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Itaconic acid and amino alcohol functionalized polyethylene as compatibilizers for polyethylene nanocomposites

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ABSTRACT

The compatibilization provided by itaconic acid (IA) and 2-[2-(dimethylamino)-ethoxy] ethanol (DMAE) functionalized polyethylene for forming polyethylene-based nanocomposites was studied and compared. IA was grafted into PE by melt mixing to obtain PEgIA (compatibilizer 1), thereafter, PEgIA was reacted with DMAE also by melt mixing to obtain PAgDMAE (compatibilizer 2). PE-clay nanocomposites were prepared by melt mixing polyethylene with each of the two quaternary ammonium modified montmorillonite clays (Cloisite 30B and Nanomer I28E) plus each of the two previously prepared compatibilizers (PEgIA and PEgDMAE). FTIR characterization confirmed the formation of these two compatibilizers. All the compatibilized nanocomposites had better clay exfoliation–intercalated compared to the uncompatibilized PE nanocomposites. X-ray diffraction and transmission electron microscopy results, as well as the mechanical properties attained showed that the PEgDMAE with the I28E clay produced the better exfoliated–intercalated nanocomposites. Samples with C30B clay did not show any intercalation improvement, as compared to the uncompatibilized samples, which was attributed mainly to the smaller initial intergallery spacing of this clay. Finally, it is concluded that the PEgDMAE offers an outstanding capability for preparing highly exfoliated PE clay nanocomposites.

1. Introduction

Polyethylene is one of the most widely used polyolefin polymers because of its low cost, low density, low-temperature toughness, low moisture absorption, and ease of processing and recycling. However due to the lack of any polar group in its backbone, it is difficult to get the exfoliated and homogenous dispersion of the clay layer at the nanometer level in the polymer matrix. When preparing polyolefin based nanocomposites by melt compounding, the exfoliation and dispersion of nanoclays depends on the organic modifier of the nanoclay, the initial interlayer spacing, the concentration of functional groups in the compatibilizer and the compatibilizers overall concentration in the composite, the viscosity of the plastic resin, and the operational conditions, such as screw configurations of extruders, rpm, temperature and residence time. Polyolefin–clay nanocomposites have received special attention because of their improved properties at very low loading levels compared with conventional microsized filler composites. Recent studies have focused on the uniform dispersion of modified clay particles in the nonpolar matrix to increase their physical and mechanical properties. Among these improved properties are mechanical, dimensional, gas barrier, thermal stability and flame retardancy with respect to the bulk polymer [1–4]. The dispersion of clay particles in a polymer matrix can result in the formation of three types of composites. The first is a conventional composite that contains the original clay particles called tactoids of 1–10 μm in size, comprised by hundreds of platelets or laminates stacked together by strong attraction forces. In this case, the clay tactoids are distributed simply as a discrete and segregated phase, which results in a composite with poor mechanical properties. The second is an intercalated polymer–clay nanocomposite, which is formed by the infiltration of one or more molecular chains of polymer into the clay host galleries or laminates. The third type is an exfoliated polymer–clay nanocomposite, characterized by the delamination and dispersion of the original tactoids into hundreds of clay laminates of 10–100 nm. In this case, the nanoclay laminates are fairly well dispersed forming a compatibilized and monolithic structure with much better mechanical properties.

In the case of PE based nanocomposites, clay exfoliation has been achieved by compounding organo-modified montmorillonite (MMT), using maleic anhydride grafted polyethylene (PEgMA) as compatibilizer, by melt mixing [1,2,5,6]. Other PE's modified with polar monomers have found wide application as compatibilizers in binary polymer blends as well as in polymeric composites rein-

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forced with glass fibber and nanoclay [7]. Itaconic anhydride is a chemical compound that presents a closed ring which can be easily opened by temperature or mechanical stress to form itaconic acid, also known as methylen-succinic acid which is one of the three acids obtained from the distillation of the citric acid. Opposed to the maleic anhydride, IA is one of the few acids produced by micro-organisms and has less-toxic characteristics.

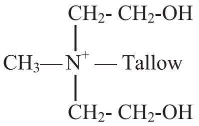
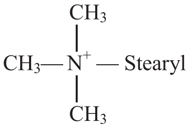
Our interest in polyolefin modified clay composites enters on the development of other methods of generating nanocomposite structures, and the understanding of polymer–filler interactions in these systems. The application of itaconic acid can be considered interesting because of their carboxylic bifunctionality and because itaconic acid is produced from non-oil based renewable natural resource, i.e. by large scale fermentation of molasses, a by-product from the sugar industry [8]. Recent reports [9–11] have been focused on using amine modified polyolefins as compatibilizer in polyolefin–clay nanocomposites. The exfoliation observed in these systems could be related to the polar and chemical interactions that occur between the carboxylic and the amine groups through an amination–imidation reaction. Some studies involve the enhancement of the adhesion between the polymer matrix and siliceous fillers by including ionomers in nanocomposite formulations [12–14]. On the contrary, other studies have demonstrated the limited capacity of maleated polyolefins as in situ compatibilizers to exfoliate organoclay by a melt compounding approach [15–17]. Typically these composites are hybrid materials that contain a mixture of exfoliated, intercalated structures, as well as large tactoid clay particles. The purpose of the present work is to obtain different functionalized PE's such as PEgIA and PEgDMAE, this last one was produced by the reaction of PEgIA with an amine alcohol, and to study their effectiveness as compatibilizers for PE-nanoclay nanocomposites. The ability of these modified PE compatibilizers to exfoliate and disperse two different organo clays was determined by X-ray diffraction (XRD) and electronic microscopy (STEM) and the influence of these compatibilizers on mechanical properties was examined.

2. Experimental methods

2.1. Materials

The PE matrix polymer is of commercial grade from Dow Plastics (LDPE 133A) with a melt index of 0.22 g/10 min. The PEgIA used was obtained in our lab by melt grafting using itaconic acid from Sigma–Aldrich and Di-cumyl peroxide from Sigma–Aldrich as initiator. The PEgIA obtained contains 0.6 wt.% IA. The MMT organoclays used were one modified with N-trimethyl stearyl quaternary ammonium (Nanocor I28E) from Nanocor Inc. and other with N-methyl, tallow, bis-2-hydroxietyl quaternary ammonium (Cloisite 30B) from Southern Clay Products Co. Also used were, a tertiary amino alcohol, DMAE, 2-[2-(dimethylamino)-ethoxy] ethanol and 2,6-Di-tert-butyl-4-methylphenol (BHT, 99%) from Sigma–Aldrich, which were reagent grade and were used without further purification. The main characteristic of the materials used are presented in Table 1.

Table 1
Main characteristics of the materials used.

LDPE	Dow 133 A (MFR 0.22 g/10 min)
IA	Itaconic acid from Sigma–Aldrich
DCP	Di-cumyl peroxide from Sigma–Aldrich
PEgIA	Polyethylene grafted itaconic acid (0.6 wt.% IA)
DMAE	2-[2-(dimethylamino)-ethoxy] ethanol from Sigma–Aldrich
BHT	2,6-Di-tert-butyl-4-methylphenol from Sigma–Aldrich
PEgDMAE	Polyethylene grafted amine alcohol
Nanoclay C30B	N-methyl, tallow, bis-2-hydroxietyl quaternary ammonium from Southern Clay Products Inc. % Weight loss ignition: 30% d_{001}, Intergallery spacing: 1.80 nm  $CH_3\text{—}\overset{CH_2\text{-}CH_2\text{-}OH}{\underset{CH_2\text{-}CH_2\text{-}OH}{N^+}}\text{—}\,Tallow$ Talow: fatty acids of 14, 16 and 18 C atoms (5% C14, 30% C16, 65% C18).
Nanoclay I28E	N-trimethyl stearyl quaternary ammonium from Nanocor Inc. % Weight loss ignition: 33% d_{001}, Intergallery spacing: 2.4 nm  $CH_3\text{—}\overset{CH_3}{\underset{CH_3}{N^+}}\text{—}\,Stearyl$ Stearyl: fatty acids of 18 C atoms

2.2. Preparation of polyethylene–clay nanocomposites

The PEgIA was obtained using a method previously reported in literature [18]. The amino alcohol modified PE, was obtained by first drying the previously prepared PEgIA at 90 °C for 24 h and then premixing it with BHT in a Banbury type mixing chamber (Brabender PL2000) equipped with roller type rotors. After 2 min of mixing and when all the polymer was melted, the amino alcohol (DMAE) was added, in sealed PE bags in order to avoid their evaporation, and the mixing was continued for 12 min at 170 °C and 60 rpm, forming the PEgDMAE.

Nanocomposites were prepared by compounding the required amounts of either PEgIA or PEgDMAE, plus LDPE and the organoclay (I28E or 30B) with 500 ppm of BHT in a Werner and Pfleiderer co-rotating twin screw extruder, with an $L/D = 29{:}1$ and $D = 30$ mm, operating at 190 °C and 100 rpm. Thereafter, 120 × 120 × 2 mm laminates were prepared by compression molding at 190 °C, from which appropriate test specimens were taken for the different analyses as X-ray diffraction and mechanical properties.

2.3. Evaluation of nanocomposites

The Fourier transform infrared spectra were recorded on a Nicolet 550 at 4 cm^{-1} of resolution and 30 scans. X-ray diffraction of the clays and nanocomposites, in order to evaluate the evolution of the clay d_{001} reflection, was performed in a Siemens D5000 using Cu Kα X-ray radiation. Ultrathin sections for STEM analysis were cut from the compression molded laminates with a diamond knife at −95 °C using a Leica microtome attached to a closed chamber with circulating liquid N_2. The STEM observations were performed with a Jeol-JSM7104F with a STEM modulus and a field emission gun at an accelerating voltage of 200 kV. Tensile properties were determined on samples obtained by compression molding using an Instron model 4301 upgraded for computerized data acquisition. Young Modulus was determined using an extensometer at a crosshead speed of 0.51 cm/min. The rheological properties were measured with an Instron capillary rheometer (model 4467), using a die with an L/D of 27.55 and D equal to 1 mm, at 195 °C.

3. Results and discussion

3.1. FTIR characterization

Fig. 1 compares the FTIR spectra for the different modified PE's. Fig. 1a, for the pure PEgIA, shows the characteristic absorption bands at 1720 cm^{-1} associated with the carbonyl C═O stretching band. The disappearance of the carbonyl stretching absorption at 1720 cm^{-1} associated with the carboxylic acid of IA in Fig. 1b, indicates a considerable extent of reaction between IA and the amino alcohol. For the PEgDMAE (Fig. 1b) new absorption bands at