Interaction of Liquids at Solid Substrates

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In Interaction of Liquids at Solid Substrates; Alexander, A.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1968.

Interaction of Liquids at Solid Substrates

A symposium sponsored by
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Chemistry at the 154th
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Illinois, Sept. 11-12, 1966.

Allen L. Alexander

Symposium Chairman

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FOREWORD

Advances in Chemistry Series was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers distributed among several journals or not published at all. Papers are refereed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications. Papers published in Advances in Chemistry Series are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.

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PREFACE

At the first meeting of the Division of Organic Coatings and Plastics Chemistry (then known as the Division of Paint and Varnish Chemistry) of the American Chemical Society in 1923, W. D. Harkins arranged a Symposium on the Wetting Power of Paint and Varnish Liquids. Papers by Harkins and associates dealt with such subjects as the flocculation of pigments as a result of the low heat of wetting of hydrophilic oxides in non-polar liquids. They demonstrated that the addition of a polar molecule to the liquid markedly increased the heat of wetting in which case pigments remained dispersed. F. E. Bartell described the use of the contact angle between liquids and solids to measure the preferential absorption of liquids by solids and the displacement of one liquid by another when both are in contact with a solid. These were the first of a series of contributions which have resulted in marked improvement in dispersion stability resulting from a better understanding of the surface properties of solids and their reaction with liquids with which they come in contact.

Through the years other symposia arranged by cooperating divisions of ACS have featured subsequent developments concerned with wetting. It is not surprising that many of these have been co-sponsored with the Division of Colloid and Surface Chemistry. In 1927 and 1928 papers by F. E. Bartell and H. S. Osterhof described the use of the adhesion tension cell and in 1930-31 papers by Harkins and Dahlstrom described further the wetting and absorption of pigments and their effect on flocculation, dispersion, and settling in paints. Subsequently, Bartell with C. W. Walton described the wetting characteristics of antimony sulfide in which it was shown that these characteristics could be changed from organophilic to hydrophilic in accordance with the chemistry of the surface layer.

In April 1955 Zisman, Fox, and Hare described the wetting properties of organic liquids on high-energy surfaces which introduced new concepts about the mechanism of the reactions occurring between solids and liquids. It is interesting to note further that Zisman's team received the first Carbide Award for this work. As the result of this and his many subsequent contributions concerning the contact angle, wetting, and adhesion, it is fitting, indeed, therefore, that in the present symposium the introductory paper has been contributed by Zisman.

In the present instance, interest in the interactions at interfaces between liquids and solid substrates has greatly expanded beyond those

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areas and concepts in which earlier workers were interested. A greater understanding of the wetting of fibers by polymers in the formation of composites has opened up new vistas resulting in major industries. Periodic symposia devoted entirely to this subject are scheduled regularly. Recently, the development of blood pumps and artificial implants in medical applications have raised entirely new problems in the blood/material interface. In recognition of the critical importance of many problems in this area still unsolved, several papers are included for which a more detailed introduction is made separately.

The availability of new highly sophisticated instrumentation has made it possible to study more intelligently the character of the surfaces of solids with which liquids may react in a variety of circumstances. Equal progress has been made by polymer chemists in the preparation of pure monomers, polymers, including solids, of known surface constitution and crystal structure. Thus, it has become possible to carry on highly effective research with adequate surface-chemical control of gas and liquid adsorption, wetting, adhesion, emulsification, foaming, boundary friction, inhibition and a variety of other areas of interest to the coatings and plastics industry.

In the present symposium most recent work in a number of these areas is described. This symposium, therefore, may be considered another in a series over a period in excess of 40 years in which progress in the field of wetting, adhesion, absorption, and other phenomena critical to the coatings and plastics industry has been offered by the Division of Organic Coatings and Plastics Chemistry.

Annandale, Va. A. L. ALEXANDER
November 1968

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The Solid/Liquid Interface—An Essential and Active Frontier of Science

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In this introductory review to the symposium, attention is given to the causes of the serious disagreements in the data reported in the literature on solid/liquid interfaces. The demanding and often-ignored experimental requirements stem principally from the overriding influence on numerous properties of solid/liquid interfaces of the outermost molecular composition of the solid surface and the properties of the first adsorbed monolayer. Available methods for purifying chemicals and new and highly specific surface chemical techniques are doing much to assist investigators. Many promising subjects of current research interest about solid/liquid interfaces are briefly discussed along with relevant literature. Finally, a brief background is given concerning the timeliness and need for each paper being offered in the symposium.

Each paper presented at this symposium reported progress in an important area of research on molecular processes at solid/liquid interfaces. Despite the obvious importance of such interfaces in both fundamental and applied science, it is no exaggeration to say that progress was painfully slow until about 20 years ago. However, since then both experimental and theoretical research on the subject has become increasingly active, exciting, and productive. That this symposium should be held under the auspices of the A.C.S. Division of Organic Coatings and Plastics Chemistry is especially appropriate, for the results of these research activities have become highly relevant to many of the important unsolved problems encountered in the science and technology of both organic coatings and plastics chemistry.

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Some General Problems and Concepts

Solid surface constitution and surface-structure sensitive properties have long defied the attack of chemists, physicists, metallurgists, engineers, and biologists; the difficulties have been especially vexing to those who have tried to understand in fundamental terms the great variety of phenomena occurring at solid/liquid interfaces. Much of the confusion and complexity encountered arose from (a) lack of adequate definition and control of each solid surface involved and (b) lack of appreciation of the necessity for the often laborious and expensive efforts required to obtain liquid-phase materials having adequate purity to guarantee reproducible surface behavior.

Why must such well-controlled materials and the associated special research techniques be used in surface-chemical research? The answer is that extreme chemical purity and care in manipulating materials which are in the interface, or are able to migrate to it, are necessary to avoid obtaining incorrect, unreproducible, or confusing experimental data. Inadequate attention to these requirements are responsible, I believe, for the already large mass of data which burdens so much of the older literature with confusing or misleading data and conclusions. The fundamental cause of these special requirements arises from the fact first pointed out by Langmuir (*40*) that the properties of the first adsorbed monolayer have an overriding influence on many surface-chemical and surface-physical properties. Highly indicative examples of the truth of the above statement have appeared in numerous publications on the influence of adsorbed monolayers on the surface and interfacial tensions of liquids, solid/solid friction, adhesion, liquid spreading, wetting and the contact angle, gas adsorption on solids, surface viscosities, evaporation-barrier films, surface electrostatic properties of metals, electrode potentials of metals in electrolytes, passivation effects, hydrogen overvoltage, and on a host of colloidal phenomena. When several surface-active species of compounds are present, their competitive adsorption behavior can be complex; frequently, the dominating influence arises from a compound present in trace concentrations. Experimental reproducibility, identification of the important variables, and an understanding of the dominant mechanism have resulted only after investigators learned to control and identify their surface-chemical system. For these reasons it is essential in research on the solid/liquid interface that there be good control of the composition of the liquid and solid as well as the real area of the solid/liquid interface; in addition, there is usually need for controlling the composition, packing, and orientation of the first adsorbed monolayer formed at that interface.

Help in coping with these problems came after World War II as the result of: (a) the increased commercial availability of organic compounds

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of high purity, (b) improved distillation and selective adsorption methods for small volume liquid samples, and (c) the evolution and increasing availability of powerful physical tools for studying solid surfaces. In connection with items (a) and (b), the rapid evolution and commercial availability of sophisticated gas/liquid chromatographic equipment for the analysis (or preparation) of extraordinarily pure liquids and gases has been a great boon to all chemists. Especially important is the fact that such methods are highly effective and adaptable even when applied to very small quantities of material. In recent years it has become possible to obtain commercially numerous chemicals already purified by chromatographic methods. As regards item (c), a list of the especially helpful physical tools for observing solid surfaces should include: the electron microscope, the electron-scan microscope, the electron diffraction apparatus, the multiple attenuated infrared reflection (MAIR) spectroscope, the optical ellipsometer, and a variety of extraordinarily sensitive radioactive tracer methods and the necessary associated equipment.

Noteworthy progress has been made by polymer chemists in preparing pure monomers and polymers, as well as solid polymers, of known surface constitution and crystal structure. The continued efforts for more than a decade by solid state physicists and metallurgists have resulted in methods and equipment for preparing an impressive variety of extraordinarily pure solid materials for research on the properties of metals, semiconductors, and single crystals.

Because of the availability of these new methods, devices, and purer materials, it has become more feasible to carry on effective research with adequate surface-chemical control of gas and liquid adsorption, wetting, adhesion, emulsification, foaming, boundary friction, corrosion inhibition, heterogeneous catalysis, electrophoresis, electrode surface potentials, and a variety of other subjects of interest in the surface-chemical and allied fields of research. In view of the present situation, serious investigators should now be able to report results in the scientific literature which will have much more value than ever before. There is no excuse for any investigator's taking such inadequate care in controlling surface composition or surface-active contaminants as was common in over 50% of the research publications in surface and colloid science in the past.

Our own investigations have concerned: (a) liquid spreading on solids and the laws relating the equilibrium contact angle and the critical surface tension of wetting to solid and liquid constitution (*26, 27, 28, 53, 54, 62*), (b) liquid/liquid displacement from solid surfaces (*1, 5*), (c) the properties of adsorbed monolayers on solids and their relation to the monolayer retraction method (*28, 54, 62*), (d) the surface electrostatic potentials of adsorbed organic monolayers on metals (*9, 10, 11, 58, 59*), (e) the effects of surface constitution on adhesion and abhesion (*60*),

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(f) the effect of an adsorbed monolayer on boundary friction and wear in rubbing solids (*13, 15, 45, 46*), and (g) the surface chemistry of silicones (*24, 25*) and fluorochemicals (*3, 4, 21, 22, 23, 34, 35, 36, 37, 51, 52*). I believe these studies have all taught reliably and well about the dominating influence in surface phenomena of the need for controlling the composition of both solids and liquids. They have also resolved many fundamental and applied problems, revealed new and unsuspected surface properties and materials, and helped stimulate more interest in surface chemistry.

Although much has been published about the role of wetting and spreading of the liquid adhesive in forming an adhesive joint (*17, 18, 61, 62, 63*), many investigators and users of adhesives are still not aware of why it is so important, despite the difficulties of preparing joints free from interfacial voids (*2, 48*). Our own recent research has shown clearly why and to what extent such voids cause a significant loss of strength in composite materials and water resistance (*2, 48, 63*). One of the most promising chemical measures is the use of "coupling agents," which are a class of adhesion-promoting agents now finding increasing applications (*33, 47, 56*). There is much yet to be learned and practiced about the proper way to use these materials (*63*), and I believe the result of current efforts will be illuminating and also of much applied value; we are witnessing the evolution of a new and important chapter in the subject of the surface chemistry of the solid/liquid interface.

Major effects of extremely thin films of adsorbed water on surface phenomena on hydrophilic solid surfaces, for example the great effect on surface potentials of metals, have been recognized for many years (*9, 10, 11, 58, 59*); our own recent investigations have demonstrated that the first adsorbed monolayer of water exercises a profound influence on the wetting and surface energy properties of high-energy hydrophilic solid surfaces including glasses and minerals (*6, 55*) and metals (*7*). Despite the large amount of past research on the surface oxidation of metals (*39*), an important gap still exists. I believe we need to learn much about the effect of each type of metal oxide on the wetting and adhesive properties of metals. When a stress-induced failure occurs in an adhesive joint involving a metallic solid, the observed results may have arisen from a cohesive failure either within the surface oxide or within the metal. Either adsorbed water or water included in the oxide structure may play an important role in determining the cohesive failure of the oxide. Another possibility is that an adhesive failure may have occurred between the oxide layer and the underlying metal. Similar problems exist when sulfides, sulfates, nitrides, phosphates, phosphides, or other inorganic compounds are present at the joint interface.

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On the Papers Presented at This Symposium

The first three of the following papers in this symposium are concerned with coupling agents. These investigations were stimulated by the reaction of an NRL team of surface chemists to the published industrial research of the past decade on glass-reinforced plastics and other composite materials. Present commercial practices still appear to involve more art than science (*63*), and these papers give adequate evidence that there are opportunities for both basic and applied research on the subject.

Craver and Taylor's (*16*) contribution is important to the subject of solvent interactions with polymeric solids; it is especially thought provoking that this work may have opened a new avenue of approach on the subject of the mechanism of plasticization.

Schick and Harvey (*49*) summarize an interesting investigation of the effect of the choice of solvent on the conformation of a polymer adsorbed at the solution interface with Spheron 6 carbon black. A noteworthy conclusion concerns the occurrence of extended and looped configurations of the adsorbed polymer molecules formed from good or poor solvents, respectively.

Many important industrial processes for plastic products now depend on some form of surface oxidation to change the surface-chemical composition of organic plastics designed for use as coatings or thin foils. More definitive published information has been needed about the surface-chemical processes involved, the effective methods for modifying or controlling the surface properties of the organic polymer, and the extent to which surface oxidation causes the deterioration of useful properties. The work of Fox, Price, and Cain (*29*) is a valuable contribution to answering all three questions. Their paper reports an effective surface-chemical investigation of the photochemical changes in the surface of a well-defined organic polymer. It may surprise many chemists to realize that, despite the sustained and often large research effort in photochemistry during the past 30 years, little has been done on the photochemistry of the solid/gas interface; obviously, much more attention needs to be directed to this important subject. The simultaneous use by these authors of polymer chemistry, the relation of the contact angle to surface constitution, and multiple attenuated internal reflection (MAIR) spectroscopy in the infrared is an impressive demonstration of the power of interdisciplinary research.

Lee (*41, 42*) offers a valuable contribution on the mechanism of reinforcement and especially on the role of adhesion and wetting in elastomeric adhesives, pressure-sensitive tapes, nonpigmented organic coatings, and composites such as resin-reinforced rubbers or thermoplastics. I am sure it will generate much discussion. Lee (*43*) presents a semiquantitative treatment of the relationship between the cohesive energy density, the solid surface tension, the critical surface tension of wetting, and the glass temperature of a high polymer. This paper is by no means rigorous or quantitative, but it is nevertheless interesting and imaginative.

Bertolucci, Jantzef, and Chamberlain (*8*) report briefly on their work using single-reflection, attenuated, total-reflection, infrared spectroscopy to study the mechanism of adsorption on hydroxy-apatite crystals of citric acid, tartaric acid, sodium citrate, oxytetracycline hydrochloride, and glycine. This work has been of interest to many chemists, but it also has particular pertinency to current research on dental adhesives and the effect of pretreatment of the tooth cavity wall.

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Although early surface chemists gave much attention to the spreading and adsorption of monolayers on liquid mercury, except for the bearing the results had on later research concerning polarography, relatively little attention has been given to the subject on the past 30 years. This is surprising in view of the stimulating and important investigations early in this century by Henri Dexaux (*19, 20*). Also, let me recall the early work of W. D. Harkins and co-workers (*30, 31, 32*) who measured the spreading coefficient and work of adhesion of the large variety of compounds able to spread spontaneously on the surface of clean liquid mercury to form monomolecular films. The report by Schwartz, Ellison, Klemm, and Otto (*57*) on the water wettability of condensed adsorbed films of fatty acids on mercury is an interesting and valuable contribution.

Schonhorn and Ryan (*50*) discuss the results of recent work which is a logical extension of their earlier investigation on the effect of the morphology of the surface region of a plastic on its adhesive joint strength. In effect, they point out how increasing polymer crystallinity in the vicinity of the free surface can increase its ability to form stronger joints by increasing its local cohesive strength. Their results are of much interest, although they are not surprising. Over ten years ago Bowers, Clinton, and I in an investigation on the frictional properties of polyethylene and its halogenated derivatives (*14*) found that the surface regions of such plastics, as normally produced, were so amorphous as to exhibit greater boundary friction and therefore greater tendency to fail cohesively than the regions just beneath. Since friction research has proved that a good joint usually fails by a cohesive failure in the weaker material (*13*), an amorphous surface structure gives a plastic a lower adhesive joint strength.

Bikerman (*12*) gives a derivation of an equation which the author considers theoretically more sound than the well-known equation of

Thomas Young for the contact angle of a liquid with a solid. The derivation and reliability of the Young equation has been especially well discussed in recent years (*38, 44*). Although I do not believe Bikerman's new treatment is sound, it is an interesting approach nevertheless.

Young and Rouch (*60*) report on progress in investigating the potentialities of a titanium organic compound designed to react with E-glass and silica by a chelating mechanism and so form a new type of coupling agent. Their work is original and promising, and it will attract much attention.

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Conclusion

In closing, I believe it deserves emphasis that any new contribution concerning new surface phenomena or any new mechanism operating at the solid/liquid interface has a high probability of evoking a wider range of interest than even the author may realize. A surface-chemical mechanism occurring at one type of solid/liquid interface may reappear again and again in unobvious but nevertheless related phenomena or processes of interest to mankind. For example, a more detailed mechanistic understanding of the role of coupling agent in glass/resin-reinforced plastics can contribute guidance to help make a major advance in another field. Examples are possible uses in dental adhesive restorative materials, in improving rubber tires, in increasing the water resistance and adhesion of paints, in biological adhesives, and in improving the properties of plastic foils and laminates for packaging or other uses.

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2.

Chlorophenylalkyl-substituted Carboxylic Acids and Silanes Designed as Adhesion Promoters

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Eight new surface active molecules having a terminal p-*chlorophenyl substituent, a polymethylene spacer, and reactive carboxyl or alkoxysilane groups have been prepared. Such structures form monolayers which promote adhesion between a solid substrate and an organic resin because they expose a relatively high energy chlorophenyl outer surface which is easily wet by the resin. Preparative methods are outlined for the monocarboxylic acids* p-$ClC_6H_4(CH_2)_{n-1}CO_2H$, *(where* n *is 12, 14, 18, and 20), for the dicarboxylic acids* p-$ClC_6H_4(CH_2)_{12}CH(CO_2H)CH_2CO_2H$ *and* p-$ClC_6H_4(CH_2)_{12}CH(CO_2H)CH_2CH_2CO_2H$, *and for the substituted silanes* p-$ClC_6H_4CH_2CH_2Si(OMe)_3$ *and* p-$ClC_6H_4CH_2CH_2Si(OEt)_3$. *The compounds are characterized by conventional criteria. NMR spectra establish the para position of the chloro substituent. GLC shows that the purities of the acids generally exceed 97.5%. Principal impurities are the unchlorinated analogs and lower homologs.*

Most commercial finishes for glass fiber form surfaces which are not readily wet by the resins used for glass fiber impregnation. To correct this deficiency in adhension, redesign of existing "coupling agents" or "adhesion promoters" has been proposed (*16*). The new concept utilizes monolayers of appropriate design for promoting adhesion between an organic resin and a solid substrate (*see* Figure 1). The new structures reported here feature a terminal chlorophenyl substituent

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exposing an outer surface which is readily wet by resins, a polymethylene spacer allowing outward orientation of the exposed group, and at the opposite end a reactive group capable of chemically bonding to the solid substrate. More than one reactive group in the molecule may be desirable; for example, we have investigated the use of one or more carboxyl groups. In the case of two terminal carboxyl groups, they should be separated by more than one carbon atom to avoid sensitivity to decarboxylation. Alternatively, the single carboxyl group may be replaced with $-SiCl_3$, $-Si(OEt)_3$ or other groups.

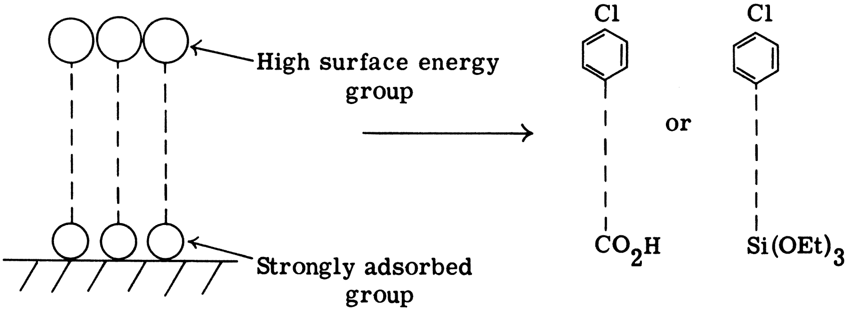
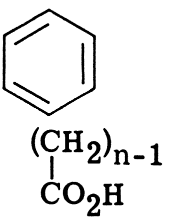


Figure 1. Structural concept for adhesion promoters

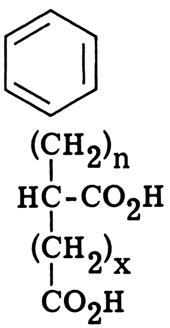
The present study outlines methods for preparing four new monocarboxylic acids, two new dicarboxylic acids, together with one known and two new substituted silanes. All comply with the above structural concepts. Structures of the six acids are given below.

Monocarboxylic acids



n = 12, 14, 18 and 20

Dicarboxylic acids



n = 12

x = 1 and 2

All six of the chlorophenyl-substituted carboxylic acids are derived from acid chlorides of long-chain aliphatic half esters. To prepare these uncommon intermediates in sufficient amounts, practicable preparative methods had to be developed. Methods are given for converting appropriate α,ω-dicarboxylic acids to the corresponding acid chloride half esters.

Certain of the *p*-chlorophenyl-substituted carboxylic acids are related products in a multistep synthesis. A schematic outline of synthetic procedures is presented to clarify these relationships. Properties of seven new *p*-chlorophenyl-substituted intermediates and six new *p*-chlorophenyl-substituted carboxylic acids are reported. All of the 13 new compounds have been characterized by conventional criteria. Both gas-liquid chromatography and nuclear magnetic resonance are used to assess the purity of the carboxylic acids and their intermediates.

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Synthetic Methods

α,ω-Dicarboxylic Acids. DODECANEDIOC AND OCTADECANEDIOC ACID. The dodecanedioc acid, m.p. 125°-127°C., was purchased from Aldrich Chemical Co., Milwaukee, Wisconsin. Hünig's 1.6 gram preparative procedure for octadecanedioc acid (*6*) was scaled up for 90 gram batches in accordance with his large scale method for docosanedioc acid (*7*). Recrystallization from methyl ethyl ketone, gives octadecanedioc acid (m.p. 121°-124°C.; 57% yield; 96% purity). The principal impurity is tridecanedioc acid.

Diesters. DIETHYL DODECANEDIOATE AND DIETHYL OCTADECANEDIOATE. The respective diesters were prepared in 99.4% and 99.0% purities by the method reported for diethyl adipate (*9*). Physical properties observed for the respective diesters agree with reported values (*1, 2, 15*).

Half Esters. ETHYL HYDROGEN DODECANEDIOATE AND ETHYL HYDROGEN OCTADECANEDIOATE. Practicable methods had to be developed for converting the diethyl esters to the respective half esters in batches as large as 100 grams. The improved process gives a relatively high conversion of the reacted diester to the half ester and allows a quantitative recovery of the unreacted diester which can be submitted to another batch operation.

Alcoholic sodium hydroxide solution (26 ml. of 1*N*) is added dropwise during 30 min. to a stirred mixture of diethyl dodecanedioate (15.0 grams; 0.0524 mole) and ethyl alcohol (30 ml.). Water (60 ml.) is added and stirring is continued (*ca.* 15 min.) until the pH reaches 8.0. Extraction of the aqueous mixture with petroleum ether (30°-60°C. boiling range; 2 × 120 ml.) removes unreacted diethyl dodecanedioate (8.60 grams; 0.0300 mole). Acidification of the aqueous layer with 600 ml. of 0.1*N* hydrochloric acid precipitates ethyl hydrogen dodecanedioate and dodecanedioc acid. Both acids are extracted with ether (2 × 150 ml.). After drying and concentrating the extract, the residue is melted by warming to 60°C., poured into 250 ml. of petroleum ether and allowed to stand for 1 hour at 25°C. for equilibration. Precipitated dodecanedioc acid is removed by filtration (1.80 grams; 0.0078 mole). The filtrate is cooled

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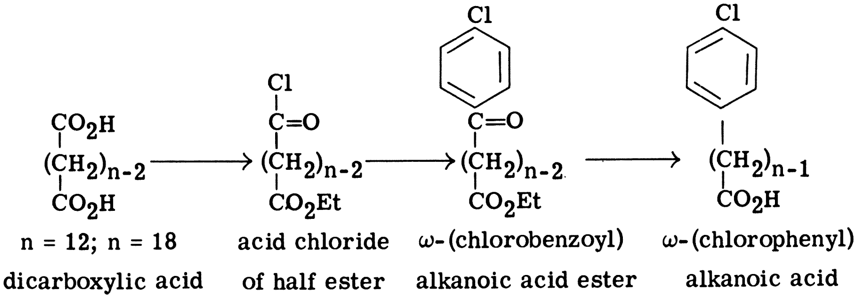
to −10°C. and filtered to collect the ethyl hydrogen dodecanedioate, 3.72 grams; 0.0144 mole; m.p. 49°-50°C. in agreement with the reported value (*8*). The yields based upon the amount of diester consumed are 64.3% half ester and 34.8% diacid, a total of 99.1%. Yields based upon the diester used are 27.5% half ester, 14.9% diacid, and 57.3% recovered diester, a total of 99.7%.

Diethyl octadecanedioate can be prepared by the same stoichiometry provided that the diester is dissolved in four times as much alcohol (4 × 30 ml.), that the saponification step is performed at 60°C., and that the final mixture of diacid and half ester is resolved in hexane. The modified procedure yields ethyl hydrogen octadecanedioate melting at 71.5° to 72.5°C. in agreement with the literature value (*1*). Yields based upon the amount of diester consumed are 90.0% half ester and 3.3% diacid. Based upon the amount of diester used, they are 44.4% half ester, 1.6% diacid and 51.0% recovered diester.

Acid Chlorides of Half Esters. The half esters are converted to the corresponding half ester acid chloride by allowing each to stand overnight with two equivalents of thionyl chloride. Unreacted thionyl chloride is removed at reduced pressure. The residual acid chlorides are used for the preparation of the keto esters.

Keto Esters. ω-(*p*-CHLOROBENZOYL)ALKANOIC ACID ESTERS. The intermediate keto esters, $p\text{-ClC}_6\text{H}_4\text{CO(CH}_2)_{10}\text{CO}_2\text{Et}$ and $p\text{-ClC}_6\text{H}_4\text{CO(CH}_2)_{17}\text{CO}_2\text{Et}$, were synthesized from α,ω-dicarboxylic acids *via* the major steps shown in Scheme I.

SCHEME I



Acid chlorides of the respective half esters are converted to the desired keto esters by Friedel-Crafts reactions resembling those developed by Fieser for preparing the ω-(*p*-chlorobenzoyl)nonanoic acid ester (*5*). The keto esters are converted to the respective keto acids through saponification with 10% alcoholic potassium hydroxide, acidification and recrystallization from toluene. Yields of the keto acids based upon the respective acid chlorides are 75 and 79%. Properties of the keto acids and their derivatives are given in Tables I and II.

Monocarboxylic Acids. ω-(*p*-CHLOROPHENYL)ALKANOIC ACIDS. The saturated acids $p\text{-ClC}_6\text{H}_4(\text{CH}_2)_{11}\text{CO}_2\text{H}$ and $p\text{-ClC}_6\text{H}_4(\text{CH}_2)_{17}\text{CO}_2\text{H}$ of Scheme I result from the Wolff-Kishner reduction (*4*) of the corresponding ω-(*p*-chlorobenzoyl)alkanoic acids. Respective yields of the acids

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Table I. Analysis and Properties of Intermediates

No.	Compound	B.P. (°C./mm. Hg)	M.P. (°C.)	N.E.	
				Calcd.	Found
1.	p-$ClC_6H_4CO(CH_2)_{10}CO_2H$	—	105-107	324.9	324.0
2.	p-$ClC_6H_4CO(CH_2)_{16}CO_2H$	—	110-112	409.0	409.9
3.	p-$ClC_6H_4(CH_2)_{12}OH$	199/1.0	32-34	—	—
4.	p-$ClC_6H_4(CH_2)_{18}OH$	—	58-60	—	—
5.	p-$ClC_6H_4(CH_2)_{12}Br$	210/1.0	—	—	—
6.	p-$ClC_6H_4(CH_2)_{18}Br$	—	44-46	—	—
7.	p-$ClC_6H_4(CH_2)_{12}CH(CO_2Et)CO_2Et$	245/1.5	—	—	—

		Analyses (%)					
		C		H		Cl	
No.	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found
1.	$C_{18}H_{25}ClO_3$	66.55	66.56	7.66	7.66	10.91	10.86
2.	$C_{24}H_{37}ClO_3$	70.48	70.53	9.12	9.21	8.67	8.83
3.	$C_{18}H_{29}ClO$	72.82	72.83	9.85	10.02	11.94	11.95
4.	$C_{24}H_{41}ClO$	75.65	76.05	10.86	10.98	9.31	8.90
5.	$C_{18}H_{28}BrCl$	60.09	59.55	7.85	7.80	9.85 22.21[a]	9.85 21.17[a]
6.	$C_{24}H_{40}BrCl$	64.93	64.50	9.08	9.02	7.99 18.00[a]	8.46 18.85[a]
7.	$C_{25}H_{39}ClO_4$	68.39	68.49	8.95	8.90	8.08	8.00

[a] Bromine assays.

Table II. Analysis and Properties of Carboxylic Acids

No.	Compound	M.P. (°C.)	N.E.	
			Calcd.	Found
8.	p-$ClC_6H_4(CH_2)_{11}CO_2H$	67-68	310.9	313.0
9.	p-$ClC_6H_4(CH_2)_{13}CO_2H$	70-70.5	337.4	338.9
10.	p-$ClC_6H_4(CH_2)_{17}CO_2H$	74-75	395.0	396.0
11.	p-$ClC_6H_4(CH_2)_{19}CO_2H$	78-79	423.1	424.0
12.	p-$ClC_6H_4(CH_2)_{12}CH(CO_2H)CH_2CO_2H$	87-88	198.5	198.9
13.	p-$ClC_6H_4(CH_2)_{12}CH(CO_2H)CH_2CH_2CO_2H$	85-86	205.5	206.7

		Analyses (%)					
		C		H		Cl	
No.	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found
8.	$C_{18}H_{27}ClO_2$	69.55	69.68	8.75	8.80	11.41	11.65
9.	$C_{20}H_{31}ClO_2$	70.88	70.65	9.22	9.31	10.46	10.37
10.	$C_{24}H_{39}ClO_2$	72.97	73.26	9.95	10.26	8.98	8.61
11.	$C_{26}H_{43}ClO_2$	73.81	73.83	10.24	10.31	8.38	8.31
12.	$C_{22}H_{33}ClO_4$	66.57	66.60	8.38	8.40	8.93	8.88
13.	$C_{23}H_{35}ClO_4$	67.22	67.52	8.58	8.63	8.63	8.56

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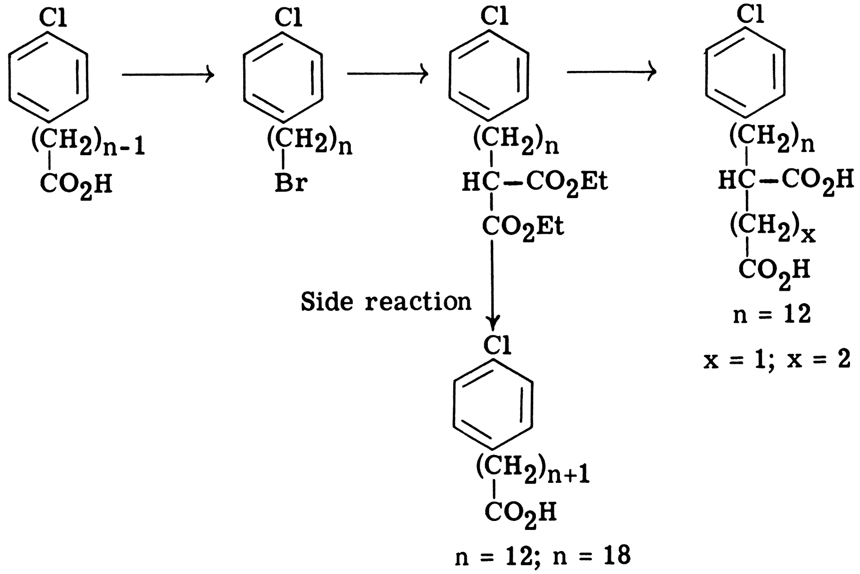
after work-up and recrystallization from heptane (−10°C.) amount to 80 and 95%. The other homologous acids, p-$ClC_6H_4(CH_2)_{13}CO_2H$ and p-$ClC_6H_4(CH_2)_{19}CO_2H$ are derived from appropriate monoalkylated malonic esters shown in Scheme II through saponification, acidification, and decarboxylation.

SCHEME II



Alcohols. ω-(p-Chlorophenyl)dodecyl Alcohol and ω-(p-Chlorophenyl)octadecyl Alcohol. These alcohols are obtained in greater than 95% yields from $LiAlH_4$ reductions of the appropriate monocarboxylic acids.

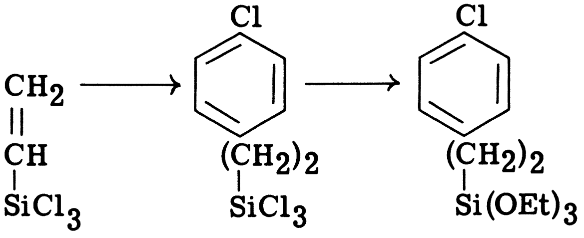
Bromides. ω-(p-Chlorophenyl)dodecyl Bromide and ω-(p-Chlorophenyl)octadecyl Bromide. Conversion of the alcohol to the corresponding bromide is accomplished by Collins' method (*3*). The respective bromides are purified by distillation in 84% yield, and by recrystallization from alcohol in 78% yield.

Monoalkylated Malonic Acid Esters. Diethyl ω-(p-Chlorophenyl)-dodecylmalonate and Diethyl ω-(p-Chlorophenyl)octadecylmalonate. These intermediate diesters of Scheme II are prepared by reaction of sodio diethyl malonate (0.30 mole) and the appropriate ω-(p-chlorophenyl)alkyl bromide (0.28 mole), using modifications of the method by Ramart-Lucas Papadakis (*12*). This leads to the crude diethyl ω-(p-chlorophenyl)dodecylmalonate (b.p. 245°C./1.5 mm.; 59% yield). The higher boiling diethyl ω-(p-chlorophenyl)octadecylmalonate is prepared by a similar procedure which omits the distillation step.

Dicarboxylic Acids. ω-(p-Chlorophenyl)dodecylsuccinic Acid and 2-[ω-(p-Chlorophenyl)dodecyl]glutaric Acid. Scheme III outlines major steps in the synthesis of the two dicarboxylic acids. The final step requires alkylation of the diethyl ω-(*p*-chlorophenyl)dodecylmalonate by modifications of the method by Ramart-Lucas and Papadakis (*12*). Briefly, the monoalkylated malonic ester (0.11 mole) is converted to the sodio derivative and then condensed with 0.11 mole of either $BrCH_2CO_2Et$ or $BrCH_2CH_2CO_2Et$ to yield triesters which after saponification, acidification, and decarboxylation lead to residues containing the respective dicarboxylic acids. Principal components of these residues are the desired dicarboxylic acids—*e.g.*, either *p*-$ClC_6H_4(CH_2)_{12}CH(CO_2H)CH_2CO_2H$ or *p*-$ClC_6H_4(CH_2)_{12}CH(CO_2H)CH_2CH_2CO_2H$, and the monocarboxylic acid, *p*-$ClC_4H_6(CH_2)_{13}CO_2H$, arising from the saponification and decarboxylation of unreacted diethyl ω-(*p*-chlorophenyl)dodecylmalonate. The decarboxylated residue is dissolved in a mixture of ether (400 ml.) and benzene (400 ml.), and the mono and dicarboxylic acids are coprecipitated as ammonium salts by bubbling an excess of ammonia through the solution. The two ammonium salts are collected by filtration. The mono and dicarboxylic acids are regenerated by acidification of the ammonium salts, followed by ether extraction and concentration of the ether extract. After being carried through their ammonium salts three times, the regenerated mixed acids are resolved by dispersing the mixture in boiling hexane (1000 ml.) and allowing it to equilibrate at room temperature. The precipitated dicarboxylic acid is collected and recrystallized again from hexane to yield the analytically pure dicarboxylic acid (30–35% yields). The monocarboxylic acid is precipitated by cooling the filtrate to −10°C. A recrystallization of this precipitate from toluene leads to the analytically pure ω-(*p*-chlorophenyl)tetradecanoic acid (25–30% yields), reported in Table II.

Substituted Silanes. 2-(*p*-CHLOROPHENYL)ETHYLTRICHLOROSILANE, 2-(*p*-CHLOROPHENYL)ETHYLTRIMETHOXYSILANE, AND 2-(*p*-CHLOROPHENYL)-ETHYLTRIETHOXYSILANE. Steps in the synthesis of *p*-$ClC_6H_4(CH_2)_2SiCl_3$ and *p*-$ClC_6H_4(CH_2)_2Si(OEt)_3$ are shown in Scheme III.

SCHEME III



The chlorophenylethyltrichlorosilane is prepared by condensing vinyltrichlorosilane and chlorobenzene, employing Wagner's variation of the Friedel-Crafts reaction (*14*). Ethanolysis of the product yields the triethoxy compound. The trimethoxy compound is prepared by reaction of 1 mole of the chlorophenylethyltrichlorosilane and 3 moles of methanol in ether using pyridine as a hydrogen chloride acceptor. Properties of the substituted silanes are given in Table III.

Table III. Analysis and Properties of Substituted Silanes

No.	*Compound*	*B.P. (°C./mm. Hg)*	n_D^{20}	d_4^{20}
14.	p-$ClC_6H_4(CH_2)_2SiCl_3$[a]	95/0.5	1.5313	1.3442
15.	p-$ClC_6H_4(CH_2)_2Si(OMe)_3$	107/0.5	1.4883	1.1315
16.	p-$ClC_6H_4(CH_2)_2Si(OEt)_3$	114/0.5	1.4757	1.0574

Analyses (%)

		C		*H*		*Si*		*Hydrolyzable Cl*	
No.	*Formula*	*Calcd.*	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*
14.	$C_8H_8Cl_4Si$	—	—	—	—	10.25	10.02	38.8	39.6
15.	$C_{11}H_{17}$-ClO_3Si	50.66	50.44	6.67	6.52	10.77	10.93	0.00	<0.006[b]
16.	$C_{14}H_{23}$-ClO_3Si	55.52	54.86	7.65	7.50	9.27	9.51	0.00	<0.10[c]

[a] Ref. *11* reports n_D^{20} 1.5310 and d_4^{20} 1.3450.
[b] Total chlorine assay: calcd., 13.60; found, 13.71.
[c] Total chlorine assay: calcd., 11.28; found, 11.26.

Results and Discussion

Conventional criteria such as melting points, elemental assays, etc. generally indicate that the reported compounds are of high purity but furnish no information concerning the nature of the impurities. In the case of compounds of such high molecular weights, these criteria may not detect significant amounts of homologs or other compounds containing similar functional groups. In the present study gas-liquid chromatography proved to be an indispensable tool in determining the amounts of such impurities and in assisting in their identification.

Contaminants may arise from impure starting materials, incomplete reactions and secondary reaction products. A knowledge of these factors serves to limit the list of probable contaminants to a small number. Tentative identifications of some of the contaminants shown as minor peaks in the chromatograms were assigned by matching their retention times (or retention temperatures) with those of probable contaminants. In the case of the six carboxylic acids of Table II, the contaminants are known to be carboxylic acids, since the method of purification involves repeated precipitations as the ammonium salts. The tridecanedioc acid observed in the octadecanedioc acid (compound 10 of Table IV) is considered the source of the lower homolog impurity ω-(p-chlorophenyl)-octadecyl bromide (compound 6 of Table IV).

Intermediates, carboxylic acids, and silanes bearing the terminal p-cholorophenyl substituent are characterized by conventional criteria in Tables I, II, and III. For further assessment of purity the intermediates and carboxylic acids were analyzed by gas-liquid chromatography. For this analysis methyl esters of the acid compounds were prepared by perchloric acid catalyzed esterification. All analyses were performed on a Beckman GC 4 equipped with a thermal conductivity detector and a temperature programmer. The stainless steel columns, 1/8 inch o.d. and 6 feet in length, were packed with 3% SE-30 on 60/80 mesh Chromosorb W. Samples were chromatographed under a variety of temperature conditions in order to obtain a good resolution of the contaminants. Table IV gives the retention temperatures of the various compounds from a single temperature program, in which the temperature was raised 5.7° per minute from an initial 200°C. and helium flow was 21 ml. per minute. Semiquantitative information concerning the impurities shown in Table IV was obtained from the chromatograms by the area normalization method. Calculated purities of the six final acid products ranged from 95 to better than 99%.

Table IV. Results of Gas-Liquid Chromatography of Intermediates and Carboxylic Acids[a]

			Probable Impurities and their Amounts (%)	
Compound Number	*Retention Temperature °C.*	*Purity %*	*Unchlorinated Analog*	*Others*
1	248	98.9	0	
2	289	96.6	0	
3	235	96.6	1.4	
4	279	97.0	0.8	
5	243	96.4	1.2	
6	286	90.0	1.3	2.9[b], 3.5[c]
7	252	83.0	2.0	
8	236	99.6	0.4	
9	249	99.1	0.9	
10	278	96.0	0	4.0[d]
11	290	98.7	0.5	
12	276	97.4	2.6	
13	282	94.7	1.8	

[a] Gas-liquid chromatography conditions given in text.
[b] Compound number 4, p-$ClC_6H_4(CH_2)_{18}OH$.
[c] p-$ClC_6H_4(CH_2)_{13}Br$.
[d] p-$ClC_6H_4(CH_2)_{12}COOH$.

The typical monocarboxylic acid p-$ClC_6H_4(CH_2)_{13}CO_2H$ has been analyzed by proton nuclear magnetic resonance. The nuclear magnetic resonance spectra show that the chlorine substitution is more than 95% para, and that 1 to 2% of the aromatic rings carry no chlorine substituent (*10*).

Both mono- and dicarboxylic acids of Table II have low melting points ranging from 67° to 88°C. Both types of acids are soluble in com-

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mon solvents such as ethyl alcohol, benzene, chloroform, and hexane (60°C.). The low solubility of the dicarboxylic acids in hexane at 25°C. provides a method for separating mixtures containing both types of acids. The three substituted silanes of Table III are high boiling liquids requiring storage in evacuated sealed ampoules to prevent hydrolysis.

Nuclear magnetic resonance studies support the hypothesis that compounds whose syntheses involve both the Wolff-Kishner reduction and the $LiAlH_4$ reduction contain small amounts of the unchlorinated analogs. Chromatography of these compounds and their derivatives shows an impurity whose retention value is approximately equivalent to that of a homolog of two carbon numbers less than the main compound. It seems reasonble to suppose that this impurity is the suspected unchlorinated analog which would have about the same molecular weight as such a homolog. It is also significant that no such impurity is seen in keto acid precursors which have not been subjected to reductive procedures.

Principal impurities found in the six *p*-chlorophenyl-substituted carboxylic acids of this study are homologs and unchlorinated analogs. Such impurities in the amounts found should not interfere in applications for which the compounds were made. Wettability studies on the compounds are reported in the present symposium (*13*).

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3

Preparation and Wettability of Terminally Chlorophenyl-substituted Carboxylic Acid Films

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A new class of surface-active compounds was designed to adsorb on solids to improve the adhesion of liquids, resins, and protective coatings without necessitating chemical interaction with both the adherend and adhesive. Terminally para-chlorophenyl-substituted dodecanoic, dodecylsuccinic, and dodecylglutaric acids were designed as potential coupling agents (or adhesion promoters). Their adsorbed monolayers were prepared by melt or solvent retraction. The wettability and high critical surface tensions (γ_c around 40 dynes/cm.) obtained are consistent with other chlorine-rich surfaces. Structural changes among acids containing the ω-(p-*chlorophenyl)dodecyl moiety affect monolayer wettability little, but can increase adsorption strength. Shortening the aliphatic chain from chlorophenyldodecanoic to chlorophenylacetic acid influences the wettability properties, but permits the use of solvents such as water to accommodate many practical applications.*

In the past decade, increasing attention has been given to improving adhesion in solid joints by designing "coupling agents" or "adhesion promoters." Some types are alleged to interact chemically with both the solid adherend surface and the polymeric adhesive. Coupling agents, such as the silanes (*15*) and certain coordination complexes of chromium (*8*), were introduced in the past decade to prevent loss of strength of glass fiber-reinforced plastics during prolonged water immersion—*i.e.*, to improve or promote wet strength. Such compounds have been alleged to function as coupling agents by compound formation with both adherend and adhesive, but there is much uncertainty yet as to the extent

In Interaction of Liquids at Solid Substrates; Alexander, A.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1968.

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of compound formation as well as the precise mechanism. Until recently, there was much debate about their value in improving wet strength (*15*) in composite materials.

Our understanding of the mechanism of adhesion and of the sources of weakness and failure in adhesive joints has increased greatly in the past decade, and increasing importance is being assigned to the wetting and spreading of the liquid adhesive for optimizing joint strength (*19, 20, 21*). An unanswered question is—to what extent is a chemical reaction at the joint interface necessary to promote formation of a strong joint? A related and important question is—must the coupling agent react chemically with both adhesive and adherend? Many physicists have long contended that intimate molecular contact of adhesive and adherend, without surface-chemical interaction, is sufficient to develop adequately high strength in adhesive joints.

But we must recognize that if the joint is subsequently to be exposed to occasional or long-term immersion in water, which may cause hydrolysis or corrosive attack, etc., surface-chemical reaction may be essential to prevent early joint failure. Therefore, chemisorbed coupling agents may be necessary for long joint life under water-immersion conditions. The question then arises—are the available agents the most suitable for all systems and uses? We think they are not. Several new classes of surface-active materials have therefore been designed and synthesized at NRL (*9*) as candidate adhesion promoters. We will present here progress of our current investigation of carboxylic acid derivatives containing terminal *p*-chlorophenyl substituents as suggested several years ago (*21*). The molecules of these materials were designed to be sufficiently surface active to chemisorb on the solid adherend surface; the adsorbed monolayer of coupling agent was to present an outermost surface on which the liquid adhesive could spread spontaneously without chemically reacting with that film surface.

Since many organic adhesives and paints are applied as solutions or dispersions having low surface tension, it might be supposed that they would invariably spread spontaneously on those adherends having high-energy surfaces, and so the use of an adhesion promoter to improve wetting would be unnecessary. Such is usually not the case, however, because innumerable materials, as commonly applied, do not spread spontaneously on the many high-energy solid surfaces which quickly adsorb either water or undesirable organic contaminants. An important and unrecognized function of the adsorbed film of adhesion promoter is to prevent such contamination; hence, it can serve as a "priming" or preliminary protective coating for the high-energy solid surface during the period prior to application of the liquid adhesive or coating. A second and related function is to prevent the adsorption of undesirable contaminant materials that migrate toward the high-energy adherend surface from the liquid adhesive after it has been applied. In either case, a firmly bound adsorbed monolayer of the adhesion promoter will prevent or repress such contamination of the adherend surface by organic substances, or by water, which could: (a) interfere with spontaneous spreading by the liquid adhesive, (b) interpose a weakly bound layer at the interface, or (c) introduce a plane of easy parting after solidification of the adhesive (*19, 20*).

However, if the adsorbed film of coupling agent is to serve well as a thin-film protective coating prior to application of the adhesive, the agent molecule should be designed to coat the adherend with an external surface having the following characteristics: (a) it should be sufficiently inert chemically; (b) it should have a low surface energy; and (c) it should form a hydrophobic barrier film in order to avoid the accumulation of an outermost adsorbed layer of water for the reasons just cited. In addition, the film of coupling agent should have a critical surface tension for spreading (γ_c) which is more than, equal to, or only slightly below, the surface tension (γ_{LV}) of the liquid adhesive as it is applied. For example, a value of γ_c of 32 dynes/cm. would permit the organic liquids used in most common paint compositions to spread readily over the surface without void formation or excessive trapping of air bubbles. If a partially cured polymeric adhesive is to be applied, however, the normally low solvent content would require γ_c to be around 36–40 dynes/cm. In either case, the result would then be to minimize the formation at the adhesive-adherend interface of regions where high stress concentration or a plane of easy cleavage or parting could develop (*21*).

Figure 1 presents schematically the role of a surface-active adhesion promoter in an adhesive joint. The desired wetting properties are obtained by incorporating an appropriately chosen atomic grouping at the outer end of the oriented adsorbed molecule. The opposite end of the molecule can comprise one or more polar groups each of which is able to adsorb, as independently as possible, on the adherend surface either by strong physical or chemical adsorption. The coupling agent would thus be highly resistant to displacement by solvents or by surface-active components in the liquid adhesive. Since the small size of the water vapor molecule makes moisture permeation of organic coatings a constant threat to the integrity and longevity of adhesive joints, the coupling agent should be more hydrophobic in constitution than hydrophilic. Finally, where there is a chemical reaction between coupling agent and adherend, the product should have optimum water-immersion resistance by not being soluble in water and by being as resistant as possible to hydrolysis.

Coupling agents presently used in glass fiber-reinforced plastics were designed to have an outermost exposed atomic grouping which is

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supposed to react chemically with molecules of the liquid adhesive, for example by vinyl polymerization. One common problem is that γ_c of an adsorbed monolayer of such a coupling agent is too low relative to the surface tension (γ_{LV}) of the liquid adhesive as it is being applied; hence, spontaneous spreading cannot take place. Another problem is that the adherend surface can become contaminated before the coupling agent has been applied. If the coupling agent is applied in advance as a protective film, it must be designed properly to prevent the chemical reactivity of the outermost portion of that film from causing serious problems such as: (a) lower oxidation or thermal stability, (b) ability to adsorb moisture, when in contact with either the atmosphere or the liquid adhesive, or (c) generation of reaction products which may be toxic, corrosive, or otherwise detrimental to joint strength. Item (a) can be a problem with the vinylsilanes. Item (b) can be a problem with a coupling agent having a hydrophilic substituent on the omega carbon. Item (c) is also important, since any harmful reaction products are concentrated within a few angstrom units of the joint interface.

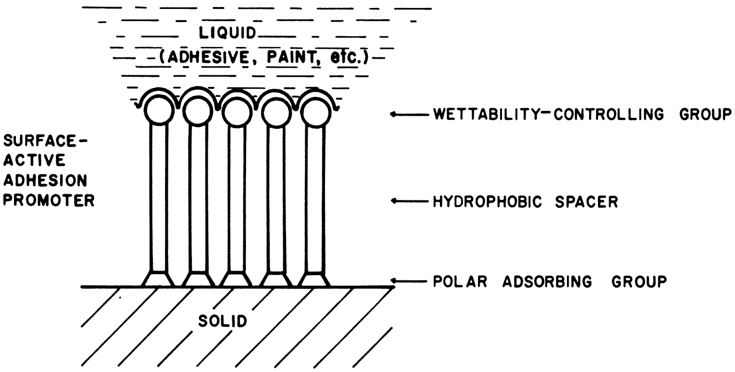

Figure 1. Schematic representation of a surface-active coupling agent

An outermost chemical group having an especially suitable structure for a coupling agent is the *p*-chlorophenyl group (*21*). An adsorbed close-packed monolayer containing such a group will present a surface which is rich in outermost covalently bonded chlorine atoms. Based on much previous research at NRL (*6*), chlorine-containing materials, such as high-energy surfaces coated with certain adsorbed monolayers or many chlorinated vinyl polymeric solids, are known to have outermost surface compositions which are very hydrophobic, are resistant to chlorine hydrolysis, and yet have critical surface tensions of wetting of 40 dynes/cm. or more at 20°C. By attaching to a chlorophenyl group a sufficiently long aliphatic chain in the para position, the chain can serve as a flexible

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Table I. Formulas and Melting Points of

Identifying Symbol	*Name*
	Monocarboxylic acids
A	ω-(*p*-chlorophenyl)acetic acid
B	ω-(*p*-chlorophenyl)dodecanoic acid
	Dicarboxylic acids
C	ω-(*p*-chlorophenyl)dodecylsuccinic acid
D	2-ω-(*p*-chlorophenyl)dodecylglutaric acid

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hydrophobic spacer between the two extremes of the coupling molecule; hence, that molecule can adsorb in the desired monolayer configuration with chlorophenyl group outermost and the carboxylic acid group (or groups) innermost. These considerations led us to prepare and investigate (9) the use of adsorbed monomolecular layers of ω-(*p*-chlorophenyl)-alkyl-substituted mono- and polycarboxylic acids as coupling agents. The use of two or more acid groups per molecule is advantageous because of the resulting decrease in the tendency of heat or solvents to desorb the film. Moreover, carboxylic acid groups should be particularly effective in promoting adsorption and adhesion to "basic surfaces" such as the hydroxyapatite constituent of teeth, many common oxide-coated metals, and various kinds of glasses and ceramics.

To ascertain whether these materials are effective as adhesion promoters and really do operate by the mechanisms proposed above, it was necessary to develop methods suitable for applying the compounds to the solid adherend surface as close-packed adsorbed monomolecular layers and prove that the resulting adsorbed monolayers really had the molecular orientation needed to optimize spreading and wettability. These two topics are the subject of the present paper. Research is in progress on (a) developing the most appropriate techniques for applying these materials in adhesive and coating investigations, (b) investigating the strength and water resistance of the resulting joints and protective coatings, and (c) comparing the results obtained with these and presently used coupling agents.

Experimental Materials and Techniques

The ω-(*p*-chlorophenyl)alkyl derivatives which were investigated are listed in Table I by name, structural formula, and melting point. All four acids were white crystalline solids. The simple letter designation given in the first column will be used hereafter to identify each compound. Compounds B, C, and D are all new compounds, synthesized, purified, and characterized at NRL by our associates, J. G. O'Rear, P. J. Sniegoski, and F. L. James (9). Compound A is a commercial product

ω-(*p*-Chlorophenyl)alkyl-Substituted Carboxylic Acids

Formula	*Melting Point (°C.)*
$ClC_6H_4(CH_2)_nCOOH$	
$ClC_6H_4CH_2COOH$	103-104
$ClC_6H_4(CH_2)_{11}COOH$	64-66
$ClC_6H_4(CH_2)_nCH(COOH)(CH_2)_{x-1}COOH$	
$ClC_6H_4(CH_2)_{12}CH(COOH)CH_2COOH$	87-88
$ClC_6H_4(CH_2)_{12}CH(COOH)(CH_2)_2COOH$	85-86

obtained from K and K Laboratories, Inc. Its purity was 99.0% as determined by P. J. Sniegoski from a gas-liquid chromatographic analysis of its methyl ester similar to that employed to characterize Compounds B, C, and D (*9*). Thus, each preparation was pure enough to be used by us as received. When it was necessary to apply the acid from organic solution, solvents were used which had been carefully purified by distillation and chromatographic adsorption. Aqueous solutions were made using grease-free, singly distilled water.

Adsorption experiments were conducted on chromium, platinum, cadmium, and zinc; the sources and preparation of these metal specimens have been reported previously (*16*). In preparing adsorbed, monomolecular layers by adsorption directly from the molten pure acid (*5*), the clean adsorbing substrate was first heated to a temperature just above the melting point of the acid (*see* Table I), a few crystals of the acid were sprinkled on the surface, and the resulting pool of molten acid was teased over the whole surface with a previously freshly flamed platinum wire. If spontaneous retraction of the liquid acid did not occur, the specimen was allowed to cool and all of the solidified material adhering on top of the adsorbed monolayer was removed by appropriate solvent treatments as discussed below.

The wettability properties of the acid film remaining on the metal were determined by measurements (at 20°C.) of the angle of contact exhibited by sessile drops of a series of purified organic liquids whose source and methods of purification have been described by us elsewhere (*7*). Measurements with a direct reading goniometer telescope (*4, 7*) were made by the drop profile method on the slowly advancing contact angle (θ) obtained by adding successive small increments of liquid to the sessile drop (*19, 20*).

Wetting Properties of Monolayers of ω-(p-Chlorophenyl)dodecylglutaric Acid on Chromium

The new compound, ω-(*p*-chlorophenyl)dodecylglutaric acid (D in Table I), is of particular interest as a coupling agent because it has two potentially active acid adsorbing groups at one end of the molecule. These carboxylic acid groups are separated by a hydrocarbon chain of sufficient flexibility to permit both groups to adsorb simultaneously on the adherend; therefore, the coupling agent should have an increased adsorptivity, as well as a decreased tendency to desorb when hot or exposed to solvents.

Emphasis was first placed on the adsorptive behavior of Compound D on the surface of chromium because that metal has the following desirable properties: (a) it is an excellent adsorbent for carboxylic acid groups (*5*); (b) a large body of data is available on the properties of adsorbed, monomolecular films of aliphatic (*16*), partially fluorinated (*13*), fully fluorinated (*2*), and chloro-fluoro carboxylic acids (*2*); (c) the metal surface can be readily and reproducibly cleaned by standard metallographic polishing techniques; and (d) there is a hard, coherent, thin-film oxide on the surface (*18*).

The "melt method" of applying the adsorbed monolayer was attempted first because the absence of solvent molecules prevents the competition for adsorption sites and the possibility of mixed film formation (*3*). In the past, when the melt method was used for the preparation of films of aliphatic or fluorinated acids, the molten acid spontaneously retracted because the surface tension (γ_{LV}) of the melt was sufficiently larger than the value of γ_c of the monolayer-coated surface (*12, 19, 20*). In the case of the chlorophenyl-substituted carboxylic acids, however, the difference between γ_{LV} and γ_c was not sufficient to promote liquid retraction; hence, the adsorbing surface always remained covered with the bulk acid which coated it with a solidified layer as the specimen cooled. Therefore, to prove the existence of an underlying, adsorbed, condensed, and adherent monomolecular layer of the coupling agent, it was necessary, first, to remove the surplus acid from the surface and, second, to measure various liquid contact angles on the coated surface after successive solvent treatments designed to remove any residual acid not firmly bound to the chromium surface.

Table II presents the results of some wettability measurements on adsorbed monolayers prepared from molten Compound D on pure, polished, clean, chromium surfaces after solvent treatment had been used to remove all surplus solidified acid. A series of successive solvent treatments was applied to each coated specimen (*see* first four columns of Table II) using liquids which have been shown to be good solvents for Compound in the bulk (*9*). These liquids were either absolute ethyl alcohol or benzene at or above 20°C., or *n*-hexane at or above 60°C. In the remaining columns are listed the average values of the slowly advancing contact angles measured by the drop-buildup method on from three to five different drops. Measurements were made on sessile drops of water, thiodiglycol, and methylene iodide. These three "diagnostic" liquids were chosen because of their high surface tensions (72.8, 54.0,

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and 50.8 dynes/cm. at 20°C., respectively) and because they differed greatly in molecular diameter (*17*) and hydrogen-bonding ability. The contact angles of Table II reveal unequivocally that the solvent treatment removed all of the visible coating of D and left behind a surface of the same reproducible wettability with respect to the three diagnostic liquids. The result was the same regardless of the choice of the solvent. As the residual adsorbed film was then found solvent-resistant—*i.e.*, there were no further changes in wettability—it could be concluded that the residual film was only a monolayer thick.

Table II. Solvent Resistance of ω-(*p*-Chlorophenyl)dodecylglutaric Acid Monolayers on Chromium (Monolayer Prepared by the Melt Method[a])

	Successive Treatments on a Single Specimen			*Advancing Contact Angles (in degrees) at 20°C.*		
Solvent	*Temp.*	*Treatment*	*Treatment Period*	*Water 82*	*Thiodiglycol*	*Methylene Iodide*
Specimen #1						
Ethyl alcohol	20°C.	Rinse	5 min. (10 cc.)	82	49	35
Specimen #2						
Ethyl alcohol	20°C.	Rinse	1 min.	81½	49	36½
Ethyl alcohol	20°C.	Rinse	1 min.	82		
Ethyl alcohol	20°C.	Immersion	15 min.	82		
Ethyl alcohol	78.5°C.	Immersion (boiling)	15 min.	81	48½	36½
Ethyl alcohol	—	Soxhlet extraction	15 min.	81½	48½	36
Benzene	—	Soxhlet extraction	15 min.	82		35
Specimen #3						
Benzene	20°C.	Rinse	5 min.	82		34½
Benzene	20°C.	Rinse	5 min.	82		35
Benzene	20°C.	Soxhlet extraction	15 min.	83		34½
Specimen #4						
n-Hexane	—	Soxhlet extraction	15 min.	80	49	33½
n-Hexane	—	Soxhlet extraction	15 min.	79		

[a] Each specimen was prepared by contact for 60 to 90 minutes with the molten acid at from 90° to 96°C.

In addition to the observations on the three diagnostic liquids required to establish the reproducibility of films formed from the melt, contact angle (θ) measurements (Table III, last column) were made on

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several other liquids having surface tensions (γ_{LV}) ranging at 20°C. from 27.6 dynes/cm. for *n*-hexadecane to 63.4 dynes/cm. for glycerol. Figure 2 is a plot of cos θ *vs.* γ_{LV} for the three diagnostic liquids as well as ten additional liquids. The majority of the data points fall within a narrow rectilinear band of approximately the same spread or width and location as were reported by Ellison and Zisman (*6*) for the chlorine-rich surface of smooth, clean, bulk poly(vinyl chloride). By analogy with their treatment of the data for that solid surface, we have used the intercept of the lower limb of the narrow band in Figure 2 to assign the value γ_c = 39 dynes/cm. for the adsorbed monolayer of Compound D. Complete spreading was observed with three hydrocarbon liquids (hexadecane, dicyclohexyl, and 1-methylnaphthalene) whose surface tensions at 20°C. were less than 39 dynes/cm. The one exception to data points falling within the narrow band was ethylene glycol, whose contact angle was higher than would have been predicted on the basis of its surface tension; one possible explanation was that excessive moisture pickup from the air occurred during contact of the liquid with the monolayer-coated surface. No contact angle measurements have been reported previously for ethylene glycol on any other chlorine-rich surfaces to indicate whether this liquid also behaved abnormally on them.

Table III. Effect of Acid Structure on Wettability of Films from Melt[a]

		Contact Angles on			
Wetting Liquids	γ_{LV} *At 20°C. (dyne/cm.)*	*Chlorophenylacetic Acid*	*Chlorophenyldodecanoic Acid*	*Chlorophenyldodecylsuccinic Acid*	*Chlorophenyldodecylglutaric Acid*
Water	72.8	74°	81°	82°	82°
Glycerol	63.4				69°
Formamide	58.2	63°	70°	70°	67°
Thiodiglycol	54.0	42°	50°	51°	49°
Methylene iodide	50.8	33°	33°	32°	34°
Ethylene glycol	47.7				57°
sym-Tetrabromoethane	47.5	26°	25°	25°	25°
α-Bromonaphthalene	44.6	16°	18°	18°	17°
o-Dibromobenzene	42.0				12°
Tricresyl phosphate	40.9				21°
α-Methylnaphthalene	36.4				6°
Dicyclohexyl	32.8		spread	spread	spread
Hexadecane	27.6		spread	spread	spread

[a] Films adsorbed on chromium during 1-hour contact with molten acid; solidified surplus acid removed with ethanol at 20°C.

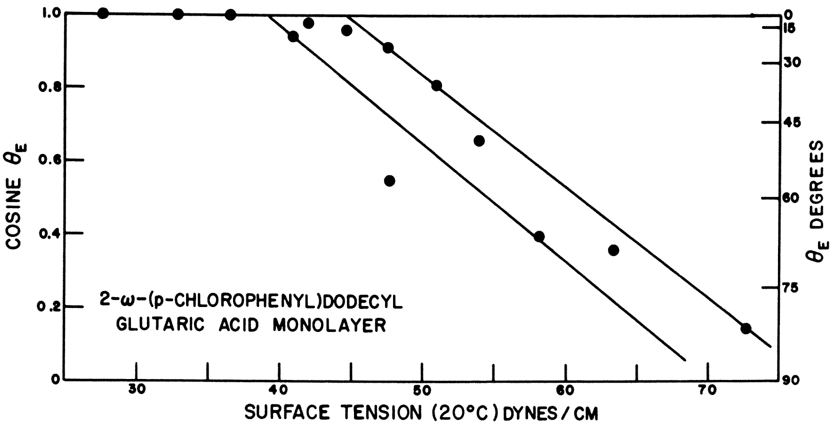

Figure 2. Wettability of ω-(p-*chlorophenyl)dodecylglutaric acid monolayers adsorbed on chromium by the melt method*

Because of the potential application of Compound D as a coupling agent for protective coatings or for dental restorative systems, methods of preparing the monolayer were sought which would not require heating the adherend as much as required in the melt method, but which would nevertheless result in reproducible adsorbed monolayers having the same desired molecular orientation and the closest possible molecular packing. The high γ_c of the monolayer formed by the melt method showed that it would be necessary to use solvents of high surface tension if spontaneous retraction was to be obtained for films formed by adsorption from solution. The theoretically and practically most obvious solvent to use was water. Unfortunately, Compound D is not soluble in water; even the use of added alkali in the water was of little help. Thus far, attempts to isolate the monolayer hydrophobically from aqueous solution have failed. An alternate approach being investigated is to convert the water-insoluble acid into a more soluble form, such as a salt, and form the desired adsorbed monolayer from application of an aqueous solution of the salt at the most suitable pH for that solid substrate (*11*).

Greater success was achieved with aqueous solutions of a nonaqueous component which is miscible with water and is also a good solvent for Compound D. Solutions containing weight concentrations of D from 4×10^{-5} to 2×10^{-4} were tried using weight ratios of from 1:7 to 11:1 of ethanol to water. The metal specimen was always immersed in each solution for one hour at 20°C. Partial or incomplete retraction on chromium was observed for all solutions except those with very high water contents (and consequently, high surface tensions). Complete retraction was observed for the 1:7 ratio; the surface tension corresponding to such

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an aqueous ethyl alcohol solution is 43.8 dynes/cm. (*1*). Despite incompleteness of retraction from solutions containing lower proportions of water, contact angle measurements with distilled water on the retracted areas were all from 60° to 75°. These values are to be compared with the hydrophobic contact angle of 82° characteristic of monolayers obtained by the melt method; they, therefore, indicate hydrophobic contact angles of from 73 to 92% of the value characteristic of the most condensed monolayers. Such high surface coverages by the adsorbed film may prove adequate for many applications of coupling agents since usually it will rarely be practicable to use the melt method, and treatment with an appropriate aqueous solution of Compound D will often be more convenient and safer.

Attempts to increase the contact angles of the diagnostic liquids by changing metal immersion conditions were not effective with the ethyl alcohol–water solutions. These attempts included: (a) increasing the concentration of D by a factor of as much as four, (b) prolonging the immersion period from 1 to 64 hours, or (c) raising the temperature of immersion from 20°C. to 50°C.

When pure ethyl alcohol was used as the solvent for Compound D, no retraction of the solution was observed from a chromium surface immersed for 1 hour at 20°C. After evaporation of the solvent, the coated chromium surface exhibited hydrophobic contact angles ranging from 60° to 70°. However, contact angles of 80° were obtained after the chromium surface had been immersed in the same solution for 19 hours at 50°C.

Nitrobenzene is a fair solvent for Compound D and has a surface tension (43.3 dynes/cm.) which is comparable to the γ_c of films of Compound D formed by the melt method. Dilute solutions of D in nitrobenzene in weight concentrations of from 9×10^{-5} to 6×10^{-4} showed more limited retraction and lower contact angles than were obtained using films prepared by the melt method. Greater success in approximating the high contact angles of films formed from the melt resulted on subjecting the monolayer-coated chromium surface, after removal from the nitrobenzene solutions, to various surface treatments (to be described below) after all molecules of D surplus to the monolayer had been removed.

A most significant result was that the adsorbed films formed on chromium from the molten pure acid at elevated temperatures exhibited the same contact angle, regardless of the application of a variety of postadsorption treatments. These treatments included: (a) immersion in distilled water at 20°C. from 1 to 16 hours, (b) immersion in distilled water at 100°C. for 1 hour, and (c) exposure to steam in a closed system at 125°C. for 1 hour. Such immunity to postadsorptive treatment was

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not observed, however, with films of Compound D formed at 20°C. by adsorption from organic or aqueous ethyl alcohol solution. As previously stated, such films, when initially prepared, exhibited uniformly lower contact angles than those prepared by the melt method. After the following postadsorptive treatments, these coatings invariably showed increased contact angles. The treatments effective in increasing the contact angles included: (a) immersion in distilled water at 20°C., (b) prolonged rinsing with steaming distilled water, and (c) heating for 5 minutes in air at 70°C. and 50% RH. In every instance the contact angle of the diagnostic liquid increased; about half of the postadsorptive treatments increased the contact angles to the values obtained by the melt method. In no case did the contact angle exceed the values observed for the same liquids on films from the melt.

It is concluded that postadsorption exposure to moisture or heat, either singly or in combination. is very effective in increasing the contact angles exhibited by adsorbed monolayers of Compound D on chromium; hence it should also increase the ability of the film to serve as a coupling agent. The effectiveness of heat treatment subsequent to adsorption in increasing the contact angle is consistent with the above observation that the contact angles for a film adsorbed from solution at elevated temperatures are high and approach those for a film adsorbed from the melt.

Effect of Changing the Solid Adherend

The effects of changes in the solid adherend on the wettability of films of acid D adsorbed from the melt are shown in Table IV. The four metals reported here are arranged in order of increasing atomic radii (last column). Experimental values of the contact angles for each of the three diagnostic liquids were closely the same for all four metal adherends. Despite the considerable variation in chemical reactivity and atomic radii of the unoxidized metallic substrates, this finding is reasonable because this dicarboxylic acid molecule can not adlineate well on the surface in close packing, and the flexibility in the aliphatic glutaric acid chain allows the molecule to adsorb about as readily on metals having different metal lattice parameters. Several differences will be observed in the methylene iodide contact angles of Table IV. A value of 36°, which is not significantly different from the value given here for chromium, was observed with zinc, but there was a marked whitening of the underlying zinc and a decrease in the hydrophobic contact angle from 80° to 50° in the surface area attacked. A significantly lower value of 29° was exhibited by methylene iodide on cadmium; however, there was no evidence of chemical attack of this metal surface.

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Table IV. Effect of Metal Adherend on Wettability of ω-(*p*-Chlorophenyl)dodecylglutaric Acid Films from the Melt[a]

			Contact Angles (in degrees)			
Substrate	*Cleaning Procedure*	*Solvent for Removal of Surplus Acid*	*Water*	*Thiodiglycol*	*Methylene Iodide*	*Atomic Radii of Metals*[c]
Chromium	Polished (*11*)	Benzene	82	50+	34	1.27
		Ethyl alcohol	82	49	35	
		n-Hexane (hot)	80	49	33	
Zinc	Polished (*11*)	Benzene	80	50	36[b]	1.38
		Ethyl alcohol	81		35[b]	
Platinum	Flamed foil	Ethyl alcohol	80	48	32	1.39
	Polished bulk material (*11*)	Ethyl alcohol	82	50	35	
Cadmium	Polished (*11*)	Benzene	82	51	29	1.54

[a] Films prepared on metal by contact for 60 to 90 minutes with molten acid at temperatures from 90° to 96°C.

[b] Produced discoloration on surface which could not be removed by ethanol but could be eliminated by metallographic polishing. Discolored area showed a decrease in water contact angle to 50°.

[c] *See* Reference *10.* Radii given in angstrom units.

In addition to film preparation by adsorption from the melt, Compound D was also adsorbed on pure platinum surfaces by adsorption from solution in nitrobenzene, ethyl alcohol, and ethyl alcohol-water solutions. As was true of films adsorbed on chromium, adsorption on platinum from solution resulted in surface coatings exhibiting lower contact angles than those formed from the molten acid. The same post-adsorption treatments were also effective in increasing the contact angles of films of Compound D on platinum.

Effect of Structure and Homology of Coupling Agents

Research is still in progress on the effects of changes in the structures of these new types of acid coupling agents. Some interesting comparisons can be made between the mono- and dicarboxylic acids containing the same ω-(*p*-chlorophenyl) substituent attached through a long aliphatic chain.

The insensitivity of wettability to changes in the dicarboxylic acid portion of the molecule is revealed by comparison of the data in Table III for the sustituted succinic acid (column five) and the substituted glutaric acid (column six).

Similarly, no significant change in wettability is observed when the dicarboxylic segment of the molecule is replaced by a single carboxyl

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group as in the case of the ω-(*p*-chlorophenyl)dodecanoic acid (column four), when prepared by the melt method. Monolayers of this same acid (Compound B) adsorbed on chromium from ethyl alcohol solution at 20°C. exhibited lower hydrophobic contact angles (71° to 75°). Subsequent application of moist heat to the surface films, however, resulted in wettability comparable to that for films formed from the melt—*i.e.*, contact angles of 82°, 53°, and 37° for water, thiodiglycol, and methylene iodide, respectively.

The above data indicate that the packing of the terminal substituents in the close-packed monolayer is the same for both the mono- and dicarboxylic acids. This becomes understandable from consideration of the molecular models. In Figure 3 the silhouettes of Stuart-Briegleb molecular models from Compounds B and D are shown. Both three-dimensional models were arranged to be as coplanar as possible so that differences in molecular cross-sectional areas could be judged from differences in their silhouettes in the plane containing the maximum number of carbon atoms. For both compounds this arrangement involved having the chlorophenyl substituent tilted with respect to the long axis of the extended aliphatic chain so that all phenyl carbon atoms could be in the same plane as the zigzag arrangement of aliphatic carbon atoms. A slight rotation toward the lower end of the alkyl chain would be sufficient in Compound D to bring the plane of the extended-chain glutaric acid moiety into coplanarity with most of the carbon atoms of the substituent in the 2-position. Such a rotation would increase the maximum dimension of the molecule perpendicular to the silhouette shown since the overall thickness of the chlorophenylalkyl substituent is determined by the alkyl chain. This increase might be easily accommodated, however, in the relatively open space around the alkyl chain.

Figure 3 makes it apparent that the size of the chlorophenyl group limits the closeness of packing of the Compound B molecules if they adsorb in the configuration shown. In the case of Compound D, however, the limitation to close-packing in the plane of the projection is due to the glutaric acid moiety when in extended configuration. Closer packing might be attainable if the flexibility of the hydrocarbon chain between the two carboxylic acid groups facilitates their closer approach. Figure 3 also reveals that the differences in cross-sectional area between the chlorophenyl group and the glutaric acid moiety are not large; therefore, it is unlikely that the configuration of the latter can be deduced solely by contact angle considerations.

An interesting effect of varying the structure of the acids can be seen on comparing the behavior of films of two dicarboxylic acids differing in the length of chain between the acid groups. Studies in progress have found that films of the substituted succinic acid (Compound C),

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adsorbed on chromium after prolonged contact with dilute nitrobenzene solution, exhibited contact angles of 80°, 50°, and 32° for water, thiodiglycol, and methylene iodide, respectively. The closeness of these results to those reported above for Compound D is evident. As predicted, the wettability of all these new acid coupling agents is determined by the chemical constitution of the exposed chlorophenyl group, with little or no effect on wetting properties arising from minor variations in packing density owing to the nature of the polar adsorbing groups. The latter, however, may have a profound effect on the ease and strength of attachment of the adsorbed adhesion promoters on adherends of different physical and chemical properties.

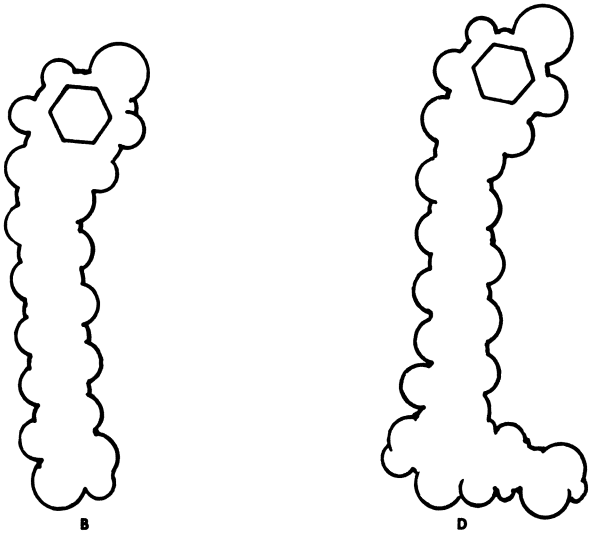

Figure 3. Silhouettes of molecular models of Compounds B and D in their extended configurations

Methods of Applying Coupling Agents

The melt method of preparing adsorbed monolayers of these coupling agents is well suited to establishing that monolayer adsorption occurs with the predicted molecular orientation, but it has several obvious disadvantages for application of these materials under practical conditions. These disadvantages include the requirement for elevated temperatures (intolerable for many biological and dental applications), the inefficient use of the coupling agent, and the necessity for solvent or mechanical removal of excess agent material. Therefore, appropriate investigations are required to determine the most suitable way to apply the film of coupling agent for each contemplated use.

Results of studies of monolayers adsorbed from organic solution reported above indicate the feasibility of incorporating the agent molecule directly in a liquid paint or adhesive formulation. By appropriate changes in the length of the aliphatic chain in the molecule, it is possible to alter the solubility of the coupling agent to suit its application in many organic solvents. Ideally, the solubility of the coupling agent in the protective coating or adhesive should be large enough to allow there to be a reasonable working concentration in the liquid phase but it should not be so large that the molecule will have a short average lifetime of adsorption at the adherend/liquid interface.

For application of the coupling agent as a primer coating, it is desirable to have a method of application that: (a) can be used at room temperature, (b) will give spontaneous retraction of the generating solution, and (c) will involve the use of solvents which are inexpensive, nontoxic, and nonflammable. Unfortunately, the deliberate building in of a high γ_c in the monolayer of coupling agent restricts the choice of solvents to liquids which have high surface tensions as well as appropriate solvency at room temperatures.

The most desirable liquid to use as a solvent would be water, from the standpoints of surface tension, cost, toxicity, and freedom from fire hazards. However, Compounds B, C, and D are not sufficiently water soluble to permit their isolation as hydrophobic monolayers from aqueous solution (*11*). Nevertheless, homologous acids having lower proportions of hydrophobic to hydrophilic substituents are available which do have appropriate water solubilities.

As an example, hydrophobic monolayers of chlorophenylacetic acid (Compound A) can be prepared from aqueous solution. The variation in their hydrophobic behavior with changes in pH (owing to added acid or alkali) and with solution concentration proved identical with that reported previously by us for other carboxylic acids (*11*). Thus, sessile drops of water exhibited their highest or "peak" contact angle (θ_p) on films prepared over a comparatively limited pH range and one that was closely associated with the "natural" pH of the solution. At any given solution concentration, decreasing the pH from the peak range resulted in an abrupt decrease in hydrophobic contact angle or even failure of the aqueous solution to show retraction. Increasing the pH above the peak range also resulted in a decrease in hydrophobic contact angle, but it was more gradual, leading to a "plateau" region occurring unsymmetrically on the alkaline side of the peak in the θ-*vs*-pH curve. As before (*11*), increases in solution concentration shifted the peak pH region to a more acidic range, increased the pH range over which hydrophobic behavior could be obtained, and increased the value of θ_p. Eventually, however, a solution concentration was reached above which further

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increases in concentration did not affect θ_p. The limiting value of θ_p = 64° was obtained for distilled water on films of Compound A adsorbed from concentrations of 7.5×10^{-4} and 3.9×10^{-3} moles/liter. This is to be compared with the water contact angle of 74° reported for films of this same acid formed by the melt-retraction method (third column of Table III). It should be noted that there was no difference in the contact angle of methylene iodide on films of A from the melt (33°) and from aqueous solutions of the concentration and pH range corresponding to peak hydrophobic behavior (33°). Not unexpectedly, significantly lower values of the methylene iodide contact angle were observed on films which did not exhibit maximum hydrophobic behavior.

Finally, the contact angles for organic liquids with surface tensions below 50 dynes/cm. were not greatly different on melt-formed monolayers of A than on comparably formed monolayers of B, C, and D—*cf.* Table III. Thus, the value of γ_c for Compound A also is in the desirable range for improving adhesion. Ultimate conditions of usage of the adhesive joint—*i.e.*, in the presence or absence of moisture, bulk water, etc.—should therefore determine whether water-insoluble coupling compounds with their protective, long, aliphatic spacers should be employed or whether the conveniently applied water-soluble acids should be preferred.

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Conclusion

The results presented here prove that these new carboxylic acid coupling agents do adsorb strongly on a variety of high-energy surfaces in the specific orientation (chlorine atoms outermost) which had been predicted (*2*) to be most useful for improving adhesion. In so doing they present an outermost surface specifically designed to have good wetting by most liquid adhesives, high resistance to oxidative or hydrolytic attack, and limited tendency to adsorb aqueous or organic contamination. The lack of retraction observed for the generating medium from the monolayer-coated surface is evidence of how well the adsorbed monolayer fulfills the requirement for good wetting by organic liquids. Moreover, the resistance of the monolayer to solvent extraction and washing treatments, which are far more rigorous than those required to remove bulk acid, provides evidence of how strongly adsorbed and resistant to removal these agent films are.

Research is continuing on new and more convenient methods of applying the acid agents and on the behavior of the agents on metals other than those reported here. Work also is in progress on certain nonmetallic surfaces which might be expected to interact with carboxylic acid coupling agents, such as certain types of glass, α-alumina, hydroxyapatite, certain ceramics, and some minerals.

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4

The Wettability of Ethyl- and Vinyltriethoxysilane Films Formed at Organic Liquid Silica Interfaces

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Adsorbed films of ethyltriethoxysilane and vinyltriethoxysilane were formed on silica and alumina by retraction from hydrocarbon solution and their wettabilities and water-stabilities determined. The vinyltriethoxysilane films were generally more oleophobic, more hydrophobic and more resistant to contact with water than the films formed by the ethyl analog. Neither adsorbate formed stable films on α-alumina. The addition of low molecular weight organic acids or bases to the adsorbate solution resulted in both the ethyl and vinyl compound forming hydrophobic and water-stable films on silica and α-alumina. Films of p-*chlorophenyl-β-ethyltrichloro, -trimethoxy, and -triethoxysilane were also studied and found to be water-stable and to have wettabilities characteristic of a surface comprised of closely-spaced* p-*chlorophenyl groups.*

Various trialkoxysilanes have been found to improve the adhesion of organic polymers to glass and other inorganic solids, especially when the bond is to be exposed to high relative humidities. For example, glass filament-resin composite materials are seriously degraded by water (*5*), the attack presumably occurring at the glass/resin interface. However, this water sensitivity can be reduced by applying certain trialkoxysilanes as finishing agents to the glass fiber. Little is known about the mechanism by which the trialkoxysilanes improve the wet strength of adhesive bonds. It is generally assumed that the mechanism involves the adsorption of the trialkoxysilane at the resin/substrate interface to form a "bridge" between adhesive and adherend (*17*). It would appear from available evidence that alkoxysilanes can be specifically adsorbed at

In Interaction of Liquids at Solid Substrates; Alexander, A.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1968.

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liquid/glass interfaces (*18*) and that this adsorption involves an interaction with the silanol groups, ~Si—OH, on the substrate surface (*2*, *8*).

The present paper describes the adsorption of ethyltriethoxysilane (ETES) and vinyltriethoxysilane (VTES) at various organic-liquid/silica interfaces. Films formed by these compounds on silica and glass from solution in nonpolar organic liquids were found to be oleophobic and so could be isolated by retraction; that is, the substrate on which the films had been formed emerged dry from the solution, thus allowing direct examination of the adsorbed layer.

This paper also deals with the adsorption of β-(*p*-chlorophenyl)ethyltriethoxy- and trimethoxysilanes which, because of the terminal *p*-chlorophenyl group, should form resin-wettable films. In the manufacture of glass-resin-composites it is critically important that the impregnating resin liquid spontaneously spread over the finish coating on the glass. Zisman (*21*) has suggested finishing agent molecules having terminal *p*-chlorophenyl groups since adsorbed films of these molecules will expose a close-packed array of *p*-chlorophenyl groups at the air/film interface and, as a result, will have critical surface tensions greater than 40 dynes/cm. The majority of resin liquids will spread spontaneously on surfaces having critical surface tensions greater than 40 dynes/cm. Shafrin and Zisman have shown that monolayers of *p*-chlorophenyl-terminated alkyl carboxylic acids on metals do have critical surface tensions of 40-45 dynes/cm. (*14*).

Experimental Procedures

Materials. The ethyltriethoxysilane (b.p. 159°-161°C. at 760 mm. Hg, $n_D^{20} = 1.3912$) and vinyltriethoxysilane (b.p. 160°C. at 760 mm. Hg, $n_D^{20} = 1.4257$), were obtained from Union Carbide Corp., Silicones Division. They were distilled and stored in desiccators. The β-(*p*-chlorophenyl)ethyltrichlorosilane (b.p. 95°C. at 0.5 mm. Hg, $n_D^{20} = 1.5313$), -triethoxysilane (b.p. 114°C. at 0.5 mm. Hg, $n_D^{20} = 1.4757$) and -trimethoxysilane (b.p. 105°C. at 0.3 mm. Hg, $n_D^{20} = 1.4883$) were prepared by J. G. O'Rear at this laboratory (*9*). The solvents from which these materials were adsorbed, α-chloronaphthalene and monoisopropylbicyclohexyl, and the organic liquids used for contact angle measurements, were reagent grade chemicals from which polar contaminants had been removed by percolation through activated adsorbents. The organic acids and bases listed in Tables I, II, and III were obtained as reagent grade chemicals and were used without further purification.

A solution containing both the ethyltriethoxysilane monomer and its polymeric hydrolysis products was prepared by shaking a 1% (by wt.) solution of the distilled monomer in α-chloronaphthalene with aqueous 0.01*N* HCl. The two phases were shaken intermittently for about four weeks until a finely divided precipitate—presumably polymeric material—appeared in the aqueous phase. The two phases were then separated. The organic phase was washed first with 0.1*N* $NaHCO_3$, then with distilled water until the washings were neutral, and finally centrifuged to remove dispersed water.

Table I. The Wettability of Films Produced by Ethyltriethoxysilane with Organic Acids and Bases

			Film Wettability			
			initial		*after 1 hr. water "desorption" test*	
Added Catalyst	*ETES/ Catalyst mole ratio*	*Substrate*	γ_c^* *dynes/ cm.*	θ_{H_2O} *deg.*	γ_c^* *dynes/ cm.*	θ_{H_2O} *deg.*
None	—	silica, air-dried	33	63	—	41
None	—	silica, flamed	34	70	—	50
propionic acid	20	silica, air-dried	24	71	—	70
propionic acid	4	silica, air-dried	26	73	26	62
bromopropionic acid	4	silica, air-dried	26	73	25	63
acetic acid	10	silica, air-dried	30	81	—	70
acetic acid	10	silica, flamed	32	96	—	104
n-propylamine	10	silica, air-dried	30	97	32	90
n-propylamine	4	silica, air-dried	36	104	36	105
n-propylamine	4	silica, flamed	38	105	38	105
n-propylamine	4	α-alumina, air-dried	35	101	35	101
piperidine	4	silica, air-dried	30	89	31	91
pyridine	4	silica, air-dried	27	76	30	63

Table II. The Wettability of Films Produced by Vinyltriethoxysilane with Organic Acids and Bases

			Film Wettability			
			initial		*after 1 hr. water "desorption" test*	
Added Catalyst	*VTES/ Catalyst mole ratio*	*Substrate*	γ_c^* *dynes/ cm.*	θ_{H_2O} *deg.*	γ_o^* *dynes/ cm.*	θ_{H_2O} *deg.*
none	—	silica, air-dried	30	80	—	44
none	—	silica, flamed	24	80	—	72
acetic acid	10	silica, air-dried	30	78	—	63
acetic acid	10	silica, flamed	36	90	34	80
n-propylamine	4	silica, air-dried	no retraction		35	103

The silica surfaces used were fused silica microscope slides (1 × 2 × 1/16 inches, A. H. Thomas and Co.) and the alumina surfaces were 3/4 inch diameter, 1/8 inch thick, synthetic, α-alumina discs (synthetic sapphire, Linde Division, Union Carbide Corp.). The specimens were cleaned by heating in a mixture of equal parts of sulfuric and nitric acid, given a preliminary rinse in hot tap water and then soaked in three suc-

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cessive baths of hot distilled water. The specimens were then dried in a clean glass oven at about 100°C. for 15-30 min. Surfaces prepared in this fashion are referred to in this report as "air-dried." Flamed surfaces were prepared by playing the flame of an oxyhydrogen torch over the surface of an air-dried specimen, holding the flame at each position until the area showed white heat. After these cleaning and drying procedures the specimens were completely wet by water, indicating that the surfaces were not contaminated by organic material.

Table III. The Wettability of *p*-Chlorophenylethylsilane Films on Silica[a]

	Wettability				
	initial		*after water "desorption"*		
Adsorbate	γ_c^* *dynes/cm.*	θ_{H_2O} *deg.*	γ_c^* *dynes/cm.*	θ_{H_2O} *deg.*	*Method of Forming Film*
p-$ClC_6H_4CH_2CH_2$-$SiCl_3$	42	83	42	85	Vapor deposition at 25°C. for 10 min.
p-$ClC_6H_4CH_2CH_2$-$Si(OCH_3)_3$	43	81	43	81	Vapor deposition at 70°C. for 10 min.
p-$ClC_6H_4CH_2CH_2$-$Si(OC_2H_5)_3$	no retraction		43	86	1% adsorbate + 0.1% *n*-propylamine in α-chloronaphthalene for 20 hours
p-$ClC_6H_4CH_2CH_2$-$Si(OCH_3)_3$	—	30	—	<20°	Vapor deposition at 25°C. for 30 min.
p-$ClC_6H_4CH_2CH_2$-$Si(OCH_3)_3$	39	71	40	60	1% adsorbate in α-chloronaphthalene for 20 hours
p-$ClC_6H_4CH_2CH_2$-$Si(OC_2H_5)_3$	no retraction		43	56	

[a] Air-dried.

Methods. The adsorption studies were carried out by immersing the clean substrate specimen in the adsorbate solution for a specified length of time, withdrawing it slowly, and allowing the solution to retract from the film-coated surface. The solvents were selected to have high enough surface tensions (γ_{LV}) to retract from the majority of the adsorbed films encountered in the experiments. All solution preparations and adsorption experiments were conducted in glove bags maintained at 25°C. and at 400–800 p.p.m. of water vapor by a positive pressure of air that had been passed over Drierite and molecular sieves.

The adsorbed films were characterized by determining the critical surface tension (γ_c) of each by the method of Zisman (*20*) which consists of determining the advancing contact angle exhibited on the adsorbed film by each member of a series of test liquids. The cosines of the contact angles ($\cos \theta$) are plotted against the surface tensions of the test liquids. A straight line is obtained and the intercept of this line with $\cos \theta = 1$ is the critical surface tension value for the adsorbed film. Because of the somewhat unusual nature of the films investigated in this study, the critical surface tension is designated as γ_c* rather than the conventional symbol, γ_c. The reason for this choice is that there are limitations to the significance of the critical surface tension values obtained here. These limitations are partly because of the wide range in polarity of the test liquids used. The choice of these liquids was necessary to cover with a single set of liquids the range of critical surface tensions presented by the adsorbed films studied. The preferred test liquids would be the *n*-alkanes since many of the literature values of γ_c were determined using this homologous series but, unfortunately, the *n*-alkanes do not cover the range of surface tensions needed. In one instance, where a comparison between the *n*-alkanes and the miscellaneous liquids was possible (Figure 1), it was found that the miscellaneous group gave an estimate of 21 dynes/cm. compared with a value of 26 dynes/cm. from the *n*-alkanes. For surfaces of higher γ_c* the discrepancy between the two series is probably smaller because the extrapolation to cos θ = 1 is shorter.

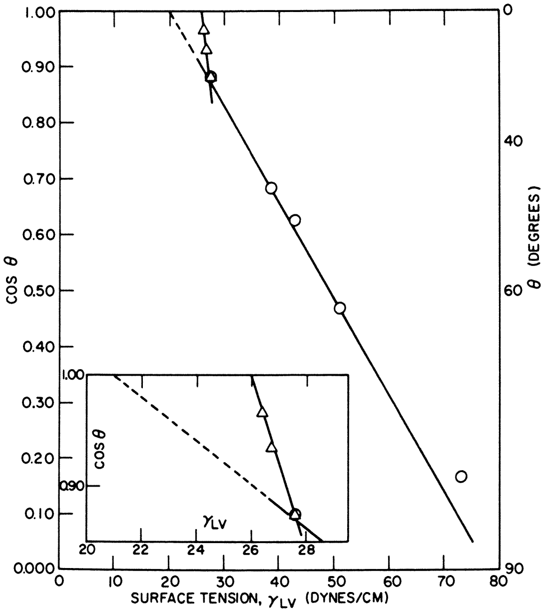

Figure 1. Comparison of cos θ vs. γ_{LV} *plots for the* n*-alkanes (—△—) and the test liquids of this study (—○—) on a triethoxysilane film. (VTES on flamed silica after 20 hrs. from a 5% solution in α-chloronaphthalene)*

The test liquids used to determine γ_c* were hexadecane (γ_{LV} = 27.6 dynes/cm.), bicyclohexyl (γ_{LV} = 33.0 dynes/cm.), α-methylnaphthalene (γ_{LV} = 38.6 dynes/cm.), α-chloronaphthalene (γ_{LV} = 42.9 dynes/cm.), methylene iodide (γ_{LV} = 50.8 dynes/cm.) and water (γ_{LV} = 72.8 dynes/cm.). All contact angle measurements were made at about 45%

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RH and at 25°C. using the sessile drop method. Surface tensions were measured at 25°C. using the duNouy ring method. Unless otherwise noted in the text, the contact angles were reproducible to ±2° and the critical surface tensions to ±0.5 dynes/cm.

The effect on the films of prolonged contact with water was determined by allowing water to fall dropwise onto the film-covered substrates for a specified length of time. The effect of this treatment was judged by determining the water contact angle and critical surface tension for the area of the test surface struck by the water drops and comparing this value with that of the original film. The drops fell from a height of 30 cm. at a rate of 2 drops/second. The test plates were held in a Büchner funnel at an angle of about 20° to the horizontal. Under these conditions the drops flash-spread over about one-half the area of the specimen surface and each drop ran off the plate into the funnel before the next drop struck. For simplicity, this test is referred to as the "water desorption test" even though changes other than physical desorption are involved.

Results

Ethyltriethoxysilane (ETES). The critical surface tensions of the ETES films obtained on silica by retraction from 1% solutions in α-chloronaphthalene are plotted in Figure 2A. The adsorption time—*i.e.*, the abscissa—is the time the silica substrate was allowed to remain in contact with the adsorbate solution. Adsorption times longer than 20 hours did not produce any further decrease in $\gamma_c{}^*$ and solutions containing 0.1% and 5% ETES gave values within 1 dyne/cm. of those in Figure 2A. Attempts to obtain ETES films from solution in isopropylbicyclohexyl were unsuccessful—the solutions did not retract from the test surfaces even after 20 hours adsorption time. Isopropylbicyclohexyl has a surface tension of 34.4 dynes/cm. so if the ETES adsorbed to form films having $\gamma_c{}^*$ values of 33-35 dynes/cm., as it had from α-chloronaphthalene, then the bicyclohexyl solution would not be expected to retract.

The contact angles exhibited by water on the ETES films were anomalous in that in plots of cos θ *vs.* γ_{LV} they frequently did not fit the straight line relationship exhibited by the data for the organic liquids. An example of the failure of the water contact angle to correlate with the organic-liquid data is given in Figure 3. For long adsorption times, 10–20 hours, the deviation of the water data points from the straight line decreased but the anomaly did not disappear even after 170 hours. In addition, the water contact angles were difficult to reproduce. The values changed measurably after only a few seconds on the surface and it was rarely possible for a water drop to slide freely over the surface when the test plate was tilted. This behavior was in distinct contrast to that of the organic liquids for which the contact angles were generally reproducible and stable, with the drops easily mobile over the surfaces.

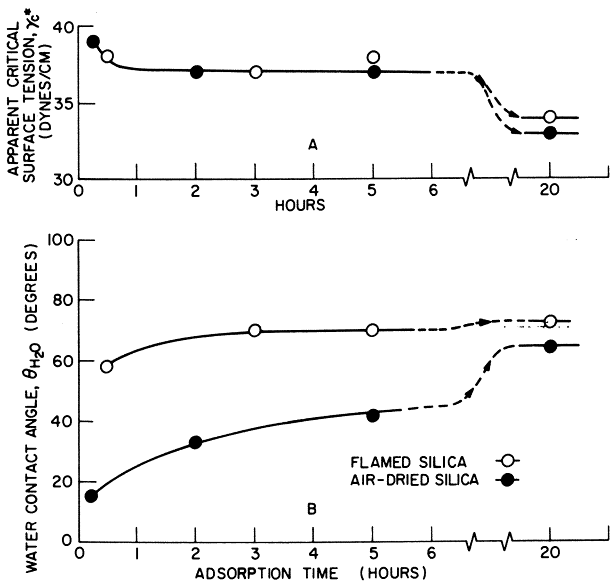

Figure 2. The change in apparent critical surface tension (A) and water contact angle (B) with adsorption time for ETES films on air-dried silica (—●—) and on flamed silica (—○—). (1% ETES in α-chloronaphthalene)

In view of the singular behavior of water on these ETES films, it was the general practice in this investigation to determine the value of γ_c^* using only the organic liquids and to plot the water contact angles separately as a function of adsorption time. In Figure 2B the water contact angle data are presented for the films formed on silica by ETES from a 1% solution in α-chloronaphthalene. The angles for the films on flamed silica were consistently higher than the corresponding angles for films on air-dried silica although after 20 hours adsorption time they approached the same value.

ETES films could not be obtained on alumina substrates by retraction. Retraction did not occur from solutions of the triethoxysilane even up to concentrations of 5%, and adsorption times of many days. This was the case using both air-dried and flamed alumina and for α-chloronaphthalene or isopropylbicyclohexyl as the solvent.

The water desorption test of the ETES films on silica showed a continuous decrease in the water contact angle, θ_{H_2O}, for desorption times up to 60 min. (Figure 4). There was a simultaneous decrease in the organic liquid contact angles—and thus an increase in γ_c^*—but these changes were less pronounced than the changes in θ_{H_2O}.

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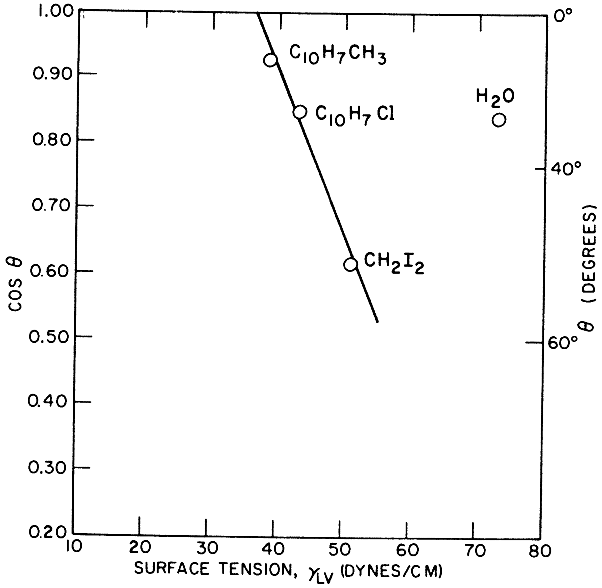

Figure 4. The change in θ_{H_2O} in the water "desorption" test for ETES films on silica. (1% ETES in α-chloronaphthalene)

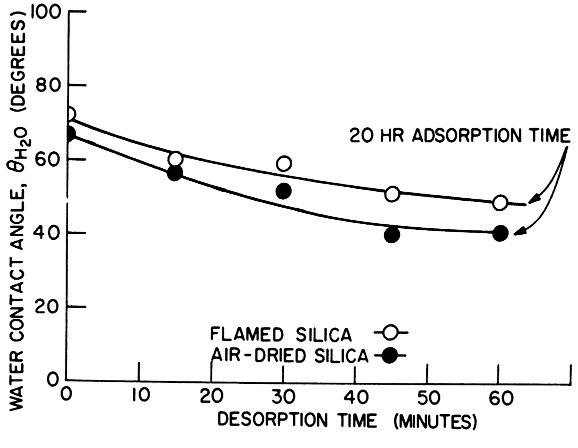

Figure 3. The failure of θ_{H_2O} to correlate with the organic liquid wetting data in γ_{LV}-cos θ plots. (ETES on air-dried silica after 2 hrs. from 1% solution in α-chloronaphthalene)

Vinyltriethoxysilane (VTES). The vinyltriethoxysilane films obtained on silica were more oleophobic (lower γ_c* values) and more hydrophobic (higher θ_{H_2O} values) than the films formed from corre-

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sponding ETES solutions. In Figure 5 the wetting data are presented as a function of adsorption time for the VTES films from α-chloronaphthalene solutions on flamed silica. The most interesting feature of these data was the pronounced concentration effect. For each concentration there was a different limiting value of γ_c^* and θ_{H_2O}; the higher concentration solutions had lower γ_c^* and higher θ_{H_2O} limits than the dilute solution. In addition the rate of film formation indicated by the decrease in γ_c^* was greater the higher the concentration.

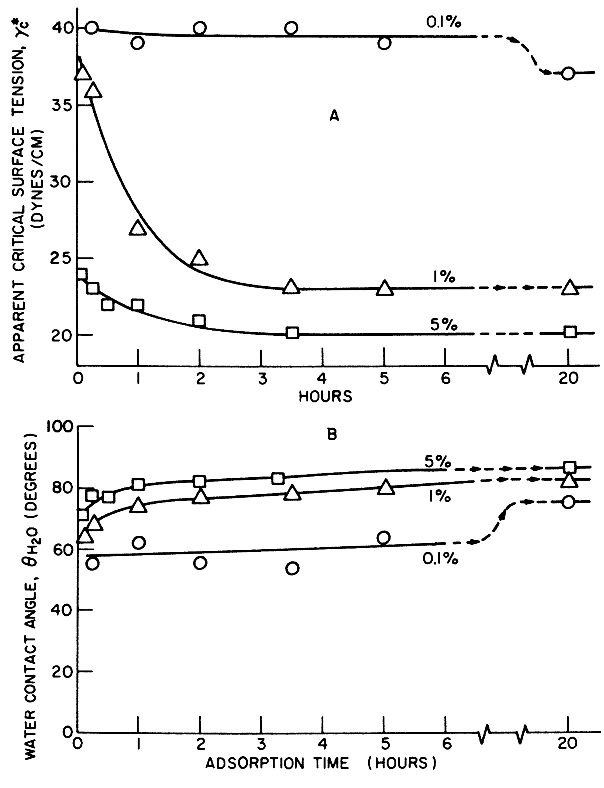

Figure 5. Effect of adsorbate concentration on the change in apparent critical surface tension (A) and water contact angle (B) with adsorption time for VTES films on flamed silica

The results obtained for VTES on air-dried silica are presented in Figure 6. They indicate a concentration effect although the behavior is more complex than that of the films on flamed silica. For the more concentrated solutions γ_c^* passes through a minimum with increasing contact time. The minimum was reached most quickly in the most concentrated solutions. Subsequent to the minimum the increase in γ_c^* was

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complete within 20 hours adsorption time although the final γ_c^* attained was seldom the same from one experiment to the next. For instance, γ_c^* values from 28 to 32 dynes/cm. were observed after 20 hours adsorption time for the 1% solution.

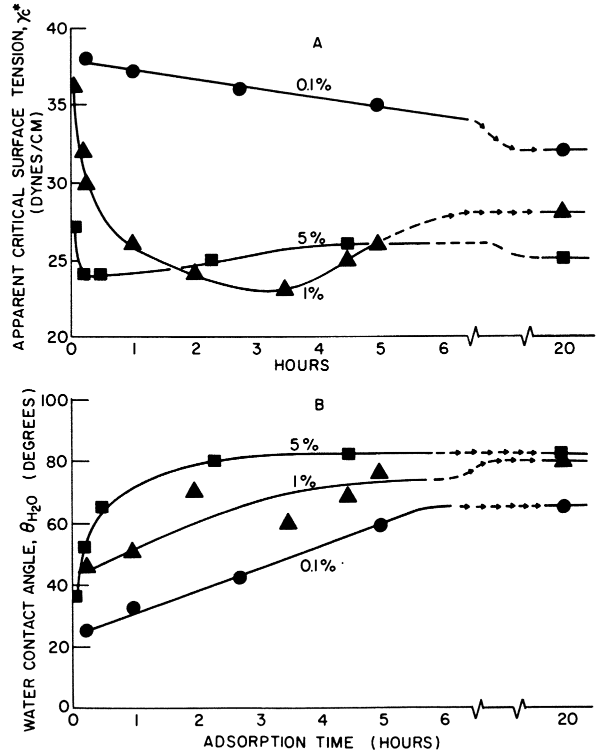

Figure 6. Effect of adsorbate concentration on the change in apparent critical surface tension (A) and water contact angle (B) with adsorption time for VTES films on air-dried silica

The water contact angle data for VTES on air-dried silica (Figure 6B) indicate a gradual increase in θ_{H_2O} with time. The rate of increase and the ultimate value of θ_{H_2O} after 20 hours adsorption time were both greater at the higher concentrations.

The θ_{H_2O} values for the VTES films were anomalously low on air-dried silica, as had been found for the ETES films. The anomaly persisted even when the adsorption time was extended to many days. On flamed silica, however, the anomaly was small or did not appear at all for films obtained from the 1% and 5% solutions after 2 hours or more adsorption time.

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In the water desorption test the VTES films on flamed silica proved to be more resistant to change than the VTES films on air-dried silica. This difference is illustrated by the data in Figure 7. On air-dried surfaces after one hour adsorption time the VTES produced a film that initially had a low water contact angle and was not significantly altered in the desorption experiment. By allowing 20 hours contact with the solution a more hydrophobic film was obtained but it was quickly "desorbed" to a condition equivalent to that for only an hour adsorption time. On flamed silica, in contrast, the film adsorbed after 20 hours adsorption time showed only a slight tendency to lose its hydrophobic character.

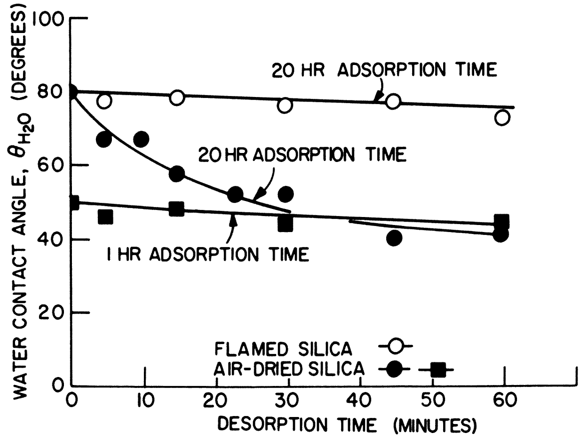


Figure 7. The change in θ_{H_2O} in the water "desorption" test for VTES films on silica (1% VTES in α-chloronaphthalene)

VTES films could be obtained on α-alumina by retraction from VTES-(α)-chloronaphthalene solutions. This contrasts with the failure of ETES solutions to retract from α-alumina. However, neither the organic liquid or water would give stable contact angles on the films formed by VTES.

Acid-Base Catalyzed Adsorption. It was found that the addition of low molecular weight organic acids and bases to the adsorbate solutions produced ETES and VTES films that were much more hydrophobic and resistant to the water desorption test than the films formed by the triethoxysilanes alone. Tables I and II list the values of γ_c* and θ_{H_2O} for the films produced in the presence of various acids and bases. Also included are the data for the films formed by ETES and VTES alone. In all cases the adsorption time was 20–24 hours, the solvent was α-chloronaphthalene and the triethoxysilane concentration was 1% by weight.

The adsorption process was apparently complete within 20 hours since the same γ_c^* and θ_{H_2O} values were obtained at 48 hours and 72 hours. Note that without ETES or VTES present, solutions of these acids and bases in α-chloronaphthalene did not retract from the silica test plates.

Before reaching the values listed in Tables I and II, γ_c^* usually went through a minimum within 1–3 hours adsorption time. Two examples of this minimum are shown in Figure 8A. For these same films θ_{H_2O} increased continuously as indicated in Figure 8B. The water contact angle, θ_{H_2O}, increased rapidly during the first three hours of adsorption and then more slowly to the final value at 20 hours. These changes in γ_c^* and θ_{H_2O} with adsorption time are typical of all the films formed by the trialkoxysilanes in the presence of an acid or base.

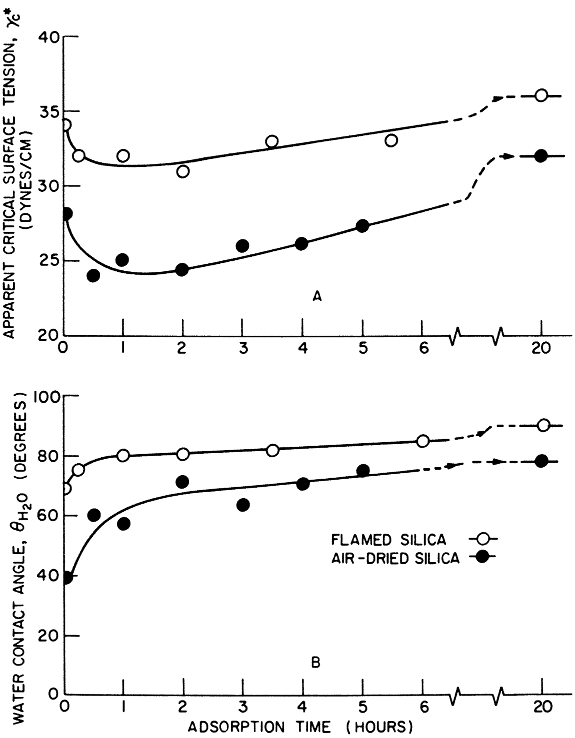


Figure 8. Adsorption of ETES in the presence of acetic acid. The change in apparent critical surface tension (A) and water contact angle (B) with adsorption time for films on flamed silica (—○—) and air-dried silica (—●—). (1% ETES and 0.03% acid in α-chloronaphthalene)

The resistance of these films to alteration in the water desorption test is also indicated in Tables I and II and further illustrated by the data in

Figure 9. For the most part, the films produced in the presence of acids and bases were highly resistant to change in the water desorption test—even the film formed on alumina (Table I). Some exceptions to this water stability were the ETES and VTES films formed on air-dried silica using the organic acids (Tables I and II) and the ETES film produced using pyridine as the catalyst.

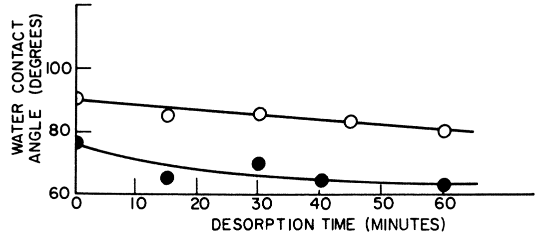


Figure 9. The change in θ_{H_2O} in the water "desorption" test for ETES films formed on silica using acetic acid catalyst. —O— flamed silica, —O— air-dried silica (20 hrs. adsorption time, 1% ETES, and 0.03% acetic acid in α-chloronaphthalene)

Retraction of the solutions containing *n*-propylamine with ETES or VTES was often incomplete or failed to occur at all. When one of these solutions did retract it did so very slowly, taking up to 10 minutes to clear the surface; normally retraction takes only a few seconds. It was noticed that failure to retract or to retract completely was almost always associated with the appearance of a finely divided precipitate in the adsorbate solution. No difficult retraction or precipitate formation was encountered in using the other acid or base catalysts. In fact, difficult retraction was observed only for the *n*-propylamine-containing solutions when the ETES (or VTES)-amine mole ratio was 4 to 1. Normal retraction occurred for the solution of ETES and *n*-propylamine at a mole ratio of 10.

If retraction was incomplete, the silica or alumina plates were subjected to the "water desorption test," and it was consistently found that the water displaced the thin visible layer of adsorbate solution. This water treatment left the surface dry and free of visible film: γ_c^* and θ_{H_2O} determinations were made on these "washed" surfaces (Table II).

To determine the effect of polysiloxane molecules in the adsorbate solution on film properties, a solution was prepared containing polymerized ETES as well as the ETES monomer. This solution was used to generate films on air-dried silica. The changes in γ_c^* and θ_{H_2O} with adsorption time are indicated in Figures 10A and 10B. The $\gamma_c{}^*$ values were low even after 20 hours adsorption time and the limiting values of θ_{H_2O} was approached rapidly. In the water desorption test these films proved to be very stable (Figure 10C). Retraction was quite rapid from these solutions and no precipitate appeared in the solution during the adsorption experiments, although one did appear after the solution had stood for many days.

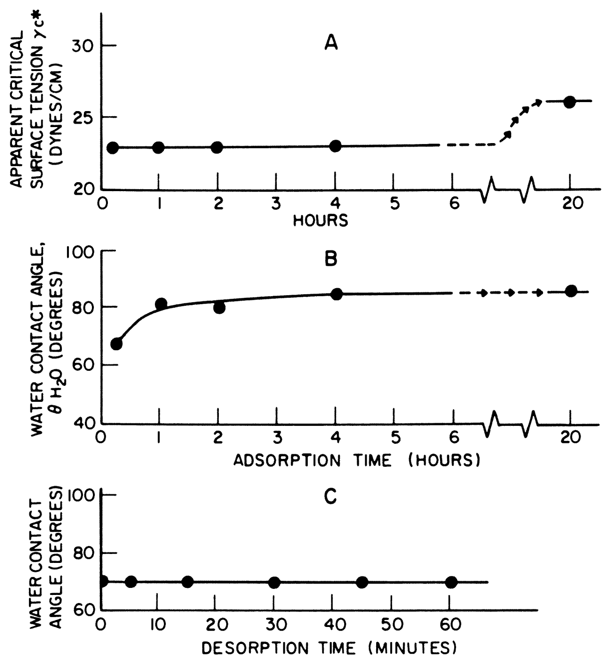


Figure 10. The properties of films generated by an ETES polymer-monomer solution on air-dried silica. The change in $\gamma_c{}^*$ (A) and θ_{H_2O} (B) with adsorption time and the change in θ_{H_2O} (C) in the water desorption test (20 hrs. adsorption time)

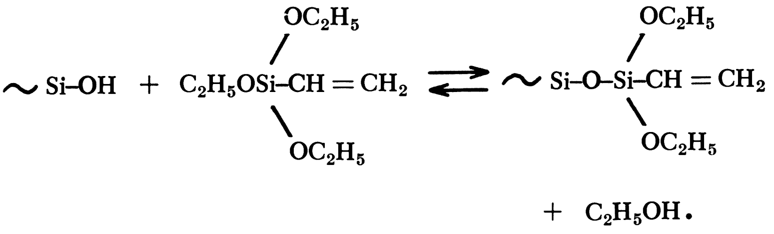
The β-(p-chlorophenyl)ethylsilane Derivatives. Data on the wettability of the β-(chlorophenyl)ethylsilane films are given in Table III. These films were formed by vapor deposition as well as by adsorption from solution. Critical surface tensions of 40-45 dynes/cm. and θ_{H_2O} of 80°-86°C. were obtained by vapor deposition of the trichloro derivative at 25°C., the trimethoxy derivative at 70°C. and from a solution of the triethoxy compound with n-propylamine. These films were all water stable. The other films formed by the triethoxy and trimethoxy compounds from solution without catalyst, and by the trimethoxy vapor at room temperature, had θ_{H_2O} values less than 80° and were not water-stable. Vapor deposition was carried out by suspending a clean silica surface over the liquid in a closed container.

Discussion

Some insight into the chemical constitution of the adsorbed trialkoxysilane films can be derived from their wettability characteristics. However, caution must be exercised in making these interpretations. Because of the complexity of the adsorption process there can be a number of possible configurations for the adsorbed molecules in these films. Some of these configurations may not be distinguishable from wettability data alone. In the discussion that follows a general model is proposed for the structure of all the films reported and postulates are offered as to how various factors might influence the detailed configuration of the model. Using the proposed model and these postulates an attempt is made to explain at least some of the observed wettability data.

Some of the experimental results suggest that one or more chemical reactions are involved in the adsorption of ETES and VTES. For example, the times required for film formation to become complete are longer than is usually associated with physical adsorption. Also, the differences in the films formed on alumina compared with silica suggest a specificity toward the silica substrate—at least in the absence of added acid or base. Finally, the results obtained by adding acids and bases to the adsorbate solution suggest a catalytic effect on film formation.

There are two reactions of the adsorbate molecules that are probably involved in the adsorption process on silica. The first is between the adsorbate molecules and the surface silanols (~Si—OH);



$$\sim\text{Si-OH} + C_2H_5O\overset{\overset{OC_2H_5}{/}}{\underset{\underset{OC_2H_5}{\backslash}}{Si}}\text{-CH}=CH_2 \rightleftharpoons \sim\text{Si-O-}\overset{\overset{OC_2H_5}{/}}{\underset{\underset{OC_2H_5}{\backslash}}{Si}}\text{-CH}=CH_2 + C_2H_5OH. \qquad (1)$$

Various studies indicate that certain alkoxysilanes react with surface silanol groups (*2*, *8*), but nothing appears to have been reported for ETES and VTES specifically. The second type reaction is between two adsorbate molecules to form a siloxane polymer linkage.

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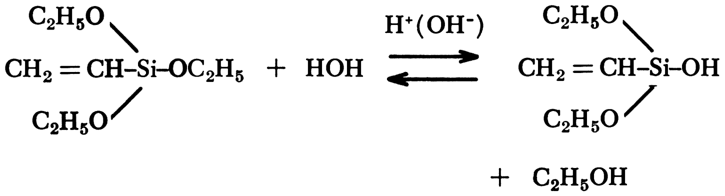
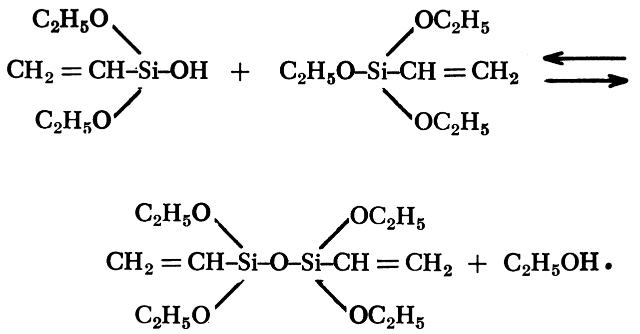


(2a)



(2b)

There is a substantial body of literature on the hydrolysis of alkoxysilanes (*16*) including a study of ETES (*15*). Note that all three reactions, (1, 2a, and 2b), are probably subject to acid-base catalysis, but only for reactions of type 2a has catalysis been demonstrated (*15, 16*).

The films generated in these experiments are best visualized as polysiloxane networks having at least an occasional chemical attachment to the surface. (The surface attachments to silica are very likely siloxane linkages as in Reaction 1. The question of the attachments to alumina is discussed below.) This network model implies that Reactions 1, 2a, and 2b all contribute to the adsorption process. However, there will be differences in the extent of polymer formation and the extent of surface attachments depending upon which triethoxysilane is involved and the conditions under which it is adsorbed. The water required for the polymerization reaction was probably available on all the surfaces studied. This would be true even for the flamed silica since those surfaces were cooled in air containing 400 p.p.m. of water. This water content is believed sufficient to promote the reforming of most surface silanol groups lost by flaming and to allow the adsorption of at least a partial monolayer of molecular water.

In order to explain the wettability results for the trialkoxysilane films, it is necessary to postulate that the following five factors are important in the adsorption process on silica:

(1) The number of specific siloxane attachments made to the surface will depend in part on the reactivity of the alkoxysilane and in part on

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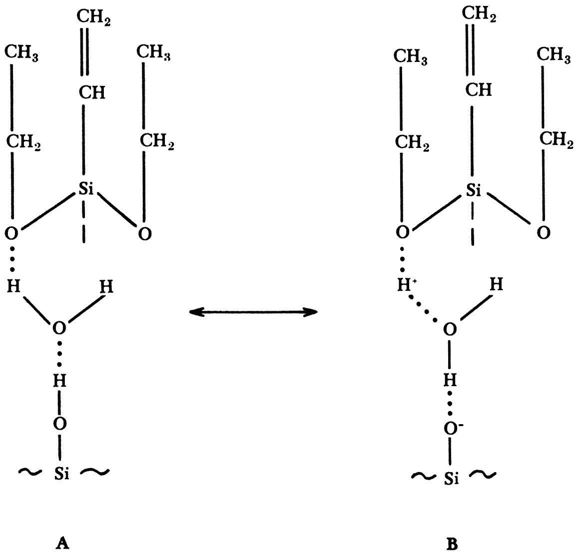
the acidity of the individual surface silanol groups. It is assumed that there is a high but undetermined density of silanol groups on both air-dried and flamed surfaces. In general, the sites on any given surface will vary widely in chemical activity. This dependence of the extent of surface attachments on adsorbate and adsorbent reactivity reflects the fact that when an alkoxysilane molecule approaches a surface silanol the reaction rate must be fast enough for bond formation during the time the adsorbate molecule is physically held at the surface site.

(2) Few of the individual trialkoxysilane molecules will make multiple attachments to the surface. This limitation exists because there is little probability that an adsorbing alkoxysilane molecule will make an initial, single attachment and then rotate about this bond until one or both of the remaining ethoxy groups are properly positioned for reaction with surface silanols. Consequently, the formation of multiple attachments is a slow process. It is likely to be outrun by the reaction of the remaining ethoxy groups with other triethoxysilane molecules to form siloxane linkages. Also, when the adsorbate solution is concentrated the number of trialkoxysilane molecules available at the surface is large, so that most silanols on the silica will have reacted with separate molecules before many multiple attachments can be made. Only for dilute adsorbate solutions is there likely to be an appreciable number of multiply-attached triethoxysilane molecules.

(3) The number of surface attachments will be limited if the molecules are prevented access to the surface silanols by adsorbed water or any other adsorbate that can H–bond to the silanol group.

(4) The surface silanols can still catalyze the polymerization of triethoxysilane molecules even if there is one or more adsorbed layers of water on the surface. Presumably the triethoxysilane molecule H–bonds to the surface *via* water molecules after which it requires only an electron shift to make a silanol proton available to the alkoxysilane molecule. This sequence is illustrated by the following structures:



A B

The H–bonds are indicated by dotted lines and the bond from the silicon to the third ethoxy group behind the plane of the paper by a dashed line. Since one molecule of water disappears for each siloxane linkage formed (Reaction 2a), some of the surface molecular water is removed as the reaction proceeds. As this occurs, the ~Si—OH sites on the surface will become exposed and accessible for direct reaction.

(5) Differences in adsorption behavior on air-dried and flamed silica are attributed to differences in the rate at which water within the silica can diffuse to the surface—the rate being much less for the flamed surfaces. Therefore, any adsorbed molceular water that is removed from the air-dried surfaces as a result of polymer formation (Postulate 4) will be quickly replaced by molecular water held in the silica immediately below the surface. On the other hand, for flamed silica the rate of replacement is believed to be much slower. In general the presence of molecular water in glass and in fused silica surfaces is well established (*6*) and preliminary studies using infrared spectroscopy confirm its presence in the silica plates used here. Flaming would remove a large portion of this interior water from the first one or two microns below the surface.

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Plausible explanations can be given for the various wettability results in terms of the proposed model. In doing so certain interpretations are made of the wettability parameters, γ_c^* and θ_{H_2O}. The apparent critical surface tension, γ_c^*, reflects the density of methyl and methylene (and sometimes vinyl) groups in the surface of the adsorbed film, including the ethyl of unhydrolyzed ethoxy groups. The water contact angle, θ_{H_2O}, will be more sensitive than the organic wetting liquids to any polar groups with which water can H–bond. The contact angle of water will also be affected if the water hydrolyses ethoxy groups to make the film surface more polar.

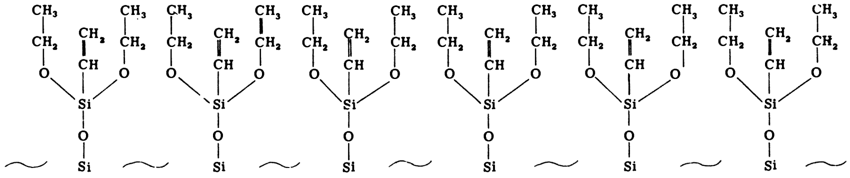
In the "desorption" experiments changes in film characteristics are assumed to include the displacement of physically adsorbed or entangled molecules, the hydrolysis of ethoxy groups and possibly the hydrolysis of some ≡Si—O—Si≡ linkages.

Ethyltriethoxysilane–Silica. The properties of the ETES films on silica indicate that this triethoxysilane does not react extensively with the surface silanols, probably because of the low hydrolytic reactivity of this particular alkoxysilane. There is obviously some adsorption of ETES since retraction does occur from the α-chloronaphthalene solutions. However, the poor water stability of the resulting films shows that the adsorbate is not strongly held to the surface—*e.g.*, the disparity between θ_{H_2O} and the organic-liquid wetting data and the marked decrease in θ_{H_2O} during the water desorption tests. Evidently, the ETES is too poorly reactive to interact with the surface silanols either to form extensive surface attachments or an adsorbed polysiloxane network (*see* Postulates 1 and 4). Consistent with this interpretation is the fact that in low-polarity solvents the hydrolysis of ETES requires catalysis by strong acids or bases (*15*).

Vinyltriethoxysilane–Silica. The VTES appears to be more reactive than ETES and therefore able to interact more extensively with the surface silanols. On flamed silica the coverage by VTES gives a high density of hydrocarbon groups (low γ_c*, Figure 5A) at least at the high concentrations. These films are stable toward water since the θ_{H_2O} values are consistent with the organic liquid wetting data and the films resist water desorption (Figure 7).

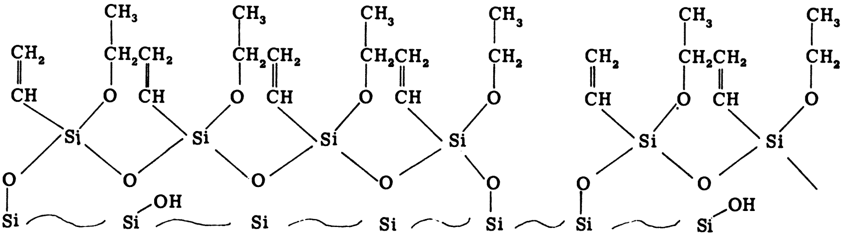
In a preliminary study here the VTES was found to be slightly more hydrolytically reactive than the ethyl compound. Also, a higher hydrolytic sensitivity for VTES than for ETES can be justified on theoretical grounds. If *p–d*–bonding can occur between the silicon atom and the vinyl group (*3, 4*), then structures such as $\overset{+}{C}H_2—CH{=}\overset{-}{Si}(OC_2H_5)_3$ may be important in the hydrolysis reaction mechanism. The increased electron density on the silica would serve to weaken the $\equiv$Si—O— bond. Similar ionic structures cannot be written for ETES.

Two different configurations are proposed for the adsorbed molecules in the VTES films on flamed silica. Both models attempt to account for the surprisingly low critical surface tensions exhibited by the films from 1% and 5% solutions. An apparent critical surface tension of 20 dynes/cm.—or 26 dynes/cm. as determined using *n*-alkanes (Figure 1) —is usually associated with closely-spaced hydrocarbon groups. Examination of molecular models indicates that to obtain such close spacing there must be an average of at least one unreacted ethoxy group remaining on each absorbed triethoxysilane. One configuration that satisfies this requirement has each adsorbed molecule singly attached to the surface;



C

Alternately, the film could consist of short vinylsiloxane polymer segments bridging from one point of surface attachments to another—*i.e.*,



D

As suggested earlier, the water necessary for polymerization was probably available even on the flamed silica. The molecular models suggest that to obtain a close spacing of hydrocarbon groups in a film of polyvinylsilane the polymer segments must be held against the surface as in structure D. If the polymer units were attached to the surface but allowed to extend in a random fashion into the adsorbate solution, a larger proportion of polar groups would be accessible to a contacting liquid.

The contention that polymer adsorption can result in oleophobic (low γ_c*) and water stable films is given support by the results using the ETES polymer-monomer solution (Figure 10). In this case preformed polymer was present in the solution along with the monomer ETES, and the resulting films had a wettability not unlike those formed by the 1% and 5% VTES solutions on flamed silica. The water stability of these films can be explained by a film structure that is predominately polymer units. Desorption then requires the simultaneous breaking of many bonds which is a statistically unlikely event.

There are at least three possible explanations for the relatively high γ_c* values of the films from the 0.1% VTES solutions. (a) As suggested by Postulate 2, the VTES molecules may form multiple attachments to the surface. If so, the number of unreacted ethoxy groups in the adsorbed film will be less than in the films formed at the higher concentration where only singly attached molecules (Structure C) or polymer molecules (Structure D) are expected. (b) The high γ_c* values may merely indicate sparse coverage of the surface. If a significant part of the adsorbate at the higher concentrations is physically held then at the lower concentration the surface density of these weakly held molecules will be lower. (c) At the low solution concentrations the rate of Reactions 1, 2a, and 2b may be too slow to give full surface coverage even within the maximum adsorption time allowed, which was about three days.

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There is not enough information to differentiate between these highly speculative explanations.

VTES films on air-dried silica differ in both wettability and water stability from the VTES films on flamed silica (Figures 5, 6, and 7). These differences are attributed to a greater rate of water diffusion to the surface from the bulk of the air-dried silica during the course of the adsorption process than occurs in the case of flamed silica (*see* Postulate 3). On air-dried silica the continued supply of water to the surface is believed significantly to reduce the formation of surface attachments. This would explain the poor water resistance of these films.

The minimum in γ_c* observed after a few hours adsorption time for VTES on air-dried silica (Figure 6A) probably corresponds to an initial surface coverage by small polymer fragments and unreacted VTES molecules H–bonded to the surface. At these early stages of adsorption the θ_{H_2O} values were highly unstable indicating easy disruption of the film. Subsequent reaction of the adsorbate molecules to form further polymer linkages and possibly surface attachments would explain the increase in water stability after 20 hours. A gradual loss of ethoxy groups from the film will accompany these processes and would contribute to the increase in γ_c* at the later adsorption times (Figure 6A).

The Effect of Acid and Base Catalysts. The addition of organic acids and bases to the adsorbate solution is believed to promote considerably more polymer formation and possibly more surface attachments in the films formed by ETES and VTES than when either triethoxysilane is adsorbed without added catalyst. In fact, from the triethoxysilane-catalyst solutions, the adsorption process is likely to continue beyond the initial surface coverage by "monolayer" films such as Structure C or D. Any unreacted ethoxy groups in the initially adsorbed film are highly susceptible to hydrolysis because of the ready availability of catalyst in the overlying solution. The water necessary for hydrolysis is available from the silica substrate or from the adsorbate solution into which trace amounts may have been introduced inadvertently during preparation. Therefore, polymer buildup on the surface will continue until one of the reactants becomes depleted or until steric factors limit further polymerization. The net effect of these processes is reflected in the observed change in γ_c* with adsorption time (Figure 8). The minimum in γ_c* at 1 to 3 hours adsorption time reflects the high density of unreacted ethoxy groups in the initial film. The subsequent increase in γ_c* corresponds to the loss of the ethoxy groups as this initial film becomes more cross-linked and there is a gradual buildup of randomly oriented polymer segments.

The films generated by the triethoxysilane-(*n*)propylamine solutions (at adsorbate/amine mole ratios of 4 or greater) differed in a number of ways from the films formed by any of the other adsorbate solutions:

(a) the films were strongly hydrophobic—*i.e.,* high θ_{H_2O}—but at the same time surprisingly oleophilic (high $\gamma_c{}^*$); (b) retraction from these solutions was slow and oftentimes incomplete; and (c) a finely divided precipitate was observed in these adsorbate solutions. In connection wtih the $\gamma_c{}^*$'s of these films it should be noted that in the cos θ–*vs*–γ_{LV} plots the wetting data did not give as exact a linear relationship as was obtained for the other films of this study. Instead, the wetting data showed a marked scatter through which a best fit straight line was drawn. Because of this scatter, there is an uncertainty of ±5 dynes/cm. in the $\gamma_c{}^*$ values for the *n*-propylamine catalyzed films in Tables I and II.

It is believed that the above phenomena result because adsorption in this case leads to the rapid formation of relatively thick polymer films. It would also appear that these films can be penetrated and perhaps swelled by the organic test liquids. The visible precipitates observed in the triethoxysilane-(*n*)propylamine solutions are presumed to be particles of high molecular-weight polysiloxane. This suggests that the rate of polymer formation is greater in these amine catalyzed solutions than in the other adsorbate-catalyst solutions. Undoubtedly, much smaller polysiloxane units were present in the adsorbate solution before the particle became visible. Thus, the buildup of the adsorbed film may include small preformed polymer aggregates as well as the triethoxysilane monomer. In fact, if adsorption proceeds rapidly enough molecules of solvent, catalyst, unreacted triethoxysilane monomer, and polymer are likely to be trapped in the adsorbed network without actually being chemically linked to it.

The slow and incomplete retraction of the solutions containing *n*-propylamine is attributed in part to the presence of weakly-held polysiloxane material on an underlying, more coherent film. The fact that the solution retracts at a low contact angle (about 20° to 30°) cannot completely explain the inordinately slow retraction. It is more likely that a loose, gel-like polymeric structure impedes and in some instances prevents the withdrawal of the retracting liquid. When retraction failed to occur, the residual solution was easily displaced by water. Undoubtedly, this "displacement" is a complex process of desorption, liquid-liquid displacement and hydrolysis of the polymer film.

The wettability of these films is adequately explained when they are viewed as more-or-less thick polymer networks into which solvent and other molecules are entangled. The high $\gamma_c{}^*$ values obtained reflect both the random oriented polymer segments and the inclusion in the film of the relatively high surface tension solvent—*i.e.,* α-chloronaphthalene (γ_{LV} = 42.9 dynes/cm.). However, the θ_{H_2O} values for these films are much higher than was to be expected from their $\gamma_c{}^*$ values. This discrepancy is best illustrated by reference to the work of Shafrin and Zisman (*13*)

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who have studied the relation between θ_{H_2O} and γ_c* for over 60 organic polymers and adsorbed organic films. They found that for a given value of γ_c* there is a corresponding upper limit for θ_{H_2O}. On this basis those films in Tables I and II having a γ_c* value of 38 dynes/cm., for example, should have a θ_{H_2O} value of not over 85° which is 20° lower than the 105° observed. Other examples of such unusually high water contact angles are underlined in Tables I and II. Note that in all cases these polysiloxane films had been deposited from solutions containing *n*-propylamine as the catalyst. This apparent discrepancy between observed and predicted water contact angles in no way invalidates the generalizations made by Shafrin and Zisman. The comparison is made to emphasize the unusual oleophilic-hydrophobic character of these films. The explanation for the discrepancy is probably that molecules of the organic test liquids penetrate and perhaps swell these polysiloxane layers, thus raising their apparent critical surface tension. The unusually large deviation of the wetting data from a straight line relationship also suggests specific interactions between the individual test liquids and these polysiloxane films. Shafrin and Zisman, of course, purposely excluded from their data any systems in which there were strong, specific interactions between surface and wetting liquid.

β-(*p*-Chlorophenyl)ethlytrialkoxy(trichloro-)silanes–Silica. The β-(*p*-chlorophenyl)ethyl compounds formed films having the wettability expected for closely-spaced *p*-chlorophenyl groups—*i.e.*, $\gamma_c^* = 40\text{-}45$ dynes/cm. and $\theta_{H_2O} = 80°\text{-}90°$ (Table III). These are the same values found by Shafrin and Zisman for films of *p*-chlorophenyldodecylglutaric acid on chromium (*14*). The easily hydrolyzed trichloro compound formed water-stable films spontaneously at 25°C. having the expected wettability. The less hydrolytically reactive trialkoxy compounds required elevated temperatures—*e.g.*, the vapor deposition of the trimethoxy compound at 70°C., or required a catalyst—*e.g.*, the triethoxy compound from a solution containing *n*-propylamine. There were no demonstrable differences in the ability of the two trialkoxy compounds to form water-stable films even though the trimethoxysilanes are usually more hydrolytically reactive than the corresponding triethoxysilanes (*7*).

Adsorption of ETES and VTES on Alumina. In the absence of acid or base catalysts it was not possible to obtain ETES films on α-alumina by retraction and the VTES films were unstable toward the organic test liquids as well as water. This failure of both the ETES and VTES to form strongly held films can be attributed to the weakly basic character of alumina surfaces. The isoelectric point of alumina is usually at a pH of 7.5 to 9.0 (*11*) which is a rough measure of the base strength of the ∼Al—OH surface groups. Silica, on the other hand, has an isoelectric point at a pH of 2, signifying a moderately strong acid character for the

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$\sim$Si—OH group. In terms of acid-base strength, the alumina presents a much less chemically active surface for trialkoxysilane hydrolysis than does silica.

The hydrolytic stability of $=$Al—O—Si$\equiv$ surface attachments is questionable if such bonds are formed. Experience with organic aluminosiloxane polymers has shown that the $=$Al—O—Si$\equiv$ linkage does not have the stability usually associated with the $\equiv$Si—O—Si$\equiv$ group especially toward water (*19*).

When *n*-propylamine was introduced into the ETES adsorbate solution the resulting films on alumina had the same wettability and water stability as the films obtained on silica from a similar solution. It can be reasonably assumed that the amine catalyzed the formation of an adsorbed polyxiloxane network on the alumina. However, it is again questionable whether the water stability of these films can be attributed to the formation of $=$Al—O—Si$\equiv$ surface attachments. The water stability is more likely owing to the highly polymeric structure of the film.

Implications for the Use of Trialkoxysilanes as Finishing Agents. The water stability of the adhesive bond between organic resins and inorganic adherends is significantly improved by precoating the inorganic surface with certain trialkoxysilane finishing agents. These compounds have proved useful for such adherends as glass (*17*), aluminum (*1*), porcelain (*10*), and natural tooth surfaces (*12*). The finishing agent coating may be applied from aqueous or nonaqueous solution or as an additive in the adhesive resin liquid.

There are three important implications of this investigation for the use of trialkoxysilanes as finishing agents when applied from nonaqueous solutions or when used as resin additives. (a) The trialkoxysilane can serve to chemically scavenge water adsorbed on the adherend surface and trace amounts of water in the liquid resin. (b) The adsorbed polysiloxane network can serve as a hydrophobic barrier to the entry of bulk water into the interfacial region. It may also hinder readsorption of water, at least in the case of glass, by chemically combining with hydrophilic surface groups. (c) The extent to which the trialkoxysilane will serve to scavenge water and form an adsorbed, hydrophobic barrier will depend on its hydrolytic reactivity and the conditions under which it is applied—*i.e.*, the amount and type of acid or base present, the amount of water present, the acid-base character of the substrate, etc.

The trialkoxysilane compounds thus satisfy two requirements indicated by Zisman (*21*) for useful finishing agents. They are able to displace water from the substrate surface and to prevent its readsorption. However, it was pointed out (*21*) that the applied film of finishing agent must be resin-wettable—*i.e.*, $\gamma_c{}^* > 40$ dynes/cm., to allow good contact between adhesive and adherend. The results with the *p*-chlorophenyl-

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terminated compounds demonstrate that, by the proper chemical design, the trialkoxysilanes can be made to meet this wettability requirement.

Acknowledgment

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5

Solvent Effects on Adsorption at the Polymer/Solid Interface

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The adsorption of polystyrene-^{14}C (PS-^{14}C, $M_w = 292{,}000$) on Graphon carbon black was studied from six solvents covering a range of solvent power. The results indicate increased adsorption of PS-^{14}C on Graphon with decreasing solvent power. Similarly, correlation between the adsorption of PS-^{14}C on Graphon and the hydrodynamic dimensions of PS-^{14}C in solution is good; i.e., *A_s increases with decreasing end-to-end root-mean-square length of the polymer in solution $(<\bar{r}^2>)^{1/2}$. It is postulated that under conditions of weak segment-surface interaction a uniformly adsorbing polymer like polystyrene attaches itself to the Graphon surface from good solvents as a flat oriented monolayer; from a poor solvent the polymer assumes a loop or coil structure in which only part of the polymer segments are attached directly to the Graphon surface.*

Comprehensive reviews dealing with the adsorption of polymers at solid-liquid interfaces have recently been published by Hughes and Frankenberg (*13*), Patat, Killman, and Schliebener (*18, 19*), Rowland, Bulas, Rothstein, and Eirich (*21*), Kipling (*14*), and Stromberg (*9, 27*). The factor of primary interest in the problem at hand, the effect of solvent on polymer adsorption in nonaqueous systems, has been the subject of several investigations (*2, 6, 8, 11, 12, 15, 16, 20, 22, 25, 28*). In general, a marked dependence of polymer adsorption on solvent used was observed. Several of these data support the contention that polymers are strongly adsorbed from poor solvents and that the reverse holds true for good solvents (*11, 12, 15, 16, 22, 25, 28*). However, this strict dependence of adsorption on solvent power is overshadowed in many cases by the interaction between polymer and adsorbent (*8*), strong competition between solvent and polymer for the surface of the adsorbent (*2, 17,* *20*), or molecular weight effects (*16*). Therefore, it appeared desirable to establish a rigorous correlation between solution and surface properties as a function of solvent power in a well-characterized system under conditions in which the adsorbent surface was at all time in contact with the equilibrium solution of the adsorbate.

The system described in this investigation is polystyrene-^{14}C adsorbed on Graphon carbon black (graphitized Spheron 6) from six solvents comprising a wide spectrum from good to poor solvent power. Well-characterized materials were selected to elucidate the conformation of polymer molecules at the solid/liquid interface. So far two models have been postulated to describe the conformation of the adsorbed polymer molecules at the solid/liquid interface (*9, 13, 14, 18, 19, 21, 27*). In the first model the polymer assumes a loop or coil structure in which only a fraction of the polymer segments are attached directly at the interface, and in the second model the polymer forms a relatively flat and compressed interfacial layer with many segments attached to the solid substrate.

Experimental

Graphon black, kindly furnished by the Cabot Corporation, was the adsorbent; and its physical properties are listed in Table I. The term "Graphon" refers to Spheron 6 which had been heated to 2,700°–3,200°C. This graphitized nonporous carbon black is a unique form of carbon with uniform surface and high surface area. The Graphon samples were dried for 12 hrs. at 140°C. and stored *in vacuo* before use in the adsorption experiments.

Labelled polystyrene-^{14}C (PS-^{14}C) was the adsorbate. Two batches were prepared by an identical procedure with only one of them containing radioactive ^{14}C. The labelled polymer was used for the adsorption measurements, whereas the unlabelled polymer was used for the determination of the solution properties. The polystyrene was prepared by emulsion polymerization of redistilled styrene. In order to remove unreacted monomer the polystyrene was freeze-dried from benzene solution.

Table I. Properties of Graphon Carbon Black

Manufacturer	Cabot
Code number	S6-D4
Nitrogen surface area (sq. meter/gram)	89.70
Electron microscope surface area (sq. meter/gram)	117.00
Electron microscope particle diameter $\overline{d}_n$ (mμ)	23.50
Electron microscope particle diameter $\overline{d}_A$ (mμ)	27.60
Nitrogen particle diameter d_A (mμ)	36.00

The viscosity-average molecular weight of the polystyrene sample, $M_v = 251{,}000$, was calculated from intrinsic viscosity measurements in toluene and butanone-2 solutions (*see* Table II) by the Mark-Houwink equation $[\eta] = K'M^a$. The constants were $K' = 1.7 \times 10^{-4}$ and $a = 0.69$ for the toluene solutions at 25.0°C. and $K' = 3.9 \times 10^{-4}$ and $a = 0.58$ for the butanone-2 solutions at 25.0°C. (29, *30*). For comparison the weight-average molecular weight $M_w = 292{,}000$ was determined from light scattering measurements in toluene solutions. The specific activity of the labelled polystyrene sample was 0.0055 mc./gram.

The solvents were of analytical grade and were used without further purification with the exception of benzene, which was redistilled and stored over sodium pellets.

The adsorption experiments were run in 50-ml. glass-stoppered Erlenmeyer flasks filled with 25 ml. adsorbate solution and 0.125 gram adsorbent. The flasks were agitated by a mechanical shaker enclosed in an air thermostat at 25.0°C. After 40-hr. agitation periods, the suspensions were centrifuged; then the concentration of the unadsorbed polymer was determined by radioactive assay (^{14}C) of aliquots of the supernatant liquid on planchets in a Geiger-Müller Counter with a decade scaler and a printing timer. All counts were run in duplicate or triplicate. The reproducibility of the adsorption experiments was within ±2.5%. Rate studies have confirmed that there is no measurable increase in amount of polystyrene adsorbed on Graphon from benzene solutions after 36 hrs.

Table II. Effect of Solvent on the Adsorption of Polystyrene-^{14}C on Graphon at 25.0°C.

	Solution Properties				*Surface Properties*
Solvent	μ[a]	$[\eta]$, *dl/gram*[b]	*a*[c]	$(\langle \bar{r}^2 \rangle)^{1/2}$, A.[d]	A_s, *mg./gram*[e]
Benzene	0.430	0.95	0.74	509	55
Toluene	0.434	0.90	0.69	500	40
Dioxane	0.472	0.85	—	491	129
Butanone-2	0.485	0.51	0.58	414	160
Ethyl acetate	0.485	0.49	—	409	160
Cyclohexane (θ-solvent)	0.499	0.25	0.50	326	175

[a] Thermodynamic compatibility constant. It has recently also been denoted to the symbol χ_1.

[b] Intrinsic viscosity: $[\eta] = 0.025$ signifies a rigid sphere.

[c] Exponent in Mark-Houwink equation $[\eta] = K'M^a$: $a = 0.5$ signifies a rigid sphere or compact coil and $a = 1.4$ a rodlike or highly extended molecule.

[d] $(\langle \bar{r}^2 \rangle)^{1/2}$: end-to-end, root-mean-square length derived from the Flory-Fox equation $[\eta] = \Phi \frac{(\langle \bar{r}^2 \rangle)^{3/2}}{M}$ where $\Phi = 2.1 \times 10^{21}$ is the universal constant. Data calculated on the basis of $M_w = 292{,}000$.

[e] A_s: extrapolated saturation concentration from adsorption isotherm plots of *A* in mg. polystyrene-^{14}C adsorbed per gram of Graphon *vs.* concentration of supernatant liquid in mg./ml.

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Results and Discussion

It is a well known fact that the configuration of polymer molecules in solution changes markedly with solvent power (*1, 29, 30*). This phenomenon has been utilized in this study to advance our experimental knowledge of the conformation of polymer molecules at the solid/liquid interface from a correlation of solution with adsorption properties of a specific polymer-solvent system. Such a correlation is given in Table II for the molecular dimensions of a polystyrene sample in six solvents, comprising a wide spectrum from good to poor solvent power, with the corresponding adsorption data at the Graphon/solution interface.

The Flory-Huggins theory is generally applied to define the thermodynamic properties of a polymer solution (*1*). It gives an expression for experimentally obtainable quantities such as the partial molar free energy of mixing.

$$\Delta F_1 = kT\left[ln(1 - v_2) + \left(1 - \frac{1}{x}\right)v_2 + \mu_1 v_2^2\right]$$

where x is the degree of polymerization. ΔF_1 may be experimentally determined from colligative property measurements. Thus, the compatibility constant μ is a useful empirical parameter from which the solvent power of a polymer solution may be determined. Its value increases with decreasing solvent power up to 0.55, when phase separation occurs. The μ values listed in the first column of Table II are taken from an osmotic pressure study of Schick (*23, 24*) on polystyrene ($M_n = 540{,}000$ or $M_v = 890{,}000$), with the exception of the value for benzene, which is taken from Breitenbach and Frank (*5*). The results in Table II are listed in increasing order of μ values, or in other words, decreasing solvent power. The two extremes in this correlation are benzene and the θ-solvent cyclohexane. The intrinsic viscosities listed in the second column decrease with decreasing solvent power, which is a direct consequence of the contraction of the swollen polymer coil with decreasing solvent power (*1, 29, 30*). The same holds true for the exponent "*a*" in the Mark-Houwink equation shown in the third column, which decreases with decreasing solvent power (*1, 29, 30*). The dimensions of the flexible polystyrene molecules calculated by the Flory-Fox equation (*7*) are listed in the fourth column. It is evident that the dimensions of the polystyrene coils decrease with decreasing solvent power, which, as will be shown below, influences markedly the adsorption of polystyrene at the solid/liquid interface. The quantity $(\langle r^2 \rangle)^{1/2}$ reaches a minimum for the θ-solvent when the polymer forms a compact coil.

The adsorption isotherms of polystyrene-^{14}C on Graphon from these six solvents are plotted in Figure 1 in terms of mg. PS-^{14}C adsorbed per gram Graphon *vs.* concentration of supernatant liquid in mg. PS-^{14}C per ml. solution. The solubility limit precluded the study in cyclohexane solutions (θ-solvent) at equilibrium concentrations exceeding 1 mg./ml. The adsorption isotherms of these systems with the exception of dioxane rise rapidly to a plateau at an equilibrium concentration of approximately 1 mg./ml., as noted generally with polymers. Marked differences in plateau level, however, have been observed. These indicate increased adsorption of polystyrene-^{14}C onto Graphon with decreasing solvent power. The former is expressed in the fifth column of Table II by A_s—*i.e.,* the extrapolated saturation concentration of the adsorption isotherms—and the latter by the μ value. A similar correlation has been established between the degree of adsorption and the hydrodynamic properties. The adsorption—*i.e.,* A_s—increases with decreasing end-to-end, root-mean-square length—*i.e.,* $(<\bar{r}^2>)^{1/2}$. Thus, the observed differences in A_s may be attributed to greater area required for adsorption of the better solvated, swollen polymer molecule, as well as to changes in the solvent-surface interaction. The latter represents essentially competition for the surface between the solvent and the polymer segment (*20*).

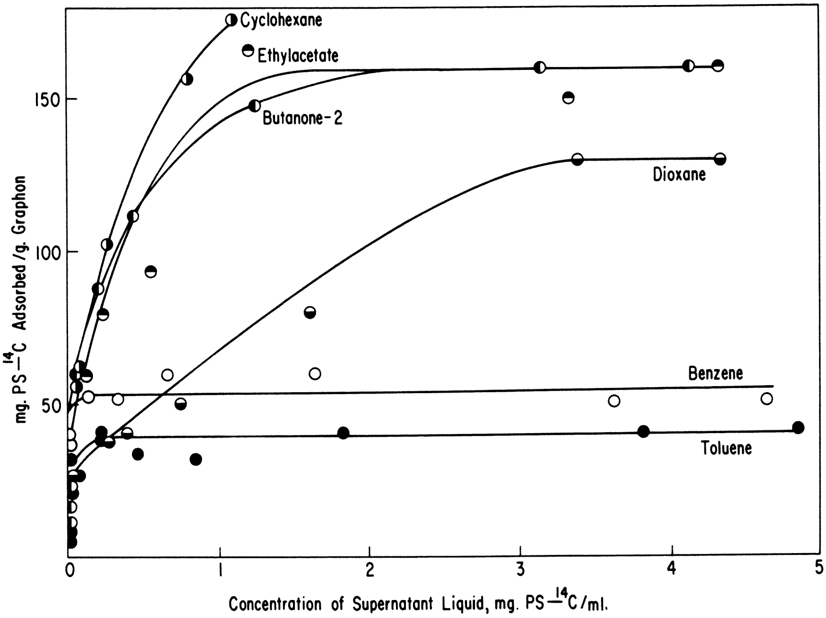

Figure 1. Adsorption isotherms of polystyrene-^{14}C on Graphon at 25.0°C.

The data of Table II have been reexamined in terms of the two models proposed for the structure of flexible polymers at the solid/liquid interface, and the pertinent data are listed in Table III. In the first column are given the areas per monomer unit of the completely uncoiled polystyrene

Table III. Adsorption of Polystyrene

Solvent	*Area per Monomer Unit, A.², of Unfolded Polystyrene Molecules at the Graphon Solution Interface*[a]	*Cross-Sectional Area of Polystyrene Coils in Solution, cm.²/Molecule*[b]	*Amount of Polystyrene Adsorbed on Graphon, gram/cm.²* [a]
Benzene	28.2	20.3×10^{-12}	6.13×10^{-8}
Toluene	38.7	19.7×10^{-12}	4.47×10^{-8}
Dioxane	12.0	18.9×10^{-12}	14.4×10^{-8}
Butanone-2	9.7	13.4×10^{-12}	17.9×10^{-8}
Ethyl acetate	9.7	13.1×10^{-12}	17.9×10^{-8}
Cyclohexane	8.9	8.34×10^{-12}	19.5×10^{-8}

[a] *See* Table I for surface area of Graphon by N_2 adsorption.
[b] Calculated from $(<\bar{r}^2>)^{1/2}$; *see* Table II.

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molecules with every segment attached to the surface sites of the nonporous Graphon. In this flat orientation the areas per monomer unit decrease with decreasing solvent power. Only for the good solvents—*i.e.*, benzene and toluene—was the observed area comparable to that of the monomeric styrene. Thus, in good solvents it may be assumed that the polymer forms a relatively flat and compressed interfacial layer with many segments attached to the solid surface. As evidenced from the large cross-sectional areas in column two, the swollen coils in these good solvents are prone to uncoil to assume the conformation suggested. However, this model is ruled out by the relatively much smaller areas per monomer unit for the medium and poor solvents in which the polymer forms tighter coils, *viz.*, first column. The alternate model is suggested for the medium and poor solvent systems in which the polymer assumes a loop or coil structure with only a fraction of the polymer segments being attached to the surface sites of the nonporous Graphon (*26*). These conclusions are corroborated by the data listed in the third column. From the better solvents less than 6×10^{-8} grams polystyrene/cm.² Graphon was adsorbed; whereas from medium and poor solvents, from 14.4×10^{-8} to 19.5×10^{-8} grams/cm.² was adsorbed. Frisch, Hellman, and Lundberg (*10*) made similar observations for polystyrene adsorbing from toluene onto carbon (3×10^{-8} gram/cm.²). A simple flat monolayer requires only 5×10^{-8} gram/cm.² (5 A. layer if polymer has density of 1) (*9, 27*). Thus, the amount adsorbed in a medium or poor solvent must be more than a simple monolayer. As cited above for these systems a monolayer of coils which are attached to the surface without any appreciable change in shape and bonded to the surface by only a few peripheral monomer units is a plausible model (*14, 21*). Steinberg (*25*) has proposed a model in which the segment density in the interfacial layer of adsorbed polymer molecules progressively decreases as the distance from the surface increases.

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Results reported in Table II follow the pattern that adsorption of polystyrene-^{14}C on Graphon is favored from a poorer solvent. Experiments are reported here and in the following paragraph which have been performed to test the reversibility of this adsorption. With this aim in mind, (1) the displacement of polystyrene-^{14}C from Graphon by the original solvent and (2) the stepwise adsorption from different solvents were studied. The data of Table IV imply that no appreciable desorption in the original solvent was observed with all six solvent systems. Once adsorbed from a particular solvent, according to Steinberg (25), polymers do not desorb appreciably in that solvent because the multiplicity of adsorbing sites energetically favors adsorption, resulting in very small desorption rate constants.

Results for the stepwise adsorption of polystyrene-^{14}C on Graphon from different solvents are shown in Table V. In the first two sets of experiments, data are given for an original concentration of 0.4 mg. polystyrene-^{14}C/ml. or 0.2 mg./ml., respectively, in all three adsorption steps. In the second set the original concentrations in step two or three correspond to the supernatant liquid concentration in the preceding step.

On changing the environment from toluene to butanone-2 (the poorer solvent) additional polymer was adsorbed. However, on reverting the environment back to toluene most of the additional polymer was desorbed. It is worth noting that in the second set of experiments the final and original systems were almost alike. These results may again be qualitatively explained in terms of changes in area required by the polymer molecule to attach itself at the solid/liquid interface. The area

Table IV. Effect of Solvent on the Desorption of Polystyrene-^{14}C from Graphon

Solvent[a]	*Equil. Conc. mg. PS-^{14}C/ml.*	*% wt. PS-^{14}C Desorbed*
Benzene	0.27	0
Benzene	0.18	2
Toluene	0.19	0
Toluene	0.13	0
Dioxane	0.183	0
Dioxane	0.136	0
Butanone-2	0.31	0
Butanone-2	0.20	0
Ethyl acetate	0.31	0
Ethyl acetate	0.21	0
Cyclohexane	0.51	0
Cyclohexane	0.32	0

[a] Experimental procedure: (1) 40-hr. agitation cycle, (2) replacement of 10 ml. of supernatant solution in dispersion by 10 ml. of fresh solvent, and (3) 40-hr. agitation cycle.

Table V. Stepwise Adsorption of Polystyrene-^{14}C on Graphon from Different Solvents

Step	Orig. Conc. of PS-^{14}C, mg./ml.	Solvent[a]	Amount Adsorbed (mg./gram) or Desorbed in Step	Total PS-^{14}C Adsorbed (mg./gram)
1	0.4	Toluene	39 ads.	39
2	0.4	Butanone-2	56 ads.	95
3	0.4	Toluene	40 des.	55
1	0.2	Toluene	26 ads.	26
2	0.2	Butanone-2	40 ads.	66
3	0.2	Toluene	22 des.	44
1	0.4	Toluene	38 ads.	38
2	0.22	Butanone-2	36 ads.	74
3	0.08	Toluene	27 des.	47
1	0.2	Toluene	28 ads.	28
2	0.07	Butanone-2	14 ads.	42
3	0	Toluene	10 des.	32

[a] Experimental procedure: (1) 40-hr. agitation cycle, (2) replacement of supernatant solution, (3) 40-hr. agitation cycle, etc.

per segment decreases as the polystyrene is desolvated on changing the environment from good to poor solvent, thus creating additional available surface. Increased adsorption may take place on these additional free surface sites. The reverse holds true for changes of environment from poor to good solvent.

In summary, it is postulated that under conditions of weak segment-surface interaction a uniformly adsorbing polymer like polystyrene attaches itself, in the concentration regions represented by the plateaux in the adsorption isotherms, to the Graphon surface from good solvents approaching a flat oriented monolayer. In contrast, from a poor solvent the polymer assumes a loop or coil structure in which only part of the polymer segments are attached directly to the Graphon surface. Thus, both models postulated are useful to describe the conformation of the adsorbed polymer molecules at the solid interface with each being applicable for different solvent media.

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6

Wettability and Constitution of Photooxidized Polystyrene and other Amorphous Polymers

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*The effect of ultraviolet irradiation in air on the wettability of thin films of amorphous polymers has been studied. With poly(vinyl chloride), poly(methyl methacrylate), poly(*n-*butyl methacrylate), poly(ethylene terephthalate), and polystyrene the changes in contact angles for various liquids with irradiation time are a function of the nature of the polymer. A detailed study of polystyrene by this technique and attenuated total reflectance spectra, both of which are sensitive to changes in the surface layers, indicates that the contact angle method is one of the most sensitive tools for the study of polymer photooxidation in its early stages. The method is useful in following specific processes and in indicating solvents to be used in the separation and isolation of photooxidation products.*

Polymers, under normal conditions, are in contact with atmospheric oxygen and are subjected to varying temperatures, humidities, and exposures to light. A polymer is most likely to undergo photochemical change at or near its surface, where the maximum absorption of highest energy radiation will occur and where the highest concentration of oxygen will be found. If the change is sufficiently slow, the polymer surface should be in a state of dynamic equilibrium with its environment, and it should be amenable to study by the methods of surface chemistry.

The wettability of a surface by liquids of known surface tension is a well-established parameter reflecting the constitution of that surface.

In Interaction of Liquids at Solid Substrates; Alexander, A.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1968.

Contact angles for a variety of liquids on pure amorphous polymer surfaces have been reported by Zisman and co-workers (*12, 13*). They have also shown (*8*) that the diffusion of low-molecular weight compounds from within a solid polymer film to its surface results in adsorption and a subsequent change in the wettability of that surface by specific liquids. In a few instances (*9, 10*), contact angle measurements have been used to show that surface changes in polymers are induced by ionizing radiation.

We have investigated the effect of ultraviolet radiation on a number of amorphous polymer surfaces in air. Polystyrene was selected for detailed study. The photooxidation of this polymer has received considerable attention in the past (*6*). Some confusion has developed, at least in part because of the high stability of the material. Impurities and secondary reactions must loom large under such conditions, since heavy doses of radiation are required to build up sufficient product concentrations for observation. Usually, transmission spectra have been utilized to determine the changes taking place, and these necessarily involve the unchanged bulk of any strongly-absorbing material such as polystyrene.

To avoid interference by products formed in secondary reactions during photooxidation, it is necessary to observe the changes as near the beginning of the process as possible. In this report, we will show that contact angle measurements and other analytical methods which are restricted in application to the surface layers are well-suited to the early detection and study of the photooxidation of polymer surfaces.

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Experimental

Materials. Spectroscopic-grade solvents were used; where fluorescence or contact angle measurements were to be made, appropriate purification steps were taken. The tetrahydrofuran was distilled from lithium aluminum hydride. For contact angle measurements, the following liquids and their surface tensions (dynes/cm.) at 20° were used: water, 72.6; formamide, 58.2; ethylene glycol, 47.7; methylene iodide, 50.8; 1-bromonaphthalene, 44.6; and *n*-hexadecane, 27.6.

Two of the polystyrene samples were benzoyl peroxide-initiated commercial materials; one of these had been on the shelf for over twenty years. The poly(*n*-butyl methacrylate) and the poly(vinyl chloride) were also commercial materials. The poly(methyl methacrylate) and the third polystyrene sample were prepared under nitrogen from freshly distilled monomers by bulk initiation with azobisisobutyronitrile (AIBN). Each of the above samples was purified by two reprecipitations from tetrahydrofuran solution with methanol and dried in vacuum at 65°C. for at least 24 hours. The poly(ethylene terephthalate) was a sample of 5-mil Mylar Type A sheet which had been cleaned by detergent washing and water rinsing, followed by vacuum-drying at room temperature for 16 hours.

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Apparatus. Contact angle measurements were made on a Model A-100 Ramé-Hart version of the NRL Contact Angle Goniometer. Exposures were carried out in a forced-draft hood with the unfiltered radiation from a General Electric UA-3 medium-pressure mercury lamp. Spectra were recorded on a Perkin-Elmer Model 350 ultraviolet spectrophotometer, a Beckman IR-12 infrared spectrophotometer with a Wilks Model 7 internal reflectance attachment, and an Aminco-Bowman Spectrofluorometer with a 1P28 photocell.

Procedure. With the exception of poly(ethylene terephthalate), 20μ films of each polymer were prepared by the evaporation of approximately 4% solutions in quartz or glass dishes of 50 cm.^{2} area for extraction experiments. For contact angle measurements, films were evaporated on acid-cleaned microscope slides by a dipping technique. Tetrahydrofuran was used with poly(vinyl chloride), methylene chloride with the other polymers.

Once laid, the polystyrene films were further purified by exhaustive extraction with methanol or *n*-heptane; the progress of extraction was followed by the ultraviolet spectra of the extracts. These preirradiation extractions showed considerable variation in purity among the three polystyrenes in spite of reprecipitation measures. The degree to which solvents can remain with a 20μ film is suggested by the need of seven days of continuous methanol or *n*-heptane extraction to remove all of the extractable benzene from a film laid from that solvent and dried in vacuum at 65°C. for 24 hours. For film laid from methylene chloride, an optically clean *n*-heptane extract was obtained from the AIBN-initiated sample within a few hours, but up to 48 hours were required for the benzoyl peroxide-initiated samples. The extracted 20μ polystyrene films were essentially non-absorbing above 285 mμ, no absorption attributable to material other than polystyrene could be observed, and only one peak (337 mμ) was seen in the fluorescence spectrum in methylene chloride. Once the films were purified by extraction, the products and wettability changes resulting from irradiation were the same for all polystyrene samples and were independent of the solvent from which the films were laid.

Films were irradiated at 30°C. at a right angle to the direction of air flow; the distance from the lamp was 9 inches. Exposures in vacuum were carried out in a quartz cell described elsewhere (*11*). Following exposure, the films were extracted as indicated in the discussion. Contact angles were measured by the advancing contact angle technique (*5*) on both unextracted and extracted films on the slides; values given are an average of four or more contact angles falling within a range of less than four degrees. Separate films were used for each exposure/extraction and contact angle measurement except where indicated, and no film was reexposed after such determination.

Literature values of the contact angles for various liquids on four of the five polymers used in this work are given in Table I. These values may be compared with those for our unirradiated polymers. In the case of polystyrene, exhaustive methanol or *n*-heptane extraction followed by drying did not result in a change in contact angles, and residual extractant could not be observed by means of frustrated multiple internal reflectance (FMIR) spectra of the films.

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Table I. Literature Values of Contact Angles of Liquids on Polymers[a]

		θ_E, *degrees*			
Liquid	$\gamma_{LV^{\circ}}$	*Poly(vinyl chloride)*[b]	*Poly(methyl methacrylate)*[c]	*Poly(ethylene terephthalate)*[d]	*Polystyrene*[e]
Water	72.8	87 (87)	76 (70)	81 (78)	91 (91)
Formamide	58.2	66 (63)	63 (56)	61 (54)	74 (71)
Methylene iodide	50.8	36 (24)	42 (39)	38 (32)	35 (−)
α-Bromonaphthalene	44.6	11 (9)	18 (16)	15 (16)	15 (17)

[a] $\gamma_{LV^{\circ}}$, liquid surface tension; θ_E, equilibrium contact angle; values in parentheses taken from Figures 1, 2, 4, and 5.
[b] Ref. *3* and *14*.
[c] Ref. *8*.
[d] Ref. *3* and *4*.
[e] Ref. *3* and *4*.

Results and Discussion

The general applicability of the contact angle method to the empirical observation of photooxidative changes in polymer films is indicated by the results shown in Figures 1, 2, 3, 4, and 5 and in the more detailed results for polystyrene described below. While these are fairly high-energy surfaces (critical surface tensions of 33-43 dynes/cm. at 20°C. (*12*) prior to irradiation, they are typical of surfaces to be expected in the coatings field. It is evident that the changes in wettability, reflected by the contact angles, during irradiation are a function of the chemical nature of the polymer and its surface. On a time basis, part of the variation is a consequence of differences in the absorption spectra of the polymers; comparison should perhaps be made on an energy absorbed basis and an intensity basis as well. Certainly, the greatest photooxidative change must occur in the surface where the contact angle is being measured, but it must also be borne in mind that partial attenuation of the incident energy, as in the case of poly(methyl methacrylate) with 254 mμ radiation, should lead to degradation throughout the film.

That photooxidation is indeed responsible for the observed changes is indicated by a comparison with the results obtained with films irradiated in vacuum. Both polystyrene and poly(*n*-butyl methacrylate) irradiated in vacuum showed no changes in contact angles after exposures up to 120 min.; with poly(ethylene terephthalate), contact angles for all of the liquids tended to increase slightly.

Polar and non-polar wetting liquids were used, and these were chosen to give a wide range of surface tensions. Compared with the original polymers, oxygenated moieties in the surfaces would be expected to interact more strongly with hydrogen-bonding liquids, but might very

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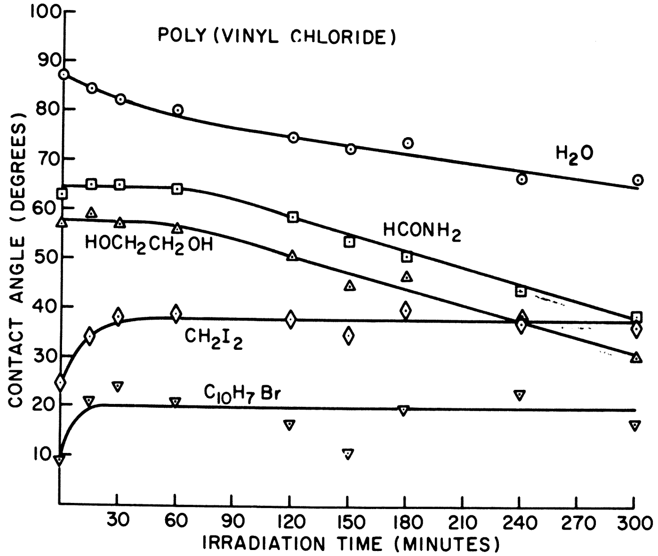

Figure 1. Contact angle changes with various liquids on a film of poly(vinyl chloride) irradiated in air

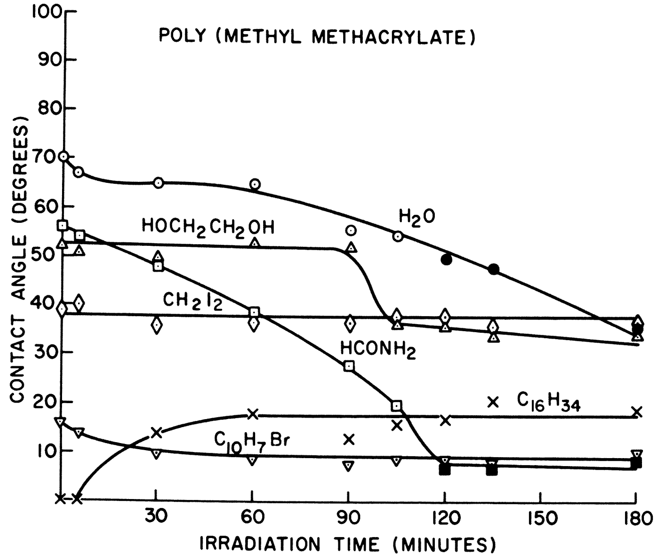

Figure 2. Contact angle changes with various liquids on a film of poly(methyl methacrylate) irradiated in air

well be less readily wet by the non-polar liquids. That such is the case can be seen in the generally decreasing contact angles for water, formamide, and ethylene glycol as exposure increased. Methylene iodide,

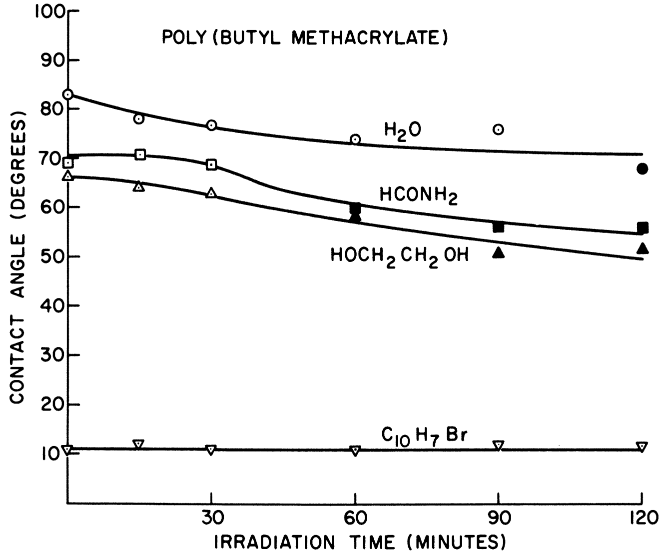

Figure 3. Contact angle changes with various liquids on a film of poly(butyl methacrylate) irradiated in air

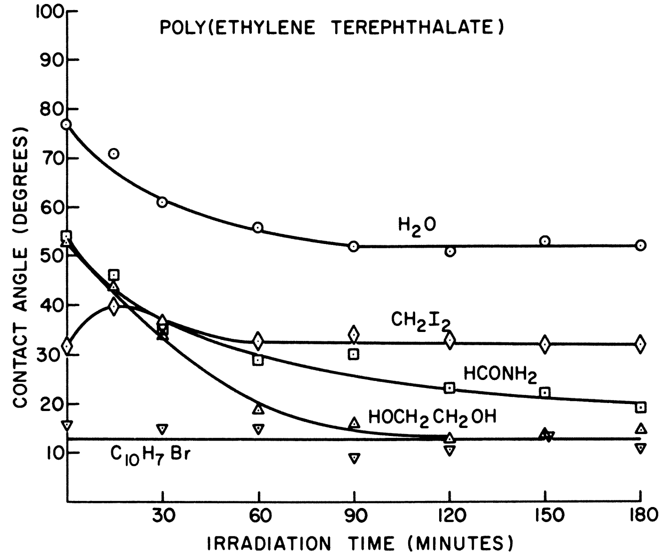

Figure 4. Contact angle changes with various liquids on a film of poly(ethylene terephthalate) irradiated in air

1-bromonaphthalene, and *n*-hexadecane, on the other hand, initially spread or gave low contact angles; as irradiation progressed, these angles either remained constant or tended to increase.

To relate the wettability changes more firmly to the photooxidation processes and products, a detailed study was carried out with polystyrene. This polymer was selected because the formation of oxidation products in the hydrocarbon surface gave rise to large changes in wettability and because these products would be readily accessible to optical methods of analysis. The ultraviolet absorption spectrum of polystyrene shows a sharp cut-off, and the extinction coefficients for the radiation absorbed are sufficiently high that almost all of the photochemical reaction should be confined to the surface layers.

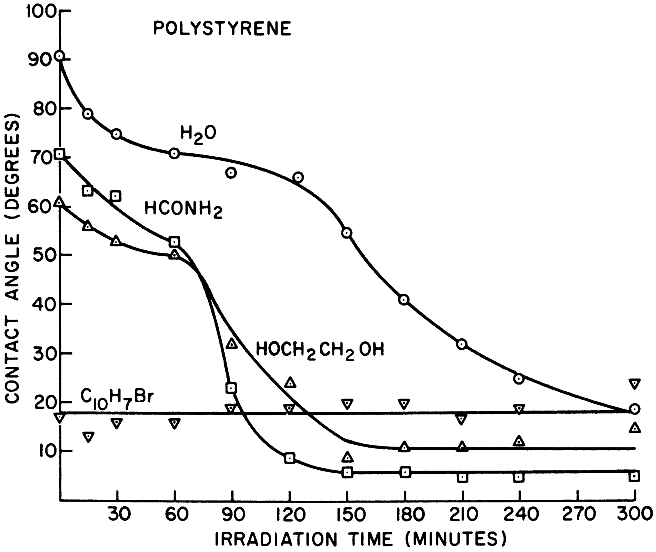

Figure 5. Contact angle changes with various liquids on a film of polystyrene irradiated in air

As a first approach, the changes in the critical surface tension for wetting, γ_c, with time of irradiation were determined. Unextracted exposed films were used. For high-energy surfaces of this kind, a homologous series of wetting liquids having the requisite surface tensions was not available, and therefore a series of water-ethyl alcohol mixtures (*1*) was utilized. Plots of the surface tensions of these mixtures against cos θ exhibited considerable curvature. Such behavior would be expected where the composition of a mixture of two hydrogen-bonding liquids is being varied. Extrapolation of these plots to cos $\theta = 1$ gave γ_c values which were low compared with the reported value (*3, 4*) of 33 dynes/cm. for polystyrene, a result also encountered with these mixtures on polyethylene (*1*). A plot of γ_c against exposure time, shown in Figure 6, is

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roughly linear, which suggests that the ratio of products affecting the contact angles is constant. The plot also indicates that γ_c changes can be an early indicator of photooxidation product formation; exposures of about 100 times those used here were necessary to give reasonable changes in the transmission infrared spectra of 20μ films.

Ultraviolet transmission spectra of irradiated films showed absorbance changes similar in sensitivity to those of γ_c. The spectrum itself only showed a general absorbance increase in the 220–400 mμ region, with a slight indication of band formation near 315 mμ. Plots of absorbance increases against exposure time were linear for 285 mμ (ketonic carbonyl formation) and 315 mμ, with the absorbance increase amounting to 0.32 and 0.25, respectively, for 20μ films exposed 300 min.

Other than as a demonstration of sensitivity to photooxidative change, these results are somewhat deceptive. A mixture of photooxidation products, primarily acids (7), has been formed in the surface layers of the film. The absorption maximum for the carboxyl group is generally in the vicinity of 210mμ. Each of the compounds present in the surface would be expected to exert its own effect, a function of its nature and concentration, on the contact angle of the wetting liquid. An examination of the specific effect of each product is therefore warranted.

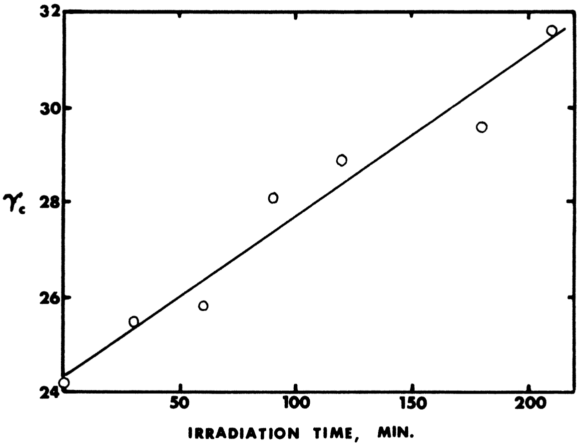

Figure 6. Critical surface tension for wetting (γ_c) of polystyrene as a function of irradiation time

Some product removal by solubilization in the wetting liquid occurred during the contact angle measurement. This was readily shown by changes in the ultraviolet absorption spectra of extracts of the surface with the same solvent. The products soluble in water, at least, were not surface-active, since a water extract of an irradiated polystyrene surface exhibited the same contact angle as pure water on an unirradiated polystyrene surface.

Solubilization of products in wetting liquids may be the key to the real utility of the contact angle method of assessing photooxidation changes in polymer surfaces. Liquids which wet but do not dissolve the polymer itself can be used to extract specific products from the surface. The extent to which products are removed can be followed by contact angle measurements on the residual material. The contact angle thus provides a guide to the separation of products and can give an indication of their rates of formation.

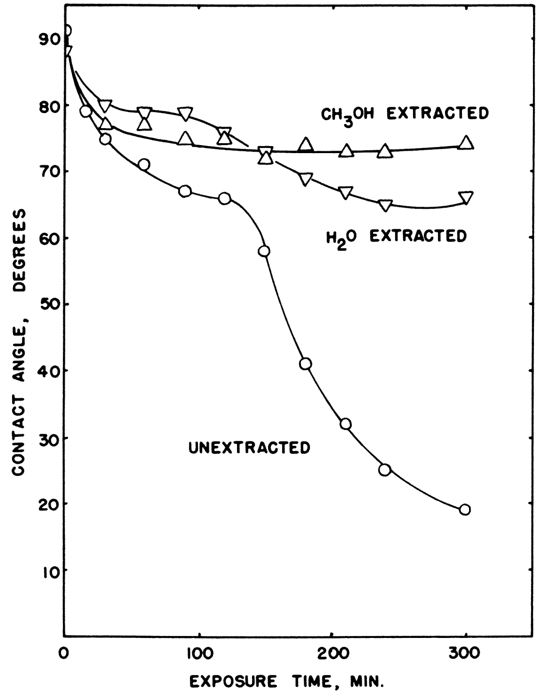

Figure 7. Effect of photooxidation product removal on water contact angles with polystyrene

This can be demonstrated with polystyrene. During photooxidation, three types of products will form: (a) material which volatilizes during the irradiation and therefore does not affect the contact angle; (b) extractable products; and (c) residual non-extractable products, mostly polymeric. In Figures 7 and 8 are shown plots of the contact angles for water and for ethylene glycol, respectively, on irradiated polystyrene

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films just after exposure and after exposure and extraction with water or methanol. Contact angles for formamide are similar to those in Figure 8. Each point represents a separate sample of film. The curves for unextracted material indicate at least two overall processes taking place; plots of $1/\theta$ against exposure result in two straight lines, the significance of which cannot be ascertained at the present time. Evidently, both water and methanol remove the more rapidly forming group of products, but to different extents since contact angles on the residual films differ. A comparison of the water and ethylene glycol contact angle curves suggests a more rapid solubilization of products in water than in ethylene glycol and this in itself constitutes a lead to product separation. A detailed description of the separation and identification of the products of polystyrene photooxidation will be the subject of a separate communication.

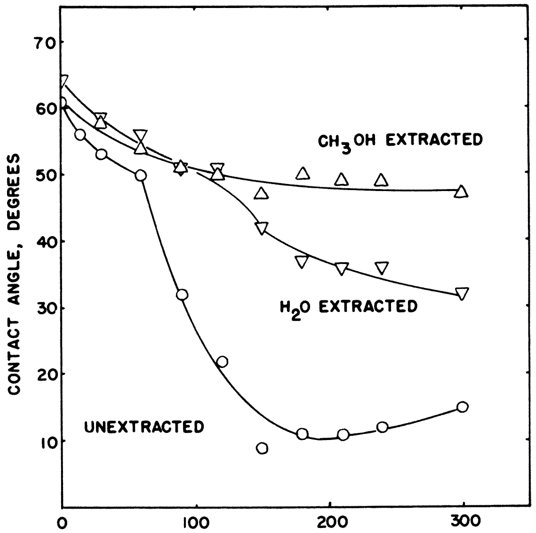

Figure 8. Effect of photooxidation product removal on ethylene glycol contact angles with polystyrene

Partial pictures of the irradiated polystyrene surfaces before and after each extraction were obtained by means of FMIR spectra of a film pressed on a KRS-5 prism. The spectra for a film exposed 5 hours are shown in Figure 9. The only significant change was a broad complex band in the carbonyl-stretching region near 1725 cm.$^{-1}$; other bands are shown for reference, since reproducible optical contact of the film with

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the prism was not always possible. In the present case, the FMIR spectra are more sensitive to product changes than are transmission spectra.

After each stage of extraction of this single film, a newly constituted surface remained. The changes in the concentration of products, mostly carboxylic acids (7), are indicated by the relative intensities of the carbonyl bands. A rough relation between these and the contact angles for water is shown in Figure 10. The relative sensitivities of the two methods are emphasized by the fact that a 5 hour exposure was needed to give significant changes in the FMIR spectra, while a much shorter exposure, 2 hours, was quite sufficient to produce large changes in the contact angles. As shown in Figure 7, a surface nearly saturated with products was attained at an exposure much earlier than 5 hours.

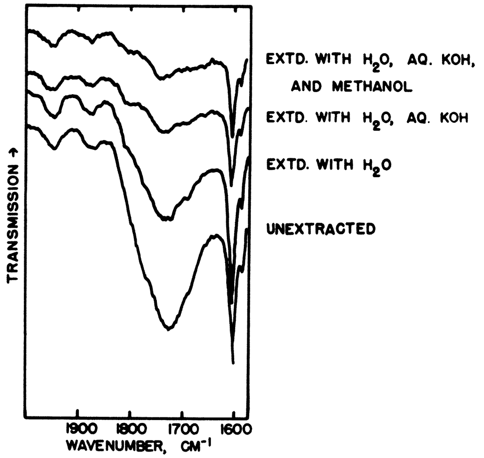

Figure 9. Carbonyl-stretching region in polystyrene irradiated 5 hours in air at 30°C.; FMIR spectra

Attempts to reconstitute a photooxidized surface by reevaporation of various extracts on both unirradiated and irradiated polystyrene surfaces were only partially successful. Deposition of the material from a methanol extract on unirradiated polystyrene, a film irradiated 2.5 hours and extracted with water, and on a film irradiated 2.5 hours and extracted with methanol reduced the water contact angle by 55°, 50°, and 51°, respectively. The same experiments with a water extract, either as such or evaporated to dryness and redissolved in methanol, produced erratic results both from film to film and on the same film. The latter result may be due to the formation of islands of material. Such inconsistencies may be the result of differences in the way various photooxidation products reorient on redeposition or to changes in the orientation of desorbable molecules in the substrate during the extraction or the redeposition process.

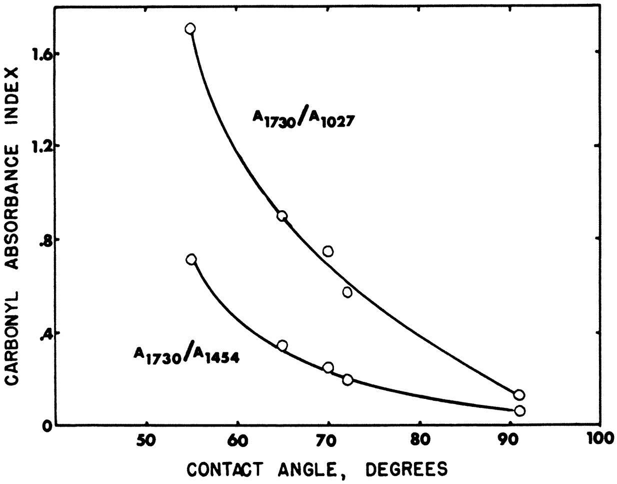

Figure 10. Relation between the relative carbonyl absorbance for polystyrene irradiated 5 hours and the water contact angle on a film irradiated 2 hours

Conclusions

An empirical relationship has been shown between the contact angles for wettability of a polymer film and the degree to which photooxidation products have accumulated in the surface layers of the film. Changes in wettability of polymer films during photooxidation are markedly dependent on the nature of the polymer. In the detection and identification of the earliest processes and products of surface photooxidation, the wettability method is far more sensitive than the infrared transmission or attenuated reflectance spectra and is about as sensitive but more specific than the ultraviolet transmission spectrum. Contact angle measurements themselves can be used as leads in the selection of solvents for the separation and identification of photooxidation products formed in the surface layers of a polymer film and are potentially useful in establishment of rates of specific processes.

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7

Adhesion of High Polymers III.

Mechanisms of Adhesion at the Rubber-Resin Interface in Hetrophase Systems

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Rubber-resin heterophase systems are classified as (1) resin as the disperse phase, (2) rubber as the disperse phase, (3) grafted rubber latex particles as the disperse phase, and (4) filled graft rubber as the disperse phase. Adhesion mechanisms related to these systems are discussed. Special emphasis is made on the last two systems which involve grafting. The graft rubber isolated from the fourth system is characterized. The graft rubber is shown to function as a compatibilizer and as an adhesive or a coupling agent for the rubber-resin interface.

Particulate organic composite materials containing both a rubber and a resin can be so familiar as to be unrecognized as such—*e.g.*, elastomeric adhesives (*63, 67*), pressure-sensitive tapes (*63*), non-pigmented organic coatings, or commonly recognized composites such as resin-reinforced rubbers (*10*) or rubber-reinforced thermoplastics (*2, 10, 55*). Though appearances and functions of these materials differ, the fundamental principles underlying the chemistry at the interface and mechanisms of reinforcement are similar.

Dobry and Boyer-Kawenoki (*14*) concluded that for polymers, compatibility is the exception and incompatibility is the rule. For a heterogeneous system, incompatibility is an advantage for reinforcement, provided that the adhesion at the interface is strong enough to withstand the applied stresses. The nature of adhesion depends on the type of interface—*e.g.*, liquid-liquid, liquid-solid, or solid-solid. In the case of two polymers at the liquid-liquid interface, a rubbery polymer-to-rubbery polymer adhesion (R-R adhesion) (*35, 36*) is likely to determine the

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process, while at the liquid-solid interface, a rubbery polymer-to-glassy polymer adhesion (R-G adhesion) should predominate. Though the latter is our major interest in this study, we also briefly discuss the adhesion at the liquid-liquid interface of transitory rubber-resin systems.

We are specifically interested in the system in which a liquid-solid interface reaction has taken place. An example of this type of reaction is the chemical grafting of a rubber with a monomer at the interface. The function of the grafted rubber as an adhesive has been postulated (*11, 29, 46, 64*) but has never been proved. Since the grafted rubber is the key to bridging two incompatible polymers together, we devoted a major portion of our experimental work to the characterization of the grafted polymer as an adhesive at the interface.

Classification of Rubber-Resin Systems. Rubber-resin heterophase systems can be classified into four types according to the main constituent in the disperse phase:

(1) Resin as the disperse phase
(2) Rubber as the disperse phase
(3) Grafted rubber latex particles as the disperse phase
(4) Filled graft rubber as the disperse phase

RESIN AS THE DISPERSE PHASE. Several kinds of resins (*10*) have been used to reinforce rubbers—*e.g.*, phenolic or coumarone resins for natural rubber, styrene-butadiene resin for styrene-butadiene rubber, etc. One other important system, pressure-sensitive adhesive, also belongs to this class. These adhesives generally contain a low molecular weight resin functioning as a tackifier. In 1957, Wetzel (*68*) and Hock (*19*) found that these adhesives were actually two-phase systems (Figure 1). Under the normal condition, the dispersed phase is the resin plus low molecular weight rubber and the continuous phase is the rubber saturated with resin.

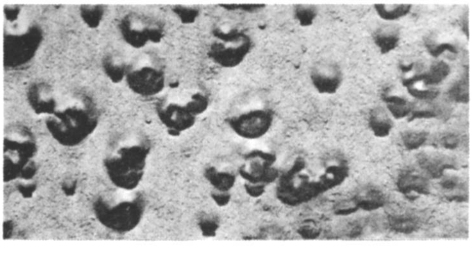

Figure 1. Electron-micrograph of two-phase pressure-sensitive adhesive

(Magnification, 11,000 ×), dark phase = resin, 3.2 pentalyn H and natural rubber by Hock (17)

They also reported a phase inversion taking place at high resin concentrations (Figure 2). After the phase inversion, the tack value of the adhesive dropped to zero.

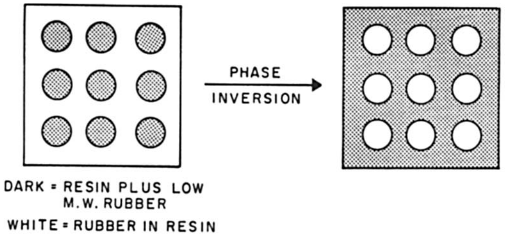

Figure 2. Phase inversion of rubber-resin phases in pressure-sensitive adhesives discovered by Wetzel and Hock in 1957

Prior to this discovery, in 1954 Silberberg and Kuhn (*62*) were first to study the polymer-in-polymer emulsion containing ethylcellulose and polystyrene in a nonaqueous solvent, benzene. The mechanisms of polymer emulsification, demixing, and phase reversal were studied. Wetzel and Hock's discovery would then equate the pressure-sensitive adhesive to a polymer-polymer emulsion instead of a polymer-polymer suspension. Since the interface is liquid-liquid, the adhesion then becomes one type of R-R adhesion (*35, 36*). According to our previous discussion, diffusion is not operative unless both resin and rubber have an identical solubility parameter. The major interfacial interaction is physical adsorption, which, in turn, determines adhesion. Our previous work on the wettability of elastomers (*37, 38*) can help predict adhesion results. Detailed studies on the function of tackifiers have been made by Wetzel and Alexander (*69*), and by Hock (*20, 21*), and therefore the subject requires no further elaboration.

RUBBER AS THE DISPERSE PHASE. In polyblend systems, a rubber is masticated mechanically with a polymer or dissolved in a polymer solution. At the conclusion of blending, a rubber is dispersed in a resin as particles of spherical or irregular shape. We can further subdivide this system into three classes according to the major intermolecular forces governing adhesion: (a) by dispersion forces—*e.g.*, the polyblend of two incompatible polymers, (b) by dipole interaction—*e.g.*, the polyblend of polyvinyl chloride and an acrylonitrile rubber (*56*), and (c) by covalent bond—*e.g.*, an epoxy resin reinforced with an acid-containing elastomer reported by McGarry (*43*).

In general, rubber particles in all these classes are non-porous and compact. An electron micrograph of a polystyrene-rubber blend (Figure 3) can illustrate the general feature of the disperse phase. The adhesion

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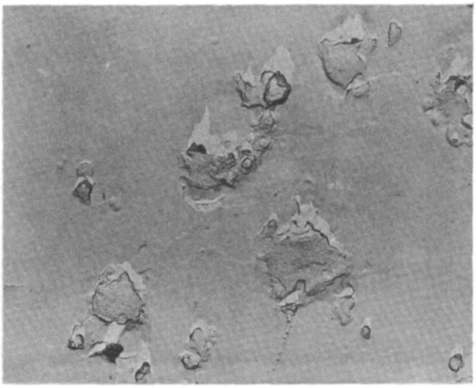

Figure 3. Electron-micrograph of polystyrene-rubber blend by the solvent-etch-double replica method

(Magnification, 8670 ×), dark phase = odd-shape rubber particles

between these two incompatible phases can be increased by so designing the components in the rubber copolymer or by the addition of a third component to act as an adhesive or a compatibilizer. A recent review in this regard written by Bohm (8) should be consulted for the mechanisms of compatibilization.

Grafted Rubber Latex Particles as the Disperse Phase. ABS polymers or acrylonitrile-butadiene-styrene polymers, can be generally made by piggy-back grafting of a polybutadiene latex with styrene and

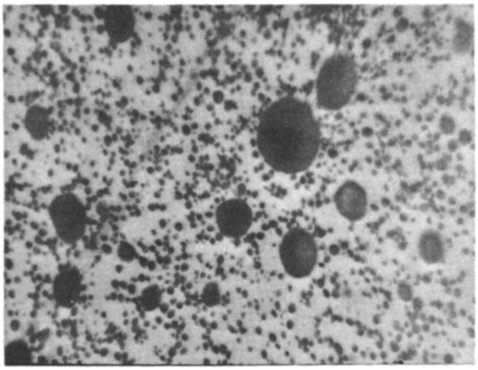

Figure 4. Electron-micrograph of grafted latex ABS polymer by the osmium tetroxide technique

(Magnification, 12,530 ×), dark phase = grafted latex particles

In Interaction of Liquids at Solid Substrates; Alexander, A.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1968.

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acrylonitrile monomers (*4, 13*). Grafting predominantly takes place on the surface of these latex particles. Undoubtedly a certain fraction of monomers can diffuse into the latex particles and will polymerize and/or graft onto rubber within the particles. A recent electron micrograph of a typical ABS polymer (Figure 4) made with the osmium tetroxide technique (*27*) shows convincingly that these particles are uniform and relatively nonporous. In Figure 5, we illustrate the change of the particle surface polarity by the piggy-back grafting. These outer shells (*17*) were actually the interface responsible for bonding between the two phases. As a result of grafting, besides the surface polarity, molecular configuration, intermolecular forces and rheological properties change accordingly. On the basis of these properties, in 1955, Hayes (*18*) patented the use of the graft copolymer to compatibilize styrene copolymers and polybutadiene. The configuration of the methyl methacrylate–natural rubber graft copolymer was studied by Merrett (*45*). He introduced the colloid chemistry terminology for the graft copolymer—*e.g.*, micelles and stabilization which were not commonly used in the polymer literature at that time. However, it would probably be more appropriate to use the term compatibilization for liquid-solid and solid-solid interfaces. Despite the confusion in terminology the graft copolymer can be also considered as an adhesive (Figure 6) for these interfaces in addition to being a compatibilizer.

FILLED GRAFT RUBBER AS THE DISPERSE PHASE. Rubber-modified polystyrene is generally obtained by polymerization grafting of a rubber in the presence of styrene monomer. The polymerization is carried out totally or partially in mass with the aid of shearing agitation, as patented by Amos *et al.* (*1*). The study on the initial stage of this type of polymerization was first published by Bender (*5*), and phase inversion similar to that discovered for the two-phase pressure-sensitive adhesives was observed. The mechanism of particle formation has also been reviewed (*47*).

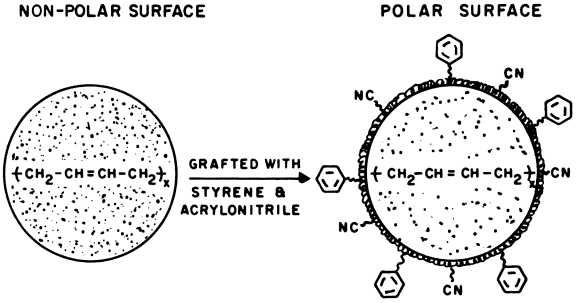

Figure 5. Polybutadiene latex particles are grafted with relatively polar monomers predominantly on the surface

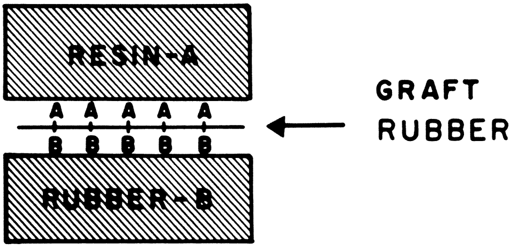

Figure 6. Adhesion at the rubber-resin interface in the rubber-reinforced thermoplastics, type III (assuming that most of the grafting takes place on the surface of latex particles)

However, no reports of surface energetics at the interface have yet been published.

The rubber particles were examined with an electron microscope after the sample was treated with osmium tetroxide (*27*). The micrograph (Figure 7) clearly indicates the porous nature of the rubber phase and the occlusion of polystyrene. We therefore classify this type of rubber phase as filled graft rubber. Since grafting takes place before and after the rubber chain is coiled, therefore, for this case, the monomer is grafted onto the rubber both within and without the rubber phase. Polybutadiene is thus made more compatible to the polymer matrix surrounding the rubber phase and the polymer filling the rubber phase. Here we have an

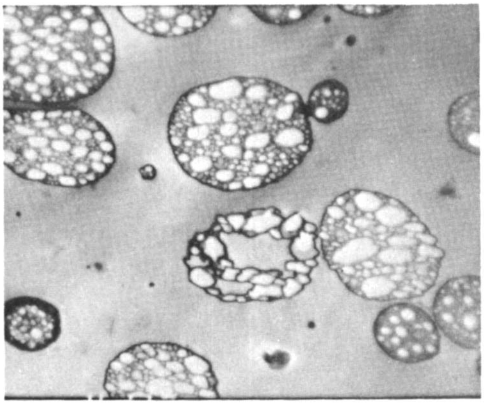

Figure 7. Electron-micrograph of rubber-reinforced polystyrene by graft polymerization

The sample was prepared by osmium tetroxide technique (magnification, 8670 ×), dark phase = rubber particles, white spots in the particles are occluded polystyrene interface or two interfaces of resin-rubber-resin, and the graft rubber acts as an adhesive for the solid-solid interface (Figure 8).

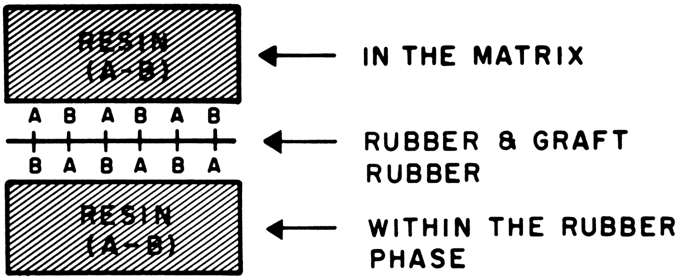

Figure 8. Adhesion at the resin-rubber-resin interface in the rubber-reinforced thermoplastics type IV, A and B are comonomers

Since these rubber particles are highly filled with a homopolymer or a copolymer, the rubber is already reinforced with a resin to give a higher modulus particle than the grafted rubber latex. On the basis of the uniqueness of these rubber particles, this process is also more appropriate in manufacturing high-strength medium-impact ABS polymer (*31*), or rubber-reinforced styrene-methyl methacrylate copolymer (*32*). The physical features of the rubber phase in an ABS polymer prepared by a polymerization grafting process are shown in an electron micrograph (Figure 9) prepared by the osmium tetroxide technique.

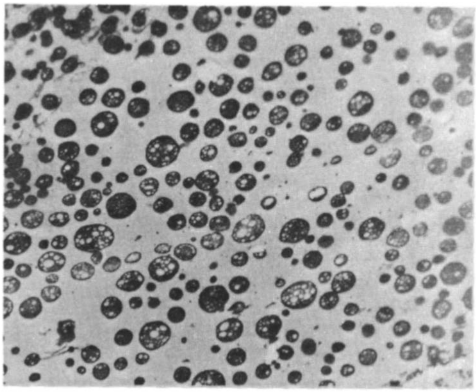

Figure 9. Electron-micrograph of an ABS polymer by graft polymerization

The sample was prepared by osmium tetroxide technique (magnification, 4130 ×)

Mechanisms of Reinforcement. Both rubber reinforced with a filler (*49, 50*) and thermoplastics reinforced with a rubber (*29, 55*) have been reviewed especially with respect to the mechanism of reinforcement. According to Nielsen (*50*), Kerner's equation (*28*) is appropriate to describe the moduli of both of these systems provided perfect adhesion exists at the interfaces:

$$\frac{E\ (\text{filled})}{E\ (\text{unfiled})} = \frac{G\ (\text{filled})}{G\ (\text{unfilled})} =$$

$$\frac{G_\mathrm{F}V_\mathrm{F}/[(7-5_\nu)G_\mathrm{p} + (8-10_\nu)G_\mathrm{F}] + V_\mathrm{p}/[15(1-\nu)]}{G_pV_F/[(7-5_\nu)G_p + (8-10_\nu)G_\mathrm{F}] + V_\mathrm{p}/[15(1-\nu)]}$$

Where G_p and G_F are the shear moduli of the plastic matrix and the filler respectively, ν is Poisson's ratio of the matrix, and V is the volume fraction. *E's* are Young's moduli. Recently this relation was verified for the rubber-reinforced thermoplastics (*29*). The effect of adhesion at the rubber-resin (or rubber-filler) interface has been studied (*49, 57, 58*) with mathematical models.

Theories regarding functions of rubber in the rubber-reinforced thermoplastics are also derived on the basis of the same premise of a perfect adhesion. In 1965, Newman and Strella (*48*) pointed out that both the original micro-crack theory proposed by Merz, Claver, and Baer (*46*) and the myriad-crack hypothesis suggested by Schmitt and Keskkula (*59*) failed to explain the reinforcement mechanism. They suggested, in turn, that the cold-draw of the glassy matrix is the key to the achievement of high elongation.

A most significant advance in recent years was made by Bucknall and Smith (*9*) who established the reinforcement mechanism on the craze theory (*25, 26*). According to their theory, the differences between reinforced and un-reinforced polystyrene simply lie in the maximum size and concentration of the craze-bands. The rubber dispersed in the matrix serves to increase the numbers of craze-bands. Without good adhesion achieved by grafting, the rubber fails to sustain tensile stresses at some stage in the crazing process. After the breakdown at the rubber-resin interface, large voids are generated to weaken the composite. We demonstrate this type of break with the model shown in Figure 10.

Bucknall and Smith's theory has been further confirmed by recent work. Matsuo (*42*) published electron micrographs of stress-crazed rubber-reinforced polymers and found his results to be in good agreement with those of Bucknall and Smith. Recently, Arends (*3*) related the cold-flow of thermoplastics to Eyring's theory of viscous flow and enlarged the scope of their theory.

Grafting and Adhesion. From the discussion in the preceding paragraph, it can be concluded that the reinforcement in rubber-resin systems

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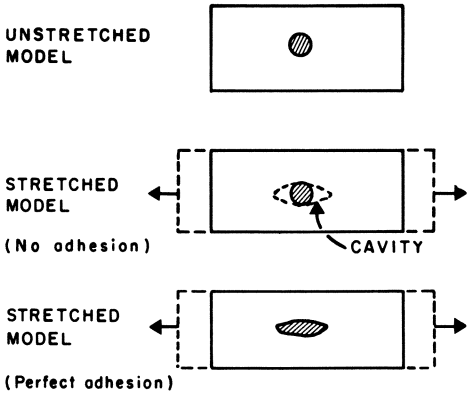

Figure 10. Adhesion and rubber-resin interface in rubber-reinforced thermoplastics

▨ *Rubber phase*

can only be achieved where a good adhesion is obtained at the interface. The adhesion mechanism (*24, 51, 52, 53, 54 66*) related to the first two systems described earlier are better understood and need not be discussed further. However, the adhesion mechanisms related to the last two systems, which involve grafting, deserve a detailed study.

Grafting of monomers onto rubber has been reviewed, (*2, 13, 30, 70*). A recent paper reported the cationic grafting of rubber (*65*). We do not intend to elaborate further on this subject. The general agreement is that grafting takes place right after initiation. During our study of the rubber-reinforced polystyrene we found that grafting took place throughout the process. Difficulties arose when crosslinking intervened, rendering the graft rubber insoluble. In the coming sections, we describe the separation, the characterization and the determination of Zisman's critical surface tension (*71, 72*) of the graft rubber phase before it is heavily crosslinked. Mechanisms of adhesion are discussed on the basis of these findings.

Experimental

Preparation of Graft Copolymer. The graft copolymers used for this study were prepared with agitation in a 2-liter resin flask equipped with a stainless steel stir-tube. The feed mixture for the polybutadiene grafted with styrene contained 200 grams of "Diene" rubber (Firestone) and 1,800 grams of styrene monomer, while the one for the polybutadiene grafted with both styrene and acrylonitrile contained 200 grams of "Diene" rubber, 500 grams of acrylonitrile and 1,300 grams of styrene. The prepolymerization was carried out in the absence of a catalyst at 105°C. for the former and at 100°C. for the latter, to a solid content

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between 35-40% before the rubber phase became highly cross-linked and insoluble. The resultant prepolymer contained the homopolymer or the copolymer, the ungrafted and grafted polybutadiene.

Separation of Polybutadiene. The ungrafted and grafted polybutadiene were separated from the homopolymer or the copolymer by the following precipitation technique:

Prepolymer (40 grams) was dispersed in methyl ethyl ketone (1,000 ml.). The dispersion was divided into several centrifuge tubes and centrifuged at 9,500 r.p.m. The supernate containing the monomer and the soluble polymer was decanted, the precipitate containing the rubber phase was re-washed with methyl ethyl ketone. We used a set of the singly-precipitated polybutadiene for the study and found that they contained a good portion of occluded polystyrene. We then used a double precipitation technique to remove the occluded polystyrene (or poly (styrene-co-acrylonitrile)). The first precipitate was redissolved in benzene and an equivalent of 0.1% of Ionol was added to the benzene solution (106 ml.). (Note: Ionol is 2,6-di-tert-butyl-*p*-cresol.) To the clear solution, methyl ethyl ketone (900 ml.) was gradually added. The doubly-precipitated polybutadiene contained both the grafted and the ungrafted portions and undoubtedly a remaining trace of polystyrene. We found that the double precipitation was necessary but the rubber was very sensitive to oxidation at room temperature, even after an addition of Ionol prior to the precipitation.

Determination of the Degree of Grafting. For a detailed quantitative study, we generally separated the grafted and the ungrafted polybutadiene. However, for this study, we were only interested in the extent of grafting in the polybutadiene during the initial polymerization. Therefore, the two portions of polybutadiene were not separated, and the degree of grafting was determined by infrared on the basis of both trans-poly(1,3-butadiene)(~964 cm.$^{-1}$) and poly(1,2-butadiene)(909 cm.$^{-1}$). The amount of styrene grafted was determined on the basis of phenyl-ring mode at 1493 cm.$^{-1}$ (Figure 11) while the cyano group absorption was measured at 2245 cm.$^{-1}$. The amount of Ionol was not enough to affect the phenyl-ring mode.

Determination of Critical Surface Tension. The method for the determination of contact angles was described in previous papers (*37, 38*). For this study, we used only one goniometer manufactured by Râme-Hart, Inc. The temperature was controlled at 20°C. with an environmental chamber. The precision was ±2° for the contact angle measurement. The liquids used were alcohols, Polyglycols P-1200, 15-200, and E-200, ethylene glycol, formamide, glycerol, and water.

The styrene-acrylonitrile copolymers were prepared in the form of a thin film. The graft polybutadiene solution was coated on a glass slide. But, for the graft polymer containing acrylonitrile, it was undesirable to use the glass slide because of the induced orientation, therefore, we used a Mylar film to support a thick smooth film of the graft rubber.

Preparation of Electron-micrographs. The polystyrene-rubber polyblend sample was etched by solvent according to the technique developed by Traylor. A double replica technique was used to prepare the sample. The first replica was methylcellulose, the second platinum and carbon, 800 A. thick.

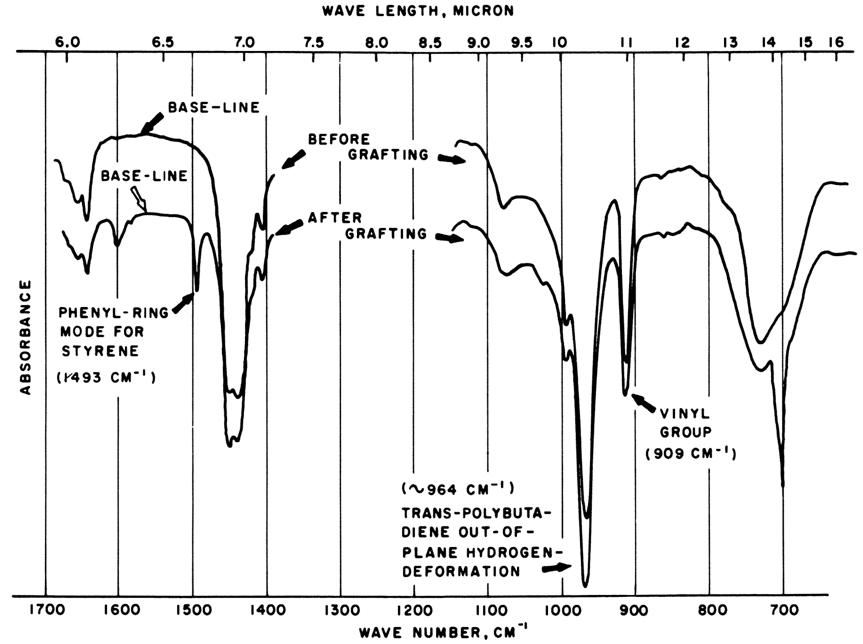

Figure 11. Infrared spectra of polybutadiene before and after moderately grafting with styrene, doubly precipitated

Other electron-micrographs were prepared according to Kato's technique (*27*). Osmium tetroxide made the rubber particles dark and distinct. The thickness of the ultrathin specimen was 1000 A.

Results and Discussion

Wettability of Elastomers and Copolymers. The wettability of elastomers (*37, 38*) in terms of critical surface tension was reported previously. The elastomers commonly used for the reinforcement of brittle polymers are polybutadiene, styrene-butadiene random and block copolymers, and butadiene-acrylonitrile rubber. Critical surface tensions for several typical elastomers are 31 dyne/cm. for "Diene" rubber, 33 dyne/cm. for both GR-S1006 rubber and styrene-butadiene block copolymer (25:75) and 37 dyne/cm. for butadiene-acrylonitrile rubber, ("Paracril" BJLT nitrile rubber). The copolymerization of butadiene with a relatively polar monomer—*e.g.*, styrene or acrylonitrile—generally results in an increase in critical surface tension. The increase in polarity is also reflected in the increase in the solubility parameter (*34, 39, 40*) and in the increase of glass temperature (*40*). We also noted a similar increase in critical surface tensions of styrene-acrylonitrile copolymers with the

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increase in acrylonitrile content (Figure 12). The critical surface tension of polystyrene determined by our method is 36 dyne/cm., and values for these copolymers vary between 37 and 43 dyne/cm. Parallel increases in both the solubility parameter and glass temperature have also been noted for the copolymers.

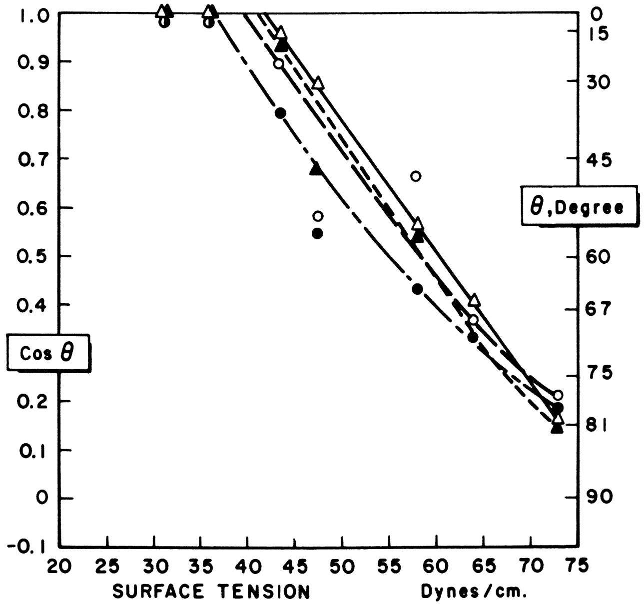

Figure 12. Wettability of styrene copolymers

			γ_c (Dynes/cm.)
△	*Acrylonitrile*	*32%*	*43*
▲	*Acrylonitrile*	*25%*	*42*
○	*Acrylonitrile (exptl.)*	*16%*	*40*
●	*Acrylonitrile (exptl.)*	*6%*	*37*

Compatibility of polymers implies a semi-quantitative measure can be used to predict whether two or more polymers are compatible. The use of one of the semi-quantitative approaches, solubility parameter, was demonstrated by Hughes and Britt (22). It was concluded (8) that one parameter was insufficient to predict the compatibility. In this paper, we now introduce critical surface tension which is determined from the surface properties of a polymer. Though both of these parameters have been related by Gardon (15), we are inclined to use the latter because we can further describe the wettability between two polymers. For instance, by the use of γ_c, we can predict equally well that compatibility between polystyrene and polybutadiene can be improved if butadiene is

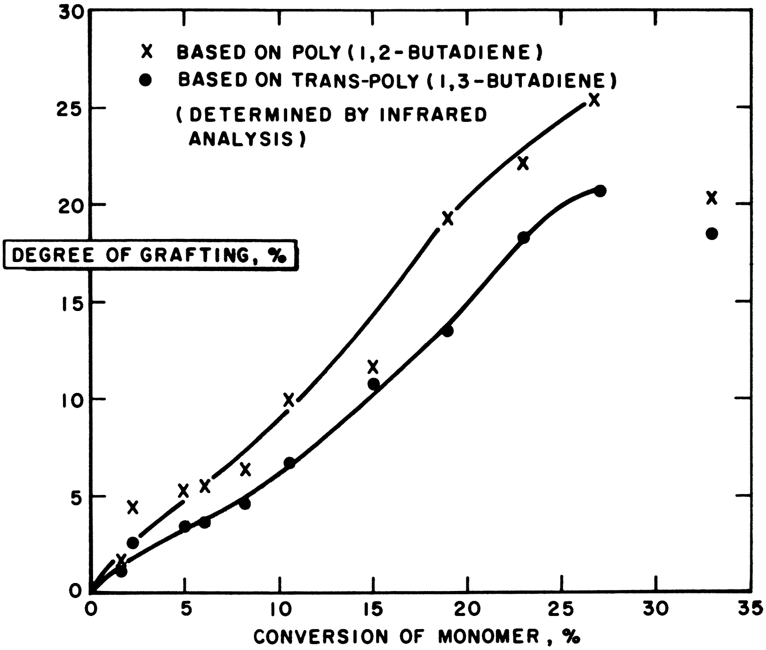

Figure 13. Degree of grafting of polybutadiene vs. *conversion of styrene monomer, singly precipitated*

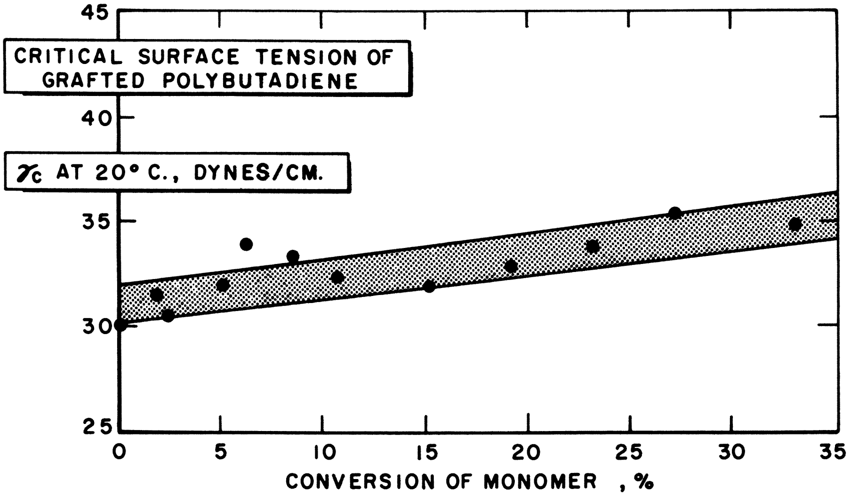

Figure 14. Effect of monomer conversion on critical surface tension of polybutadiene grafted with styrene, singly precipitated

allowed to form a copolymer of styrene or if a styrene-butadiene copolymer can be added to compatibilize the two incompatible polymers.

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Thermodynamic Work of Adhesion. One other important aspect of surface energetics (*71, 72*) is the use of surface free energy to calculate the maximum reversible work of adhesion, W_{ad}, which has been correlated to the adhesive strength (*41, 44*) and should not be equated to the strength of an adhesive joint (*6*). Since neither wetting nor adhesion is controlled purely by thermodynamic factors, we should use the maximum reversible work of adhesion, W_{ad} on the basis of an idealistic approach. When all other variables are equal, we can use W_{ad} to compare the effectiveness of adhesives for a specific substrate.

By definition, W_{ad} is the sum of surface free energies of a liquid (F_{lv}) and a solid in vacuum (F_s) minus the interfacial free energy (F_{sl}) according to Dupre's equation:

$$W_{ad} = F_s + F_{\mathrm{lv}} - F_{\mathrm{sl}} \tag{1}$$

For an amorphous solid polymer, $F_s \simeq \gamma_s$, and F_{sl} has been theorized to be negligible (*71, 72*). By assuming $\Phi = 1$ (*62*) (Φ is the interaction parameter), we then obtain

$$\gamma_c \rightarrow \gamma_s \tag{2}$$

Since this work of adhesion has been correlated (*41, 44*) with the adhesive strength, we can presumably use W_{ad} to estimate the theoretical maximum adhesive strength between a rubber and a resin for all four systems discussed in this paper. For example, the work of adhesion between polystyrene and polybutadiene is 67 dyne/cm., and that between polystyrene and styrene-butadiene copolymer is 69 dyne/cm.

Wettability of Graft Copolymers. One of the difficulties in studying the graft copolymer is the separation of the grafted portion from the occluded copolymer. Without a nearly clean separation, it is impossible to determine whether the wettability is for the occluded copolymer or for the grafted rubber or for both. We shall demonstrate this by using both the singly and the doubly precipitated rubber obtained during the mass polymerization of polystyrene. In Figure 13, we show the apparent degree of grafting at 27% conversion increased to 21% as determined on the basis of vinyl group absorption and 25.5% on the basis of the trans isomer absorption. The critical surface tensions of these fractions also increase with the percent conversion of the monomer (Figure 14). The data fall within a band instead of a straight line. This result is expected in view of the limited precision of the contact angle determination and the possible contamination with the occluded polystyrene.

A separate polymerization was carried out under identical conditions but, for this experiment, the polybutadiene fraction was separated by the double precipitation described in the *Experimental* section. As expected, the apparent degree of grafting was in general 50% lower than that

In Interaction of Liquids at Solid Substrates; Alexander, A.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1968.

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obtained by the single precipitation (Figure 15). Apparently a large portion of the occluded polystyrene could be removed by a second precipitation. The doubly precipitated polybutadiene fractions were very sensitive to oxidation, and oxidation tended to increase γ_c. Therefore, an additional amount of Ionol was added prior to the second precipitation.

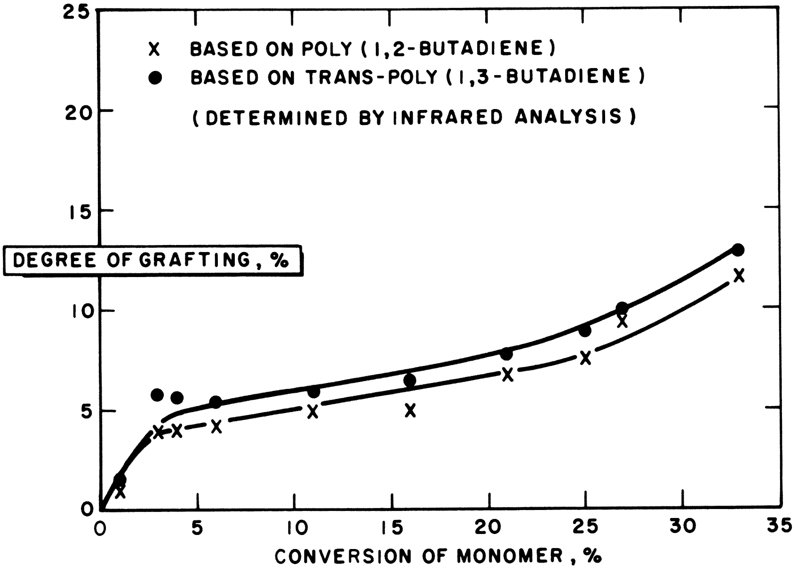

Figure 15. Degree of grafting of polybutadiene vs. *conversion of styrene monomer, doubly precipitated*

The critical surface tensions of the doubly precipitated fractions versus conversion are shown in Figure 16. Here we note an abrupt rise in γ_c and then a plateau band between 34 and 35.5 dyne/cm. These increases in γ_c, though higher than expected, could be caused predominantly by the grafting of styrene to the rubber as observed in normal random copolymerization (*37, 38*).

The graft polybutadiene containing both styrene and acrylonitrile prepared in a separate experiment was isolated by a double precipitation. The experimental value for the degree of grafting was calculated on the basis of the trans isomer of polybutadiene (Figure 17). Except for two fractions, the styrene contents are within the shaded band. We note that both the styrene and the acrylonitrile contents increase slightly. This phenomenon might be caused by the polymerization temperature which was lower than in the previous two experiments (100°C. instead of 110°C.).

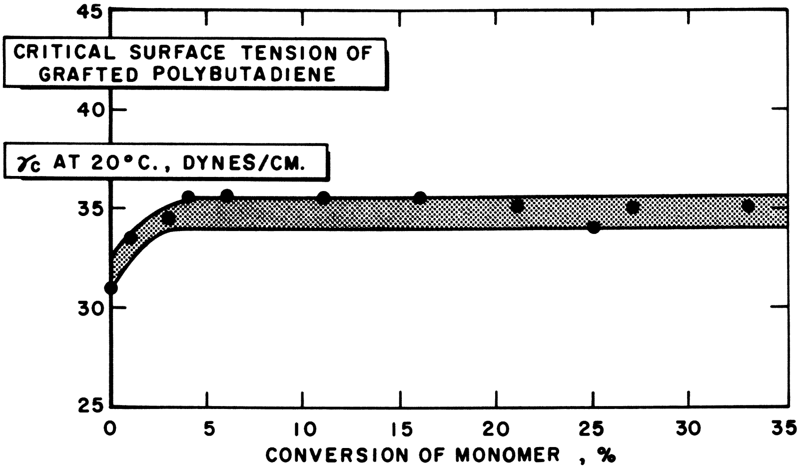

Figure 16. Effect of monomer conversion on critical surface tension of polybutadiene grafted with styrene, doubly precipitated

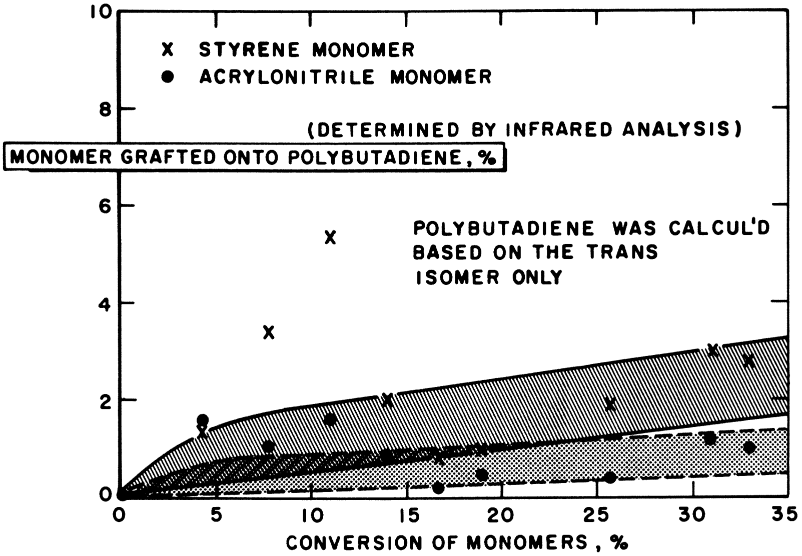

Figure 17. Styrene and acrylonitrile grafted onto polybutadiene vs. *monomer converted, doubly precipitated*

Despite this low degree of grafting, γ_c's increase with the increase in percent conversion (Figure 18). The shaded band shows the magnitude. However, the rate of increase in γ_c is not in proportion to the rate of increase in the degree of grafting. The double precipitation could be

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accompanied by an undue oxidation of polybutadiene, but the infrared analysis did not show any absorption band related to the oxidized product.

In spite of this discrepancy, the γ_c's for polybutadiene after being lightly grafted with styrene and acrylonitrile, show the same trend as those for polybutadiene after it has been grafted with styrene. Critical surface tension of grafted polybutadiene increases with the extent of grafting, though the rate of increase is somewhat greater than expected. We further noted that the γ_c of the polybutadiene, after it had been partially grafted, lies somewhere between the γ_c's of both the homopolymer (or the copolymer) and the ungrafted polybutadiene.

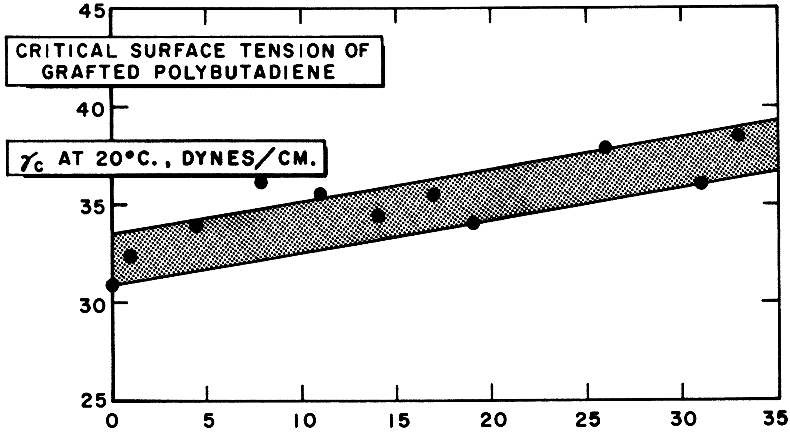

Figure 18. Effect of monomer conversion on critical surface tension of polybutadiene grafted with styrene and acrylonitrile, doubly precipitated

Functions of Graft Copolymers at the Interfaces. AT THE LIQUID-LIQUID INTERFACE. During the early stage of polymerization, the interface is rubber-to-rubber or liquid-to-liquid. The substitution of the graft rubber for the ungrafted rubber of the interface tends to lower the interfacial tension (γ_{12}) according to Good and Girifalco equation (*16*):

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\Phi(\gamma_1\gamma_2)^{1/2} \tag{3}$$

Where Φ, the interaction parameter, is assumed to be unity. If we neglect the presence of the monomer in both phases, we can use the following critical surface tension values to estimate γ_{12}: γ_1 (polystyrene), 36; γ_2 (ungrafted polybutadiene), 31 and γ_2 (grafted polybutadiene), 34, dyne/cm. The estimated γ_{12}'s are 0.2 dyne/cm. for the ungrafted polybutadiene interface and —0.2 dyne/cm. for the grafted polybutadiene interface.

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A negative or zero interfacial tension is a necessary condition for the emulsification which leads to the phase inversion reported by Bender (*5*). This is one of the most important criteria for the particle formation mechanism. Unfortunately this surface energetics aspect has not been discussed by previous workers.

A zero or negative interfacial tension also implies the compatibilization of two phases (*12*). An inter-diffusion at the molten stage can take place under this condition. We could expect the graft side chain to diffuse into the polymer phase and the grafted rubber main chain to diffuse into the rubber phase as shown in Figure 6. On the whole, we can conclude that grafting tends to make rubber more compatible with the polymer phase.

AT THE LIQUID-SOLID INTERFACE. The maximum work of adhesion, W_{ad}, for the grafted rubber-polymer interface is always higher than that for the ungrafted rubber-polymer interface. During the course of polymerization, most of the rubber is grafted and lightly cross-linked. If the rubber is still rubbery at the end of the polymerization, we can consider the interface to be liquid-solid at room temperature. By using the same example as in the preceding paragraph, we can show that W_{ad} is 70 dyne/cm. for the grafted rubber-polystyrene interface and 67 dyne/cm. for the ungrafted rubber-polystyrene interface. We thus conclude that the graft rubber is a better adhesive than the ungrafted rubber.

Factors Affecting the Interfacial Bond. Besides grafting, the adhesion between a rubber and a resin can be achieved by forming hydrogen bridges, by causing dipole-interaction or by creating covalent bonds. We shall not elaborate further on this. The factors which adversely affect the interfacial bond need to be briefly discussed on the basis of the adhesive concept. The first factor is cross-linking, as determined by the swelling index of the rubber phase. The higher the degree of cross-linking or the lower the swelling index, the less rubbery the rubber phase becomes. The rigid rubber phase, even if it is grafted, cannot function as an adhesive but introduces unnecessary stress at the interface. Consequently the rubbery adhesive is replaced by a solid phase; therefore, the final interface is actually solid-solid instead of liquid-solid.

The second deterimental factor is the thermal or the thermal oxidative degradation of the rubber phase at elevated temperatures. As reported previously, the oxidative degradation (*33*) is enhanced by the presence of metallic impurities. As a result of these modes of degradation, the rubber phase loses unsaturation upon further crosslinking or cyclization (*61*) or both. Although the polarity of rubber may be increased; the rigidity is also increased simultaneously to nullify the gain in polarity. As a consequence, the rubber loses its function as an elastomeric adhesive at the interface. A similar detrimental effect of degradation in the pressure-sensitive adhesives is well known (*20, 21, 69*). In rubber-reinforced thermoplastics, the degradation of rubber generally causes de-wetting of the rubber-resin interface. Therefore, upon stretching or under tensile stress, rubber no longer functions as a reinforcing medium, and toughness and impact resistance of the composite drastically decrease.

Conclusions

Rubber-resin heterophase systems were classified as (1) resin as the disperse phase, (2) rubber as the disperse phase, (3) grafted rubber latex particles as the disperse phase and (4) filled graft rubber as the disperse phase. Adhesion mechanisms related to these systems were discussed. Special emphasis was made for the last two systems which involved grafting. The graft rubbers isolated from the fourth system were characterized. Critical surface tensions of polybutadiene after being grafted lightly with styrene and with styrene and acrylonitrile were found to lie between those of the two phases. Consequently, the graft rubber was shown to function as a compatibilizer and as an adhesive or a coupling agent for the rubber-resin interface. Degradation and excessive cross-linking of the rubber phase tended to reduce adhesion at the interface.

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8

Adhesion of High Polymers IV.

Relationships Between Surface Wettability and Bulk Properties of High Polymers

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Critical surface tensions (γ_c) *of a series of functional polymers were determined. These results are compared with those calculated on the basis of solubility parameter* (δ) *according to the following equation:*

$$\gamma_c{}^{0.43} = 0.24\ \delta\Phi V_m{}^{0.14}$$

where Φ *is the interaction parameter defined by Good and Girifalco and* V_m *is the molar volume. Another comparison is made with parachor* (P) *according to the following equation:*

$$\gamma_c = P^4 V_m{}^{-4}\Phi^2$$

The analysis of variance and the method of regular regression are used in evaluating the results. Equation improvements are discussed. The difficulties in predicting surface tensions of polymers on the basis of bulk properties are emphasized.

In recent years, developing interests in surface energetics and adhesion of liquid-like polymers, or polymer liquids, have prompted both theoretical and experimental work on surface tension. Unlike low molecular weight liquids, polymer liquids have not been extensively studied. Bondi and Simkin (*1*) mentioned surface tension in their study on high molecular weight liquids. Roe (*28*) applied both the cell theory of polymer liquids and the hole theory of surface tension of simple liquids to develop an approximate theory of surface tensions of polymer liquids. His approach has met some degree of success. Notably, both Bondi's and Roe's work are somewhat related to the cell theory introduced by Prigogine and

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co-workers (*24*). Prigogine used one of the important parameters, 3*c*, to describe molecular flexibility in terms of the external degree of freedom. This parameter resembles the number, *n* intuitively developed by Hayes (*8*). The use of Hayes' degree of freedom together with other parameters in correlating surface wettability and glass temperatures of polymers (*16*) was reported previously.

Besides the theoretical work, two important experimental approaches deserve mention:

1. The direct measurement of surface tensions of polymer melts (*10, 27, 29, 30, 37*) generally yields values somewhat greater than those obtained indirectly, depending on the method and the instrument. Unfortunately, structure correlation studies cannot be undertaken until more direct surface tension data have been obtained.

2. The convenience of applying indirect measurements in terms of critical surface tension has contributed to their extensive use. Zisman (*39, 40*) originally assumed that both interfacial tension and the spreading pressure are negligible for low-surface-energy solids. Contrary views have been stated by Johnson and Dettre (*11*). Melrose (*21*) showed that the interfacial tension was actually measurable, and recently Neumann and Sell (*22*) refined the measurement by taking into account spreading pressure. One rather noticeable complication is the induced orientation reported by Ray and co-workers (*26*), and more recently discussed by Cuthrell (*3*) in terms of the environmental effect. Despite these limitations, we found that the consideration of the critical surface tension was technically useful and theoretically sound in comparing the surface energetics of polymers on a relative scale. For instance, we found that the wettability of rubbers could be readily characterized by critical surface tensions (*15*).

The purpose of this paper is to use data already aquired on critical surface tension for a correlation with solubility parameters and parachors of polymers. The theoretical background of these parameters is briefly mentioned. The evaluation of the calculated values is then discussed. Because of the complexity of the polymer conformation on the surface, we do not imply that a straight-forward relationship between the surface and the bulk properties is available, even in the case of a liquid-like amorphous polymer. Another purpose of this paper is, therefore, to point out the complicating factors and the difficulties in predicting the surface wettability on the basis of bulk properties.

Theoretical Background

Solubility Parameter and Surface Tension. Cohesive energy density (CED) (*9*) is the energy, in calories per cubic centimeter, necessary for an infinite separation of the molecule in 1 cubic centimeter of liquid versus the action of intermolecular attraction:

$$\text{CED} = \delta^2 = (\Delta H_v - RT)/V_m \qquad (1)$$

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where δ is the solubility parameter (cal./cc.)$^{1/2}$, ΔH_v is the molar heat of vaporization (cal./mole), R is the gas constant (cal./mole-deg.), T is the temperature (°K.), and V_m is the molar volume (cc./mole).

An empirical relationship between the solubility parameter and the liquid surface tension of a nonpolar liquid was obtained by Hildebrand and Scott (*9*)

$$\delta = 4.1\ (\gamma_l/V_m^{1/3})^{0.43} \tag{2}$$

where γ_l is the liquid surface tension (dyne/cm.), and the unit for 4.1 is (cal./cc.)$^{1/2}$ (dyne/cm.)$^{-0.43}$ (cc./mole)$^{0.14}$. Recently we have reexamined this relationship (*17*) and found that it can be applied to nearly all non-oxygenated liquids including polar amines and nitriles.

Despite the approximation, Zisman's critical surface tension (*39, 40*) still provides the most convenient means of expressing the surface tension of a solid. Later Gardon (*6*) suggested a possible linear relationship between the critical surface tension γ_c and the solubility parameter for liquid-like polymers. He also proposed the following relation between solid surface tension and critical surface tension:

$$\gamma_s = \gamma_c/\Phi^2 \tag{3}$$

where Φ is the ratio between the reversible work of adhesion ($\gamma_A + \gamma_B - \gamma_A\gamma_B$) and the geometrical mean of the work of cohesion of the two components. For low energy solids (*6*), Φ is greater than 0.8 but less than 1. This parameter, Φ, is the interaction parameter introduced by Good and Girifalco (*7*).

On the basis of Equations 2 and 3, we then derived one empirical equation especially for nonpolar polymers (*16*).

$$\gamma_c^{0.43} = 0.24\ \delta\Phi^{0.86}V_m^{0.14} \tag{4}$$

or we can simplify it into Equation 5

$$\gamma_c^{0.43} = 0.24\ \delta\Phi V_m^{0.14} \tag{5}$$

We later found (*17*) that a slight modification was needed for polyesters and polyethers and this equation did not apply to poly(vinyl alcohol) and nylon.

The molar volume in these equations is difficult to assign. This was found to be a problem in the case of a polar liquid. Recently Roe (*29*) pointed out that, in the case of polymeric liquids, the thickness of the transition layer depends not only on the size of the repeat unit but also on the degree of correlation between successive structural units, or, in other words, on the flexibility of the polymer chain. It is, therefore, not appropriate to use the cube root of the molar volume as a measure of the thickness of the monomolecular layer at the vapor-liquid interface.

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Molecular Orientation and Surface Tension. One disconcerting fact is the molecular orientation of nonsymmetrical and polar liquids. With orientation, the surface of these liquids may represent only a part of the molecules. For this type of liquid, a correlation between the surface and the bulk properties could present a problem. The original assumption made by Hildebrand and Scott (*9*) was that nonpolar liquid molecules assume a spherical symmetry. The general application of their equations to liquids without a spherical symmetry is really remarkable. However, we noted (*17*) that deviations were found for nearly all oxygenated liquids. In the case of polymers, the molecular orientation is expected to play a more important role. This could be one of the reasons that the relationship between surface and bulk properties of polymers is rather sporadic. In the *Experimental* section, we shall explain the importance of the induced orientation (*3, 26*) with respect to obtaining a surface tension reading for a polar polymer.

As a result of molecular orientation, it would appear less appropriate to use the cube root of the molar volume as a measure of the thickness of the monomolecular layer at the vapor-liquid interface. An accurate calculation of the monomolecular layer thickness requires a precise theoretical model of the structure of a liquid or a polymer which is beyond the scope of this paper. An example of this kind of approach is given by Roe (*28*) in his paper on polymeric liquids.

Parachor and Surface Tension. Kleeman (*12*) and Macleod (*18*) separately found an empirical equation to correlate density and surface tension of a liquid

$$\gamma = C(D - d)^4 \qquad (6)$$

where C is a constant, D and d is the density of liquid and vapor respectively. This simple relation appears to hold over a wide range of temperature and forms the foundation of Sugden's parachor — P (*36*):

$$P = \frac{\mathrm{M}}{D - d}\gamma^{1/4} \qquad (7)$$

where M is the molecular weight in gram/mole, and P is in (dyne/cm.)$^{1/4}$ (cc./mole). The dimension is $[\mathrm{M}]^{1/4}[T]^{-1/2}[L]^3$.

When the vapor density is negligible, Equation 7 can be written in terms of molar volume of a liquid, V_m:

$$P = \frac{\mathrm{M}}{D}\gamma^{1/4} = V_m\gamma^{1/4} \qquad (8)$$

Hence, a comparison of parachors for different compounds, according to Sugden, is a comparison of molar volumes at temperatures at which the liquids have the same surface tension.

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Table I. Physical Properties of Organic Liquids Used

Hydroxy-Containing Compounds	*Source*	*Molecular Weight*	*Specific Gravity 25/25°C.*
Polyglycol P-1200	Dow	1200 (Aver.)	1.003
Polyglycol 15-200	Dow	2600 (Aver.)	1.053
Polyglycol E-200	Dow	200 (Aver.)	1.124
Ethylene glycol	Dow	62.1	1.113
Formamide	Reagent	45	1.134^{20}
Glycerol (U. S. P.)	Dow	92.1	1.252
1-Octanol	Reagent	130.2	0.827_4^{20}
1-Heptanol	Reagent	116.2	0.822_4^{20}
n-Butyl alcohol	Reagent	74.1	0.810_4^{20}

In 1965, Roe (*27*), Marwedel (*20*), and Lee and co-workers (*13*) independently suggested that parachor could be used to calculate the surface tension of a polymer. We, therefore, use the following equation for the calculation:

$$\gamma_c = P^4 V_m^{-4} \Phi^2 \qquad (9)$$

The calculated results were used to compare with those obtained by us and by others (*34*). The causes of deviations are discussed in the later section.

Experimental

Preparation of Samples. In obtaining a reliable critical surface tension, the sample preparation was very important. For most polymers, we used a heat-cleaned microscope slide to support a film cast from a solution containing 5% by weight of polymer. The solvent was first slowly evaporated. The semi-dry film was further dried at 50°C. under vacuum to remove the remaining trace of solvent. As reported previously we detected the effect of orientation, or the environmental effect, caused by the polar silicate surface which supported the polymeric film (*15*). Therefore, for polar polymers, we attempted to preserve the orientation of polar groups at the air-solid interface by using a polar film to mold the polymer. The polar film was either Mylar or "Kapton" polyimide H-film. H-film was used especially for polymers of high glass temperatures. No mold-release agent was used, and no attempt was made to remove the static charges on the surface.

Determination of Contact Angle. At the beginning of this work, no commercial unit was available; therefore, we built a goniometer after the model described by Fort and Patterson (*5*). This goniometer was made to observe the surface of a drop which was used to be the center of rotation, and the angle at which extinction occurred was equal to the

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for the Determination of Critical Surface Tension

$(n)_d^{25}$	*Viscosity (Centistokes) at 25°C.*	*Surface Tension dyne/cm. at 20°C.*	*Water (Percent)*
1.448	160	31.3	0.11
1.459	360	36.6	0.29
1.459	40	43.5	0.36
1.430	15	47.5	0.97
1.445^{20}	300	58.2	0.11
1.468	435	64.0	0.37
1.429^{20}	10.8^{20}	26.7	0.26
1.424^{20}	8.7^{20}	25.6	0.20
1.399^{20}	3.5^{20}	24.6	0.27

contact angle. The angles of appearance and disappearance, which should be the same within one degree, were recorded. Precision was good, being within plus or minus one degree. With this type of goniometer, we only read from one point of the liquid on a fresh polymer sample at 15, 30, and 45 minute intervals. For high viscosity liquids, the initial reading at 0 minute could be erroneous, but after 15 minutes, the liquid reached equilibrium and the reading changed only slightly, if any. The physical properties of these liquids are listed in Table I. Since the viscosities of these liquids varied, we preferred to take readings at more than one time interval. For this goniometer, the work was carried out in a dark room between 20° and 25°C. with 20-30% R. H.

For contact angles above 90°, we later used the NRL-contact-angle goniometer Model A-100 manufactured by Râme-Hart, Inc. according to the unit used by Zisman. The techniques in obtaining contact angles were described by Zisman and co-workers (*39, 40*). Because of its simplicity especially without the use of a dark room, most of our later work was conducted with NRL goniometer. According to Fort and Patterson (*5*), despite two different principles involved in these two types of goniometer, the readings were equivalent and interchangeable.

The hydroxy compounds used in this experimental work generally did not attack the surface of polymers. Another advantage of using the hydroxy compounds was to provide liquids which could interact with the substrate besides dispersion forces. However, two of the polar liquids—*e.g.*, formamide and ethylene glycol—used were unsatisfactory as observed by others (*39, 40*). Since no other substitute was found at the time of this study, they were used especially for the high surface tension region. Therefore, for polar polymers with $\gamma_c > 40$ dyne/cm., the determined values were somewhat less accurate than those for polymers with $\gamma_c < 40$ dyne/cm. A typical $\cos\theta - \gamma_{lv}$ plot is illustrated in Figure 1. The observed results and the sources of polymers are listed in Table II. Since most of these polymers were obtained commercially, we did not receive complete information regarding the detailed characterization of each polymer—*e.g.*, molecular weight and molecular weight distribution.

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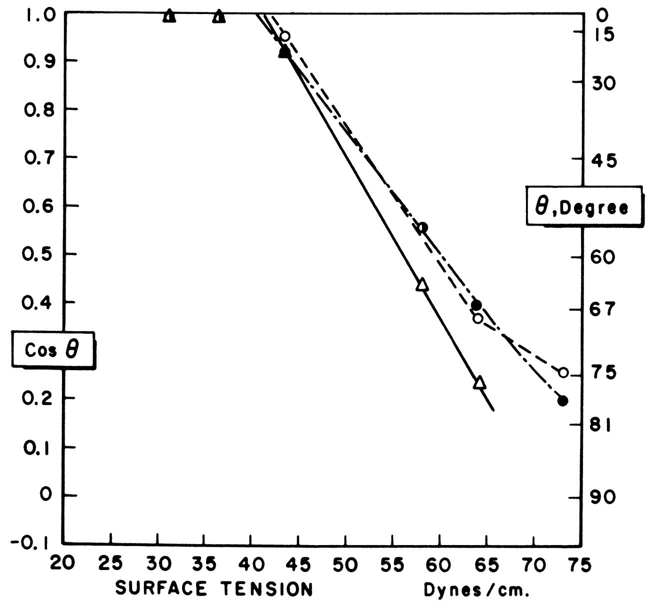

Figure 1. Wettability of functional polymers (aromatic polar)

	γ_c (dyne/cm.)
○—*"Phenoxy plastics" (Bakelite)*	*43*
△—*Polycarbonate (G. E. "Lexan")*	*42*
●—*"Polysulfone" (Union Carbide)*	*41*

Results and Discussion

In Table III, critical surface tensions of thirty-nine polymers are reported, calculated on the basis of Equation 5 by assuming $\Phi = 1$. In other words, these calculated results are equivalent to the calculated solid surface tensions (γ_s). Solubility parameters of several polymers listed in the table were calculated on the basis of Small's constants (*35*), and all molar volumes were calculated on the basis of the molecular weight of the repeat unit and the density of the polymer. The results in Table III were used to prepare a graph (Figure 2) for the comparison between the calculated and the observed critical surface tensions of these polymers. The data are rather scattered, and the calculated values are generally lower than those observed directly. The following factors may be contributing to the deviations:

1. As pointed out by Roe, the calculation of the monolayer thickness on the basis of the cube root of the molar volume of a polymer is rather inaccurate (*29*).

2. The original Hildebrand and Scott equation was obtained on the premise that nonpolar liquids possessed a spherical symmetry. For liquids without symmetry, the molecules tend to orient. The result of orientation could contribute to the departure of the surface properties from the bulk properties of polar and hydrogen-bonded liquids. This departure should be enhanced in the case of a long-chain polymer.

3. Under a separate study (*17*), we found that oxygenated liquids generally do not follow the Hildebrand and Scott equation. For the simplest oxygenated liquids—*e.g.*, ethers and esters—the proper equation should be:

$$\delta = 3.6\left(\frac{\gamma_1}{V_m{}^{1/3}}\right)^{0.56} \tag{10}$$

On the basis of Equation 10, we modified Equation 4 into Equation 11 for polyethers and polyesters.

$$\gamma_c{}^{0.56} = 0.28\,\delta\Phi V_m{}^{0.19} \tag{11}$$

With the modification, we still did not observe any substantial improvement in the overall correlation.

4. It should be noted that some of the polymers in Table III are crystalline or semicrystalline—*e.g.*, poly(vinyl alcohol), nylon, and poly(ethylene oxide). It is known that the crystalline structure tends to alter the liquid-like properties of polymers (*6*).

5. There are some uncontrollable factors affecting the determination of critical surface tension—*e.g.*, the type of liquids used, the type of interaction between a liquid and a solid, the homogeneity of surface, etc. An ideal correlation should be made from the direct surface tension, if available, of a polymer melt.

The critical surface tensions reported in Table IV were calculated on the basis of Equation 9 by assuming $\Phi = 1$. The parachor values for the repeat unit were calculated on the basis of the recommended values published by Quayle (*25*). For hydrogen-bonded polymers, we attempted to correct the parachors by subtracting the values allowed for hydrogen bridges formed at maximum sites from the original readings. For instance, two hydrogen bridges were counted per repeat unit of poly(6-aminocaproic acid), nylon-6. Even with this correction, the calculated critical surface tensions for both nylon-6 and nylon-6,6 are still higher than the observed values. The data in Table IV suggest that this actually happens to most other polymers besides nylons.

The deviations between observed and calculated values in both Tables III and IV were subjected to the analysis of variance (*23*) (tested at the F. 99 level). The computed results indicate that there is a significant difference between these two methods of calculation. The coefficients of correlation for these two proposed relationships were calculated

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Table II. Sources and Observed Critical

Polymers	*Sources*
Polyacrylonitrile	Exptl., Dow-Badische
Poly(ethylene oxide)	"Carbowax" 4000
"Phenoxy Plastics"	Bakelite
Polycarbonate	"Lexan," GE
Poly(2-chlorostyrene)	Exptl., Dow
"Polyphenylene Oxide"	GE "PPO"
Poly(methyl acrylate)	Exptl.
Poly(vinyl formal)	"Formvar," Monsanto
Poly(formaldehyde)	"Delrin" Acetal resin, duPont
Poly(methylstyrene), mixed isomers	Exptl., Dow
Polystyrene	Styron 666, Dow
Poly(ethyl methacrylate)	Exptl.
Poly(propylene oxide)	Exptl., Dow
Poly(vinyl methyl ether)	"Gantrez" M, General Aniline
Poly(4-tert-butylstyrene) (96% p-)	Exptl., Dow
Poly(vinyl butyral)	"Butvar," Monsanto
Poly(butyl acrylate)	Exptl.

from these data by the method of regular regression (23). A similar set of computation was carried out after three highly hydrogen-bonded polymers were removed from the lists. (These three polymers were nylon-6, nylon-6,6 and poly(vinyl alcohol)). Both results are tabulated as follows:

	Mean		*Variance*		*Standard Deviation*		*Correlation Coefficient*	
Method	*(1)*	*(2)*	*(1)*	*(2)*	*(1)*	*(2)*	*(1)*	*(2)*
Solubility parameter	−5.88	−8.51	158.73	60.65	12.60	7.79	0.731	0.762
Parachor	8.65	8.22	182.14	171.40	13.50	13.09	0.299	0.178

[a] Column 1 includes the data for the three hydrogen-bonded polymers; while Column 2 does not.

It is important to note that the correlation coefficient is slightly increased in the case of the solubility parameter but decreased in the case of the parachor after the three hydrogen-bonded polymers were removed from the Tables.

The computed results indicate that compared with the solubility parameter relationship, the existing parachor relationship has a lower

Surface Tensions of Functional Polymers

Density d *(gram/cc.)*	*Solubility Parameter* δ *(cal./cc.)*$^{1/2}$	*Critical Surface Tension* γc *(dyne/cm.)*
1.17	12.5	44
1.12	8.6 (calc.)	43
1.17-1.18	10.2 (calc.)	42
1.20	10.2 (calc.)	42
1.25	10.5 (calc.)	42
1.06	10.7 (calc.)	41
1.22	10.1	41
1.23	7.3 (calc.)	38
1.43	9.7 (calc.)	36
1.04	9.8 (calc.)	35
1.04	9.1	36
1.11	8.9	33
1.00	8.0 (calc.)	32
1.04	8.0 (calc.)	29
0.95	8.6 (calc.)	29
1.05	7.1 (calc.)	28
1.10	8.7	28

correlation coefficient. The problems mentioned include the lack of accurate density data for polymers and the difficult assignment of molar volume. In light of recent work, an important problem is represented by Macleod's exponent, p, in Equation 6, which has been assumed to be four. Wright (*38*) found that this exponent need not be four. Therefore, the Sugden parachor can take a general form:

$$P = \frac{M}{D - d}\gamma^{1/p} \qquad (12)$$

Marwedel (*19*) showed that p was less than four and actually differed with respect to the polarity of a liquid.

Recently Roe (*29*) reported that the p values for polymers were smaller than those for monomers. For instance, the following p values were found: 3.0 for poly(ethylene oxide), 3.2 for both polyethylene and polypropylene, 3.3 for branched polyethylene, 3.5 for poly(dimethyl siloxane), and 4.1 for poly(butene). Here the relationship between p and polarity is not well defined. But if the exact value of p is known for each homolog of compounds or polymers, we should be able to obtain a higher correlation coefficient and a lower standard deviation.

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Table III. Relationships Between Solubility Parameters

Equation: $\gamma_c^{0.43} = 0.24\ \delta \Phi V_m^{0.14}$

Polymers	*Solubility Parameter*[a] δ *(cal./cc.)*$^{1/2}$
Poly(tetrafluoroethylene)	6.2
Poly(vinyl butyral)	7.1 (calc.)
Poly(chlorotrifluoroethylene)	7.2
Poly(1,2-butadiene)	7.2 (calc.)
Poly(vinyl formal)	7.3 (calc.)
Poly(dimethyl siloxane)	7.6
Poly(vinylidene fluoride)	7.8
Poly(2-methylpropene)	7.9
Polyethylene, high density, d = 0.95	7.9
low density, d = 0.91	7.9
Poly(propylene oxide)	8.0 (calc.)
Poly(vinyl methyl ether)	8.0 (calc.)
Poly(2-methyl-1,3-butadiene), *trans*	8.1
Poly(2-methyl-1,3-butadiene), *cis*	8.1
Poly(1,3-butadiene), *trans*	8.4
Poly(1,3-butadiene), *cis*	8.4
Poly(*tert*-butylstyrene)	8.6 (calc.)
Poly(ethylene oxide)	8.6 (calc.)
Poly(vinyl fluoride)	8.8 (calc.)
Poly(ethyl methacrylate)	8.9
Poly(2-chloro-1,3-butadiene)	9.0
Poly(methyl methacrylate)	9.1
Polystyrene, atactic	9.1
Polypropylene	9.2
Poly(ethyl acrylate)	9.4
Poly(vinyl acetate)	9.4
Poly(vinyl chloride)	9.5
Poly(formaldehyde)	9.7 (calc.)
Poly(methylstyrene mixed isomers)	9.8 (calc.)
"Phenoxy Plastics"	9.9 (calc.)
Poly(methyl acrylate)	10.1
Polycarbonate	10.2 (calc.)
Poly(2-chlorostyrene)	10.5 (calc.)
"Polyphenylene Oxide"	10.7 (calc.)
Poly(ethylene terephthalate)	10.7
Poly(vinylidene chloride)	12.2
Polyacrylonitrile	12.5
Poly(vinyl alcohol)	12.6

and Critical Surface Tensions of Polymers

(assuming $\Phi = 1$, then $\gamma_c = \gamma_s$)

Molar Volume V_m *(cc./mole)*	*Critical Surface Tension*[b] γ_c *(dyne/cm.)*		Δ
	Calc.	*Obs.*	
45.5	9	18*	−9
135.0	18	28	−10
56.2	14	31*	−17
56.4	14	25	−11
81.5	16	40	−24
78.8	17	24*	−7
36.4	14	25*	−11
63.0	18	27	−9
29.6	14	31	−17
31.0	14	31	−17
58.0	18	32	−14
55.6	17	29	−12
72.4	20	30	−10
75.0	20	31	−11
58.2	20	31	−11
60.1	20	32	−12
169.0	29	29	0
39.2	17	43	−26
32.0	20	28*	−8
103.0	27	33	−6
72.0	25	38	−13
84.8	27	38	−11
100.0	28	36	−8
46.2	23	29	−6
91.0	30	37*	−7
72.2	28	37*	−9
44.6	25	39	−14
21.0	22	36	−14
113.0	36	35	+1
243.0	45	43	+2
70.5	32	41	−9
212.0	46	42	+4
111.0	43	42	+1
115.0	45	41	+4
143.0	51	43*	+8
58.0	47	40	+7
45.4	46	44	+2
34.2	45	37*	+8

Table III.

Polymers	*Solubility Parameter*[a] δ *(cal./cc.)*$^{1/2}$
Poly(6-aminocaproic acid) (Nylon 6)	13.6
Poly(hexamethylene adipamide) (Nylon 6,6)	13.6

[a] Most of the solubility parameter values were obtained from data compiled by H. Burrell (2). The calculated values were computed on the basis of Small's constants (*35*).

Table IV. Relationship Between Parachors

Equation: $\gamma_c = P^4 V_m^{-4} \Phi^2$

Polymers	*Parachor*[a] *P* *(Repeat Unit)*	*M.W. (gram/mole) (Repeat Unit)*
Poly(tetrafluoroethylene)	122.4	100.0
Poly(chlorotrifluoroethylene)	151.5	116.5
Poly(dimethylsiloxane)	154.4	74.1
Poly(vinylidene fluoride)	101.2	64.0
Poly(1,2-butadiene)	145.4	54.1
Poly(2-methylpropene)	152.6	56.1
Poly(vinyl fluoride)	90.6	46.0
Poly(vinyl butyral)	328.6	142.0
Poly(*tert*-butylstyrene)	342.1	160.1
Poly(vinyl methyl ether)	136.1	58.0
Poly(propylene)	116.3	42.1
Poly(2-methyl-1,3-butadiene), *trans*	183.0	68.1
Poly(2-methyl-1,3-butadiene), *cis*	183.0	68.1
Polyethylene, high density	80.0	28.1
low density	80.0	28.1
Poly(1,3-butadiene), *trans*	146.7	54.1
Poly(1,3-butadiene), *cis*	146.7	54.1
Poly(propylene oxide)	126.1	58.0
Poly(ethyl methacrylate)	259.3	114.1
Poly(ethyl acrylate)	223.8	100.0
Poly(methylstyrene), mixed isomers	287.1	118.1
Polystyrene, atactic	249.1	104.1
Poly(formaldehyde)	59.8	30.0

Continued

Molar Volume V_m *(cc./mole)*	*Critical Surface Tension*[b] γ_c *(dyne/cm.)* *Calc.*	*Obs.*	Δ
100.0	73	42*	+31
182.0	87	46*	+41

[b] The critical surface tensions marked with asterisk (*) were obtained from data compiled by E. G. Shafrin (*34*). Other values were determined by us.

and Critical Surface Tensions of Polymers

(assuming $\Phi = 1, \gamma_c = \gamma_s$)

Polymer Density[b] *d* *(gram/cc.)*	*Molar Volume* V_m *(cc./mole)*	*Critical Surface Tension*[c] γ_c *(dyne/cm.)* *Calc.*	*Obs.*	Δ
2.20	45.5	53	18*	+35
2.07	56.2	53	31	+22
0.94	78.8	15	24*	−9
1.76	36.4	63	25*	+38
0.96	56.4	44	25	+19
0.91	63.0	33	27	+6
1.44	32.0	63	28*	+35
1.05	135.0	36	28	+8
0.95	169.0	16	29	−13
1.04	55.6	33	29	+4
0.91	46.2	36	29	+7
0.94	72.4	40	30	+10
0.91	75.0	33	31	+2
0.95	29.6	53	31	+22
0.91	31.0	44	31	+13
0.93	58.2	36	31	+5
0.91	60.1	33	32	+1
1.00	58.0	23	32	−9
1.11	103.0	40	33	+7
1.10	91.0	36	35*	+1
1.04	113.0	44	35	+9
1.04	100.0	40	36	+4
1.43	21.0	69	36	+33

Table IV.

Polymers	*Parachor*[a] *P* *(Repeat Unit)*	*M.W.* *(gram/mole)* *(Repeat Unit)*
Poly(vinyl acetate)	183.8	86.0
Poly(vinyl alcohol)	94.3	44.1
	79.9	44.1
Poly(methyl methacrylate)	218.3	100.1
Poly(2-chloro-1,3-butadiene)	186.4	88.5
Poly(vinyl chloride)	119.7	62.5
Poly(vinyl formal)	208.6	100.0
Poly(vinylidene chloride)	159.4	96.6
Poly(methyl acrylate)	183.8	86.0
"Polyphenylene Oxide"	268.9	121.0
Polycarbonate	524.4	254.0
Poly(2-chlorostyrene)	266.8	138.6
"Phenoxy Plastics"	624.7	284.0
Poly(ethylene oxide)	99.8	44.0
Poly(ethylene terephthalate)	376.7	192.2
Poly(6-aminocaproic acid)	274.0	113.2
(Nylon 6)	245.2	113.2
Poly(acrylonitrile)	131.6	53.1
Poly(hexamethylene adipamide)	548.0	226.3
(Nylon 6,6)	490.4	226.3

[a] The parachors were calculated on the basis of the recommended values published by O. R. Quayle (*25*). For the hydrogen-bonded compounds, we attempted to correct the parachors subtracting the value allowed for the hydrogen bridge per possible site from the original readings).

[b] The densities reported in the literature were determined between 20°-25°C.

Conclusions

Critical surface tensions of functional polymers were experimentally determined. This set of data and the data on elastomers obtained previously were used to elucidate the proposed solubility parameter–surface tension relationship and the proposed parachor–surface tension relationship. The results show that the former has a higher correlation coefficient than the latter. The correlation coefficients, including three highly hydrogen-bonded polymers, are 0.731 for the former and 0.299 for the latter. Otherwise, they are 0.762 for the former and 0.178 for the latter. For the size of samples examined, we can conclude that the proposed solubility parameter–relationship is more effective than the proposed parachor–relationship in calculating critical surface tension of a polymer.

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Continued

Polymer Density[b] d (gram/cc.)	Molar Volume V_m (cc./mole)	Critical Surface Tension[c] γ_c (dyne/cm.)		Δ
		Calc.	Obs.	
1.19	72.4	40	37	+3
1.29	34.2	58	37*	+21
1.29	34.2	30	37	−7
1.18	84.8	44	38	+6
1.23	72.0	44	38	+6
1.40	44.6	53	39	+14
1.23	81.5	44	40	+4
1.66	58.0	58	40	+18
1.22	70.5	44	41	+3
1.06	115.0	30	41	−11
1.20	212.0	36	42	−6
1.25	111.0	36	42	−6
1.17	243.0	48	43	+5
1.12	39.2	44	43	+1
1.34	143.0	40	43*	−3
1.13	100.0	58	43*	+15
1.13	100.0	36	43	−7
1.17	45.4	69	44	+25
1.24	182.0	83	46*	+37
1.24	182.0	53	46	+7

[c] The critical surface tensions marked with asterisk (*) were obtained from Table (III-113) compiled by E. G. Shafrin (*34*). Other critical surface tension values were determined by us. The differences between the calculated and the observed are listed under Δ.

However, both equations need improvements, and none of these equations at this stage can be used for the prediction of critical surface tension or surface tension of a polymer with sufficient accuracy. The problems of the difficult assignment of the thickness of the monolayer at the interface, of the molecular orientation, of crystallinity and of hydrogen bonding could contribute to the sporadic results regarding the calculated critical surface tensions.

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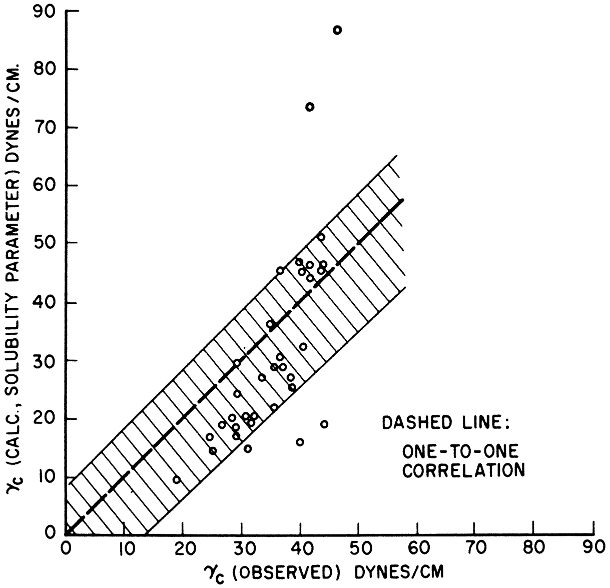

Figure 2. Comparison of the observed and the calculated critical surface tensions of polymers (on the basis of solubility parameter)

Laboratory in carrying out the analysis of variance. The author appreciates the help of Ryong-Joon Roe of E. I. duPont de Nemours and Co. for sending his manuscript prior to publication and E. G. Shafrin of the Naval Research Laboratory for discussing experimental techniques in the determination of critical surface tension. The author is indebted to both referees for many valuable comments.

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9

Chemistry at Organic-Inorganic Interfaces

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The single reflection ATR infrared spectra of a series of synthetic and natural calcium phosphates were examined for changes resulting from adsorption of organic molecules. The asymmetric P—O$^-$ stretching frequency (ν_3) at 1027 cm.$^{-1}$ underwent a high frequency shift of up to 9 cm.$^{-1}$ as a result of adsorption of citric acid, tetracycline, and certain other polar molecules. Similarly, the P—O stretching frequency of the P—O—C group in trialkyl phosphates was shifted to higher frequencies by hydrogen bonding with water and phenol. The relationship between the high frequency shift and the properties of the solid phase is discussed. A tentative explanation is offered for the shift in the lattice absorption frequency as a result of surface modification.

Infrared spectrophotometry has been applied very effectively to the study of adsorbed molecules and the changes which occur in the spectrum of the adsorbate as a result of interaction with the adsorbent. Excellent bibliographies on this subject are presented by Eischens and Pliskin (*4*) and Little (*9*).

In addition to providing an insight into changes that occur in the adsorbed phase, infrared spectra of organic-inorganic systems should also provide some indication of changes occurring in the adsorbent phase. Further, such changes should also be related to adsorption and adhesion mechanisms. Very little attention has been paid to spectral changes in adsorbents and, as pointed out by Amberg (*1*), such changes when they occur have usually been neglected. Certainly, there are undoubtedly many cases in which spectral changes are obscured because of broad intense absorption bands such as Si—O and P—O in silicates and phosphates.

In Interaction of Liquids at Solid Substrates; Alexander, A.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1968.

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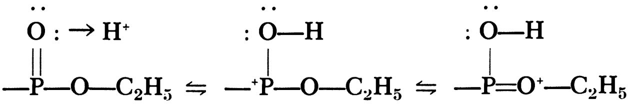
The object of this work was to study the interaction of adsorbed organic molecules with a tooth-mineral (hydroxyapatite) adsorbent. Of especial interest was the extent to which the response of the mineral phase could be observed by infrared spectroscopy.

Results

Model Compound Study. Homogeneous systems of triethyl phosphate (TEP) with phenol and with water were chosen as models for heterogeneous systems. Spectra of these systems provided a basis for expecting changes in the spectrum of solid adsorbent phases. Table I includes the data for a 1 : 1 mixture of TEP and water and a 5% TEP-5% phenol solution in benzene. The O—H stretching frequencies of both water and phenol were shifted to lower frequencies. Likewise, the C—O stretching in phenol and the P=O stretching in TEP were shifted to lower frequencies, as expected (*4, 9*). Two additional shifts were observed in our work. The P—O and C—O stretching in the P—O—C_2H_5 group is reported (*2*) at 973 and 1033 cm.$^{-1}$, respectively. Each band was shifted, either by water or phenol, by 2 to 3 cm.$^{-1}$.

On the basis of the data of Hardy and co-workers (*6*) and of Fletcher and co-workers (*5*), it is assumed that the structure of a 1 : 1 complex of triethyl phosphate and water is one in which hydrogen bonding occurs on the oxygen atom of the phosphoryl group (P=O). The O—H stretching frequency of the proton donor and the P=O stretching frequency of the proton acceptor are shifted to lower frequencies as expected. In this work the effect of hydrogen bonding was also observed in the C—O—P bonds of the phosphate ester groups. The C—O stretch at 1033 cm.$^{-1}$ was shifted toward lower frequencies (*2*), while the P—O stretch at 973 cm.$^{-1}$ was shifted, both by water and phenol, to higher frequencies. This high frequency shift is readily explained on the basis of polarizability of the ether oxygen atom, which may share its electrons with phosphorus as the P=O link is polarized by hydrogen bonding:



$$\begin{array}{ccc} \ddot{O}:\rightarrow H^+ & :\ddot{O}-H & :\ddot{O}-H \\ \| & | & | \\ -P-O-C_2H_5 \leftrightharpoons & -{}^+P-O-C_2H_5 \leftrightharpoons & -P=O^+-C_2H_5 \end{array}$$

This explanation is similar to that discussed by Bellamy (*3*) for the inductive and mesomeric effects in acids, acid chlorides, esters, and amides.

These data confirm Bellamy and Beecher's assignment (*2*) of the 1033 cm.$^{-1}$ band to C—O and the 973 cm.$^{-1}$ band to P—O in the P—O—C_2H_5 linkage.

Table I. Infrared Spectra of Hydrogen-Bonded Triethyl Phosphate Infrared Absorption Maxima (cm.$^{-1}$)

Assignment	*TEP*	*Phenol*	*TEP-Phenol 1:1 Mixture*	*Water*	*TEP-Water 1:1 Mixture*	*Shift*
O—H stretch in phenol		3309	3279			30
P=O stretch	1271		Combined doublet at 1250 & 1205			Both the P=O and C—O stretching modes were shifted
C—O stretch		1258				
C—O stretch	1033[a]		1031			Small but definite shift
P—O stretch in P—O—C_2H_5	973[a]		976			Small but definite shift to a higher frequency
O—H stretch in water				Broad about 3450		Peak broadened & shift not measurable
P=O stretch	1272				1261	11
C—O stretch in P—O—C_2H_5	1033				1031	Small but definite shift
P—O stretch in P—O—C_2H_5	973				976	3; small but definite shift to a higher frequency

[a] Reference 2.

Crystalline Phosphate Studies. On the basis of the results with triethyl phosphate, a series of calcium phosphates was examined by infrared spectrophotometry. Pertinent properties of these materials are summarized in Table II, and their spectral characteristics are shown in Table III. None of the synthetic hydroxyapatites [$Ca_{10}(PO_4)_6(OH)_2$] had the stoichiometric Ca/P ratio of 1.667, although they showed the apatite lattice structure. A typical infrared transmission spectrum (between 1500 and 700 cm.$^{-1}$) of a dry powder synthetic hydroxyapatite is shown in Figure 1.

The intense absorption of the P—O structure obscures all detail in this region. The use of single attenuated total reflection technique, coupled with scale expansion, resulted in the spectrum shown in Figure 2. The maxima in the asymmetric P—O$^-$ stretching band is readily measured.

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Table II. Properties of Calcium Phosphates

Sample	*Ca/P*	*Specific Surface*[a] *meter^2/gram*	*X-ray Pattern*
Hydroxyapatite—synthetic			
Sample No. 1	1.62	180	Hydroxyapatite
Sample No. 2	1.64	104	Hydroxyapatite
Sample No. 3	1.64	152	Hydroxyapatite
Sample No. 4	—	120	Amorphous
Natural (contains fluoride)[b]	1.667[b]	0.8	—
Fluoroapatite—synthetic	—	50	Fluoroapatite
Hydroxyapatite—commercial			
Biogel HTP	1.53[c]	62	—
Kerr-McGee	1.57 (1.66[c])	27.4	Hydroxyapatite
Calcium Phosphate			
Baker A.R. (Tricalcium Phosphate)	1.53	36	Hydroxyapatite
Synthetic	1.54	97	Whitlockite [β-$Ca_3(PO_4)_2$]

[a] Measured by the flow method of nitrogen adsorption.

[b] Crystal from Gerlos Zillerthalen, Austrian Alps, courtesy Stanford University Geology Department; Ca/P ratio is assumed.

[c] Data supplied by the manufacturer.

Table III. Major Absorption Band of Synthetic and Commercial Phosphates from 5000 to 400 cm.$^{-1}$

Material	*Sodium Chloride Region, cm.$^{-1}$*			*Potassium Bromide Region, cm.$^{-1}$*		
Hydroxyapatite—synthetic						
Sample No. 1	1091	1027	960	625	592	554
Sample No. 2	1096	1026	960	absent	592	553
Sample No. 3	1093	1028	960			
Sample No. 4	1092	1024	960			
Apatite—natural	1093	1042	961			
Fluoroapatite—synthetic	1097	1030	963			
Hydroxyapatite—commercial						
Biogel HTP	1086	1020	960	621	592	551
Kerr-McGee	1092	1027	961	622	591	554
Calcium Phosphate						
Baker A.R. (Tricalcium Phosphate)	1090	1027	960	623	592	552
Synthetic No. 2	1100	1028	absent			

The infrared spectra of these materials were taken before and after they were exposed to solutions of a variety of adsorbates. It was found that citric acid, tetracycline (as the HCl salt), and certain other organic

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molecules cause a shift in the asymmetric P—O⁻ stretching frequency at 1027 to 1028 cm.$^{-1}$.

Table IV includes the pertinent data for the effect of selected adsorbates upon synthetic hydroxyapatite. The adsorbates were chosen for their molecular structures or for their importance to dental problems. The frequencies reported in Table IV are accurate and reproducible to ±2 cm.$^{-1}$. Therefore, only the values of shifts of 9 cm.$^{-1}$ for citric acid and 5 cm.$^{-1}$ for oxytetracycline HCl are of significance for synthetic hydroxyapatite Sample No. 1. By way of contrast, tartaric acid caused no shift in the 1027 peak of Sample No. 1, which had a specific surface of only 180 meter^2/gram, although it did cause a shift for Sample No. 2 which had a specific surface of only 104 meter^2/gram. Further, Sample No. 3, with a specific surface of 152 meter^2/gram was not affected by either citric acid or tetracycline·HCl.

The data in Table IV for the three samples of hydroxyapatite summarize the range for shifts in these samples of hydroxyapatite. Shifts have not been observed in commercially available hydroxyapatites, one sample of natural apatite, or calcium phosphates. Likewise, calcium phosphates prepared by methods which yield high specific surface have also not responded in this manner to adsorbates.

The asymmetric stretching frequency of the P—O⁻ ion is the only vibration of the PO_4^{3-} ion in the 5000 to 400 cm.$^{-1}$ region noticeably affected by adsorbed molecules.

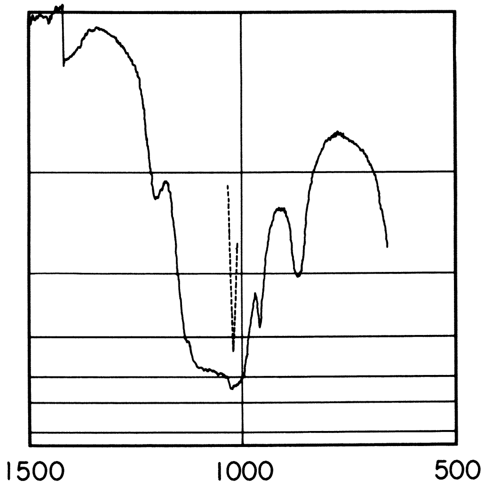

Figure 1. Transmission spectrum of synthetic hydroxyapatite

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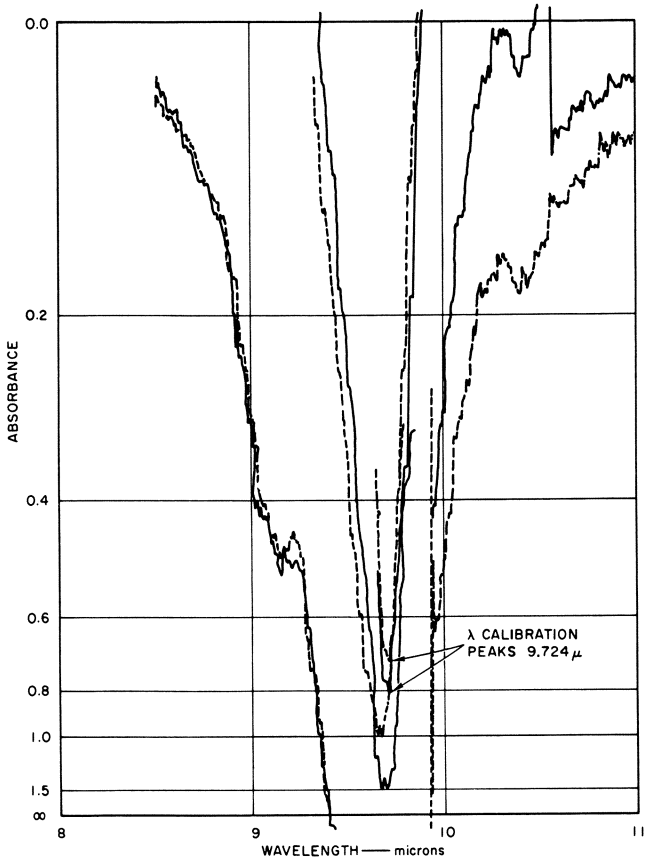

Figure 2. Single reflection ATR spectra of synthetic hydroxyapatite

--- *Absorbed citric acid*
—— *Plain material, pH adjusted with HCl to pH 4.08*

Discussion

The high frequency shift in the asymmetric P—O^- stretching frequency caused by adsorption on hydroxyapatite appears to be a perturbation of lattice bonds as a result of surface changes. The minimum specific surface necessary to cause a lattice shift by a particular adsorbate has not been ascertained. The difference in sensitivity between different preparations of hydroxyapatite is shown in Table IV. These differences are best explained, at present, by differences in surface groups resulting from minor differences in washing procedure. Rootare, Deitz, and Carpenter (*10*) discuss hydrolysis reactions of surface phosphate ions and the

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formation of complexes on the surface of hydroxyapatite crystals. The extent of hydrolysis and the concentration of surface complexes should have a pronounced effect on the adsorption of organic molecules by hydroxyapatite crystals.

Table IV. Effect of Adsorbed Molecules upon the Infrared Spectrum of Synthetic Hydroxyapatites

Sample No. 1

Adsorbate	*Adsorption Peak (cm.$^{-1}$)*	*Shift (cm.$^{-1}$)*
None	1027	0
Citric acid	1036	9 (high frequency)
Tartaric acid	1025	2
Sodium citrate	1028	1
Oxytetracycline · HCl	1032	5 (high frequency)
Glycine	1028	1

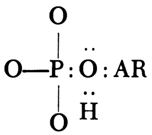
Sample No. 2

Adsorbate	*Adsorption Peak (cm.$^{-1}$)*	*Shift (cm.$^{-1}$)*	
None	1026	0	
Citric acid	1031	5	(high frequency
Tartaric acid	1031	5	
Tetracycline · HCl	1032	6	
Oxytetracycline · HCl	1033	7	
Phenol	1030	4	
Gelatin	1031	5	

Sample No. 3

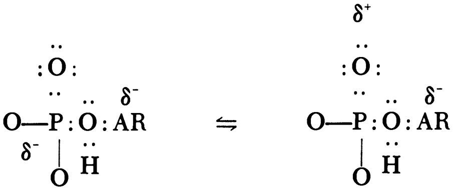
Adsorbate	*Adsorption Peak (cm.$^{-1}$)*	*Shift (cm.$^{-1}$)*
None	1029	0
Citric acid	1032	3 (high frequency)
Tetracycline · HCl	1029	0

The observed high frequency shifts in the 1026–1028 cm.$^{-1}$ band of high-surface hydroxyapatites may be explained by the following physical picture of adsorption: an adsorbed molecule, AR, containing an electrophilic group, A—*e.g.*, citric acid—coordinates with the oxygen of a surface —P : O : H group, giving the structure



$$\mathrm{O{-}\overset{\overset{\displaystyle O}{|}}{\underset{\underset{\displaystyle O}{|}}{P}}:\underset{\underset{\displaystyle H}{\cdot\cdot}}{\overset{\cdot\cdot}{O}}:AR}$$

where the three noncoordinated oxygen atoms are in the lattice of the crystal. The decrease in electron density around the surface oxygen is transferred by inductive effects through the P atom to the adjacent lattice oxygens, resulting in an increased electron density between the P and O atoms in the lattice.



This results in a shift to a higher frequency, in a manner analogous to the triethyl phosphate-phenol system.

This explanation of the observed shift is tentative, pending further clarification.

Experimental

Synthetic hydroxyapatites were prepared by the method of Hayek and co-workers (7, 8), modified to produce a product of small particle size. The products were isolated by washing the gel slurry with water until free of nitrate ion. The resultant suspensions were then spray-dried with a Minor Type 53 Niro Atomizer (Copenhagen, Denmark). The resultant dry products were in the form of porous, spherical polycrystalline agglomerates of 5 to 8 μ average diameter. The specific surfaces of these products ranged from 104 to 180 meter^2/gram.

Commercial hydroxyapatite sample No. 1 was Biogel HTP from Biorad Laboratories. Commercial Sample No. 2 was obtained from the Kerr-McGee Corporation.

Natural hydroxyapatite from Gerlos, Zillerthalen, in the Austrian Alps, was supplied by the Stanford University Department of Geology. The calcium phosphate used was Baker A. R. Grade.

Infrared spectra were obtained on a Perkin Elmer 221 spectrophotometer, using a Connecticut Instrument Company single-reflection attenuated total reflectance attachment and 5X scale expansion. The sample was placed as a dry powder on a KRS-5 prism. This arrangement provided the very short sample path length required to obtain resolution of the broad, intense phosphate band. Figure 1 shows the transmission spectrum of a dry powder sample of hydroxyapatite. Figure 2 shows the single reflection ATR spectra of untreated hydroxyapatite and the mineral containing adsorbed citric acid. A wavelength marker was used for each spectrum to ensure correct alignment of the two spectra. The shift, though small, was real and reproducible.

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Acknowledgments

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10

Wettability of Monolayers of Fatty Materials on Mercury

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Monolayers of normal straight chain fatty alcohols and carboxylic acids in the C_{12} to C_{20} range were spread on mercury in a Langmuir type film balance apparatus. On each of the films a droplet of water was placed and the contact angle was measured at various values of the film pressure. Thus, the mutual relationships among film pressure, molecular packing and contact angle were determined for each fatty material. The materials fell into two groups depending on chain length. Among the shorter chain compounds the contact angle changed continuously as the molecular area decreased during the film's "two dimensional phase change." On films of the longer chain compounds the contact angle remained essentially constant throughout the phase change.

This study concerns the wettability of a surface consisting of a metal substrate covered by a monomolecular layer of a polar long chain fatty compound. More specifically it concerns the relationship between the contact angle of water on such a surface and the packing density of the molecules within the monolayer. This problem was studied by Bartell and Ruch (*1*) using platinum and chromium as the metallic substrates, and *n*-octadecylamine as the long chain polar compound. Starting with a closely packed monolayer, they progressively attenuated it by solvent washing, measuring the degree of attenuation or molecular depletion by an ellipsometric method. At different degrees of depletion measurements were made of contact angle and contact angle hysteresis, using hexadecane and water as the test liquids. Although the contact angle changed in a reproducible manner, neither the homogeneity nor the uniformity of coverage of the depleted monolayer could be clearly defined in these systems.

Techniques for spreading monolayers of polar long chain compounds on mercury in a Langmuir type film balance, and for measuring their surface area-pressure properties, have been described by one of the present authors (*3*). Using these techniques, it has proved possible to measure continuously the change in contact angle of a water droplet superposed on the monolayer, as the film pressure is controllably varied. This has now been done for monolayers of the normal C_{12}–C_{20} fatty acids and the normal primary C_{14}–C_{18} alcohols on the mercury substrate.

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Experimental

Apparatus and Materials. The Langmuir film balance, modified for use with mercury, was essentially identical with that described by Ellison (*3*). A Plexiglass trough was fabricated to fit the metal frame so that only 350 cc. of mercury were required. Mylar film, 0.001 inch thick, was used in a single piece to form both the balance float and a frame for the entire trough. The Mylar was adherent to the clean mercury surface and thus by using Mylar film for the compression barriers also, leakage of the organic monolayers during compression was avoided. The dimensions of the framed surface were 61.8 cm. by 12.0 cm., and the effective length of the balance float was 11.0 cm.

A goniometer telescope was used to observe the sessile water drops and to measure their contact angles. The water drops were applied to the surface from a microburet which was firmly mounted on a micromanipulator. Contact was maintained between the water drop and the capillary tip of the microburet, thus allowing water to be added to or withdrawn from the drop in determining hysteresis. The capillary was a needle of sufficiently small dimension not to distort materially the sphericity of the drop's surface. All measurements were made at room temperature, which ranged from 23°–25°C.

Instrument grade (triple distilled, analyzed) mercury and reagent grade benzene (analyzed) were obtained from Fisher Scientific Co. Ultra High Purity Nitrogen gas was purchased from Air Products and Chemicals, Inc. Locally purchased bottled distilled water was redistilled from a Yoe type glass still. The distillate had a surface tension of 72 dynes/cm. and a resistance of greater than 2 megohms/cc.

The fatty acids and alcohols were purchased research grade materials. Their melting points are shown in Table I.

Procedure. The Plexiglas trough was cleaned prior to use by washing with sodium tripolyphosphate solution, followed by thorough rinsing with hot tap water and finally with distilled water. The Mylar film was cleaned by rinsing thoroughly with reagent grade acetone. In a typical experiment, the mercury surface was swept with the compression barriers on both sides of the balance float, and the torsion head was adjusted to zero scale reading. A solution of the polar fatty compound in benzene was prepared, and the concentration determined accurately. Concentrations in the range of 4 × 10^{-4} molar were suited to the size of the trough and to the dosages dispensed. An exact volume of this solution, usually 100 to 200 microliters, was metered onto the surface from a micropipet. After waiting about five minutes for the deflection of the torsion head to become constant, indicating substantially complete evaporation of the benzene, the tip of the water syringe was put into place close to the float and a drop of water was pushed out onto the liquid surface. The syringe tip was kept in contact with the water drop, so that by advancing or retracting the plunger water could be added to or withdrawn from the drop. Thus, both advancing and receding contact angles could be formed. The barrier was advanced carefully by hand in steps of 1 cm. After each advance the new film pressure (π_f) was recorded, and advancing (θ_A) and receding (θ_R) contact angles of the water drop were measured. At all except the very highest values of π_f the contact angle hysteresis was less than 4°, which is on the borderline of insignificance in view of the inherent errors of measurement. Only the advancing angles are represented in the diagrams of Figure 1 and are simply designated θ. In a typical run, the time elapsed between each advance of the barrier was less than two minutes.

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Table I. Melting Points of *n*-Paraffinic Acids and Alcohols Used in Forming Monolayers on Mercury

Acids	*Experimental m.p. °C.*	*Literature m.p. °C.*
C_{12}	42.5 ± 0.5	43.0
C_{14}	54.5 ± 0.5	54.4
C_{16}	60.0 ± 0.5	62.8
C_{18}	69.0 ± 0.5	69.6
C_{20}	75.0 ± 0.5	75.4
Alcohols		
C_{14}	36.5 ± 0.5	37.6
C_{16}	49.0 ± 0.5	49.3
C_{18}	56.5 ± 0.5	57.9

Equilibrium film pressures (π_e) of the polar fatty compounds were measured by a slight modification of the method described previously (*3*). The mercury surface was swept clean, and the torsion head adjusted to zero scale reading. With the barrier open, several crystals of the material to be measured were scattered on the surface. Within about three minutes the initial rapid random movement of the crystals had ceased and the film pressure reading had become constant. This reading was recorded as π_e. It was checked by moving in the barrier, which temporarily increased the reading. Within about 15 minutes, however, the reading slowly returned to its initial value, presumably because of recrystallization of the compressed film on the nuclei formed by the original floating crystals.

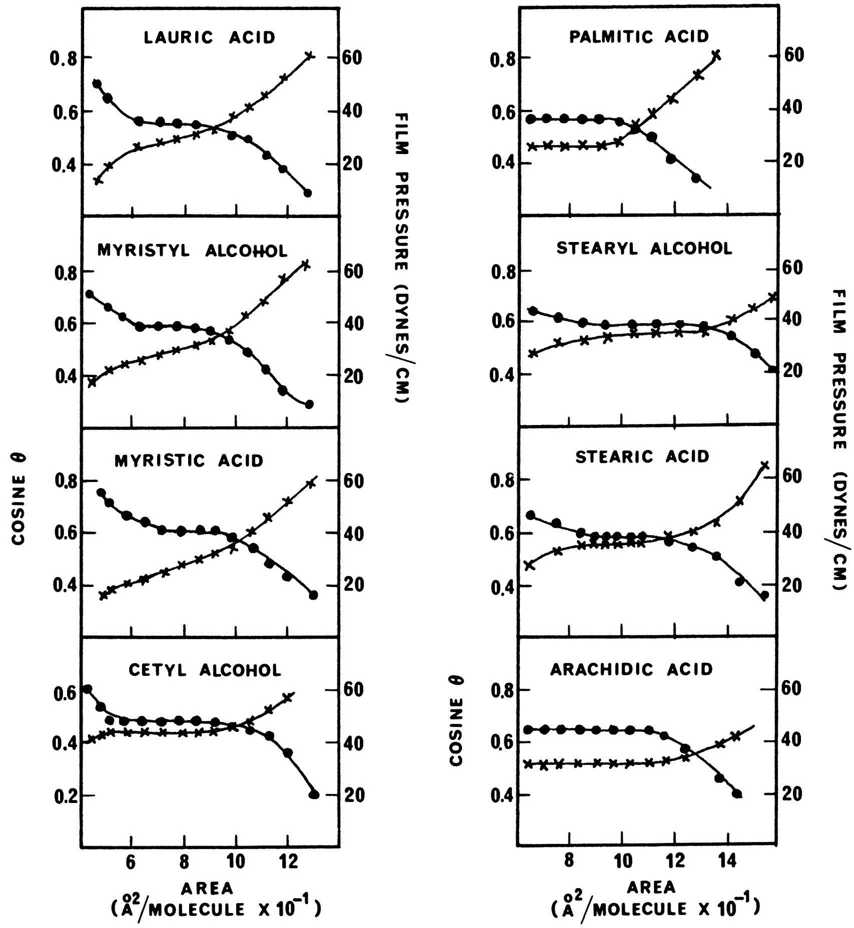

Figure 1. Film pressures and contact angles of fatty polar monolayers as functions of molecular packing

●—*Film pressure* vs. *area*
×—*Cosine θ* vs. *area*

Results

Figure 1 shows the data for all eight fatty polar compounds tested. Considering first the curves of film pressure *vs.* area-per-molecule, it is evident that all the compounds give curves of the same form. As the area is reduced the pressure at first rises: there then follows a region in which the pressure remains constant as the area is progressively decreased. This region has been associated with a change in orientation of the molecules in the monolayer, the long axis of the molecule changing from a parallel

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to a perpendicular position with respect to the mercury surface. At the end of the constant pressure region, as the area is reduced still further the pressure again rises until the region of film collapse is reached. This region is off the scale in the diagrams of Figure 1. The pressure and area-per-molecule at which collapse occurs is not exactly reproducible although it is sharply defined in any single run. The onset of the collapse region is indicated experimentally by movement of the water droplet, which keeps its distance from the barrier as the barrier is advanced. In the constant pressure region the water droplet remains stationary when the barrier is advanced. On a film which collapses, for example, at an area of 26 $A.^2$ the water droplet will usually start to move when the barrier is advanced from 32 $A.^2$ to 30 $A.^2$ equivalent area. Neither the area-per-molecule nor the film pressure at which the constant pressure region starts is exactly reproducible from run to run on the same compound; nor is the numerical value of the constant pressure itself. The film pressure-area curve is quite reproducible, however, in the high area region where the pressure is less than π_e. This confirms previous reports of the behavior of those fatty polar films on mercury. It also conforms with the ideas of Cary and Rideal (2) on the stability and collapse of monolayers on aqueous substrates. These ideas have been discussed previously in connection with mercury substrates by one of the present authors (3). The inherent metastability of these films at pressures greater than π_e is responsible for the lack of point-to-point reproducibility in the π-A isotherms. There is no evidence of any chemical interaction between atmospheric constituents and either the film or the substrate.

The curves of contact angle (plotted here as cos θ rather than θ) *vs.* area-per-molecule fall into two distinct groups. For lauric acid, myristyl alcohol, and myristic acid the contact angle increases steadily although not linearly as the film is compressed. There are no apparent correlations or correspondences between these curves and the corresponding film pressure-area curves. For the other five compounds, however, the contact angle at first increases as the film is compressed, then remains substantially constant over a considerable area range, and finally increases again as the area approches the range of collapse. The range of constant contact angle coincides exactly with the range of constant film pressure.

The measured values of π_e for the eight fatty compounds used in this study are shown in Table II.

The values for lauric acid, stearic acid, and stearyl alcohol are 5 to 7 dynes/cm. higher than those reported previously. This probably reflects a difference in the purity of the mercury used rather than the polar fatty compounds. Very small traces of metallic impurities in mercury have been shown to alter its surface properties greatly.

Table II. Equilibrium Spreading Pressures (π_e) on Mercury at 25°C.

Material	*(dynes/cm.)*
lauric acid	44.5
myristyl alcohol	41.5
myristic acid	42
cetyl alcohol	39
palmitic acid	40
stearyl alcohol	35
stearic acid	35
arachidic acid	32

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Hysteresis of the contact angle was very slight except for the C_{12}–C_{14} compounds in the high pressure region at which the films collapsed. As an example a myristic acid film similar to that of Figure 1, at 28 A.^{2}/molecule showed a π_f value of 71 dynes/cm. and no collapse. The contact angle of water at this value showed the same slight (3°–4°) hysteresis encountered at higher areas. In going from 28 to 26 A.^{2}/molecule, π_f rose to an initial value of 82 dynes/cm. but fell back rather rapidly, indicating collapse. At this area θ_A was 100° and θ_R was 88°-90°, and these values did not change within a substantial period of observation.

Discussion

The difference between the contact angle vs. area curves of the C_{12}–C_{14} compounds and the C_{16}–C_{20} compounds can be explained as follows: In the C_{12}–C_{14} monolayer systems the water drop at all times (within the ranges of π_f and area measured) sits on top of the monolayer and does not make molecular contact with mercury. Therefore, θ responds to changes in the molecular packing density (defined as the reciprocal of the area per molecule), but is essentially unaffected by changes in film pressure. In the C_{16}–C_{20} systems the water drop is in molecular contact with the mercury, and the fatty polar monolayer acts as a piston at the periphery of the water-mercury interface. The contact angle therefore responds to the film pressure, remaining constant while π_f remains constant, regardless of the increase in molecular packing density.

It may be somewhat surprising that the shorter fatty polar compounds effectively make the mercury "water-repellent" whereas the longer ones do not. The situation can be pictured, however, as one in which the relative affinities of bulk water and fatty monolayer for the mercury surface determines which substance displaced the other. Among the polar fatty compounds π_e, at any given temperature, can be taken as an index of affinity between the spread material and the mercury. On this basis the C_{12}–C_{14} compounds in Table II have greater affinity for mercury than the C_{16}–C_{20} compounds. The water-mercury affinity at the operating temperature evidently has a value such that water can displace the C_{16}–C_{20} films but not the C_{12}–C_{14}. Unfortunately, the most reliable published values of π_e for water on mercury (*4*) were determined by a different experimental procedure and are not strictly applicable in this case. They are, however, well within the range that would support the above picture.

The nearly linear form of the cos θ *vs.* area curves for the C_{12}–C_{14} compounds contrasts sharply with the form of Bartell and Ruch's curves for progressively depleted monolayers of octadecylamine on solid metallic substrates. This is not surprising in view of the many differences between the two systems. The comparison of hysteresis effects is interesting. The Bartell and Ruch curves show high hysteresis of the water contact angle on the close-packed films, and a rather sharp diminution of hysteresis when the film is about 60% depleted. This is qualitatively similar to the effect we noted that significant hysteresis only occurred at the highest packing density we could obtain on the mercury, which was considerably less than that of a close-packed monolayer on chromium or platinum.

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11

The Effect of Polymer Surface Morphology on Adhesion and Adhesive Joint Strengths

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The morphological character of the surface region of polyethylene has been considered with respect to adhesion and adhesive joint strength. By melting polyethylene onto a high energy surface—e.g., *gold or aluminum—extensive nucleation and the formation of a transcrystalline region in the polymer occurs. Dissolution of the metal rather than peeling the metal from the polymer leaves the surface region of the polymer intact. The polymer sheet is now amenable to conventional structural adhesive bonding. Apparently the weak boundary layer on polyethylene is a consequence of the morphology in the surface region and is influenced by the method of preparation.*

The quest for surface treatments of polymers with respect to adhesive bonding has proven fruitful in a practical sense but, until recently, the underlying principles have been somewhat elusive (*5, 16*). Apparently, what is of prime importance in preparing strong adhesive joints with polymers exhibiting weak boundary layer behavior is the nature of the surface morphology and the effect an applied stress has on it. In this paper we shall demonstrate, using polyethylene, that the weak boundary layer behavior normally present in many melt crystallized polymers is a function of the surface region morphology of the polymer and is therefore dependent on how the polymer sheet is prepared. Indeed, by controlling the nucleation and subsequent crystallization, we will show that a surface region may be generated, in crystallizable polymers, that is amenable to conventional adhesive bonding.

Concomitant with this change in the morphology of the surface region, there is a marked change in the wettability even though the chemical constitution is unchanged. This change in wettability has been

In Interaction of Liquids at Solid Substrates; Alexander, A.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1968.

related to a change in the surface crystallinity, being strongly dependent upon the nature of the substrate used to prepare the polymer.

Experimental

Materials. Marlex 5003 polyethylene (PE) was supplied by the Phillips Petroleum Company, Bartlesville, Oklahoma.

Epoxy resin DER332LC (Dow Chemical Co., Midland, Michigan) is a diglycidyl ether of bisphenol A, having an epoxy equivalent weight of 179 maximum (the pure material would have an epoxy equivalent weight of 170), a total chloride content less than 0.1% by weight, and a viscosity of 6400 centipoises maximum at 25°C.

Diethylaminopropylamine (Miller-Stephenson Chemical Co., Inc., Philadelphia) was distilled under nitrogen through a 6-inch Vigreux column and the first fraction discarded. The product distilling at 68°C. and 26-mm. pressure was stored in the dark in tightly stoppered glass containers prior to use.

The epoxy adhesive consisted of 100 parts by weight of the above resin and seven parts by weight of the diethylaminopropylamine, thoroughly mixed and used immediately.

The metal tensile-shear adherends were of 2024-T3 aluminum (Aluminum Co. of America). Their dimensions were 5 by 1 by 1/16 inch. The surface of the aluminum was prepared by first vapor-degreasing in trichloroethylene and then etching for seven minutes at 65°C. in the following solution:

Sodium dichromate ($Na_2Cr_2O_7 \cdot 2H_2O$)	1 part by weight
Water	30 parts by weight
Sulfuric acid (95%)	10 parts by weight

After etching, the specimens were rinsed for five minutes in running tap water and for one minute in running distilled water, and then dried in a forced air oven at 60°C. Specimens were stored in desiccators over Ascarite and removed just prior to use.

Film Preparation. Polymer films (10 mil thick) were prepared by compression molding for one half hour at 175°C. between evaporated gold films on glass microscope slides or sheets of 0.7 mil aluminum foil (Reynolds Aluminum Wrap) which had been chemically etched as above.

After molding, to avoid damaging the surface region of the polymer by peeling from the aluminum, the foil was dissolved by immersion in a sodium hydroxide solution (from 10% to concentrated) which was surrounded by an ice bath to avoid overheating of the specimens. The residual black oxide (trace metal contaminants) was removed by rinsing in concentrated hydrochloric acid. Neither the hydrochloric acid nor the sodium hydroxide treatment affects the surface region of the polyethylene with respect to wettability (γ_c measured before and after exposure is unchanged) and joint strengths. No residual aluminum or metal contaminants were detected using electron microprobe techniques or atomic absorption spectroscopy (AAS).

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The gold films were prepared by vapor depositing about 3000A. of gold on microscope slides (3 by 1 by 1/16 inch). The thickness of the gold film is not crucial provided that a continuous film is generated. Sections of polyethylene film were placed between gold-coated microscope slides to form sandwiches. These sandwiches were molded under similar conditions to the aluminum composites described earlier. After cooling the composites, the gold was dissolved either by amalgamation with mercury or by exposing the composites to a concentrated aqueous solution of sodium cyanide. After a typical cyanide treatment, a final rinse in concentrated hydrochloric acid removed any trace of surface residue—*i.e.*, carbonates. No residue of gold on the polymer was detected in either case using electron microprobe techniques. Atomic absorption spectroscopy (AAS) indicates that from zero to 1/100 of an equivalent monolayer of gold remains after the removal treatments. Small flecks of gold may have been encapsulated on cooling the polymer. Poor reproducibility of the AAS results indicates this. If the real surface area were greater than the geometric area, which is likely, the residue would be far less than the estimated 1/100 of an equivalent monolayer. Neither aqueous cyanide solution nor mercury affects the wettability of polyethylene.

Two other substrates, Mylar and polytetrafluoroethylene (PTFE) separated easily from the polyethylene upon cooling.

ATR infrared techniques using KRS-5 crystals and transmission infrared showed no evidence of oxidation after dissolution of the aluminum or gold. No evidence of a change in the surface constitution of polyethylene was observed using similar infrared techniques.

Thermal History. The polyethylene was molded at 175°C. for varying lengths of time, then cooled by circulating cold water through the press platens. The rate of cooling had no apparent effect on either the mechanical strength of the surface region or the wettability.

Density. The bulk density of the polymer films before and after molding were measured in a density gradient column at 23°C. All the polyethylene samples had the same density of 0.955 gram/cc.

Adhesive Joints. For the measurement of tensile-shear strengths, standard composite test pieces consisting of aluminum-epoxy adhesive-polyethylene film-epoxy adhesive-aluminum were prepared for bonding in a special device designed to maintain a half-inch overlap. The thickness of the epoxy adhesive was maintained constant by insertion of a piece of 0.003-inch-diameter gold wire in each glueline between the aluminum and the polyethylene. Clean gloves and tweezers were used in all specimen preparations to avoid possible contamination. Bonding was accomplished, at approximately 20 p.s.i. pressure, by placing weighted stacks of composites in forced air ovens at specified temperatures for 16 hours. The bonded specimens were tested in tensile shear in accordance with ASTM D1002-64, except that the jaw separation rate was 0.1 inch per minute.

Wettability. A description of the contact angle goniometer and the scheme used in determining the critical surface tension of wetting (γ_c) are described elsewhere (*15, 18*).

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Results and Discussion

The tensile shear strengths of joints prepared using polyethylene which had been molded at 175°C. for varying lengths of time are shown in Figure 1. Preparation of the joints is confined to temperatures below the melting point of the polyethylene. It is important to note that if the polymer is peeled or removed from the metal other than by dissolution of the metal, the resultant joint strengths are comparable to those obtained for films generated against both PTFE and Mylar (bottom line, Figure 1).

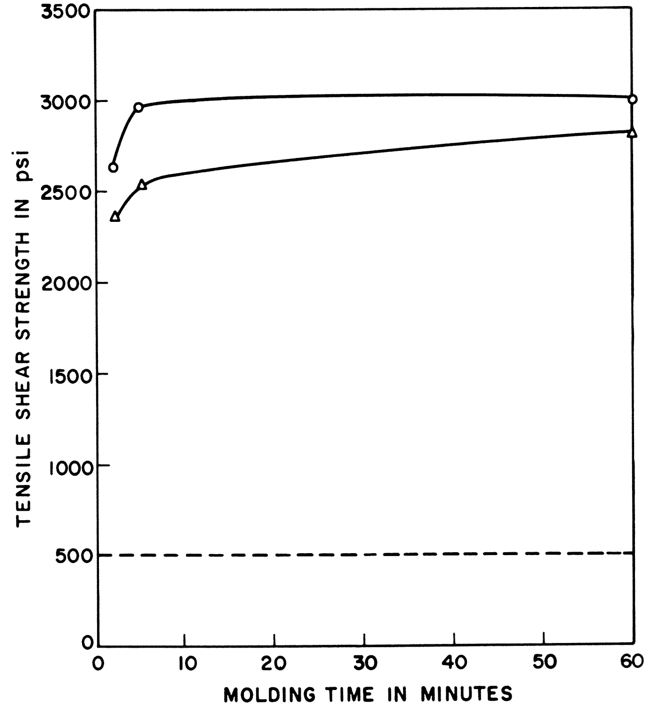

Figure 1. The tensile shear strength of the composite aluminum-epoxy adhesive-polyethylene film-epoxy adhesive-aluminum cured at 82°C. plotted as a function of molding time at 175°C.

▲— *Polyethylene film nucleated and solidified in contact with etched aluminum surface (subsequently dissolved from substrate)*
●— *Polyethylene film nucleated and solidified in contact with gold (subsequently dissolved from substrate)*
(- - -)— *Molded against low energy surface (PTFE or Mylar)*

Although a large number of substrates have been used to nucleate and crystallize polyethylene (*14*), only the wettabilities of polyethylenes

Table I. Wettability of

Liquid	γ_{LV}, *dynes/cm.*	γ_{LV}^d, *dynes/cm.*	$\sqrt{\gamma_{LV}^d}/\gamma_{LV}$, *l./(dynes/cm.)*$^{1/2}$
Water	72.8	21.8	0.0641
Glycerol	63.4	37.0	0.0959
Formamide	58.2	39.5	0.1080
α-Bromonaphthalene	44.6	44.6	0.1497

generated against gold, PTFE, and the single crystal aggregates are illustrated in Table I. The wettability of the aluminum-generated surface is essentially that of the single crystal aggregate.

Adhesive Joint Strength. Generally, to facilitate removal from molds or substrate surfaces, crystallizable polymers have been prepared in contact with low energy surfaces—*i.e.*, PTFE, Mylar—mold release agents or high energy surfaces—*i.e.*, metals, metal oxides—for short times at low temperatures—*i.e.*, just above the melting point of the polymer. This procedure generally results in the formation of considerable interfacial voids and a small real area of contact between the polymer melt and the nucleating phase.

The rate of wetting has been shown to be proportional to the surface tension of the polymer melt (γ_{LV}) and inversely proportional to the melt viscosity (η) (*15*). Since the melt viscosity varies strongly with temperature, to preclude interfacial voids at low temperatures, it is important to allow for sufficient time to insure extensive interfacial contact between the polymer melt and the adjacent substrate.

Figure 2a illustrates a poorly wetted substrate. Although the thermodynamic requirements for spreading are fulfilled—*i.e.*, $\gamma_{SV} \geqslant \gamma_{SL} + \gamma_{LV}$—spreading may not take place because of the kinetic requirements (*15*). Enhancement of wetting may be accomplished by employing higher temperatures or longer times, or both if convenient, bearing in mind that degradation of the polymer is to be avoided. Since η decreases quite drastically with temperature, relatively short times at elevated temperatures are required to achieve extensive interfacial contact between the polymer melt and the substrate (Figure 2b).

Since we can form strong adhesive joints by melting onto a high energy surface we can inquire whether the surface generated at the high energy solid-polymer melt interface is amenable to adhesive bonding when the metal is removed. As shown in Figure 1 it is important to remove the metal by dissolution rather than by peeling. Peeling removes the surface region of interest. This can be seen by examining the bondability of the damaged polymer and foil surfaces after peeling the foil

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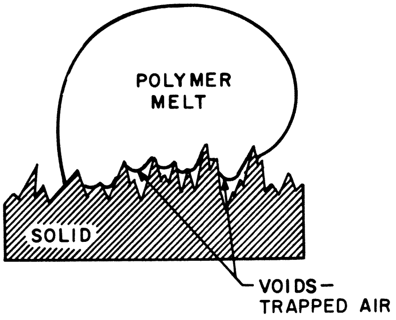
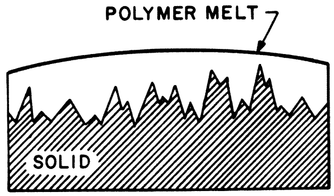
Polyethylene at 20°C.

Single Crystal Aggregate		*Nucleated*			
		Teflon		*Gold*	
θ, deg.	*Cos θ*	*θ, deg.*	*Cos θ*	*θ, deg.*	*Cos θ*
93	−0.052	94	−0.070	84	0.105
67	0.391	79	0.191	53	.602
55	0.574	77	0.225	41	.755
Spreads	1.000	35	0.818	Spreads	1.000

from the polymer. In both cases the joint strengths are low (bottom line, Figure 1). When the foil is peeled, failure occurs in the surface region of the polymer exposing two new surfaces which are not amenable to adhesive bonding.



(a) NOTE LOW REAL AREA
OF INTERFACIAL CONTACT



(b) NOTE LACK OF VOIDS
FROM TRAPPED AIR IN
PORES AND CREVICES

Figure 2. (a) Poorly wetted interface and (b) extensive intermolecular contact between liquid and solid

The residue on a peeled aluminum foil which had been molded against polyethylene at 175°C. for one hour was examined by Gel Permeation Chromatography (GPC) to determine the nature of the molecular weight distribution and to determine whether any fractionation occurred at the metal-polymer melt interface. The polymer was dissolved off the foil and examined. The $M_{\bar{W}}$ and $M_{\bar{N}}$ values for the surface region formed at the solid-liquid interface were 47,600 and 8,180, respectively. The corresponding values for the bulk polymer were 45,100 and 9,300, respectively. Apparently, there is no fractionation taking place as a result of the extensive nucleation and growth of the transcrystalline region (Figure 3). Whatever species are present in the polymer are accommodated into the crystal structure. However, while the molecular weight distributions may be similar, because of morphological differences the mechanical strengths of the surface regions are different.

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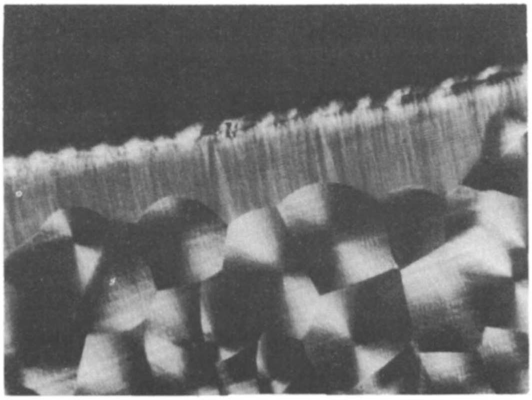

Figure 3. The transcrystalline region generated at a high energy solid-polymer melt interface after solidification. The depth of the transcrystalline region is estimated to be about 25μ

Strong joints with epoxy adhesives can be made to polyethylene surfaces which have been oxidized by a variety of techniques (*4*, *5*). The general belief has been that the presence of polar groups on the polymer surface creates an affinity for the polar epoxy adhesive which improves wettability and results in a strong adhesive joint.

Wettability has long been considered to be of primary concern in being able to form strong adhesive joints with the low energy crystalline polymers. Hansen and Schonhorn (*5*) have demonstrated that if the weakness in the surface region of a polymer is removed, without changing

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its wettability, strong joints can be prepared. In fact, Schonhorn and Hansen (*17*) have shown that lowering the wettability by, for example, exposing polyethylene to fluorine gas and creating a polytetrafluoroethylene-like surface is not detrimental, provided the weak boundary layer has been eliminated in the process. The critical surface tension of wetting (γ_c) of the fluorinated surface is about 20 dynes/cm., similar to polytetrafluoroethylene.

Surface treatments (oxidation) are probably effective because they, like CASING (crosslinking by activated species of inert gases) (*5*, *16*), eliminate the weak boundary layer normally present on the surface of polyethylene. During CASING, the polymer molecules at and near the surface are knitted together to form a cross-linked matrix having high mechanical strength. A cross-linked skin on polyethylene has been observed after surface treatment by corona discharge and chemical etching (*2*, *11*, *21*). This probably accounts for the strong joints formed by the use of these techniques (Figure 4). The mere presence of polar groups would not be sufficient if they were organized in a layer having low mechanical strength.

To demonstrate the presence of the weak boundary layer in polyethylene formed at a low energy surface, we attempted to eliminate it by several techniques and to observe the resultant joint strengths obtained with a conventional epoxy adhesive in the composite: aluminum-epoxy adhesive-polyethylene-epoxy adhesive-aluminum. The bottom curve in Figure 4 is based on joint strength data obtained from untreated polyethylene film (molded against PTFE). All experiments were performed below the melting point of polyethylene since above the melting point it will spread on the cured epoxy adhesive surface and in this process will preclude the formation of the weak boundary layer and result in relatively strong joints (*19*). When polyethylene is nucleated in the presence of a high energy surface, a transcrystalline region (*1*, *3*, *6*, *12*) is formed at the solid-liquid interface on cooling (Figure 3). Apparently, this results in generation of a region at the interface whose characteristic strength is similar to if not greater than that of the bulk polymer (*10*).

It was felt that the weak boundary layer was comprised of low molecular weight polymer molecules which were forced to the surface during recrystallization of the melt (*7*, *8*) in contact with a low energy surface, so we hoped to minimize their presence by molding well characterized single crystal aggregates of polyetheylene (*18*). However, on molding against a low energy surface, weak boundary layers were generated and only slight increases in joint strength were observed (Figure 4). Wettability of the molded "single crystal aggregate" was essentially the same as an untreated film but considerably different from the freshly precipitated single crystal aggregate (*18*).

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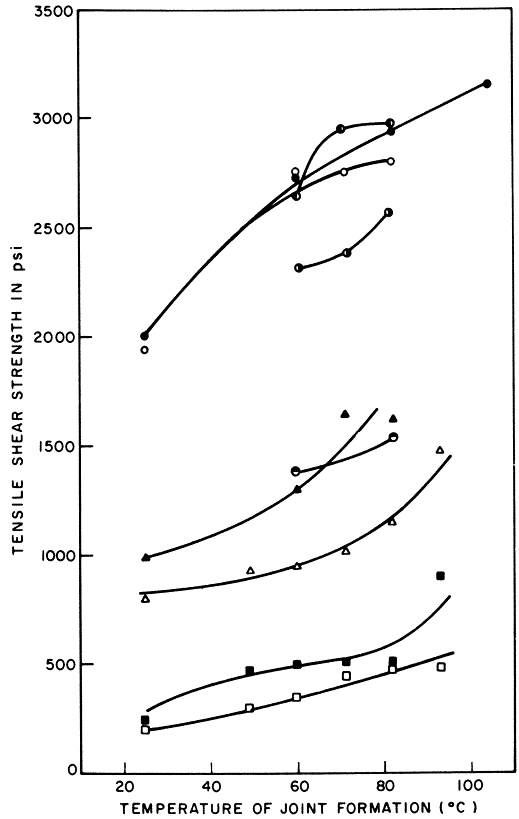

Figure 4. The tensile shear strength of the composite aluminum-epoxy adhesive-polyethylene-epoxy adhesive-aluminum plotted as a function of the temperature of the joint formation

□—*Untreated polyethylene (molded against PTFE) (no surface treatment)*

■—*Marlex 5003 polyethylene crystallized from 0.04% solution in xylene at 85°C. then molded into 10 mil. sheets at 160°C. No surface treatment*

△—*Polyethylene film (untreated) exposed to vapors of a boiling 1.1 hexane, heptane mixture for 5 minutes*

▲—*Polyethylene film (untreated) irradiated with a Van de Graaff generator to a dose of 10 Mrads*

○—*Polyethylene film exposed to glass cleaning solution at 80°C. for 4 minutes*

●—*CASED polyethylene, exposed to activated helium at 1 mm. pressure and high power for 5 seconds*

◓—*Polyethylene film generated against vapor degreased aluminum foil (subsequently removed by dissolution)*

◑—*Polyethylene film generated against vapor degreased and chemically etched aluminum foil (subsequently removed by dissolution)*

◐—*Polyethylene film generated against gold*

We resorted to other techniques such as solvent extraction (*16*). Specimens suitable for joint strength measurement were prepared and then extracted in a boiling 1:1 hexane-heptane solution for several minutes. The specimens were not swelled appreciably, and resultant joint strengths were considerably greater than those obtained with untreated film. Again γ_c was about 35 dynes/cm. When boiling octane was used to extract the low molecular weight polymer from polyethylene film, considerable swelling occurred. Upon removal of the solvent, additional lower molecular weight material was transported to the solid-air interface and only weak joints could be obtained.

The weak boundary layer was partially eliminated by bombardment of the polymer with high energy electrons. The results in Figure 4 show that stronger joints were obtained—but not shown is the fact that bulk properties of the polymer were seriously affected. Although the γ_c was raised, since irradiation was done in air, joint strengths were about the same as those obtained by the solvent extraction technique.

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The uppermost curves in Figure 4 are results obtained with surface treatment techniques which result in both cross-linking and strengthening of the weak boundary layer without affecting bulk properties of the polymer. High joint strengths were obtained after both CASING (five seconds in excited helium) and after etching with glass cleaning solution (four minutes at 80°C.). Glass cleaning solution treatment of polyethylene like all oxidative surface treatments causes ablation of some of the polymer at the surface and changes wettability. The results for the films generated against the gold are comparable to those of the CASING technique.

It is interesting to note that the joint strengths for films generated against gold are in excess of those prepared with films generated against etched aluminum. Vapor degreasing the aluminum foil without a chemical etch is only as effective as high energy electron bombardment in eliminating the weak boundary layer.

The importance of the chemical etch on the aluminum cannot be over-emphasized. Surface layers from rolling oils or weak oxides may obviate any desired effects.

By examining the strength of joints prepared over an extensive temperature range which includes the molten region, we note some striking features (Figure 5). The data for the melt crystallized polymer sheet that was peeled from the mold have been reported previously (*19*). We compare these data with the data of this report to point out the significance of the undisturbed transcrystalline region. The joint strengths are considerably higher than the same materials which have a damaged transcrystalline region. From the above analysis we can conclude that

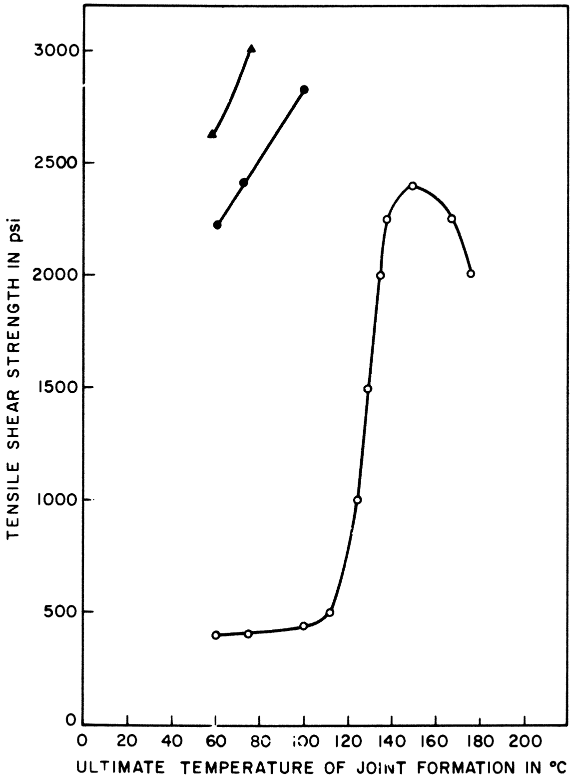

Figure 5. The tensile shear strength of the composite aluminum-epoxy adhesive-polyethylene-epoxy adhesive-aluminum plotted as a function of the temperature of the joint formation

○—*Data Ref.* 19

●—*Transcrystalline region (TCR) polyethylene generated at 175°C. for ½ hour against etched aluminum (substrate removed by dissolution)*

▲—*TCR polyethylene generated at 175°C. for ½ hour against gold (substrate removed by dissolution)*

the weakness in the surface region of polyethylene is not an intrinsic property of the polymer but is dependent on the manner in which it is formed from the melt. If care is taken in the preparation of the polymer sheet to prevent any mechanical work on the surface region, then it is possible to prepare this polyethylene for adhesive bonding without resorting to cross-linking of the surface region. Extraction of the transcrystalline region films in boiling xylene showed no evidence of a gel fraction. We speculate that what is increasing the mechanical strength of the surface region, as a result of the extensive nucleation, is considerable entanglement of the polymer chains. There is a strong competition

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for these chains since so many nuclei are formed. Effectively, each entanglement may be considered to be a cross-link.

Wettability and Surface Morphology. Surface chemical studies on crystallizable polymers have ignored, in general, the nature of the nucleating phase—*i.e.*, vapor, solid, or liquid—and the details of formation of the polymer melt-nucleating phase interface which on solidification by cooling results in a polymer solid-nucleating phase interface (*22*).

Extensive heterogeneous nucleation of polyethylene melts on high energy surfaces results in generation of transcrystallinity in the interfacial region [(S-L) → (S-S)] (*1, 3, 6, 12*). Koutsky, Walton, and Baer (*9*) have observed that there is a variation in the extent in supercooling which may depend upon surface energy and interatomic spacing in the substrate. Effective nucleating agents allowed for only small supercoolings. Sharples (*20*) has concluded that stresses at the interface set up during cooling from the melt are important in determining the subsequent morphology. Wettability studies coupled with a modified Fowkes-Young approach to interfacial phenomena (*18*) have indicated that gold is a more effective nucleating agent than the alkali halides and alkaline earth salts (*9*). Since a large number of nuclei are generated at the solid-liquid interface, provided that extensive contact has been established between the substrate and the molten polymer, the spherulites are inhibited in their lateral growth and only propagate in a direction transverse to the plane of the film. Apparently, as a result of this extensive nucleation on high energy surfaces, there is generated a plane of spherulitic cores which exhibit a density, as computed from wettabilities, similar to the single crystal density (Table II).

Table II. Surface Density and Crystallinity of Polyethylene Films as Determined by Wettability at 20°C.

Nucleating Phase	ρ_s *grams cm.*$^{-3}$	*Percent Crystallinity*
Nitrogen (vapor)	0.855	0
Polytetrafluoroethylene	0.855	0
Aluminum	0.949	63.2
Single crystal aggregate	0.949	63.2
Gold	1.007	93.6

Low energy surfaces—*e.g.*, Teflon, Mylar, etc.—are apparently ineffective nucleating agents. When polymers are cooled in contact with these surfaces, nucleation is precluded at the S-L interface and is apparently initiated in the bulk. Sufficient supercooling has not occurred at the solid-liquid interface to nucleate the interfacial region before nucleation occurs in the bulk. Apparently, this is the reason for the lack of a well defined transcrystalline region when polyethylene is nucleated against a

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low energy solid. As crystallization proceeds in the bulk, polymer molecules which cannot be accommodated into the crystal lattice during crystallization are rejected to the interface and reside there in an amorphous or liquid-like state (*7*, *8*). When prepared against low energy surfaces, polymers have surface regions which have densities, as computed from wettabilities, corresponding to the amorphous solid. This is illustrated in Figure 6 where a typical Fowkes type plot is constructed of the data in Table I. Here, the values for γ_s are, 36.2 ergs/cm.^{2} for the low energy nucleated surface, 53.6 ergs/cm.^{2} for the single crystal aggregate and 69.6 ergs/cm.^{2} for the gold nucleated surface. To estimate the surface density, the authors have modified the Fowkes-Young equation (18)

$$(\mathrm{Cos}\ \theta)_{a,ac,c} = \frac{2\left(\dfrac{\rho_s{}^{a,ac,c}}{\rho_s{}^{a}}\right)^2[(\gamma_{LV}{}^{d})_p\gamma_{LV}{}^{d}]^{1/2}}{\gamma_{LV}} - 1 - \frac{\pi_e}{\gamma_{LV}} \qquad (1)$$

where θ is the contact angle of the sessile drop of liquid on the polymer surface, ρ_S is the surface density, γ_{LV} is the surface tension, the subscript p refers to the polymer, the superscript d refers to the dispersion component of the surface free energy, the superscripts *a*, *ac*, and *c* refer to amorphous, partially crystalline and crystalline, respectively, and π_e is the spreading pressure (γ_S-γ_{SV})—the difference between the surface free energy of the surface of the polymer in vacuum and in equilibrium with the vapor of the wetting liquid. We have ignored π_e/γ_{LV} in our computation since $\theta > 0$ (*18*).

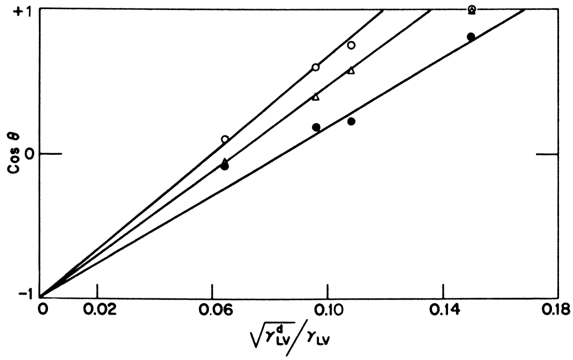

Figure 6. A Fowkes-Young plot of the wettability data for a variety of polyethylene surfaces

●—*Nucleated at low energy surface (PTFE)*
△—*Single crystal aggregates and nucleated against etched aluminum*
○—*Nucleated against gold*

In Interaction of Liquids at Solid Substrates; Alexander, A.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1968.

When the surface density of the solid is essentially that of the amorphous solid or supercooled liquid, Equation 1 becomes the familiar Fowkes-Young expression (*18*). Based on the generally accepted value of $\rho_S{}^a$ for polyethylene, $\rho_S{}^{ac}$ values are computed. From these values, the specific volumes are obtained. The percent crystallinity in the surface region is computed from the specific volume. Table II lists the values of $\rho_S{}^{ac}$ and the percent crystallinity of these films.

Employing high energy surfaces for the nucleation of polymer melts is only effective if sufficient time is allowed for the polymer melt to achieve extensive and intimate contact with the substrate. If sufficient time has not been allowed, considerable interfacial voids will result and nucleation will generally occur in the bulk, generating an amorphous surface region in the polymer. If sufficient time is allowed for spreading to occur, interfacial voids are precluded with nucleation occurring predominantly at the S-L interface. As evidenced from Tables I and II, the vapor phase is a poor nucleating agent.

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12

Polymer Solvent Interactions by Ultrasonic Impedometry

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Some unexpectedly complex liquid solid interactions have been detected and studied by ultrasonic impedance measurements (ultrasonic impedometry). Small amounts of water and alcohols have pronounced effects on the physical state of hydrophilic polymers; specifically, the high frequency shear modulus and crystallinity index of a poly(vinyl alcohol) film increases with water content to a maximum before normal solution phenomena occur. These effects are attributed to the increased molecular order owing to water hydrogen bonded between polymer chains. The unusual effects of moisture on a novel poly(vinyl chloride)/plasticizer system and on hydrophilic polymers other than poly(vinyl alcohol) are also described.

In our studies on the cellulose pulp/water system and the various viscoelastic changes which take place in this system during drying (5), we found Mason's ultrasonic shear impedance device (*12*) to be a most useful and versatile tool, capable of monitoring rapid changes in the shear stiffness of systems undergoing polymerization, coagulation, or other liquid-solid transitions. The work we are reporting here relates to a variety of transient changes in the high frequency shear modulus (stiffness) of polymer films induced by wetting of the films with polar solvents or near solvents. These transient effects are particularly marked in the case of poly(vinyl alcohol) films which are in contact with liquid water.

Methods and Procedures

The technique of ultrasonic impedometry was developed by Mason and McSkimmin of Bell Telephone laboratories for measuring the complex mechanical shear modulus of polymer liquids (*11, 12*). They described three relaxation modes for the systems—configurational elasticity, long chain entanglement, and chain segment twisting. Litovitz and co-workers used this high frequency technique in their investigation of the viscoelastic properties of associated liquids (*13, 17*). Myers and co-workers have monitored the liquid-solid transitions associated with the coalescence of latexes and the drying of linseed oil (*15, 16*). Barlow and Lamb studied the high shear rate behavior of lubricating oils at pressures up to 1,000 atmospheres and at frequencies up to 85 megahertz (*1*). Hunter, Montrose, and Shively have studied the viscoelastic constants of short-chain polymers using this technique (*10*).

In ultrasonic impedometry, the test sample is subjected to a high frequency cyclic shear strain by a plane-polarized, pulsed ultrasonic shear wave which is generated within a quartz echo bar as shown in Figure 1. The test material is placed on top of the bar and the ultrasonic wave is generated in the bar by means of a piezoelectric crystal bonded to one end of the bar and driven at resonant frequencies by an electrical impulse from a pulsed oscillator. The pulse generator emits a radio frequency electrical pulse of 2 to 80 Mhz. lasting about 5 microseconds and repeating about 400 times per second. The packet of ultra-sound is reflected from the test surface and is received at the other end of the bar by a second piezoelectric crystal where it is reconverted to an electrical signal and displayed on an oscilloscope as a series of peaks of decreasing amplitude. The geometry of the echo bar is such that the original pulse is reflected back and forth creating the pulse echo pattern shown in Figure 1. In favorable cases, as many as 50 echoes can be observed.

With a test sample on the optically flat top surface of the bar, the pulse echo train is reduced in amplitude. This attenuation is owing to the refraction of part of the ultrasonic wave into the test sample at the frequency used. The ratio of successive peak amplitudes may be measured on the oscilloscope and expressed in decibels loss per echo. From this, the loss per echo with no sample on the bar can be substracted to give a value Δdb which is related to the mechanical shear impedance of the sample. Rapid changes can be conveniently monitored by a recorder which follows the peak signal of a selected echo.

The polymeric films used in our studies were prepared by allowing a dilute solution of the polymer in a suitable solvent to evaporate on the test surface of the impedometer bar. Film thicknesses were varied over the range 10-100 microns by appropriate choice of solution volume and concentration. The poly(vinyl alcohols) (PVA) used in our work were Monsanto's Gelvatol 20-30 and 20-90. These are 88% hydrolyzed products and have molecular weights of 10,000 and 125,000 respectively. They behaved similarly in their responses to wetting, humidification, and redrying.

The test frequency used was normally 2.5 or 5.0 Mhz. A spot check showed that the transient effects found were more pronounced at higher frequencies (up to 60 Mhz.).

Theory of Ultrasonic Impedometry

The amount of attenuation suffered by the pulse echoes depends directly on the shear mechanical impedance, Z, of the polymer film. For

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viscoelastic materials Z has resistive and reactive components, R and X (units of mechanical ohms). The relation of R and X to shear stiffness G and shear viscosity η is given by:

$$G = (R^2 - X^2)/\rho \tag{1}$$

and

$$\eta = 2RX/\omega\rho \tag{2}$$

where ρ is the density of the material and ω is the circular frequency of the measurement. As discussed in greater detail elsewhere (5), the component R is dependent almost solely on the measured attenuation of the pulse echo amplitude. The component X is much more difficult to measure accurately (involving small phase shifts at high frequency) and, in our work was not measured.

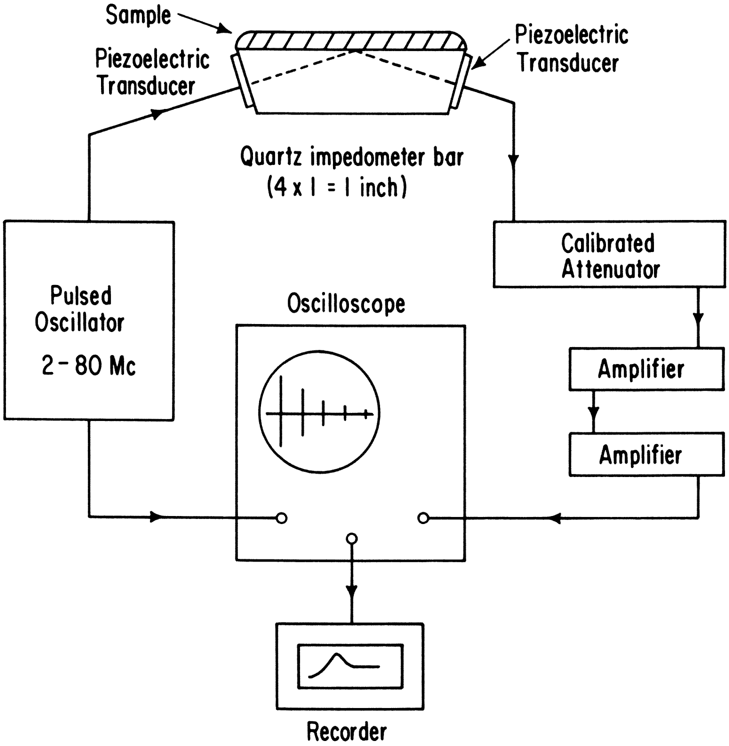

Figure 1. Ultrasonic Impedometer

For Newtonian liquids, $X = R$ and therefore shear stiffness G, by Equation 1, is zero. Viscosity is then given by the function $2R^2/\omega\rho$. This will hold approximately true into the megacycle frequency range for

In Interaction of Liquids at Solid Substrates; Alexander, A.;
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liquids with a normal viscosity below about 100 cp. Thus, water for instance, will still have a viscosity of 1 cp. at 10 Mhz. and above.

For elastic solids, such as those we are dealing with experimentally in this work, X approaches zero and thus the shear stiffness is simply R^2/ρ which is a direct function of the measured echo attenuation Δdb. An increased attenuation means increased R and therefore increased shear stiffness. Superficially, this would appear to be opposite to the usual interpretation of "attenuation" or "dampening" in other dynamic mechanical test methods. For example, in torsion pendulum type tests, a rubbery polymer gives a rapidly damped oscillation. Actually, there is no discrepancy at all because in the technique we are using the wave amplitudes measured on the oscilloscope screen are those not entering the sample. More energy escapes from the quartz bar as the polymer film approaches the mechanical impedance of quartz. The reader should be cautioned to keep in mind the different meaning which "attenuation" has in ultrasonic impedometry as opposed to its use in traditional dynamical testing techniques.

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Results and Discussion

Poly(vinyl alcohol)/Water. When distilled water is poured onto the surface of poly(vinyl alcohol) films dried onto the impedometer bar, the initial response is not the expected decrease in stiffness caused by the solvating effect of the water, but rather a marked increase in stiffness followed by a slow relaxation as shown in Figure 2. (The Δdb scale on this and most following graphs has been adjusted to read as change in Δdb from the initial value. Thus, the zero point is for the dried polymer film. The absolute value Δdb for dried polymer films ranged from 1 to 16 Δdb depending on film thickness and polymer type.)

This unusual effect of increased high frequency shear stiffness on initial contact with water was evident even when the water was applied as vapor. With thin films of PVA, the Δdb increases rapidly with even a single moist breath blown on the sample and then returns to its initial value slowly as the sorbed water diffuses out of the film. By blowing moist air continuously over a dried PVA film, the Δdb can be made to pass through a maximum just as it does when liquid water is applied. These responses are shown schematically in Figure 2a.

The same curious effects occur when the moisture sequence is reversed. An experiment of this sort is shown in Figure 3, where we equilibrated a PVA film with a 100% relative humidity atmosphere and then recorded the Δdb change as this film dried out in a 50% relative humidity atmosphere.

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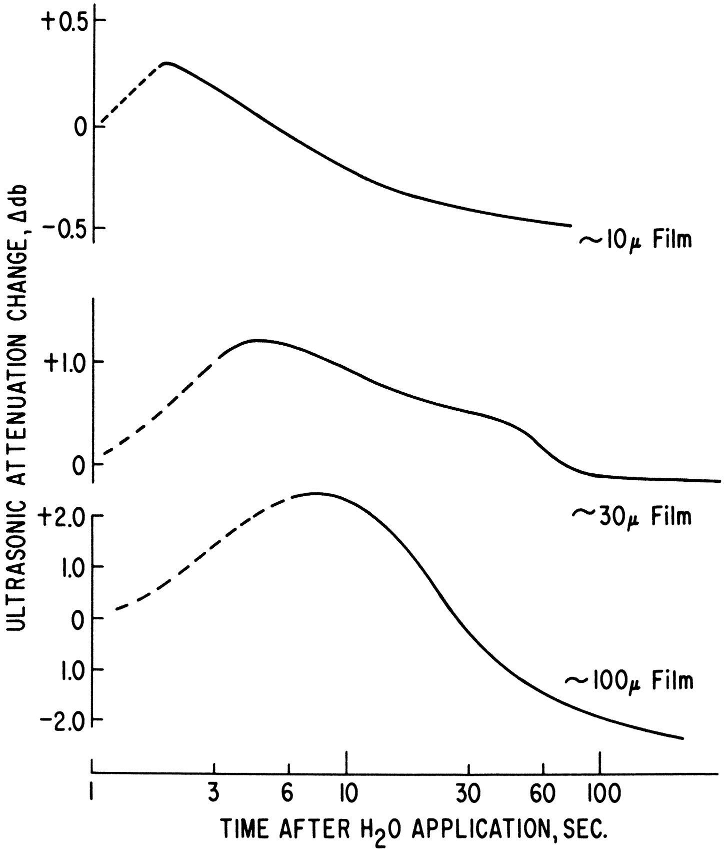

Figure 2a. . Poly(vinyl alcohol): water interaction

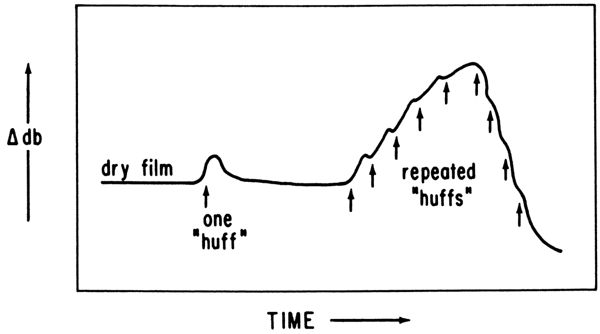

Figure 2b. Response of PVA film to breath moisture (schematic)

To check the possibility that this anomalous mechanical behavior might be caused by a solvent gradient within the polymer film or by

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some bulk effect of water at the interface, another PVA film (Gelvatol 20-30, 200 μ thick) was prepared on an impedometer bar and dried over phosphorus pentoxide for one week. It was then conditioned successively at relative humidities of 50, 65, 75, 85, and 93%. The film was equilibrated at each humidity for 48 hours. Moisture content (weight gain) and Δdb were measured at intervals during each two day conditioning period. The data are given in Table I and Figure 4. Note that the stiffness of the PVA film increases with increasing moisture content until the normal solvent effect of water comes into play in the region between 85 and 95% relative humidity. During each approach to equilibrium, as shown by the dotted line, the shear stiffness passes through a maximum indicating that the transient moisture gradient in the film also causes an increase in Δdb.

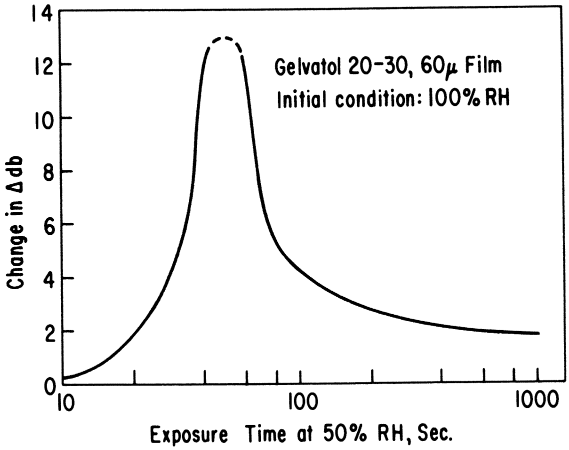

Figure 3. Dehumidification of PVA film

Mason (*11*) has shown that the high frequency shear stiffness of a polymer is largely a measure of the mobility of segments of the polymer chain. We propose that water molecules acting individually or in small clusters serve as molecular crosslinks through hydrogen bonding between adjacent polymer molecules or neighboring chain segments. If the lifetime of these crosslinks is longer than the frequency used to measure mechanical stiffness, in our case 10^{-7} second, then one would expect to see an increased stiffness owing to adsorbed water which could not be measured by traditional mechanical testing methods operating at much lower frequencies. What would look very rigid at 10^7 c.p.s. might appear quite flexible in a conventional torsion pendulum or tensile tester. Thus, it is conceivable that the "static" modulus would be reduced by the adsorption of moisture under the experimental conditions we have used

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here even though the "high frequency" modulus is increased within this range.

Several findings in the literature support this view. For example, density measurements in other hydrophilic polymer systems (collagen and gelatin) have revealed a maximum upon the addition of water (*7*). The density maximum was attributed to the formation of water bridges, doubly hydrogen-bonded structures, joining accessible chains in closer alignment. Also, thermodynamic interpretation of sorption isotherms indicate that polymer/water molecular contacts are favored over water/water contacts in some hydrophilic polymers up to relative humidities of 80% and over (*19*). In earlier work, Zimm suggested that the effect of water molecules on protein structure could give rise to an entropy loss—*i.e.*, increased ordering— of considerable magnitude (*21*).

Table I. Humidification of PVA Film

% Relative Humidity	*Conditioning Time, Hrs.*	*Moisture Content %*	Δdb *at 5 MHz.*
0	(1 week)	0	15.0
50	1	1.0	15.0
50	4	2.1	—
50	24	3.5	15.6
50	46	3.8	15.6
65	5	7.7	16.7
65	22	10.9	16.1
65	28	11.2	16.2
75	2	13.7	17.5
75	66	20.4	17.9
80	6	23.2	19.6
80	24	27.2	20.0
93	22	47.9	16.8

In a study of PVA/water relations, it was found that a marked reduction in PVA swelling results from pretreatment of the polymer films by exposure to a high humidity atmosphere (*18*). The explanation was that the chain segments, allowed greater freedom of motion by the absorbed water, could assume configurations favorable for growth of new ordered regions. Other workers have found large interactions of PVA with water, as measured by changes in specific volume (*20*). Russian workers have shown by heat capacity and torsion techniques that the plasticizing action of water on a hydrophilic polymer (rayon) consists "not only in increasing the flexibility of the molecular chains but also in increasing their orderedness" (*14*). Crosslinking of polyethylene glycol derivatives with water molecules has been indicated by yield value measurements (*9*). Thus, frequent reference has been made to the organizing influence of water on hydrophilic polymers.

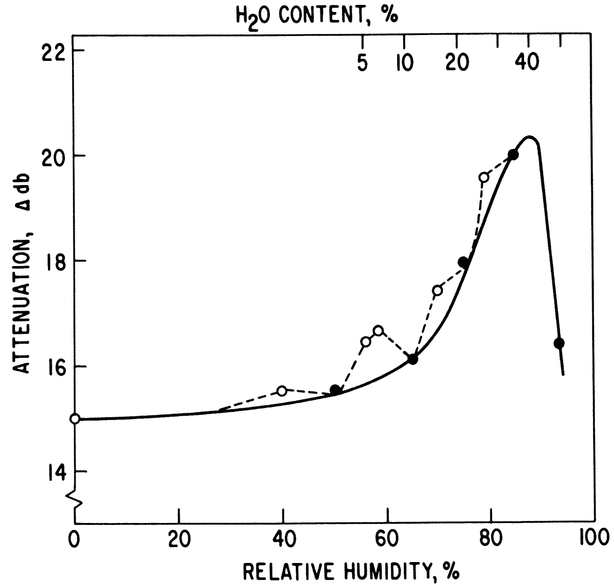

Figure 4. PVA humidification

—●— *Equilibrium*
—○— *Approach to equilibrium (schematic)*

If water acts as a crosslinking agent, it should increase the molecular ordering in the polymer film and this effect should be detectable by x-ray diffraction techniques. PVA films were prepared on glass slides that were conditioned at 0, 30, and 85% relative humidity. X-ray diffractograms of these films are presented in Figure 5, with analytical data in Table II. At 0% relative humidity, only a broad amorphous band is present. At 30% relative humidity, a peak at $2\theta = 19.3°$ appears; at 85% relative humidity, a second peak at $2\theta = 22.2°$ is barely evident. These peaks are characteristic of the PVA crystalline phase (*3*). The intensity of the amorphous phase defraction halo decreases with increasing relative humidity. It appears, therefore, that water induces the aggregation of small crystallites (which contribute to the amorphous pattern (*2*)) into groups large enough to be detected by x-ray as being truly crystalline. In a study of the swelling behavior of PVA in water, Priest made reference to earlier unpublished work where the x-ray diffraction pattern for PVA became sharper on humidification (*18*). Thus, the effect of moisture in increasing the Δdb of PVA films correlates with structural changes in the polymer as viewed by x-ray techniques.

Poly(vinyl alcohol)/Methanol. When methanol is used instead of water, the increase in attenuation is not as rapid as that with water but

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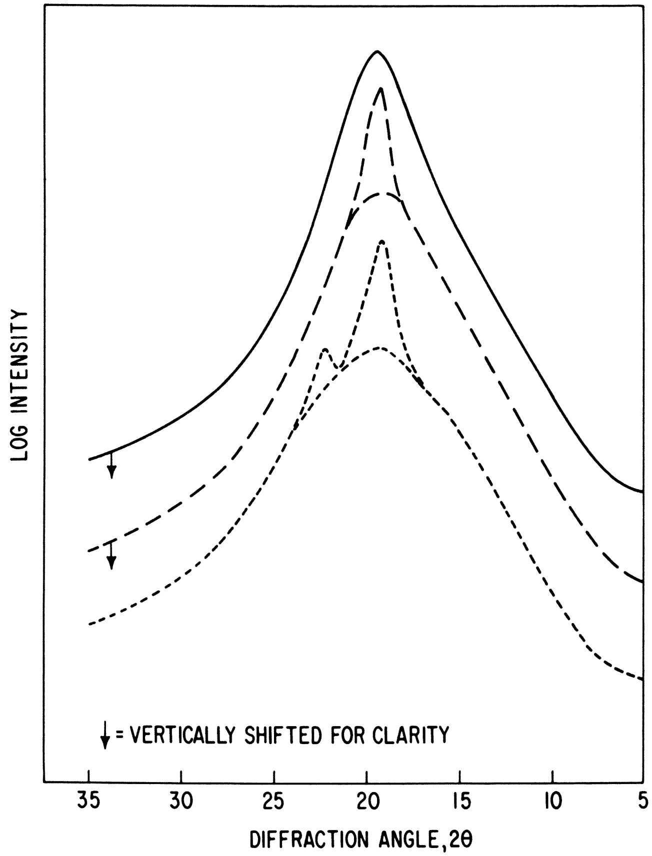

Figure 5. X-ray diagram poly(vinyl alcohol)

0% Relative Humidity ————
30% Relative Humidity — — —
85% Relative Humidity - - - - - -

Table II. Effect of Water Vapor on Poly (vinyl alcohol) Crystallinity

		Peak Intensity			
		Broad	*Structure*		
Sample Condition	*% RH*	*2θ: 19.5*	*19.3*	*22.2*	*Crystallinity Index*
Dry	0-5	46.5	—	—	0
Lab Air	30	41.0	11.5	—	28
Humid	87	34.0	12.5	5	64
Redried	0-5	46.5	12.5	—	27

the peak intensity is more persistent as is shown in Figure 6. Ethyl alcohol has a similar response, but the intensity is only 1/10 as great.

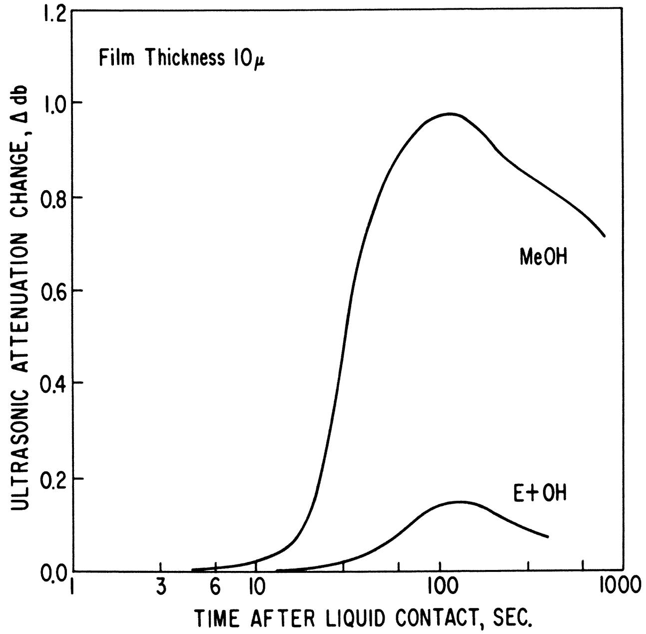

Figure 6. Poly(vinyl alcohol): methanol interaction

Propyl alcohol, butyl alcohol, benzene, and octane show no effect. These results correlate with the relative hydrogen bonding capabilities of the alcohol series. Apparently methanol is also capable of forming hydrogen bonding crosslinks between poly(vinyl alcohol) chain segments but without dissolving the polymer. Ethyl alcohol with its increasing molecular volume is still capable of forming some hydrogen bonding crosslinks, perhaps only in the more readily accessible regions of the polymer network while the higher alcohols—propyl alcohol, butyl alcohol, etc., if they are hydrogen bonded, do not form crosslinks which are detectable at the frequencies we used.

Because methanol is not actually a solvent for PVA, some interesting sorption/desorption cycling experiments can be conveniently run on PVA films without disrupting the film integrity. As noted above, methanol produces a slow increase of shear stiffness (Δdb) when layered on PVA. The time scale and curve shape are suggestive of a diffusion process (liquid into polymer). By removing the liquid layer, we should permit methanol to evaporate from the film and thus reverse the effect. The

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results shown in Figure 7 are surprising. The first application of methanol produced a slow increase in Δ*db* as before. The excess methanol was drawn off the surface by syringe at point B. We then expected to see Δ*db* return slowly to the initial value as the film dried out. Removal of the liquid layer (at B) caused a decrease in attenuation until the film surface appeared dry (at C). Then, as methanol evaporated from within the film, the Δ*db* passed through a very high maximum. A second flooding of the surface after air drying resulted in an immediate increase in Δ*db* in contrast to the slow build up on initial wetting. After the first wetting, the sequence of responses to subsequent wetting/drying cycles was remarkably reproducible. Perhaps the first wetting is unique in that it "opens up" the surface structure of the film, permitting rapid penetration of methanol into the film on succeeding rewettings.

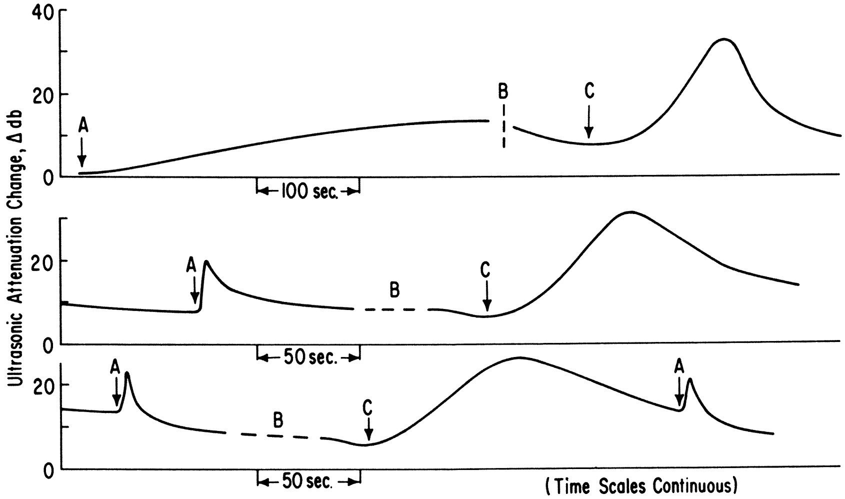

Figure 7. Poly(vinyl alcohol): methanol interaction

Polymer: Gelvatol 20–30
Film thickness = 50 μ
Frequency = 5 MHz.
Film Δdb = 6.0

A: MeOH added
B: MeOH drawn off
C: Polymer surface dry

Another example of an intriguing cycling effect resulted from an experiment in which we crosslinked the surface of PVA film by painting the film with borax solution. The surface was now visibly less receptive to water (droplets did not spread), but the film Δ*db* was unchanged. Methanol wetting produced the curious doubled peaked increase in Δ*db* shown in Figure 8. By redrying the film in a vacuum oven (50°C.), the position of the first peak (upon rewetting with methanol) was gradually shifted to longer times. The second peak position was unchanged. Appar-

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ently, whatever was causing the early peak was being modified or removed by the alcohol, resulting in longer times required for subsequent methanol additions to reach the unmodified region of the film.

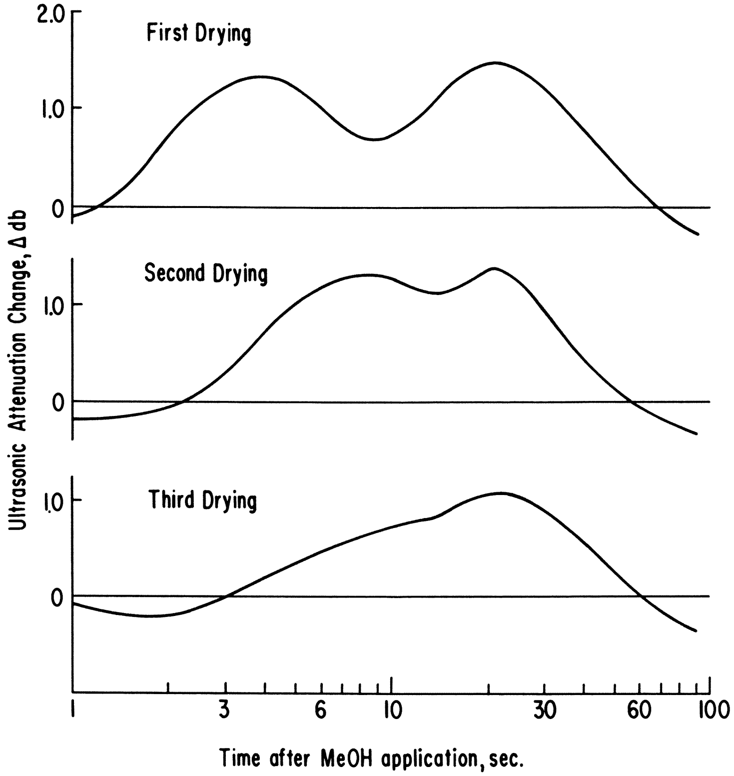

Figure 8. Poly(vinyl alcohol) crosslinked: methanol interaction

Polymer: Gelvatol 20–30
Film thickness = 65 μ
Frequency = 5 MHz.

Other Polymers. Other hydrophilic polymers also exhibit the shear stiffness anomaly when contacted with hydrogen bonding solvents. Films of amylose respond to water and dimethylsulfoxide as shown in Table III. When wet with water, there is a comparatively large increase in attenuation followed by a slow decline to a level plateau. We attribute this leveling out to the comparative water insolubility of retrograded amylose. Dimethyl sulfoxide is a much stronger solvent for amylose than is water and the increase in stiffness which is followed by a rapid decay to zero indicates complete film solution as was the case with water on PVA. The

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peak height is lower with DMSO because rapid solution prevents attainment of maximum stiffening effect.

Other hydrophilic polymers including gelatin, casein, and poly(vinylpyrrolidone) all respond like PVA when contacted by water; there is a rapid increase in modulus followed by film solution.

Even though cellulose fiber mats are discontinuous rather than homogeneous films, a sheet prepared from well mascerated cellulose fibers will exhibit this same response to water as does PVA. A more detailed treatment of cellulose fiber water interactions has been given elsewhere (*5*).

Hydrophobic polymers and films, such as paraffin wax and poly(vinyl chloride), show no change in stiffness modulus when flooded with water. On the other hand, butyl alcohol on a paraffin wax film causes a slow, slight increase of stiffness modulus over a period of several minutes. The effect of benzene on paraffin films is similar to that of methanol on PVA. A poly(vinyl chloride) film is unaffected by plasticizers such as dimethyl and diethyl phthalate over short time periods. However, PVC gives rise to the ultrasonic modulus anomaly when contacted with tetrahydrofuran, a strong solvent for PVC. The plasticizing effect of dibutyl phthalate on polystyrene has been demonstrated by ultrasonic impedometry (*16*). No anomalies were found.

Table III. Response of Amylose Films to Wetting (Film Thickness: 10 μ)

	Change in Δdb *from dry film value after wetting surface with:*	
Time after Wetting (sec.)	*Water*	*Dimethyl sulfoxide*
0 (dry)	0	0
2	2.1	0.8
5	1.4	−0.1
10	1.2	−0.1
30	1.0	−0.1
∞	0.8	−0.1

Other Transient Interactions. The PVA/borax example dealt with the effects of surface exposure of a two-component polymer system to a wetting liquid. We discovered a practical example of this class of phenomena in a plasticized poly(vinyl chloride) (PVC) system. A peculiar plasticizer (tetraethyl methylene bisphosphonate) for PVC has been found (*6*) which has the unusual property of exuding out of PVC immediately upon exposure to high humidity. The plasticizer quickly re-enters the resin when the humidity is reduced. A film of 60% resin and 40% plasticizer was solvent cast from tetrahydrofuran onto an impedometer bar and was subjected to sudden high humidity exposure.

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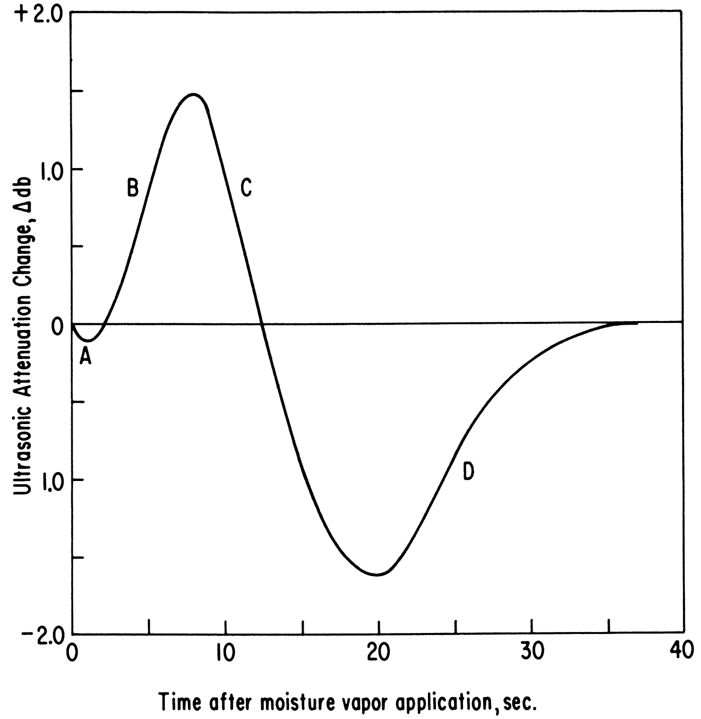

Figure 9. Resin: plasticizer: moisture interaction

Resin: poly(vinyl chloride)—Opalon 650
Plasticizer: 40% tetraethyl methylene bisphosphonate
A — D = See *text*
Film thickness = 4 mg./cm.^{2}
Frequency = 5 MHz.

The response obtained is shown in Figure 9. Our interpretation is: at A—sorption of small amount of moisture vapor enhances the plasticizing effect and reduces the shear rigidity. At B—water vapor at the film surface draws plasticizer out of the resin, leaving the film more rigid. Plasticizer can be seen and felt on the surface at this point. At C—film is losing adhesion to the quartz surface. At D—plasticizer is returning to the resin (observed) and film re-adheres to the surface, returning to its original state.

Supplementary experiments support this interpretation: (a) films equilibrated at 50% R.H. had lower rigidity than one equilibrated at 0% R.H.—suggesting behavior at A, (b) film equilibrated at 100% R.H. separated from quartz surface, (c) abrupt humidity changes have no effect on PVC or the plasticizer separately.

A mundane example which we include for its novel complexity is the effect of water wetting ordinary cellophane adhesive tape. The tape

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provides a highly complex substate (cellophane, plasticizer, adhesive, and other components). The tape was pressed onto the impedometer bar and wetted with water. A complex response would be expected of a complex system if the attenuation changes previously observed on simpler systems were not of trivial origin—*e.g.*, instrument effects. The response shown in Figure 10 is quite complex and reproducible (particularly along the time axis). A double layer of type (Curve B) gave a similar response shifted to longer times and smaller amplitudes. We do not pretend to be able to interpret the behavior depicted in Figure 10, but it is certain that some subtle liquid-solid interactions are responsible as well as gross effects such as separation at the cellophane/adhesive interface.

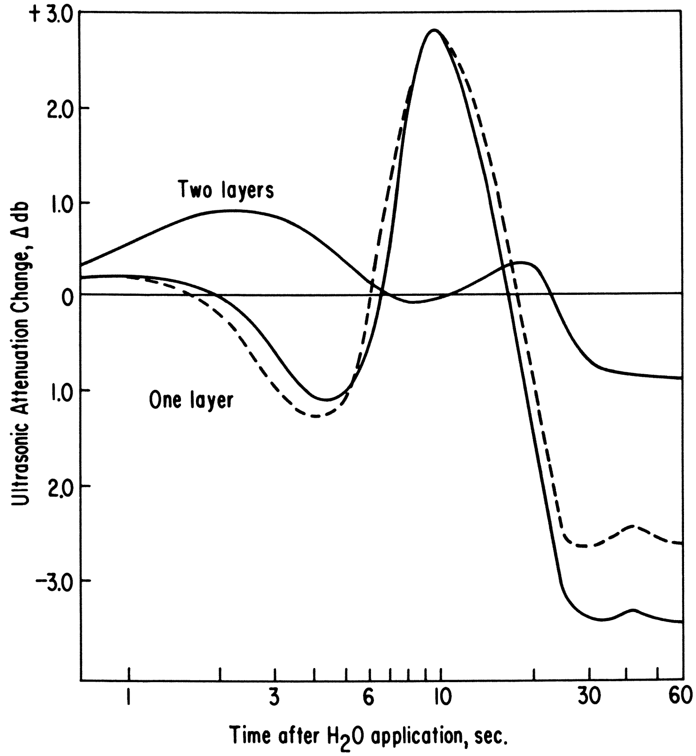

Figure 10. Cellophane tape/water interaction

Frequency = 2.5 MHz.

Summary and Conclusions. "Simple shear is by far the most important type of deformation in studies of viscoelastic bodies, because [for example] the absence of a volume change facilitates interpretation of the behavior in molecular terms" (*8*).

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The sequence of events which we have detected at ultrasonic frequencies when hydrophilic polymers are contacted by strongly hydrogen bonding solvents involves a sharp increase in shear stiffness followed by a more or less rapid decrease to attenuation levels close to that of the solvent.

We attribute the initial increase in stiffness to water hydrogen bonding polymer chains with consequent increase in order. This stage is followed by progressive solvation of the polymer film, plasticization, and solution. Water vapor produces increased organization in poly(vinyl alcohol) either through crosslinking or through increased molecular mobility. This is manifested by the increased sharpness of the x-ray diffraction pattern and by the increased high frequency shear stiffness of the humidified films. The molecular bridging hypothesis has been used by others to explain density maxima in humidified collagen and gelatin, the "bound" water phenomena in living organisms, and the bonding of cellulose fibers in papermaking.

The hydrogen bonds in liquid water have an average lifetime of less than 10^{-10} second as measured by dielectric relaxation times (*4*). But the hydrogen bonds between water and a polymer could exist for longer than 10^{-7} seconds. Such a structure would appear "permanent" at the frequencies used in the ultrasonic impedometer (10^7 cycles/sec. range), and should demonstrate a measurable shear stiffness at these frequencies.

The case for increased organization in hydrophobic films caused by nonhydrogen-bonding solvents is not as well documented. It is difficult for us to see how benzene can increase the shear modulus of paraffin wax or how tetrahydrofuran can do the same for poly(vinyl chloride). It is possible that we are dealing with a van der Waals bonding in swollen polymers in these cases but much more evidence would be needed before a definite theory can be advanced.

The use of the shear-reflectance impedometer has permitted us to observe polymer-solvent interactions in thin films and to monitor transient effects which are not readily accessible by other techniques. This suggests that this technique could be applied to the study of polymer-solvent interactions in other related research areas such as the diffusion of solvents into films, physical effects at pigment-polymer surfaces, or the nature of the interface between living cell surfaces and aqueous media.

Acknowledgment

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13

Blood/Material Interface Problems Confronting Artificial Heart Development

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The Artificial Heart Program of NIH has 15 contracts trying to discover materials compatible with blood. We know that foreign materials become coated with adsorbed protein within a few seconds after being exposed to blood and that the clotting process does not begin until some time later. Hageman factor is activated at the blood/material interface, but how and why this leads to clotting is not clear. Other proteins may be involved. Blood agitated in contact with foreign material will hemolyze, perhaps days later. The surfaces of blood vessels in contact with blood have a "slime layer" that contains heparinoid complexes, the function of which is not understood. Hydrogels, which simulate this layer, show promise. Related to these programs is the need for better methods for determining protein denaturation.

Probably the most serious technical obstacle standing in the way of the development of satisfactory blood pumps of many varieties is the blood/material interface problem. There is no material today which has been proven to be satisfactorily compatible with blood. This is not a problem that can be solved by the physicians and hematologists alone but must be solved by a team effort involving these individuals and also the physical and polymer chemists and others whose expertise is periodically required. Recognizing the enormity of this problem the Artificial Heart Program of the National Heart Institute has established several projects in this field. These projects include the following:

(1) Attempts to develop more stable and more satisfactory heparin surfaces on various polymers.

(2) Studies attempting to develop materials with very low surface free energy.

In Interaction of Liquids at Solid Substrates; Alexander, A.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1968.

(3) Attempts to develop polyelectrolyte complex resins in the form of hydrogels which would be compatible with blood.

(4) Attempts to develop polymeric hydrogels which would be compatible with blood.

(5) Attempts to develop new base polymers which are more compatible with blood.

(6) Attempts to develop silicones which are more compatible with blood.

(7) Attempts to develop polymeric electrets with negatively charged surfaces which are more compatible with blood.

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There are a number of projects to study the effects that result from the contact of blood with some of these foreign materials. The last group is probably the most critical group. There is no satisfactory *in-vitro* test for blood/materials compatibility, nor is there a completely satisfactory *in-vivo* test. It is possible that there is sufficient information available today fully to define the problem if it could be organized properly. It might then be possible to place more emphasis on areas and techniques of importance. Many of the materials that are being tested today do look promising with the tests that are available. Investigators continue to find more and more materials which do not clot blood when passed in test tubes made of these materials for long periods of time, well beyond the time normally required for clotting resulting from the activation of Hageman factor.

What is some of the information that we have today? In the first place much of the information available today is inconclusive and still more theoretical than factual. For example, we know that blood practically never clots in direct contact with a foreign material. That statement always requires clarification. We know that foreign materials become coated with adsorbed protein within a very few seconds after being exposed to blood and that the clotting process does not begin until some time after that occurs. How many steps there are between the protein contact with a foreign material and the actual clotting of blood is somewhat speculative, but certainly there is good evidence that Hageman factor, one of the proteins in the blood, is activated as a result of this blood/material contact and this activated Hageman factor, in turn, initiates a chain reaction which results in the conversion of fibrinogen to fibrin, the matrix of blood clots. We know that the Hageman factor in blood, if it becomes adsorbed on a surface, certainly does not remain fixed there. It is even possible that the activation of Hageman factor results from the activation of some other protein which does remain more firmly attached to the material, but this has not been demonstrated.

What actually happens in the activation of Hageman factor? Is it a chemical reaction? We know that Hageman factor can be activated and clotting still prevented as a result of the addition of oxylate or citrate to the blood to tie up the calcium ion. This blood containing activated Hageman factor can then be allowed to stand for a period of time and the Hageman factor will be deactivated. Whatever the reaction that is involved, therefore, it is a reversible reaction and probably does not require any apparent chemical resynthesis.

Since Hageman factor is thought to be helical in form, as is true with other blood proteins, it is possible that the adsorption forces between it and the surface result in an unfolding of the helix with exposure of certain active sites which in turn initiate the clotting of blood. This seems like a reasonable theory, but of course at this stage can be considered nothing more than that.

What happens to the other proteins that are adsorbed on foreign materials? We know that many proteins are quite firmly bound to the surface and that it is difficult to wash some of these off. We also know that many of these proteins have definite biological function other than merely osmotic activity. We also know that the strength of these adsorption forces varies with different proteins, but apparently a dynamic state exists with proteins being adsorbed, desorbed, and new proteins adsorbed. It would seem quite coincidental if Hageman factor were the only one of these proteins that altered its biological function as a result of this adsorption and desorption. It seems quite obvious that materials which are compatible with blood must not appreciably alter any of the vital blood proteins.

Heparin has been ionically bonded to surfaces for some time and more recently it has been co-valently bonded to various materials. Some of these surfaces are quite stable and the heparin remains on the surface in high concentration for long periods of time. There is no longer any doubt that heparin surfaces *per se* retard clotting and do not require that the heparin be in solution at the surface to accomplish this. The heparin on the surface retards clotting and its action in doing this may be somewhat different than its action when in solution. Proteins, however, are still adsorbed onto heparin surfaces and the adsorption is fairly strong. The fact that Hageman factor is not apparently activated by these heparin surfaces does not necessarily mean that other proteins are not altered. Again at this time our information is far from conclusive on this subject.

We know that blood that has been in contact with foreign materials and agitated under these conditions hemolyzes. We know that some of this hemolysis or destruction of the red cells takes place because of

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abnormal flow conditions within the pumping devices. We also know that some of these conditions that seem to destroy blood in blood pumps and oxygenators exist in the body and do not cause hemolysis there. We know that the material itself apparently plays some role in this hemolysis, but the extent of this role is not altogether clear. There is also evidence that some of the adverse effects on the red blood cell do not result in destruction of the cell at that time, but that this may occur days later. Direct contact with a foreign material apparently shortens the life of red cells. There is also some evidence that red cells which have been in contact with a foreign material do not function in the transport of CO_2 and O_2 as well as they normally do. Much of this information is still poorly understood, to say the least, but again there does appear to be some reaction between the foreign material and the red blood cell. The materials themselves are noted for the fact that they are usually chemically inert so the interaction between the red cell and foreign material is probably not a chemical reaction in the usual sense of the term. Again it may be that proteins in the wall of the red cell may be affected in much the same way as Hageman factor and possibly other blood proteins are affected.

We also know that patients who have been kept on oxygenators for long periods of time develop problems which are poorly understood but if these problems are allowed to continue they inevitably result in death. Animals that are put on total heart replacement using an artificial heart pump also die eventually with some very poorly understood physiologic changes. These changes may well result from denatured enzymes and hormones within the body.

The changes that take place seem to differ somewhat depending on whether the blood merely passes over a foreign material or whether it is actively pumped by a foreign material. It is possible that the combined action of the adsorption forces of protein on foreign surfaces and the forces created by the flexing diaphragm may exceed some of the forces of the chemical bonds, causing rupture of protein chains and breakdown of some of these proteins to polypeptides. These polypeptides may pass through capillary walls into the extravascular spaces upsetting the osmotic equilibrium and creating some of the edema that is frequently seen under these circumstances. Again, it appears that the degree of difficulty that arises from use of oxygenators, artificial kidneys, artificial blood pumps and the like is dependent on the amount of blood coming in contact with a foreign material. Thus, oxygenators which are used to oxygenate the entire "cardiac" output can be used for only a few hours while if only a tenth of the cardiac output is oxygenated this period of time can be greatly extended. Artificial kidneys which allow only a

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fraction of the total minute volume of the heart to pass through them can also be used for long periods of time. Cardiac assist pumps seem to develop difficulty if they pump a very large fraction of the total cardiac output for long periods of time.

It might be wise at this time to take a quick look at the ideal surface, the surface of blood vessels. The immediate surface in contact with blood is somewhat of a "slime layer" which contains heparinoid complexes. The concentration of these heparinoid complexes, however, is not high and it is not clearly understood how important they are. It is because of the existence of this "slime layer" that hydrogels were expected to show promise, the theory being that it would be difficult for protein to be adsorbed onto a surface which was 80 to 90% water and, since the protein would not be well adsorbed, denaturation might be minimized. These hydrogels that have been tested to date have not been quite as encouraging as had been hoped but this is not altogether the fault of the materials themselves. There is certainly hope that as time goes on and more work has been accomplished in this field that we can learn whether these hydrogels do in fact have promise.

All of this tends to indicate that we may be making a mistake when we look only at the clotting problem resulting from the blood/material interaction. This may merely be a very visible effect of the denaturation of one particular protein in the blood. The solution of the clotting problem may very well only allow us to recognize the fact that other factors are involved and that we have failed to look at the total picture.

Two programs may be required: (1) development of better methods for determining the denaturation of protein and (2) development of materials which are satisfactorily compatible with blood. The former is a very difficult problem which may almost prove to be insurmountable for many years. We know that the biological function of some of the enzymes in the body can be altered by very minor changes of certain critical side chains and that we do not have good tests for this biological function for many enzymes. *In-vivo* testing is difficult since the body is continuously trying to correct the abnormalities which it sees. For example, the level of plasma hemoglobin in the body is determined in part by the body's ability at that moment to remove the plasma hemoglobin from the blood and this ability varies considerably from time to time as a result of factors that are only partially understood. The same is true with the infusion of altered proteins. The body will remove them and replace them just as rapidly as it possibly can and its ability to do this will vary as a result of many factors that will probably be only partially understood for many years. The development of materials which are truly compatible with blood is also very difficult. One of the first problems in achieving this, of course, is to determine what is incompatible about presently available materials. On the other hand, only as a result of developing better materials are some of the more subtle problems recognized. There must, therefore, be a constant exchange of information between these groups.

There obviously is a great need for the chemists in the nation to work in this field from many points of view.

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Characteristics of Heparinized Surfaces

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Heparin can be attached to a variety of surfaces by means of complex formation with quaternary ammonium salts. Depending on the method used to attach heparin, the resulting surfaces may or may not release heparin when contacted with blood plasma. The removal of heparin from surfaces by plasma protein fractions was studied and it was found that alpha-globulins removed greater amounts than any other fraction. Heparinized surfaces adsorb proteins when exposed to blood or plasma. However, with the possible exception of thrombin, there is no consistent pattern of protein adsorption which can be related to their nonthrombogenicity.

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Heparin has been chemically bonded to a number of polymers to produce surfaces which do not cause coagulation of contacted blood (*5, 6, 7*). The nonthrombogenicity of these surfaces has been demonstrated both in *in vitro* tests and in a limited number of *in vivo* experiments. Bonding of heparin to these polymers has been effected through complex formation with quaternary ammonium groups covalently attached to the surfaces. Because of the potential uses of these materials in the cardiovascular system, it is essential that they retain their nonthrombogenicity during prolonged exposure to blood and that they do not cause damage to blood elements.

The permanency of the bonded heparin on a number of selected polymer systems has been measured using radiolabeled heparin (^{35}S). It has been found that the loss of heparin after prolonged exposure to distilled water and isotonic saline at 37°C. is almost negligible for heparinized polypropylene, silicone rubber, and Hydrin rubber. On the other hand, polypropylene loses 70% of its originally bound heparin after exposure to plasma for three hours. Hydrin rubber and silicone rubber lose only from 0 to 5%. The loss of heparin on the polypropylene may be attributed to displacement of the heparin molecules by a protein or combination of proteins. A series of experiments was performed in which

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the removal of heparin from polypropylene by a series of plasma proteins was measured. The proteins were dissolved in buffered physiological saline and contacted with the heparinized surfaces for 30 minutes in a static system at 25°C. After the exposure period, the surfaces were rinsed, dried, and recounted. Techniques for preparing and determining amounts of surface-bonded heparin by radioisotope labeling have been described in a previous publication (3). The results of this present study are shown in Table I.

Table I. Removal of Heparin from Polypropylene by Individual Proteins

Protein	*Concentration mg./ml.*	*Percent Loss*
γ-globulin[a]	10.0	54
α-globulin[a]	4.0	92
β-globulin[a]	4.0	56
Fibrinogen[b]	3.6	64
Hageman factor[c]	0.01	64
Albumin[a]	20.0	59

[a] Cohn fractions (bovine).
[b] Obtained from Gallard-Schlessinger, 95% clottable (bovine).
[c] Purified 5000 times from bovine plasma.

It can be seen that α-globulin removes more heparin than do any of the other plasma proteins. The reason for the loss of heparin from the polypropylene surface and not from the silicone rubber is not understood since the same chemical reactions are used to effect bonding to both polymers.

The stability of the heparin/amine complex is affected by the structure of the amine. A series of studies has been performed in which the effect of amine structure on heparin bonding and retentivity was measured by radioisotope techniques. The results indicated that quaternary ammonium salts are more effective in binding heparin than are primary, secondary, and tertiary amines, and that amines containing alicyclic or aromatic structures are more effective in binding heparin than are those containing only straight chains (2). A study was also made on ratio of the number of surface quaternary ammonium sites to the number of heparin tetrasaccharide units which were bound. In this study, silicone rubber and polypropylene surfaces were aminated with tritiated dimethylaniline and pyridine according to previously described techniques (7) and then heparinized with ^{35}S heparin. The relative amounts of amines and heparin were determined by scintillation counting (3). Results from this study are presented in Table II.

Table II. Ratio of Number of Amine Sites to Amount of Bound Heparin

Surface	*Moles Alkylated Dimethyl-aniline per cm.^{2} × 10^9*	*Moles Alkylated Pyridine per cm.^{2} × 10^9*	*Moles Heparin Tetrasac-charide per cm.^{2} × 10^9*	*Ratio of Dimethyl-aniline to Heparin*	*Ratio of Pyridine to Heparin*
Styrene-grafted polypropylene	6.51		0.607	10.8/1	8.8/1
Styrene-grafted polypropylene		2.57	0.294		
Silicone rubber	15.2		3.03	5.0/1	6.3/1
Silicone rubber		18.5	2.82		
Styrene-grafted silicone rubber	55.7		4.74	11.8/1	15.5/1
Styrene-grafted silicone rubber		59.4	3.84		

From the above data it may be seen, first of all, that the ratio of amine sites to heparin tetrasaccharide units is affected by the type of surface to which these groups are attached. This may be owing to the conformation of the surface. A microscopically rough surface would prevent complete association of all of the amine sites with heparin sulfate groups because of the large size of the heparin molecule. The data also show that many amine groups are necessary to bind a heparin tetrasaccharide unit. Each of these units contains seven negatively ionized groups, and thus the theoretical ratio of amine sites to tetrasaccharide units would be 7/1. As can be seen from Table II, the experimentally obtained ratios range from 5/1 to 15/1. As a corollary experiment, the ratio of heparin tetrasaccharide units to the number of moles of free quaternary ammonium salts was determined in solution by equilibrium dialysis experiments. The results showed that the ratios of phenyltrimethylammonium iodide and methylpyridinium iodide to heparin tetrasaccharide units were respectively 3.3/1 and 3.0/1. The lower values obtained from solution indicate that it is unlikely that all the quaternary ammonium sites on the polymer surface are complexed with an anionic site on the heparin molecule.

The mechanism by which heparinized surfaces maintain their nonthrombogenicity has been investigated by a number of experimental techniques. The evidence indicates that the absence of clotting in *in vitro* experiments is not caused by heparin release into the blood because normal clotting occurred in heparinized vessels to which either tissue thromboplastin or an activating surface such as kaolin was added. In addition, a number of surfaces which contained large amounts of heparin caused clotting in contacted blood. These surfaces presumably did not

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have a uniform covering of heparin and the unheparinized portions of the surface caused activation of the contact system. If the mechanism by which heparinized surfaces maintained fluidity of contacted blood was merely the release of heparin into the blood, one would expect that any heparin-containing surface would be nonthrombogenic.

An important factor in the interaction of foreign surfaces with blood is the rapid adsorption of plasma proteins onto such surfaces when they are exposed to blood (*4*). For this reason the adsorption of radioactively tagged blood components on heparinized and unheparinized surfaces was measured. Proteins were dissolved in approximate physiological concentrations in a buffered (pH 7.35) physiological saline solution and the solutions were exposed to the test surfaces for 2 hours at 37°C. in a static system. After the exposure, the surfaces were rinsed with physiological saline and distilled water and then dried. The amount of protein on the surfaces was determined in a 2π-gas flow proportional counter (*7*). As shown in Table III, although both heparinized surfaces were nonthrombogenic, there is no consistent pattern of either increased or decreased adsorption of the proteins caused by the heparinization. Increased adsorption on both heparinized surfaces was seen only with fibrinogen and thrombin. With heparinized silicone rubber, the increase in adsorption of thrombin was very great. Thus, the absence of clotting in blood exposed to heparinized surfaces appears not to be associated with differences in protein adsorption. A possible explanation for their nonthrombogenicity may be that they do not cause activation of Hageman factor and thus coagulation *via* the intrinsic pathway (*1*) is not initiated. In experiments performed at Battelle with purified Hageman factor, it was found that exposure to heparinized surfaces caused no increase in the amount of activated Hageman factor. Exposure to an unheparinized surface, on the other hand, caused partial activation of the Hageman

Table III. Ratio of Adsorption of Proteins on Heparinized Surface to Unheparinized Surface

Protein	*Concentration mg./ml.*	*Silicone*	*Polypropylene*
Fibrinogen[a]	3.8	1.3	1.6
γ-globulin	10.0	0.86	1.6
β-lipoprotein	4.0	0.70	1.4
α-lipoprotein	4.0	4.5	0.9
α-globulin	4.0	0.78	1.43
Human serum albumin	20.0	0.65	1.2
Thrombin	0.1	24	3.8
Hageman factor	0.01	—	1.7

[a] Source of all proteins same as in Table I.

factor preparation. The results were complicated by the fact that a quaternary ammonium surface (which was also thrombogenic) caused no apparent activation of Hageman factor. Thus, further work must be done before more definite conclusions can be drawn. Work is now in progress on the adsorption of other coagulation factors onto heparinized surfaces and on the effect of exposure to heparinized surfaces on the effect of exposure to heparinized surfaces on clotting factor activity.

Conclusion

It has been shown that heparinized surfaces can be made which lose either no heparin or extremely small amounts of heparin upon exposure to plasma. These surfaces adsorb proteins and with the exception of thrombin, there is no consistent pattern of protein adsorption which can be related to their nonthrombogenicity.

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Heparin Bearing Coatings or Surfaces: Quantitative Relations

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The amounts of heparin removed from solution, and of heparin adsorbed on cationic surfaces, were determined using ^{35}S labelled heparin. The averages agree in order of magnitudes but the surface shows large local variation, confirmed by autoradiographs. Initial strike effects do not level out in 48 hours exposure to aqueous heparin solution. However, uniform heparin deposit is obtained by dipping the cationic surface at a steady rate. Minimum heparin loading for anticoagulant effect (clotting time longer than 100 min.) approximates 0.3 $\mu g./cm.^2$ for graphite-benzalkonium-heparin and polyvinylpyridine-heparin surfaces, and also for cellulose nitrate lacquers containing benzalkonium-heparin complex. Electrolyte in the heparin solution reduces the amount adsorbed, with greater effect on polyvinylpyridine than on graphite-benzalkonium surfaces.

The discovery by Gott, Whiffen, and Dutton (*4*) that heparin adsorbed upon a suitably receptive surface could prevent blood from clotting has inspired much work on the preparation of heparin bearing plastic surfaces. Coagulation tests, *in vitro* or *in vivo,* tend to be "go-no go" tests and have seldom been used to determine quantitative relations between the amount of heparin on the surface, the mechanism of binding to the surface, and the anticoagulant effectiveness. Quantitative data are needed to give evidence on the theoretical question, whether heparin introduced on a surface acts there, or by going into solution; and the practical questions, of the most suitable modes of binding heparin to a surface for long term *in vivo* effectiveness and for fabrication of prosthetic systems.

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Advances in Chemistry; American Chemical Society: Washington, DC, 1968.

Earlier quantitative estimates of the amount of heparin initially present on anticoagulant surfaces are summarized in Table I. These estimates should be regarded as indicating orders of magnitude rather than precise measurements.

Table I. Reported Amounts of Heparin on Anticoagulant Surfaces

Surface	*Method*	*Heparin* μ*g./cm.*^{2}	*Reference*
Graphite-benzalkonium	^{35}S, direct	3 or less	*10, 11, 12*
	Chemical, depletion	0.24	*3*
	^{3}H, direct	2	*6, 7*
	^{3}H, direct	3 to 1	*5*
	^{35}S, direct	1.6	*2*
Cation grafted to silicone rubbers or polypropylene	^{35}S, direct	1 to 15.7	*2*
Polyvinylpyridine	Chemical, depletion	3	*3*
Cellulose, ethyleneimine	^{3}H, direct	4 to 700	*6, 7*

Materials

Heparin Bearing Surfaces. GBH. Graphite-benzalkonium surfaces (GB) have been treated with sodium heparin to make the graphite-benzalkonium-heparin (GBH) surfaces described by Gott (*4*). The graphite (Dag 154, Acheson Colloids, 1 part, plus 3 parts ethyl alcohol) was applied to films of polyester (Mylar) by painting, spraying, or dipping and draining.

PVPYRH Poly-4-vinylpyridine (PVPyr) prepared by conventional persulfate catalyzed polymerization was dissolved in ethyl alcohol or methyl Cellosolve (2 to 3% solution) for application to polyester film substances. These films adsorb heparin from solutions of sodium heparin to produce anticoagulant surfaces (PVPyrH). Films were painted on, or spread by knife coating.

CBH. The sparingly water soluble compound of heparin with an organic base (BH), such as benzalkonium—*e.g.*, "Zephiran" (Winthrop) or cetyl trimethyl ammonium bromide or octadecyl amine can be dissolved in ethyl alcohol and mixed with an organic polymer matrix—*e.g.*, collodion in ether and alcohol (*4*). Such lacquer mixtures are designated CBH.

Methods

Adsorption Studies. SACKS. GB or PVPyr surfaces were made into flat sacks, sealed on three sides by a heat sealing polyester film coated with a polyolefinic adhesive (Seal-Lamin, Seal Inc., Shelton, Conn.). The fourth side was similarly sealed after introducing the solution containing heparin leaving an air bubble enclosed. Such flat sacks, with two coated faces each 12 × 12 cm. (288 cm.^{2} for adsorption) and over all dimensions of 14 × 14 cm. were held between flat discs at a spacing such that the

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enclosed air bubble would travel around the inside edge, taking up about 1/3 of the enclosed volume, thus stirring the contents when the disc assembly was rotated. An assembly of sacks and discs was rotated in a thermostat for 20 hours or longer. The sacks were partially opened by snipping off one corner, drained, and rinsed, then opened by slitting along the sealed edges.

DIPPED FILMS. Short term adsorption effects were examined by dipping films, coated onto one or both sides of a polyester sheet, into heparin solutions. Insertion and removal was either by hand or in special cases by a constant rate mechanism. The films were let hang without stirring in the solution for an interval after dipping. Narrow containers were used to minimize volume of solution required.

Determination of Heparin. CHEMICAL. Modifications of the methods of Warren and Wysocki (*9*) and Bassiouni (*1*) were used. Where plasma or blood was not involved, a direct titration of the heparin with azure A, either measuring the dye removal or redissolving the precipitate, was used.

RADIO TRACER. Heparin labelled on the *N*-sulfate with ^{35}S was obtained from Calbiochem Co. Specific activity was 0.65 mc./grams, 140 U heparin/mg. This could be counted in a liquid scintillation system, to determine depletion from solution. Internal standards of ^{14}C compounds were used to determine efficiency. The labelled heparin adsorbed on a surface could be counted on a 2×2 cm. or 1 inch diameter portion supported on a planchet in a gas flow Geiger counter. A calibration curve was prepared by evaporating known amounts of labelled heparin on a similar area of the adsorbing surface. The calibration curve was linear over a greater range, and with a higher count per microgram of labelled heparin, for PVPyr surfaces than for GB surfaces, which indicates more absorption of radiation by the graphite layer.

AUTORADIOGRAPHS. The surfaces bearing adsorbed labelled heparin were dried, then placed in direct contact with "No Screen" x-ray film (Kodak NS-2). The adsorption sacks could be opened on three sides, then two film sheets inserted so that autoradiographs of both surfaces could be obtained. "Register" of the two films was established by making identifying notches after assembly. Darkening was seen only on the side in contact with heparin, indicating that all the ^{35}S beta radiation was absorbed in the film and its cellulose acetate base, total thickness 9 mils. Trials with the planchet counter show that a 5 mil polyester film reduces the count to 6 to 7% of that with direct exposure; with a representative PVPyr film on polyester the count falls to 4%, and with a GB film on polyester, to 1.6%. Hence, even in autoradiographs with adsorption of heparin on both surfaces, the effect observed is more than 90% from the adjacent surface. Autoradiographs show no effect, within the time of exposure used, of labelled heparin adsorbed on a polyester control, although a small adsorption can be detected by direct planchet counting. The autoradiographs were made at different stages in the decay of the ^{35}S; the exposure times therefore varied, in order to obtain the pattern, from 3 to 45 days.

DYEING OF HEPARIN ON PVPYR. The transparent films of polyvinylpyridine permit demonstration of the presence of heparin, and some judgment of the uniformity of adsorption, by staining with a basic dye such as toluidine blue or azure A, which combine with heparin to form relatively insoluble compounds. A PVPyr film stained with either dye is faintly blue; if heparin has been absorbed, a reddish color appears in much greater strength. The redness (metachromatic effect) indicates that this is the compound of the dye with heparin. Some heparin also leaves the surface and forms a precipitate in the solution.

COAGULATION TESTS. Fresh, citrated normal "non-contact activated" human plasma, used within 6 hours of drawing the blood, was used throughout unless specially indicated. This was platelet rich plasma. The plasma was kept in an ice bath until just before use, when it was warmed in small lots to room temperature. All handling and tests were conducted in plastic (polystyrene, polyethylene, poly(vinyl chloride)) or in siliconized glass unless specifically noted. The first 5 mil of blood was discarded, to minimize tissue or traumatic influence. Typical recalcification clotting time in plastic was 20 minutes; in glass, 8 minutes; in glass with 5 minutes of deliberate activation by rolling as a film on the glass wall before recalcification, 3 minutes, showing that the contact activation system (Factors XII, XI) was present ready for activation.

Two types of surfaces were made: "Cones"—a portion of film was folded twice, as in preparing filter paper for a funnel, then opened out to form a cone. "Flat surfaces"—a convenient area of film, usually the 2 × 2 cm. specimen on which the adsorbed heparin had been determined by the planched counter, was placed in a Petri dish, along with a separate portion of cotton or filter paper saturated with water. Citrated plasma (0.2 ml.) was pipetted onto the center of the specimen; then $0.05M$ $CaCl_2$ solution (0.2 ml.) was added, and the mixture was stirred with a Teflon stirring rod without touching the film and with the least possible spreading of the large drop. The Petri dish cover was then used to prevent evaporation or air-borne contamination. Direct visual observation, or observation with a low power, long working distance stereo microscope permitted determination of the first appearance of fibrin. The liquid or gel condition could be checked by tipping the Petri dish. In some work, the plasma was recalcified in a plastic test tube, then quickly transferred to the film, with generally similar results, but shorter clotting times.

Results

Uniformity of Adsorption. Regrettably, autoradiographic testing of uniformity of adsorption was begun somewhat late in the work, after the necessity for this was recognized from irregularities of dyeing, of coagulation tests, and of planchet counts on small areas.

Planchet counts show ratios as high as 30:1 between areas of strong adsorption and weak adsorption. The average of a large number of 2 × 2 cm. areas, however, shows a general correspondence to the over-all average as determined by depletion, as shown in Table II. Hence, some general guidance on adsorption can be obtained from depletion measurements, although for any great degree of precision, uniform adsorption is required.

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Table II. Comparison of Adsorption of Heparin on P_4VPyr-Mylar Surface, by Depletion (Indirect, Average for 288 cm.^{2}) and by Planchet Count (Direct, for 4 cm.^{2})

Initial Heparin Available in Solution[a] *μg./cm.*^{2}	*Adsorbed Heparin by Depletion μg./cm.*^{2}	*Adsorbed Heparin on 2 × 2 cm. Squares*	
		Individual μg./cm.^{2}	*Average μg./cm.*^{2}
3.4	1.87	2.28, 1.96, 0.92 1.26, 1.90	1.66
0.34	0.34	0.07, 0.46, 0.53 0.10, 0.49, 0.61 0.76, 0.45, 0.05 0.06, 0.07	0.29
0.17	0.17	0.29, 0.21, 0.24 0.30, 0.23	0.25
0.034	0.034	0.050, 0.060, 0.020 0.087, 0.082	0.060

[a] Amount in original solution divided by area.

Autoradiographs of GBH surfaces sometimes show a "strike" where the aqueous solution of heparin was delivered by a pipette, and ran down the film, as seen in Figure 1, which shows the two sides of an adsorption sack with graphite-benzalkonium surface. The match of the adsorption pattern on the two surfaces indicates that it was a matter of initial contact with solution, not a property of the surfaces. This pattern was produced on an initially dry GB surface. The solution was 90% cold heparin, 10% tagged heparin, at 67 μg. tagged heparin/ml. The average heparin adsorption, calculated as total (10× radioactive heparin adsorption) from depletion of the solution, was 2.7 μg./cm.^{2} Sack was rotated 20 hours, with a bubble, at 37°C.

Figure 2 shows two sides of a GBH sack which was wet with water before introducing the heparin solution. Ten ml. of heparin solution were introduced into 5 ml. of water, avoiding initial contact with the walls. The pattern appears to be related to the circular rotation of the bubble. Other initially wet or dry sacks showed similar rotation-suggesting patterns, not the flow-strike patterns of Figure 1. Heparin concentration was 648 μg./ml. in the initial 15 ml. mixture; sacks were rotated 48 hours with bubble at 37°C. Average adsorption of heparin, by depletion of solution, is 4.0 μg./cm.^{2}.

Figure 3 shows one side of a polyvinylpyridine sack, initially dry. Ten ml. of heparin solution were introduced into the dry sack, followed by 5 ml. water, avoiding contact with the walls. (This was part of the same experiment as Figure 2). The pattern was matched on the other side and appears to be related to the bubble, its location in early stages

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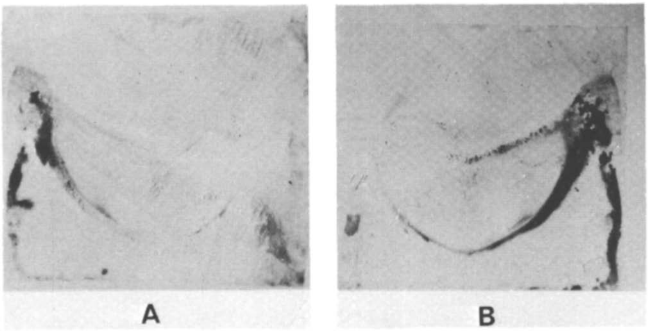

Figure 1. Autoradiographs showing uneven adsorption of heparin on an initially dry graphite-benzalkonium surface. A and B are the two sides of a flat adsorption sack. Flow from the point of initial contact of the solution is indicated with an initial "strike" which did not level in 20 hours rotation, with a bubble, at 37°C. Average heparin adsorption 2.7 μg./cm.²

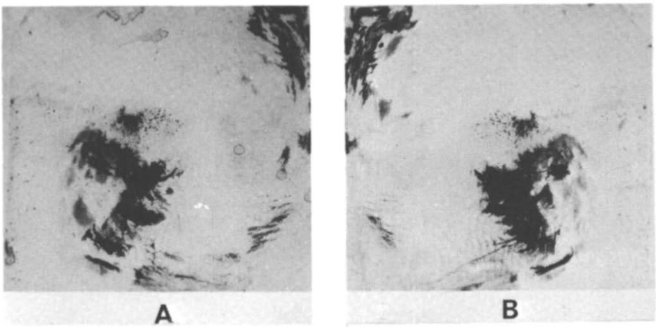

Figure 2. Autoradiographs showing uneven adsorption on an initially wet graphite-benzalkonium surface. A and B are two sides of a flat adsorption sack, 10 ml. heparin solution introduced into 5 ml. water, avoiding contact with the walls. Sack rotated 48 hours with bubble at 37°C.; initial heparin concentration 638 μg./ml. in 15 ml.; average heparin adsorption 4.0 μg./cm.²; autoradiograph exposure 72 hours

of exposure prior to rotation, and its path during rotation (48 hours at 37°C.). A fold or crack in the heparin adsorbing film can also be seen in the lower third. The generally darker tone, for the same solution concentration, age of heparin, and time of autoradiograph exposure agrees with the depletion and planchet count measurements in indicating more heparin adsorbed per unit area on the PVPyr films than on the GB films, at least as we prepare them. This may indicate more cationic sites available on PVPyr, but we lack information to compare total cations available or the specific surface areas and depth of penetration, so this observation

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is purely empirical relating only to the particular way in which these films have been prepared. PVPyr sacks which were initially wet show similar patterns. Initial mixture concentration was 648 μg. heparin/ml.; average adsorption, by depletion, 7.6 μg./cm.^{2}.

Figure 4 shows the relatively even adsorption on polyvinylpyridine surfaces spread by knife coating and dipped into radioactive heparin solution (500 μg./ml.) for 6 minutes. Six discs each 1 inch in diameter were die cut from each of two duplicate preparations which were similar in visual evenness to the ones shown. Planchet counts gave the results shown below:

	A	*B*
	μg./cm.^{2}	*μg./cm.^{2}*
	1.88	1.52
	1.64	1.43
	1.78	1.47
	1.58	1.44
	1.45	1.45
	1.43	1.27
Average	1.63	1.43
Standard Deviation	0.17	0.08
Coefficient of Variation	12%	6%

Influence of Electrolytes. Presence of electrolyte of low molecular weight in the solution with the heparin reduces the amount of heparin adsorbed, and promotes leveling, as would be expected from the fact that the relatively water-insoluble complexes or compounds of heparin and other mucopolysaccharides are increasingly dissociated and the mucopolysaccharide brought into solution by increasing electrolyte concentrations (*8*). Since Gott (*4*) and most other surgeons have applied heparin from solution in 0.15*M* NaCl, the practical formation of GBH anticoagulant surfaces on surgical implants has probably involved much less non-uniformity than many of our experiments.

The two types of surface, GB and PVPyr, differ in the effect of electrolyte on heparin adsorption. On GB, the heparin adsorption is unchanged between 0.15*M* and 0.5*M* NaCl, but drops by half at 1.0*M;* on PVPyr the adsorption is unchanged between 0.05*M* and 0.15*M*, but drops to close to zero at 0.5*M*. These results were all obtained in adsorption sacks. Autoradiographs indicated that we had not found the conditions for uniform adsorption, although logically adsorption can be expected to be more uniform under conditions in which initial strike can be prevented, or leveled by equilibrium adsorption and desorption during longer exposure.

We are engaged in obtaining more uniform surfaces from which more precise and accurate adsorption isotherms can be obtained. Results

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Figure 3. Autoradiograph showing uneven adsorption on an initially dry polyvinylpyridine surface. Rotated with bubble 48 hours at 37°C. Heparin concentration 638 μg./ml., average heparin adsorption 7.6 μg./cm.^{2}. Autoradiograph exposure 72 hours (comparable with Figure 2). In the lower third there is a fold or crack line in the film, probably introduced before the sack was made

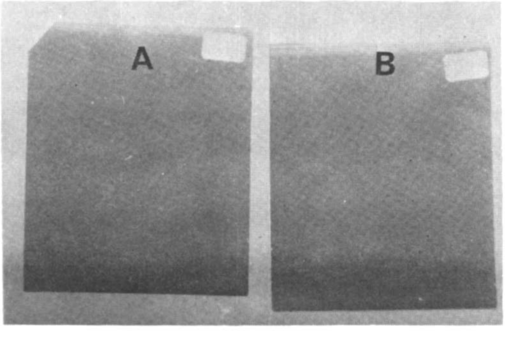

Figure 4. Relatively even autoradiograph of two portions of polyvinylpyridine film, A and B. There is some gradation from top to bottom, but the uniformity is high compared with Figure 1 through 3. This was dipped into heparin solution, held immersed 6 minutes, then withdrawn and rinsed. Planchet counts of die cut one inch circles taken from a pair of surfaces similar in visual evenness are given in the text, showing coefficients of variation of 12 and 6% for duplicates

obtained by depletion analysis can only indicate the average adsorption over the whole area. However, such analyses indicate that all the heparin available, up to an average of about 3 μg/cm.^{2}, will be adsorbed on GB surfaces. The level for complete exhaustion by PVPyr films appears to be higher, *ca.* 10 μg./cm.^{2}. However, the autoradiographs show that the true maximum may be much higher.

Effect of Thickness of Adsorbing Film. Earlier studies of effect of film thickness (3) indicated that the trend between graphite film thickness and amount of benzalkonium adsorbed was small, from about 2 to 4 μg. benzalkonium per cm.^{2} for variation from 200 to 1000 μg. graphite per cm.^{2}. The analyses by chemical methods for heparin adsorbed were not precise enough to show any trend. Chemical analysis did show that from 1.5 to 7.5 μg. of heparin was absorbed on from 400 to 1000 μg. of PVPyr per cm.^{2}, but the range of heparin was so great at each PVPyr level that no clear trend could be seen. More recent autoradiographic studies with each kind of film indicate that for brief exposures to heparin solution in distilled water there is indeed a trend for more heparin to be adsorbed on thicker films of either kind.

Uniform Adsorption by Uniform Mechanical Exposure. If an adsorbing film is introduced into the solution at a uniform rate, the "strike" effect can be made uniform. Autoradiographs such as Figure 4 show that this can be accomplished, or at least that much more uniform adsorption can be obtained by dipping than by exposure in sacks. Whether the heparin so adsorbed is the same in its equilibrium relations to solutions is yet to be determined, but it appears similar in anticoagulant effect.

Minimum Heparin Binding for Anticoagulant Effect. Using autoradiographs as guides, selection of relatively uniform areas on which the heparin can be determined by planchet counting has permitted estimates of relation to the anticoagulant effect. Table III shows some results, which indicate that for GBH surfaces, the limit lies between 0.2 and 0.3 μg. heparin/cm.^{2}.

Table III also shows results on PVPyrH films prepared by brief dipping and demonstrated to be uniform by autoradiographs. Here the effect of increasing amount of heparin per unit area appears more graded, but again close to 0.3 μg. heparin/cm.^{2} is needed to delay clotting longer than 100 minutes.

Minimum Heparin in a Lacquer. Earlier work (3) using coagulation tests in cones showed that the anticoagulant effect of a lacquer containing heparin-benzalkonium compound (GBH) depended not only on the total amount of heparin in the lacquer, but also required a minimum concentration. Variation of heparin content at constant film thickness (5 microns) indicates a critical level between 0.3 and 0.5 μg./cm.^{2}; variation of film thickness at 0.3 or 0.6% BH in the film indicates a similar critical level, but at 0.075% BH in the GBH film, no amount of film or heparin, up to 1.5 μg./cm.^{2} or 50 microns thickness showed anticoagulation.

Table III. Minimum Heparin Binding for Anticoagulant Effect

Tests:

COAGULATION TIME: 0.2 ml. citrated plasma placed on flat surface, recalcified with 0.1 ml. M/20 $CaCl_2$, stirred with a Teflon strip. Controls are Mylar polyester surfaces.

HEPARIN: determined on each test portion by planchet count.

A. Relatively uniform GBH areas from long-time adsorption sacks, selected with guidance of autoradiographs

Heparin μg./cm.^{2}	*(Darkening of Film)*	*Coagulation Time, min.*	
		Fibrin	*Clot*
0.0	control	25	25
0.17	light	25	35
0.51	medium	100+	—
1.2	heavier	100+	—

B. Uniform areas produced by dipping, checked for uniformity by autoradiographs

Surface	*Heparin μg./cm.^{2}*	*Coagulation Time, min. Fibrin*
Control	0	27
GBH	0.05	37
	0.09	63
	0.27	100+
Control	0	26
PVPyrH	0.08	50
	0.9	48
	0.13	47
	0.25	68
	0.29	84
	0.31	100+

Discussion

Earlier data (3) obtained with tests in cones and chemical determination suggested that the anticoagulant effect of heparin introduced on the wall was greater than that to be expected if all the heparin were dissolved in the plasma. This conclusion requires checking with more uniform heparin layers and improved coagulation test techniques on flat surfaces. It is known that some heparin goes into solution in plasma from GBH or PVPyrH surfaces, as prepared by us, and it seems probable that this is generally true for any adsorbed heparin system in which the

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heparin is held to the surface by ionic bonds. Hence, the effect of the dissolving heparin could be greater in the diffusion layer near the surface than if uniformly distributed through the solution. We believe that the answer to the question whether the heparin is acting while adsorbed may be approached either by more precise quantitative studies, the road to which now seems open, or by conclusive showing of effectiveness of heparin covalently or completely bound to the surface. From a practical point of view, the anticoagulant effectiveness of heparin bound to a surface by different basic groups should be of importance with respect to duration of effectiveness, and amount of heparin required.

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16

Heparin Covalently Bonded to Polymer Surface

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Cross-linked polystyrene beads were para-*nitrated on the surface then reduced to the aminopolystyrene and finally converted by phosgenation to isocyanato-polystyrene. Coupling to sodium heparin was achieved at room temperature in formamide. The covalently bound heparin beads were non-clotting for twenty-four hours when tested by Lee-White method. Special antithrombogenic hydrogel tubes were used for the tests since other surfaces induced clotting. A similar synthetic sequence to surface modify injection molded polystyrene rings for* in vivo *testing in canine hearts yielded badly distorted pieces which were only moderately antithrombogenic. The roughened surface was thought to have contributed to clot formation. The use of cross-linked copolymers of* N-*vinylphthalimide later reduced to the amine was shown to be a route which allowed distortion-free polymers containing pendant isocyanate groups for heparin coupling.*

Much work on heparin-quaternary ammonium complexes has been reported as an outgrowth of the original publications by Gott (2, 3) which showed their value as antithrombogenic surfaces for prosthetic heart valves. The GBH surfaces (graphite-benzalkonium chloride-heparin coating) of Gott have superior antithrombogenic properties when compared with glass, polycarbonates, and silicone. Leininger *et al.* (8) and Merrill *et al.* (9) further developed this approach by using cationic modifications of a number of polymer surfaces including polypropylene, polystyrene, and polyethylenimine grafted onto cellulose as substrates for complexing the heparin.

In Interaction of Liquids at Solid Substrates; Alexander, A.;
Advances in Chemistry; American Chemical Society: Washington, DC, 1968.

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One of the most difficult problems yet to be overcome in the development of a workable artificial heart is that of thrombosis on the surface of the prosthetic materials (*2*) used in its construction. Although the GBH type surfaces of Gott and later workers are of research promise, there is concern that for long term implantation the heparin which is electrostatically complexed to the surface may ultimately become depleted owing to dissociation (*5, 6*). Thus, the prosthetic device may become susceptible to clotting. If heparin were to be covalently bonded to a substrate in a biologically stable manner which did not cause a loss of its antithrombogenic nature, we would then have a non-migratable form of heparin. The method used to bond heparin covalently to a polymer substrate and a preliminary demonstration of the antithrombogenic value *in vitro* of such a surface constitute the basis for this paper. We also bonded heparin ionically to a polymer substrate in much the same way as Leininger did (*8*) since this surface is known to have good *in vivo* antithrombogenic character and could thus serve as a good *in vitro* control.

Covalent Linking Reaction

In order that the heparin remain biologically active after fixation to a polymer substrate, the covalent bond must be achieved *via* functional groups on the heparin molecule, which are non-essential for its biological activity. Further, the binding reaction should be performed under reaction conditions which themselves do not cause loss of the antithrombogenic character of the heparin.

The functional groups of heparin suitable for formation of a covalent bond include the alcohol, carboxylic acid, and amino groups. The structure of heparin is shown in Figure 1. The amino groups readily react with

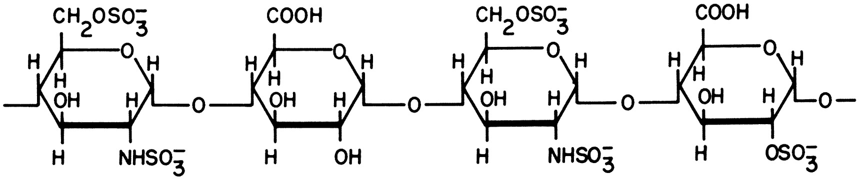

Figure 1. Proposed heparin molecule

Molecular weight: 12,000
Sulfate group: 4-5 per unit

acylating and alkylating agents and aldehydes and isocyanates as well as with diazonium salts. The hydroxy groups react with acylating agents,

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isocyanates; and they also couple with diazonium salts. Covalent bonds can also be established between carboxylic acid groups in heparin and a polymer substrate containing a nucleophilic group such as an amino group, by employing cross-linking agents. The dicyclohexylcarbodiimide and diisocyanates are typical examples of cross-linking agents which can react under mild environmental conditions.

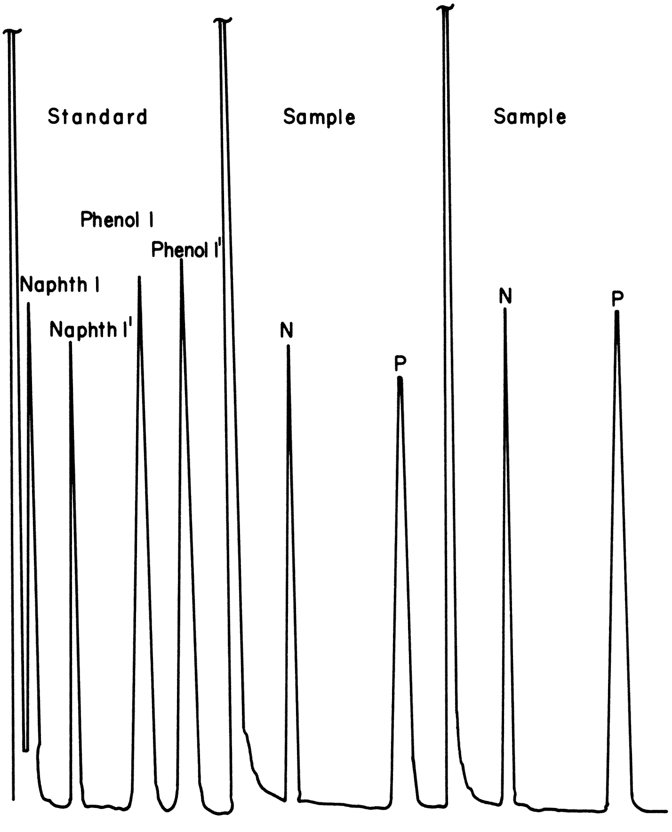

Figure 2. Gas chromatographic identification for isocyanate group

In one of the recent studies on the chemical coupling reaction, Axen (*1*) succeeded in bonding an enzyme covalently onto an insoluble polymer by employing the isothiocyanate as the chemical coupler. The enzyme retained all its catalytic activities. The method used by us to attach heparin onto a polymer substrate made use of a pendant isocyanate

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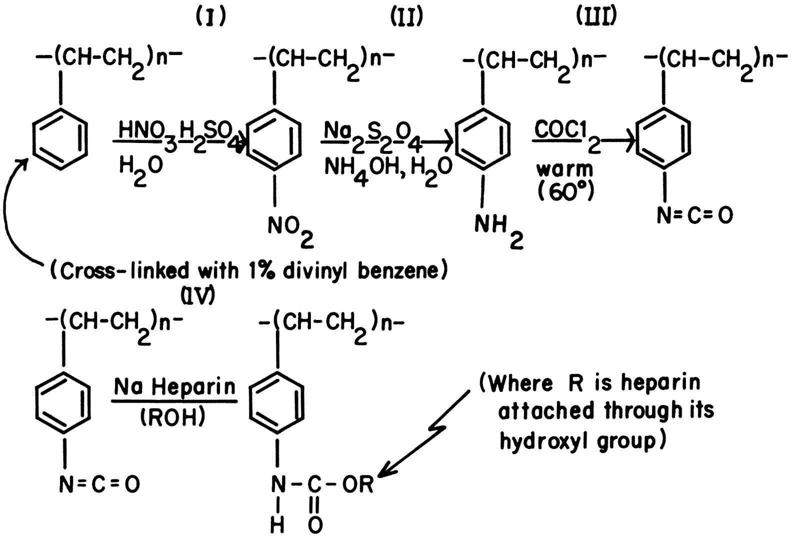
group on a polymer backbone. We find that the isocyanate coupling reaction for bonding the heparin (which is in its sodium salt form) must proceed under very mild conditions. Extremes of pH and high reaction temperatures must be avoided in order to minimize the hydrolysis of the naturally occurring sulfate and amidosulfate groups in heparin. Formamide was unique among many solvents tested in being able to dissolve sodium heparin at room temperature. Cross-linked polystyrene beads were used as the starting point for the formation of polystyrene-isocyanate. The amount of heparin which bonded to this substrate was determined by sulfur microanalysis of the final product after it had been washed exhaustively with water. It is desirable to use cross-linked polystyrene rather than homopolymer styrene, as the latter has a tendency to swell and dissolve in some of the reactions and a distorted surface may result.

Materials and Methods. The stepwise sequence for the synthesis of polystyrene-isocyanate and subsequent reaction with heparin is shown below:



Preparation of *p*-Nitropolystyrene (I). A polystyrene which is cross-linked to the extent of 1% with divinylbenzene and passed through a screen of 24 mesh, and retained on a screen size of 50 mesh, was used as a polymer substrate. To a solution of 5 ml. of concentrated nitric acid was added 15 grams of the cross-linked polystyrene beads. The reaction was carried out at 60°C. for half an hour with stirring. The product was filtered and washed with water several times and then thoroughly washed with methanol on a Büchner funnel. The product was dried under vacuum for 24 hours. Microanalysis showed that 0.7% by weight of nitrogen

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Advances in Chemistry; American Chemical Society: Washington, DC, 1968.

was incorporated. The IR spectra of *p*-nitropolystyrene showed a medium absorption at 7.5 microns because of the nitro group. A different pattern of absorption peaks from that of polystyrene was also observed in the higher wave length area.

PREPARATION OF *p*-AMINOPOLYSTYRENE (II). Reduction of the *p*-nitropolystyrene was accomplished by using sodium dithionite or stannous chloride as the reducing agent. Five grams of *p*-nitropolystyrene (I) was suspended in a solution containing 20 ml. of water, 25 ml. concentrated ammonium hydroxide, and an excess amount of sodium dithionite. The mixture was refluxed for 24 hours with stirring. The product was filtered out and washed with distilled water several times. The resultant *p*-aminopolystyrene was diazotized with nitrous acid. We were able to show the presence of *p*-aminopolystyrene by coupling with phenol and aniline to give intense yellowish and red colors respectively.

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CONVERSION TO ISOCYANATE DERIVATIVES (III). The amino groups were converted to isocyanate groups by treatment of the amino-polymer with phosgene gas in hexane. Into the suspension of 5 grams of well dried *p*-aminopolystyrene (II) in 300 ml. hexane, a constant stream of phosgene gas was passed for 6 hours after which the mixture was refluxed. After cooling to room temperature, the product was filtered under nitrogen atmosphere and washed thoroughly with hexane. It was used directly for the coupling reaction. The isocyanate content was determined by gas chromatography using naphthalene as a non-reactive internal standard and phenol as a coupling agent both dissolved in toluene. Figure 2 shows the duplicates of the quantitative identification of the isocyanate groups. The "Standard" consists of phenol as a coupling reagent, naphthalene as an internal standard and toluene as a solvent. The "Sample" consists of the standard solution and the isocyanate-polystyrene. It was observed that the height difference between naphthalene and phenol in the "Standard" appreciably diminished compared to the "Sample" in which phenol and isocyanate-polystyrene reacted for a few minutes. The minimum content of the isocyanate group was calculated from the depletion of phenol as being 244 p.p.m. by weight of isocyanate per gram of polymer.

FIXATION OF HEPARIN (IV). Heparin was coupled to *p*-isocyanatopolystyrene by the following procedure. Five hundred mg. of heparin was dissolved in 50 ml. of freshly distilled formamide at room temperature with stirring. Into this clear solution, 100 grams of freshly made *p*-isocyanato-polystyrene (III) was added and the resulting suspension stirred for 24 hours at room temperature under a nitrogen atmosphere. At the end of this period, the reaction product was collected on a filter and exhaustively washed with water to remove all unreacted heparin. Finally, it was washed further with methanol and dried under vacuum for 24 hours. Microanalysis indicated that the sulfur content of the final product was 0.19% by weight. This corresponds to 1.7% of heparin fixed to the polystyrene surface. Parallel controls show that when isocyanate groups are absent, no sulfur is found in the product. The above result is interpreted as evidence of covalent bonding of the heparin to the polystyrene backbone.

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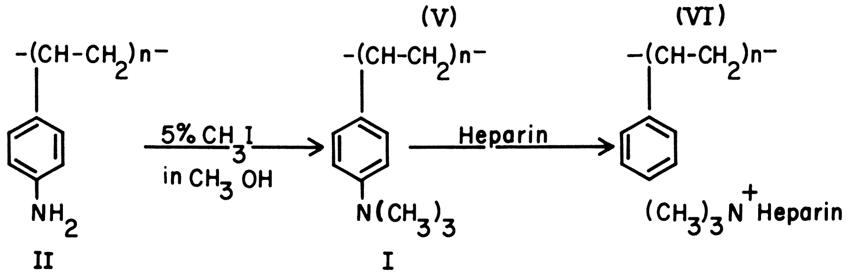
Synthesis of Trimethylaminopolystyrene Iodide and Its Reaction with Heparin

Reaction Scheme:



Preparation Procedures. Five grams of *p*-aminopolystyrene (II) prepared as before from cross-linked polystyrene was refluxed with 5% CH_3I in CH_3OH for 10 hours. The product was filtered, washed with water and methanol, and then dried under vacuum. This quaternary ammonium polymer further reacted with 50 mgm. of heparin in water solution to form the complex (VI). The sulfur microanalysis showed 0.9% by weight.

Determination of Anti-Clotting Activities of Covalently Bound Heparin Beads

The above samples were sent to the University of Pennsylvania Hospital for *in vitro* testing of the antithrombogenic character of the covalently bound heparin and the ionically bound heparin on polystyrene.

The procedure used for determination of clotting time is a modification of a Lee-White Clotting Test. Before each test was undertaken, the surface of each sample was thoroughly washed with distilled water and oven dried. Blood used in these tests was obtained from a normal human volunteer and was used as drawn without citration. The twenty cc. of blood used for each test were drawn from an antecubital vein. In order to ensure that the blood which was used in each test was of a low tissue thromboplastin concentration, a two syringe technique was used and only the last 6 cc. of blood taken were used in the test; the first 14 cc. were discarded. Time measurement was started as soon as the blood entered the tube and stopped upon the onset of clot formation. Occasionally, when the sample was observed not to have clotted within thirty minutes, a portion of the blood was removed from the tube and placed on a piece of gauze and carefully examined for slight evidence of clot formation. The samples which were used for the above test were as follows:

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(1) Polystyrene beads (50 mesh), 1% cross-linked by divinylbenzene.

(2) Aminopolystyrene synthesized from 1.

(3) Trimethylaminopolystyrene-heparin ionically bonded complex beads synthesized from 1.

(4) Poly-*p*-isocyanatostyrene-heparin covalently bonded beads synthesized from 1.

Each different test was conducted both in glass tubes and in hydrogel tubes (*4*). It was apparent that a glass tube was not suitable for conducting the blood clotting test for evaluating the polystyrene beads, since the glass tube itself induces clotting. In order to obviate the clotting effect by glass, we chose a hydrogel tube which was shown to be non-clotting to whole blood after 24 hours of contact (*4*). The hydrogel used for the above test was a copolymer hydrogel of 16.4% acrylamide and 5% dimethylaminoethyl methacrylate, cross-linked by 0.1% methylenebisacrylamide.

To prevent hemolysis of the blood in the hydrogel tubes, it was necessary to keep the gel pH and salinity equivalent to that of blood. This was done by adjusting the pH of the monomer solution to 7.38 by phosphate buffer solution and 0.85% of sodium chloride was added.

Five mg. and fifty mg. of each polymer sample were placed in the hydrogel tubes and the clotting tests conducted in duplicate. The results are presented in Table I.

Table I. Lee-White Clotting Test

	In Glass Tube (minutes)	*In Hydrogel*[a] *(minutes)*
Polystyrene beads (5.0 mg.)	11; 11	26; 36
Polystyrene beads (50 mg.)	11; 11	16; 16
Aminopolystyrene (50 mg.)	11; 11	38; 34-1/2
Aminopolystyrene (50 mg.)	11; 11	21; 19-1/2
Trimethylaminopolystyrene–heparin ionic complex (5 mg.)	11; 11	2811/2; 24
Trimethylaminopolystyrene–heparin ionic complex (50 mg.)	11; 11	21; 16-1/2
Isocyanate-polystyrene–heparin covalent (5 mg.)	11; 11	720; 41 (owing to air bubbles)
Isocyanate-polystyrene–heparin covalent (50 mg.)	11; 11	16; 16
Hydrogel-control		720; 720

[a] 16.4% Acrylamide, 5% Dimethylaminoethyl methacrylate, and 0.1% Methylenebisacrylamide copolymer hydrogel. 0.85% NaCl added and pH 7.38 buffered.

When glass tubes were used as containers for the beads, all of the samples clotted within eleven minutes. The rapid clotting is ascribed

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to the overriding effect of the glass surface of the tube. However, when these same bead samples were placed in the hydrogel tubes, significant differences in clotting time were obtained. It was observed that the polystyrene beads, the polyaminostyrene beads, and the polytrimethylaminostyrene-heparin ionically bonded beads caused clotting in less than 35 minutes. However, one of the poly-*p*-isocyanatostyrene-heparin covalently bonded bead samples gave a greater than 720 minutes clotting time, which is appreciably longer than the ionically bonded heparinized surface and comparable to the non-clotting behavior of the gel surface itself. The sample of blood was not clotted after 24 hours, although the actual Lee-White test was carried out for only 12 hours (720 min.).

One of the samples which contained 5 mg. of covalently bonded heparinized beads had only 41 minutes clotting time which is very much shorter than the other sample, but still longer than the ionically bonded heparin complex beads. This shortened clotting time was attributed to an air bubble which was trapped by a mechanical error while the technician was adding the blood into the tube dropwise. The technician predicted *a priori* that this particular sample would have a low value for clotting time.

In trials where we greatly extended the surface area of the polymer beads containing covalently bonded heparin, we found significantly lower clotting time. With the 50 mg. samples which had ten times the surface area, rapid clotting was observed in all cases. This is an indication that either total surface or excess heparin at the blood interface is of significance. We have had several occasions in other tests where relatively large amounts of heparin polymerized into hydrogels showed shorter clotting times than similar gels with lesser amounts of heparin.

Summary

A method of covalently bonding heparin to a polymer substrate is presented. The synthetic route consists of coupling heparin covalently with polyisocyanatostyrene. This reaction was made possible by the fact that formamide is a room temperature solvent for sodium heparin and this allowed a liquid-solid interface reaction to take place. Lee-White clotting tests *in vitro* (in hydrogel tubes) showed these surfaces to be non-clotting after 24 hours whereas untreated controls and surfaces of GBH type clotted in approximately 25–35 minutes.

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