

# Aging and Annealing Behavior of Polycarbonate Surfaces Modified by Direct-Current Glow Discharge in Air

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**ABSTRACT:** Aging and annealing a polycarbonate (PC) polymer surface treated by direct-current (dc) glow discharge tend to revert it back to its virgin (pristine) state existing before surface modification by glow discharge. This structural recovery during aging and annealing has been studied in terms of the contact angles of test liquids and surface energy and correlated to the parameters of surface treatment such as the treatment time and power. Samples stored in hydrophobic environments such as air and treated by dc glow discharge at higher power levels show less recovery during aging than those treated at lower power levels. Similarly, a longer exposure time at a power level of 2.04 W decreases the extent of structural recovery in terms of surface energy during aging in air.

At higher power levels, the higher kinetic energy of plasma species involved during dc glow discharge results in greater thickness of the damaged layer of the polymer surface, and so a PC sample exposed to dc glow discharge at a higher temperature also recovers at a slower rate during the initial phase of aging, whereas samples with surfaces modified by dc glow discharge at room temperature but annealed at a higher temperature show a relatively rapid recovery during the initial phase of aging. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 700–708, 2009

**Key words:** ageing; annealing; ESCA/XPS; polycarbonates; surfaces

## INTRODUCTION

The surface modification of polymers has been carried out with techniques such as direct-current (dc) glow discharge, which causes increased surface energy primarily through the modification of its polar component due to dipolar interactions and a minor change in the dispersion component due to van der Waals interactions.<sup>1–3</sup> Thus, improved surface wetting and adhesion needed for various industrial applications, such as construction, sports, automobiles, packaging, and medical applications, are obtained.<sup>3–8</sup> It is, therefore, essential that the surface, once modified, be stable and retain its modified characteristics for a long period of time. The stability of the modified surface is threatened by structural recovery of the surface, which reverts toward its original (pristine) unmodified state during storage over a period of time. The acceptability and utility of any surface modification technique will depend on the kinetics of this structural recovery, which is commonly known as aging. Efforts should then be directed to understanding the aging behavior of sur-

faces of polymers modified by glow discharge.<sup>2–7,9–14</sup> Storing a surface modified by glow discharge at elevated temperatures for different times is called annealing. Structural recovery at these elevated temperatures may also be interesting for deriving a strategy for ascertaining the stability of modified polymer surfaces.

Among various polymers, polycarbonate (PC) is a very promising material because of its good transparency, toughness, high tensile strength and impact resistance, and high heat resistance and rigidity. These properties make PC an ideal material for various demanding applications. Although its low hardness, low scratch resistance, and degradation by UV radiation as well as its poor wettability demand the modification of the surface properties of PC, good adhesion between the surface of the polymer and adhesive/coated material is also necessary. Thus, the stability of the surface properties after modification for prolonged periods in different environments and at different temperatures is of paramount importance, and there is a need to restrict surface recovery toward the untreated state during aging.

In the past, efforts have been made to understand and minimize the effect of aging on the modified surfaces of polymers in different hydrophilic and hydrophobic environments.<sup>15–24</sup> The aging of

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polymer surfaces modified by alternating-current glow discharge [radio frequency (RF), micro-wave (MW), and electron-coupled-resonance (ECR)] and ion irradiation has been studied extensively<sup>12,25–27</sup> in different environments. However, there have been very few investigations<sup>17</sup> on the aging of polymer surfaces modified by dc glow discharge.

In this study, the effects of aging and annealing on PC samples modified by exposure to dc glow discharge in air were investigated. The aging of PC surfaces treated for surface modification for different times of exposure and at different power levels was carried out in ambient air, and annealing at different temperatures of samples treated at room temperature (ambient) by dc glow discharge was also carried out. The aging of samples treated by dc glow discharge at higher temperatures was also performed during storage in ambient air at room temperature.

## EXPERIMENTAL

For surface modification, PC substrates ( $2 \times 2 \times 0.3 \text{ cm}^3$ ) with a specific gravity of  $1.2 \text{ g/cm}^3$  and a molecular weight of approximately 30,000 (manufactured by Lexon, Inc., and supplied by M/S GE Plastics, Gurgaon, India) were used.<sup>28,29</sup> These substrates were first cleaned three times in doubly distilled water and in isopropyl alcohol ultrasonically and dried before being stored in desiccators for about 4 h before subjection to a glow-discharge treatment.

The discharge was carried out in an assembled dc glow discharge setup with a glass chamber about 450 mm high and 300 mm in diameter.<sup>30</sup> The chamber was connected to a diffusion pump with a speed of 800 L/min backed by a rotary oil pump with a capacity of  $12 \text{ m}^3/\text{h}$ . A pressure of  $10^{-5}$  mbar could be attained in the vacuum chamber. However, the operating pressure used for this study was 0.3 mbar (30 Pa). The discharge was produced between a pair of 4-mm-thick Al plates with a diameter of 100 mm. The choice of the electrode material was dictated by the low sputtering yield to reduce contamination by the electrode material. The gap between electrodes was kept at 4.5 cm. The substrates were placed on the anode (lower electrode), which was connected to the ground, and the cathode (upper electrode) was connected to a power supply with a voltage range of 0–5000 V.<sup>30,31</sup>

The contact angle on the PC surface was measured by the sessile drop method with two probe liquids such as deionized water and formamide.<sup>28–31</sup> The contact angle could be measured with an accuracy of  $\pm 2^\circ$ , which included the error due to evaporation of the probe liquids and random error in the contact angles as estimated from six measurements on different drops for each liquid. From the contact-angle

data for sessile drops of water and formamide, the polar and dispersive components were estimated with the geometric mean relation.<sup>30,32</sup> On the addition of the polar and dispersive components, the total surface energy for PC was estimated. The error in the surface energies was observed to lie in the range of  $\pm 0.8 \text{ mJ/m}^2$ , which was estimated on the basis of the contact angle.

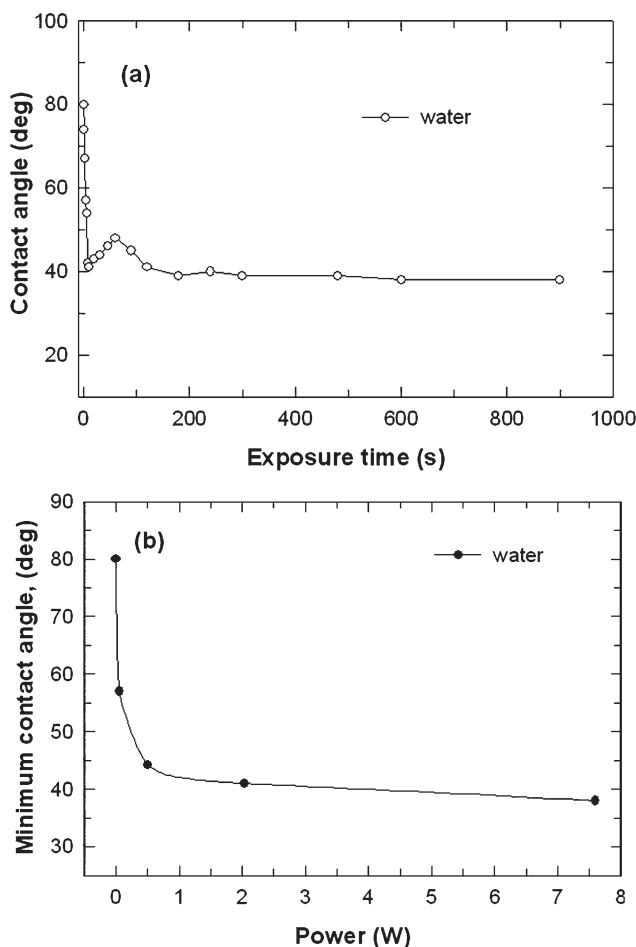
Atomic force microscopy (AFM) was carried out with a Nanoscope IIIA scanning probe microscopy atomic force microscope (Digital Instruments) made by Veeco probes, Santa Barbara, CA. The contact-mode technique was used to obtain the surface roughness. The surface roughness from the topographic images was obtained with the help of inbuilt Nanoscope software available for scanning probe microscopy.

Electron spectroscopy for chemical analysis (or X-ray photoelectron spectroscopy) was carried out with the help of a PerkinElmer model 1257 X-ray photoelectron spectrometer (Massachusetts, USA) with a nonmonochromatic Mg  $K\alpha$  radiation source with an energy range of 0–1236.5 eV at 15 kV (power = 100 W). The operating pressure in the analysis chamber was kept at  $3.0 \times 10^{-8}$  torr throughout the experiments. Wide-scan survey spectra were obtained in the binding energy (BE) range of 0–1000 eV with a pass energy of 60 eV, whereas narrow-scan spectra were carried out in the BE range of approximately 20 eV around each signal peak of C1s, O1s, and N1s with a pass energy of 40 eV. During the analysis, the X-ray beam with a spot size of 2.5 mm was incident at an angle of  $35^\circ$  to the surface of the substrate, and electrons, having a normal take-off angle, were detected with a hemispherical electron energy analyzer mounted at the normal position of the sample surface.

The aging and annealing studies were carried out in air at room temperature as a function of the storage time for samples stored at different temperatures. Annealing studies at different temperatures were carried out in an oven at atmospheric pressure. The temperature of the oven was controlled accurately with a proportional–integral–differential temperature controller with an accuracy of  $\pm 1.0^\circ\text{C}$ . For annealing at low temperatures, the samples were stored in a freezer in air-tight boxes. Silica gel was also placed inside the box to remove water vapor surrounding the sample. For samples stored at low temperatures, the contact-angle measurements were made after the samples had attained equilibrium with the environment in about 8–10 min.

## RESULTS AND DISCUSSION

The variation of the contact angle with the time of exposure at different power levels is shown in



**Figure 1** Variation of (a) the contact angle of water with the time of exposure at 2.04 W and (b) the initial minimum value of the contact angle with the power for the time of exposure after dc-glow-discharge treatment on PC.

Figure 1(a,b). Figure 1(a) reveals a significant change in the contact angle after exposure to dc glow-discharge plasma in the presence of air. A rapid change in the wetting angle can be observed until 10 s of exposure at the power level of 2.04 W, at which point the contact angle of water attains a value of approximately 40° from its initial value of 80° observed on an as-received PC sheet. However, further exposure results in decreased wetting until 60 s of exposure

time at the power level of 2.04 W. The contact angle decreases with continuing exposure before saturation, as shown in Figure 1(a). Table I shows that the change in the contact angle is due to the dominating change in the polar component of the surface energy. The change in the dispersion component of the surface energy is relatively small but in the opposite direction. Figure 1(b) shows the variation of the minimum contact angle with increasing power of the dc glow discharge used to treat PC samples in air. The wettability of the surface treated to attain the minimum contact angle increases with increasing power, as indicated by the increased reduction in the contact angle. Table II shows that with increasing power of the dc glow discharge, the polar component of the surface energy increases, whereas the dispersion component decreases. The decrease in the contact angle with either a longer time of exposure or higher power leads to more collisions with higher kinetic energy species, and this results in the scission of long chains and their functionalization and cross-linking. Different polar functional groups such as C=O and C—O<sup>7</sup> help to increase the polar and total surface energies of PC. The smaller the fragment size is of the chain, the larger the mobility is. The hump in the contact angle observed here has also been noted in various other polymers during glow-discharge/plasma treatment.<sup>25,33,34</sup> It has been inferred that as the functionalization of chains takes place, a competing mechanism of chain scission and crosslinking, which prevents the movement of various functional groups, also takes place during glow discharge. These competing mechanisms may be responsible for the hump. It is also necessary to retain the fragmented functionalized chain at the surface to prevent the aging effect. For this reason, the variation of the contact angle as a function of the aging time in air on PC samples with surfaces exposed to dc glow discharge at 2.04 W for exposure times of 10, 60, and 900 s to attain the initial minimum contact angle, the end of the hydrophobic change (i.e., the hump), and the saturation in the contact angle, respectively, is shown in Figure 2. A rapid increase in the contact angle, indicating structural recovery of

**TABLE I**  
Surface Energies of the PC Surfaces Modified by dc Glow Discharge with the Time of Exposure at a 2.04-W Power Level and Percentage Recovery in the Surface Energies After Aging

State of the sample	Surface energy before aging (just treated; mJ/m <sup>2</sup> )			Recovery to as-received values of the different components of the surface energy after aging (%)					
				Aged for about 10 h			Aged for about 500 h		
	Polar	Dispersive	Total	Polar	Dispersive	Total	Polar	Dispersive	Total
As received	6.89	25.67	32.56	—	—	—	—	—	—
Treated for 10 s	34.84	21.05	55.89	28.47	88.31	16.59	68.37	148.70	56.32
Treated for 60 s	29.49	22.57	52.05	12.87	89.35	0.72	52.47	86.77	46.99
Treated for 900 s	37.51	20.53	57.85	29.16	166.92	0.63	52.05	244.94	12.49

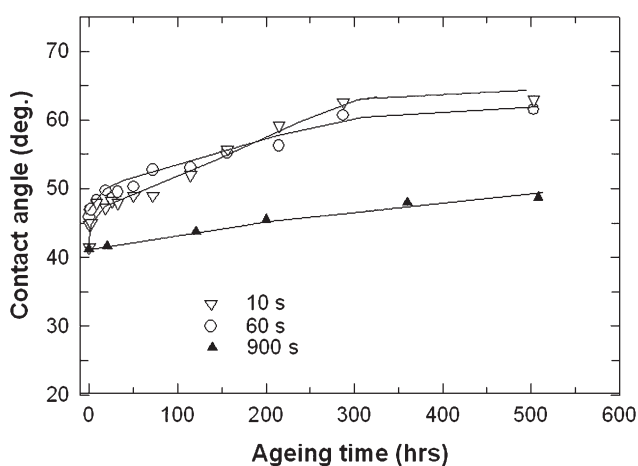
**TABLE II**  
**Surface Energies of the PC Surfaces Modified by dc Glow Discharge at Different Power Levels to the Maximum Surface Energy and Percentage Recovery in the Surface Energies After Aging**

State of the sample	Surface energy before aging (just treated; mJ/m <sup>2</sup> )			Recovery to as-received values of the different components of the surface energy after aging (%)					
				Aged for about 10 h			Aged for about 660 h		
	Polar	Dispersive	Total	Polar	Dispersive	Total	Polar	Dispersive	Total
As received	06.89	25.67	32.56	—	—	—	—	—	—
Treated with 0.50 W	34.63	19.27	53.90	66.33	187.18	30.08	90.77	203.75	58.24
Treated with 2.04 W	34.84	21.05	55.89	28.48	88.31	16.58	74.81	189.82	51.99
Treated with 7.60 W	37.23	22.57	59.8	27.42	71.61	24.96	71.75	264.51	49.81

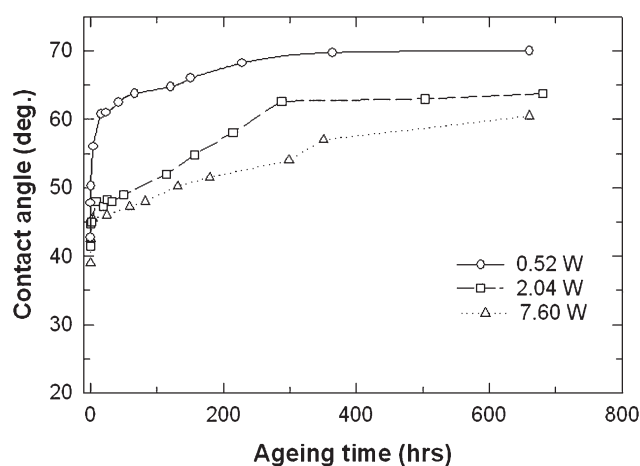
the treated surface, can be observed within the first 10 h of aging. Thereafter, the contact angle increases slowly and reaches saturation after a long aging time of about 500 h. The aging behavior of PC suggests that, in general, there are two different relaxation mechanisms responsible for the aging effect. There is a rapid rise in the contact angle that occurs within the first few hours, and a second mechanism is responsible for a slow rise in the contact angle over a few hundred hours.<sup>35</sup> For the samples treated for a longer time of exposure, such as 900 s, the second mechanism is more pronounced during aging. The recovery during aging is larger (16.59%) from the contact angle minimum for the 10-s-treated surface even with an aging time of 10 h. However, for a longer exposure time corresponding to the peak of the hump or saturation, the extent of recovery is relatively very small at 0.72% and 0.63%, as shown in Table I. Therefore, it is apparent that a longer exposure time under glow discharge decreases the mobility of the fragmented and functionalized chains, possibly because of increased crosslinking. However, at a longer aging time of 500 h, even the chain fragments of larger sizes and lower mobility move away

from the surface during 10–500 h of aging, and this leads to about 40.0% recovery (i.e., 56.32 – 16.56 ~ 40) of the surface energy in PC exposed to glow discharge for attaining the minimum contact angle. In the PC surface exposed to attain a contact angle corresponding to the peak of the hump, there is a still larger recovery of about 46% between 10 and 500 h, as shown in Table I. However, longer exposure to dc glow discharge to attain contact-angle saturation results in a smaller recovery of 12.49% even after 500 h of aging. It is possible that there is extensive crosslinking during longer exposure, but the damage may extend even to the subsurface and may be reflected in the mechanical properties.

The aging behavior of samples exposed to dc glow discharge to attain the minimum contact angle at different power levels is shown in Figure 3. The general behavior of the contact angle as a function of the aging time is very similar to that of the samples treated at 2.04 W with increasing exposure times (Fig. 2). Here too, the samples treated at a higher power recover predominantly by the slower (second) relaxation mechanism during aging versus that observed during the aging of PC treated at a



**Figure 2** Variation of the contact angle of water with increasing aging time for PC samples modified by exposure to dc glow discharge for different times at a power level of 2.04 W.



**Figure 3** Variation of the contact angle of water with increasing aging time for PC samples modified by dc glow discharge to attain the minimum contact angle at different powers.

lower power. Similarly, the structural recovery during aging is larger (30.08%) from the contact angle minimum even with aging for 10 h for the surface treated at a lower power level up to the initial minimum time of treatment. However, for a higher power, the extent of recovery is lower for 2.04 and 7.6 W; the corresponding recoveries are 16.58 and 24.96%, respectively, as shown in Table II. Therefore, this may be attributed to the fact that the surface treated at a higher power level under glow discharge decreases the mobility of the fragmented and functionalized chains; it may also be inferred that this is due to the increased crosslinking of polymer chains. With prolonged aging of approximately 660 h, the chain fragments of larger sizes and lower mobility move away from the surface during 10–660 h of aging, and this leads to recovery of approximately 28% (i.e.,  $58.24 - 30.08 = 28.16$ ) for a surface treated at a lower power level of 0.52 W in dc glow discharge for attaining the minimum contact angle. However, using a higher power of dc glow discharge to attain saturation in the contact angle results in a smaller recovery of 49.81% even after 660 h of aging. However, there is very little difference in the recovery with a longer duration of aging at a higher power in comparison with the other process parameter, that is, the treatment time for longer exposure at a power level of 2.04 W. However, it still shows that there is an increase in chain crosslinking from lower to higher power levels, just like the exposure time parameter, and the surface damage may also extend even to the subsurface because of the collision of higher energy species of glow discharge on the surface; this may be reflected in mechanical problems, as observed for PC adhesively joined to mild steel at different power levels. This behavior seems to be common for most of the polymers for which aging behavior has been reported.<sup>2,18,19,21</sup> Similar aging behavior has been observed in polypropylene surfaces modified by exposure to oxygen plasma, as reported by Morra et al.,<sup>20</sup> and also in poly(ether ether ketone) film surfaces modified by exposure to RF plasma, as reported by Brennan et al.<sup>21</sup> Gil'man et al.<sup>7</sup> studied the aging of PC surfaces modified by alternating-current (50 Hz) glow-discharge plasma; the initial recovery of the contact angle was much slower than the results obtained in this study, but the general behavior was still the same.

The relaxation of the surface modified by glow discharge may be attributed to the following effects: (1) the migration or orientation of polar groups created during surface modification and (2) the motion of low-molecular-weight oxides (LMWOs).

It is of course not known which mechanism is responsible for rapid or slow recovery during aging. It is generally believed that aging causes inward or out-

**TABLE III**  
Variation in the Surface Roughness of PC Treated by dc Glow Discharge at a 2.04-W Power Level for 10 s and Then Aged in Air

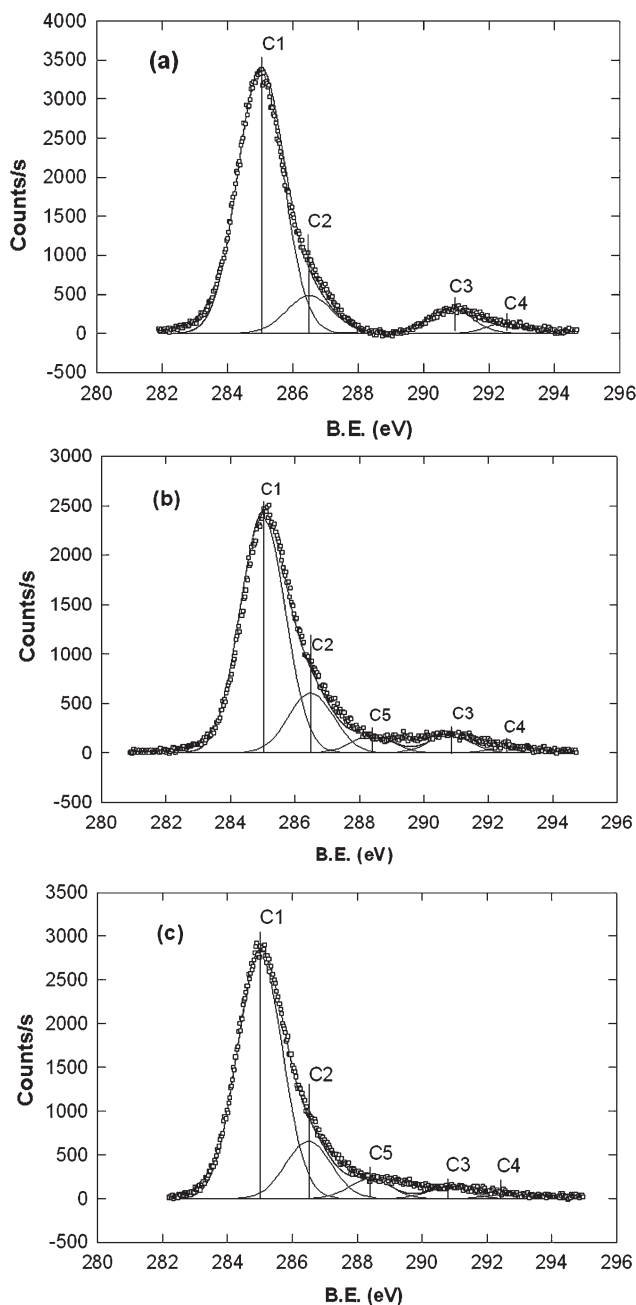
PC	Aging time (days)	Area ( $\mu\text{m}^2$ )	RMS (nm)	RA (nm)
Untreated	0	8.895	10.064	8.402
Treated	1	8.894	2.915	2.292
Treated and aged	70	8.892	2.808	2.002

ward diffusion of oxygen containing polar groups, depending on the environment during aging.<sup>18</sup>

Restructuring of the surface, which involves limited movement, may be taking place faster. The diffusion or migration of polar functional species generated on the surface by glow discharge into the subsurface may involve longer times, and the change due to it should be relatively slow. There is also a high density of LMWO fragments on the surface generated by a longer treatment, and it may help to restrict the diffusion further through the subsurface layer, as pointed out earlier<sup>7,10,12–14</sup> in studies on the aging of polymers surface-modified by RF glow discharge at different powers and for different exposure times. The higher power thickens the depth of modification, and the LMWOs may stay in the subsurface region and restrict the migration of polar groups into the subsurface or the movement of unmodified chains from the bulk region to the surface.

The surface roughness was observed by AFM to determine the changes from either the restructuring or rearrangement of polar species of PC on the modified surface before and after aging, as shown in Table III. There is a very slight change in the roughness root mean square (RMS) from 2.9 to 2.8 nm due to 70 days of aging of the modified surface of the sample treated at a power of 2.04 W for 10 s. The corresponding change in the average roughness (RA) is from 2.2 to 2.0 nm in a scanning area of  $8.894 \mu\text{m}^2$ . Thus, the roughness does not change much with aging, and there is possibly very little change in the surface topography of PC during aging in air. The results show that the dynamic motion of the surface and rearrangement of molecular chains do not affect the surface roughness. Therefore, it can be inferred that aging is primarily due to the reorientation of polar species and their diffusion.

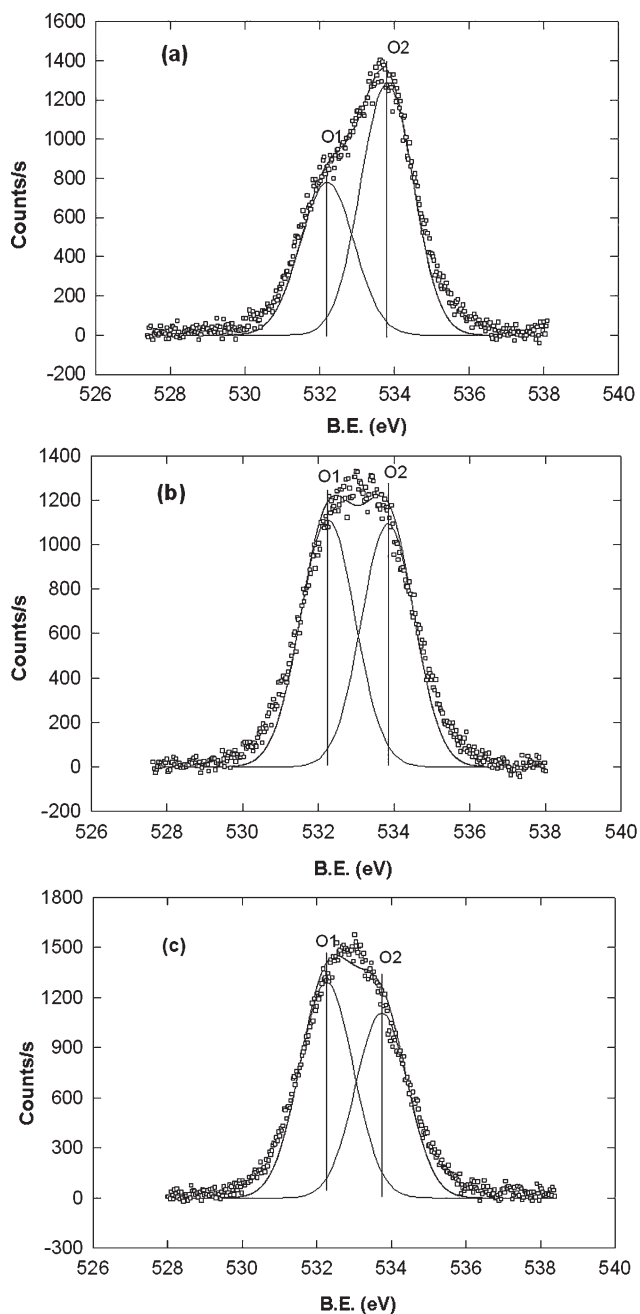
An X-ray photoelectron spectroscopy analysis of the modified PC surface stored for the longest time of 70 days was carried out to determine the changes in the polar functional groups and atomic concentrations of C, O, and N after aging. For the identification of these groups and the atomic percentage concentrations of these groups, narrow-scan spectra of untreated, treated (at 2.04 W for 10 s), and aged



**Figure 4** Deconvoluted narrow-scan spectra of the C1s peak for samples: (a) as-received surface, (b) surface modified by dc glow discharge at 2.04 W for 10 s, and (c) surface modified and aged in air for 70 days.

PC samples were obtained for C1s and O1s spectra, as shown in Figure 4(a–c) and Figure 5(a–c), respectively. The atomic percentages of O and C were calculated on the basis of an area analysis of deconvoluted C1s and O1s spectra in a narrow range. The theoretical estimates of the percentages of C and O atoms from the structural formula, full width at half-maximum, peak assignment, and other references used for deconvolution have been discussed elsewhere.<sup>30</sup> The assignment of the peak positions of the functional groups was carried out

according to Vallon et al.<sup>22</sup> and Zajickova and co-workers.<sup>13,14</sup> The deconvoluted peaks were assigned to different chemical bonds marked C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, C<sub>4</sub>, and C<sub>5</sub>, which correspond to C–C/C–H, C–O, O–(C=O)–O,  $\pi$ – $\pi^*$ , and O–C=O/C=O bonds, respectively. Figures 4(a–c) and 5(a–c) also show the deconvoluted peaks for the aforementioned conditions in the narrow range spectra of C1s and O1s, respectively.



**Figure 5** Deconvoluted narrow-scan spectra of the O1s peak for samples: (a) as-received surface, (b) surface modified by dc glow discharge at 2.04 W for 10 s, and (c) surface modified and aged in air for 70 days.

**TABLE IV**  
Atomic Composition of Carbon and Oxygen in the As-Received Surface of PC and in the Modified Surfaces Before and After Aging in Air for 70 Days

Sample state	C (atom %)	O (atom %)	O/C ratio
Untreated	86.40	13.60	0.157
Treated for 10 s with 2.04 W	82.42	17.67	0.214
Aged 70 days	84.09	15.91	0.188

The calculated atomic O/C ratio is given in Table IV, and the O/C ratio of the modified surface, 0.21, decreases during 70 days of aging to 0.18. This result follows the general correlation of the contact angle increasing with the O/C ratio decreasing because of the decreasing polar component and total surface energy. This can be attributed to the folding of surface chains and resulting reduction of the interfacial energy of the modified PC surface in contact with air. Therefore, it can be concluded that during aging, the decrease in the polar functional groups is the dominant mechanism instead of other changes leading to changes in the surface topography. However, from the concentration of functional groups, it has been found that C—O shows a very slight change in magnitude, whereas the concentration of C=O decreases after 70 days of aging. The concentrations of O—(C=O)—O and shake-up satellites ( $\pi$ - $\pi^*$ ) also decrease, as shown in Table V. The decrease in the concentration of O—(C=O)—O and shake-up satellites ( $\pi$ - $\pi^*$ ) shows that the aromatic character of the PC surface decreases during aging.<sup>10,13,14</sup> The extent of the decrease in the O/C ratio is much higher during the aging of the PC surface modified by RF glow discharge.<sup>13,14</sup>

Figure 6 summarizes the variation of the contact angle of water droplets on the PC surface modified by dc glow discharge at 2.04 W for 10 s as a function of the annealing time. When aging is carried out at temperatures higher than room temperature ( $\sim$  300 K), it is called annealing. Samples aged at 273 K, a

temperature lower than room temperature, show a small change in the contact angle, and this implies reduced/negligible motion of polar groups. On the other hand, the contact angle of a sample annealed at a higher temperature of 413 K increases rapidly and reaches a saturation value. The rate of the increase in the contact angle is much slower for samples aged at approximately 300 K. Very similar behavior has also been reported for the surface of polypropylene modified by exposure to oxygen plasma, as observed by Morra et al.<sup>20</sup> Gupta et al.<sup>9</sup> reported similar results for the surface of a polyester film modified by exposure to argon plasma. The contact angle of water increases more rapidly for samples annealed at 293 K and saturates to a higher value versus that observed in samples aged at 253 K. The different saturation values of the contact angle for samples stored at different temperatures suggest that apart from the motion of functional groups, there are some other mechanisms operative during aging/annealing. To investigate this, PC samples were exposed to dc glow discharge at 2.04 W for 10 s at temperatures higher than room temperature. Figure 7 shows the variation of the contact angle as a function of the storage time (at room temperature) during aging in air. The PC surface modified at a higher temperature (413 K) by dc glow discharge shows a much smaller change in the contact angle in comparison with samples with surface modification carried out at room temperature (300 K).

Samples treated at 413 K (near the glass-transition temperature of PC) show a smaller contact angle after treatment and during aging and saturate to a relatively low contact angle, 38°, after aging for 500 h. PC samples modified at 373 and 300 K reach the contact-angle saturation values of 40 and 65°, respectively.

The aging behavior of samples with surfaces modified at higher temperatures suggests that aging involves other mechanisms besides the motion of

**TABLE V**  
Concentration of Chemical Functional Groups Just After Treatment and After Aging in Air (Hydrophobic Medium) for 70 Days

Peak	BE (eV)	Assigned functional groups	Untreated	Treated	
				Just after treatment	After aging for 70 days
C <sub>1</sub>	285	C—C, C—H	78.13	70.59	73.87
C <sub>2</sub>	286.5	C—O, C—N,	11.25	17.98	17.19
C <sub>3</sub>	290.8	O—(C=O)—O	7.21	4.95	3.06
C <sub>4</sub>	292.6	$\pi$ - $\pi^*$	2.93	1.52	1.09
C <sub>5</sub>	288.4	C=O, O—C=O	—	4.95	4.75
O <sub>1</sub>	532.2	C=O	37.9	54.52	51.12
O <sub>2</sub>	533.8	C—O	62.09	45.48	48.87

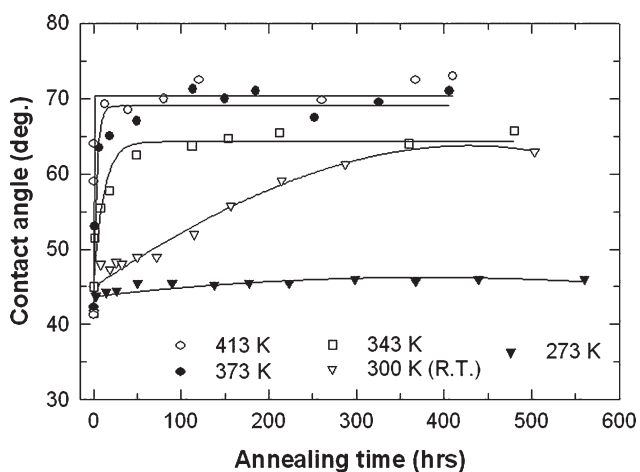
The treated samples were subjected to 2.04 W for 10 s in an air dc glow discharge. The results are also given for the untreated sample.

functional groups, crystallinity, crosslinking, and LMWO formation on the modified surfaces, which may be responsible for the observed aging behavior. However, the contribution of different mechanisms could not be quantified and definitely discussed.

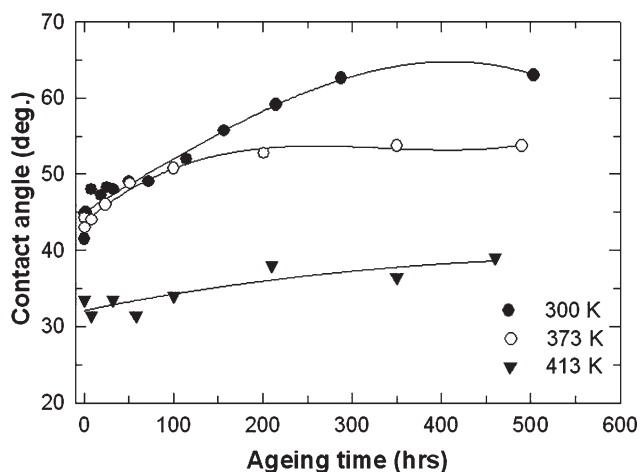
The total surface energy in the case of aging at the lower temperature of 273 K decreases to approximately  $53 \text{ mJ/m}^2$  after approximately 550 h of aging from the as-modified surface energy of approximately  $56 \text{ mJ/m}^2$ , which is very slight. As for the highest annealing temperature of 413 K, the surface energy decreases to approximately  $33.45 \text{ mJ/m}^2$  after annealing for 410 h from that of the as-modified PC surface, which is approximately  $56 \text{ mJ/m}^2$ . During high-temperature annealing, the surface energy approaches that of the as-received state, corresponding to a surface energy of approximately  $32.57 \text{ mJ/m}^2$ .

The total surface energy with the polar and dispersion components for samples of PC with the surface modified by dc glow discharge at elevated temperatures and aged in ambient air was also estimated from the corresponding contact-angle data. A slower decrease in the surface energy can be observed in the PC samples with the surface modified at higher temperatures. The surface energy shows very little reduction during aging for PC with the surface modified by glow discharge at 413 K and decreases to approximately  $58 \text{ mJ/m}^2$  from the as-modified surface energy of approximately  $62 \text{ mJ/m}^2$  during aging at room temperature; this is also an indication of maintaining the total surface energy for a longer duration.

The decrease in the polar component of the surface energy during aging is maximum for PC samples with the surface modified at room temperature and is minimum in the samples with the surface



**Figure 6** Variation of the contact angle of water with the annealing time for PC samples modified by dc glow discharge at 2.04 W for 10 s and annealed at different temperatures (R.T. = room temperature).



**Figure 7** Variation of the contact angle of water with the ageing time for PC samples modified by dc glow discharge at 2.04 W for 10 s at different temperatures and then stored at room temperature.

modified at 413 K. It has been found that beyond an aging time limit of approximately 250 h, the polar component saturates, regardless of the temperature at which surface modification is carried out. This shows that no further change is taking place with respect to polar groups after this period, and the surface becomes stable with the interacting medium by minimization of the interfacial energy. There is no appreciable change in the dispersion component of the surface energy.

## CONCLUSIONS

The surface of PC after dc-glow-discharge modification shows the following behavior during aging and annealing in a hydrophobic environment (air):

- During aging at a lower power, the dynamics of polar species are greater than the dynamics at a higher power in a hydrophobic medium (air). Thus, the exposure of PC at a higher power level prevents the aging effect for a longer period in air.
- Similarly, a longer duration of exposure at a particular power (2.04 W) also helps to restrict the migration/diffusion of polar groups for a prolonged period of storage in air.
- The O/C ratio of the treated PC surface decreases after aging, and this indicates a reduction mainly of oxidized polar groups such as  $\text{C}=\text{O}$ , whereas there is a negligible change in the roughness of the surface after aging for the same aging period as observed by AFM.
- Annealing at a higher temperature increases the dynamics of the polar groups and therefore decreases both the wetting and total surface energy of the modified PC.



- During aging, fast recovery to an untreated state is restricted for a PC surface treated at high temperatures by dc glow discharge; this may be due to the deep penetration of polar groups and restrictions by LMWOs.

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