Journal of Thermal Analysis and Calorimetry, Vol. 87 (2007) 3, 811–814

THERMAL AND MECHANICAL PROPERTIES OF PE/ORGANOCLAY NANOCOMPOSITES

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Polyethylene/montmorillonite clay nanocomposites were obtained via direct melt intercalation. The clay was organically modified with four different types of quaternary ammonium salts. The objective of this work is to study the use of montmorillonite clay in the production of nanocomposites by means on rheological, mechanical and crystallization properties of nanocomposites and to compare to the properties of the matrix and PE/unmodified clay nanocomposites. In general, the tensile test showed that the yield strength and modulus of the nanocomposites are close to the pure PE. Apparently, the mixture with Dodigen salt seems to be more stable than the pure PE and PE/unmodified clay.

Keywords: *nanocomposite, organoclay, polyethylene, thermal stability*

Introduction

Smectite is the name of a sodium, magnesium, calcium, iron, potassium and lithium aluminosilicate group which is the main clay mineral constituent of montmorillonite. The clay minerals of this group present two-dimensional layers formed by fusing two silica tetrahedral sheets with an edge-shared octahedral sheet of either alumina or magnesia [1]. These clays can interact with organic compounds to form complexes with varying stabilities and properties. The organoclays were obtained by the addition of quaternary ammonium salts (containing at least 12 carbon atoms) to aqueous dispersions of sodium smectite clays. In these dispersions the clay particles or layers must be separated from one another and not be stacked, in order to facilitate the introduction of the organic compounds. Consequently, some of the cations, typically Na^+ and/or Ca^{2+} – they compensate the charge deficiency which is generated by isomorphous substitution within the layers – are replaced by the organic cations of quaternary ammonium salts that were adsorbed on the negative sites of the clay surfaces [2].

Polymer nanocomposites are materials that presented excellent properties such as thermal stability and flammability. Small amounts of organoclays (<10 mass%) used in the polymer matrices influence significantly several properties, such as mechanical, thermal, optical, electric, dimensional, flammability and barrier due to the large contact area between polymer and clay on a nanoscale as reported in [3–7]. With regard to their easy preparation and properties an important group is the polymer-silicate nanocomposites. In general, to facilitate the intercalation of the silicate layers with the polymer, the clay is modified by a quaternary ammonium salt through a cation change reaction, because the ammonium salt changes the surface of the clay from hydrophilic to organophilic. Polyethylene/organoclay nanocomposites have been prepared by melt intercalation technique. Due to the combination of many important properties, e.g. low mass, low cost, good processability, etc. [5, 8–11], polyethylene (PE) is a widely used substance in this field. In general, PE/clay nanocomposites are produced by melt intercalation and in situ polymerization [10]. However, it should be mentioned that the reaction products and the clay itself can catalyze the degradation of the polymer. As it was pointed out by Ray and Okamoto [12] and Zhao *et al*. [13] the thermal stability of the PE/clay nanocomposites has distinguished importance.

The aim of the present work is to prepare organophilic clays by using different types of quaternary ammonium salts and then their addition in 5 mass% to a polyethylene matrix in order to evaluate the rheological, crystallization and mechanical properties of the produced nanocomposites.

Experimental

Starting materials

The pristine clay used was Na-montmorillonite (MMT, Brasgel PA, Boa Vista/PB, Northeast of Brazil) sup-

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1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
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plied by Bentonit União do Nordeste with a cation exchange capacity (CEC) of 90 meq/100 g. The interlayer spacing (d_{001}) obtained by XRD was 12.5 Å. MMT was dried at 60°C for 48 h prior to use.

The quaternary ammonium salts used for the modification of MMT were: alkyl dimethyl benzylammonium chloride (DOD, Dodigen; $C_{19}H_{32}N^+(CH_3)_2Cl^-$), cetyl trimethyl ammonium chloride (GEN, Genamin; $C_{16}H_{33}N^+(CH_3)_3Cl^-$), esthearil dimethyl ammonium chloride (PRAEP, Praepagen; $(C_{16}H_{33})_2N^+(CH_3)_2Cl^-$) all industrial grades supplied by Clariant/Brazil and cetyltrimethylammonium bromide (BRO, Bromide; $C_{16}H_{33}N^+(CH_3)_3Br^-$), industrial grade from Vetec/Brazil. High density polyethylene (PE), HI-760UV, supplied by Braskem/Brazil, was used as matrix.

Preparation of the organophilic montmorillonite and nanocomposites

An aqueous solution containing about 20.0 g of quaternary ammonium salts (Dodigen, Genamin and Praepagen) was added to a 2000 mL glass flask containing 32 g of Na^+-montmorillonite (MMT) passing through a 200 mesh sieve, and 768 mL of distilled water. The mixtures were mechanically stirred for 20 min. The resulting organo-montmorillonite (OMMT) was washed with distilled water for several times to remove excess salts, dried at 60°C for 48 h and finally ground in order to pass through a 200 mesh sieve according to the procedure described by Araújo *et al.* [14–17] and Barbosa [5]. The bromide salt was used as received.

Mixtures of PE containing 5 mass% of montmorillonite clay (unmodified and salt modified ones) were obtained by a Torque Rheometer Haake with internal mixer, operating at 190°C, 60 rpm for 7 min. After mixing, the nanocomposites were prepared by compression molding at 200°C. Tensile tests to investigate the mechanical properties were done using a universal tensile Loyd LR/10KN machine with a crosshead velocity of 50 mm min^{-1} according to ASTM D638. Izod impact test was carried out on notched specimens at room temperature using a CEAST, model Resil 2.75J, according to ASTM D256. Minimum five parallel measurements were done for each test.

Thermal analysis

Thermal stability was investigated using a Shimadzu model DSC 50 equipment at 10°C min^{-1} heating rate from 20 to 360°C in an air.

Results and discussion

Rheological properties

Figure 1 presents the torque curves *vs*. time for the pure PE and its mixtures with the unmodified (AST) and modified clays with Dodigen, Praepagen and Genamin salts and in the presence of bromide salt. The systems were named as: PE/AST for polymer mixture with the unmodified clay: The salt modified ones were named as Dodigen (PE/ACT-DOD), Praepagen (PE/ACT-PRAEP) and Genamin (PE/ACT-GEN) and in the presence of the bromide salt (PE/AST-BRO).

According to Fig. 1, there are no significant differences between the curves. Apparently, neither deterioration nor any change in the polymer matrix occurred.

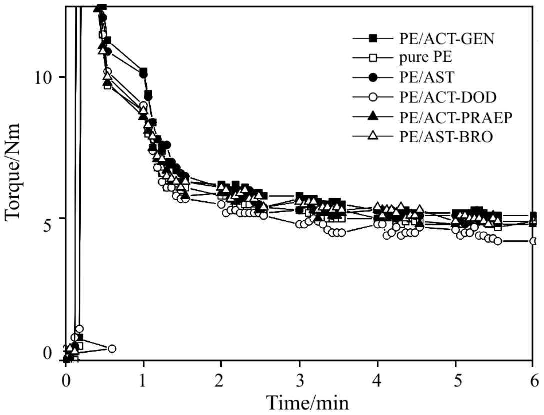

Fig. 1 Rheological curves of PE and its nanocomposites

Thermal behavior

Figure 2 summarizes the curves of DSC of the pure PE and its mixtures. It can be seen that there was no change in the melting temperatures of the mixtures. Apparently, the presence of the clay with the Dodigen salt somewhat delays the degradation. However, these differences are not so significant compared to the pure PE.

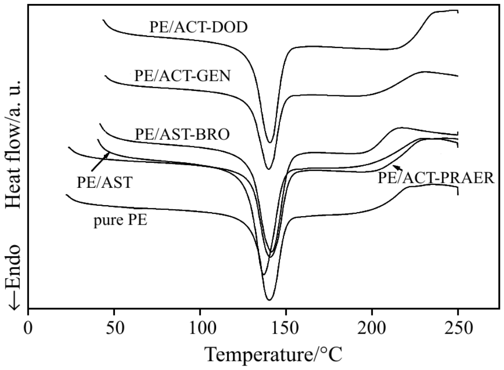

Fig. 2 DSC curves of PE and its nanocomposites

Table 1 Mechanical properties of the PE matrix and its nanocomposites

Material	Tensile modulus/GPa	Yield strength/MPa	Elongation at break/%	Izod impact strength/J m^{-1}
Pure PE	0.7±0.01	22.5±0.5	11.1±0.7	30.4±0.8
PE/AST	0.8±0.04	21.6±0.4	9.7±0.5	24.0±0.3
PEA/ACT-DOD	0.8±0.05	19.5±0.9	9.1±1.0	27.9±1.7
PE/ACT-PRAEP	0.9±0.07	20.8±0.6	8.8±0.8	24.6±0.9
PE/ACT-GEN	0.9±0.07	21.0±1.3	8.9±0.8	21.4±0.7
PE/ACT-BRO	1.1±0.04	20.0±0.9	8.6±3.7	29.2±1.6

Mechanical properties

Table 1 shows the yield strength, tensile modulus, elongation at break and Izod impact strength of the pure PE and its nanocomposites. The PE+ACT/GEN, PE+ACT/PRAEP and PE+ACT/BRO systems have larger values of the tensile modulus and they are higher compared to the pure polyethylene. In general, the yield strength, elongation at break and Izod impact strength of systems were lower compared to the PE matrix. The Izod impact strength of the nanocomposites containing modified clays with Genamin and Bromide showed remarkable difference compared to other systems. However, it can be observed too, that the standard deviation of the systems with ACT/BRO was higher than ACT/GEN. In agreement with Zhao *et al*. observation [13], according to the results obtained for the modulus and the elongation, the clay itself contributes for the rigidity increase of the PE matrix. As it was reported in [18–20], in general, when low amounts of modified layered silicates are used, the mechanical properties are the same as those for pure polymers. Xu *et al*. [21] reported that the worse properties of nanocomposites can be attributed to the weak interactions between polymer and clay, which can be attributed to the non-polar nature of the polymer matrix. Hence, a sufficient level of layer separation has to achieve to reduce layer–layer attraction of clay and favors the intercalation/exfoliation of the polymer into organoclay. In other words, the larger the organic species of the quaternary ammonium salts, the larger the separation of clay layers [22]. Systems with Nylon6 that has functional groups in its structure promote a remarkable interaction with the organoclay [3, 14, 22–24]. It can happen that in the used mixing equipment the shear rate is insufficient to promote the full exfoliation or dispersion of the particles in nano-scale compared to a twin screw extruder. The mechanical and thermal properties and morphology of the obtained PE nanocomposites in extruder will be studied and reported later.

Conclusions

Four different types of quaternary ammonium salts were used to modify the montmorillonite clay. PE/clay nanocomposites, which were prepared by melt intercalation in order to study the effect of the salts and organoclay on the thermal stability and mechanical properties of PE. No significant differences were found in the organophilic properties of clay modified with different types of quaternary ammonium salts. The torque values for all the studied systems practically did not change comparing all the systems to the clay and the pure polyethylene. Thermal analysis using DSC confirmed that the presence of the unmodified and the salt-modified clay did not alter the crystallinity of the PE. Furthermore, it seems the presence of the salt delays the polymer matrix degradation. The tensile modulus of the PE systems prepared with unmodified clay and quaternary ammonium salts modified clay did not present significant difference but the modulus was higher compared to the pure polyethylene. The yield strength and elongation at break of the systems with unmodified and salt-modified clay were smaller than the pure polyethylene. Probably, the presence of clay increased the rigidity of the PE matrix.

Acknowledgements

The authors acknowledge Braskem for the kind supply of PE, Bentonit União do Nordeste for the supply of the clay, Clariant for the supply of the quaternary ammonium salts, RENAMI (Rede de Nanotecnologia Molecular e de Interfaces), FAPESQ/MCT/CNPq (Fundação de Apoio a Pesquisa do Estado da Paraíba) and CNPq are also acknowledged for the financial support.

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DOI: 10.1007/s10973-006-7758-0