polymer communications

Preparation of laminates having isotropically molecular orientation of a liquid crystalline polymer in poly(ethylene terephthalate) matrix

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Morphological and structural properties of laminates consisting of extruded sheets of liquid crystalline polymer (LCP)/poly(ethylene terephthalate) (PET) blend were investigated. In laminates obtained by compression moulding the two blend sheets with the extrusion directions at right angles, the LCP fibril axes lay in various directions in the PET matrix, and consequently they looked like mechanically isotropic materials.

(Keywords: liquid crystalline polymer; poly(ethylene terephthalate); blend sheet)

Introduction

Rigid-chain polymers that form thermotropic liquid crystalline states tend to be easily oriented parallel to the direction of flow. This feature of thermotropic liquid crystalline polymers (LCPs) is almost preserved in the blended melt containing conventional thermoplastic polymers such as poly(ethylene terephthalate) (PET)[1]. In most cases, moulded or extruded parts obtained from the melt blends of these polymers contain separate phases, composed of both the oriented fibrous structures of the LCP phase and the unoriented structures of the conventional thermoplastic polymer phase[1–5]. Therefore, LCPs are believed to play a role as a reinforcement in moulded or extruded parts of the blends. The mechanical properties of the moulded or extruded blend parts perpendicular to the direction of molecular orientation of the LCP polymers, however, are very inferior to those parallel to the orientation direction[6]. The anisotropy of the mechanical properties is one of the shortcomings of moulded or extruded parts of blends containing LCPs.

Recently, Dutta *et al.* have investigated the mechanical properties of quasi-isotropic laminates using extruded films of LCP/fluoropolymer blend as a prepreg[7]. We have examined in detail the structural, thermal and mechanical properties of extruded sheets and strands of blends containing liquid crystalline copolyester and copolyesteramide with PET, and have found that the modulus and strength of the blends are mainly dependent upon content and morphology of the LCPs, and also that the blend sheets have a striking anisotropy of the mechanical properties[8–10]. In order to decrease the anisotropy of mechanical properties of the LCP/PET blend sheets, laminated plates have been prepared using extruded sheets of the LCP/PET blends. In this paper, we have examined the structural properties of the laminated plates of the blend sheets.

Experimental

The LCP used in this work is a commercial polymer, Vectra A 950 (Polyplastics Co., Japan), prepared from hydroxybenzoic acid and hydroxynaphthoic acid. PET is also a commercial product, SA1206 (Unitika Co., Japan). The two-component polymers, mixed by a rotor in the form of pellets, were dried in an oven at 90°C for 14 h and then at 150°C for 4 h. LCP contents in the LCP/PET blends were 40, 50 and 60 wt%.

The mixed pellets of the two-component polymers were melt-blended at 300°C using a single-screw extruder equipped with a coat-hanger die which was composed of a crosshead with diameter 15 mm, manifold, damming zone, and die lip area, as reported in a previous paper[11]. The die lip area was 20 mm long in the flow direction and 120 mm wide. The gap of the die lip was adjusted to 0.75 mm. The LCP/PET blend sheets were extruded at 310°C and at a pressure of 20–45 kg cm^{-2} into a water bath. The thickness of extruded blend sheets ranged from 0.3 to 0.6 mm. The blend sheets were dried at 100°C *in vacuo* and were used as a prepreg for preparing laminated plates. Laminates were obtained by compression moulding two sheet prepregs, crossing each other in the extrusion direction, at 300°C and 30 kg cm^{-2} for about 10 min *in vacuo*.

X-ray diffraction patterns of extruded sheets and laminated plates were obtained at room temperature with an X-ray generator (Rigaku Co.) having Ni-filtered Cu Kα radiation and a flat-plate camera. The morphology of the surfaces of sheets and laminated plates fractured at room temperature or at the temperature of liquid nitrogen was observed using a scanning electron microscope (SEM) (model DS-130, Akashi Co.). The fractured surfaces were coated with gold before observation.

Results and discussion

Figure 1 shows lateral surfaces of the extruded sheet of LCP/PET 50/50 blend, which were fractured parallel and perpendicular to the extrusion direction. The LCP component forms fibrous structures elongated almost parallel to the extrusion direction in the continuous phase of PET in the blend sheet (*Figure 1b*). Fractured cross-section surfaces of the LCP fibrils embedded in the PET phase can also be seen in *Figure 1a*. The thickness

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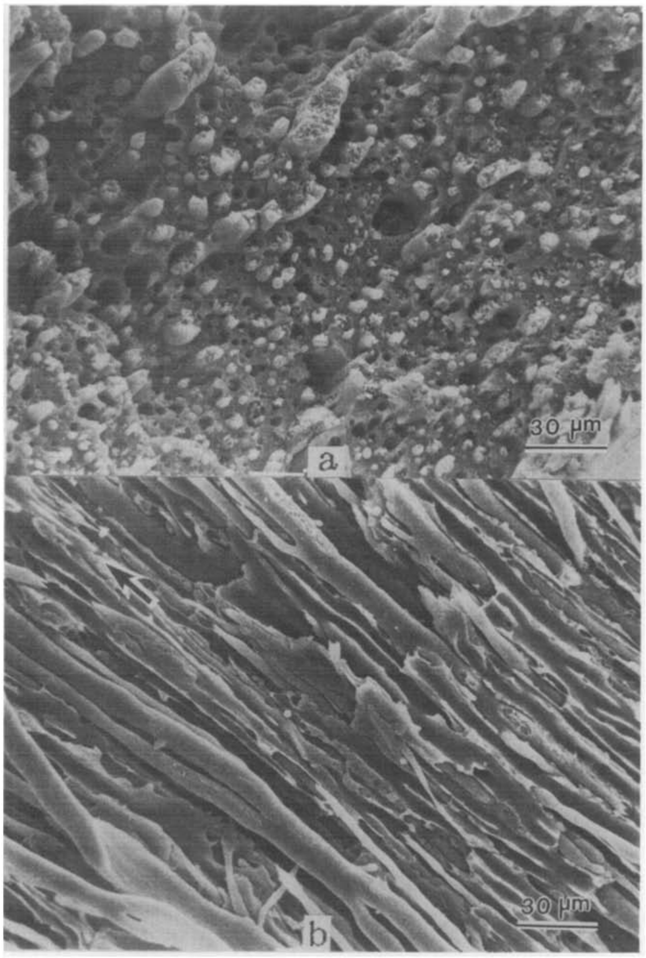

Figure 1 SEM micrographs of lateral surfaces of an extruded sheet of LCP/PET 50/50 blend, fractured perpendicular (a) and parallel (b) to the extrusion direction. An arrow in (b) indicates the extrusion direction

of most LCP fibrils is less than 10 μm. *Figure 1b* shows that thinner LCP fibrils frequently diverge from thicker ones. This result implies that a network of the LCP fibrils exists in the LCP/PET blend sheets. This network increased with increasing content of LCP in the blend. The LCP fibrils in the blend sheets tended to become thinner with increasing the draw ratio of the sheets. The PET component is an amorphous and unoriented structure in the blend sheets, as reported in a previous paper[8]. Therefore, the PET phase acts as a matrix in the blend sheets.

The dynamic tensile modulus of extruded sheets was investigated by using a Rheovibron. The modulus parallal to the extrusion direction for LCP/PET 50/50 blend sheet was 10 GPa at room temperature, while that parallel to the extrusion direction for a pure PET sheet was 2.2 GPa. However, the modulus perpendicular to the extrusion direction for the former sheet was almost the same as, or a little lower than, that for the latter sheet. There was not much difference between the modulus parallel and perpendicular to the extrusion direction for the pure PET sheet. These results reveal that a tensile modulus parallel to the extrusion direction of PET sheet is improved by blending with LCP, while that perpendicular to the extrusion direction is almost unchanged. The improvement in tensile modulus of LCP/PET blend sheets is attributed to the formation of fibrous structures in the blends, as shown in *Figure 1*.

Figure 2 shows a fractured lateral surface of a plate laminate of the two LCP/PET 50/50 blend sheet prepregs. LCP fibrils, very similar to those observed in *Figure 1*, can be seen in the PET matrix in *Figure 2*. However, the direction of the LCP fibril axis in about half of the fractured lateral surface is almost perpendicular to that in the other half of the surface, as seen in *Figure 2*, because the extrusion direction of one of the two sheet prepregs made a right angle with the extrusion direction of the other sheet prepreg in the laminate. It should be noted that the two sheet prepregs are fastened together by the PET component in the blend, as shown in *Figure 2*. This result reveals that the PET component acts as an effective adhesive agent at the interface between the two sheet prepregs.

Figure 3 illustrates wide-angle X-ray diffraction patterns for an extruded sheet of LCP/PET 50/50 blend and the laminate shown in *Figure 2*. The diffraction pattern of *Figure 3a* demonstrates that the PET component in the blend sheet is amorphous and has an unoriented structure, and that the LCP component is crystalline and has a more or less oriented structure showing equatorial reflection of 0.45 nm[8,10]. This oriented structure of the LCP component in the blend sheet corresponds to the fibrous structure observed in *Figures 1* and *2*. On the other hand, the LCP component in the laminate shows

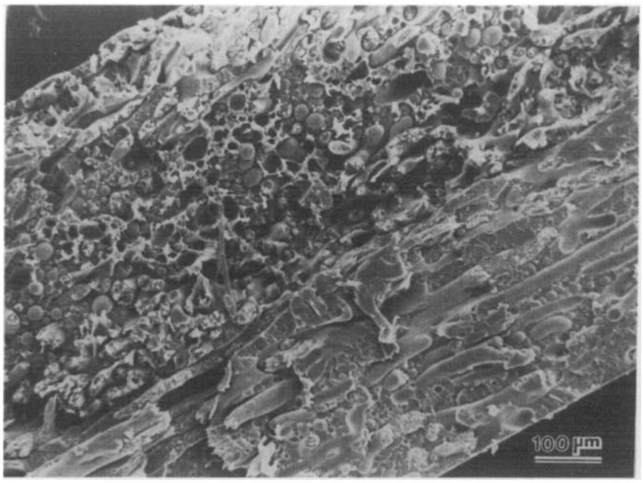

Figure 2 SEM micrograph of fractured lateral surface of a laminate of LCP/PET 50/50 blend

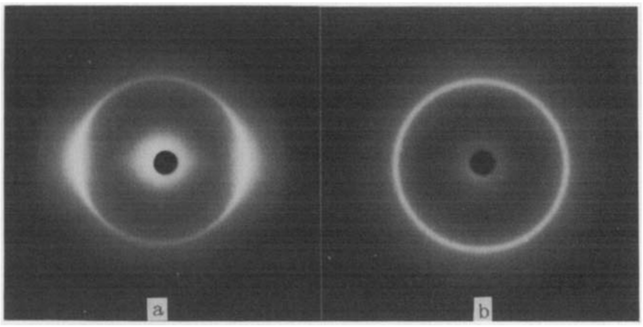

Figure 3 Wide-angle X-ray diffraction patterns of an extruded sheet (a) and a laminate (b) of LCP/PET 50/50 blend. The extrusion direction of the sheet (a) is vertical and the incident direction of the X-ray beam is perpendicular to the surface of the sheet

a reflection of a ring pattern indicating no oriented structure, as might be expected from the structural properties seen in *Figure 2*, though the PET component remains amorphous and unoriented (*Figure 3b*). This result reveals that the orientation of LCP fibrils, that is, LCP molecules, disappears when two sheet prepregs are laminated with their extrusion directions at right angles. Consequently, the laminate of the LCP/PET blend looks like an isotropic material having no orientation of the LCP molecules.

An extruded sheet of LCP/PET blends could be fractured easily by hand parallel to the extrusion direction at room temperature, while it was very hard to do so perpendicular to the extrusion direction. On the other hand, the laminate of LCP/PET blends mentioned above was isotropically much tougher, regardless of the extrusion direction of the sheets in the laminate. Probably, the laminate has little anisotropy of mechanical properties. The tensile modulus and strength of the laminate will be examined in detail in future work.

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