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Miscibility of a nematic liquid crystalline polymer pair

Tsung-Tang Hsieh[a], Carlos Tiu[b], George P. Simon[c,*]

[a]UMC, Advanced Technology Development, Hsin-Chu 30077, Taiwan, ROC
[b]Department of Chemical Engineering, Monash University, Clayton, Vic. 3800, Australia
[c]School of Physics and Materials Engineering, Monash University, Clayton, Vic. 3800, Australia

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Abstract

This work investigates the miscibility of two commercially important thermotropic main chain liquid crystalline polymers (LCPs), Vectra A950 and Vectra B950, using dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC) and positron annihilation lifetime spectroscopy (PALS). Although previously reported to be either miscible or show a compositional-dependent miscibility, they are shown here to be immiscible based on DMA, DSC and PALS results. The latter technique is somewhat more novel in its use to assess miscibility, by probing the free volume of the blends and comparing this to rule-of-mixtures values of the two components. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Thermotropic liquid crystalline polymer; Miscibility; Blend

1. Introduction

Miscibility between different liquid crystalline polymers (LCPs) can be an interesting issue given the dual polymeric and liquid crystalline nature of these materials. For example, the behaviour observed for low molecular weight liquid crystals (LMWLCs) is that those of the same class (e.g. nematic) are generally miscible [1], whereas blends of different polymers without strong interactions between different macromolecules tend to be immiscible [2]. The related literature to date shows that the polymeric characteristics of LCPs often dominate as far as miscibility is concerned, since many nematic LCPs have been found to be immiscible [3–6] and, occasionally, miscibility of LCPs of the different classes (e.g. nematic and smectic [7]) has been reported.

Miscibility of polymer pairs is often determined by thermal and/or mechanical methods, such as differential scanning calorimetry (DSC) or dynamic mechanical analysis (DMA). For miscible systems, a single glass transition temperature (T_g) is observed and moves in temperature location in proportion to concentrations of the constituents, as well as often varying likewise in intensity. For immiscible blends, two distinct T_gs belonging to the pure components occur, remaining constant in temperature location, the peak size varying in magnitude according to the component concentration. Morphological observation such as by electron microscopy can also serve as complementary evidence to confirm the conclusion drawn from above-mentioned techniques, provided the electron densities of the various phases differ sufficiently. Whilst this may be enhanced by staining, for example, not all polymers are so amenable to this technique — LCPs with low solvent uptake being an example of this.

Total miscibility between two widely used and commercially important LCPs, Vectra A950 and Vectra B950, was reported recently [8], although an earlier study by Kenig et al. [9] on the same materials indicated a more complicated scenario, composition-dependent miscibility. Our research laboratory has reported results on a number of LCP blends in recent times [6,10–12] in terms of their rheology, miscibility and free volume. The aim of this paper is to investigate this system and attempt to clarify the difference in miscibilities reported by both groups [8,9] using similar techniques. In addition, a more novel sub-atomic technique, positron annihilation lifetime spectroscopy (PALS), which probes excluded or free volume in the blends is used to assess the miscibility or otherwise of these polymers. Given that synergies are often observed in the blending of two LCP phases [10] (such as lower viscosity or higher modulus) and that the components of this blend series are readily available (albeit often in a filled form) it is a blend worthy of further investigation.

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* Corresponding author. Fax: +61-3-9905-4940.
E-mail address: george.simon@spme.monash.edu.au (G.P. Simon).

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2. Experimental

The materials studied are Vectra A950 and Vectra B950 obtained from Ticona (USA) (formerly Hoechst-Celanese). Vectra A950 (referred to as Vectra A hereafter) is a well-studied copolyester, which consists of 73 mol% *p*-hydroxybenzoic acid (HBA) and 27 mol% 2-hydroxy-6-napthoic acid (HNA). Vectra B950 (referred to as Vectra-B) is a terpolymer, a polyesteramide, which consists of 60 mol% HNA, 20 mol% terephthalic acid (TA) and 20 mol% aminophenol (AP).

All materials were dried in a vacuum oven at 100°C for 4 h prior to being processed and measured. A Haake Rheomix 600 internal mixer equipped with two sigma rotors was used to prepare blends in the presence of 0.2% trans-esterification inhibitor (based on total weight of the blend), Irganox 1098 (Ciba-Geigy). The mixture was processed at 320°C for 5 min with a rotor speed of 20 rpm under a nitrogen atmosphere.

DMA was carried out on a Rheometrics RDAII in a torsion mode. Measurements were conducted in a 2°C step with a soaking time of 1 min for thermal equilibrium in an environmental chamber purged with dry nitrogen and a frequency of 1 Hz over a temperature range from 50 to 180°C was employed.

A DuPont 9900 thermal analyzer equipped with a differential scanning calorimetric (DSC) module was used to study the thermal transitions of the blends. All of the samples of 10–15 mg were initially scanned over a temperature range from 50 to 300°C at a heating rate of 20°C/min and cooled to 50°C at a cooling rate of 20°C/min immediately upon reaching the final temperature. All samples were again scanned from 50 to 300°C at the same heating rate. The measurements were carried out in a nitrogen atmosphere. The reported results were taken from the second heating runs of the experiments to avoid any experimental artefact arising from previous thermal and mechanical treatments.

Free volume properties were measured by PALS. Theories and details of the PALS technique and its application to polymers, and in particular to polymer blends, can be found elsewhere [6,13] and references therein. In short, it uses a sub-atomic probe, the positron (anti-particle of the electron) to probe the volume between polymer chains. The positron is injected into the plastic coupons (ca. 1.5 mm thick) from an appropriate, decaying radioactive source. Whilst the positron itself eventually gets annihilated by an electron, other species consisting of positrons and electrons in different coupled spin states are also formed. Of these, one forms within free volume sites and is long-lived. The species is known as *ortho*-positronium (*o*-Ps) and its lifetime (τ_3) and intensity (I_3) are indicative of the size and concentration of free volume sites, respectively. This lifetime can be converted by a semi-empirical equation (see the various general references on PALS given above) into a radius, R, and thus a volume, V ($=(4/3)\pi R^3$), of the free volume sites. Provided that there is little chemical interaction between the polymer and the sub-atomic species (such as may cause quenching of positronium formation, and is absent in the polyester systems being studied here), the result allows a characterisation of the average free volume properties. Further, it is possible to obtain a comparative measure of the free volume fraction, h, expressed in per cent can be determined [14] from the equation

$$h = CI_3V \tag{1}$$

where V is in Å^3, I_3 is in per cent and C is empirically determined from comparison with pressure–volume–temperature data and is found to be approximately 1.8×10^{-3} in many glassy polymer systems [14–17]. In any case, it is only viewed as a comparative value in this work (often people present simply a number such as VI_3).

The PALS experiments were carried out on an automated EG&G Ortec fast–fast coincidence system using a ^{22}Na source of approximately 30 μCi contained between very thin titanium foils at 22 ± 1°C. The resolution of the instrument obtained from the ^{60}Co prompt curve was 280 ps and the source correction was negligible and not removed.

3. Results and discussion

Fig. 1 shows the tan δ curves of the Vectra-A + Vectra-B blends as a function of temperature. T_g of Vectra-A is found to be at 100°C whilst Vectra-B exhibits its glass transition at around 135°C. T_gs of both Vectra-A and Vectra-B can be observed in blends containing 25 and 50% Vectra-B, whilst the single tan δ peak shown by the 75% Vectra-B blend shifts slightly to a lower temperature and is very close in temperature location and height to that of neat Vectra-B. The single transition observed for the 75% Vectra-B blend is not interpreted as an indication of molecular miscibility, since if this was the case addition of 25 wt% Vectra-A should be able to significantly reduce the blend T_g. They thus appear to be rather immiscible according to the DMA

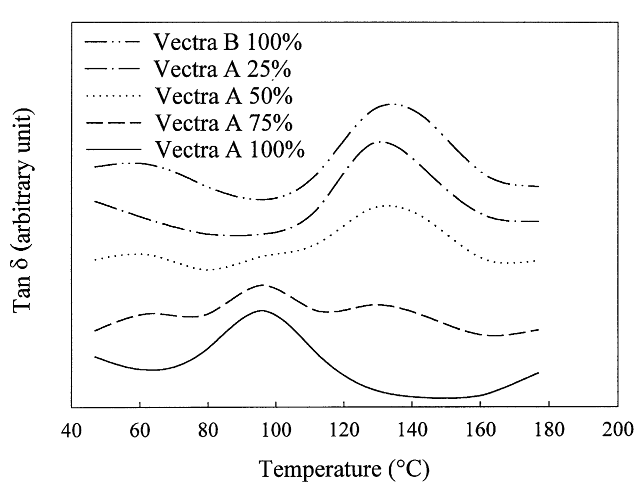

Fig. 1. Dynamic mechanical tan δ spectra of the Vectra-A + Vectra-B blends in a torsion mode at 1 Hz.

results, although not quite in the standard fashion. A secondary relaxation can be seen at about 50°C for the Vectra-B material and blends and has previously been ascribed to the local motion of the HNA unit [18]. Its precise location depends on the HNA concentration and the nature of the other groups to which it is attached [19]. It is found to occur at lower temperatures in Vectra-A alone, at about 20°C, and thus out of the range of the data shown here.

It is pertinent to examine the chemical structures of both materials in relation to expectations of miscibility or otherwise. Vectra-A and Vectra-B have similar molecular architectures as they both contain some significant component of HNA units, which introduce an offset effect on the otherwise all-para molecular chains [20]. However, immiscibility of Vectra-A + Vectra-B blends is likely to arise from the strong hydrogen bonds forming in Vectra-B between nitrogen atoms of amide groups and oxygen atoms of amide and ester groups. This may lead to a cohesive Vectra-B phase, which excludes the Vectra-A component. In addition, Vectra-B has a more complicated molecular chemistry than Vectra-A, because Vectra-B is a copolyesteramide rather than simply a copolyester as is Vectra-A. The non-appearance of the glass transition of Vectra-A in the tan δ trace of the 75% Vectra-B blend is expected to result from low content of Vectra-A and its weak glass transition relaxation, which really only shows as a slightly diluted, marginally shifted Vectra B relaxation maxima.

DMA of the Vectra-A + Vectra-B blends has also been studied by Kenig et al. [9] and somewhat different damping behaviour (two peaks for the 25% blend and one peak for the 50 and 75% Vectra-B blends) was observed and a different interpretation was given. They concluded that the blend miscibility is composition dependent with better miscibility occurring at higher Vectra-B content (the 75% Vectra-B blend). The heating rate used was 5°C/min and the applied frequencies were 3–10 Hz, which are both greater than those used in the present study (ca. 2°C/min and 1 Hz) and thus a possible reason for the contrasting results. The resolution of DMA or other thermal techniques is highly heating rate and frequency dependent, that is, lower the heating rate and frequency, the better the resolution. The T_g of the Vectra-A component is very weak for the 50% Vectra-B blend as seen in Fig. 1, whilst it became unnoticeable in Kenigs' study (Fig. 4 of Ref. [9]). The relatively higher T_g values reported by Kenig et al. [9], 110°C for Vectra-A and 150°C for Vectra-B, further demonstrate the influence of the higher heating rates and frequencies used. It should be noted that neither precise details of blending times and temperatures were given, nor special precautions were taken for the possibility of transesterification.

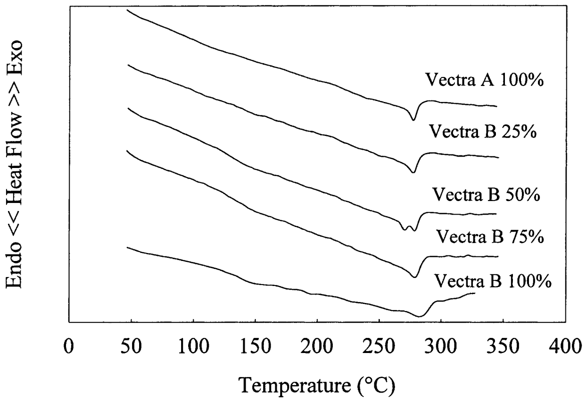

Fig. 2. DSC thermograms of the Vectra-A + Vectra-B blends.

DSC measurements were also carried out on the Vectra-A + Vectra-B blends and the results are shown in Fig. 2. Vectra-A shows an endothermic peak at 278°C, whilst melting point of the Vectra-B is at 282°C. The 25 wt% Vectra-B blend has an endothermic peak at 275°C and the 75 wt% Vectra-B displays an endothermic peak at 280°C. By contrast, the 50% Vectra-B blend shows two peaks occurring at 272 and 281°C, respectively. From the DSC results, the 50 wt% Vectra-B blend exhibits two melting processes ascribed to Vectra-A and Vectra-B phases, which indicates phase separation in the crystalline regions of the blend. A single and reduced melting point of a LCP + LCP blend has previously been considered as an indication of blend miscibility [8] but co-crystallization of polymer pairs has been considered to be unlikely [21]. This is because, in addition to the thermodynamic molecular affinity required for amorphous polymers to be miscible, crystalline structures and factors such as matching of crystallization kinetics would be required. The use of melting points as an indicator of miscibility is more difficult since semi-crystalline LCPs, such as Vectra-A and Vectra-B, typically have a degree of crystallinity of about 20% for quenched samples [22]. The melting behaviour of the minor component may not be shown strongly in a DSC trace, and further be reduced in magnitude by dilution in a blend. Whilst the melting phenomenon only relates to the crystalline regions of the LCPs, DMA predominantly probes the more abundant amorphous phase of the LCPs. DMA is thus a more sensitive technique to determine the miscibility of LCP + LCP blends, with DSC and crystalline melting peaks as a supplementary method. For blends of Vectra-A and Vectra-B, both DMA (amorphous region) and DSC (crystalline region) results indicate that they are largely immiscible. The differences in molecular chain interactions seem to dominate the miscibility behaviour of Vectra-A and Vectra-B, although both are nematic and contain some concentration of HNA units.

The more recent study by Hakemi [8] concluded that Vectra-A and Vectra-B were fully miscible. His blends were prepared by repeated heating and cooling (3–4 times) of the mixed LCPs, instead of melt blending, which is commonly employed for polymer blend preparation. The evidence presented in support of the miscibility is based on DSC results where it was found that the T_g of the blends are all around 135°C and only one melting point for each blend is observed, which is lower than those of the component

LCPs. Transesterification occurring in polymers containing ester linkages at elevated temperatures is a common phenomenon [23] and thus needs to be taken into consideration. As the mixture in Hakemi's study [8] was repeatedly heated in DSC, with no specified precaution taken to inhibit such reaction taking place between Vectra-A and Vectra-B, transesterified block copolymer or even random copolymer may result, rather than a polymer blend. Therefore, the single and also lower melting point determined might come from transesterified materials. The transesterified, blocky LCP is likely to have a lower melting point as it has been known that complication of molecular structure leads to difficulty in crystallisation and a lower melting point as a result [20]. Other evidence provided by Hakemi [8] in favour of miscibility was that the blends showed only the characteristic T_g of the Vectra-B. However, since Vectra-A shows a very weak glass transition, which has a much lower strength than that of Vectra-B (Fig. 1), it would be difficult to detect from DSC thermograms even if it exists (Fig. 2).

PALS has been applied to the study of vacancy-type defects in metals, ceramics and semi-conductors for many years. The analogue of the vacancy-type defect in metals measured by the *o*-positronium lifetime in polymers is the free volume of their amorphous region. As mentioned earlier, the average free volume size (V) in Å^3 is the PALS property presented as a function of concentration in this paper and the results are shown in Fig. 3, as is the total free volume fraction h (%). The average free volume size is found to be around 38 Å^3 for Vectra-A and 31 Å^3 for Vectra-B. The free volume size of the blends is either very slightly higher than the weighted average (the 25 and 50% Vectra-B blends) and much greater than the weighted average (the 75% Vectra-B blend). In contrast, it has been shown in a number of instances (and summarised, for example, in Ref. [13]) that the PALS volume size of miscible polymer blends is usually smaller than the rule of mixtures value determined from the value of the components, that is, it shows a negative deviation from linear additivity. This has been surmised to be due to the favourable intermolecular interactions, which draw molecular chains closer together [13] and has been demonstrated in molecular modelling of miscible polymer blends [24,25]. This appears to add weight to the idea that Vectra-A + Vectra-B blends are not miscible. Indeed, as in this system, a clearly immiscible thermoplastic blend of polystyrene and poly(vinyl acetate) was also found to slow a slight positive deviation from the rule of mixtures, ascribed to being due to the extra free volume arising at the interface [26].

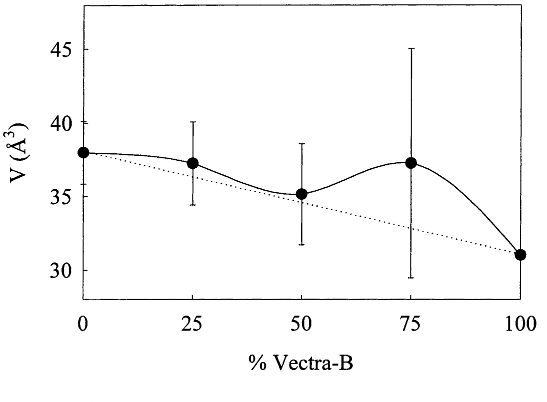

Fig. 3. Average free volume (V) of the Vectra-A + Vectra-B blends derived from PALS parameters.

4. Conclusions

Blends of two LCPs, Vectra-A and Vectra-B were prepared and their miscibility investigated. Although early studies showed that these blends were either fully miscible or displaying composition-dependent miscibility, the present study confirmed the immiscibility of the blends. Double tan δ peaks in DMA spectra were observed for the 25 and 50% Vectra-B blends, whilst the 75% Vectra-B blend showed a single tan δ peak due to dilution-out of the weak glass transition of Vectra-A. DSC results showed two melting points for the 50% Vectra-B blend and one melting point for the other blends. Average free volume size of the blends derived from PALS parameters indicate that the 75% Vectra-B blend has much larger free volume than predicted from linear additivity of the components, which supports the immiscibility interpretation of the blends if the interface is 'poor' in the sense that free volume resides at it.

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