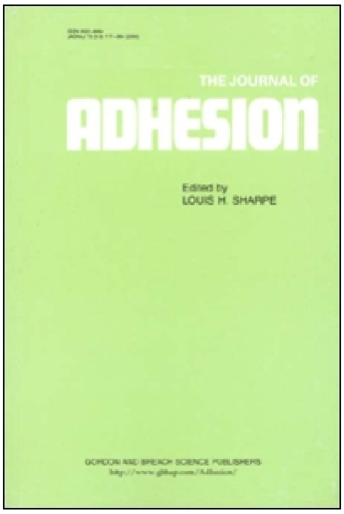
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

The Adhesion of Polymers to Each Other and to Fibres

William C. Wake[a]
[a] The City University, London, England

To cite this Article Wake, William C.(1972) 'The Adhesion of Polymers to Each Other and to Fibres', The Journal of Adhesion, 3: 4, 315 — 324

To link to this Article: DOI: 10.1080/00218467208072202

URL: http://dx.doi.org/10.1080/00218467208072202

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Adhesion, 1972, Vol. 3, pp. 315–324

Printed in Northern Ireland

The Adhesion of Polymers to Each Other and to Fibres†

WILLIAM C. WAKE

The City University,
London, England

(*Received November* 4, 1971)

Autohesion is a diffusion process but adhesion between different polymers is best secured by forming cross-links at the interface. The nature of the polymer surface is but imperfectly understood and its surface free energy can vary with preparation of the sample. The surface may vary from a liquid or pseudo-liquid to one more cross-linked or saturated than the bulk material. The use of solvents in securing adhesion between polymers can adversely affect the bond and solvent from a wiped surface is absorbed and is detectable after 2 weeks. The reactions of elastomers with fibres is discussed and involves both chemical reaction and morphological complexity. RFL treatment gives molecular adsorbed films of resin on latex particles. The RF modification "Pexul" seeks to match properties of resin and fibre whilst maintaining the usual reactivity, surface and chemical of RF resins. Surface halogenation of polymers is shown with model liquids to lead to hydrogen bond formation, thus explaining the improved adhesion of polyurethane. Mechanical interaction of elastomers and textiles is emphasized by reference to new information on penetration of elastomer into the yarn as well as into the weave. The joining of rubber-textile composite sheets is discussed.

INTRODUCTION

The autohesion of polymers is now well established as a diffusion process[1] but a critical examination[2] of polymer diffusion shows that it is unlikely to be a major factor in the adhesion of unlike polymers. Evidence has been adduced[3] that maximum adhesion between different polymers is achieved when the solubility parameters of the polymers are similar, thus tending to support mutual solubility, and therefore diffusion, as a condition of good adhesion but it is equally true that the vapour degreasing of metal with

---

† This paper was presented at the *Symposium on Recent Advances in Adhesion* during the 162nd National American Chemical Society Meeting, September, 1971.

solvent before bonding with a polymer appears most efficient when the solubility parameter of the solvent approximates closest to that of the polymer[4,5]. The apparent unity of these phenomena may lie in a relationship between surface energy and solubility parameters which has been identified empirically[6] and which has more recently shown[7] to have a rational basis enabling the surface free energy to be calculated from the heat of evaporation and the molecular volume.

Where elastomers of similar cross-linking reactivity are concerned, such as natural rubber and SBR, the lack of compatibility can be masked, as it were, by cross-linking under conditions to form chemical bridges between the two polymers although such unions are not necessarily proof against dynamic fatigue when failure at the interface occurs. It appears probable that to achieve the permanent union of dissimilar polymers it is necessary to modify the surface of one or both and also to accompany this by the specific interaction of a chemical linkage across the interface.

NATURE OF THE POLYMER SURFACE

There are two sorts of polymer surface to be discussed; the ideal surface on which we think we make measurements and the real surface which participates in adhesion joints. These surfaces can be very different things. The ideal surface is the one that is invoked in terms of the bulk structure of the polymer and for which surface energies and other intellectually important concepts are invented. Half-way between these two types are the surfaces which participate in measurements such as critical surface tension which are carried out on specially prepared or cleaned, real surfaces. Consider for example polymethyl methacrylate for which γ_c has been recorded with a range of values. Owens and Wendt[8] record 39 mN.m^{-1}, almost identical numerically with their estimate of the free surface energy, suggesting that the surface molecules are almost completely orientated with dipolar portions screened from the surface by back bone or methyl groups. Yet the use of a solvent will secure such strong adhesion to a metal that we assume a different, much more polar surface exists at the interface formed under these conditions than at the polymer-air surface formed by evaporation of the same solvent. An indication that this is indeed so is given by measurements of the contact angle of water on methyl methacrylate under conditions to eliminate the spreading pressure[9] and record a surface free energy, ascribable to dispersion forces only, of 69 mJ.m^{-2}, almost twice that mentioned above, and to which is to be added a non-dispersion component of 25.5 mJ.m^{-2} giving a total surface free energy of 94.5 compared with 40.2 mJ.m^{-2}. Of course, when a polymer is deposited on a metal a very high energy surface is involved of infinite polarizability. However, in addition to dipole orientation effects which this would produce, there is evidence of alteration in the surface density of the polymer[10]. The polymer surface, even when free from foreign molecules, may not be free from "impurities". In his early demonstration of the "weak-layer theory" Bikerman[11] showed that recrystallized polyethylene behaved far better than untreated material and ascribed this to the removal of oxygenated material, liquid in nature. The surface properties of the purified polyethylene, as indicated by contact angle with water, showed no change though it is likely that more recent work with hydrocarbon solvents would show a difference in the critical surface tension which can only arise from a real difference in surface energy. Moreover, the critical surface tension usually quoted for polyethylene of about 31 $mN.m^{-1}$ can only differ from that for pure n-hexatriacontane (given as 21 $mN.m^{-1}$)[8] by virtue of polarity since the lower density of polyethylene would reduce rather than increase the value.

The Bikerman concept of the weak layer[12] has been very fruitful in focusing attention on the combined morphology and composition of adhesive and therefore of polymer surfaces. Certainly, many polymers are compounded with a liquid plasticiser which will, if present, always exist as a surface layer. However, even when a liquid is not present and where material of sufficiently low molecular weight to escape any cross-linking process is absent, a quasi liquid surface to elastomeric materials is thought to exist[13]. Such a layer would be less resistant to shear than the bulk polymer and very much less resistant to cleavage, a phenomenon which would be described as tearing in the bulk polymer. The quasi-liquid, if it exists, arises from the nature of elastomeric cross-linking processes. Quantitative interpretation of the elastic behaviour of cross-linked networks has shown the need to correct the equations used to allow for the effect on the network of the ends of chain molecules. Estimates for the proportion of the total polymer involved in these "loose ends" varies with theoretical treatment from M_c/M (Tobolsky) to $2M_c/M$ (Flory) where M_c is the molecular weight between cross-links and M is the molecular weight before cross-linking. About 5% of elastomeric material will be involved in loose ends and they are likely to consist of chain lengths averaging 160 carbon atoms in the case of natural rubber for which most data is available. Because of their relative mobility, those near enough the surface to migrate to it will tend to do so giving an enhanced surface concentration.

However, in addition to the possibility of a weak surface layer there is strong evidence with some vulcanized elastomers that the cross-linking density differs on the surface to its average value in the bulk material. This has been demonstrated by adhesion studies carried out under particularly careful conditions to obviate surface contamination and which showed that although there was no difference between an original surface and a newly cut surface of vulcanized polychloroprene, a very definite difference existed with butadiene-acrylonitrile copolymers[14]. This difference was independent of surface smoothness and was eliminated by ageing the rubber. The last fact points to a degree of oxidative cross-linking on the surface preventing diffusion and/or reaction of a vulcanizable adhesive of the same polymer with that of the surface layer.

The mode of preparation of a polymer surface for adhesion can therefore influence its surface composition in subtle ways not always easily discernable by a single measuring operation.

Where mutual diffusion is possible adequate adhesion is easily obtainable but cross-linking inhibits diffusion. The bond between an unvulcanized rubber and the same rubber previously vulcanized can usually be separated at the plane of the vulcanized material. Swelling of the vulcanized rubber by solvent followed by application of a solution of the rubber to the swollen surface and then slow removal of solvent results in a weaker, not a stronger joint. When a solution of rubber is applied to dry rubber, some solvent evaporates from the surface but some diffuses into the rubber until the concentration gradient is reversed by continuance of evaporation from the surface. In such a situation solvent is retained for long periods. In fact experiments showed a 50% gain in adhesion measured in direct tension if the film of adhesive was first dried on a glass plate and then applied as a sandwich filling between discs of vulcanized rubber and moulded at 140°C compared with applying the same rubbery adhesive in a solvent to the surfaces and prolonged drying by vacuum after the usual substantial period of air drying. The cycling of solvent concentration at the interface does not seem conducive to diffusion of polymer ends into the rubber. Indeed, residual solvent may plasticize the interface for a very long time. For example, Carter[15] has shown that wiping a polymer surface with a cotton wool swab soaked in solvent leads to rapid surface penetration by the solvent which is removed only after many days. Using a plasticized PVC, and wiping the surface with a swab thus transferring 5.0 mg. cm^{-2} of methyl ethyl ketone, Carter found that immediately after wiping a large amount of solvent is present in the surface although plasticiser has also been removed. Maximum penetration appeared to take about an hour but measurable quantities persisted for two weeks.

SURFACE CHEMICAL REACTIVITY OF POLYMERS

In spite of confidence in the ability of secondary valency forces adequately to account for adhesive strength, and that they do so in fact is demonstrated by the ability to displace paint films by moisture and then re-establish adhesion by removal of water[16], the practical technologist has preferably used adhesive systems in which surface chemical reaction is believed to occur with the formation of primary valency links across the interface. Typical among these is the use of isocyanates for linking elastomeric and fibre forming polymers. The reaction of isocyanates with the elastomer is adequately accounted for by adventitiously introduced hydroxyl groups. There are sufficient of them to give a moderately cross-linked material and arise from oxidation during processing. Isocyanate reaction with textile is not so easily explained. End group reaction with the textile-polymer lacks conviction without some knowledge of the occurrence of hydroxyl or amine end groups in the surface. There are only two reactions of substituted amides with isocyanates of which the writer is aware. The first leads to direct attachment of the phenyl isocyanate which was used.[17]

$$\text{Ar.NCO} + \text{R'CO.NH.R''} \longrightarrow \text{ArNH.CO.NR''.CO.R'}$$

The second is an interchange reaction reported to occur at elevated temperatures[18].

$$\text{Ph.CO.NH.CH}_3 + \text{Ph.NCO} \xrightarrow{120^\circ\text{C}} \text{Ph.CO.NH.Ph.}$$

Neither of these reactions have been investigated in the context of textile surfaces and some workers believe diffusion into the amorphous regions of the textile filament, followed by reaction with the regain moisture content is more plausible than direct chemical reaction.

An interesting, indirect use of surface chemical reactivity has been the surface halogenation treatment of elastomers recommended by the Shoe and Allied Trades Research Association (SATRA)[19] in which the nature of the elastomer surface is altered in its behaviour towards other elastomers capable of hydrogen-bonding but is virtually unchanged where this is not possible. It is worth briefly reviewing the evidence for this mechanism. The mechanism of halogenation is not relevant here; as applied to unsaturated diene polymers or copolymers it may be assumed that the double bond is saturated with chlorine without any elimination of hydrogen chloride.

It is well-known that the adhesion of a polyurethane polymer applied to a cross-linked butadiene-styrene copolymer is poor but when the substrate is halogenated, a permanent bond is easily formed.

The critical surface tension of a butadiene-styrene (B-S) copolymer is 33 mN.m^{-1}, chlorination raises this to about 41 mN.m^{-1} but this change reflects only the increase due to dispersion forces. It is possible from the contact angles shown by certain liquids with the surface before and after chlorination of a B-S copolymer to show that the improved bonding with polyurethane is associated with specific polar interaction rather than just the increases in the dispersion forces[20]. Table I shows the contact angle, surface tension, and the work of adhesion, W_A, calculated from the Dupré-Young equation W_A for three liquids on a butadiene-styrene substrate before and after chlorination of the surface.

TABLE I

Liquid	Surface Tension mN.m^{-1}	Before Chlorination		After Chlorination	
		θ	W_A mJ.m^2	θ	W_A m.J.m^2
Trixylyl phosphate	38	34°	69	29°	71
Glycerol	63.2	84°	70	61°	94
Formamide	58.2	75°	73	42°	102

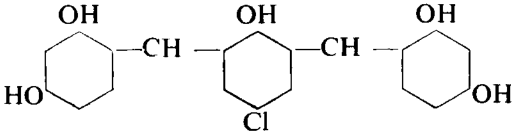
Tricresyl phosphate has been shown to behave in its wetting behaviour on surfaces as if it were a completely apolar body, surface attraction being dependent solely on dispersion forces[21]; trixylyl phosphate behaves similarly. This is reflected in the very slight change in the work of adhesion on chlorination of the surface. Glycerol and formamide, by contrast, show specific polar interactions and, in the case of formamide, hydrogen bond formation could be anticipated from the -NH group to the chlorine atoms on the surface. This is certainly reflected in the large increase in the work of adhesion. It is also reflected in the peeling strength, for a clean, newly cut surface of a B-S rubber showed a peeling strength with a polyurethane of only 5kg. per 25 mm. width but chlorination raised this to 22 kg. per 25 mm. This is a major improvement in specific adhesion of the surface towards a polymer known to participate in hydrogen bonding.

OTHER ELASTOMER-FIBRE INTERACTION

The widespread use of resorcinol-formaldehyde resin in conjunction with latices as a means of bonding elastomers to textiles involves an interaction more complex than that across a simple interface. An essential need in tyre construction is to transmit large forces from an elastomer to the textile and since the stress which can be transferred is limited, the force can only be accommodated by increasing the surface area over which transfer occurs.

This is achieved by using an adhesive system which, unlike most rubber-textile interactions, penetrates into the structure of the yarn, taking advantage of the high surface area which exists inside the yarn by coating individual filaments. The adhesive is easily shown to be the resin and not the latex but the resin is very brittle and tyre cord has to withstand high frequency deformation. The system which has evolved empirically enables a highly flexible composite to be achieved by adsorbing the resin on to the latex particles thus avoiding the formation of the brittle three-dimensional bulk resin and using instead a two-dimension resin on a spherical surface. The adsorption of the resin on to the latex has recently been studied[22] and the maturation period known to be essential in the preparation of the adhesive "dip" involves the replacement of other surface active material by oligomers of resorcinol-formaldehyde.

Given the morphology of this complex system, the question arises as to the possibility and nature of any chemical reaction. Speculation allied to experiments with model compounds has suggested reaction of the resin with natural rubber with the formation of chromans. Smely, Dogadkin and Tutorskii quoted by Mzourek and Smely[23] postulate a reaction between amide groups on the textile and methylol groups on the resin but most speculation has suggested hydrogen bond interaction of the resorcinol-formalde-hyde resin with the textile. An extremely interesting development has been the modified resorcinol resins introduced by ICI Fibres, Ltd. for bonding rubbers to polyester fibre[24] under the registered trade name 'Pexul'. The essential feature of the Pexul process is the use of a proportion of a trinuclear resorcinol derivative[25] which is essentially;



This compound is capable of reaction with terminal methylol groups of the ordinary resorcinol-formaldehyde oligomer but also possess an affinity for polyester not possessed by the ordinary compound. The compound was placed in contact with polyester film (Melinex) and heated as for normal curing and multiple internal reflection IR spectroscopy in the film showed[25] a shift in the carbonyl stretching frequency from 1720 cm^{-1} to 1695 cm^{-1} with broadening of the peak. It suggested to Mather that resorcinol and neither the chlorine nor the hydroxyl p-chlorophenol was responsible for the bonding. Additionally, rapid ebullioscopic measurements with dimethyl terephthalate indicated an association of either one molecule of Pexul with each carbonyl group of the di-ester or four molecules with two molecules of diester. Hydrogen bonding is fairly clearly implicated but other features are present in the system. The solubility parameter of polyester is 10.3 and that of resorcinol 16.0; the substituted resorcinols are closer to the polyester. Additionally, the chlorine substituent prevents chain branching by the addition of methylolated phenols to the central nucleus. All these features play some role in a complex situation[25].

MECHANICAL INTERACTION OF ELASTOMER AND TEXTILE

The superior adhesion of rubbers to cotton compared to untreated rayon has long been known to be associated with the penetration of staple ends into the rubber rather than of rubber into the textile[26]. Indeed, with the exception of the aqueous latex system used for tyre cords, it has usually been assumed that elastomer as applied by spreading from a dough or with a calender, penetration occurs into the weave but not into the yarn[27]. It now appeais that if excess elastomer is applied to the surface of a textile and the composite so formed is press moulded under conditions such that a hydrostatic pressure is applied to the elastomer for a relatively long time, considerable penetration into the weave of the textile can occur[28]. In the calendering process the pressure operates for an extremely short period as also in spreading from a dough. In subsequent vulcanization, either pressure is absent or small as in hot air or wrapped autoclave procedures or fabric-to-fabric contact precludes the existance of a hydrostatic pressure forcing elastomer into the textile. Undoubtedly some penetration occurs in the manufacture of belting and hose but it has not been quantitatively assessed and the extent of its influence on the measured adhesion is an unknown factor in technology.

In most applications where elastomers and textile interact, it is the textile which carries the stress even if the stress is transmitted to the textile through the elastomer. The interface through which this stress is transferred needs to be sufficient in area for its task. Where joints are necessary the transfer of stress gives rise to additional problems. Because of the highly extensible nature of the adherends, a lap joint of a coated textile fails in the cleavage mode by a peeling back from the ends of the joint. This failure is determined by the peeling strength and, apart from influencing the time before failure is complete, is independent of overlap length. Looked at from one viewpoint sewing together of the adherends is a confession of failure to obtain high enough peeling strength to enable the bond to accept a shear load increasing with increasing area. From another viewpoint however, it can be argued that if it is necessary to reinforce the elastomer, one cannot expect union of the elastomer to take the load when there is a break in the reinforcement; sewing serves to join the reinforcement just as an elastomeric adhesive joins the coating. The stress distribution in such joins can, in fact, be calculated and investigated by quite simple methods[20].

CONCLUSIONS

The adhesion of different polymers to each other whether as sheets or fibres or of cross-linked polymers by an adhesive of similar constitution, presents a number of problems. Solutions accepted by present day technology are most satisfactory where direct chemical reaction across the interface or at least hydrogen bond formation is involved. With heavy duty elastomer-textile composite constructions joining of sheets of already cured material presents the double problem of adhesion between the surfaces and correcting for the discontinuity of the fabric reinforcement. The means of overcoming this particular problem cannot be regarded as either completely satisfactory or elegant and new means would represent a considerable technological advance.

References

1. S. S. Voyutskii, *Autohesion and Adhesion of High Polymers*, transl. S. Kaganoff (Interscience, New York, 1963).
2. R. M. Vasenin, quoted by W. C. Wake in *Treatise on Adhesion and Adhesives*, Vol. II, Ed. R. L. Patrick, (Dekker, New York, 1969), Chapter 4.
3. Y. Iyengar and D. E. Erickson, *J. Appl. Polym. Sci.* **11**, 2311–2324 (1967).
4. J. H. Engel & R. N. Fitzwater, *Adhesion and Cohesion*, Ed. P. Weiss, (Elsevier, New York, 1962), p. 89.
5. J. C. Sherlock and L. L. Shreir, *Brit. polym. J.* **1** (**1**), 34 (1969).
6. J. L. Gardon, *J. Phys. Chem.* **67**, 1935 (1963).
7. T. P. Hobin, Ministry of Technology, U.K. Report (1968), to be published in the *J. Adhesion*.
8. D. K. Owens and R. C. Wendt, *J. Appl. Polym. Sci.* **13**, (**8**), 1741 (1969).
9. Y. Tamai, K. Makuuchi and M. Suzuki, *J. Phys. Chem.* **71**, 4176 (1967).
10. H. Schonhorn, *J. Polym. Sci.* **B5**, 919 (1967). K. Hara and H. Schonhorn, J. Adhesion **2**, 100 (1970).
11. J. J. Bikerman, *Adhesive Age* (**2**) 23 (1969).
12. J. J. Bikerman, *The Science of Adhesive Joints*, 2nd. Ed., (Academic Press, New York, 1968).
13. R. H. Norman and W. C. Wake, J. Adhesion, **1**, (**1**), 7 (1969).
14. W. C. Wake, *Treatise on Adhesion and Adhesives*, Vol II, Ed., R. L. Patrick (Dekker, New York, 1969), Chapter 4.
15. A. R. Carter, *Bonding Progress* **1** (**2**), 25 (1970) Issued by the Shoe and Allied Trades Research Association, Kettering, England.
16. Paint Research Station, Teddington, Private Communication.
17. M. Busch, G. Blume, and E. Pungs, *J. Prakt. Chem.*, **79**, 513 (1909).
18. P. F. Wiley, *J. Amer. Chem. Soc.* **71**, 3746 (1949).
19. A. R. Carter, *Halogenation of Vulcanized Rubbers to Improve Adhesion* (Shoe and Allied Trades Research Association, Kettering, 1969).

20. L. Greenwood and W. C. Wake, Paper given at Paris Rubber Conference, June 1970.
21. F. M. Fowkes, *Treatise on Adhesion and Adhesives*, Vol. I. Ed. R. L. Patrick (Dekker, New York, 1967), Chpater 9.
22. D. D. Eley and L. B. Pawlowski, *J. Coll. Interface Sci.* **29**, (**2**), 222 (1969).
23. Z. Mzourek and Z. Smely, *Plaste U. Kaut.* **11** (7), 410 (1964).
24. R. B. Pearson, *Textile-to-Rubber Adhesion* (ICI Fibres, Ltd. Harrogate, 1969).
25. J. Mather, *Brit. Polym. J.*, **3** (2), 58–62 (1971).
26. E. M. Borroff and W. C. Wake, *Trans. Inst. Rubber Ind.* **25**, 140 (1949).
27. W. C. Wake, *Adhesion*; *Fundamentals and Practice* (Ministry of Technology, MacLaren, MacLaren, London, 1969), p. 118.
28. K. W. Allen, T. Slezak-Glijer and W. C. Wake. To be published in J.I.R.I.