Abstract: Solution-cast thin films of poly(ethylene 2,6-naphthalate) (PEN) were isothermally crystallized at 190°C on the highly oriented ultra-thin friction-transfer layer of polytetrafluoroethylene (PTFE), after being melted at 300°C. Transmission electron microscopy (TEM) of the films showed that PEN crystallized in an oriented fashion on the layer. Selected-area electron diffraction (ED) indicated that the crystals in the PEN films are mostly the α-form, as expected from our thermal condition for crystallization. The ED pattern from the untilted specimen was characterized by the fairly intense arc-shaped 010 reflection on the equator. A series of ED patterns, which were obtained from the same specimen area tilted at various angles around the axis parallel or perpendicular to the chain axis of PTFE in a TEM column, suggested that the crystallites of PEN α-form are preferentially oriented with their chain axis being parallel to the chain axis of PTFE and moreover, with their (100) planes being parallel to the surface of the PTFE layer.

1. Introduction

Polytetrafluoroethylene (PTFE) is known to act as a substrate to orient low-molecular-weight compounds and other polymers on it [1-5]. Various techniques have been reported to prepare PTFE films as a substrate [1,3], and one of them shows that a highly oriented ultra-thin "friction-transfer layer" of PTFE can be prepared by mechanical deposition onto a smooth glass surface [3, 4]. Really on the layer, oriented structures of various polymers as well as many low-molecular-weight compounds are obtained [3, 5-8]. One of such polymers is poly(ethylene terephthalate) (PET), which is crystallized in an oriented fashion on the layer [3]. Poly(ethylene 2,6-naphthalate) (PEN; is one of the high-performance polymers for wide use, and has naphthalene rings in its main chain in place of all the benzene rings of PET. Taking account of the similarity in chemical structure between PEN and PET, it seems reasonable to expect that PEN will crystallize in an oriented fashion on the friction-transfer layer of PTFE.

PEN crystallizes in at least two different crystal forms: α and β [9-11]. These two forms grow according to thermal conditions [10, 11] and/or by drawing [12, 13]/high-speed melt-spinning [14-16]: The pressure is also an important factor [17]. Wide-angle X-ray diffraction using synchrotron radiation revealed that at crystallization temperatures (Tc) up to 200°C only the α-form appeared in the specimens which had been melted at 300°C [10]. It was, however, reported that PEN crystallized exclusively in the α-form at Tc < 220°C [18]. In any case, when PEN is crystallized isothermally at Tc = 190°C after being melted at 300°C, only the α-form can be expected to grow.

Recently, we have reported transmission electron
microscopy (TEM) of the spherulitic morphology in a PEN thin film crystallized isothermally at 190°C from the melt (300°C) [19]. All the crystals of PEN thus crystallized were the α-form. Furthermore, most of the crystallites were preferentially oriented with their (001) planes being parallel to the film surface and with their (010) ones being parallel to the radial direction of the 2-dimensional spherulite. We here present a TEM study on preferential orientation of PEN, which was crystallized isothermally at 190°C on the friction-transfer layer of PTFE, after being melted at 300°C.

2. Experimental

PEN pellets (Mn =17,000; TN-8050 Lot. 51-6-103) were kindly supplied by Teijin Limited. An 0.1wt% solution of PEN in 1,1,1,3,3,3-hexafluoro-2-propanol, which is regarded as a good solvent with low degradation effect on PEN as well as on PET [20, 21], was prepared at room temperature (RT). A glass slide covered with an ultra-thin friction-transfer layer of PTFE, which layer had been prepared with our homemade apparatus (the temperature of the glass slide = ca. 300°C, the contact pressure = ca. 0.5MPa, and the sliding speed = 0.45mm/s). The glass slide coated with PTFE was dipped into the “warm” solution (about 40°C; for uniform wetting) of PEN, and then the remaining solvent was evaporated from the glass slide under an ambient condition. The glass slide with a dried thin film of PEN was placed on the thermostated hot stage (Mettler FP-82) for optical microscopy, and the crystallization was carried out as follows: melted at 300°C for 5min, cooled down to 190°C, held at 190°C for 1 h, and finally cooled down to RT by quenching.

The specimens, namely thin composite films of PEN and PTFE were coated with vapor-deposited C, under vacuum. (Some of the specimens were shadowed with Au before coating with C. The shadowing angle was tan⁻¹ (1/4), and the shadowing direction was nearly perpendicular to the sliding direction for making the friction-transfer layer.) The composite film was detached from the glass by using a poly(acrylic acid) backing film, which was solidified from a 25% aqueous solution and can be dissolved again in water, and then the film was floated off on the water surface. Finally, this film was mounted on a Cu grid for TEM.

The morphological observation and selected-area electron diffraction (ED) experiment were carried out with a transmission electron microscope (JEOL JEM-200CS) operated at 200kV. For specimen tilting, a specimen-rotating holder (JEOL EM-SRH10) was utilized. Selected-area ED patterns from the specimen area of ca. 8 μm in diameter and morphological images were recorded onto Kodak SO-163 or Mitsubishi MEM films, which were all developed at 20°C for 5min with Mitsubishi Gekkol (full strength).

3. Results and Discussion

The crystal structure of the α-form of PEN was analyzed by Mencik [9]. This form belongs to the triclinic system (space group = P1) with the unit cell parameters: a = 0.651nm, b = 0.575nm, c (chain axis) = 1.32nm, α = 81.33°, β = 144° and γ = 100°. Figure 1 illustrates the crystal lattice of the α-form, viewed along the chain axis (c-axis). In this figure, the c-axis, which is normal to the sheet of the figure, is pointing upward. One chain stem, in which the naphthalene rings and their adjacent planar carbonyl units are all parallel to one another and are on a certain single plane [18], passes through the unit cell. All the ED patterns in this report were well indexed with the cell parameters of the α-form, except for some cases in which a strong meridional reflection appears (See Fig.5).

Typical morphology of PEN crystallized isothermally at 190°C from the melt on the PTFE layer is shown in Fig.2. Terrace-like entities, some of which are indicated with arrowheads, are to be PEN. The PTFE layer is not uniform in continuity but is separated

![Fig. 1 Crystal lattice of PEN α-form [9], viewed along the chain axis (c-axis). The c-axis is normal to the sheet of this figure and pointing upward. Circles indicate carbon or oxygen atoms.](image-url)
into fibrous domains with different widths, as demonstrated in Fig. 2. Breakages have already been present in as-prepared friction-transfer layers of PTFE in our experiments, though it was reported that the as-prepared layers of PTFE were fairly uniform in continuity and thickness [4]. From the ED patterns and morphological observation of the layers which were shadowed with Au and then coated with C, however, we confirmed in advance that each fibrous domain in such layers is practically uniform in thickness with its top surface being basically parallel to the (100) crystallographic plane [4], and that no structural changes occur by the solvent for PEN and/or by thermal treatment up to 300°C which is lower than the melting temperature (or “isotropization temperature”) of PTFE [22, 23].

Figure 3(a) shows a representative ED pattern of PEN crystals grown on the PTFE layer. The rings in the pattern, which have uniform intensity distribution along their individual Debye-Scherrer circles, are from Au, and they (especially, the innermost ring of 111) were used as a reference to calibrate the camera length. The innermost intense arc-shaped reflection on the equator was indexed as 010 from the PEN α-form: this is one of the characteristic reflections to identify a crystal under consideration as the α-form. Though the 001 reflection could also be assigned to this intense reflection because the calculated lattice spacing of the (100) plane is similar to that of (010), it was ruled out by taking into consideration that the absolute value of structure factor of 001 is much smaller than that of 010 [9], as was mentioned in our previous work [19]. Other two intense reflections marked with letters A and B are from highly oriented PTFE: 100 on the equator and 0015 on the meridian. On the equator, a weak arc-shaped reflection is also recognized and it should be indexed as 020 from the PEN α-form. On the basis of these results, it is deduced that most of the crystallites of α-form are oriented with their (010) planes being parallel to the incident electron beam direction (and, of course, to the c-axis of PTFE) and accordingly being perpendicular to the PTFE surface. Some other faint ring-like reflections are also observed in Fig. 3(a), which seem to come from unoriented PEN.

In order to determine which crystallographic plane of the α-form is in contact with the PTFE surface, the specimen was tilted around the axis parallel or perpendicular to the chain axis (c-axis) of PTFE. When the specimen was tilted around the meridional axis, namely around the PTFE c-axis, the intensity of the 001 reflection from PTFE increased with increasing tilting angle, attained its maximum at 30° (Fig. 3(b)), and then decreased again (Fig. 3(c)). From this result, the top surface of the friction-transfer layer was confirmed to be basically parallel to the crystallographic (100) plane of PTFE [4]. In Fig. 3(b), the 010 reflection of the PEN α-form becomes faint, but no other new reflections appear. By tilting around the same meridional axis by about 55°, a new arc-shaped reflection appears on the equator, which is indexed as 110 of the α-form, and the 010 reflection has almost disappeared (Fig. 3(c)). On the other hand, when the specimen is tilted by about 50°
around the axis perpendicular to the PTFE c-axis, two sets of the weak arc-shaped reflection appear in the resulting ED pattern, being at an azimuthal angle, $\theta = \pm \text{ca. 50°}$, away from the equator (see Fig.4): In this case, the ED pattern from the untilted specimen was, of course, practically similar to Fig.3(a). This reflection is indexed as 112 from the $\alpha$-form.

To explain the results mentioned above, two important considerations must be given to the angle between the crystallographic planes with different indices for the PEN $\alpha$-form. According to our calculation based on the unit cell parameters of the $\alpha$-form, the following two things can be expected: Firstly, if the (100) plane is parallel to the substrate surface (PTFE), the (010) plane is nearly parallel to the incident electron beam direction without specimen tilting because the angle between (100) and (010) planes is computed to be 85°. Taking account of some orientation fluctuation of crystallites, this condition will give the 010 reflection on the equator without tilting. The (110) plane makes an angle of 60° with (010). Accordingly, it is expected that the 110 reflection will appear on the equator when the specimen is tilted by 60° (for Fig.3(c), about 55°) around the PTFE c-axis. Secondly, the (112) plane makes an angle of 47° with (010). It is, therefore, expected that the 112 reflection will appear at $\theta = \pm 47°$ (in Fig.4, $\theta = \pm \text{ca. 50°}$) in the ED pattern when the specimen is tilted by about 50° around the axis perpendicular to the PTFE c-axis. Both of the above-mentioned expectations have experimentally been fulfilled, as demonstrated in Figs.3(c) and 4.

As has already been frequently the case for oriented overgrowth of a crystalline polymer on the surface of a crystalline substrate, the polymer chains are apt to lie down parallel to the substrate surface [2, 3]. Hence, the orientation of PEN chains on PTFE was expected reasonably to be in the same manner. On the basis of our experimental data, it should be concluded that the (100) plane of the PEN $\alpha$-form is in contact with the
Fig. 4  Selected-area ED pattern taken from the tilted specimen, which contains numerous crystallites of PEN on the PTFE layer (melted at 300°C for 5min and then crystallized at 190°C for 1 h).

The specimen was tilted in the TEM column around the axis perpendicular to the c-axis of PTFE by about 50° (i.e., the tilting axis is horizontal).

(100) face of PTFE, and expectedly that the c-axis (chain axis) of the α-form is parallel to the PTFE c-axis, plausibly in an epitaxial fashion. The inter-stem distance in the (100) plane of PTFE is reported as 0.566nm [22], and that in the (100) plane of PEN α-form is computed to be \( b \cdot \sin \alpha = 0.568 \text{nm} \). Therefore, the degree of lattice mismatch is estimated at

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\left| \frac{0.568 - 0.566}{0.566} \right| \times 100 / 0.566 = 0.4 \% \]

which value is sufficiently within the accepted range of lattice mismatches for epitaxy (<15%) [2]. This result also explains well the epitaxial crystallization of PEN on PTFE with both their c-axes being parallel to each other and their respective (100) planes being in contact with each other.

Figure 5 shows an example of the ED patterns from some of the untilted specimens. A pair of arrowheads indicate a strong reflection that could be occasionally observed on the meridian. This reflection cannot be indexed with the α-form, and accordingly might be indexed as 011 of the β-form of PEN by using its unit cell parameters: triclinic, \( a = 0.926 \text{nm}, b = 1.559 \text{nm}, c = 1.273 \text{nm}, \alpha = 121.6°, \beta = 95.57°, \gamma = 122.52° \) [11]. However, further investigation is needed to associate this reflection with the β-form or a new crystal modification of PEN.

References and Notes