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Compatibility studies of poly(ether imide) with liquid crystal mixtures

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The miscibility of poly(ether imide) (Ultem) and liquid crystal 4-[(2S)-2-methylbutoxy]-N-[[4-[(5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluorodecyl)oxy]phenyl] methylene] benzenamine (MTOPMB) were investigated at 30 ^{o}C in dilute chloroform solutions by viscometric analysis. The intrinsic viscosity and interaction parameters were determined for individual components and binary Ultem/MTOPMB mixtures in compositions such as 80/20, 60/40, 40/60 and 20/80 (w/w) in chloroform solutions. The miscibility criteria on the basis of the sign of Δb_m, $\Delta b'_m$, $\Delta b''_m$ and $\Delta[\eta]_m$ which are the difference between their experimental and ideal values were used in viscometric analysis. The data suggested that the studied binary mixtures were immiscible except the one of Ultem/MTOPMB: 80/20 (w/w). The miscibility of the mixtures was also studied by differential scanning calorimetry (DSC) and polarised light optical microscopy (POM).

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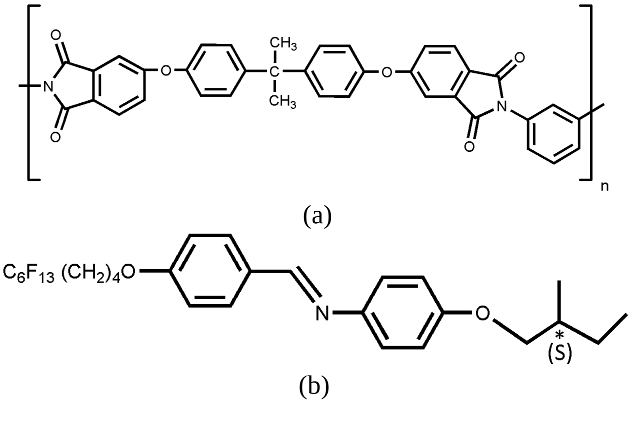
1. Introduction

Polyether imides such as Ultem, a well-known class of engineering thermoplastic polymers, offer exceptional thermal, chemical and mechanical stability and available in large quantities. Their cost is close to other thermoplastic polymers that offer similar performance and significantly more economical than small batch thermoplastic polymers. Ultem has higher diffusion selectivity due to their fused ring structure and rigid backbone. Its high glass transition temperature allows higher pressure and temperature applications without plastic deformation [1].

Mixing of materials with different physical characteristics leads to produce new functional materials for practical applications [2]. Recently, mixtures of polymers and low molecular weight liquid crystals have received considerable attention in scientific area due to their great potential for various modern applications, such as new displays, memory storage and holographic devices [3-5]. The multicomponent nature of these materials provides some properties that cannot be realized with the individual components alone [6]. The miscibility of the mixtures of a polymer and a liquid crystal (LC) mainly depend on the chemical structure, mesophase properties, molecular weight and concentration of the components [7-9]. There have been number of techniques to study the miscibility of mixtures such as DSC, neutron scattering, inverse gas chromatography, electron microscopy, etc. [10,11]. Most of the techniques may be complicated, costly and time consuming. However, viscosity is simple, low cost and rapid technique and provides valuable information to determine polymer-polymer miscibility [12-16]. Although viscosity has been widely used to investigate the miscibility of polymer mixtures, it is a novel technique for determination of miscibility of a polymer with a LC.

In this work, we have studied the miscibility and morphology of binary mixtures of a polymer and a LC, i.e., Ultem and MTOPMB by solving them in chloroform. Their miscibility parameters were found by viscosity measurements at 30 ^{o}C as suggested by several research groups such as Krigbaum and Wall [17], Catsiff and Hewett [18] and Garcia et al. [19]. DSC and POM measurements were also carried out to analyze the miscibility, thermal properties and morphology of the mixtures. Chemical structures of Ultem and MTOPMB were given in Scheme 1.



Scheme 1. Chemical structure of Ultem (a) and MTOPMB (b).

2. Experimental

2.1. Materials and instrumentation

All viscosity measurements were performed at 30 ^{o}C using Schott visco system AVS 470. Stock solutions of the binary and ternary systems were freshly prepared by dissolving appropriate amount of polymers in chloroform into a concentration of 0.3 g/10 cm^3 solutions. For each measurement, 5 cm^3 stock solution was loaded into the viscosimeter and diluted by adding 2 cm^3 chloroform to yield several lower concentrations. The efflux time of each solution was taken as the average of four readings agreed within ±0.5%.

The morphology and thermal properties of Ultem/MTOPMB mixtures were investigated using POM and DSC. Microscopy was performed on a Leitz Laborlux 12 Pol polarizing microscope, equipped with a Linkam THMS 600 hot stage and a Linkam TMS93 temperature controller. DSC-thermograms were recorded on a Perkin-Elmer DSC-7, with a 10 Kmin^{-1} heating and cooling rate.

2.2. Theoretical background on viscosity

Huggins' equation for a mixture is written as [20]

$$(\eta_{sp})_m / c_m = [\eta]_m + b_m c_m \tag{1}$$

where c, $(\eta_{sp})/c$, $[\eta]$, and b are concentration, reduced viscosity, intrinsic viscosity and interaction parameter of the polymer in the solution, respectively, while subscript "*m*" denotes "mixture". The miscibility of the components of a mixture is estimated by comparison of the experimental and ideal values of b_m and $[\eta]_m$.

Krigbaum and Wall [17] have defined the ideal value of the interaction parameter b_m^{id} as

$$b_m^{id} = b_1 w_1^2 + b_2 w_2^2 + 2 b_{12}^{id} w_1 w_2 \tag{2}$$

by defining b_{12}^{id} as a geometric mean;

$$b_{12}^{id} = b_1^{1/2} b_2^{1/2} \tag{3}$$

where w is weight fraction of the component in the mixture and subscripts 1 and 2 indicates the polymer and LC, respectively.

Catsiff and Hewett [18] have defined the ideal value $b_{12}^{id'}$ as an arithmetic mean

$$b_{12}^{id'} = (b_1 + b_2)/2 \tag{4}$$

On the other hand, Garcia et al. [19] have stated that the Eq. (2) proposed by Krigbaum and Wall was mathematically erroneous and have defined the ideal value of the interaction parameter $b_m^{id''}$ as

$$b_m^{id''} = b_1 w_1^2 + b_2 w_2^2 \tag{5}$$

Garcia et al. have also proposed another miscibility criterion based on the difference between the experimental and ideal values of $[\eta]_m$ assuming that the intrinsic viscosity can be treated as an excess property. The value of $[\eta]_m^{id}$ has defined as

$$[\eta]_m^{id} = [\eta]_1 w_1 + [\eta]_2 w_2 \tag{6}$$

3. Results and discussion

The synthesis of MTOPMB was carried out by the p-toluenesulfonic acid catalyzed condensation of the semifluorinated alkyloxybenzaldehyde and (S)-4-(2-methylbutoxy)-aniline in toluene. The preparation procedure, spectroscopic data and the liquid crystalline properties for the imine mesogen MTOPMB have been reported in a previous study [21]. The phase transition temperatures and enthalpies of the LC are shown in Table 1.

Table 1. The phase transition temperatures of the MTOPMB.

Compound	T/ °C [ΔH / kJ mol^{-1}]
MTOPMB [21]	Cr 94 [28.3] (SmX* 70 [1.3]) SmC* 118 [0.2] SmA 142 [4.2] Iso

[a] Enthalpy values in brackets, heating rate 10 K min^{-1}; abbreviations: Cr= crystalline, SmA= nontilted smectic phase, SmC*= chiral smectic C phase, SmX = low temperature mesophase with unknown structure and Iso= isotropic liquid phase; monotropic transition is in parentheses.

Fig. 1 shows the lines plotted according to Eq. 1, i.e. variation of reduced viscosity (η_{sp}/c) with total concentration, c of the mixtures of Ultem/MTOPMB in the compositions: 100/0, 80/20, 60/40, 40/60, 20/80 and 0/100 by weight, respectively in the chloroform solution at 30 ^{o}C.

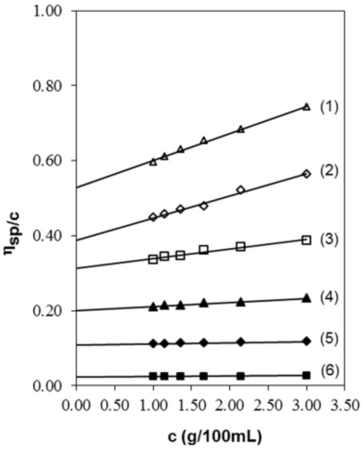


Fig. 1. Reduced viscosity values (η_{sp}/c) against total concentrations of the Ultem and MTOPMB and their mixtures of Ultem/MTOPMB the following compositions: 100/0 (1), 80/20 (2), 60/40 (3), 40/60 (4), 20/80 (5) and 0/100 (6) by weight at 30 ^{o}C in chloroform.

The intrinsic viscosities and interaction parameters of the mixtures and individual components have been determined from the intercept and slope of the linear lines in the Fig. 1. The data were collected in Table 2.

Table 2. Experimental dilute solution viscosity data of the mixtures and individual components at 30 ^oC in chloroform.

Ultem/MTOPMB at 30 ^oC in chloroform	b_m (cm^6/g^2)	$[\eta]_m$ (cm^3/g)	r^2
100/0	0.0723	0.5281	0.9962
80/20	0.0588	0.3882	0.9863
60/40	0.0255	0.3137	0.9693
40/60	0.0108	0.2002	0.9626
20/80	0.0029	0.1089	0.9357
0/100	0.0016	0.0220	0.9260

The miscibility parameter of the mixture is obtained as a difference between the experimental interaction parameter b_m, and their corresponding ideal values proposed by Krigbaum and Wall in the Eqs. 2 and 3; by Catsiff and Hewett in the Eqs. 2 and 4; and by Garcia et al. in Eq. 5. Similarly, the miscibility parameter based on intrinsic viscosity is obtained as the difference between the experimental intrinsic viscosity and ideal one found from Eq. 6. The criteria related to miscibility are that the mixture is miscible if $\Delta b_m = b_m - b_m^{id} > 0$ or $\Delta b'_m = b_m - b_m^{id'} > 0$ or $\Delta b''_m = b_m - b_m^{id''} > 0$ or $\Delta[\eta]_m = ([\eta]_m - [\eta]_m^{id}) < 0$ since attractive intermolecular forces are present between the components of the mixture. In the case of $\mathbf{\Delta} b_m < 0$ or $\mathbf{\Delta} b'_m < 0$ or $\mathbf{\Delta} b''_m < 0$ or $\mathbf{\Delta}[\eta]_m > 0$, the mixture is immiscible since repulsive intermolecular forces are present. If the difference is vanishing neither attractive nor repulsive intermolecular forces are present.

All of the miscibility parameters of Ultem/MTOPMB mixtures obtained from viscosity measurements were given in Table 3. According to the miscibility criteria given above, the values in the Table 3 suggest that the components are miscible if the ratio of MTOPMB is 20% in the mixture but they become immiscible if the ratio of LC in the mixture increases.

Table 3. Numerical values of miscibility parameters for the mixtures.

Ultem/ MTOPMB at 30 ^oC in chloroform	Δb_m (cm^6/g^2)	$\Delta b'_m$ (cm^6/g^2)	$\Delta b''_m$ (cm^6/g^2)	$\mathbf{\Delta}[\eta]_m$ (cm^3/g)	Miscibility
80/20	0.009	0.001	0.012	-0.039	Miscible
60/40	-0.006	-0.018	-0.001	-0.012	Immiscible
40/60	-0.007	-0.019	-0.001	-0.024	Immiscible
20/80	-0.004	-0.013	-0.001	-0.014	Immiscible

DSC was used to investigate the validity of the miscibility criteria based on viscosity by comparing the thermograms of Ultem/MTOPMB in the composition of 80/20 (miscible) and 20/80 (immiscible) with that of individual MTOPMB given in Fig. 2.

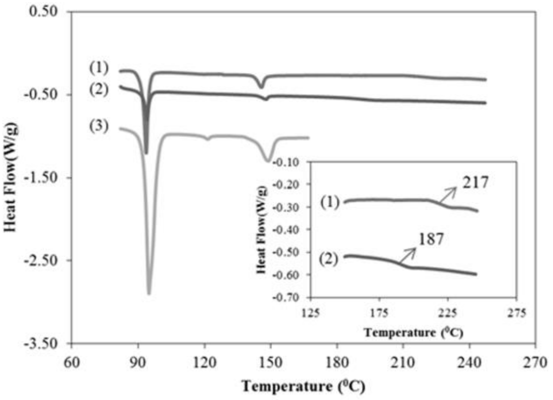


Fig. 2. DSC scans of compound MTOPMB (3), Ultem/MTOPMB in the ratio 80/20 (2) and 20/80 (1) during the second heating process.

The glass transition temperature (T_g) of Ultem was determined in our previous studies as 220 ^oC. In Fig. 2, the T_gs of Ultem/MTOPMB: 80/20 and 20/80 were determined as 187 and 217 °C, respectively. It was seen that T_g of the former mixture (miscible) was considerably lower than that of Ultem although the T_g of the latter one (immiscible) was almost unchanged. Since it is well known that an impurity in a polymer decreases its T_g if it is miscible whilst the T_g of the polymer does not change considerably in the case of immiscibility, DSC results support the result obtained by viscosimetry that the mixtures of Ultem/MTOPMB: 80/20 and 20/80 are miscible and immiscible, respectively.

The morphology of the mixtures of Ultem/MTOPMB was investigated by POM in the mesomorphic temperature range of MTOPMB. The imine mesogen MTOPMB shows smectic polymorphism [20]. The transition temperature of MTOPMB from smectic mesophase to isotropic mesophase is 142 °C. The samples of Ultem/MTOPMB (80/20 and 20/80) were heated to approximately 15 °C above the smectic-isotropic transition temperature of the MTOPMB. Left for about 15 min in the isotropic state, then they were cooled slowly at a rate of 5 °C/min. Fig. 3 shows photomicrographs at 130 °C of pure components and Ultem/MTOPMB (80/20 and 20/80) mixtures. Fig. 3 shows photomicrographs at 130 °C of pure components and Ultem/MTOPMB (80/20 and 20/80) mixtures.

The birefringent regions of MTOPMB in the composition Ultem/MTOPMB (80/20) slightly appear in Ultem-rich domains. In regions rich in MTOPMB, the isotropic-smectic transition occurs at 138 °C. As mentioned in Reference [3], liquid crystals which are impured with a polymer may show a decrease in their phase transition temperatures. This observation indicates that in these regions Ultem molecules are partially mixed with liquid crystal component.

The phase segregation between Ultem and MTOPMB occurs for composition in Ultem/MTOPMB (20/80) (at 130 °C, see Fig. 3d). The typical morphology of Ultem and texture of smectic mesophase independently appears in Ultem/MTOPMB (20/80) mixture. The isotropic-smectic phase transition in liquid crystal-rich regions occurs as observed for pure liquid crystal component MTOPMB. It is obvious that the observations on the morphology of MTOPMB confirm the results obtained from viscosity measurements related to its miscibility with Ultem. These results suggest that viscosimetry is a reasonable method in determination of miscibility of a polymer with a liquid crystal.

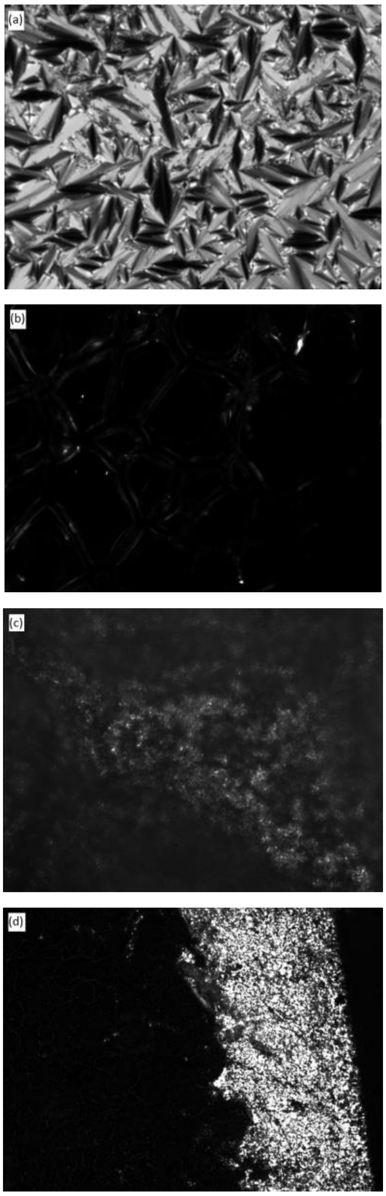


Fig. 3. Optical polarized photomicrographs as observed on cooling at 130 ^{o}C for pure components and mixtures in different composition of Ultem/MTOPMB; (a) smectic A texture of MTOPMB; (b) amorphous Ultem; (c) Ultem/ MTOPMB: 80/20 and (d) Ultem / MTOPMB: 20/80.

4. Conclusions

The miscibility of Ultem and MTOPMB was investigated by viscosity, DSC and POM. According to the viscosity results, the studied mixtures are immiscible except the one in the composition of Ultem/MTOPMB: 80/20. The DSC and POM techniques support the viscosity results. This study suggests that miscibility criteria proposed by Krigbaum and Wall, Catsiff and Hewett, Garcia et al. can be used accurately in determination of the miscibility of a polymer with a LC at least for the mixtures studied in this study. In conclusion, it can be stated that viscosity technique can be expanded to determine the miscibility behavior of a polymer with a LC.

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