Preparation of PE Nanocomposites Using Pristine Nano Clay via Alkyl Ammonium Solution Injection in a Twin-Screw Extruder

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ABSTRACT: In this study, saline water was used as a preintercalating agent for pristine clay surface to assist clay dispersion in one-step melt state process. The solution contains dodecyl trimethyl ammonium chloride salt in distilled water and was injected into the twin-screw extruder using a high pressure dosing pump. To investigate the effect of dissolution of alkyl salt on clay dispersion, two samples with the same compositions were prepared through both salt solution and pure water injection which was compared with organo-modified prepared sample. The resultant compounds were characterized using x-ray diffraction (XRD), transmission electron microscopy (TEM), differential scanning calorimetry (DSC), and dynamic rheological measurements (RMS). Tensile and notched-Izod impact properties of the samples were measured as well. The XRD results showed no peak for the sample containing 2 wt % pristine clay, prepared via injection of salt solution representing exfoliated microstructure. In addition, TEM images showed proper dispersion and distribution of clay platelets in the matrix. Furthermore, RMS results showed that the slop of the storage modulus has been declined and for the sample using saline, the variation was prominent as a result of network structure formation. Tensile results also showed an increase of tensile modulus in the range of about 22% for the sample containing 2 wt % clay. Izod impact strength in the sample prepared via injection of salt solution showed fracture energy comparable to neat polyethylene. Additionally, the crystallization data in terms of degree of crystallinity, melting, and crystallization temperatures of samples represented no noticeable change compared to neat polyethylene. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 1344–1351, 2012

Key words: polyethylene (PE); nanocomposites; clay; melt

INTRODUCTION

Nanocomposites are a new class of composites, for which at least one dimension of the dispersed particles is in the nanometer range. Clay containing polymeric nanocomposites currently resulted in a tremendous interest from both academics and industries. In this class of composites, by dispersing at nanoscale a small amount of clay (usually less than 5 wt %) within a polymeric matrix, a large array of properties can be significantly improved.[1–3]

The most commonly used types of layered silicates in the formation of polymer/layered silicate (PLS) nanocomposites belong to the 2 : 1 phyllosilicate family. Structurally, the crystals consist of two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. Layer thickness is on the order of 1 nm while the lateral dimension can vary from 30 to 200 nm. Montmorillonite (MMT) is the most common type of layered silicate currently used in research, while mica, talc, hectorite, and saponite are examples of lesser used 2 : 1 phyllosilicates. These clays typically exist as stacks of individual silicate layers held together by van der Waals forces resulting in gap spacings on the order of 1 nm.[4,5]

Polyethylene is a general purpose polymer with high amount of usage in industries such as packaging, automobile, appliances, etc. The importance of these industries are clear; packaging industry plays a consequential role in economic development; as a result, development and improvement in this industry can help economic growth by increasing the efficiency of food marketing and other products and by adding value to exports.[6] Using nanocomposites in this area has an essential role in this development. Nanocomposites improve mechanical, thermal, and barrier properties of pure polymers.[7]

Several systems with different methods such as *in situ* polymerization, solvent blending, and melt intercalation on polymer/clay nanocomposites (PCNs) have been studied since Toyota's group developed Nylon-6/MMT nanocomposites via

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in situ polymerization.[8,9] Polymer melt intercalation with a variety of commercial polymers has been shown to be a more efficient and environmentally friendly alternative to traditional processes.[10–12]

Besides conventional methods of nanocomposites preparation, there are new innovative methods which lead to reducing the cost and steps of preparation.[13–16] In these techniques, one of the characteristics of clay minerals, i.e., their swelling in water is used to disperse and exfoliate clay platelets. Hasegawa et al.[13] introduced a novel melt compounding process using the Na-montmorillonite water slurry for preparing the nanocomposites consisting of Nylon 6 and Na-montmorillonite without any surfactant. Clay particles dispersed homogeneously in the nanometer level in water and the resultant nanocomposites had strength, modulus, and heat distortion temperature much higher than those of neat Nylon 6. Furthermore, WAXS patterns and TEM micrograph show exfoliation of the sample prepared by this method. In this method, through introducing clay slurry in the extruder by a pump, the clay slurry is reduced to fine droplets containing clay platelets; after that the water evaporates in contact with the melt leaving the silica layers dispersed; finally the water vapor is removed under vacuum. Although Hasegawa et al. achieved very good results for Nylon-6 nanocomposites, the main disadvantage of their method was that a large amount of water was pumped into the extruder to reduce the high viscosity of the clay slurry. To enhance this method, Yu et al.[14] fabricated nylon nanocomposites without pretreatment with water by a small amount of water. In this method, water is injected into the extruder barrel to aid swelling of MMT. TEM micrograph showed uniform dispersion of clay platelets in polymeric matrices. With the aid of water, mechanical properties, and thermal stability of resultant Nylon-6 nanocomposites were greatly improved in comparison with those of the nylon/pristine MMT microcomposite obtained without water and the Nylon-6/OMMT nanocomposite obtained with and without water. In another work, Fedullo et al.[15] prepared Nylon-6 nanocomposites by extrusion with a water injection system. They showed the mechanism for formation of these nanocomposites and the driving forces leading to the exfoliation/intercalation of the Na$^+$ MMT in Nylon-6 matrices. Based on their results, the injected water enhanced the polarity and the fluidity of the polyamide chains and increased the interlayer spacing of pristine MMT. In this condition, polyamide chains diffuse between the platelets and are adsorbed on the silicate surface. Adsorption of polyamide chains on the clay surface enhance the clay compatibility with the matrices and reduce the electrostatic interaction between the clay platelets. Nylon-6 was not the only polymer which
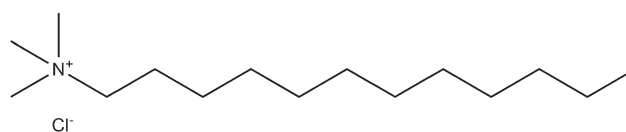

Figure 1 Dodecyl trimethyl ammonium chloride structure.

is used in the water injection melt compounding process. Kato et al.[16] used a similar method for preparation of polypropylene clay nanocomposites. The main difference of their work is usage of two compatibilizers to prevent aggregation of clay platelets in the matrices; it was because of much more hydrophobic nature of PP in comparison to Nylon-6. Based on TEM and XRD results, the silicate layers of the clay mineral were exfoliated and dispersed uniformly in the matrices. The resultant polypropylene nanocomposite had almost the same properties as a conventional polypropylene-clay nanocomposite.

The objective of this work is to introduce a novel method of producing polyethylene matrix due to its huge usage in industries to find a commercialized approach of preparation. Alkyl ammonium salt solution was used as a preintercalating agent for clay surface to assist clay dispersion in a one-step melt state process. Polyethylene nanocomposite was prepared via injection of solution into the mixture of polymer melt and pristine clay. The solution contains dodecyl trimethyl ammonium chloride salt in distilled water which is the first step to the clay surface. Afterward, with evaporation of water, polyethylene grafted anhydride maleic acts to stabilize the clay surface in the polyethylene matrices.

EXPERIMENTAL

Material

The base polymer used in this experiment is high density polyethylene provided by Sabic® with trade name of HDPE B4660 (MFI = 0.7 g/10 min, 190°C, and 2.16 kg) based on ASTM D1238, with a density of 0.961 g/cm^3. Maleic anhydride grafted polyethylene, PE-*g*-MA, (Fusabond® E100) was purchased from DuPont^{TM}, USA to enhance matrices compatibility with nanoclay, its melt flow rate is 2 g/10 min with a nominal density of 0.954 g/cm^3. Sodium-montmorillonite (Na-MMT) under the trade name of Cloisite Na+ with a cation exchange capacity of 0.92 meq/g, was provided by Southern Clay Products (Gonzalez, TX) and organic modified clay under trade name of Nanofil SE 3000 is provided by Süd-Chemie AG, Germany. The average powder particle size is about 8 μm. Besides PE-*g*-MA, an alkyl ammonium salt is also used for *in situ* treatment of clay to enhance its compatibility with matrix. Dodecyl trimethyl ammonium chloride (Figure 1) was obtained

Figure 2 Scheme of laboratory corotating intermeshing twin screw extruder.

from Xiamen Pioneer Technology Inc., China with purity >99%. The water used for injection is a distilled one.

Preparation of nanocomposites using saline water

Compounding of nanocomposites has been done using a laboratory corotating intermeshing twin screw extruder from Brabender with length to diameter ratio of 40 and diameter of 20 mm. There are three mixing zones composed of kneading blocks to enhance the clay dispersion. The first mixing zone starts at 0.25 L and is about 0.1 L long, the second is at 0.5 L and about 0.1 L long, and the third is at 0.75 L and 0.06 L long, and the scheme of the screw is shown in Figure 2. There are four heating zones along the extruder barrel followed by the die heater. The temperatures of these five zones were set at 180, 190, 200, 205, and 205°C, respectively. The screw speed was 200 rpm and the feeding rate in all the samples was 1.3 kg/h. The solution containing dodecyl trimethyl ammonium chloride salt in distilled water was injected into the barrel through DLS 2/20 dozing pump made by ETATRON, Italy, which can produce 20 bar pressure. This pressure is high enough to compensate saturated pressure of water at 205°C (about 16 bars). The screw design contains blocks to prevent back flow of water vapor to the hopper. At the final step of compounding, the water was removed from the vent by vacuum. The extruded clay/polyethylene compounds were cooled in a water bath and then pelletized. The residence time in twin screw extruder was approximately 2 min. Sample made by organic modified clay was also prepared with the same instrument and operation condition as mentioned for water and solution injected samples.

After compounding, the resulting clay/polyethylene nanocomposites as well as the neat polyethylene were injected into dumbbell using a 130-g injection molding machine (ENGEL, Germany). The injection temperature was 210°C with cycle time of 3 s and cooling time of 25 s. The injection pressure and mold pressure for all samples were 1800 and 2200 psi, respectively.

Nanocomposite of polyethylene was prepared with 2 wt % of clay and salt amount of 0.25 equivalent of clay is abbreviated to PE-Nano1. For the sake of comparison, another sample is prepared with the same composition prepared with different method of incorporation of alkyl ammonium salt; in this sample, distilled water injected and the salt fed to the extruder with other materials, abbreviated as PE-Nano2. Besides, neat polyethylene sample and sample with organic modified clay were produced under the same condition for comparison to Nano1 and PE-Nano2 samples, and these samples are named PE and PE-Nanofil, respectively. The samples' code and composition are shown in Table I.

Characterization

Dispersion of the silicate layers in the composites was evaluated by an x-ray diffractometer, x-ray diffraction (XRD) patterns were obtained through a Philips X'Pert equipped with Cu KR generator (λ = 1.5404 Å) at a scan rate of 0.02° per second ranging from 1.5° to 30°. Its generator tension is 40 kV and generator current is 40 mA.

Besides XRD, the TEM images of polyethylene nanocomposites samples were acquired to investigate the level of dispersion and distribution of clay platelets. TEM observations of the PE samples were done on ultra-thin sections of the injection molded samples perpendicular to the direction of flow using a FEG Philips model TEM instrument. These ultra-thin sections were produced by the freeze-cutting method using a microtome.

To study the dynamic rheomechanical response of samples, a small-amplitude oscillatory shear was applied to the sample, and the resultant shear stress was measured as

$$\sigma(t) = \gamma_0[G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t)].$$

TABLE I
Samples' Name and Composition of Each Sample

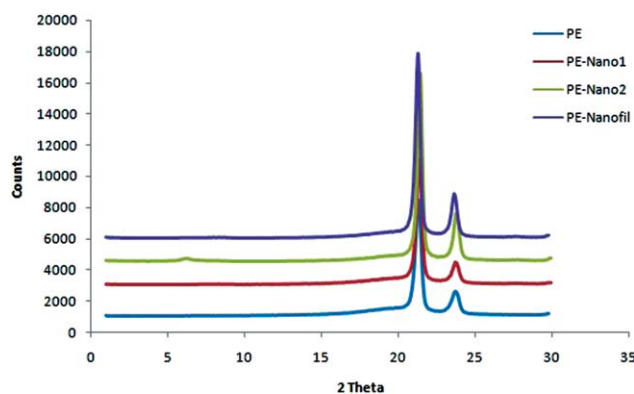| Sample name	Clay content (%)	Clay type	PE-g-MA (%)	Salt (eq)	Water flow rate (kg/hr)	Extruder flow rate (kg/hr)
PE	0	–	0	0	1	1.3
PE-Nano1	2	Na-MMT	9	0.25	1	1.3
PE-Nano2	2	Na-MMT	9	0.25	1	1.3
PE-Nanofil	2	NanofilSE3000	9	–	–	1.3

Figure 3 XRD patterns for PE, PE-Nano1, PE-Nano2, and PE-Nanofil samples with 2 wt % clay. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The storage modulus (G') and complex viscosity (η) were measured as a function of angular frequency (ω) using a Paar Physica, UDS200 rheometer. The rheometer was operated in the dynamic oscillatory mode with parallel plate geometry of 25 mm diameter and 1-mm gap. Dynamic frequency sweep tests were executed in the frequency range of 0.05–1000 sec^{-1} using a strain amplitude of 1%, proven to be in the linear viscoelasticity range by means of strain sweep measurements at temperatures of 205°C.

Tensile tests were conducted on Galdabini instrument based on ASTM D638 at a cross speed of 50 mm/min and 2N preload. Impact test are done by U-F impact tester from Ueshima Seisakusho Ltd., Japan, under conditions of ASTM D256 and 30 kgf cm load at room temperature. Thermal properties of samples were evaluated on an instrument from 25 to 220°C at a heating rate of 10°C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

XRD results

The XRD results for PE-Nano1, PE-Nano2, PE-Nanofil, and neat PE samples are shown in Figures 3 and 4. No diffraction peak is observed for PE-Nano1 and PE-Nanofil samples at low 2θ values but a small peak at about 6° is visible for PE-Nano2 sample which corresponds to basal spacing of 1.5 nm, it can be related to either alkyl ammonium salt or absorbed water molecules layers. The montmorillonite surface can absorb up to four layers of water molecules which increases the basal spacing to 1.9 nm, this process is a preintercalating step in the process of nanocomposites. Afterward, the alkyl ammonium salt can be absorbed on the surface of clay platelets, and vacuum venting at the end of the extruder will evacuate the final nanocomposite from water molecules. Furthermore, all the samples were

dried in an oven overnight, so the increase in basal spacing in PE-Nano2 may be for the presence of alkyl ammonium salt. PE-Nano1 sample showed no peak, which could be an indication of the exfoliated microstructure for the nanocomposite. However, it might be verified with other characterization methods including TEM and RMS methods. XRD results of PE-Nano1 is comparable with sample prepared by organic modified clay which show the practicability of the new method of production of polyethylene nanocomposites and also the effectiveness of the alkyl ammonium salt solution as an intercalating agent; in the case of PE-Nano1, due to better dispersion of the alkyl ammonium chains in water and good interaction with clay surface and consequently by donating hydrophobicity nature, the basal spacing of the silicate layers increases which results in easier diffusion of the polymer and compatibilizer chains between the layers. Although in the PE-Nano2 sample, the diffraction peak appears in basal spacing of 1.5 nm, the intensity of the peak is low and it shows that other clay stacks are dispersed by interaction of salt modifier and clay surface. However, the extent of modification and dispersion is lower than those of PE-Nano1 which uses salt solution for injection. WAXD patterns of neat polyethylene characterized by two peaks individually located at 2θ values of 21.3 and 23.7 correspond to the orthorhombic phase of polyethylene. These peaks also present in both nanocomposites, indicating no change in crystal structure.

TEM observations

To support the dispersion of clay, the silicate layers were observed by TEM. TEM image of PE-Nano1 is shown in Figure 5. The dark lines are cross section of silicate layers which show a homogeneous distribution of clay platelets in the polymeric matrices. The size of dark line show clay stacks in a well-dispersed condition. Although some small stacks of
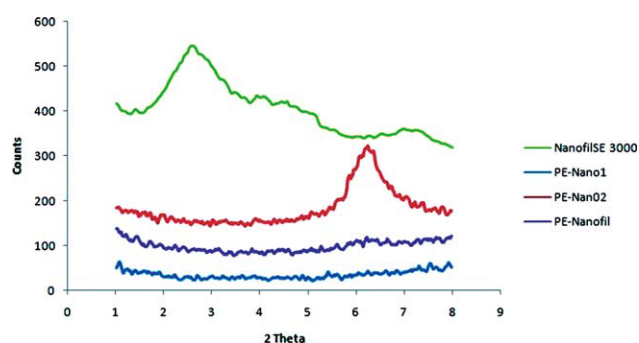

Figure 4 XRD patterns for Nanofil SE 3000, PE-Nano1, PE-Nano2, and PE-Nanofil samples with 2 wt % clay in shorter range. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
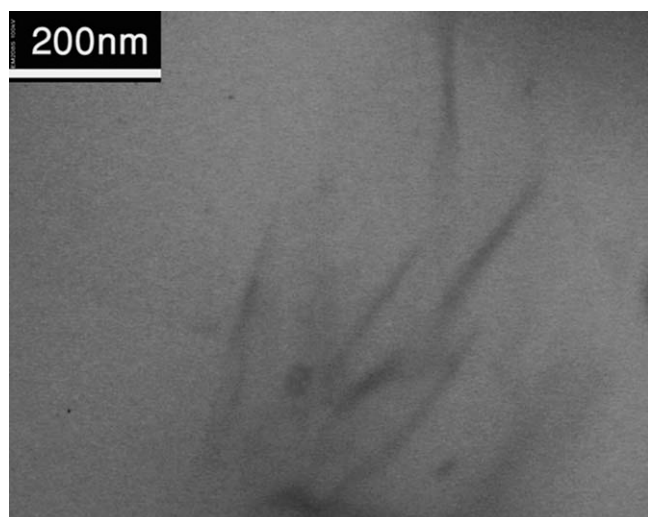
Figure 5 TEM micrographs of PE-Nano1 sample.

clay are visible, generally speaking PE-Nano1 shows appropriate level of clay dispersion. The results show high level of distribution and dispersion of silicate layers which resulted in clay stacks with high aspect ratio. The dispersion of PE-Nano1 sample demonstrates that the solution injection method using alkyl ammonium salt is a favorable method for production of PE nanocomposites.

RMS results

In polymer nanocomposites, the study of rheological properties is instructive for several reasons because the rheological properties are indicative of melt processing behavior; furthermore, the rheological properties of particle-filled materials are sensitive to the structure, particle size, shape, and surface characteristics of the dispersed phase, and as a result, rheology potentially offers a means to assess the state of dispersion in the nanocomposites[17]

Storage modulus of PE-Nano1, PE-Nano2, and PE-Nanofil samples compared to neat PE are shown in Figure 6. All the samples show higher storage modulus at lower frequencies as a result of the percolated structure formation in these samples. Galgali et al.[18] showed the origination of this behavior in nanocomposites in frictional interactions between the silicate layers and polymer chains that caused a solid-like behavior. Furthermore, Ren et al.[19] proposed that solid-like behavior in the terminal zone is due to the percolated network of anisotropic clay platelets.

As Figure 6 shows, all three samples showed deviation from neat polyethylene in the terminal zone but those of PE-Nano1 and PE-Nanofil are more pronounced, indicating higher deviation by dramatic change in comparison to PE-Nano2 which is evidence of solid-like behavior due to percolated network of clay platelets as reported previously.[18–20]
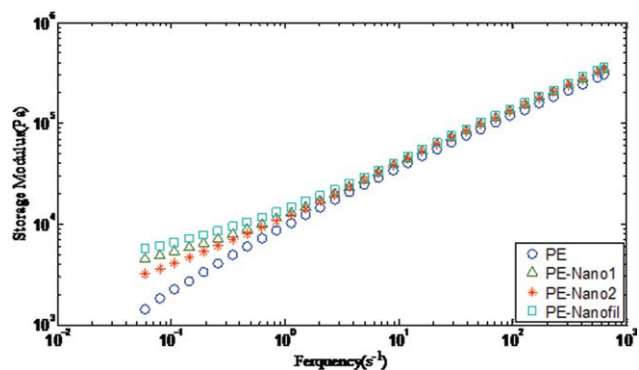
Figure 6 The storage modulus against angular frequency of PE-Nanofil (square), PE-Nano1 (triangle), PE-Nano2 (asterisk), and neat polyethylene (circle) samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The more dispersion and distribution of platelets, the more possibility of network formation. These results are in agreement with XRD and TEM results. Based on XRD results, PE-Nano1 and PE-Nanofil had better dispersion and no peaks were observed in its diffractogram, but in PE-Nano2, some stacks of clays were kept unchanged and their basal spacing showed a small difference compared to pristine clay.

The power law equation was fitted for viscosity against the frequency curve of most of the polymeric systems:

$$\eta = k\omega^{n-1}$$

The exponent of n in the power law equation in low frequencies is used as a measure of clay dispersion.[21] It is based on the fact that at low angular frequencies, the rheological response is characteristic of the unperturbed filler structure in the system. Complex viscosity against angular frequency of the samples is shown in Figure 7. Like storage modulus
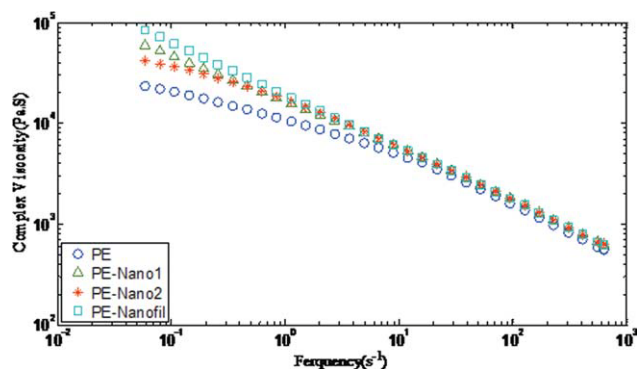

Figure 7 The complex viscosity against angular frequency of PE-Nanofil (square), PE-Nano1 (triangle), PE-Nano2 (asterisk), and neat polyethylene (circle) samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Tensile Properties of PE Composites in Compare
to Neat PE

Sample name	Tensile modulus (N/mm^2)	Tensile strength (N/mm^2)	Stress at break (N/mm^2)	Elongation at break (%)
PE	988 ± 12	25.2	12.8	205
PE-Nano1	1213 ± 17	28.8	13.9	154
PE-Nano2	1131 ± 20	27.7	15.8	183
PE-Nanofil	1257 ± 57	26.6	13.4	195

curves, samples showed deviation from neat polyethylene behavior at the low frequency region; the slop and n exponent has changed and viscosity is higher than those of polyethylene. In the high frequency region, the house of cards structure cannot follow the shear-induced disturbance, and the dynamics of nanocomposite system is mainly controlled by the liquid polymer melt.[22] For PE-Nano1 and PE-Nanofil, the change in slope and n exponent is more striking and a viscosity upturn can be seen at low frequencies. The change in slope originates from the ease of shear thinning behavior in polyethylene nanocomposites based on both anisotropic filler and structure formation by high aspect ratio silicate layers.[23] Based on XRD, TEM and storage modulus results, the PE-Nano1 had better dispersion and distribution of clay platelets, resulting in higher potential for network formation in a certain percent of clay. In the other words, all these results revealed that there is a strong potential for producing polyethylene clay nanocomposite through this novel route: injection of aqueous solution of alkyl ammonium salts via melt mixing.

Mechanical properties

As a basic concept, incorporation of a layered silicate in a polymer matrix results in significant improvements of Young's modulus.[23–26] The main reason for resistance against straining is due to high modulus of silicate layers. Hence, when a relatively softer matrix such as polymers is reinforced with such fillers, the polymer, particularly that adjacent to the filler particles, becomes highly restrained mechanically. This makes the filler to carry a considerable portion of an applied load, the assumption for this mechanism is that the bonding between the two phases is adequate.[27] Table II shows the tensile properties of PE-Nano1, PE-Nano2, and PE-Nanofil samples compared to neat PE. It is obvious that all the three composites showed an enhancement in tensile modulus as compared to pure PE. The enhancement in tensile modulus for PE-Nano1, PE-Nano2, and PE-Nanofil are 22%, 14%, and 27%, respectively. This difference comes back to variation of dispersion and distribution of samples which is discussed before in XRD,

TEM, and RMS results. PE-Nano1 had better dispersion and no peak was observed in its XRD diffractogram but in PE-Nano2 some stacks of clay in the matrix phase remained unchanged. In PE-Nanofil, better modification of surfaces comparing with PE-Nano1 has led to proper mechanical properties. Furthermore, based on the storage and complex viscosity results, distribution of silicate layers were in proper condition in PE-Nano1, due to better dispersion and distribution of the clay particles in PE-Nano1 where interfacial interaction between the polymer and silicate layer has been increased in it. It seems as a result of better distribution of alkyl ammonium salt in saline water, the interaction of silicate layers with alkyl ammonium salt has been improved.

Table II also shows the yield stress and stress at break of samples. The effect of nanofiller addition on tensile strength is not as clear as in the case of the modulus since in some cases[23,28–30] increase in tensile strength and some other cases [26,31] reduction of tensile strength upon nanocomposite formation have been reported.

Both tensile strength and stress at break showed enhancement compared with PE but this increment is more pronounced in PE-Nano1 with regard to its tensile modulus results. This is because of the difference in the level of dispersion in samples, PE-Nano2 had a lower level of exfoliation, aspect ratio, and surface area; therefore, the reinforcement mechanism does not work well in this case. Tensile strength and stress at break of PE-Nano1 is commensurate with those of PE-Nanofil indicating proper level of enforcement due to appropriate modification of pristine clay platelets in aqueous solution injection process.

Fracture energy acquired through impact test is also shown in Figure 8. As it is shown, PE-Nano1
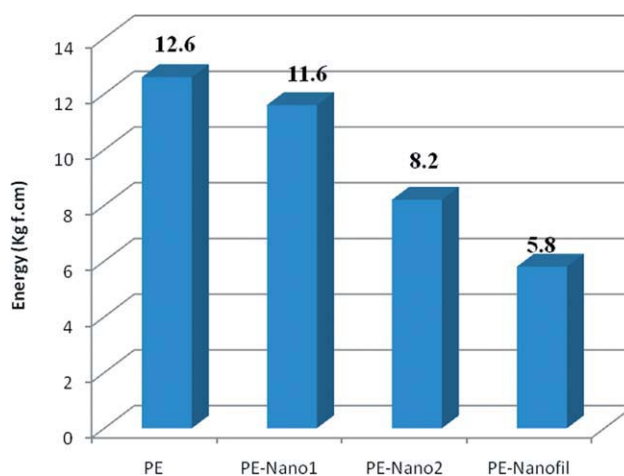
Figure 8 Fracture energy of PE nanocomposites in comparison to neat PE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Thermal Properties of Polyethylene Nanocomposites
Prepared via Injection of Saline Water (PE-Nano1) and
Distilled Water (PE-Nano2)

Sample name	Degree of crystallinity (%)	Melting temperature (°C)	Crystallization temperature (°C)
PE	64.9	132	120
PE-Nano1	65.0	132	121
PE-Nano2	66.4	132	120
PE-Nanofil	63.1	132	124

has comparable impact strength with PE but those of PE-Nano2 showed about 35% lower impact strength than PE sample. The brittle behavior of nanocomposites probably originates from the formation of microvoids due to deboning of clay platelets from the polymer matrix upon failure.[32] Usually, microvoids are formed around the large inhomogeneities. These microvoids will merge into larger cracks causing embrittlement, ultimately resulting in reduced toughness.[33] It is probable that in PE-Nano2, formation of these microvoids have led to reduction in toughness but in PE-Nano1, because of its proper dispersion, the size of microvoids are comparable with well-dispersed silicate layers; therefore, their size will be below the critical size of the crack, eventually their fracture energy is comparable to polyethylene. Other researchers also reported reduction in the impact strength in PE-based nanocomposites, indicating that the incorporation of clay into semicrystalline thermoplastics usually results in toughness reduction,[33] which is observable in the PE-Nanofil sample. In this case, the fracture energy is even lower than PE-Nano2 meaning that the nanocomposite prepared by Nanofil SE 3000 sample does not show a proper balance of mechanical properties as a result of the high level of chain confinement between clay platelets; in the other words, higher reinforcement with clay particles has lead to resistance to plastic deformation.[34]

DSC results

The crystallization data in terms of degree of crystallinity, melting, and crystallization temperatures of samples are summarized in Table III. The percentage of crystallinity was estimated using a value of heat of fusion of 293 J/g for 100% crystalline PE.[35] Except small changes, no noticeable change in degree of crystallinity, melting point, and crystallization temperature is observed. Deshmane et al.[36] also reported no change in crystallization of PE nanocomposites and attributed it to weak interaction between polyethylene and clay. Maiti et al.[11] reported that although clay particles act as nucleating agents for

the crystallization of matrix, the linear growth rate and the overall crystallization rate are not meaningfully influenced by the presence of clay. Furthermore, confinement of chains and segments in the presence of clay hinder the segmental rearrangement during crystallization and restrict the formation of perfect crystals in the polymer matrix.[37]

CONCLUSIONS

Polyethylene nanocomposites were prepared with the aid of alkyl ammonium solution as a preintercalating agent for clay surface to assist clay dispersion in one-step melt state process. In this process aqueous solution was injected into the mixture of polymer melt and pristine clay within a laboratory scale twin-screw extruder. The solution contains dodecyl trimethyl ammonium chloride salt in distilled water and was injected into the twin-screw extruder using a high pressure dosing pump.

The XRD results showed no peak for sample containing 2 wt % pristine clay which was prepared via injection of salt solution representing exfoliated microstructure which was similar to the result of organo-modified clay; in addition, the XRD results for other samples using distilled water the peak was shifted to lower 2θ values indicating intercalated morphology. TEM images also showed uniform distribution and dispersion of clay particles in polyethylene matrix for PE-Nano1 sample. Furthermore, for the aqueous solution injected sample, RMS results showed that the slop of the storage modulus has been declined and has been reached to a near plateau which is evidence of the network structure for this sample. In complex viscosity curves, deviation from neat polyethylene behavior in low frequency region was observed; the slope and n exponent has changed and viscosity is higher than those of polyethylene. Change in slope and viscosity upturn in saline water solution injected sample confirms better dispersion and formation of network in this nanocomposite; all the rheological results acquired for PE-Nano1 sample were on a par with those of nanocomposite prepared with organo-modified clay. Tensile results also showed an increase of tensile modulus in the range of about 22% for sample prepared via injection of alkyl ammonium solution which was in the same range of nanocomposite prepared with organo-modified clay. Furthermore, Izod impact strength in sample prepared via injection of salt solution had energy of fracture comparable to neat polyethylene, while the other sample showed about 35% reduction in impact strength. The crystallization data in terms of the degree of crystallinity, melting, and crystallization temperatures of samples had no noticeable variation comparing with the neat polyethylene.

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