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Fatigue behaviour of injection-moulded polymer blends of polypropylene and liquid crystalline polyester

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Fatigue processes in injection-moulded blends of polypropylene (PP) and a liquid-crystalline polyester (LCP) were investigated with reference to variations in the inner microstructure and the dynamic viscoelastic properties under cyclic tensile loading. For neat PP, whitening caused by inter-spherulite and/or inter-lamella microcrazing was observed over a wide range within the specimen, and the storage modulus E' and the loss tangent $\tan \delta$ monotonically decreased and increased, respectively, until fracture. For the neat LCP specimen, on the other hand, the molecular orientation progressed all over the specimen during fatigue, and, as a result, E' remained almost constant and $\tan \delta$ clearly decreased, until they were drastically reversed just before fracture. In the blends containing over 40 wt% of the LCP, the influence of LCP was so strongly reflected as to reduce $\tan \delta$ during fatigue and to extend the fatigue lifetime. In addition, it was observed that the PP and the LCP phases closely attach to each other under loading. Such morphological change in the blended specimens with higher LCP content was also considered to contribute to a decrease in $\tan \delta$ during fatigue and to the extension of their fatigue lifetimes. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Polymer blends have been extensively studied and developed to exhibit high performance and new functions to meet various industrial demands[1,2]. In general, the mechanical properties of the newly developed polymeric materials are mainly evaluated in terms of dynamic viscoelasticity, quasi-static tensile and/or compressive behaviour and impact strength. The fatigue property, however, is also an important subject for further applications of them to the structural components. The fatigue performance is usually characterized by the relationship of applied stress–amplitude to lifetime, i.e. S–N curve, and the crack growth rate under cyclic loading, which often leads to Paris' law, as well as for other engineering materials[3]. However, these evaluating methods cannot offer significant information on the inner structural changes in the material during the fatigue process.

A new type of equipment for the fatigue test has been developed to enable one to perform the continuous measurement of dynamic viscoelastic properties under cyclic loading until fracture[4,5]. The dynamic viscoelastic factors well reflect the microstructure of polymers at the molecular level. Therefore, the fatigue tests using this

type of equipment seem useful for elucidating the fatigue mechanisms in detail, and may contribute to the development of high fatigue-performance polymer blends.

In this study we discuss the fatigue process in injection-moulded blends of polypropylene (PP) and a liquid-crystalline polyester (LCP) from the viewpoint mentioned above. The polymer blends using LCPs are often regarded as *in situ* composites[1,6-8], because LCPs with high rigidity due to a rod-like molecular structure can be well aligned in the flow direction under the injection moulding. Although their quasi-static mechanical properties have so far been investigated[1,9-12], the dynamic fatigue behaviour has not been sufficiently studied, as yet[12]. Thus, we conducted the dynamic viscoelastic analysis of fatigue of PP/LCP blends, and interpreted the results both from the morphological observations in scanning electron microscopy (SEM) for the blends and polarized Fourier transform infrared (*FT*i.r.) microspectroscopy on molecular orientation for LCP.

EXPERIMENTAL

Materials and sample preparation

The materials used were commercially available PP, M1700 (Asahi Chemical Co. Ltd) and a thermotropic LCP, Rodrun LC3000 (Unitika Co. Ltd). This LCP was a copolymer consisting of *p*-hydroxybenzoic acid and

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poly(ethylene terephthalate). These pellets were mixed at different weight fractions without any compatibilizer, and then dried in air at 80°C for 4 h. They were extruded by a single screw extruder, Raboplastomil (Toyo Seiki Co. Ltd), under mixing at a cylinder temperature of 230°C and at a screw rotating speed of 150 rpm. The pellets made by the extrusion were again dried in air at 80°C, and subsequently placed in an injection moulder, model J75SS2 (Nippon Seiko Co. Ltd). The dumbbell-shaped specimens with gauge length of 60 mm, width 10 mm and thickness 3 mm were moulded at outlet and mould temperatures of 230 and 40°C, respectively, following the recommendation of the supplier. Only the rectangular gauge region was used in the experiments after cutting off both sides of the dumbbell-shaped specimen.

Dynamic viscoelasticity

Dynamic viscoelastic measurements were conducted by means of equipment that served both as a dynamic viscoelastic meter and as a fatigue tester, Fatigueron, VFA-1KNA (Orientec Co. Ltd). This testing machine has been newly developed to perform not only general characterization of the viscoelastic factors under small oscillating strain, but also simultaneous and continuous measurements of their variations during fatigue until fracture under increasing amplitudes of cyclic strain and/or stress. The prototype of this fatigue tester was first made by Takahara and co-workers[4,5]. The storage modulus, E', and the loss tangent, tan δ, in the flow direction under injection were measured under a sinusoidal strain of the amplitude of 4.2×10^{-4} at a heating rate of 2°C min^{-1} from -150°C to a certain temperature, at which the specimen was so elongated as to make the measurement impossible at applied stress levels (2.33 MPa for neat PP, and 3.33 MPa for neat LCP) under an auto-tension mechanism for preventing slack of the specimen.

Dynamic viscoelastic analysis of fatigue process

Variations in E' and tan δ during fatigue were simultaneously and continuously measured until fracture by using also the new type of fatigue tester mentioned above. All the tests were conducted in air at room temperature (23 ± 2°C) under the same loading condition, i.e. the sinusoidal tensile stress along the flow direction under injection at the maximum stress of 25 MPa, a stress ratio of 0.04 and applied frequency of 10 Hz.

Observation of inner morphology

The morphology in the blends was observed under transmitted light by means of an optical microscope, Axioplan (Carl Zeiss, Inc). A thin slice (10 μm thick) of as-moulded specimens was prepared in the flow direction by using a microtome, model HM340 (Microm Inc.).

The inner part of the fatigue-fractured specimen of PP was exposed in the direction parallel to the flow direction by using the knife of the above microtome. Its cut surface was sputter-coated with a thin layer of gold and then observed under reflected light with Normarski contrast using the above optical microscope.

For PP/LCP blends, the inner parts of the as-moulded and the fatigued specimens were also exposed and gold-coated in the same way as that for the fatigue-fractured PP specimen mentioned above. The observations were

performed by using SEM with a field emission gun, model S4000 (Hitachi Co. Ltd).

For neat LCP, the as-moulded and the fatigued specimens were fractured along the flow direction at the temperature of liquid nitrogen. The fracture surfaces were observed by SEM after the same treatment as that for the blend specimens.

Polarized FTi.r. microspectroscopy on molecular orientation in neat LCP

In order to evaluate the microstructural variation in LCP during fatigue at molecular level, the polarized *FT*i.r. microspectra were measured by a *FT*i.r. micro-spectrometer with a MCT detector, model 8900μ (Japan Spectroscopic Co. Ltd), following the procedure which Kaito *et al.*[13] have applied to the analysis of the molecular orientation in the extruded LCP sheets. The as-moulded and the fatigued specimens were micro-tomed in the flow direction to a thickness of 5 μm. The polarized spectra were obtained by changing the polarization direction. A small square region of 20 μm × 20 μm was analysed under transmission mode; 16 scans of 4 cm^{-1} resolution were conducted.

In the above cases the SEM observations and the *FT*-i.r. measurements for the fatigued specimens were always made for the specimens, which were unloaded and removed from the apparatus before fracture, when their tan δ values indicated the minimum under cyclic loading. This trend of tan δ will be precisely described below.

RESULTS AND DISCUSSION

Dispersion of PP and LCP phases

Figure 1 presents the optical micrographs of inner morphology of the blends with different LCP contents. For every sample, the skin, the intermediate and the core regions may be broadly distinguished, as well as for other injection mouldings. In addition, the LCP phase, which is seen in black in the figure, is clearly recognized to be separated from the PP phase.

For the specimen of 20 wt% LCP content, numerous fine fibrils of LCP oriented in the flow direction are seen in the skin and the intermediate regions, while LCP disperses in the form of minute spheres in the core region. For the composition of 40 wt% LCP, the LCP phase becomes much longer and thicker, and is partially fibrous even in the core region. Increasing the fraction of LCP to 60 wt% extends the LCP phase to form a thick network structure in the core region. In the specimen of higher LCP content of 80 wt%, the PP phase penetrates into the crevice between the enlarged LCP domains.

Dynamic viscoelastic properties

The storage modulus, E', and the loss tangent, tan δ, measured at 1 Hz, are shown in *Figure 2* as a function of temperature. The numbers in the figure denote the LCP contents. For neat PP, glass and secondary transitions are observed at about -10 and 60°C, respectively, while neat LCP indicates glass transition at about 60°C and clear secondary transition at -60°C. For the blended specimens these relaxations are influenced in their intensity, but not affected at their temperatures, by the composition, as is generally observed for immiscible binary systems[2]. The value of E' increases monotonically
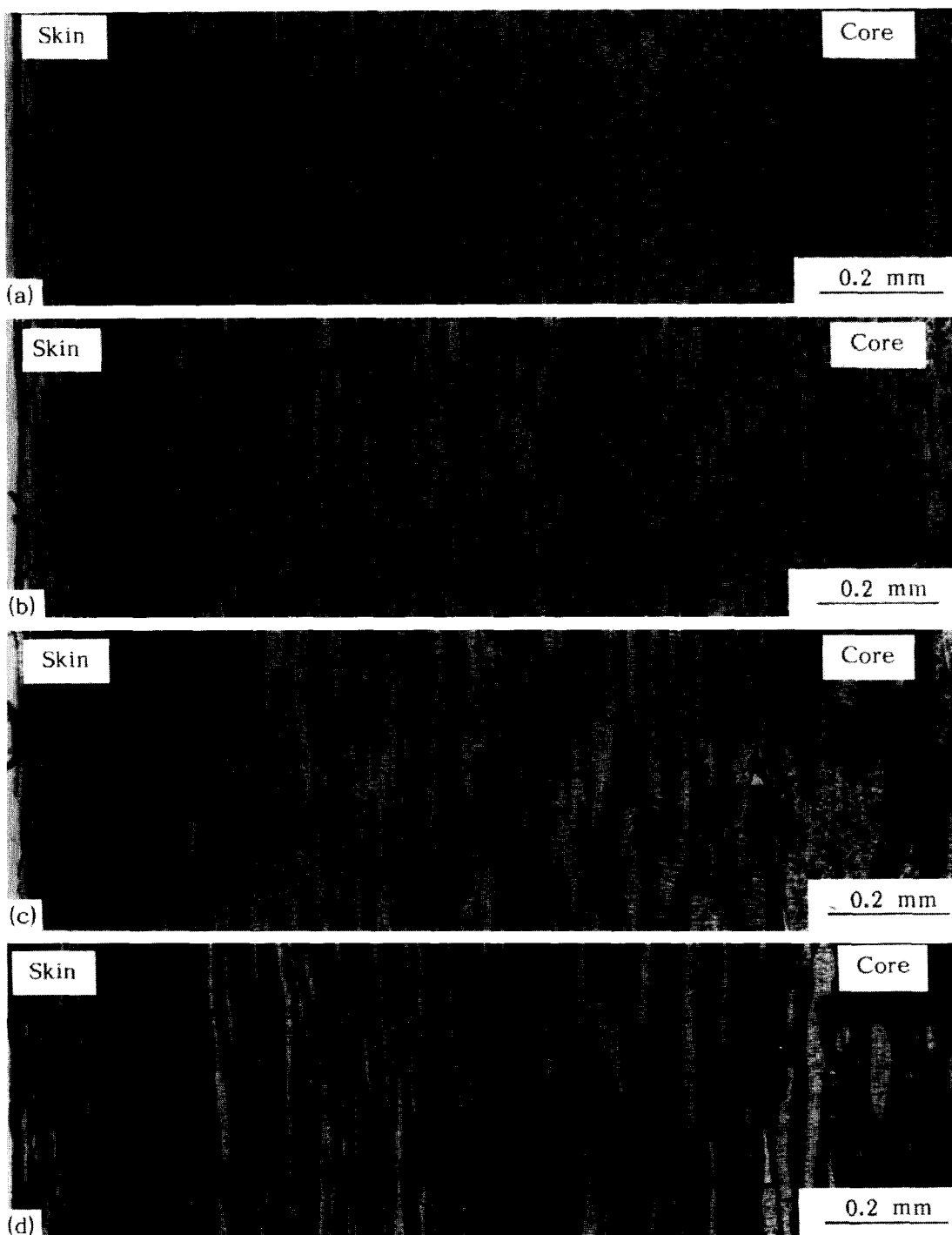
Figure 1 Inner morphology of the blends with different LCP contents: (a) 20 wt%; (b) 40 wt%; (c) 60 wt%; (d) 80 wt%

with increasing LCP content. The tan δ value, however, increases with an increase in the LCP content at temperatures below $-10°C$ and above $60°C$, but the relationship is completely reversed between -10 and $60°C$. The large relaxation at about $-60°C$ caused by the LCP phase will be worth examining with reference to the impact strength at low temperature.

Variations in the dynamic viscoelastic properties during fatigue

Figure 3 shows variations of E' and tan δ with loading time during fatigue for the specimens with different LCP contents. The numbers in the figure again denote the

LCP weight fraction. For neat PP, E' and tan δ monotonically decrease and increase, respectively, until fracture, followed by whitening over a wide range within the specimen. An optical micrograph of the inner morphology of the whitened PP specimen is shown in *Figure 4*, which was taken under Nomarski contrast. It is suggested that the whitening phenomenon results from microcrazing at inter-spherulite and/or inter-lamellar regions[14]. This microfracture process may contribute to an increase in tan δ during fatigue. In the case of neat PP, fracture took place in a highly necked region, where the specimen was locally softened to a greater extent. According to the measurement of surface temperature
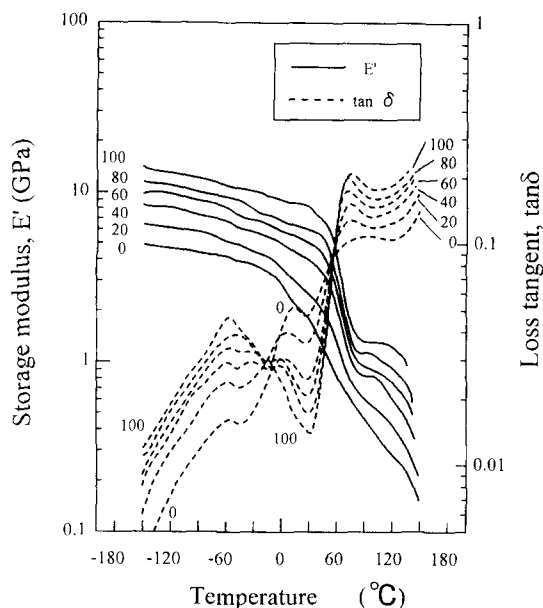
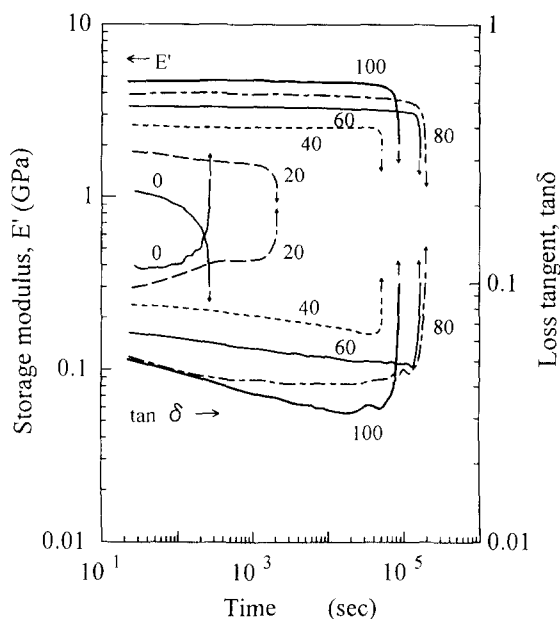**Figure 2** Dynamic viscoelastic properties of PP/LCP blends measured at 1 Hz. The numbers denote the LCP weight fractions

Figure 3 Variations in the dynamic viscoelastic properties under cyclic tension. The numbers denote the LCP weight fractions

Figure 4 Optical micrograph of the inner mophology of the fatigue-fractured PP followed by whitening. The arrow denotes the loading direction

by an i.r. radiation thermometer, the temperature at this region finally increased to about 90°C. Therefore, the fatigue failure of neat PP under the present stress condition may be classified as thermal failure. This type of fatigue failure is generally observed for other engineering polymers at relatively high stress level[3].

For neat LCP, on the other hand, E' remains almost constant, while $\tan\delta$ clearly decreases, with progress of the fatigue process. Just before fracture, E' and $\tan\delta$ drastically decrease and increase, respectively. It is clear that the fatigue lifetime of LCP is much greater than that of PP under the same stress condition. Fracture was observed to start in a skin layer and to exhibit a manner of brittle fracture without large deformation and/or necking.

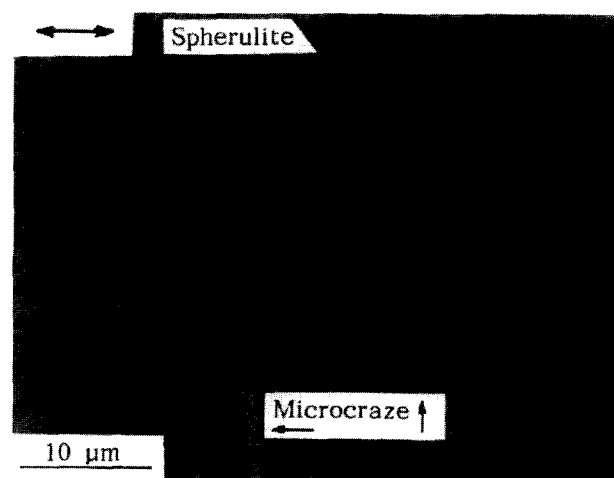With regard to the behaviour of blended specimens,

the fatigue lifetime increases with an increase in LCP content. It is noted that the fatigue lifetime surpasses that of neat LCP in cases of its higher content (60 and 80 wt%). In the blended specimens of LCP fractions over 40 wt% the variations in dynamic viscoelastic properties are so influenced by LCP as to show a decrease in $\tan\delta$ during fatigue.

Variations in inner morphology of blends

The SEM micrographs of the inner morphology of the intermediate regions of the as-moulded and the fatigued specimens with 40 wt% LCP are presented in *Figures 5a* and *b*, respectively. The picture of the fatigued structure was taken after removing the specimen from the apparatus, when $\tan\delta$ indicated the minimum value before fracture. In the as-moulded specimen a creviced (fibrous) structure in the LCP phase and a gap between the PP and LCP phases are clearly observed. After fatigue, however, the structure of the LCP becomes much denser, and PP and LCP phases closely attach to each other. It seems curious that such adhesion takes place between the two phases despite there being no compatibilizer, because PP has a simple structure consisting of aliphatic hydrocarbon chains, and LCP has more rigid polar chains with an aromatic component. Although precise mechanisms remain to be elucidated, the $-CH_2-CH_2-$ units in LCP may possibly have some effect on such adhesion with the aid of heat generation in the PP phase by the hysteresis loss under cyclic tension, as Mather has pointed out[15].

Microstructural changes in neat LCP

Figure 6 presents the polarized microspectra for the skin layer of the as-moulded specimen of neat LCP. The solid line denotes the spectrum measured under polarization perpendicular to the flow direction under injection, while the broken line is that parallel to the flow direction. There are clear differences between these absorbances. These differences mean that the molecular chains are highly oriented in the flow direction in the skin layer. Such anisotropy is conveniently expressed by a dichroic ratio, which is, in this case, given by the ratio of absorption intensity in the flow direction to that in the perpendicular direction. Here, we note the dichroic ratio
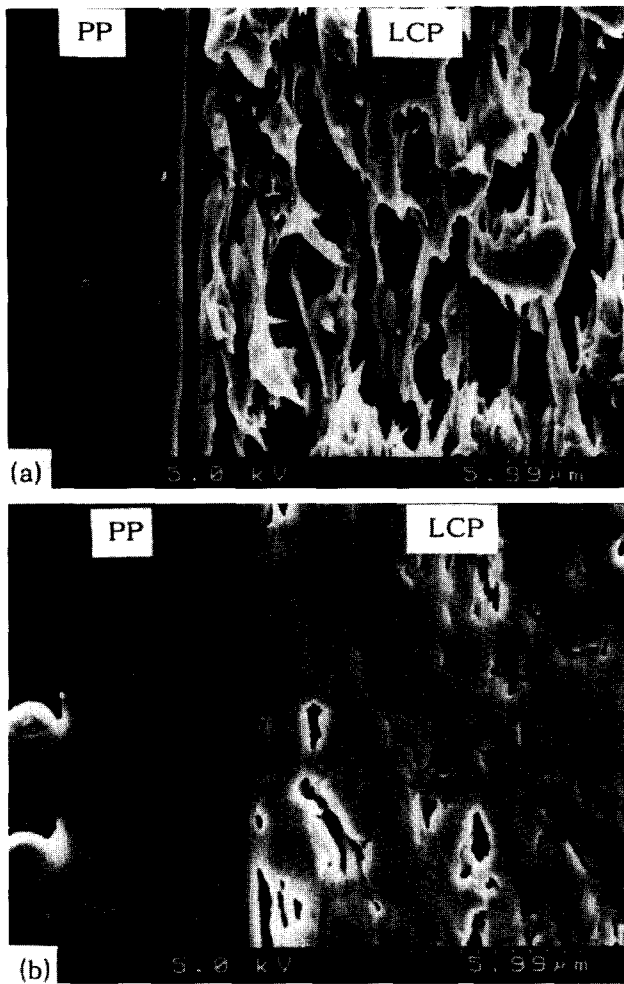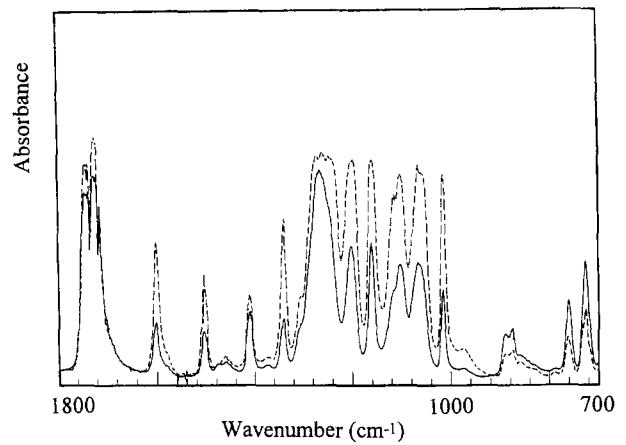
Figure 5 Scanning electron micrographs of intermediate regions of the specimen with 40 wt% LCP: (a) as-moulded specimen; (b) fatigued specimen
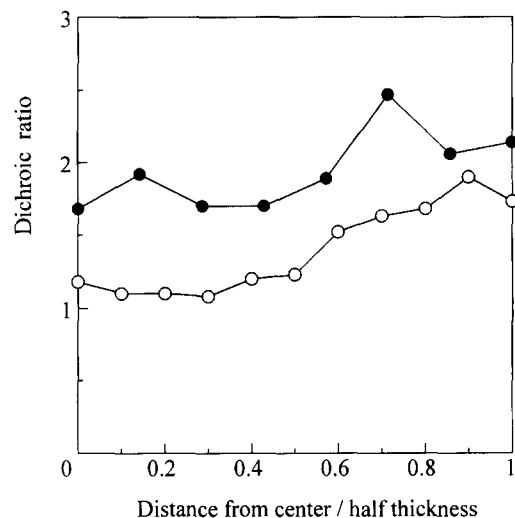

Figure 6 Polarized micro-*FT*i.r. spectra for the skin layer of the as-moulded LCP specimen: (—) perpendicular polarization; (— — —) parallel polarization


Figure 7 Molecular orientation profile in a LCP represented by the dichroic ratio corresponding to the vibration of the benzene ring in the main chain: (O) as-moulded specimen; (●) fatigued specimen

for the absorbance at $1602\,cm^{-1}$ due to the skeletal vibration of the benzene ring in the main chain of LCP.

Measuring the spectra from the core to the skin layer in the same way provides a profile of molecular orientation. *Figure 7* shows the relationship between the dichroic ratio corresponding to the vibration of the benzene ring and the distance from the centre of the neat LCP specimen, which is here normalized by the half thickness of the specimen. The open circles represent the dichroic ratio for the as-moulded specimen, and the filled circles denote that for the fatigued specimen, which was unloaded when the tan δ value was regarded to take the minimum during the test. In the as-moulded specimen the dichroic ratio is about 1.2 in the core region, indicating an approximate isotropic state, and gradually increases towards the surface layer, resembling the trend in the extruded LCP sheets[13]. A relatively low value over the entire surface may result from the fact that the molecular orientation is suppressed by rapid cooling when molten polymer is in contact with the mould wall under injection. For the fatigued specimen, on the other hand, the dichroic ratio is so enhanced over all the specimen as to show a high value of 1.7 even in the inner core region.

SEM micrographs of the morphology of inner core regions of the as-moulded and the fatigued LCP

specimens are presented in *Figures 8a* and *8b*, respectively. The latter was taken after removing the specimen from the apparatus, when tan δ indicated the minimum value before fracture, as for the *FT*i.r. measurement. Curved and crossed fibrils are seen in the as-moulded specimen[13], while fibrils are, as a whole, oriented in the flow direction in the fatigued specimen. Since the molecular chains will align in the direction of the fibril axis, the fibril orientation may accord with the enhancement of molecular orientation during fatigue.

The micro-*FT*i.r. measurements and the SEM observations mentioned above may provide an interpretation that a decrease in tan δ during fatigue for the specimens with higher LCP content is attributed both to the molecular orientation in the LCP phase and to adhesion between the PP and the LCP phases advancing under cyclic tension.

CONCLUSIONS

Fatigue processes of injection-moulded PP/LCP binary blends were investigated from viewpoints of variations in
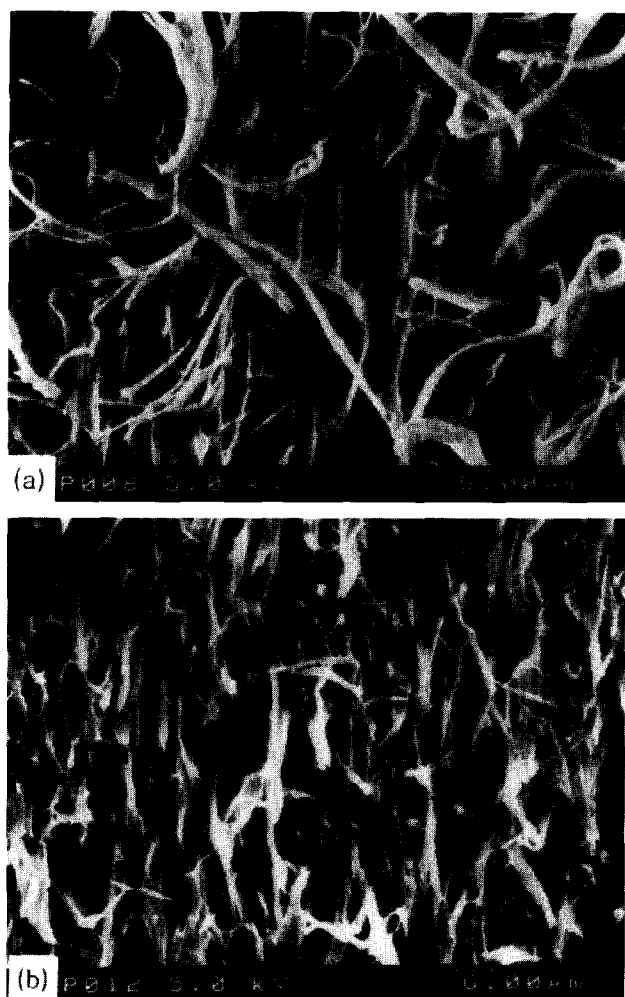
Figure 8 Scanning electron micrographs of the inner core region of neat LCP: (a) as-moulded specimen; (b) fatigued specimen

the dynamic viscoelastic properties and the inner microstructure under cyclic tension. The fatigue lifetime increases with an increase in the fraction of LCP, but surpasses the lifetime of neat LCP in cases of its higher content. For the specimens containing over 40 wt% of LCP, E' remains almost constant, while $\tan \delta$ clearly decreases with the progress of fatigue process. Such fatigue behaviour quote opposes the trend of neat PP and is strongly influenced by LCP. The SEM observations of

inner morphology reveal that the LCP phase transforms from an original creviced structure to a much closer one, and attaches closely to the PP phase. In addition, the polarized micro-*FT* i.r. analyses for neat LCP indicate the molecular orientation to be enhanced over all the specimen in the loading direction under cyclic tension. These microstructural changes may be strongly reflected in the variations in the dynamic viscoelastic properties of the specimens with higher LCP content during fatigue. It will be required in future to elucidate the mechanism of adhesion between the PP and the LCP phases advancing under cyclic tension.

ACKNOWLEDGEMENTS

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