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A Study of Surface Dynamics of Polymers. II. Investigation by Plasma Surface Implantation of Fluorine-Containing Moieties

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Synopsis

Macromolecules at the surface of a polymeric solid have considerable mobility, and the specific arrangement of functional groups of macromolecules at the surface is dictated by the environmental conditions in which the surface is placed. Consequently, the change of environmental conditions, such as immersion in water or placement in a biological surrounding, could cause a considerable degree of change in the surface characteristics of a polymer from those evaluated in the laboratory against ambient air. The mobile nature of a polymer surface can be investigated by surface-implanting fluorine-containing moieties, mainly $-\text{CF}_3$, by the plasma implantation technique and following the disappearance and reappearance of fluorine atoms on the surface. The disappearance rates (based on the immersion time in water at room temperature) of ESCA F_{1s} signals, the decay rates of (advancing) contact angle of water, and the recovery of these values on heat treatment of water-immersed samples were measured as a function of crystallinity of polymer samples (at three levels of crystallinity) for poly(ethylene terephthalate) and nylon 6.

INTRODUCTION

The surface dynamics of polymer solids are considerably different from those of more rigid materials such as metals and ceramics, due to the high mobility of macromolecules at the surface. Macromolecules have a high degree of freedom in determining their conformations according to the immediate neighboring phase. Consequently, macromolecules may orient themselves at the surface in a manner which is considerably different from that in the bulk phase of the polymer. For this reason, it is often difficult to predict the surface properties of polymers from the chemical nature of the molecules. Experimental evidence which supports the concept that the surface characteristics of polymers are determined by the specific surface configurations of samples, but not by the chemical structure of polymers, have appeared in the literature.¹⁻¹¹ For example, a highly water-swollen gel of hydrophilic polymer shows an extremely high water contact angle at the gel/air interface, whereas the same gel exhibits highly hydrophilic characteristics at the gel/water interface.² Surface analysis by ESCA revealed very few ion-exchange groups on the surface of an ion-exchange resin under the conditions of ESCA measurement in vacuum.⁵

The "surface configuration," which is used in this paper to describe the specific arrangement of chemical moieties at the surface, depends on the surrounding medium. Hence, the surface configuration of a polymer sample can not be described without specifying the surrounding medium. Such

changes in the surface configuration may generally be described by the term "surface dynamics", which deals with the change of surface characteristics due to the variations of environmental conditions. Although the overall net change due to the shift of the environmental conditions, such as the ones described above, can easily be observed, quantitative study is difficult without adequate surface labeling techniques and model cases.

In part I of this series of studies⁷ we demonstrated that the decay of hydrophilic character, introduced by plasma treatment of hydrophobic polymers, is primarily due to surface dynamic changes rather than the loss of chemical moieties due to their instability in the ambient conditions. It is postulated that the decay of the hydrophilic character of the surface over time after treatment is due to rotational and/or diffusional migration away from the surface of hydrophilic moieties that are introduced only on the surface by the plasma treatment. According to this postulate, the hydrophobic groups introduced onto a polymer surface would not decay in air. On the other hand, it also predicts that similar decay would be observed if the treated sample were kept in water; i.e., the rotational and diffusional migration of hydrophobic moieties away from the water/polymer interface would cause decay of the hydrophobic character when the treated samples are immersed in water.

In the research reported in this paper, the surface implantation of fluorine-containing moieties by a CF_4 plasma treatment is used to label the surface of nylon 6 and poly(ethylene terephthalate) (PET), and the decay of the hydrophobic character thus acquired is examined as a function of time of immersion in water in order to investigate the nature of the surface dynamic changes occurring in response to the shift of the surrounding conditions from air/polymer to water/polymer.

EXPERIMENTAL

Polymer Samples

Nylon 6 Films

A special batch of unoriented film without surface treatment (thickness 40 μm) was provided by courtesy of Toray Co., Ltd., Japan. The surface of the film was cleaned with a nonionic detergent solution (Scoarol 400, 2 g/L for 20 min) and a sodium phosphate solution (2g/L for 10 min, repeat twice). The samples were rinsed well with distilled water and dried in air overnight. An air-dried sample was fixed on a stretching device (width 4.3 cm, length 10 cm) and subjected to annealing at a preset temperature (205 and 220°C) in a circulating air oven for 10 min to produce (stretched) samples with varying degrees of crystallinity. The degree of crystallinity was determined at 25°C by density measurement using a density gradient column made of toluene and carbon tetrachloride.

PET Films

Special batches of biaxially oriented films, with three different degrees of crystallinity and without any surface treatment (thickness 50 μm) were

provided by courtesy of Toray Co., Ltd., Japan. The films were cleaned, using the procedure described above, and were used in the following experiments. The crystallinity was determined by density measurements at 25°C by using benzene and carbon tetrachloride.

Plasma Treatment of Films

A plasma reactor, IPC-1001-148 AN (International Plasma), capacitive coupling of rf (13.56 MHz) by external electrodes, was used to treat the film. CF_4 (without carrier gas) was used at a fixed flow rate of 50 $\text{cm}^3(\text{STP})/\text{min}$. The treatment was carried out at a pressure of 0.7 torr with an applied wattage of 50 W for 2 min.

Contact Angle Measurement

The advancing contact angle of water was measured by the following procedure. First, a droplet of water (2.7 μl) was placed on the center part of a film, and a photograph of the profile of the water droplet on the surface was taken. Every 20 s additional water (2.7 μl) was added to the water droplet, and a photograph was taken immediately. The procedure was repeated five times. By measuring the contact angles of the water droplets shown on the photographic prints, the advancing contact angle of water on the sample was determined.

ESCA Measurement

A Shimadzu ESCA 750 with a data analysis system was used for the measurements of C_{1s} , F_{1s} , O_{1s} , and N_{1s} peaks, using aluminum foil-filtered MgK_α x-rays (8 kV, 30 mA). The major emphasis of our ESCA analysis is on the accurate estimate of the number of fluorine atoms at the surface and, to a lesser extent, on the confirmation of types of fluorine-containing carbons.

Since the absolute intensity of F_{1s} peaks may change due to factors involved with the equipment, the reliability of the absolute value of the peak intensity is questionable. The efforts to normalize the peak intensity by taking the ratio F/C or the atomic percent at the surface, on the other hand, involve a similar extent of ambiguities when the surface modifications which introduce atoms that were not present in the original sample are employed. Because the CF_4 plasma treatment introduces additional C, F, and O atoms onto the surface of the substrate film, it was decided to use the peak intensity measurement to describe the total amount of fluorine atoms. In order to minimize the effect of sensitivity drift of the equipment, the following procedure was adopted.

On each set of measurements, the C_{1s} spectrum of a reference sample of PET film was taken, and the intensity of the C_{1s} peak at 285 eV was compared with that measured in the previous run. The calibration factor was computed from the ratio of the peak intensities in order to compensate for the decrease in sensitivity of ESCA due to contamination of the anode. If a significant decrease in the sensitivity was noticed, the equipment was readjusted following the baking procedure. By this procedure, the variation of the F_{1s} peak intensity (due to surface dynamic changes) could be examined with

reasonable accuracy, although the absolute values might not be directly compared with data taken by other equipment.

Preparation of Water-immersed Samples

Water immersion of plasma-treated samples was carried out at 25°C, immediately after the plasma treatment. After a preset immersion time (5, 30, 60, 90, and 120 min), a sample was picked out of the water and immediately placed in liquid nitrogen and was then allowed to freeze for 15 min. The frozen sample was freeze-dried at -113°C in order to preserve the surface configuration at the end of a certain time of immersion in water. The freeze-dried samples were used for measurements of the contact angles of water and of ESCA peaks.

RESULTS AND DISCUSSION

Reversible Changes of Contact Angles of Water Due to the Immersion of CF₄ Plasma-treated Films

The CF₄ plasma-treated films showed high contact angles of water, and no sign of decay was observed while the samples were kept in air. However, significant decreases in the contact angles were observed after those samples were immersed in water. The decay of the contact angle upon immersion in water could possibly be caused by washing off loosely adhering plasma treatment products or by the detachment of some hydrophobic moieties through chemical reactions with water. In order to examine these possibilities, contact angles of water were measured for plasma-treated samples which were subsequently treated in the manner described in Table I.

The results indicate that the contact angle for the plasma-treated nylon film is decreased from 108.5° to 64.3° by boiling the sample for 30 min. The contact angle of water for the boiled sample is very close to that for the untreated film. This fact alone might appear to support the concept of washing-off; however, the boiled sample regained the contact angle to 104.3°

TABLE I
Change of Contact Angle of Water on the Surface of CF₄ Plasma-treated Polymer Films on Various Subsequent Treatments

	Nylon 6 (degrees)	PET (degrees)
No treatment	63.5	69.0
CF ₄ plasma	108.5	98.0
CF ₄ plasma and submerged 60 min	85.3	73.8
Above are heat treated	104.3	93.5
	(160°C, 10 min)	(180°C, 10 min)
CF ₄ plasma and heat treated	106.5	91.5
	(160°C, 10 min)	(180°C, 10 min)
CF ₄ plasma and heat treated and submerged 60 min	67.3	71.3
CF ₄ plasma and boiled 30 min	64.3	65.0
Above heat treated	104.3	86.8
	(160°C, 10 min)	(180°C, 10 min)

upon heat treatment at 160°C for 10 min. Similar loss and recovery of the contact angle was also observed with PET films, as shown in the table. These results confirm that the decay of the contact angle of water upon the treated films' immersion in water is primarily due to surface dynamic changes of the treated samples but not due to washing off the hydrophobic moieties formed by the plasma treatment.

Influence of the Experimental Procedures on the Crystallinity of the Films

According to the results shown in Table I, rotational and diffusional migrations of hydrophobic moieties (formed only on the surface by the plasma treatment) away from the water/film interface seem to be the major phenomenon which accounts for the decay of the hydrophobic character of the surface. Such migration processes are anticipated to be hindered by the

TABLE II
Contact Angle (degrees) of Water on Nylon 6 Films with Various Degrees of Crystallinity after CF₄ Plasma and Heat Treatments

	Crystallinity (%)					
	25.0		39.6		46.1	
	No plasma	CF ₄ plasma 2 min	No plasma	CF ₄ plasma 2 min	No plasma	CF ₄ plasma 2 min
No treatment	63.1	106.0	62.9	106.6	62.3	109.3
Heat treated 100°C, 10 min	62.7	106.3	62.2	105.9	62.0	108.6
Heat treated 130°C, 10 min	62.8	106.5	63.4	106.3	62.9	107.8
Heat treated 160°C, 10 min	63.8	106.3	63.4	105.5	62.6	108.1

TABLE III
Contact Angle (degrees) of Water on Pet Films with Various Degrees of Crystallinity after CF₄ Plasma and Heat Treatments

	Crystallinity (%)					
	25.4		37.7		50.7	
	No plasma	CF ₄ plasma 2 min	No plasma	CF ₄ plasma 2 min	No plasma	CF ₄ plasma 2 min
No treatment	63.8	101.0	64.9	101.3	67.0	100.0
Heat treated 100°C, 10 min	63.4	99.6	64.8	99.6	66.3	99.8
Heat treated 140°C, 10 min	62.4	98.8	63.5	100.4	67.5	99.4
Heat treated 180°C, 10 min	62.8	97.8	64.4	100.0	66.1	96.7

TABLE IV
ESCA F_{1s} Intensity (cps) of Nylon 6 Films with Various Degrees of Crystallinity
after CF₄ Plasma and Heat Treatments

	Crystallinity (%)		
	25.0	39.6	46.1
No treatment	—	—	—
CF ₄ plasma	2.04 × 10 ⁵	2.02 × 10 ⁵	2.05 × 10 ⁵
CF ₄ plasma and heat treated 100°C, 10 min	1.92	1.94	1.92
CF ₄ plasma and heat treated 130°C, 10 min	1.81	1.75	1.81
CF ₄ plasma and heat treated 160°C, 10 min	1.51	1.62	1.63

TABLE V
ESCA F_{1s} Intensity (cps) of PET Films with Various Degrees of Crystallinity
after CF₄ Plasma and Heat Treatments

	Crystallinity (%)		
	25.4	37.7	50.7
No treatment	—	—	—
CF ₄ plasma	2.00 × 10 ⁵	1.92 × 10 ⁵	2.02 × 10 ⁵
CF ₄ plasma and that treated 100°C, 10 min	1.96	1.88	1.85
CF ₄ plasma and heat treated 140°C, 10 min	1.68	1.74	1.72
CF ₄ plasma and heat treated 180°C, 10 min	1.56	1.56	1.52

presence of crystalline phases in the samples; i.e., the higher the crystallinity, the more difficult the migration.

In order to examine the effect of the crystallinity of the film, it was first determined whether the plasma treatment would influence the crystallinity of the substrate film. Although it was anticipated that the surface modification by low temperature plasma employed in this study would not influence the crystallinity of films, it was necessary to determine if this was the case because the crystallinity of a sample is an important parameter in this study. It was confirmed that the plasma treatment and the heat treatment of the plasma-treated sample do not change the crystallinity of the films. Results of the plasma treatment and also of the heat treatment of plasma-treated

TABLE VI
Contact Angle (degrees) of Water on Nylon 6 Films with Various Degrees of Crystallinity
after CF₄ Plasma and Water Immersion

	Crystallinity (%)		
	25.0	39.6	46.1
No treatment	63.5	61.9	62.3
CF ₄ plasma	108.9	108.0	108.0
CF ₄ plasma and suberged 5 min	92.3	95.2	98.9
Above submerged 30 min	85.1	87.9	90.6
Above submerged 60 min	78.8	83.4	86.6
Above submerged 90 min	78.1	81.8	86.1
Above submerged 120 min	77.9	83.5	85.0

samples (at three levels of crystallinity) are shown in Tables II and III (contact angle of water) and in Tables IV and V (ESCA F_{1s} peak intensity).

Decay of Hydrophobicity upon Immersion of Films in Water

The decay of hydrophobicity manifested by the contact angles of water or of ESCA F_{1s} peak intensity is observed in nylon 6 and PET films as shown in Tables VI–IX. There is a direct linear correlation between the contact angles of water and the intensity of ESCA F_{1s} peaks as shown in Figure 1. This

TABLE VII
Contact Angle (degrees) of Water on PET Films with Various Degrees of Crystallinity after CF_4 Plasma and Water Immersion

	Crystallinity (%)		
	25.4	37.7	50.7
No treatment	62.2	63.7	67.1
CF_4 plasma	108.3	108.0	107.5
CF_4 plasma and submerged 5 min	72.8	76.0	80.5
Above submerged 30 min	47.4	53.9	66.6
Above submerged 60 min	41.9	46.4	54.2
Above are submerged 90 min	38.7	44.1	49.3
Above are submerged 120 min	34.6	42.5	49.1

TABLE VIII
ESCA F_{1s} Intensity (cps) of Nylon 6 Films with Various Degrees of Crystallinity after CF_4 Plasma and Water Immersion

	Crystallinity (%)		
	25.0	39.6	46.1
No treatment	—	—	—
CF_4 plasma	2.04×10^5	2.04×10^5	2.04×10^5
CF_4 plasma and submerged 5 min	1.67	1.75	1.84
Above submerged 30 min	1.51	1.58	1.71
Above submerged 60 min	1.27	1.68	1.66
Above submerged 90 min	1.44	1.49	1.61
Above submerged 120 min	1.40	1.53	1.61

TABLE IX
ESCA F_{1s} Intensity (cps) of PET Films with Various Degrees of Crystallinity after CF_4 Plasma and Water Immersion

	Crystallinity (%)		
	25.4	37.7	60.7
No treatment	—	—	—
CF_4 plasma	2.01×10^5	2.03×10^5	2.01×10^5
CF_4 plasma and submerged 5 min	1.49	1.68	1.79
Above submerged 30 min	1.36	1.45	1.50
Above submerged 60 min	1.32	1.44	1.53
Above submerged 90 min	1.26	1.45	1.52
Above submerged 120 min	1.32	1.40	1.48

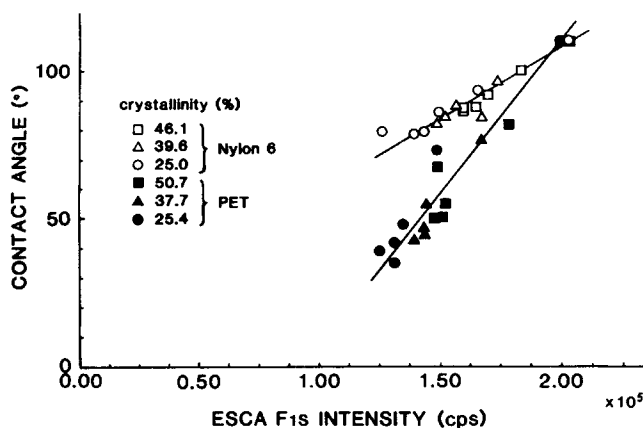


Fig. 1. Correlation between contact angle of water and ESCA F_{1s} intensity of CF_4 plasma-treated nylon 6 and PET films.

correlation confirms that the increase and the decrease of the contact angle of water on the surface of plasma-treated films are due mainly to the change in the surface concentration of fluorine-containing moieties and enable us to deal with the decay phenomena by either one of these measurements.

A parameter which describes the surface character (contact angle of water, or ESCA F_{1s} peak intensity) for a sample immersed in water for t minutes, A_t , is found to be related to the parameter of the original (unimmersed) film, A_0 , by the following equations, which generally describe diffusion-controlled chemical reaction in polymer matrices where the extent of reaction is proportional to the diffusion path length:

$$A_t = A_0 t^{-k}$$

or

$$\log A_t = \log A_0 - k \log t.$$

A typical decay in the hydrophobic character of the treated sample as a function of immersion time in water is shown in Figure 2 as log-log plots based on the above equation for the contact angle of water (PET) and water immersion time. The entire decay curve does not always fit the linear relationship; however, the initial portion of the decay curve can be expressed by the above equations. The value of k can be calculated from the initial linear portion of a log-log plot. Because log-log plots are involved in the determination of values of ks , contact angle (rather than $\cos \theta$) is used throughout this paper.

The parameter k may be taken as describing the surface dynamic mobility of polymers. The parameter is related to the ease of rotational and diffusional migrations of hydrophobic moieties from the surface into the bulk of a film. The values of ks , for nylon 6 and PET, both by the contact angle and by ESCA F_{1s} peak intensity, are compared as a function of the degree of crystallinity in Figure 3.

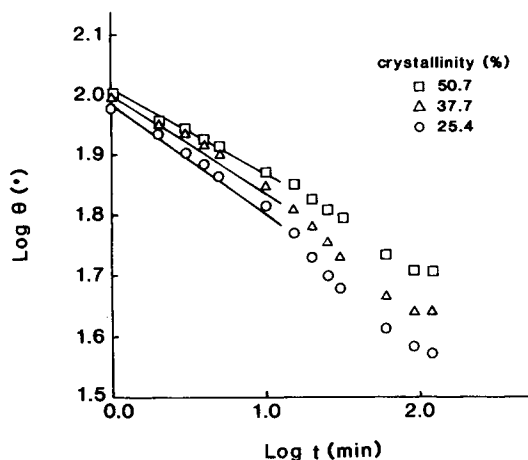


Fig. 2. Decay characteristics of contact angle of water on CF_4 plasma-treated PET films with varying degrees of crystallinity upon water immersion.

The value of k depends on the type of measurement used in the computation. This dependency is anticipated because the sensitivity of measurement to the surface dynamic change is different for each type of measurement. While the contact angle of water may reflect the surface character of the top atomic layer, ESCA measurement may respond only when the variation occurs at the depth equivalent to the electron escape depth. Because of this factor, k_s (contact angles) for PET are 4–8 times greater than for nylon 6, but k_s (ESCA) for PET are by and large the same as those for nylon 6.

It is interesting to note that k_s for PET are larger than those for nylon 6, which is the opposite of what one might expect based on the known characteristics of the polymer; e.g., molecular structures, steric hinderance, chain stiffness, T_g , and modulus. The results also demonstrate that the surface dynamic characteristics of a polymer may not be predicted adequately from the chemical structure or other properties of the polymer.

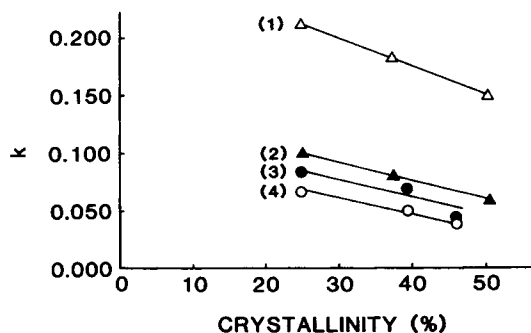


Fig. 3. Effect of crystallinity on the mobility parameter k for PET and nylon 6 films: (1) PET, contact angle; (2) PET, ESCA F_{1s} ; (3) nylon 6, ESCA F_{1s} ; (4) nylon 6, contact angle.

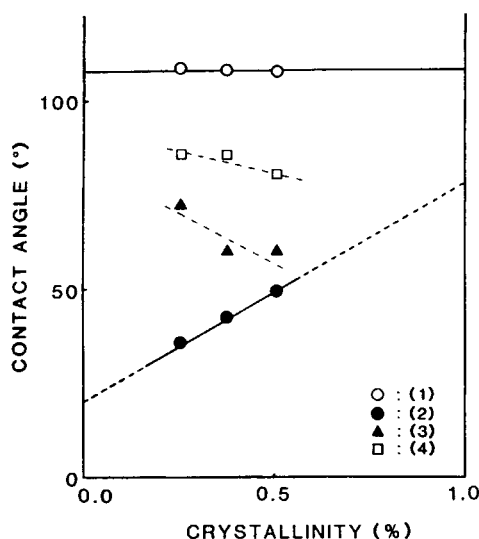


Fig. 4. Contact angle of water on CF_4 plasma-treated PET films, which are subsequently treated differently, as a function of the degree of crystallinity of films: (1) CF_4 plasma treatment, no further treatment; (2) CF_4 plasma treatment, and water immersion for 120 min; (3) CF_4 plasma treatment, water immersion for 120 min and heat treatment at 100°C for 10 min; (4) CF_4 plasma treatment, water immersion for 120 min and heat treatment at 180°C for 10 min.

Recovery of Hydrophobicity on Heat Treatment of Samples Immersed in Water

As shown in Table 1, part of the loss of hydrophobicity observed for the water-immersed samples is recoverable on subsequent heat treatment, indicating that migrations of hydrophobic moieties caused by the water are reversible, at least partially. The reversible aspect was investigated with samples of varying degrees of crystallinity. All samples were first immersed in water for 120 min and freeze dried. Then, films were heat-treated at different temperatures for 10 min.

The trends found for the decay and the recovery of hydrophobicity may be seen in a typical figure where these changes are plotted against the degree of crystallinity of film shown in Figure 4. Typical changes of ESCA peak profiles are shown in Figure 5. These results indicate that the buried fluorine-containing moieties migrate toward the surface on heat treatment. It should be reiterated that no inward migration of fluorine-containing moieties occurred upon heat treatment of unimmersed films as described earlier.

ESCA C_{1s} peaks shown in Figure 5 indicate that the major fluorine-containing moieties are $-\text{CF}_2-$ and $-\text{CF}_3$. The ESCA profiles of C_{1s} peaks for CF_4 plasma-treated films are significantly different from those for plasma polymers of fluorine-containing monomers, which generally show many peaks located within 285–295 eV and in which the peak height of CF_3 is usually smaller than the peaks appearing at lower binding energy levels.¹² This confirms that the CF_4 plasma treatment used in this study is not a plasma polymerization process but is plasma implantation of fluorine containing moieties largely consisting of $-\text{CF}_2-$ and $-\text{CF}_3$ groups.

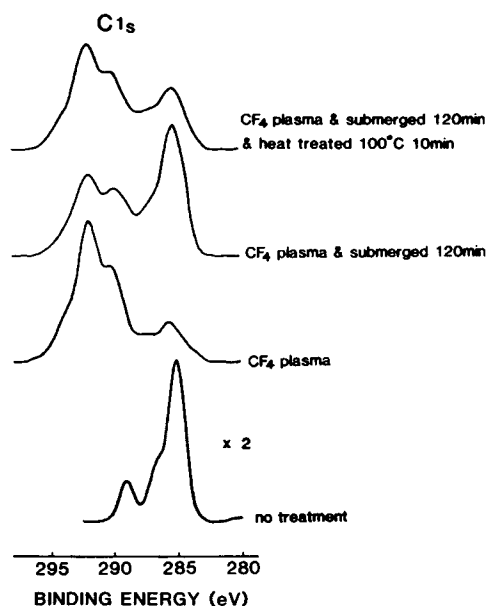


Fig. 5. Changes of ESCA signals of PET film (crystallinity 25.4%) upon the sequential treatments.

As is clearly shown in Figure 5 (and also in Tables II–V), the effect of CF_4 plasma treatment is independent of the crystallinity of the film indicating that the implantation of fluorine-containing moieties takes place without regard to crystalline and amorphous regions at the surface. However, the decay of hydrophobic character, manifested either by the contact angle of water or by the intensity of the ESCA F_{1s} peak, is dependent on the crystallinity of the sample. The lower the crystallinity of the sample, the greater is the decay observed when the sample is immersed in water. The extent of decay is more or less proportional to the amorphous content.

On the other hand, the extent of recovery when a wet film is heat treated does not follow the same pattern; i.e., the extent of recovery decreases much more steeply with the increase of crystallinity. As a result, at the end of a cycle of water immersion and heat treatment, samples with higher crystallinity exhibit a lower degree of hydrophobicity than do samples with lower degrees of crystallinity.

The fact that the decay and the recovery do not follow the same pattern seems to indicate the difference in the basic principles responsible for these two processes. This aspect may be explained by considering (1) the three-phase model of semicrystalline polymers and (2) the difference between driving forces for these two processes.

With the two-phase model, only crystalline and non-crystalline (amorphous) domains are considered. With the three-phase model, an additional domain (transitional region) is considered in the non-crystalline phase. In the transitional region, macromolecules are not in a crystalline phase; but their mobility is largely restricted by the presence of the crystalline phase. Consequently, molecules in the transitional domain behave in a significantly different manner than molecules in the rest of the noncrystalline phase.

The significance of the transitional domain is dependent on the phenomenon under consideration or on the nature of the measurements. Whereas most physical methods used to determine the amount of the crystalline phase would not detect the presence of the transitional domain, results of wide-line NMR studies^{13, 14} of the effect of heat treatment of fibers (nylon 6 and PET) strongly support the presence of the transitional domain.

The transitional domain seems to play an important role in the transport of relatively small molecules such as dyes in the polymer matrix. The abnormal increase of dye absorption by fibers made of the same polymers used in this study, which were heat-treated at relatively high temperatures and which showed significant increases in crystallinity, has been explained satisfactorily by adapting the three-phase model.¹⁵⁻¹⁷ In this case, the increase in crystallinity was achieved evidently at the expense of macromolecules in the transitional domain, yielding larger free volume elements in the transitional domain.

Because the surface dynamic changes discussed in this study are related to the diffusion of labeled portions of macromolecules within a polymer matrix, the role of the transitional domain is different from that observed in the dyeability study. Nevertheless, adaptation of the three-phase model is well justified in our effort to elucidate the mechanisms for surface dynamic changes.

By virtue of the definition of the transitional domain, only the rotational migration, which can be achieved without conformation changes of macromolecules involving a larger segmental motion, can take place in the transitional region. Rotational migration refers to the burying motion of the surface-implanted fluorine-containing moieties by the rotational motion of a molecule around the axis of the long chain but does not refer to the simple (free) rotation of a fluorine-containing carbon atom along the axis of a C—C bond. Because of the bond angle of C—C—C, such a rotation often requires rearrangement of larger segments adjacent to the rotating bond.

With the consideration of allowable modes of migration of moieties in amorphous and transitional domains, it is possible to distinguish the rotational migration, which is the only allowable mode of migration in the transitional region, and diffusion, which is the dominant mode in the amorphous region. The results of this study indicate that the decay is a consequence of both of the migration processes, but the recovery is the consequence of diffusion only. The preliminary results of a study on the activation energies of these two processes seem to confirm this postulation. The details of the study on activation energies will be presented elsewhere in due course. A schematic representation of this postulation based on the three-phase model for semicrystalline polymers is given in Figure 6.

Why these two processes (i.e., rotation and diffusion) occur in different ways in the decay and in the recovery may be explained by the difference in the nature of the driving force for those processes. Although the decay process proceeds via migration by rotation and diffusion driven by the interfacial free energy difference between polymer and surrounding phases, the recovery of hydrophobicity may be visualized as a segregation process driven by the local free energy difference within a macromolecule which requires a higher degree of mobility involving a larger segment of the molecule. For this reason,

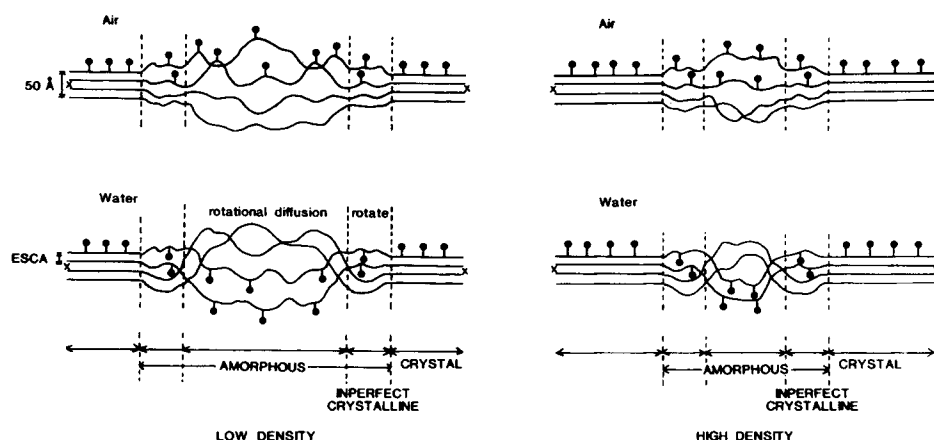


Fig. 6. Schematic representations of the modes of migration of fluorine-containing moieties from the surface in crystalline, amorphous, and transitional regions for films of low and high degrees of crystallinity.

recovery requires heat treatment at a sufficiently high temperature and is usually not observed upon drying of wet samples at ambient temperature.

Because of the presence of the transitional regions (volume fraction y), the increase of the volume fraction x of crystalline regions decreases the volume fraction of amorphous region ($1 - x - y$) to less than the value based on the two-phases model ($1 - x$). Thus, the domain in which the recovery process takes place diminishes more steeply with the increase of crystallinity than the two-phase model would predict, which accounts for the reduced recovery of hydrophobicity observed for films with a higher degree of crystallinity.

CONCLUDING REMARKS

Plasma implantation of fluorine-containing moieties on the surface of polymeric films provides a unique opportunity to investigate the surface dynamic aspects of polymer surfaces. It should be reiterated that the major emphasis of this study is on the surface mobilities of nylon 6 and PET films, and that surface fluorination by the low-temperature plasma is used as a means of labeling the surfaces. Therefore, the k parameters calculated in this study are meant to indicate the mobility of molecules at the surface of the original (untreated) polymer but not the efficacy or the durability of the surface modification. The mobilities thus obtained may include the effect of perturbation due to the labeling in a fashion comparable to the "isotope effect" in the radioactive labeling.

Although a number of investigations in recent years point out that modified polymer surfaces are dynamic entities, the highly mobile nature of (unmodified) polymer surfaces have in general not been taken into consideration in interpretation of most surface-related phenomena. In most cases, a polymer surface is represented as a rigid unperturbable plane. For instance, in dealing with many surface phenomena such as protein adsorption on polymer surfaces, biocompatibility of polymers, and surface modifications of polymer surfaces

by various means, the mobile nature of macromolecules at the interface has been largely ignored.

The surface dynamic data described in this paper clearly indicate that polymer surfaces are not as rigid as heretofore intuitively assumed or considered. The fact that PET showed such a large mobility at room temperature (below T_g) may provide enough impetus to reexamine many intuitive assumptions made in dealing with various surface or interfacial phenomena associated with polymers.

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