Organoclay/thermotropic liquid crystalline polymer nanocomposites. Part VI: Effects of intercalated organoclay on nanocomposite morphology, thermal and rheological properties

Youhong Tang*†, Ping Gaoa, Lin Ye, Chengbi Zhao and Wei Linb

aDepartment of Chemical and Biomolecular Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong, China; bCentre for Advanced Materials Technology, School of Aerospace, Mechanical and Mechatronic Engineering, The University of Sydney, Sydney, NSW 2006, Australia; cCentre for Advanced Marine Materials, School of Civil Engineering and Transportation, South China University of Technology, Guangzhou 510641, China

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A study of a typical intercalated structure of a thermotropic liquid crystalline polymer (TLCP) with organoclay was performed to elucidate the influence of intercalated organoclay on the TLCP molecules, especially on their liquid crystallinity, thermal and rheological properties. The intercalated structures were confirmed in TLCP and organoclay formed molecular interactions with TLCP molecules in the system. Such intercalated structures caused the glass transition temperature of the nanocomposite to become invisible in thermal measurement and also caused loss of liquid crystallinity. The TLCP molecules inside the organoclay galleries showed higher thermal stability and transition temperatures, but the orderly structure of the TLCP molecules outside the galleries was destroyed by the organoclay, causing the TLCP to display lower thermal stability and transition temperatures than pristine TLCP. At 185°C, where TLCP is in the nematic phase, the nanocomposite had three orders of magnitude higher viscosity in the linear viscoelastic region than that of TLCP, with chain mobility and relaxation time slowed due to the intercalated effects in the nanocomposite. Steady shear altered the domain sizes and oriented the highly anisotropic organoclay layers or tactoids along the shear direction.

Keywords: intercalation; clay; liquid crystalline polymer (LCP); rheology

1. Introduction

The conformation of polymeric chains in the vicinity of flat walls or free surfaces has been studied extensively in recent years, motivated by the many applications where the behavior of confined chains is critical. Such applications include coatings and flow of molecular solutions in capillaries. Increased interest has recently been focused on

*Corresponding author. Email: tang@aeromech.usyd.edu.au.
†Current address: Centre for Advanced Materials Technology, School of Aerospace, Mechanical and Mechatronic Engineering, The University of Sydney, Sydney, NSW 2006, Australia.
polymer intercalated into 2:1 mica-type phyllosilicates, such as montmorillonite and synthetic hectorites, as model systems for studying the structure and dynamics of nanoscopically confined polymers. Both recent experimental results and simulations suggest that many dynamic models can be applied to describe these confined molecules, and that the distance from the confining surface appears to be a critical parameter in understanding which dynamic modes are appropriate [1,2].

Polymers confined at molecular length scales display structures and dynamics that differ from their bulk systems. Depending upon the nature of the polymers and the confining surfaces, confinement may either enhance or reduce molecular mobility and relaxation [3]. Moreover, experimental studies using surface forces apparatus (SFA) have indicated that the dynamics of nanoconfined polymers were characterized by a viscosity increase up to three orders of magnitude greater than the bulk values. Solid-like responses to imposed shear and confinement-induced ‘sluggish’ behavior suggested the existence of a ‘pinned’, ‘immobilized’ layer adjacent to the confining surfaces [4–10]. Pioneering studies by Vaia et al. [11] utilized a simple X-ray diffraction-based scheme to investigate the kinetics of polystyrene intercalation in octadecylammonium-exchanged fluorohectorite in a quiescent condition. Manias et al. [12] reported X-ray diffraction and small-angle neutron scattering in characterization of the intercalation dynamics of polystyrene into 2 nm galleries of alkylammonium ion-exchanged fluorohectorite, a mica-type layered silicate. Experimental studies by Wallace et al. [13] showed that strongly attractive interactions increase the glass transition temperature (\(T_g\)) near a surface, whereas less attractive interactions reduce \(T_g\) in polystyrene thin films supported on hydrogen-terminated silicon substrates and on silicon native-oxide surfaces, respectively. Meanwhile, the interparticle spacing effect on \(T_g\) of poly(methylmethacrylate)–silica and poly(2-vinyl pyridine)–silica nanocomposites has been studied carefully [14]. Other methods, such as dielectric relaxation spectroscopy measured in polystyrene thin films labeled with a dye [15], changing of temperature-dependent fluorescence intensity by embedded a fluorescence tag in poly(methyl methacrylate) [16] were used to analyze the nanostructure effects on \(T_g\).

In parallel with the experimental studies, molecular dynamics simulations have been used to clarify the associated microscopic models and the phenomenological observations of macroscopic properties. Such simulations have revealed that the dynamics of chain molecules undergo radical changes in the vicinity of solid surfaces, to the extent that both chain mobility [17] and chain relaxation times [18] can be slowed by three orders of magnitude near a physisorbing surface.

In this study, a model thermotropic liquid crystalline polymer (TLCP)/organoclay system was analyzed using a series of characterization methods to elucidate the influence of organoclay intercalated with the TLCP molecules, especially on their liquid crystallinity and thermal and rheological properties.

### 2. Experimental

#### 2.1. 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 [19]. 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 nanocomposite was prepared by a combination of ultrasonication, centrifugation, solution casting and heating-shearing separation methods. The detailed preparation steps have been reported previously [20]. TLCP and the 3.0 wt% organoclay/TLCP nanocomposite left in the barrel of a capillary rheometer after heating-shearing separation (subsequently referred to as TC3 dark) [20] were characterized using various methods, detailed in the following section.

2.2. Characterization

A Fourier transform infrared (FTIR) spectrometer (Bio-Rad FTS 6000, USA) was used at ambient temperature with an attenuated total reflectance (ATR) mode with or without polarizer light for thin film. Spectral resolution was maintained at 2 cm\(^{-1}\). Dry nitrogen gas was used to purge the sample compartment to reduce the interference of water and carbon dioxide in the spectrum. Wide-angle X-ray diffraction (WAXRD) was conducted at ambient temperature using a Philips powder X-ray diffraction system (Model PW 1830, The Netherlands). WAXRD was performed with Cu K\(\alpha\) radiation of wavelength 1.5406 Å. The film preparation steps were the same as those previously reported [21]. Transmission electron microscopy (TEM) images were obtained at 200 kV with a transmission electron microscope (JEOL 2010, Japan) with the same preparation as previously reported [21].

Thermal stability analysis was carried out using a Hi-Res TGA 2950 thermogravimetric analysis apparatus (TA Instruments, USA). The test was carried out in air and N\(_2\) with a heating rate of 20.0°C/min from 50.0°C to 600.0°C. The phase transition temperatures of TLCP and TC3 dark were determined via differential scanning calorimetry (DSC, PYRIS diamond, Perkin-Elmer Instruments, USA), using indium as the calibration standard, with heating or cooling rates of 10.0°C/min under nitrogen atmosphere.

The mesophase structures of the liquid-crystalline phases of TLCP and TC3 dark were investigated by polarized optical microscopy (POM) using an Olympus microscope BX 50 with a Cambridge shear system CSS450 connected to a hot stage. Mesophase structure images at different temperatures were obtained after removing any shear history and anchored defects, as previously described [20].

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 0.02 g cm. For all tests reported here, 25 mm parallel plate fixtures were used. All measurements were performed at 185°C in a N\(_2\) atmosphere. A controlled thermomechanical history was performed before testing [20].

3. Results and discussion

3.1. Interactions between TLCP and organoclay

Figure 1 shows FTIR spectra of TLCP and TC3 dark. The absorption peak at 1062 cm\(^{-1}\) in the TLCP associated with the asymmetric stretching peak of \(-\text{C}–\text{O}–\) (in \(-\text{Ar}–\text{C}–\text{O}–\text{Ar}–\)) shifted to 1055 cm\(^{-1}\) in TC3 dark. The peak shift is the result of the interaction between the positive charged N\(^+\) ion in the surfactant 2M2HT located on the surface of the organoclay with the \(-\text{C}–\text{O}–\) group in the TLCP molecules. No peak shift occurred for the symmetric stretching peak of \(-\text{C}–\text{O}–\) (in \(-\text{Ar}–\text{C}–\text{O}–\text{Ar}–\)), which appeared at 1012 cm\(^{-1}\). The relative intensity ratios between the two stretching modes changed. Compared with the TLCP, the ratio between the symmetric and asymmetric stretching mode was significantly increased for TC3 dark, indicating that symmetric stretching was enhanced in TC3 dark.
In Figure 1, peaks at 1092 cm$^{-1}$ and 1180 cm$^{-1}$ belong to the –C–O– groups in stretching mode (in –CH$_2$–C–O–Ar–). There is no peak shifting but the ratio between the relative intensity of symmetric and asymmetric stretching peaks has changed for the different materials. For TLCP the symmetric intensity was greater than the asymmetric intensity, whereas for TC3 dark the asymmetric intensity was much greater than the symmetric intensity. Symmetric stretching was suppressed in the TC3 dark material.

The peaks at 1110 cm$^{-1}$ and 1130 cm$^{-1}$ are aromatic =C–H in-plane deformation vibrations. Discussion of these peaks is provided when the polarized light FTIR result is reported.

With horizontally (vertically) polarized IR on the film surface plane, if the stretching direction is parallel to the horizontal (vertical) direction, the intensity of this mode will be enhanced. If the stretching direction is vertical to the horizontal (vertical) direction, the intensity of this mode will be suppressed. Comparing the spectra of the materials with two perpendicular directions, we can obtain further information about the direction of the molecules in the films.

Figure 2 shows the FTIR spectra of TLCP and TC3 dark with polarized IR light. For the absorption peak at 1062 cm$^{-1}$ (the asymmetric stretching peak of –C–O–), TC3 dark shows a red shift in the horizontal condition compared with the TLCP spectrum. Also the relative intensity ratio of the symmetric to asymmetric increased for TC3 dark in both directions, especially in the horizontal direction. For peaks at 1092 cm$^{-1}$ and 1180 cm$^{-1}$, the symmetric peaks of –C–O– in TC3 dark were suppressed in both directions compared with TLCP. For TLCP, symmetric stretching in the vertical direction was also suppressed. Due to the different directions of deformation vibration for the two types of C–H (four C–H bonds), the peaks at 1110 and 1130 cm$^{-1}$ are associated with the =C–H in-plane (ip) deformation vibrations and the peaks at 755 cm$^{-1}$ and 765 cm$^{-1}$ are associated with the =C–H out-of-plane (op) deformation vibration. With vertically polarized light, the C–H ip stretching spectra for TC3 dark and TLCP were the same, but with horizontally polarized light the C–H ip stretching peak at 1110 cm$^{-1}$ in TLCP shifted to a higher wavenumber of 1120 cm$^{-1}$ for TC3 dark, and the other C–H ip stretching peak at 1130 cm$^{-1}$ in TLCP disappeared completely in TC3 dark, as shown in Figure 2.
3.2. Organoclay dispersion and morphological analysis

XRD is a useful and simple measurement to characterize clay morphology in nanocomposites. The position of the (001) plane diffraction peak observed in the XRD pattern can be used to determine the interlayer distance of clay layers according to the Bragg equation, \( \lambda = 2d \sin \theta \), where \( \lambda \) is the wavelength of incident wave, \( d \) is the spacing between the planes in the atomic lattice, and \( \theta \) is the angle between the incident ray and the scattering planes. Typical WAXRD patterns for organoclay, TLCP and TC3 dark are shown in Figure 3. The \( d \)-spacing of organoclay, originally at 2.35 nm, shifted to a higher value, 3.27 nm, as the gallery expanded to accommodate the intercalating polymer. Second-order reflection is very common, and intercalated nanocomposites may have up to 13-order reflections [22].

TEM is an extremely useful technique for providing complementary information about WAXRD ‘silent’ nanocomposites. In addition to a description of the spatial correlations
of organoclays, TEM provides a means to discern the homogeneity of the mixing process. Bright-field TEM images of TC3 dark are shown in Figure 4. Small magnification graphs (Figures 4a and 4b) show the dispersion of organoclays in the polymer matrix with most displaying agglomerations of size 20–50 nm. The peaks in the WAXRD patterns are attributed to the agglomerated layers. The periodic alternating dark and light bands represent the layers of organoclay and the inter-layers, respectively, with a spacing of ~3 nm between the organoclay layers (Figure 4c). The pristine organoclay exhibits the same microstructure as that observed in Figure 4c but with a smaller interlayer spacing.

3.3. Thermal properties

Figure 5 illustrates the TGA curves of organoclay with TLCP and TC3 dark in air and \( N_2 \) atmosphere. The TGA curves show clearly that at beginning of weight loss, the TLCP had better thermal stability in both oxidation and decomposition conditions than TC3 dark. This phenomenon may be caused by the agglomerated clay destroying the orderly structure of TLCP molecules that lie outside the organoclay galleries. With the loss of that orderly structure, the thermal stability of TC3 dark decreased. However, the TGA curves show that at high temperatures TC3 dark had greater thermal stability than TLCP. This effect is caused by the intercalated TLCP molecules in the organoclay gallery. With enhancement by organoclay, the thermal stability of the TLCP molecules inside the gallery improved, giving rise to greater thermal stability than that of pure TLCP. From the TGA curves it can be seen that two kinds of TLCP molecules exist in TC3 dark. One is the TLCP molecules outside the organoclay gallery, where the orderly structure of the TLCP has been destroyed by organoclay clusters; the other is the TLCP molecules inside the organoclay gallery, where the TLCP molecules are intercalated in the gallery.

Glass transition in thin (10–150 nm) supported polystyrene films has been extensively studied by several methods, including ellipsometry, X-ray reflectivity, positron annihilation lifetime spectroscopy and brillouin light scattering [13]. Although many of the findings remain controversial, some consensus has been reached. Specifically, it is believed that where strong specific interaction exists between the polymer and the surface, the glass transition temperature increases. In efforts to explain these results, some researchers [23] have proposed the existence of a 50 nm immobilized, rigid, ‘dead’ layer of polymer adsorbed on the solid surfaces, where no \( T_g \) is observed and the polymer and segmental dynamics are believed to be inhibited. Manias et al. [24] studied the glass transition of polystyrene in much more severe confinement of 2 nm using DSC and nuclear magnetic resonance
(NMR), and no glass transition was detected in the confined systems. It seems evident that there is no clear transition in these ultra-confined polymers within the 2 nm slit pores. This is consistent with extensive studies investigating the glass transition of polyethylene oxide intercalated in similar slit pores, employing DSC and thermal stimulated dielectric depolarization [25].

Curves of the first and fifth DSC heating and cooling cycles of TLCP and TC3 dark are shown in Figure 6. From the first heating curves it is evident that the glass transition temperature of the TLCP, originally 121.7°C, became invisible in the TC3 dark. In TC3 dark, the two melting temperatures exist, just as in TLCP, but they have shifted to lower temperatures due to the severe segmental distribution [19]. These shifts may have been caused by destruction of the orderly structure of TLCP by the presence of agglomerated organoclay clusters. After a few heating and cooling cycles, defects within the TLCP have been annealed out, causing the crystal-to-nematic transition temperature to shift to higher temperatures, especially the peak at 145.3°C originally in the first TLCP heating curve. The enthalpy has decreased because of the slow crystallization rate for TLCP. For TC3 dark, in the fifth heating curve, the two peaks have merged during annealing, forming a broad peak centering on a higher temperature than either of the peaks in the first heating curve. Both curves demonstrate that annealing can effectively decrease the density of defects and that intercalated organoclay structures dramatically influence the thermal properties of TLCP.

Figure 5. TGA of organoclay, TLCP and TC3 dark in air (a) and N₂ (b) conditions.

Figure 6. DSC of first and fifth (a) heating and (b) cooling curves of TLCP and TC3 dark.
3.4. Liquid crystallinity and mesophase structure

Figures 7a–7d show optical micrographs of TLCP and TC3 dark at 185°C obtained using polarized light. The TLCP micrograph shows textures surrounding regions of different colors (blue, yellow and pink), which indicate domains with different orientation before shearing (Figure 7a), and once steady flow was reached, a monodomain with few defect structures was formed in TLCP (Figure 7c). For TC3 dark, Figure 7b show that no nematic mesophase exists at this temperature because of the intercalation structures between the organoclay and TLCP molecules and the destruction by organoclay clusters of the ordered structures of the TLCP. After sufficient shearing at this temperature, domain structures were completely destroyed by the strong shearing force. Smaller domains remained in TC3 dark, with more homogeneous domains than the original sample. Even after 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 seen in Figure 7d. When the temperature was increased to 230°C, for TC3 dark (Figure 7f), only a few nematic structures were observed and no nematic–isotropic transition phenomenon occurred after steady shear, although it would have occurred at 230°C for TLCP [19] (Figure 7e). From these images it is clearly observed that the degree of liquid crystallinity of TC3 dark was much lower than that of TLCP; also the nematic mesophase was suppressed by the intercalation structure and destroyed by the tactoids of organoclay.

3.5. Rheological characterization

Rheology measurements on the TC3 dark nanocomposite were performed using a conventional melt-state rheometer in both oscillatory and steady shear modes. These experimental studies provided an insight into the relaxation of polymer chains when intercalated in organoclay layers, as well as the role of shear in orienting the layered structures.

TC3 dark displayed a shear-thinning behavior, whereas TLCP displayed a strain-independent viscosity at low strain at 185°C, as shown in Figure 8. Comparing the viscosities in the linear viscoelastic region, TC3 dark had more than three orders of magnitude higher viscosity than TLCP. Strong intercalated effects gave rise to these large differences. Also the critical strain magnitude shifted to lower strain units, with intercalated morphology formed in the nanocomposite.

As shown in Figure 9, in the nematic state of 185°C, the slope of the log $G'$ versus log $\omega$ plot in the terminal region for TLCP was much lower than 2. We attribute this observation to the polydomain structures in TLCP [16]. For TC3 dark in the lower frequency region, the log $G'$ curve is parallel to that of the TLCP but almost 10^4 higher in magnitude than that of TLCP. A downward trend in the terminal region of the log $G'$ versus log $\omega$ plot is discernible in both materials, consistent with the report by Huang and Han [26]. In the higher frequency region, the curves differ between the two materials. The TLCP has relatively higher slopes than the TC3 dark, i.e. $G'$ and $G''$ are 0.725, 0.398 for TLCP and 0.232, 0.447 for TC3 dark, respectively. Both materials lack the characteristic homopolymer-like behavior, i.e. $G' \sim \omega^2$ and $G'' \sim \omega$. It thus appears that intimate contact between the polymer and the organoclay layers has led to an alteration of the relaxation dynamics of the polymer, causing the low-frequency plateau in the moduli and the low-strain non-Newtonian viscosity behavior.

Conceptually, if one examines the dynamics at various nonlinear strain amplitudes on a fixed time scale, the response reflects the dynamic structure and relaxation processes perturbed by strains on that time scale. Figure 10 shows curves of TLCP and TC3 dark in stress relaxation mode in nonlinear regions. TLCP displayed a rapid initial decay followed...
Figure 7. POM of TLCP (left column) and TC3 dark (right column) (a, b) before and (c, d) after shear at 185°C and (e, f) relaxation at 230°C.

by plateaus in the long relaxation time in high nonlinear regions. These relaxation curves cannot be superimposed on each other simply by shifting in a vertical direction. This means that the time–strain factorability \( G(t, \gamma) = G(t)h(\gamma) \), where \( G(t) \) is the memory function.
and $h(\gamma)$ is the damping function) is not applicable to the nematic region of TLCP. The failure of time–strain factorability for TLCP in the nematic region is believed to be attributable to variations in its morphology as affected by the level of applied shear strain. Similar phenomena have been reported by other research groups [27]. TC3 dark evidenced a much slower decay rate throughout the measured relaxation time. The relaxation modules were
nearly constant during the entire relaxation period within a time scale of $10^2$ s, and a rapid relaxation trend is observed for the long nonlinear relaxation time in the higher relaxation region (strain = 700.0%). These curves can be superimposed on each other simply by vertical shifting within a 100 seconds relaxation time. The fact that the time–strain superposition principle can be applied to the dependence of $G(t, \gamma)$ by a damping function $h(\gamma)$ in the time scale of $10^{-1}$–100s and $h(\gamma)$ seems to agree with Wagner type expressions:

$$h(\gamma) = \exp(-k \gamma^n).$$

Mackley et al. [28] tested a Wagner-type damping function for various polymeric and colloidal fluids. They found that Equation (1) worked adequately for most classes of materials, such as kaolinite suspensions, most closely resembling our study systems here. Ren and Krishnamoorti [29] conjectured that the high anisotropic silicate layers or tactoids responded to the external flow and oriented when subjected to moderate and larger strain amplitudes. This behavior is analogous to that of liquid crystals and other meso-structured materials [30–32]. On the basis of the low volume fractions of added filler and the reproducibility of the shear thinning, a hypothesis such as confinement-induced shear thinning of the tactoids can be suggested. This implies that in whole regions, the correlations between the confined molecules do not have time to relax, and higher strain amplitude or longer time is needed to disengage the strongly correlated molecules.

Time-dependent shear stress data for the start-up of steady shear at the same shear rate for TLCP and the intercalated TC3 dark are shown in Figures 11a and 11b, respectively. Both exhibit viscoelastic behavior, with the presence of a stress overshoot at the beginning and achievement of final steady state. Further, the shear stress data do not exhibit any time-dependent oscillations as would be expected for anisotropic systems with particle tumbling or rotation.

Different mechanisms have been speculated for these nonlinear observations, including shear-thinning of a polymer network which is formed by bridging the particles [33,34], confinement-induced enhanced shear thinning of the polymers, rheology of the anisotropic filler particles, and modified particle dynamics and stress contributions arising from their suspension in a viscoelastic matrix [29,35,36]. These observations have been rationalized by invoking either the enhanced shear-thinning of the polymer matrix in the gaps between the filler particles, arising due to the higher shear rates [37], or the presence of an

![Figure 11](image-url). Step rate tests with shear rate at 0.5 $1/s$ at 185°C for (a) TLCP and (b) TC3 dark.
agglomerated network structure of the colloidal particles [38]. In some instances, the latter has also been shown to manifest as a yield stress at the lower shear rates [39].

As shown in the POM images in Figure 7, the structural domains for TC3 dark before and after sufficient steady shearing at 185°C became smaller than its original domains and caused small domains to flow more fluently between two plates. Compared with the WAXRD curves (Figure 3), the peak position for TC3 dark before and after steady shear was unchanged, but the relative intensity increased after shearing. Therefore, considering the above mechanisms and the fact that in our own system TC3 dark did not show the presence of agglomerated network structures with steady shear, the steady state shear behavior of TC3 dark may have arisen due to the higher shear rates in the gaps between the organoclay clusters and to the dramatic decrease of domain sizes.

6. Conclusions

A typical intercalated structure of TLCP molecules with organoclay was characterized in this study. Intercalated structures were confirmed, with interactions existing between the organoclay and TLCP molecules. Intercalated structures caused the TLCP glass transition temperature to become invisible in thermal measurement. The dynamics of the intercalated structures were characterized using rheological analysis at 185°C, where the liquid crystallinity and mesophase structure of the TLCP was lost in the nanocomposite. The viscosity of the nanocomposite increased by more than three orders of magnitude in the linear viscoelastic region, and the chain mobility and chain relaxation time were decreased by virtue of the presence of intercalation. Steady shear effectively decreased the nanocomposite domain sizes and oriented the highly anisotropic organoclay layers or tactoids along the shear direction.

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