Residual Reactivity for Surface Grafting of Acrylic Acid on Argon Glow-Discharged Poly(ethylene terephthalate) (PET) Films

YOU-LO HSIEH* and MEIPING WU†

Division of Textiles, University of California, Davis, California 95616

SYNOPSIS

The wettability of poly(ethylene terephthalate) (PET) films in water was significantly improved upon exposure to argon glow discharge. Depending upon the lengths of glow-discharge exposure, the water contact angle (CA) of the untreated film (73.1° ± 0.1°) was reduced to between 33.7° and 41.0° on the argon glow-discharged films. Wettability decay was observed during the initial few days. Depending upon the treatment time, the water CA stabilized 4–7 days after the treatment and the extent of the wettability decay ranged from 4.3° to 7.6°. The residual reactivity of the glow-discharged surfaces was captured by exposing the glow-discharged PET to acrylic acid in the liquid and vapor phases. Optimal water CAs of 54.0° and 41.9° were achieved in the liquid-phase and the vapor-phase exposures, respectively. Wettability decay of these acrylic acid-grafted PET surfaces was very small (0°–1.9°) for the liquid-phase reactions and negligible (0.3°–0.6°) for the vapor-phase reactions. The near absence of wettability decay or the greater stability of the grafted surfaces suggested the almost complete dissipation of the residual reactivity through reactions with acrylic acid. Surface morphology of the untreated as well as the acrylic acid-grafted PET surfaces were examined and detailed by scanning electron microscopy.

INTRODUCTION

It is well recognized that surface wettability and adhesion of polymers can be significantly improved by low-temperature plasma in nonpolymer-forming gases. The active species generated in a low-temperature plasma, or glow discharge, can activate the top molecular layers on the surface without affecting the bulk of the polymer. Low-temperature plasma is also known for its higher efficiency and effectiveness in inducing surface modification on polymers than that of most chemical and thermal methods.[1] Even though the properties of the modified surfaces are highly dependent on the equipment and the conditions and there is still a lack of understanding of the exact nature and mechanisms of surface changes

on polymers, the superior performance properties of the low-temperature plasma-modified polymer surfaces have attracted strong interest in their applications.

The improved wettability on the plasma-modified polymer surface has been attributed to the induced polar groups,[2-4] surface oxidation,[5] and surface roughness.[6,7] On most polymer surfaces, the superior wettability acquired was not permanent. The reduction of the acquired wettability or wettability decay has been explained by the reorientation of the hydrophilic groups toward the bulk of the polymer[8,9] and surface contamination.[9]

In one of our previous studies,[10] glow-discharge-induced water wettability on poly(ethylene terephthalate) (PET) films was enhanced and stabilized by treating PET in strong interacting organic solvents prior to the glow discharge. It was believed that the solvent treatments increased molecular order on the film surface. The solvent-induced molecular order lowered chain mobility, thus restricting the reorientation of the glow-discharged polar

---

groups, resulting in less wettability decay. In another study, drastic wettability decay was observed during the initial few days following the glow discharge on PET films and fabrics.[11] The wettability decay was associated with increased surface oxygen content and slight weight gain. This observation implied the existence of residual reactivity and the dissipation of this residual reactivity through reactions with atmospheric compounds.

If the wettability decay is an indication of residual reactivity decay on PET surfaces, this reactivity can be utilized for grafting with substances present in the immediate environment following the glow discharge. This study was intended to gather additional evidence on the residual reactivity on glow-discharge PET and to further illustrate the relationship between wettability decay and reactivity decay. Because of the hydrophobic nature of the PET, surface
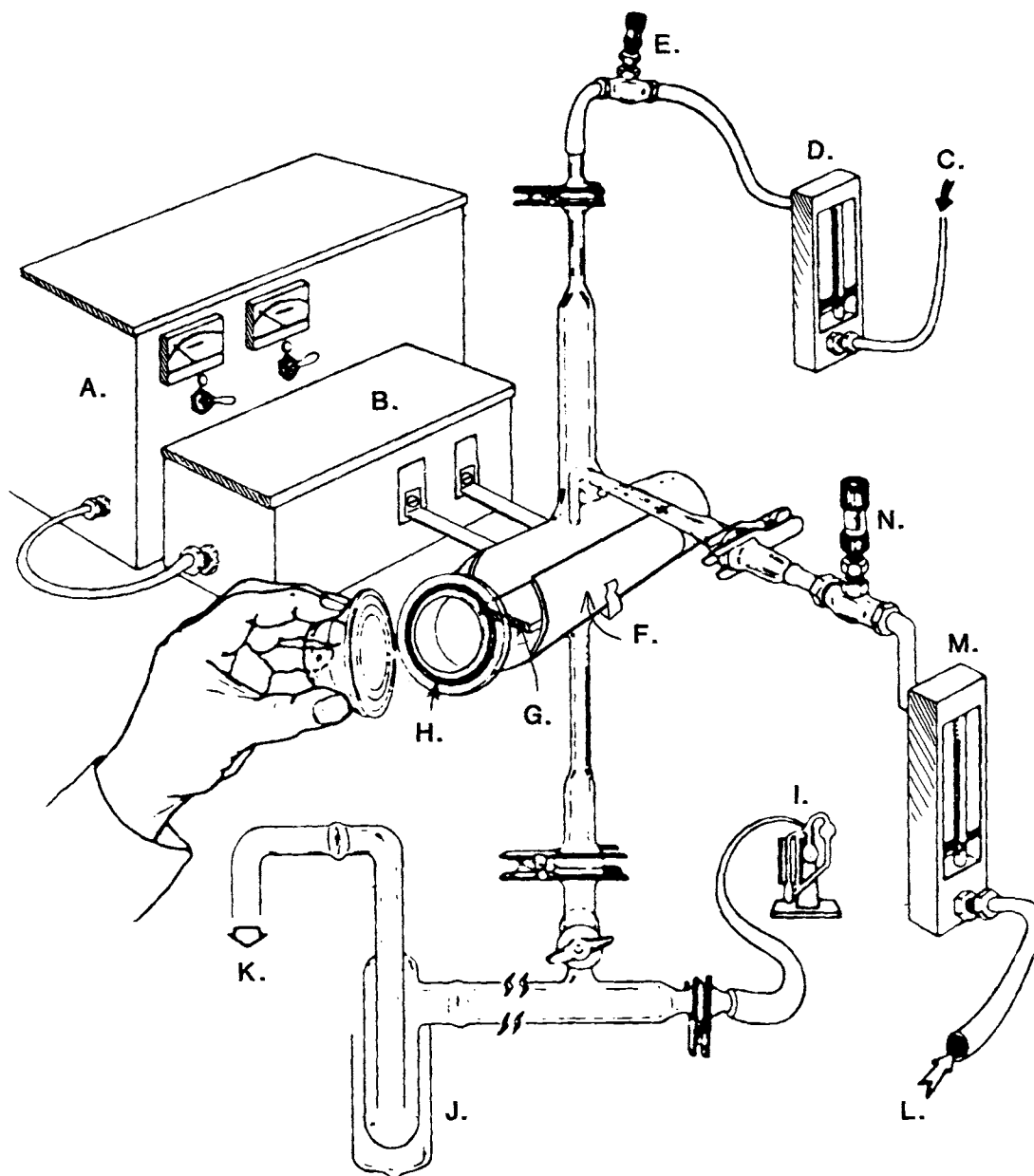
Figure 1 Glow-discharge system: (A) radio-frequency generator; (B) resonance (inductive and capacitive) assembly with a watt meter; (C) inlet for system carrier gas; (D) flowmeter; (E) flow control needle valve; (F) copper electrodes; (G) substrate; (H) rubber O-ring; (I) pressure gauge; (J) reactive gas trap; (K) outlet to vacuum pump; (L) inlet for monomer; (M) flowmeter; (N) flow control needle valve.

Table I   Water Contact Angles of PET Films* as Affected by Argon Glow Discharge at a Power Level of 30 Watts

Glow Discharge Time, Minute	Time After Glow Discharge, Day					Total Decay
	1	2	4	7	10	
0.5	41.0 (0.5)	42.8 (0.5)	44.8 (0.4)	46.3 (0.5)	46.3 (0.4)	5.3
1	39.9 (0.4)	41.7 (0.5)	44.0 (0.4)	44.1 (0.4)	44.3 (0.4)	4.4
2	39.2 (0.5)	40.8 (0.5)	43.2 (0.5)	43.4 (0.4)	43.5 (0.4)	4.3
5	33.7 (5.4)	36.0 (3.7)	39.4 (1.6)	40.8 (0.6)	41.3 (0.6)	7.6

* CA of untreated PET is 73.1 (0.1).
Number in ( ) denotes the standard deviation of 30 measurements from three specimens.

changes via reactions with any hydrophilic compound, such as acrylic acid, could be easily evaluated by changes in wettability. Preliminary experiments were performed to confirm the lack of adsorption of acrylic acid on the cleaned PET films. PET films were exposed to acrylic acid for 1 h and then rinsed in deionized water. The water contact angle on the acrylic acid-exposed films remained the same as the untreated PET films. In this study, the glow-discharged PET films were exposed to acrylic acid in the liquid and vapor phases. The residual reactivity and its decay was verified by monitoring changes in surface wettability and topography of glow-discharged and acrylic acid-exposed surfaces.

EXPERIMENTAL

The poly(ethylene terephthalate) (PET) used in this study was the Melinex type O films (300 gauge in thickness) from ICI Americas, Inc. These films were biaxially oriented and annealed at 210°C. Film specimens were cut into a 1.5 × 4.0 cm² size and cleaned with a detergent solution (0.1% Triton X), followed by rinsing in deionized water and trifluorotrichloroethane. They were air-dried before use. All experiments were conducted on triplicated film specimens.

The glow-discharge system has been previously described.[11] Briefly, a 13.56 MHz radio-frequency generator was used to generate the glow discharge (Fig. 1). The treatments were performed in argon with a flow rate of 52.5 cc/min at a system pressure

of 1.5 Torr. The glow-discharge films were then rinsed thoroughly with deionized water to remove any redeposited materials from etching of the surface.

The inhibitor in acrylic acid was removed by passing the monomer through neutralized alumina oxide immediately before use. For the liquid-phase reactions, the glow-discharge films were immersed in concentrated acrylic acid for various periods ranging from 1 h to 10 days. Since the dissipation of the activity depends on the time following the glow discharge, a constant time was allowed between the extinction of the glow discharge and the contact with acrylic acid on all glow-discharged films. A period of 4 min was necessary to bring the chamber to atmospheric pressure by purging of the glow-dis-

Table II   Initial Water Contact Angles* of Acrylic Acid Grafted PET in Liquid Phase

Reaction Time	Glow Discharge Time, Minute		
	0.5	1	2
1 h	56.2 (0.3)	52.1 (0.5)	52.6 (0.4)
4 h	58.0 (0.3)	53.9 (0.3)	53.7 (0.3)
1 day	58.8 (0.4)	54.4 (0.5)	54.4 (0.4)
2 days	58.6 (0.3)	54.6 (0.2)	54.7 (0.3)
4 days	59.0 (0.2)	54.7 (0.3)	55.1 (0.3)
7 days	59.5 (0.2)	55.1 (0.3)	55.5 (0.2)

* Data shown were taken 1 day after PET film were taken out of the liquid AA.
Number in ( ) denotes the standard deviation of 30 measurements from three specimens.
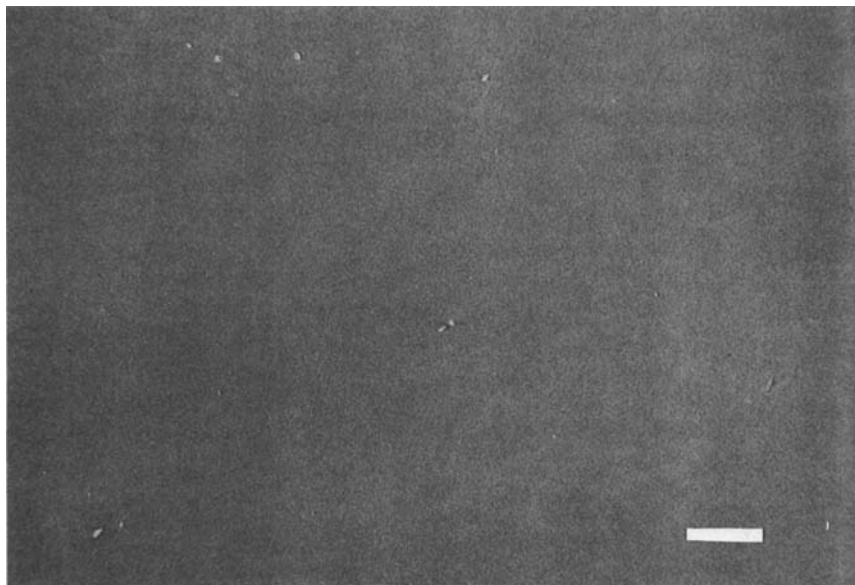
Figure 2 Untreated PET surface: (a) bar = 4.95 μm; (b) bar = 0.25 μm; (c) bar = 0.13 μm.

charge chamber with argon gas. The exposure of the glow-discharged films to the atmosphere lasted less than 5 s.

For the vapor-phase reactions, the N valve (in Fig. 1) was opened to allow acrylic acid vapor to enter the chamber. The admission of acrylic acid vapor was administrated by the pressure differentiation between the chamber (1.5 Torr) and the monomer reservoir (atmospheric pressure) at the same time the glow discharge was extinguished. After either the liquid- or vapor-phase reaction, the films were rinsed with deionized water and immersed in a water bath in a reciprocal shaker for 30 min to remove nonbonded substances, such as the adsorbed and trapped acrylic acid and the oligomers. The films were then dried in a vacuum desiccator for 2 days.

Surface wettability was determined by water wetting contact angle (CA) measurements of 0.5 mL droplets of doubly deionized-distilled (DDD) water on a microscopic goniometer. The advancing CA angle of each droplet was taken approximately 20 s after the deposition of the droplet. Surface morphology was examined under a scanning electron microscope (SEM). Each film's specimen was coated with a 300 Å layer of gold by intermittent sputtering to avoid possible heat damage to the film. The SEM evaluation was conducted on a side-entry goniometer-type stage with small probe sizes of either 30 or 100 Å for better resolution at high magnifications.

RESULTS AND DISCUSSION

Argon Glow Discharge

Water contact angle (CA) of the untreated PET films averaged 73.1° (±0.1°). Upon exposure to argon glow discharge, water wettability of the treated PET films was greatly improved as shown by the significantly reduced CAs (Table I). The water CAs decreased with increasing glow-discharge time. The average CAs between the consecutive exposure times were significantly different at the 0.05 level except for that between 1 and 2 min. Glow discharge up to 2 min caused relatively uniform wettability changes as indicated by the little CA variations at different locations on one film as well as among films. Large variations in CAs were observed on the films glow discharged for 5 min, indicating less uniform surface changes on the films.

Wettability decays were observed on all glow-discharged PET films. The extents and patterns of the decays varied among the different exposure lengths. The CA increases were most obvious during the first few days. The CA increases ranged from 4.3° to 7.6° but seemed to be independent of the glow-discharge lengths. The CAs on the PET films glow discharged for 1 min stabilized 7 days after the treatment, whereas the CAs on those glow discharged longer reached stabilization after 4 days. The stabilized CAs
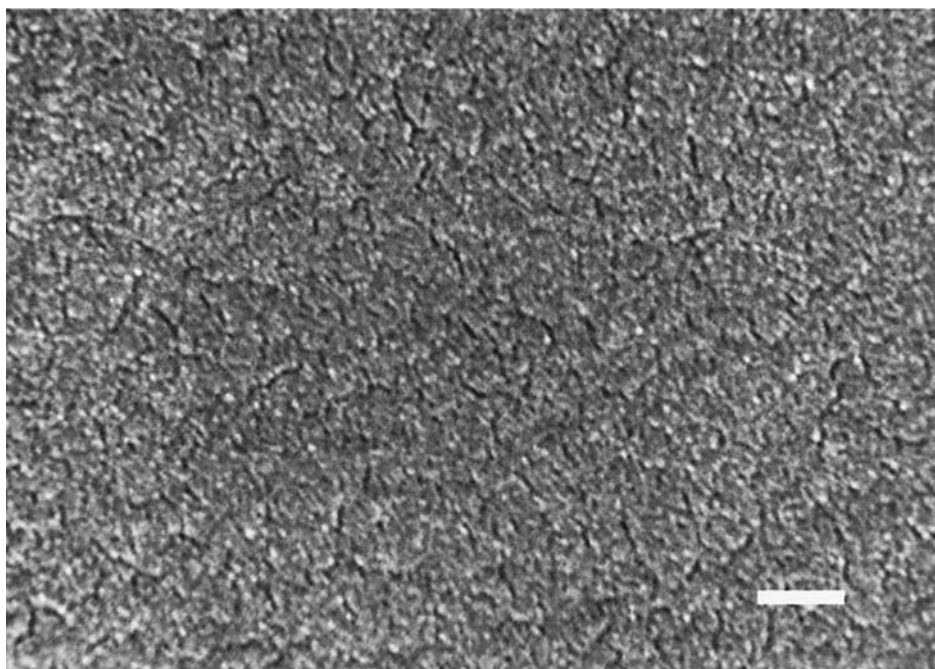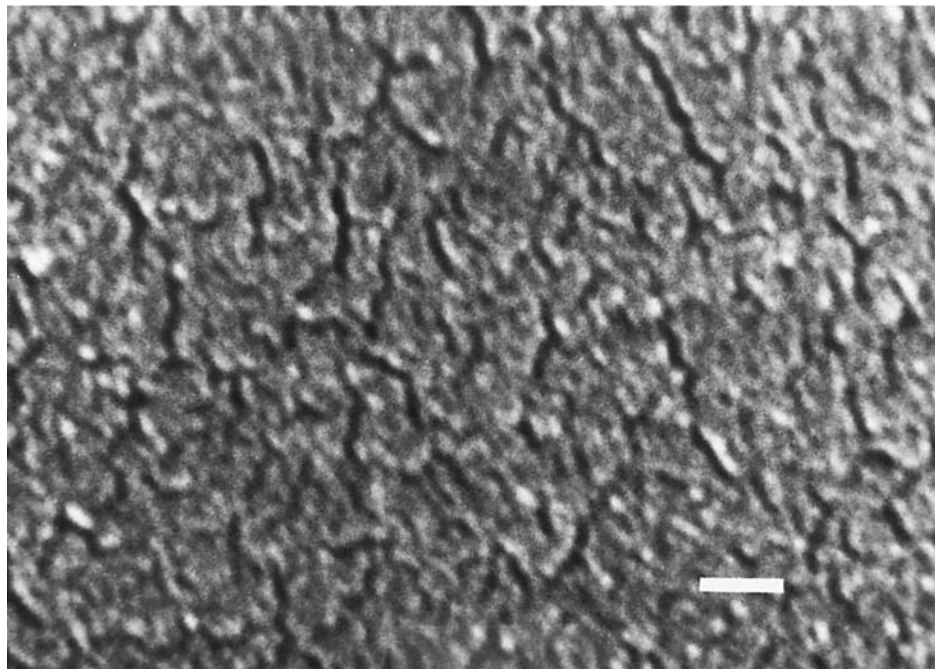
Figure 2   (*Continued from the previous page*)

showed that the water wettability was positively related to the glow-discharge time.

At magnifications up to 2000, the untreated PET surface appeared smooth [Fig. 2(a)]. Irregular hairline patterns became apparent at higher magnifications (15,000) [Fig. 2(b) and (c)]. These microscopic patterns were also found on the PET surfaces glow discharged for 1 min, suggesting no significant change in surface morphology at this glow-discharge level. As the glow-discharge time was
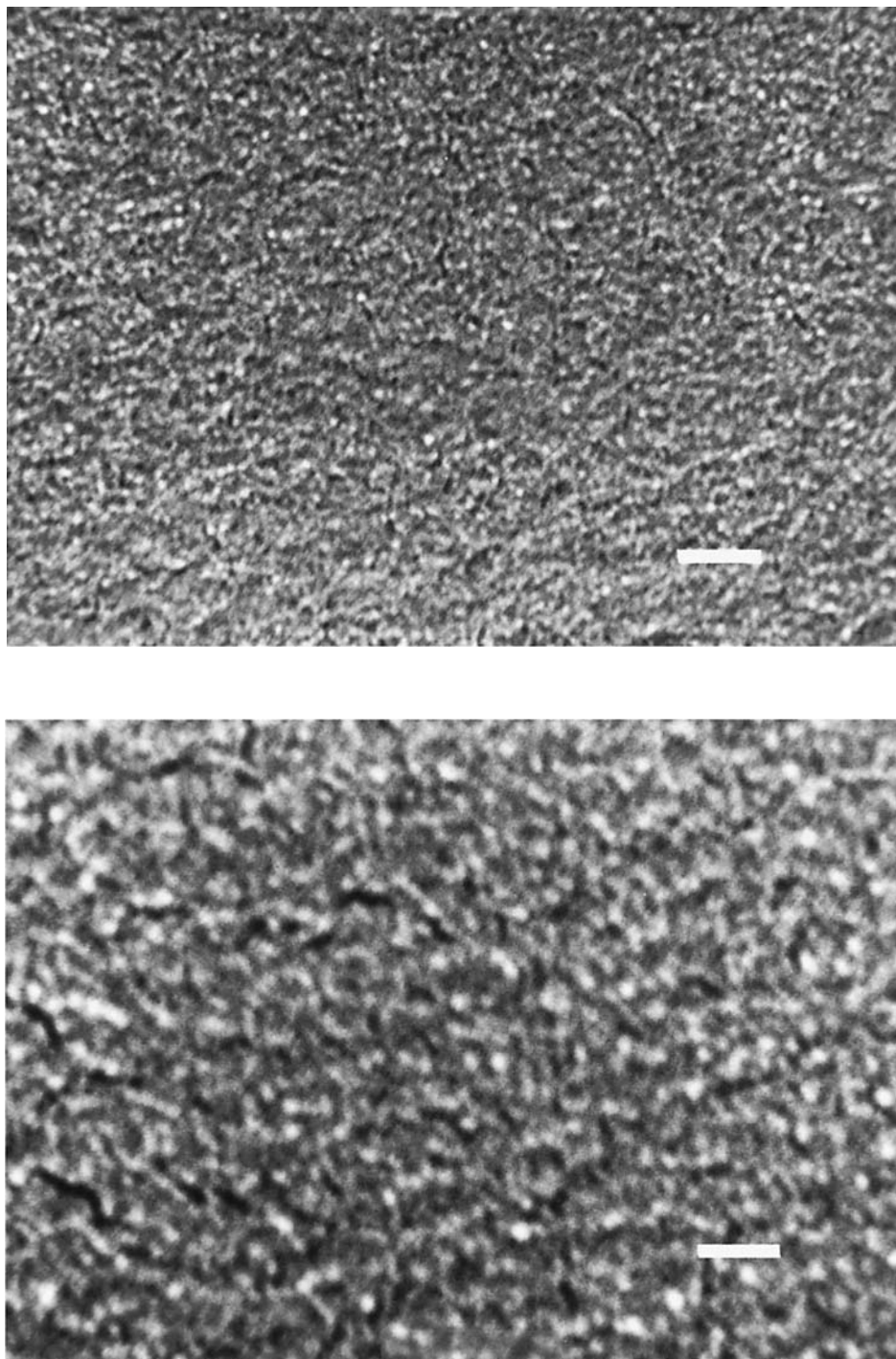
Figure 3   PET surfaces glow discharged in argon for 5 min: (a) bar = 0.25 μm; (b) bar = 0.13 μm.

prolonged to 2 min and longer, some distinct surface changes were observed. The hairline patterns became less distinct [Fig. 3(a) and (b)] as the sign for etching or removal of the surface layer. The dis-

appearance of the hairline patterns along with the etching process confirmed the surface nature of these microscopic features. Since etching by the glow discharge occurs more readily on amorphous domains

Table III   Stabilized Contact Angles of Acrylic Acid Grafted PET in Liquid Phase

| Reaction Time | Time to Reach Stabilization, Days | | Glow Discharge Time, Minutes | | |
	After Monomer Immersion	Total	0.5	1	2
1 h	10	10	57.9 (0.4)	54.0 (0.4)	54.2 (0.1)
4 h	7	7	58.6 (0.2)	54.9 (0.3)	55.2 (0.3)
1 day	7	8	59.7 (0.3)	55.2 (0.2)	55.5 (0.3)
2 days	7	9	59.3 (0.3)	55.4 (0.4)	55.5 (0.3)
4 days	4	8	59.5 (0.1)	55.2 (0.4)	55.5 (0.2)
7 days	1	8	59.5 (0.2)	55.1 (0.3)	55.5 (0.2)

Number in ( ) denotes the standard deviation for 30 measurements from three specimens.

of polymers, the even etching effects on the surface suggested that the surface may be uniformly amorphous. The microscopic hairline patterns may be microcracks resulting from differential cooling and contraction of the amorphous surface.

Another change on films glow discharged for 2 min was the sporadic polygonal crystals on the surfaces [Fig. 4(a–c)]. These crystals may be the oligomers migrated to and crystallized on the PET surface. Both heat and solvent treatments have been shown to cause the migration to and the crystallization of oligomers on the surfaces of PET films[12] and fibers.[13–16] The polygonal crystals observed on the argon glow-discharged PET were similar in shape to those found from heat treatments.[13–16] However, the sizes of these crystals were approximately one magnitude smaller than those observed on heat-treated PET. The appearance of these crystals suggested that the energy generated from the glow-discharge conditions studied was sufficient to

promote chain mobility and oligomer migration to the surface. The much smaller dimension of these crystals may be explained by the surface nature of the glow-discharge treatment. Since the glow discharge does not penetrate into the bulk, the effects from the generated energy were limited to the surface, causing migration of oligomers in the surface region.

As the glow-discharge time increased to 5 min, nothing resembling crystal formation was found [Fig. 5(a–b)]. However, patches of substances with similar dimensions as those crystals [Fig. 4(a–c)] were observed. Even after a 2 min glow discharge, the crystals appeared to be surrounded by sputtered substances [Fig. 4(a–c)]. It was thought that the migration and surface recrystallization of oligomers and etching effects coexisted. During shorter glow discharge, the crystals were generated and slightly etched. As glow-discharge time was lengthened, etching effects became dominant. The patches of

Table IV   Water Contact Angles of Acrylic Acid Grafted PET in Vapor Phase: Continuous Pumping for 10 Minutes

| Ar Glow Discharge | Time Following Acrylic Acid Reaction, Day | | | | | | Total Decay |
	1	2	4	7	10	20	
0.5 m	35.6 (0.6)	41.3 (0.4)	43.4 (0.4)	44.9 (0.3)	46.9 (0.2)	50.2 (0.4)	14.6
1 m	35.2 (0.2)	42.3 (0.1)	43.2 (0.4)	45.5 (0.4)	46.6 (0.1)	51.9 (0.2)	16.7
2 m	40.6 (0.4)	46.3 (0.4)	46.6 (0.4)	47.0 (0.5)	47.1 (0.5)	— —	6.5

Number in ( ) denotes the standard deviation of 30 measurements from three specimens.
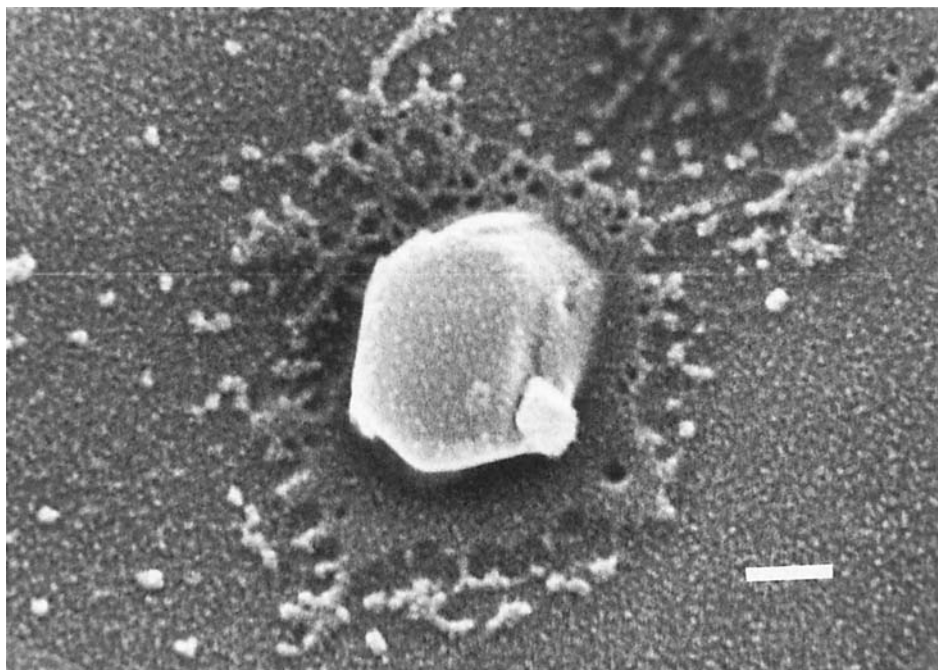
Figure 4 PET surfaces glow discharged in argon for 2 min: (a, b, and c): bar = 0.25 μm.

materials observed after a 5 min glow discharge were possibly the etched crystals. The substances appeared to be the redeposition and sputtering of the etched crystals.

Since surface wettability is strongly governed by surface roughness, topographical changes should be kept at a minimum in order to study the effects of surface reactivity. To achieve minimum surface roughness, glow-discharge exposure lengths up to 2 min were used for the following reactions.

Liquid-Phase Reactions

To investigate whether this wettability decay on argon glow-discharged PET surface was residual reactivity, the activated surfaces were exposed to acrylic acid in the liquid phase. The water wettability decay of the glow-discharge films occurred during the first 4–7 days. To capture the residual reactivity, the glow-discharged PET films were immersed in acrylic acid for up to 7 days. Table II lists the initial CAs taken 1 day after the reaction. Within the 1 h reaction series, better water wettability was associated with longer glow-discharge time. However, CAs increased as time in acrylic acid lengthened. From the initial CA readings, the most wettable surface was the film treated in argon glow discharge for 1 min and exposed to acrylic acid for 1 h.

The wettability decay patterns as illustrated by CA increases are shown in Figure 6(a–c). For all three glow-discharge lengths, wettability decays decreased as the liquid-phase reaction times with acrylic acid increased. After 7 days in acrylic acid, the water CAs of the grafted surface remained unchanged. Overall, the CA decays on the liquid-phase grafted surfaces were no more than 1.9°, which were much lower than those (4.3°–7.6°) observed for the glow-discharged PET.

After the complete stabilization of the CAs, the most wettable PET surface was from the 1 min argon glow discharge to the 1 h immersion in the acrylic acid condition (Table III). For the 0.5 min glow-discharge series, water CAs were not significantly changed after the 1 day liquid-phase reaction. As glow-discharge time lengthened to 1 and 2 min, the liquid-phase reaction time required to obtain water CAs with insignificant decay was 4 h. Little or no CA decay observed on the liquid-phase-grafted PET surfaces implies near depletion of the residual reactivity in the shorter liquid-phase reactions and total depletion at the longer reaction time.

The comparisons on the decay patterns of the glow-discharged-only and the liquid-phase-grafted PET films showed some insight into the residual reactivity. Though CA decays lasted 4–7 days for the glow-discharged PET, a longer time in the liquid
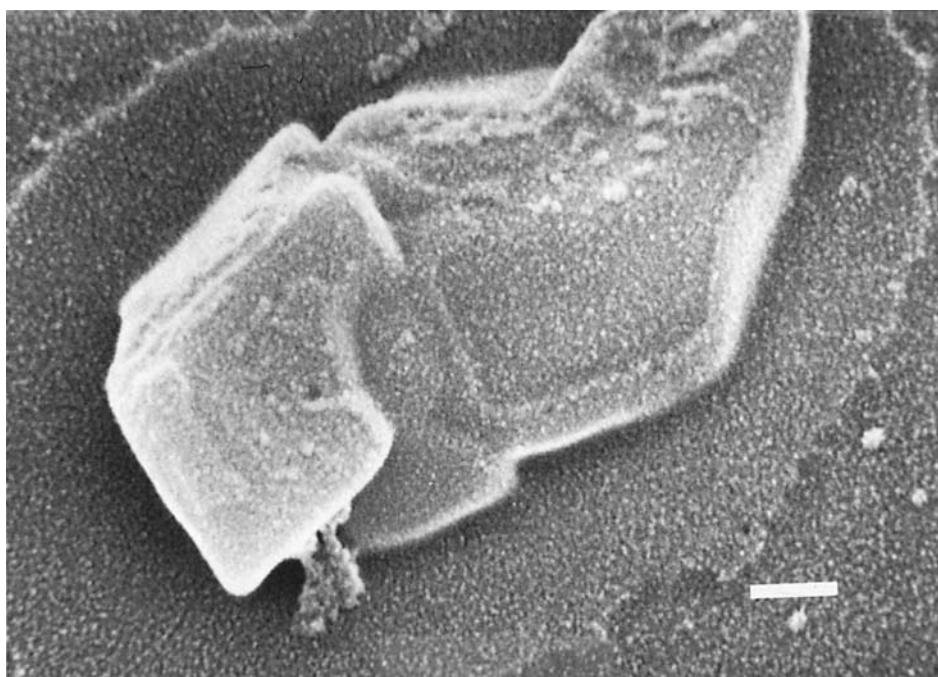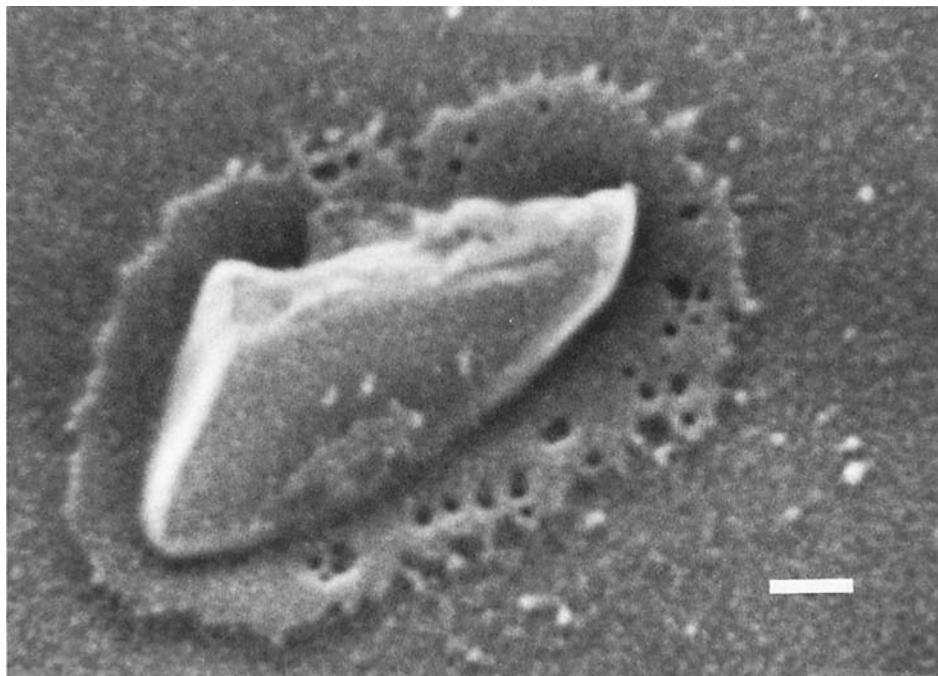
Figure 4 (*Continued from the previous page*)

phase was necessary to eliminate the CA decays. This indicated that the residual active species on glow-discharged PET surfaces dissipated faster in air than in acrylic acid. When compared with the glow-discharged PET, the less wettable but more stable surfaces of the liquid-phase-grafted surfaces also reflected the different nature of these surfaces. The very little CA decay suggested that the residual
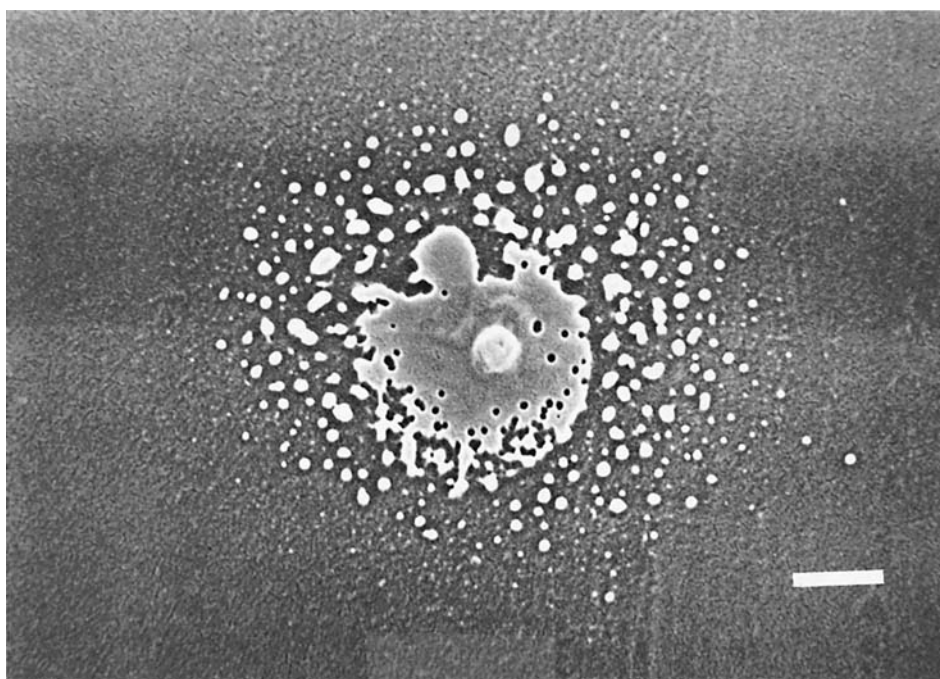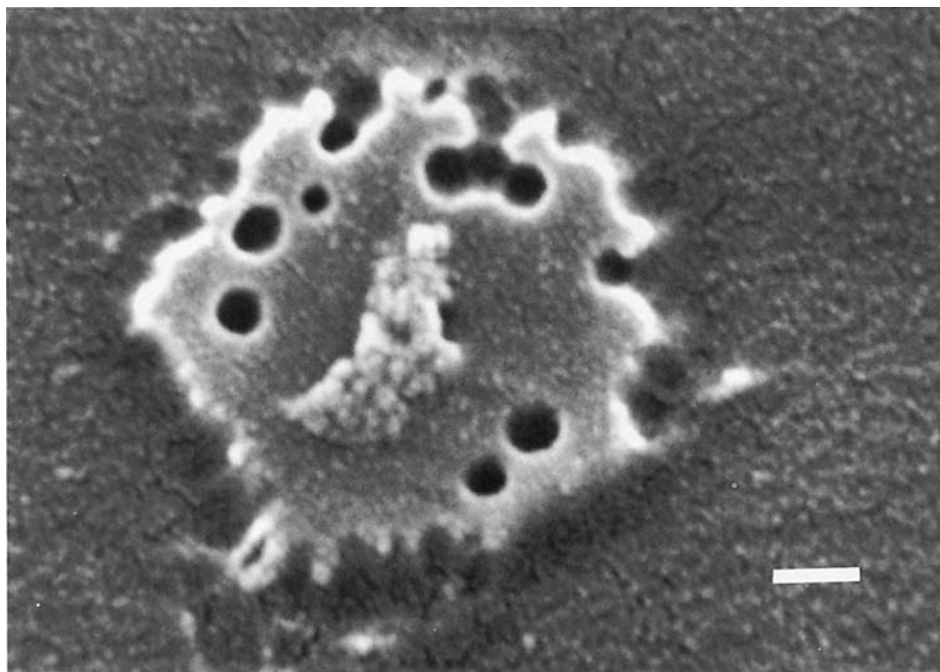
Figure 5   PET surfaces glow discharged in argon for 5 min: (a) bar = 0.20 μm; (b) bar = 0.99 μm.

reactivity was almost completely consumed by reacting with acrylic acid. Surface hydrophilicity is governed by the density and types of polar groups on the surface. A possible explanation for the less wettable grafted surfaces was the replacement of the more polar functional groups on the glow-discharged

Table V   Water Contact Angles of Acrylic Acid Grafted PET* in Vapor Phase: No Pumping for 10 Minutes

AA Vapor Time, Minutes	Time Following Acrylic Acid Reaction, Day					Total Decay
	1	2	3	4	5	
5	46.8 (0.3)	47.2 (0.4)	47.5 (0.3)	47.6 (0.3)	47.7 (0.3)	0.9
10	46.2 (0.3)	46.2 (0.4)	47.0 (0.3)	47.1 (0.4)	47.2 (0.3)	1.0
15	45.8 (0.4)	46.3 (0.3)	46.7 (0.3)	46.9 (0.4)	47.0 (0.3)	1.2
20	45.9 (0.4)	46.4 (0.4)	46.6 (0.3)	46.8 (0.4)	47.0 (0.3)	1.1

* Argon glow discharge lasted 1 minute.
Number in ( ) denotes the standard deviation of 30 measurements from three specimens.

surfaces by the less polar acrylic acid. The hydroxyl groups on acrylic acid might also be less accessible for hydrogen bonding with water because of the increased molecular bulk on the grafted surfaces.

The scanning electron micrographs of the 1 h liquid-phase-reacted PET film surfaces were similar in appearance among the various lengths of glow-discharge time. The surfaces were evenly spotted with small spherical particles [Fig. 7(a)] and clusters [Fig. 7(b)]. The sizes of these particles ranged from 0.1 to 1 μm. The particles melt upon extended electron exposure in the scanning electron microscope. These particles may be from the polymerization of acrylic acid, but further research is needed to verify this. Upon longer immersion in acrylic acid, the hairline pattern disappeared from the surface (Fig. 8).
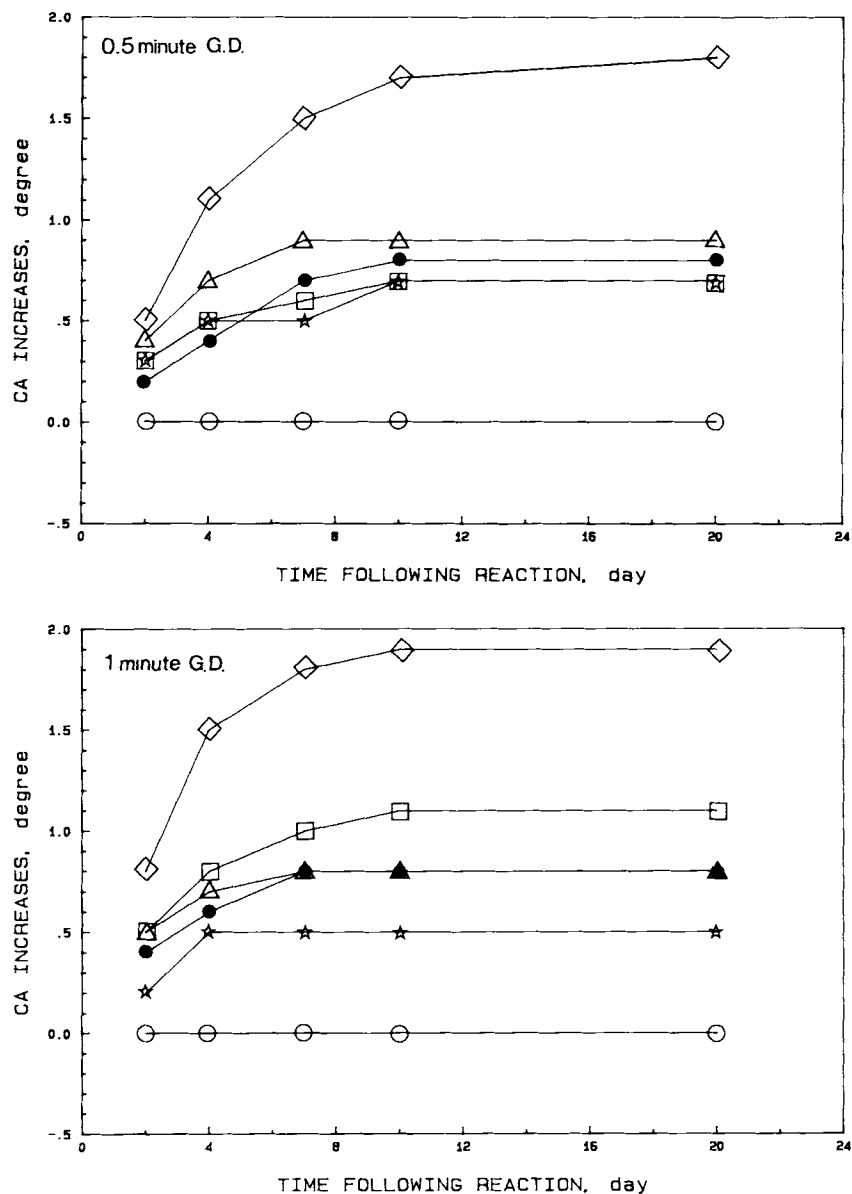
Vapor-Phase Reactions

The effects of vapor-phase reactions were evaluated under three vapor admission conditions. In the first one, acrylic acid vapor was admitted to the glow-discharge chamber immediately after the extinction of the glow. The vapor was let in for 10 min, during which time the chamber pressure was kept at 1.5 Torr by continuous pumping. The water CAs taken 1 day after the reactions on this vapor-phase-grafted PET films (Table IV) were actually lower than those glow discharged (Table I). However, unlike the liquid-phase-grafted PET films, the wettability of this vapor-phase-reacted surface was not stable. The wettability decay and the stabilized CAs were both higher than those of the glow-discharged PET surfaces.

Table VI   Water Contact Angles of Acrylic Acid Grafted PET in Vapor Phase: Combined Pumping Condition for a Total of 10 Minutes

Ar Glow Discharge	Time Following Acrylic Acid Reaction, Day					Total Decay
	1	2	4	7	40	
0.5 m	41.3 (0.1)	41.6 (0.1)	41.8 (0.1)	41.9 (0.1)	41.9 (0.1)	0.6
1 m	46.1 (0.2)	46.3 (0.1)	46.5 (0.1)	46.7 (0.1)	46.7 (0.1)	0.5
2 m	47.2 (1.2)	47.4 (1.0)	47.9 (0.8)	48.0 (0.7)	47.5 (0.1)	0.3

Number in ( ) denotes the standard deviation of 30 measurements from three specimens.

Figure 6 Wettability decay of acrylic acid-grafted PET in liquid-phase reaction (0.5, 1, and 2 min glow discharge); reaction time: 1 h (◇), 4 h (□), 1 day (△), 2 days (●), 4 days (★), and 7 days (○).

Although the reasons for the superior wettability of the first vapor-phase-grafted PET films were not known, the significant wettability decay indicated extensive uncaptured residual reactivity. The lack of reaction was thought to be due to the low amount of acrylic acid vapor in the chamber under the continuous pumping condition. In the attempt to increase the vapor concentration, the pump was turned off during the vapor admission period. While the acrylic acid vapor was admitted, the chamber pressure was found to remain at 1.5 Torr for the lengths of time studied. Under this second vapor-phase condition, the CA stability of the grafted PET surfaces (1 min glow discharge) was very much improved (Table V) as compared to the previous vapor-phase condition (Table IV). The very low wettability decay indicated the near absence of activated species on the surface. The water CAs on these films were significantly lower than those on the liquid-phase-grafted ones (Table III), but were not as low as the glow-discharged surfaces (Table I). Both the CAs and CA decay were independent of the lengths of the vapor-phase reaction.

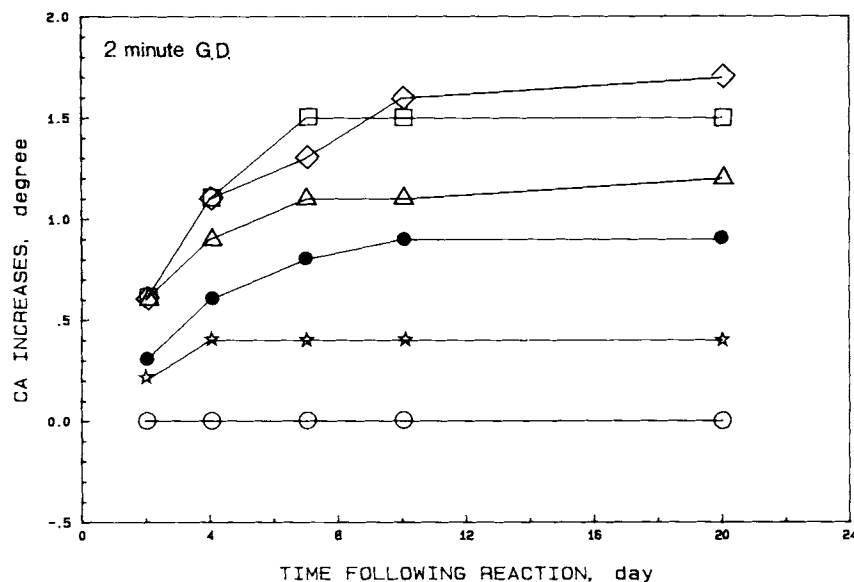In the previous two vapor-phase conditions, the

Figure 6   (*Continued from the previous page*)

lowest initial CAs resulted from the continuous pumping condition and higher CA stability was achieved by admitting acrylic acid vapor without pumping. In the third vapor-phase condition, two prior approaches were combined to maximize their effects. Acrylic acid vapor was admitted immediately after glow discharge with the pump running for 5 min and then with the pump turned off for another 5 min. Table VI lists the CAs of PET films glow discharged for 0.5, 1, and 2 min prior to the exposures to acrylic acid vapor. The lowest glow-discharge time of 0.5 min produced the most wettable surface, with a CA of 41.9°. The most promising result of this combined vapor-phase procedure was achieving the least CA decays (0.3°–0.6°) (Table VI).

The surface of acrylic acid-grafted PET under the optimal vapor-phase condition appeared relatively smooth under the scanning electron microscope. Examination at a higher magnification reveals a surface (Fig. 9) similar to the glow-discharged surface [Fig. 3(b)].

The major differences in wettability and wettability decay between films modified in the liquid phase and vapor phase could be explained by how the acrylic acid molecules were covalently bonded to the glow-discharge-activated PET surfaces. In the liquid-phase reaction, the reactive species on the PET surface were surrounded by abundant acrylic acid, allowing not only grafting but also cross-linking of acrylic acid on the surface. Cross-linking could reduce the mobility and possibly the density of sur-

face polar groups, resulting in less wettable surfaces. In the vapor phase, on the other hand, cross-linking was less likely due to the separated nature of the acrylic acid molecules in the vapor. Since surface-adsorbed acrylic acid should have been removed by the after-reaction washes in either case, it was reasonable to believe that differences resulting from these two types of reactions are due mainly to the structural difference of the bonded acrylic acid.

SUMMARY

The water CA of the untreated Melinex PET films was 73.1°. Upon glow-discharge treatment in argon, wettability of PET was improved significantly. The water CA was reduced to 41.0° after a 0.5 min treatment, and to 33.7°, after a 5 min treatment. The improved wettability decayed with time. Water CAs of the argon glow-discharged PET stabilized 4 days after the treatments of 1, 2, and 5 min. But the equilibrium CA was not reached until 7 days after the 0.5 min treatment. Total CA decay ranged from 4.3° and 4.4° for the 2 and 1 min treatments to 7.6° for the 5 min treatment. Scanning electron micrographs showed irregular hairline patterns on the untreated PET surface at 15,000 magnifications and higher. The surfaces of the PET films glow discharged for up to 1 min remained similar to the untreated ones. The appearance of polygonal crystals and the disappearance of the hairline patterns were observed
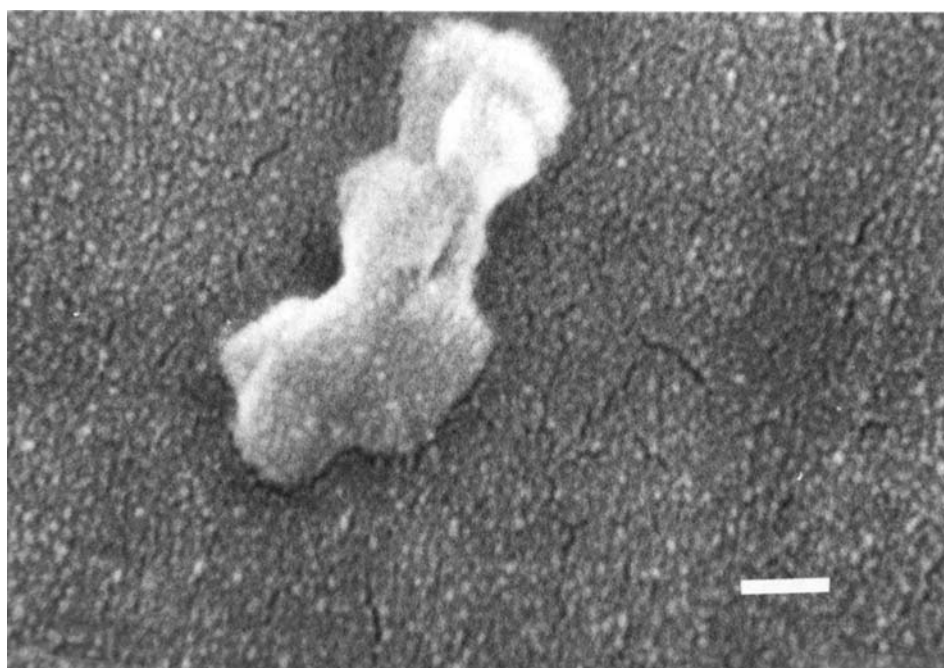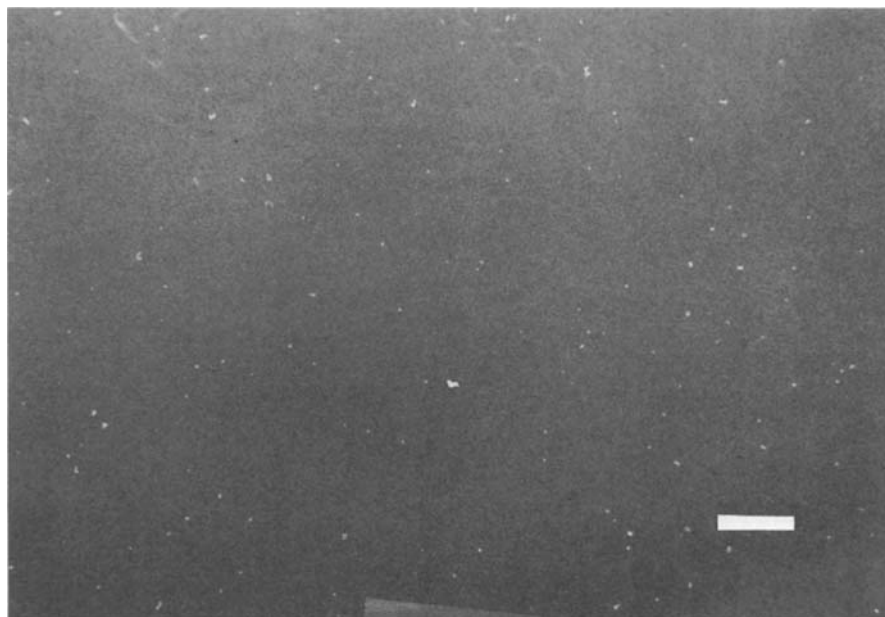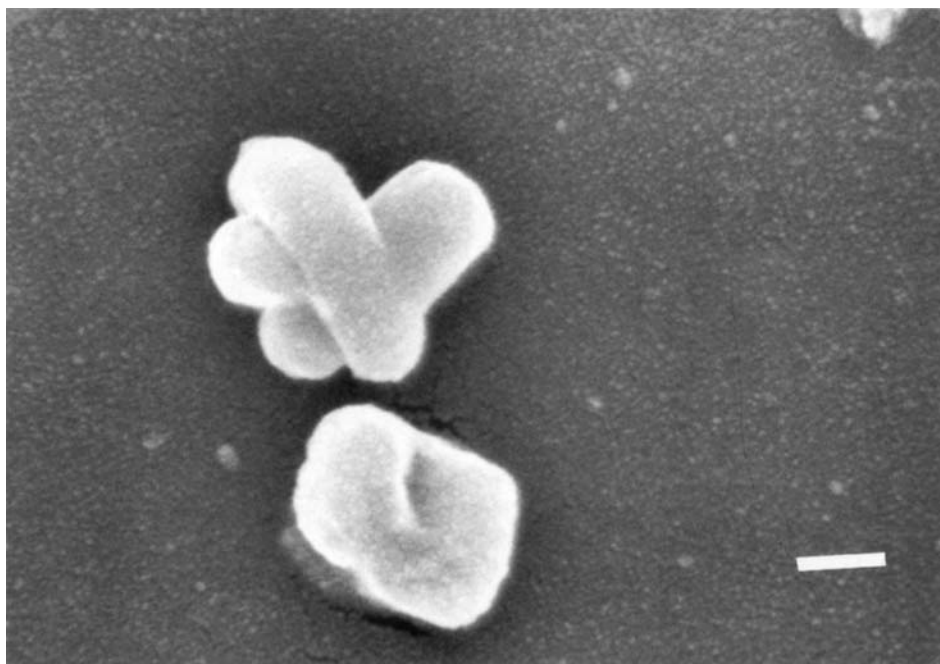
Figure 7   Liquid-phase grafting of acrylic acid (1 h immersion) on PET after 0.5 min argon glow discharge: (a) bar = 9.90 μm; (b) bar = 0.17 μm.

on PET surfaces glow discharged for 2 min and longer. The hairline patterns that were thought to be surface microcracks of mostly amorphous PET became less noticeable with increasing glow-discharge time. Polygonal crystals were similar in shape to, but approximately one magnitude smaller than, those found on heat-treated PET fibers and films. These polygonal crystals were increasingly etched with longer glow discharge and were sputtered away, leaving mostly patches of redeposited substances.
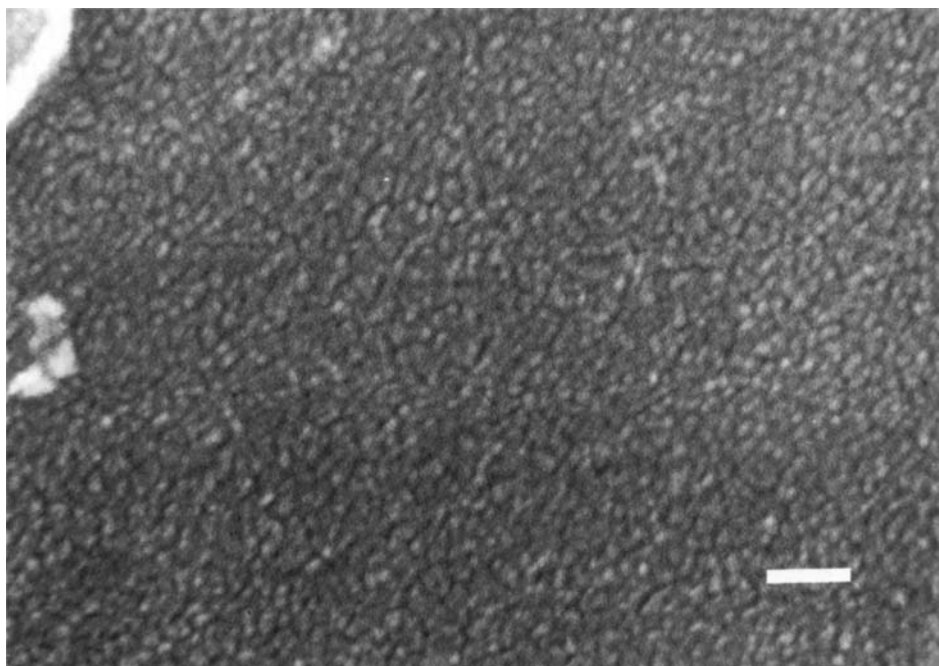
In the liquid-phase reactions, longer glow-discharge time produced lower CAs. Lengthening liq-

Figure 8 Liquid-phase grafting of acrylic acid (4 day immersion in acrylic acid) on 1 min argon glow-discharged PET; bar = 0.20 μm.

uid-phase reaction time, on the other hand, slightly increased CAs. A water CA of 54.0° was achieved by 1 min glow discharge followed by a 1 h reaction in acrylic acid. Wettability of the grafted surface decays with time to a lesser degree (up to 1.9°) than did the PET treated with argon glow discharge alone. Particles, individual and clusters sized from 0.1 to 1.0 mm, were found on the grafted surfaces after the

Figure 9 Vapor-phase (10 min under the combined condition) grafting of acrylic acid on PET initiated by 1 min argon glow discharge; bar = 0.10 μm.

liquid-phase reactions. As reaction in acrylic acid was prolonged, the hairline patterns disappeared from the surfaces.

In the vapor-phase reactions, the CAs varied significantly by changing the vapor admission conditions, but the CAs were not affected by the length of acrylic acid admission time. A water CA of 42.9° was obtained in the optimal vapor-phase condition. The vapor-phase-reacted surfaces also had negligible CA decay (0.3°–0.6°). Surfaces of grafted PET in the vapor-phase reaction were similar to the glow-discharged PET surfaces.

Substantial residual reactivity on argon glow-discharged PET surfaces was demonstrated by the significant changes on surface wettability by reactions with acrylic acid. A wide range of surface wettability produced from reacting with acrylic acid under different conditions illustrates the potential of glow-discharge-activated PET surface for further reaction to achieve specific chemical functionality. Along with results of another study,[11] surface wettability decay on glow-discharged PET was attributed to both residual reactivity and reorientation of polar groups on the surface. The wettability decay could be reduced either by proper solvent treatment prior to glow discharge[10] or by reaction with hydrophilic compounds as found in this study.

REFERENCES

1. H. V. Boenig, *Plasma Science and Technology*, Cornell University Press, Ithaca, NY, 1982, Chap. 2.
2. J. M. Burkstrand, *J. Vac. Sci. Tech.*, **15**, 233 (1978).
3. D. T. Clark and A. Dilks, *Characterization of Metal and Polymer Surfaces*, L. H. Lee, Ed., Academic Press, New York, 1977, Vol. 2, p. 101.
4. H. Yasuda, H. C. Marsh, S. Braandt, and C. N. Reilley, *J. Polym. Sci. Poly. Chem.*, **15**, 991 (1977).
5. M. M. Kadash and C. G. Seefred, Jr., *Plast. Eng.*, **41**(12), 45, (1985).
6. R. H. Hansen, J. V. Pascale, T. DeBenedicts, and P. M. Rentzepis, *J. Polym. Sci. A*, **3**, 2205 (1965).
7. A. M. Wrobel, M. Kryszwsik, W. Rakwski, M. Okoniewski, and S. Kubacki, *Polym. Phys.*, **19**, 908 (1978).
8. D. Briggs, D. G. Rance, C. R. Kendall, and A. R. Blythe, *Polymer*, **PB21PB**, 895 (1980).
9. H. Yasuda and A. K. Sharma, *J. Appl. Polym. Sci.*, **19**, 1285 (1981).
10. Y.-L. Hsieh, D. A. Timm, and M. Wu, *J. Appl. Polym. Sci.*, **38**, 1719 (1989).
11. Y.-L. Hsieh and E. Y. Chen, *Ind. Eng. Chem. Prod. Res. Dev.*, **24**, 246 (1985).
12. M. M. Millard, J. J. Windle, and A. E. Pavlath, *J. Appl. Polym. Sci.*, **17**, 2502 (1973).
13. J. Derminot, R. Hagege, and J. Jacquenmart, *Bull. Sci. ITF*, **5**(20), 355 (1976).
14. A. Perovic and D. K. Murti, *J. Appl. Polym. Sci.*, **29**, 4321 (1984).
15. A. Perovic and P. R. Sundararajan, *Polym. Bull.*, **6**, 277 (1982).
16. A. L. Cimecioglu, S. H. Zeronian, K. W. Alger, and M. J. Collins, *J. Appl. Polym. Sci.*, **32**, 4719 (1986).