Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Arao Manhique [a d], Walter W. Focke [b], Andreas Leuteritz [c] & Carvalho Madivate [d]

[a] Institute of Applied Materials, Department of Chemistry, University of Pretoria, Pretoria, South Africa

[b] Institute of Applied Materials, Department of Chemical Engineering, University of Pretoria, Pretoria, South Africa

[c] Leibniz Institute of Polymer Research Dresden, Dresden, Germany

[d] Department of Chemistry, Universidade Eduardo Mondlane, Maputo, Mozambique

Available online: 02 Mar 2012

To cite this article: Arao Manhique, Walter W. Focke, Andreas Leuteritz & Carvalho Madivate (2012): Layered Double Hydroxides as Nano Additives in Poly(ϵ-caprolactone), Molecular Crystals and Liquid Crystals, 556:1, 114-123

To link to this article: http://dx.doi.org/10.1080/15421406.2012.635925

Mol. Cryst. Liq. Cryst., Vol. 556: pp. 114–123, 2012

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.635925

Layered Double Hydroxides as Nano Additives in Poly(ε-caprolactone)

ARAO MANHIQUE,[1,4,*] WALTER W. FOCKE,[2] ANDREAS LEUTERITZ,[3] AND CARVALHO MADIVATE[4]

[1]Institute of Applied Materials, Department of Chemistry, University of Pretoria, Pretoria, South Africa
[2]Institute of Applied Materials, Department of Chemical Engineering, University of Pretoria, Pretoria, South Africa
[3]Leibniz Institute of Polymer Research Dresden, Dresden, Germany
[4]Department of Chemistry, Universidade Eduardo Mondlane, Maputo, Mozambique

Poly(ε-caprolactone) nanocomposites were prepared by melt compounding with organo-modified layered double hydroxides (LDH). The LDH were intercalated with stearic acid (LDH-stearate) or with sodium dodecyl sulphate (LDH-SDS). Nanocomposites morphology was studied by XRD and TEM. Thermal properties were analysed by TG and DSC. Although both systems showed presence of a mixed morphology, exfoliated and intercalated, LDH-stearate nanocomposites showed a better dispersion of inorganic platelets. TEM images showed the presence of individual platelets in the PCL matrix. LDH-SDS nanocomposites.

Keywords Polycaprolactone; nanocomposites; exfoliation

Introduction

Poly(ε-caprolactone) (PCL) is a biodegradable polymer with potential applications in the field of bioengineering and packaging. It features a low melting temperature range (59°C–64°C) and a low glass transition temperature (≈ −60°C). The low melting point complicates processing and the poor mechanical properties have hampered widespread use [1–3]. The addition of small amounts of benign inorganic fillers may lead to an improvement of some of these characteristics [1]. Layered double hydroxides (LDH) have been used in this regard.

Property improvement by LDH or by other nanofillers is intrinsically dependent on the compatibility of the filler with the parent polymer. The compatibility will impact directly on the degree of exfoliation that can be achieved. It will therefore influence the property improvement. Compatibility can be achieved by intercalation of suitable organic molecules into the clay layers.

*Address correspondence to Arao Manhique, Institute of Applied Materials, Department of Chemistry, University of Pretoria, Pretoria, South Africa. E-mail: araomanhique@uem.mz

Organoclay nanocomposites can be prepared in three different ways: (1) direct intercalation, where the polymer is directly intercalated in the clay matrix; (2) *in situ* polymerization, where monomers are imbibed into clay structure prior to polymerization; (3) and co-precipitation, which involves simultaneous formation of clay layers and intercalation [4]. Nanocomposites are generally characterized by XRD and TEM. A complete exfoliation may result in the disappearance of the clay basal reflections. It is important to note, however, that other changes can result in basal reflections apparently disappearing. TEM provides direct information on the morphology of the nanocomposites but the representativeness of the sample can be questioned [5].

Direct intercalation by melt processing is the most environmentally and commercially advantageous processing technique for nanocomposites preparation [6, 7]. However Nhlapo et al. [8] reported a phase transition above 85°C and complete melting above 120°C in LDH-stearate. If this were true, this would make the material unfit for melt processing with conventional thermoplastics that require higher processing temperatures. This investigation was aimed to study the intercalation of LDH-stearate in the low melting poly (ε-caprolactone) polymer. The hope of this investigation was a clearer picture of propensity of LDH-stearate to exfoliation.

Experimental

Materials

Poly(ε-caprolactone) (PCL 6500) with an average molecular mass of 50 000, was supplied by Solvay Interox Ltd (UK). Two nanofillers were used, i.e. layered double hydroxide modified either with stearic acid (LDH-stearate) or with sodium dodecyl sulphate (LDH-SDS). The LDH is a commercial product from Chamotte Holdings South Africa with composition corresponding to 2.1:1 (Mg:Al) on a mole basis. Modification was conducted according to the procedure reported by Nhlapo et al. [8].

Compounding and Injection Moulding

The organoclays and the polymer were dried overnight in a vacuum oven at 60°C. The dried mixture was compounded in a Brabender Plasticorder (Duisburg EHT 50, German) for 6 min at a speed of 120 rpm. The compounded samples were injection moulded in a DACA Microinjector (USA) at 90°C.

Characterization

X-ray diffraction analyses were conducted in a XRD 3003 θ/θ (Seifert-FPM Freiberg/Sa.) instrument, over the range of $2\theta = 0.5$ to 30° in symmetric reflection, long secondary Soller collimator. Cu-Kα radiation (monochromatization by a primary multilayer system) was used at 40 kV and 30 mA. The step-scan mode was 10 s per point.

FTIR spectra were recorded in a Bruker Opus Spectrophotometer. TEM images were recorded in a JEOL JEM–2100F. Thermogravimetric analyses were conducted in a Mettler Toledo A851 TGA/SDTA instrument. Approximately 20 mg of the sample were placed in 150 μl alumina pan and subjected to 10°C/min heating program from 25 to 800°C. DSC experiments were performed in a Mettler Toledo Star^e SW instrument. Samples were heated from −70 to 140°C at 10°C/min and hold isothermally at 140°C and allowed to cool afterwards at the same rate.

Results and Discussion

X-Ray Powder Diffraction and TEM

XRD was used to verify the exfoliation of the LDH in the composites. The complete loss of the clay XRD reflections are expected for a completely delaminated or exfoliated nanocomposite. However, low clay concentrations and a loss of symmetry can also lead to such a collapse. Diffractograms of the PCL-LDH-stearate and the PCL-LDH-SDS composites are presented in Fig. 1. No significant changes were observed in position of the XRD peaks. However higher order peaks became weaker or even disappeared. This indicated that exfoliation was not completely achieved and that LDH crystalline structure was at least partially preserved. Based on these XRD results one can assume that, at best, a microcomposite structure was achieved. A clearer understanding of the morphology can be obtained by analysing TEM micrographs.

Low magnification micrographs (Fig. 2) reveal that LDH-SDS composites featured a more uniform filler distribution than LDH-stearate composites. LDH-SDS composites, according to this image seem to have a good distribution of LDH particles in PCL matrix as opposite to LDH-stearate composites. However this distribution can also indicate a poorer

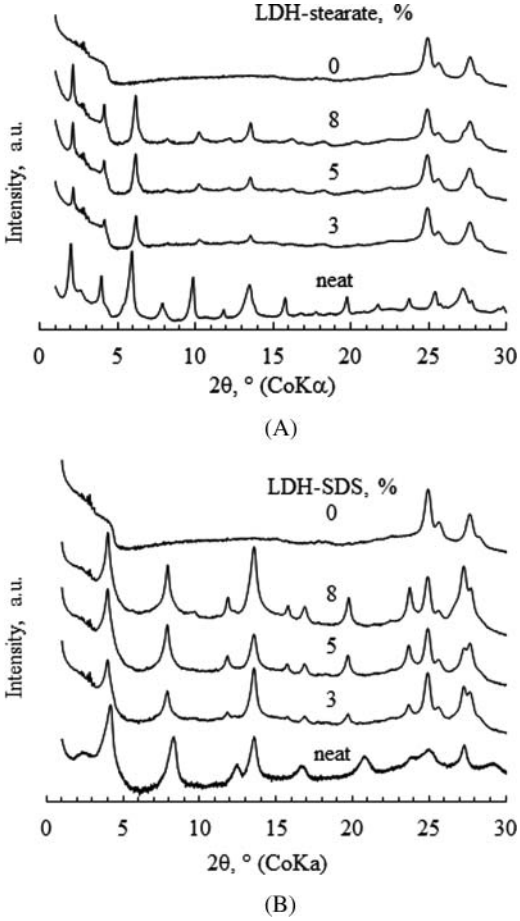


Figure 1. XRD diffractograms of nanocomposites. (a) Poly(ε-caprolactone)/LDH-stearate, and (b) Poly(ε-caprolactone)/LDH-SDS.

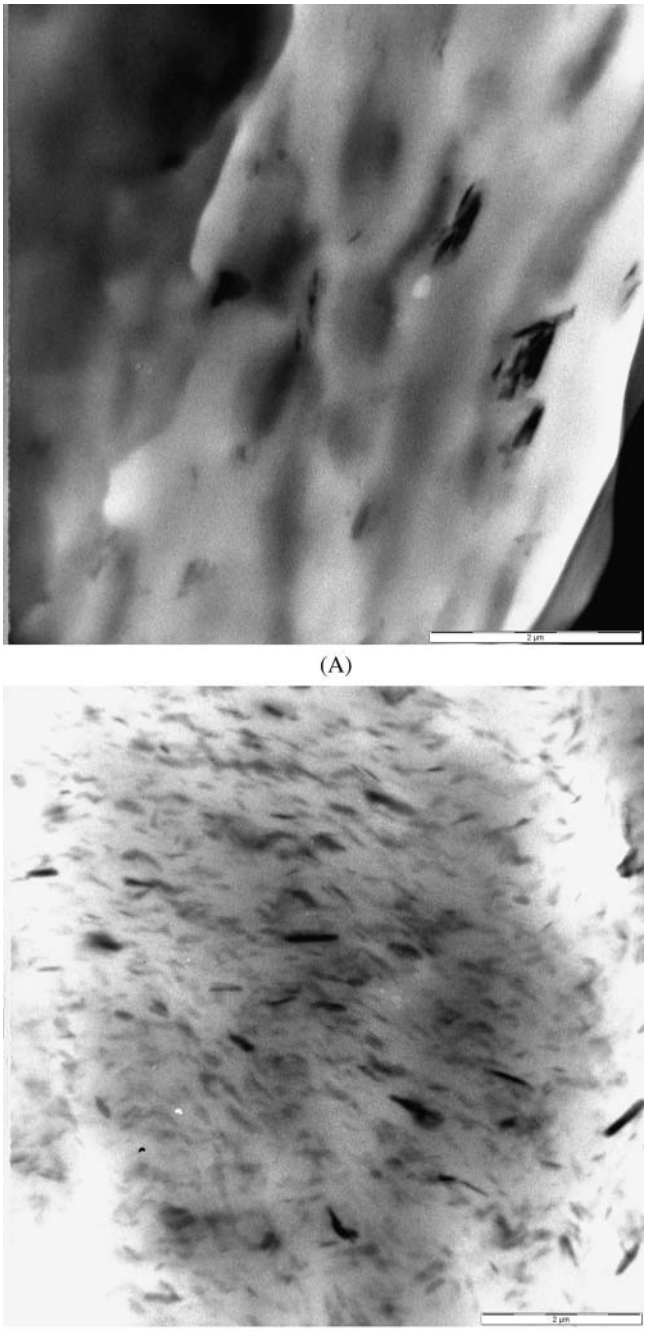
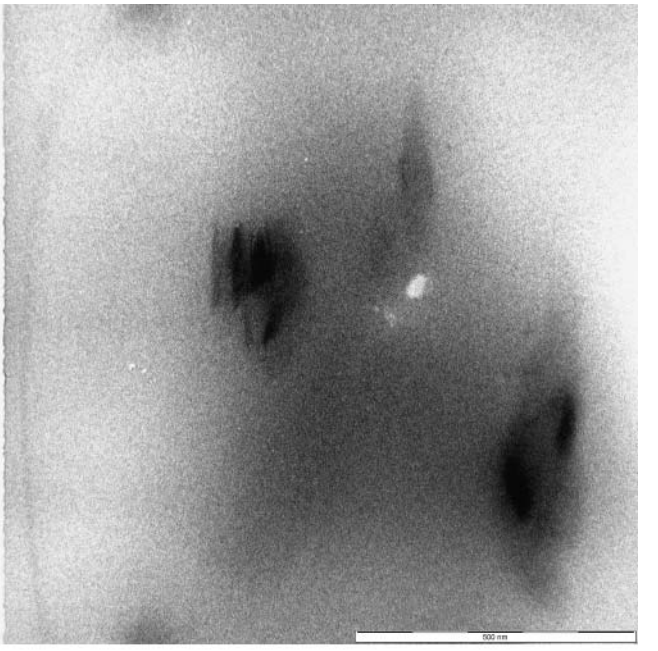
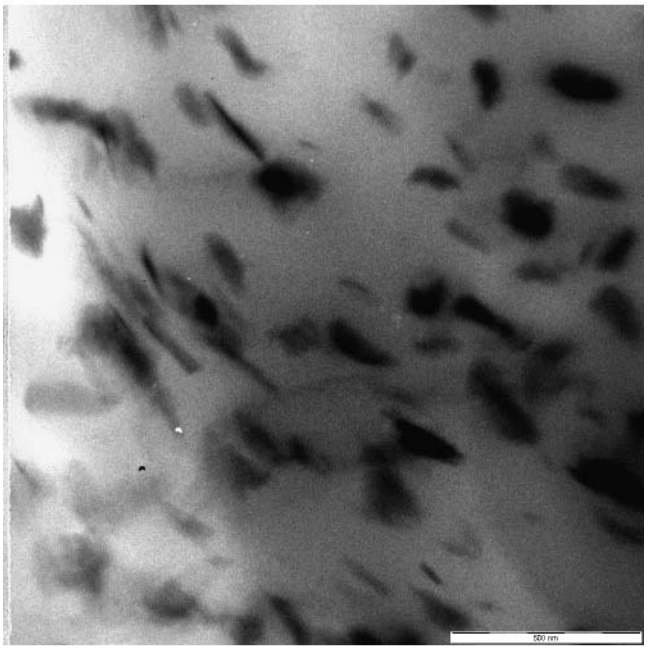


Figure 2. Low magnification TEM image of PCL composites prepared in this work. (a) LDH stearate; (b) LDH-SDS.

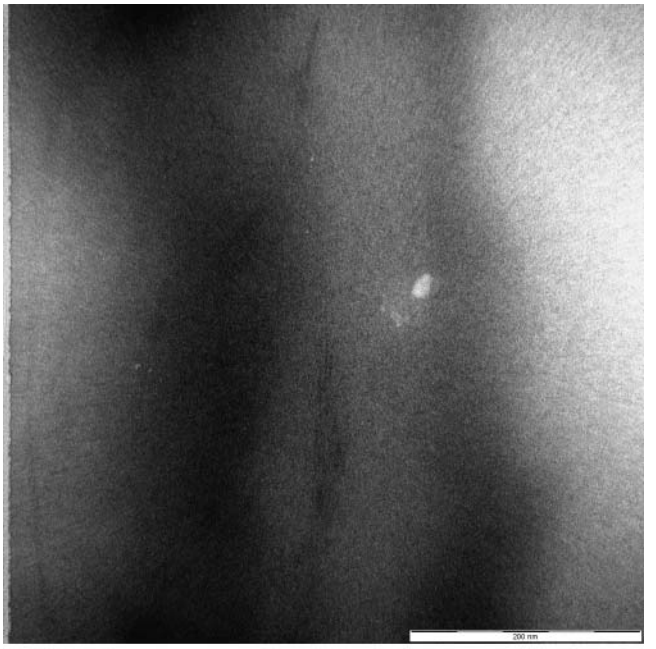


(A)

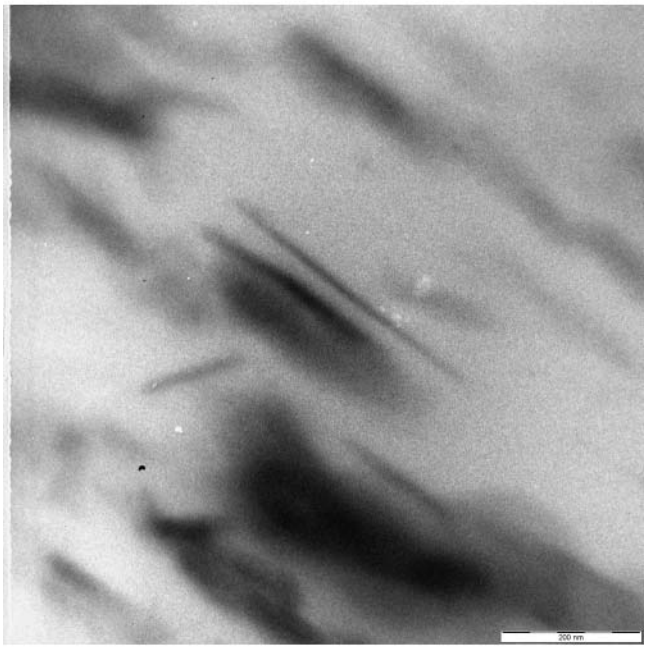


(B)

Figure 3. TEM images of (a) poly(ε-caprolactone)/LDH-stearate, and (b) LDH-SDS nanocomposites.



(A)



(B)

Figure 4. High magnification TEM images of poly(ε-caprolactone) nanocomposites. (a) LDH-stearate, and (b) LDH-SDS.

distribution at the nanometer scale. Thus in LDH-stearate a better Nano scale distribution might have been achieved. In fact, medium magnification TEM images showed the presence of a higher density of tactoids in LDH-SDS composites compared to LDH-stearate (Fig. 3). However individually dispersed particles (highlighted) are present in polymer matrix of both nanocomposites indicating that a mixed morphology was achieved. The LDH platelets are present in the form of individual particles as well as tactoids.

A higher magnification image shows that some LDH-stearate crystals in nanocomposites are present as groups of crystals are assembled in piles with different arrangements (Fig. 4(a)). LDH platelets in LDH-SDS nanocomposites are present as tactoids, indicating a lesser extent of exfoliation/intercalation in this system. These tactoids are sparsely dispersed in the polymer matrix (Fig. 4(b)). These particles will show a limited symmetry resulting in the disappearance of higher order reflections on the XRD diffractogram as was observed by Costa et al. [9].

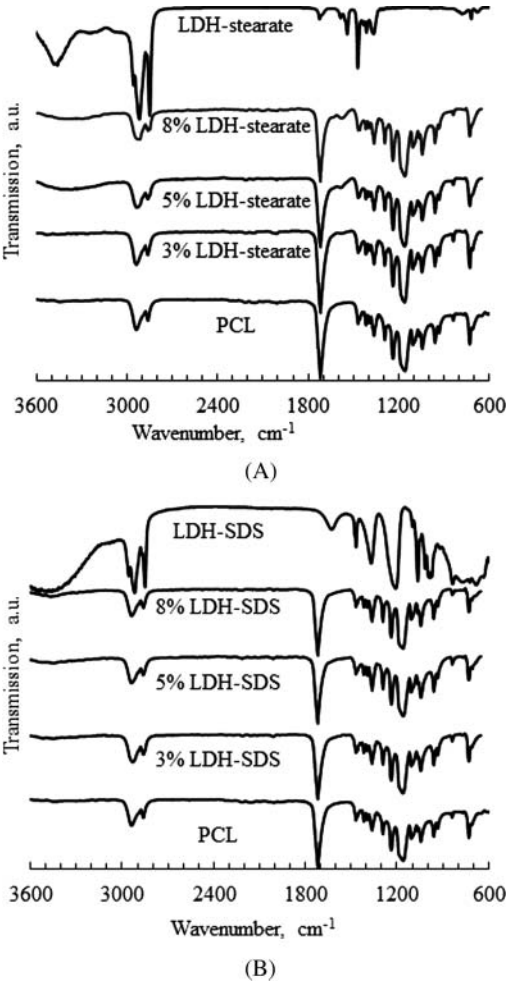


Figure 5. FTIR spectra of nanocomposites. (a) Poly(ε-caprolactone)/LDH-stearate; (b) Poly(ε-caprolactone)/LDH-SDS.

FTIR Analysis

FTIR spectra are shown in Fig. 5. The bands at 2860, 2917, and 2936 cm^{-1} in PCL spectrum are attributed to C—H stretch vibration modes. Carbonyl stretching is observed at 1718 cm^{-1}. C—O—C and C—C stretching in crystalline phase band are present at 1292 cm^{-1}, while the same absorptions in the amorphous phase are observed at 1157 cm^{-1}. Other bands observed are 1238 cm^{-1} (asymmetric C—O—C stretching), and CH_2 rocking at 1394, and 729 cm^{-1} [10–13]. The presence of LDH in the PCL nanocomposites is confirmed by the presence of additional bands below 800 cm^{-1} which are due to M-O vibrations, Figs 4(a) and 4(b). Bands related to O-H groups (not shown here) were observed at 3100–3600 cm^{-1}.

Thermal Properties

Figure 6 illustrates thermogravimetric analyses results for neat polymer and nanocomposites. The thermal degradation temperature of PCL composites is lower compared to the neat

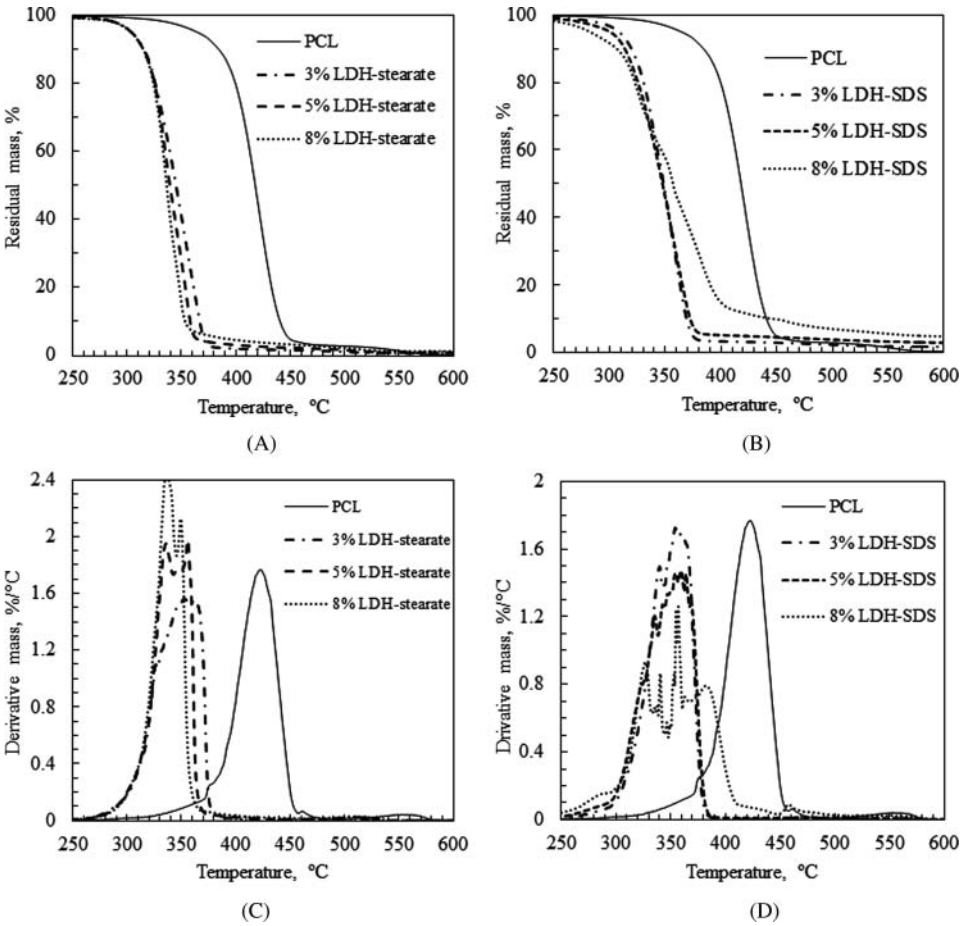


Figure 6. Thermogravimetric response of Poly(ε-caprolactone) nanocomposites. TG curves of (a) PCL/LDH-stearate; (b) PCL/LDH-SDS; DTG curves of (c) PCL/LDH-stearate, and (d) and PCL/LDH-SDS nanocomposites.

polymer. One of the explanations for such behaviour could be the degradation promoted by the OH groups present in the LDH structure. This was also observed Du et al. [13] in poly(propylene carbonate). Peng et al. [12] attributed such behaviour to the earlier decomposition of LDH compared to the parent polymer. This was also observed by Nhlapo et al. [8]. DTG curves (Fig. 6(c) and 6(d)) show that PCL degradation occurred in multiple steps.

Figure 7 shows DSC curves for neat PCL and the nanocomposites. The melting temperatures of both LDH-stearate and LDH-SDS nanocomposites are close to the melting temperature of parent polymer (Fig. 7(a) and 7(b)) indicating that the crystal structure of PCL is maintained in agreement with the observation of previous authors [14, 15]. Figures 7(c) and 7(d) indicate a slight decrease in the crystallization temperature of LDH-stearate nanocomposites. LDH-SDS nanocomposites showed a slight increase in crystallization temperature to 29°C for a 3% clay loading. This was expected since LDH layers act as nucleating agents as was observed for other clays. However, above this point

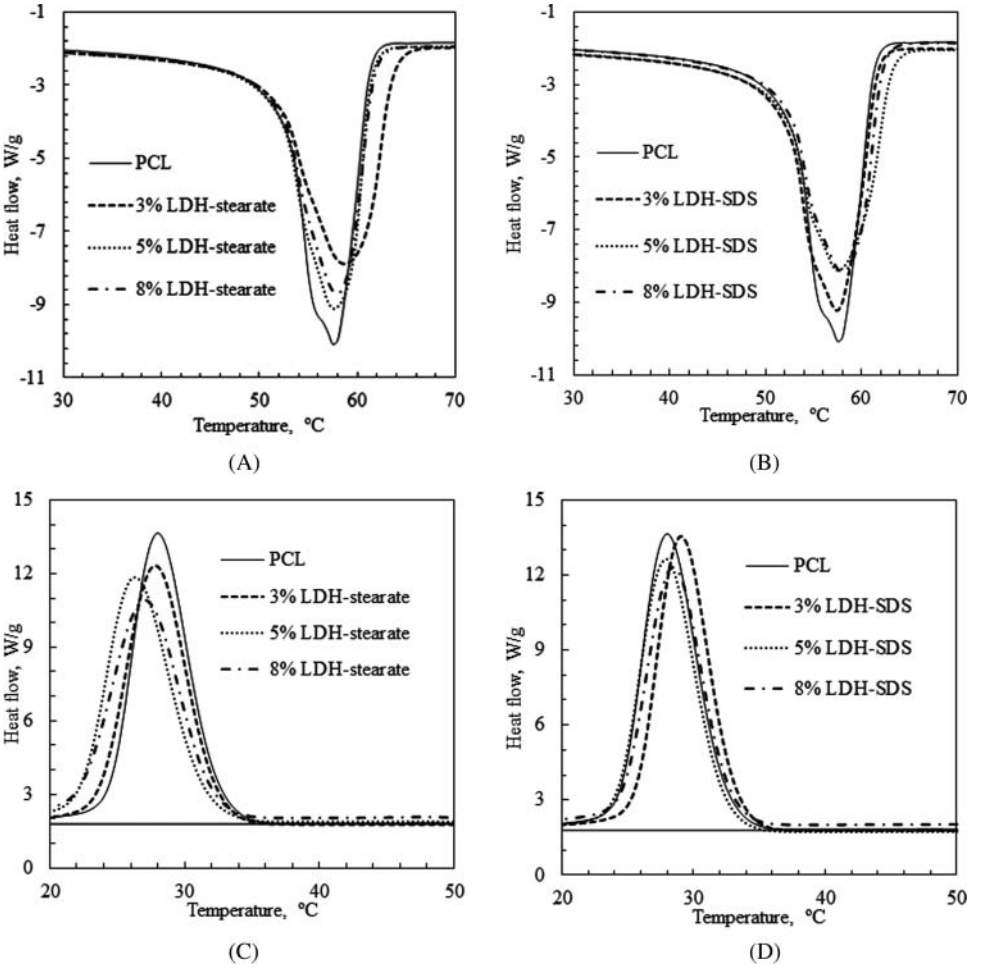


Figure 7. DSC curves of PCL and PCL nanocomposites. Melting endotherms of (a) PCL/LDH-stearate, and (b) PCL/LDH-SDS nanocomposites. Crystallization exotherms of (c) PCL/LDH-stearate, and (d) PCL/LDH-SDS nanocomposites.

the crystallization temperature decreased. The behaviour for LDH higher loadings can be understood in terms of the explanation offered by Di et al. [14]. The presence of organic surfactant in LDH galleries leads to interactions with PCL molecules. This effect increases with increasing LDH concentration [14].

Conclusions

PCL/LDH-stearate and LDH-SDS nanocomposites were prepared via melt intercalation. The Nanocomposites morphology was studied by XRD and TEM while thermal properties were studied by TG and DSC. FTIR studies confirmed the presence of LDH in PCL matrix. XRD and TEM results indicated a mixed morphology. Both systems showed the existence of a dispersed (exfoliated) LDH platelets as well as the presence of tactoids. A better matching of polymer-filler properties was observed with LDH-stearate as TEM results indicated a better dispersion of filler particles in this latter system. DSC results showed that the presence of LDH-SDS did affect crystallization of PCL.

Acknowledgments

This work is based on research supported by the National Research Foundation (NRF) through the Institutional Research Development Programme (IRDP); the South Africa/Mozambique Collaboration Programme, and the South Africa/Germany Research Collaboration Programme. Financial support from the Bundesministerium für Forschung (BMF) and the Leibniz Institute for Polymer Research in Dresden, is also gratefully acknowledged.

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