Adhesion of Plasma Polymer Films to Metal Substrates

INTRODUCTION

A study of the bonding of thin plasma polymer films to polymeric substrates has been reported recently.[1] Regardless of the nature of the polymer (polystyrene or polyacrylonitrile), the adhesion as measured by a Scotch tape peel test was shown to be a function of the chemical structure of the substrate and not of the plasma polymer. Additionally, exposure of such bonds to various solvents (water, dimethyl formamide, hexane, or polyethylene glycol E200) for periods up to 120 hr resulted in no deterioration of the bond strength of such films to the substrates. It was, therefore, concluded that when adhesion occurs, a chemical bond is probably formed.

Deposition of plasma polymer films on metals has been described.[2,3] Adhesion to FPL-etched aluminum has been reported to be very good.[3] In this note, the bonding of such films to a variety of untreated metal surfaces is described.

EXPERIMENTAL

Substrates were sandblasted, sanded with silicon carbide paper (through 600 grit), hand polished with a soft cloth and metal polish for 20 min, ultrasonically cleaned for 10 min in detergent solution, then ultrasonically cleaned for 10 min in methylene chloride, rinsed with acetone, and blown dry with nitrogen. Wettability of the metal surfaces was determined by measuring the advancing contact angle of sessile drops at 24°C with an NRL goniometer (Rame-Hart, Inc.). The test liquids used and the procedures followed have been detailed previously.[4] This method allows us to determine the polar (γ^P) and dispersion (γ^D) contributions to the overall surface energy $\gamma = \gamma^P + \gamma^D$. The results obtained are presented in Table I. Film deposition was via the procedure described in reference 5. Briefly, this involves the polymerization of a monomer gas (acrylonitrile or styrene) in the afterglow region of an LFE PDS-302 electrodeless rf glow-discharge apparatus. Monomer pressure of 10 μm and 10 W power provides deposition rates on the metal substrates of 14 and 20 Å/min for the respective monomers. Adhesion was measured by a 90° peel test with Scotch tape in the plasma film.

RESULTS AND DISCUSSION

From the adhesion tests (Table II), it can be seen that, for metals unlike polymeric substrates, adhesion of plasma polymer is a function of both the nature of the substrate and the polymer film. Adhesion of polyacrylonitrile to steel and aluminum may be due to the more polar character of plasma polymerized polyacrylonitrile ($\gamma^P = 45$, $\gamma^D = 18$) as compared to polystyrene ($\gamma^P = 5$, $\gamma^D = 37$).

For those polymers to which the films adhered, samples were soaked in water at ambient for 1 hr (Table III). For the more-polar substrates (aluminum, steel, and titanium), film adhesion failed probably due to intrusion of water at the metal-film interface. (Retention of adhesion of both films on copper is probably the result of the highly hydrophobic character of the metal and the inability

TABLE I
Surface Energetics of Metals

	γ^P	γ^D	γ
Titanium	39	25	64
Nickel	10	29	39
Copper	27	27	54
Aluminum	38	25	63
Steel	25	26	51

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TABLE II
Adhesion of Plasma Films to Metal Substrates

Metal	Polyacrylonitrile	Polystyrene
Aluminum	Adheres	Does not adhere
Steel	Adheres	Does not adhere
Nickel	Adheres	Adheres partially
Copper	Adheres	Adheres
Titanium	Adheres partially	Does not adhere

TABLE III
Adhesion of Plasma Films to Metal Substrates After 1 hr Water Soak

Metal	Polyacrylonitrile	Polystyrene
Aluminum	Does not adhere	—
Steel	Does not adhere	—
Nickel	Adheres partially	Does not adhere
Copper	Adheres	Adheres
Titanium	Does not adhere	—

of water to displace the adhesive at this hostile interface.) The failure of the surface energetics analysis (Table I) to confirm this conclusion may be due to the plasma acting as a means for cleaning the metal surface prior to film deposition. If so, the data in Table I do not represent the true surface energetics at the time of film deposition.

This report is a portion of a review article covering our work.[6]

References

1. L. W. Crane and C. L. Hamermesh, "Adhesion of Thin Plasma Polymer Films to Plastics," presented at Symposium on Adhesion Measurement of Thin Film, Thick Film, and Bulk Coatings, American Society for Testing of Materials, Philadelphia, November 1976.

2. M. R. Wertheimer and H. P. Schreiber, *Am. Chem. Soc. Coat. Plast., Prepr.*, **37**(1), 401 (1977).

3. P. J. Dynes and D. H. Kaelble, *J. Nonomol. Sci.*, **A-10**, 535 (1976).

4. T. R. Hollahan and T. Wydeven, *Science*, **179**, 500 (1973).

5. C. L. Hamermesh and P. J. Dynes, *J. Polym. Sci. Lett.*, **13**, 663 (1975).

6. T. Smith, D. H. Kaelble, and C. L. Hamermesh, "Mechanism of Plasma Polymerization," presented at International Symposium on Surface Properties, University of Missouri at Rolla, August, 1977.

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