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MISCIBILITY IN LOW MOLECULAR MASS LIQUID CRYSTAL-SEMICRYSTALLINE POLYMER BLENDS

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Abstract

Miscibility in blends of semicrystalline polymers (poly(ethylene) adipate and poly(tetrahydrofuran)) and liquid crystal cholesteryl palmitate was investigated by means of differential scanning calorimetry and polarizing optical microscopy. Some (concentration-dependent) miscibility was found. A more pronounced miscibility exhibits the polyester-based blends probably due to the similar chemical structure of the two components and stronger interactions between the two components.

Keywords: blend, liquid crystal, polyester, polyether

Introduction

The science and technology of polymer blends has emerged as a major tool for designing and improving polymeric materials. A relatively new field of importance is that of polymer blends containing liquid crystals (LC). Low molecular mass liquid crystals in polymer matrices constitute interesting systems from many points of view. Many studies concerning phase behavior, miscibility, morphology, properties have been carried out on such blends [1–5]. Also, these systems can be used in interesting applications [6–9]. Liquid crystal displays have become popular as low voltage, low power devices due to the molecular optical anisotropy of these materials. Semicrystalline polymers can be used as non-interactive supports for liquid crystals in these devices. Because of these applications, liquid crystal–polymer blends have attracted considerable attention in the microelectronics industry. In this case, however, an immiscible polymer–liquid crystal blend is advantageous because one is interested in preserving the birefringent behaviour of the liquid crystal impregnated in polymeric substrate.

The aim of this work is to report some results concerning the characterization of binary blends of cholesteryl palmitate (CP), which is a low molecular mass liquid crystal with two isotropic semicrystalline polymers: poly(ethylene adipate) (PEA) (M_n=2000 g mol^{-1}), poly(tetrahydrofuran) (PTHF) (M_n=1000 and 2000 g mol^{-1}). CP was chosen because undergoes phase transitions at moderate temperatures. So, it was not nec-

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essary to heat the blends to temperatures at which the polymers might undergo thermal degradation, most likely at the ether linkage. Differential scanning calorimetry and polarizing optical microscopy were used as experimental probes of miscibility.

Experimental

Materials

Poly(ethylene adipate) (PEA) with endcapped hydroxyl groups is a commercial product purchased from Fibrex SA, Savinesti, Romania (M_n=2000 g mol^{-1}). Poly(tetrahydrofuran) (PTHF) with M_n=1000 and 2000 g mol^{-1} are commercial products purchased from BASF. Cholesteryl palmitate (CP) was obtained from Nopris SRL, Cluj Napoca, Romania and used as received. This LC compound presents two types of mesophases, i.e. cholesteric and smectic mesophases: (*m.p.* (C→Ch) 74.5°C, (Ch→I) 80°C, (Ch→S) 73.5°C (monotropic)) (as determined by DSC, 4°C min^{-1}). 1,2-dichloroethane (DCE) (Aldrich) was used as received.

Blend preparation

The polymers and CP were separately dissolved in DCE to form 2 and 0.8 g dL^{-1} solutions, respectively. Then, the solutions were mixed to the final ratio and the mixtures were stirred for 5 h. After that, the solvent was slowly evaporated at room temperature. In order to remove the residual solvent, the samples were dried in a vacuum oven at 50°C for several days.

Measurements

Thermal analysis was performed using a differential scanning calorimeter (Mettler DSC-12 E), at heating rates of 4°C min^{-1}, nitrogen flow 50 mL min^{-1} and the sample sizes were 5–10 mg. Scanning was conducted from 20 to 100°C on heating and from 100 to 30°C on cooling. The transition temperatures were obtained from extrapolated onset of the endothermic and exothermic peaks. The heats of the transitions were calculated from the areas of the endothermic and exothermic peaks, using the cut-and-weigh technique. Indium (*m.p.*=156.6°C, ΔH=28.42 J g^{-1}) was used as calibration standard for the heat of fusion calibration. These values were obtained in the first heating and cooling runs.

The microscopic observations were undertaken with a IOR MC1-type polarizing microscope equipped with a heating stage (magnification 150×).

Results and discussion

In Figs 1 and 2 the DSC curves (first heating runs) of PEA/CP and PTHF 2000/CP blends, respectively, are depicted. The appearance of the first-order thermodynamic transitions, characteristic of the liquid crystalline component, in the DSC curves of the blends provides evidence of phase separation. The Ch → I transition temperature of the liquid crystal in the studied blends is not distinguishable. It must be mentioned that at a heating rate of 1°C min^{-1} even for 80% (mass) CP in the blends this peak is hardly visible.

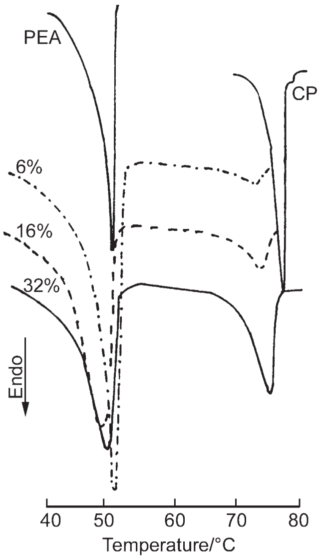

Fig. 1 DSC curves (first heating runs) of the pure PEA and CP and of the corresponding blends with different amounts of CP (% mass CP)

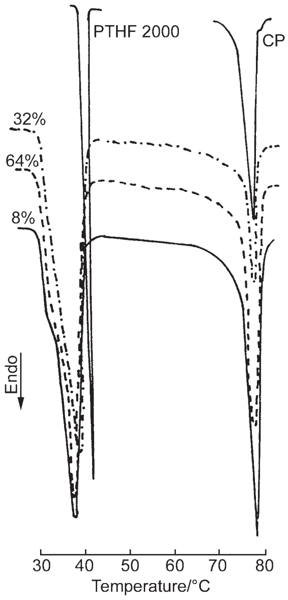

Fig. 2 DSC curves (first heating runs) of the pure PTHF 2000 and CP and of the corresponding blends with different amounts of CP (% mass CP)

It was found that blending affects the melting behavior of the two components of the blends. The melting points of the polymers and of the liquid crystal are shifted down a few degrees with the increasing content of CP and polymer, respectively. This is anologous to the phenomenon of melting point depression [10] and provides evidence for some (concentration-dependent) miscibility of the two components. The melting point of liquid crystal represents the temperature of the crystal to the first liquid crystal transition. The thermodynamic parameters of the blends studied are listed in Tables 1, 2 and 3. At lower concentrations of the liquid crystal, the *LC* peaks are not evidenced in the DSC scans. Also at a heating rate of 1°C min^{-1} these peaks are not visible.

Table 1 Thermodynamic parameters of the PEA/CP blends

CP/ mass%	T_1/°C	ΔH_1/ J g^{-1} blend	ΔH_1/ J g^{-1} PEA	T_2/°C	ΔH_2/ J g^{-1} blend	δ	ΔH_2/ J g^{-1} CP	T_3/°C	ΔH_3/ J g^{-1} blend
0	47.5	99.47	99.47	–	–	–	–	–	–
2	51.0	82.58	84.26	65.5	0.98	0.992	49.00	50.5	1.49
4	49.2	82.37	85.80	66.2	3.30	0.975	82.50	51.2	4.59
6	50.0	74.64	79.40	67.8	3.42	0.974	57.00	52.2	5.72
10	44.0	79.42	88.24	68.2	8.59	0.931	85.90	54.8	9.19
16	42.5	80.61	95.96	69.5	11.84	0.899	74.00	52.3	9.05
32	43.8	55.01	80.89	71.7	23.02	0.757	71.93	56.2	21.53
64	43.9	51.69	143.58	72.0	41.75	0.169	65.23	57.5	38.63
80	42.8	40.53	202.65	72.2	42.15	–	52.68	55.8	42.03
100	–	–	–	74.5	139.58	–	139.58	54.5	102.44

Table 2 Thermodynamic parameters of PTHF 1000/CP blends

CP/ mass%	T_1/°C	ΔH_1/ J g^{-1} blend	ΔH_1/ J g^{-1} PTHF	T_2/°C	ΔH_2/ J g^{-1} blend	δ	ΔH_2/ J g^{-1} CP	T_3/°C	ΔH_3/ J g^{-1} blend
0	32.0	113.31	113.31	–	–	–	–	–	–
4	31.2	77.35	80.57	77.0	0.40	0.997	10.00	–	–
6	30.0	87.48	93.06	77.0	0.28	0.997	4.66	–	–
8	32.5	45.24	49.17	76.5	2.61	0.979	32.62	63.5	4.62
16	29.8	75.20	89.52	76.5	5.01	0.957	31.31	71.0	4.84
32	30.2	56.80	83.53	75.5	23.43	0.753	73.21	68.5	16.66
64	30.2	42.27	117.41	76.0	53.14	–	83.03	64.5	43.34
80	30.5	31.72	158.6	75.0	49.02	–	61.27	67.0	43.07
100	–	–	–	74.5	139.58	–	139.58	54.5	102.44

Table 3 Thermodynamic parameters of PTHF 2000/CP blends

CP/ mass%	T_1/°C	ΔH_1/ J g^{-1} blend	ΔH_1/ J g^{-1} PTHF	T_2/°C	ΔH_2/ J g^{-1} blend	δ	ΔH_2/ J g^{-1} CP	T_3/°C	ΔH_3/ J g^{-1} blend
0	34.0	162.63	162.63	–	–	–	–	–	–
4	34.5	106.59	111.03	–	–	–	–	–	–
6	33.0	105.19	111.90	–	–	–	–	–	–
8	33.2	110.48	120.08	77.0	0.33	0.997	4.125	58.0	6.62
16	33.7	90.97	108.29	77.0	1.90	0.983	11.87	65.0	13.34
32	33.5	100.06	147.14	76.0	25.99	0.726	81.21	64.2	23.65
64	33.0	82.17	228.25	76.7	41.29	0.178	64.51	66.3	36.83
80	33.2	70.77	353.85	76.7	48.17	–	60.21	66.2	41.11
100	–	–	–	74.5	139.58	–	139.58	54.5	102.44

T_1 and ΔH_1 – melting point and heat of fusion of polymer;
T_2 and ΔH_2 – melting point and heat of fusion of liquid crystal;
T_3 and ΔH_3 – crystallization temperature and heat of smectic→crystal transition;
δ – mass fraction of liquid crystal dissolved in polymer matrix

As can be seen, the melting points of the polymers are shifted down a few degrees and a somewhat more pronounced depression is observed at the blends based on PEA. Also, the heat of fusion of the polymers decrease with the increasing content of the low molecular mass liquid crystal. These facts show some degree of miscibility in the isotropic (polymer-rich phase). The same behaviour for all the blends studied is observed. As for the liquid crystal component, it can be seen that at the PEA/CP blends the melting points are slightly shifted to lower temperatures and this fact evidences some extent of miscibility in the LC-rich phase. In the blends with PTHF the melting points of CP are very little affected for all the compositions. But, for all the blends, the heat of fusion of CP decreases with increasing the content of the polymer. Taking into account that the appearance of the melting transitions of the liquid crystal means phase separation, the equation shown in [11] was applied in this study and the mass fraction of liquid crystal dissolved in the polymer matrix was calculated as follows:

$$\delta=1-(\Delta H_{\mathrm{b}})/(\chi\Delta H_{\mathrm{LC}}) \tag{1}$$

where δ – mass fraction of liquid crystal dissolved in the polymer matrix, χ – mass fraction of polymer in the blend, ΔH_{b} – heat of fusion of the liquid crystal in the blend, ΔH_{LC} – heat of fusion of pure liquid crystal.

It can be seen from Tables 1, 2 and 3 that δ decreases with decreasing the content of polymer in the blends. This fact evidences the concentration-dependent miscibility found for these blends.

As a conclusion, in the PEA-based blends, the melting points of both components are more affected than those of PTHF-based blends. This fact shows an improved miscibility in the blends with poly(ester) probably because of the similar chemical structure of the two components and because stronger interactions between the two components are involved. Also, the blends with a lower molecular mass polymer (PTHF 1000) show a somewhat more pronounced depression of the melting points than PTHF 2000 due to the entropic contribution to the miscibility.

The thermal behaviour of the blends was studied on cooling, too. The liquid crystal → crystal transition temperature (T_3) and corresponding heats are listed in Tables 1, 2 and 3. It can be seen, that blending affects this transition temperature of the liquid crystal for all blends. The associated heats decrease with increasing the content of the polymers. The crystallization of the polymers could not be evidenced in these investigation conditions. For some of the PTHF-based blends the LC peaks corresponding to the two mesophases, i.e. cholesteric and smectic mesophases, appear on DSC scans. The transition temperatures and the corresponding heats and entropy changes decrease with adding the polymer component (Tables 4 and 5). The heat of I→Ch transition was used in Eq. (1) and it was found that the mass fraction of liquid crystal dissolved in polymer matrix decreases with decreasing content of polymer in the blends. As for the blends with PEA, only the crystallization peaks are evidenced, showing once again that, the blends with PTHF are characterized by a higher degree of phase separation.

Table 4 Transition temperatures, heats of transitions and entropy changes for PTHF 1000-based blends

CP/ mass%	T_4/°C	ΔH_4/ J g^{-1} blend	δ	ΔS_4/ J g^{-1} K^{-1}	T_5/°C	ΔH_5/ J g^{-1} blend
8	68.5	0.33	0.90	$9.6\cdot10^{-4}$	65.0	0.33
32	76.0	0.45	0.81	$1.3\cdot10^{-3}$	72.2	0.42
64	76.5	0.92	0.28	$2.6\cdot10^{-3}$	72.5	1.22
80	76.0	1.13	–	$3.2\cdot10^{-3}$	72.0	1.30
100	78.8	3.59	–	$1.02\cdot10^{-2}$	73.5	3.97

Table 5 Transition temperatures, heats of transitions and entropy changes for PTHF 2000-based blends

CP/ mass%	T_4/°C	ΔH_4/ J g^{-1} blend	δ	ΔS_4/ J g^{-1} K^{-1}	T_5/°C	ΔH_5/ J g^{-1} blend
32	76.2	0.37	0.84	$1.0\cdot10^{-3}$	73.0	0.37
64	76.5	0.64	0.50	$1.8\cdot10^{-3}$	72.5	0.69
80	76.2	0.81	–	$2.3\cdot10^{-3}$	72.8	1.16
100	78.8	3.59	–	$1.02\cdot10^{-2}$	73.5	3.97

T_4, ΔH_4 and ΔS_4 – I → Ch transition temperature, heat of I → Ch transition and entropy change at I → Ch transition of the liquid crystal; T_5 and ΔH_5 – Ch → S transition temperature and heat of Ch → S transition of the liquid crystal

As mentioned before, the appearance of the first-order thermodynamic transitions, characteristic of the liquid crystalline component in the DSC curves of the blends evidence phase separation. The phase separation of the studied blends was found by polarizing optical microscopy, too. The appearance of the mesophases was observed at an amount of 16% (mass) of liquid crystal for both PEA- and PTHF-based blends. As presented before, at the blends with PEA the peaks corresponding to the two mesophases of cholesteryl palmitate were not evidenced by DSC curves (first cooling runs). These can be explained with the resolution limits of the instruments used. At concentrations lower than 16% only the crystallization of the low molecular mass liquid crystal was observed. At the PEA-based blends it was found that, the liquid crystal affects the crystallization of the polymer, i.e. on cooling from isotropic state a spherulitic morphology that is typical of semicrystalline polymers was formed. The fact that only the crystallization of PEA is affected by cholesteryl palmitate may be explained with the presence of stronger interactions in these blends.

Also, by microscopic observations it was found that the transition temperatures were altered by blending evidencing the concentration-dependent miscibility found by means of DSC.

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