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A new approach to characterize crystallinity by observing the mobility of plasma treated polymer surfaces

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Abstract

We describe in this paper a novel method to characterize crystallinity by observing the difference in chain mobility of oxygen plasma treated polymer surfaces, and further compare the crystallinity with the values obtained by X-ray diffractometry (XRD) and differential scanning calorimetry (DSC). We modified polymer surfaces with an inductively coupled plasma system to introduce polar functional groups. The immobility parameters of plasma modified surfaces were obtained by measuring contact angles as a function of storage time in air. Due to highly restricted chain mobility in the crystalline region, the crystallinity can be estimated by the fraction of immobile polar groups remaining after chain reorientation.

Keywords: Surface; Crystallinity; Immobility

1. Introduction

What constitutes a surface from the perspective of one technique can be the bulk from the perspective of another, or also under different conditions with the same technique. Although several techniques [1] were introduced for the characterization of a surface, the wetting characteristics of polymer solids must be a direct consequence of the phenomenon on the polymer surface [2–4]. In the attempt to understand the wetting behavior of polymeric solids in an environment of interest, two important issues will be addressed: (1) quantitation of crystallinity from the surface properties; and (2) comparison of those values with the bulk crystallinity.

Plasma surface treatment is a proper technique for these purposes because of many advantages over other techniques including the modification of just the outermost atomic layers of a substrate [5,6], selection of desired chemical reaction pathways [7], minimization of thermal degradation [7], and rapid treatment [8]. Among the most interesting phenomena with a plasma treatment are the surface dynamics, which deal with the change of surface characteristics due to the variations of environmental conditions [9–12]. The high energy components in the amorphous region tend to be buried beneath the polymer–air interface as a result of the thermodynamic drive to minimize the surface energy [13–19]. However, chain mobility mainly occurs in the amorphous region and the mobility in the crystalline region is fairly limited because of an orderly packed structure [20]. The preferred chain-reorientation enables the estimation of crystallinity at the surface by demonstrating the fraction of immobile polar groups on the surface. The immobility parameters of modified surfaces can be deduced from the equations suggested by Chatelier et al. [21,22]. Based on the author's understanding, this is the first attempt to estimate crystallinity from surface properties although a variety of phenomena at the surface have been explained through the crystallinity of polymers. The obtained crystallinity was compared with the bulk crystallinity from X-ray diffractometry (XRD) and differential scanning calorimetry (DSC).

2. Experimental

2.1. Preparation of polymer films

Poly(ethylene terephthalate) (Aldrich, M_v 18,000) was melted and cast on a slide glass at 260°C, and a home made frame was used to control film uniformity. The cast polymer was quenched into cold water immediately after melting in order to prevent crystallization of the polymer. After immersing into water, the films were dried at ambient

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conditions for 24 h. The crystallinity was obtained by adjusting annealing time at 130°C with the amorphous polymer.

2.2. Plasma surface modification of polymer films

An inductively coupled RF plasma system operating at 13.54 MHz was used for plasma treatment of the polymers. Specimens were mounted on a flat sample holder and the chamber was evacuated to a base pressure of 10^{-4} Torr or lower. Treatment was performed at an operating pressure of 100 mTorr for 1 min with an RF power of 180 W while introducing only oxygen gas. Samples treated with a plasma were immediately used for characterizations, and stored in the air.

2.3. Contact angle measurement

The contact angles between the distilled water and the specimens were measured at room temperature using a Goniometer (RAME-HART, MODEL100-00 115 1119), with a droplet technique [23]. Measurements were performed in quadruplicate on specimens stored for various periods of time; standard deviations typically were 1–2°.

2.4. Differential scanning calorimetry (DSC)

DSC analysis was carried out on polymers using a differential scanning calorimeter (Perkin–Elmer, DSC-4). In each case approximately 10 mg of polymer was sealed into an aluminum pan. The pan was placed in the heating chamber of the apparatus on a heat sensor. A reference pan was placed alongside it on a separate sensor. The DSC trace was recorded through a preset temperature program from 30 to 300°C at a rate of 20°C/min. The melting enthalpy was obtained from the area under a peak by using a data acquisition program. XRD, Wide angle X-ray scattering spectra were taken on a diffractometer (Rigaku, SWXD Series) with a counting step of 0.05°, count time per step of 2 s, and a scanning angle sector 2θ of 10–50°.

3. Results and discussion

Fig. 1 shows the contact angles of O_2 plasma treated surfaces stored in air (crystallinity of the polymers was shown in Table 1). The surfaces of polymeric solids are relatively mobile, in comparison to those of ceramic, or glassy solid counterparts [4]. This means that polymeric solids can adopt different surface configurations in different environments, so as to minimize the total free energy of the system. The relaxation of a polymer surface to orient itself and equilibrate to a new environment will, however, be highly dependent on its physical properties such as surface crystallinity and density. According to simulations performed by Mansfield and Theodorou [24] there is considerable enhancement of atomic mobility in the outermost region (surface) compared to the internal regions (bulk) as a consequence of the decreased surface density and increased free volume. In fact the surface consists not only of a solid phase but also of transition phases with liquid-like or vapor-like behavior [25].

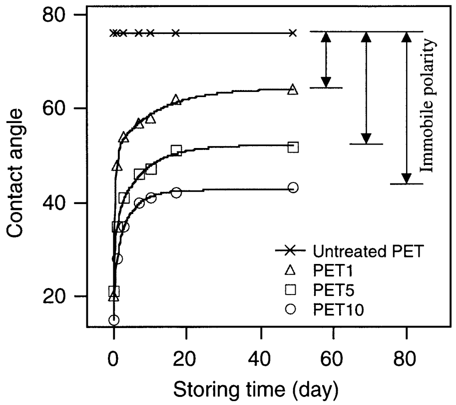

Fig. 1. Effect of crystallinity on the surface dynamics of oxygen plasma treated PET surfaces annealed at 130°C.

As can be seen in the figure, the contact angle of oxygen plasma treated surfaces is near zero immediately after the treatment because of polar moieties introduced to the surface. However, storage in air allows the hydrophobic recovery to occur at the surface. A semicrystalline surface having an orderly packed structure recovers its hydrophobicity partially, while an amorphous surface does completely. In the figure, the surface annealed for a longer period demonstrated a lower contact angle after completion of the recovery because of the highly crystalline structure. The difference in contact angle between an untreated surface and a hydrophobicity-recovered surface represents the immobile polar groups remaining in the crystalline region of the surface, and the fraction of immobile polar groups is considered as the crystallinity of a polymer. The hydrophobic recovery is directly related to the content of polar groups beginning to disappear when the surface contacts nonpolar environments. The decay of polar groups on the surface is indicated by the change of water contact angle measured as a function of time. Contact angle and

Table 1
Crystallinity of PET samples annealed at 130°C

Sample	Annealing time (h)	Crystallinity	
		DSC	XRD
PET1	1	21.71	11.14
PET2	2	23.80	16.27
PET3	3	24.32	20.58
PET4	4	25.89	27.97
PET5	5	29.55	30.79
PET6	6	29.81	30.99
PET7	7	29.81	31.27
PET8	10	30.33	32.51
PET9	12	31.12	33.03
PET10	24	37.13	33.08

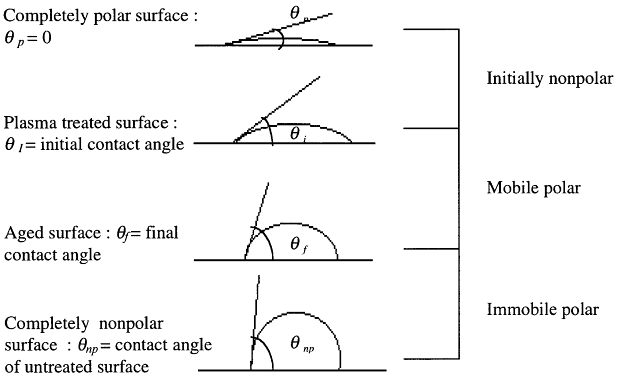

Fig. 2. Four situations of a water contact angle according to the surface conditions.

XPS data suggest an exponential time course for the migration of mobile polar groups into the bulk [26,27]. Based the suggestion of Chatelier et al. [21,22] the fraction of immobile polar groups can be estimated. Plasma treated polymer surfaces contain both high and low surface energy regions, which are primarily formed by introducing polar groups on the nonpolar polymer surface. Based on the Cassie's suggestion [2], the equilibrium contact angles of heterogeneous surfaces can be modified into

$$\cos \theta_\eta = f_p \cos \theta_h^p + f_{np} \cos \theta_h^{np} \tag{1}$$

where f_p and f_{np} are the fraction of polar groups and nonpolar groups on the surface, respectively. θ_h^p, and θ_h^{np}, are the equilibrium contact angle of pure polar and pure nonpolar surfaces. In general, the fraction of nonpolar groups is expressed as $f_{np} = 1 - f_{np}$. And f_p is expressed as a sum of mobile, f_m, and immobile polar fraction, f_{im}, in the polymer chains.

$$\cos \theta_h = f_{im} + (1 - f_{im}) \cos \theta_h^{np} + f_m (1 - \cos \theta_h^{np})\, e^{-t/\tau} \tag{2}$$

Two different methods were considered to obtain the fraction of mobile and the fraction of immobile polar groups: (a) comparison of the experimentally obtained curve function with Eq. (2); (b) calculation based on the following model. As shown in Fig. 2, four situations of a contact angle are possible. The cosine value expresses the area of polar groups because surface tension is directly related to the polar group content. The total area occupied by polar groups is the difference between the completely polar surface and the completely nonpolar surface. The fractions of mobile and immobile polar groups can be obtained by the following equations:

$$f_m = (\cos \theta_i - \cos \theta_p)/(\cos \theta_p - \cos \theta_{np}) \tag{3}$$

$$f_m = (\cos \theta_f - \cos \theta_{np})/(\cos \theta_p - \cos \theta_{np}) \tag{4}$$

where f_m is the fraction of mobile polar groups, f_{im} the fraction of immobile polar groups, θ_i is the contact angle right after plasma treatment, θ_f the contact angle after aging, θ_p the contact angle of a completely polar surface and θ_{np} the contact angle of a completely nonpolar surface. As can be seen in Table 1, both methods showed a close correlation between the derived equation and experimental data and the fraction of immobile polar groups, f_{im}, is considered the crystallinity.

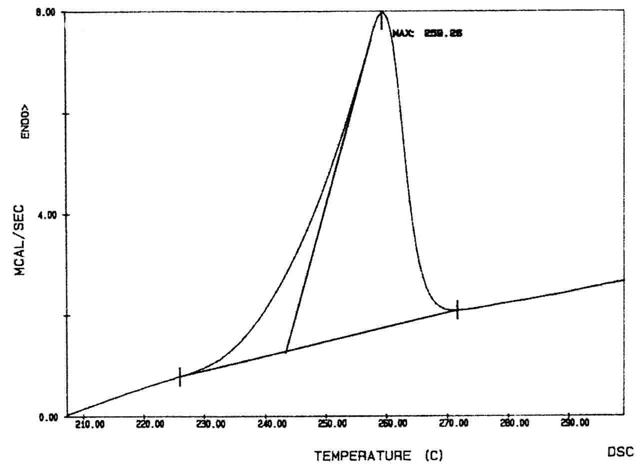

Fig. 3. X-ray diffraction of the PET film.

The crystallinity obtained from the immobility parameter was compared with the values from DSC and XRD which are widely used to characterize the crystallinity. In DSC, the heat capacity changes are observed in a polymer sample with changes in temperature. Since the sample absorbs more heat due to its higher heat capacity, second order transitions or glass transitions cause abrupt changes in curve shape. Fig. 3 represents a DSC thermogram at the range of fusion, where the melting temperature is determined as a maximum point at the range. Melting enthalpy was obtained from the area under a peak, and the crystallinity was calculated by dividing the melting enthalpy by the fusion energy of 100% crystalline PET, 26.9 kJ/mol [28,29].

When a polymer has a highly stereoregular structure with little or no chain branching or it contains highly polar groups that give rise to strong dipole–dipole interactions, it can exist in crystalline form. Such crystallinity is unlike that of low molecular weight compounds but exists instead in regions of the polymer matrix where an orderly packing of polymer molecules is possible. It should be mentioned that stereoregularity does not automatically lead to crystallinity. A molten stereoregular polymer, upon rapid cooling, may solidify in a metastable amorphous state. Crystallinity can frequently be induced, however, by heating slowly to impart to the polymer molecules sufficient motion to allow them to line up in an order.

XRD is also used for calculating the crystallinity. Crystalline PET has a triclinic structure with one monomer per unit cell, and the following parameters: $a = 4.56$ Å, $b = 5.94$ Å, $c = 10.75$ Å, $\alpha = 98.5°$, $\beta = 118°$, $\gamma = 112°$ [30]. The strong diffraction peaks are located at $2\theta = 17$, 23.0, and 26.5° as shown in Fig. 4. The vertical lines exhibit the locations of diffraction peaks expected from reports. The peaks are considered as the strong reflections for the (0-11), (010), (−110), and (100) reflections based on the crystal structure of PET. In order to subtract the amorphous halo from the spectrum, an appropriate curve fitting, which centers at $2\theta = 23.5°$, was performed. The smooth line, which centers at $2\theta = 23.5°$, represents the amorphous halo curve-fitted with a polynomial function. The amorphous halo was subtracted from the spectrum to acquire the area of diffraction peaks. The crystallinity was calculated from the areas under the amorphous peak and crystalline peaks with the equation as follows [31].

$$\text{Crystallinity}(\%) = A_c/(A_c + A_a) \times 100 \tag{5}$$

A_c is the area of the crystalline peak and A_a is the area of the amorphous peak. The curve fitting to obtain the areas under crystalline peaks was performed with a Lorentzian function. Basically, three apparent peaks were considered for the curve fitting after subtracting the halo region from the spectrum. Table 2 summarizes the crystallinity obtained by DSC and XRD. The comparatively higher value of crystallinity from the immobility parameters is due to the incomplete reorientation of polar groups in amorphous region. As polar groups rotate into the bulk region, dipole–dipole interaction or hydrogen bonding with polar contents near surface restricts the reorientation of polymer chains. The restricted mobile groups in the amorphous region contribute to increase the immobile polar fraction, i.e. crystallinity.

4. Conclusions

The reorientation of polymer chains occurs in the amorphous region where mobile polar groups migrate or rotate into the bulk. The chain mobility at the surface is closely related to crystallinity, which can be estimated from the fraction of immobile polar groups on the polymer surface treated with an oxygen plasma. The immobility parameters of modified polymer surface can be obtained by a contact angle measurement. The fraction of immobile polar groups remaining after relaxation represented the crystallinity of a polymer.

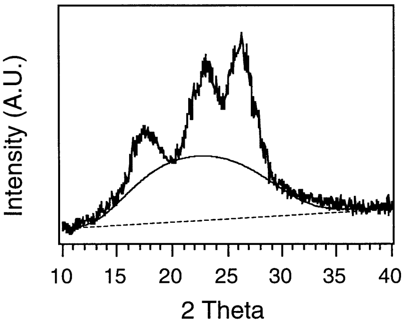

Fig. 4. Determination of a melting point and melting enthalpy from a DSC thermogram.

Table 2
Comparison of the fractions of mobile and immobile polar groups

Polymer	$^*f_m$	$^*f_{im}$	$^*f_m$	$^*f_{im}$
PET1	0.75	0.18	0.82	0.06
PET2	0.58	0.29	0.54	0.35
PET3	0.52	0.37	0.52	0.34
PET4	0.62	0.29	0.63	0.28
PET5	0.58	0.31	0.69	0.24
PET6	0.61	0.34	0.63	0.31
PET7	0.62	0.35	0.63	0.30
PET8	0.48	0.41	0.56	0.30
PET9	0.52	0.44	0.53	0.42
PET10	0.31	0.58	0.30	0.57

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