Effect of Organoclay on the Orientation and Thermal Properties of Liquid-Crystalline Polymers

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The preparation and thermal and thermo-mechanical properties of nanocomposites based on liquid-crystalline polymers (LCP) and organically-modified layered silicate (OMLS) is described. From XRD patterns, very little smectic ordering is present in the pure LCP; in the nanocomposites, the polymer chains tended to orient in the direction of the dispersed clay layers. According to the DSC results, during first heating, the first melting peak represents the crystalline to nematic transition and, after that, a broader isotropization takes place. Although TGA of the samples showed a single-step decomposition through chain scission under an inert atmosphere, in air the nanocomposites underwent a two-step process, with onset of degradation at a higher temperature. The first step is mainly due to chain scission and the second is due to oxidative reactions.

Introduction

Liquid-crystalline polymers (LCP) are well known for their excellent properties, such as high strength and stiffness, low melt viscosity, and their high chemical and thermal resistance.[1,2] Recently, the blending of thermotropic LCP with thermoplastics has attracted much attention because of the self-reinforcement effect of LCP due to their rigid-rod-like molecular structure. In such LCP/thermoplastics blends, the LCP acts as reinforcing element like nanoclay in nanocomposites by offering a large surface area. The advantages of incorporation of a few percent of LCP in thermoplastic matrices are: (i) improvement in processability because of the lower viscosity of the LCP, and (ii) the improvement in mechanical properties by uniform microfibrillation of the LCP in the matrix polymer.[3] Over the last decade, many polymers such as poly(propylene),[4] polystyrene,[5] poly(methyl methacrylate),[6] poly(ethylene terephthalate),[7] poly(vinyl alcohol),[8] poly(butylene succinate),[9] and polylactide,[9b,10] have been used for the preparation of nanocomposites with either pure or organically-modified clay. However, there remain very few reports regarding LCP-based nanocomposites with clay. Vaia et al.[11] reported the reversible intercalation between organoclay and LCP in the nematic state. According to them, much better intercalation of polymer chains in the clay galleries is possible with a prolonged annealing time. Zhang et al.[12] showed that
the glass-transition temperature and the mechanical properties of LCP/clay nanocomposites were enhanced compared to virgin polymer. Recently, Huang et al.\[13\] reported on the dispersion characteristics and rheology of nanocomposites based on organoclay and thermotropic LCP with pendent functional groups. In another report\[14\] they confirmed the very high degree of dispersion of organoclay in the LCP matrix, because of the formation of hydrogen bonds between the pendent pyridyl group in the LCP and the hydroxyl group of the surfactant residing at the surface of organoclay. According to Shen et al.\[15\] the polar epoxy groups in liquid-crystalline epoxides make it possible to diffuse into the clay galleries. The modifier present in the organoclay catalyzes the epoxy ring-opening reaction with a diamine curing agent. Chang et al.\[16\] also prepared aromatic thermotropic LCP nanocomposites and focused on the morphology and thermal properties. Up to now, however, nobody has focused on how the structure of the LCP changes after the preparation of the nanocomposites with organoclay, and how the clay particles affect the properties of the LCP. Therefore, the main objective of this study is to understand the effect of the organoclay on the structure of the LCP and hence on the mesophase transitions and crystallization, and on the thermo-mechanical properties of the LCP. Thermogravimetric analyses (TGA) have been carried out to determine the inorganic part present in the nanocomposite samples and the thermal stability of the nanocomposite samples under both oxidative and inert environments.

**Experimental Part**

**Materials**

The commercially-available, main-chain, thermotropic liquid-crystalline polymer, Vectra B950, used to prepare the LCP-organoclay nanocomposites was supplied by Ticona. The chemical formula of Vectra B950 is shown in Figure 1.

The organoclay Closite® 20A (C20A) was purchased from Southern Clay Products. It is a natural montmorillonite (MMT) modified by dimethyl dihydrogenated-tallow quaternary ammonium salt with cation exchange capacity of 95 meq per 100 g.\[17\] Figure 2 shows the molecular structure of the surfactant.

The polar solubility parameters (\(\delta\)) for the LCP and organic modifier of C20A were estimated roughly from the group-contribution method of Fedors\[18\] and the values were 25.6 J\(^1\)cm\(^{-3/2}\) and 16.9 J\(^1\)cm\(^{-3/2}\) respectively. The reason for selecting C20A for the preparation of the nanocomposites was the higher thermal stability of the surfactant of C20A compared to other Closite clays at the processing temperature, and the larger interlayer spacing between the silicate layers (2.45 nm, estimated from the XRD results). To determine the thermal stability of C20A at the processing conditions, the TGA ramp test was performed and, according to this result, C20A lost \(\approx 8\%\) of its initial weight at 270°C in 25 min. The C20A sample was kept at 270°C for 5 min and it showed an extra \(\approx 4\%\) weight loss. Since the nanocomposites were prepared by melt extrusion where the residence time of the samples inside the extruder was \(\leq 2\) min, the degradation of C20A didn’t significantly affect the properties of the nanocomposites. All of these materials were dried at 110°C for 24 h under vacuum before blending to avoid degradation caused by moisture. The thermal treatment also improves the performance of the LCP, such as a dramatic improvement in tenacity. This improvement is usually due to the increase in molecular weight, as well as in the degree of perfection of the crystallinity.\[13\]

**Nanocomposite Preparation**

Nanocomposites were prepared by melt extrusion in a Haake twin-screw extruder at a screw speed of 30 rpm. The barrel temperatures used were 260, 270, and 270°C and the temperature of the capillary die was 270°C. After collecting the nanocomposite samples from the extruder, they were dried under vacuum at 110°C for 24 h to remove any water and then moulded under different conditions, according to the needs of different experiments. Initially the samples were moulded using a Carver laboratory press at 300°C, under 2 MPa pressure for 2 min, and the sample thicknesses were \(\approx 12\) mm. For the study of non-isothermal crystallization kinetics, the sheet of highly-crystalline samples was prepared by using a Carver model: 4393.4PR3B02 at 300°C, under 2 kg pressure for 2 min, and then slowly cooled for about 4 h by passing air through the plates.

**Characterization Techniques and Conditions**

All of the characterizations were carried out using isothermally-annealed, moulded samples. The X-ray diffraction analyses in the small-angle (\(2\theta = 0–30°\)) and wide-angle (\(2\theta = 21–69°\)) regions were performed using a Siemens-500 diffractometer in the transmission mode. The beam was Cu K\(_\alpha\) (\(\lambda = 0.154\) nm) operated at 40 kV, and 40 mA.

The morphology of the fractured surface of the moulded nanocomposites was investigated by scanning electron microscopy (SEM, JEOL model JSM-820 apparatus) operated at an accelerating voltage of 15 kV. The samples were fractured in...
nanocomposites were LCPCN1.4 and LCPCN3.4, respectively. The sample was 3.4%; hence the abbreviations used for these samples was 1.4% and that in the second batch nanocomposite the inorganic part present in the first batch nanocomposite was determined using both air and nitrogen atmospheres. The amount of the inorganic part present in the nanocomposite was studied by conventional DSC. In order to do that, all of the samples went through the same experimental cycle: heating from room temperature to 350°C at a rate of 10°C·min⁻¹, then cooling to 20°C at the same rate as heating and further heating up to 350°C at a heating rate of 10°C·min⁻¹. To study the non-isothermal crystallization dynamics, the samples were melted at 350°C at a heating rate of 20°C·min⁻¹, kept at that temperature for 5 min to destroy all the previous thermal history, cooled to 20°C at different cooling rates: 5, 10, 20 and 30°C·min⁻¹ and then re-melted up to 350°C at a heating rate of 20°C·min⁻¹ as soon as cooling was finished. The DSC samples were weighed such that all of the samples had an identical LCP content. The sample weight was maintained at low levels (3–4 mg) for all measurements in order to minimize any possible thermal lag during the scans.

The thermo-mechanical properties of the LCP and its nanocomposites were examined using a Rheometric Scientific Analyzer (RSA) in dual-cantilever bending mode. The storage modulus (E'), loss modulus (E'') and tanδ values were determined at a constant frequency of 6.283 rad·s⁻¹, with a strain amplitude of 0.02% (determined after the strain sweep tests at different temperatures), a heating rate of 2°C·min⁻¹ and in the temperature range 0 to 200°C.

Thermo-Gravimetric Analyses (TGA) were carried out by using a TA Q500 instrument in the temperature range 25 to 900°C under both air and nitrogen atmospheres. The amount of the inorganic part present in the nanocomposite samples was determined using TGA. According to TGA data (conducted under air), the amount of the inorganic part present in the first batch nanocomposite sample was 1.4% and that in the second batch nanocomposite sample was 3.4%; hence the abbreviations used for these nanocomposites were LCPCN1.4 and LCPCN3.4, respectively.

Results and Discussion

Structure of the Nanocomposites

The XRD patterns not only provide information about the dispersion of the silicate layers in the polymer matrix but also the mesophase structures present in the LCP and the orientation of the directors can be predicted from the X-ray diffractionograms. The most well-known technique, XRD in the small-angle region, was used to determine the intercalation of polymer chains in the nanoclay galleries. Figure 3 shows the XRD patterns of the pure C20A powder and nanocomposites in the small-angle region. The characteristic (001) peak of the C20A powder appeared at 2θ = 3.6° (d = 2.45 nm). In both nanocomposites the characteristic peak intensity of C20A was not only significantly reduced due to the dilution effect of clay but also shifted to 2θ = 2.28° and 2θ = 2.32° for LCPCN1.4 and LCPCN3.4, respectively. These peak shifts towards lower angles indicate the intercalation of polymer chains inside the clay galleries. The variation of clay content, however, doesn’t show a significant change in the basal spacing: in both nanocomposites it remains almost the same (d = 3.85 nm). Thus it is expected that the dispersion of the clay platelets in the polymer matrix should be better in the LCPCN1.4 nanocomposite sample. The XRD patterns plotted in the range 2θ = 8 to 27° are shown in Figure 4. It is clear from the Figure that the nanocomposites have the same mesophase structure or, in other words, the same type of crystal formation at 2θ ≈ 11.8° and 2θ ≈ 19.4°. In the case of nanocomposites, however, a shoulder peak accompanied with the second crystalline peak appears. This may be due to the growth of the same kind of crystal with a different size distribution or orientation. The XRD analyses in the wide-angle region show the formation of different types of crystals in the nanocomposite samples as compared to neat LCP (Figure 5). The effect of clay concentration on the crystal growth can be visualised directly in the XRD pattern at 2θ ≈ 43.2°. The XRD powder patterns in Figure 6 and 7, show the diffraction patterns of the oriented samples and also show how the orientation of the LCP crystallites changed after addition of organically-modified layered silicate (OMLS) in various proportions. Thus it is possible to tune the orientation of LCP by adding the filler. For extruded materials, the structure and mechanical properties were found to be closely related to the extrusion conditions. Thus the...
The orientation of LCP in nanocomposites may depend on factors such as the draw ratio of the extruder, and the condition of moulding for example. Here, the effect of these above-mentioned factors were minimized by moulding all the samples under the same conditions. Although C20A hasn’t too much interaction with the Vectra B950, it can change the mesophase structure. It is clear from Figure 6 that because of the ordered structure of the layered silicate, nanocomposites exhibit more and more ordered structures, compared to the pure polymer, with an increase in nanoclay loading. From Figure 6 it is prominent that LCP exhibits diffuse rings with a sharp ring as an outer shell, whereas the nanocomposites exhibit sharp and intense diffractions at the shell and in the core. The nematic phase is characterized by the molecules having no positional order, rather than they tend to align in the same direction. On the other hand, in the smectic phase the molecules maintain the general orientational order of the nematic phase, but also tend to align themselves in layers.
Although detailed studies on the mesophase transition and crystal growth are ongoing, one can expect from Figure 6 and 7 that very little smectic-like ordering is present in the pure LCP, whereas in the nanocomposites, polymer chains not only tend to orient in the direction of the dispersed clay layers, but the ordering in alignment is also improved.

SEM images of the LCP/clay nanocomposites are shown in Figure 8. The only thing observed here is that the fracture surfaces of these nanocomposites have a febrile morphology. The dispersion of the clay platelets in the LCP matrix can be visualized by the TEM observations shown in Figure 9. The intercalated clay layers can be visualized directly as the black entities in the TEM images. The TEM images show that the dispersion of organoclay is much better with a lower clay concentration and an increase in the clay concentration results in more and more agglomeration and hence almost no change in the basal spacing.

**Thermal Properties**

Melting and Crystallization Behavior of Virgin Polymer and As-Prepared Nanocomposite Samples

To study the mesophase transitions and crystal-growth behavior of all of the samples, the method mentioned in...
the characterization part was followed. Different parts of Figure 10 represent respectively (a) the first heating, (b) cooling and (c) subsequent heating. Different thermal parameters determined from the cooling and the second heating cycles are tabulated in Table 1. According to Figure 10a the $T_g$ of neat LCP was affected after addition of organically-modified layered silicate. In the nanocomposites, chain relaxation associated with the $T_g$ is possibly due to the enhancement of ordering in the direction of the clay lamellae. A further increase in temperature resulted in a sharp transition that is associated with a wider one. The first melting peak represents the crystalline to nematic transition and after that a broader isotropization takes place.

During cooling from the isotropic state, as shown in Figure 10b and Table 1, the crystallization-onset temperature ($T_{c,on}$) shifted towards higher temperatures. This is due to the nucleation effect of the organoclay, by offering a large surface area to start the crystallization. The crystallization-peak temperatures ($T_c$) however remained almost the same, for the samples examined here. The enthalpy of crystallization ($\Delta H_c$) also remained almost unaltered after addition of the clay. It is noticeable that LCP and its nanocomposites showed a very small value of the transition enthalpy because their chain rigidity prevents molecules folding, and the mesophase transitions generally occur by segregation of the rigid chain molecules.[1] The half time of crystallization ($t_{1/2}$), defined as the time required to attain a relative degree of crystallinity of 50%, can be estimated from the Equation (1).

$$t_{1/2} = \frac{T_{c,on} - T_c}{\phi}$$

where, $\phi$ is the cooling rate. The results are summarized in Table 1. It is clear from Table 1 that the $t_{1/2}$ value of the nanocomposite samples remains almost the same as that of the pure polymer.

During the second heating, as observed in Figure 10c, the enthalpy-relaxation phenomena associated with $T_g$ is not as prominent as in first heating cycle. According to Table 1, the $T_g$ of pure polymer remained unaltered in the nanocomposite samples with lower clay content, but it shifted towards slightly lower temperatures when the clay loading increased. This indicates that with increase an in the clay concentration, the movement of chain segments starts earlier. As soon as the samples cross $\approx 200{^\circ}C$, a complex but continuous phase transition or consecutive melting - recrystallization/crystal orientation - remelting mechanism takes place. A comprehensive study of the phase morphology is still under investigation.

The temperatures of the two prominent and one broad transition were denoted by $T_{m1}$, $T_{m2}$ and $T_{m3}$, respectively in Table 1. Chung et al.[1] have already reported that, depending on the annealing time, during isothermal crystallization Vectra B950 shows sometimes two or sometimes one melting peak. Here, according to Figure 10d, it is clear that, the pure Vectra B950 exhibited very little crystal orientation just before $T_{m2}$; the nanocomposites exhibited a more pronounced crystal-orientation effect at $270.75{^\circ}C$ and $269{^\circ}C$ for LCPCN1.4 and LCPCN3.4 respectively. Since Vectra B950 is a fully-aromatic, main-chain random copolymer, the distribution of molecular sequences within the polymer itself may not be so even. Further, in contrast to ref.[1] chain rigidity prevents molecules folding, and the transitions generally occur by segregation of rigid-chain molecules. Probably, because of these reasons LCP shows such a complex melting phenomenon and incorporation of the organoclay creates further complexity. The appearance of three endothermic peaks in the DSC also supports the XRD results. From the XRD patterns (Figure 6 and 7) it was clear that the smectic-like ordering improved in the nanocomposites and also with an increase in clay loading. Thus the three melting peaks in the DSC thermogram originates from (i) melting, $T_{m1}$; (ii) transition from a more-ordered structure (smectic) to a less ordered structure (nematic), $T_{m2}$; and (iii)
isotropization, $T_{m3}$. According to Table 1, for the nanocomposite samples $T_{m1}$, $T_{m2}$ and $T_{m3}$ were shifted towards the lower-temperature region, compared to the virgin VectraB950 sample, because organoclay facilitates the segregation of the rigid chains of Vectra B950. Since organoclay induces a more and more ordered structure in the nanocomposites, the values of the enthalpy of fusion ($\Delta H_f$) increase with the clay loading as reported in Table 1.

Non-Isothermal Crystallization Behavior

The characteristic parameters of non-isothermal crystallization (from the cooling and second heating runs) are tabulated in Table 2. Figure 11 and 12 represent, respectively, the exothermic and endothermic plots during non-isothermal crystallization and subsequent heating. According to Table 2 for all the three samples studied here, the crystallization-peak temperature ($T_c$) shifted towards

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{c, \text{on}}$</th>
<th>$T_c$</th>
<th>$\Delta H_c$</th>
<th>$t_{1/2}$</th>
<th>$T_g$</th>
<th>$T_{m1}$</th>
<th>$T_{m2}$</th>
<th>$T_{m3}$</th>
<th>$\Delta H_f$</th>
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<tr>
<td>LCP</td>
<td>232.22</td>
<td>223.90</td>
<td>2.39</td>
<td>0.83</td>
<td>134.01</td>
<td>267.77</td>
<td>277.11</td>
<td>293.99</td>
<td>5.47</td>
</tr>
<tr>
<td>LCPCN1.4</td>
<td>236.83</td>
<td>223.11</td>
<td>3.15</td>
<td>1.37</td>
<td>134.21</td>
<td>265.22</td>
<td>276.16</td>
<td>291.09</td>
<td>7.15</td>
</tr>
<tr>
<td>LCPCN3.4</td>
<td>238.28</td>
<td>224.42</td>
<td>3.31</td>
<td>1.39</td>
<td>132.13</td>
<td>264.22</td>
<td>275.33</td>
<td>290.67</td>
<td>8.06</td>
</tr>
</tbody>
</table>
lower temperature with an increase in the cooling rate because, with an increased cooling rate, the molten samples experience a shorter time to crystallize and hence complete crystallization was not possible with higher rates. For nanocomposite samples, however, there is no significant change in the $T_c$ and $\Delta H_f$ values.

The effect of the cooling rate and clay concentration on the subsequent heating scan can be visualized directly in Figure 12. For LCP, at a lower cooling rate ($5^\circ C \cdot min^{-1}$) the two transition processes are clearly visible. With an increase in the cooling rate ($10^\circ C \cdot min^{-1}$), the first transition ($T_{m1}$) shifted slightly towards a higher temperature and the second transition ($T_{m2}$) shifted toward a lower temperature. A further increase in the cooling rate resulted in the two transitions being merged into one, with a further reduction of the $\Delta H_f$ values. The LCPCN1.4 nanocomposite sample also exhibited a similar trend to the pure LCP sample. The increase in clay content resulted in the presence of two distinguishable transitions for a cooling rate of $20^\circ C \cdot min^{-1}$. With an increase in the clay content, the intensity of the first transition was enhanced. In all three samples, however, (especially noticeable in LCPCN3.4 sample) the intensity of the first transition reduced and the second one improved, and finally at a heating rate $30^\circ C \cdot min^{-1}$, the two transitions merged into one. These observations can be explained as follows: with a decreased cooling rate during non-isothermal crystallization, the samples get more time to organize crystals and as a result there is a possibility of attaining a more-ordered structure. Thus, during heating the first thermal event corresponds to a more-ordered to less-ordered transition and the second thermal event corresponds to isotropization.

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analyses were carried out to understand the response of the pure LCP and its nanocomposites to an oscillatory deformation under the bending mode as a function of temperature. The effect of organo-filler on the storage flexural modulus ($E’$), loss modulus ($E''$) and tan$\delta$ values were respectively recorded in Figure 13a, b, and c. The improvement of both moduli of the nanocomposites and, of course, with an increase in the filler concentration in the whole range of temperature studied here, is because of the reinforcement effect of the organoclay. Although the first relaxation process is not so prominent in Figure 13a, a relaxation at around $40^\circ C$ affects the viscous behavior and hence the glass-rubber transition. The DSC thermogram (Figure 10c) also supports this relaxation phenomenon. The tan$\delta$ (the ratio $E’/E’’$) generally determines the molecular-mobility transitions, such as $T_g$. According to Figure 13c, the nanocomposites also show the same relaxation process like LCP, but the first relaxation (first tan$\delta$ peak) shifts towards lower temperatures for the nanocomposite samples, compared to virgin polymer. The second tan$\delta$ peak (which is comparable to the $T_g$ values reported in Table 1) remained unaltered after addition of the clay. The temperatures corresponding to these tan$\delta$ peaks are given in Table 3.

Thermogravimetric Analysis

The thermogravimetric analyses were carried out under both nitrogen and air atmosphere. Figure 14 and 15 show the thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTGA) curves under the nitrogen and air atmosphere respectively. Under an inert atmosphere.
atmosphere, the polymer shows a single-step decomposition by random chain scission of the polymer \cite{1} as determined by both the TGA and the DTGA curve in Figure 14. In the case of the nanocomposite samples, initially the degradation starts a little earlier because of the decomposition of the organic modifier present in the organoclay \cite{23} but after around 8% degradation the nanocomposites show a much higher thermal stability. If 10% of degradation is considered to be the onset of the main degradation process, then, according to Table 4, the nanocomposites exhibit a higher stability against thermal decomposition, compared to pure LCP. Thus, at this stage,
the clay platelets act as an insulator; in the course of the heating, however, they act as a heat source and enhance char formation at a lower temperature. For better dispersion of the nanoclay in the LCPCN1.4 sample, the char formation starts faster than in the other nanocomposites. The DTGA curves of the nanocomposites show a very small, but distinct, transition at 448 °C and 432 °C for the LCPCN1.4 and LCPCN3.4 samples respectively. The probable reason is that the dispersion of clay platelets in the LCP matrix results in some chain scission of the long, rigid LCP chains and these small-length chains decompose by further chain scission at a lower temperature. Finally

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\tan1}$ °C</th>
<th>$T_{\tan2}$ °C</th>
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<tbody>
<tr>
<td>LCP</td>
<td>61.67</td>
<td>138.89</td>
</tr>
<tr>
<td>LCPCN1.4</td>
<td>57.22</td>
<td>138.89</td>
</tr>
<tr>
<td>LCPCN3.4</td>
<td>56.11</td>
<td>138.89</td>
</tr>
</tbody>
</table>

Figure 13. DMA data for LCP and its nanocomposites: (a) storage flexural modulus, (b) loss modulus and (c) tanδ as a function of temperature.

Figure 14. a) TGA thermograms and b) first-derivative TGA (DTGA) curves of neat LCP and its nanocomposites under nitrogen atmosphere.
the maximum decomposition also occurs by structure-bond rupture or by chain scission. Like under an inert atmosphere, in an air atmosphere, the nanocomposites exhibit higher values of the onset of degradation, as reported in Table 4. According to Chung et al. [1], Vectra B950 shows two-step decompositions under air atmosphere: the first degradation step is mainly due to chain scission, with some extent of oxidation, and the second degradation step is due to oxidative reactions. Thus the first step is mainly a charring process and the second step is a char-combustion process. In the DTGA curves in Figure 15b, the first intense peak represents the char formation process and the second intense peak represents the char combustion process. Here also, the nanocomposites exhibit a two-step char formation process, like under the inert atmosphere, and a two-step char-combustion process.

**Conclusion**

In order to study the effect of organically-modified layered silicate on the structure, orientation and hence the other properties of LCP, nanocomposites of LCP were prepared with two different amounts of layered-silicate loading. XRD diffraction patterns in the small-angle region were used to determine the intercalation of the polymer chains in the nanoclay galleries. In both nanocomposites the characteristic peak intensity of C20A was not only significantly reduced due to the dilution effect of clay, but also shifted towards the lower-angle side, indicating the intercalation of polymer chains inside the clay galleries. The effect of clay concentration on the crystal growth can be visualized directly in the XRD patterns in the wide-angle region. The XRD patterns in both the small- and wide-angle regions represent the diffraction patterns of the oriented samples and also show how the orientation of the crystallites changed after addition of organoclay with different concentrations. Thus it is possible to tune the orientation of LCP by adding the filler. From these patterns one can expect that very little smectic-like ordering is present in the pure LCP, whereas in the nanocomposites, the molecules not only tend to orient in the direction of dispersed clay layers, but the ordering in alignment also improved.

SEM images of the fracture surfaces of the LCP/clay nanocomposites show a febrile morphology. TEM images show the dispersion of organoclay is much better with a lower clay concentration and that an increase in clay concentration results in more and more agglomeration.

During the first heating cycle of as-prepared samples, analyzed by DSC, the \( T_g \) of the neat LCP was affected after

![Figure 15](image-url)
addition of organically-modified layered silicate. In the nanocomposites, the chain relaxation associated with the T_g is possibly due to an enhancement of the ordering in the direction of the clay lamellae. A further increase in temperature results in a sharp transition associated with a wider one. The first melting peak represents the crystalline to nematic transition, and after that, a broader isotropization takes place. The crystallization-peak temperatures (T_m) of the LCP remained the same after nanocomposite preparation. During subsequent heating after crystallization, the T_g of the pure polymer remained unchanged in the nanocomposites with the lower clay content, but shifted toward a slightly lower temperature region when the clay percentage increased. This indicates that, with an increase in clay loading, the movement of the chain sites and, of course, with an increase in the filler content, the improvement of both moduli of the nanocomposites is mainly due to the reinforcement effect of the organoclay. Although under an inert atmosphere, in the case of the nanocomposite samples, initially the degradation started a little earlier, because of the decomposition of the organic modifier present in the organoclay, but after around 8% degradation, the nanocomposite samples show a much higher thermal stability. Here the decomposition occurs by structure-bond rupture or chain scission.

Under an air atmosphere, the nanocomposite samples exhibited higher values of the onset of degradation, along with the two-step decomposition. The first degradation step was mainly due to the chain scission with some extent of oxidation and the second degradation step was due to oxidative reactions. Thus, the first step is mainly a charring process and the second step is a char-combustion process.

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