

Solvent- and Glow-Discharge-Induced Surface Wetting and Morphological Changes of Poly(ethylene Terephthalate) (PET)

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Synopsis

The effects of argon glow discharge and selected organic solvents on the surface wettability of poly(ethylene terephthalate) (PET) and on the wettability decay of glow discharged PET films were studied. Glow discharge in argon (30 W/1 min) drastically reduced the initial water contact angle (CA) measurement of PET from 67.0 to 26.2°. The glow-discharge-induced wetting, however, decayed during the first 7 days and stabilized at 33.1°. Treatments in dimethyl sulfoxide, dimethyl formamide, pyridine, and water at 80°C caused some improvement in surface wettability as shown by decreases of water CAs in the range of 53–56°. When the solvent and glow discharge treatments were applied consecutively on PET, additive effects on improving surface wettability were observed. The stabilized water CAs of the solvent-and-glow-discharged films ranged from 25.0 to 32.1° depending upon the solvent type. The solvent treatments prior to glow discharge either reduced the extent of CA decay or the time taken to reach stabilization on PET films. Scanning electron microscopic evaluation showed no difference between the solvent-treated and the untreated PET surfaces, but a finely etched surface was observed on the glow discharged PET at a 40,000 magnification and above. The distinctly different surface of the DMSO-and-glow-discharged PET indicated that morphological changes on PET surface were induced by the solvent.

INTRODUCTION

For any polymer, the surface may have very different characteristics than its bulk. Some of the differences have been explained by the fact that organic macromolecules have varying degrees of flexibility for chain movement and reorientation. The mobility of macromolecules has been shown to allow the surfaces of polymers to remain at their most stable forms, i.e., at their lowest energy levels. This has been observed in the migration of lower-energy component in polymer mixture^{1,2} and in copolymer³ and of low-energy additives^{4–6} in polymers to their surfaces. Because surface wettability relates directly to surface energy, more energetically stable surfaces result in less wettable surfaces.

Surface wettability has been related to crystallinity and density of polymers. For polyethylene single crystal aggregates, a high-density crystalline structure was found to be more wettable than a low density amorphous one.⁷

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Higher surface tensions were also correlated with increasing crystallinity and density on several commercial PET films.⁸ However, drawing of poly(ethylene terephthalate) (PET) filaments which increased both density and crystallinity rendered the surfaces less wettable.⁹ Though higher density and crystallinity in the bulk are recognized in all above cases, it remains unclear how the surface is affected by the increased order in the bulk.

Solvent-induced crystallization (SINC) on initially unoriented and amorphous PET occurs when certain strongly interactive solvents whose solubility parameters are close to those of amorphous PET were used.¹⁰⁻¹³ On amorphous PET, formation of crystallites and voids was evident in the bulk as well as on the surface of the substrates.^{14,15} Relatively little work has been reported on SINC of oriented and partially crystalline PET. Results of one study have shown that solvent diffusion and crystallization decreased with increasing orientation and crystallinity in the substrate.¹⁴ In contrast to the amorphous PET, the surface of highly drawn film remained smooth after solvent treatment.

A well-recognized and effective means of improving surface wettability of many polymers is low temperature plasma. The improved wettability has been attributed to the increasing amount of polar groups,^{6,16,17} surface oxidation,¹⁸ and increased surface roughness.^{19,20} Our previous work on glow discharging poly(ethylene terephthalate) (PET) in argon, air, and nitrogen showed that the acquired wettability decayed with time.²¹ This decay stabilizes after several days and the stabilized surface still retains much of its acquired wettability. The lowered wettability on the glow discharged PET surface was believed to be from the subsequent reactions of the residual free radicals with atmospheric compounds. This decay was also explained by others to be from the reorientation of the hydrophilic groups toward the bulk of the polymer^{21,22} and possible surface contamination.²²

This study was intended to investigate whether and how selected organic solvents influenced the surface wettability of semicrystalline PET. In addition, it was of interest to study the effect of organic solvents on stability of glow discharge modified PET surfaces. Selection of strong interacting organic solvents²³ and optimum conditions of glow discharge²¹ were based on the results of two prior studies.

EXPERIMENTAL

PET used in this study was Mylar films from Du Pont. Films were thoroughly cleaned with trichlorotrifluoroethane to remove surface impurities and residues prior to use. Reagent grade dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF) and pyridine were used as the strong interacting solvents and doubly-deionized-distilled (DDD) water was used as the noninteracting solvent. Solvent treatments were performed in a temperature-controlled silicone oil bath at each predetermined temperature for 2 min. After solvent treatments, the films were cooled in air and extracted in methanol for 4 h to remove residual solvents. Three films were used for each condition.

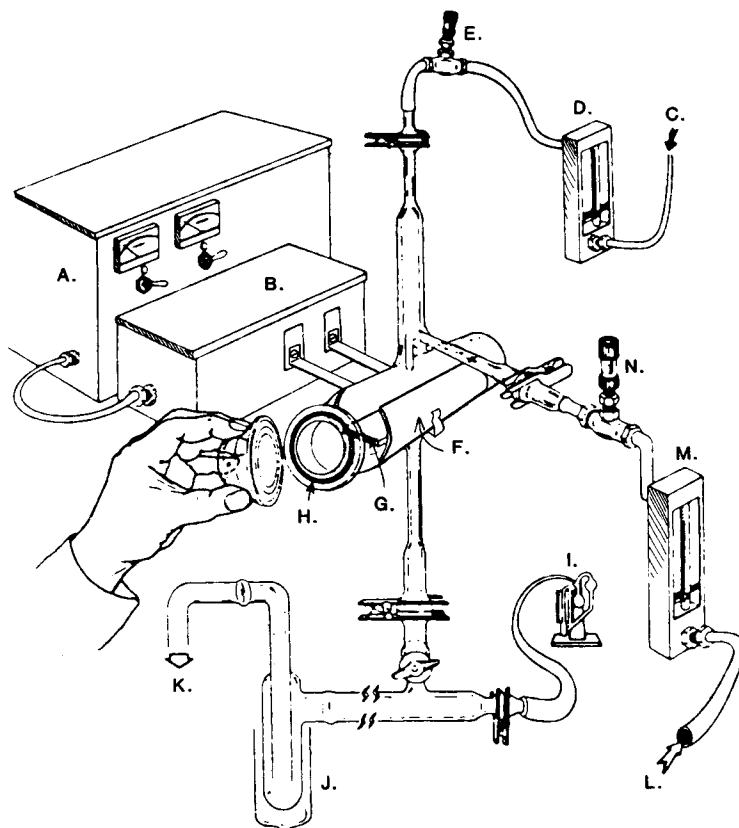


Fig. 1. Glow discharge system: (A) radio frequency power generator; (B) resonance (inductive and capacitive) assembly with a watt meter; (C) inlet for system carrier gas; (D) flow meter; (E) flow control needle valve; (F) copper electrode; (G) substrate; (H) rubber O-ring; (I) pressure gauge; (J) trap; (K) outlet to vacuum pump; (L) additional inlet for gas (e.g., monomer); (M) flow meter; (N) flow control needle valve.

The glass reactor and the glow discharge system is illustrated in Figure 1. Glow discharge was generated by a 13.56 MHz radio frequency generator. The energy was capacitively coupled to a pair of external copper electrodes which are shaped closely to the sides of the cylindrical specimen chamber. Though the power is adjustable during the discharge, power level was established and stabilized prior to the experiment and was kept stable during the treatment. The specimen chamber has a volume of 415 mL with an inner diameter of 6 cm and is about 15 cm long. Each film sample was supported by a thin glass frame at a stationary and horizontal position in the center of the specimen chamber. Air in the system was first displaced with argon by flushing argon through the chamber with the outlet open. The outlet was then closed and the pump turned on. Continuous flow of argon was adjusted to 52.5 cc/min. When the pressure in the chamber was stabilized at 0.3 torr, the glow discharge was turned on at a power level of 30 W for 1 min. The glow region had a volume of 445 cc including the tubings above and below the main chamber. The pressure

remained at 0.3 torr for the entire glow discharge period. After the glow was turned off, pressure in the reactor was brought back to equilibrium with the atmospheric pressure by raising the argon flow rate. For each glow discharge condition, three films were used.

Surface wettability of the films was determined by water contact angle (CA) measurement and Zisman's critical surface tension (CST). Fifteen measurements of water CA were made on each film with 0.5 μL droplets of doubly-deionized-distilled (DDD) water using a microscopic goniometer. Contact angle measurement of glow discharged and solvent-and-glow-discharged films were made 1 h after the glow discharge treatment. Readings were taken 1 min after the deposition of a droplet. Critical surface tensions of the films were derived by the Zisman's method which involves the CA measurements using liquids with known surface tensions (γ). The liquids used were DDD water ($\gamma = 72.6$ dyn), glycerol ($\gamma = 62.6$ dyn), triethylene glycol ($\gamma = 46.0$ dyn), and 1-bromonaphthalene ($\gamma = 43.1$ dyn). Fifteen CA measurements using each of these liquids were made with a 0.5 μL capillary. Linear regression of the liquid surface tensions and the cosine of the CAs was performed for each film. The extrapolation of surface tension at cosine $\theta = 1$ gave the CST for wetting of each film.

Surface morphology was studied by scanning electron microscopy. Each film was thinly coated with a layer of gold 300 \AA in thickness. Sputter coating was performed intermittently to avoid possible heat damage to the film surface. Films were examined on a side-entry goniometer type stage with small probe sizes of either 30 or 100 \AA for better resolution at high magnifications.

RESULTS AND DISCUSSION

Argon Glow Discharge

Water CA value of the untreated film was determined to be $67.0^\circ (\pm 0.1)^\circ$. The water CA of the glow discharged film (at 30 W for 1 min) taken 1 h after the treatment was lowered to $26.2^\circ (\pm 0.1)^\circ$. Gradual decay of wettability was observed during the first 7 days and leveled off at $33.1^\circ (\pm 0.09)^\circ$ (Fig. 2). Some free radicals and ions of lesser reactivity can be long-living enough for further reactions after the glow discharge. During storage, these residual reactive species can cause changes in surface chemistry contributing to the wettability decay in glow discharged PET.

When untreated film was extracted in methanol in addition to being cleaned, a slightly lower CA of 66.1° was measured. When the extracted films were glow discharged under the same condition, the CA taken 1 h after the treatment was 25.0° . The slightly more wettable surfaces due to extraction were consistent on the untreated and the glow discharged (CAs taken 1 h after treatment) films. However, the decay of wettability on the extracted films occurred much sooner and leveled off to the same extent as the ones without prior extraction after only 2 days. Though extraction did cause some differences in the initial CAs and the rate of CA decay on glow discharged films, water CAs after stabilization were the same whether the substrates were extracted or not. Therefore, extraction was not included as a cleaning process.

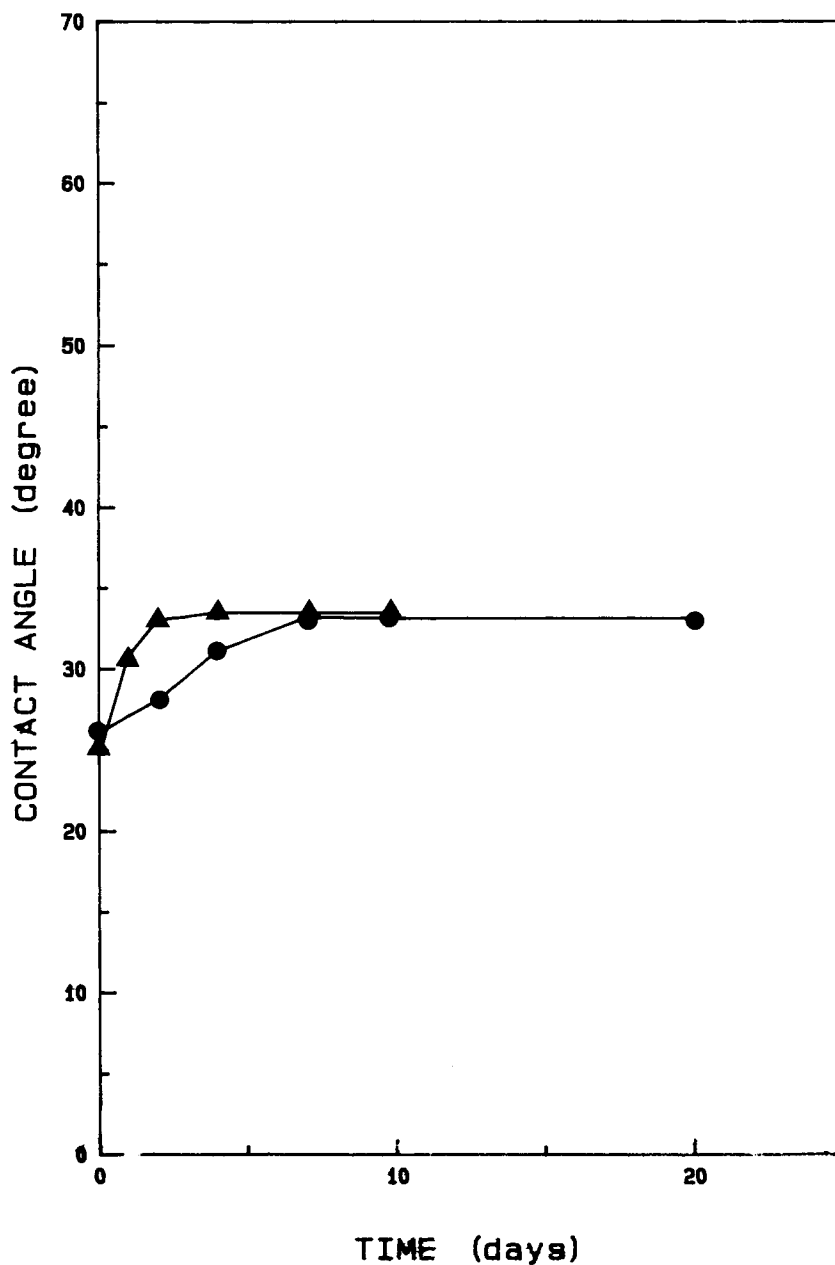


Fig. 2. Water CAs of argon glow discharge PET films: (●) cleaned with trichlorotrifluoroethane, (▲) cleaned with trichlorotrifluoroethane and extracted with methanol.

DMSO and Glow Discharge Treatments

The effect of solvent temperature was first evaluated with DMSO at temperatures ranging from just above the glass transition temperature (T_g) of PET, i.e., 80°C, to 160°C. Wettability of the solvent treated films were improved as indicated by the lowered water CAs in the range of 53–56° (Fig.

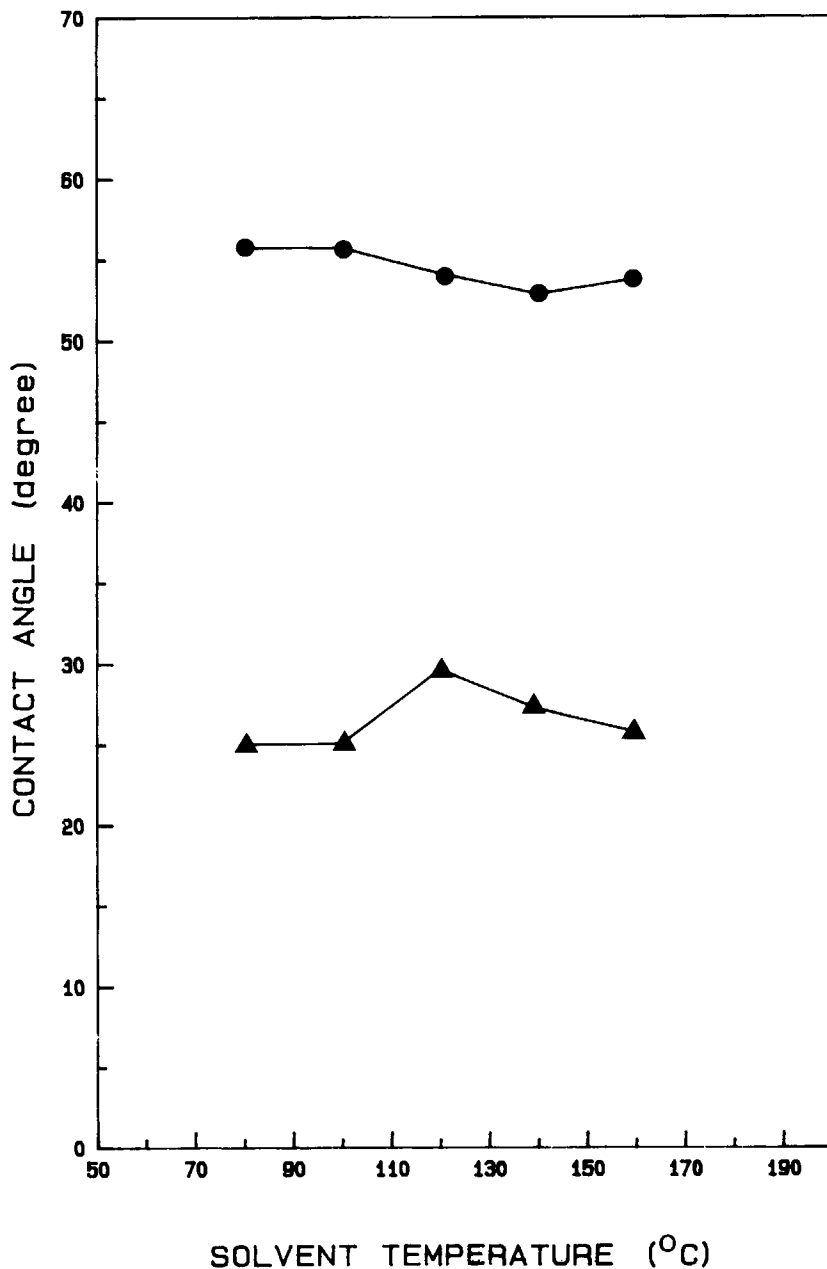


Fig. 3. Water CAs of DMSO and DMSO-and-glow discharged PET films: (●) DMSO only; (▲) DMSO and glow discharge.

3). There were no distinctive trends among the temperatures studied. Though DMSO did not decrease the water CA as much as the glow discharge, the DMSO-induced water wettability did not change with time.

As these solvent-treated films were glow discharged, further improvement in wettability was observed. The CA measurements of the stabilized surfaces of the DMSO-and-glow discharged PET were in a range from 25.0° to 28.5°.

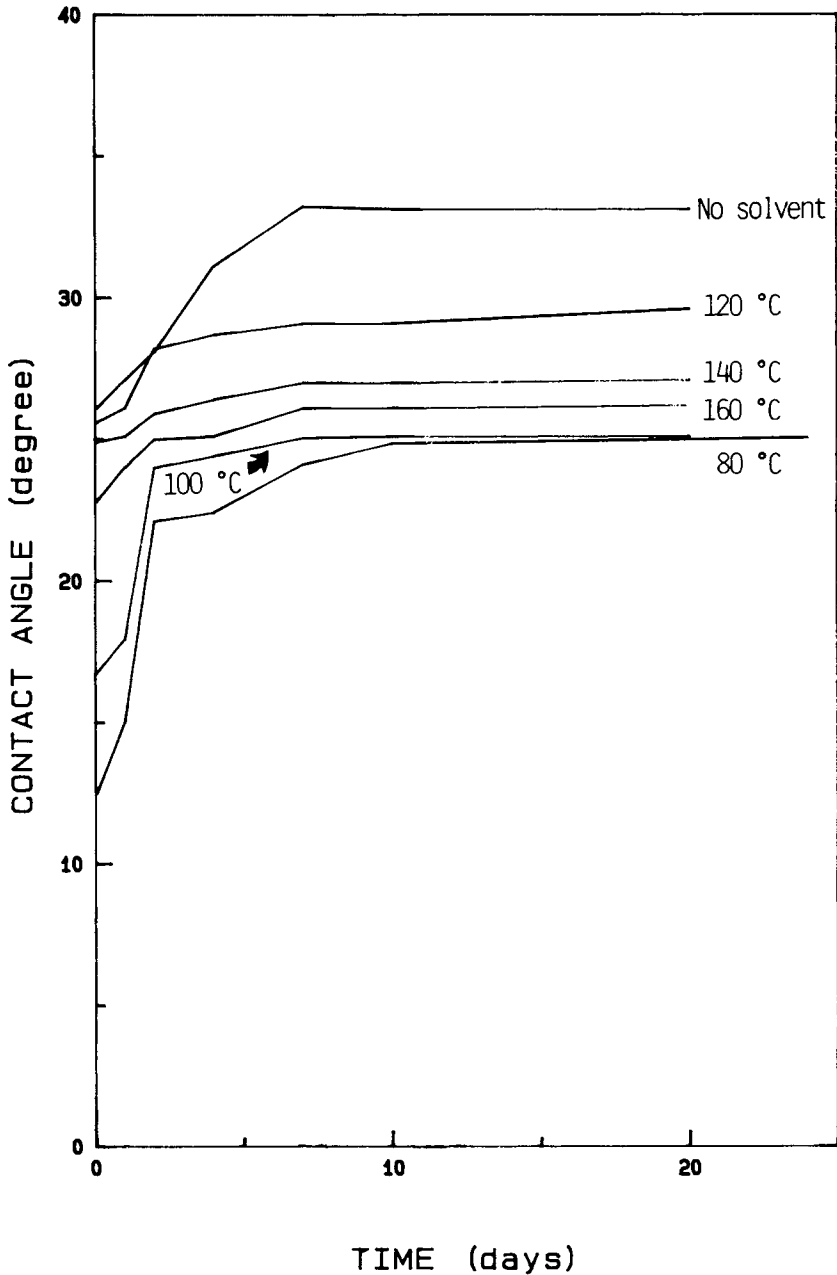


Fig. 4. Water CA decays of DMSO-treated PET films at different solvent temperatures.

This small range of 3.5° was similar to the one (3.0°) observed on the films treated with DMSO alone at the same solvent temperature range. An additive effect of the glow discharge and DMSO treatments on improving wettability of PET were observed.

Decay of wettability with time was still observed on the films that were both solvent treated and glow discharged (Fig. 4). At the end of the stabilization period, i.e., 7–10 days after the glow discharge treatment, different

TABLE I
Wettability Decay (deg) of Glow Discharged and DMSO-and-Glow-Discharge-treated PET during Stabilization

DMSO treatment	Water contact angle		
	1 h after glow discharge	Stabilized	Increase during stabilization
None	26.1 (0.1)	33.1 (0.1)	7.0
80°C	12.5 (0.09)	25.0 ^a (0.08)	12.5
100°C	16.8 (0.09)	25.1 (0.1)	8.3
120°C	25.1 (0.09)	28.5 (0.1)	3.4
140°C	24.1 (0.1)	27.0 (0.1)	2.9
160°C	23.8 (0.1)	25.6 (0.1)	1.8

^a CA measurements stabilized 10 days after the glow discharge treatment. All others stabilized after 7 days.

extents of CA decay were observed at the solvent temperatures studied (Table I). For PET solvent treated at lower temperatures of 80 and 100°C, the initial CAs (taken 1 h after glow discharge) were much lower than for those at higher solvent temperatures. But these films also had greater CAs decays than those treated at higher temperatures. Greater wettability decay at lower DMSO temperatures suggests that greater chain mobility may be induced by the solvent at lower temperatures than the higher ones. Increased chain mobility allows reorientation of the glow-discharge-induced surface functional groups to assume the most stable surface, thus, lower surface tension and higher contact angle. Considerably less CA decay in DMSO-treated PET at temperature of 120°C or higher suggests that molecular order may be increased by a combination of solvent and thermally induced changes. The increased molecular order which may be related to higher crystallinity and/or molecular alignment can restrict molecular flexibility to reorientation, thus limiting wettability decay.

Solvent and Glow-Discharge Treatments

The lowest solvent temperature of 80°C coupled with glow discharge resulted in the most wettable surface and therefore was chosen to be the solvent temperature for other test solvents. Treatment in DMF, pyridine, and water at 80°C also resulted in improved wettability (Fig. 5). The wettability of the DMSO-, DMF-, and pyridine-treated surfaces was stable with time but those treated in water showed decay of the acquired wettability during the first 2 days. As these films were glow discharged, their wetting characteristics were further improved. Similar trends in CA decay were observed as with DMSO. A clear additive effect from these solvent and argon glow discharge treatments was again observed. All four solvents not only enhanced the final wettability of the solvent-and-glow-discharged PET, but also shortened the time for stabilization (Table II). As observed earlier with DMSO, the increases in CAs during stabilization were about the same for DMF and higher for pyridine and water. The effectiveness of these solvents in inducing wettability is in the descending order of DMSO, pyridine, DMF, and water, as indicated by their CAs of 25.0, 27.5, 28.6, and 32.0°, respectively.

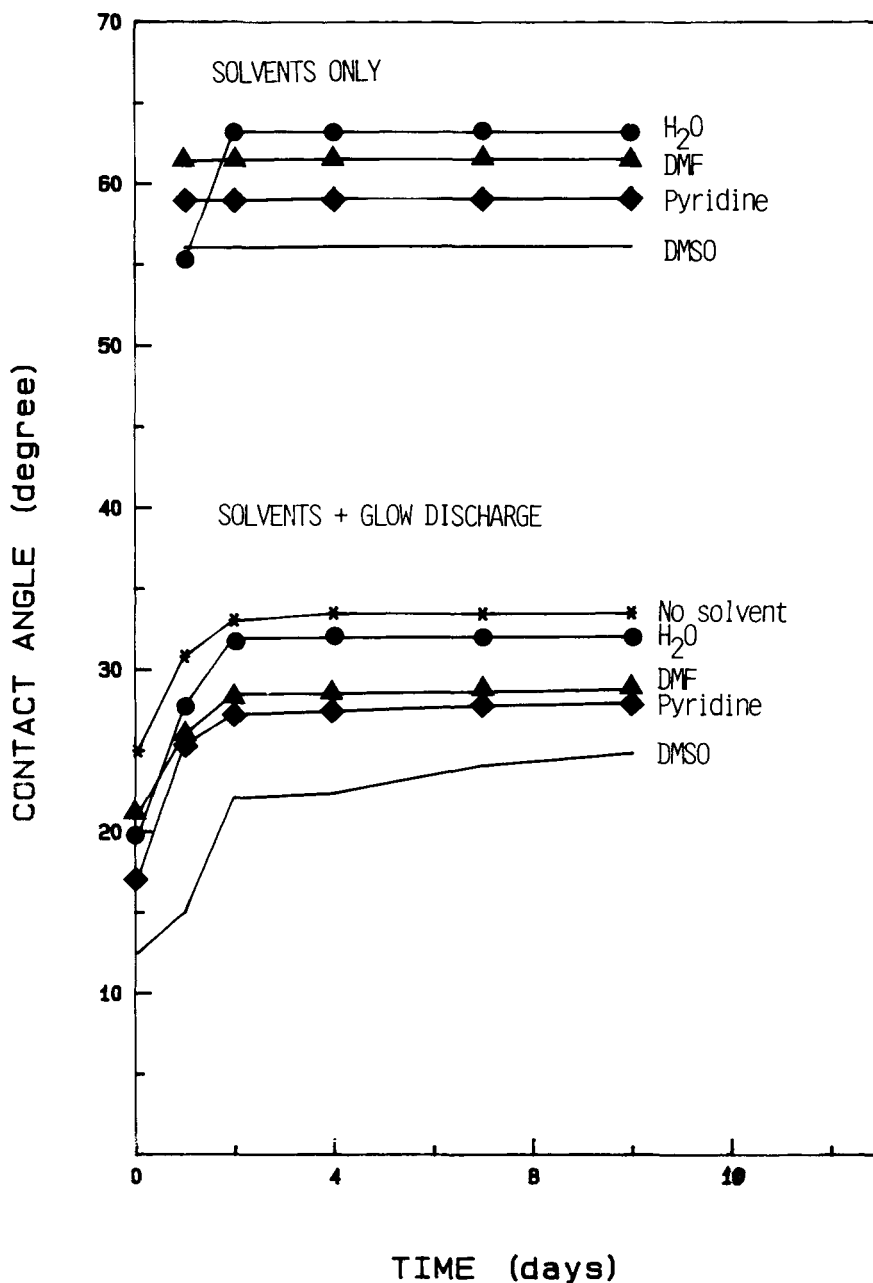


Fig. 5. Water CAs of solvent and solvent-and-glow-discharge-treated PET films.

Two forms of wettability decay on PET were observed with the combination of solvent and glow discharge treatments. At a lower temperature of 80°C, stabilization of CAs was reached in shorter time when PET were treated in water, pyridine, and DMF than when treated in DMSO. On the other hand, the extents of CA decay were significantly lessened by DMSO treatments at higher temperatures of 120°C and above. As DMSO tempera-

TABLE II
Wettability Decay (deg) of Solvent-and-Glow Discharge-Treated PET
during Stabilization

Solvent	Water contact angle		
	1 h after glow discharge	Stabilized	Increase during stabilization
Water	19.6 (0.1)	32.0 ^a (0.1)	12.4
Pyridine	17.0 (0.1)	27.5 ^a (0.1)	10.5
DMF	21.0 (0.1)	28.6 ^a (0.1)	7.6
DMSO	12.5 (0.09)	25.0 (0.08)	12.5

^a CAs stabilized 2 days after the glow discharge treatment.

ture increased, the extents of wettability decay decreased. This further supports the hypothesis that increasing order of molecular arrangement on the surface of semicrystalline PET is induced by both thermal and chemical energies. The altered wettability decay patterns by solvents and heat also confirm the earlier observation^{20,21} that the wettability decay of glow discharged PET is partially caused by reorientation of surface molecules.

Critical Surface Tension

The Zisman's critical surface tension (CST) values of the untreated, solvent-treated, and solvent/glow-discharge-treated PET films were derived from the CAs of selected liquids (Table III). The improvement of surface wettability by the glow discharge alone was indicated by a significantly reduced water CA and a slightly increased critical surface tension. Water CAs of films were also reduced by the solvent treatment, but their CSTs remained basically unchanged. On the other hand, the solvent-and-glow discharge treatment produced surfaces with lowest CAs but a wide range of CST values. Though the derivation of CSTs for the solvent-and-glow-discharged surfaces was consistent among the liquids used, the wettability of these surfaces as indicated by their water CAs was not correlated with their CSTs. For

TABLE III
Critical Surface Tensions of Untreated, Solvent-Treated, Glow Discharged (g.d.),
and Solvent-and-Glow-Discharged-Treated PET

	Water contact angle (deg)	Critical surface tension (dyn/cm)
Untreated	67.0 (1.0)	38.7 (.99)
DMSO	56.1 (.07)	39.6 (.99)
P	59.1 (.08)	38.3 (.96)
DMF	61.6 (.08)	37.7 (.89)
H ₂ O	63.2 (1.0)	39.6 (.99)
g.d.	33.1 (0.09)	41.8 (.99)
DMSO/g.d.	25.1 (0.1)	40.6 (.99)
P/g.d.	28.0 (0.1)	35.1 (.98)
DMF/g.d.	28.8 (0.1)	11.6 (1.0)
H ₂ O/g.d.	32.1 (0.1)	12.9 (.99)

example, the DMSO-glow-discharged surface had a lowest water CA of 25.1° and yet maintained the same CST as the untreated PET. The water CA of the water-glow-discharged PET remains similar to that of the glow-discharged surface, but the CST of the modified surface is much lower. These CST data imply the complexity of the modified surfaces and their different interaction with the test liquids.

Surface Morphology

The scanning electron micrograph of the untreated PET film at a 5000 magnification showed a smooth surface [Fig. 6(a)]. At a higher magnification of 40,000, however, interconnecting hairlines were observed throughout the untreated film surface [Fig. 6(b)]. On the solvent treated films, no morphological changes were seen despite the type of solvent used (Fig. 7). At about 5000 magnification, the glow discharged surface also appeared to be smooth. More surface detail became evident at 40,000 magnification [Fig. 8(a)]. The glow discharged surface had finer and more extensive hairlines and a coverage of irregularly shaped particles. Since etching occurs faster in the amorphous and less ordered regions of the polymer, the increased hairlines after glow discharge may be the indication of where the amorphous and less ordered regions are on the surface. The particles appear shallow in depth and are closely intact with the surface [Fig. 8(b)]. They may be the partially etched away surface material and/or oligomers. On the solvent-and-glow-discharged PET [Fig. 9(a)], the domains surrounded by hairlines were larger and more defined as compared to glow-discharged alone surface [Fig. 8(a)]. The surface was evenly but not fully covered by spheres and their clusters [Fig. 9(a)]. These spheres, which have diameters in the range of 40–80 nm, are more removed from the surface as compared to the particles in Fig. 8. These spheres melt upon extensive exposure to the electron beam on SEM [Fig. 9(b)] whereas those seen in Figure 8 did not.

Surface morphological changes were evident from the glow discharged surfaces with [Figs. 9(a) and 9(b)] and without [Figs. 8(a) and 8(b)] prior DMSO treatment, whereas solvent treatments alone did not impose any morphological surface changes. Upon glow discharge, the increased sizes of domains between hairlines on the DMSO-treated PET indicated solvent-induced order on the surface. The distinctly different responses of the topical particulates to electron beam exposure further suggests that those on glow discharge surface may be crosslinked whereas those on the solvent-and-glow-discharged surface are likely crystalline.

CONCLUSION

1. Strong interacting organic solvents improved surface wettability of PET in the descending order of DMSO, pyridine, and DMF. The solvent-induced wettability was not strongly influenced by solvent temperature but was stable with time.

2. An additive effect on improving surface wettability of PET was observed by solvent and glow discharge treatments. Depending upon solvent type, solvent treatments prior to glow discharge either reduced the extent in wettability decay or the time taken to reach stabilization of CAs. It is thought



Fig. 6. SEMs of untreated PET film: (a) bar = 1.99 μm ; (b) bar = 248 nm.



Fig. 6. (Continued from the previous page.)

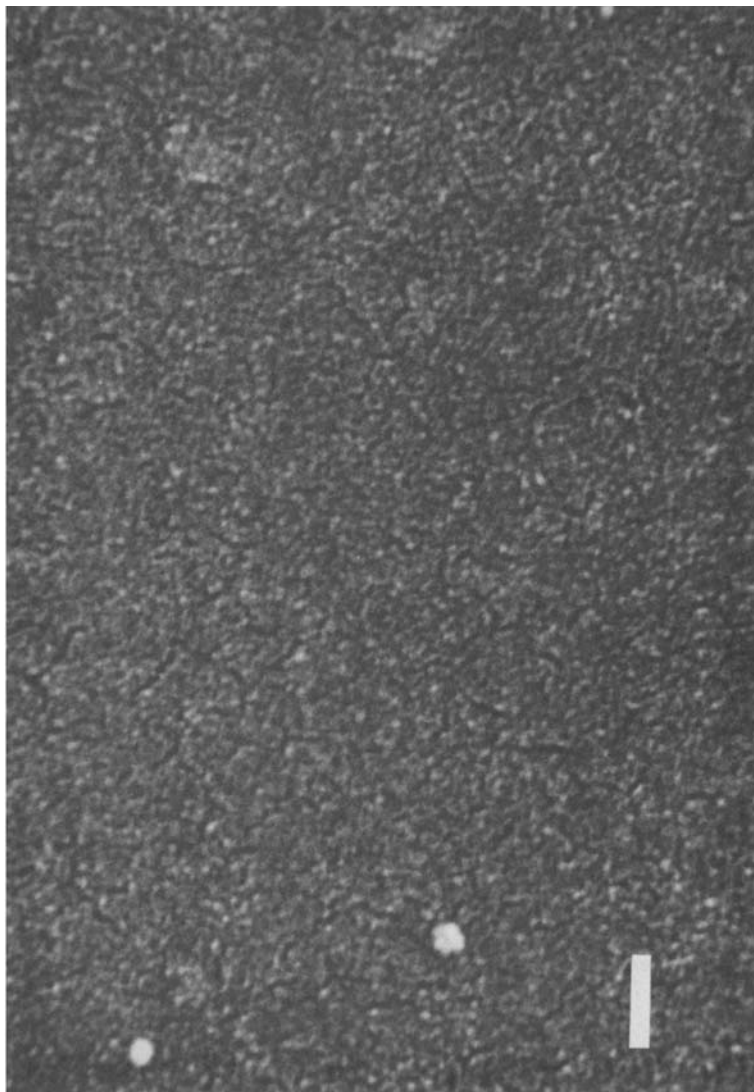


Fig. 7. SEM of DMSO (at 70°C for 2 min) treated PET film: bar = 248 nm.

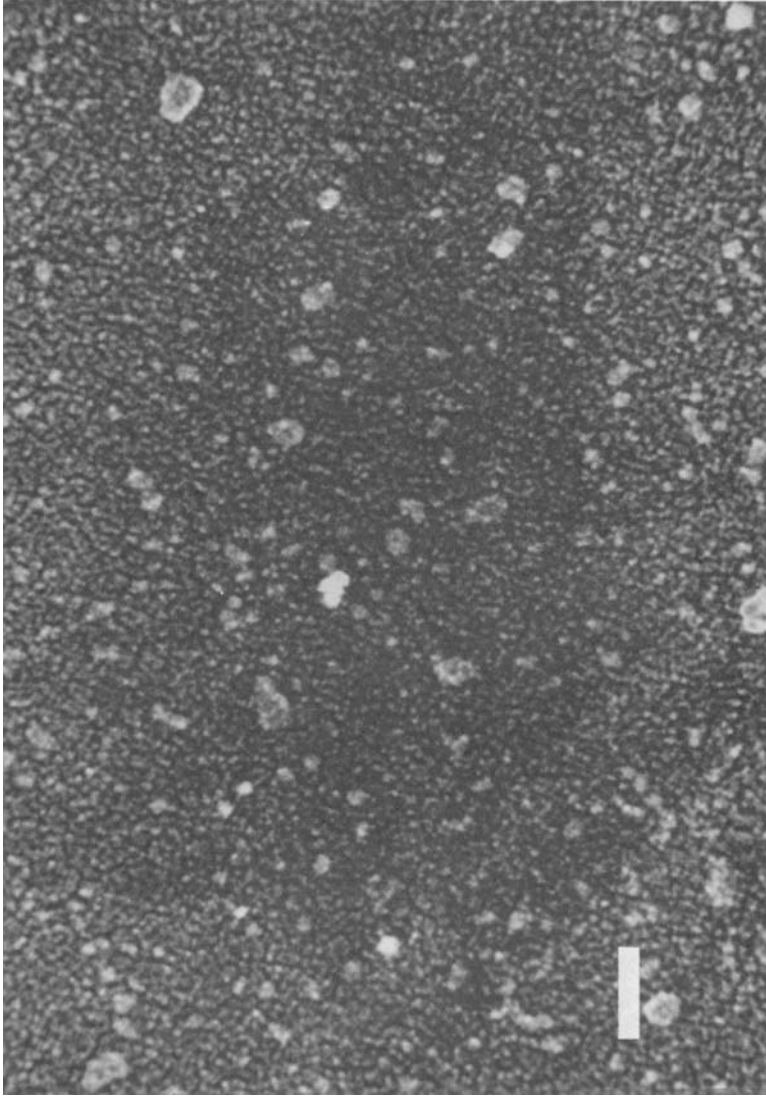


Fig. 8. SEMs of argon glow discharged (at 30 W for 1 min) PET film: (a) bar = 248 nm; (b) bar = 99 nm.

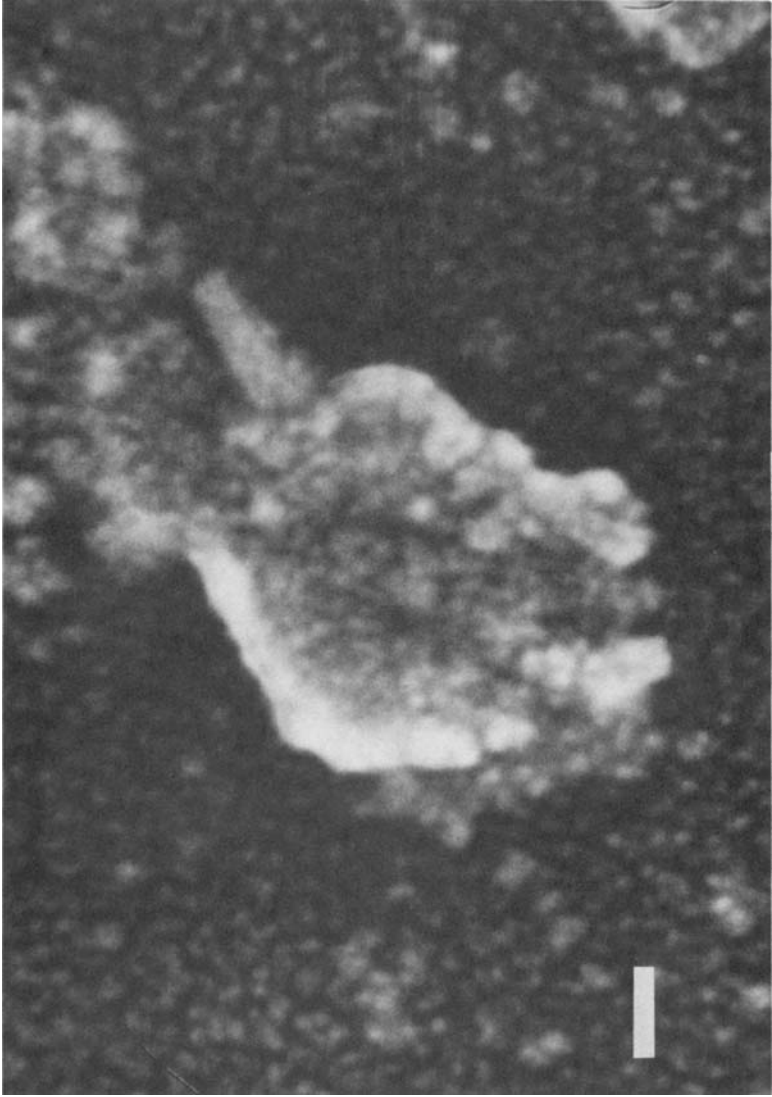


Fig. 8. (Continued from the previous page.)

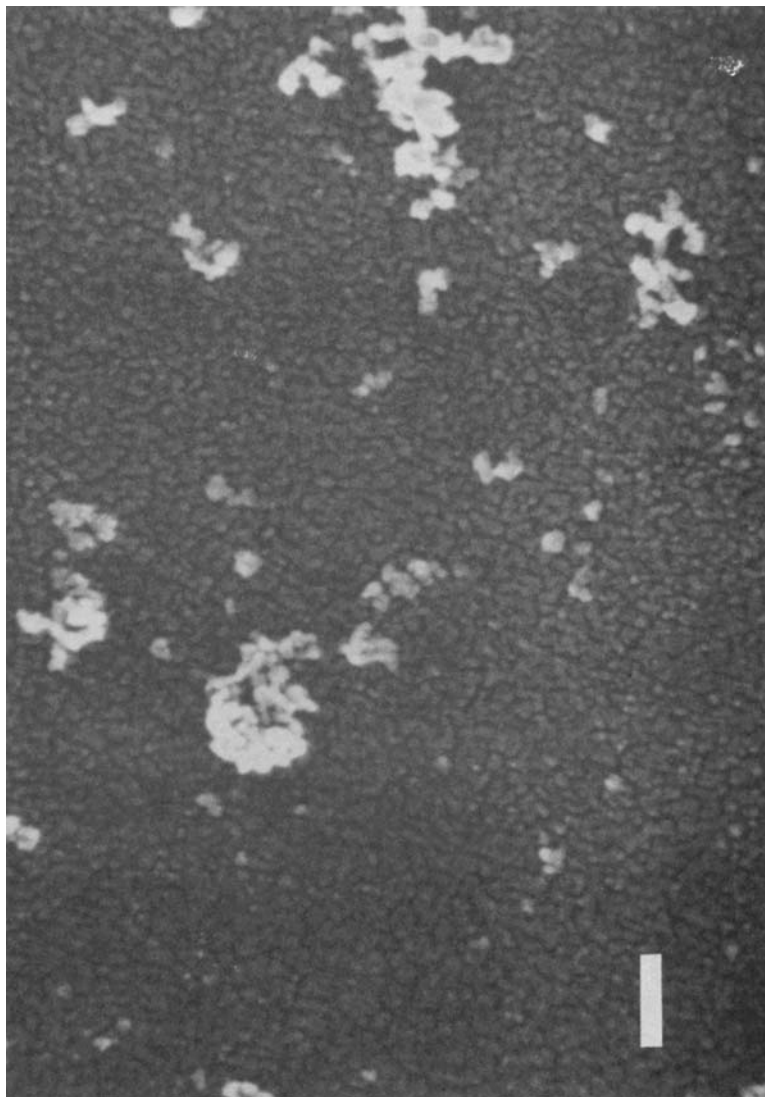


Fig. 9. SEMs of DMSO-and-glow-discharged (same conditions as those in Figs. 7 and 8) PET film: (a) bar = 248 nm; (b) bar = 99 nm.

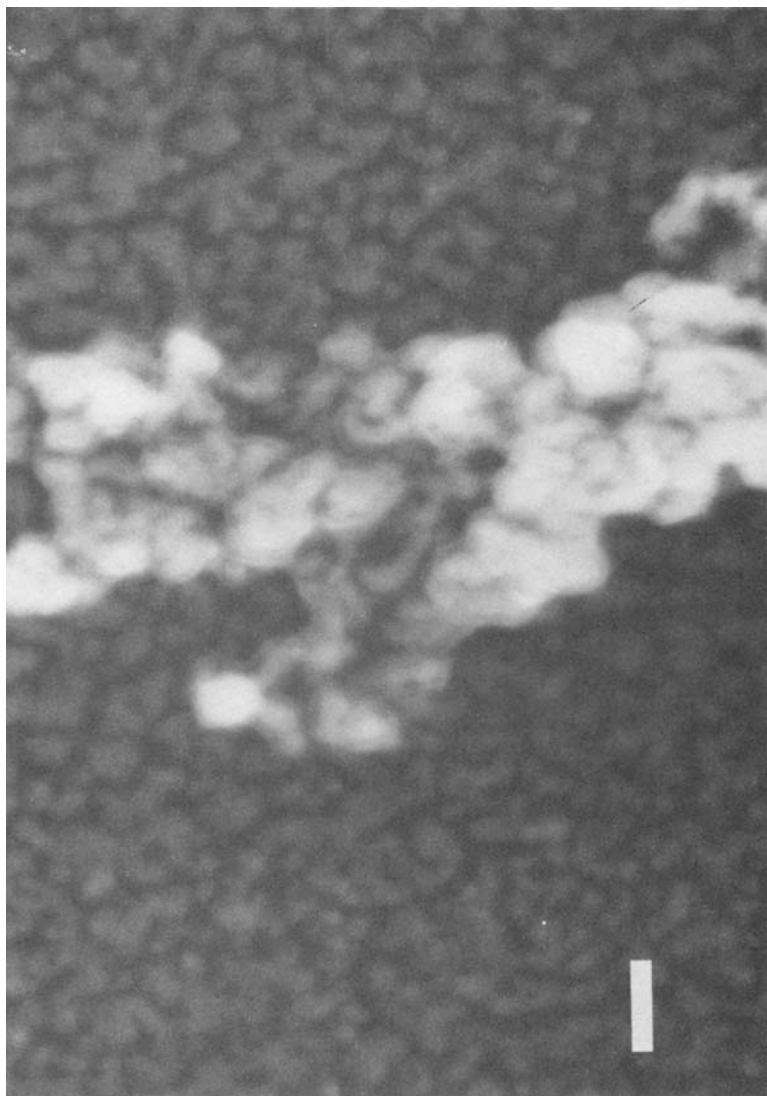


Fig. 9. (Continued from the previous page.)

that wettability decay can be attributed to the reorientation of surface molecules to a larger extent and residual surface reactions to a lesser extent.

3. The solvent-treated surfaces had similar appearance as the untreated PET. On the argon-glow-discharged PET, a finely etched surface was observed only at magnification of 40,000 or higher. Solvent treatments changed the way the PET surfaces were affected by glow discharge.

4. Solvent-and-glow discharge treatments produced PET surfaces with high wettability with a range of critical surface tensions.

References

1. M. Langsam and G. J. Mantel, *J. Appl. Polym. Sci.*, **19**, 2235 (1975).
2. R. W. Phillips and R. H. Dettre, *J. Colloid Interf. Sci.*, **56**, 251 (1976).
3. M. Toyama, A. Watanabe, and T. Ito, *J. Colloid Interf. Sci.*, **47**, 802 (1974).
4. M. K. Burnett, *Polym. Eng. Sci.*, **17**, 450 (1977).
5. N. L. Jarvis, R. B. Fox, and W. A. Zisman, *Adv. Chem. Ser.*, **43**, 317 (1964).
6. J. M. Burkstrand, J. M., *J. Vac. Sci. Technol.*, **15**, 233 (1978).
7. H. Schonhorn and F. W. Ryan, *J. Phys. Chem.*, **70**, 3811 (1966).
8. J. T. J. Burger, *J. Appl. Polym. Sci.*, **20**, 1143 (1976).
9. L. Penn, C. K. Nuta, and L. Rebenfeld, *Text. Res. J.*, **51**, 774 (1981).
10. L. Rebenfeld, J. P. Makenewicz, H.-D. Weigmann, and G. L. Wilks, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C15**(2), 279 (1976).
11. T. Okada, Y. Shimano, and I. Sakurada, *Jpn. Atomic Energy Res. Inst.*, 35 (1973).
12. W. R. Moore and R. P. Sheldon, *Polymer*, **2**, 315 (1961).
13. B. H. Knox, H. D. Weigmann, and M. G. Scott, *Text. Res. J.*, **45**, 203 (1975).
14. C. J. Durning, L. Rebenfeld, W. D. Russel, and H. D. Weigmann, *J. Appl. Polym. Sci.*, **24**, 1341 (1986).
15. H. Jameel, H. D. Noether, and L. Rebenfeld, *J. Appl. Polym. Sci.*, **27**, 773 (1982).
16. D. T. Clark and A. Dilks, *Characterization of Metal and Polymer Surfaces*, L. H. Lee, Ed., Academic, New York, 1977, Vol. 2, p. 101.
17. H. Yasuda, H. C. Marsh, S. Brandt, and C. N. Reilley, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 991 (1977).
18. M. M. Kadash and C. G. Seefried, Jr., *Plast. Eng.*, 45 (December 1985).
19. R. H. Hansen, J. V. Pascale, T. DeBenedicts, and P. M. Rentzepis, *J. Polym. Sci., Part A*, **3**, 2205 (1965).
20. A. M. Wrobel, M. Kryszewski, W. Rakwski, M. Okoniewski, and S. Kubacki, *Polym. Phys.*, **19**, 908 (1978).
21. Y.-L. Hsieh and E. Y. Chen, *Ind. Eng. Chem., Prod. Res. Dev.*, **24**, 246 (1985).
22. H. Yasuda and A. K. Sharma, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 1285 (1981).
23. Y.-L. Hsieh, C. Pugh, and M. S. Ellison, *J. Appl. Polym. Sci.*, **29**, 3347 (1984).

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