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Research paper

Effect of clay surface modification and organoclay purity on microstructure and thermal properties of poly(L-lactic acid)/vermiculite nanocomposites

M. Jesús Fernández *, M. Dolores Fernández, Ibai Aranburu

Departamento de Ciencia y Tecnología de Polímeros, Facultad de Química, Universidad del País Vasco (UPV/EHU), Paseo Manuel Lardizábal 3, 20018 San Sebastián, Spain

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A B S T R A C T

Vermiculite (VMT) was successfully modified by cationic exchange of hexadecyltrimethyl ammonium ions, covalent grafting of glycidoxypropyl trimethoxy silane, and combining grafting and intercalation. The complete removal of excess surfactant from VMT resulted in a change in the interlayer structure and higher thermal stability of the organoclay mineral. The organosilane grafted on the clay mineral edges improved the thermal stability of the organoclay mineral. The organoclay minerals were melt compounded with poly(L-lactic acid) (PLLA), and the effect of the nanofiller concentration, type of modification and organoclay mineral purity on the nanostructure and thermal properties of nanocomposites was investigated. The removal of excess surfactant and organosilane functionalization enhanced the dispersion level of the organoclay mineral. PLLA degradation that occurred during nanocomposite processing depended on the clay mineral concentration, the extent of clean surface and the clay mineral dispersion state. The removal of excess surfactant and organosilane functionalization improved the thermal stability of nanocomposites.

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1. Introduction

In the last decades, there has been a strong emphasis on the development of polymeric nanocomposites, where at least one of the dimensions of the filler material is of the order of a nanometer. The nanofillers have a unique combination of characteristics, such as size, mechanical properties, and low concentrations necessary to improve many physical and chemical properties of a polymer matrix. In addition, many polymer nanocomposites can be fabricated and processed in ways similar to that of conventional polymer composites, making them particularly attractive from a manufacturing point of view.

In general, nanofillers provide reinforcing efficiency because of their high aspect ratios. The properties of a nanocomposite are greatly influenced by the size scale of its component phases and the degree of mixing between the two phases. Polymer nanocomposites based on layered silicates can be classified into three different types, depending on the extent of separation of the silicate layers: phase-separated, intercalated and exfoliated nanocomposites (Alexandre and Dubois, 2000). In each case, the physical properties of the resultant composite are significantly different. Exfoliated nanocomposites have higher phase homogeneity than the intercalated counterpart. Hence the exfoliated structure is more desirable in enhancing the properties of nanocomposites. However, complete exfoliation (single platelet dispersion) and hence the preparation of homogeneous nanocomposites are a very difficult issue since flocculation takes place owing to the hydroxylated edge–edge interaction between the clay mineral layers.

The lack of affinity between hydrophilic silicate and hydrophobic polymer causes agglomeration of the mineral in the polymer matrix. To render layered silicates miscible with those polymer matrices, it is required to convert the hydrophilic silicate surface to an organophilic. Generally, this can be done by ion-exchange reactions with organic cations (typically cationic surfactants) (Ray and Okamoto, 2003), by grafting of organic functionalities to the hydroxyl groups present at the edge of the clay mineral layers and by a combination of these two methods. Pristine-layered silicates usually contain exchangeable inorganic cations in the interlayer and surfactants such as organoalkylammonium salts can exchange with these cations in the interlayer through ion exchange reactions, and results in a larger interlayer spacing. Using the grafting approach, a covalent linkage can be achieved through the reaction between the reactive hydroxyl groups and organoalkoxysilanes in order to provide functional organic moieties. The silane molecules can react at the external broken edges of the clay mineral crystalline sheets, remaining the interlayer spacing unchanged, or at the layer surface of the clay mineral sheets, in this case an interlayer expansion occurs. Using that modification method, organic groups can be introduced into the clay mineral, which may interact with the polymer matrix to enhance the compatibility in the nanocomposite material.

The type of clay mineral and its content, the chemical nature of the clay mineral modifier, clay mineral functionalizations, the nature of polymer, and the processing route are the most important parameters

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* Corresponding author. Tel.: +34 943015353; fax: +34 943015270.
E-mail addresses: mjesus.fernandez@ehu.es (M.J. Fernández), mariadolores.fernandez@ehu.es (M.D. Fernández).

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in defining the state of dispersion of organoclays in polymers and, hence, the properties of the prepared composite. The organoclay purity is another aspect that can have an effect on the properties of the composites. It has been reported that the presence of excess surfactant has a strong influence on the thermal stability and the interlayer structure of the organoclays (Cui et al., 2008a; Davis et al., 2004; Elban et al., 2012; He et al., 2006; Le Pluart et al., 2002; Xi et al., 2005; Xie et al., 2001). Thus, the morphology and properties of the polymer nanocomposites can be affected by the extent of clean surface (Cui et al., 2008b; Mittal, 2008; Morgan and Harris, 2003).

Poly(lactic acid) (PLA), a compostable biodegradable thermoplastic, is of increasing commercial interest because it is made from renewable resources (Auras et al., 2004; Garlotta, 2002; Gupta and Kumar, 2007; Lim et al., 2008), and is used in a variety of applications. 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 (Ray and Okamoto, 2003).

Hectorite, saponite, and montmorillonite have been the most commonly used layered silicates for the preparation of PLA nanocomposites (Pandey et al., 2005). Thus far, a relative small number of studies have been reported on the preparation of PLA nanocomposites based on vermiculite (VMT) (Fernández et al., 2013; Zhang et al., 2007). VMT is a clay mineral that occurs extensively in nature. It is a 2:1 clay, consisting of an Al octahedral sheet, sandwiched between two Si tetrahedral sheets, and these three sheets form a layer. Compared with montmorillonite, hectorite and saponite, VMT is much cheaper and has larger cation exchange capacity (CEC).

The aims of this study were, firstly, to synthesize organo-VMTs by cation exchange reaction with alkylammonium ions, and by combining ion exchange reaction and silane grafting; secondly, to prepare organoclay mineral nanocomposites based on PLA by melt blending, and investigate the effect of the clay mineral content, the modification process, and the elimination of the excess surfactant in the organophilic clay mineral on the morphology and thermal properties of PLA nanocomposites based on organo-VMTs. Organo-VMTs were characterized by X-ray diffraction, FTIR, and thermogravimetry. The morphology and thermal properties of the PLA/organo-VMT nanocomposites were characterized by X-ray diffraction, microscopy, thermogravimetry, and differential scanning calorimetry.

2. Materials and methods

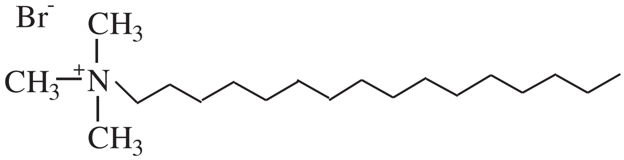
2.1. Materials

The VMT used in this work was purchased from Sigma-Aldrich with grade number 3, its cation exchange capacity (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). The surfactant used was hexadecyltrimethyl ammonium bromide (HDTMA) (Structure 1) with a purity of 99% as supplied by Sigma-Aldrich, and it was used without any further purification. The silane coupling agent, (γ-glycidoxypropyl) trimethoxy silane (GPS) (Structure 2), was supplied by Sigma-Aldrich. Poly(L-lactide) (PLLA) (3051D) was manufactured by NatureWorks LLC. The D-isomer content of PLLA is 3.7–4.6%, the residual monomer content is less than 0.3 wt.%, with a number-average molecular weight of 70,000 g/mol and a polydispersity index of 1.67, as measured by gel permeation chromatography (GPC), and was dried under vacuum at 60 °C before use.

2.2. Preparation of chemically treated vermiculite samples

2.2.1. Sodium exchanged vermiculite (Na-VMT)

100 g of the milled pristine VMT was refluxed in 500 mL of 4 M NaCl solution for 48 h, filtered and washed thoroughly with distilled water till the absence of chloride ions was confirmed ($AgNO_3$ test), then dried at 80 °C under reduced pressure.



Structure 1. HDTMA.

2.2.2. Alkylammonium exchanged vermiculite

The VMT was organically modified by a cation-exchange reaction between Na-VMT and HDTMA. 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 Na-VMT was preliminarily dispersed in deionized water by using a mechanical stirrer, and heated at 75 °C. The alkylammonium solution was added to the dispersion of the clay mineral particles, and the mixture was exchanged for 24 h at this temperature using vigorous stirring. The resulted organoclay mineral was collected by filtration and repeatedly washed with hot deionized water while stirring until no halide ions were detected upon adding 0.1 M aqueous $AgNO_3$. Then, the product was dried under reduced pressure at 60 °C to a constant weight. Another two organoclay minerals were prepared in the same way as above except that the purification method to remove any excess surfactant that may exist was different; one was washed with hot deionized water followed by Soxhlet extraction in ethanol for 1–4 days, and the other was washed with hot deionized water, followed by Soxhlet extraction in ethanol for 1 day and then ethanol acidified with acetic acid of pH = 4 under reflux for 12 h. The sample washed only with hot water was denoted as OVMT-w, the one washed with hot water followed by Soxhlet extraction in ethanol was denoted as OVMT-e, while the one treated with acidified ethanol OVMT.

2.2.3. Grafting of organic silane onto vermiculite (VMTS)

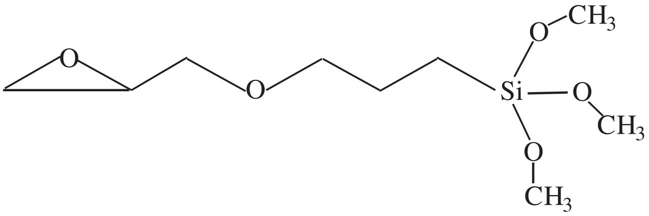
First, the silane coupling agent (GPS) was hydrolyzed at pH 4.0 for 18 h with acetic acid in ethanol (90 wt.%)/deionized water (10 wt.%) mixture at room temperature. Then Na-VMT was added and the mixture was heated with reflux at 70 °C for different times. At the end of the reaction, the mixture was allowed to cool with stirring. The reaction product was diluted with 1-propanol five times to remove any soluble homocondensates, then filtered and repeatedly washed with ethanol at room temperature. The product, denoted as VMTS, was dried in an oven under a vacuum at 50 °C for at least 48 h.

2.2.4. Grafting of organic silane onto organo-vermiculite (SOVMT)

The silane-grafted organo-VMT (SOVMT) was prepared from OVMT-e, after Soxhlet extraction for 1 day, in the same way as VMTS.

2.2.5. Alkylammonium exchanged silanized vermiculite (OVMTS)

The silane-grafted vermiculite (VMTS) was organically modified by a cation-exchange reaction between Na-VMTS and HDTMA in the same way as OVMT. The product was denoted as OVMTS.



Structure 2. GPS.

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