

Effect of PEGMA/amine silane compatibilizer on clay dispersion of polyethylene-clay nanocomposites

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Received: 17 June 2009 / Revised: 10 August 2009 / Accepted: 21 September 2009 /
Published online: 11 October 2009
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Abstract The compatibilization effects provided by an amine silane modified polyethylene (PEgAS) versus those by a maleated polyethylene (PEgMA), for forming PE–clay based nanocomposites, were studied. PEgAS was prepared by condensation reaction between PEGMA and g-(aminopropyl) triethoxy silane (APTS). It had the triethoxy-silane functionality on one end and was solution mixed with an organomodified clay (Cloisite 20A) to promote the reaction of the silane groups with the hydroxyl groups on the surface of the clay. The obtained masterbatches were then compounded with PE to obtain PE–clay nanocomposites by melt blending in a twin screw extruder, using different compatibilizers and clay contents. FTIR, XRD, STEM, and Instron were used to characterize the structural, morphological, and mechanical properties of the nanocomposites. Results showed that the PEgAS formed more exfoliated–intercalated morphology and better mechanical properties, especially in modulus and tensile strength as compared with PEGMA composites and neat PE. The Young modulus was 35% higher, and the tensile strength was 18% higher with PEgAS composites.

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Keywords Amine silane · Nanoclays · Polyethylene · Compatibilizer

Introduction

In recent years, there is a growing interest, both from academia and industry, in new class of composite materials in which the filler is dispersed into the polymer matrix at a nanometer scale. Among the different nano fillers used to prepare these kinds of materials, layered silicates are particularly attractive as they can be easily added to a melt polymer matrix by using common processing equipment. Layered silicates are composed of sheet-like platelets that are about 1 nm in thickness and 100–1000 nm in width and length, so they possess high aspect ratios and large surface areas. The high aspect ratio of the clay platelets permits significant reinforcement at relatively low loadings. However, the main key challenge to realize this potential is to achieve a high degree of exfoliation or intercalation of the silicate layers within the polymer matrix using a convenient and adequate process, like melt compounding.

Polymer–clay nanocomposites have received special attention because of their improved properties at very low loading levels compared with conventional filler composites. It is well known that the enhancement in properties is related to a homogeneous dispersion and exfoliation of the organoclay in the polymer matrix [1–3]. However, this dispersion depends on several factors, such as the polymer polar groups [4, 5] and the structural characteristics of the clay modifier [6, 7]. It is well known that the dispersion of clay tactoids in a polymer matrix can result in the formation of three types of composites: (1) conventional composites that contain clay tactoids dispersed simply as a segregated phase; (2) intercalated polymer–clay nanocomposites, which are formed by the infiltration of one or more molecular layers of polymer into the clay host galleries; and (3) exfoliated polymer–clay nanocomposites as characterized by low clay content, a monolithic structure, and a separation between clay layers that depend on the polymer content of the composite. Exfoliation is particularly desirable for improving specific properties that are affected by the degree of dispersion and the resulting interfacial area between polymer and clay nanolayers [8–10].

Polyethylene (PE) exhibits an attractive combination of low cost, low density, and extraordinary versatility in terms of properties, applications, and recycling. Like many polyolefins, PE lacks the intrinsic thermodynamic affinity with current organoclays to form well-exfoliated nanocomposites [11, 12]. The use of a compatibilizing agent has proved to be a partial solution to this problem. Maleated polyolefin such as PEgMA has become a widely accepted compatibilizing agent for polyolefin-based nanocomposites [13, 14]. Even though these nanocomposites containing a maleated polyolefin are not as well exfoliated as those based on more polar polymers such as nylon [15], this approach has shown several benefits. Recent reports [16–18] have been focused on using amine-modified polyolefins as compatibilizers in polyolefin–clay nanocomposites. The exfoliation observed in these systems could be related with polar and chemical interactions that occur between the maleic anhydride and the amine groups through an amination–imidation reaction. Some other studies involved the enhancement of the adhesion

between polymer matrix and siliceous fillers using different compatibilizers systems [18, 19]. Other reports discussed the incorporation of silane-coupling agents in the preparation of polymer–clay nanocomposites for increasing the organic–inorganic interaction [20–23].

The main purpose of this study is to study the structural, morphological, and mechanical properties of PE–clay nanocomposites using an amine silane modified polyethylene (PEgAS) as a compatibilizer. The PEgAS has not been reported in the open literature as a compatibilizer for PE–clay systems. This compatibilizer was obtained by condensation reaction between amine group of APTS and the maleic anhydride moiety of PEGMA. It has the triethoxy silyl group capable of reacting with the hydroxyl group on the clay surface to form a linkage between polymer and clay. This would increase the interaction and dispersion of the clay in the polymer matrix and provide another option in the manufacturing of PE/clay hybrid nanocomposites. Although an amine silane modified polypropylene (PPgAS) was used as compatibilizer for PP–clay nanocomposites [20], this is the first time that an amine silane polyethylene (PEgAS) is used as a compatibilizer in a PE/organoclay nanocomposite system.

Experimental

Materials

The PE (LDPE 133A) matrix polymer was of commercial grade from Dow Plastics with a melt index of 0.22 g/10 min. The PEGMA, a maleated LLDPE Fusebond E MB 226DE, was supplied by DuPont and contained 0.9 wt% maleic anhydride groups and had a melt index of 0.91 g/10 min. The montmorillonite organoclay (MMT), modified with a dimethyl, dihydrogenated tallow quaternary ammonium salt (Cloisite 20A), was from Southern Clay Products Co. APTS was from Sigma-Aldrich, which was reagent grade and used without further purification.

Compatibilizer and nanocomposites preparation

In order to prepare the PEgAS compatibilizer, a xylene solution of PEGMA was prepared under reflux. After PEGMA dissolution, APTS was added into the hot xylene solution with stirring at 80 °C. The clay suspension was prepared by dispersing organoclay into xylene and heated to 85 °C with stirring until the suspension became clear. This clay suspension was added into the above solution of the condensation reaction product of PEGMA and APTS. Then methanol and water, in acidic condition, were added to the above mixture and were allowed to react for more than 3 h. The products were precipitated in an excess of methanol for several times. The nanocomposites were prepared by compounding the required amounts of the above-prepared PEgAS/clay masterbatch, PEGMA, and LDPE in a Werner and Pfleiderer twin screw extruder, with an L/D = 29:1 and D = 30 mm, operating at 190 °C and 100 rpm in corrotating mode. The samples were pelletized and mixed again by passing through the twin-screw extruder in a two-step mixing at 190 °C and 200 rpm. The compatibilizing agent to clay proportion was fixed at a ratio of

Table 1 Nanocomposite formulations

Sample	PE (wt%)	PEgMA (wt%)	PEgAS (wt%)	Clay (wt%)
LDPE	100	0	0	0
PE/PEgMA-16/4%	80	16	0	4
PE/PEgMA-20/4%	76	20	0	4
PE/PEgAS-16/4%	80	0	16	4
PE/PEgAS-16/PEgMA-4/4%	76	4	16	4
PE/PEgAS-24/6%	70	0	24	6
PE/PEgAS-24/PEgMA-6/6%	64	6	24	6

4:1. The clay, PE, PEgMA, and PEgAS nanocomposites' composition is detailed in Table 1.

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 (XRD) of the nanocomposites, to evaluate the evolution of the clay d_{001} reflection, was performed in a Siemens D5000 using Cu $K\alpha$ X-ray radiation. The X-ray samples were obtained from compression moldings to avoid a preferred orientation of the clay. FE-SEM with STEM modulus (Field Emission Scanning Electron Microscopy with STEM modulus) is a technique that combines the electron transmission and scanning of the sample. Ultrathin sections for STEM analysis, approximately 70–100 nm in thickness, were cut from the compression molded samples with a diamond knife using a Leica microtome. These observations were performed with a Jeol-JSM7401F at an accelerating voltage of 30 kV. Tensile properties were analyzed on an Instron model 4301 upgraded for computerized data acquisition. All tests were done in triplicate.

Results and discussion

The manufacture of hybrid nanocomposite materials that involve the combination of a polymer matrix and inorganic fillers such as PE-nanoclay requires the use of a coupling or compatibilizing agent to reduce the interfacial tension between phases and improve the performance of the nanocomposites. In this study, a coupling agent was prepared by the reaction of a PEgMA and amino silane (APTS) by a condensation reaction between amine groups of amino-silane and the maleic anhydride of PEgMA in xylene solution.

The reaction is outlined in the scheme of Fig. 1 according to data reported in the literature [20]. The obtained coupling agent (PEgAS) has the triethoxy silane functionality group at one end and it is attached to polymer segments through the amidation reaction of amine groups with maleic anhydride groups of PEgMA. This coupling agent is then mixed with the organomodified clay (Cloisite 20A) suspension to promote the reaction between the triethoxy silyl group of the silane

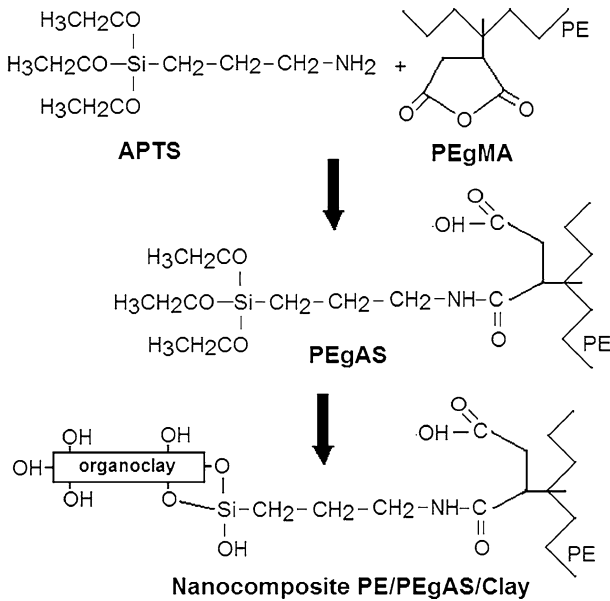


Fig. 1 Scheme reaction of APTS and PEGMA to form PEGAS and its interaction with clay

(PEGAS) and the hydroxyl groups on the surface of the clay. The final product of the condensation reaction is precipitated, washed, and dried to obtain a masterbatch of the clay into the coupling agent matrix.

The content of non-reacted amino-silane is removed with different washes. After the formation of Si–O–Si links between the PEGAS and the organoclay during preparation of the masterbatch, the PE segments of PEGAS can easily be entangled with the polymer PE matrix during melt mixing in a twin-screw extruder to prepare hybrid nanocomposites. These nanocomposites could then be prepared with different contents of PEGAS and PEGMA to assess whether the inclusion of an additional PEGMA content has influence on the degree of dispersion, intercalation, and exfoliation of nanoclay. Thus, the effect of different contents of clay, PEGMA, and PEGAS (Table 1) on the final nanocomposite properties could be determined.

FTIR characterization

Infrared spectroscopy is a useful tool to observe the formation or disappearance of several chemical bonds. Functionalized materials with specific polar groups usually show a characteristic FTIR spectrum. In the present study, the analysis by FTIR can provide information about the formation of new bonds during the preparation of the coupling agent PEGAS. It has been reported by several authors [22, 24] that silanes can interact with metal oxides such as clay by adsorption and the formation of Si–O–Si links generating a surface coating on the inorganic phase. Figure 2 compares the FTIR spectra of pure amino-silane, PEGMA, and the prepared nanocomposites. The characteristic peaks near 3285 and 3355 cm⁻¹ of the pure

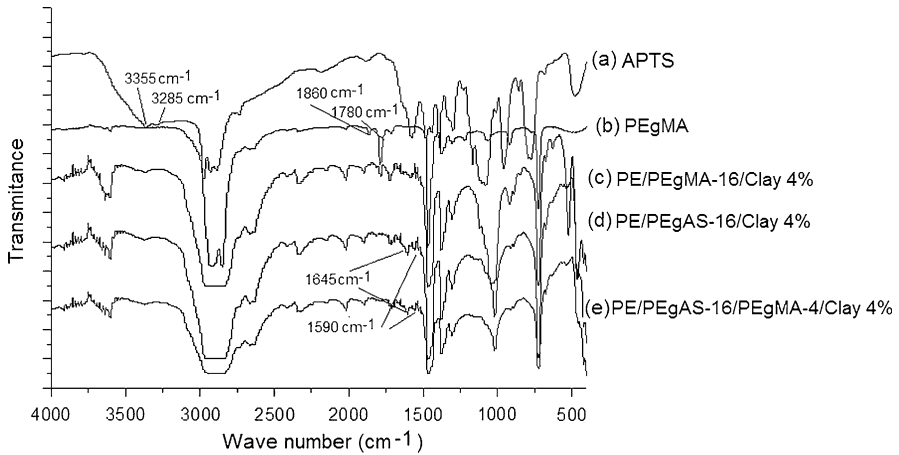


Fig. 2 FTIR spectra of (a) APTS, (b) PEGMA, (c) PE/PEGMA-16/Clay-4%, (d) PE/PEgAS-16/Clay-4%, and (e) PE/PEgAS-16/PEGMA-4/Clay-4%

amino-silane are attributed to the stretching of the primary amine group ($-\text{NH}_2$). For the PEGMA, the carbonyl group ($\text{C}=\text{O}$) stretching of the maleic anhydride can be observed near 1780 and 1860 cm^{-1} . These two carbonyl peaks are significantly diminished in the samples of nanocomposites with clay, PEGMA and PEGAS. This could be attributed to the reaction between amine groups of amino-silane and the maleic anhydride of PEGMA that caused the decline or disappearance of these peaks. The spectra for the nanocomposites with PEGAS show peaks near 1645 and 1590 cm^{-1} corresponding to the stretching vibration of $\text{C}=\text{O}$ group of amide (Amide I at 1645 cm^{-1}) and the stretching vibration of the deformation of the NH group for the Amide II band at 1590 cm^{-1} . This comparative information, obtained from the spectra, provides reliable evidence that a covalent bond between PEGMA and the amino-silane exists indicating that the anhydride ring of PEGMA is opened by the inclusion of the primary amine group of amino-silane. Similar results are reported in the literature [25, 26]. Many literature reports have shown that the amino-silane can bind to the surface of inorganic fillers such as clays by adsorption and chemical bonding to the particles coated with a layer of silane. This study suggests that the silane interacts with clay according to the scheme outlined in Fig. 1. Although the characteristic peaks of $\text{Si}-\text{O}-\text{Si}$ link appear, according to reports in the literature [22, 24], between 1000 and 1100 cm^{-1} in the spectra for the nanocomposites with PEGAS in Fig. 2, they cannot be distinguished since there are overlapping peaks making it difficult to identify them. Despite this and as already mentioned, it is well known that silane groups interact with the surface of the clay to form $\text{Si}-\text{O}-\text{Si}$ links.

XRD characterization

The XRD technique is useful for characterizing nanocomposites based on polyolefins using coupling or compatibilizing agents to determine the degree of

organo-clay exfoliation [27]. Thus, if the diffraction signal from the d_{001} in a clay nanocomposite disappears, we could say that there is a total clay exfoliation. On the other hand, if the d_{001} diffraction peak only decreases and shifts to lower 2θ angles, it would indicate an intercalation and/or partial exfoliation in the nanocomposite. This has been found for most polyolefins using a compatibilizing agent between polymer and nanoclay. Using the XRD technique, the prepared nanocomposites from PE and organo-clay using PEGAS and PEGMA were characterized. Taking the diffraction pattern of the clay as a reference, it was possible to determine the degree of clay exfoliation. The nanoclay Cloisite 20A is an organically modified clay with a surfactant of the type of a quaternary ammonium salt, which separates the clay plates reducing the interactions between them and permitting a greater interaction with polymer system. It is noteworthy that the intercalation of polymer chains within the galleries of the clay depends on the concentration of clay as well as the polarity of the surfactant organic modifier of the clay. A new diffraction pattern implies that nanolayers have been separated and that a nanostructured system has been formed indicating that the molecular chains of the polymer are intercalated into the galleries of the clay [27].

Figure 3 shows the XRD patterns for organoclay and the different nanocomposites. The interlayer distance in the clay can be calculated from the position of the peak at a certain angle 2θ , which corresponds to d_{001} plane diffraction of the clay. This figure shows that the diffraction peak d_{001} for organoclay is about 3.6° , which corresponds to an intergallery spacing of 2.46 nm calculated from the Bragg law. The clay surfactant, alkylammonium salt, converted the surface of this clay from hydrophilic to hydrophobic and increased the spacing between layers. This obtained results of 2θ angles and intergallery spacing between layers were very similar to those reported by other authors.

All the PE nanocomposites show two characteristic 2θ peaks, one between 9° and 10° which corresponds to the crystalline phase of PE and other diffraction peak

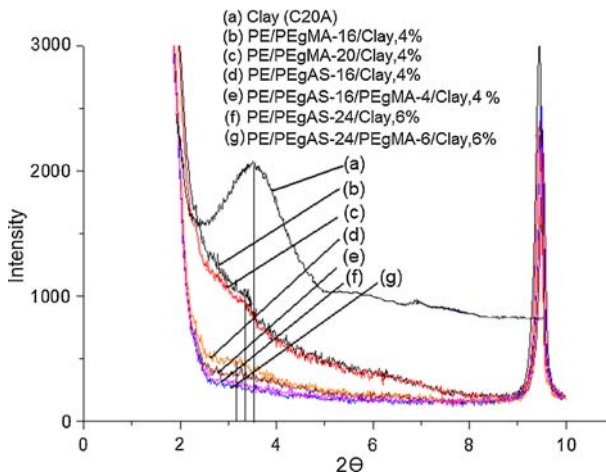


Fig. 3 XRD patterns of C20A clay and PE nanocomposites with different clay content and compatibilizers

corresponding to d_{001} plane of the clay between 2° and 4° . The addition of clay does not significantly change the crystalline phase of PE as there is no displacement of the peak corresponding to the crystalline phase around 9.5° .

It is known that to achieve a good degree of exfoliation, where most of the clay layers are dispersed and exfoliated in the polymer matrix, a very good interaction between the polymer matrices with the surface of clay layers is required. This could be achieved using polar polymers such as polyamides and other polar systems.

However, when using non-polar polymers such as PE, a compatibilizing agent is required to promote interactions with the clay. It becomes clear that all the nanocomposite systems with different clay contents and compatibilizing agents (PEgAS and PEGMA) present d_{001} diffraction peaks at lower angles than those observed for the organo-clay, which suggests that a better degree of exfoliation–intercalation is achieved when using the modified PE as compatibilizer. It is noted that for the two samples with only PEGMA at 16 and 20%, both have a very significant depression of the d_{001} diffraction peak which appears as a shoulder near a 2θ angle of 3.3° corresponding to an intergallery spacing of 2.68 nm for both cases. However, for the higher PEGMA content the diffraction signal is slightly lower in intensity, indicating that, at this content, there is a better degree of intercalation–exfoliation. All the nanocomposites with PEGAS present a significant reduction in the d_{001} diffraction peak intensity with an almost disappearance of this peak. This indicates that a better degree of exfoliation–intercalation in these compounds has been achieved, and the clay is more separated or intercalated and there are fewer aggregates or tactoids. While there is no defined peak, the inflection or change of slope of the curve is taken as the diffraction peak. The two nanocomposites, 4% clay and 16% PEGAS and 16% PEGAS with 4% PEGMA, show diffraction peaks much less defined and close to 2θ angles of 3.19° , corresponding to an intergallery spacing of 2.70 nm. Finally, the last two nanocomposites with 6% clay do not show a defined peak making it difficult to identify a characteristic signal or an intergallery spacing, but suggests a much better degree of exfoliation–intercalation, which needs to be confirmed by STEM analysis.

STEM characterization

The images displayed in this section are obtained by means of scanning electronic microscopy with an STEM modulo. Making a comparative analysis between the evaluated nanostructure materials by the STEM technique would allow us to relate the obtained micrographs to the previously obtained XRD results. Figure 4a and b shows the images for the nanocomposites from 4% clay with PEGMA and PEGAS. When only PEGMA is used, it appears only a slight clay exfoliation is observed, with formation of noticeable number of clay aggregates or tactoids. This indicates that certain degree of exfoliation–intercalation is achieved which agrees with the XRD results, where the diffraction peak for this compound moved toward smaller angles. On the other hand, when only the PEGAS compatibilizer is used, the obtained morphology shows a much better degree of exfoliation, revealing fewer numbers of clay aggregates or tactoids with noticeable separation between its layers. This also corresponds well with the XRD results in which higher interlayer

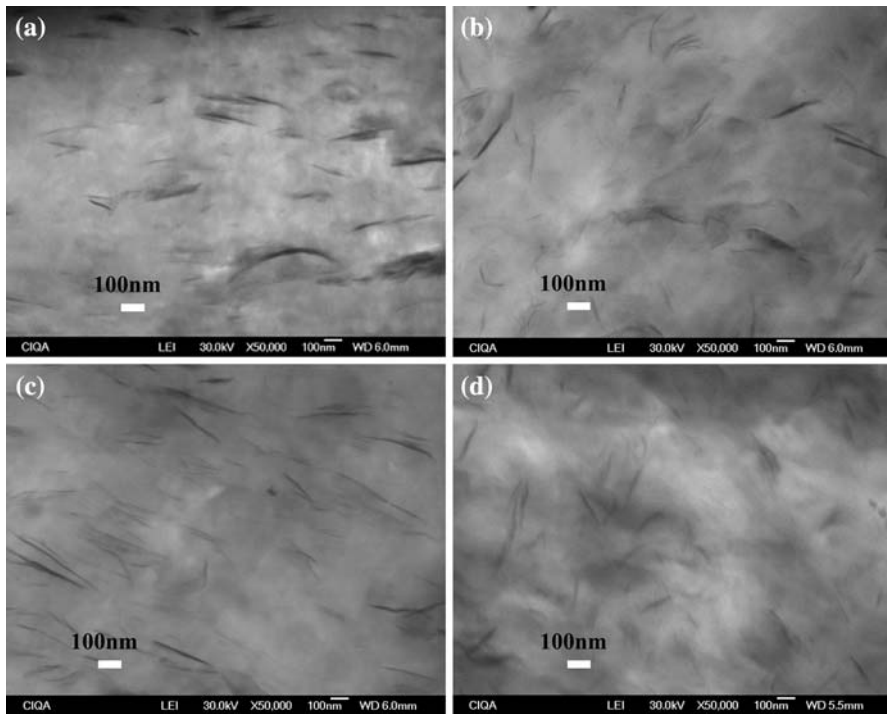


Fig. 4 STEM micrographs of **a** PE/PEgMA-16/Clay-4%, **b** PE/PEgAS-16/Clay-4%, **c** PE/PEgAS-16/PEgMA-4/Clay-4%, and **d** PE/PEgAS-24/Clay-6%

spacing was observed and where, in some cases, a characteristic diffraction peak was not possible to be observed. In the case when both compatibilizers were used together, the image (Fig. 4c) shows a more exfoliated and intercalated morphology which suggests a synergist effect of both compatibilizers. Increasing the clay content to 6% (Fig. 4d) with PEGAS, the morphology is quite homogeneous revealing a more dispersed and exfoliated structure. Indicating higher exfoliation–intercalation with greater spacing between layers, a result also confirmed by XRD.

Mechanical properties

It is known that a homogeneous dispersion of clay nanolayers in a polymer matrix provides maximum reinforcement via load transfer and deflection of cracks resulting from an applied load. Interactions between exfoliated nanolayers with large interfacial area and the surrounding polymer matrix lead to higher tensile strength, modulus, and thermal stability. Conventional polymer–filler composites containing micron-size aggregated tactoids also improve stiffness and modulus, but at the expense of tensile strength, elongation, and toughness [28–30]. The mechanical properties of flexural modulus, tensile strength, and elongation at break of the samples were determined to establish the effect of the compatibilizing system on these three properties. The mechanical properties of nanocomposites are directly

Table 2 Mechanical properties for the nanocomposites

Sample	Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
LDPE	201 ± 3.0	12.3 ± 0.8	502 ± 10
PE/PEgMA-16/4%	239 ± 1.4	15.1 ± 1.5	267 ± 11
PE/PEgMA-20/4%	243 ± 1.8	15.8 ± 0.3	295 ± 9
PE/PEgAS-16/4%	295 ± 2.3	16.9 ± 0.5	318 ± 7
PE/PEgAS-16/PEgMA-4/4%	305 ± 3.2	16.6 ± 0.3	330 ± 10
PE/PEgAS-24/6%	322 ± 3.0	17.0 ± 1.3	225 ± 5
PE/PEgAS-24/PEgMA-6/6%	348 ± 2.8	17.3 ± 0.5	243 ± 10

related to the homogeneous clay dispersion and exfoliation or intercalation in the polymer matrix. A more homogeneous clay dispersion would result in higher modulus but at the expense of deformation and toughness such as elongation at break and impact resistance. It is, therefore, important to achieve an appropriate compound reinforcement by an homogeneous stress and failure distribution resulting from the application of a load. It was reported [9] that interactions between the intercalated or exfoliated nanoclays with the polymer matrix showed relatively large interfacial areas that led to improved mechanical properties. It was also reported [31] that conventional polymer composites filled with aggregates at a micrometer level or tactoids also improved stiffness, but a decrease in tensile strength, elongation, and toughness. One of the main advantages of incorporating a nanoclay into a polymer matrix is the improvement of its mechanical properties, in particular, modulus or stiffness and yield stress while barely causing a reduction in deformation compared with conventional fillers [32].

Table 2 shows the mechanical properties of the nanocomposites at different clay and compatibilizer contents. All the nanocomposites achieve higher modulus and tensile strength than the neat PE, while as expected elongation is significantly decreased with the addition of clay. This reduction in elongation of the PE–clay nanocomposites as compared with the unfilled polymer is attributed to the fact that fillers generally decreases the ductility of polymers and similar trends are also seen for nanocomposites [33]. A reduced elongation at break often means a reduced energy to break but there are exceptions to this [31].

When increasing the clay content from 4 to 6%, a corresponding increase in modulus and tensile strength and a decrease in elongation at break are observed. The tensile strength and modulus of the nanocomposites containing PEgAS containing 4% of clay show higher values than the compound with PEgMA: Young's modulus at 24% higher and tensile strength at 12% higher. This could be attributed to the fact that PEgAS promotes higher interactions between the organic phases of PE with the surface of clay, allowing an improvement in the mechanical performance of these compounds. When comparing the combined effect of both compatibilizers (PEgMA and PEgAS), it can be said that the incorporation of both favors polar interactions between the polymer matrix and nanoclay presenting a slightly better mechanical performance of these systems compared with those with only one compatibilizer.

Samples with the combination of both compatibilizers resulted in highest modulus values of 305 MPa, when using 4% of clay and 348 MPa when using 6% of clay. According to the obtained results, it is clear that there was a better interaction between the nano-layers of the galleries of the organo-clay and the polar groups of the compatibilizing agent, PEGAS, enhancing the mechanical reinforcement by reducing the content of tactoids or failure points, and favoring an intercalated–exfoliated morphology that allowed the stress dissipation and greater reinforcement against deformation. This was also confirmed by XRD and STEM results. On the other hand, as was expected, the incorporation of organo-clay in a polymeric matrix tended to reduce the elongation at break. As shown in Table 2, the elongation at break of the nanocomposites follows this trend. The contribution of PEGAS could be observed when comparing the samples PE/PEGMA-16/4% with PE/PEGAS-16/4% in which the samples with PEGAS show higher elongations. In general, it can be said that the addition of PEGAS reduces the tendency of the clay to form aggregates in a PE matrix and favors the formation of intercalated–exfoliated structures that provides a better mechanical reinforcement of the compound.

Conclusions

The PEGAS compatibilizer was successfully synthesized by a chemical condensation reaction between amine groups of APTS and maleic anhydride groups of PEGMA. This compatibilizer provided strong links between the clay surface and the silane groups attached to the compatibilizer favoring strong interactions between clay and PE matrices. Noticeable increase in the degree of exfoliation–intercalation was obtained when using this compatibilizer as observed by XRD and STEM. Significant mechanical reinforcement, especially in modulus and tensile strength, was obtained for the compounds with PEGAS and only a slightly improvement when using combinations of both compatibilizers (PEGAS and PEGMA). PEGAS can certainly provide another option in the manufacturing of PE/clay hybrid nanocomposites.

Acknowledgments The authors gratefully acknowledge the financial support of CONACyT (CB-2005-C-24605) and would also like to thank A. Herrera-Guerrero, M. C. Gonzalez-Cantu, J. Zamora-Rodriguez, J. A. Sanchez-Molina, M. Lozano-Estrada, M. L. Lopez-Quintanilla, G. Mendez-Padilla, J. Rodriguez-Velázquez and J. F. Zendejo-Rodriguez for their assistance in the sample preparation and characterization and to T. Trejo-Villanueva and P. Flores-Siller for their assistance in technical data acquisition.

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