Influence of microstructure developed during drawing on surface properties of poly(ethylene terephthalate) film

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(Received 8 December 1993; revised 15 March 1994)

We have measured the surface wettability of poly(ethylene terephthalate) (PET) film drawn to different draw ratios at strain rates of 0.56 and 0.01 s^{-1} and a draw temperature of 90°C. The probe liquid was demineralized water. We believe that the observed changes in advancing and receding work of adhesion—and in the wetting hysteresis indicated by their difference—reflect a lowering of the energy state of the film surface during drawing, due to increases in 'amorphous orientation' and the onset of crystallization. Orientation-induced interaction between PET molecules may reduce the availability of sites that would otherwise interact with water.

(Keywords: poly(ethylene terephthalate); surface energy; wettability)

INTRODUCTION

Drawing of amorphous, unoriented poly(ethylene terephthalate) (PET) film above the glass transition temperature causes molecular alignment along the extension direction and eventually induces crystallization. We have previously reported the changes in bulk morphology resulting from hot drawing[1–3], and *Figure 1* shows some of the results that are relevant to the present study. The development of molecular orientation in the non-crystalline regions (*Figure 1a*), determined by the intrinsic fluorescence method described in ref. 3, is dependent on strain rate: orientation increases more slowly at lower strain rates because the PET chains have more time to relax during extension. *Figure 1b* shows the effects of drawing on the development of crystallinity. Crystallization starts earlier at higher strain rates because the critical amorphous orientation for crystallization is reached at lower draw ratios.

The aim of the present investigation is to determine whether these microstructural changes influence the surface properties of the film, as reflected by changes in water wettability. We will compare, therefore, the wetting properties of PET films hot-drawn at two strain rates to various draw ratios, for which the microstructural development has already been characterized. Previous work on PET fibres has indicated that there is a general decrease in wettability with increasing draw ratio[4].

The wetting experiment is able to characterize the chemical heterogeneity of a smooth surface from the nature and extent of its interaction with a fluid of known properties. Instrumentation used in the present study monitors such interaction in terms of advancing and receding wetting forces as a suspended film sample is immersed and then withdrawn from the liquid at a set rate—an adaptation of the Wilhelmy plate experiment[5,6]. Provided that scanning is slow enough that the system remains in near equilibrium, changes in the wetting force reflect the chemical heterogeneity of the surface. A chemically homogeneous surface produces smooth curves of wettability *versus* meniscus traverse, with the receding curve exactly duplicating the advancing one. Surfaces are usually heterogeneous, however, producing irregular curves with wetting hysteresis.

Johnson and Dettre[6] demonstrated how wetting hysteresis can arise from surface heterogeneity using a model consisting of homogeneous high- and low-energy sites. The family of curves from their analysis is summarized schematically in *Figure 2*, which shows the advancing and receding wettability for a bicomponent surface as a function of its energy composition. The surface energy composition is expressed as the surface area fraction that is low energy (low wettability). Regions 1 and 5 are homogeneous surfaces consisting of high- or low-energy sites. In such cases there is no difference between the advancing and receding wettability. The advancing wettability decreases rapidly as soon as small portions of low-energy surface are introduced (region 2), but the receding wettability remains constant until the percentage of low-energy surface is very high (region 4). The interpretation of wetting hysteresis is summarized as follows: (1) the absence of hysteresis indicates a homogeneous surface; (2) the advancing mode primarily measures wetting force due to low-energy surface constituents, and the receding mode primarily measures wetting force due to high-energy constituents; and (3) surfaces that are predominantly low energy display poor reproducibility of receding wettability values, whereas

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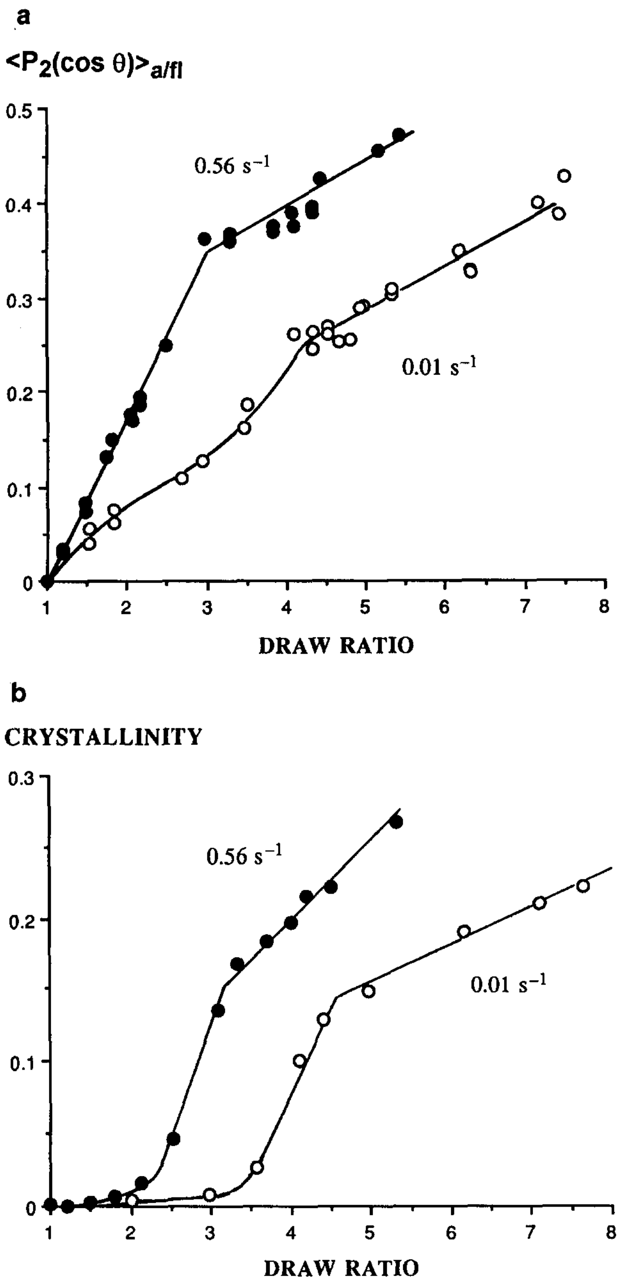

Figure 1 Draw ratio dependence of (a) amorphous orientation and (b) volume fraction crystallinity for PET film drawn at two strain rates[3]

scatter in advancing wettability values indicates a predominantly high-energy surface.

EXPERIMENTAL

Material

Amorphous, unoriented PET film was provided by Goodyear. The number-average molecular weight is 21 000 (intrinsic viscosity of $0.66\,\mathrm{dl\,g^{-1}}$) deduced from intrinsic viscosity measurements of polymer solutions in *o*-chlorophenol.

Deformation procedures

We have investigated two different kinds of PET specimens: specimens that were drawn unrestrained, with reduced width after drawing (simple extension), and specimens drawn at constant width (pure shear). The sample geometries used in constant width and unrestrained drawing are shown in refs 1 and 3, respectively. During drawing of the wide samples[1], the segments near the edge become narrow, but only the constant-width segments in the centre of the strips were used for the wettability measurements.

It is well known that the uniaxially oriented molecules of samples drawn in simple extension possess cylindrical symmetry, whereas pure shear deformation imparts planar as well as axial orientation, especially in the crystalline regions[7]. Except for this, the microstructural development during hot-drawing appears to be very similar for these two deformation modes[1,3]. For surface studies, however, it is noteworthy that the surface area remains constant during unrestrained drawing, but increases in proportion to draw ratio when drawing at constant width.

The film strips were mounted in the jaws of an Instron tensile tester, enclosed in a furnace. The furnace was heated to 90°C, which took 30–40 minutes, and the film was drawn at the selected strain rate as soon as this temperature was reached. At the end of the drawing process, the specimen was immediately quenched by opening the furnace door.

For unrestrained specimens, nominal strain rates of 0.56 and $0.01\,\mathrm{s^{-1}}$ were used. For constant-width specimens, the nominal strain rates were 0.42 and $0.01\,\mathrm{s^{-1}}$. Detailed microstructural characterization of the unrestrained and constant-width specimens drawn under identical conditions was reported by us elsewhere[1,3].

Wetting measurements

Advancing and receding wetting forces were monitored using a technique based on the Wilhelmy balance principle[8]. This technique and the wetting apparatus developed at TRI/Princeton are described in detail elsewhere[9].

The wetting force was monitored as a function of meniscus position by moving the balance platform upward to measure the advancing wettability and downward to scan the receding wettability. Scanning of the film was always parallel to the draw direction, and a weight was placed at the bottom of the film to stabilize it during the measurement. The probe liquid was demineralized water. The wetting measurement is computer-controlled including data processing. Slow platform velocities ($0.5\,\mathrm{mm\,min^{-1}}$) permit measurement of the meniscus at quasi-equilibrium, which is important be-

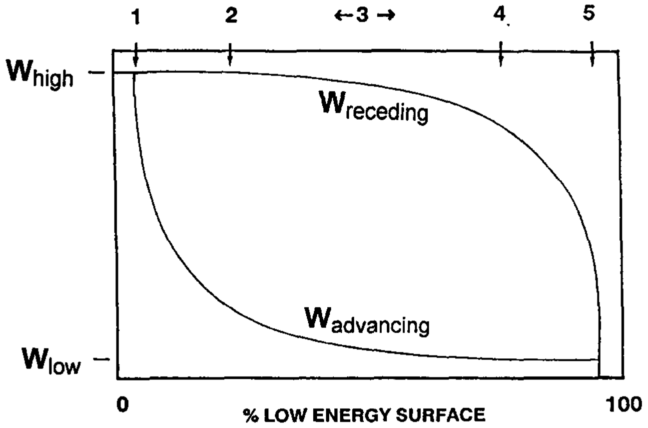

Figure 2 Schematic showing wetting hysteresis of a heterogeneous surface, from the analysis of Johnson and Dettre[6]

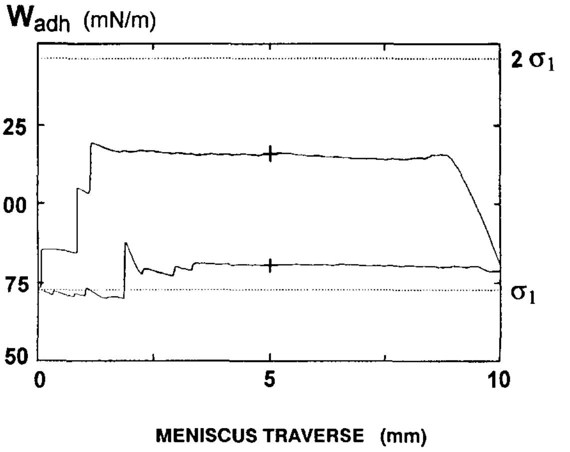

Figure 3 Example of a typical wetting measurement of PET film with water as probe liquid

cause contact angle values are then independent of the liquid travel rate[10]. The measurements were made under standard temperature and humidity conditions. The work of adhesion, W_{adh}, is defined as the work required to separate a solid–liquid system at the interface. Using the known surface tension of the liquid γ_{LV}, and the measured perimeter of the sample P, W_{adh} can be calculated from the microbalance mass measurement M:

$$W_{adh} = \gamma_{LV} + (Mg/P) \qquad (1)$$

where g is the acceleration due to gravity.

Figure 3 is an example of a typical wetting measurement on PET film with water as probe liquid. The work of adhesion is given as a function of meniscus position. The irregularity at the beginning accompanies immersion of the film; the bottom of the film touched the surface after 2.5 mm, and then the hook of the weight that keeps the film straight touched the surface after 3.0–4.0 mm. The measurement reached equilibrium after 4.5 mm, when the hook was fully submerged. By setting a mark at this point, we can erase the initial data. The result of the measurement is a wetting hysteresis curve with the advancing wettability for the film immersion and the receding wettability for the film withdrawal direction. The W_{adh} data were found to be reproducible to approximately $\pm 1.0\,\mathrm{mN\,m^{-1}}$.

From *Figure 3*, we can deduce that this film is homogeneous on a macroscopic scale because there is no scattering along the advancing and receding curve, but the film is heterogeneous at the microstructural level because hysteresis occurs. The hysteresis indicates that the surface contains sites with different energies. As mentioned above, low-energy sites have a dominant influence on the advancing wettability, and the receding wettability is more sensitive to high-energy sites.

Measurement of end-group concentration

We have attempted to determine relative changes in concentration of end-groups (mainly carboxylic groups) on the film surface, using adsorption of a cationic, fluorochrome dye, rhodamine B. The PET film was treated for 5 min at pH 8.0–8.5 in a 0.0025% solution of the dye. Dyeing was carried out at room temperature, well below the T_g of the film, thereby minimizing diffusion of the dye into the film interior. The film was then washed in demineralized water.

Excitation of the dye in the range 515–580 nm produces emission fluorescence with a maximum, λ_{em}, at ~600 nm. The treated film was therefore excited and scanned at λ_{em} in a Leitz MPV 1.1 microscope with a Plomoepak fluorometry attachment. The scanning speed was $180\,\mu\mathrm{m\,s^{-1}}$, and the total distance scanned was 5.4 mm. The measured fluorescence intensity is assumed to increase with increasing dye adsorption, which would reflect increased end-group concentration on the film surface.

RESULTS

Wettability of unrestrained specimens

The effect of draw ratio on the advancing water wettability of unrestrained PET film is shown in *Figure 4a*, where the work of adhesion, representing the wetting properties, is given as a function of draw ratio for film drawn at strain rates of 0.56 and $0.01\,\mathrm{s^{-1}}$. The work of adhesion decreases with increasing draw ratio, with most of the change occurring at low draw ratios. The effect of

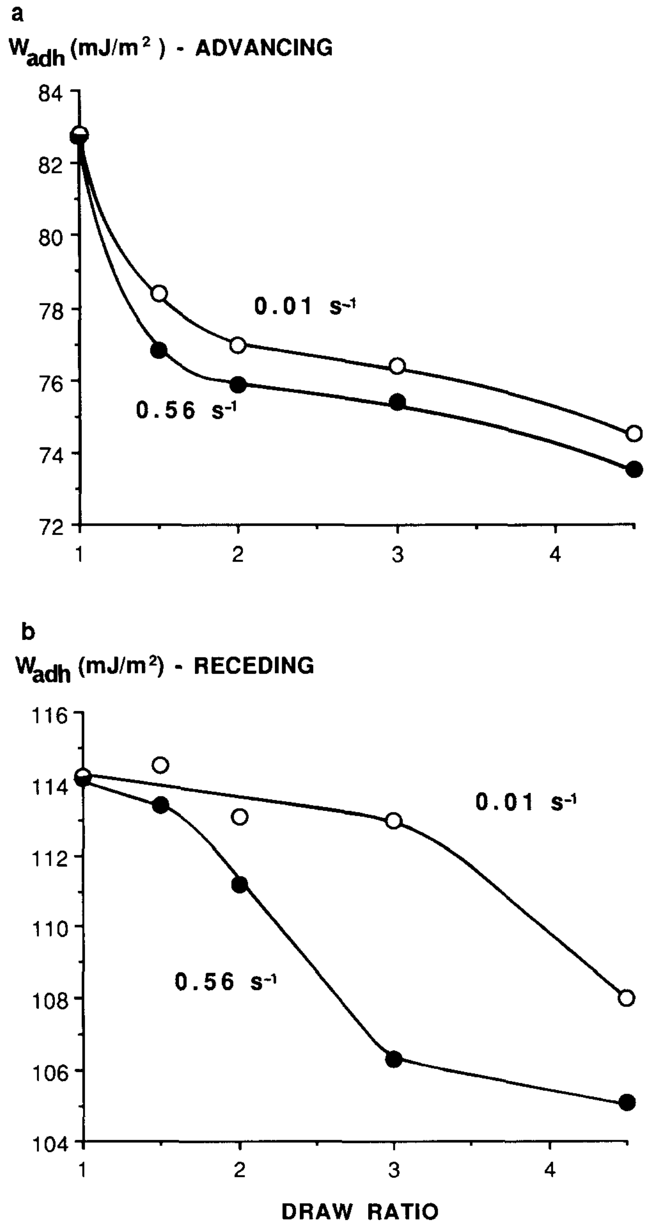

Figure 4 Influence of draw ratio on (a) advancing and (b) receding work of adhesion for specimens drawn unrestrained at two strain rates

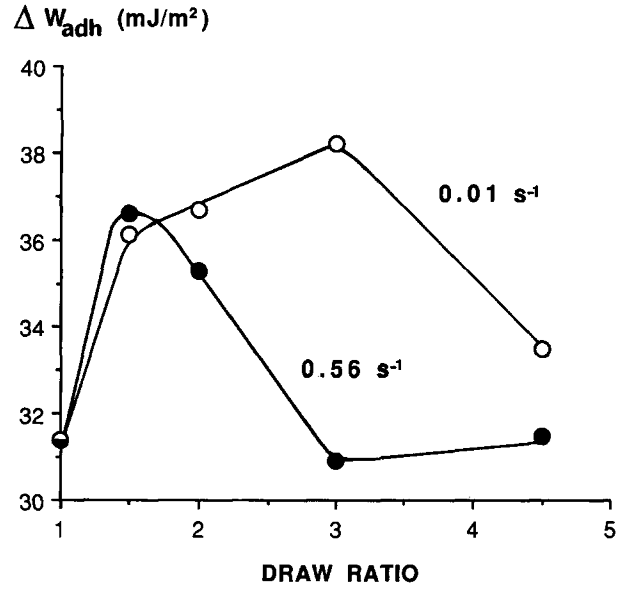

Figure 5 Wetting hysteresis as a function of draw ratio for specimens drawn unrestrained at two strain rates

strain rate, however, is small: the work of adhesion seems to decrease somewhat more slowly and remains slightly higher at the lower strain rate, but the statistical significance of these differences is doubtful. Since advancing wettability is most sensitive to initial changes in the energy composition of the surface (see *Figure 2*), we can deduce from the decrease in work of adhesion that molecular orientation induced at low draw ratios forms low-energy sites on the surface. These low-energy sites (which would have low wetting or non-wetting properties) must be formed by amorphous orientation because in the low draw ratio range only amorphous orientation is taking place (*Figure 1*). Crystallization appears to have little influence on the advancing wettability because there is no significant change at higher draw ratios where crystallites are formed.

The effect of unrestrained drawing on the receding wetting behaviour is shown in *Figure 4b*. As would be expected, the receding wetting behaviour is quite different from the advancing because the receding wetting mode is more responsive to high-energy sites. Since wettability in the receding mode is insensitive to initial changes in the composition of energy sites at the surface, drawing to low draw ratios has an insignificant influence on receding wettability. As soon as crystallization starts at higher draw ratios, however, receding wettabilities are reduced, indicating that crystallinity further increases the proportion of low-energy sites on the film surface. The influence of strain rate on the point at which receding wettability starts to decrease is consistent with the fact that crystallization starts earlier at higher strain rates. For example, at the strain rate of $0.56\,s^{-1}$ crystallization starts at draw ratio 2, whereas at the strain rate of $0.01\,s^{-1}$ it starts at draw ratio 3 to 3.5 (*Figure 1a*). This correlates directly with the draw ratios at which the receding wettability starts to decrease. It is also noteworthy that, in the case of the $0.56\,s^{-1}$ strain rate, the decrease in receding wettability abruptly levels off at a draw ratio of about 3, which coincides with the onset of the slower crystallization regime [regime 2 (ref. 1)]. For the $0.01\,s^{-1}$ strain rate, our wetting data do not extend into regime 2.

We have calculated the wetting hysteresis—the difference between the receding and advancing work of adhesion—at each draw ratio to summarize the effects obtained. *Figure 5* shows wetting hysteresis as a function of draw ratio at the two strain rates studied. At low draw ratios, hysteresis increases because the initial reduction in polymer–liquid interaction due to amorphous orientation only shows up as a decrease in the advancing wetting force, with the receding wettability remaining approximately constant. There is no difference between the two curves because these effects are essentially independent of strain rate. As soon as crystallization starts, the proportion of high-energy surface is abruptly reduced. This change decreases the receding wettability but does not influence the advancing wettability which, in this range, is insensitive to changes in the energy composition of the surface. The hysteresis is therefore reduced. The difference between the two curves is due to crystallization starting earlier at the higher strain rate.

Wettability of constant-width specimens

The wetting behaviour of the samples drawn at constant width is similar to that of unrestrained samples (*Figure 6*). The advancing wettability (*Figure 6a*) decreases with increasing draw ratio, then levels off at a draw ratio of about 2, and the strain rate has no significant influence on advancing wettability. Low draw ratios have little influence on the receding wetting force (*Figure 6b*), but when crystallization starts, this force decreases significantly. An important difference, however, between specimens drawn unrestrained and at constant width is the magnitude of the wettability changes. In the case of constant-width drawing, the decreases in wettability are much smaller. An explanation for this difference will be discussed later.

Sung *et al.*[11] measured the contact angle of a water drop deposited on the horizontal surface of PET film specimens with different draw ratios. Their results seem to indicate that contact angle is independent of draw ratio. However, the sessile drop method on a horizontal surface does not distinguish between advancing and receding contact angles and, when they differ, would provide some uncertain value between the two. Therefore our data and those of Sung *et al.* are not comparable.

End-group concentration

It is necessary to consider the possibility that drawing PET film could change the concentration of end-groups on the surface, which could influence wetting properties. To determine relative changes in end-group concentration we measured the relative amount of a fluorescent, cationic dye adsorbed on the film surface (see Experimental section). *Figure 7* shows typical sections of microfluorometer scans for films with draw ratios of 1.0, 2.0 and 4.5, and *Table 1* gives average fluorescence intensities for each draw ratio. For the film drawn unrestrained, there is no detectable change in fluorescence intensity with draw ratio, indicating that the end-group concentration is not influenced by this type of deformation. For film drawn at constant width, there seems to be a significant decrease in fluorescence intensity at a draw ratio of 4.5. It is possible that the large increase in surface area accompanying constant width drawing is responsible for this apparent decrease in end-group concentration. At any rate, the absence of any measureable change in end-group concentration at the surface of

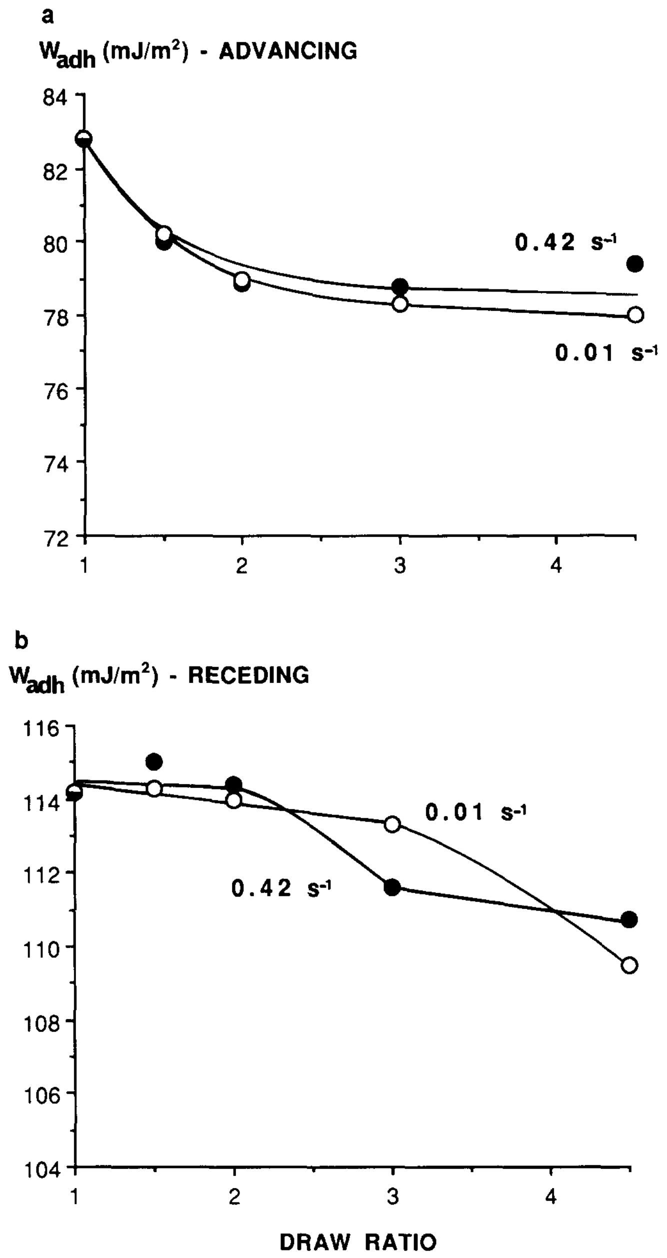

Figure 6 Influence of draw ratio on (a) advancing and (b) receding work of adhesion for specimens drawn at constant width at two strain rates

unrestrained specimens indicates that carboxyl groups are not responsible for the deformation-induced decreases in advancing and receding wettability.

DISCUSSION

Comparison of the experimental results with the calculated curves of the Johnson and Dettre model provides a good basis for interpretation of the observed effects. An example is the rapid decrease of the advancing wettability at low draw ratios before reaching a constant value at higher draw ratios. The Johnson and Dettre analysis predicts this response from the introduction of low-energy sites on the surface. The model can also explain the delayed decrease of the receding wetting force, since it predicts that the fraction of high-energy surface can be reduced substantially without influencing the receding wettability.

The Johnson and Dettre analysis contains additional basic information about the wetting measurement which should be discussed. For example, the analysis shows that the wetting experiment cannot detect any change in surface energy when the proportion of low-energy sites is between ~20% and 80% because there can be no significant change in the values of the advancing and receding wetting force in this range. Problematic, too, is the determination of any absolute energy value between the highest and lowest energy because the measurement provides only relative changes of two variable parameters, i.e. the advancing and the receding wetting forces. These are serious limitations for surface characterization by wetting measurements and should be taken into account.

There remains an important question: why does orientation of PET molecules result in a general decrease of surface energy? One could certainly expect the opposite result. Closer packing of molecules through orientation and crystallization should increase the concentration of interactive sites on the surface and therefore *increase* wettability. Evidence for this behaviour has been reported: high-density, crystalline polyethylene was found to be more wettable than low-density, amorphous polyethylene[12]; and the water wettability of a series of alkanes was found to increase with their density[6]. On the

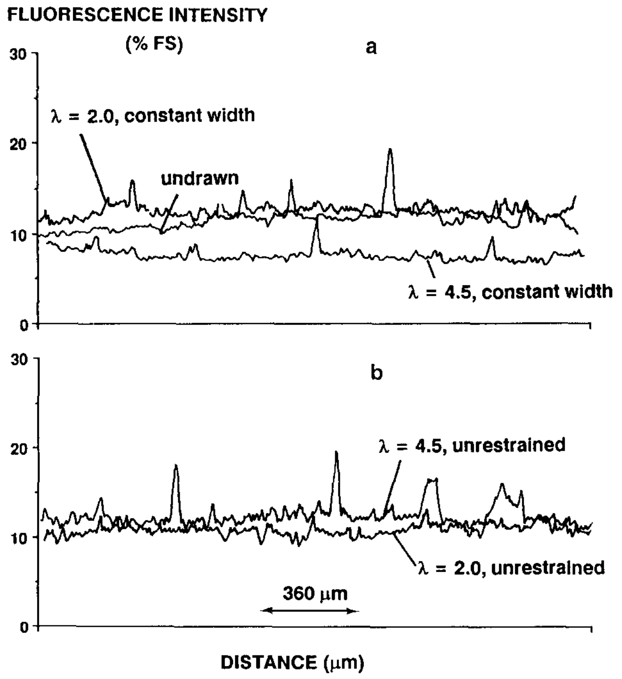

Figure 7 Microfluorometer scans of a fluorochrome dye adsorbed on PET film, showing fluorescence intensity (% full scale) *versus* scanning distance along the film for (a) an undrawn specimen and specimens drawn at constant width, and (b) specimens drawn unrestrained

Table 1 Average fluorescence intensity of fluorochrome dye adsorbed on PET film, obtained from a 5 mm microfluorometer scan

	Fluorescence intensity (% FS)	
λ	Constant width	Unrestrained
1.0[a]	12.0 ± 1.5	12.0 ± 1.5
2.0	12.5 ± 1.5	10.5 ± 1.5
4.5	7.5 ± 1.0	11.5 ± 2.0

[a] Undrawn specimen

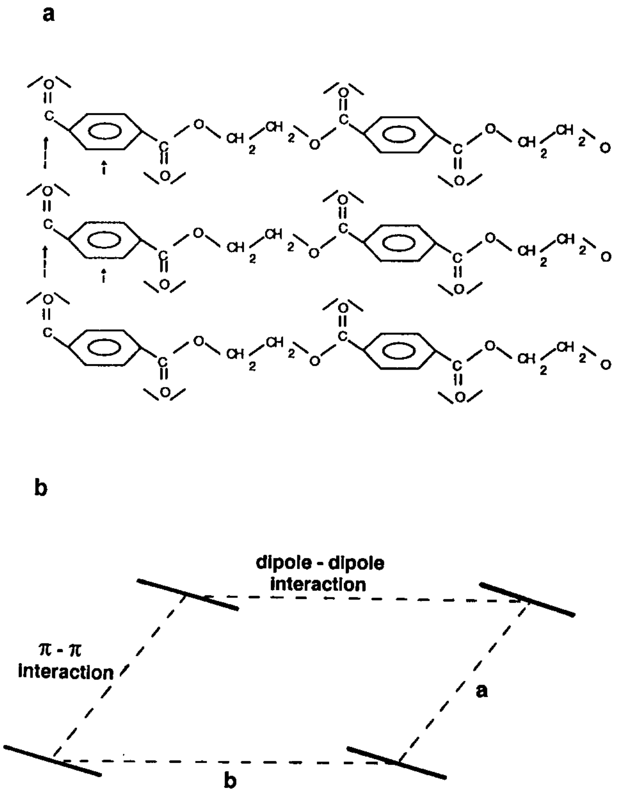

Figure 8 Schematics showing (a) interactions of adjacent PET chains in the benzene ring layer (– – – →) and between layers (– →), and (b) basal plane of PET unit cell and molecular interactions

other hand, studies involving controlled changes in packing density of adsorbed monolayers showed decreasing wettability with increasing density[13,14]. An explanation for this behaviour is that lower packing density results in a less sharp interface between solid and liquid, allowing some interpenetration of liquid and solid[6]. Greater interpenetration permits greater interaction between liquid and solid, and consequently the apparent wettability is higher in the less dense solid.

The latter interpretation could account for the decreasing wettability of PET film with increasing draw ratio. To elaborate, we will consider the molecular structure and molecular interactions of PET chains. As soon as non-crystalline PET film is extended, amorphous orientation takes place, such that polymer chains are oriented along the extension axis. Molecular orientation permits greater interaction between the chains, as illustrated in *Figure 8*. There are polar interactions between the carbonyl groups of the chains in the layer, and π–π interactions between aromatic rings of adjacent layers. As a result of these orientation-induced interactions, PET is in a lower energy state, and interactions with water are reduced. In other words, interaction between PET molecules increases the proportion of non-wetting (low-energy) sites per molecule by depleting the availability of sites capable of interacting with water molecules. Since crystallization involves high alignment and close packing of chains, it would be particularly effective at decreasing polymer/liquid interactions in this way. Before crystallization begins, however, amorphous orientation has already decreased the advancing work of adhesion to a roughly constant value (indicative of reaching its insensitive range), so the influence of crystallization can only show up as a decrease in receding wettability. *Figure 9* provides a schematic representation of the influence of molecular orientation on wettability, as proposed above, in terms of the Johnson and Dettre analysis.

This interpretation of our data assumes that, in the absence of close packing, the liquid penetrates beyond the outermost atoms of the surface molecules, and suggests that as a result of interchain interactions, close packing prevents access to interactive sites which are, even slightly, below these atoms. So, in the absence of close packing, the liquid must penetrate the solid to a minimum depth somewhat less than one molecule in diameter, which seems plausible. Of course, the ease of interpenetration depends on the nature of the liquid as well as of the solid, so that use of a probe liquid other than water might show an entirely different response to changes in the packing density of PET film.

It is also necessary to discuss the observation that the decreases in advancing and receding wettability with increasing draw ratio are smaller in the constant-width specimens than in the unrestrained specimens. This is despite the fact that the levels of crystallinity and the axial orientation of the molecules are essentially the same in these two modes of deformation[1,3]. One explanation for the difference in wettability is that it arises from the planar orientation of molecules and crystallites in the constant-width specimens. With increasing draw ratio at constant width, there is an increasing tendency for the benzene ring planes to align parallel to the surface of the film, whereas the unrestrained films retain cylindrical symmetry[7]. This parallel arrangement may somehow enhance accessibility of water molecules to interactive sites on the polymer chains.

Another explanation for the wettability difference of unrestrained and constant-width drawn specimens is that extension at constant width greatly increases the surface area and may open the structure in the plane of the film; i.e. there may be lower in-plane packing density in the amorphous regions of the constant-width specimens than in the unrestrained ones, resulting in a more diffuse interface between solid and liquid. As discussed earlier, greater interpenetration of water and polymer would increase wettability.

CONCLUSIONS

As soon as amorphous, unoriented PET film is drawn, the advancing wetting force decreases quite sharply and

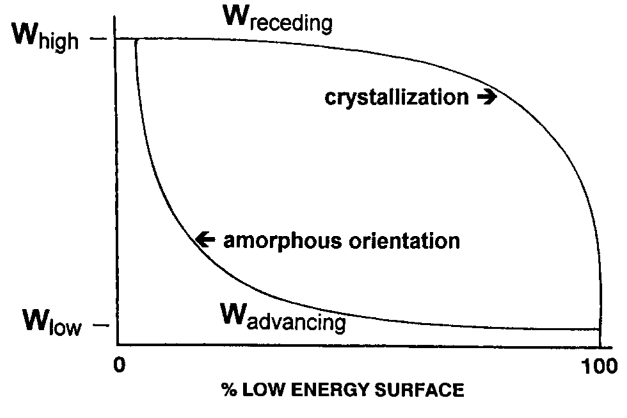

Figure 9 Interpretation of the influence of molecular orientation and crystallization on advancing and receding wettability, in terms of the model of Johnson and Dettre

then levels off at a draw ratio of about 2. The receding wetting force remains constant until crystallization starts, and then decreases abruptly. For the lower strain rate, the decrease in receding wettability starts at a higher draw ratio than for the higher strain rate, as does crystallization. The rapid decrease in advancing wetting force before reaching a constant value, and the delayed decrease in receding wetting force, are explicable in terms of Johnson and Dettre's model of an energetically heterogeneous surface. On the basis of this bicomponent model, drawing appears to increase the proportion of low-energy surface (at the expense of higher-energy surface that would interact more strongly with water). We propose that orientation-induced interaction between PET molecules depletes the availability of sites capable of interacting with water, reducing surface energy.

Drawing in simple extension (unrestrained) and in pure shear (constant width) show similar wetting behaviour, but the magnitude of the decreases in advancing and receding wettability are smaller in pure shear. Possibly the planar orientation of the constant-width specimens enhances polymer/liquid interaction, or perhaps the increased surface area reduces in-plane packing density, permitting increased interpenetration and interaction between polymer and liquid.

ACKNOWLEDGEMENTS

This study was undertaken in connection with the TRI project 'Structure and Properties of Polyester Film', supported by a group of Corporate Participants. The authors thank Drs Rebenfeld, Weigmann and Kamath for helpful discussions, and Ms Sigrid Ruetsch for performing the microfluorometry experiment. One of us (F.H.) is grateful for financial support from Deutsche Forschungsgemeinschaft (DFG).

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