Wettability of Glow Discharge Polymers

ASHOK K. SHARMA,* FRANK MILLICH, and ECKHARD W. HELLMUTH, *Polymer Division, Department of Chemistry, University of Missouri–Kansas City, Kansas City, Missouri 64110*

Synopsis

Treatment of good adhering glow discharge polymerized propylene (GDPP) coatings with reactive gas plasma from oxygen, nitrogen, or water (produced in a tubular reactor operation at 27.1 MHz) results in surfaces characterized by more hydrophilic interactions. Zisman's plots indicate a change in surface energy after such treatment. Transmission electron microscopy depicts that the pronounced improvement in wettability of GDPP polymer after oxygen plasma treatment in part results from the high surface development in the polymer. However, the effect is not permanent. The wettability of plasma-treated polymer diminishes with time and reaches a limiting value in 2–3 months indicating structural rearrangements at the polymer surface. Argon, carbon monoxide, or bromotrichloromethane plasma does not change the polymer surface wettability significantly. In contrast to the O_2 plasma-treated GDPP polymer, a glow discharged polymer synthesized from ϵ-caprolactam maintains its inherent hydrophilicily over an extended period of time.

INTRODUCTION

Surface modification of conventional polymers by treatment with nonpolymer forming gas plasma (such as from Ar, He, N_2, O_2, etc.) has gained great importance in the last few years. The resulting polymers are generally more hydrophilic[1–3] and show improved adhesive bonding to metals and polymers.[4–8] ESCA studies indicate incorporation of oxygen functionalities after such treatment.[9–12] The use of gas plasmas for surface modification of glow discharge polymer has been less common.[13,14] In the past,[15] we reported improvement in wettability of glow discharge polymerized propylene (GDPP) polymer by oxygen plasma treatment. Oxygen was preferred because oxygen plasmas are well characterized.[15–20] In the present study, detailed investigations of the oxygen plasma treatment of good adhering glow discharge polymerized propylene coatings have been conducted. Other gas plasmas such as from N_2, Ar, CO, H_2O, and $BrCCl_3$ vapors have been explored. A novel hydrophilic glow discharge polymer from ϵ-caprolactam is also discussed.

EXPERIMENTAL

The glow discharge reactor and the method of polymer synthesis has been described elsewhere.[21] An inductively coupled tubular glass reactor operating at a radio frequency (RF) of 27.12 MHz was employed. The freshly deposited polymer coatings were treated with O_2, N_2, Ar, CO, H_2O, or $BrCCl_3$ vapor plasma without exposure to the air. The plasma treatment was conducted in a fashion similar to argon etching used for substrate preparation prior to polymer depo-

* Present address: Graduate Center for Materials Research, University of Missouri–Rolla, Rolla, MO 65401.

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sition. The gas was supplied through the monomer mixing system. Only coatings with good adhesion can be studied for plasma modification.

The contact angle between a liquid and polymer surface which provides a measure of the wettability of the surface was determined by a technique similar to the ASTM standard D724-45 (1971). A drop of the test liquid (deionized H_2O–CH_3OH mixtures, ethylene glycol, formamide, or glycerine) was deposited on the conditioned (RH 52 ± 1%) test specimen placed on a jack stand. A hypodermic syringe capable of providing 80 drop/ml or disposable transfer pipets (40 drops/ml) were conveniently used for this purpose. The drop was illuminated from the top with a microscope lamp. The contact angle formed by the drop was measured by a microscope goniometer developed for this purpose and described earlier.[15] The drop size was successively increased until a constant contract angle was produced. Several readings were taken; each time a new drop was placed at a different site on the specimen and the average value reported. This method gave a value of 107° for the contact angle of H_2O on polytetrafluoroethylene film which is fairly close to the value (108°) reported in the literature.[22] Critical surface tensions were obtained from Zisman's plots.[23]

RESULTS AND DISCUSSION

The contact angle of H_2O on oxygen-etched film was 20–48° depending on the conditions of plasma treatment in contrast to the 92 ± 4° for the untreated propylene glow discharge polymer. Variation in plasma exposure time from 2 to 20 min did not change the contact angle significantly. Similarly, a change in O_2 flow rate had little effect on the magnitude of contact angle, although the polymer etching rate was changed. The latter passed through a maximum at 310 μmole min^{-1} with an increase in oxygen flow rate. An increasing RF power decreased the contact angle, improved the wettability, and increased the rate of polymer etching.

The results of contact angle measurement with CH_3OH–H_2O mixtures and the pure solvents or a propylene glow discharge polymer deposited on a glass substrate (condition of polymerization: monomer flow rate 326 μmole min^{-1}, polymerization time 30 min, substrate position (60 mm from electrode) before and after 3 min of oxygen plasma etching (oxygen pressure, 40 mtorr, power setting 175 mA) are given as Zisman's plot in Figure 1. This plot allows extrapolation to zero contact angle ($\cos \theta = 1$) to give the critical surface tension of the solid surface. Any liquid with surface tension equal to or less than the critical surface tension of solid surface will form a zero contact angle. The measurements were made immediately after the plasma treatment. The results for untreated GDPP film (curve A) extrapolate to a value of 23×10^{-3} N/m for the critical surface tension. Zisman has listed a range of 20–24 $\times 10^{-3}$ N/m, for a surface having a monolayer of methyl groups.[24] The results for the oxygen-etched film surface are indicated by curve B. A much reduced contact angle is observed with each of the liquids for the oxygen-etched surface; the critical surface tension of the solid on extrapolation gives a value of 58×10^{-3} N/m which corresponds to a polymer surface having unsaturation or a high concentration of carbon–oxygen chemical bonds.[25] This is not surprising; ESCA studies of oxygen-etched conventional polymer surfaces has shown that oxygen is incorporated into the film surface after such treatment.[9–12] However, the infrared

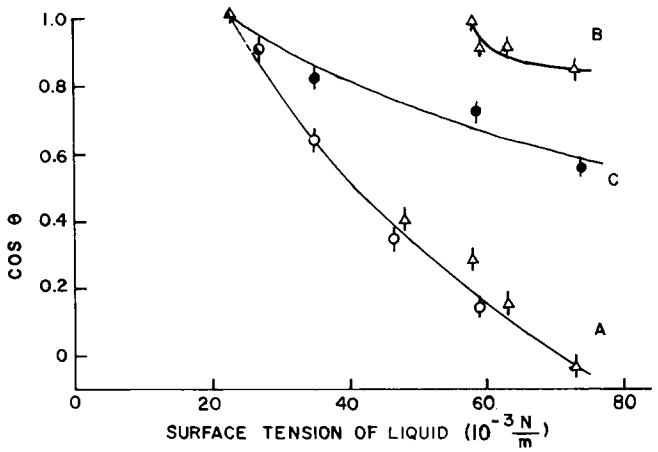

Fig. 1. Cosine of contact angle θ vs. surface tension of liquids (○) H_3OH–H_2O; (△) pure polar compounds for: (A) freshly obtained glow discharge polymerized propylene coating on glass (polymerization time, 30 min; monomer flow rate, 320 μmole min^{-1}; substrate position, 60 mm from RF coil); (B) polymer immediately after 3 min of oxygen plasma etching at an oxygen pressure of 40 mtorr; and (C) one-month old O_2 etched polymer.

spectra of the polymer collected from sleeve 2 (−45 to +155 mm from electrodes), of the reactor (which in the course of experiments was exposed several times to propylene and oxygen plasma) failed to show quantitative changes in the chemical composition of the surface layer. Elemental analysis performed on this polymer gave a C:H:O ratio of 1:1.59:0.06, which was the same as that of the untreated polymer.

The effect of oxygen plasma treatment is, however, not durable. Curve C in Figure 1 represents the behavior of oxygen-etched polymer surface after aging in air for over one month. An increased contact angle (compared to the freshly etched polymer) is observed with each of the liquids, and the critical surface tension now has a much lower value of 22.5×10^{-3} N/m indicating that the surface is predominantly comprised of methyl groups. Figure 2 shows the variation in the contact angle of an etched polymer (aged at 52 ± 1% RH) with water as a function of time. A saturation value of 65 ± 5° is reached after a period of two to three months. High discharge power and the longer etching time gave the most durable effect.

In order to investigate the effect of gas type on surface wettability, a series of discharges in various gases were conducted keeping polymerization and other etching parameters constant in each experiment. The degree of modification in each case was determined by measuring the contact angle of water immediately after the treatment. The results are shown in Table I along with the etching rate of different gas plasmas. Oxygen and water produced the most wettable surfaces and have the highest etching rates (200 ± 40 Å/min at the conditions listed in Table I) followed by nitrogen and carbon monoxide. Bromotrichloromethane was practically ineffective in improving the hydrophilicity of the polymer, although the color of the polymer film changed from almost colorless to deep yellow after treatment. The negative etching rate of $BrCCl_3$ results from the reaction of polymer with the active halogen species created in plasma.

It was noticed that the pressure in the reactor increased (from 44 → 70 mtorr) during treatment with O_2 and H_2O plasmas. This was probably due to the for-

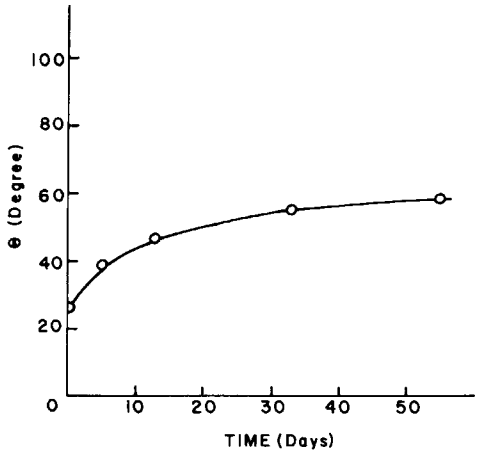

Fig. 2. Variation in contact angle of oxygen plasma etched glow discharge polymerized propylene coating on glass substrate with H_2O vs. aging of polymer at 52 ± 1% RH. (Polymerization time, 2 hr; monomer flow rate, 340 μmole min^{-1}; substrate position, center of RF coil; oxygen pressure, 40 mtorr; etching time, 5 min.)

mation of atomic oxygen in the discharge, which is very reactive and converts the solid polymer into gaseous products (by breaking bonds) besides making it hydrophilic.

Investigation of the oxygen plasma treated polymer surface by transmission electron microscopy[24] showed differences in the surface structure of the polymer (compared to the untreated one). The electron micrographs in Figure 3 show the surfaces of (A) an untreated polymer (obtained at a monomer flow rate of 326 mole/min., at the center of the RF coil and 30 min discharge time) and (B) the polymer etched with oxygen for 3 min (propylene flow rate 340 mole min^{-1}, time 50 min, center position, oxygen pressure 40 mtorr). The surface of polymer treated with oxygen plasma developed microroughness, which is absent at the untreated polymer surface. It is known that the wettability of the polymer depends on the surface roughness.[26,27] The pronounced improvement in the wettability of the GDPP polymer may be associated with changes in the surface structure. Morphological study of the oxygen-etched polymer surfaces is, however, complicated by the fact that it is sometimes difficult to obtain replicas of the surface because the replicating material adheres very tightly to these surfaces.

TABLE I
Wettability as a Function of Gas Type

Etching gas[a]	Contact angle with water, ±4°	Etching rate, Å (±40 Å/min)
Oxygen	32°	200
Nitrogen	50°	0
Water	31°	200
Argon	75°	20
Carbonmonoxide	69°	
Bromotrichloromethane	91°	−100
Control[b]	92°	

[a] Etching time: 5 min, etching gas pressure: 40 ± 2 mtorr.
[b] Monomer flow rate: 270 ± 15 μmole min^{-1}; polymerization time: 2 hr.

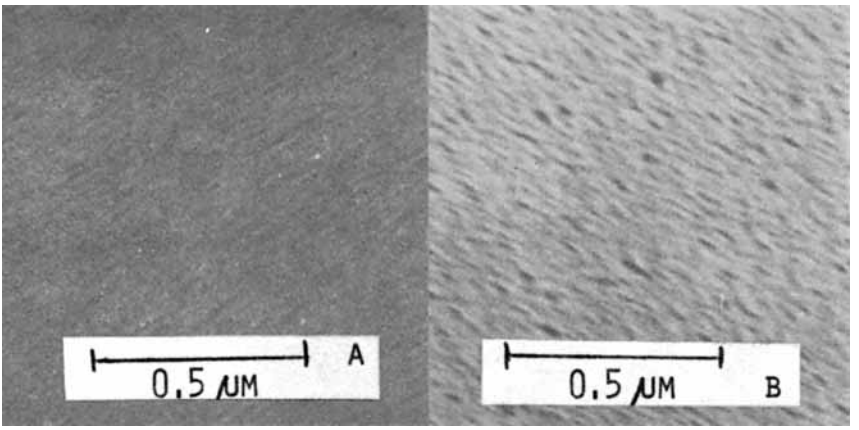

Fig. 3. Transmission electron micrograph of glow discharge polymerized propylene: (A) obtained at a monomer flow rate of 386 μmole min^{-1} (60350×) without oxygen etching; (B) after oxygen plasma etching for 3 min at oxygen pressure of 40 mtorr (61200×).

The reason for the drift in surface wettability values for the oxygen plasma etched GDPP polymer is not clear. The microroughness created by oxygen plasma treatment should stay constant with time. An explanation based on the formation of oxygen functional groups after oxygen plasma treatment[9–12] does not seem to be adequate because the concentration of such groups in plasma-formed polymers is known to increase with time. However, it is possible that the oxygen functionalities produced at the polymer surface by oxygen plasma treatment slowly gets embedded in the bulk of the polymer and those produced by interaction with atmospheric air are not all available at the polymer surface. The latter view is supported by the fact that inspite of rather high concentration of radical sites available in glow discharge polymers, the oxygen uptake is quite slow and continues over an extended period of time.[21] The interaction of freshly oxygen-etched GDPP polymer with $1.66 \times 10^{-5}M$ solution of 1.1 diphenylpicryl hydrazyl reagent in benzene and aging of the oxygen-etched polymer at 52 ± 1% RH showed no significant differences from the untreated polymer which suggest that the concentration of free-radical sites produced by oxygen plasma treatment are not significant and may not play an important role in the improvement of wettability.

In contrast to the oxygen-etched glow discharge polymerized propylene polymer the wettability of glow discharge polymerized ϵ-caprolactam[21] stayed constant over a period of 54 days (contact angle with H_2O, 56 ± 4°). Zisman's plot gave a critical surface tension of 43×10^{-3} N/m for such a surface which is close to that observed for conventional nylon 66 polymer (46×10^{-3} N/m).[23] The presence of argon in the glow discharge reduced the wettability of the polymer and gave a critical surface tension value of 32×10^{-3} N/m for this polymer.

In conclusion, the wettability of glow discharge polymerized propylene, similar to that of conventional polymers, can be improved by selective gas plasma treatment. Increase in microroughness and polar functionalities by plasma treatment, or both, may play an important role in polymer hydrophilicity although the latter is a more logical choice.

References

1. A. M. Wrobel, M. Kryszewski, W. Rakowski, M. Okoniewski, and Z. Kubackl, *Polymer*, **19,** 908 (1978).

2. V. G. Tobakarev, V. I. Grinewich, A. I. Maksimov, and V. V. Rybkin, *Tzv. Vyssh. Uchebn, Zaved, Khlm. Tekhnol.*, **22**(2), 184 (1979).

3. T. Tsunoda, K. Chiba, and M. Eukumura, *Kobunshi Ronbunshv*, **35**(4), 223 (1978).

4. Y. V. Lupin, L. S. Myakisheva, and M. A. Shulman, *Mekh. Polim.*, **2,** 365 (1978).

5. T. A. Rudik, A. A. Trofimova, D. I. Sharfutdinova, and N. V. Sibriyakova, *Plast. Massy*, **1,** 58 (1979).

6. Y. M. Podgorny, M. A. Shulman, and P. Auzans, *Plast. Massy*, **1,** 56 (1979).

7. J. Janaka and L. Ambroz, *Folia Fac. Sci. Nat. Univ. Purkynianae Brun.*, **18**(3), 57 (1977).

8. Y. Takei and H. Tomaki, *Jpn. Kokai Tokyo Koho*, **78,** 129, 262 (1978).

9. A. R. Bylthe, D. Briggs, G. R. Kendall, D. G. Rance, and V. J. I. Zichy, *Polymer*, **19**(11), 1273 (1978).

10. H. Yasuda, H. C. Marsh, S. Brandt, and C. N. Reilley, *J. Polym. Sci., Polym. Chem. Ed.*, **15,** 991 (1977).

11. D. T. Clark and A. Dilks, in *Characterization of Metal and Polymer Surfaces*, Vol. 2, L. H. Lee, Ed., Academic, New York, 1977, p. 86.

12. M. M. Milard, in *Characterization of Metal and Polymer Surfaces*, Vol. 2, L. H. Lee, Ed., Academic, New York, 1977, p. 86.

13. H. Yasuda, *J. Macromol. Sci., Chem.*, **A10**(3), 383 (1976).

14. G. D. Sasho, *J. Macromol. Sci., Chem.*, **10,** 559 (1976).

15. A. K. Sharma, F. Millich, and E. W. Hellmuth, *J. Appl. Phys.*, **49**(10), 5055 (1978).

16. R. H. Hansen, J. V. Pascale, T. Debenedicks, and P. M. Rentzebis, *J. Polym. Sci. Part* A **3,** 2205 (1976).

17. M. L. Kaplan, *Chemtech*, 620 (1971).

18. A. M. Trozzolo and F. H. Winslow, *Macromolecules*, **1,** 98 (1968).

19. J. T. Herron and H. L. Schiff, *Can. J. Chem.*, **36,** 1159 (1958).

20. D. D. Wagman, W. H. Evans, V. B. Parker, F. Hallow, S. M. Bailey, and R. H. Schumn, *Selected Values of Chemical and Thermodynamic Properties*, Nat. Bur. Stand., Tech. Note 270-3, Jan. 1961, U.S. Government Printing Office, Washington, DC 20402.

21. A. K. Sharma, F. Millich, and E. W. Hellmuth, in *Plasma Polymerization*, M. Shen and A. T. Bell, Eds., ACS Symp. Ser. 108 Am. Chem. Soc., Washington, DC, 1979.

22. W. A. Zisman, *Adv. Chem. Ser. No. 43*, Am. Chem. Soc., Washington, DC, 1964.

23. W. A. Zisman, in *Encyclopedia of Polymer Science and Technology*, Vol. 1, Wiley, New York, 1964, p. 454.

24. A. K. Sharma, F. Millich, E. W. Hellmuth, *J. Appl. Polym. Sci.*, **26,** 2197 (1981).

25. A. W. Adamson, *Physical Chemistry of Surfaces*, Interscience, New York, 1967, p. 352.

26. P. W. Adamson, *Physical Chemistry of Surfaces*, Wiley, New York, 1960, chaps. 5, 8.

27. A. Passerone, in *Science and Technology of Surface Coatings*, B. N. Chapman and J. C. Anderson, Eds., Academic, London, 1974, p. 198.

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