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Characterization of polymer-liquid crystal blends

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Blends of semi-crystalline polymers (polyethylene adipate and two poly(ester-urethane)s) with liquid crystal cholesteryl palmitate with different compositions were prepared by solution casting. One of the poly(ester-urethane)s was based on 2,4-tolylene diisocyanate (TDI) and the other one on 4,4'-diphenylmethane diisocyanate (MDI). The miscibility and phase transition were investigated over the whole range of concentration by differential scanning calorimetry and polarizing optical microscopy.

Keywords: liquid crystal, blend, polyester, poly(ester-urethane).

INTRODUCTION

A relatively new field of importance is that of polymer blends containing liquid crystals (LC). Low molecular weight liquid crystals in polymer matrices constitute interesting systems from many points of view. Many studies concerning the phase behaviour, miscibility, morphology and properties have been performed on such blends,[1–5] and some of these systems can be used for electro-optic applications.[6–9] Also, LC compounds may act as plasticizers and short reinforcing materials.[10,11] Liquid crystal displays have become popular as low voltage, low power devices due to the molecular optical anisotropy of these materials. Semi-crystalline 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 it is of interest to preserve the birefringent behaviour of the liquid crystal impregnated in the polymeric substrate.

In this paper some results concerning the characterization of binary blends of cholesteryl palmitate, which is a low molecular weight liquid crystal, with isotropic semi-crystalline polymers (polyethylene adipate and poly(ester-urethane)s) will be reported. The latter polymers were chosen in order to study the influence of urethane groups on the miscibility of these blends. Differential scanning calorimetry and polarizing optical microscopy were used as macroscopic experimental probes of miscibility.

EXPERIMENTAL

Materials

Poly(ethylene adipate) (PEA) with endcapped hydroxyl groups was a commercial product purchased from Fibrex SA, Savinesti, Romania (M_n = 2000).

2,4-Tolylene diisocyanate (TDI), and 4,4'-diphenylmethane diisocyanate (MDI) (Merck) were distilled prior to utilization under reduced pressure. Propan-2-ol and 1,2-dichloroethane (DCE) (Aldrich) were used as received. Cholesteryl palmitate (CP) was obtained from Nopris SRL, Cluj Napoca, Romania. This LC compound presents two types of mesophases, *i.e.,* cholesteric and smectic mesophases: (m.p. (C-Ch) 78 °C, (Ch-I) 81 °C, (Ch-S) 73 °C (monotropic)), as determined by DSC (4 °C/min).

A two-step addition reaction was used to prepare the poly(ester-urethane)s (PEA-MDI and PEA-TDI). The first step was the preparation of the NCO-terminated prepolymer, as follows. PEA was dehydrated for 3 h at 120 °C. Subsequently, TDI and MDI, respectively, were added to the vigorously stirred PEA. The reaction between the diisocyanates and macrodiol was carried out at 90 °C for 1 h under a nitrogen atmosphere. The amount of diisocyanate and PEA was controlled at a NCO : OH mole ratio of 3 : 1. The second step was the reaction of the free isocyanic groups with 2-propanol. The reaction temperature was allowed to cool to 40 °C when 2-propanol was added. The polymers were precipitated in water and dried under vacuum for several days.

The purity of polymers was checked by IR (Specord M 80) and ^{1}H-NMR (C 60 HL NMR at 60 °C in DMSO-d_6 using TMS as internal reference) analyses. Thus, the IR spectra of the polymers exhibit intense absorption bands of urethane carbonyl at 1740 cm^{-1}, the NH of urethane linkages gave a signal at 3370 cm^{-1}, the bands at 2980 cm^{-1} were ascribed to aliphatic groups, while the ester band was found in the range of 1100–1300 cm^{-1}.

The ^{1}H-NMR spectra of polymers showed peaks at 4.2 ppm which were assigned to the methylene protons from ethylene glycol and peaks at 2.3 and 1.6 ppm which were assigned to the methylene protons from adipic acid. The methine protons were observed at 4.5 ppm while the methyl protons from 2-propanol were observed at 1.2 ppm. The phenyl protons resonate at 6.7–7.5 ppm and the N–H proton absorption of the urethane linkage at 8.9 and 9.2 ppm. The methylene protons from MDI resonate at 3.8 ppm and the methyl protons from TDI resonate at 2.2 ppm. Also, the ratio of the integrals confirms the structure and composition of the polymers.

Blend preparation

The polymers and CP were separately dissolved in DCE to form 2 g/dL and 0.8 g/dL solutions, respectively. Then, the solutions were mixed to the final ratio and the mixtures were stirred for 5 h. Subsequently, 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), at heating and cooling rates of 4 °C/min, a nitrogen flow of 50 mL/min and sample sizes of 5–10 mg. The scanning was conducted from 20 °C to 100 °C when heating and from 100 °C to 30 °C when cooling. The melting temperatures of the polymers was taken as the onset of the melting process while the melting and crystallization temperatures of the low molecular weight liquid crystal were obtained from the maxima of the endothermic and exothermic peaks, respectively. The enthalpies were calculated from the areas of the endothermic and exothermic peaks, respectively. The enthalpies were calculated from the areas of the endothermic and exothermic peaks, using the cut-and-weigh technique. These values were obtained in the first heating and cooling runs. The calibration was done using indium as standard material.

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

RESULTS AND DISCUSSION

The melting behaviour of PEA-MDI/CP and PEA-TDI/CP blends, are presented in Fig. 1 and Fig. 2, respectively.

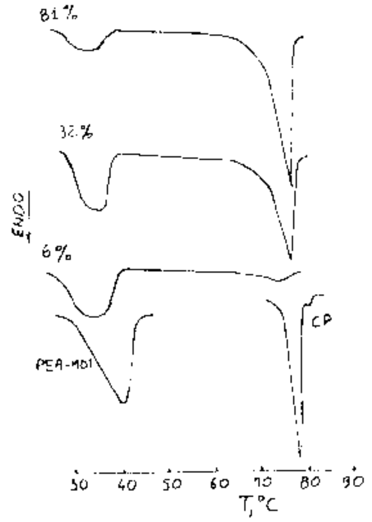

Fig. 1. DSC thermograms (first heating runs) of PEA-MDI/CP blends.

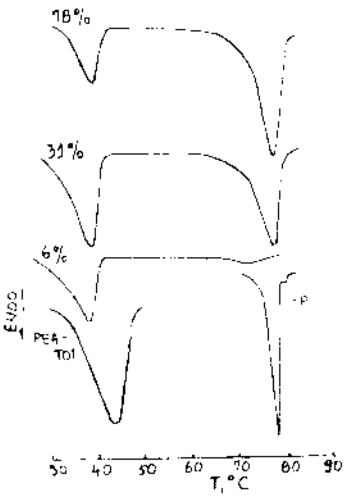

Fig. 2. DSC thermograms (first heating runs) of PEA-TDI/CP blends.

The appearance of the first-order thermodynamic transitions, characteristic of the liquid crystalline components, in the DSC thermograms of the blends provides macroscopic evidence of phase separation. The isotropization temperature of the liquid crystal in the studied blends was not distinguishable. It was found that blending affects the melting behaviour of the two components of the blends. The melting temperatures of the polymers and of the liquid crystal are shifted down a few degrees with increasing content of CP and polymer, respectively. This is analogous to the phenomenon of melting point depression[12] and provides evidence for some (concentration-dependent) miscibility of the two components. Also, it can be noticed that the melting endotherms of PEA-MDI in the blends are broader than the melting endotherm of the neat polymer. The thermodynamic parameters of the blends studied are listed in Tables I – III. At lower concentrations of the liquid crystal, the LC peaks are not evidenced in the DSC scans.

As can be seen, the melting temperatures of the polymers are shifted down a few degrees and a somewhat more pronounced depression is observed with the blends based on PEA. The melting temperatures of PEA-TDI are lower than the melting temperature corresponding to the neat polymer, but these values do not change with blend composition. The melting enthalpy of the polymers decreases with increasing content of the low molecular weight liquid crystal. These facts show some degree of miscibility in the isotropic (polymer-rich phase). The urethane polymers exhibit higher degrees of phase separation with the TDI-based blends being more phase separated. The variation of melting enthalpy of polymers as a function of CP content is depicted in Fig. 3. The same behaviour for all the studied blends was observed. It can also be seen that melting temperatures of the liquid crystal component are slightly shifted to lower temperatures, a fact which evidences some degree of miscibility in the LC-rich phase, and the melting enthalpy of the CP decreases with increasing content of the polymer. The melting point depression of cholesteryl palmitate is more pronounced as compared with the polymers, suggesting an improved miscibility in the LC-rich phase. The variation of melting enthalpy of the liquid crystal as a function of polymer content is portrayed in Fig. 4. For all the blends studied the same behaviour was observed.

TABLE I. Thermodynamic parameters of the PEA/CP blends

% CP mass	T_1/°C	H_1/J/g blend	H_1/J/g PEA	T_2/°C	H_2/J/g blend	H_2/J/g CP	T_3/°C	H_3/J/g blend	p
0	47.5	99.47	99.47	–	–	–	–	–	–
2	51.0	82.58	84.26	71.5	0.99	49.5	49	1.49	0.63
4	49.2	82.37	85.8	73	3.32	83	50	4.59	0.38
6	50.0	74.64	79.40	74	3.44	57.33	51	5.72	0.56
10	44.0	79.42	88.24	74	8.62	86.2	51	9.18	0.31
16	42.5	80.61	95.96	74.5	11.88	74.25	50	9.04	0.36
32	43.8	55.01	80.89	76	23.08	72.12	54	21.51	0.24
64	43.9	51.69	143.58	76	41.84	65.37	56	38.6	–
80	42.8	40.53	202.65	76	42.24	52.8	54.5	42.00	–
100	–	–	–	78	139.85	139.85	53	102.36	–

T_1 and H_1 - melting temperature and enthalpy of the polymer; T_2 and H_2 - melting temperature and enthalpy of the liquid crystal; T_3 and H_3 - crystallization temperature and enthalpy of the liquid crystal; p - portion of liquid crystal dissolved in the polymer matrix.

TABLE II. Thermodynamic parameters of the PEA-MDI/CP blends

% CP mass	T_1/°C	H_1/J/g blend	H_1/J/g PEA-MDI	T_2/°C	H_2/J/g blend	H_2/J/g CP	T_3/°C	H_3/J/g blend	p
0	29.7	50.99	50.99	–	–	–	–	–	–
2	26.2	25.73	26.25	71.5	3.08	154	46	1.18	–
4	27.5	28.29	29.46	74	3.82	95.5	48	2.22	0.28
6	26.5	26.85	28.56	74.5	5.23	87.16	49	3.76	0.33
8	28.5	33.57	36.48	75	6.79	84.87	53	4.33	0.34
16	27.5	30.65	36.48	76	17.06	106.62	50	2.84	0.09
32	29.2	25.83	37.98	77	33.12	103.5	50.5	20.27	–
65	29.3	20.4	58.28	77	54.39	83.67	51.5	35.07	–
81	27.3	13.49	71	77.5	58.03	71.64	52	46.06	–
100	–	–	–	78	139.85	139.85	53	102.36	–

T_1 and H_1 - melting temperature and enthalpy of the polymer; T_2 and H_2 - melting temperature and enthalpy of the liquid crystal; T_3 and H_3 - crystallization temperature and enthalpy of the liquid crystal; p - portion of liquid crystal dissolved in the polymer matrix.

TABLE III. Thermodynamic parameters of the PEA-TDI/CP blends

% CP mass	T_1/°C	H_1/J/g blend	H_1/J/g PEA-TDI	T_2/°C	H_2/J/g blend	H_2/J/g CP	T_3/°C	H_3/J/g blend	p
0	34.8	53.82	53.82	–	–	–	–	–	–
2	32.5	47.44	48.4	72.5	2.71	135.5	–	–	0.011
4	33.5	30.67	31.94	73	3.78	94.5	–	–	0.296
6	33	42.46	45.17	73	6.02	100.33	–	–	0.236
8	33.5	44.01	47.83	74.5	8.51	106.37	–	–	0.173
31	33.2	29.24	42.37	77	32.4	104.74	50	46.87	–
47	33.5	29.66	55.96	77.5	46.6	99.27	51	68.17	–
78	34.0	21.87	99.40	77.5	50.7	65	52.5	51.25	–
100	–	–	–	78	139.85	139.85	53	102.36	–

T_1 and H_1 - melting temperature and enthalpy of the polymer; T_2 and H_2 - melting temperature and enthalpy of the liquid crystal; T_3 and H_3 - crystallization temperature and enthalpy of the liquid crystal; p - portion of liquid crystal dissolved in the polymer matrix.

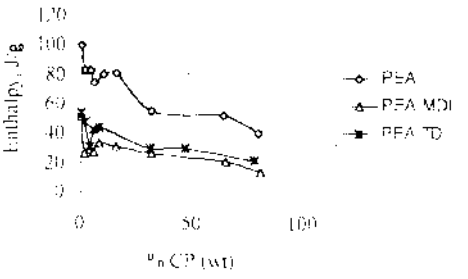

Fig. 3. Variation of the melting enthalpy of the polymers as a function of the CP content.

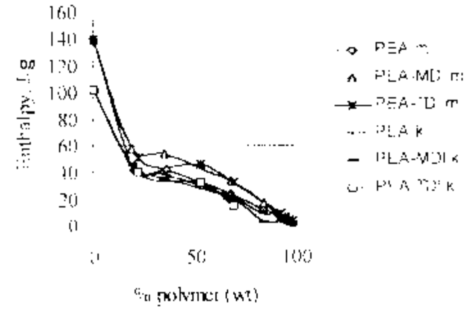

Fig. 4. Variation of the melting and crystallization enthalpies of CP as a function of the polymer content.

Taking into account that the appearance of the melting transitions of the liquid crystal means phase separation, the portion of the liquid crystal dissolved in the polymer matrix was calculated as follows using the equation.[13]

$$p = 1 - H_2/(f\ H_{LC}) \tag{1}$$

where, p – portion of liquid crystal dissolved in the polymer matrix; f – weight fraction of polymer in the blend; H_2 – melting enthalpy of the liquid crystal in the blend, J/g CP and H_{LC} – melting enthalpy of pure liquid crystal (H_{LC} = 139.85 J/g CP).

It can be seen from Tables I – III that, in general, p tends to decrease with increasing content of liquid crystal. This fact evidences the concentration-dependent miscibility found for these blends.

The thermal behaviour of the blends was studied on cooling too. The crystallization temperatures and enthalpies are listed in Tables I – III. It can be seen, that blending affects the crystallization temperatures of the liquid crystal for all blends. The associated enthalpy decreases with increasing content of polymer (Fig. 4). The crystallization of the polymers could not be evidenced under these investigation conditions. The isotropic-cholesteric and cholesteric-smectic transition were not observed in the cooling runs of the DSC thermograms. This is in contrast with the thermal behaviour of the polytetrahydrofuran-cholesteryl palmitate blends studied,[14] where the above mentioned peaks were observed in the cooling scans. This fact shows that the polyether-based blends are more phase separated and weaker interactions are involved, as compared with the blends taken in this study.

The phase separation of these blends was also studied by means of polarizing optical microscopy. The appearance of the mesophases was observed for the TDI-based blends at a lower content of liquid crystal (4 % mass) than for the other two blends (16 % mass). For example, the photomicrograph at 60 ºC after cooling from isotropic state, of the 8/92 CP/PEA-TDI blend is presented in Fig. 5 in which the texture, consisting of birefringent spots dispersed in an isotropic background, can be seen. Crystallization of the low molecular weight liquid crystal was observed for all the compositions studied. It was observed that the liquid crystal affects the crystallization of the polymers, *i.e.,* on cooling from the isotropic state a spherulitic morphology, typical of semi-crystalline polymers, was formed. For example, the photomicrograph at 30 ºC, after cooling the same blend as presented in Fig. 6 from isotropic state is shown. The above mentioned spherulitic morphology can be seen from this photograph.

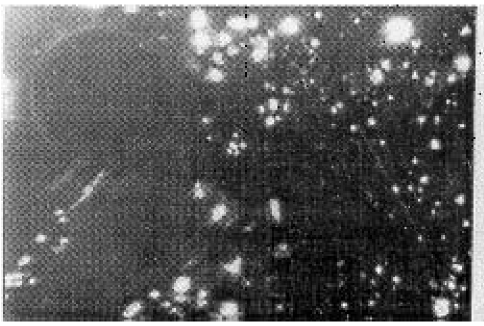

Fig. 5. Photomicrograph at 60 ºC of the 8/92 CP/PEA-TDI blend after cooling (150).

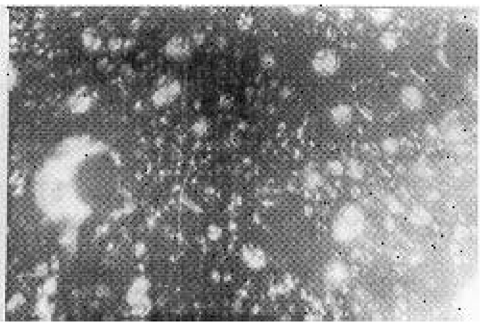

Fig. 6. Photomicrograph at 30 ºC of the 8/92 CP/PEA-TDI blend after cooling (150).

ИЗВОД

КАРАКТЕРИЗАЦИЈА СМЕШЕ ПОЛИМЕР–ТЕЧНИ КРИСТАЛ

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Припремљене су смеше различитих састава полу-кристалних полимера (полиетилен адипата и два поли(естар-уретан)а са течним кристалима холестерил палмитата ливењем из раствора. Један од поли(естар-уретан)а има као основу 2,4-толилен диизоцијанат (TDI), а други 4,4´-дифенилметан диизоцијанат (MDI). Диференцијалном скенирајућом калориметријом и оптичком микроскопијом са поларизованим светлом испитиване су мешљивости и фазни прелази у целој области концентрација.

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REFERENCES

1. J. R. S. Rodrigues, A. Kaito, V. Soldi, A. T. N. Pires, *Polym. Int.* **46** (1998) 138
2. C. C. Riccardi, J. Borrajo, R. J. J. Williams, H. M. Siddigi, M. Dumon, J. P. Pascault, *Macromolecules* **31** (1998) 1124
3. Z. Q. Lin, H. D. Zhang, Y. L. Yang, *Macromol. Theory Simul.* **6** (1997) 1153
4. M. Pracella, B. Bresci, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect A* **266** (1995) 23
5. G. M. Russell, B. J. A. Paterson, C. T. Imrie, S. K. Heeks, *Chem. Mater.* **7** (1995) 2185
6. H-K. Jeong, H. Kikuchi, T. Kajiyama, *New Polym. Mater.* **5** (1998) 103
7. C. Carfagna, E. Amendola, M. Giamberini, H. Hakemi, S. Pane, *Polym. Int.* **44** (1997) 465
8. L. Carpaneto, A. Ristango, P. Stagnaro, B. Valenti, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **290** (1996) 213
9. C-L. Lin, L-C. Chien, *Macromol. Rapid Commun.* **16** (1995) 869
10. A. K. Kalkar, A. A. Bhalwandar, *Polym. Sci.* **2** (1994_) 573
11. A. K. Kalkar, V. V. Kunte, A. A. Deshpande, *Macromol. New Front., Proc.IUPAC Int. Symp. Adv. Polym. Sci. Technol,* **1** (1998) 239
12. P. J. Flory, *Principles of Polymer Chemistry,* Cornell University Press, Ithaca, 1953, p. 568
13. S-C. Peng, J-W. Yu, S-N. Lee, *J. Polym. Sci. B: Polym. Phys.* **35** (1997) 1373
14. D. Filip, C. I. Simionescu, D. Macocinschi, I. Parashiv, (submitted).