Organoclay/thermotropic liquid crystalline polymer nanocomposites. Part V: morphological and rheological studies

Youhong Tang · Ping Gao · Lin Ye · Chengbi Zhao · Wei Lin

Abstract Small amounts of organoclays in different sizes and concentrations were added into thermotropic liquid crystalline polymer (TLCP) by a combination method of ultrasonication, centrifugation, and solution casting (and shear-induced phase separation). Four kinds of organoclay-modified TLCP composites were obtained. TC3 UP was a kind of organoclay which displayed a marked shear-induced phase separation phenomenon at 190 °C and higher temperatures. TC3 UP could be separated into a TLCP-rich part, TC3 white, and an organoclay-rich part, TC3 dark. TC3 white was an organoclay-modified TLCP with fully exfoliated organoclay of a uniform size of 15–25 nm well dispersed in the TLCP. TC3 dark had a typical intercalated model structure with some TLCP molecules confined in organoclay galleries. TC3 FS was an organoclay-modified TLCP with organoclay of comparable size to that of the fully extended TLCP molecule, i.e., 85 nm. The organoclay layers dispersed into the polymeric matrix as a few randomly organized organoclay layers or stacks of layers in the quiescent condition in organoclay-modified TLCPs. The larger organoclay size or higher concentration of organoclay in the composites (such as, TC3 UP and TC3 dark) caused a greater proportion of the layers or stacks be hydro-dynamically impeded in the quiescent state, resulting in the filler–filler interaction becoming important and in fact dominating the long-term viscoelasticity of the composites. Additionally, the ease with which the organoclay structure could be altered by flow was considerably enhanced, primarily because of filler–filler interactions. Organoclay size has primary effect on the liquid crystallinity of TLCP. Small or comparable organoclay size with the fully extended TLCP molecule in TC3 white and TC3 FS has weak or negligible negative influence on the liquid crystallinity of TLCP, while larger organoclay size totally damages the liquid crystallinity of TLCP. The morphologies, liquid crystallinity as well as the linear and non-linear viscoelastic behaviors of organoclay-modified TLCPs have been characterized in detail.

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Introduction

Liquid crystalline polymers are typical examples of self-ordered polymeric systems, due largely to their intrinsic molecular anisotropy. The properties of liquid crystalline polymers are strongly influenced by flow-induced changes in the degree of molecular orientation during processing [1].

Interactions of layered silicates causing the presence of domains similar to those found in studies of liquid

crystalline and ordered block copolymer systems have been analyzed by many researchers. Clarke et al. [2] used a diffraction technique to investigate the orientational alignment of anisotropic clay under flow. In studies by Mourchid et al. [3], laponite particles interacted at the sol–gel transition and were not totally free to be separated. One possible reason is that the total Gibbs energy was minimized to align neighboring particles in order to save free volume and reduce their excluded volume interaction [4]. Extensional flow was applied to a thin film of sepiolite suspension in an extension cell of the four-roll mill. Near a critical volume fraction, the behavior of the colloidal suspension changed from that of an isotropic system to that of a nematic system. In the isotropic behavior domain, flow reversal left no permanent orientation during the relaxation process while in the nematic behavior domain, permanent orientations of the structure were observed [5].

Nanocomposites based thermotropic liquid crystalline polymer (TLCP) and organoclay, have been studied by several groups with different foci [6–9]. Organoclay size and concentration have substantial effects on the properties of TLCP. For example, the liquid crystallinity of the hybrids was lost when the organoclay content exceeded 6.0% in TLCP with an alkoxy side-group and an organoclay (Closite 25 A) prepared by the melting intercalation method [6]. The formation of hydrogen bonds caused a very high degree of dispersion of organoclay but a considerable loss in the degree of liquid crystallinity in a nanocomposite with a segmented main-chain liquid crystalline polymer having a pendent pyridyl group (PyHQ12) with Closite 30B [9].

In this study, four types of organoclay-modified TLCPs were prepared by a combination of ultrasonication, centrifugation, and solution casting methods (some also with a shear-induced phase separation method). The morphologies of the organoclays in TLCP and the effects of the organoclays on the liquid crystallinity linear and non-linear rheological behaviors of the TLCP were characterized. The influence of purification on the rheological behavior of the TLCP was also elucidated.

Experimental

Materials and sample preparation

TLCP, a copolyester containing 30% *p*-hydroxybenzoic acid (*p*-HBA), 35% hydroquinone (HQ), and 35% sebacic acid (SA) in mole fraction, was synthesized and supplied by B.P. Chemicals Ltd, UK. The as-received TLCP is a light brown powder that has been characterized previously [10]. The organoclay Closite 20A is a natural montmorillonite modified with dimethyl dihydrogenated tallow alkyl quaternary ammonium chloride. It was kindly supplied by Southern Clay Products, USA. The as-received TLCP was purified by chloroform and precipitated by methanol at room temperature [11]. 3 wt% as-received organoclay/as-received TLCP (TC3 UP), 3 wt% treated organoclay/as-received TLCP (TC3 FS) have been prepared by a combination of ultrasonication, centrifugation, and solution casting methods [11, 12]. TC3 white and TC3 dark have been prepared by using shear-induced phase phenomenon of TC3 UP [13]. TC3 UP was extruded using a capillary rheometer (Göttfert Rheograph 2003A, Germany) at 190 °C at a low speed (5.0 1/s) [11].

Characterization

Wide angle X-ray diffraction (WAXRD) was conducted at room temperature on a Philips powder X-ray diffraction system (Model PW 1830, The Netherlands). WAXRD was conducted with Cu Kα radiation of wavelength 1.5406 Å. Transmission electron microscopy (TEM) images were obtained using a transmission electron microscope at 200 kV (JEOL 2010, Japan). The mesophase structures of the liquid crystalline phase of the TLCP and organoclay-modified TLCPs were investigated by polarized optical microscopy (POM) using an Olympus microscope BX 50 with a Cambridge shear system CSS450 connecting a hot stage (Linkam Scientific Instruments Ltd., UK). Mesophase structure images were obtained at different temperatures after any shear history and anchored defects had been removed from the measured sample [11]. Controlled strain rheological measurements were carried out using an Advanced Rheometric Expansion System (ARES) (TA instruments, USA) with a 200 g-cm transducer within the resolution limit of 0.02 g-cm. 50 mm cone and plate fixtures with nominal cone angle 0.04 rad and nominal gap 0.0508 mm, as well as 50 mm parallel plate fixtures were used for all tests reported here. All measurements were performed at 185 °C in N_2 atmosphere (TC3 UP measurements were performed at 190 °C), where TLCP has been shown to exhibit stable rheological properties in the nematic phase. Care was taken to ensure that a controlled thermomechanical history was achieved [11].

Results and discussion

Organoclay dispersion and organoclay-modified TLCPs morphology

The structure and morphology of polymer-organoclay nanocomposites depend on the interaction of the polymer with the organoclay and the dispersion of organoclay in the polymer matrix. XRD is a useful and simple measurement

to characterize clay morphologies in nanocomposites. The position of the (001) plane diffraction peak observed in the XRD pattern can be used to determine the interlayer distance of the clay layers according to the Bragg equation.

In TC3 white, the (001) plane diffraction peak observed in the XRD pattern disappeared, compared with the pattern of as-received organoclay with d-spacing of 2.35 nm, as shown in Fig. 1. This observation suggests that the organoclay layer distance in TC3 white may become larger than that of as-received organoclay, due either to the formation of an exfoliated structure in the TLCP matrix, or to the heavy agglomeration of organoclay, or simply to the low concentration of organoclay. The corresponding peaks in TC3 dark and TC3 FS shifted to higher values of 3.27 nm and 3.40 nm, respectively, as the gallery expanded to accommodate the intercalating polymer. Second order reflection is very common, and intercalated hybrids may have up to 13 orders of reflection [14]. The corresponding XRD peak of TC3 UP also displayed a lower angle but
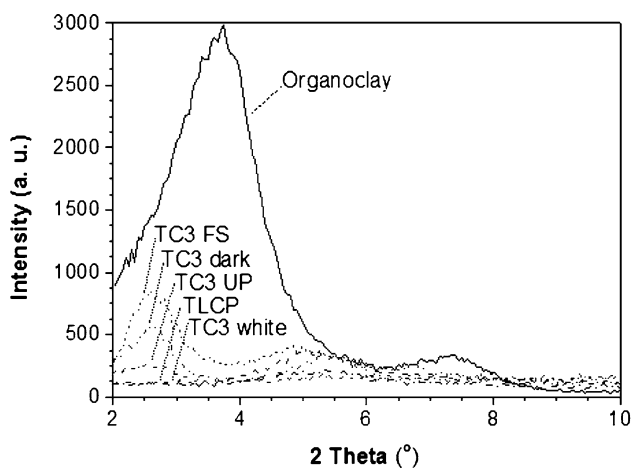
Fig. 1 WAXRD patterns of organoclay, TLCP, and organoclay-modified TLCP blends

took the form of a plateau with low intensity rather than a sharp peak. This suggested that the spaces between layers in the TC3 UP became larger than the as-received organoclay and formed a partially intercalated structure in the TLCP.

XRD and TEM are complementary techniques, in that one technique can provide information missed by the other in analyzing the morphology of layered silicates in polymeric matrix, especially for exfoliated structures. Typical TEM photographs of TC3 white are shown in Fig. 2. The dark plates, 15–25 nm in length, are the organoclays with surfaces paralleling the observed plane. The organoclays were fully exfoliated and well dispersed in the TLCP matrix without any agglomeration.

Bright field TEM images of TC3 dark and TC3 FS are shown in Figs. 3 and 4. Small magnification graphs (Figs. 3a and 4a) show the dispersion of the organoclays in the polymer matrix at both magnification levels, with most displaying agglomerations of size 20–50 nm for TC3 dark and 10–20 nm for TC3 FS. The peaks in the XRD patterns are attributed to the agglomerated layers. The periodic alternating dark and light bands represent the layers of organoclay and the interlayers, respectively, with about 3 nm between the organoclay layers (Figs. 3b and 4b). The as-received organoclay exhibited the same microstructure as that observed in Figs. 3b and 4b but with a smaller interlayer spacing. Moreover, Fig. 4b shows that the organoclay size is uniform and within the range of 100–200 nm, which is comparable with the chain length of a fully extended TLCP molecule based on its number average molecular mass of 14,000 kg/kmol, i.e., ∼85 nm [15].

For the TC3 UP, organoclays were well dispersed in the TLCP with some agglomeration of about 50 nm in size, as shown in Fig. 5a. Figure 5b displays high magnification images of TC3 UP which show that the clay formed
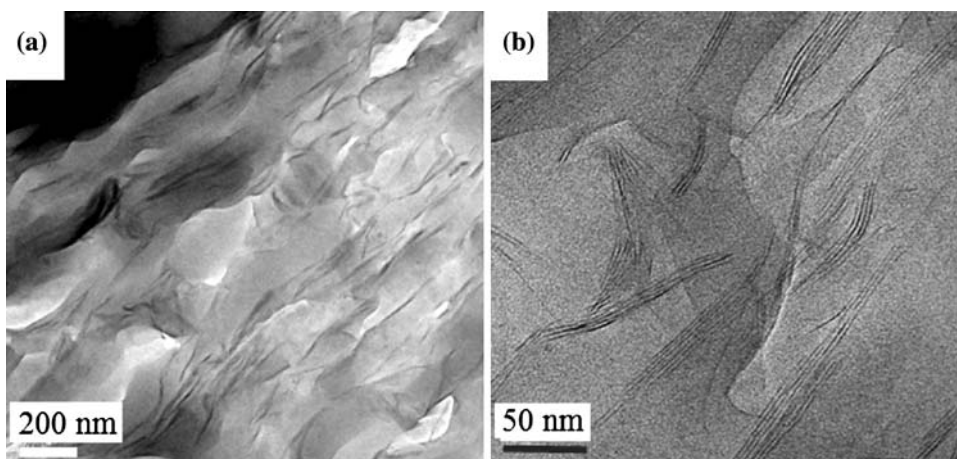
Fig. 2 TEM images of TC3 white with different magnifications
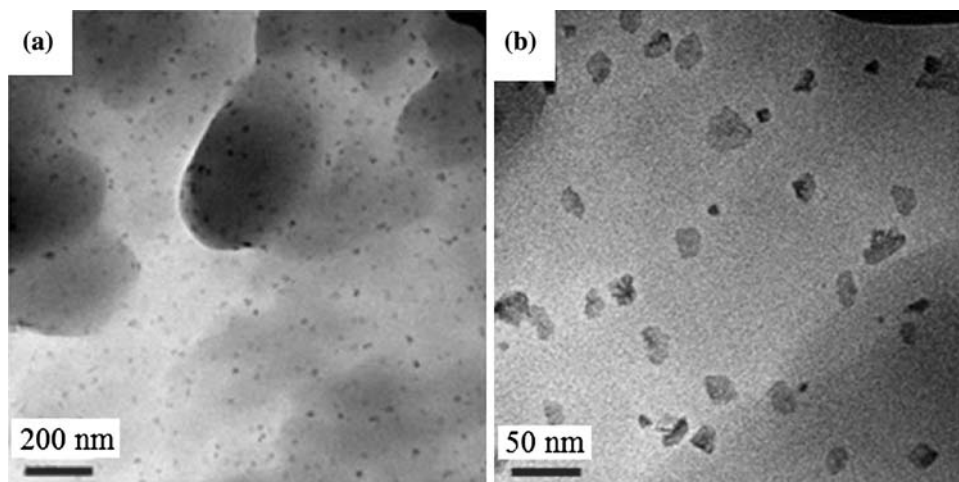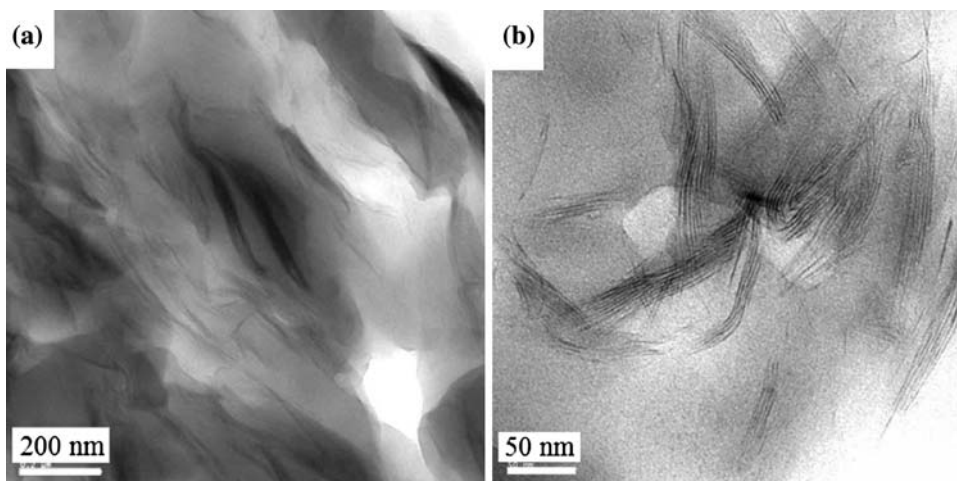
Fig. 3 TEM images of TC3 dark with different magnifications
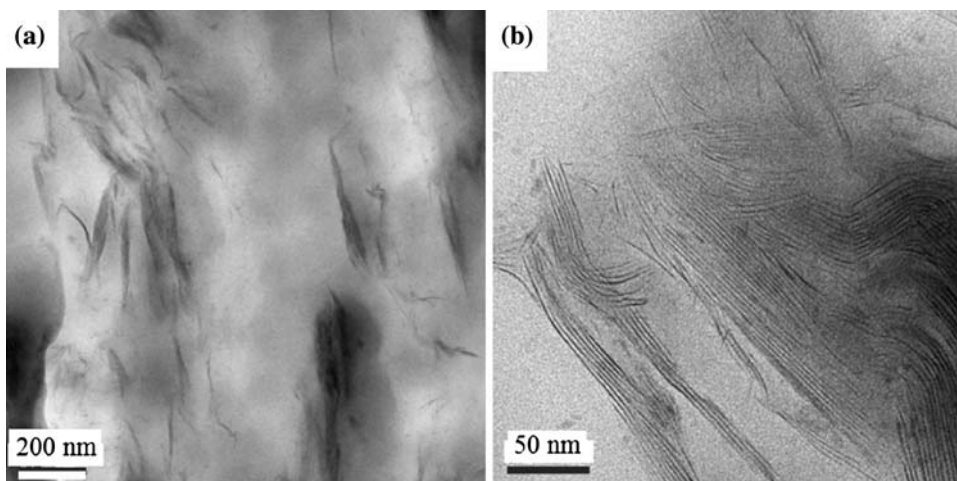
Fig. 4 TEM images of TC3 FS with different magnifications

Fig. 5 TEM images of TC3 UP with different magnifications

partially intercalated structures with d-spacing approximately 4–5 nm on average; the presence of the broad shoulder in the XRD pattern is attributed to these non-exfoliated layers which are parallel in the agglomerated layers.

Liquid crystallinity

Purified TLCP and the organoclay-modified TLCPs were sheared at a steady shear rate of 0.5 1/s for 3600 s and then relaxed in the CSS 450 system at 185 °C (190 °C for

TC3 UP) with the nominated gap being 20 μm. Pictures were taken simultaneously with the POM. Figures 6, 7, 8, 9 display the in situ microstructure evolution of the purified TLCP and organoclay-modified TLCPs using polarization transmission optical microscopy. The incident polarization was oriented along the flow direction and the analyzer was oriented perpendicular to this polarization.

The POM image in Fig. 6a of TC3 UP before shearing at 190 °C shows the domains (mainly dark yellow) with few other colors. Clear agglomeration exists after shearing at 190 °C, as shown in Fig. 6b. Shear-induced phase separation occurred, with two part structures appearing: a polymer-rich part and an organoclay-rich part. Semi-solid materials can be detected in the organoclay-rich part, whereas the TLCP-rich part shows a monodomain with few defect structures, similar to the pure TLCP texture in the same condition. Figure 6c shows the POM images of TC3 UP after steady shearing at a shear rate of 0.5 1/s for 1800 s
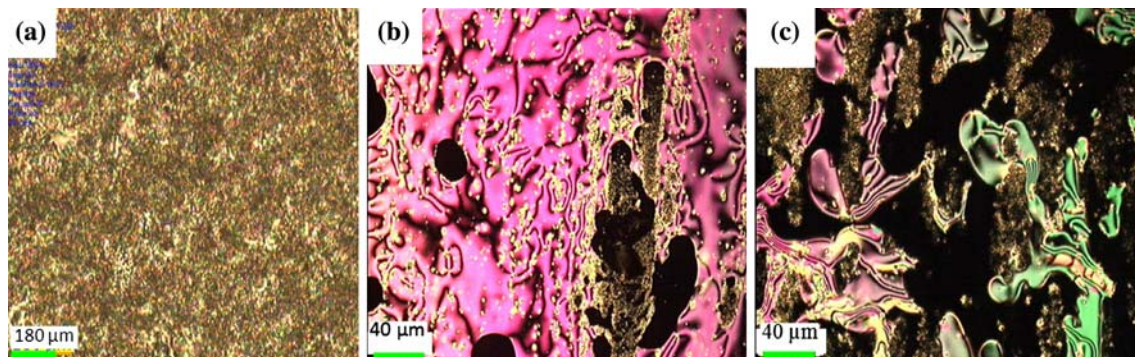
Fig. 6 POM images of TC3 UP **a** before and **b** after shear 0.5 1/s for 3600 s and relaxation at 190 °C **c** after shear 0.5 1/s for 1800 s and relaxed at 230 °C
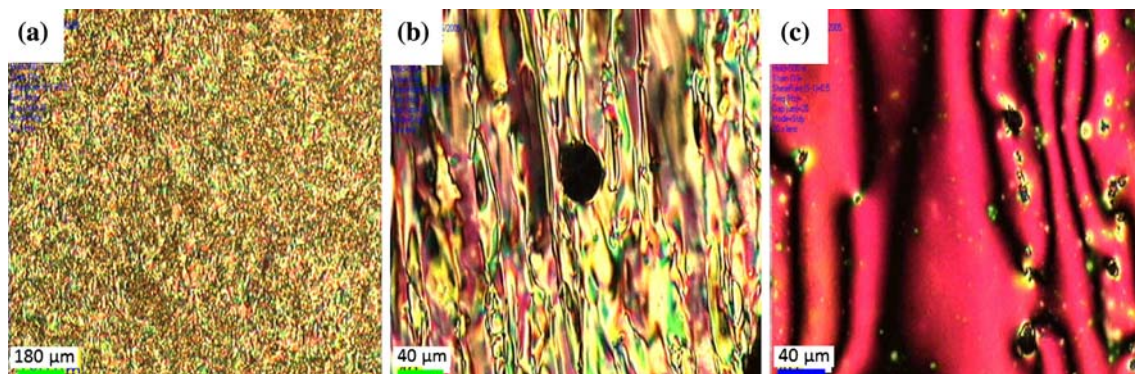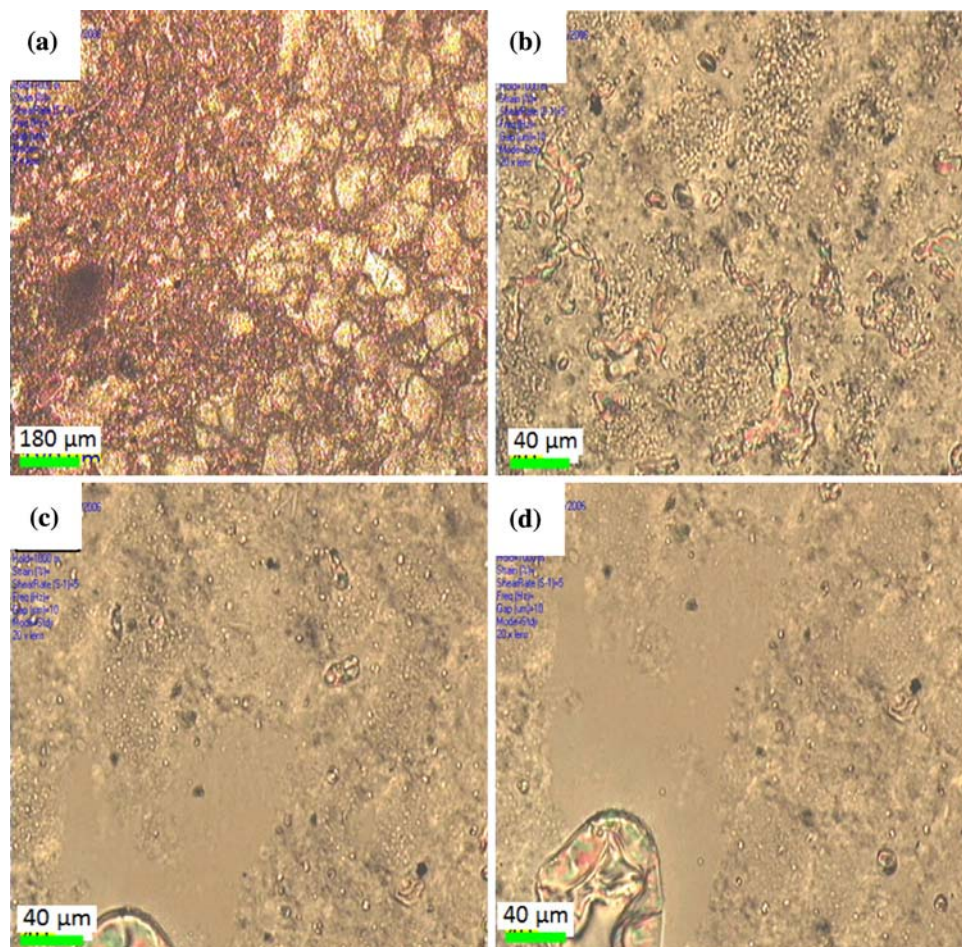

Fig. 7 POM images of purified TLCP at 185 °C **a** before, **b** during, and **c** after steady shear 0.5 1/s
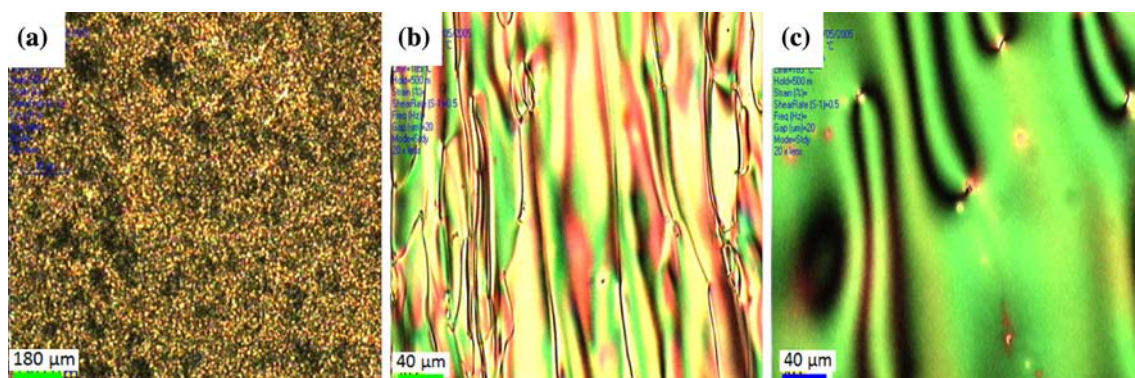
Fig. 8 POM images of TC3 white at 185 °C **a** before, **b** during, and **c** after steady shear 0.5 1/s

Fig. 9 POM images of TC3 dark **a** before **b** after steady shear 0.5 1/s at 185 °C, after steady shear **c** at 230 °C and **d** at 240 °C


at 230 °C, at which pure TLCP produced isotropic–nematic biphase structures. There is an obvious image of isotropic–nematic biphase structures in the polymer-rich part, and semi-solid structures still present in the organoclay-rich part. TC3 UP can be separated into TC3 white and TC3 dark by using the shear-induced phase separation phenomenon, as described before [11]. The liquid crystallinity of TC3 white and TC3 dark is described below.

Microstructures of the melted purified TLCP and TC3 white in the quiescent state at 185 °C are shown in Figs. 7a and 8a, respectively. The TLCP micrograph shows textures surrounding regions of different colors (blue, yellow, and pink) which indicate domains with different orientation. Compared to the TLCP, TC3 white shows domains (mainly dark yellow) with only a few colors. At the start of the shear flow, the domain textures became deformed, stretched and aligned along the shear direction. A gradual increase in the light intensity was observed. During shearing, the TLCP (in Fig. 7b) exhibited colorful textures (yellow, red, and blue with some dark areas), whereas the TC3 white (Fig. 8b) exhibited one main color (yellow with a few blue and red areas). Microstructures of relaxation after flow cessation are illustrated in Figs. 7c and 8c. Once

steady flow was reached, a monodomain with few defect structures was formed. With the same shear history, the static texture of the TC3 white was similar to that of the purified TLCP. The existence of fully exfoliated organoclays did not affect the mesophase structure of the TLCP, which attribute to the good dispersion of organoclays and their small size.

Figure 9a shows TC3 dark at 185 °C with polarized light. The image shows that no nematic mesophase existed at this temperature, because the organoclay layers confined the TLCP molecules in the galleries and tactoids of the organoclays destroyed the ordered structures of the TLCP. After sufficient shearing at this temperature the TLCP domain structures were completely destroyed by the strong shearing force. Smaller domains remained, with more homogeneity than the original sample. Even when TC3 dark was relaxed at 185 °C for more than 3600 s, no nematic structure formed and the degree of liquid crystallinity was very low, as shown in Fig. 9b. When the temperature was increased to 230 °C (Fig. 9c) and 240 °C (Fig. 9d), only a few nematic structures were observed and no nematic–isotropic transition phenomenon occurred, although it would normally occur at 230 °C for TLCP.
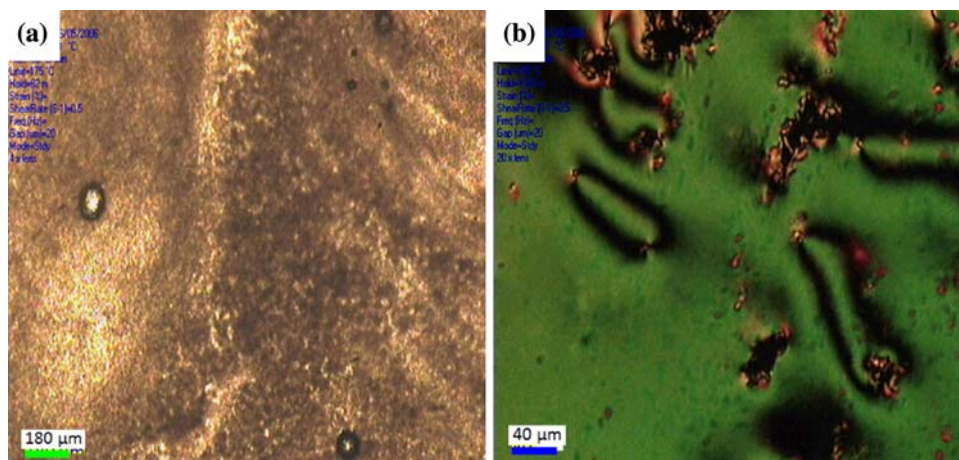
From these images it is clearly observed that the degree of liquid crystallinity was much lower than that of TLCP and the nematic mesophase was destroyed by the large organoclay sizes and strong intercalated interactions between organoclay and TLCP.

Figure 10 shows POM photographs of TC3 FS under different conditions. Figure 10a shows the original TC3 FS morphology under polarized light at 175 °C. At this temperature the TC3 FS has already melted but shows no mesophase structures. The light intensity is uniform, with only small domains. After steady shear at 185 °C for 3600 s at 0.5 1/s and relaxation for a sufficient time, as shown in Fig. 10b, the mesophase structures are similar to those of the TLCP. Careful observation of the entire image reveals that there are still some features which are believed to be organoclay interacting strongly with the TLCP molecules and forming clusters. However, the density of these clusters is low and the domain sizes are not large. The liquid crystallinity of TLCP did not affect much by the presence of organoclays with comparable size of the fully extended TLCP molecules.

Linear viscoelasticity behaviors

The transitions in the TLCPs (with and without purification) and organoclay-modified TLCPs from linear to non-linear viscoelastic behaviors, as manifested in dynamic strain sweep experiments, are shown in Fig. 11. It can be seen that in the linear viscoelastic region where the strain amplitude is below the critical value, as-received TLCP (AR TLCP) exhibits approximately five times greater complex viscosity than the purified TLCP (P TLCP), because of the removal of impurities and the catalysis generated during the synthesis process. In comparison with the purified TLCP, TC3 dark shows the highest complex viscosity, with an increase of more than three orders of magnitude; TC3 UP shows more than two orders of
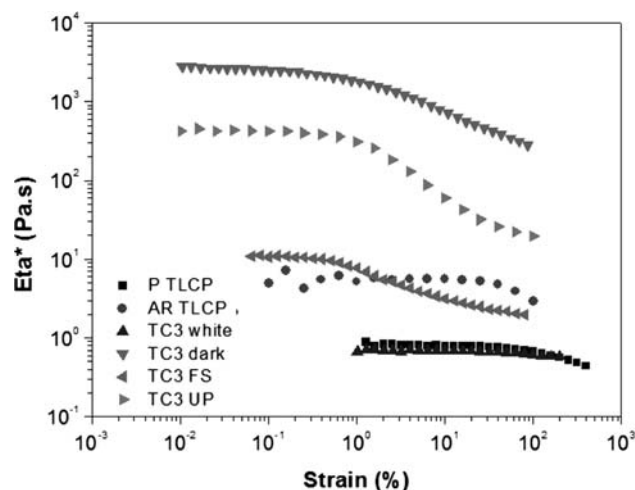
Fig. 11 Complex viscosities of TLCPs and organoclay-modified TLCPs in dynamic strain sweep at 185 °C (TC3 UP at 190 °C)

magnitude higher complex viscosity; TC3 FS shows less than one order of magnitude higher complex viscosity; TC3 white shows similar complex viscosity to that of the purified TLCP. On the other hand, in the nematic phase, the textures of the TLCP are very stable, giving a very large linear viscoelastic response region. All materials exhibit the expected shear-thinning behavior, with the critical strain amplitude for the transition decreasing dramatically from about 20.0% for the TLCPs and TC3 white to 1.0% for TC3 FS, 0.3% for TC3 UP, and 0.1% for TC3 dark. Furthermore, the strain amplitude dependence of complex viscosity in the shear-thinning regime is different for the organoclay-modified TLCPs. Comparing the complex viscosity in the linear region with the complex viscosity at 100% strain (non-linear region), TC3 UP is about 25 times higher, TC3 dark is about 15 times higher and TC3 FS is about 6 times higher, whereas TC3 white is almost the same.
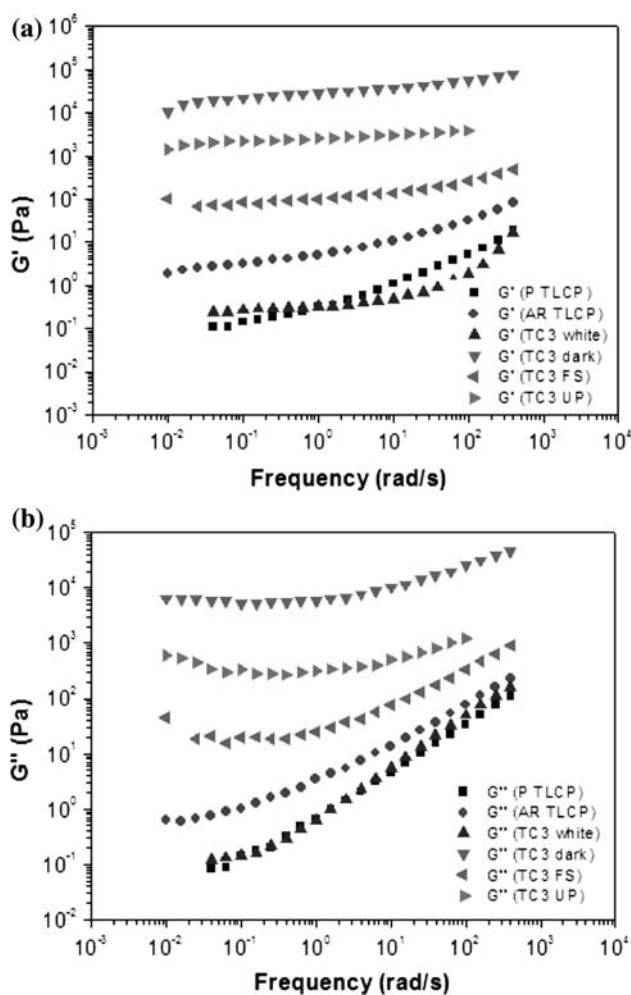
Fig. 12 a Storage and **b** loss modulus of purified TLCP and organoclay modified TLCPs in dynamic frequency sweep at 185 °C (TC3 UP at 190 °C)

Dynamic frequency sweeps at strains well within the linear viscoelastic regime of each material were performed in a range of frequencies covering five decades (0.01–1000 rad/s). The results, shown in Fig. 12 exhibit the storage modulus G′ and loss modulus G″ of the TLCPs and organoclay-modified TLCPs.

The slopes in the terminal region for G′ and G″ were 0.12 and 0.31 for TC3 white, and 0.30 and 0.55 for purified TLCP. Pseudo-solidlike behaviors existed in the purified TLCP and TC3 white, with the TC3 white exhibiting more solid-like behavior than the purified TLCP. The polydomain structure in its bulk state is the reason for the behavior of purified TLCP [16]. The percolated network formed by the exfoliated organoclay with the purified TLCP molecules enhances those polydomain structures, causing more solid-like behavior in the low frequency region in TC3 white. At high frequencies, TC3 white showed a gradual change of slope to -0.21, whereas purified TLCP maintained the same slope. In this region, the slopes of G′ and

G″ for purified TLCP were 0.70 and 0.86 and for TC3 white were 1.83 and 0.92. There were dramatic differences between the two materials. The slopes for TC3 white approached the theoretical values for polymers with flexible chains, which are 2 and 1, respectively.

For TC3 dark in the low frequency region, the slopes of G′ and G″ curves were smaller and G′ and G″ were more than three-order higher in magnitude than those of the as-received TLCP. Negative slopes in the low frequency regions were also reported recently by Huang and Han [9, 17], who attributed this phenomenon to the influence of strong attractive interaction. It appears that the intimate contact between the polymer and the inorganic sheets leads to an alteration of the relaxation dynamics of the polymer, causing the low-frequency plateau in the modules and the low-strain non-Newtonian viscosity behavior.

With careful analysis of the slopes of modules in low and high frequency regions for TC3 FS, it is clearly seen that in the low frequency regions TC3 FS holds terminal regions, with slopes of G′ and G″ being -0.079, -0.383. With treated organoclay introduced into the TLCP matrix, network structures still existed and enhanced the solid-state behavior of as-received TLCP in the low frequency region. In high frequency regions the entanglements were destroyed but weak interactions still existed. From the phenomenological aspect, the rheological curve of TC3 FS is a combination of the curves of TC3 dark and as-received TLCP, with a trend in the low-frequency region similar to that of TC3 dark and a trend in the high-frequency region similar to that of as-received TLCP.

The dependence of dynamic modulus on frequency was measured for TC3 UP at 190 °C. In the low frequency regions, the G′ curve had a similar trend to that of TC3 dark and TC3 FS and the G″ curve was similar to that of TC3 FS, which means that a solid-like structure also existed in the TC3 UP. In the high frequency region, the G″ curve showed a trend approaching that of the as-received TLCP curves, as in the TC3 FS.

Because the organoclay layers dispersed into the polymeric matrix as a few randomly organized organoclay layers or stacks of layers in the quiescent condition, it was expected that in the quiescent state, a greater proportion of the layers or stacks would be hydro-dynamically impeded, resulting in the filler–filler interaction becoming important and in fact dominating the long-term viscoelasticity of the composites. Additionally, the ease with which the organoclay structure could be altered by flow was considerably enhanced, primarily because of filler–filler interactions. It is not surprising, then, that the threshold strain amplitude for the onset of shear-thinning decreased with additional organoclay and the strain amplitude dependence of the shear-thinning was enhanced for the nanocomposites. Also, different organoclay sizes and

concentrations displayed different levels of interaction in the nanocomposites. In TC3 dark, by virtue of the intercalated structures, high concentration and large organoclay size, the interactions of fillers as well as of filler-polymer molecules became significant and dominant. High complex viscosity, low critical strains, and significant shear-thinning behavior were observed. In TC3 UP, its partially intercalated and partially exfoliated structure, mixed sizes, and high concentration of organoclay, as well as the shear-induced phase separation phenomenon, caused the TC3 UP to show the most dramatic shear-thinning change (complex viscosity in the linear region/complex viscosity at 100% strain >25). In TC3 FS, because the organoclay was of uniform size and of comparable size to that of fully extended TLCP molecules, interactions of fillers and of filler-TLCP molecules were not significant. Because of this specific structure the nanocomposite displayed comparable complex viscosity in the linear region and similar complex viscosity in the non-linear region to the as-received TLCP. In TC3 white, the low organoclay concentration, uniform small organoclay size and fully exfoliated structures caused filler–filler interaction to become negligible. Non-bond interactions of filler-TLCP molecules dominated the rheological behaviors of TC3 white, with similar complex viscosity but different viscoelastic behaviors in the linear viscoelastic region.

Steady shear behaviors

The application of steady shear was sufficient to align the structure and characterize the non-linear behavior of the samples. Figure 13 shows the normalized stress curves of the TLCPs and organoclay-modified TLCPs at typical steady shear rates. With the exception of the first few
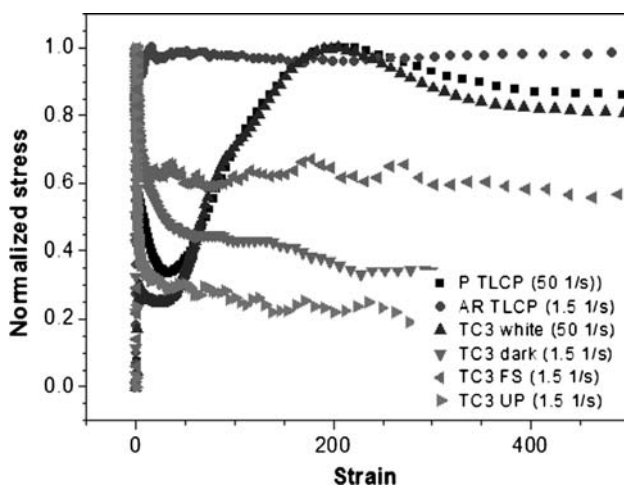
Fig. 13 Normalized stress evolution curves for purified TLCP and organoclay modified TLCPs at 185 °C (TC3 UP at 190 °C) with shear rate 1.5 1/s (50.0 1/s for purified TLCP and TC3 white)

minutes of shearing, the stress decreased monotonically with continued shearing, finally reaching a plateau value.

For the purified TLCP and TC3 white, in the first few minutes of shearing the stress showed one or more peaks, before monotonically decreasing. Overshoot was a common phenomenon in the TLCP and its nanocomposite, implying that some network structures were destroyed by shearing. Two overshooting peaks and one undershooting peak appear for both materials in Fig. 13. Magda et al. [18] reported similar findings in a dioctyl phthalate solution of high molecular weight polystyrene. They suggested that the first and second overshoots at a high shear rate were due to chain stretching and shear-induced demixing, respectively. Rheological experiments were carried out on a certain concentration solution under shear flow by Kume et al. [19], who considered that the second overshoot was related to the development of a butterfly pattern and the formation and growth of shear-induced structures.

Figure 13 shows the normalized strain-dependent shear stress curves for the start of steady shear at the same shear rate for the as-received TLCP, TC3 dark, TC3 FS, and TC3 UP. All exhibit viscoelastic behavior, with the presence of a stress overshoot at the beginning and eventual achievement of final steady state. Furthermore, the shear stress data do not exhibit any time-dependent oscillations as would be expected for anisotropic systems with particle tumbling or rotation.

The efficiency of steady shear in orienting TLCP molecules under the same shear strain values can be determined by the ratio of normalized overshooting and steady state values. The as-received TLCP had the lowest efficiency, with almost no overshooting occurring (ratio ≈ 1) and the TC3 UP had more than seven times higher values (ratio > 7). One reason for the huge difference between the overshooting and steady state values for TC3 UP is that the temporary network structures originally existing in the nanocomposite were permanently destroyed; a second but important reason is the occurrence of phase separation during steady shearing. The organoclay-rich phase had a semi-solid morphology. It adhered to the testing fixtures during shear and was lubricated by the TLCP-rich phase on its surface. Only TLCP-rich phase between the fixtures, was measured, which accounted for most of the total measured viscosity.

Figure 14 shows the apparent shear viscosities of TLCPs and organoclay-modified TLCPs with different shear rates at 185 °C (TC3 UP values were characterized at 190 °C). All materials show shear-thinning phenomena. Originally, the viscosity difference was almost four orders of magnitude higher at a low shear rate for the different organoclay-modified TLCPs, but they gradually merged (or displayed a merging trend) with the increase in shear rate. In the purified TLCP and TC3 white, the shear rate could reach
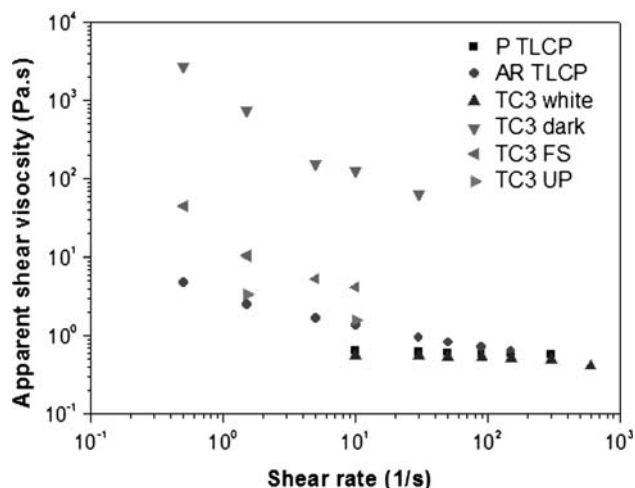
Fig. 14 Apparent shear viscosity of purified TLCP and organoclay modified TLCPs in steady shear at 185 °C (TC3 UP at 190 °C)

almost 1000 1/s. It was also observed that the as-received TLCP displayed a much higher steady shear viscosity than that of the purified TLCP at the same shear rate.

Figure 14 further shows that the viscosities of the organoclay-modified TLCPs were less than 10 Pa s when the shear rate was greater than 2.0 1/s (except TC3 dark), and TC3 white had much lower viscosity than the as-received TLCP. These values were exceptionally low, even among the TLCPs. Some studies show that a small amount of a similar type of as-received TLCP effectively reduced the viscosity of high density or high molecular mass polyethylene (HDPE or HMMPE) at a processing temperature close to the nematic transition region of the TLCP [20, 21]. If the organoclay-modified TLCPs are blended with HDPE or HMMPE, this low viscosity will produce an extremely small viscosity ratio, which is an important factor influencing the rheological properties of a blend system. A significant bulk viscosity reduction can be achieved by blending a small amount of organoclay-modified TLCP, which will be evaluated in the further studies.

Conclusions

Four kinds of organoclay-modified TLCPs, i.e., TC3 white, TC3 dark, TC3 FS, and TC3 UP, were prepared by a combination of ultrasonication, centrifugation, and solution casting (and shear-induced phase separation) methods. The effects of organoclay size and concentration on the morphologies, liquid crystallinity, and rheological properties of organoclay-modified TLCP composites have been studied. The organoclay layers dispersed into the TLCP matrix as a few randomly organized organoclay layers or stacks of layers in the composites. Larger organoclay size or higher

concentration of organoclay, especially higher concentration, made the filler–filler and filler–polymer interactions become important and dominated the long-term visco-elasticity of the composites. The organoclay structures could be easily altered and those interactions would be efficiently destroyed by the steady shear to make composites have much lower viscosities in the steady state of shear. Organoclay size has primary effect on the liquid crystallinity of TLCP. Smaller or comparable organoclay size with the fully extended TLCP molecules has weak or negligible negative effect on the liquid crystallinity of TLCP, while layer size of organoclay totally damages the liquid crystallinity of TLCP. The organoclay-modified TLCPs maintained low steady shear viscosities at high shear rates, which were comparable with that of TLCP. They are promising candidates as viscosity reduction agents for polyethylene, functioning in a similar manner to TLCP at a processing temperature close to the nematic transition region of TLCP.

References

1. Romo-Uribe A, Lemmon TJ, Windle AH (1997) J Rheol 41:1117
2. Clarke SM, Rennie AR, Convert P (1996) Europhys Lett 35:233
3. Mourchid A, Lecolier E, van Damme H, Levitz P (1998) Langmuir 14:4718
4. Schmidt G, Nakatani AI, Han CC (2002) Rheol Acta 41:45
5. Pignon F, Magnin A, Piau JM, Fuller GG (2001) 2nd international conference on self-assembled fibrillar networks
6. Zhang GL, Jiang CL, Su CY, Zhang HZ (2003) J Appl Polym Sci 89:3155
7. Chang JH, Ju CH, Kim SH (2006) J Polym Sci B Polym Phys 44:387
8. Vaia RA, Giannelis EP (2001) Polymer 42:1281
9. Huang WY, Han CD (2006) Macromolecules 39:257
10. Gao P, Lu XH, Chai CK (1996) Polym Eng Sci 36:2771
11. Tang YH, Gao P, Ye L, Zhao CB (2010) J Polym Sci B Polym Phys (accepted)
12. Tang YH, Gao P, Ye L, Zhao CB, Lin W (in review) J Mater Sci
13. Tang YH, Gao P, Ye L, Zhao CB, Lin W (submitted) J Mater Sci
14. Chiu FC, Lai SM, Chen JW (2004) J Polym Sci B Polym Phys 42:4139
15. Chan CK, Gao P (2005) Polymer 46:10890
16. Onogi S, Asada T (1980) Rheology, vol I. Plenum Press, New York
17. Huang WY, Han CD (2006) Polymer 47:4400–4410
18. Magda JJ, Lee CS, Muller SJ, Larson RG (1993) Macromolecules 26:1696
19. Kume T, Hattori T, Hashimoto T (1997) Macromolecules 30:427
20. Chan CK, Whitehouse C, Gao P (1999) Polym Eng Sci 39:1353
21. Chan CK, Whitehouse C, Gao P, Chai CK (2001) Polymer 42:7847