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ORIGINAL CONTRIBUTION

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Influence of drawing and heat treatment on surface free energies of polyethylene terephthalate fibers

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Abstract The surface free energies of polyethylene terepthalate fibers with different draw ratios were experimentally determined by contact angle measurements in *n*-alkane/water systems. The dispersive component of the surface free energy increased with increasing draw ratio, whereas the nondispersive one remained almost constant. After heat treatment, the dispersive surface free energy increased, but was reduced above 140 °C. The nondispersive component increased by heat treatment at 190 °C. The increases in the density and birefringence of the fibres due to the drawing and heat treatment suggested that the increase in the dispersive surface free energy was caused by the increase in the atomic density at the fiber surface due to drawing and heat treatment. ESCA results indicated that the increment in the non-dispersive surface free energy due to heat treatment was caused by the addition of functional groups to the fiber surface due to heat treatment.

Key words Surface free energy – polyethyleneterephthalate – drawing – heat treatment – contact angle

Introduction

Surface free energy is one characteristic of materials, and experimental [1–12] and theoretical [13, 14] investigations for the determination of surface free energies of solids have been carried out. Sacher [2] has pointed out that the "standard" surface free energy may not exist for polymers because of their actual differences due to material sources and variations during manufacture. The molecular weight dependence of the surface free energy of polydimethylsiloxane has been reported by Sauer et al. [6]. Eckersley and co-workers [8] have shown that the experimentally determined surface free energies of polymethyl methacrylate-co-butyl acrylate emulsion polymer films were lower than the calculated values because of the exudation of the oligomeric or polymeric pseudosurfactant to the surface of the films. In a previous paper [3], we reported that dyeing with a reactive dyestuff caused a decrease in the surface free energy of nylon 6. The above experimental findings suggest that the experimental determination of the surface free energy of a given synthetic polymer is needed for the understanding of various phenomena at interfaces.

In general, synthetic fibers are drawn to four or five times in their length after spinning in order to obtain closely packed and highly-oriented structures of the molecules. In addition, a variety of techniques for surface modification is applied to the fibers to achieve better surface properties. Although the changes in surface free energies of the fibers due to surface modification have been experimentally observed [15–18], the effects of drawing and heat treatment have not been systematically investigated. It is worthwhile evaluating the surface free energy of drawn and heat treated fibers from the viewpoint of the effect of the density of the fiber.

In the present study, the effects of drawing and heat treatment on surface free energies were examined by contact angle measurements using polyethylene terephthalate (PET) fibers which have been widely used as clothing and industrial materials. The contact angle can be measured by various techniques such as sessile drop, horizontal meniscus, and Wilhelmy gravitational techniques [19, 20]. The Wilhelmy technique has the advantage of accurate and reproducible contact angle measurements because the angles can be calculated from the weight recordings. In addition, the weight recordings have no buoyancy effect for fibrous solids. Hence, the Wilhelmy technique was employed for the measurements of contact angles in the PET fiber/*n*-alkane/water systems. Dispersive and nondispersive surface free energies of the fibers were determined from the angles.

Experimental

Materials

Polyethylene terephthalate, PET, (intrinsic viscosity: 0.95, TiO_2-free) was melt-spun to a monofilament having a diameter of about 400 μm using a screw extruder. Undrawn monofilaments were kept in a cool condition (0 °C–5 °C) before drawing and heat treatment. The monofilaments were drawn in water at 60 °C in the draw ratio (DR) of 3.5 to 5.0 in which no necking points of the fibers by drawing were found. They were then fixed on a frame under tensionless state and heat-treated at 120–190 °C $\pm$ 1 °C for 15 min in a circulating air oven. The monofilaments were cut to a length of ca. 2 cm, and were successively purified by extraction with water and ethyl ether.

Extrapure grade *n*-alkanes (*n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane and *n*-decane) and doubly distilled water were used for the contact angle measurements.

Contact angle measurements

Advancing and receding contact angles of water in the PET fiber/*n*-alkane/water systems were measured by the Wilhelmy method using an electrobalance (Cahn Instruments Inc., C-2000) and a reversible elevator (Burleigh Instruments Inc., Inchworm Motor). The experimental details have been described elsewhere [21–25]. Weight recordings were obtained during a fiber immersion-emersion cycle at the three-phase boundary velocity of 0.3 mm/min in the plateau region where the contact angles were independent of the velocity, since the contact angles in the plateau region are considered to be the "thermodynamically significant contact angles" [22, 24, 26]. The cycle was repeated two more times using the same part of the same fiber, and the reproducibility was checked. The weight recordings of the PET fibers had no buoyancy slope. The contact angle was calculated from the wetting force by the Wilhelmy equation using the effective perimeter of the fiber which was determined from the weight recording obtained at the *n*-pentane/air interface [22].

Contact angle measurements were carried out in a room maintained at a constant temperature (20 °C) and a constant relative humidity (65%).

Measurements of density

The density of the PET fibers was measured at 25 °C using a density gradient column with a mixture of ligroin and carbon tetrachloride.

Measurements of birefringence

Birefringence of the fibers was measured using a polarizing microscope (Nikon optiphotopol) fitted with a Babinet's compensator. The optical path length, i.e., the diameter of the monofilament, was determined using an eye piece micrometer attached to the microscope.

ESCA

Electron Spectroscopy for Chemical Analysis (ESCA) spectra were obtained using an ULVAC-PHI ESCA 5600 spectrometer. Samples for the measurements were prepared by placing the cut fibers side by side on a slide glass. The beam was focused approximately 400 μm (drawn) or 800 μm (undrawn filaments) in diameter using a minimum area omni-focus lens. Measurements were done with a MgK_α source at 15 kV 400 W.

Results and discussion

Figure 1 shows the effect of the draw ratio on birefringence, Δn, and density, ρ, of the PET fibers. Obviously, the values of Δn and ρ increased with increasing draw ratio. The increase in Δn indicates the increase in the degree of orientation of the polymer chains parallel to the fiber axis. From the values of density, the crystallinity of the fiber,

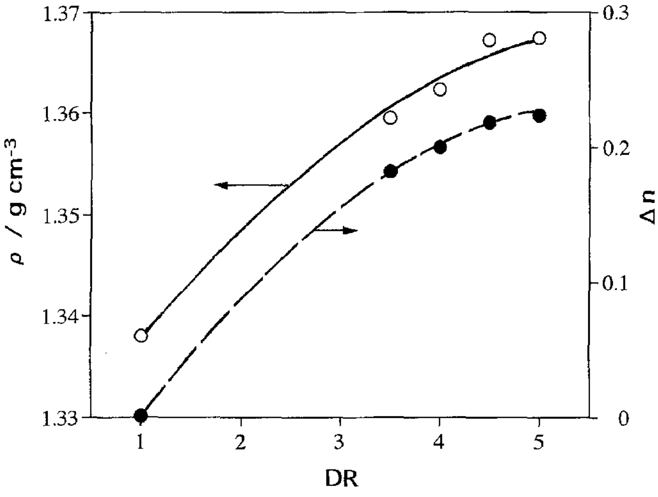

Fig. 1 Density, ρ(○), and birefringence, Δn(●), as a function of draw ratio, DR, for polyethylene terephthalate fibers

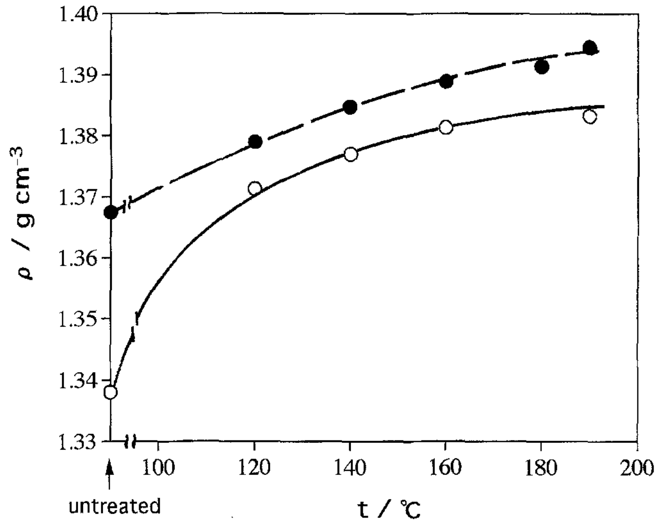

Fig. 2 Density, ρ, as a function of heat treatment temperature, t, for polyethylene terephthalate fibers. ○: undrawn fiber, ●: drawn fiber ($DR = 5$)

X_{cw}, can be calculated according to the following formula:

$$X_{cw} = \frac{\rho_c(\rho - \rho_a)}{\rho(\rho_c - \rho_a)} \tag{2}$$

where ρ is the density of the fiber, and ρ_c and ρ_a are the densities of the crystalline and amorphous PET with the values of 1.455 g/cm^3 and 1.335 g/cm^3, respectively [27]. The X_{cw} value of the undrawn fiber is approximately 0.03, suggesting a mostly amorphous phase. After drawing, X_{cw} increased with increasing draw ratio, and reached 0.28 at $DR = 5$.

The effect of heat treatment temperature on density of the fiber is given in Fig. 2. In either case of the undrawn and drawn ($DR = 5$) fibers, the density, ρ, and hence, the crystallinity, X_{cw}, of the fibers increased with increasing temperature, and the value of X_{cw} reached approximately 0.4 and 0.5 at 190 °C for the undrawn and drawn ($DR = 5$) fibers, respectively. It was found that the drawn ($DR = 5$) fibers with the higher degree of orientation obtained the higher crystallinity by the heat treatment.

Assuming that Young's equation holds for the PET fiber/n-alkane/water system, one can obtain the following expression using the equation with respect to interfacial free energy corresponding to the extended Fowkes' equation [22, 28]

$$\gamma_w - \gamma_o + \gamma_{ow}\cos\theta_w = 2(\gamma_s^{d})^{1/2}[(\gamma_w^{d})^{1/2} - (\gamma_o)^{1/2}] + 2(\gamma_s^{nd}\gamma_w^{nd})^{1/2} \tag{1}$$

where γ is the surface free energy, and θ the contact angle. The subscripts s, w, and o refer to solid, water, and n-alkane, and the superscripts d and nd refer to the dispersive and nondispersive components, respectively. Since a linear relation was found between $\gamma_w - \gamma_o + \gamma_{ow}\cos\theta_w$ and $(\gamma_w^{d})^{1/2} - (\gamma_o)^{1/2}$, the dispersive and nondispersive surface free energy was calculated from the slope and the intercept of the plot. In a previous study [23], we carried out the experimental determination of surface free energies of the carbon fibers exposed to an atomic oxygen beam. The dispersive surface free energy from advancing contact angles and the nondispersive one from the receding angles were justified by the results of the surface analysis of the fibers. According to this experimental finding, the dispersive and nondispersive surface free energies of the PET fibers were determined from the advancing and receding contact angles, respectively.

The obtained surface free energies of the PET fibers with different draw ratios are shown in Fig. 3. The dispersive component increased from 19 mJ/m^2 to 34 mJ/m^2 by drawing. On the other hand, the nondispersive one was found to be independent of the draw ratio.

The effect of heat treatment temperature on the surface free energy is presented in Fig. 4. In both cases of the undrawn and drawn fibers, the dispersive component of the surface free energy increased with increasing temperature, and then decreased above 140 °C. The nondispersive component was little affected by the heat treatment except the drawn ($DR = 5$) fibers treated at 190 °C.

In general, the dispersive surface free energy relates to the number of volume elements per unit volume in the surface region, i.e., surface density [29, 30]. The dispersive surface free energies of the PET fibers, γ_s^{d}, are plotted versus the bulk density of the fibers, ρ (Fig. 5). In the case

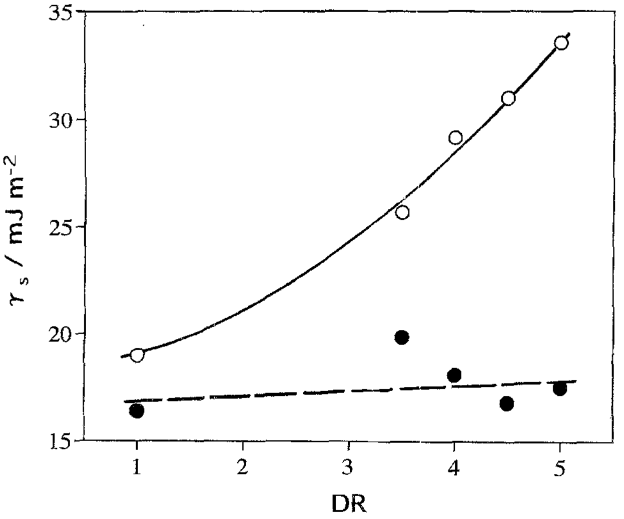

Fig. 3 Effect of draw ratio, *DR*, on surface free energy of polyethylene terephthalate fibers, γ_s. ○: dispersive, ●: nondispersive

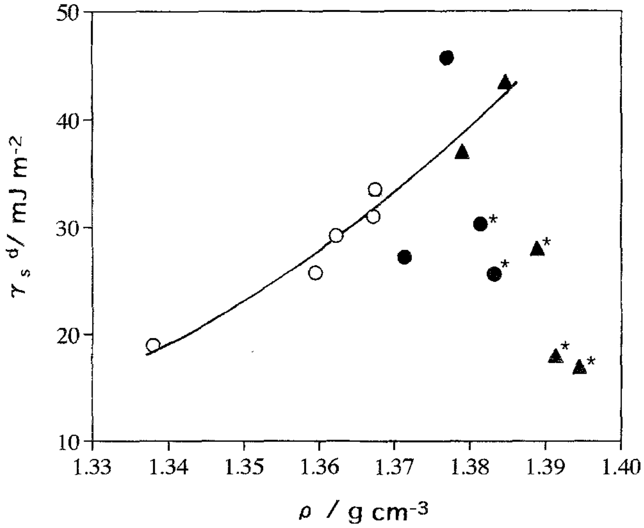

Fig. 5 Relation between dispersive surface free energy, $\gamma_s{}^d$, and density, ρ, for polyethylene terephthalate fibers. ○: $DR = 1$–5, ●: undrawn, $t = 120$–$140\,^\circ$C, ▲: $DR = 5$, $t = 120$–$140\,^\circ$C, ●*: undrawn, $t = 160$–$190\,^\circ$C, ▲*: $DR = 5$, $t = 160$–$190\,^\circ$C

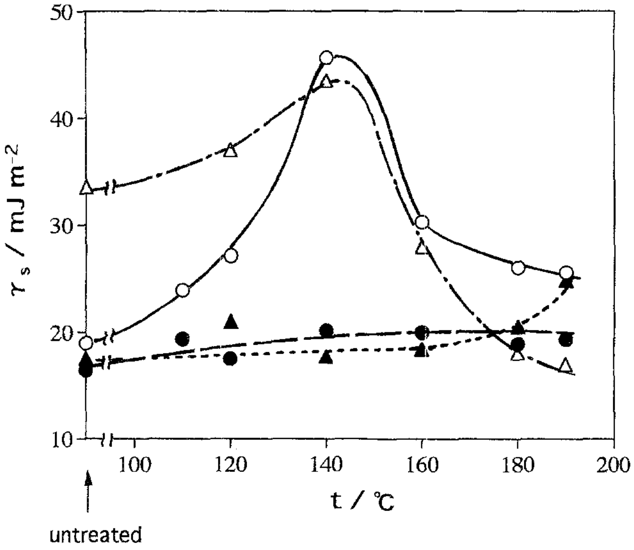

Fig. 4 Effect of heat treatment temperature, *t*, on surface free energy of polyethylene terephthalate fibers, γ_s. ○: undrawn fiber, dispersive, ●: undrawn fiber, nondispersive, △: drawn fiber ($DR = 5$), dispersive, ▲: drawn fiber ($DR = 5$), nondispersive

of the fibers having different draw ratios without heat treatment (the curve shown by the open circles in Fig. 5), the $\gamma_s{}^d$ value increased with increasing ρ. This result is probably attributed to the increase in the surface density of the fiber due to drawing [25]. The results of the heat treated fibers are plotted using the closed circles (undrawn fibers) and closed triangles (drawn fibers) in Fig. 5. The data obtained above 140 °C are represented by the symbols with asterisks, which deviate from the curve in Fig. 5. This suggests that the reduction in the surface density takes place above 140 °C in spite of the increase in the bulk density of the fiber. The reduction in surface density may be caused by concentration of the ends of the polymer chains to the surface layer of the fiber [31] or by the exudation of a catalysis such as sodium or magnesium methoxide [32]. Concentration of the polymer chain ends or the exudation of the catalysis will result in the increase in $\gamma_s{}^{nd}$. However, little increase in $\gamma_s{}^{nd}$ in the range of 140 °C–180 °C is shown in Fig. 4. This also indicates the absence of the surface contamination of the fiber. Hence, the experimental results in Fig. 5 suggest that the partial melting or disorder of orientation in the fiber surface layer takes place by the heat treatment above 140 °C. The experimental findings that the 4% increase in the bulk density resulted in the two-fold value of $\gamma_s{}^d$ and that the decrease in $\gamma_s{}^d$ took place in spite of the increase in the bulk density suggest that the change in the surface density due to drawing and heat treatment is different from that in the bulk density of the fiber. Since it is too difficult to determine the surface density of the PET fiber, no experimental confirmation is obtained in the present study.

The nondispersive component of the surface free energy of the fiber increased by heat treatment at 190 °C. The nondispersive surface free energy is generally related to the chemical composition of the surface [23, 25]. In order to analyze the functional groups formed on the fiber surface treated at 190 °C, we used the micro ESCA system, which

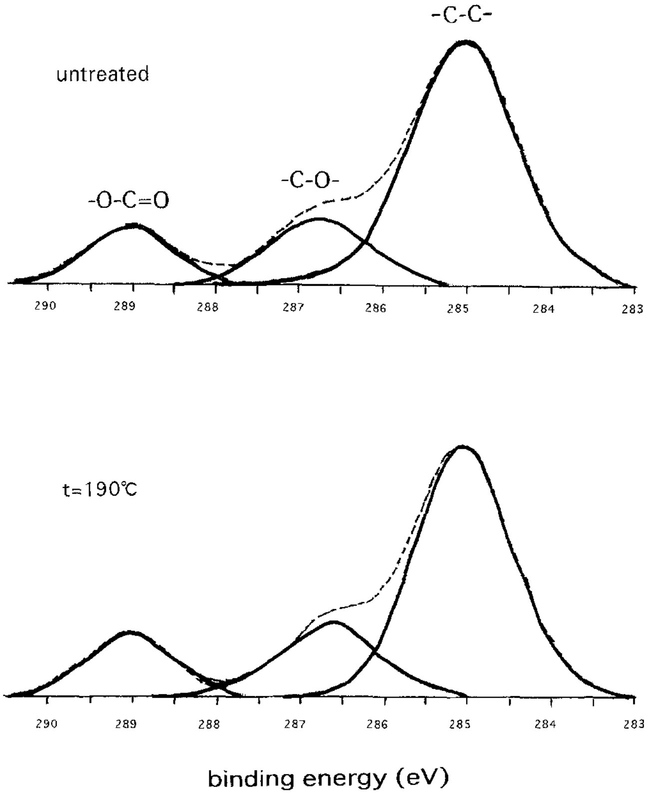

Fig. 6 ESCA C_{1s} spectra of undrawn polyethylene terephthalate fibers

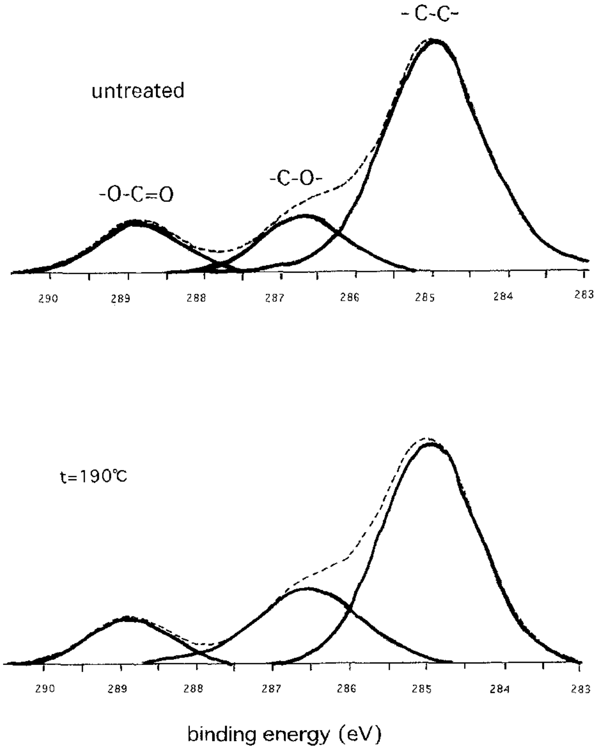

Fig. 7 ESCA C_{1s} spectra of drawn ($DR = 5$) polyethylene terephthalate fibers

allowed to apply for surface analysis of fibers. The ESCA spectra signals of the carbon region detected on the PET fiber surfaces showed more than one peak, and each peak was attributed to a different chemical group. We deconvoluted the complex peak in the C_{1s} region into three peaks (Figs. 6 and 7). The binding energies of 285.0 eV, 286.6 eV and 289.1 eV are attributed to the carbon in the –C–C–, –C–O– and –O–C=O groups, respectively [33, 34]. The surface concentrations of elements calculated through their peak areas are given in Table 1. The relative percentage of carbon in the –O–C=O groups negligibly changed, whereas that in the –C–O– groups increased due to heat treatment, especially for the drawn ($DR = 5$) fibers. In the previous papers [23, 25], we have investigated the surface free energy of the carbon fibers oxidized by atomic oxygen exposure and by electrolysis. It has shown that the nondispersive surface free energy largely increased with increasing atomic concentration of oxygen in the surface layer of the carbon fiber. Although the ESCA results in the present study are semiquantitive, it is found that the increase in the nondispersive component is caused by the formation of functional groups on the fiber surface due to heat treatment in air.

Table 1 ESCA defected surface composition of poly(ethylene terephthalate) fibers

PET fibers	–C–C–	–C–O–	–O–C=O
$DR = 1$, untreated	70.52	16.65	12.83
$DR = 1$, 190 °C	65.93	20.28	13.80
$DR = 5$, untreated	72.23	14.95	12.82
$DR = 5$, 190 °C	64.22	24.67	11.11

Conclusions

The experimental determination of surface free energies from contact angle measurements was carried out using PET fibers with different draw ratios and heat treatment temperatures. The dispersive component of the surface free energy increased as the draw ratio increased. For both the undrawn and drawn ($DR = 5$) fibers, the dispersive component of the surface free energy increased due to heat treatment, and then decreased above 140 °C. The density and birefringence of the fibers were found to increase due to the drawing and heat treatment, indicating that the increase in the dispersive surface free energy was caused by the increase in the atomic density at the fiber surface due to drawing and heat treatment. It was suggested that the decrease in the surface atomic density took place in spite of the increase in the bulk density of the fiber above 140 °C.

The nondispersive component almost did not change by drawing and heat treatment, but increased due to heat treatment at 190 °C. ESCA results indicated that the increment in the nondispersive surface free energy was caused by the formation of functional groups on the fiber surface.

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