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Polyethylene and polypropylene nanocomposites based on a three component oligomerically-modified clay

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Abstract

Polyethylene and polypropylene nanocomposites were prepared using a novel oligomerically-modified clay that contains three components, styrene, lauryl acrylate and vinylbenzyl chloride. The nanocomposites were prepared by directly melt blending the polymers with the clay and they were characterized by X-ray diffraction and transmission electron microscopy, to understand their morphology, and their thermal stability, flammability and mechanical properties were evaluated using thermogravimetric analysis, cone calorimetry and mechanical testing, respectively. The reduction in peak heat release rate is about 60% at 5% inorganic clay loading and 70% at 8% inorganic clay loading.

Keywords: Oligomerically-modified clay; Thermogravimetric analysis; Cone calorimetry; Mechanical testing

1. Introduction

Polymer–clay nanocomposites have been of great interest since the research at the Toyota Company found that polyamide-6-clay nanocomposites gave greatly enhanced mechanical properties, along with a large increase in the heat distortion temperature, at only 5% clay loading [1]. The clay is highly organophobic, which means that it must generally be organically-modified by treatment with some organophilic agent, in order to obtain nanocomposites with polymers. The backbones of polyethylene (PE) and polypropylene (PP) are very non-polar; research shows that maleic anhydride grafted polymer has to be used as a compatibiliser [2–4] in order to produce either PE or PP nanocomposites by melt blending. Previous work [5] has shown that PE and PP nanocomposites can be formed based on an oligomerically-modified clay, namely "lauryl clay", which contains 75% oligomer and 25% inorganic clay. The oligomer used in lauryl clay contains lauryl acrylate along with one or two units of vinylbenzyl chloride to permit the formation of the ammonium salt to modify the clay.

In this work, a terpolymer surfactant, containing styrene in addition to the lauryl acrylate and vinylbenzyl chloride, was used to modify the clay, and then the modified clay was directly melt blended with PE and PP to form nanocomposites.

2. Experimental

2.1. Materials

The majority of the chemicals used in this study, including low-density polyethylene (melt index 190 °C/2.16 kg, 7 g/10 min), isotactic polypropylene (melt index 230 °C/2.16 kg, 4 g/10 min), vinylbenzyl chloride, styrene, lauryl acrylate and 2,2′-azobisisobutyronitrile (AIBN) were acquired from the Aldrich Chemical Company. Sodium montmorillonite was provided by Southern Clay Products, Inc.

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2.2. Synthesis of vinylbenzyl chloride, styrene and lauryl acrylate terpolymer

A 115 g (0.48 mol) portion of lauryl acrylate, 50 g (0.48 mol) styrene and 9.2 g (60 mmol) vinylbenzyl chloride along with 400 ml THF were placed in a 1000 ml three-necked round bottom flask, equipped with a magnetic stirrer, nitrogen inlet and a condenser. The solution was first stirred for 10 min then gently refluxed under nitrogen for 10 min. Then 9.8 g (60 mmol) AIBN was added to the solution in one portion. The system was kept at a gentle reflux for 12 h, then the terpolymer was precipitated by pouring it into a large amount of methanol. A 145 g portion of a colorless terpolymer was collected after filtration. The number average molecular weight is 6200 (PDI = 1.24). ^{1}H NMR: ($CDCl_3$, ppm) 7.1 (br, 29H), 6.7 (br, 20H), 4.5 (br, 2H), 3.8 (br, 18H), 2.3 (br, 19H), 1.9 (br, 20H), 1.6 (br, 18H), 1.3 (br, 162H), 0.9 (t, 27H).

2.3. Synthesis of the ammonium salt of the terpolymer

The procedure was similar to previous work [5]. To a solution of 145 g terpolymer in 400 ml THF in a 1000 ml round bottom flask was added a large excess of triethylamine. The solution was stirred at room temperature for 2 h then kept at gentle reflux for another 10 h under nitrogen. The solvent was evaporated at 70 °C under vacuum and 150 g of the terpolymer salt was collected. A new broad peak in the NMR spectrum at 3.4 ppm may be assigned to the methylene group attached to the nitrogen of the ammonium salt. The methyl group adjacent to the methylene is in the 1.3 ppm region.

2.4. Preparation of the oligomerically-modified clay

The procedure is the same as previously reported [5]; the resulting clay, which contains the three component oligomer, is known as triclay.

2.5. Preparation of the polymer–clay nanocomposites

All nanocomposites were prepared using melt blending in a Brabender Plasticorder at 60 rpm and 185 °C for 3 min; the calculated amount of polymer and triclay was put into the Brabender mixer at the same time. After 3 min blending, the mixture was removed from the chamber and allowed to cool to room temperate. The composition of the nanocomposites is given in Table 1.

Table 1
Composition of polymer–clay nanocomposites

No.	PE or PP	Triclay	Inorganic clay loading (%)
1	96	4	1
2	88	12	3
3	80	20	5
4	68	32	8

2.6. Instrumentation

X-ray diffraction (XRD) was measured on a Rigaku Geiger Flex, 2-circle powder diffractometer equipped with Cu–Kα generator ($\lambda = 1.5404$ Å) at 50 kV and 20 mA, scanning from 1 to 10° at 0.1 step. All the samples were compression moulded into 20 mm × 15 mm × 1 mm plaques for XRD measurements. Bright field transmission electron microscopy (TEM) image was obtained at 120 kV, at low-dose conditions, with a Phillips 400T electron microscopy. The sample was ultramicrotomed with a diamond knife on a Leica Ultracur UCT microtome under cryogenic conditions to give a 70-nm-thick section. The section was transferred to carbon-coated Cu grids of 200 mesh. The contrast between the layered silicate and the polymer phase was sufficient for imaging, so no heavy metal staining of sections prior to imaging was required. Thermogravimetric analysis (TGA) was carried out on a Cahn TG131 unit under nitrogen at a scan rate of 20 °C/min from room temperature to 600 °C at 50 mg scale. Temperatures are reproducible to ±3 °C while the fraction of non-volatile is repeatable to ±3%. Cone calorimetry was performed on an Atlas CONE-2 according to ASTM E 1354-92 at an incident flux of 35 kW/m^2 using a cone shaped heater. Exhaust flow was set at 24 L/s and the spark was continuous until the sample ignited. Cone samples were prepared by compression moulding the composites into 100 mm × 100 mm × 3 mm square plaques. Typical results from cone calorimetry are reproducible to within about ±10%. These uncertainties are based on many runs in which thousands of samples have been combusted [6]. Tensile properties were measured using MTS Alliance RT/5 tensile test machine at a crosshead speed of 25.4 mm/min. The reported values are based on the average of five determinations. Molecular weights were determined using a DAWN EOS MALLS (Wyatt Technologies) coupled with a W-410 RID (Waters Corporation) using Waters Ultrastyragel columns HR4, HR3, HR1 in series; the mobile phase was THF.

3. Results and discussion

3.1. X-ray diffraction (XRD) measurement on the clay and its nanocomposites

The XRD pattern of the triclay is shown in Fig. 1; this is the same pattern that was seen for lauryl clay [5].