The Use of Acetylene Glow Discharge for Improving Adhesive Bonding of Polymeric Films*

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Synopsis

Coating of polyethylene (PE), poly(vinyl fluoride) (PVF), poly(tetrafluoroethylene) (PTFE), and poly(vinyl chloride) (PVC) films with flow discharge-polymerized acetylene was investigated. The influence of glow discharge experimental conditions on the nature of the coated layer, the films' wettability, surface roughness, and adhesive joint strength was determined. It was found that coating of these films with plasma-polymerized acetylene led to the formation of a rough, crosslinked, irremovable layer with an improved wettability. The presence of the plasma-polymerized acetylene on the film surface lead to a large improvement in the adhesive joint strength of these films with epoxy adhesive. Best results were obtained with films coated at a low acetylene flow rate. Increase in glow discharge power and treatment time lead to a further improvement.

INTRODUCTION

The treatment of polymeric films by glow discharge plasma is a recommended method when seeking improvement in adhesive bonding.[1] Exposure of films to a glow discharge plasma may lead to chemical and morphological changes at the film surface. The chemical modifications that are frequently encountered in such treatments result in the formation of new functional groups at the film surface. The new functional groups may improve the wettability of the film surface and its adhesion strength. Glow discharge treatment may also lead to the formation of a crosslinked surface which has high cohesive strength and is ideal for production of strong adhesive joints.[2] Thus, for example,[1] nitrogen glow discharge plasma treatment of PE led to an improvement in adhesive joint strength. This improvement was attributed primarily to increase in cohesive strength of the polymer in the surface region through the formation of a densely crosslinked matrix. Glow discharge treatment may also cause chemical degradation and crystallization[3-5] at the film surface which may lead to morphological changes, such as an increase in surface roughness. Roughening of the film surface may also improve its adhesive bonding. Unreactive gases such as nitrogen and argon are commonly used for such glow discharge treatments. All favorable chemical and morphological changes that improve the adhesive joint strength of a treated film cannot always be achieved. Results vary with the gas and polymer used.

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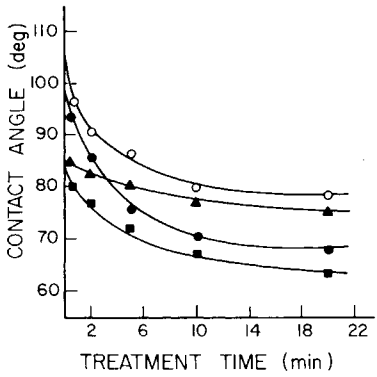


Fig. 1. Dependence of contact angle with water of films coated with plasma-polymerized acetylene on glow discharge treatment time. Glow discharge conditions: pressure, 0.10 torr; acetylene flow rate, 0.21 mmole/min; discharge current, 15 mA; discharge voltage, 750 V. (○) PTFE film, (▲) PVC film, (●) PE film, (■) PVF film.

It was interesting to find out whether chemical and morphological changes such as introduction of new and reactive functional groups, crosslinking, and roughening of the film surface can be achieved simultaneously by the use of a reactive gas for the glow discharge treatment. A reactive gas that will polymerize in the plasma and will coat the film surface with an irremovable rough, crosslinked polymeric layer with new and reactive functional groups may be useful for such treatment. It is well known[6–8] that acetylene polymerizes in glow discharge plasma. It was reported that the polymer obtained contains mainly double bonds, is highly crosslinked, and contains also trapped free radicals. These free radicals eventually react with air, oxygen, and water and are replaced by hydroxyl and carbonyl groups.

It was of interest to find out whether acetylene glow discharge can be used for

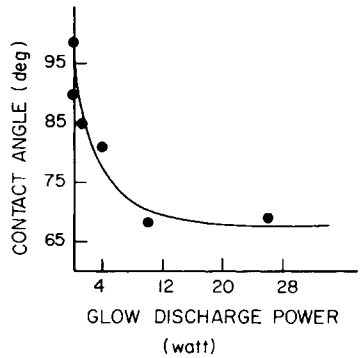


Fig. 2. Dependence of contact angle with water of PE film on glow discharge power. Glow discharge conditions: pressure, 0.10 torr; acetylene flow rate, 0.21 mmole/min; glow discharge treatment time, 20 min.

the coating of films with plasma-polymerized acetylene. It is expected that the presence of a rough crosslinked coating with new functional groups, including trapped free radicals at the film surface, will improve wettability and adhesion properties of these films.

The present work deals with the coating of PE, PVF, PTFE, and PVC films with glow-discharge-polymerized acetylene. The influence of glow discharge conditions on the film's contact angle with water, surface morphology, and adhesive joint strength were investigated.

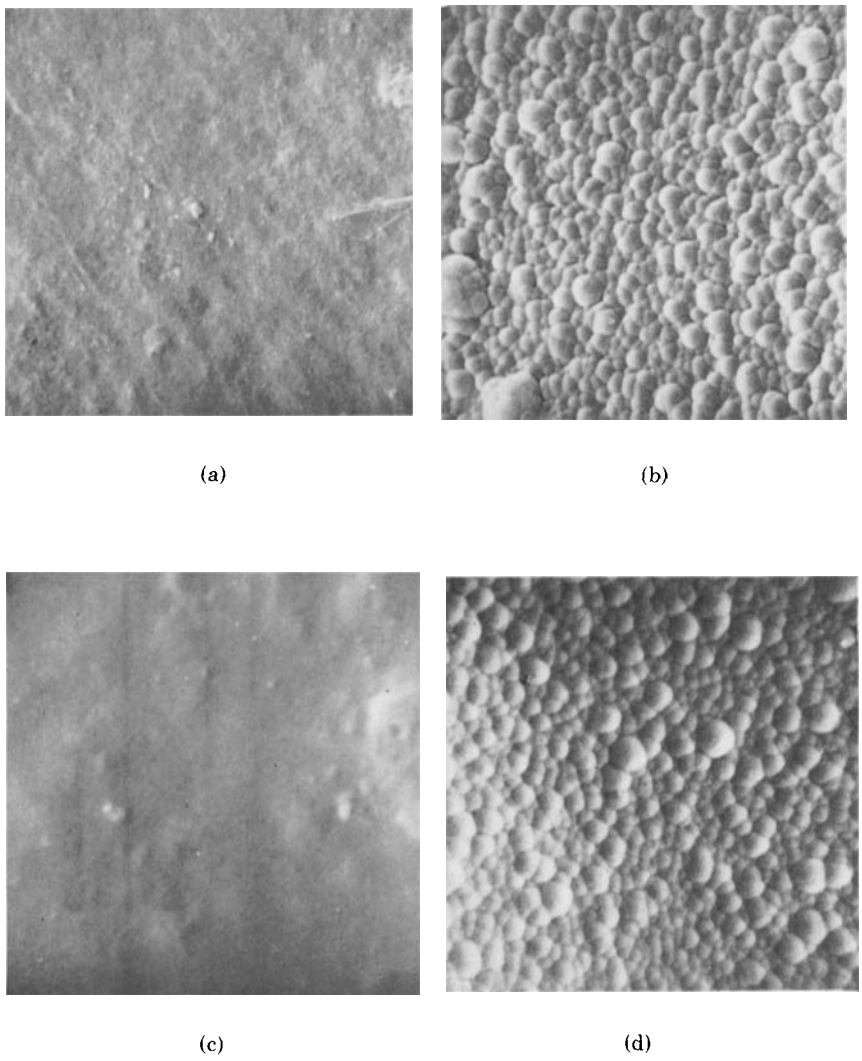


Fig. 3. Change in surface morphology due to acetylene glow discharge treatment. Glow discharge conditions: pressure, 0.10 torr; acetylene flow rate, 0.21 mmole/min; discharge current, 15 mA; discharge voltage, 750 V; treatment time, 10 min. (A) untreated PE film, (B) acetylene glow-discharge-treated PE film, (C) untreated PVC film, (D) acetylene glow-discharge-treated PVC film. Photographs were taken at the same magnification (×10,000).

EXPERIMENTAL

Materials

PE film 0.10 mm thick (Hazorea), PVC film 0.20 mm thick (Haogenplast) containing 20% dioctyl phthalate (as determined by extraction), PVF film 0.03 mm thick (ACC-2 Fortin), and PTFE 0.20 mm thick (du Pont) were used.

PE, PVF, and PTFA were cleaned by immersing them in isopropanol at 60°C for 10 min, rinsing with methanol, and then drying at 50°C for 4 hr. PVC films were cleaned with cotton soaked with petroleum ether, rinsed with methanol, and allowed to dry at room temperature.

Acetylene of 99.6% purity (Matheson Gas Products Company) was used for the glow discharge. Slow-curing epoxy adhesive Araldite (Ciba) was used.

Glow Discharge

Glow discharge of acetylene was carried out in apparatus which has already been described.[9] Glow discharge was carried out in a flow system using ac power supply (50 Hz) and platinum electrodes. The reaction cell consisted of a glass tube of 3 cm i.d. and 50 cm long which was cooled by a water jacket. Films (10 × 20 cm) were introduced into the reaction cell, folded in such a way that they remained attached to the cylindrical cell wall. In this arrangement the films were exposed to the glow discharge only at their inner side; therefore, each experiment was repeated, exposing the other side of the film to the glow discharge under the same experimental conditions.

In operation, the cell with the film inside was evacuated to $<10^{-3}$ torr and then isolated from the high-vacuum source. Acetylene was then admitted into the cell and the cell was evacuated again, allowing the gas to flow at the required flow rate for 10 min before the glow discharge experiment was carried out. During glow discharge, a decrease in pressure in the reaction cell due to polymerization of acetylene was always observed.

Adhesive Joint Strength

Adhesive joints were prepared by sandwiching the treated and untreated films between epoxy-coated aluminum strips. Aluminum strips (Alclad 2024T3, 4 × 1 in., 1/16 in. thick) were used for this purpose. The strips were degreased with

TABLE I
Contact Angle with Water of Films Coated with Plasma-Polymerized Acetylene at Different Acetylene Flow Rates[a]

Acetylene flow rate, mmole/min	Contact angle, degrees							
	PE		PVF		PTFE		PVC	
	Unrinsed	Rinsed[b]	Unrinsed	Rinsed[b]	Unrinsed	Rinsed[b]	Unrinsed	Rinsed[b]
0.00	99	99	85	85	104	104	85	85
0.21	68	68	63	63	78	78	75	75
0.46	135	80	130	65	128	100	130	105
0.76	140	86	137	73	135	100	135	105

[a] Plasma conditions: treatment time, 20 min; current, 15 mA; discharge voltage, 750 V.
[b] The film was rinsed with methanol.

acetone and then etched in sulfochromic acid solution according to procedure described in the literature.[10] The strips were rinsed in water for 10 min and then in distilled water and were allowed to dry at 70°C. Overlapping of the two strips was always 1 × ½ in. The aluminum strips were kept under pressure of 5 psi at 60°C for 4 hr. Tensile shear strength was determined according to ASTM D1002-64 using Hounsfield tensometer.

Contact Angle Measurements

Contact angle was determined 4 hr after glow discharge treatment and 1 min after deposition of the water drop. Measurements were made on both sides of the water drop and were repeated five times.

Mechanical Property Evaluation

Mechanical properties were determined according to ASTM D882-67 using an Instron model 1114.

Infrared Measurements

A Wilks model 9T multiple internal reflection attachment was used in conjunction with a Perkin–Elmer model 225 infrared spectrophotometer.

RESULTS AND DISCUSSION

The possible use of acetylene glow discharge for surface modification of PE, PVF, PTFE, and PVC was investigated. It was found that acetylene glow discharge can be used for coating of these films with a polymer derived from acetylene. The nature of the coated layer varied with the glow discharge conditions and was dependent mainly on the acetylene flow rate. Most experiments were conducted at four different flow rates, between 0.21 and 1.89 mmole/min, which corresponds to 0.1–0.7 torr. The plasma-polymerized acetylene layer was insoluble in organic solvents, as expected for such crosslinked polymer.[6]

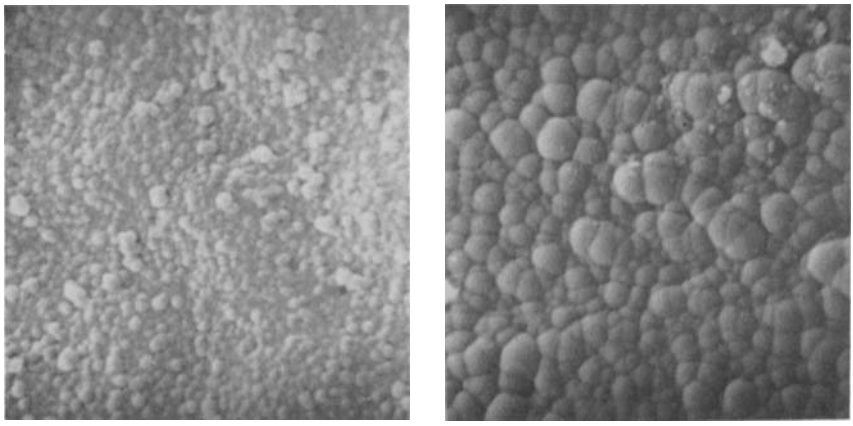
Glow discharge treatment at low flow rates (0.21 mmole/min or lower) yielded insoluble irremovable glossy transparent coating. At other higher flow rates, opaque, powdery coating was always formed. Although the coating formed at these flow rates were always insoluble, it could be partially removed by physical means.

ATR spectra of acetylene-plasma-treated films revealed the presence of unsaturation and oxygen incorporation. While unsaturation is the direct result of plasma polymerization of acetylene, oxygen incorporation is attributed to reaction of trapped free radicals with air.[7,8] Absorption of carbon–carbon double bonds (1600, 1640 cm^{-1}), peroxide (1240 cm^{-1}), C–O (1020 cm^{-1}), and C–H adjacent to a double bond (800 cm^{-1}) could be identified. ATR measurements, repeated over period of four months, of films which were kept at room temperature revealed the development of strong carbonyl absorption. Similar results were obtained within a few days when the treated films were kept at 80°C. The appearance of carbonyl groups in plasma-polymerized acetylene has already been reported.[6,7]

TABLE II
Mechanical Properties of Acetylene Glow Discharge-Treated Films[a]

	PE		PVC		PVF		PTFE	
	Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated
Initial modulus, kg/cm^2	1150	1290	4000	4350	10330	13330	5830	6250
Yield point stress, kg/cm^2	138	168	160	200	413	560	140	150
Yield point strain, %	12.0	13.0	4.0	4.6	4.0	4.2	2.4	2.4
Tensile strength, kg/cm^2	252	208	365	308	906	866	420	400
Extension at break, %	594	374	304	230	184	176	300	277

[a] Acetylene glow discharge conditions: acetylene flow rate, 0.21 mmole/min; current, 15 mA, voltage, 750 V; treatment time, 20 min. Mechanical properties were determined according to ASTM D882-67.



(a) (b)

Fig. 4. Change in PE film surface morphology with discharge treatment time. Glow discharge conditions: pressure, 0.10 torr; acetylene flow rate, 0.21 mmole/min; discharge current, 15 mA discharge voltage, 750 V; (A) treatment time 2.0 min, (B) treatment time 10.0 min. All photographs were taken at the same magnification (×10,000).

The coating of a film with plasma-polymerized acetylene should change its wettability. The influence of plasma conditions such as treatment time, plasma power, and gas flow rate on contact angle with water of acetylene-plasma-treated films was investigated. It was found that with four different films investigated, acetylene plasma treatment led always to improvement in the film wettability.

Dependence of contact angle with water on plasma treatment time for the four different films is described in Figure 1. Treatment was carried out at the lowest acetylene flow rate. Increase in treatment time, up to 20 min, lead to a decrease in contact angle with water. The lowest contact angles obtained for the four

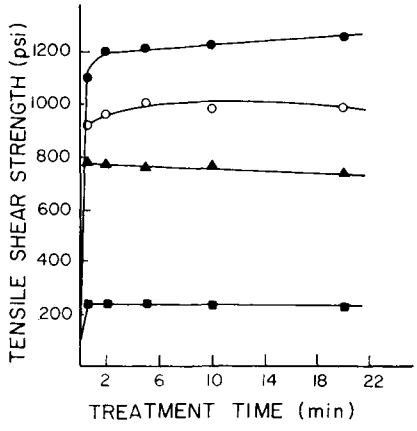


Fig. 5. Dependence of tensile shear strength of the composite aluminum–epoxy adhesive–acetylene glow-discharge-treated PE–epoxy adhesive–aluminum on glow discharge treatment time at different acetylene flow rates. Glow discharge conditions: discharge current, 15 mA; discharge voltage, 750 V. (●) 0.21 mmole/min acetylene flow rate, (○) 0.46 mmole/min acetylene flow rate, (▲) 0.76 mmole/min acetylene flow rate, (■) 1.81 mmole/min acetylene flow rate.

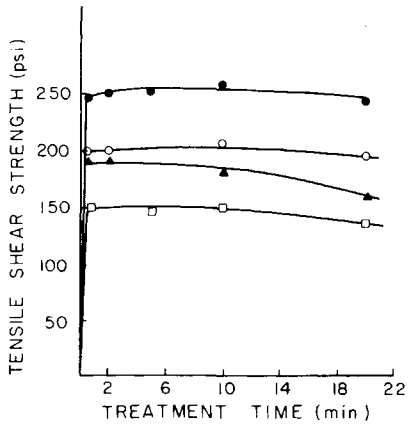


Fig. 6. Dependence of tensile shear strength of the composite aluminum–epoxy adhesive–acetylene glow-discharge-treated PTFE–epoxy adhesive–aluminum on glow discharge treatment time at different acetylene flow rates. Glow discharge conditions: discharge current, 15 mA; discharge voltage, 750 V. (●) 0.21 mmole/min acetylene flow rate, (○) 0.46 mmole/min acetylene flow rate, (▲) 0.76 mmole/min acetylene flow rate, (□) 1.89 mmole/min acetylene flow rate.

different films were 68° for PE film, 63° for PVF film, 75° for PVC film, and 78° for PTFE. Acetylene plasma power effect on contact angle with water of the treated PE film is similar (Fig. 2). Increase in plasma power, up to 10 W, lead to a decrease in contact angle with water.

The influence of acetylene flow rate on contact angle with water of the four different films is reported in Table I. Since the coated layers formed at acetylene flow rates higher than 0.21 mmole/min were powdery and could be partially removed, the contact angle was determined twice. Contact angle was determined on the film as obtained after the plasma treatment and again after removing part

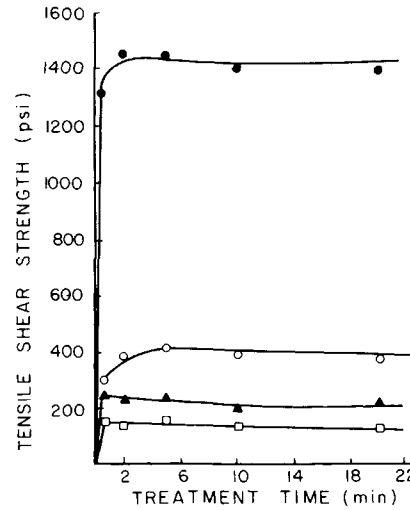


Fig. 7. Dependence of tensile shear strength of the composite aluminum–epoxy adhesive–acetylene glow-discharge-treated PVF–epoxy adhesive–aluminum glow discharge treatment time at different acetylene flow rates. Glow discharge conditions: discharge current, 17 mA; discharge voltage, 750 V. (●) 0.21 mmole/min acetylene flow rate, (○) 0.46 mmole/min acetylene flow rate, (▲) 0.76 mmole/min acetylene flow rate, (□) 1.89 mmole/min acetylene flow rate.

of the powdery coating by rinsing with petroleum ether. Improvement in contact angle with water was found for all four different films which were coated with an unpowdery plasma-polymerized acetylene coating. At high acetylene flow rates when powdery coatings were obtained, no improvement in contact angle with water was found when the films were not rinsed with methanol. After rinsing, some improvement had been observed with PE and PVF films. The contact angles with water obtained did not reach those of the films coated at the lowest acetylene flow rate. The contact angles with water of PTFE and PVC films were improved after rinsing, yet the contact angle of PVC was higher and that of PTFE was almost the same as those of the uncoated films.

The coating of a film with plasma-polymerized acetylene should change the morphology of the film surface. Those changes in samples which were coated at the lowest acetylene flow rate were followed by scanning electron microscopy. Coating of PE and PVC films with plasma-polymerized acetylene resulted in roughening of the film surface (Fig. 3). Increase in plasma treatment time led to an increase in extent of acetylene polymerization, which affected surface morphology. Changes in surface morphology with plasma treatment time can be observed (Fig. 4). The polymer buildup, at the film surface, starts at definite localized centers which later grow and expand with plasma treatment time.

Glow discharge treatment is commonly used for surface modification of polymers. In order to find out whether bulk properties were affected during acetylene plasma treatment, tensile properties of the treated films were determined (Table II). Practically no change in tensile properties was found. The effects of acetylene glow discharge treatment were limited to the film surface.

The presence of new functional groups—trapped free radicals—and an irremovable, crosslinked rough polymeric layer with an improved wettability at the film surface should improve adhesive joint strength of these films.

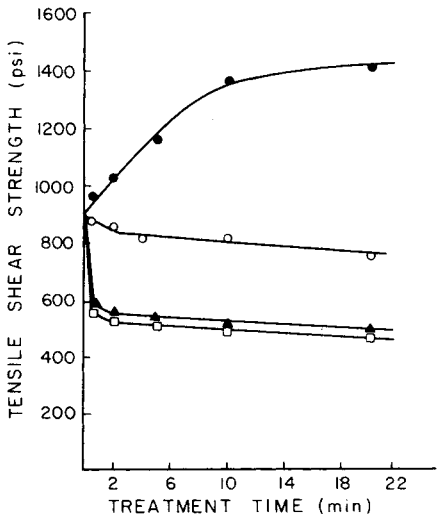


Fig. 8. Dependence of tensile shear strength of the composite aluminum–epoxy adhesive–acetylene glow-discharge-treated PVC–epoxy adhesive–aluminum on glow discharge treatment time at different acetylene flow rates. Glow discharge conditions: discharge current, 15 mA; discharge voltage, 750 V. (●) 0.21 mmole/min acetylene flow rate, (○) 0.46 mmole/min acetylene flow rate, (▲) 0.76 mmole/min acetylene flow rate, (□) 1.89 mmole/min acetylene flow rate.

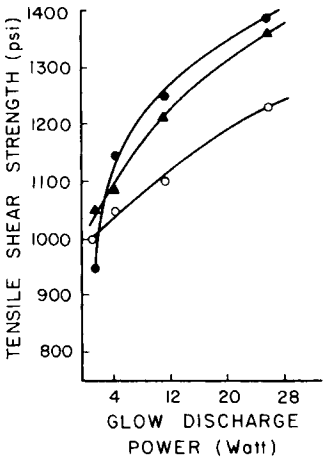


Fig. 9. Dependence of tensile shear strength of the composite aluminum–epoxy adhesive–acetylene glow-discharge-treated PE–epoxy adhesive–aluminum on glow discharge power. Glow discharge conditions: acetylene flow rate, 0.21 mmole/min. (○) 0.5 min treatment time, (▲) 5.0 min treatment time, (●) 20.0 min treatment time.

The four different films that were subjected to acetylene glow discharge plasma under different plasma conditions were used for the preparation of adhesive joints. Adhesive joints were prepared by sandwiching the film between epoxy-coated aluminum strips. Tensile shear strength of these joints never exceeded the value of 2200 psi obtained with such a joint without the presence of a film.

The dependence of joint strength on acetylene plasma treatment time at different gas flow rates is described in Figures 5 through 7. Similar behavior was obtained with PE, PVF, and PTFE films. The maximum joint strength obtained under the experimental conditions was reached within a short time. Joint strength was determined by the nature of the coating. At high flow rates when powdery coating was formed, tensile shear strength was lower than that obtained with a film which was coated at the lowest flow rate (0.21 mmole/min) in which irremovable nonpowdery coating with a better wettability was formed. Increase in acetylene flow rate lead to a decrease in joint strength. When PVC film was subjected to acetylene glow discharge treatment (Fig. 8) improvement in joint strength was observed only in the lowest gas flow rate, but longer plasma treatment time was needed to reach this improvement. At high flow rates, when

TABLE III
Maximal Tensile Shear Strength of the Composite: Aluminum–Epoxy Adhesive–Acetylene Plasma-Treated Film–Epoxy Adhesive–Aluminum[a]

Film	Film width, mm	Tensile shear strength, psi	
		Untreated	Treated
PE	0.10	90	1250
PVF	0.03	10	1450
PVC	0.20	900	1450
PTFE	0.20	10	250

[a] Glow discharge conditions: see Figs. 5–8. Tensile shear strength was determined according to ASTM D 1002-64.

powdery coating was formed, deterioration in joint strength was observed. Here, too, decrease in acetylene flow rate led to an increase in joint strength. It can be seen that the nature of the coating is important for good adhesion. The maximum values of tensile shear strength obtained for the four different films are reported in Table III. With PE and PVF films, failure occurred mainly in the film itself. With PVC and PTFE films, failure occurred always at the film boundary layer.

Plasma power affects extent of polymerization of acetylene and therefore may contribute to the adhesive joint strength of the treated films. The dependence of adhesive joint strength of PE film on plasma power was determined (Fig. 9). Experiments were carried out at different plasma treatment times and at the lowest acetylene flow rate. It can be seen that increase in plasma power which lead to increase in the extent of polymerization of acetylene on the film surface lead to an increase in joint strength.

We conclude that treatment of polymeric films such as PE, PVF, PTFE, and PVC with acetylene glow discharge can improve their adhesive bonding. The nature of the coated layer is of essential importance. At low flow rates, a wettable, rough, crosslinked layer can be obtained and good adhesion can be reached. At this low flow rate, adhesion strength can be improved further by controlling plasma power and plasma treatment time.

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