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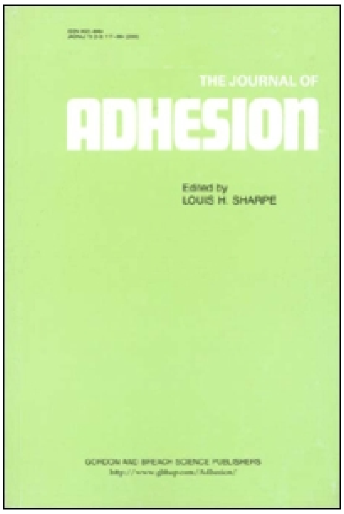

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Effect of Activated Gas Plasma on Surface Characteristics and Bondability of RTV Silicone and Polyethylene[†‡]

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An RTV silicone and high density polyethylene are exposed in an activated gas plasma for varying times and varying conditions. Both oxygen and argon are used. Changes in critical surface tension of wetting as determined by contact angle measurements are reported. Bondability of the treated surfaces is evaluated with both the aged bonds and aged surfaces prior to bonding being evaluated. In contradiction to some of the recent work reported in the literature on the effect of activated inert gas on surface characteristics, contact angles always decreased on the materials studied indicating an increase in surface energy. The significance of the results on present adhesion theories is discussed.

INTRODUCTION

The use of activated gas plasmas to improve adhesion to difficult to bond surfaces of materials such as polyethylene originated about 1956.[1] Surface treatment of polyethylene films by Tesla coil brush discharge and glow discharge were methods investigated. Improved adhesion was attributed primarily to surface oxidation.

Schonhorn and co-workers,[2,3,4] in later work, made use of an "electrodeless" discharge process to improve adhesion to various polymers including polyethylene. A low pressure activated gas plasma environment was produced in an rf field. Inert gases such as helium at approximately 1 Torr pressure were used and the process for improving adhesion was designated CASING

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

(Crosslinking by Activated Species of Inert Gas). The observed increase in bond strength was reported to result from elimination of weak boundary layer material and the formation of a high density crosslinked surface region of high cohesive strength. A unique feature reported for the treatment was that it produced no change in critical surface tension (γ_c) of the treated surface.

DeLollis and Montoya[5] previously reported the improved bondability of an RTV silicone rubber after exposure to oxygen in a low pressure rf glow discharge. In an extension of that study, both RTV silicone rubber and polyethylene were treated in rf activated argon and helium environments. We observed changes in γ_c with treatment conditions and variations in bond strength and wettability with time.

EXPERIMENTAL

Pure, high density polyethylene was obtained from Phillips Petroleum Company as MARLEX 6065 fluff. Both molded films, approximately 0.008" thick, and films deposited on glass microscope slides from hot reagent grade toluene or xylene solutions (0.3%) were used for contact angle measurements to obtain γ_c values. After preparation, samples were stored until use in vacuum desiccators protected from light.

The silicone rubber used was General Electric RTV 630, a dimethyl, vinyl addition type. Sheets approximately ⅛" thick were cast on clean aluminum forms from thoroughly mixed and degassed batches. No release agent was used. All cast sheet stock was cured at 160 ± 5°F for 5 hours. Discs for tensile adhesion specimens and for the contact angle measurements in connection with bond strength studies were punched from sheet with a 1⅛" diameter die and stored in all-glass containers until use. Strips 1 × 3" were cut from sheet on a clean metal shear for contact angle measurements used in $\cos \theta$ *vs* γ_L plots.

Contact angles were measured by the technique described by Zisman[6,7] using a Ramé-Hart NRL contact angle goniometer. Temperature and relative humidity in the laboratory were within the ranges of 21–24°C and 20–30% respectively. Four to six contact angle measurements on each drop were averaged for three or more drops. Precision was within ±2°, except for angles below 10° and greater than 85°. As noted by Lee[8] equilibration time varies with different liquids, consequently advancing angle readings were taken at time intervals from 1 to 15 minutes. For untreated low energy surfaces contact angles reached equilibrium in 5 minutes or less. Since the rate of spreading of different liquids varied widely on activated surfaces, values for contact angles were established on the basis of repeatibility at a given time interval for each combination of liquid, polymer, and surface treatment conditions. Caution was necessary to avoid errors introduced by such factors as evaporation of volatile liquids and swelling of the silicone rubber by some liquids.

The nonhomologous series of liquids used for contact angle determinations are included in Table I. Liquids with appropriate surface tensions and sufficiently different dispersion and polar component ratios were selected to reflect the characteristics of both treated and untreated surfaces. Critical surface tension values were taken as the intercept of $\cos\theta = 1.0$ from Zisman[9] type plots of $\cos\theta$ as a function of surface tension of the liquid γ_L.

TABLE I
Wettability of surfaces with various liquids

Liquid	Surface Tension (γ_L) (dynes/cm) at 20°C	Measured Contact Angles (degrees) Untreated RTV 630	Treated[a] RTV 630	Untreated Polyethylene	Treated[a] Polyethylene
8.3 M K_2CO_3	110.8	109.6	21.6		48.7
Water	72.8	99.5	10.6	97.5	19.0
Glycerol	63.4	91.5	6.8	85.2	10.5
Formamide	58.2	85.5	0	77.3	0
α-bromonaphthalene	44.6		0		0
Tricresyl phosphate	40.9	64.5	0	42.0	
Hexadecane	27.6	38.0	0		
Acetic acid	27.2	37.5	0	0	0
Carbon tetrachloride	26.1	26.0			
Dodecane	25.4	24.0			
Critical Surface Tension (γ_c)[dynes/cm]		19–22	59–61	30–32	58–60

[a] rf activated argon plasma, 10 minutes at 150 watts, 0.6 Torr.

Reference 5 describes tensile adhesion specimens formed by bonding RTV 630 or polyethylene discs between aluminum plugs. We used a mineral filled version of the following standard Sandia casting resin formulation to bond the RTV.

SANDIA LABORATORIES SRIR
(Semirigid Inspectable Resin)

Epon 828 (Shell Chemical Company)	100 pbw
HHPA (Hexahydrophthalic Anhydride)	76 pbw
P 11-80 (Dow Chemical Polyol)	66 pbw
BDMA (Benzyl Dimethyl Amine)	2 pbw

Neo Novacite, a silica filler (Malvern Minerals Company, Hot Springs, Arkansas), was added to the standard formulation in the amount of 488 pbw to give a more easily processed paste. Specimens were cured for 24 hours at 160 ± 5°F. This formulation was selected since cure proceeds at an intermediate temperature by anhydride reaction and there is less likelihood of adverse reaction with RTV silicones than with amine curing systems. Glycerol contact angle measurements were used to compare with bond strengths of treated and untreated silicone rubber.

Adhesive bond strength and contact angles were determined for RTV samples immediately after argon plasma treatment and at different time intervals after treatment. These specimens were exposed to ambient laboratory conditions during the time between treatment and bonding and are designated as "aged surfaces". Another set of tensile adhesion specimens was made immediately after treatment and tested at later times. This set is referred to as having "aged bonds".

The adhesive used for bonding polyethylene to aluminum was Shell Epon 828/DEAPA, cured at 160 ± 5°F for 5 hours.

Polymers were treated in a Tracerlab LTA 600A low temperature asher as described by Hansen and Schonhorn.[2] The type of gas, pressure, rf power and times were varied.

RESULTS

Results of contact angle measurements on untreated and argon treated RTV 630 and Marlex 6065 are shown in Table I. Essentially, the same results were obtained with both materials using a helium discharge. Results obtained by treatment with argon plasma are sufficient to demonstrate clearly the increased wettability and effective critical surface tension which result from the so-called CASING treatment.

The critical surface tension of 20–23 dynes/cm obtained for the untreated RTV 630 is in good agreement with a reported value of 24 dynes/cm.[10] The γ_c observed for untreated polyethylene (30–32 dynes/cm) compares well with the 31 dynes/cm reported by Zisman[11] and Lee.[12] The γ_c for RTV 630 treated with the rf plasma increased by a factor of about three. The treatment of polyethylene approximately doubles γ_c. Treatment for shorter times and/or lower power settings gives values which lie between the two extremes seen in Table I.

Results of bondability studies are shown in Tables II and III. Change of contact angle with time and bond strength change with time to aged surfaces are shown in Table II. The contact angle approaches an apparent equilibrium in about 4 hours. The increase in contact angle with time occurs at about the same rate as that observed by White[13] for initially clean polar surfaces. The decrease in bond strength continues during a period in which contact angle appears to remain constant (1 to 7 days). After 30 days contact angle had increased to 80° and bond strength had become negligible. The percent cohesive failure was determined visually and with a low power microscope (40×).

TABLE II
Contact angle and bond strength of aged, treated RTV Silicone surfaces

Time After Treatment[a]	Contact[b] Angle (degrees)	Tensile Strength (psi)[c]	Cohesive Failure, %
No treatment	102	<10	0
<30 minutes	16	384	100
4 hours	49		
24 hours	53	250	90
48 hours	54		
7 days	54	102	30
30 days	80	fell apart on handling	0

[a] rf activated argon plasma, 10 minutes at 250 watts, 1 Torr.

[b] measured with glycerol.

[c] RTV 630 bonded to aluminum.

TABLE III
Strength of aged bonds[a]

Aging Time[b]	Tensile Strength (psi)	Cohesive Failure, %
None	450	100
2 weeks	409	100
1 month	363	100

[a] Treatment and specimens same as those for Table II.

[b] Time elapsed after tensile adhesion specimen assembly. Environment: Laboratory ambient.

Table III shows the results of aging tensile adhesion specimens which were all prepared at the same time to freshly treated surfaces. The failures are all cohesive in the silicone rubber. The failure level decreases with time and appears to reflect a change in the polymer rather than a change in the interface.

The contact angle formed by glycerol on the argon plasma treated RTV is initially far below that observed on the untreated surface. If treated RTV 630 is allowed to remain in the LTA 600 reactor chamber under vacuum after the rf generator is turned off the low contact angle remains constant for times up to 24 hours. The same behavior was observed for argon and helium treated polyethylene for as long as it remained in the chamber under vacuum (48 hours).

Tensile adhesion specimens of polyethylene film treated 30 minutes at 50 watts in argon gave an average strength of 3780 psi for 10 specimens. The total range was 3475–4680 psi. Failure was mainly cohesive in the film. Bond strength of specimens using untreated film was negligible.

DISCUSSION

The results show that treatment of polydimethylsiloxane rubber and pure, high density polyethylene with rf activated plasmas of inert gases is effective in improving both bondability and wettability of the surfaces. The striking feature in our work is the observed increase in wettability of treated surfaces. The increase in critical surface tension with plasma treatment is in direct contradiction with results reported by Schonhorn *et al.*[2,3,4]

We have found scattered reports by other workers who have always observed increased wettability with improved bondability using gaseous discharge methods. Malpass and Bright[14] reported that after glow discharge treatment of polyethylene in either argon or hydrogen, the contact angle "falls to immeasurable low values" in 10–20 minutes. They suggested that oxidation of treated surfaces on exposure to air might explain their observations but did not comment on how oxidation might take place. Hall *et al.*[15] have produced improved bondability in a variety of thermoplastics treated with rf activated helium. Subsequent correspondence[16] indicated that considerably reduced contact angles of water were seen on various surfaces, including polyethylene. Blais, *et al.*[17] observed increased wettability by water and sebacyl chloride of polypropylene treated in nitrogen and argon corona discharges. They also observed topographical changes, increased unsaturation, and crosslinking on corona treated surfaces and proposed that improved bondability may result from roughening or "mound" formation leading to improved wettability, weak layer consolidation and interpenetration of the polypropylene film and a subsequently deposited nylon coating.

The general problem of chemical characterization of surfaces is a difficult one and progress in this field has been limited by the lack of adequate analytical tools. The absence of direct experimental evidence as to chemical nature of gas plasma treated polymer surfaces reflects the general problem.

The evidence that the surfaces of many polymers exposed to inert gaseous discharges contain material which is more highly crosslinked, is of higher density and greater cohesive strength than the bulk polymer is conclusive. However, it is doubtful that these conditions are sufficient to account completely for the higher surface energies observed and we are not aware that a mechanism to account for the phenomenon has been clearly proposed or demonstrated. Among several chemical or physical processes which may be occurring, several would seem to warrant careful investigation. It is possible that alkyl radicals in the surface region are very rapidly quenched on exposure to atmospheric oxygen and decay through the peroxy radical to a carbonyl which gives a higher energy surface. Photochemical effects of ultraviolet radiation present in inert gaseous discharges also may make a large contribution to altering surface characteristics. Other possibilities to be considered are that high energy material is being RF sputtered[18] from the chamber wall and deposited on polymer surfaces and that chemical changes on treated surfaces may influence adhesion and wetting behavior. Preliminary evidence obtained in our laboratory concerning the role of some of these phenomena is sufficiently conclusive to warrant discussion.

Exhaustive studies of radiation effects in bulk polymers have been conducted. Crosslinking, chain scission and rearrangement are several types of reactions which may occur simultaneously. It is well established that polyethylene and polydimethylsiloxanes are polymers in which crosslinking predominates. Trapped radicals are intermediate products. Electron spin resonance studies of the Marlex 6065 polyethylene sealed in quartz tubes containing Ar at ~1 Torr and subjected to RF discharge show the presence of free radicals with essentially the same structure as those produced by γ-irradiation and electron bombardment. After 24 hours at room temperature there was no appreciable decay in samples which remained sealed in the argon atmosphere. The presence of radicals was not detected in samples exposed to air for less than 5 minutes. (The broad band of hydroperoxide radicals would not have been detected in the equipment used.) Any change with time of measured γ_c values which might be caused by migration of low molecular weight to the surface after treatment would have been evident in this kind of experiment. Lawton, *et al*[19] reported that two stable species of radicals are formed in electron and γ-irradiated polyethylene in a nitrogen atmosphere. At room temperature, one species decays in approximately 6 days while the other is stable for thousands of hours. Momentary exposure to air (O_2) destroys these radical species. Loy[20] has shown that hydroperoxide radicals are formed rapidly on exposure of irradiated polyethylene to air.

The work of Hansen *et al*[21] on the surface oxidation of polyolefins and that of Hollahan and Carlson[22] on oxidation of polymethyl silicone surfaces by oxidizing plasmas constitute further evidence that under certain conditions an addition of polar groups to polymer surfaces by free radical mechanisms does occur. As noted by Hollahan, Kaplan and Kelleher[23] reported hydroperoxide formation via peroxy radical formation on cis-polybutadiene surfaces by $O_2(^1\Delta_g)$ from a microwave plasma.

Ultraviolet irradiation has been utilized for many years as a method of producing free radicals in solids. Crosslinking of polyethylene by ultraviolet was reported in 1956 by Oster[24] who later presented evidence that crosslinking involved a free radical mechanism.[25] We have observed crosslinking and increased critical surface tension in both polyethylene and polymethylsiloxane rubber in oxygen free atmospheres after long time exposure to ultraviolet from a high pressure mercury lamp. In the presence of O_2, the oxidation reaction predominated over crosslinking. As would be expected, lower contact angles were formed by water and glycerol on oxidized surfaces.

During the course of our work, we learned that Dr. Martin Hudis[26] of the General Electric Research Center had obtained crosslinking of polyethylene by ultraviolet irradiation from an RF hydrogen discharge. Hudis used LiF as a window material. By adapting our experimental apparatus to allow physical isolation of samples from the plasma as Hudis had done, we obtained comparable results using an argon discharge. Both fused silica and LiF ports were used.†

The possible contribution of sputtered high energy wall material has also been investigated. It was found that in the argon discharge Si and B, probably in the form of oxides, i.e. glass, was deposited on copper and carbon surfaces. Replacing the Pyrex reactor chamber with a polyethylene lined acrylic chamber of identical dimensions did not change the results obtained with either polymer in the glass chamber. Although it appears likely that some surface contamination of polymer samples by sputtered wall material may occur during the plasma treatment, the phenomenon does not contribute significantly to the alteration of surface characteristics.

The possibility that surfaces might be electrically charged after plasma treatment was examined early in our investigation. No static charge could be detected with a leaf electrometer and exposure to α-source discharge devices had no effect on contact angles measured. Kim and Goring[27] reported changes in surface morphology of polyethylene after corona discharge treatment in oxygen and air. It was suggested that the "bump" formation observed might result from migration of low molecular weight degradation products to electrically charged areas on the surface. No surface morphological changes resulted from corona treatment in N_2, H_2, He and *A*. Kim,

† The UV transmission of the LiF ports used (Harshaw, UV Grade) changed rapidly in both A and H_2 discharges. A strong absorption peak in the 2400–2550 Å region develops. The effect of this change had a pronounced influence on the rate of change on polymer surfaces. After the absorption peak became very strong, the effects on silicone rubber became negligible.

Evans and Goring[28] investigated corona-induced autohesion of polyethylene treated in oxygen containing gases and N_2. They reported "noncorrelation of adhesion with wetting tension" and suggested that autohesion might be enhanced by some kind of electret formation in corona treated films. Heterogeneously distributed surface charges on films treated for short times in air, O_2, and N_2 coronas were indicated by Lichtenberg figures developed by dusting surfaces with a light dielectric powder (viz. jeweler's rouge). If any inference was intended that a relationship exists between wetting tension (γ_c) and *autohesive* bond strength and γ_c and bond strength of epoxy adhesives to polyethylene or silicone rubber treated in RF discharges of noble gases such as A and He, the relationship is not obvious. In our work, repeated attempts to develop Lichtenberg figures on polyethylene treated in RF discharges of A were completely unsuccessful.

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