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Shear-induced interactions in blends of HMMPE containing a small amount of thermotropic copolyester HBA/HQ/SA

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Abstract

Shear-induced interactions between high molecular mass polyethylene (HMMPE) melt and a thermotropic liquid crystalline copolyester, HBA/HQ/SA (TLCP) were investigated using large amplitude oscillatory shear and capillary shear. Polarized optical microscopy (POM) observations show that the mono-domain nematic TLCP droplets embedded inside a HMMPE melt may be readily elongated using large amplitude oscillatory shear. The HMMPE melt adjacent to the elongated TLCP filament was observed to crystallize faster than that in the matrix away from the interface. TEM analysis on the 1 wt% TLCP/HMMPE blend quenched after capillary shear shows that there are strong interfacial interactions between the elongated TLCP filament and the HMMPE matrix. Long range PE lamellae orientational order up to 2 μm away from the TLCP filament surface were observed, with all the lamellae surface normal parallel to the TLCP fiber. Additionally, a strong interfacial compatibility between the TLCP filament and the HMMPE matrix with an interfacial thickness of ∼30 nm has also been observed. The enhanced interfacial compatibility is attributed to the –CH$_2$– group interactions due to chain alignment in both components at their interface. These results provide a fundamental insight to other TLCP containing thermoplastics where compatibilities may be present due to segmental interactions.

Keywords: Shear-induced interactions; Interfacial thickness between TLCP and HMMPE; Molecular ordering in HMMPE

1. Introduction

Blends containing small amounts of a thermotropic liquid crystalline polymer (TLCP) in a matrix of thermoplastic are of technical interest for two main reasons: Firstly, use of TLCPs to enhance the mechanical properties of the matrix polymer through in situ formation of fibrous TLCP dispersion during processing, it may be possible to develop ‘self-reinforced’ composites that exploit the outstanding tensile properties of fibers made from LCPs [1,2]. Secondly, it is known that TLCPs can act as a flow modifier, effecting substantial pressure drop reductions during melt extrusion [3]. For both effects, the formation of fibril form droplets during processing has been found to be crucial [4]. It is believed that the changes in bulk viscosity were due to the interfacial slip between the elongated low viscosity TLCP and the matrix polymer.

In a series of publications, we have reported that the addition of 0.2–1 wt% TLCP to a high molecular mass polyethylene may lead to viscosity reductions between 88 and 95% [5–7]. The TLCP is a ter-polyester containing hydroxy-benzoic acid, *para*-benzoic acid, and sebacic acid, in the mole ratio 30:35:35. SEM studies on the etched outer surface of extrudates have shown strong interfacial interactions between TLCP filaments and HMMPE matrix [7].

While extensive literatures are available on the interfacial properties of mixtures of flexible polymers [8], very few studies on the interface between a liquid crystalline polymer and a flexible polymer, in which there is an additional length scale associated with nematic order, have been reported. The recent molecular dynamics simulation on the equilibrium structure of a mixture of LCP molecules with a flexible amorphous polymer shows that a diffuse interface gives a much lower interfacial tension than a sharp interface. These interfacial structures were caused by a far-field homeotropic and a planar LCP nematic order, respectively [9]. Direct experimental observations on the interfacial structure have not been reported mainly due to the domain texture of the embedded TLCPs.

In this paper, we focus on the interface between an elongated mono-domain TLCP filament and a high molecular

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mass polyethylene matrix. Two different types of flow fields have been applied: large amplitude oscillatory shear was applied on the mono-domain nematic TLCP melt droplet embedded within a HMMPE matrix to investigate the subsequent crystallization behaviour in molten HMMPE; capillary shear was applied to produce extrudate surfaces at high wall shear stresses. Transmission electron microscopy was used to investigate the interfacial structure between the dispersed TLCP filament and that HMMPE matrix.

2. Experimental section

2.1. Materials

The high molecular mass PE (HMMPE), Marlex HXM TR-570 used in this study was kindly supplied by Phillips Petroleum International Inc., USA. The weight averaged molecular weight of TR-570 is about 350,000 kg/kmol. The themotropic liquid crystalline copolyester (TLCP) used in this study was synthesized and kindly supplied by B.P. Chemicals Ltd, UK. This TLCP is a main chain copolyester containing mole fractions of 30% *p*-hydroxybenzoic acid, 35% hydroquinone and 35% sebacic acid (HBA/HQ/SA). Its number and weight average molecular weights are, respectively, $\bar{M}_n = 7000$ and $\bar{M}_w = 25,000$ kg/kmol, as determined from GPC.

The as received TLCP is a light brown powder that has been characterized before [10]. Prior to all experiments, the TLCP powder was vacuum dried at 120 °C for at least 48 h to remove any residual moisture.

2.2. Polarized optical microscopy (POM)

The POM experiments were carried out on the Cambridge Shearing System CSS 450 in conjunction with an Olympus microscope BX 50. Single TLCP droplets were dispersed into the HMMPE matrix for the optical measurements. The sample was prepared by sandwiching a thin TLCP fiber of diameter ∼20 μm into a pair of ∼1 cm^2 thin HMMPE films at 185 °C, at which temperature the TLCP is in the fully nematic phase, between the optical glasses inside the Cambridge Shearing System CSS 450. The gap was set at 50 μm and sufficient time (approx. ∼1.5 h) was allowed for the complete relaxation of the TLCP melt filament into defect free nearly spherical droplets. Elongation of the near spherical TLCP droplets was effected by applying large amplitude oscillatory shear at a maximum strain amplitude of 400%. Crystallization of PE was monitored between linearly cross-polarized light at 120 °C.

2.3. Transmission electron microscopy (TEM)

Electron micrographs were taken on a JOEL JEM 100 CX II electron microscope at an accelerating voltage of 100 kV. The samples used for the TEM were obtained from the capillary rheometer experiments. Both pure HMMPE and 1 wt% TLCP/HMMPE blend samples were extruded at 190 °C through the 1.3 mm diameter capillary die with a length to diameter ratio (*L*/*D*) of 30. All samples were taken at the wall shear stress of 0.11 MPa. The extrudate morphology was quenched using compressed air at the capillary die exit. In order to enhance the phase contrast, the samples were stained with a ruthenium tetraoxide (RuO_4) vapor for 4 days before being embedded into empoxy resin. The embedded samples were ultra-microtomed into about 100 nm thick sections at room temperature. All images were obtained from sample sections microtomed along the flow direction as depicted in Fig. 1.

3. Results and Discussion

3.1. Polarized optical microscopy (POM)

3.1.1. Un-oriented TLCP droplet

In order to investigate the effect of molecular alignment within the dispersed TLCP droplets on the morphology of the neighboring HMMPE matrix, single droplets of monodomain nematic TLCP were prepared. These monodomain droplets were obtained by the capillary instability method as described elsewhere [11]. Fig. 2(a) shows the POM micrograph of the nearly spherical TLCP droplet embedded inside the HMMPE matrix at 185 °C. The TLCP droplet displays a gray birefringent color implying no preferred global molecular alignment within the sample. The system was cooled at a cooling rate of 30 °C/min to 120 °C. In order to facilitate the identification of the interface, a pale blue ring was artificially superimposed on the rim of the TLCP droplet. A small size shrinkage was observed within the TLCP domain at 163 °C, corresponding to the crystallization temperature of the TLCP melt. A series of banded textures began to appear as shown in Fig. 2(b). Uniform scattering structures began to emerge within the HMMPE melt after the system has reached to 120 °C for about 1 min and 40 s (Fig. 2(c) and (d)). Rapid increase in

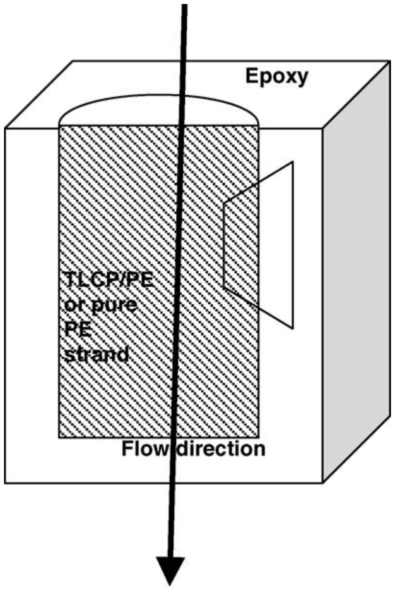

Fig. 1. Schematic diagram showing the geometry of the polymer strand embedded inside the epoxy resin. The trapezoid insert indicates the position where ultra-thin films are sectioned from.

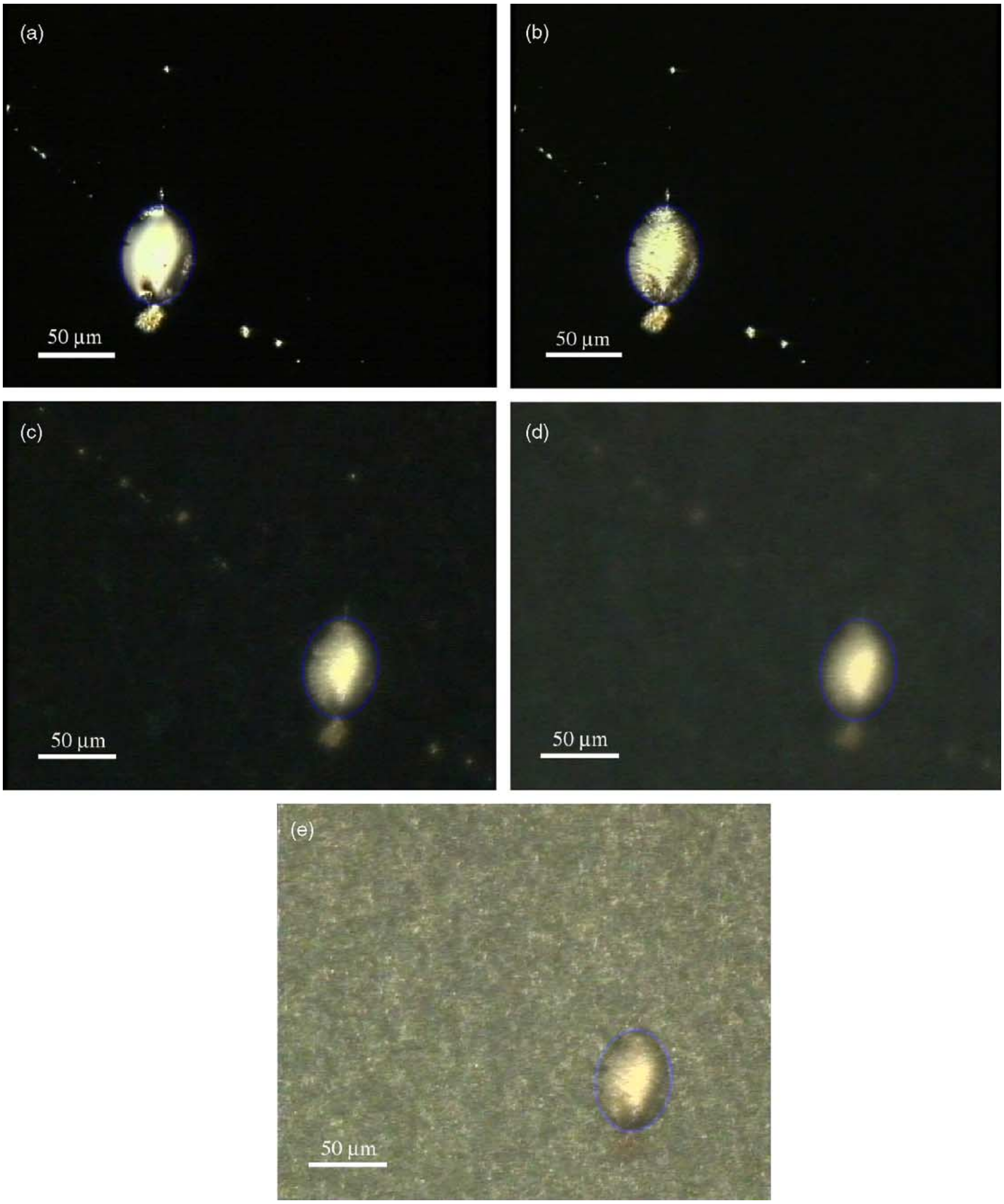

Fig. 2. PE crystallization process under the influence of the nearly spherical TLCP particle, which was cooled from the initially monodomain pure nematic TLCP droplet, observed between crossed polarizers. Cooling rate was at 30 °C/min. (a) Monodomain TLCP droplet obtained by annealing at 185 °C for at least 2 h; (b) micrograph captured at 163 °C displaying the onset of TLCP crystallization; (c) and (d) the onset of PE crystallization after annealing at 120 °C for 1 min and 40 s and 1 min and 50 s, respectively; and (e) annealing for 2 min and 30 s at 120 °C.

overall birefringence is observed with little further change observed after 2 min and 10 s (Fig. 2(e)).

3.1.2. Elongated TLCP droplet

The structure evolution at the interface between the elongated TLCP particle and HMMPE matrix is very different and intriguing. The initially nearly spherical droplet TLCP embedded within the HMMPE matrix was deformed into elongated droplet to an aspect ratio of ∼7 at a strain amplitude of 400% and a frequency of 1 rad/s. The image captured 1 s after the cessation of shear shows clear molecular anisotropy along the flow direction (Fig. 3(a)). Multiple retardation bands or Newton's rings are visible. The system was cooled to 120 °C at a cooling rate of 30 °C/min. Again, a small shape retraction was observed when the TLCP melt began to crystallize at 163 °C (Fig. 3(b)). At this point, the TLCP particle is 202 μm long and 29 μm wide with the aspect ratio unchanged at 7. A series of bands formed due to crystallization are again observed but appear to having their normals parallel to the initial flow direction. A pale blue ring superimposed on the TLCP rim is also used to identify the TLCP/HMMPE interface.

The crystalline TLCP particle shows little further change in size upon further cooling to 120 °C. One minute after annealing

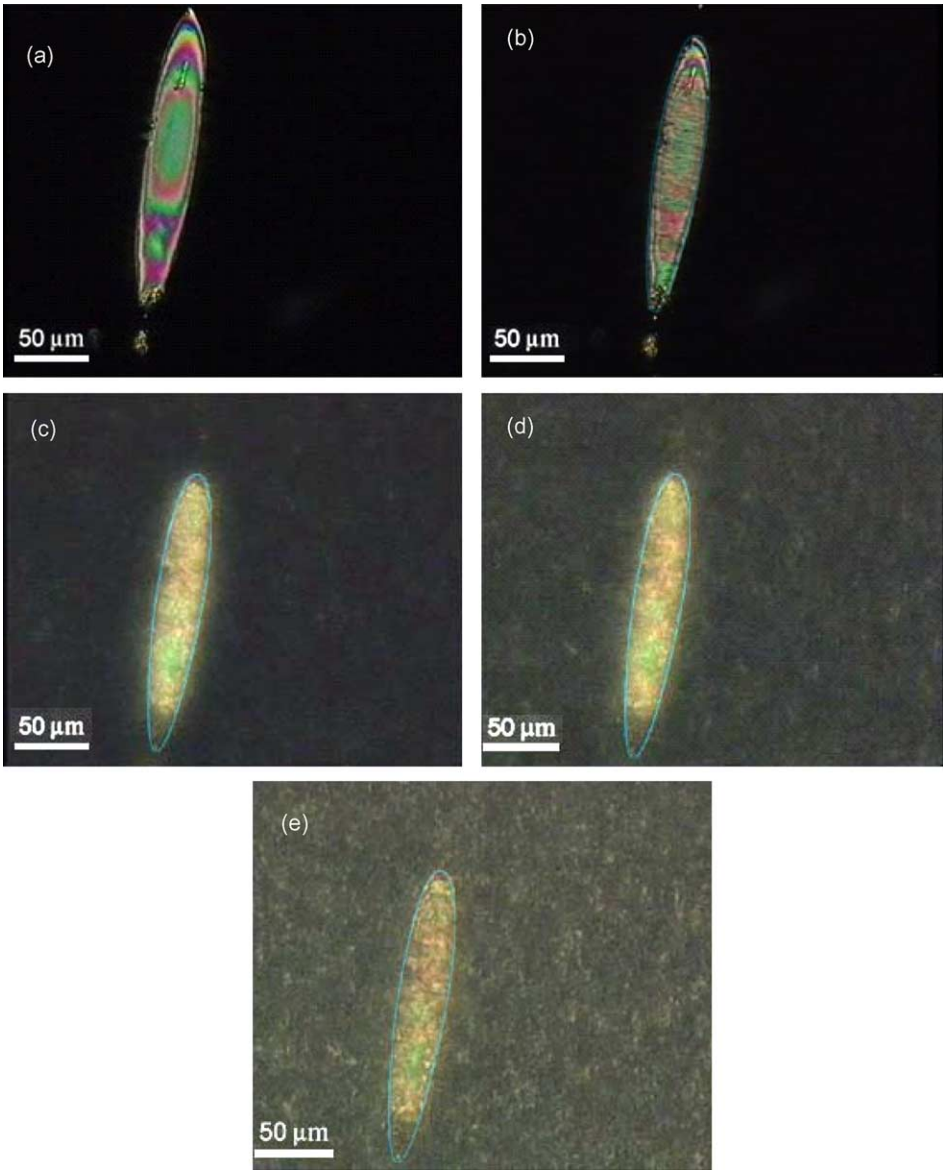

Fig. 3. PE crystallization process under the influence of elongated TLCP particle, which was cooled from the initially monodomain pure nematic TLCP droplet, observed between crossed polarizers. (a) One second after cessation of a large amplitude oscillatory shear at a strain of 400% and a frequency of 1 rad/s, $T = 185$ °C; (b) micrograph captured at 163 °C displaying the onset of TLCP crystallization; a pale blue ring around the TLCP particle was inserted to indicate the interface between the TLCP particle and the PE matrix; (c) onset of PE crystallization after annealing for 1 min at 120 °C. A thin layer of birefringent material can be identified around the TLCP particle; (d) further development of the transcrystallization region and the onset of PE crystallization in the bulk away from the interface after annealing for 1 min and 10 s at 120 °C; and (e) annealing for 1 min and 30 s at 120 °C.

at 120 °C, a layer of birefringent material began to emerge, covering the entire TLCP particle. In addition, a thin ring of such birefringent material of thickness ~10 μm is also observed, Fig. 3(c). The thickness of the ring increases with increasing annealing time. About 1 min 30 s later, the matrix began to crystallize (Fig. 3(d)). Nearly steady state crystallization within the matrix was reached after about 1 min and 50 s (Fig. 3(e)).

A number of literatures concerning the nucleation effects of TLCP on thermoplastics crystallization have been published [12–15]. The work by Tjong et al. [15] demonstrated that the TLCP could act as a row-nucleating site when Vectra was added to PP. Since, all commercial main chain TLCPs display multi-domain structures, molecular alignment effects within the dispersed TLCP particles cannot be investigated. As a result, no literatures were available to demonstrate how molecular ordering within the dispersed TLCP particle may affect the molecular organization in the neighboring matrix polymer. This is the first report to show such effects. Our experimental observations suggest that only elongated TLCP particles may induce molecular order in the neighboring PE phase and hence increase the rate of PE crystallization. This is further supported through TEM studies at the TLCP and HMMPE interface shown below. On the other hand, nearly spherical TLCP particles without any preferred molecular alignment initially did not have any effects on the PE crystallization rate or PE chain conformation changes.

The alignment-induced stronger interfacial interactions may be attributed to the flexible spacers of the SA segments within the dispersed TLCP domains. The chain alignment within both components at the interface may assist better molecular contact between SA segments and the neighboring PE molecules and hence enhanced interfacial compatibility. Enhancement of compatibility between TLCP containing flexible spacers with thermoplastics has been observed before [16].

3.2. Transmission electron microscopy

Transmission electron microscopy was used to study the interface of TLCP/HMMPE blend containing 1 wt% TLCP after capillary extrusion. Pure HMMPE extruded at a similar wall shear stress was also examined for comparison. Sections containing the interface of TLCP fiber particles embedded in HMMPE were ultra-microtomed along the flow direction. In order to enhance the phase contrast, the as microtomed thin films were stained with a ruthenium tetraoxide (RuO_4) vapor for 15 and 30 min, respectively.

3.3. Microstructure of HMMPE

Fig. 4 is a micrographs of the HMMPE thin section prepared along the flow direction of the extrudate surface. The flow direction was indicated using a black arrow superimposed on the micrographs. In order to have a clearer structural elucidation, the thin section has been annealed for 24 h at 124 °C. The interface between the extrudate outer surface and the epoxy resin for embedding the section is to the left hand side of the micrograph.

The PE extrudate surface displays a row-nucleated shish-kebab structure which is usually observed when PE crystallization takes place under stress [17,18]. Apparently, the long fiber crystals formed by extended high molecular mass fractions act as the nucleation sites for the growth of folded PE crystals. The row-nucleated regions extend up to about 200 nm diameter. However, outside these few row-nucleated areas, all PE lamellae are randomly oriented.

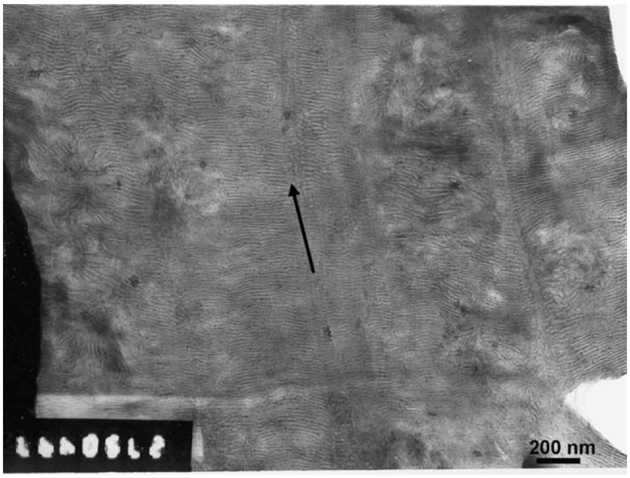

Fig. 4. TEM micrograph of the lateral section of the PE extrudate surface after annealing prepared parallel to the flow direction.

3.4. One weight percent TLCP/HMMPE blend

The micrographs of the 1 wt% TLCP/HMMPE prepared at a similar wall shear stress to that of the pure HMMPE extrudates

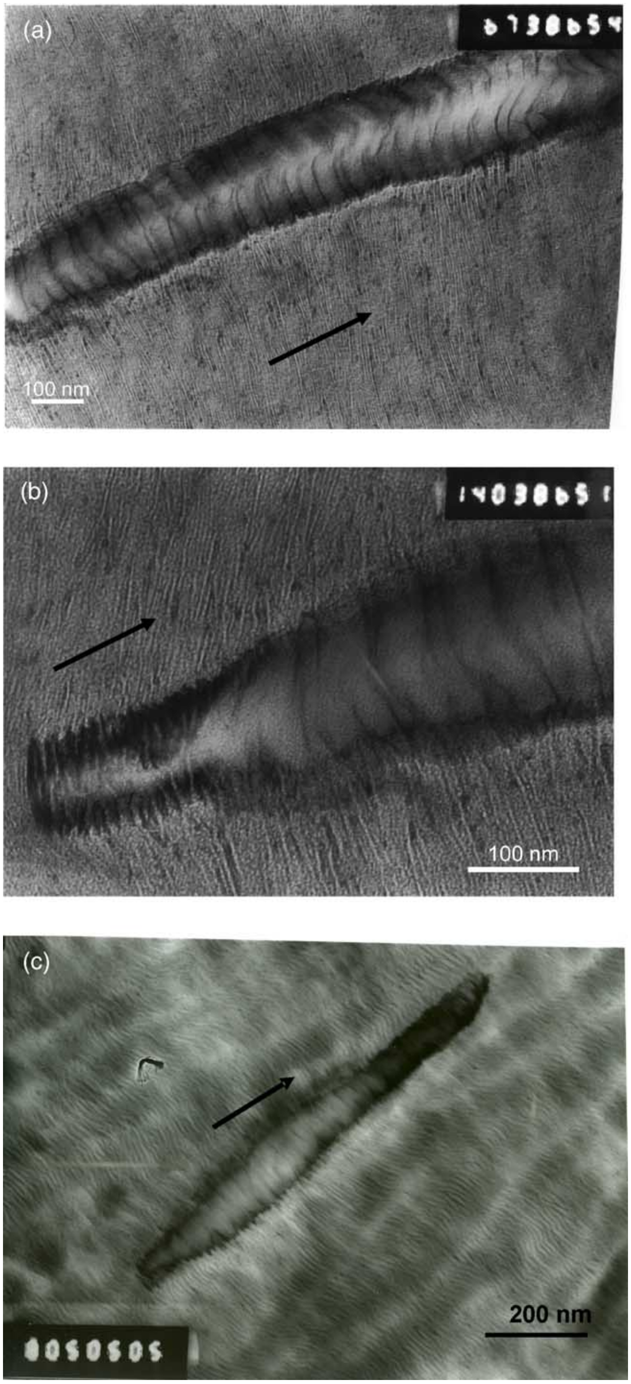

Fig. 5. TEM micrographs of the lateral section of the 1 wt% TLCP/HMMPE blend extrudate surface prepared parallel to the flow direction. (a) and (b) Un-annealed blend surfaces at different magnifications; and (c) the blend surface after annealing for 24 h at 124 °C.

are shown in Fig. 5(a)–(c). There are a number of intriguing features shown in these micrographs: firstly, a global alignment of the PE lamellae can be seen clearly (Fig. 5(a)). All PE lamellae's surface normals are parallel to the flow direction aligning with the TLCP filament. The maximum diagonal distance from the lower left hand corner to the upper right hand corner is about 4 μm. Secondly, strong interfacial compatibilities may be seen clearly between the aligned TLCP filament and the adjacent PE matrix, Fig. 5(b). An interfacial layer with thicknesses of up to 30 nm may be readily identified. In this region, strong ingrowth of PE lamellae into the TLCP fiber, particularly around the tip of the TLCP filament (Fig. 5(b)), can be observed. Thirdly, the embedded TLCP fibre displays a regular banded structure, and the bands are all perpendicular to the chain alignment direction within the TLCP filament. The average inter-band distance is about 37 nm. The chain length of a fully extended TLCP molecule based on its number average molecular mass of 14,000 kg/kmol is ~85 nm. Thus, the chains within the embedded TLCP were highly extended by capillary flow.

Annealing of the 1 wt% TLCP/HMMPE blend leads to the usual lamellar thickening within the PE matrix also reveals the large internal stresses within the blend surface. Significant lamellar thickening in PE crystals from 6 to 11.6 nm is shown in Fig. 5(c). More significantly, the originally well-aligned parallel-stacked PE lamellae show a modulated wavy texture with some periodical patterns as a result of the stress relaxation process. The large distortion is partially attributed to the small thermal expansion coefficient of the dispersed TLCP fibers. In comparison with the pure HMMPE extrudate surface, it is clear that the wavy structures observed in the blend were not caused by the quenching process. It is due to the higher chain alignment in the PE phase induced by the elongated oriented TLCP fiber.

The above observations are consistent with our earlier studies [7]. SEM micrographs on the quenched extrudates showed that slender TLCP filaments with widths of 40–210 nm and lengths up to 5 μm existed at about 30–50 nm below the top surface of the extrudates. Stacks of PE lamellae were observed to have their plane surfaces normal to the flow direction consistent with the structure shown in Fig. 5(a)–(c). However, individual lamella could not be observed directly using SEM.

Our previous experiments have shown that the melt viscosity of the TLCP is extremely low (~1 Pa S at 10 rad/s) [10]. The viscosity ratio between the TLCP and the PE matrix is extremely large ($>10^5$). The stability of the elongated TLCP filaments also implies that the interfacial tension between the oriented TLCP fibre and the molten PE matrix is very small. The alignment induced compatibility is consistent with the molecular dynamics observations by Li and Denn [9], where a diffuse interface shows a much lower interfacial tension between the isotropic polymer and a nematic LCP.

4. Conclusions

Crystallization of HMMPE under the influence of both oriented and un-oriented TLCP has been studied using POM and TEM. Elongated TLCP droplet of mono-domain texture can be readily elongated by large strain oscillatory shear flow. Faster crystallization rate in the PE phase adjacent to the elongated TLCP filament has been observed under POM.

TEM micrographs show that the dispersed TLCP filaments show high level of molecular orientation along the flow direction. The PE lamellae on both pure HMMPE and the 1 wt% TLCP/HMMPE extrudate surfaces show preferred alignment normal to the flow direction. However, the blend surface show a much longer range orientation compared to the pure HMMPE. The alignment correlation distance is up to 1.8 μm in the blend which is at least ten times that of the pure PE extrudate. This high level of alignment is attributed to the stronger interaction between the two constituents during flow caused by molecular alignment and entanglement reductions at the interface. The PE lamellae adjacent to the TLCP filament are almost two times thicker than those away from the interface.

A strong interfacial diffusion has been found between the oriented TLCP filament and the HMMPE matrix with an interfacial thickness up to 30 nm. This is attributed to the flexible spacer effects within the SA units on the main chain TLCP.

Annealing process has been found to be effective in causing lamellar thickening in PE. The lamellae thicknesses increase from ~6 to 9.5 nm in pure HMMPE and 11.6 nm in the 1 wt% TLCP/HMMPE blend. Stress relaxation during the annealing process shows that the PE chains in the blend surface have much better alignment than those in the pure PE extrudate surface.

Our studies on the alignment induced compatibilities between thermotropic main chain TLCP and the molten PE matrix may also serve to provide a fundamental insight to other molten thermoplastics containing TLCPs. Most commercial TLCPs show multidomain textures due to their high melt viscosity. Such non-equilibrium textures have hindered the fundamental understandings on the interfaces between a TLCP melt and a thermoplastic polymer when segmental interactions may be present. Our report may be the first to clearly demonstrate molecular orientation effects in nearly mono-domain main chain TLCPs on the order development in the neighboring polymer melts when segmental compatibilities are present.

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