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SHORT COMMUNICATION

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Banded texture in sheared a semiflexible thermotropic liquid-crystalline polyester and its graft copolymers with polyolefins

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Abstract The formation of banded texture both in a semiflexible thermotropic liquid-crystalline polyester (SBH 112, synthesized from sebacic acid, 4,4′-dihydroxybiphenyl and 4-hydroxybenzoic acid, from Enirícerche, Milan) and in a blend of SBH with graft copolymers, consisting of a polyolefin (polyethylene or polypropylene) backbone and SBH grafts (COPPE, COPPP) has been studied by polarization microscopy and by scanning electron microscopy. The influence of the preparation conditions upon the perfection, characteristics and thermal stability of the banded texture has been investigated. The results show that the banded texture formed in SBH sheared films possesses greater perfection, smaller band width and larger angle of deviation, and higher thermal stability than the banded texture formed in COPPE and COPPP prepared under similar conditions. It has been assumed that the chain rigidity of the macromolecules of the system is mainly responsible for the formation and perfection of the banded texture.

Key words Banded texture · Semiflexible liquid-crystalline polymer and its graft copolymers with polyolefins · Formation conditions · Thermal stability · Molecular chain rigidity

Introduction

The study on the morphology of liquid-crystalline polymers (LCPs) in the oriented state has been of considerable interest because the final products preserve the high orientation of their macromolecules after processing in the mesomorphic state. The so-called banded texture is one of the morphological characteristics of a LCP subjected to shear or elongational flow in the mesomorphic state. Band formation is a phenomenon common to all solid films formed in the sheared lyotropic or thermotropic mesophase, nematic or cholesteric, of main-chain and side-chain LCPs. It is shown that the band texture is not formed during the shear but during the cessation of the shear [1]. The alternating dark and bright bands observed in a polarizing microscope have been shown to be an optical effect. The macromolecular chains are, in fact, oriented in the direction of shear. The angle of deviation varies from a couple of degrees up to 45° depending on the polymer, in an alternative opposite sense. The aligned macromolecule chains are aggregated into zigzag fibrils 100–200 nm thick. The average width of the bands, i.e. the periodicity of fibril bending ranges, from 0.5 to 10 μm, depending on the nature of the polymer [1].

Concerning the thermotropic LCP, the formation process of the banded texture has been studied mainly for wholly aromatic rigid LCPs. It has been shown that the optical texture obtained is determined by the shear rate: rapid shear rates generally favor the banded texture, while slower shear rates lead to the formation of the tight texture [2]. The annealing of the film at the temperature of shear does not influence the behavior of the bands obtained from a random aromatic copolyester [3]. The perfection of the banded texture has been shown to improve with increasing molecular weight of the aromatic polyester fractions [4]. Both the band width and the angle between the optical axis and the shear direction depend on the molecular weight [4]. The banded texture is formed only above a certain critical molecular weight [5]. For polymers with lower molecular weight the disordered tight texture is formed after cessation of shear [5]. The thermal stability of a quenched banded texture has been investigated [4, 6]. The bands remain almost unchanged during heating up to the melting transition and subsequent cooling [4, 6]. In contrast, the bandwidth as well as the extinction angle of the bands are very dependent on the cooling conditions for the two types of aromatic main-chain LCPs [7]. The influence of substrate surfaces upon the formation behavior of a banded texture and its thermal stability have been studied for an aromatic X-shaped main-chain liquid-crystalline polyester [8]. An irregular banded texture forms when the glass substrate is replaced by a Teflon sheet [8].

Banded texture formation in the sheared polymeric liquid-crystalline state is far from being understood, although many authors have put forward some explanation from limited facets of observations. Different mechanisms for the phenomenon of banding in sheared polymeric liquid crystals have been proposed. A suggested scheme points to the existence of restoring forces, which provide axial compression, producing the buckling of uniaxially oriented birefringent fibrous entities [9]. The banded formation has been discussed on the basis of a contraction mechanism and has been explained as the result of a zigzag rearrangement of straightforward oriented fibrils under certain contraction effects [7]. A suggestion has been made that a retraction process along the nematic director at the cessation of shear provides a mechanism for crumpling the microstructure and, thus, for banded texture formation [5]. The formation of a banded texture is explained by the slow effect which the constricting elastic force of macromolecules has upon the relaxation [10]. It has been concluded that the band texture phenomenon can be adequately explained by nematic director relaxation; the rapid lateral relaxation is attributed to the large value of the splay constant in polymeric liquid crystals [11].

More experimental facts regarding the conditions and factors affecting band texture formation have to be exploited in order to explain this phenomenon, connected also with the mechanical properties of the LCP [12]. It has been shown that the anisotropic mechanical properties of LCPs are related to the wavelength of the banded texture. By adjusting the shear distortion appropriately one can control the mechanical properties of LCPs by an order of magnitude [12].

In this work the banded texture formation in a semiflexible thermotropic liquid-crystalline polyester has been studied. The aim was to investigate the influence of the conditions of the formation (temperature of shear, cooling conditions) upon the characteristics of the banded texture and its thermal stability. The formation of a banded texture in graft copolymers consisting of a polyolefin backbone and LCP grafts has been also studied.

Experimental

Materials

The LCP was a semiflexible copolyester synthesized as described before [13, 14] from sebacic acid (S), 4,4′-dihydroxybiphenyl (B) and 4-hydroxybenzoic acid (H), in a molar ratio S:B:H 1:1:2, supplied by Eniricerche, Milan. The inherent viscosity of SBH, measured in pentafluorophenol at 60 °C, with a concentration of 0.1 g/dl, was 1.01 dl/g. This LCP has a crystalline to nematic phase transition temperature of 230 °C and a nematic to crystalline transition temperature of 217 °C [14].

The graft copolymers consisting of polyethylene (PE-*g*-SBH) or polypropylene (PP-*g*-SBH) backbones and SBH branches were synthesized via reactive blending of functionalized PE or functionalized PP with a semiflexible liquid-crystalline polyester SBH, as described elsewhere [15, 16]. The reactive blends were fractionated with boiling toluene and xylene, which are good solvents for polyolefins [15, 16]. The insoluble xylene fractions of the reactive blends have been shown to contain about 73–75% SBH (about 25–27% of corresponding polyolefin) and to consist of unreacted SBH and some polyolefin-*g*-SBH copolymer [15, 16]. The copolymer is built of a polyolefin backbone and SBH grafts [15, 16]. No unbounded polyolefin remains in the insoluble fractions [15, 16]; thus, they consist of a blend comprising unreacted SBH and some polyolefin-*g*-SBH copolymer. The adhesion between both components is extremely strong because the SBH grafts of the copolymer are miscible with bulk SBH [15, 16].

The xylene-insoluble fractions of the reactive blends are indicated as COPPE and COPPP, respectively.

Methods

Sheared films of the polymers (SBH, COPPE, COPPP) were prepared using the technique described by Donald et al. [17]. Small blocks were cut from the sample, placed onto a clean glass slide and melted to form the mesophase. Each polymer was melted at two temperatures above the polymer melting point −10 and 30 °C. The melted polymers were then sheared using a razor blade at almost equal shear rate. The sheared films were transferred quickly onto the hot stage of the microscope, preliminarily preset at the temperature of shear. For each sample one sheared film was rapidly quenched on a metal block and one sheared film was cooled to room temperature at a rate of 10 °C/min.

Optical microscopic observations were performed using a Leitz Ortholux polarizing microscope equipped with a Mettler FP-50 hot stage. The Hv diffraction patterns of small-angle light scattering were obtained using the microscope as a diffractometer and applying a Bertran lens. The microscope was preliminarily calibrated using a diffraction lattice with a definite distance between the lines.

The scanning electron microscopy (SEM) observations were performed using a JEOL T300 apparatus. The polymer films were fractured in liquid nitrogen and the fracture surfaces were contrasted with gold.

Results and discussion

In order to establish the influence of the temperature of shear on the texture formed, the SBH sample was sheared at two temperatures: 240 °C (10 °C above the polymer melting point) and 260 °C (30 °C above the melting temperature), applying almost equal shear rate. The optical microscope observations show that when the sample is sheared at 240 °C a tight texture always forms, while the shear at higher temperature leads to the formation of a banded texture in the sample. As the shear rate applied in both cases is almost equal, this result indicates that the formation of a banded texture depends not only on the shear rate [2] but also on the appropriate temperature of shear. In both types of texture the molecules lie in layers and there is a strong correlation between the layers in the banded texture, while in the tight texture this correlation is less pronounced [2]. It could be assumed that the formation of the banded texture requires an appropriate viscosity of the polymer melt obtained at higher temperature. All successive experiments of the shear of the polymer samples were done at 30 °C above the melting point.

It should be noted that under these conditions the banded texture appears immediately after the shear of SBH, while there is an induction period of 1–2 min for the occurrence of banded texture in COPPE or COPPP. The sheared films were cooled using two different cooling conditions: the quench of the film on a cold metal plate and slow cooling to room temperature. The microscopic observations on the morphology of the films at room temperature show the preservation of the banded texture in the quenched as well as in the cooled films. Moreover, the direct observation of the film during the slow cooling process evidences that no changes occur in the banded texture at the crystallization temperature of the samples. That means that the crystallization of the LCPs does not influence significantly the molecular order obtained in the nematic state during the shear process.

Parallel bands with alternate brightness extending in a direction perpendicular to the shear direction are observed in both types of SBH films, quenched and slowly cooled (Fig. 1). The banded texture appears perfect and regular; the bands of clear boundaries have a great extension and cover the entire view field of the microscope (Fig. 1). The micrograph taken at large magnification (Fig. 1b) reveals small strips on the surface of the bands, which are almost perpendicular to the bands extension and travel in an almost a zigzag manner along the shear direction. It could be assumed that these strips correspond to the molecular fibrils formed during the shear, the sinusoidal path of which along the shear direction is responsible for the formation of the banded texture. The Hv diffraction pattern of the banded texture obtained in SBH films is a typical grating pattern (Fig. 1a).

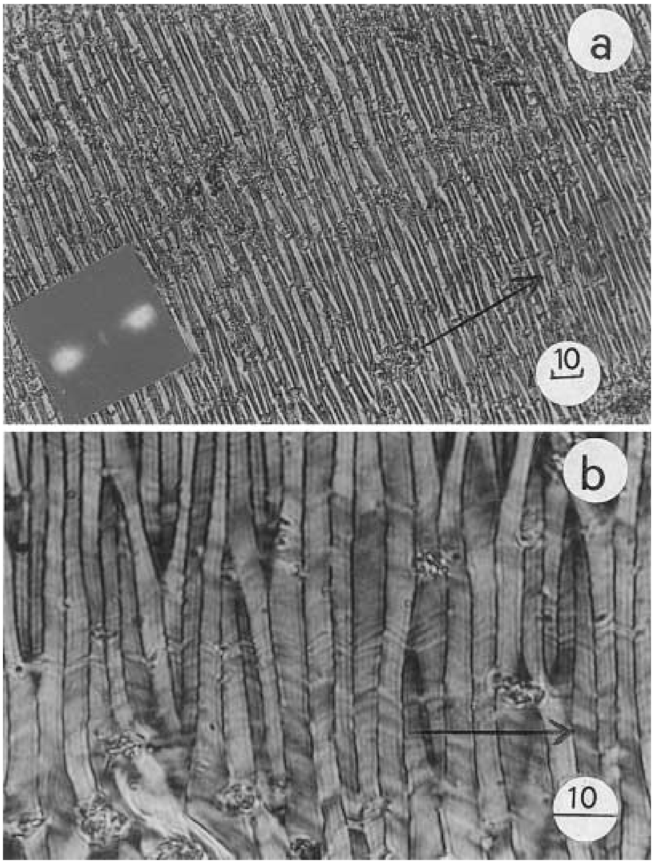

Fig. 1 Optical micrographs of the banded texture formed in film of a semiflexible copolyester synthesized from sebacic acid, 4,4′-dihydroxybiphenyl and 4-hydroxybenzoic acid (*SBH*): **a** sheared at 260 °C, quenched on a metal block and corresponding Hv pattern; **b** sheared at 260 °C, cooled at a rate of 10 °C/min to room temperature. The *arrows* indicate the shear direction. The magnification is given by a scale in microns

The banded texture formed in the films of COPPE and COPPP is not so regular in shape and has in some cases a short extension (Fig. 2). The Hv diffraction pattern is also a typical grating pattern (Fig. 2a). These results are in agreement with the fact that the banded texture is not formed in flexible polymers. Evidently, the total flexibility of COPPE and COPPP, being in fact blends of SBH with polyolefin-*g*-SBH copolymer, is greater than the flexibility of the pure SBH. It could be assumed that the greater chain flexibility and the blend character of COPPE and COPPP result in the formation of an imperfect banded structure. On the other hand, a banded texture is formed in COPPE and COPPP in spite of the availability of some flexible polyolefins in them. The formation of a banded texture is possible owing to the total rigidity of the system which is favorable enough.

The banded texture obtained is characterized by the width of the bands and by the directions of the optical axes of the bands. The band width is determined by direct microscopic measurements and from the Hv diffraction patterns. The sheared films of the samples give Hv patterns, corresponding to the diffraction from strips with a constant spacing, *D*, where *D* is the width of the band. The average value of the band width *D* over the scattering volume is determined from the equation [4, 18]

$$D = \lambda/2\sin(Q_\mathrm{m}) \ ,$$

where λ is the wave length of the light and Q_m is the angle of the incident and scattered beams corresponding to the maximum pattern intensity.

Another characteristic of the banded texture is the angle θ between the shear direction and the optical axes of the bands. The scheme of a polymer fibril with a sinusoidal path, obtained during the shear with regard to the shear direction and to the optical axes of the polarizer and the analyzer of the microscope, is shown in Fig. 3. The optical axes of the bands deviate from the shear direction alternately by an angle $+\theta$ or $-\theta$ (Fig. 3). The value of the angle θ is determined by the rotation of the film with respect to the direction of the polaroids. During the rotation at a certain angle θ the dark band changes into a bright one, while the bright band turns into a dark one. The data for the band width determined by direct measurement and from the Hv pattern of small-angle light diffraction as well as θ angle values are given in the Table 1.

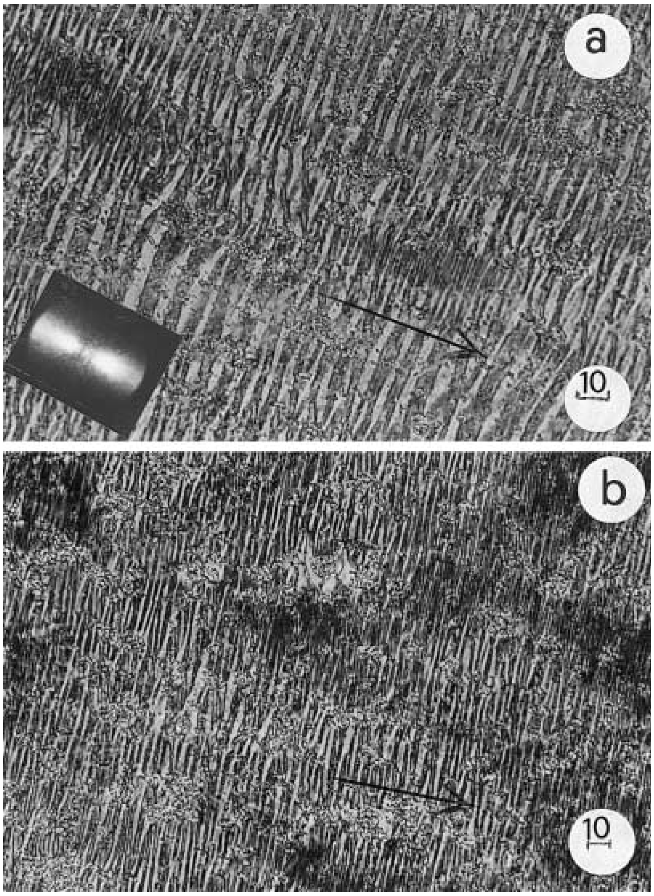

Fig. 2 Optical micrographs of the banded texture formed in films of **a** a blend of SBH with a graft copolymer consisting of a polyethylene backbone and **b** a blend of SBH with a graft copolymer consisting of a polypropylene backbone, sheared at 260 °C, quenched on a metal block and corresponding Hv pattern (**a**). The *arrows* indicate the shear direction. The magnification is given by a scale in microns

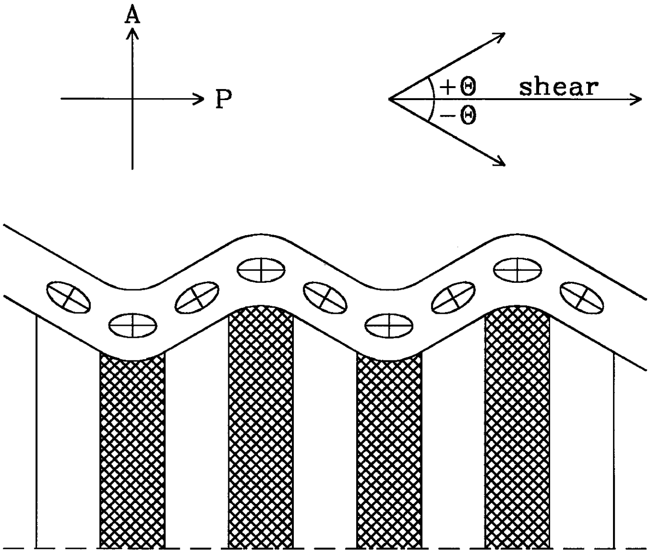

Fig. 3 Scheme of the polymer fibril with a sinusoidal path with regard to the shear direction and to the optical axes of the polarizer and the analyzer of the microscope. The change in the optical axes of the fibril with angle of deviation $+\theta$ or $-\theta$ along the shear direction, which is responsible for the appearance of alternately dark and bright bands, is also shown

Table 1 Characteristics of the banded texture of the samples: a semiflexible thermotropic liquid-crystalline polyester synthesized from sebacic acid, 4,4′-dihydroxybiphenyl and 4-hydroxybenzoic acid (*SBH*); a blend of SBH with graft copolymers, consisting of a polyolefin (polyethylene or polypropylene) backbone and SBH grafts (*COPPE*, *COPPP*)

Sample	Band width (direct measurement) (μm)	Band width (from Hv pattern) (μm)	θ (degrees)
SBH quenched	3.0–3.5	3.6	25 ± 2
SBH cooled	3.0–3.5	3.5	23 ± 2
COPPE quenched	4.0–4.5	4.3	17 ± 2
COPPE cooled	4.5–5.5	4.5	20 ± 2
COPPP quenched	5.0–5.5	4.9	21 ± 2
COPPP cooled	5.5–6.5	5.5	19 ± 2

As seen, the banded texture formed in the SBH sample is characterized by larger θ angle values and by lower values of the band width than the corresponding values of the banded texture formed in COPPE or COPPP (Table 1). It could be assumed that this is due to the rigidity of the SBH molecular chains, which is higher than that of the materials COPPE and COPPP. Moreover there is a good agreement between the values of the band width obtained by direct measurement and those obtained from Hv diffraction patterns (Table 1). The difference between the values of the band width and the angle θ for quenched and cooled samples is almost negligible. These results show that the cooling regime of the sheared films almost does not influence the main characteristics of the banded texture. However, the data show a clear tendency of increasing angle θ and of decreasing band width when the rigidity of the molecular chains increases.

The thermal stability of the banded texture obtained was investigated by heating the cooled films to a temperature above the melting temperature of the polymer. The microscopic observations show that the banded texture formed in the SBH sample remains almost unchanged during the melting transition and disappears at a temperature 40–50 °C above the melting temperature. During the cooling process the banded texture in SBH reappears with approximately the same perfection and contrast as those of the texture before the thermal treatment. The results are in agreement with those of other authors [3, 4, 6] and show that the molecular order obtained by shear in the mesomorphic state is not destroyed by heating. It could be assumed that this good thermal stability of the banded texture obtained by shear in the semiflexible LCP is due to the limited molecular motions of the polymer segments in the mesomorphic state, which are very similar to the molecular motions in the solid state for the LCPs [19]. Concerning the thermal stability of the imperfect banded texture formed in COPPE or COPPP it should be noted that this texture is less stable when it is subjected to thermal treatment. Short bands with large width reappear when the samples are cooled after having been heated to 40–50 °C above their melting point. The results show that the more perfect banded texture formed in the more rigid polymer sample possesses higher thermal stability than the banded texture formed in COPPE and COPPP, containing a greater number of flexible chains.

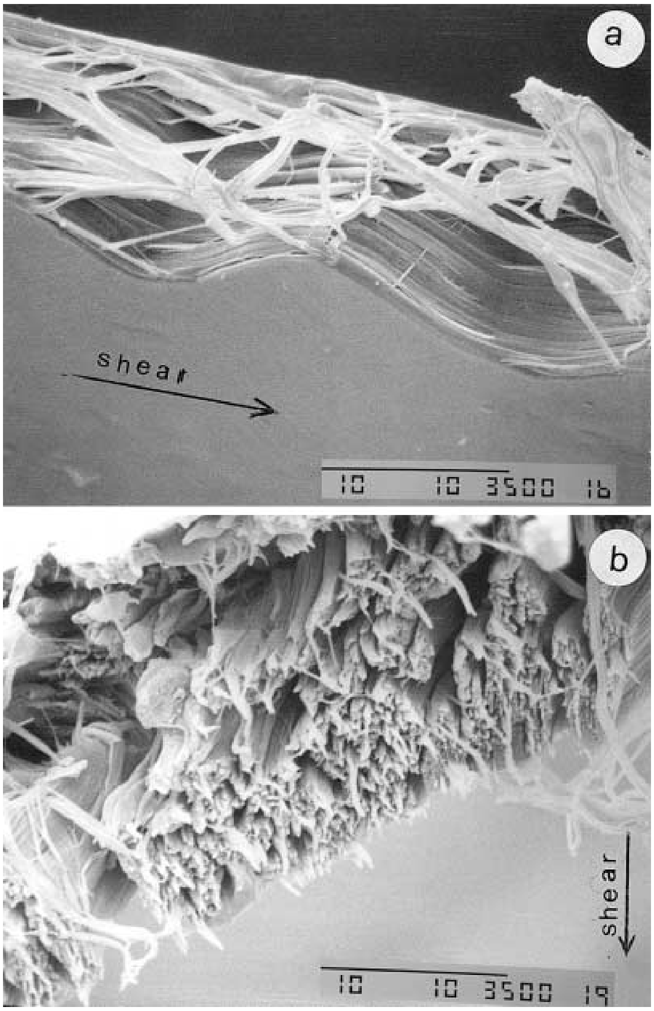

Fig. 4 Scanning electron microscope micrographs of the fracture surfaces of SBH sheared film: **a** fracture along the shear direction; **b** fracture perpendicular to the shear direction

In order to investigate the arrangement of the structural units of the banded texture formed, the sheared film of the SBH sample was fractured in liquid nitrogen and the fracture surface was examined by SEM. The micrographs of the fracture surfaces of the SBH sheared film are shown in Fig. 4. The micrographs of these fracture surfaces either parallel (Fig. 4a) or perpendicular (Fig. 4b) to the shear direction reveal that the film is composed of ribbon-like fibrils of about 1–2 μm in diameter. The fibrils travel along the shear direction in a sinusoidal manner (Fig. 4a) and the angle of deviation from the shear direction of about 20–30° is in good agreement with the optical microscope observations. The length of the waves corresponds well to the width of the bands determined previously. The fibrils are arranged in layers parallel to the film surface. It should be emphasized that the fibrils near the bottom surface of the film (i.e. the surface near to the glass slide) are almost linear, having lost the sinusoidal character of their arrangement. It could be assumed that this is due to the fact that the shear stress applied to the upper surface of the film decreases continuously along the film thickness and consequently it cannot produce sufficient orientation of the macromolecules situated on the glass surface. On the other hand, the lowest oriented SBH layer which is in closest contact with the glass might not relax sufficiently after the shear because of the strong adhesion between the glass surface and this polymer layer.

The results show that the banded texture formed in SBH sheared films is characterized by greater perfection, smaller band width and larger angle of deviation, and higher thermal stability than the banded texture in COPPE or COPPP formed under similar conditions. The latter materials (COPPE and COPPP) are composed of SBH and some polyolefin-*g*-SBH copolymers, constructed by a polyolefin backbone and long SBH grafts [15, 16]. Evidently COPPE and COPPP possess higher degrees of crystallinity and higher flexibility of the molecular chains than the pure SBH sample does. It could be assumed that the chain rigidity of the molecules in COPPE and COPPP is not enough for their packing into fibrils, the common relaxation of which is responsible for the formation of a perfect banded texture after the cessation of the shear. It is known that the molecules in flexible chain polymers may also orient along the shear direction but the relaxation takes place easily as a result of random thermal motions of individual molecules; therefore no regular banded texture is formed.

Conclusion

The study of the conditions of the banded texture formation in the materials studied allows the following conclusions to be drawn. The banded texture forms in films sheared at an appropriate temperature above the melting temperature of the polymer. The cooling conditions (quenching or slow cooling) almost do not influence the perfection of the banded texture formed during the cessation of the shear. Under equal conditions the pure LCP forms a banded texture which is characterized by a smaller band width, a larger deviation angle and a higher thermal stability than those of the samples composed of a blend of the LCP and polyolefin-*g*-LCP copolymer. The results are interpreted by the total higher flexibility and by the blend character of the materials COPPE and COPPP. In SBH, composed of more rigid chains, the higher forces of molecular packing cause the formation of fibrils oriented along the shear direction, the common relaxation of which forms a perfect banded texture with high thermal stability after cessation of the shear.

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