Friction-induced molecular orientation of thin polymer films and bulk surfaces

F. Katzenberg, H. Liebertz, and J. Petermann

Lehrstuhl für Werkstoffkunde, FB Chemietechnik, Universität Dortmund, D-44221 Dortmund, Germany.

Abstract: This paper reports the possibility to produce highly uniaxially oriented thin films of thermoplastic polymers by friction transfer onto smooth, rigid substrates. The resulting degree of orientation and thickness of these films depends on parameters such as sliding rate, pressure and substrate temperature. Moreover, an uniaxial orientation in the friction contact area of the sliding polymer bar takes place, too. This gives the possibility, to uniaxially orient nanometer thin layers on the surface of non-oriented polymer bulk material.

1. Introduction

The formation of ultra-thin, highly uniaxially oriented PTFE-films by the friction transfer method of Tabor et al. is well known since 1964(1,2). For example, oriented PTFE thin films were used directly for TEM investigations(3,4) or to induce molecular orientation of numerous polymers by epitaxial overgrowth(5,6,7,8).

It is found now that it is possible to orient numerous other thermoplastic polymers directly by the friction transfer method. The degree of orientation and the thickness of these thin films do not always have the same quality as those known for conventional methods (i.e. melt spinning[9], spin coating[10] or Langmuir-Blodgett method[11]). But the orientation of low-molecular weight, insoluble and even amorphous polymers in form of thin films and thin surface orientation on polymeric bulk materials is possible.

2. Experimental

The oriented thin films discussed in this paper were prepared by sliding a surface of a polymer rod on a clean glass slide, simply by hand. The polymer and the glass were heated to the same temperature. The temperature, pressure and sliding rate were varied in that manner till homogeneous thin polymer layers of the desired thickness and degree of orientation arise. The friction transfer is not committed to glass substrates. Other smooth and rigid substrates, i.e. metal surfaces or PMMA, can also be used. The resulting layers were directly floated off on water, picked up on copper TEM grids and used for investigations of their structure and morphology in a Philips CM200 transmission electron microscope (TEM) operated at 200kV. The electron diffraction patterns were taken exclusively without using a selected-area aperture. The diameter of the specimen area used for diffraction was approximately 30μm. A qualitative judgement about the degree of orientation, surface roughness and thickness can be made by optical microscopy, using polarization and phase contrast. Atomic force microscopy (AFM), on a DME Rasterscope 3000 operated in contact mode, was used to reveal the surface topography of the polymer thin films.

To demonstrate the supposed orientation in a thin surface layer of the sliding counterpart, the oriented overgrowth of PE onto iPP, called epitaxy, was used as a probe. “Epitaxy” describes the growth of a guest crystal on the surface of a host crystal in one or more strictly defined crystallographic orientations (12). PE
crystallizing on uniaxially oriented iPP forms a
cross-hatched structure with the PE molecules being
inclined at about ±50° to the molecular direction of iPP.
The friction contact area of an iPP rod was covered
with a thin non-oriented HDPE layer. After melting the
PE at 160°C and following its crystallization on the iPP
surface, the morphology of the iPP/PE layer was
observed by AFM.

3. Results and Discussion

In Figures 1.a-d, electron diffraction patterns of some
friction-transfer oriented thermoplastic polymers are
shown. The sliding direction, accordingly the
orientation of the molecular axis, is indicated by an
arrow. For other polymers, their temperatures used for
preparation, and a qualitative judgement about the
thickness and the degree of orientation are shown in
Table 1. Their preparation temperature is well below
their melting temperature, and for some of them even
below their T_g (PC and LCP). At moderate
temperatures, all the resulting polymer thin films can
be detached easily from the substrate by floating them
off on water. At higher substrate temperatures,
detachment by floating off on water is impossible. The
reason why the polymer thin films show high adhesion
at high transfer temperatures may result from the
roughness of the films, which is lowest at the high
temperatures and consequently leads to more contact
area. In TEM bright-field micrographs no crystal
morphologies are visible. For example, the TEM
bright-field micrograph of HDPE (Fig. 2 (left)) does
not show any morphological contrast. But, after
annealing the HDPE friction-transfer film at 125°C, a
lamellar morphology has developed. Figure 2 (right)
shows the TEM bright-field micrograph of the annealed
HDPE friction-transfer film. For both the films, the
molecular orientation is unchanged, as seen from the
inserted electron diffraction patterns, which are
identical for the unannealed and annealed film. The
orientation direction is indicated by an arrow. Using
phase contrast in underfocus conditions, the darker
contrast correlates to the crystalline and the brighter
contrast to the amorphous areas. The highly oriented
crystalline lamellar morphology of HDPE is visible.
This leads to the suggestion that the original crystal
morphology may be of a micellar kind and transforms
upon annealing into a lamellar morphology[13].

Table 1 Friction transferable polymers, the transfer temperatures and a qualitative estimation
of the thickness and the degree of orientation of the films. (+ good, o medium, - poor)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Degree of orientation</th>
<th>Layer thickness</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE BASF 6021D</td>
<td>+</td>
<td>+</td>
<td>20-100</td>
</tr>
<tr>
<td>LDPE BASF 1810H</td>
<td>o</td>
<td>+</td>
<td>20-90</td>
</tr>
<tr>
<td>UHMWPE Hoechst</td>
<td>+</td>
<td>+</td>
<td>20-100</td>
</tr>
<tr>
<td>PB-1 Huels</td>
<td>+</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>iPP BASF 1100H</td>
<td>+</td>
<td>o</td>
<td>20-120</td>
</tr>
<tr>
<td>sPP non-commercial; Fina</td>
<td>+</td>
<td>+</td>
<td>20-100</td>
</tr>
<tr>
<td>iPS Polysciences</td>
<td>+</td>
<td>+</td>
<td>20-200</td>
</tr>
<tr>
<td>sPS Idemitsu</td>
<td>+</td>
<td>+</td>
<td>20-200</td>
</tr>
<tr>
<td>aPS BASF 143E</td>
<td>o</td>
<td>+</td>
<td>80</td>
</tr>
<tr>
<td>PC Bayer</td>
<td>o</td>
<td>-</td>
<td>50</td>
</tr>
</tbody>
</table>
| LCP (4,4 dihydroxybiphenyl monosubstituted
terephhalic acid) non-commercial| +                     | -               | 80              |
| PVDF Daikin Corp.              | +                     | o               | 50              |
| PVDF TrFE Daikin Corp.         | +                     | o               | 50              |
| PTFE Hoechst                   | +                     | +               | 20-300          |
friction temperature may therefore be compensated by the other two parameters.

Friction transfer of both amorphous and crystalline sPP result in a highly oriented crystalline sPP film. This indicates, that the friction transfer mechanism contains a phase transition, and that the resulting crystal phase and chain conformation of the friction-transfer thin film is independent of the physical state of the original polymer.

The mechanism of friction transfer can be explained with two different concepts:

1. Appropriate combinations of sliding rate and pressure lead to temperatures within a thin surface layer that are higher than the melting point or the glass transition temperature, respectively. By sliding the polymer rod, its melt is transferred to the supercooled substrate and crystallizes in an oriented state, because the flow gradient is high enough to avoid relaxation of

Fig. 1 Electron diffraction patterns of friction-transfer oriented PTFE (a), HDPE (b), iPS (c), PC (d). The sliding direction is equivalent to the molecular axis of the polymer thin films and indicated with the arrow.
Fig. 2 TEM bright-field micrographs of the original friction-transfer oriented HDPE thin film (left), and after annealing at 125°C for 30min (right). Without annealing, no morphologies are visible. After annealing, a lamellar morphology has developed. Using phase contrast in underfocus conditions, the darker contrasts correlate to the PE lamellar crystals and the brighter to the amorphous regions. The sliding direction and therefore the crystallographic c-axis is indicated by the arrow.

The oriented molecules (9).

2. The other conceivable mechanism is plastic deformation, involving a complete destruction of the original structure and subsequent transformation into a fibrillar morphology (14,15,16,17). It is comparable to the orientation mechanism of tensile cold drawing.

The diffraction patterns of friction-transfer sPP (Fig. 3.a) and PVDF (Fig 3.b) thin films exhibit two crystal phases of “all-trans” and “helical” chain conformations (18,19,20,21).

The sPP used for the friction transfer has a degree of tacticity of about 85%. Melt drawing of this sPP results in a highly oriented thin film containing a crystal structure with the helical conformation (22). In contrast, cold drawing results in a two-crystal-phase structure containing phases with “all-trans” (tttt) and “helical” (ttgg) conformations, comparable to the results from friction transfer (Fig. 3.a) (23). Very pronounced on the diffraction patterns is a diffraction spot on the meridian, which corresponds to a chain repeat distance of a [tg"tg"] chain conformation, not reported till now for sPP in the literature.

Fig. 3 Electron diffraction patterns of friction-transfer oriented sPP (a) and PVDF (b). Both diffraction patterns show a two-crystal-phase structure of “all-trans” and “helical” chain conformations. Characteristic reflections of both phases are indicated.

The occurrence of the [tttt] chain conformation leads to the suggestion that the orientation mechanism of the friction transfer method may involve a cold-drawing orientation (concept 2), too.

Crystallizing PVDF from the melt results in the
\(\alpha\)-phase, containing a helical chain conformation \((tg^*tg^-)\) [21]. In contrast to sPP, the \(\alpha\)-phase transfers completely into the piezoelectrically active \(\beta\)-phase by high mechanical drawing. The corresponding diffraction patterns are consistent with the \(\beta\)-phase \((tt)\) [21,24]. The friction transfer mechanism may therefore be a mixture of both concepts \((1+2)\), because the electron diffraction pattern of our friction-transfer PVDF (Fig. 3.b) exhibits a two-crystal-phase structure containing also the helical conformation \((\alpha\)-phase). A possibility, in which both mechanisms can appear, is shown in the sketch in Figure 4. The polymer rod and the substrate are illustrated. By sliding the polymer rod over the substrate, a thin molten layer in the friction contact area appears and transfers to the substrate, where the layer crystallizes in a high flow gradient (concept 1). The molten surface layer is of such a small thickness \((<10\text{nm})\), that not the complete macromolecule is in the molten state but only its segments in direct contact to the substrate. These segments apart from direct contact with the substrate may then be plastically deformed but be a part of the transferred layer (concept 2). Therefore, both processes (concepts \(1+2\)) may play a role in the formation of the transferred film. This suggests that a very thin zone of the friction contact area may also be oriented. A direct proof of this suggestion by x-ray diffraction, electron diffraction or optical polarization contrast was not successful, probably due to difficulties in sample preparation. But indirect evidence of the surface orientation is accomplished by using the phenomenon of epitaxy between oriented iPP and HDPE [25,26,27,28,29] as a probe. When crystallizing HDPE onto an oriented iPP film, an epitaxial orientation of the PE macromolecules occurs, with the PE chains being inclined at \(\pm 50^\circ\) to the iPP chain direction. Figure 5 shows an AFM image of a thin PE layer, which was put as a non-oriented film on the friction contact area of the iPP rod, heated to 160°C and subsequently recrystallized at room temperature. The typical cross-hatched morphology of epitaxially crystallized PE is visible. The appearance of the epitaxial PE morphology leads to the conclusion, that uniaxial surface orientation can be achieved by simply sliding a smooth and rigid substrate over a polymer surface.

Additionally, our observations may also have strong resemblance to linear friction welding [30] and may give us a tool to further investigate molecular mechanisms.

**Fig. 4** The friction transfer mechanism elucidating sketch, showing the sliding polymer rod, with a thin molten surface layer in direct contact to the substrate and with a transformation zone, where additional plastic deformation appears.

**Fig. 5** AFM contact-mode image of PE, crystallized at the friction contact area of an iPP rod. The typical epitaxial arrangement of PE lamellar agglomerates is visible. The molecular direction of the iPP substrate is indicated by an arrow.
occurring during this type of welding process.

4. Conclusion

The friction transfer method offers an easy possibility to orient several thermoplastic polymers in form of ultra-thin films. By this method, highly uniaxially oriented polymer thin films can be produced by simply sliding the polymer over a smooth and rigid substrate. Moreover, it is possible to obtain an orientation in a thin layer of the friction contact area by the same procedure. Two mechanisms may be responsible for the orientation: (1) oriented crystallization from a highly strained thin molten layer on the sliding surface of the polymer and (2) molecular orientation by the plastic deformation in the friction contact area.

Acknowledgement

The financial support of the Volkswagen Foundation is gratefully acknowledged.

References