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An exfoliation of organoclay in thermotropic liquid crystalline polyester nanocomposites

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Dedicated to Prof. Jung-Il Jin of Korea University, Seoul, Korea, on the occasion of his 60th birthday

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Abstract

A thermotropic liquid crystalline polyester (TLCP) with an alkoxy side-group was synthesized from 2-ethoxyhydroquinone and 2-bromoterephthalic acid. Nanocomposites of TLCP with Cloisite 25A (C25A) as an organoclay were prepared by the melting intercalation method above the melt transition temperature (T_m) of the TLCP. Liquid crystallinity, morphology, and thermo-mechanical behaviors were examined with increasing organoclay content from 0 to 6%. Liquid crystallinity of the C25A/TLCP hybrids was observed when organoclay content was up to 6%. Regardless of the clay content in the hybrids, the C25A in TLCP was highly dispersed in a nanometer scale. The hybrids (0–6% C25A/TLCP) were processed for fiber spinning to examine their tensile properties. Ultimate strength and initial modulus of the TLCP hybrids increased with increasing clay content and the maximum values of the mechanical properties were obtained from the hybrid containing 6% of the organoclay. Thermal, morphological and mechanical properties of the nanocomposites were examined by differential scanning calorimetry (DSC), thermogravimetric analyzer (TGA), polarized optical microscope, electron microscopes (SEM and TEM), and capillary rheometer. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Thermotropic liquid crystalline polyester; Organoclay; Nanocomposite

1. Introduction

Thermotropic liquid crystalline polymers have already been established as high performance commercial engineering polymers. This is due to their specific chemical structures, high strengths, high moduli, low viscosities, and other good mechanical properties [1–4]. The structure-property relationships of thermotropic liquid crystalline polyesters (TLCPs) have been the subject of much research [4–7]. In spite of their inferior physical strength when compared with lyotropic liquid crystalline polyamides, TLCPs are attracting a great deal of interest based on their melt processability [8,9].

Although wholly aromatic TLCPs exhibit very attractive mechanical properties, they generally have high melting points, thus making them difficult to process [10,11]. Inclusion of flexible alkyl groups in otherwise wholly aromatic polyesters not only lowers the melting point, but also improves solubility and increases mixing entropy. Thus, despite the predictable reduction in mechanical properties, these polyesters possess considerable advantages in some applications and show improved interfacial adhesion between the two phases [5,12,13].

Nanocomposites possess unique properties, such as stiffness, strength and gas permeability, for their dispersion structure [14–18]. The methods used for creating nanocomposites include in situ polymerization, solution intercalation, and melting intercalation [19,20]. Of them, melting intercalation can be used with the most polymers, especially thermoplastic materials, but it needs a polymer that has good process properties in the melting state. In recent years much attention has been paid to layered clay/polymer nanocomposites, since these represent advanced plastic materials prepared via the melting intercalation method.

In our previous paper [21], large improvements were achieved in the thermal stabilities of TLCP nanocomposites by using organo-montmorillonite. This enhancement of the thermal stabilities explains reasonably well the dispersed structure of clay in the nanocomposites caused by the formation of the large aspect ratio of the clay particles.

For this paper, we synthesized TLCP with an alkoxy side group base on a nematic liquid crystalline phase. We also examined the correlation between the thermo-mechanical

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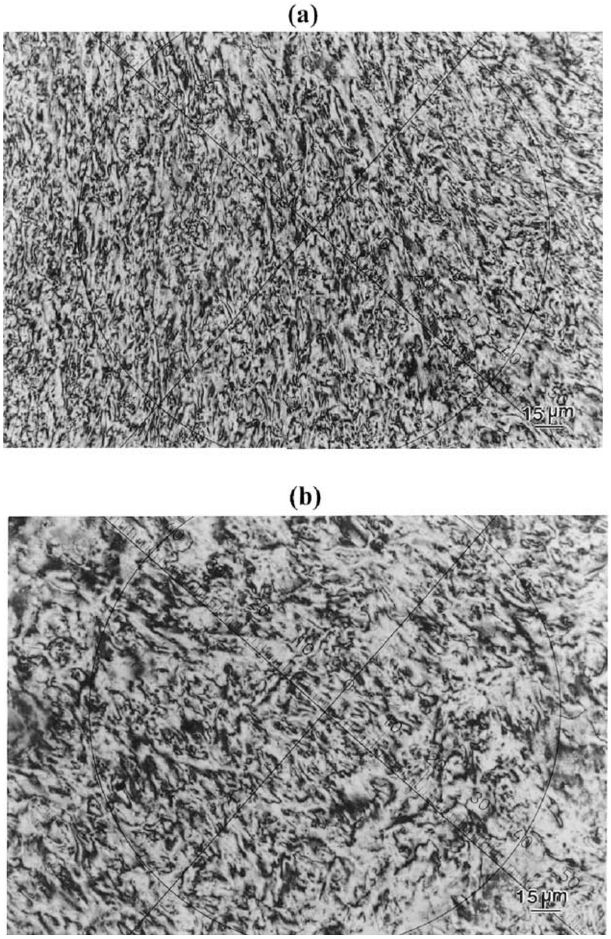


Fig. 1. Optical micrographs of TLCP taken at (a) 197 °C and (b) 210 °C (×250).

properties and the clay content in TLCP nanocomposites with variances in the dispersed morphology of the clay particles. The general goal of this work was to use a minimum amount of clay in the hybrids and still obtain thermo-mechanical properties significantly superior to those of matrix polymer.

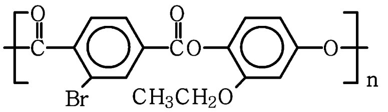
2. Experimental

2.1. Monomer synthesis

All reagents were purchased from Aldrich Chemical Co. Commercially available solvents were purified by distillation. The compound 2-ethoxyhydroquinone was synthesized via a multi-step route, and 2-bromoterephthalic acid was purchased from Aldrich Chemicals.

2.2. Polymer preparation

The TLCP was prepared by direct polycondensation of equivalent weights of the appropriate 2-ethoxyhydroquinone and 2-bromoterephthalic acid in the presence of thionyl chloride and pyridine. The detailed procedure was earlier described by us [22], as well as by Lenz et al. [23]. The ethoxy side group and Br on the TLCP not only lowers the melting point, but also improves some applications, as mentioned in the previous section. The polymer formed was thoroughly washed with methanol, with dilute HCl, and then with water prior to drying at 60 °C in a vacuum oven.



Inherent viscosity of the TLCP was 0.64 dL/g which was measured at 30 °C at a concentration of 0.2 g/dL solutions in a phenol/1,1,2,2-tetrachloroethane = 50/50 (v/v) mixture. Fig. 1 shows the thread nematic textures for pure TLCP at both 197 and 210 °C.

2.3. Preparation of C25A /TLCP nanocomposites

Cloisite 25A (organically modified MMT; C25A) was obtained from Southern Clay Product, Co. Since the synthetic procedures for C25A/TLCP nanocomposites with different weight percent (wt%) organoclay are very similar, only a representative example for the preparation of the C25A/TLCP (2 wt%) is given. 50 g of TLCP and 1 g of C25A were dry-mixed and melt-blended at 190 °C, within the nematic region of the polymer, for 30 min using a mechanical mixer. For simplicity, the hybrids will be referred to as 0% C25A/TLCP, 2% C25A/TLCP, 4% C25A/TLCP, and so on, in which C25A and TLCP represent the organoclay and polymer components used to prepare the hybrids, respectively, and the number denotes the organoclay weight percent in the hybrid.

2.4. Extrusion

The TLCP hybrids were processed for fiber spinning to examine their tensile properties. The dried blends were pressed at 160 °C, 2500 kg/cm^2 for a few minutes on a hot press. The film-type blends were dried in a vacuum oven for 24 h prior to being extruded through the die of a capillary rheometer. From the capillary rheometer, the hot extrudates were immediately drawn at constant take-up speed to form extended extrudates having the same diameters. The cylinder temperature of the extruder was 190 °C and the mean residence time in the capillary rheometer was about 2–3 min.

To identify chemical reactions such as transesterification and thermal degradation at the processing temperature, annealing was conducted for 4% C25A/TLCP hybrid at 190 °C. DSC thermograms of the heat-treated hybrids are shown in Fig. 2. When heat treatment time increased from 10 to 60 min at 190 °C, there were no significant changes in the DSC scans. Chemical changes thus do not take place to any appreciable extent at the extrusion processing temperature 190 °C. It was also confirmed by ^{1}H- and ^{13}C-NMR spectroscopy that no detectable transesterification reaction occurred in TLCP under the processing condition.

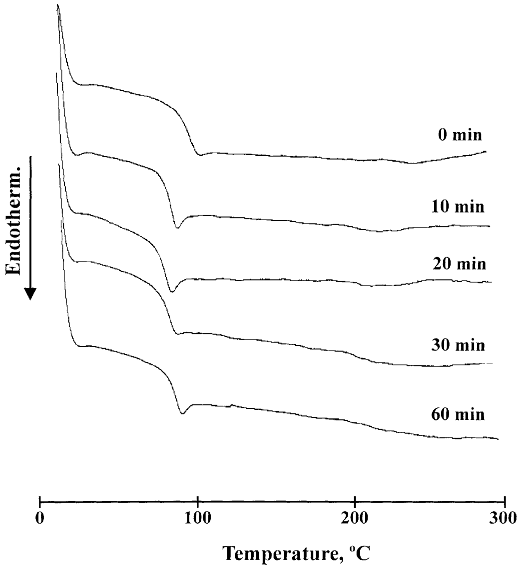


Fig. 2. DSC thermograms of 4% C25A in TLCP hybrid annealed at 190 °C for different times.

2.5. Characterization

The thermal and the thermogravimetric analyses of hybrids were carried out under N_2 atmosphere on Du Pont 910 equipment. The samples were heated and cooled at a rate of 20 °C /min. Wide-angle X-ray diffraction (XRD) measurements were performed at room temperature on a Rigaku (D/Max-IIIB) X-ray Diffractometer, using Ni-filtered Co-Kα radiation. The scanning rate was 2°/min over a range of $2\theta = 2–30°$. Tensile properties of the extrudate were determined using an Instron Mechanical Tester (Model 5564) at a crosshead speed of 2 mm/min. The specimens were prepared by cutting strips 5 by 70 mm long. An average of at least eight individual determinations was obtained. The experimental uncertainties in tensile strength and modulus were ±1 MPa and ±0.05 GPa, respectively.

A polarizing microscope (Leitz, Ortholux) equipped with a Mettler FP-5 hot stage was used to examine the liquid crystalline behavior. The morphology of the fractured surfaces of the extrusion samples was investigated using a Hitachi S-2400 scanning electron microscope (SEM). The fractured surfaces were sputter-coated with gold for enhanced conductivity using an SPI Sputter Coater. TEM photographs of ultrathin section polymer/organoclay hybrid samples were taken on an EM 912 OMEGA (CARL ZEISS) transmission electron microscope using an acceleration voltage of 120 kV.

3. Results and discussion

3.1. Dispersibility of organoclay in TLCP

The XRD patterns of C25A, pure TLCP, and their TLCP hybrids with 2–6% C25A were represented in the region from $2\theta = 2–15°$ in Fig. 3. The interlayer spacing was observed in $2\theta = 5.64°$ ($d = 18.14$ Å) for C25A. A peak was observed in $2\theta = 4.69°$ ($d = 21.98$ Å) for pure TLCP. When the amount of organoclay increased from 2 to 6%, C25A/TLCP hybrids showed a same peak at the same position ($2\theta = 4.69°$). In the TLCP hybrids with 2–6% C25A, no obvious clay peaks appeared in their X-ray diffraction curves. This indicated that these clay layers were exfoliated and dispersed homogeneously in the TLCP matrix. This was also direct evidence that the C25A/TLCP hybrids formed nanocomposites.

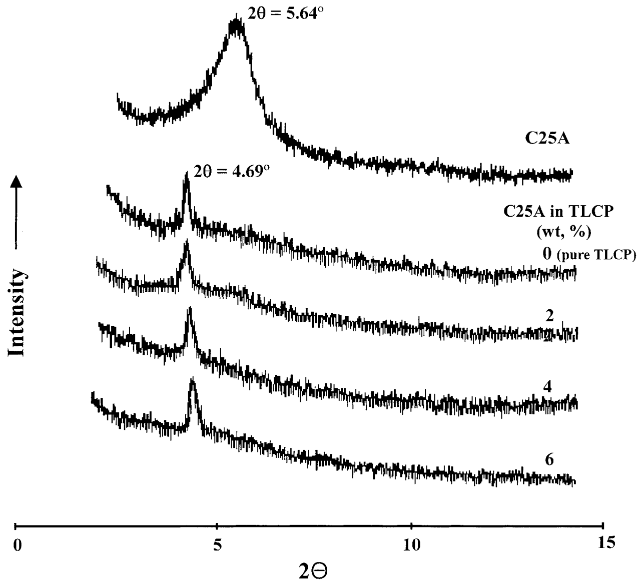


Fig. 3. XRDs of C25A and C25A/TLCP hybrids.

Unfortunately, XRD is unable to detect regular stacking exceeding 88 Å. One may note that the commonly used definition of an exfoliated nanocompoisite is based on layer spacing larger than this value. In reality, it was the electron microscopic analyses that evidenced the formation of nanocomposites.

Fractured surfaces of the films were viewed under SEM. A comparative analysis of the SEM photograph for TLCP hybrids with different clay content exhibiting the fibrous and platelet orientation distribution morphology including overall projection, as shown in Fig. 4.

More direct evidence of the formation of a true nanocomposite is provided by TEM of an ultramicrotomed section. TEM micrographs of TLCP with different C25A content from 2 to 6% are shown in Fig. 5(a)–(c), respectively. The dark lines are the intersections of the clay layer of 1-nm-thickness and the spaces between the dark lines are interlayer spaces. This TEM photograph proves that most clay layers of organoclay were exfoliated and dispersed homogeneously into the TLCP matrix. This is consistent with the observation of XRD studies shown in Fig. 3. In conclusion, we were able to successfully synthesize TLCP nanocomposites using C25A via a melting intercalation

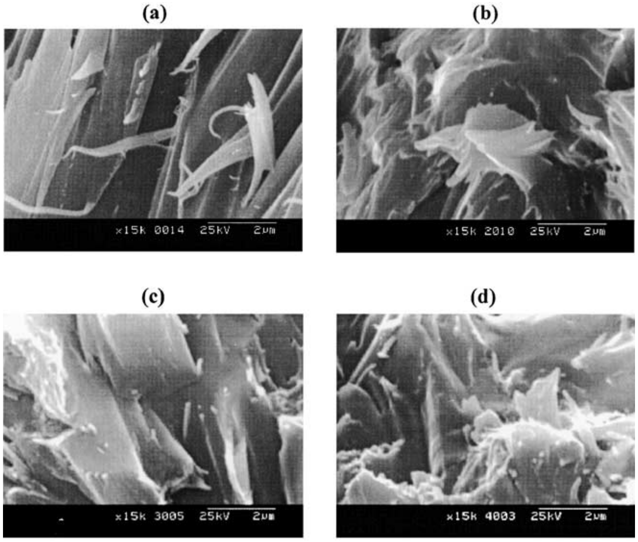


Fig. 4. SEM photomicrographs of (a) 0% (pure TLCP), (b) 2%, (c) 4%, and (d) 6% C25A in TLCP hybrids.

method. Considering the preceding results, the existing state of clay particles could be determined to affect the thermal behaviors and the tensile mechanical properties for each organoclay/polymer hybrid.

3.2. Thermal behaviors

The thermal properties of TLCP hybrids with different contents of C25A are listed in Table 1. The glass transition temperatures (T_g) of TLCP hybrids linearly increased from 92 to 98 °C with clay loading from 0 to 4 wt% and leveled off at the content range of more than 4 wt% of organoclay. The increase in the T_g of these hybrids could be the result of two factors. First, the effect of small amounts of dispersed clay layers on the free volume of TLCP is significant, and does influence the glass transition temperature of TLCP hybrids. The second factor is ascribed to the confinement of the intercalated polymer chains within the clay galleries, which prevents segmental motions of the polymer chains.

DSC traces of the pure TLCP and the hybrids are shown in Fig. 6. The endothermic peak of the pure TLCP appears at 143 °C and corresponds with the melt transition temperature (T_m). Maximum transition peaks of the TLCP hybrids containing different clay contents in the DSC thermograms are slightly increased to 150 °C (see Table 1). This increase in the thermal behavior of the hybrids may result from the heat insulation effect of the clay layer structure, as well as the strong interaction between the organoclay and TLCP molecular chains. The isotropic transition temperatures (T_i) of pure TLCP was virtually unchanged regardless of organoclay loading, compared with the TLCP hybrids. Fig. 7 shows the thread nematic textures for 2 and 6% C25A/TLCP hybrids, respectively. Regardless of the clay content in the hybrids, liquid crystallinity of the C25A/TLCP hybrids was observed when organoclay content was up to 6%.

In addition to having a higher melting point, thermal degradation properties of TLCP hybrids also show improvement.

Table 1
Thermal behavior values of C25A/TLCP hybrids

clay (wt%)	T_g (°C)	T_m (°C)	T_i (°C)	T_D^{i} [a] (°C)	wt_R^{600} [b] (%)
0 (pure TLCP)	92	143	225	330	37
2	95	150	226	352	42
4	98	150	225	352	44
6	98	149	225	353	47

[a] Initial weight reduction onset temperature.

[b] Weight percent of residue at 600 °C.

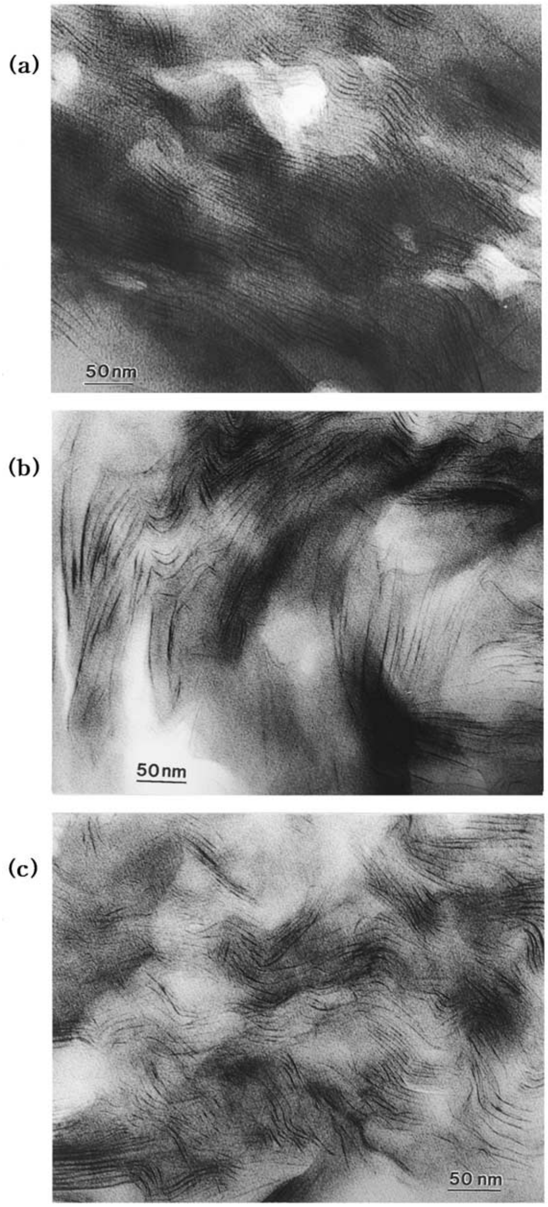


Fig. 5. TEM photomicrographs of (a) 2%, (b) 4%, and (c) 6% C25A in TLCP hybrids.

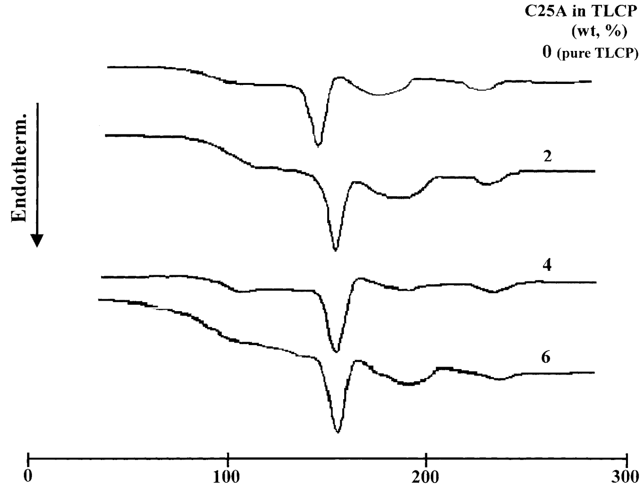


Fig. 6. DSC thermograms of C25A and C25A/TLCP hybrids.

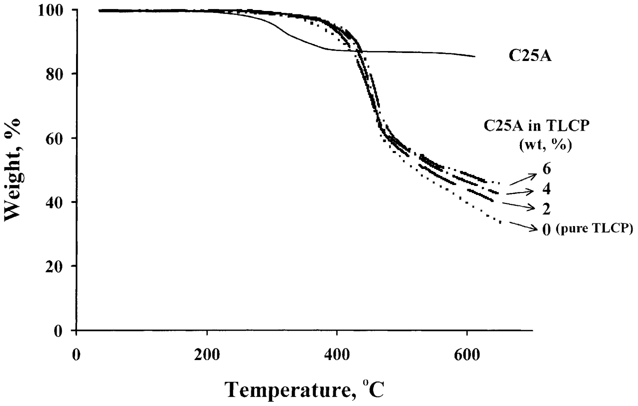


Fig. 8. TGA thermograms of C25A and C25A/TLCP hybrids.

A comparative thermal gravimetric analysis (TGA) of pure TLCP and three nanocomposites with 2–6% C25A is shown in Table 1 and Fig. 8. TGA curves do not show weight loss below 100 °C, as shown in Fig. 8, indicating no water remained in the samples. The weight loss due to the decomposition of TLCP and its hybrids was nearly the same until a temperature of about 300 °C. After this point, the initial thermal degradation temperature (T_D^i) was influenced by organoclay loading in hybrids. Table 1 summarizes T_D^i of the C25A/TLCP hybrids (at 2% weight loss) increased with the amount of organoclay. T_D^i was observed at 352–353 °C depending on the composition of the clay from 2 to 6 wt% in the TLCP hybrids, with a maximum increase of 23 °C in the case of the 6% C25A/TLCP as compared with that of the pure TLCP. Weight of the residue at 600 °C increased with clay loading from 0 to 6%, ranging from 37 to 47%. This enhancement of the char formation is ascribed to the high heat resistance exerted by the clay itself.

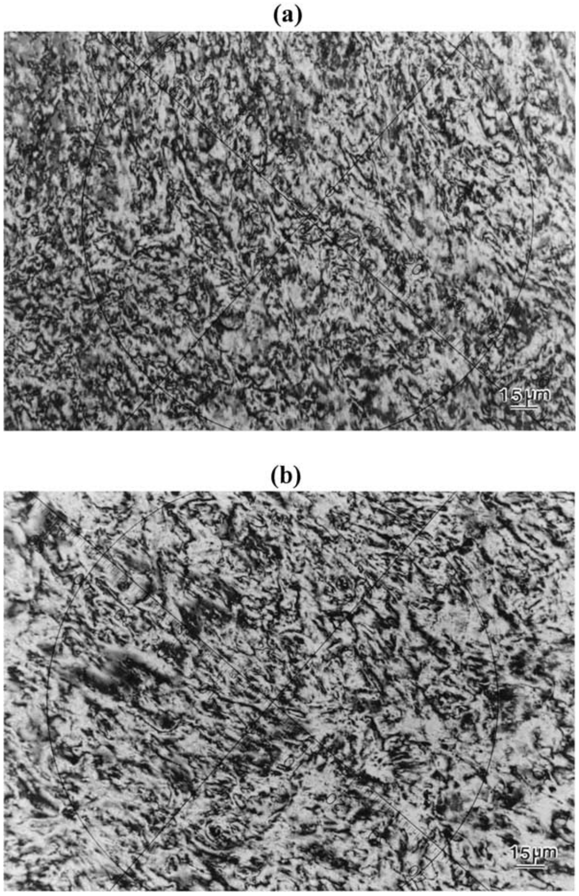


Fig. 7. Optical micrographs of (a) 2% and (b) 6% C25A in TLCP hybrids taken at 200 °C (×250).

Considering the above results, it is consistently believable that the introduction of inorganic components into organic polymers can improve their thermal stability on the basis of the fact that clays have good thermal stability [24,25].

3.3. Tensile properties

The pure TLCP and the TLCP hybrids were extruded through a capillary die with draw ratio (DR) = 1 to examine the tensile strength and modulus of the extrudates. The DR was calculated from the ratio of the diameter of the drawn extrudate to that of the extruder die.

The tensile mechanical properties of pure TLCP and its hybrid fibers are listed in Table 2. The tensile strength and initial modulus of C25A/TLCP hybrids increased with corresponding increases in the amount of organoclay. The

Table 2
Tensile properties of C25A/TLCP hybrid fibers

Clay (wt%)	Ult. Str. (MPa)	Ini. Modu. (GPa)	E.B.[a] (%)
0	11.03	2.91	2
2	15.10	4.03	1
4	16.15	4.38	1
6	17.28	5.76	1

[a] Elongation percent at break.

ultimate tensile strength of TLCP hybrid fibers increased as the organoclay contents increased. When the C25A was increased from 0 to 6% in hybrids, the strength linearly improved from 11.03 to 17.28 MPa. The ultimate strength of 6% C25A/TLCP was 1.6 times higher than that of pure TLCP.

The same kind of behavior was observed for the initial moduli. For example, the initial tensile modulus of 2% C25A was 4.03 GPa, which was about 140% higher than the modulus of pure TLCP. When the organoclay in TLCP reaches 6%, the modulus increases about 2.0 fold (5.76 GPa) over that of the pure TLCP.

This large increase in tensile property of hybrids owing to the presence of organoclay can be explained as follows: the amount of the increase of tensile property by clay layers depends on the interactions between rigid, rod-shaped TLCP molecules and layered organoclays, as well as on the rigid nature of the clay layers. Moreover, the clay was much more rigid than the TLCP molecules, and did not deform or relax as the TLCP molecules did. This improvement was possible because organoclay layers could be highly dispersed and exfoliated in the TLCP matrix. This is consistent with the general observation that the introduction of organoclay into a matrix polymer increases its strength and modulus [26,27].

The percent elongation at break of all samples, however, decreases from 2 to 1% and then remains constant with clay addition.

4. Conclusions

An aromatic thermotropic LCP with ethoxy side group was synthesized and its optical texture was nematic. The addition of 2–6% C25A to a TLCP maintains liquid crystallinity. C25A was exfoliated and dispersed homogeneously in the matrix polymer. This was direct evidence that the C25A/TLCP hybrids formed nanocomposites. This was also cross-checked using XRD and TEM.

In general, thermal behaviors (T_g, T_m, and T_D^i) of the hybrids were enhanced with increasing clay content from 0 to 6 wt%. On the other hand, the isotropic transition temperatures (T_i) of the hybrids were unchanged regardless of organoclay loading.

Hybrids of different C25A contents were extruded with DR = 1 from a capillary rheometer to investigate the mechanical properties of the hybrids. The ultimate strength and initial modulus of the hybrids increased with increasing C25A content. When the amount of organoclay in TLCP reached 6 wt%, a 1.6-fold increase in the ultimate strength and a 2.0-fold increase in the initial modulus were obtained, as compared with the strength and modulus of the pure polymer matrix. In this system, it was found that small additions of organoclay were enough to improve the properties of the matrix polymer, TLCP.

Acknowledgements

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