Band pattern development in shear-oriented thermotropic copolyester extrudates

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The mechanism of band pattern development in shear-oriented thermotropic copolyester extrudates is explained in terms of residual longitudinal tension. A liquid-crystalline copolyester consisting of 40 mol% poly(ethylene terephthalate) and 60 mol% *p*-oxybenzoate is extruded at 220°C in a wide shear-rate range without elongational deformation. These extrudates exhibit band patterns perpendicular to the extruded direction in the core layer after development of skin–core structures at high shear rates. The band pattern causes characteristic cone-shaped fracture surfaces after tensile tests. Moreover, in the core layer, cracks along band patterns are detected by optical and scanning electron microscope observations. These morphological characteristics are caused by a molecular orientation distribution in the radial direction, which also causes the distribution of thermal and mechanical properties. The mechanism of band pattern development is analysed by assuming that longitudinal tension is concentrated in the core layer during the cooling process. This stress is induced by differences in both Young's modulus and longitudinal linear expansion coefficient between the skin and core layers. The quantity of the residual stress is estimated roughly by a thermal mechanical analysis.

(Keywords: thermotropic copolyester; shear; extrudate; band pattern; skin–core structure; molecular orientation)

INTRODUCTION

The morphology of a thermotropic copolyester consisting of 40 mol% poly(ethylene terephthalate) (PET) and 60 mol% *p*-oxybenzoate (PHB)[1] has been investigated from various viewpoints. Donald *et al.* have indicated that thermotropic liquid-crystalline polymers exhibit banded textures caused by shearing between glass slides and observed these structures precisely[2-8]. Banded structures were also investigated in lyotropic[9,10] and other thermotropic[11-14] polymers.

We have investigated properties of PET/PHB extrudates with widely changed molecular orientations induced by shear and elongational stresses[15]. Judging from the property changes, molecular orientation depends less on shear stress than on elongational stress. To investigate the shear stress dependence of molecular orientation, therefore, it is important to avoid elongational deformation. Only when extruded at a high shear rate do PET/PHB extrudates exhibit characteristic structures, which may be caused by a shear stress distribution in the radial direction. Most characteristic is a banded structure perpendicular to the longitudinal direction, which develops in the core layer of a skin–core structure. We call it 'band pattern' to distinguish it from so-called 'banded texture'.

This paper deals with the morphological and physical changes in PET/PHB extrudates with increase in the shear rate. Band pattern development is explained in terms of residual longitudinal tension caused by distributions in thermal and mechanical properties in the radial direction after rapid cooling of the extrudates.

EXPERIMENTAL

Material

The material used was a thermotropic nematic copolyester consisting of 40 mol% PET and 60 mol% PHB with an inherent viscosity of 0.67 dl g^{-1}, which was measured at 30°C in 50:50 (by weight) phenol–tetrachloroethane at a concentration of 0.50 g/100 ml. This copolyester was prepared as described by Jackson and Kuhfuss[1]. The stable liquid-crystalline temperature range of the copolyester is from 220 to 300°C[16].

Extrusion

PET/PHB copolyester was extruded at 220°C using a capillary viscometer with a capillary 1.0 mm in diameter and 5.0 mm in length (*Figure 1*). The extrusion temperature was limited to low values in order to make extrudates stably over an extensive shear-rate range. The shear rate for extrusion was varied from 6 to 6080 s^{-1}. To avoid deformation-induced molecular orientation, the take-up speed was controlled to be the same as the extrusion speed. The extrudate diameter, therefore, was kept constant over all the shear-rate range. All the extrudates were immediately quenched in water.

Morphological observations

PET/PHB extrudates were microtomed in the extruded direction to a thickness of 6 μm for longitudinal cross-section observation. Optical transmitted micrographs were taken with a polarizing microscope between crossed polarizers in a diagonal position. Optical

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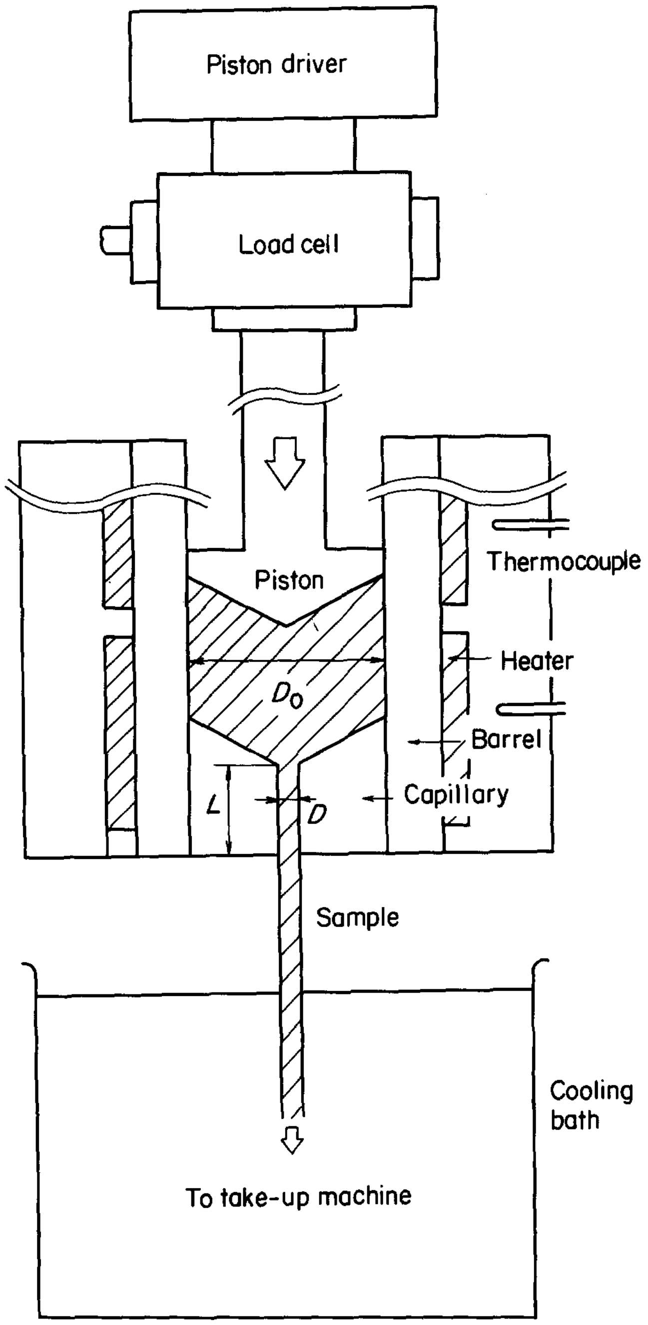

Figure 1 Schematic diagram of extrusion apparatus

retardations were measured under these conditions by a beam 50 μm in diameter and birefringence values were determined. The fracture surfaces after tensile tests and the longitudinal cross-sections of the extrudates were observed by scanning electron microscopy (SEM).

Property measurements

Young's moduli of samples were measured by a viscoelastometer. Elongations at break and tensile strengths were measured by a tensile test machine. Longitudinal linear expansion coefficients were measured by a thermal mechanical analyser (t.m.a.) in tension mode and determined by averaging the values in the temperature range from −20 to 20°C. Details of property measurements are mentioned elsewhere[15].

RESULTS

Band pattern development

Figure 2 shows optical micrographs of microtomed PET/PHB extrudates taken between crossed polarizers in a diagonal position. The extrudates at low shear rates show homogeneous textures in the radial direction. The extrudates at shear rates above 122 s^{-1} exhibit skin–core structure. The skin layers seem homogeneous and show interference colours induced by birefringence over all the shear-rate range above 122 s^{-1}. Core layers at shear rates above 608 s^{-1}, however, exhibit band patterns with dark and bright layers perpendicular to the extruded direction, although the core layer at 122 s^{-1} seems homogeneous. In the region adjacent to the skin layer, the band patterns change their direction, becoming parallel to the extruded direction and then disappear into the skin layer.

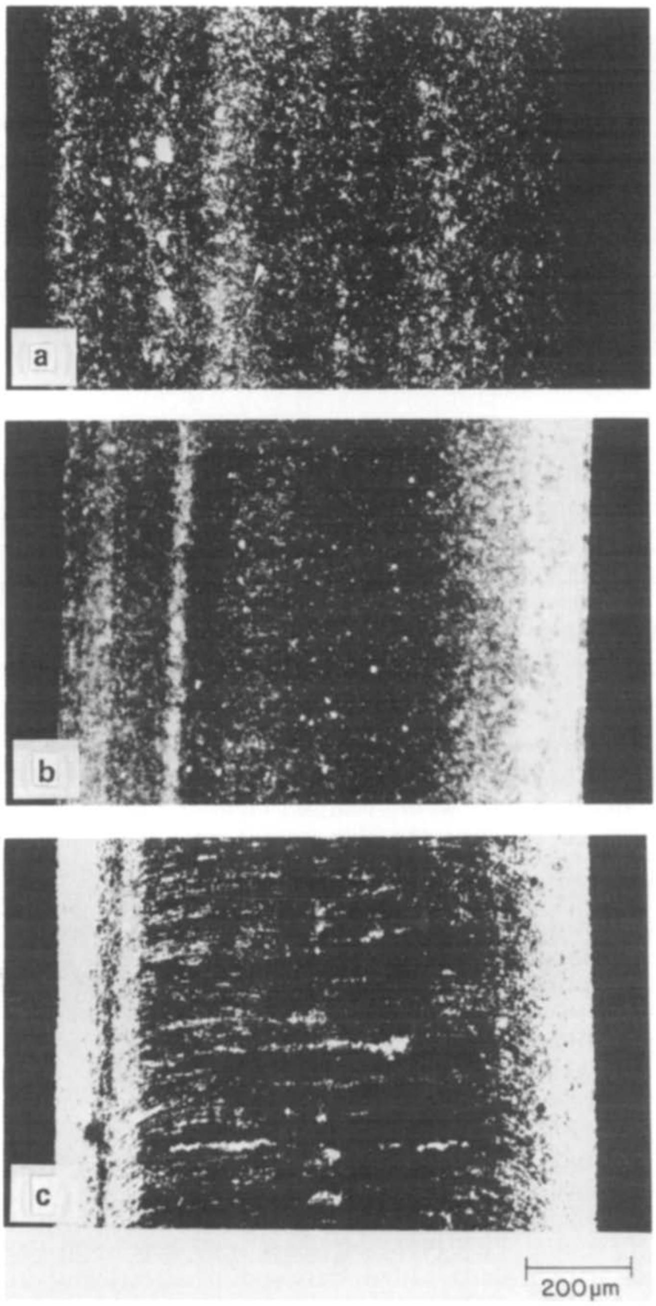

Figure 2 Optical micrographs of microtomed extrudates between crossed polarizers in diagonal position. Shear rates (s^{-1}): (a) 6; (b) 122; (c) 6080. Sample thickness 6 μm. The extrusion direction is vertical

Structural changes between the skin and core layers are clear and drastic. The thicknesses of skin layers are about 150 μm and change little with changes in the shear rate.

Figure 3 shows higher-magnification optical micrographs of the core layer of microtomed extrudates at shear rates of 122, 608 and 6080 s^{-1}. It is clear that no band patterns exist in the core layer at 122 s^{-1} even though the extrudate exhibits skin–core structure. Band patterns at intervals of a few micrometres are observed at shear rates above 608 s^{-1}. There are no changes in these intervals with changes in the shear rate.

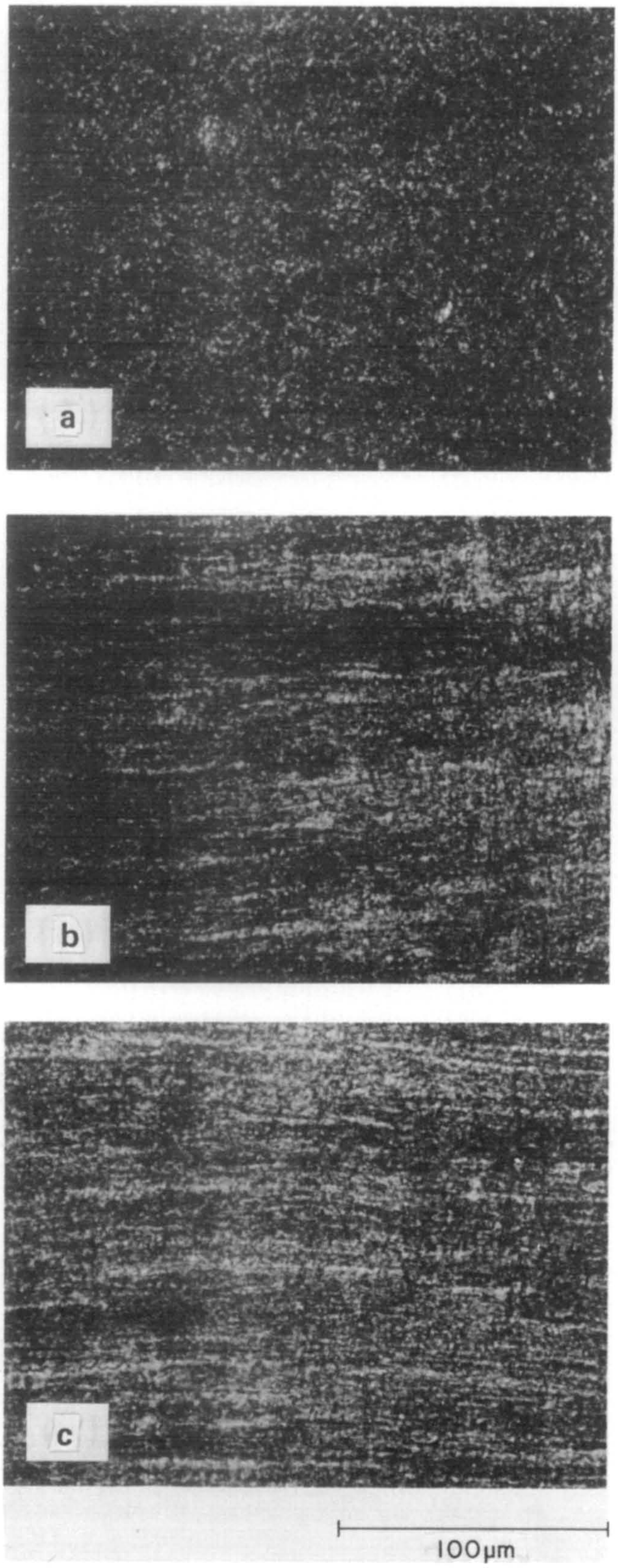

Figure 3 High-magnification optical micrographs of the core layer of microtomed extrudates. Shear rates (s^{-1}): (a) 122; (b) 608; (c) 6080. Sample thickness 6 μm. The extrusion direction is vertical

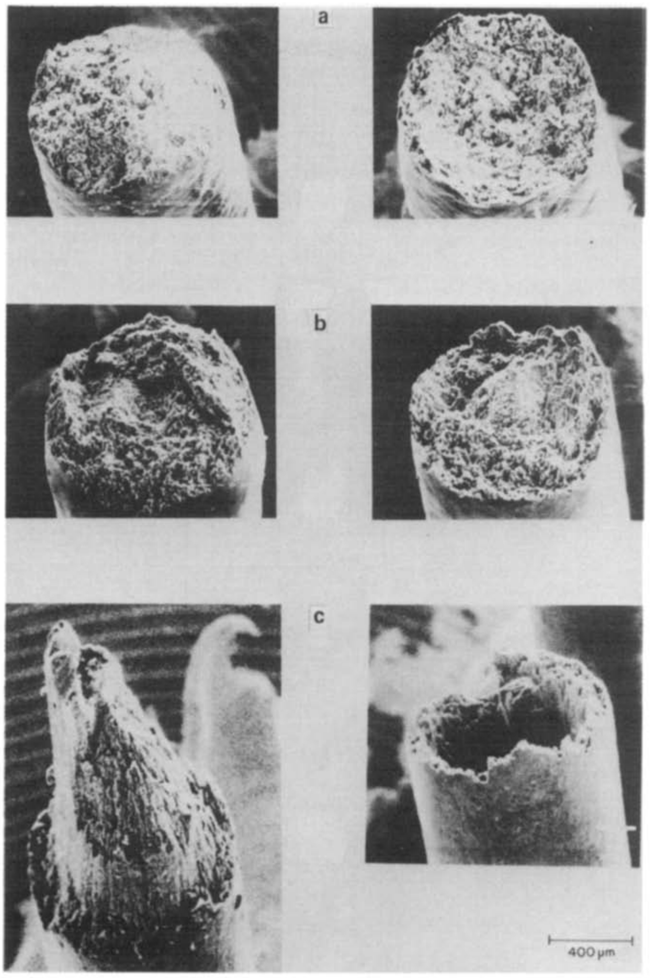

Figure 4 Scanning electron micrographs of paired fracture surfaces of the extrudates taken after tensile tests. Shear rates (s^{-1}): (a) 6; (b) 122; (c) 6080

Fracture surface observation

Figure 4 shows SEM micrographs of the paired fracture surfaces at the same breaking points, taken after tensile test. PET/PHB extrudates at shear rates lower than 122 s^{-1} show relatively flat fracture surfaces. At shear rates above 608 s^{-1}, however, the inner parts of the fracture surfaces become uneven, resulting in characteristic convex and concave cone-shaped surfaces. The outer parts of the fracture surfaces remain flat even when extruded at high shear rates. The thickness of the outer part is about 150 μm. This corresponds to the thickness of the skin layer (*Figure 2*). The flat outer part of the fracture surface, therefore, corresponds to the skin layer and the inner part corresponds to the core layer.

Characteristic uneven fracture surfaces are not only caused by skin–core structure but greatly dependent on band pattern development, because an extrudate at a shear rate of 122 s^{-1} exhibits a simple flat fracture surface even if it shows skin–core structure (*Figure 2*). The change in fracture surfaces corresponds to band pattern development in the core layer (*Figure 3*). The characteristic cone-shaped fracture surface in the core layer is caused by band patterns and fractures occur along the band patterns. Moreover, the boundaries of the inner and outer parts of the fracture surfaces are discontinuous, which means that the fractures of the two parts occur independently of each other. This result indicates that the mechanical binding force between molecules of the skin and the core layer is weak when the core layer exhibits band patterns.

Figure 5 shows higher-magnification SEM micrographs of the skin layer of the fractured surfaces. From these micrographs, it is clear that oriented fibrous textures develop with increases in the shear rate in the skin layer. On the other hand, no fibrous texture development was observed in the core layer even at the highest shear. That is, textures similar to the skin layer at the lowest shear rate were observed. The microtextures of the skin and the core layer are different in molecular orientation, which indicates the cause of skin–core structure development because microtexture is directly affected by molecular orientation. Moreover, microtexture in the fracture surface was not affected by band pattern development. This indicates that, in the core layer, molecular orientation accompanied by band pattern development does not occur.

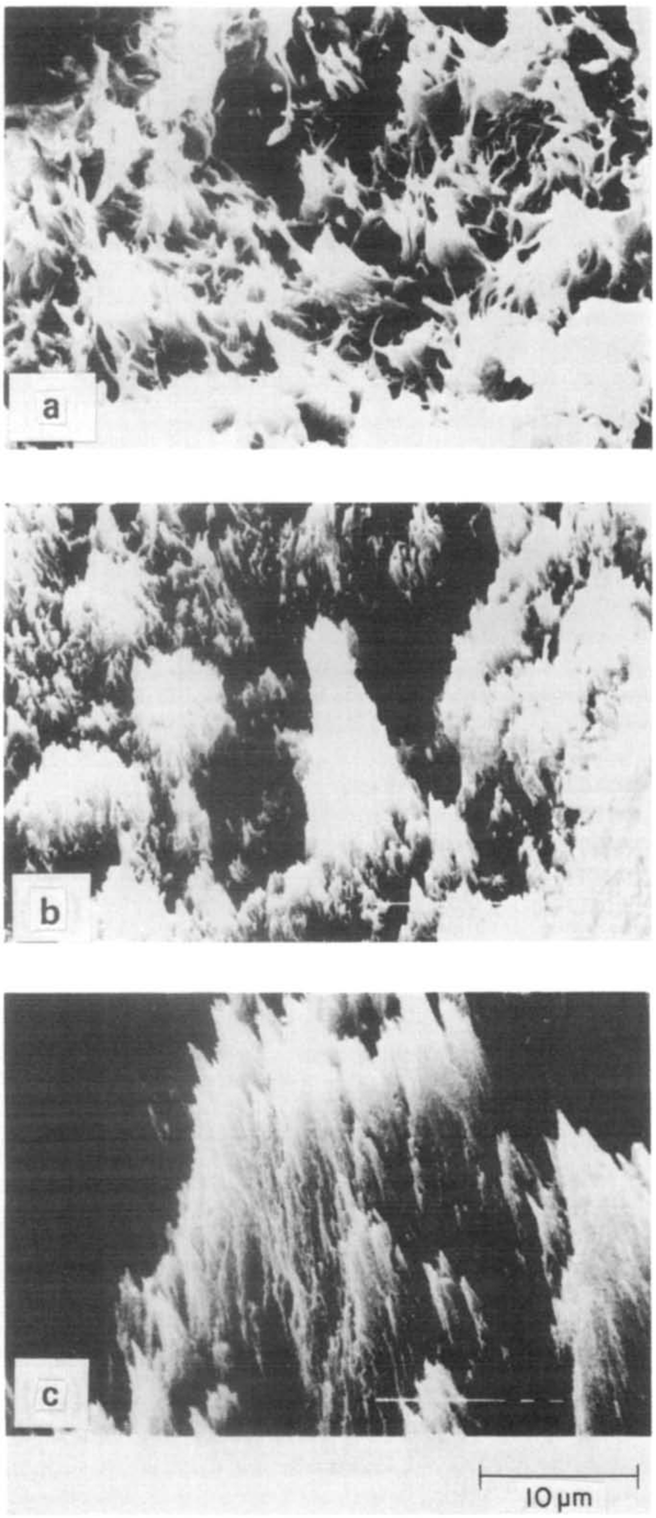

Figure 5 High-magnification scanning electron micrographs of fractured skin layer surfaces of the extrudates. Shear rates (s^{-1}): (a) 6; (b) 122; (c) 6080

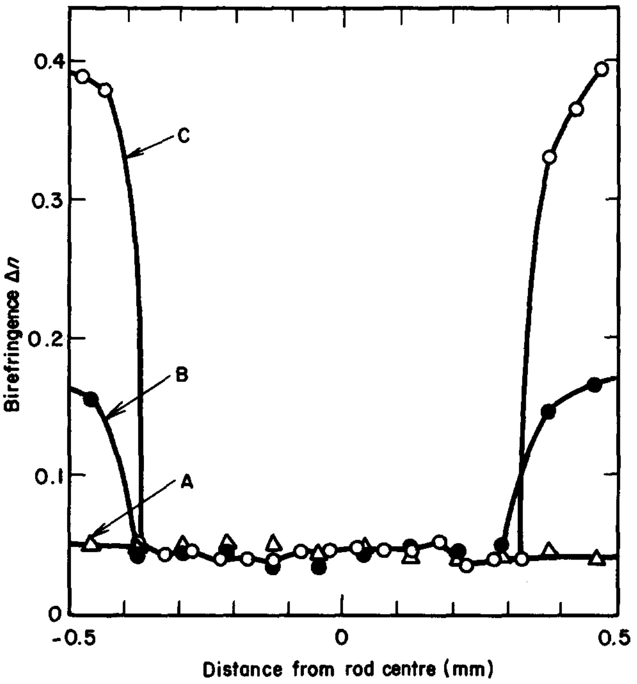

Figure 6 Change in birefringence distribution in the radial direction with shear rate. Shear rates (s^{-1}): A, 6; B, 122; C, 6080

Orientation distribution

Optical micrographs of the extrudate's longitudinal cross-section in diagonal and extinction positions indicate that the oriented PET/PHB copolyester exhibits birefringence (*Figure 2*). *Figure 6* shows the birefringence distribution change with shear rate in the radial direction for the extrudates. Birefringence values of the core layer with a band pattern were determined by the values at bright layers because the dark layers were not transparent. The value of birefringence increases only in the outer part of the longitudinal cross-sections, which correspond to the skin layer of the skin–core structure. The thickness of this part is, therefore, about 150 μm and changes little with increase in the shear rate. The core layer maintains very low birefringence values even when extruded at the highest shear rate. This birefringence distribution change with shear rate indicates that the molecular orientation induced by shear is concentrated only in the skin layer of the extrudates. This result also indicates that the skin–core structure is directly caused by an orientation distribution in the radial direction and that the band pattern develops when the difference in molecular orientation between two layers is larger than a certain value.

Cracks along band patterns

Cracks are observed along band patterns in the extrudates at shear rates of 608 and 6080 s^{-1} (*Figure 7*). Only a few, short (20–40 μm in length) cracks were observed at 608 s^{-1}. There were more, longer cracks (about 100 μm in length) at 6080 s^{-1}. These cracks were also observed by SEM. *Figure 8* shows SEM micrographs of a longitudinal cross-section of the extrudate at 6080 s^{-1} for skin and core layers. Cracks along band patterns with thickness of less than 10 μm are observed in the core layer while there was no fracture in the skin layer. The intervals between these cracks were from 10 to 60 μm. These cracks may have developed due to the treatments needed for the SEM observations, because fractures observed by optical micrographs were much fewer and shorter than these defects (*Figure 7*).

Density changes of extrudates were measured, but there were no clear changes in density with shear rate. For all the extrudates, free radicals induced by rupture of molecular segments were not detected by electron spin resonance (e.s.r.) measurements. These results indicate that there are no microfractures such as voids or cracks in the extrudate even at the highest shear rate. The cracks that were detected by optical and SEM observations, therefore, indicate that core layers with band patterns can easily get partially ruptured and they may have been generated during the preparation for observation.

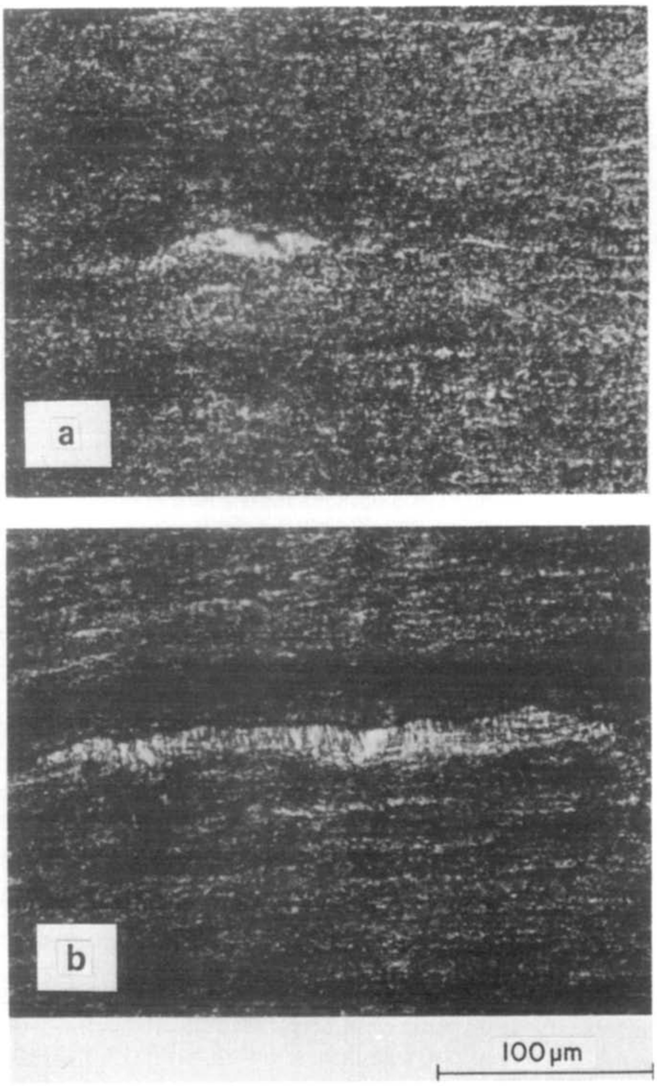

Figure 7 High-magnification optical micrographs of cracks along band patterns. Shear rates (s^{-1}): (a) 608; (b) 6080. Sample thickness 6 μm. The extrusion direction is vertical

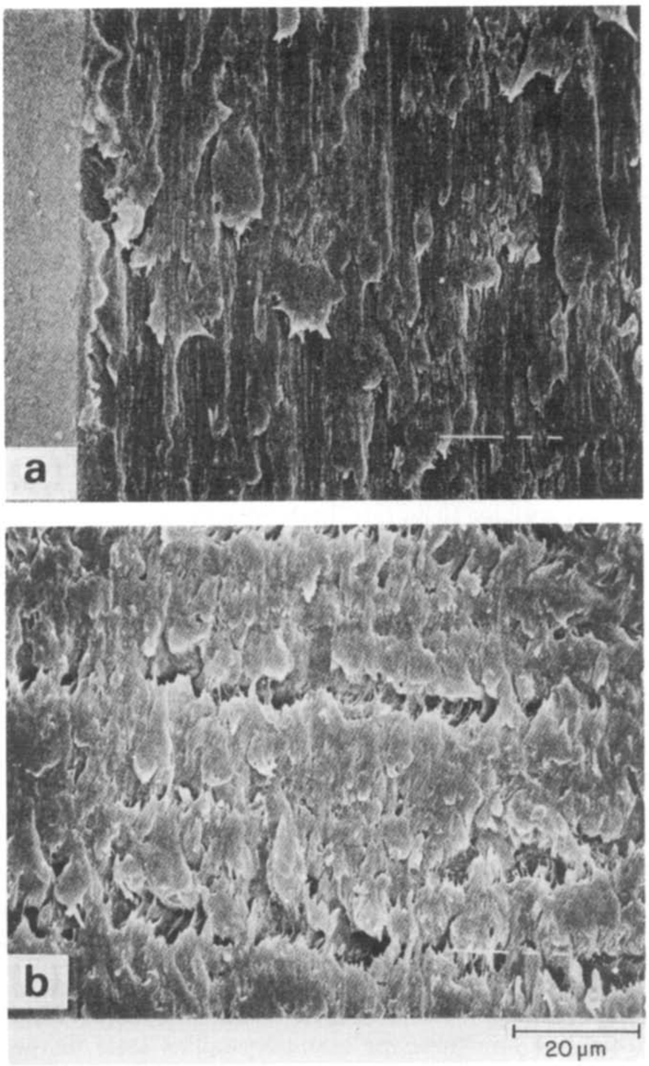

Figure 8 High-magnification scanning electron micrograph of cross-section of an extrudate at a shear rate of 6080 s^{-1}: (a) skin layer; (b) core layer. The extrusion direction is vertical

DISCUSSION

Mechanism of band pattern development

As shown above, the band pattern development is closely related to the skin–core structure. The skin layer exhibits high molecular orientation, as indicated by the fibrous textures on fracture surfaces (*Figure 5*), and high values of birefringence (*Figure 6*). The core layer with band patterns exhibited no clear molecular orientation (*Figure 6*). The difference in the degree of molecular orientation between the skin and core layers increases with shear rate, resulting in significant differences in properties.

On the other hand, highly oriented PET/PHB extrudates with elongational deformation show homogeneous structures in the radial direction and do not exhibit a skin–core structure or band pattern[17]. This result also indicates that band patterns are caused by a molecular orientation distribution in the radial direction.

From measured values of the Young's modulus and longitudinal linear thermal expansion coefficient of

PET/PHB extrudates, changes in these values for the skin and core layers with shear rate are estimated by assuming that skin layers are of homogeneous molecular orientation and that core layers exhibit no changes in their molecular orientation over all the shear-rate range. The Young's modulus of the core layer (E_c) is, therefore, assumed to be unchanged (equal to the value at the lowest shear rate). The Young's modulus of the skin layer (E_s) is calculated from the measured value (E) of the extrudate by:

$$E = a_s E_s + (1 - a_s) E_c$$

where a_s is the fraction of skin layer. The value of a_s is estimated to be 0.51 because the thickness of the skin layer remained unchanged (about 150 μm). *Figure 9* shows the changes in the values of E (——), E_s and E_c (–––) with shear rate. The value of E increased almost linearly with log shear rate. In the shear-rate range above $600\,\mathrm{s}^{-1}$, where band patterns develop, the values of E_s were more than three times the values of E_c.

Changes in linear expansion coefficients of skin and core layers (α_s and α_c) are also estimated. The value of α_c is assumed to be unchanged (equal to the value at the lowest shear rate), and the value of α_s is then calculated from the measured value (α) of the extrudate by:

$$E = a_s \alpha_s E_s + (1 - a_s) \alpha_c E_c$$

Figure 10 shows the changes in α (——), α_s and α_c (–––) with shear rate. The linear expansion coefficient decreased from $2 \times 10^{-5}\,\mathrm{K}^{-1}$ to zero with increases in the shear rate. The differences between the values of α_s and α_c are larger than $2 \times 10^{-5}\,\mathrm{K}^{-1}$ in the shear-rate range above $600\,\mathrm{s}^{-1}$. These differences in linear expansion coefficient would cause the difference in changes in longitudinal dimension between skin and core layers during cooling from the liquid-crystalline state to the quenched temperature, if there is no molecular binding between skin and core layers.

We can roughly estimate the difference in changes in longitudinal dimension during cooling. *Figure 11* shows changes in the longitudinal dimensions of the PET/PHB extrudates with two different molecular orientations with temperature, detected by a t.m.a. with a low tension. Judging from the birefringence values of the two extrudates, two curves correspond to the skin and core layers of the PET/PHB extrudate at about $600\,\mathrm{s}^{-1}$. Assuming that changes over 180°C are equal to each other, the difference in longitudinal dimension changes can be estimated to be a few per cent. This difference in the longitudinal dimension results in a residual longitudinal tension in the core layer because the Young's modulus of the skin layer is far larger than that of the core layer at about $600\,\mathrm{s}^{-1}$ (*Figure 9*). Moreover, compressive stress in the outer layer is small. Considering that solidification starts from the outer skin layer, this effect is definitive.

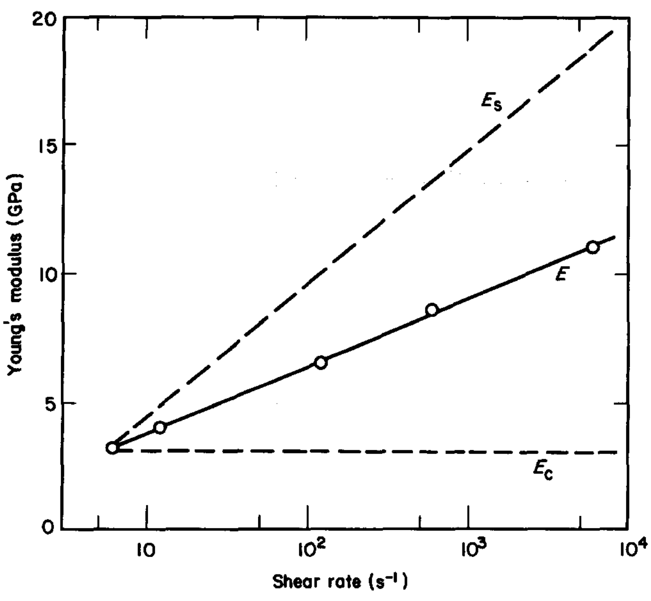

Figure 9 Changes in Young's moduli with shear rate: circles indicate measured average values; broken lines are calculated changes for skin and core layers

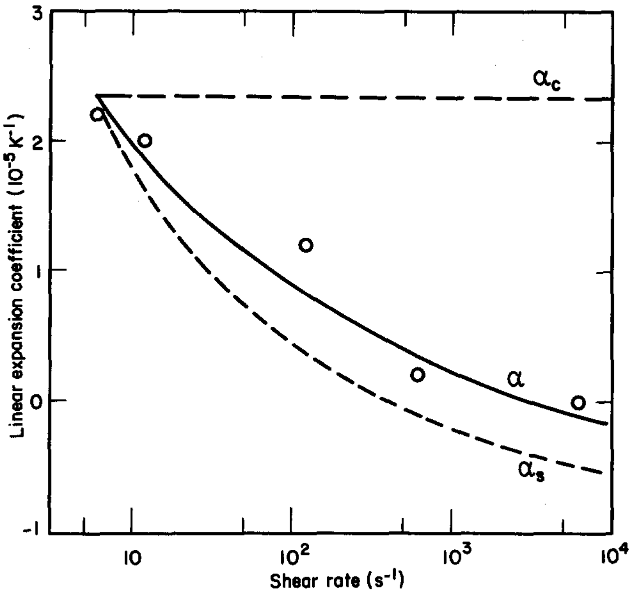

Figure 10 Changes in longitudinal linear expansion coefficients with shear rate: circles indicate measured average values; broken lines are calculated changes for skin and core layers

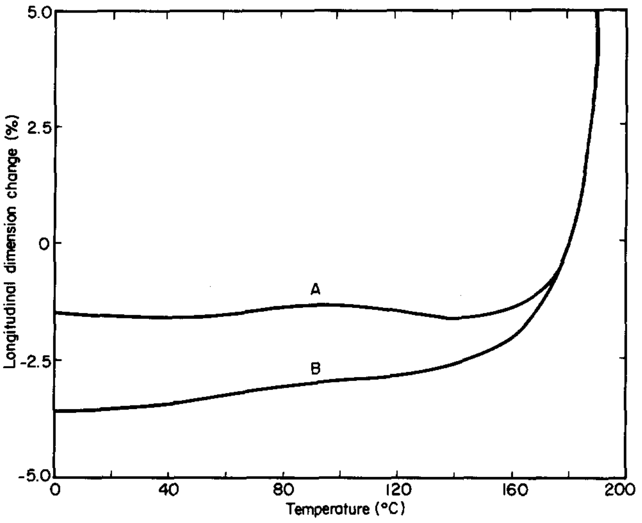

Figure 11 Changes in the longitudinal dimension of PET/PHB extrudates with temperature, measured by t.m.a.: A, an extrudate with high molecular orientation similar to the skin layer of the extrudate at about $600\,\mathrm{s}^{-1}$; B, an extrudate without clear molecular orientation similar to the core layers

On oriented poly(ethylene terephthalate) (PET) fibres, a phenomenon similar to band patterns was observed. That is, upon drawing of a PET fibre, transverse lines appear on it near the drawing limit[18]. These lines are caused by longitudinal tensions similarly to core layers with band patterns of PET/PHB extrudates. Molecules on these lines are kept elongated near to the limit. If this fibre is forced to elongate more, these lines spread and the fibre becomes fractured. This determines the drawing limit.

Comparing with this result, it can be said that band patterns were caused by a microconcentration of tension. Core layers just before the band pattern development are in a nearly fully elongated state to the longitudinal direction. If core layers are more elongated, micro non-uniformity (or a kind of microdefect) may be generated to release the longitudinal tension a little, then this non-uniformity may be spread perpendicular to the longitudinal direction, resulting in band pattern development. Core layers with band patterns, therefore, are easy to fracture along band patterns. The cracks along band patterns shown in *Figures 7* and *8* support this consideration.

A difference in residual stress between skin and core layers generates a shear stress concentration on the border of the core layer on the skin layer. A change in direction of band pattern near to the skin layer, as shown in *Figure 2c*, can represent the existence of this shear stress. This changing direction of the band pattern of this part may indicate an increase in the shear stress. The shear stress is largest at the boundary. The binding force between molecules of the skin and core layers can be weakened by this very large shear stress, as detected by tensile tests (*Figure 4*). This explains the wide step change in birefringence values between skin and core layers (*Figure 6*).

Characteristics of liquid-crystalline polymer

As mentioned above, band pattern development is similar to the transverse line development in some drawn PET fibres. The significant difference between these two phenomena is that PET fibres exhibit molecular orientation with longitudinal tension in the solid state while PET/PHB copolyester does not. This difference occurs because liquid-crystalline polymers deform only by melt drawing and cannot do so by hot drawing, while PET can deform by hot drawing. This is a characteristic property of liquid-crystalline polymers and makes band pattern development easy in the core layer during rapid cooling.

Banded textures[2-9] of the same material may be different from these band patterns in the extrudates because, in our case, no zigzag structure or rotation of the extinction position was observed by polarizing microscopy[3]. The banded texture, moreover, appears when quenched from the highly oriented liquid-crystalline state, while the band pattern appears when quenched from a scarcely oriented state. The band pattern develops without molecular orientation and indicates the existence of residual longitudinal tension. It is noted that a liquid-crystalline film between two slide glasses can be compressed by these slide glasses during cooling after it is sheared to orient highly at elevated liquid-crystalline temperatures, because the linear expansion coefficient of a highly oriented liquid-crystalline polymer in the orientation direction is negative. The relation between so-called banded texture and such a cooling effect is, however, not clear.

Band patterns have been observed for other liquid-crystalline polymer extrudates[14] and injection mouldings[19]. In the case of injection mouldings, it is natural that the band pattern develops nearly parallel to the skin layer. More or less, a structure with a band pattern shows a state with low Young's modulus that is easy to break. Consequently, it is important to prevent liquid-crystalline polymer products from developing a band pattern.

CONCLUSIONS

PET/PHB copolyester extrudates were oriented only by shear stress in the liquid-crystalline state and were quenched. Changes in properties such as Young's modulus and linear expansion coefficients, which are determined by the average value of orientation distributions in the radial direction, were relatively small but orientation distributions in the radial direction increased with increases in the shear rate. This resulted in a skin–core structure and then in a band pattern perpendicular to the extruded direction in the core layer at high shear rates. Some morphological characteristics caused not simply by skin–core structure development but predominantly by band pattern development were observed. The extrudates with band patterns exhibited cone-shaped fracture surfaces after tensile tests. By optical and SEM observations, cracks were detected along band patterns, although these may be caused by the treatments needed prior to observation. These cracks indicate that longitudinal tension was applied in the core layer during the cooling process because of a significant distribution in Young's modulus and the linear expansion coefficient in the radial direction. Band pattern development is explained by this residual longitudinal tension in the core layer.

It is necessary to pay attention to the cooling effect to analyse the solid morphology of liquid-crystalline polymers with an orientation distribution.

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