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Adhesion Of Glow Discharge Polymers To Metals And Polymers

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Synopsis

Adhesion of glow discharge polymers to metals and polymers in an adhesive joint was measured by lap-shear test and immersion in hot water of 70°C for an extended time. A glow discharge polymer was deposited onto polymers [polyethylene and poly(tetrafluoroethylene)] and metals (aluminum and stainless steel) prior to when the polymer and metal were joined. It is found that the lap-shear strength is enhanced by coating the surfaces of these substrates with plasma film produced from methane, ethylene, and acetylene, and that deterioration of the adhesive bonding part, when immersed in hot water of 70°C, is strongly dependent on the gas used as well as operational conditions where a polymer film is formed. The adhesion of a polymer produced from methane on the polymer and metal is strong enough to apply for durable, adhesive joints.

INTRODUCTION

Glow discharge polymerization is unique in the capability of producing a highly crosslinked, pinhole-free, thin film of organic polymers. In addition, when the plasma film is deposited on the polymer, the properties of the polymer surface are able to be widely varied without changing the bulk properties of the polymer. This distinguished process has already been attempted for some application such as improvement of blood compatibility and permeability of gas and liquid.

Adhesive bonding of an inert polymer such as polyethylene, poly(tetrafluoroethylene), or metal such as stainless steel is difficult unless a special surface treatment with, for example, flame or chromic sulforic acid,[1] is done. The attempt by Schonhorn et al.,[2–4] who demonstrated the surface treatment of a polymer with the activated species of inert gas created by radio frequency discharge for improvement of adhesion, is suggestive. Bonding strength is strongly dependent on the thickness of a crosslinked layer created by interaction with activated species, indicating that a uniformly crosslinked layer at the surface is important to obtain strong adhesion.

We have already reported the manner by which any substrate is able to be uniformly, in respect to film thickness, coated over with plasma films.[5] This technique, in this study, was applied for improvement of adhesive bonding, and adhesion was examined as a function of the material, the gas used, and the operational conditions where plasma film was formed.

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EXPERIMENTAL

Substrates provided for the measurement of adhesive strength were high-density polyethylene(provided from McMaster-Carr., 8624N12 type), poly(tetrafluoroethylene) (Teflon) (McMaster-Carr., 8546K12 type), aluminum (from Metal Good Co., 1100-F), and stainless steel (from Metal Good Co., 304 type), and their dimensions were 9.5 ($\frac{3}{8}$ in.) × 23 × 4.8 ($\frac{3}{16}$ in.) mm as shown in Figure 1. The surface of these substrates was sanded, washed with acetone, methanol, and distilled water for 10 min using an ultrasonic cleaner, and then stored in a desiccator over a silica gel. Prior to plasma-polymer coating the substrates were further cleaned by argon etching for 10 min using the same apparatus as that for plasma polymerization, and then coated with plasma polymers.

Plasma polymerization was carried out by an apparatus which utilized capacitive coupling of a 10-kHz audio frequency (af) source and a magnetic enhancement. The basic plasma polymerization system and the experimental procedure were the essentially same as those reported elsewhere.[5] An aluminum plate [12 in. (30.5 cm) diameter] capable of rotating around an axis placed on the top of the electrodes was positioned midway between aluminum electrodes [6 in. (15.2 cm) square] the separation of which was 6 in. and on which substrates were mounted, and then kept rotating at approximately 60 rpm by the inductive force of a magnet placed out of the bell jar during glow discharge polymerization.

Monomer gases used in this study were methane, ethylene, and acetylene which were commercially provided from Ideal Gas Products and Matheson, and their purities were above 99.5%. For all polymerization, unless otherwise noticed, the monomer flow rate of approximately 2.0 cm³(STP)/min, the total pressure before glow discharge of 30 mtorr, and the constant current of 250 mA were employed. These operational conditions maintained the most stable glow discharge without arcing. The pressure changes in the system and the voltage level between electrodes were continuously recorded during polymerization with a MKS Baratoron pressuremeter and a Hewlett-Packard digital multimeter 3435A, respectively. The deposition rate was measured with a thickness monitor (Veeco model QM-31) positioned midway between the electrodes. The deposition rate (r in mg/cm²) on the substrate mounted on the aluminum plate was directly related to a thickness monitor reading (R, in KÅ), and calculted by the following empirical equation which has been reported elsewhere[5]:

$$r = 0.434 \times 10^{-2}R - 0.243 \times 10^{-2}$$

A, B: SUBSTRATE(ALUMINUM, STAINLESS
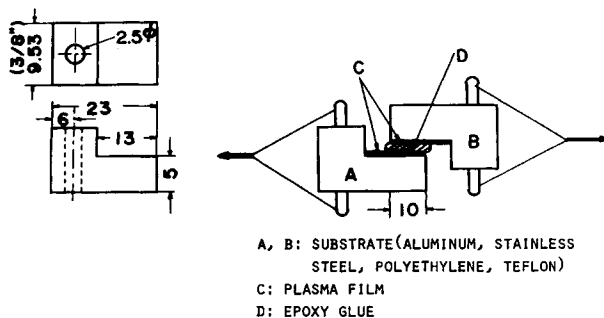STEEL, POLYETHYLENE, TEFLON)
C: PLASMA FILM
D: EPOXY GLUE

Fig. 1. Shema of specimen for measurement of adhesion; unit: mm.

For the measurement of adhesive strength standard composite test pieces consisting of substrate/plasma polymer/adhesive/plasma polymer/substrate, as shown in Figure 1, were prepared for bonding with a special device designed to maintain a 10-mm overlap. The specimens were lightly weighed and allowed to cure for 24 h at 60°C in an air-circulating oven. The adhesive used was a mixture of epoxide and harder (Conap Inc., Easy Poxy) at a ratio of 1:1 by weight without filler material. The bonding strength was evaluated by lap-shear strength using an Instron universal testing instrument at a peeling speed of 5 mm/min and immersion in hot water of $70 \pm 0.5°C$ for the extended time necessary for the specimen to separate itself.

Contact angles of water, glycerol, formamide, diiodomethane, and tricresyl phosphate were measured by a drop-on plate method using a cathetometer with a goniometer eyepiece. The contact angle data were analyzed according to Kaelble's method,[6] and the dispersive contribution, γ_s^d, and the polar contribution, γ_s^p, were calculated.

RESULTS AND DISCUSSION

Lap-Shear Strength

Results for lap-shear strength are listed in Table I. Gases used for glow discharge polymerization were methane, ethylene, and acetylene which had a different deposition rate of polymers created by plasma. Under operational conditions employed in this study the deposition rate was $1.5_5 \times 10^3$ Å/h for methane, $2.5_2 \times 10^3$ for ethylene, and $3.5_6 \times 10^3$ for acetylene. By coating substrate surfaces with these plasma polymers of approximately 2000 Å thickness, as shown in Table I, lap-shear strength was markedly increased. The lap consisting of polyethylene/plasma polymer/epoxy adhesive/plasma polymer/aluminum as well as stainless steel increased to approximately 50 kg/cm^2 in lap-shear strength. The improvement seems to be almost independent of the gases used for polymerization. Similarly, in the case of the lap consisting of poly(tetrafluoroethylene) instead of polyethylene and aluminum as well as stainless steel, the lap-shear strength improvement by coating substrate surfaces with plasma film was also observable. The bonding strength, regardless of the gases used for polymerization, increased to approximately 40 kg/cm^2. Failure always occured at the cohesive layer of plasma polymers rather than the adhesive layer.

The feasibility of forming strong adhesive joints between an epoxy adhesive and a fluorocarbon polymer such as poly(tetrafluoroethylene) and poly(chlorotrifluoroethylene) as well as polyolefine such as polyethylene and polypropylene, which are very inert for adhesive bonding, has been already demonstrated by Schonhorn et al.[2-4] Their technique, called CASING (crosslinking by activated species of inert gases), is a treatment of polymer surfaces by exposing to activated species of inert gases generated by radio frequency discharge, and results in the formation of a crosslinked surface layer which has a strong, cohesive strength. Hall, et al.[7] have also investigated surface treatment with activated species of inert gases, and then recognized there was a significantly different improvement of lap-shear strength with respect to the type of polymer as well as gas and the period of the treatment. These results seem to indicate the different susceptibility of polymers to plasma when exposed to activated species

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TABLE I
Lap-Shear Strength*
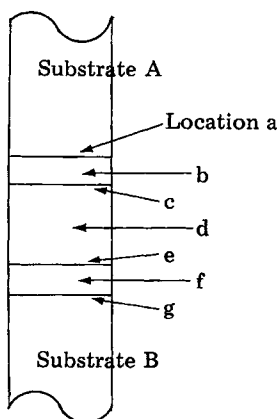
Construction of adhesive joint		Lap-shear strength (kg/cm^2)			
			CH$_4$	CH$_2$=CH$_2$	CH≡CH
Substrate A	Substrate B	Uncoated	(2000)[†]	(2000)	(2060)
PE[‡]	PE	5.8_9(b)[¶]	$24._2$(b)	24.4(b)	$20._7$(b)
PE	AL[‡]	$16._6$(b)	$47._6$(f)	$49._5$(f)	$48._2$(b)
PE	ST[‡]	$28._5$(b)	$45._1$(f)	$47._8$(f)	$46._5$(b)
T[‡]	T	2.4_7(b)	$17._9$(b)	$17._8$(b)	$17._8$(b)
T	AL	$15._8$(b)	$36._8$(f)	$40._4$(f)	$41._6$(b)
T	ST	3.8_0(b)	$38._0$(f)	$39._8$(f)	$40._3$(b)

* Operational conditions: flow rate, 2.0 cm^3(STP)/min; current of af power, 250 mA.
[†] Film thickness, in Å.
[‡] PE: polyethylene; T: poly(tetrafluoroethylene); AL: aluminum, ST: stainless steel.
[¶] Location of failure, the symbol defined as follows illustrates the location of failure:
a: interface between substrate A and plasma polymer.
b: cohesive failure of plasma polymer layer on A side.
c: interface between plasma polymer on A side and adhesive.
d: cohesive failure of adhesive.
e: interface between plasma polymer on B side and adhesive.
f: cohesive failure of plasma polymer layer on B side.
g: interface between substrate B and plasma polymer layer.

of inert gases. If organic gases such as methane, ethylene, and acetylene which are a so-called polymer-forming plasma, instead of inert gases, are used as a plasma gas; the formation of polymer films created by plasma over substrate surfaces and ablation involving crosslinking and unsaturation will occur simultaneously. Also in such a system the balance between the polymer formation and ablation must be dependent on the nature of gases and conditions under which the polymer is formed.

The comparison between inert gas plasma and organic gas plasma in treating polymer surfaces by glow discharge can be visualized in Table I. The first column marked as "uncoated" in Table I, as described in the experimental part, represents the bonding strength of lap when treated with argon etching for 5 min, and the other columns represent the strength of lap when first treated with argon etching and then coated with plasma polymers of approximately 2000-Å thickness. The table evidently indicates that the surface treatment with polymer-

forming plasma is more effective for the adhesive joint than the treatment with the nonpolymer-forming plasma.

From the measurement of the lap-shear strength, Dynes and Kaelble[8] have studied adhesive and cohesive properties of plasma film which is produced from styrene and epichlorohydrine by glow discharge polymerization and covers over surfaces of metal such as aluminum. The lap-shear strength decreases as film thickness deposited onto metal surface increases, and levels off over a film thickness of 1600 Å, where the lap-shear strength decreases to approximately 53% of the original strength. In this experiment, an arbitrarily chosen thickness of 2000 Å was used for all experiments. Consequently, the results may not represent the maximum adhesive strength obtainable by this technique; i.e., by applying thinner coating layer, the overall adhesive strength may increase further.

Deterioration of Adhesive Joint in Hot Water

To evaluate deterioration of adhesive joints consisting of substrates coated with plasma films and epoxy adhesive, the time necessary for these joining parts to peel off of themselves when immersed in hot water of $70 \pm 0.5°C$ was measured. Substrates used here were polyethylene, poly(tetrafluoroethylene), aluminum, and stainless steel, and the construction of the joints was exactly the same as that used for measurement of lap-shear strength, but widely varied conditions where plasma were formed were employed.

Results for the deterioration of adhesive joints in hot water are listed in Table II. Unexpectedly, the deterioration seems to be entirely dependent on gases used for polymerization as well as operational conditions where the polymer is formed.

The lap without coating of plasma films but subjected to argon etching stripped off readily within the period of 20 h in hot water of $70 \pm 0.5°C$, but the lap consisting of substrates coated with polymer produced from methane prior to forming adhesive joints, as shown in Table II, retained for approximately ninefold as long a time. The improvement was outstanding in the case of coating with polymer produced from methane, and polymer from ethylene followed. However, there was no advantage in treating substrate surfaces with polymer from acetylene.

Operational conditions where plasma film is formed seems to influence deterioration of adhesive joints. The ratio of W/FM, where W, M, and F represent af power supplied to maintain glow discharge, molecular weight, and flow rate of the gas introduced into a reactor, respectively, is thought to be a factor controlling glow discharge polymerization.[9,10] In operating at a low ratio of W/FM, plasma-induced polymerization, which is triggered by reactive species that are created in an electric in an electric discharge, may be predominant; at a high ratio of W/FM plasma polymerization which propagated stepwise by combination between reactive species involving an ion, an excited molecule or a free radical produced in a plasma state may occur and a higher ratio ablation may be prevailing. Therefore, generally in glow discharge polymerization, competitive plasma-induced polymerization, plasma polymerization, and ablation occur simultaneously, and the balance among these reactions may be determined by operational conditions as well as gas introduced.[11] It is, of course, in consider-

TABLE II
Deterioration of Adhesive Joint in Water of 70°C

Time necessary for adhesive joint to peel off in water of 70°C (h)

Construction of adhesive joint		Uncoated	CH$_4$			CH$_2$=CH$_2$			CHCH	Used gas
Substrate A	Substrate B			2000			2000			2000	Film thickness, Å
			1.0	2.0	10	1.0	2.0	10	2.0	Flow rate [cm³(STP)/min]
			120	90	90	120	90	90	90	af power, W
			(400)	(250)	(250)	(400)	(250)	(250)	(250)	af current, mA
PE†	PE	20(b)*	169_5(b)	178(b)	47_5(b)	79_8(b)	91(b)	19(b)	23(b)	
PE	AL†	20(b)	80_5(f)	178(b)	38(f)	40(b)	53(f)	19(b)	23(b)	
PE	ST†	20(b)	169_5(f)	141(b)	19(f)	79_8(f)	65(f)	19(f)	23(b)	
T†	T	20(b)	143_5(f)	178(b)	47_5(b)	48(b)	91(b)	19(b)	23(b)	
T	AL	20(b)	103_7(f)	127(b)	28_5(f)	40(b)	32(f)	19(b)	23(b)	
T	ST	20(b)	129(f)	103(b)	19(f)	79_8(f)	91(f)	19(f)	23(b)	

* Location of failure, the definition is the same as shown in Table I.

† PE: polyethylene; T: poly(tetrafluoroethylene); AL: aluminum; ST: stainless steel.
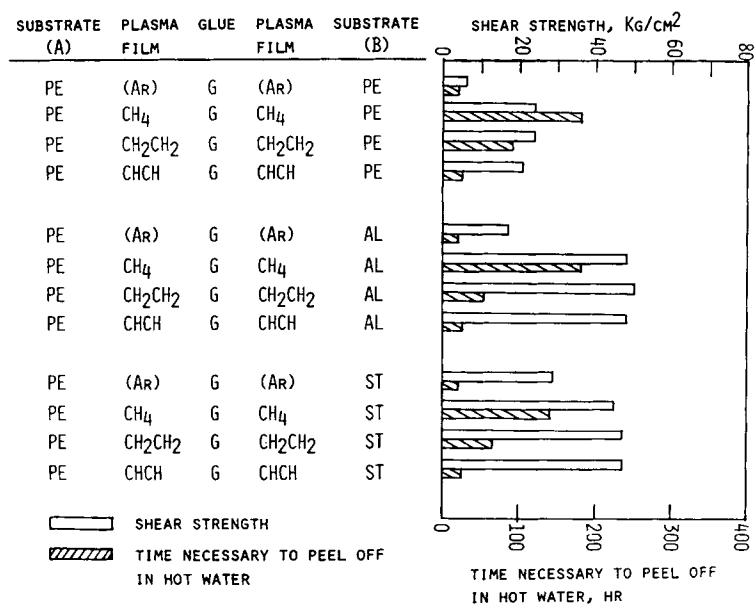
Fig. 2. Lap-shear strength and deterioration in hot water as a function of material and gas used for polymerization: PE, polyethylene; AL, aluminum; ST, stainless steel; (AR), argon etching; CH_4, plasma polymer from methane; CH_2CH_2, plasma polymer from ethylene; CHCH, plasma polymer from acetylene.

ation of the fact that properties of the deposited polymer strongly depend on operational conditions as well as the gas introduced.

The comparison shown in Table II seems to visualize accurately the influence of properties of the polymer caused by altering the conditions on deterioration of the adhesive joints; but, although changes in properties of deposited polymer are quantitatively undetermined, these changes are preceptible from the change in color of the deposited film. The color of the deposited film varied from colorless to light yellow as the ratio of W/FM increased, indicating that ablation became gradually predominant. There seems to be an optimum condition where the polymer is produced, and a moderate ratio of W/FM seems to be favorable for durable adhesive joints.

Consequently, durable adhesive strength improvement by coating substrate surfaces with plasma films prior to forming adhesive joints with epoxy adhesive is summarized in Figures 2 and 3, where the bonding strength is evaluated by two different manners.

TABLE III
Surface Energy for Plasma Film

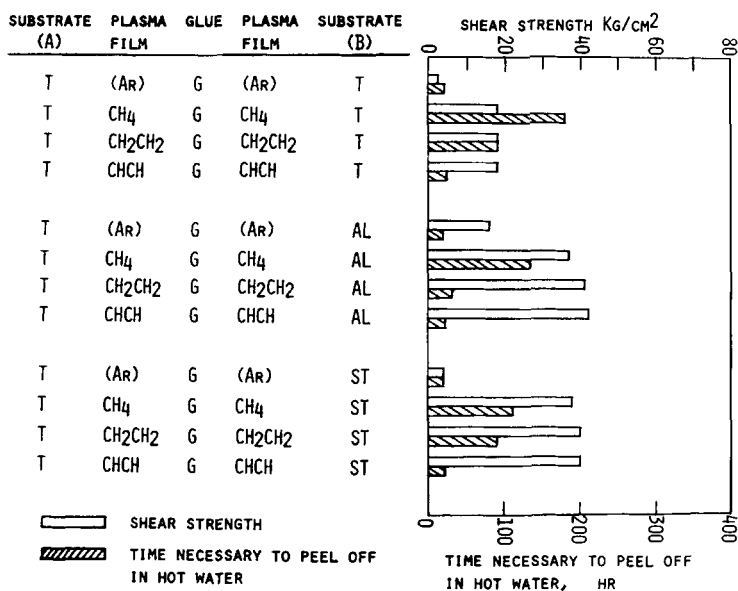| Plasma film from	Surface energy γ_s (dyn/cm)	Dispersion contribution γ_s^d (dyn/cm)	Polar contribution γ_s^p (dyn/cm)
CH_4	$45._8$	$41._5$	$4._3$
$CH_2{=}CH_2$	$41._2$	$36._0$	$5._2$
$CH{\equiv}CH$	$57._2$	$45._4$	$12._2$

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Fig. 3. Lap-shear strength and deterioration in hot water as a function of material and gas used for polymerization; T, polytetrafluoroethylene; AL, aluminum; ST, stainless steel; (AR), argon etching; CH_4, plasma polymer from methane; CH_2CH_2, plasma polymer from ethylene; CHCH, plasma polymer from acetylene.

The adhesion of the polymer produced from methane on substrates is strong enough to apply for a treatment of inert surfaces such as polyethylene, poly-(tetrafluoroethylene), and stainless steel for adhesive bonding. Inferior adhesion of the polymer from acetylene on substrate, when immersed in hot water, may be due to the facile invasion of water into an interface between the substrate surface and the plasma film, because of high surface energy contributed by polar groups, as shown in Table III. The fact that failure occurred at the cohesive rather than the adhesive layer may assist in understanding our speculation concerning failure of adhesive joints.

It is important to point out that the adhesive strength measured under a dry condition may not represent the successfulness of the joint since water vapor always penetrates to the interface of joints. In this sense, the simple immersion test such as described in Table II may provide more important and useful information on the adhesive strength, although the method provides only relative and semiquantitative data. The fact that there is no correlation between the lap-shear strength and immersion failure indicates that the adhesive strength is highly dependent on the extent of water penetration into the interface and the competitive role of water–surface interaction versus adhesive–surface interaction (adhesion). According to these data, it may well be speculated that the combination which yielded longer time, in the immersion test and lower lap-shear test strength is more useful than the combination which yielded higher lap-shear test strength but shorter time in the immersion test. This judgment seems to be particularly important in certain applications of materials where contact with liquid water cannot be avoided, such as in the biomedical application.

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