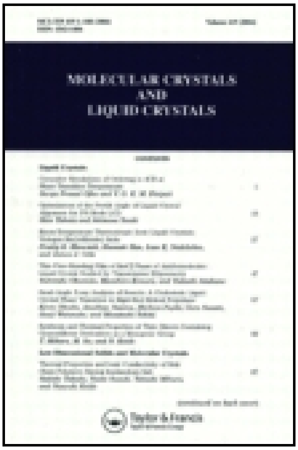

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Liquid Crystal Polymer Blends

Marek Kozlowski [a] & Anna Kozlowska [a]

[a] Wroclaw University of Technology, 1-19 Polymer Recycling Laboratory Wybrzeze Wyspianskiego 27, Wroclaw, 50-370, Poland

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Liquid Crystal Polymer Blends

MAREK KOZLOWSKI and ANNA KOZLOWSKA

Wroclaw University of Technology, I–19 Polymer Recycling Laboratory Wybrzeze Wyspianskiego 27, Wroclaw 50–370, Poland

Two-component blends of polymer liquid crystals with polysulfone or polypropylene have been investigated. Tensile properties, melt rheology and morphology of two-component systems have been presented. The orientation conditions under melt processing have been related to the phase structure and mechanical strength of the blends. Enhancement of interfacial adhesion has been attempted by means of compatibilization with the maleated modifiers.

Keywords: Liquid crystalline polymer; polymer blend; compatibilization; morphology; mechanical strength

INTRODUCTION

Polymer blends comprised of the thermoplastic matrix and liquid crystalline polymer (LCP) are still receiving considerable attention, even though a substantial interest on this group of plastics started almost twenty years ago. This has been because LCP domains may be oriented into fibers under specific processing conditions, thus forming a strengthening structure similar to that in the fiber-reinforced composites. Mechanical properties of such *in situ* composites may be fairly high, since as a rule, LCPs exhibit higher moduli and higher tensile strength than flexible thermoplastics[1-5]. The advantageous mechanical properties are caused by their chemical structure, which includes numerous aromatic units caused by their chemical structure, which includes numerous aromatic units located along macromolecules. This results in the LCPs high stiffness and high temperature resistance.

Moreover, melt viscosity of liquid crystalline polymers is very low, which makes heterogeneous blends containing LCPs easily processable. Since, in contrary to the glass fiber reinforced materials, all components of LCP-blends use to be at processing conditions in a molten state, such composites do not wear a metal surface of the processing equipment.

However, the reinforcing effect is often only hardly observed in LCP-blends. There exist two main reasons for such frustrating finding. One of them is an insufficient orientation of the liquid crystalline domains in a matrix, which reduces the mechanical strength of the entire sytem significantly below expectations. This factor deals with a morphology of LCP-blends in its geometrical aspect. Another reason concerns the interfacial region - incompatibility between components makes a transmission of the mechanical energy through the composite ineffective. In principle, the interfacial adhesion may be improved by addition of block/graft copolymers or other additives, which contain polar groups capable to interactions with the components of LCP-blends[2-4]. However, the interactions are mainly physical, thus being of moderate strength, which makes a coupling efficiency rather poor.

EXPERIMENTAL

Liquid crystalline polymers were melt mixed with polysulfone (PSF) and polypropylene (PP) in a ratio of 10/90 and 20/80. LCP/PSF blends were prepared by injection molding, whereas LCP/PP systems were obtained by extrusion. The blend components were dried before mixing at 125°C overnight.

High orientation in the blends was produced under fast drawing of a strand extruded from the capillary rheometer die. Draw ratio was calculated as a ratio of the capillary die diameter to the actual strand diameter.

Materials

The polymers forming a matrix in the blends were polysulfone Udel P1700 from Amoco, USA and polypropylene D60P from Montell, Italy. The liquid crystalline polymers were the wholy aromatic Vectra A950 from Hoechst Celanese (LCP1) and semi-flexible SBHN from Eniricerche (LCP2) [6]. In comparison to LCP1 composed of 6-hydroxy-2-naphtoic acid and *p*-hydroxybenzoic acid, LCP2 grade contained additional units derived from sebacic acid and 4,4'-dihydroxybiphenyl. Two commercial products were used for compatibilization - maleated polypropylene (PP-*g*-MAH) from Montell and maleated block copolymer styrene-butadiene-styrene (SEBS-g-MAH) from Shell. Additionally a laboratory product was used, obtained by reactive blending of SBHN and (SEBS-g-MAH) in a chamber of an internal mixer.

Test Methods

Mechanical properties were evaluated at room temperature by means of the uni-axial tension at an elongation rate of 20 mm/min, using the Lloyd LR 10K tensile machine.

Melt rheology was determined using the capillary rheometer Rheotester1000 (Goettfert), equipped with a capillary of 1 mm diameter, 30 mm length. The Rabinowitch correction was applied, whereas the Bagley correction was neglected because of a high L/d ratio. Frequency sweep oscillatory tests were also performed with a plate-plate rheometer RDA II (Rheometrics).

Morphology of cold-fractured sample surfaces, being coated with gold before observations, was examined with a Jeol JSM 5800LV scanning electron microscope.

RESULTS

PSF-LCP composites exhibited enhanced rigidity and tensile strength in comparison to polysulfone, whereas the effect of reinforcement in polypropylene-based blends was less expressed (Table I). The highest influence on tensile properties has been observed for the modulus and elongation at break. For example, an addition of 10 wt. % of LCP1 brought about an increase in the modulus of approx. 31 % and in the tensile strength of 9 %. Respective elongation at break decreased of more than one order of magnitude, reaching the values characteristic for a liquid crystalline polymer.

Further increase in LCP-content brought about a slightly less expressed change in the mechanical properties. Addition of 20 wt. % of LCP1 resulted in enhancement of a tensile modulus of ca. 54 % and a tensile strength of ca. 12 %.

TABLE I Mechanical properties of LCP-blends

Polymer blend composition	Tensile modulus, GPa	Tensile Strength, MPa	Elongation at break, %
PSF	2.48	70.0	>50
PSF/LCP1 90/10	3.25	76.3	4.4
PSF/LCP1 80/20	3.83	78.1	3.3
PP	0.89	35.0	840.0
PP/LCP1 90/10	1.37	36.3	23.2
PP/LCP1 80/20	1.86	39.2	16.7

Compatibilization was examined by addition of polypropylene grafted with maleic anhydride (PP-g-MAH) and by means of a copolymer obtained by reactive blending of LCP and maleated block copolymer styrene-butadiene-styrene (SEBS-g-MAH). The last product exhibited distinctly higher compatibilizing efficiency (Table II).

Additional improvement in mechanical properties resulted from a high orientation of extruded material, which brought about to an extensive fibrillation of the liquid crystalline domains. The reinforcing effect was higher the higher was a draw ratio. Markedly enhanced elongation at break of LCP-blends containing the LCP-based compatibilizer implies better transmission of mechanical stress through the blend.

TABLE II Mechanical properties of compatibilized LCP-PP blends

Polymer blend composition	Tensile modulus, GPa	Tensile Strength, MPa	Elongation at break, %
PP	0.89	35.0	840.0
PP/LCP1/ 90/10	1.37	36.3	23.2
PP/LCP1 80/20	1.86	39.2	16.7
PP/LCP1/comp 90/10	1.35	36.9	14.0
PP/LCP1/comp 80/20	2.14	53.0	6.0
PP/LCP2 80/20	0.68	13.4	6.0
PP/LCP2/comp 80/20	0.84	12.0	4.0
PP/LCP2/comp® 80/20	0.79	19.0	444.0
PP/LCP2/comp® 80/20*	1.34	21.4	67.2
PP/LCP2/comp® 80/20**	1.87	27.6	24.1

® Reactive blending
* Draw ratio = 5
** Draw ratio = 50

Morphology inspections by a scanning electron microscopy evidenced both the enhanced interfacial adhesion and different orientation level of a dispersed phase. Figure 1 represent PSF/LCP1 system with a low (a) and high orientation (b) of the liquid crystal polymer domains. Although both LCP-blends are of the same composition, they should be classified to different composite types: particulate (a) and fiber reinforced (b) ones. Despite diversity of the domain shape, their similar size was observed - both the spherical and fibrilar objects were of 1-3 μm diameter. This should be refered to the hydrodynamics, interfacial tension and percolation phenomena in the system. One has to stress, that the reinforcing effect was observed only under specific, strictly controlled conditions.

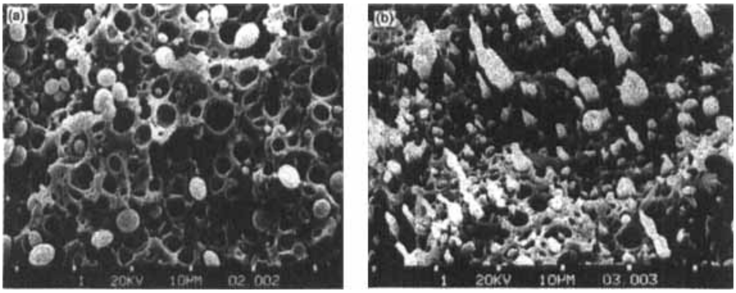

FIGURE 1 SEM micrographs of PSF/LCP1 70/30 blends prepared with low (a) and high (b) orientation level.

Melt rheology exhibited distinctly decreased viscosity of thermoplastics after addition of liquid crystalline polymers. Figure 2 shows the viscosity dependence on shear rate for polypropylene and PP blends and alloys with LCPs.

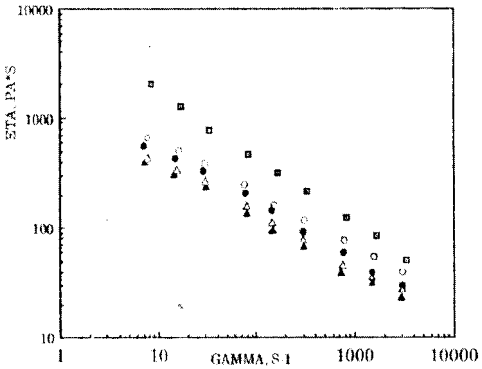

FIGURE 2 Viscosity curves of PP/LCP 90/10 systems by capillary rheometry (290°C). From top to bottom: PP - PP/LCP1 - PP/LCP1/comp - PP/LCP2 - PP/LCP2/comp.

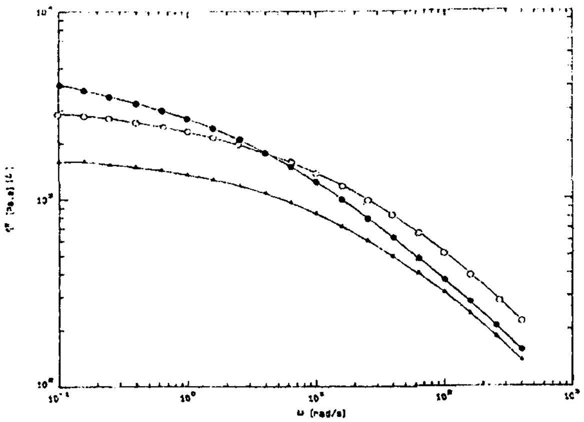

FIGURE 3 Viscosity curves of PP/LCP 90/10 (•) and compatibilized 90/10 (∇) and 80/20 (○) blends by plate-plate rheometry (290°C).

Enhanced interfacial adhesion between the matrix and LCP was evidenced at low shear rates as a slight increase in the melt viscosity (Figure 3).

CONCLUSIONS

- Thermoplastic microcomposites may be formed *in situ* under high orientation of blends composed of thermotropic LCP-isotropic polymer.
- Liquid crystal polymer blends still contain a value, which has not yet been entirely exploited. Insufficient reinforcing efficiency by LCP-fibers may be improved by compatibilizing agents.
- Reactive compatibilization and processing of LCP-blends with a high elongational stress component should provide the microcomposite material of a high mechanical strength and enhanced interfacial adhesion.

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