



Poly(L-lactic acid)/organically modified vermiculite nanocomposites prepared by melt compounding: Effect of clay modification on microstructure and thermal properties



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ABSTRACT

In this work, vermiculite (VMT) was successfully modified by organic cation intercalation (oleyl bis(2-hydroxyethyl) methyl ammonium), silane grafting (glycidoxypopyl trimethoxy silane), and combining silane grafting and alkylammonium cation intercalation. The organically modified VMTs were melt compounded with poly(L-lactic acid) (PLLA), and the effect of the nanofiller concentration and type of modification of the VMT on the nanostructure and thermal properties of the PLLA/organo-VMT nanocomposites was investigated. The effect of the melt processing conditions used in the preparation of nanocomposites on the molecular weights of the polymer matrix was determined by gel permeation chromatography (GPC). The structure of the intercalated surfactant in the modified clays was characterized by X-ray diffraction (XRD) analysis. The morphology of the nanocomposites was examined by XRD and transmission and scanning electron microscopy (TEM, SEM). The thermal behavior of the clays and nanocomposites was analyzed by differential scanning calorimetry (DSC) and thermogravimetry (TGA), and microscale pyrolysis combustion calorimetry (PCFC) was used to measure the flammability of the nanocomposites. GPC analysis showed that the molecular weights of native and unfilled extruded PLLA were similar, while the incorporation of organo-VMTs resulted in a reduction of the PLLA molecular weights. XRD and TEM investigations showed that exfoliation predominantly occurred in 2 wt% nanocomposites, whereas intercalated structures together with exfoliated clays were observed with high contents of organoclays. The double modification of the clay resulted in a higher level of exfoliation, attributed to the enhanced interactions between the end groups of the PLLA and the clay containing the epoxy groups. DSC analysis showed that the glass transition and cold crystallization temperatures of nanocomposites were slightly lower than those of neat PLLA. The crystallization enthalpies increased with the addition of organo-VMTs. However, the crystallinity of the PLLA was unaffected by the addition of clays, only the crystal size and perfection were affected. The nanocomposites prepared with 2 wt% of organoclays displayed increased thermal stability. The flammability test revealed that no significant reduction of fire hazards was caused by the presence of organo-VMTs.

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1. Introduction

Polymer clay nanocomposites are a new class of reinforced plastics formed by dispersion of nanosized clay particles in a polymer matrix which have received considerable attention in both scientific and industrial

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areas during the past decade [1–3]. With relatively low loading of clay, many physical and chemical properties of the composites improve significantly as compared to the pure polymer or to the related macro- or microcomposite [4–10]. The enhanced properties of polymer–clay nanocomposites are due to high interfacial interaction between the homogeneously dispersed nano-sized clay platelets and polymer matrix.

For compatibility reasons, clays are hydrophilic by nature and polymers mostly hydrophobic, the clay needs to be modified suitably with organic species in order to use it in the preparation of clay based polymer nanocomposites. The surface modification of clay is one of the most important steps in the preparation of nanocomposites. Clays are layered silicates with alkali or alkaline earth metal cations in the interlayer. Surfactants such as organoalkylammonium salts can exchange with the inorganic hydrated cations in the interlayer through ion exchange reactions. Another modification procedure includes the grafting of organic functionalities to the hydroxyl groups present at the edge of the clay mineral layers. Using this approach, a covalent linkage can be achieved through the reaction between the reactive hydroxyl groups and an adequate molecule. Organoalkoxysilanes can be used to provide functional organic moieties. Hydrolysis of the alkoxy groups yields in silanol groups that react with surface groups of the clay. The silane molecules can react at the external broken edges of the clay crystalline sheets, remaining the basal spacing unchanged, or at the layer surface of the clay sheets, in this case an interlayer expansion occurs. Using that modification method, organic groups can be introduced into the clay, which may interact with the polymer matrix to enhance the compatibility in the nanocomposite material.

Poly(lactic acid) (PLA), a compostable biodegradable thermoplastic, is of increasing commercial interest because it is made from renewable resources. PLA is used in a variety of applications, like packaging material and in biomedicine. The combination of PLA and layered silicates may result in a nanocomposite with remarkable improvements in its material properties when compared with those of virgin PLA [11].

Vermiculite (VMT) is a mica-type silicate, possesses a layered structure and is usually used as a packaging material for antishocking, abundant and much cheaper in comparison with montmorillonite, hectorite and saponite. However, VMTs have a large internal surface, higher cation exchange capacity (CEC) and higher negative charge on the silicate layers in comparison with others 2:1 layered phyllosilicates. Therefore, it is quite difficult to exchange cations with organic molecules because of its high interlayer charge density.

There have been some reports of the modification of Cloisites with silanes [12,13], but there are not reported studies about intercalation of onium ions and silane modification of VMT.

The aim of this work was, firstly, to synthesize organo-vermiculites by cation-exchange reaction with alkylammonium ions, and by combining ion exchange reaction and silane grafting; secondly, to prepare organoclay nanocomposites based on PLA by melt compounding method, and investigate the effect of the clay content and the

modification process on clay dispersion in the polymer matrix, and thermal properties of the nanocomposites. Organo-VMTs were characterized by X-ray diffraction, FTIR and thermogravimetry. The morphology, thermal properties, and flammability of the PLLA/organo-VMT nanocomposites were characterized by X-ray diffraction, microscopy, thermogravimetry, differential scanning calorimetry and pyrolysis-combustion flow calorimetry.

2. Experimental

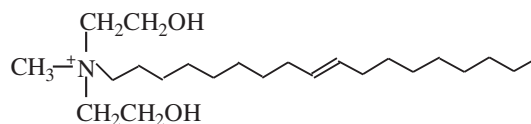
2.1. Materials

The VMT used in this work was purchased from Sigma-Aldrich with grade number 3, its CEC is 150 meq/100 g and its *d*-spacing is 12 Å (hydrated clay). Expanded VMT was ground, to obtain particles less than 40 μm in size, using an ultracentrifugal mill (Retsch ZM-200) in which the reduction of size takes place by impact and shearing effects between the rotor and the fixed ring sieve. The surfactant used was oleyl bis(2-hydroxyethyl) methyl ammonium chloride (Ethoquad O/12) labeled ETO (FW: 406.1, **Structure 1**) supplied by Akzo Nobel as active solution in isopropyl alcohol. The silane coupling agent, (γ -glycidoxypropyl)trimethoxy silane, labeled GPS (FW: 236.34, **Structure 2**), was supplied by Aldrich. Poly(L-lactide) (PLLA) (3051D) was manufactured by NatureWorks LLC. The D-isomer content of PLLA is 3.7–4.6%, and the residual monomer content is less than 0.3 wt% and with a number-average molecular weight of 70,000 g/mol and a polydispersity index of 1.67, as measured by Gel Permeation, and was dried under vacuum at 60 °C before use.

2.2. Preparation of chemically treated vermiculites

2.2.1. Alkylammonium exchanged vermiculite (OVMT)

The VMT was organically modified by a cation-exchange reaction between VMT and ETO. The required amount (1.25 equivalent of the CEC) of the alkylammonium salt was dissolved in deionized water at approximately 50 °C. 10 g of VMT were preliminarily dispersed in deionized water by using a mechanical stirrer, and heated at 85 °C. The alkylammonium solution was added to the suspension of the clay particles, and the mixture was exchanged for 24 h at this temperature using vigorous stirring. The resulted organo-clay (OVMT) was collected by filtration and repeatedly washed with hot deionized water until no halide ions were detected upon adding 0.1 M aqueous AgNO₃. Then, the organo-clay was washed with hot ethanol, and finally the product was dried under reduced pressure at 60 °C to a constant weight.



Structure 1. ETO.

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