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ORIGINAL PAPER

Preparation and properties of polyethylene-octene elastomer (POE)/organoclay nanocomposites

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Abstract Polyethylene-octene elastomer/organoclay nanocomposites were prepared by a melt blending process. It was found that the addition of a small amount of glycidyl methacrylate and a peroxide during the melt mixing induced facile intercalation of the polymer chains into the organoclay and dispersion of the clay particles on the nanometer scale, which was confirmed by X-ray diffraction and transmission electron microscopy. Enhanced mechanical properties of the nanocomposites were observed from tensile, dynamic mechanical, and tear testing. Oscillatory shear-controlled rheology in the molten state of the nanocomposites revealed a pseudo solid-like behavior as well as an enhanced shear thinning behavior.

Keywords Polyethylene-octene elastomer (POE) · Organoclay · Nanocomposite · Melt blending

Introduction

Polymer/clay nanocomposites have been of increasing interests in the past decade because they can exhibit dramatically improved mechanical and physical properties including modulus and strength, thermal stability, flammability resistance, and gas barrier properties with far less inorganic content than is used in conventionally filled polymer composites. Montmorillonite is the most commonly used clay mineral which is comprised of 1 nm thick aluminosilicate layers. The silicate layers are negatively charged and are stacked by a weak dipole force, with the gallery between the silicate layers normally occupied by Na^+. Clay surfaces can be organically

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modified by the exchange of metal cations existing between the clay layers with long alkyl ammonium ions, which enable facile intercalation of the polymer chains into the layers of the clay. Depending on the degree of polymer penetration into the organoclay layers, the silicate layers of the clay are exfoliated or the clay particles exist as regularly intercalated aggregates with larger interlamellar spacing [1, 2]. Considerable effort has been invested on the synthesis of nanocomposites with a wide range of polymers, and in particular, the fabrication of nanocomposites of olefinic thermoplastics and elastomers such as PP, PE, EPDM, and SEBS with clay is an area of intense research [3–11].

Polyethylene-octene elastomer (POE), developed by Dow Elastomers using the INSITE™ catalyst and a process technology under the brand name Engage®, is a commercially important polyolefin polymer. The polymer has a uniform distribution of comonomer and a narrow molecular weight distribution, and is produced in a broad range of grades from rubber to thermoplastics by varying the ethylene-to-octene ratio. POE is used in diverse applications including impact modifiers, packaging, and wire and cable fabrication [12]. Various inorganic fillers have been incorporated into the POE to improve its performance properties [13–17]. However, only a few studies on the POE/clay nanocomposites have been conducted. Maiti et al. and Latta et al. [18, 19] prepared POE/organoclay nanocomposites by a solution blending process. Chang et al. prepared intercalated POE/clay nanocomposites by a melt mixing process using ethylene copolymer containing glycidyl methacrylate as a compatibilizer [20].

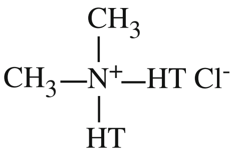
In this study, we demonstrate that POE/organoclay hybrid nanocomposites can be prepared by a melt mixing process with the addition of a polar additive such as glycidyl methacrylate (GMA) and peroxide during melt blending of the POE with the organoclay. Mechanical, dynamic mechanical, and rheological properties of the nanocomposites were investigated.

Experimental

Materials and blend preparation

Polyethylene-octene elastomer (POE) containing 18 wt% of comonomer (Engage 8003) was kindly supplied by DuPont-Dow Elastomer. Glycidyl methacrylate (GMA, 97% purity) was purchased from Aldrich and used as received. Di-tert-butyl peroxide (Trigonox B, Akzo) was used as a free radical initiator which was reported to be an effective initiator to induce grafting of GMA onto polyethylene [21].

The clay mineral used in this study is a Cloisite 20A (Southern Clay Products), which is a natural Na$^+$ montmorillonite modified with a quaternary ammonium salt, dimethyl dihydrogenated tallow ammonium chloride,



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle HT}{N^+}}-HT\ Cl^-$$

where HT is a hydrogenated tallow consisting of about 65% C18, 30% C16, and 5% C14 units.

Preparation of hybrids

POE and organoclay [3, 5, 7, and 10 parts per hundred rubber (phr)] were melt mixed at 130 °C for 5 min in an internal mixer (Haake Polylab 600) with a rotor speed of 60 rpm, and then mixture of GMA (5 wt% for POE) and peroxide (0.1 wt% for POE) was added. After the addition, the temperature was raised to 175 °C and the mixing was conducted for another 5 min. The amount of organoclay was 3, 5, 7, and 10 phr. The resultant compounds were compression molded into test pieces. The same procedure was conducted in the absence of organoclay in order to evaluate the grafting efficiency of GMA onto POE.

Characterization

The change in gallery distance in the clay after mixing with the rubber was examined using X-ray diffraction patterns recorded on a diffractometer (BEDE D-3 system) using CuKα radiation ($\lambda = 1.54$ Å) at a generator voltage of 40 kV and a generator current of 100 mA. Dispersability of the silicate layers in the composite was evaluated using transmission electron microscopy (TEM). TEM micrographs were obtained with a JEOL 200CX TEM using an acceleration voltage of 200 kV.

Ultimate tensile strength, elongation-at-break, and tensile moduli were determined using a universal testing machine (United Co., STM-10E) at 25 °C and with a cross-head speed of 500 mm/min, according to ASTM D412 specifications. Tear strength was measured as per ASTM D624 using unnicked 90° angle test pieces (die C) at 25 °C at a cross-head speed of 500 mm/min using a universal testing machine.

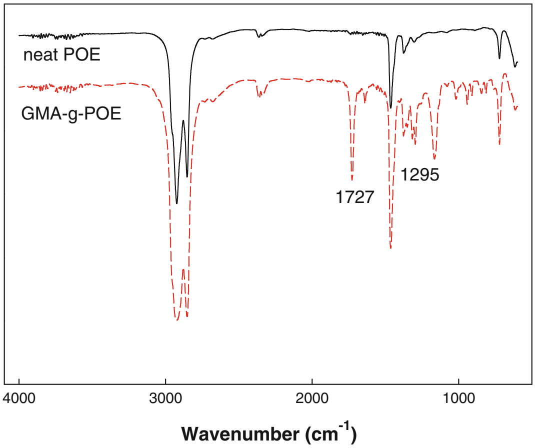
Dynamic mechanical properties of the composites were determined using a dynamic mechanical analyzer (TA Instrument DMA 2980). The sample was subjected to a cyclic tensile strain with an amplitude of 0.2% and a frequency of 10 Hz. The temperature was increased at a heating rate of 2 °C/min from −80 to 100 °C.

Melt rheological measurements (small amplitude oscillatory shear rheometry) were taken using RDA II Instrument (Rheometrics Inc.). Dynamic oscillatory shear measurements were performed at 130 °C using a set of 25 mm diameter parallel plates and a sample of 1–2 mm thickness. The frequency sweep was carried out within a frequency range of 0.1–100 rad/s at a strain of 1% (well within the linear viscoelastic range).

Results and discussion

FT-IR analysis was conducted to confirm the grafting of GMA onto POE. The FT-IR spectra of neat POE and purified GMA-g-POE samples are compared in Fig. 1. The GMA-g-POE showed new bands at 1727 and 1295 cm^{-1}, which are assigned to

Fig. 1 FT-IR spectra of neat POE and GMA-g-POE



the carbonyl stretching and to the epoxy group of GMA, respectively. This result indicates that GMA was grafted onto the POE by a melt process.

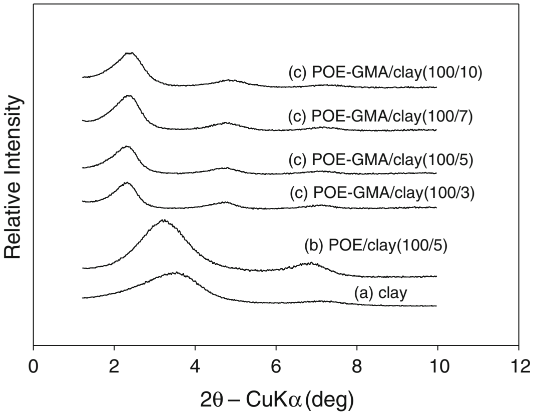
The degree of GMA grafting, which was defined as the weight percentage of GMA in POE-g-GMA, was determined by means of acid-alkali titration, which was carried out according to a procedure reported in the literature [22]. About 0.5 g of the purified sample was first dissolved in 70 mL refluxing xylene for 1 h, to which a few drops of trichloroacetic acid/xylene solution were added. The hot solution was titrated immediately with 0.05 N NaOH/CH_3OH, after adding four drops of 1% phenolphthalein in methanol as an indicator. Titration was stopped when the coloration remained for 30 s. The grafting degree (GD) can be expressed :

$$GD = [142.15 \times (V_o - V) \times c]/[1000 \times m]$$

where V (mL) and V_o (mL) represent the volume of NaOH/CH_3OH solution used for titration of grafted and blank samples, respectively; c (mol/L) is the molar concentration of the NaOH/CH_3OH solution; 142.15 (g/mol) is the molecular weight of GMA; and m (g) is the weight of the grafted sample. The grafting degree in the GMA-g-POE prepared in this study was 0.8 wt%. It was also observed that the GMA-modified POE, like unmodified POE, was completely soluble in the solvent indicating that the melt grafting process did not result in cross-linking.

X-ray diffraction (XRD) is generally employed to characterize the interlayer spacing in clay particles, which is correlated with the extent of intercalation. Figure 2 shows the XRD patterns of the organoclay and various POE/clay hybrids, where the peaks correspond to the (001) plane reflections of the clay. It is evident that there was only a marginal shift in the diffraction peak for unmodified POE/clay (100/5) system, indicating the organoclay (Cloisite 20A) is not compatible with the POE chains, even though it has long nonpolar alkyl chains (ca 65% C18, 30% C16, and 5% C14 units) on its surface. On the contrary, the diffraction peak for the hybrids prepared by in situ melt grafting of GMA appeared at a much lower angle relative to that of the organoclay. The interlayer spacing of the organoclay expanded from 2.52 nm (Cloisite 20A) to 4.18 nm in the hybrids, implying that the

Fig. 2 X-ray patterns of (*a*) organoclay (*b*) unmodified POE/clay(100/5), and (*c*) GMA-modified POE/clay with 3, 5, 7, and 10 phr clay



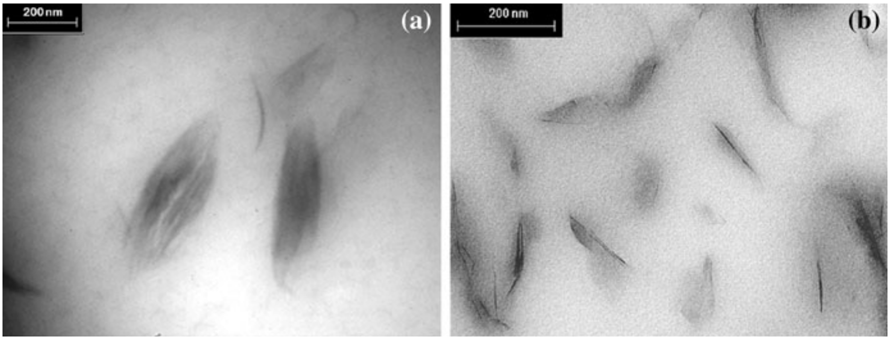


Fig. 3 TEM image of **a** unmodified POE/clay and **b** GMA-modified POE/clay nanocomposite (clay content: 5 phr)

compatibility of the POE chains with organoclay was enhanced by the introduction of GMA onto the polymer chains. Strong polarity remained even for the organically modified clay, and the presence of a small polar moiety on the nonpolar polymer chains improved the compatibility with the surface of the organoclay, which facilitated the intercalation of the polymer chains into the interlayers of the clay, as observed in other polyolefin/clay nanocomposites [3–6, 10]. The strong diffraction peak in the nanocomposite systems, however, indicates that most clay particles exist as stacks of layers or tactoids with an enlarged interlayer spacing. TEM images of an ultrathin section of a compression-molded unmodified POE/clay and GMA-modified POE/clay nanocomposite with a clay loading of 5 phr are shown in Fig. 3. The dark lines are the cross sections of the clay layers and it is apparent that clay particles of 10–40 nm thickness were dispersed uniformly in the GMA-modified POE matrix, while the clay particles are agglomerated in the unmodified POE matrix.

Figure 4 shows variations in 100% modulus, tensile strength, and elongation-at-break of neat POE/clay hybrid and the nanocomposite prepared by in situ melt grafting of GMA as a function of clay content. It can be seen that GMA-modified

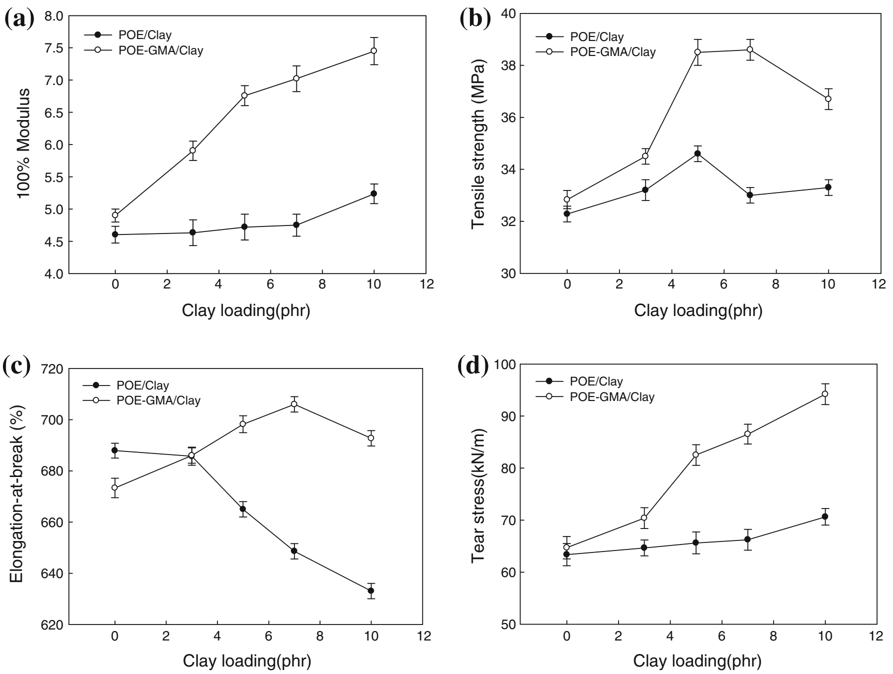


Fig. 4 **a** Tensile modulus, **b** tensile strength, **c** elongation-at-break, and **d** tear strength of POE/clay nanocomposites as a function of clay content

POE have slightly higher modulus, tensile, and tear strength with a slightly lower elongation-at-break when compared to unmodified POE. It is thought that the differences in the properties of neat POE and GMA-modified POE are partly attributed to a presence of a small amount of poly(glycidyl methacrylate) homopolymer in the POE matrix, which might be formed during the melt grafting process.

Much greater improvements in modulus and tensile strength were observed for the nanocomposite prepared by in situ melt grafting of GMA than the composite based on unmodified POE. For example, the tensile modulus at 100% elongation was marginally increased in the unmodified POE/clay (100/5), whereas a 30% increase was observed in the GMA-modified POE/clay (100/5) nanocomposite. The enhanced stiffening effect in the nanocomposites was correlated with the improved dispersion of the clay nanolayers in the hybrid, which was induced by the large extent of polymer intercalation into the clay galleries with the increased polarity of the GMA-modified POE, as confirmed by XRD and TEM. Notably, the increase in the modulus of the GMA-modified POE/clay nanocomposites was accompanied by retention of the ductility of neat POE, while a decrease in the elongation-at-break was observed in the hybrids based on unmodified POE. Similar trends in the tensile behavior have been observed in other elastomer-clay nanocomposites, which are attributed to huge interfacial action between the elastomer and clay nanolayers [19, 23, 24]. Figure 4 also shows the variation of tear strength of the hybrids with clay loading. The hybrids prepared by in situ grafting of GMA showed greater enhancement in the tear strength. With 5 phr clay loading, the tear strength was increased by 25% for the GMA-modified POE/clay nanocomposite. The uniform dispersion of the clay nanolayers in the rubber matrix is thought to form a physical barrier against growing cracks, which leads to increased resistance to tearing. These observations indicate that the intercalation of POE chains into the galleries of organoclay, even though each layer of the clay is not perfectly delaminated, can enhance the toughness, strength, and stiffness of the hybrid nanocomposite.

The value of tan δ and the dynamic storage modulus (E') from the DMA study of hybrids containing 5 phr clay are shown in Fig. 5a, b, respectively. There was no change in T_g for neat POE and its hybrid with clay, while the T_g was increased from −28 °C in GMA-modified POE to −24.2 °C in the modified POE/clay hybrid.

Further, there was a reduction in the peak maximum at the T_g, while there was no change in the values in the unmodified POE/clay hybrid. This result suggests that the molecular mobility of POE chains is restricted due to the increased interfacial interaction between the GMA-modified POE matrix and the organoclay. An enhanced storage modulus over the entire temperature range in the GMA-modified POE/clay nanocomposite is also evident from Fig. 5b. At 30 °C, for example, the

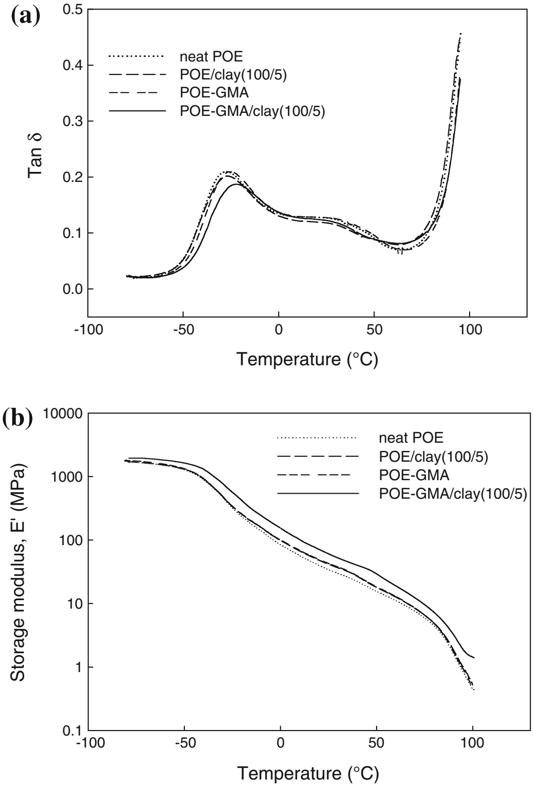


Fig. 5 Variation of **a** tan δ and **b** the dynamic storage modulus E', with temperature for neat POE, GMA-modified POE and their hybrids (clay content: 5 phr)

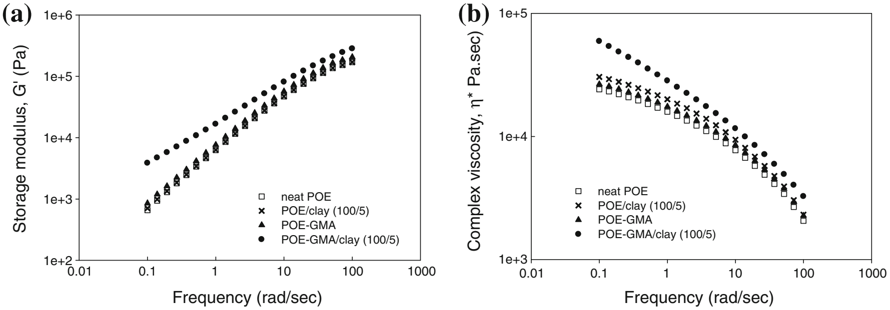


Fig. 6 Variation of **a** storage modulus, G' and **b** complex viscosity, η^* with frequency for neat POE, GMA-modified POE and their hybrids in the molten state (clay content: 5 phr)

storage modulus of the nanocomposite was increased by about 40% compared with that of the matrix polymer.

A melt rheology study was carried out to assess the microstructure of the samples in the melt state. The frequency dependence of both storage modulus (G') and complex viscosity (η^*) of POE, GMA-modified POE and their hybrid with 5 phr organoclay in the molten state is shown in Fig. 6a, b, respectively. The degree of clay dispersion affected the rheological properties of the hybrids. As shown in Fig. 6a, there was a marginal change of G' in the unmodified POE/clay hybrid as compared with the neat resin. In contrast, the storage modulus of the GMA-modified POE/clay hybrid in the melt state increased with increasing clay content, especially in the low frequency region, and this increase was accompanied by a decrease in the terminal region slope. A lower terminal slope and higher storage modulus indicates solid-like behavior of the nanocomposite, originating from the filler network in the polymer matrix. A plot of dynamic complex viscosity (η^*) versus frequency (Fig. 6b) revealed that clay induced an increase in the viscosity in the hybrids based on unmodified and GMA-modified POE, but the increase in the viscosity was much higher for the hybrid based on modified POE. Moreover, enhanced shear thinning behavior was observed for the GMA-modified POE/clay nanocomposite, implying shear-induced alignment of the well-dispersed clay nanoparticles in the matrix polymer. This type of rheological behavior is typically observed in other polymer/clay nanocomposites [8, 9, 25].

Conclusions

POE/organoclay nanocomposites were prepared by a melt mixing process. Addition of a small amount of GMA with a peroxide during melt blending induced facile intercalation of the polymer chains into the layers of the organoclay and a dispersion of clay particles on the nanometer scale. The clay nanolayers improve the mechanical properties and glass transition temperature of the elastomer. Melt state linear dynamic viscoelastic measurements for the nanocomposites revealed pseudo solid-like behavior as well as enhanced shear thinning.

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