Effect of Electrodeless Glow Discharge on Polymers

H. YASUDA, C. E. LAMAZE and K. SAKAOKU, *Camille Dreyfus Laboratory, Research Triangle Institute, Research Triangle Park, North Carolina 27709*

Synopsis

The effects of gas plasma generated by electrodeless (inductive coupling) glow discharge on polymers were investigated as functions of gas pressure, discharge power, exposure time, and type of plasma gas. A remarkable similarity between the plasma susceptibilities of low molecular weight organic compounds and polymers was observed; i.e., polymers which have ether, carbonyl, ester, or carboxylic acid attached to a nonaromatic structure are very susceptible to plasma. The weight loss was proportional to the exposure time and exposed area. The discharge power and type of gas were found to have a great influence on both the rate of weight loss and the morphology of the exposed surface. The predominant effect of plasma on polymers was found to be degradation (manifested by weight loss). The crosslinking effect was found to be marginal with many polymers; however, significant crosslinking was observed with double bond-containing polymers. The crosslinking was examined by swelling the treated films. With copolymers of styrene–butadiene, 4-vinylpyridine–butadiene, methacrylic acid–butadiene, and acrylic acid–butadiene, the crosslinking was greatly dependent on the discharge power, the butadiene content of the copolymers, and the exposure time. Both degradation and crosslinking by gas plasma were generally limited to the exposed surface; however, the propagation of crosslinking in the direction of thickness was observed with copolymers of styrene–butadiene. The plasma of organic vapor also causes degradation of plasma-susceptible polymers, particularly at high wattage, although the deposition of polymer occurs simultaneously.

INTRODUCTION

Gas plasma generated by electrodeless glow discharge can be considered as a relatively mild radiation source in so far as the effects on many vinyl monomers and organic polymers are concerned. Gas plasma initiates polymerization of monomers leading to deposition of polymers onto the surface of the discharge vessel.[1,2] Gas plasma has been used to treat the surface of polymers to improve wettability and bonding capability,[3-5] and to study the morphologic structure of the surface.[6,7] It has been postulated that the increased bonding strength is due to cleaning of the surface and crosslinking of a thin layer on the polymer surface. Therefore, three major effects generally observed by radiation, i.e., polymerization of monomers, degradation, and crosslinking of polymers, all seem to be involved with gas plasma treatment of monomers and polymers.

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Although these fundamental aspects were observed in experiments using plasma generated by various types of electric discharge, it has become evident that the details of these effects are highly dependent on the experimental conditions, such as the mode of discharge, i.e., d.c. or a.c. (inductive coupling and capacitative coupling); the frequency of the a.c.; the relative position of samples in respect to the electrodes or the coupler and to the flow of gas; size of the reaction vessel; etc. Consequently, the results found by a particular system may not entirely apply to the other systems.

This study was carried out as part of an effort to prepare composite reverse osmosis membranes by plasma deposition of polymers onto porous substrate. Therefore, it was aimed at the investigation of the magnitude of degradation and of crosslinking, particularly in comparison with the magnitude of polymer deposition from the plasma of an organic vapor.

Although convincing evidence has been presented that crosslinking of polyethylene occurs by plasma treatment and contributes to better bonding characteristics of treated surface,[3,4] it cannot be generalized that plasma can be used to introduce enough crosslinking into any kind of polymer. A similar situation has been found with γ-ray irradiation, namely, polyethylene is perhaps the only polymer into which a sufficient amount of crosslinks can be introduced by γ-ray irradiation. If a polymer is plasma susceptible, the degradation of polymer may overwhelm the polymer deposition by plasma and perhaps alter the characteristics of the substrate polymer.

The work reported here was performed concurrently with a study of polymerization of organic compounds in order to find the influence of operational factors of discharge so that it might be possible to suppress one effect and/or enhance the other in a particular application of glow discharge.

EXPERIMENTAL

The plasma apparatus used in this study and the procedure of operation is similar to that reported previously.[2]

Polymer Degradation

In the degradation experiments, a polymer sample (8.0 cm $\times$ 2.5 cm) was suspended in the center part of the discharge vessel by means of a support made of glass rod, exposing both sides of the sample (i.e., 40 cm^2 total surface) to the plasma.

Polymer samples used were commercially available polymers in thin sheet form. They were cleaned by washing with acetone in an ultrasonic vibrator for 30 minutes, dried in a vacuum oven at room temperature, and stored in a dust-free container. Polymer samples were weighed before and after the treatment to determine the rate of weight loss. Nylon 6 samples, unlike the others, showed considerable weight loss due to loss of moisture (determined by drying in a heated vacuum oven). Therefore, to obtain the polymer weight loss, the average weight loss observed for heat drying

was subtracted from the total weight loss observed for plasma-treated nylon 6 samples.

The degradation of water-soluble polymers was investigated by coating a thin layer of polymer solution on one side of a glass slide. The weight changes were calculated on the coated area.

Polymer Crosslinking

Crosslinking of polymers was examined by the swelling observed when the treated samples were immersed in the solvent from which the films were originally cast. Solvent-cast films of many polymers left a thin, insoluble layer when immersed in the solvent after treatment with gas plasma, indicating that a certain number of crosslinks were introduced by the treatment. However, most such films never became strong enough to maintain the film form in the solvent, through they are definitely insoluble and exist as a highly swollen mass. It seemed that the crosslinks introduced by plasma in ordinary polymers was not sufficient to maintain the film form, thus it was not possible to study the swelling quantitatively. In order to observe the crosslinking effect of gas plasma as manifested by experimentally controllable factors, some double bond-containing copolymers, such as styrene–butadiene (ST–BD), 4-vinylpyridine–butadiene (4 VP–BD), acrylic acid–butadiene (AA–BD), and methacrylic acid–butadiene (MA–BD), were used in this study. Copolymer samples were prepared in the laboratory by conventional free-radical polymerization.

The styrene–butadiene (ST–BD) copolymers (80:20 and 70:30 monomer mole ratios) were prepared in emulsions of the following wt-% composition: 20.0% total monomers, 77.2% H_2O, 2.2% sodium lauryl sulfate, 0.5% K_2HPO_4, and 0.1% $K_2S_2O_8$. The solutions were maintained at 60°C for 4 hr, then the polymer was precipitated in acidified MeOH (20 ml HCl:2000 ml MeOH), washed, and dried. The films were cast from a 10% solution of the polymer in toluene, and the thickness of the dried films was 1.2×10^{-3} cm.

The 4-vinylpyridine–butadiene (4VP–BD) copolymer (80:20 monomer mole ratio) was prepared in bulk monomer mixture using 0.02 wt-% 2,2-azobis(2-methylpropionitrile) as initiator. The solution was maintained at 60°C for 8 hr, then diluted with a solution of EtOH/H_2O (60:40 vol-%). The polymer was then precipitated in H_2O, washed, and dried, and films were cast from a 10% solution of the copolymer in ethanol. The thickness of the dried films was 1.0×10^{-3} cm.

The methacrylic acid–butadiene (MA–BD) and acrylic acid–butadiene (AA–BD) copolymers (80:20 monomer mole ratio) were polymerized in a 50 wt-% solution with ethanol and initiated with 0.03 wt-% 2,2-azobis-(2-methylpropionitrile) as initiator. The solutions were maintained at 60°C for 16 hr, then diluted with a solution of EtOH/H_2O (60:40 vol-%). The polymer was then precipitated in H_2O, washed, and dried, and films were cast from a 20% solution of the polymer in ethanol. The thickness

of the dried MA–BD films was 1.0×10^{-3} cm, and of the AA–BD films, 0.5×10^{-3} cm.

The samples to be treated were squares of film exactly 1 in. on a side cut from the cast films described above.   Each sample was positioned on a glass slide placed in the plasma chamber, and in this manner only the top surface was exposed to plasma.   After treatment, the swelling of the sample, as compared to an untreated control, was observed by placing the sample in a Petri dish of the casting solvent and observing the new dimensions of the swollen film.   A grid beneath the dish allowed measurement of the sample surface area without additional handling.

For the 4VP–BD, MA–BD, and AA–BD plasma-treated samples, the films remaining in the solvent after swelling were so thin that measurement of the thickness could not be done simply.   In the case of the ST–BD copolymers, plasma treatment of the samples showed some effect in the remaining thickness as well as surface area.   Because of the gelatinous nature of these swollen samples, measurement of the thickness was made manually, using a micrometer, while the sample was held in the swelling agent.

RESULTS AND DISCUSSION

Degradation

The effect of plasma is limited to the polymer surface, and the weight loss is not dependent on the thickness of the sample.   A similar observation was reported by Hansen et al.[8] with oxygen plasma and various polymers.   The time dependence of weight change is shown in Figure 1 (He at $150\,\mu$ Hg, discharge power 30 watts.)
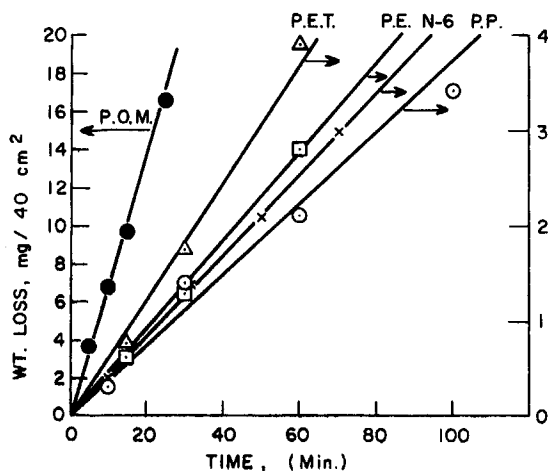

Fig. 1. Weight loss observed with plasma treatment of polymers: P.O.M., poly-(oxymethylene);   P.E.T.,   poly(ethylene   terephthalate);   P.E.,   polyethylene   (density 0.96);   N-6:   nylon 6;   P.P.,   polypropylene.   He as plasma gas, discharge power 30 watts at $150\,\mu$ Hg.
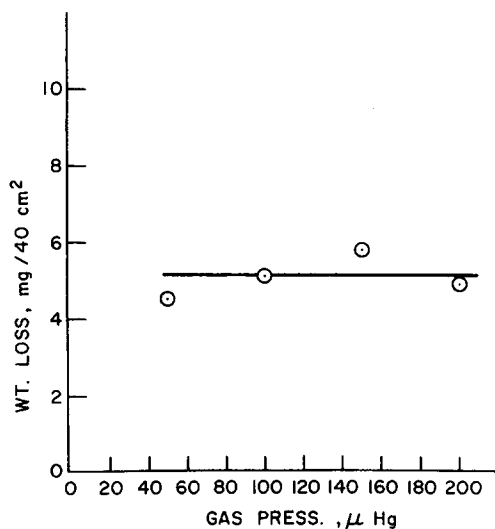
Fig. 2. Effect of gas pressure on weight loss of poly(oxymethylene) treated by He plasma at 100 watts for 10 min.
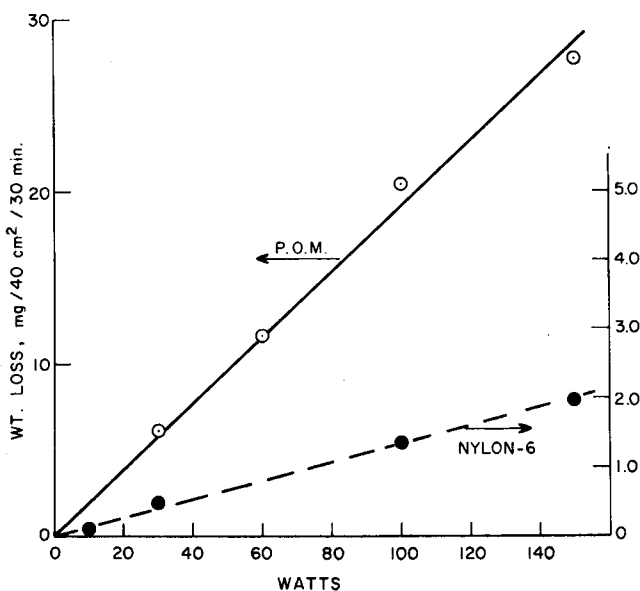

Fig. 3. Effect of discharge wattage on the rate of weight loss for poly(oxymethylene) and nylon 6. He plasma, 150 μ Hg.

The effect of type of gas is examined with poly(oxymethylene) and polypropylene using N_2 and He. With poly(oxymethylene), which showed an exceptionally high rate of weight loss, the difference due to gas was negligible, but with polypropylene the rate of weight loss for N_2, was found approximately 30% smaller than for He. This trend is opposite to the
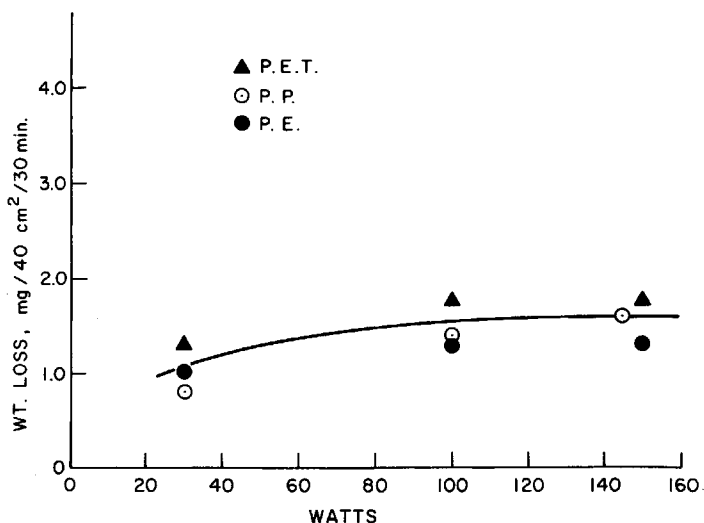
Fig. 4. Effect of discharge wattage on the rate of weight loss for poly(ethylene tereph-
thalate), polypropylene, and polyethylene.   He plasma, 150 μ Hg.

order of gas effect found in plasma polymerization.[2]   Nitrogen plasma
seems to cause less radiation damage on polymers yet accelerates more effi-
ciently the polymerization of vinyl monomers.

The effect of gas pressure was examined with poly(oxymethylene) sam-
ples under the following discharge conditions: He as plasma gas, dis-
charge power of 100 watts, and treatment time of 10 min.   The result is
shown in Figure 2.   The gas pressure does not seem to have an effect on
the rate of weight loss within the range examined in this study.

The effect of discharge power was examined with He plasma.   Poly-
(oxymethylene) and nylon 6 showed an apparently linear dependence on
the discharge power, as shown in Figure 3.   Nitrogen plasma on poly-
(oxymethylene) showed no significant difference on the power dependence
from that of helium plasma.   The discharge power has less effect on poly-
propylene, poly(ethylene terephthalate), and polyethylene, and the rates
of weight loss seem to reach plateau values at very low discharge powers,
as shown in Figure 4.

Although the degradation effect of a glow discharge is generally con-
sidered mild, it is very intense at the surface.   Since the effect of plasma
is confined to the surface, the degradation of polymer leads to a nearly
complete breakdown of relatively small numbers of molecules (at the sur-
face) into low molecular weight components which eventually vaporize
and are pumped out of the low-pressure system.   This is in strong con-
trast to the radiation damage caused by high-energy radiation which has
high penetration, such as γ-ray and x-ray.   The degradation by these high-
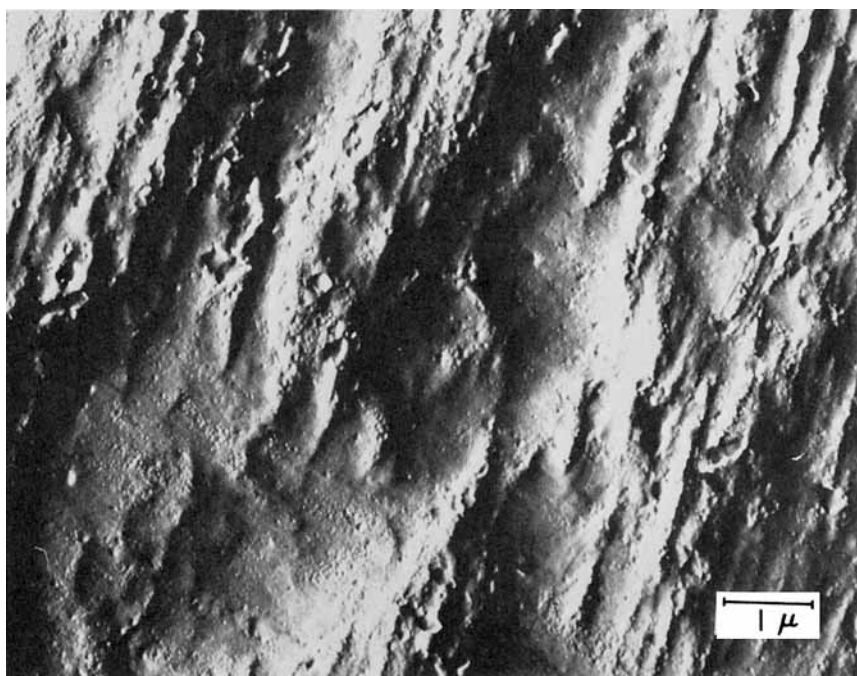energy radiations occurs in the entire bulk of a sample, but a complete

Fig. 5. Surface of nontreated poly(oxymethylene) sample.

breakdown of polymer molecules that leads to weight loss does not occur unless an extremely high dose is given.

This localized degradation of polymer at the surface is clearly seen in (transmission) electron micrographs of treated samples, as shown in Figures 5 through 12, which were obtained in the following model experiments. Knowing that the degradation effect of plasma is quite severe at the surface, it is important to examine the effect of organic vapor plasma which deposits polymer onto the substrate polymer. This is concerned with a practical question of whether the deposition of polymer from organic vapor plasma shields the underlying substrate polymer from degradation or whether the organic vapor plasma also damages the substrate polymer.

It is likely that competitive reactions of polymerization of monomer and degradation of polymer (substrate) occur simultaneously. In order to gain more insight into the competitive natures of these reactions, model experiments were carried out by using poly(oxymethylene), which was found to be extremely susceptible to glow discharge.

The results of these model experiments are summarized in Table I as the rate of weight change in plasma of various gases and the monomer styrene. It is interesting to note that poly(oxymethylene) loses weight at the highest rate in plasma of its own degraded products and trace amount of residual air, and that the addition of gas such as helium and nitrogen decreases the rate of weight loss. This is in accordance with the trend

TABLE I
Effect of Plasma Gas on Degradation of Poly(oxymethylene)
and Polymerization of Styrene onto the Substrate

Plasma	Substrate	Rate of weight change, $(g\ cm^{-2}\ min^{-1}) \times 10^6$	
		30 watts	100 watts
Vacuum $(0.2\ \mu)$	POM	−3.50	−15.8
100 μ He	POM	−3.13	−14.6
100 μ N$_2$	POM	−2.00	−11.0
40 μ ST	slide	+1.88	+1.88
40 μ ST	POM	+1.25	0.0
80 μ N$_2$ + 20 μ ST	slide	+4.40	+4.40
80 μ N$_2$ + 20 μ ST	POM	+1.50	+1.63
80 μ He + 20 μ ST	slide	+2.50	+2.50
80 μ He + 20 μ ST	POM	−0.25	−0.83
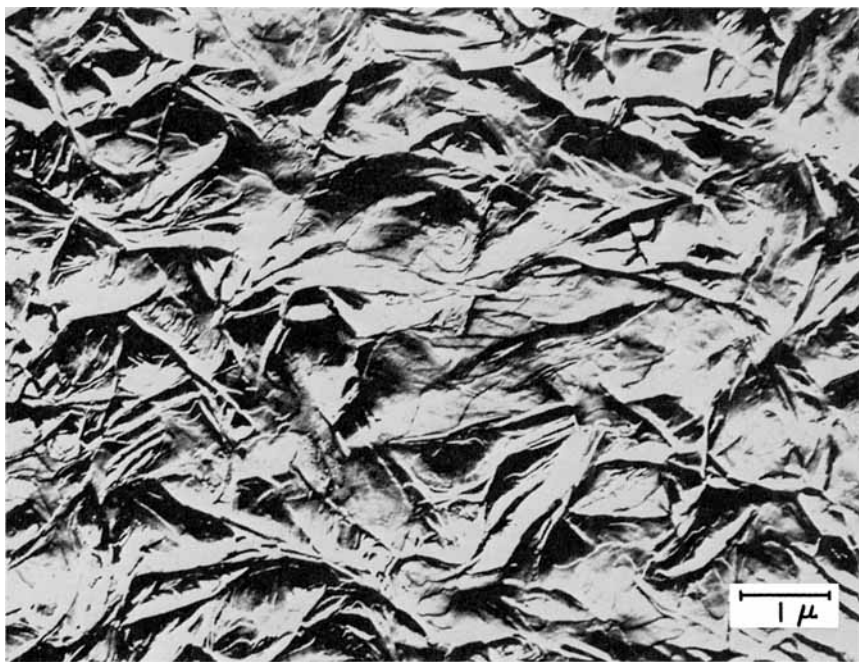
Fig. 6. Surface of annealed poly(oxymethylene) sample.

observed in the decomposition of organic compounds that the most plasma-susceptible groups are oxygen-containing groups such as ether, carbonyl, and hydroxyl groups.[9,10] When these groups decompose in plasma, they are likely to form atomic oxygen and accelerate the decomposition of the polymer.

The addition of monomer styrene apparently overwhelms the degradation of poly(oxymethylene), and the weight increase observed at low dis-
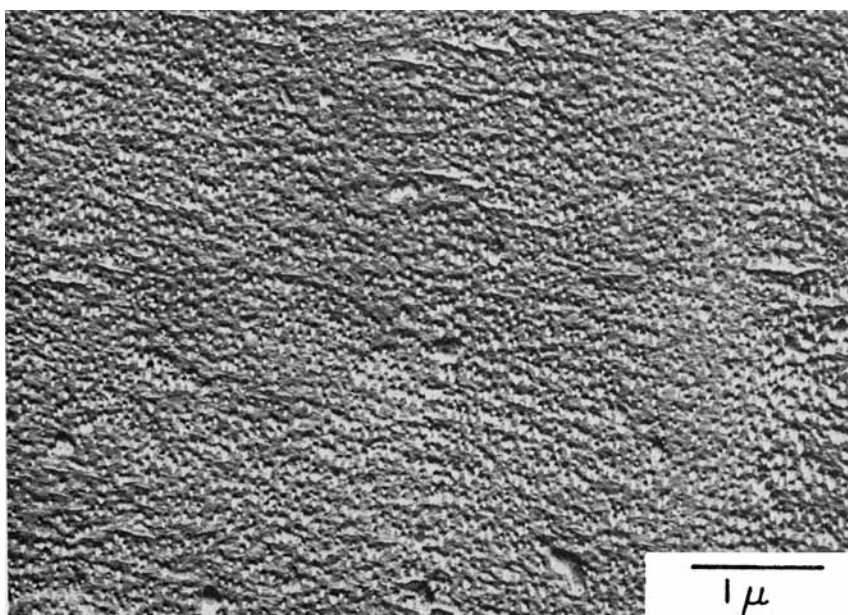
Fig. 7. Electron micrograph of surface of poly(oxymethylene) exposed to N_2 plasma (100 μ Hg) at 100 watts for 10 min. Weight change: -5.85 mg/40 cm².
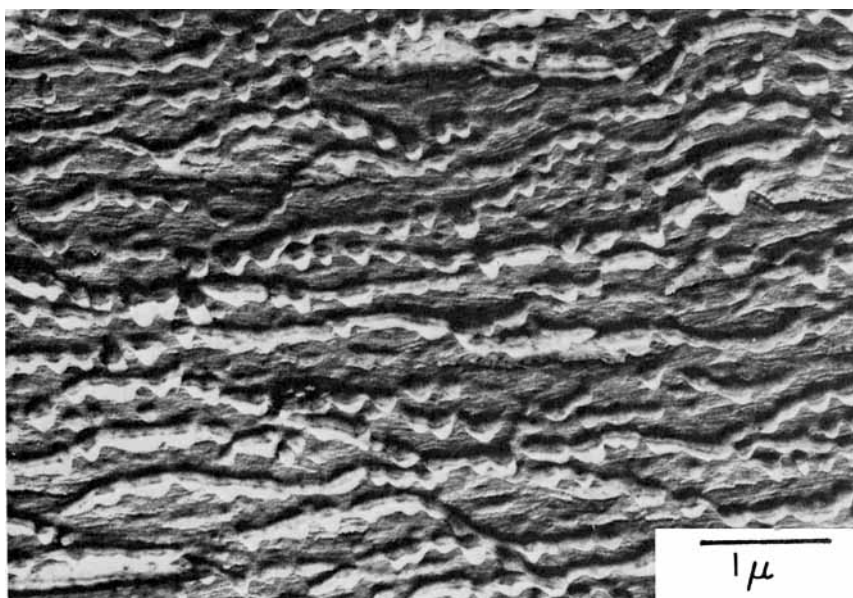

Fig. 8. Electron micrograph of surface of poly(oxymethylene) exposed to He plasma (100 μ Hg) at 100 watts for 10 min. Weight change: -5.85 mg/40 cm².
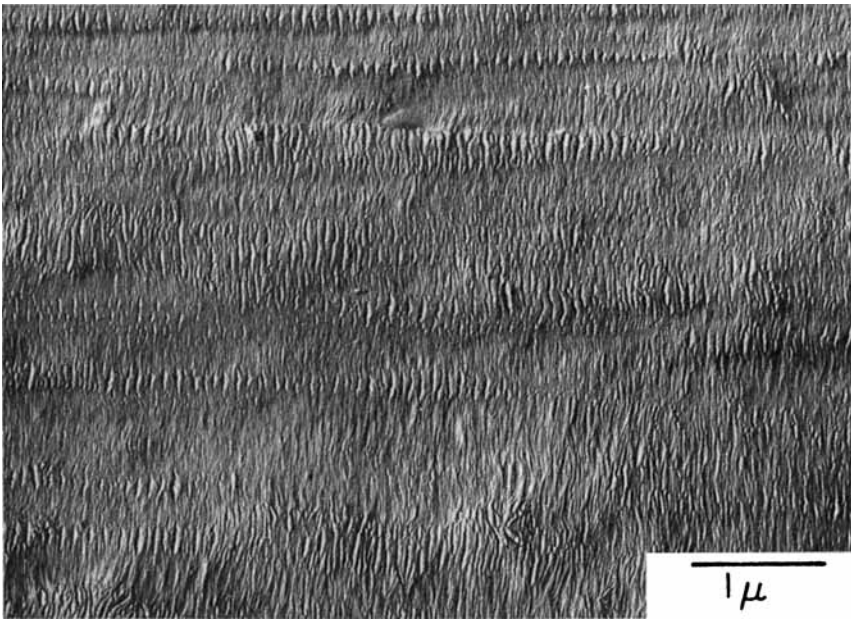
Fig. 9. Electron micrograph of surface of poly(oxymethylene) exposed to styrene plasma (40 μ Hg) at 30 watts for 10 min.   Weight change: $+0.5$ mg/40 cm^2.
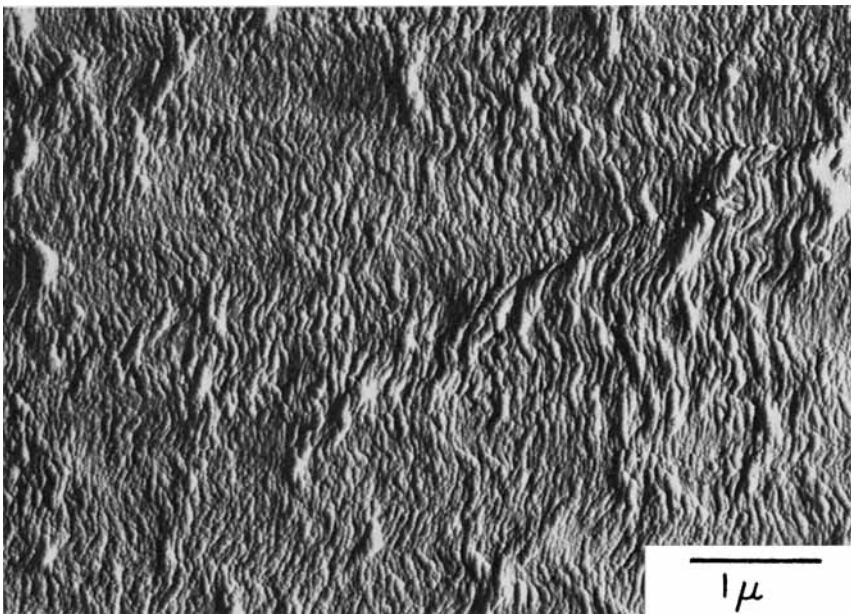

Fig. 10. Electron micrograph of surface of poly(oxymethylene) exposed to styrene plasma (40 μ Hg) at 100 watts for 10 min.   Weight change: 0 mg/40 cm^2.
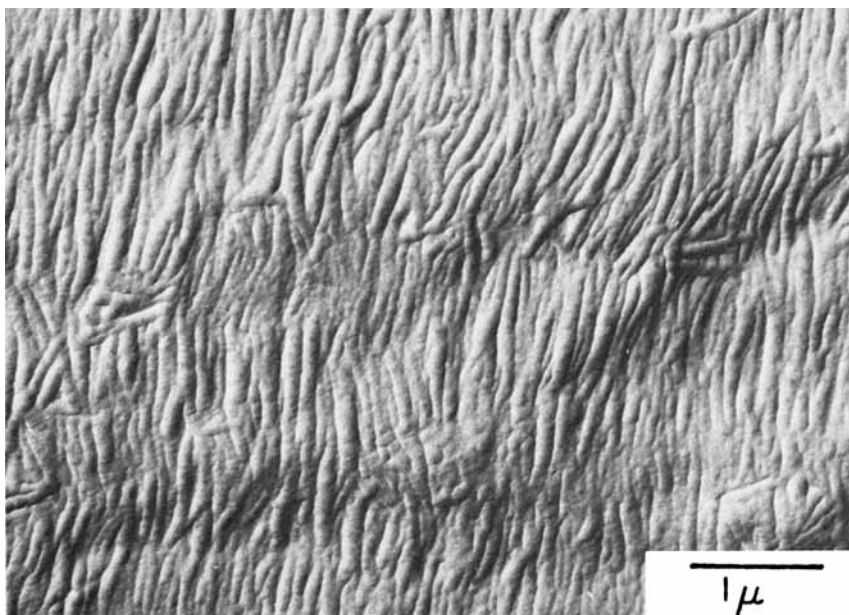
Fig. 11. Electron micrograph of surface of poly(oxymethylene) exposed to plasma of mixture of N_2 and styrene (80/20, total pressure 100 μ Hg) at 100 watts for 10 min. Weight change: $+0.65$ mg/40 cm².
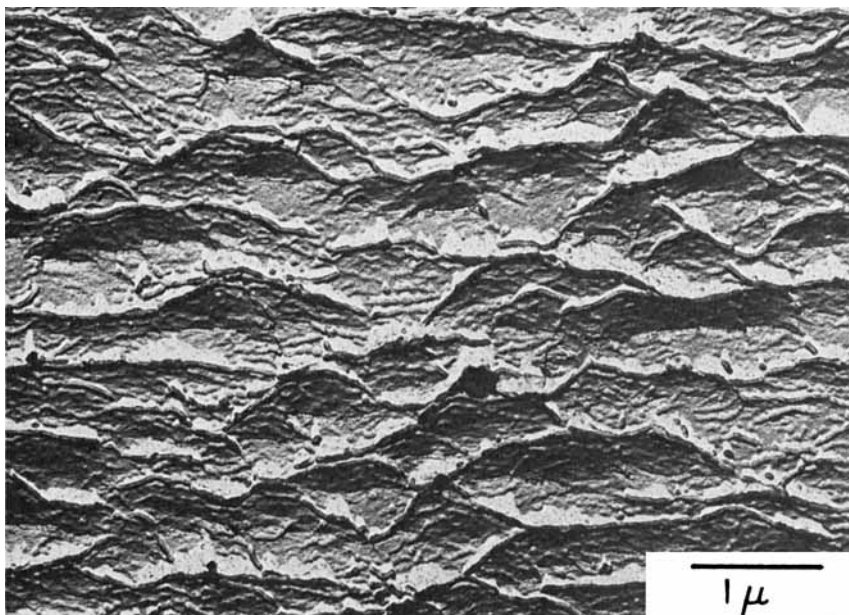

Fig. 12. Electron micrograph of surface of poly(oxymethylene) exposed to plasma of mixture of He and styrene (80/20, total pressure 100 μ Hg) at 100 watts for 10 min. Weight change: -3.3 mg/40 cm².

TABLE II
Plasma Susceptibility of Polymers Measured by the Rate
of Weight Loss in Helium Plasma

Polymer	Weight loss rate,[a] (mg cm^{-2} min^{-1}) × 10^3
Poly(oxymethylene)	17.0
Poly(acrylic acid)	16.2
Poly(methacrylic acid)	15.4
Poly(vinylpyrrolidone)	11.9
Poly(vinyl alcohol)	9.4
Poly(ethylene terephthalate)	1.7
Polyethylene	1.2
Nylon 6	1.1
Polypropylene	0.8

[a] He plasma (100 μ Hg) at 30 watts.

charge (30 watts) power was practically identical to the rate of polymer deposition onto a glass slide from monomer styrene. However, at higher discharge wattage, no weight change was observed despite the fact that there was obvious polymer deposition on the surface of the poly(oxymethylene) sample. With the addition of He, weight losses were observed at both levels of wattage. This indicates that the deposition of polymer is not enough to shield the underlying polymer from plasma degradation if high-discharge power and/or He is employed.

Notable changes in morphology of surfaces due to type of gas (i.e., nitrogen and helium), plasma of styrene (polymer deposition), and the level of discharge power can be seen in the electron micrographs shown in Figures 5 through 12. The difference between the effects of nitrogen and helium used as gas alone and also with styrene vapor is more pronounced in the morphology of the surface than in the rates of weight change. All samples were exposed to plasma for 10 min and weight changes per 40 cm^2 surface were observed after the plasma exposures cited in the figures. The morphology of the plasma-treated surface (e.g., Figs. 7 and 8) is considerably different from that of nontreated and of annealed (but not treated) samples (Figs. 5 and 6, respectively). Although annealing due to the heat effect of plasma treatment would play a role, particularly with polymers which have relatively low melting points, in the morphologic change accompanied by the plasma treatment the effect due to plasma degradation seems to overwhelm other effects with highly plasma-susceptible polymers such as poly(oxymethylene).

These differences in the morphology of plasma-treated surfaces would play a significant role in the improvement of bonding characteristics of the surface, although it is beyond the scope of this study.

With many polymers which have much lower plasma susceptibility than poly(oxymethylene), the degradation of substrate polymer might be negligible, particularly in plasma of polymerizable organic vapors. Never-

theless, these results indicate the possibility of degradation of substrate polymer when polymer is deposited from monomer plasma, and provide a useful guideline in selecting polymeric materials to be used as substrate for the plasma coating and types of gases to be used.

The plasma susceptibility of polymers is summarized in Table II as the rate of weight loss of polymer exposed to helium plasma (100 μ Hg) at 30 watts. These trends found with degradation (as manifested by observed weight loss) by plasma seem to coincide with trends found in decomposition of organic vapors in plasma, of which details are presented in reference 10. Namely, the structures which are plasma susceptible are oxygen-containing groups, particularly those attached to an aliphatic chain, and the decomposition is highly dependent on the discharge power.

Crosslinking

The crosslinking effect of plasma treatment on butadiene copolymers seems to depend on the chemical nature of the comonomer, perhaps depending on the plasma susceptibility of the comonomer unit. A major difference can be observed in the depth of the crosslinked layer. With AA–BD and MA–BD copolymers, the crosslinking seems to be limited to a very thin layer at the surface. With low-dose treatment, samples of these polymers are dissolved in the solvent, and the films completely disappear. At a certain level of plasma treatment, a thin layer of the surface remains without being dissolved, but the thickness of the crosslinked layer does not increase with further treatment.
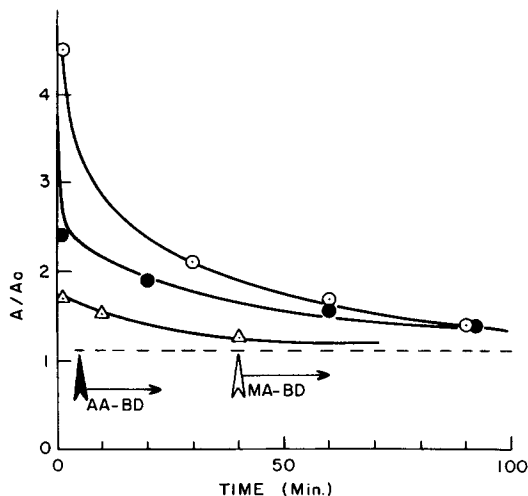

Fig. 13. Areal swelling ratio of plasma treated polymers as a function of plasma treatment time; He plasma, 150 μ Hg, 10 watts: (O) for styrene–butadiene (16% butadiene) copolymer; (●) for styrene–butadiene (24% butadiene) copolymer; (△) for 4-vinylpyridine–butadiene (20% butadiene) copolymer.

Fig. 14. Areal swelling ratio of plasma treated polymers as a function of plasma treatment time; He plasma, 150 μ Hg, 80 watts: (O) for styrene–butadiene (16% butadiene) copolymer; (●) for styrene–butadiene (24% butadiene) copolymer; (△) for 4-vinyl-pyridine–butadiene (20% butadiene) copolymer.
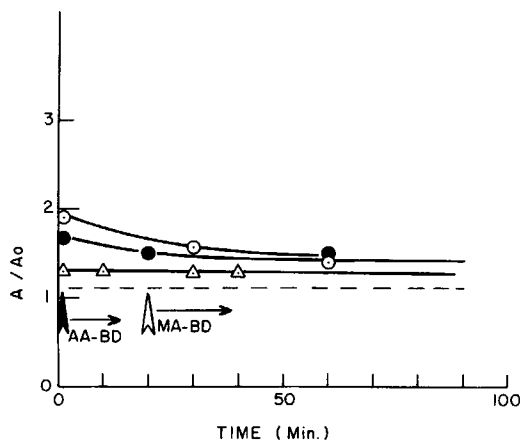
The crosslinking effect of plasma on ST–BD copolymer is quite different from that observed with AA–BD or MA–BD, and the thickness of the crosslinked layer increases with increasing exposure time.   VP–BD copolymers show an increase in thickness but not as evident as for the ST–BD copolymer.   With these samples, it is possible to measure the areal swelling ratio as a function of treatment time.   The results are shown in Figures 13 and 14.   The arrows shown in these figures indicate the time treatment (critical treatment time) necessary to produce visible self-supporting film when the treated MA–BD and AA–BD samples were immersed in the solvent from which the original films were cast.

The efficiency of crosslinking is proportional to butadiene (double bond) content, and the extent of crosslinking introduction is accelerated bv increasing the wattage of the plasma.   By increasing the wattage of the plasma, the critical treatment time decreases and the areal swelling decreases quickly to the limiting value.

It is interesting to note that the increase in thickness of the crosslinked layer (in the case of ST–BD polymer) occurs much later after the decrease in areal swelling becomes obvious, as shown in Figure 15.   The data shown in this figure were obtained with 150 watts discharge power.   At this wattage, the areal swelling practically reached the limiting value within a very short treatment time (1 min), yet the change of thickness is observed in the time scale of 30–60 min of the treatment.

The apparent maximum in thickness in Figure 15 can be explained by the increase in thickness (in dry state) and crosslinking density in the crosslinked layer, since the thickness is measured in the solvent.   The increase in crosslinked layer (in dry state) tends to increase the total swollen thickness, but the increase in crosslinking density tends to decrease the swelling
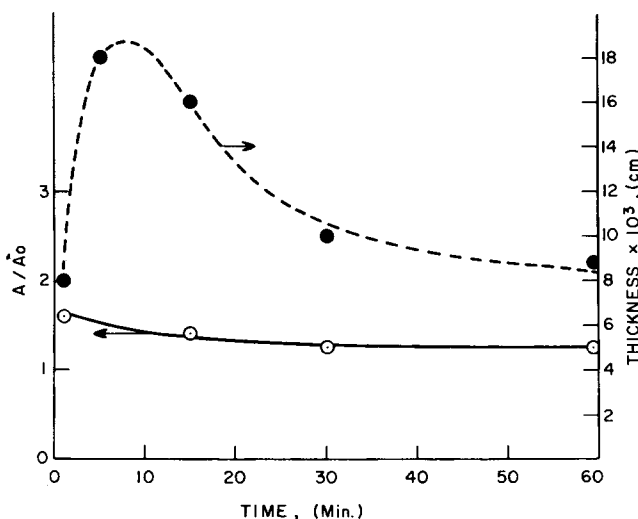
Fig. 15. Areal swelling ratio and the thickness of swollen crosslinked layer of plasma-treated copolymer of styrene–butadiene (16% butadiene) as a function of treatment time. He plasma 150 μ Hg, 150 watts.

(from dry state). These two opposing effects lead to the apparent maximum in the plot of thickness versus treatment time.

Since the increase in thickness occurs after areal swelling has reached the limiting value, it indicates that the crosslinking by plasma occurs only at the interface and, only in some special polymers, the propagation of cross-linking in the direction of thickness occurs as a secondary effect.

CONCLUSIONS

The effect of plasma on polymers, except plasma of oxygen which undoubtedly causes oxidative degradation and further oxidation of degraded components, may be summarized as follows:

The predominant effect with many polymers seems to be degradation, which leads to weight loss.

This effect is quite severe at the surface, though the effect is confined to the exposed surface.

The plasma susceptibility of polymers resembles that of low molecular weight organic compounds in plasma and depends on the type of gas used in the plasma. Polymers which contain ether, carbonyl, and hydroxyl, particularly those attached to aliphatic chains, have high plasma susceptibility.

Degradation of relatively low plasma-susceptible polymers is nearly independent of wattage. Degradation of plasma-susceptible polymers depends on the wattage of the plasma.

In plasma of organic vapor, the deposition of polymer seems to have an overwhelming effect on degradation. The deposition of polymer, how-

ever, does not always shield the polymer from degradation if the polymer has high plasma susceptibility and/or if high wattage was employed.

The morphology of plasma-treated sample is highly dependent on the type of gas, on the wattage, and on the plasma susceptibility of the polymer.

The crosslinking by the plasma seems to be rather marginal unless the polymer has low plasma susceptibility and/or high capability to crosslink.

With crosslinkable polymers, the crosslinking is highly dependent on the wattage and the number of crosslinkable double bonds.

With polymers of low plasma susceptibility, particularly with polymers that contain crosslinkable double bonds and aromatic structures, the crosslinking effect seems to extend into the bulk of the polymer sample depending on the wattage and treatment time.

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