

Toughening Liquid-Crystalline Polymers with Polyethylenes Containing Epoxy Functionality

A. Tynys, U. Hippi, J. Seppälä

Department of Chemical Technology, Helsinki University of Technology, P.O. Box 6100, FIN-02015 HUT, Finland

Received 16 July 2001; accepted 12 November 2001

ABSTRACT: To improve toughness, a liquid-crystalline polymer (LCPs) was blended with polyethylenes containing epoxy functionality in concentrations of 2, 6, and 15 wt %. The blends were prepared with a corotating twin-screw extruder and were injection-molded into specimens for mechanical testing. The effect of the amount of the epoxy-functionalized polyethylenes on the morphology and mechanical and thermal properties was studied. The toughness improved with increasing amount of functionalized polyethylene, and the blend containing 15 wt % epoxy-functionalized polyethylene had the best toughness properties. Impact

strength values up to three times higher than those of the neat LCP were achieved. However, the stiffness of the LCP concurrently decreased substantially. The morphology became much more uniform, and the melting behavior changed. The results show that considerable improvements in the toughness properties of LCPs can be achieved with epoxy-functionalized polyethylenes. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1886–1891, 2002

Key words: liquid-crystalline polymers (LCP); toughness; polyethylene (PE)

INTRODUCTION

Thermotropic, main-chain liquid-crystalline polymers (LCPs) constitute a group of polymers with unique properties. For example, the mechanical properties, dimensional stability, low melt viscosity, and heat and chemical resistance are usually superior to those of many other commonly used engineering thermoplastics. LCPs consist of linear, semirigid, rodlike molecules that are capable of aligning to a very high degree during melt flow, thereby forming a highly ordered melt phase. When the polymer melt is cooled, the orientation is retained, and this leads to highly oriented and anisotropic properties.

In addition to the high price of LCPs, their poor toughness, a result of anisotropy, is a problem in applications. For improved toughness, LCPs can be blended with more flexible polymers such as polyolefins. The problem with LCP blends has been the incompatibility of LCPs with most polymers due to structural differences. For this problem to be overcome, strong interactions between blended polymers should be formed.

Several research groups have blended LCPs with different functionalized polymers to find the functionalities that can form physical or chemical interactions

with LCPs. Maleic anhydride-grafted polyethylene¹ and polypropylene^{2–6} have been investigated as compatibilizers in polyolefin/LCP blends. Maleic anhydride-grafted compatibilizers have usually improved the tensile strength of LCP blends.^{2–5} Other properties such as the tensile modulus,^{2,6} torsion modulus, and compliance² have also been improved with these compatibilizers. It is probable that maleic anhydride-grafted compatibilizers do not react with the functional groups of the LCPs, but enhanced adhesion between the polymers is due to physical interactions such as hydrogen bonding.^{1,4,6}

Another frequently used functionality in LCP blends is acrylic acid. Acrylic acid-grafted polyolefins are usually branched with LCPs. Therefore, LCP branches of the compatibilizer are miscible with the LCP phase, and the backbone of the compatibilizer is miscible with the polyolefin part of the blend.^{7–10} Neat acrylic acid-grafted polyolefins have also been investigated as compatibilizers in LCP blends.¹¹ LCP-branched compatibilizers prepared in advance have been found to be much more effective compatibilizers than neat acrylic acid-grafted polyethylene.⁹

Compounds and polyethylenes or polypropylenes containing epoxy functional groups have been studied for compatibilization with LCP blends. Epoxy functionalities containing compatibilizers can be either low molecular mass multifunctional epoxy compounds¹² or epoxy-functionalized polymers such as ethylene glycidyl methacrylate copolymer^{3,13,14} or glycidyl methacrylate-grafted polypropylene.¹⁵ Compatibilizers based on epoxy functionality have improved

Correspondence to: U. Hippi (ulla.hippi@luuku.com).

toughness properties, such as the impact strength of LCP blends, but stiffness properties such as the tensile modulus concurrently decrease.^{1,13,14} The changes in the mechanical properties of compatibilized blends are most likely due to chemical reactions between the epoxy-functionalized polymer and the functional groups of the LCPs.¹³ Other polymers investigated for the compatibilization of LCP blends include oxazoline-functionalized polypropylene,¹⁶ chlorinated polypropylene,¹⁷ and different ionomers.^{18,19}

In this study, the toughening of a particular LCP was studied with epoxy-functionalized polyethylenes. The LCP was blended with different amounts of epoxy-functionalized polyethylenes, and the properties of the blends were investigated by mechanical testing, differential scanning calorimetry (DSC), scanning electron microscopy (SEM), and capillary rheometry.

EXPERIMENTAL

Materials

The thermotropic LCP used was Vectra B950 from Hoechst Celanese. This copolyester consisted of 2-hydroxy-6-naphthoic acid, terephthalic acid, and 4-aminophenol (52/21/21 mol/mol/mol). The LCP had a melting temperature of 280°C and a density of 1.40 g/cm³. The epoxy-functionalized polyethylenes were ethylene/glycidyl methacrylate (Lotader AX 8840) and ethylene/methyl acrylate/glycidyl methacrylate (Lotader AX 8900) from Atofina. The third epoxy-functionalized polymer was ethylene/glycidyl methacrylate (Bondfast E) from Sumitomo Chemical. The glycidyl methacrylate content of Lotader AX 8840 and Lotader AX 8900 was 8 wt %, and that of Bondfast E was 12 wt %. The methyl acrylate content of Lotader AX 8900 was 25 wt %.

Blending

Before the blending, the LCP and epoxy-functionalized polymers were dried overnight in a Conair Micro-D dehumidifying dryer. The drying temperature was 120°C for the LCP and 60°C for the epoxy-functionalized polymers. LCP blends containing 2, 6, or 15 wt % epoxy-functionalized polymers were prepared with a Werner & Pfleiderer ZSK 25 M9 corotating twin-screw extruder with the temperature profile 210–290–295–300–300–300°C and at a screw speed of 160 rpm. The melt temperature of the blends varied between 306 and 308°C. The extrudate was quenched in a water bath and pelletized.

Injection molding

The blends were injection-molded into the form of test specimens after drying overnight in a Conair Micro-D

dehumidifying dryer at 80°C. Injection molding was carried out with an Engel ES 200/40 injection-molding machine. The blends were processed at 300°C. The processing conditions were not optimized for the blends, and similar conditions were used for each blend type.

Characterization and testing

The injection-molded specimens were used for tensile and impact tests. Before testing, all samples were conditioned at 23°C and 50% relative humidity for at least 24 h.

Tensile properties were measured according to ISO 527-1993 (E) with an Instron 4204 testing machine at a test speed of 1 mm/min and with specimen type 1A for the determination of both the tensile strength and tensile modulus. An extensometer was used for determining the modulus.

The Charpy impact strength was determined according to ISO 179:1993(E) with a Zwick 5102 pendulum-type testing machine. The test was carried out with both unnotched (type 1eU) and notched (type 1eA) test specimens. A pendulum of 4 J was used for the unnotched specimens, and a pendulum of 2 J was used for the notched specimens.

DSC measurements were carried out with a Mettler Toledo DSC821^e instrument under a nitrogen atmosphere. The temperature varied from 20 to 350°C, and the rates of cooling and reheating were 10°C/min. The sample weight was equalized to 5.00 mg.

The morphology of the fractured surfaces of the specimens was investigated with a JEOL JSM-6335F field emission scanning electron microscope. The specimens were fractured after cooling in liquid nitrogen, and the fractured surfaces were sputter-coated with gold and evaporated with carbon. Electron micrographs were taken with an acceleration voltage of 5.0 kV.

Melt viscosities in the shear flow were measured with a Göttfert Rheograph 2002 capillary viscometer at 300°C. The length/diameter ratio of the die was 30/1 mm. The results included the Rabinowitch correction, but the Bagley correction was not made.

RESULTS AND DISCUSSION

Mechanical properties

The mechanical properties (tensile modulus, tensile strength, elongation at break, and Charpy impact strength of both unnotched and notched specimens) of the neat LCP and the blends containing 2, 6, and 15 wt % epoxy-functionalized polyethylenes are displayed in Table I. The primary aim of improving the toughness of the neat LCP was achieved with all blends

TABLE I
Tensile Modulus (E), Tensile Stress (σ), Elongation at Break (ϵ), and Charpy Impact Strength of Unnotched and Notched Specimens of LCP Blends Containing 2, 6, and 15 wt % Epoxy-Functionalized Polyethylene

Blend	Polyethylene content (wt %)	E (MPa)	σ (MPa)	ϵ (%)	Charpy impact strength (kJ/m ²)	
					Unnotched	Notched
LCP	—	17,200 (1,910)	112 (10)	0.9 (0.4)	15 (2.8)	13 (2.6)
Bondfast E	2	13,600 (360)	134 (14)	1.6 (0.4)	17 (2.3)	17 (3.0)
	6	12,400 (340)	141 (12)	2.2 (0.5)	24 (3.1)	20 (4.6)
Lotader AX 8840	15	9,900 (280)	164 (12)	5.0 (0.7)	47 (5.5)	24 (2.4)
	2	13,300 (510)	122 (7)	1.2 (0.2)	17 (2.7)	16 (1.5)
Lotader AX 8900	6	12,600 (580)	131 (12)	1.8 (0.5)	23 (3.7)	22 (3.5)
	15	10,400 (430)	166 (15)	4.6 (1.0)	26 (10.6)	18 (4.3)
Lotader AX 8900	2	14,000 (560)	132 (5)	1.3 (0.2)	16 (2.8)	14 (2.8)
	6	12,600 (390)	127 (7)	1.6 (0.3)	17 (3.0)	15 (3.0)
	15	10,500 (290)	134 (25)	2.8 (1.1)	34 (7.8)	23 (2.8)

Standard deviations are in parentheses.

containing epoxy-functionalized polyethylenes. The improvement in toughness was evident with the addition of 2 wt % functionalized polyethylenes, and the toughness improved with additional amounts of functionalized polyethylene. This can be seen in Figure 1. The blend containing 15 wt % Bondfast E had the highest Charpy impact strength for the unnotched specimens. This blend had an impact strength up to three times higher than that of the neat LCP. The elongation at break and tensile strength also improved when the LCP was blended with epoxy-functionalized polyethylenes. When the toughness properties of the blends improved, the modulus of the blends decreased. The decrease was already considerable with 2 wt % functionalized polyethylene, and the behavior was more pronounced when a larger amount of functionalized polyethylene was blended with LCP. This behavior is illustrated in Figure 2.

Rheology

The shear viscosities of the neat LCP, functionalized polyethylenes, and blends were measured at 300°C

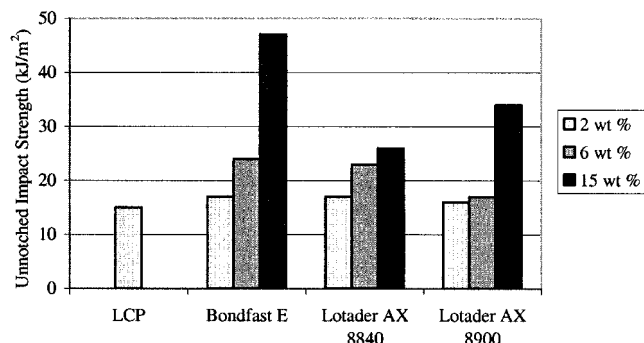


Figure 1 Charpy impact strength of unnotched specimens of LCP blends containing 2, 6, and 15 wt % epoxy-functionalized polyethylenes.

with a shear rate ranging from 100 to at least 1000 1/s. The melt viscosities of the LCP, Lotader AX 8840, and blends containing 2, 6, and 15 wt % Lotader AX 8840 are shown in Figure 3.

The neat LCP and polyethylenes had the lowest melt viscosities at the investigated shear rate area. All the LCP blends containing epoxy-functionalized polyethylene had considerably higher melt viscosities than the neat blend components. The melt viscosity of the blends rose as the amount of functionalized polyethylene in the blends increased. According to investigations by Holsti-Miettinen et al.,¹³ the remarkably high viscosities of the blends are evidence of enhanced interactions between the blend components. This is probably due to chemical reactions between the end groups of the LCP and the epoxy groups of the functionalized polyethylene.

DSC studies

A DSC analysis of the blends and neat LCP indicated that the melting behavior of the LCP changed when it was blended with epoxy-functionalized polyethylenes.

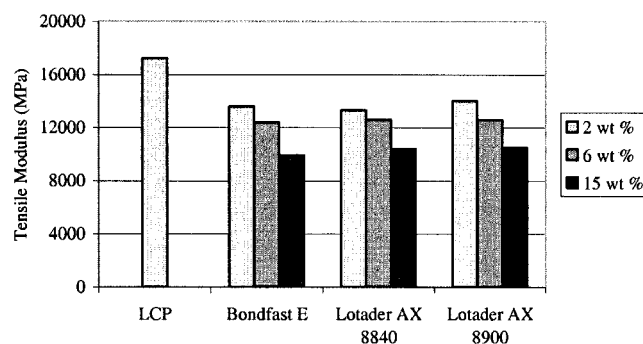


Figure 2 Tensile modulus of LCP blends containing 2, 6, and 15 wt % epoxy-functionalized polyethylenes.

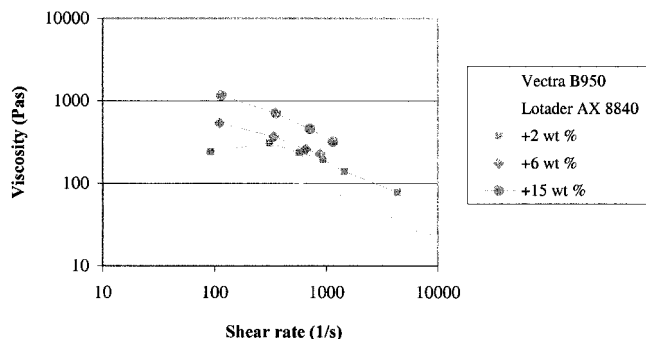


Figure 3 Melt viscosity versus the shear rate for the LCP, Lotader AX 8840, and LCP blends containing 2, 6, and 15 wt % Lotader AX 8840 measured at 300°C.

The neat LCP had two separate melting peaks at 275 and 285°C, which can be seen in Figure 4. Although the epoxy-functionalized polyethylene affected the melting behavior of the LCP, the melting temperature of the LCP was unchanged in all blends. When 2 wt % of the functionalized polyethylene was blended, the melting behavior of the LCP did not change noticeably. With a larger amount of functionalized polyethylene in the blends, the melting peaks of the LCP decreased until there was only a trace with a functionalized polyethylene content of 15 wt %. The melting peak of the functionalized polyethylene at 80°C enlarged as its fraction was increased. Therefore, the changes in the melting behavior of the LCP can be interpreted as further evidence of interactions between the two polymers.

Morphology

Clear changes in the morphology with an increasing fraction of functionalized polyethylene can be seen in Figure 5. The addition of 2 wt % functionalized polyethylene to the LCP did not cause a considerable

smoothing in the blend morphology in comparison with that caused by additions of 6 or 15 wt % functionalized polyethylene. The enhanced interactions between the blended polymers and possible chemical reactions between the functional groups of the polymers probably caused the smoothness of the fractured surfaces. SEM images of the blends offer clear support for the information obtained by other methods.

CONCLUSIONS

Blends containing an LCP as the major component and 2–15 wt % epoxy-functionalized polyethylene were studied by a number of methods to clarify the possible interactions between the blended polymers. The aim of the study was to toughen the LCP by blending it with a suitable polyethylene and to find the best blend composition for LCP toughening.

The study of the blends revealed that the toughness properties of the LCP could be improved significantly through blending with epoxy-functionalized polyethylenes. Better toughness properties could be seen in the improved elongation at break and impact strength of both unnotched and notched specimens in comparison with those of the neat LCP. The toughness properties of the blends were usually better when a larger amount of functionalized polyethylene was added to the LCP. The addition of functionalized polyethylenes gradually reduced the stiffness of the LCP; this could be seen as the decreased modulus of the blends containing functionalized polyethylene. Suitable combined properties of stiffness and toughness could be achieved with an adjusted amount of epoxy-functionalized polyethylene in the LCP. The improvement in the toughness of the LCP blends was due to strong interactions between two polymers, and this was confirmed by different characterization methods.

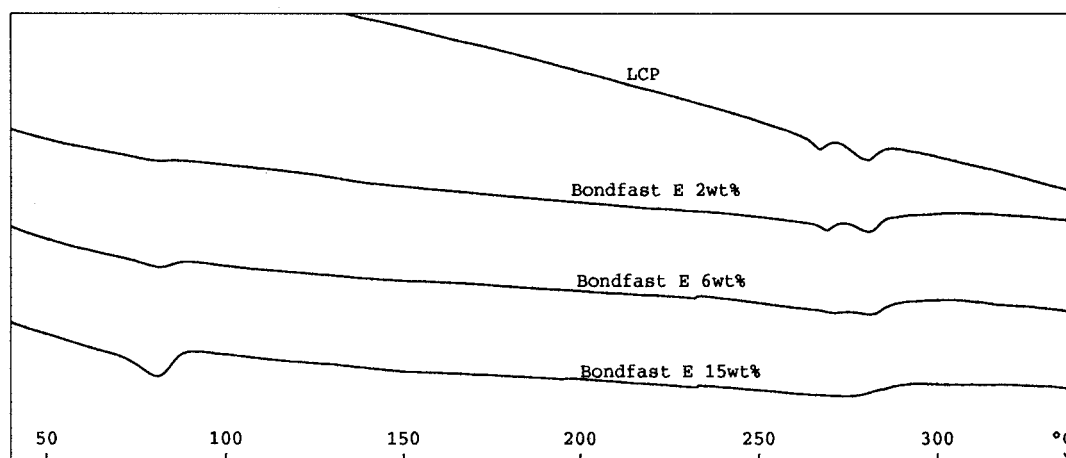


Figure 4 Melting thermograms of the neat LCP and LCP blends recorded at a sweep rate of 10°C/min.

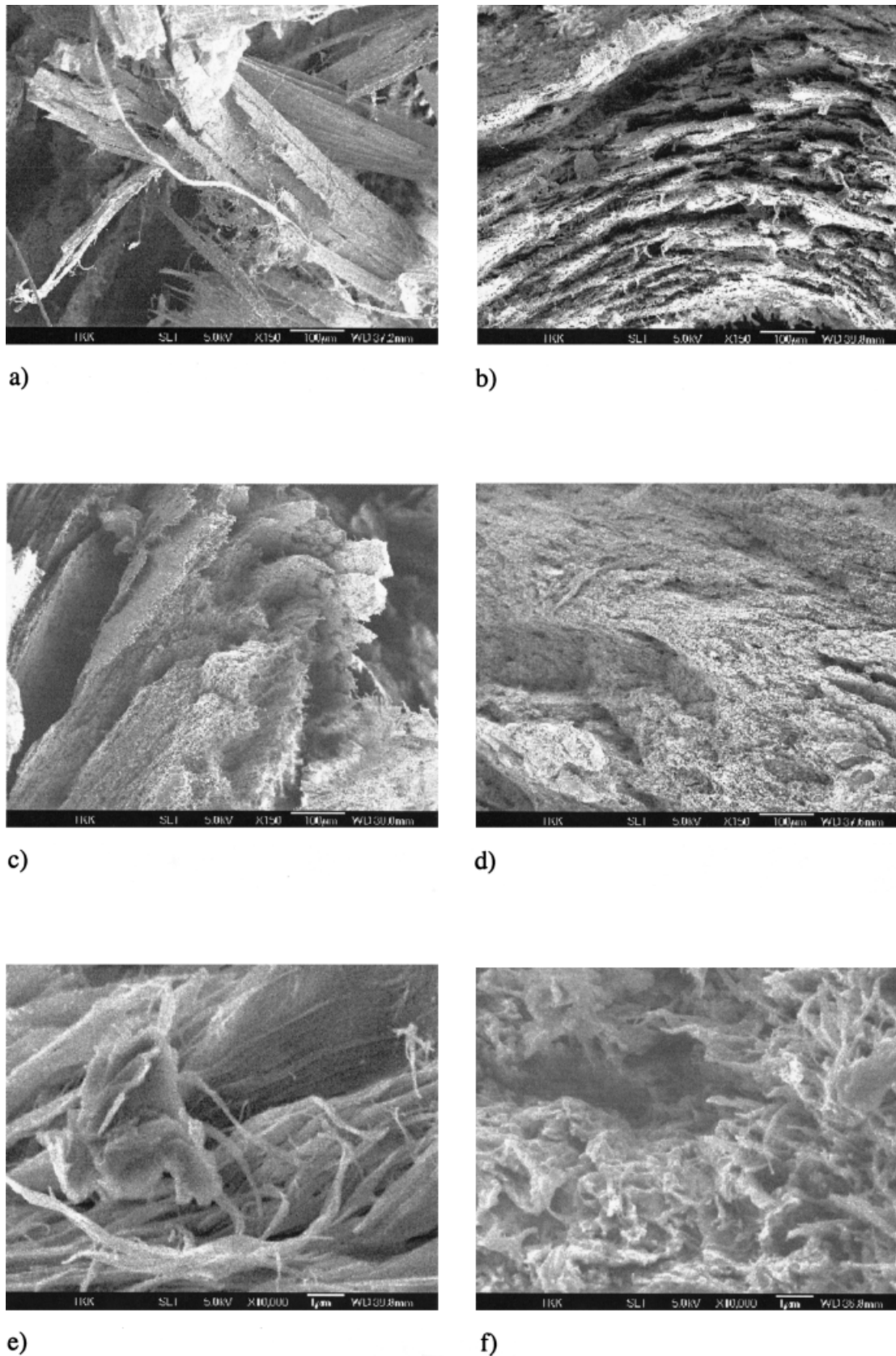


Figure 5 SEM images of the fractured surfaces of blends containing (a) 0, (b) 2, (c) 6, and (d) 15 wt % Bondfast E at a magnification of 150 \times and (e) 2 and (f) 15 wt % Bondfast E at a magnification of 10,000 \times .

The authors are grateful to Dr. Kari Lounatmaa from the Laboratory of Electronics Production Technology at the Helsinki University of Technology for the scanning electron micrographs.

References

1. La Mantia, F. P.; Scaffaro, R.; Plado, G.; Magagnini, P. L.; Paci, M. *Polym Networks Blends* 1996, 6, 171.
2. Datta, A.; Chen, H. H.; Baird, D. G. *Polymer* 1993, 34, 759.
3. Heino, M. T.; Seppälä, J. V. *J Appl Polym Sci* 1993, 48, 1677.
4. O'Donnell, H. J.; Baird, D. G. *Polymer* 1995, 36, 3113.
5. Datta, A.; Baird, D. G. *Polymer* 1995, 36, 505.
6. Kozłowski, M.; La Mantia, F. P. *J Appl Polym Sci* 1997, 66, 969.
7. La Mantia, F. P.; Scaffaro, R.; Magagnini, P. L.; Paci, M.; Chiezzi, C.; Sek, D.; Minkova, L. I.; Miteva, T. S. *Polym Eng Sci* 1997, 37, 1164.
8. La Mantia, F. P.; Scaffaro, R.; Magagnini, P. L.; Paci, M.; Minkova, L. I.; Miteva, T. S. *J Appl Polym Sci* 1999, 71, 603.
9. Minkova, L. I.; Velcheva, M.; Paci, M.; Magagnini, P.; La Mantia, F. P.; Sek, D. *J Appl Polym Sci* 1999, 73, 2069.
10. Magagnini, P. L.; Pracella, M.; Minkova, L. I.; Miteva, T. S.; Sek, D.; Grobelny, J.; La Mantia, F. P.; Scaffaro, R. *J Appl Polym Sci* 1998, 69, 391.
11. Miller, M. M.; Cowie, J. M. G.; Tait, J. G.; Brydon, D. L.; Mather, R. R. *Polymer* 1995, 36, 3107.
12. Chin, H.-C.; Chang, F.-C. *Polymer* 1997, 38, 2947.
13. Holsti-Miettinen, R. M.; Heino, M. T.; Seppälä, J. V. *J Appl Polym Sci* 1995, 57, 573.
14. Chiou, Y.-P.; Chiou, K.-C.; Chang, F.-C. *Polymer* 1996, 37, 4099.
15. Yu, L.; Simon, G.; Shanks, R. A.; Nobile, M. R. *J Appl Polym Sci* 2000, 77, 2229.
16. Scaffaro, R.; La Mantia, P. L.; Pentchev, I. T.; Hu, G.-H. *Mol Cryst Liq Cryst* 1999, 336, 169.
17. Yazaki, F.; Tsubouchi, Y.; Yosomiya, R. *Polym Polym Compos* 1993, 1, 183.
18. Dutta, D.; Weiss, R. A.; He, J. *Polymer* 1996, 37, 429.
19. Zhang, H.; Weiss, R. A.; Kuder, J. E.; Cangiano, D. *Polymer* 2000, 41, 3069.