Surfactant-induced morphology and thermal behavior of polymer layered silicate nanocomposites

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Abstract. Poly(L-lactic acid) nanocomposites were prepared by the addition of montmorillonite modified with various loadings of hexadecylammonium cation. The influence of alkylammonium on the morphology and surface charge of the clay was investigated by X-ray diffraction (XRD) analysis and electrokinetic measurements, respectively. The structural characteristics of the inorganic-organic hybrids were studied by XRD, transmission electron microscopy (TEM) and atomic force microscopy (AFM). Thermal analysis was carried out by thermogravimetric analysis (TGA) under constant nitrogen flow and under air. The results showed that high concentration of surfactant present in the clay greatly increases clay’s dispersibility into the matrix and this substantially improves the thermal stability of the pristine polymer.

1. Introduction
Polymer nanocomposites have recently received considerable attention from both academia and industry, since they are considered to be an effective way to overcome the shortcomings of conventional, mineral-filled composites. Minimal addition levels (<10 wt%) of nano-sized filler significantly enhance mechanical, thermal and barrier performance properties of the polymer [1].

Of great current interest is the use of layered silicates as nanoscopic filler material. These two-dimensional, plate-like clays such as montmorillonite (MMT) are composed of regular stacks of silicate layers bound together with weak interatomic forces. By modifying their surface through the use of surfactants, high aspect ratio nanoparticles can be created which, in turn, can be dispersed in organic phases, e.g. in polymer matrices [2]. The presence of amphiphilic molecules increases the interlayer spacing of these clays and facilitates polymer insertion; the amphiphilic molecules serve as a compatibilizer between the hydrophilic clays and the hydrophobic polymer.

Recently, biodegradable and biocompatible polymers have become quite popular in the field, because of their potential biomedical and ecological applications. Poly(L-lactic acid) (PLLA) is a biodegradable, aliphatic, thermoplastic polyester produced from agricultural resources and is used widely [3].

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Although intensive research efforts have been devoted to the improvement of PLLA properties by preparing various nanoclay-filled PLLA hybrids [4-6], the effect of the clay modification degree on the composite behavior and structure have not been identified. In order to obtain a fundamental understanding of the reinforcement caused by the layered silicates, it is necessary to define the relationship between organoclay structure and hybrid properties. The objective of this study was to prepare PLLA nanocomposites containing montmorillonite with various concentrations of hexadecylammonium cation and to investigate the surfactant role on the nanocomposite structure and thermal stability.

2. Experimental part

2.1. Materials
PLLA (M_n=81000, M_w/M_n=1.9 and 0% content in D-lactide stereoisomer) was supplied by Galactic S.A. and sodium montmorillonite (NaMMT) (Cation Exchange Capacity (CEC) =92.6 meq/100 g) was obtained from Southern Clay Products (Texas, USA). Hexadecylamine with purity of 90% and concentrated HCl were purchased from Sigma-Aldrich. All materials were used without any further purification.

2.2. Preparation of organophilic montmorillonite
Organically modified montmorillonite (C_{16}MMT) was prepared through an ion-exchange reaction between sodium montmorillonite and hexadecylammonium cation (C_{16}A). The concentration of ammonium salts was equivalent to 50%, 150% and 250% the CEC of the silicate. The content of the inorganic parts in each prepared sample was determined by thermogravimetric analysis.

2.3. Nanocomposite preparation
Nanocomposites were produced by using the solution casting technique. Initially, the organomodified material (powder form) was dispersed in chloroform. The clay suspension was sonicated for 1h with a Heat Systems-Ultrasonics Inc. W-375 sonicator. After polymer dissolution, the mixture was further sonicated for 1h. Then, the mixture was cast onto Petri dishes and kept for 48h in a chloroform atmosphere, so that a slow solvent evaporation be achieved. Eventually, the obtained nanocomposite films with inorganic contents of 3 wt% were dried in vacuum at 50°C for 24h.

2.4. Characterization
The electrokinetic potential (ζ) of both the natural and the organophilic clay was measured with an automated microelectrophoresis instrument (ZetaPlus, Brookhaven Instruments Corporation) at pH~6.5 and using Smoluchowski’s equation. At least 20 runs were conducted for each sample and the mean values were recorded.

The structure of the organomodified clay and of the nanohybrids were investigated by X-ray diffraction analysis (XRD) using a Rich. Seifert 3003 TT diffractometer and Ni-filtered CuKα radiation (λ=0.154 nm). The scanned 2θ values were ranged between 2° to 10°. The dispersion of the silicate layers into the polymer matrix was examined directly by transmission electron microscopy (TEM) bright field imaging using a Jeol 120CX microscope operating at 120kV.

Atomic force microscopy (AFM) measurements were performed on a Veeco CP-II microscope operated in intermittent-contact mode (“Tapping Mode”). A commercial silicon tip-cantilever was used with a spring constant 20-80 N/m, a resonance frequency in the 200-400 kHz range and a tip radius of less than 10 nm. In this work, the samples were microtomed at room temperature.

The thermal stability of the hybrids was investigated by thermogravimetric analysis (TGA) on a Shimadzu TGA-50 with a heating ramp of 10°C/min up to 750°C under flowing nitrogen (20 cm^3/min). The thermal stability was also investigated in isothermal conditions at 260°C in air using the same instrument.
3. Results and discussion

3.1. Organomodified clay characteristics

The electrokinetic properties of natural montmorillonite and the montmorillonite modified with various concentrations of C\textsubscript{16}A are illustrated in figure 1. Because of isomorphous lattice substitution, montmorillonite surface charge is always negative and pH independent. However, at the edges, where the lattice is disrupted, there is a pH dependent charge arising from broken bonds [7]. Electrokinoetic measurements were performed at pH ~ 6.5 where the edges are considered to be neutralized [8]. At low loading levels, C\textsubscript{16}A is adsorbed by cation exchange only. As the load increases, the surfactant is adsorbed on the clay external surfaces through both cation exchange and hydrophobic bonding. The positive charge development on the surface of the clay is due to these hydrophobic interactions [9].

Figure 2 presents the XRD patterns of natural and organophilic clay. The basal spacing of the natural clay is 11.8 Å. Addition of C\textsubscript{16}A quantity equal to 50% coverage of the CEC enhances this \( d_{001} \) spacing to 13.6 Å implying that C\textsubscript{16}A and Na\textsuperscript{+} coexist within the same interlayer space and that the basal spacing is governed by a monolayer arrangement of alkylammonium. Further increase of the surfactant quantity leads to a substantial increase of the clay \( d \)-spacing up to 18.5 Å at surfactant levels of 150% coverage of the CEC and to 24.2 Å at 250% of the CEC suggesting a bilayer and a paraffin type monolayer of alkylammonium interlayer structure, respectively [10].

![Figure 1](image1.png)  
**Figure 1.** Relationship between montmorillonite zeta potential and surfactant concentration (related to the CEC).

![Figure 2](image2.png)  
**Figure 2.** XRD patterns of montmorillonite with various concentrations (related to the CEC) of hexadecylammonium.

3.2. Nanocomposites morphology

The changes of the mineral basal spacing due to the polymer presence are described in figure 3. It appears the \( d_{001} \) peaks from the composites are shifted towards lower 2\( \theta \) values indicating expansion of the clay structure due to the polymer insertion into the silicate galleries. Only in the case where the loading amount of C\textsubscript{16}A was equal to 50% CEC, the basal spacing of the inorganic material did not change after mixing the clay with the polymer. Apparently, the surfactant quantity was not enough in order to render the layered silicate miscible with the polymer matrix.

The excellent miscibility of the silicate layers into the polymer matrix when the surfactant concentration is at 150% CEC was also confirmed by TEM observations (figure 4). Dark lines represent the cross sections of the silicate layers and the gray area corresponds to the matrix. Inspection of this figure reveals the homogeneous dispersion of clay platelets throughout the polymer matrix.
The structure of the nanohybrids was also investigated by AFM observation. Topography and phase images of PLLA nanocomposite with 150% CEC organomodified MMT are illustrated in figures 5 (a) and (b). The light phase variations in figure 5 (b) represent dispersed clay platelets and, in accordance with the TEM observations, indicate the excellent miscibility of the inorganic material into the matrix due to the surfactant presence.

Figure 3. XRD patterns of (a) organo-modified clays and (b) the corresponding PLLA hybrids.

Figure 4. TEM micrograph of PLLA and C_{16}MMT with alkylammonium concentration at 150% CEC.

Figure 5. AFM topography (a) and phase (b) images of PLLA nanocomposite with MMT modified by hexadecylammonium cation equivalent to 150% the mineral CEC.

3.3. Nanocomposites thermal stability
Thermal decomposition properties of the prepared PLLA organomodified clay nanocomposites were investigated by TGA analysis, as shown in figure 6. Introduction of organomodified clay significantly increases the polymer thermal stability provided that the clay contains adequate amount of surfactant, so that a good dispersion of the silicate platelets can be achieved.
In isothermal conditions (260 °C) and oxidizing atmosphere, the nanocomposite prepared with clay subjected to a high degree of modification exhibited the most reduced rate of polymer mass loss. The dispersed inorganic mineral decreases diffusion of both oxygen from air to the polymer and volatile thermo-oxidation products from the polymer matrix to the air [11]. As the process of volatilization continues and the nanocomposite is reduced in volume, an improvement in this barrier property is observed and is attributed to the reassembly of the dispersed silicate layers on the polymer surface [12].

![Figure 6. TGA thermographs in inert atmosphere for PLLA nanocomposites prepared by the addition of MMT containing concentrations of C_{16}A at 50%, 150% and 250% CEC.](image1)

![Figure 7. TGA curves in isothermal conditions (260 °C) and oxidizing atmosphere for pure PLLA and PLLA nanocomposites prepared by the addition of MMT with C_{16}A concentrations at 50%, 150% and 250% CEC.](image2)

4. Conclusions
Organophilic MMT with various loadings of hexadecylammonium cation was prepared through an ion exchange reaction. The surfactant presence increased the basal spacing of the clay and changed its surface charge.

PLLA nanocomposites were produced by the solvent casting method and with the various grades of the organomodified MMT prepared. Increase of the degree of clay modification led to an increased dispersion of the layered silicates into the matrix and to an improved polymer thermal stability.

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