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Flow induced chain alignment and disentanglement as the viscosity reduction mechanism within TLCP/HDPE blends

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Abstract

Experimental observations on the use of a low transition temperature thermotropic liquid crystalline polymer, TLCP(1), as a processing aid for HDPE at low concentrations of 2 wt% and less are reported. Viscosity reductions of ~93% are observed at 185°C when the TLCP is fully nematic and ~89% at 220°C when the TLCP is, initially, a nematic–isotropic biphase. HDPE extrudate distortion and melt fracture are completely eliminated for apparent shear rates up to 1000 s^{-1} at 185°C. Using a Mooney analysis, wall slip is shown to contribute to the viscosity reduction at a negligible level. At 220°C, viscosity reductions are observed at a much higher critical wall shear stress than at 185°C. This has been attributed to a flow induced phase transition from isotropic to nematic phase at 220°C.

A mechanism elucidating the viscosity reducing effects of the incorporation of TLCP into an HDPE matrix is also proposed. The TLCP droplets firstly deform into long fibrils during entry flow. This is followed by chain alignment of the nematic TLCP molecules within the nematic TLCP droplets. Such chain alignment forces the neighbouring PE molecules to align and disentangle, leading to a reduced bulk viscosity. © 2001 Published by Elsevier Science Ltd.

Keywords: Thermotropic liquid crystalline copolyesters; Wall slip; Droplet elongation

1. Introduction

Blending of thermotropic liquid crystalline polymers (TLCPs) with commercial thermoplastics is known to lead to viscosity reductions [1–3], as well as improved mechanical [4] and barrier properties [5] of the final blend product over the pure homopolymer. The improved processability brought about by the inclusion of TLCPs is beneficial in a number of ways: (i) the power requirements for extrusion are lowered; (ii) higher processing rates are possible; (iii) using TLCPs as reinforcers reduces wear and abrasion on processing equipment in comparison with glass fibre reinforcers; and (iv) homopolymers normally processed at temperatures high enough to initiate degradation may be processed at lower, less harmful temperatures. Cogswell et al. [6] were the first to state that for improved melt processing, the TLCP should be in an anisotropic state over the same temperature range as the homopolymer is melt processable. These workers also stated that such an anisotropic state could be brought about by a shear induced phase transition. Examples of the viscosity reductions observed by adding TLCPs include reductions of up to 70% for various engineering polymers blended with a polyethylene terephthalate/*p*-hydroxybenzoic acid copolymer [2] and up to 68% with as little as 2 wt% of a TLCP based on 6-hydroxy-2-naphthanoic/*p*-hydroxbenzoic acid/terephthalic acid/hydroquinone blended with polycarbonate [7]. The latter is one of the few reports where less than 5 wt% TLCP is used; other examples are James et al. [8] and Swaminathan and Isayev [9].

There is only a handful of reports concerning the processing of blends of polyethylene (PE) and TLCPs [10–15]. This is probably because: (i) most TLCPs, being wholly aromatic copolyesters and copolyesteramides, are expected to have poor compatibility and adhesion with PE; and, (ii) most aromatic TLCPs are in an anisotropic state at temperatures of 300°C or more, far above the processing temperature of PE. There are now, however, TLCPs available with the appropriate melt transitions [16,17], which may be blended with PE. La Mantia et al. [14] report viscosity reductions of 40–60% with 5 wt% of a sebacic acid/4,4′-dihydroxybiphenyl/4-hydroxybenzoic acid copolyester blended with high density polyethylene (HDPE). Whitehouse et al. [3]

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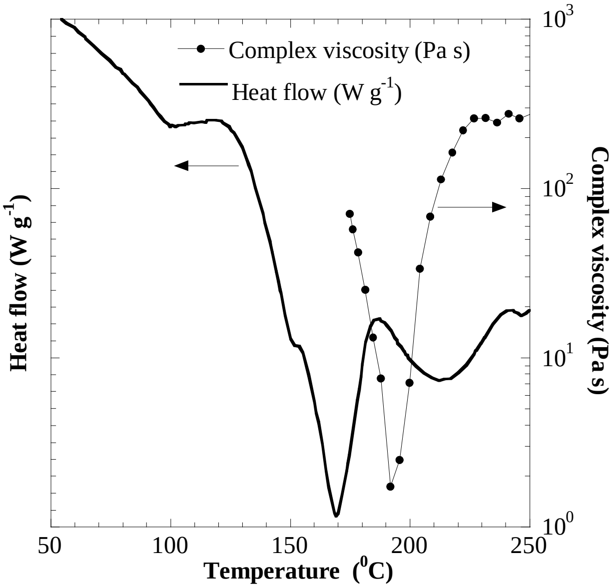

Fig. 1. Complex viscosity temperature sweep and DSC thermogram for TLCP(1) [17]. Temperature sweep experimental details: RMS800 rotational rheometer, 50 mm diam. cone and plate fixture with a cone angle of 0.04 rad, $\omega = 10$ rad s^{-1}, temperature ramp rate = 10°C min^{-1} and strain = 5%. DSC Experimental details: TA Instruments DSC2910, temperature range was from 40 to 250°C with heating and cooling rates of 10°C min^{-1} under a nitrogen atmosphere.

rheologically characterized 0.2, 0.5 and 2 wt% blends of a copolyester of hydroxybenzoic acid/hydroquinone/sebacic acid terpolymer (HBA/HQ/SA) in HDPE at 185°C when the copolyester is fully nematic, and recorded viscosity reductions of 85–90%.

Under shear and, dependent on the viscosity ratio, λ [18], the TLCP regions deform, elongate and orient to form fibrils [19–21]. It is postulated that this elongation and orientation are necessary for the viscosity reduction to occur [2,22]. Some reports talk about a lubrication effect, but do not state whether this is internal or external lubrication or if wall slip is involved. Given that PE is known to undergo slip and that fluorocarbon additives, see for example, Stewart [23], are used to induce and promote this slip at lower stress values, the question of how TLCPs cause a viscosity reduction in a PE matrix is of importance.

1.1. Objectives of the present work

The present work seeks to show whether or not wall slip is involved and, if it is, to what extent, in the viscosity reduction observed in blends of the thermotropic liquid crystalline polymer HBA/HQ/SA and HDPE [3]. This report demonstrates that wall slip is present at a negligible level and that the viscosity reduction is caused primarily by the orientation and elongation of the nematic TLCP regions within the blend, inducing molecular orientation in the neighbouring PE phase. When the TLCP is initially in the isotropic/nematic biphase, a flow induced phase transition, from isotropic to nematic, is necessary before the viscosity reduction can occur.

2. Experimental

2.1. Materials and preparation

The extrusion grade HDPE used in this study was supplied by B.P. Chemicals Ltd in the form of pellets. The 0.2, 0.5 and 2 wt% TLCP(1) in HDPE blends were also supplied by B.P. Chemicals Ltd, again in the form of pellets, having been blended using a twin screw extruder. All the pelletized materials contained a grey pigment. Prior to use, all materials were dried under vacuum at about 80°C for at least 24 h. TLCP(1) is the label used for a proprietary thermotropic liquid crystalline polymer synthesized by B.P. Chemicals Ltd, which is a copolyester of hydroxybenzoic acid, hydroquinone and sebacic acid (HBA/HQ/SA). The full synthesis and formulation of TLCP(1) are not available for publication. The rheology of this low nematic transition temperature TLCP has been described elsewhere by Gao et al. [17], who report the lowest viscosity of TLCP(1) to be at a temperature of 186°C when it is in the fully nematic regime. According to DSC and polarizing optical microscopy results, the nematic regime plateau is in the temperature range 182–191°C. From 191 to 250°C, TLCP(1) is a mixture of nematic and isotropic melts. Above 250°C, TLCP(1) is believed to be almost completely isotropic. Fig. 1 shows a plot of the complex viscosity temperature sweep made on a Rheometrics mechanical spectrometer RMS800 and the DSC thermogram for TLCP(1), confirming the phase transitions and the temperature at which the lowest viscosity was recorded.

2.2. Capillary rheometry experiments

Steady shear experiments were carried out using a Göttfert Rheograph 2003A capillary rheometer on the as-received pellet form of the materials, or in the case of the TLCP(1), the as-received powder form at 185 and 220°C. The apparent shear viscosity and wall shear stress values of all the materials were recorded in the apparent shear rate range 10–1000 s^{-1} for the blend materials and 10–10 000 s^{-1} for the pure TLCP(1). The wall shear stress and apparent shear viscosity values were calculated from piston pressure measurements, unless otherwise stated, using the formula $\tau_w = (D/4L)\Delta P$. The apparent shear rate was calculated using $\dot{\gamma}_{ap} = 32Q/\pi D^3$. A round hole capillary die with a 1 mm diameter and a length to diameter ratio of 30 was used. For the pure TLCP(1) at 180 and 220°C, a round hole capillary die of 0.5 mm diameter and $L/D = 60$ was used. Rabinowitsch corrections were applied, but Bagley corrections were neglected. The entry pressure drop is small and independent of TLCP concentration [24].

2.3. Wall slip measurements

A second set of capillary rheometry experiments were performed on the 0.5 and 2 wt% TLCP(1) in HDPE blends using a twin bore Rosand RH7 capillary rheometer at 190°C and the Mooney technique to correct for wall slip [25]. Capillary dies with diameters of 0.5, 0.7, 1.0 and 1.5 mm, all with a length/diameter (*L*/*D*) ratio of 20, were used. Two die angles, of 90 and 180°, were also utilized.

2.4. Morphological observations

A JEOL 6300F scanning electron microscope (SEM) was used to take micrographs of extrudates generated during the capillary rheometry experiments. Some samples were allowed to cool naturally on exiting from the die. Others were quenched by compressed air from a hose placed near the die exit, providing a cooling ring. This 'froze' the structure of the TLCP(1) droplets or fibrils before they could relax completely. Micrographs of the surfaces of these samples were taken before and after etching with a 10 wt% aqueous sodium hydroxide solution at 50°C. All samples were placed on aluminum stubs and sputter-coated with an ~100 Å layer of gold to minimize charging.

3. Results and discussion

3.1. Rheological characterization of pure materials

The HDPE used in this study is processable up to an apparent shear rate of ~100 s^{-1} and a wall shear stress of 0.35 MPa at 185°C. It exhibits pressure oscillation and melt fracture at higher processing rates; see Fig. 2a. The stick-slip behaviour, pressure oscillation and melt fracture are similar to those reported by Uhland [26]. At 220°C, HDPE is processable up to 540 s^{-1} and ~0.45 MPa before the onset of pressure oscillation and extrudate distortion. Wang and Drda [27], using constant pressure capillary rheometry, report τ_{crit1} values of 0.307 and 0.348 MPa at 180 and 220°C, respectively, for what we believe is a similar HDPE from the same supplier, B.P. Chemicals Ltd. These values compare favourably with those of Hatzikiriakos and Dealy [28]. It is possible to argue for a gradient change at ~0.20 MPa at both temperatures, indicating the onset of partial wall slip. Again, given previously reported τ_{slip} values [29–32], this would not be unreasonable.

For comparison, the same plot for the pure TLCP(1) is shown in Fig. 2b. At 185°C, the viscosity of TLCP(1) was too low to produce reliable piston pressure measurements at $\dot{\gamma}_{\mathrm{ap}} < 900\ \mathrm{s}^{-1}$. The same was true at 220°C for $\dot{\gamma}_{\mathrm{ap}} < 300\ \mathrm{s}^{-1}$. There are three important points to note: (i) the pure TLCP(1) is shear thinning, with power law indices of 0.8 at 185°C and 0.7 at 220°C (see Table 1); (ii) for $\dot{\gamma}_{\mathrm{ap}} < 900\ \mathrm{s}^{-1}$, the TLCP(1) exhibits a lower viscosity and wall shear stress at the lower temperature, 185°C; and, (iii) in the apparent shear rate range observed, the wall shear stress does not exceed 0.007 MPa nor is the apparent shear viscosity greater than 25 Pa s at either temperature.

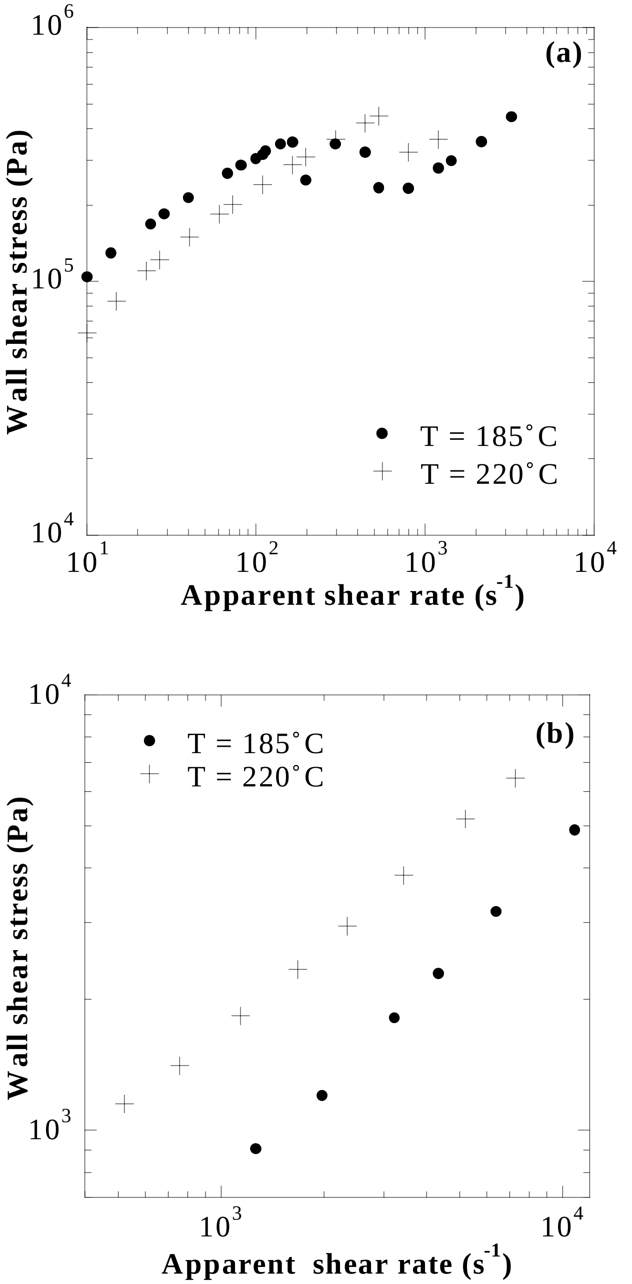

Fig. 2. Plot of wall shear stress versus apparent shear rate for pure components at 185 and 220°C: (a) HDPE, using capillary rheometry; (b) TLCP(1) using capillary rheometry and basing calculations on the measurement of pressure before die entrance.

These viscosity values indicate that the TLCP droplets are expected to deform and breakup in both the entry and the capillary regions of the capillary. However, due to the extremely low viscosity ratios, $\lambda = \eta_{\mathrm{TLCP(1)}}/\eta_{\mathrm{HDPE}}$ being of the order of 10^{-6}–10^{-4} in the wall shear stress range of interest (see Fig. 3), the droplet deformation and breakup will not be 'efficient', but probably of the tip spinning type, as the viscosity ratio does not lie in the range $0.01 \leq \lambda \leq 1.5$

Table 1
Power law curve fitting parameters for pure HDPE, pure TLCP(1) and blends at 185 and 220°C

Material	Temperature (°C)	Shear thinning zone	*n*	*K*
Pure HDPE	185	–	0.43	41 288
Pure TLCP(1)[a]	185	–	0.82	2.4
0.2 wt% TLCP(1) blend	185	Before yield	0.41	32 681
		After yield	0.47	14 559
0.5 wt% TLCP(1) blend	185	After yield	0.48	12 588
2 wt% TLCP(1) blend	185	After yield	0.34	22 633
			0.49	9638
Pure HDPE	220	–	0.48	23 883
Pure TLCP(1)[a]	220	–	0.7	13.8
0.2 wt% TLCP(1) blend	220	Before yield	0.49	19 159
			0.27	53 447
2 wt% TLCP(1) blend	220	Before yield	0.31	39 701
		After yield	0.34	22 374

[33]. However, the criteria for single droplet deformation are based on Newtonian systems in a simple shear flow field. The TLCP(1)/HDPE system under consideration is both viscoelastic and undergoing extensional flow in the capillary entrance region. Such entry region extension is shown clearly in photographs of blends of polypropylene with Vectra A900 and Vectra B900 presented by Gao et al. [34]. The presence of viscoelasticity has been found to lead to greater droplet stability, requiring higher shear stresses for breakup [35].

In general, droplet deformation and breakup in immiscible binary fluids is controlled by the capillary number, defined as

$$\kappa = \frac{(\eta_m \dot{\gamma})d}{\sigma} \tag{1}$$

where η_m is the matrix apparent shear viscosity, $\dot{\gamma}$ is the shear rate; the product of which gives the local shear stress; *d* is the droplet diameter and σ is the interfacial tension. This is the ratio of viscous forces, which cause deformation, to the interfacial tension forces, which provide droplet stability. When the capillary number exceeds a certain critical capillary number, which is a function of viscosity ratio between the dispersed phase and the dispersion phase and type of flow, irreversible droplet deformation is expected. For viscoelastic systems, the ratio of viscoelasticity has also been found to affect the critical capillary number by altering the apparent interfacial tension between the two liquids [35].

Fig. 4 shows plots of the ratio κ/κ_{cr} for the 2 wt% TLCP(1)/HDPE blends versus wall shear stress at 185 and 220°C, respectively. The critical capillary numbers, κ_{cr}, are taken from De Bruijn [36] for simple shear, Fig. 4a, and Utracki and Shi [33] for extensional flows, Fig. 4b; both were intended to describe Newtonian systems. The calculation was based on the viscosity ratios (Fig. 3) obtained by power law fitting to Fig. 2a and b; droplet diameter estimates of 0.6 μm from Whitehouse et al. [3]; and, an average interfacial tension value of 25.5 mN m^{-1} at both temperatures. This interfacial tension is an average value taken from the results of experiments carried out by Zhu [37] on a 10 wt% TLCP(1)/HDPE blend and obtained using a Taylor's droplet deformation method in the small deformation limit. A slightly lower interfacial tension value was obtained at 185°C than at 220°C, but both were of the order of 20 mN m^{-1}. Such interfacial tension values compare favourably with those reported for other TLCP containing thermoplastic blends [8,34,38].

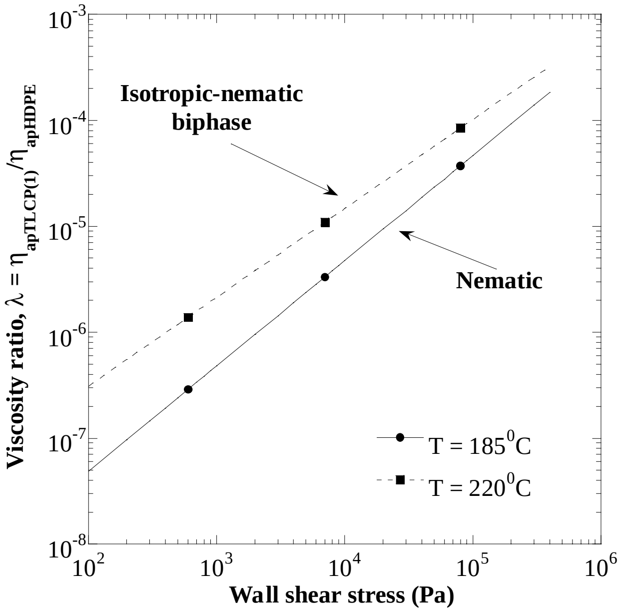

Fig. 3. Plot of viscosity ratio, $\lambda = \eta_{apTLCP(1)}/\eta_{apHDPE}$, versus wall shear stress at 185 and 220°C. All calculations based on measurements of pressure before die entry.

From Fig. 4a, no irreversible droplet deformation due to simple shear is expected in the wall shear stress range of interest at either 185 or 220°C. Irreversible droplet deformation due to extensional flow is possible at both temperatures at wall stress values above certain thresholds. Interestingly, Fig. 4b shows that the TLCP(1) blends should undergo irreversible droplet deformation at lower τ_w values at 220°C than at 185°C, due to the slightly higher λ at 220°C. It is worth repeating that the critical capillary numbers are based on completely Newtonian systems containing single droplets. Droplet coalescence during flow may lead to larger droplets and thus larger capillary numbers. It is also possible that such coalescence may result in capillary numbers exceeding the critical capillary numbers for irreversible deformation even in simple shear flow.

3.2. Flow curves at 185 and 220°C

The capillary rheometry data for the pure HDPE and 2 wt% TLCP(1) blend are presented as plots of apparent

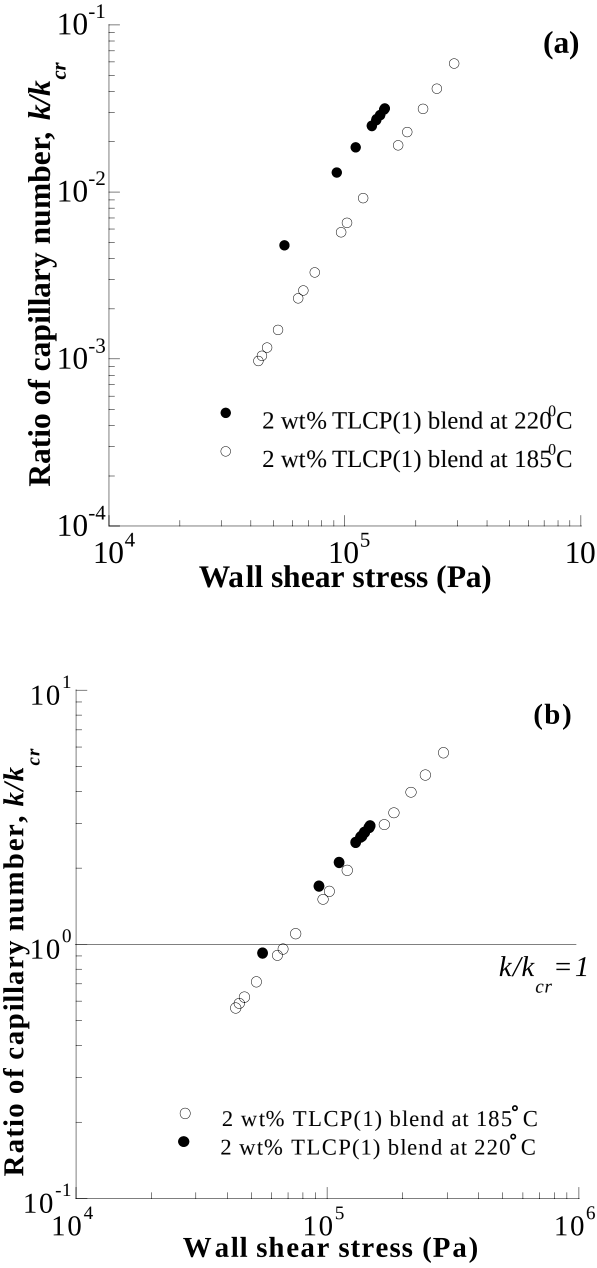

Fig. 4. Plot of κ/κ_{cr} versus wall shear stress for the 0.2 and 2 wt% TLCP(1) in HDPE blends at 185 and 220°C for (a) simple shear and (b) extensional flow.

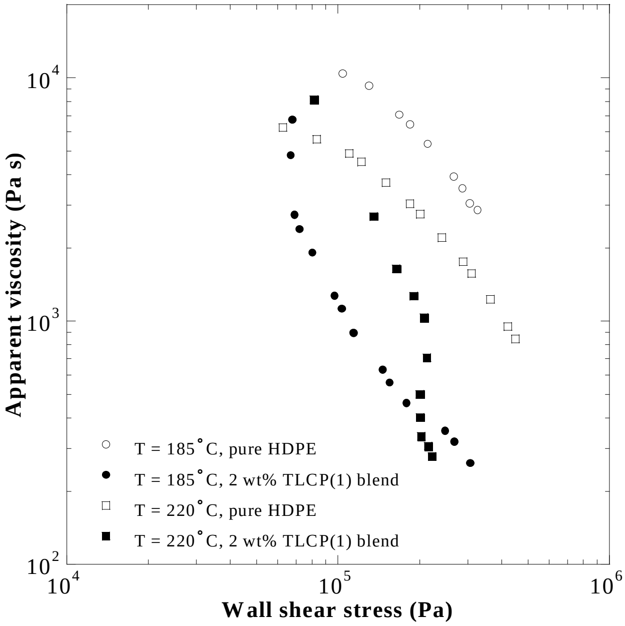

Fig. 5. Plots of apparent shear viscosity versus wall shear stress at temperatures of 185 and 220°C for pure HDPE and the 2 wt% TLCP(1) blend; data from capillary rheometry.

shear viscosity versus wall shear stress in Fig. 5. The TLCP(1) is fully nematic and a nematic–isotropic biphase at 185 and 220°C, respectively. Firstly, significant viscosity reductions are observed at both temperatures. Based on an equivalent wall stress of 0.21 MPa, the viscosity reductions at these temperatures are 93% (185°C) and 89% (220°C). Secondly, at both temperatures, a yield-like behaviour is shown by the blend where the wall stress is almost constant over a region of rapidly decreasing viscosity. However, the yield stress at 185°C is much less than that at 220°C (0.068 versus 0.18 MPa). Thirdly, it may be observed that the blend shows a higher apparent shear viscosity than the pure HDPE at low wall stress values at 220°C. Blends of TLCPs and thermoplastics having higher viscosities than the pure homopolymer at low shear rates have been reported previously [39–41]. Weiss et al. [39,40] attributed this to energy dissipation due to the tumbling and rotation of the phase-separated TLCP domains.

Finally, the yield-like behaviour at 220°C presents a slight negative gradient, whereas at 185°C, there is a positive gradient at all times. We suggest the negative gradient is due to a TLCP(1) phase transition from isotropic to nematic. TLCPs are known and theoretically understood to undergo shear-induced phase transitions when the domain orientation is sufficiently high [42,43]. Chan et al. [44] have presented the results of optical microscopy/shearing experiments demonstrating a phase transition from isotropic to nematic within a pure TLCP similar to TLCP(1). Also, a pre-transitional order in the isotropic phase of a homologous series of liquid crystals close to the isotropic to nematic transition has been experimentally observed. de Schrijver et al. [45] used a transmission ellipsometric technique to observe this surface-induced isotropic ordering. To our knowledge, the present work is the first time that evidence, although preliminary in nature, has been put forward for such a phase transition occurring when the TLCP forms the minor component of a blend. Further experiments are required to quantify the amount of isotropic phase converted to nematic. Such an isotropic to nematic phase transition explains the convergence in the λ versus τ_w plot shown in Fig. 3. Droplet elongation takes place at 185°C after the yield-like behaviour and, as was established by the experiments at 185°C, a nematic phase TLCP in either a fully

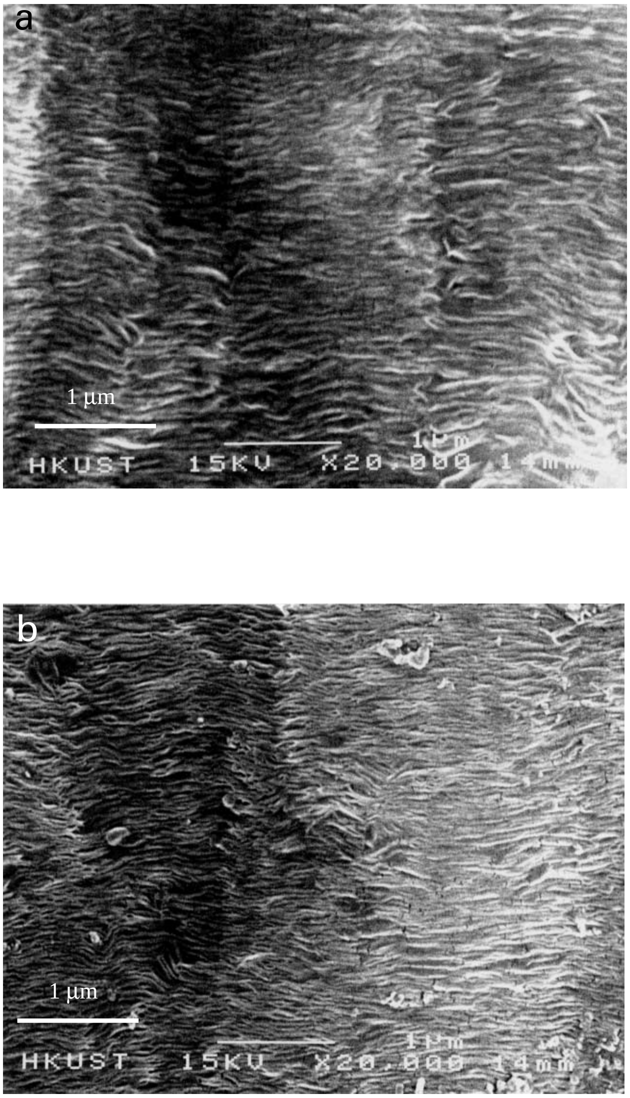

Fig. 6. SEM micrographs of extrudate surface of pure HDPE processed at 190°C, $\tau_w = 0.15$ MPa using a capillary die of 1.5 mm diameter and $L/D = 30$. (a) Prior to solvent etching; (b) after solvent etching. Direction of extrusion is vertical, i.e. down the page. Magnification 20000 ×.

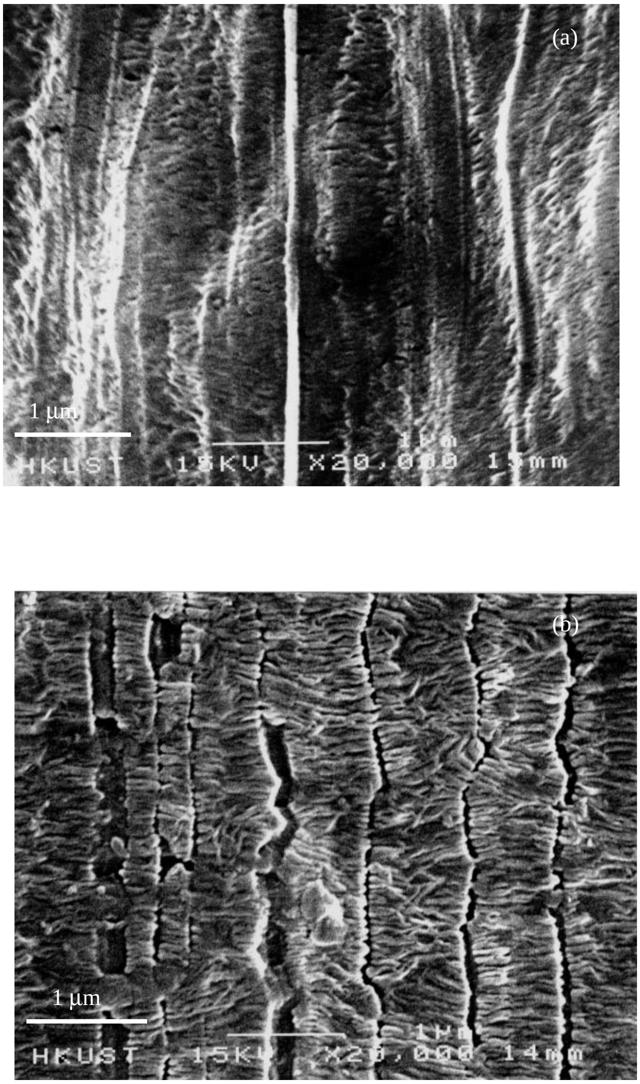

Fig. 7. SEM micrographs of extrudate surface of 1 wt% TLCP blend processed at 190°C, $\tau_w = 0.15$ MPa using a capillary die of 1.5 mm diameter and $L/D = 30$. (a) Prior to solvent etching; (b) after solvent etching. Direction of extrusion is vertical, i.e. down the page. Magnification 20000 ×.

aligned or almost fully aligned condition, was necessary for viscosity reduction. At 220°C, the irreversible droplet deformation takes place before the yield-like behaviour. The isotropic content of the TLCP droplets inhibits the nematic content from aligning as quickly as it does at 185°C. Eventually, there is enough alignment of the isotropic TLCP for it to convert to nematic. This alignment is brought about by droplet deformation; once the TLCP nematic content of the droplets becomes dominant, viscosity reduction is seen in the form of yield-like behaviour.

The extrudates of all blends are glossy and smooth, with no trace of melt fracture in the observed apparent shear rate range, up to $\dot{\gamma}_{ap} = 1000\ \mathrm{s}^{-1}$. Figs. 6 and 7 show SEM micrographs of the surfaces of rapidly quenched extrudates of pure HDPE and blend containing 1 wt% TLCP, respectively. Both samples were prepared at the same wall shear stress of 0.15 MPa and etched with a 10 wt% NaOH aqueous solution.

Both the pure HDPE and the blend surface were smooth under these wall shear stresses at magnifications less than 1000 ×. At higher magnifications, some interesting features are revealed. Firstly, prior to etching, the pure HDPE surface appears to show some regular layer textures which are aligned transverse to the flow direction: see Fig. 6a. Etching sharpens the surface topology: see Fig. 6b. The average thickness of the transverse layers is ~220 Å. We believe these are lamellar crystals with the crystal *c*-axis aligned with the flow direction. The regular patterns observed are a result of high shear stresses at the die wall–polymer interface during flow, and were preserved by rapid quenching. The improvement in contrast between

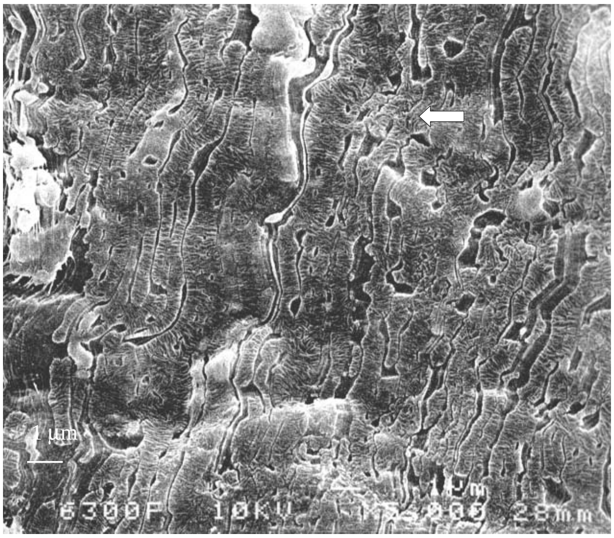

Fig. 8. SEM micrographs of extrudate surface of 2 wt% TLCP blend processed at 190°C. The surface was etched using a 10 wt% aqueous NaOH solution for a short time interval at room temperature. Direction of extrusion is vertical, i.e. down the page. Magnification 5000 × .

the etched and non-etched surfaces is due to the removal of the antioxidant Irganox 1010, which covers a large amount of the exterior surface, by the etchant. Surface composition analysis using a secondary ion mass spectroscopy technique showed the surface concentration of Irganox 1010 to be about 20% [46].

Secondly, whilst the unetched blend surface shows certain features similar to the pure HDPE prior to etching (Fig. 7a), there are also some longitudinal fibrillar striations that are embedded under a thin film. After etching for sufficient time, the surface topology again becomes sharper. Additionally, what were seen as striations are now long, thin cavities with the long dimension parallel to the flow direction. Progressive etching at different time intervals shows the cavities are due to the removal of TLCP filaments. A micrograph illustrating this observation is shown in Fig. 8. Notice one of the long slender TLCP filaments in the middle of the micrograph as indicated by an arrow. Obviously, there is some degree of filament relaxation as shown by the swollen regions along the TLCP filament. Transverse to the flow direction, the stacks of lamellar textures similar to that exhibited by the pure HDPE are also apparent. However, these lamellae are much thicker than those in the pure HDPE. The lamellar thickness is between 400 and 600 Å. This is about 2–3 times that of the pure HDPE. We attribute this to the enhancement of the chain alignment of the PE proximal to the highly aligned TLCP domains during flow.

These observations lead us to conclude the following. (i) The rapid shear thinning region corresponds to a zone where there is competition between the processes of reversible droplet elongation by entry flow and parallel flow of the two immiscible liquids. The latter gives rise to a reduced melt viscosity [47], but the former to an increase in melt viscosity [48]. (ii) The flow curves above the upper yield stresses at different TLCP concentrations correspond to blends containing irreversibly deformed TLCP fibrils. These fibrils are stable within the capillary die land: see Fig. 8. The remarkable fibre stability may be due to the high level of chain orientation of the nematic TLCP chains within these highly elongated TLCP fibrils. The TLCP chain alignment apparently also assists the orientation of PE molecules in the neighbouring domains, resulting in fewer PE chain entanglements and giving rise to a significantly reduced bulk viscosity.

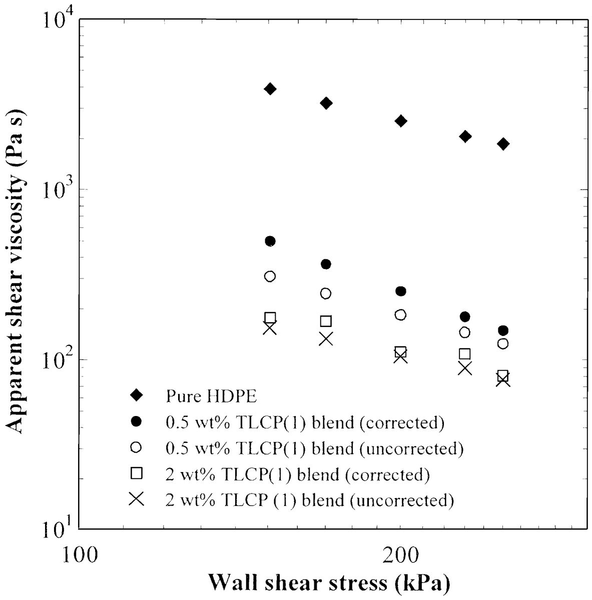

Fig. 9. Plots of shear viscosity versus wall shear stress for 0.5 and 2 wt% TLCP(1)/HDPE blends showing uncorrected values and values corrected for wall slip measured using capillary dies of *L*/*D* = 20, but a range of capillary die diameters and entry angles of 90 and 180°.

Inter-layer slip or internal lubrication has been previously presented as an explanation for viscosity reduction by TLCPs in blends with thermoplastics [49,50]. In these reports, concentrations of 10 and 30 wt% of a TLCP with a viscosity 100 times greater than TLCP(1) was used. In the present work, it is not felt that inter-layer slip provides a full explanation for the viscosity reduction. This is because: (i) of the very low TLCP(1) concentrations used; and (ii) of the strong chain alignment of the PE molecules due to the presence of highly aligned TLCP fibres. If there is co-deformation of matrix and dispersed phase there is no inter-layer slip [51].

Our wall slip measurements using dies of constant *L*/*D* ratios on a twin-bore rheometer as described above have also demonstrated that the contribution to viscosity reduction due to wall slip is negligible for the TLCP(1)/HDPE system. An example of such observations is shown in Fig. 9. Using the Mooney technique [25], the apparent shear viscosity versus true shear stress may be established and are shown together with the uncorrected data in Fig. 9. These plots show that the average contribution of wall slip to the viscosity reduction is very small: 3.9% (2.1–6.3%) for the

0.5 wt% TLCP(1) blend and 0.35% (0.18–0.52%) for the 2 wt% TLCP(1) blend. The percentage contribution values are averages over the wall shear stress ranges, the spread of values being indicated in parentheses. The lack of wall slip in TLCP/PE blends is further demonstrated by the experimental observations of Chan [24].

3.3. Proposed mechanism for viscosity reduction

An outline of a proposed mechanism for viscosity reduction is given here using irreversible thermodynamics. Two initial TLCP conditions will be considered: (1) when the TLCP is fully or predominantly nematic; and (2) when the TLCP is predominantly isotropic. It is assumed that the TLCP concentration is above the critical concentration for coalescence and the viscosity ratios are very low, i.e. 10^{-6}–10^{-4}.

3.3.1. Nematic TLCP

The viscosity reduction due to the incorporation of nematic TLCP into the HDPE matrix may be broadly divided into two regimes, the rapidly shear thinning region and the end of yield region. Within the rapidly shear thinning region, the bulk viscosity is controlled by the competition between droplet elongation and parallel flow of the blends. The droplets with diameters larger than the average critical droplet diameters may undergo irreversible elongation in the entry flow. The population of such droplets will increase as the wall shear stress increases. Additionally, droplets that are of near spherical form will experience large drag forces to migrate to the capillary wall during flow. The migration may result in increased droplet coalescence frequency, leading to larger droplets. Once the newly formed large droplet diameter exceeds the critical droplet diameter for irreversible elongation in simple shear flow they will also elongate into fibrils. The droplet migration and deformation will cause energy dissipation, leading to an increase in bulk viscosity. However, once the irreversibly deformed fibril TLCP droplets are established, parallel flow between the TLCP fibrils and the molten PE matrix becomes possible leading to viscosity reductions [47]. The PE chain orientation may also be increased when the TLCP molecules within the TLCP droplets become highly aligned in the flow direction. The enhancement in PE chain alignment has been observed indirectly when the blend was cooled after a pre-shear flow at high temperature. The PE phase immediately adjacent to the elongated TLCP domain boundary was found to crystallize faster than elsewhere. However, if the TLCP domain was not deformed, no difference in PE crystallization rate was observed. These experiments will be described in a later publication; for an initial report see Ref. [52]. Therefore, it may be argued that a combination of droplet elongation, chain alignment and parallel flow induces the rapidly shear thinning yield-like behaviour. After all droplets become fully elongated further increase in wall shear stress will no longer cause any further changes in blend melt structure. We believe this occurs at the end of the yield region or in the region where all flow curves become parallel.

3.3.2. Predominantly isotropic TLCP

In this situation, irreversible droplet deformation starts at a lower τ_w value than for a blend containing fully nematic TLCPs, due to the higher apparent viscosity ratio. Firstly, after the capillary number becomes larger than the critical capillary number for irreversible droplet elongation in the entry flow, the blend viscosity becomes lower than that of the pure PE although only a very small difference is observed. Secondly, at about a critical shear stress of 0.21 MPa, which is more than double the value of the critical shear stress for irreversible droplet elongation, a yield behaviour is observed. Immediately beyond the yield, the wall shear stress decreases slightly with increasing apparent shear rate, and later stays almost constant with further increase in apparent shear rate. We attribute the viscosity difference to the flow induced phase transition from isotropic to nematic phase within the dispersed TLCP droplets. The flow induced phase transition may be discussed within the framework of irreversible thermodynamics as shown in Eq. (2):

$$\Delta G = \Delta H_f - T\Delta S_f + \sigma \sum A_i + \int \tau\dot{\gamma}\, dt \qquad (2)$$

where ΔH_f is the enthalpy of fusion, ΔS_f is the entropy of fusion, σ is the interfacial tension between the nematic and isotropic phase of the single TLCP component, and $\int \tau\dot{\gamma}\, dt$ is the reversible shear energy input.

The fusional enthalpy term is always negative for phase transition from isotropic to nematic. But for polymers, this term is generally quite small. The fusional entropic change, the interfacial energy, and the shear work are all positive. The last two items are normally very small and can be neglected. Therefore, for flow induced phase transitions to occur, either the change of entropy has to be very small or the temperature must be close to the phase transition temperature. In other words, a high level of chain alignment within the isotropic phase during flow is crucial for any flow induced phase transitions to occur.

Once this phase transition from isotropic to nematic has taken place and the nematic content increased, the highly elongated TLCP fibrils may become more stable. The parallel flow of the elongated TLCP fibrils and the molten PE matrix will lead to a reduced bulk viscosity [47]. At a certain critical wall shear stress, the level of nematic portion within the dispersed TLCP droplets may become a dominant phase. We suspect this coincides with the yield stress on the flow curve in Fig. 5.

It should however be noted that the critical shear stress for shear induced phase transition within the TLCP droplets contained in the 2 wt% TLCP blend is many times larger than that for the single component TLCP. The rheo-optical experiments of Chan et al. [44] on the single component

TLCP showed that the critical shear stress is of the order of 100 Pa. However in the blend, the rapidly shear thinning transition does not occur until the shear stresses reach 0.2 MPa. This discrepancy is believed to be due to the inefficiency of chain alignment within the TLCP droplets contained in the blend. For isotropic TLCP chain elongation within the blend to take place, the TLCP droplets need to undergo irreversible elongation into long fibrils first. Further, molecular orientation within the deformed droplets may not be as high as in single component TLCPs, for example, it is known that for immiscible Newtonian fluids, the molecules within the tips of the dispersed droplets undergo recirculation.

Any contribution to the viscosity reduction due to wall slip has been ignored in the proposed mechanism as, if it is significant, wall slip should occur at both 220 and 185°C. For both of the cases given above, there will be deformation and alignment of the TLCP droplets in the region of the die wall–polymer interface, where the stresses are greatest.

4. Conclusions

TLCP(1) is an excellent viscosity reducing agent for HDPE, with reductions of 93% at 185°C and 89% at 220°C. These high reductions can only be achieved when the TLCP(1) is in the nematic phase and with a critical concentration globally oriented in the flow direction.

In the specific blend studied here, TLCP(1)/HDPE, the contribution of wall slip to the viscosity reduction is negligible. It is the irreversible TLCP(1) droplet deformation in the extensional flow at the capillary entrance, leading to the global alignment of nematic TLCP, which causes the viscosity reduction. When the TLCP(1) starts in the isotropic–nematic biphase at 220°C there is a phase transition from isotropic to nematic. This happens after irreversible droplet deformation has aligned the isotropic TLCP within the droplets, and there is a minimum free energy within the isotropic phase of the dispersed TLCP droplets. Significant viscosity reduction occurs once the nematic TLCP content is increased. The highly aligned nematic TLCP induces alignment in the neighbouring PE chains. It is likely there is some disentanglement within the PE matrix, which will also produce a viscosity reduction.

Wall slip contributes to the viscosity reduction at a very low level and is dependent on the TCLP(1) concentration: lower TLCP(1) concentrations having higher slip velocities. The slippage is probably of a layer or film against the die wall, the exact composition of which is being investigated. This film is highly fluid in the flow direction and is thought to contribute to the suppression of extrudate distortion.

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