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Effects of Gas Plasma Treatments on Surface Properties of Commercial Polymer Films

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Surface properties of various commercial polymer films have been studied before and after a brief exposure to low-temperature gas plasmas. The surface properties investigated include wettability by water and how well vapor-deposited aluminum adhered to the polymer surface. Excellent adhesion of aluminum was found for polymers that had been exposed to the gas plasma.

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SUMMARY

Surface properties of a number of commercial thermoplastic polymer films were investigated before and after brief exposures to rf-induced, low-temperature gas plasmas. Water wettability and adhesion of vapor-deposited aluminum to thin films (8-12 microns) of polyethylene, polypropylene, polyester, polysulfone, polycarbonate, and polyvinylidene fluoride films were studied before and after treatments with with oxygen, 96%CF_4/4%O_2, and helium plasmas. Treatment with oxygen plasmas showed the greatest change in water wettability for polyvinylidene fluoride and polypropylene films, whereas treatment with 96%CF_4/4%O_2 showed dramatic changes in wettability of polycarbonate, polysulfone, and polystyrene. Excellent adhesion of aluminum was found for polymers that had been previously exposed to gas plasmas.

INTRODUCTION

Treating polymer surfaces with low-temperature, low-pressure, rf-induced gas plasmas can modify their adhesion and wetting characteristics. The effect of reactive gas plasma treatment on materials has been summarized in an excellent review article by Liston.[1] Recently, gas plasmas have been used to modify surfaces of fluoropolymers[2] and other commercial polymers.[3]

This note summarizes our study of the wettability and adhesion of vapor-deposited aluminum to commercially available thin polymer films that have been briefly exposed to gas plasma.

EXPERIMENTAL

The following polymers were studied: polyethylene, polypropylene, polyester, polysulfone, polycarbonate, and polyvinylidene fluoride. In terms of ease of handling in cutting these samples, relative static (films adhering to each other and to plastic gloves) for the above-mentioned films could be ranked in the following order, with polysulfone having the most static and polystyrene the least static: polysulfone > polycarbonate = polyvinylidene fluoride > polyester > polypropylene > polystyrene.

Coupons that were approximately 7.5 cm X 10 cm and 8-12 microns thick were treated in a Branson/IPC (Fort Washington, PA) Model 7104 plasma etcher for four minutes at 250 watts, with a gas pressure of 150 torr and a gas flow rate of 0.3 mil/min.

Based on the chamber volume, the power density was 0.002 watt/ cm^3. We studied three separate gas plasmas: oxygen, helium, and a mixture of 90% CF_4/4% O_2. Following the various plasma treatments, a Rame-Hart telescopic goniometer was used to measure the static contact angle made by a water drop on the various film surfaces. Samples were then taped to a polyethylene carrier and metallized rapidly with approximately 100 to 150 Å of aluminum in a commercial metallizer. Elapsed time between the plasma treatments and aluminum deposition was approximately one month. Adhesion of aluminum was determined qualitatively by applying a piece of adhesive tape (Scotch 810) to the metallized polymer surface, removing the tape, and observing how much aluminum was removed from the film.

RESULTS AND DISCUSSIONS

a. Water Wettability

The contact angle between the edge of a drop of water and a film surface reflects the wettability of the film surface by water. Contact angle measurements are a simple method for determining the hydrophobic or hydrophilic nature of attached chemical groups on surfaces. Liquids similar in composition to chemical groups on the film wet the surface well, and they make smaller contact angles with the surface than liquids containing dissimilar groups. The contact angle of water with typical hydrophobic surfaces is approximately 65 to 95 degrees.

Table 1 summarizes our experimental results on wettability and adhesion of the various polymers following treatment with oxygen, helium, and CF_4/O_2. For each polymer and treatment procedure, the contact angle in degrees is listed on the left of the line; on the right side, the relative adhesion of aluminum to the sample is listed as either A, B, or C. The contact angle of water decreased following plasma treatments. Following plasma treament, the observed decrease in contact angle for all samples indicated that the polymer surfaces had become more receptive to water, i.e., improved wettability.

Helium treatment had the least effect on the contact angle of any of the polymers, with the exception of polyester. Oxygen plasma treatment had the greatest effect in the reduction of the contact angle for polyvinylidene fluoride and polypropylene; but CF_4/O_2 plasma treatment had the greatest effect in reducing the contact angle for polycarbonate, polysulfone, and polystyrene.

Table 1. Contact angle of water (in degrees) and relative adhesion of vapor-deposited aluminum (described as either A, B, or C) to surfaces of selected polymer films that have been exposed to various plasma treatments. For each polymer and treatment procedure, the contact angle is listed on the left and the relative adhesion of aluminum is listed on the right.

Polymer	Contact Angle/Adhesion of Aluminum			
	Untreated	O_2	CF_4/O_2	He
Polycarbonate	72/B	39/A	<15/A	37/A
Polysulfone	70/A	25/A	<15/A	26/A
Polyester	66/C	29/A	30/A	29/A
PVDF	71/C	40/A	70/A	57/A
Polypropylene	98/C	40/A	72/A	53/A
Polyethylene	90/C	-/-	20/A	50/A
Polystyrene	83/B	15/-	<15/-	26/-

A = excellent adhesion

B = good adhesion

C = poor adhesion

b. Adhesion

It is readily apparent from Table 1 that aluminum adhesion to polycarbonate, polyester, polyvinylidene fluoride, polyethylene, and polypropylene improves substantially after the surfaces have been exposed briefly to gas plasma. In fact, tested polymer samples exposed to <u>any</u> of the three plasmas had excellent adhesion of aluminum. Since one month had elapsed between the time that these polymers had been exposed to the gas plasmas and the time that they were metallized, the effects of plasma treatment are apparently retained, even after being exposed to air for one month.

Improved adhesion of aluminum to the various polymer surfaces and the reduced contact angles of water on the polymer surfaces following plasma treatments may be due to removal of impurity layers from the polymer surface, thus allowing better wettability and aluminum adhesion. This possibility, however, does not account for the variations in contact angle observed after exposure of the polymers to the different plasmas. A more likely possibility is that exposure to gas plasma forms reactive groups on the polymer surface which, upon subsequent exposure to oxygen in the atmosphere, may allow covalent oxygen bonds to be formed. During metallization, the aluminum can react with these oxygen groups to form strong bonds. In fact, formation of aluminum-oxygen-polymer complexes at surfaces of aluminum vapor-coated, oxygen plasma-treated polymers has been noted as improving adhesion between the metal and the polymer.[1] Since these oxygen complexes would be formed after exposure of plasma-treated polymers to air, the type of oxygen groups formed on the polymer surface should be similar, regardless of which gas plasma was studied. Perhaps this would explain why there was no apparent difference in adhesion of aluminum to polymer samples exposed to O_2, CF_4/O_2, or He plasmas. For all of the polymers studied, exposure to any of the three gas plasmas produced excellent aluminum adhesion.

The exact amount of treatment required for maximum adhesion for a given polymer can, perhaps, be further optimized by varying the power density, temperature, and total time in the plasma environment.

CONCLUSIONS

Brief exposure of various thermopolymers to a gas plasma dramatically enhances the water wettability and the subsequent adhesion of vapor-deposited-aluminum to the polymer surface.

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