Blends containing two thermotropic liquid crystalline polymers: Effects of transesterification on miscibility and rheology

Tsung-Tang Hsieh*, Carlos Tiu, Kuo-Huang Hsieh[1] and George P. Simon[2]

Department of Chemical Engineering, Monash University
Clayton, Victoria, Australia 3168
[1]*Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan*
[2]*Department of Materials Engineering, Monash University*
Clayton, Victoria, Australia 3168

Abstract

Blends of two thermotropic liquid crystalline polymers, HX2000 and Vectra A950, were prepared by melt blending. Effects of transesterification on these blends are investigated by comparing properties of the blends with and without the addition of an inhibitor, in terms of blend miscibility and rheology. Both the uninhibited and inhibited blends are found to be largely immiscible with very limited miscibility in HX2000-rich phase. No strong evidence indicates the occurrence of transesterification in the blends in the solid state. Dynamic rheological behaviour, such as shear storage modulus (G') and shear loss modulus (G") as a function of frequency, of the blends are interpreted by a three-zone model. HX2000 shows terminal-zone and plateau-zone behaviour, whilst Vectra A950 shows plateau-zone and transition-zone behaviour. The un- inhibited blends show plateau-zone behaviour up to 50% Vectra A950 content and the inhibited blends show plateau-zone behaviour up to 60% Vectra A950 content. Compositional dependence of the complex viscosities of the uninhibited and inhibited blends displayed positive deviations from additivity, which is a characteristic feature for the immiscible thermoplastic blends. When under steady shear, both the uninhibited and inhibited blends show shear thinning behaviour and their viscosities decrease monotonically with the addition of Vectra A950. Compositional dependence of the steady shear viscosities of the two sets of blends displayed negative deviations from additivity and the uninhibited blends were more viscous than the inhibited blends for the full composition range. Although limited agreement with the Cox-Merz rule is found for the inhibited blends, these two sets of blends, in general, do not follow the rule due to their liquid crystalline order and two-phase morphology. Despite being immiscible blends, transesterification, such as polymerization, in the blends might occur during the rheological characterization, supported by the facts that uninhibited blends show HX2000-dominant behaviour at lower Vectra A950 content and are more viscous than the inhibited blends. The addition of transesterification inhibitor in such blends is advised if only physical mixing is desired.

Key words : transesterification, liquid crystalline polymer, blend; rheology, positron annihilation, free volume

Introduction

Thermotropic liquid crystalline polymers (TLCPs) and their blends with thermoplastics (TPs) have been studied extensively in recent years due to their unusual behaviour such as low viscosity and high mechanical performance of TLCPs, viscosity reduction and in situ reinforcement of TP matrix by TLCP fibrils [Gotsis and Baird (1985), Berry and Siegmann (1991), Roetting and Hinrichsen (1994)]. Unlike blends of TLCPs and TPs, blends containing two TLCPs have been rarely investigated [DeMeuse and Jaffe

(1988), DeMeuse and Jaffe (1991), Roetting and Hinrichsen (1994)].

Interchange reactions, such as transesterification, commonly occur in blends containing polyesters and polycarbonates. Although these reactions can be utilized in polymer processing [Porter and Wang (1992)], they are undesirable if the physical mixing of polymers is concerned. TLCPs generally belong to the polyester family and transesterification between TLCPs has been claimed in the literature to be absent for most TLCP+TLCP blends to date [DeMeuse and Jaffe (1988), DeMeuse and Jaffe (1991)]. However, verification of the occurrence of transesterification in TLCP+TLCP blends by comparing blend systems with and without the addition of an inhibitor has not yet

been reported. In this work, the blends of two wholly aromatic TLCPs, HX2000 which has bulky substituents and Vectra A950 whose molecular linearity is offset by naphthalene units, are used as a model blend system. The blend behaviour, in terms of miscibility and rheological properties, and the effect of possible transesterification on the blend properties are studied.

Experimental

Materials and Blending

The materials chosen for this study were two nematic, wholly aromatic thermotropic copolyesters, HX2000 from DuPont and Vectra A950 (referred to as Vectra hereafter) from Hoechst Celanese. HX2000 is an amorphous TLCP and may contain phenyl hydroquinone (PHQ), terephthalic acid (TA) and p-hydroxybenzoic acid (HBA) [Magnini (1993)]. Vectra is a semicrystalline TLCP, consisting of

TA HBA

PhHQ

HX2000

HBA HNA

Vectra A950
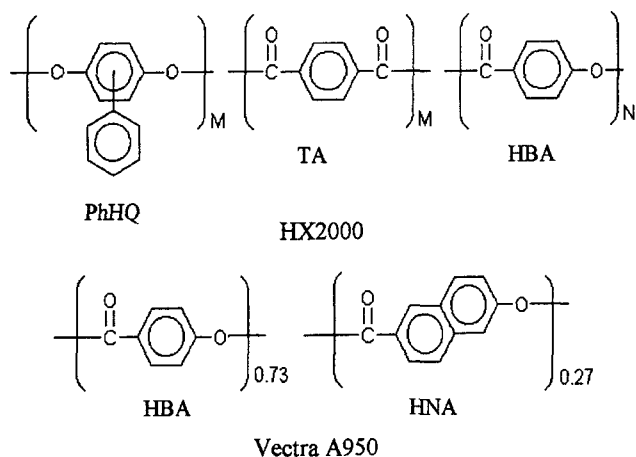
73 mol % of HBA and 27 mol% 2-hydroxy-6-naphthoic acid (HNA). The molecular weight (MW) of Vectra is about 30000, whilst there is no MW data available for HX2000. Their chemical structures are shown above.

In order to prevent any hydrolysis during blending, all polymers were dried in a vacuum oven at 100°C for 24 hours prior to processing. Blends of HX2000 and Vectra were produced by melt blending using a Haake Rheomex 252 extruder. The temperatures for the three independent heating zones and the die were 320°C, 330°C, 330°C and 330°C, respectively. A transesterification inhibitor, Irganox 1098 from Ciba-Geigy, was used in the preparation of one set of the blends and the amount of inhibitor added is 0.2% (based on total weight of the blend). Pure HX2000 and Vectra were also processed under the same conditions as their blends, and thus had identical mechanical and thermal histories.

Characterization techniques

Dynamic mechanical thermal analysis (DMTA) was

undertaken using a Perkin Elmer DMA-7 (DMA-7) and a Rheometrics dynamic analyser II (RDAII). The three-pointbend mode was employed for samples tested by DMA-7 at a frequency of 1 Hz and a scan rate of 2°C/min in an inert atmosphere with a continuous helium gas flow of 40 cm³/min. The sample dimension was 20 mm×5 mm ×2 mm.

The RDAII was equipped with rectangular torsion fixtures for oscillatory shear deformation test on solid test samples. Specimen dimensions were 50 mm×5 mm×2 mm They were oscillated at 1 Hz in 2°C steps with a soaking time of 1 minute to obtain thermal equilibrium.

A DuPont 9900 thermal analyser equipped with a DSC module was used to study the thermodynamic transitions of the materials. All samples of 10 to 15 mg were initially scanned over a temperature range from 50°C to the 350°C at a heating rate of 20°C/min and cooled to 50°C at a cooling rate of 20°C/min immediately after the furnace reached the final temperature. All samples were scanned again in from 50°C to 350°C at the same heating rate. The measurements were carried out in an inert atmosphere with a continuous nitrogen gas flow of 60 cm³/min. The reported results were taken from the second heating runs of the experiments to avoid any experimental artifact arising from previous thermal history.

Oscillatory rheological properties of the materials were investigated by RDAII at 320°C using 25 mm parallel-plate fixtures with a constant gap setting of 9 mm. The environmental chamber, where the test fixtures and samples were located, was continuously purged with dry nitrogen during measurements to avoid the occurrence of oxidation. Measurements were performed within the linear viscoelastic region obtained by strain sweep tests. No preshear was applied to the sample.

Steady shear viscosity was measured by using a Kayeness Galaxy III capillary rheometer (model D9052) at 320°C with a capillary die of diameter 0.76 mm and length 25.4 mm (L/D=33). The Rabinowitsch correction for non-parabolic velocity profiles was applied.

Results and Discussion

Miscibility of HX2000+Vectra blends

The miscibility of the HX2000+Vectra blends in the solid state was determined by measuring blend T_g behaviour using RDAII (1 Hz), DMA-7 (1 Hz) and DSC (20°C/min). The tanδ curves for the blends without the addition of inhibitor by RDAII are shown in Fig.1. The glass transition temperature (T_g) of neat HX2000 is clearly observed at 191°C, whilst Vectra shows a rather weak glass transition at 90.8°C. As seen in Fig.1 and Table 1, the T_gs of the blends associated with HX2000 phase decrease with the addition of Vectra. HX2000 and Vectra have only a very limited miscibility as the glass transitions of both pha-
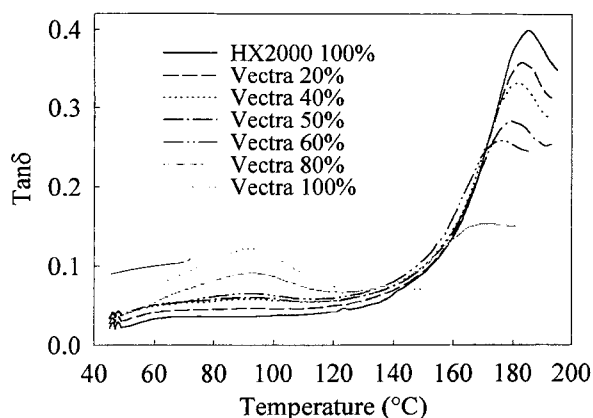
Figure. 1. Tanδ curves of the uninhibited HX2000+Vectra blends by RDAII at 1 Hz.

Table. 1 *Transition behaviour of HX2000+Vectra blends without inhibitor* determined by various techniques

	T_g (°C) (RDAII)	T_g (°C) (DMA-7)	T_g (°C) (DSC)	T_m (°C) (ΔH_f (J/g))
HX2000 100%	191	200	190.8	---
Vectra 20%	189/---[a]*	198.8/---[a]	187.5/---[a]	---[b]
Vectra 40%	187/---[a]	195.9/---[a]	186.2/---[a]	273.0(0.12)
Vectra 50%	185/---[a]	197.8/---[a]	185.9/---[a]	273.2(0.13)
Vectra 60%	181/92.8	192.0/---[a]	---[a]/---[a]	273.7(0.49)
Vectra 80%	175/92.8	192.5/ 107.3	---[a]/---[a]	274.2(0.85)
Vectra 100%	90.8	106.6	---[a]	274.7(0.90)

[a]: glass transition not observed.
[b]: heat of fusion not observed.
*: T_{g1}/T_{g2} : T_{g1} is the T_g of the HX2000 component and T_{g2} is the T_g of the Vectra component in all dual T_g entries shown.

ses change very little with composition. It appears that there is a slight solubility of Vectra within the HX2000-rich phase since the T_g decreases with its addition. By contrast, the T_gs relating to the Vectra phase in the blends remain almost the same as that of neat Vectra and become too weak to be detected when the Vectra concentration is low ($\leq$ 50% Vectra), as seen in Fig.1 and Table 1. Vectra material may be closely packed on a molecular level due to a simpler molecular structure, which may discourage the inclusion of HX2000 molecules in the Vectra phase. On the other hand, Vectra molecules are clearly able to be incorporated into the HX2000 rich-phase, since HX2000 molecules are not packed to the same degree as Vectra due to the phenyl substituents and the more complicated molecular chemistry (a terpolymer).

As TLCPs are highly anisotropic materials, different test modes used in DMTA, such as bending (DMA-7) and

torsion (RDAII), might be expected to lead to dissimilar results. The T_g values of the blends determined by DMA-7, which are also shown in Table 1, are higher than those by RDAII in general but the trend agrees well with RDAII data. This indicates that the blend structure is likely to be a random distribution of highly aligned domains. This is because the preferred direction of alignment, such as that which can be achieved by drawing, was not obtained during the preparation of test samples.

The T_gs of the HX2000-rich phase of the blends measured by DSC also decrease slightly with Vectra content. For blends with Vectra contents greater than 50%, the T_gs are too weak to be determined by DSC, as seen in Fig.2. In addition to T_g, other thermal properties, such as melting temperature (T_m) and heat of fusion (ΔH_f), of the blends were also determined by DSC, as seen in Table 1. T_ms of the blends, relating to melting of crystallites in Vectra component, change slightly with respect to the addition of HX2000 component. This indicates that there is no HX2000 component in the crystalline region of the Vectra phase. The heat of fusion, ΔH_f, of the blends decreases monotonically with HX2000 content and is about one seventh of the value of the neat Vectra with addition of only 50% HX2000. Since the HX2000 molecules do not exist in the crystalline region of the blend and the decrease in ΔH_f is not proportional to the blend concentrations, the hindered crystallization of Vectra is attributed to morphological effects. That is, compared to the bulk Vectra, the Vectra phase can not achieve the same degree of crystallinity in the blends. In addition, the incorporation of a small amount of Vectra into HX2000-rich phase, which is presumed to be unable to crystallize in that environment, may also contribute to the reduced crystallinity of the blends.

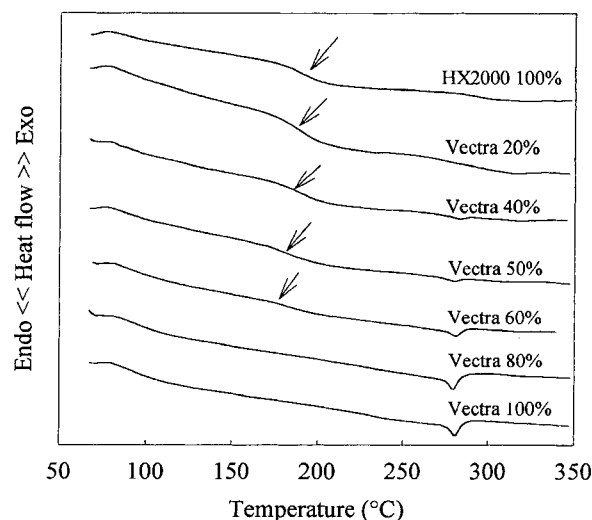Low molecular weight liquid crystals (LMWLCs) forming the same mesophase are generally miscible with each

Figure. 2. DSC thermograms of the uninhibited HX2000+Vectra blends (Arrows indicate T_g positions).

other, which has been applied in the classification of unknown LMWLCs and liquid crystalline polymers (LCPs) [Sackmann and Jaffe (1969); Billard and Vilasagar (1982)]. Both HX2000 and Vectra belong to the nematic class of TLCPs, which exhibit a one-dimensional molecular order (molecular axial direction). Unlike their low MW counterparts, blends of HX2000 and Vectra are found to be largely immiscible.

Studies of miscibility in blends containing two TLCPs to date [DeMeuse and Jaffe (1988), DeMeuse and Jaffe (1991), Roetting and Hinrichsen (1994), Jin *et al.* (1986), Yoo and Kim (1987), Kenig *et al.* (1991)] indicate that in order to achieve miscibility for TLCPs, similarities in chain chemistry and rigidity may be more important than forming the same class of mesophase. For blends of HX2000 and Vectra, the immiscibility may arise from the facts that (1) they do not contain the same comonomer in large quantity (HBA content in HX2000 is claimed to be very small [Magnini (1993)]), (2) Vectra is a copolyester and HX2000 is a terpolymer (more complicated molecular chain statistics for HX2000) and (3) HX2000 has phenylene substituents which significantly affect chain packing.

DMTA and DSC results for the inhibited blends are quite similar to their uninhibited counterparts and, therefore, are not shown here to avoid repetition. T_g, T_m and ΔH_f of the inhibited blends are listed in Table 2. Effects of the possible transesterification on blend miscibility in the solid state were verified by examining T_g, T_m and ΔH_f of the blends in Table 1 (uninhibited blends) and Table 2 (inhibited blends). Pure components, HX2000 and Vectra, show almost no difference in T_g, T_m and ΔH_f (ΔH_f is only relevant to semicrystalline Vectra as HX2000 is amorphous), with or without the use of the inhibitor during processing in an extruder. In general, T_gs (HX2000-rich phase) of the

uninhibited blend are higher than those of inhibited blends, no matter whether they were measured by DMA-7, RDAII or DSC. This difference in the blend T_g increases with Vectra concentration. The lower HX2000-phase T_gs of the inhibited blends may result from the use of an inhibitor which also functions as a plasticizing agent. The inhibitor used in this work might preferentially dissolve in HX2000-rich phase since only this phase is clearly affected. ΔH_f of the uninhibited blends decreases more slowly with the addition of HX2000, compared to their inhibited counterparts. Although there are some differences between the behaviour of the inhibited and uninhibited blends, the possible transesterification seems to have little influence on the immiscible HX2000+Vectra blends. In a largely immiscible blend system such a reaction would only occur at the interfaces and would not lead to a significant change in the bulk property (such as T_g) of an entire phase. The occurrence of transesterification in TLCP+TLCP blends have been claimed to be absent or negligible based on DSC [DeMeuse and Jaffe (1990), Lin and Winter (1992)], x-ray diffraction [DeMeuse and Jaffe (1988), DeMeuse and Jaffe

Table. 2 *Transition behaviour of HX2000+Vectra blends with inhibitor determined by various techniques.*

	T_g (°C) (RDAII)	T_g (°C) (DMA-7)	T_g (°C) (DSC)	T_m (°C) (ΔH_f (J/g))
HX2000 100%	187	200	192.7	---
Vectra 20%	183/---[a]*	194.3/---[a]	184.1/---[a]	---[b]
Vectra 40%	179/92.8	194.2/---[a]	172.8/---[a]	272.2(0.08)
Vectra 50%	175/92.8	190.8/---[a]	---[a]/---[a]	271.8(0.09)
Vectra 60%	175/92.8	185.3/---[a]	---[a]/---[a]	272.5(0.31)
Vectra 80%	165/92.8	185.3/107.2	---[a]/---[a]	274.8(0.44)
Vectra 100%	92.8	108.7	---[a]	273.4(0.95)

[a]: glass transition no observed.
[b]: heat of fusion not observed.
*: T_{g1}/T_{g2} : T_{g1} is the T_g of the HX2000 component and T_{g2} is the T_g of the Vectra component in all dual T_g entries shown.
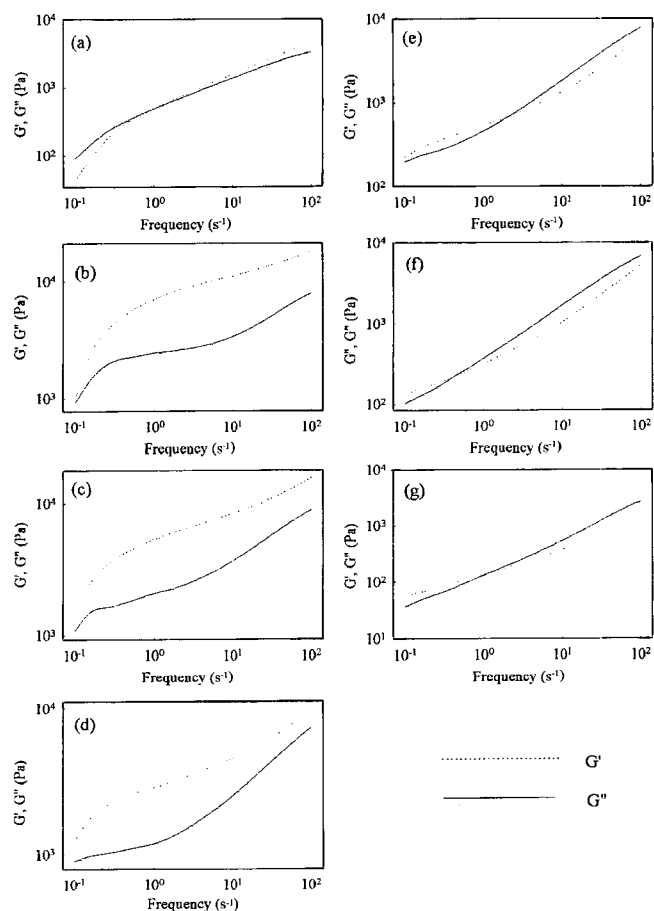

Figure. 3. G' and G" curves of the uninhibited HX2000+Vectra blends as a function of frequency at 320°C (a) HX 2000 (b) 20% Vectra (c) 40% Vectra (d) 50% Vectra (e) 60% Vectra (f) 80% Vectra (g) Vectra..

(1990)] of the uninhibited blends. Miscible TLCP+ TLCP blends showed a T_m lower than that of the fully transesterified TLCP [DeMeuse and Jaffe (1990)]. Immiscible TLCP+TLCP blends displayed two T_m, each of which has a value of its respective TLCP, and ΔH_f of the blends varied linearly with concentration [Lin and Winter (1992)]. X-ray diffraction of TLCP+TLCP blends showed meridional peaks different from that of the fully transesterified TLCP [DeMeuse and Jaffe (1988), DeMeuse and Jaffe (1990)].

Rheology

Figure 3 depicts the frequency dependence of storage moduli (G') and loss moduli (G") of the uninhibited HX2000+Vectra blends, as characterised by the RDAII at 320°C. Referring to a three-zone model [Ferry, 1989], the behaviour of HX2000 across the frequency range measured can be located in both terminal and plateau zones, as seen in Fig. 3(a). Similar terminal-to-plateau-zone behaviour has been observed for a TLCP with kinked linkages [Hsieh *et al.*, 1999] and TLCPs with flexible spacers [Shin *et al.* (1994)]. By contrast, Vectra shows the plateau zone at low frequencies, moving into a transition zone at high frequencies, as seen in Fig.3(g). This zone behaviour arises from the rigid nature of TLCP molecules rather than the effect of entanglements in flexible polymers [Hsieh *et al.*, 1999]. By characterizing the behaviour of all the blends in the manner of the three-zone model, the effect on dynamic rheology of blending of the two materials is made apparent. Blends of 20% to 50% Vectra (Fig.3(b)-(d)) appear to predominantly be in plateau zone, clearly influenced more by the behavior of HX2000. The blends of 60% and 80% Vectra (Fig. 3(e) and (f)) are very Vectra-like. It has been found that zone behaviour of the miscible TLCP+TLCP blends would be dominated by the less rigid component TLCP [Hsieh *et al.*, 1999]. As HX2000+ Vectra blends are immiscible, the major component of the blends dominate their zone behaviour. In summary, HX2000 appears to behave as a less-associated TLCP than Vectra, because the

terminal-to-plateau zone crossover frequency of Vectra has a much lower value which is beyond the accessible frequency range of RDAII. The frequency dependence of G' and G" of the inhibited blends can be seen elsewhere [Hsieh *et al.* (1998)]. The HX2000 component dominates the inhibited blend dynamic be- haviour up to 60% Vectra content, instead of 50% Vectra content as was the case for the uninhibited system.

Figure 4 gives the complex viscosities of the uninhibited blends as a function of frequency at 320°C. HX2000 shows slightly shear thickening behaviour at low frequencies (≤ 0.3 s^{-1}), which has been observed in the complex viscosity curve of another HX TLCP (HX4000) at a much higher temperature, 385°C [Bretas *et al.* (1994)]. HX2000 displays shear thinning behaviour following a shear-thickening region. By contrast, Vectra shows constantly shear thinning behaviour over the whole frequency range studied, which has been frequently reported [Kalika *et al.* (1989)]. Apparently, the initial alignment of HX2000 is less ordered than that of Vectra in the molten state. The blends display only shear thinning when the Vectra content reaches 50%. HX2000 is more viscous than Vectra, and their blends with Vectra contents less than 60% are more viscous than both pure components. Despite this increase in the blend viscosity, this behaviour is consistent with the zone behaviour in which HX2000 component is dominant up to 50% Vectra.

Complex viscosities of the inhibited HX2000+Vectra blends as a function of frequency at 320°C are shown in Fig.5. HX2000 still shows a shear thickening feature at low frequencies followed by shear thinning behaviour, whilst Vectra displays shear thinning behaviour only, the same as for their uninhibited counterparts. With the addition of 20% Vectra, the blend shows a more pronounced shear thickening feature than the neat HX2000. HX2000 is more viscous than Vectra, and only the blend containing 80% Vectra has complex viscosities intermediate between those of its constituents. The dominance of HX2000 in the blend
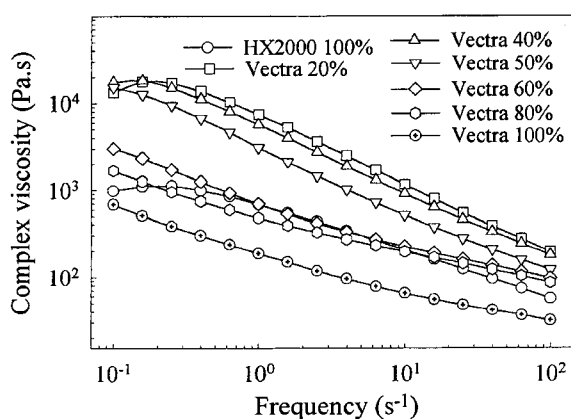

Figure. 4. Complex viscosities of the uninhibited HX2000+Vectra blends at 320°C.
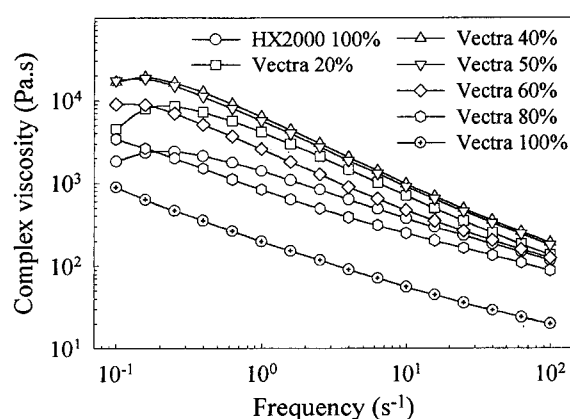

Figure. 5. Complex viscosities of the inhibited HX2000+Vectra blends at 320°C.
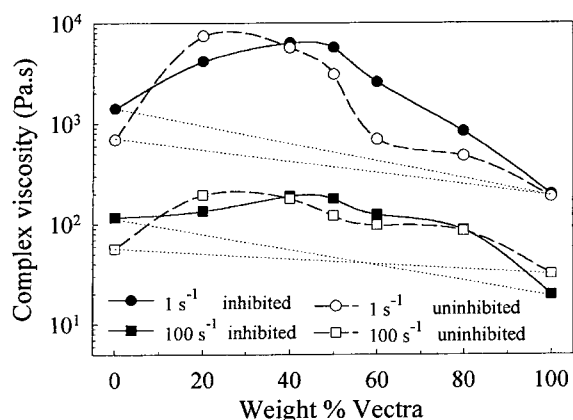
Figure. 6. Compositional dependence of the complex viscosities of the uninhibited and inhibited HX2000+Vectra blends at 320°C.

properties, as in the zone behaviour is also observed in the complex viscosities of the blends in which blends show shear thickening or a short Newtonian plateau up to 60% Vectra content. The shear thickening behaviour in the uninhibited blends is less prominent than that of the inhibited blends. The uninhibited blends become fully shear thinning at a much lower Vectra concentration (50%) than the inhibited blends which becomes fully shear thinning at 80% Vectra content. It is tempting to suggest that this difference in the complex viscosities of the inhibited and uninhibited blends may arise from some form of transesterification between HX2000 and Vectra, which makes the uninhibited blend behave more Vectralike at lower Vectra content.

Compositional dependence of the complex viscosities of the uninhibited and inhibited blends is shown in Fig.6. At two arbitrarily chosen frequencies, 1 s⁻¹ and 100 s⁻¹, complex viscosities of the blends all show strong positive deviations from the rule of mixture. This is likely to originate from the two phase morphology of the blends as immiscible TP+TP blends [Yoshikawa *et al.* (1994), Xanthos and Ponnusamy (1997), Lee and Kim (1998)] and the immiscible TLCP+TP blends [Hsieh (unpublished data)] often show positive deviations in the blend complex viscosities as a function of frequency. Yoshikawa *et al.* [Yoshikawa *et al.* (1994)] studied complex viscosities of blends of lithium or sodium-sulfonated PS ionomers (LiSPS or NaSPS) with polyamide 6 (PA6). LiSPS and PA6 formed a homogenous blend, due to strong intermolecular interactions. The compositional dependence of complex viscosities of such blends showed the rule of mixture behaviour at low frequencies and negative deviations at high frequencies. By contrast, immiscible blends of NaSPS and PA6 showed positive deviations at frequencies of 0.1, 1, 10 and 100 s⁻¹ [Yoshikawa *et al.* (1994)]. In spite of not knowing the factors governing these deviations of complex viscosities for miscible or immiscible blends, these devia-

tions can serve as characteristic features of polymer blends. Although there has been no such data reported for TLCP+TLCP blends, it appears that the above-mentioned observation is also applicable to TLCP+TL CP blends.

At the frequency of 1 s⁻¹, the uninhibited HX2000 is less viscous than the inhibited HX2000, and the uninhibited blends with Vectra content greater than 20% are also less viscous than the inhibited blends. The uninhibited and inhibited Vectra have similar complex viscosity. At the frequency of 100 s⁻¹, the blends show the same trend as at 1 s⁻¹, except that inhibited Vectra is less viscous than uninhibited Vectra. The comparison between complex viscosities of these two sets of blends appears to be inconclusive. However, extensive transesterification in the blends is unlikely since positive deviations in the compositional dependence of the complex viscosities of the uninhibited blends are observed at both frequencies, 1 s⁻¹ and 100 s⁻¹. This indicates that the uninhibited blends are still rather immiscible, as miscible blends (due to massive transesterification) are expected to show weighted-average behaviour.

Figure 7 shows the steady shear viscosities of the uninhibited HX2000+Vectra blends at 320°C measured with a capillary rheometer. Unlike the case of complex viscosity where HX2000 and blends with high HX2000 concentrations show shear thickening behaviour at low frequencies (Fig.4), shear thinning is the only feature observed for the whole blend system under capillary flow. This is probably due to the limited coverage of the low shear rate range in capillary measurements. HX2000 is much more viscous than Vectra and the steady shear viscosities of the blends monotonically decrease with increasing Vectra content.

The steady shear viscosities of inhibited HX2000+Vectra blends were found to behave in a similar manner as their uninhibited counterparts, that is, HX2000 is most viscous and the blend viscosity decreases with the addition of the Vectra component. The results can be found elsewhere
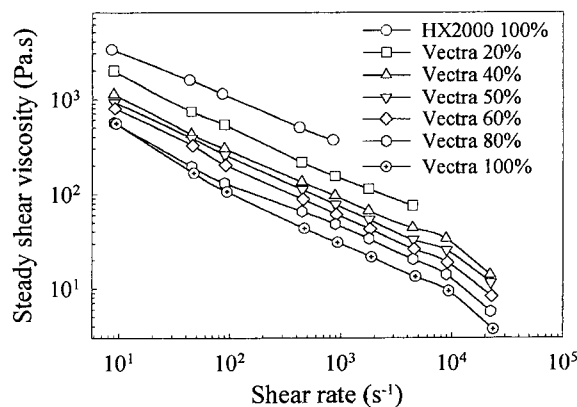

Figure. 7. Steady shear viscosities of the uninhibited HX2000+ Vectra blends at 320°C.

[Hsieh *et al.* (1998)].

Compositional dependence of the viscosities of the uninhibited and inhibited blends at two arbitrary shear rates, 100 s^{-1} and 1000 s^{-1} is shown in Fig.8. Instead of displaying a positive deviation as in complex viscosity (Fig.6), the compositional dependence of the steady shear viscosity shows a negative deviation from the rule of mixture. At the shear rate of 100 s^{-1}, a significant reduction of steady shear viscosity can be achieved in both sets of blends by blending 20% Vectra, compared to that of neat HX2000. This reduction in steady shear viscosity of the uninhibited and inhibited blend is less notable at higher Vectra compositions, and is less obvious at 1000 s^{-1} than at 100 s^{-1}. This indicates that high shear rates enhance the alignment of LC materials and thus the difference in viscosity, due to molecular packing, appears to vanish at higher shear rates. This finding can be useful in tailoring viscosity of a TLCP by the addition of another.

The comparison between the steady shear viscosities of the uninhibited and inhibited blends shows that, at all compositions, the steady shear viscosities of the uninhibited blends are greater than those of the inhibited blends, and the differences are more significant for the neat HX2000 and blends of low Vectra compositions. Transesterification has been utilized to increase MW of moulded products of PET, whose processability is favourable when MW is low, and high MW is required for final products [Porter *et al.* (1989)]. Further polymerization of Vectra has been confirmed in the molten state, supported by an increase in complex viscosity with time [Cocchini *et al.* (1991)]. HX4000 (a similar TLCP to HX2000) has also been reported to show time-dependent complex viscosity where its complex viscosity increases with time [Bretas *et al.* (1994)]. Therefore, the higher steady shear viscosities shown by the uninhibited blends may result from further polymerization (transesterification) of the TLCPs. It appears that HX2000 component is more susceptible to
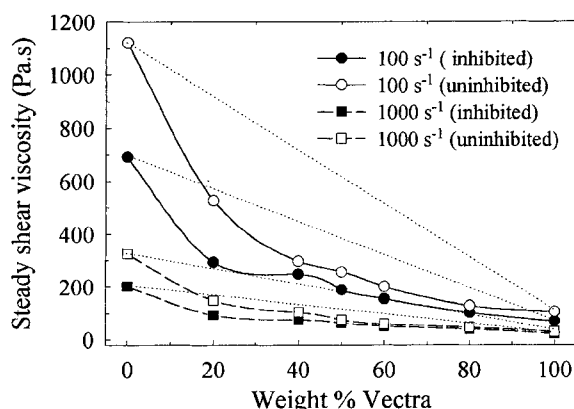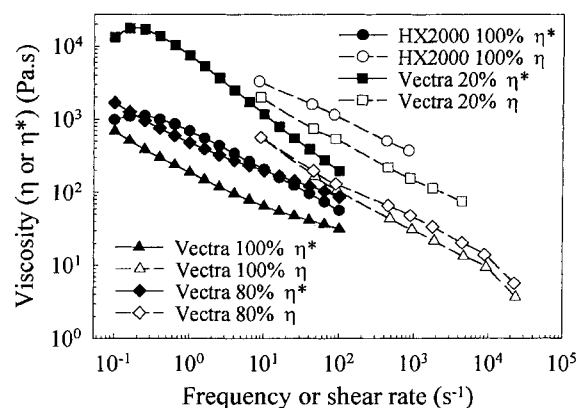
Figure. 9. Comparison of steady shear viscosities (η) and complex viscosities (η*) of the uninhibited HX2000+Vectra blends at 320°C.

transesterification than Vectra component because the uninhibited HX2000 and blends with lower Vectra contents have greater viscosity than their inhibited counterparts. Moreover, transesterification between different components may create blocky polymers, which have more complicated molecular structures than the component polymers, predominantly from reactions in the interfaces. This may also contribute to the higher viscosities of the uninhibited blends as the molecular packing of the more complicated TLCP is expected to be poor and thus more viscous. As also seen in Fig.8, the difference in viscosity reduces if higher shear is employed, despite the uninhibited blends still showing greater viscosities than the inhibited blends at all compositions.

The applicability of the Cox-Merz rule on the uninhibited HX2000+Vectra blends was examined, as seen in Fig.9. The uninhibited blends do not appear to obey the rule. The inapplicability of the rule has also been observed for HX4000 TLCP, even though both the steady shear and complex viscosities were measured by a rotational rheo-

Figure. 8. Compositional dependence of the steady shear viscosities of the uninhibited and inhibited HX2000+Vectra blends at 320°C.
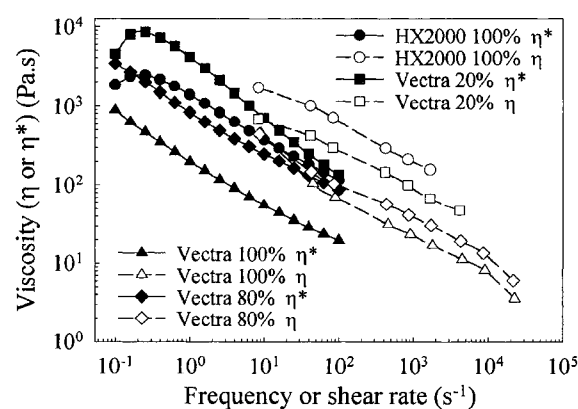
Figure. 10. Comparison of steady shear viscosities (η) and complex viscosities (η*) of the inhibited HX2000+Vectra blends at 320°C.

meter [Bretas *et al.* (1994)]. Higher shear rates are likely to align polydomain of TLCPs more effectively [Lin and Winter (1992)] than small oscillatory shear, since polydomain structure is not expected to be altered much by oscillatory shear within the linear viscoelastic region. However, for the uninhibited blends, steady shear viscosities of the blends are greater than their complex viscosities. It has been reported that some defect structures exist in TLCP melts, varying with time, and shear rates [Hsaio *et al.* (1990)]. The defect structure will reach a uniform state, which produces a steady state viscosity at a given shear rate. The Cox-Merz rule is, therefore, thought to be valid for TLCP melts only if both steady shear and dynamic shear measurements are probing the melt under a similar defect state [Gillmor *et al.* (1994)]. The proposed defect structure may help to explain a contradictory result reported by Lin and Winter [Lin and Winter (1992)], who showed good agreement of η and η^* for Vectra at 290°C. In their study, both steady shear and dynamic shear viscosities were measured by the same rotational rheometer, which may tend to result in a somewhat analogous defect state.

The inhibited HX2000+Vectra blends were also examined for the applicability of the Cox-Merz rule, as shown in Fig.10. HX2000 and Vectra do not follow the rule. However, it seems that the rule holds true for their blends to a limited extent, as seen in Fig.10 in which the 20% and 80% Vectra blends are shown. It is interesting to observe that the blends, containing two TLCPs which do not follow the rule, roughly obey the rule. In particular, their compositional dependence in complex viscosity and steady shear viscosity is totally different with the former showing a positive deviation and the latter showing a negative deviation (Fig.6 and Fig.8). This is likely to be coincidental that deviations from the rule, due to LC order and the two phase morphology, in some way manage to compensate each other.

Summary and Conclusions

Blends containing two TLCPs, amorphous HX2000 which has bulky substituents present in its main chain and semicrystalline Vectra which consists of HNA units, were prepared in this work. Effects of the potential transesterification on such blends are examined by comparing properties of blends with or without the addition of an inhibitor. Both uninhibited and inhibited blends are found to be largely immiscible due to the dissimilarity in molecular chemistry as well as in molecular packing. In addition, there is a limited miscibility in the HX2000-rich phase of the blends, which is thought to result from loose packing of HX2000. There is no clear evidence suggesting the occurrence of transesterification in the blends in the solid state. According to literature on TLCP+TLCP blends to date,

there has been no confirmation on the occurrence of transesterification in such blends in the solid state, although this reaction commonly takes place in thermoplastic polyesters. Sophisticated molecular analysis techniques, such as small angle neutron scattering (SANS) [Kugler *et al.* (1987), MacDonald *et al.* (1991)] and nuclear magnetic resonance (NMR) [Cheng *et al.* (1990)], have been shown to be potent methods in determining the occurrence of transesterification at molecular level. The application of these techniques has not been considered here because the emphasis in this work is placed on the effects of the transesterification (if any) on blend properties, such as miscibility and rheology, rather than any reaction on a molecular level.

With reference to the three-zone dynamic moduli-frequency model, in either the uninhibited blends or the inhibited blends, HX2000 shows terminal- and plateauzone behaviour, whilst Vectra shows plateau- and transition-zone behaviour. This indicates that Vectra is closely packed which may lead to a strong molecular association. The uninhibited blends show plateau-zone behaviour up to 50% Vectra A950 content and the inhibited blends show plateau-zone behaviour up to 60% Vectra A950 content. Compositional dependence of the complex viscosities of both the uninhibited and inhibited blends exhibit positive deviations from additivity, which is often found in the immiscible thermoplastic blends. When under steady shear, both the uninhibited and inhibited blends show shear thinning behaviour and their viscosities decrease monotonically with the addition of Vectra. Compositional dependence of the steady shear viscosities of both the uninhibited and inhibited blends exhibits negative deviations from additivity.

Despite solid state properties of the blends being less conclusive, rheological characterization in the molten state revealed some evidence of transesterification. It is indicated by the difference in the Vectra influence on the zone behaviour, the higher viscosities of the uninhibited blends than those of the inhibited blends, and the different applicability of the Cox-Merz rule of the inhibited and uninhibited blends. It should be noted that transesterification may predominantly occur during the rheological measurement rather than the blending process.

Properties of TLCPs have been known to strongly depend on their thermal and mechanical histories [Wissbrun (1980), Kim and Han (1994)] due to the change in LC alignment as well as chemical reactions, such as transesterification. A similar HX TLCP (HX4000) has been reported to show increasing complex viscosity with time and Vectra was observed to experience further polymerization in a rheometer. Transesterification may occur in the individual phases (a polymerization reaction) and at the interfaces in the HX2000+Vectra blends primarily during rheological measurements. It is assumed that the transes-

terification inhibitor, added during blending, was still functional when the blend was being rheologically characterized. Therefore, it is advisable that a transesterification inhibitor should be added during blend preparation or if solid state characterization is carried out on blend materials, which have undergone rheological measurements.

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