Polyethylene/Clay/Graphite Nanocomposites as Potential Materials for Preparation of Reinforced Conductive Natural Gas Transfer Pipes

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ABSTRACT: A series of high-density polyethylene/Cloisite 20A/graphite nanocomposites were prepared via melt blending for the production of polymeric pipes for natural gas transfer. The microstructural, mechanical, thermal, electrical and barrier properties of prepared nanocomposites were investigated. An intercalated morphology was observed for prepared nanocomposites. Improved mechanical properties e.g. over 148 % increase in Young’s modulus were observed by incorporating the nanoparticles into the polyethylene matrix. The thermal analysis showed that the melting point of polyethylene was slightly increased by incorporating both fillers, i.e. Cloisite 20A and graphite in it, and the crystallinity was depended on the type of filler. The results showed that the MFI values decreased by incorporating the fillers into the polyethylene matrix and further decreases were observed by increasing the contents of the filler. It was also found that a considerable amount of electrical conductivity is created in graphite loaded nanocomposites. The natural gas permeability investigations revealed of more than 51 % decrease in the permeability by incorporating 5 wt.% of Cloisite 20A to the polyethylene. It was concluded that the prepared nanocomposites due to their enhanced mechanical, thermal and barrier properties along with the conductive nature are excellent materials to be used in the production of polymeric pipes in natural gas distribution and transportation networks.

KEYWORDS: Nanocomposites; Polyethylene; Clay; Graphite; Natural gas pipeline

INTRODUCTION
For many years, steel pipes have been utilized in gas transportation and distribution networks. But, their some disadvantages such as oxidation and corrosion have restricted their application in practical usages [1, 2]. Therefore, in past years special attention have been paid to use polymers to produce a novel class of gas transportation pipelines [3]. Polymer pipes are significantly lighter than steel ones while their mechanical strengths...
are lower. In fact, when strength to weight ratio is considered, polymer pipes will be much stronger than the steel pipes. Comparing relative flexural strengths, polymer pipes are significantly more flexible than steel pipes and their connection process is easier. Furthermore, polymer pipes are highly resistant to many corrosive chemicals and compounds [4].

Polyethylene (PE) is the primary material used for production of polymeric pipes in natural gas transmission and distribution systems. It is a linear polymer prepared from ethylene that can be formed in high, medium or low density versions and is particularly easy to mold when forming. It is easy to form into pipe that is light, tough, and chemical resistant and can be spooled. Among the PE family, high density polyethylene (HDPE) is mainly used in the transportation of natural gas both in distribution lines and flowlines [4]. Because of flexibility, ease of joining and long-term durability of PE along with lower installed cost and lack of corrosion, gas companies want to install PE pipes instead of steel pipes in larger diameters and higher pressures [5]. Advantages of PE pipes over traditional metal pipes have increased scientific and industry interests in the use of PE pipelines in gas distribution networks and therefore numerous researches have been recently performed on preparation of different types of PE based gas transfer pipes [6-9].

However, some disadvantages of the PE pipes restricted their applications in gas transfer systems. The first limitation arises from the electrically insulating nature of the PE. PE pipes suffer static electricity created inside the pipe, which can not be discharged through the pipe wall and may cause fire. Furthermore, static electricity can create fine holes on the pipe surface which makes gas diffuse out of the pipe [10, 11].

Most polymers are electrically insulating and increasing their electrical conductivity can broaden their applications [10, 12]. In the recent years, conducting polymers have attracted considerable attention due to their potential application in different fields, such as antistatic coatings, electromagnetic shielding materials, semiconductors and batteries [10]. Electrically conducting polymers, consisting of conducting fillers in an insulating polymer matrix, are considered to be an important group of relatively inexpensive materials for many engineering applications such as electrical conducting adhesives, sensors and actuators, insulated coatings and films, electromagnetic interference shielding materials for electronic devices, thermal interface materials and so on [10, 12, 13]. Electrical conductivity values are typically $10^{-14}$ to $10^{-17}$ S/cm for polymers, $10^2$ S/cm for carbon black, $10^3$ S/cm for high purity synthetic graphite, and $10^6$ S/cm for metals such as aluminum and copper [10]. Conductive polymers with electrical conductivity ranging from approximately $10^{-10}$ to $10^2$ S/cm can be used for static dissipative applications [12]. Graphite is widely used to improve the conductivity of polymers due to its low cost, availability and desired conductivity.

The second problem in PE pipes is the relatively weak mechanical properties e.g. low tensile strength and elastic modulus which causes the mechanical damages and fracture of the pipe under high loads. Another problem of PE pipes is resulted from their permeable nature. In these pipes, the gas can diffuse to outside the pipe and may increase the pressure drop inside the pipe and reduce the flow rate of gas. These three problems seem to be overcome using the technology of polymer nanocomposites and by incorporating inorganic reinforcing agents such as oclays into the polymeric pipes.

Polymer-clay nanocomposites are nanoscale organic-inorganic hybrid materials, in which the silicate layers of clay with nanoscale dimensions are used to reinforce the polymer matrix [14-20]. It has been shown that the presence of clay layers inside the polymer matrix significantly improves the mechanical and physical properties of the polymer [21-26]. Furthermore, it has been shown that the presence of clay layers inside the polymer-clay nanocomposites decreases the permeability of the nanocomposites and the clay layers act as physical barriers against transfer of matters through the nanocomposite [27, 28]. Beside the clays, other nanometric fillers such as carbon nanotubes, graphene and magnetic nanoparticles are widely used for fabrication of polymer nanocomposites [29-31].

Recently, we used Cu nanoparticles to create electrical conductivity in the organically modified montmorillonite clay (Cloisite 20A) loaded PE nanocomposites for production of polymeric pipes for gas transfer applications [32]. The results showed an improvement in the mechanical properties due to the presence of reinforcing agent (Cloisite 20A) and...
an enhancement in the electrical conductivity due to the presence of conductive agent (Cu nanoparticles) in nanocomposites which were very suitable for production of gas transfer pipes. However, the main challenging problem behind the Cu nanoparticles loaded nanocomposites was possible oxidation of Cu at high melting and processing temperatures. In order to overcome this problem and also produce the economic gas transfer nanocomposite pipes, we used graphite as a readily available and inexpensive source of conductive material instead of Cu nanoparticles in the current study. In this work, PE/clay/graphite nanocomposites were prepared via melt blending and their structural, mechanical, thermal, electrical and gas permeability properties were investigated to evaluate their potentials for production of polymeric pipes for natural gas transfer.

EXPERIMENTAL SECTION

Materials

HDPE (grade 6040) having density of 0.96 g/cm³ and melting flow index (MFI) of 3.98 g/10 min (under 2.16 kg at 190°C) was supplied by Tabriz Petrochemical Co., Iran. Organically modified montmorillonite clay (Cloisite 20A) was purchased from Southern Clay Products Inc., USA. Graphite with an average particle diameter of 4 μm and having the nanoscale platelets thickness was purchased from Qingdao Tianhe Graphite Co. Ltd., China.

Preparation of nanocomposites

In order to prepare nanocomposites, an internal mixer with a blending chamber of 55 cc (Brabender W50, Germany) was used. Nanocomposites with different weight percentages of fillers, i.e. Cloisite 20A and graphite nanoparticles were prepared in the internal mixer at 180 °C at 70 rpm for a total mixing time of 10 min. At first, HDPE was added into the internal blending chamber. Cloisite 20A was then added to the polymer melt. About 3 minutes later, graphite nanoparticles were added as the second filler. Finally, the samples were cooled to room temperature. All samples were then compression molded (Toyoseiki Mini Test PRES, Germany) at 200 °C, under a pressure of 25 bar to obtain films with different thicknesses. Finally, PE nanocomposites contained 0, 1, 3 and 5 wt.% of Cloisite 20A and also 0, 2 and 4 wt.% of graphite nanoparticles were obtained. The abbreviation PCGx-y was used for samples which x shows the weight percentage of Cloisite 20A and y shows the weight percentage of graphite nanoparticles.

Characterization

The morphology of the prepared samples was examined by X-ray diffractionmetry (XRD) and Scanning Electron Microscopy (SEM). XRD was carried out on Cloisite 20A and graphite as well as on two typical nanocomposites (i.e. PCG3-0 and PCG3-2 samples) using a diffractometer (SIEMENS D5000, Germany) equipped with an X-ray generator using Cu Kα (λ= 0.15406 nm) radiation at room temperature. The diffractograms were scanned in 20 range from 2 to 50° with a rate of 2 °/min. Scanning electron microscope (KYKY-EM3200, China) was applied to observe the surface microstructure of samples. In order to perform the SEM, typical samples including the PCG0-0, PCG3-0 and PCG3-2 were broken in the liquid nitrogen and the SEM images were taken of the fracture cross sections of the samples.

Tensile, Differential Scanning Calorimetry (DSC) and MFI tests were used to determine the effects of Cloisite 20A and graphite nanoparticles on the mechanical and thermal properties of the prepared nanocomposites. Uniaxial tensile testing was used to determine the Young’s modulus, tensile strength, elongation at break and yield stress of samples. The prepared films of each specimen were cut into dumbbell shaped samples according to ASTM-D412 with 2 mm thickness. Measurements were performed using a GT-TCS-2000 tensiometer (Gotech Testing Machines Inc, Taiwan) with a constant crosshead speed of 5 mm/min at room temperature. At least three specimens of each sample were tested and the average value was reported with standard deviations. DSC was performed on some typical samples including pure PE, PCG3-0 and PCG3-2. DSC thermogram were recorded using a DSC-Netzsch-200-F3 (Germany) at a heating rate of 10 °C/min with weight of samples in the range 5 to 12 mg under an extra dry nitrogen atmosphere over a temperature range of -10 to 250 °C. MFI measurements were also accomplished on all samples according to ASTM D-1238 standard. Three specimens of each sample were tested and the average value was reported with standard deviation.
The room temperature electrical conductivity of pure PE (i.e. PCG0-0 sample) and the graphite loaded nanocomposites (i.e. PCG3-2 and PCG3-4 samples) was measured by a standard four-probe method using a Keithley 196 System DMM Digital Multimeter (USA). The data were gained after averaging at least three values.

CH₄ permeation test was performed on PCG0-0, PCG1-0, PCG3-0 and PCG5-0 samples to investigate the effect of Cloisite 20A on the barrier properties of the prepared nanocomposites against natural gas permeation. For this purpose, films with thicknesses of nearly 100 μm and permeation area of 2 cm² were used and the experiments were performed according to the constant volume and variable pressure method described in details elsewhere [33]. For each sample, three different films were tested and the average permeability values were reported.

RESULTS AND DISCUSSION

Morphology and microstructural properties

Fig. 1 demonstrates the XRD results for Cloisite 20A, graphite, nanocomposite containing 3 wt.% of Cloisite 20A (PCG3-0) and nanocomposite containing 3 wt.% of Cloisite 20A and 2 wt.% of graphite (PCG3-2). XRD profile of Cloisite 20A has a characteristic diffraction peak at 3.7° which is due to the interlayer spacing of the clay layers (Fig. 1a). On the other hand, clay loaded samples i.e. PCG3-0 and PCG3-2 have characteristic peaks at 3.44° and 3.6°, respectively, which is due to the interlayer spacing of the clay layers inside the PE matrix (Fig. 1c and d). As seen, the characteristic diffraction peak of Cloisite 20A has been shifted slightly to the lower angles in PCG3-0 and PCG3-2 samples, which reveals possible intercalation of the nanocomposites. Similar intercalated morphology for PE-clay nanocomposites with very small shifting in the clay characteristic diffraction peak has been reported previously based on XRD results and the suggested morphology was confirmed by transmission electron microscopy (TEM) [21]. This means that the d-spacing of Cloisite 20A is already sufficiently large (due to organically modification) to permit the entry of the PE chains without drastic increasing the d-spacing.

Two characteristic diffraction peaks around 22 and 24° were also observed for PCG3-0 and PCG3-2 nanocomposites which are related to the presence of PE in the nanocomposites. Furthermore, the characteristic diffraction peak of pure graphite at 26.36 ° (Fig. 1b) was observed with a lower intensity in the graphite loaded nanocomposite (i.e. PCG3-2 sample) at around 26.74 ° (Fig. 1d).

The dispersion of Cloisite 20A and graphite nanoparticles in PE matrix was observed by SEM. The SEM microphotographs of cryogenic fracture surfaces of PCG0-0, PCG3-0 and PCG3-2 samples with two magnifications are shown in Fig. 2. The SEM images indicate a nearly uniform distribution of nanoparticles inside the nanocomposites created due to the appropriate mixing and processing conditions in the samples preparation stage. It can be seen that the incorporated nanoparticles are composed of a nearly random structure without creation of the nanoparticles clusters and agglomerates.

Mechanical and thermal properties

Table 1 summarizes the mechanical properties of prepared nanocomposites derived from the stress-strain curves obtained by the uniaxial tensile test. The results show that addition of Cloisite 20A and graphite into PE matrix causes the increase in the Young’s modulus, tensile strength and yield stress, while decrease in the elongation at break of samples. For instance, incorporating 3 wt.% of Cloisite 20A into PE matrix increased the Young’s modulus, tensile strength and yield stress of the nanocomposite by 117, 13, 21 %, respectively. It can be seen also that adding the same amount of Cloisite 20A into PE created a nanocomposite.
Fig. 2: SEM microphotographs of (a) PCG0-0, (b) PCG3-0, (c) PCG3-2 samples with magnifications of 20000x and 40000x.
Table 1: Effect of Cloisite 20A/graphite contents on the mechanical properties of PE/Cloisite 20A/graphite nanocomposites.

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>Young’s Modulus (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Yield Stress (MPa)</th>
<th>Elongation at Break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCG0-0</td>
<td>369.5±38.5</td>
<td>16.0±0.3</td>
<td>11.2±0.5</td>
<td>549.0±40.0</td>
</tr>
<tr>
<td>PCG1-0</td>
<td>723.7±44.9</td>
<td>17.2±0.2</td>
<td>13.8±0.5</td>
<td>339.7±29.4</td>
</tr>
<tr>
<td>PCG3-0</td>
<td>800.4±45.3</td>
<td>18.1±0.3</td>
<td>13.5±0.4</td>
<td>159.5±49.5</td>
</tr>
<tr>
<td>PCG5-0</td>
<td>918.1±31.2</td>
<td>19.3±0.3</td>
<td>14.1±0.5</td>
<td>80.0±19.5</td>
</tr>
<tr>
<td>PCG3-2</td>
<td>819.4±28.4</td>
<td>18.2±0.2</td>
<td>14.0±0.3</td>
<td>140.0±12.2</td>
</tr>
<tr>
<td>PCG3-4</td>
<td>846.8±37.2</td>
<td>18.7±0.3</td>
<td>14.5±0.4</td>
<td>121.7±10.6</td>
</tr>
</tbody>
</table>

with 71% decreased elongation at break. From the viewpoint of the effect of graphite on the mechanical properties, the results show that the addition of 4 wt.% graphite into PE matrix containing 3 wt.% of Cloisite 20A the Young’s modulus, tensile strength and yield stress were increased 129, 17 and 29%, respectively while the elongation at break decreased 78% compared with the pure PE. Comparing the results for PCG3-4 sample with PCG3-0 showed 6, 3 and 7% increase in the Young’s modulus, tensile strength and yield stress, respectively as well as 24% decrease in the elongation at break.

The improved mechanical properties of prepared nanocomposites could be attributed to the excellent interactions created among the Cloisite 20A, graphite and PE. These interactions create some additional PE chains entanglements inside the nanocomposite and let the chains to share the external loads with the incorporated fillers and as a result, the mechanical properties improved. According to the obtained mechanical results, it can be said that the prepared nanocomposites are suitable to produce the natural gas transfer pipes with enhanced mechanical properties.

Fig. 3 shows the thermograms obtained by DSC for PCG3-0 and PCG3-2 nanocomposites. The DSC curve of the pure PE (PCG0-0) was also shown as a reference. A similar pattern was observed for all examined samples with an endothermic peak around the melting point. Using the obtained DSC curves, some important thermal properties of samples including the melting point ($T_m$), enthalpy of fusion ($\Delta H_f$) and crystallinity percentage were extracted and listed in Table 2. The crystallinity values were calculated using the $\Delta H_f$ value of 288 J/g for a 100% crystalline PE [34, 35].

As seen in Table 2, the melting points of two examined nanocomposites are slightly higher than the pure PE. From the crystallization viewpoint, comparing the obtained results for PCG0-0 and PCG3-0 samples show that by incorporating the Cloisite 20A into the PE matrix, $\Delta H_f$ and crystallinity values are decreased. In contrast, by comparing the obtained results for PCG0-0 and PCG3-2 one can find that the values of $\Delta H_f$ and crystallinity are increased by incorporating the graphite nanoparticles to the nanocomposites. In general, the presence of nanoparticles can have several contradictory effects on the fusion and crystallization behavior of polymer nanocomposites. From one point, nanoparticles can act as the start point of crystallization and cause some increments in the crystallization amount of nanocomposites. On the other side, they may prevent the polymer chains from entering crystal structures and as a result they can decrease the crystallization value of nanocomposite. Depending on the type and amount of used nanoparticles, crystallization could be either decreased or increased. Therefore, it can be said that
in our study, clay layers prevent approaching of polyethylene polymer chains together and decrease the chain crystallization. In contrast, results show that presence of graphite in the structure of nanocomposites act as a nucleus and a start point of crystallization. Therefore the sample containing graphite (PCG3-2) has a higher value of crystallinity compared to PCG0-0 and PCG3-0 samples.

The measurement of MFI is a simple and useful way to estimate the chain mobility of polymers. Table 3 summarizes the MFI values obtained for the prepared samples. The results showed that the addition of fillers both Cloisite 20A and graphite into the PE matrix and also by increasing the filler content, the MFI values decrease. The results revealed that an increase in the amount of Cloisite 20A up to 5 wt. % declines the MFI value by 33 %. Besides, for samples containing both Cloisite 20A and graphite nanoparticles, the addition of 2 and 4 wt.% graphite into the polymer matrix decreased MFI to 20 and 26 %, respectively. The decline in the MFI of the nanocomposites could also be attributed to the restricted mobility of the polymer chains and increased viscosity of melt due to the interaction between fillers and polymer matrix. The lower MFI values of the prepared nanocomposites compared to the pure PE are related to their higher melt strengths, which in turn reflect their good processability during extrusion and production of the practical natural gas transfer pipes.

**Electrical conductivity**

In order to donate the electrical conductivity to the PE/Cloisite 20A nanocomposites, the graphite as a well known conductive nanoparticle was used. The electrical conductivities of graphite loaded nanocomposites along with the pure PE as a reference were measured using the four point probe method and the obtained results are shown in Fig. 4. As seen, pure PE behaves like an insulator while by adding the conductive graphite nanoparticles in it; the electrical conductivity is created inside the non-conductive matrix. However, the electrical conductivity for the examined graphite loaded nanocomposites has not serious dependency on the graphite loading level and the electrical conductivity reaches to a saturated level over 2 wt.% loading of graphite. It seems that the created electrical conductivity in the graphite loaded nanocomposites could overcome the serious problems existing in the non-conductive PE pipes used in the practical gas transportation networks, such as explosion in the pipeline and creation of fine holes on the pipe surface.

**Barrier properties**

Porosity is an important factor which influences the permeation properties of polymers. When the gas passes through the PE pipes, it diffuses into the pores of pipe and results in reduction of the gas flow rate in the natural gas transportation. Therefore, in this study we tried to prepare clay loaded PE nanocomposites with reduced permeability. The CH₄ permeability measurements were performed on the pure PE and Cloisite 20A containing nanocomposites and the results are shown in Fig. 5. As it can be observed, all the nanocomposites have lower permeability than the pure PE and the permeability decreases as the content of Cloisite 20A is increased. Interestingly, it was found that addition of 5 wt.% Cloisite 20A to PE reduced the permeability over 51%.

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**Table 2: Thermal properties of some prepared samples.**

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>Tm (°C)</th>
<th>∆Hf (J/g)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCG0-0</td>
<td>131.5</td>
<td>120.8</td>
<td>41.94</td>
</tr>
<tr>
<td>PCG3-0</td>
<td>132.0</td>
<td>110.8</td>
<td>39.66</td>
</tr>
<tr>
<td>PCG3-2</td>
<td>132.1</td>
<td>126.8</td>
<td>46.34</td>
</tr>
</tbody>
</table>

**Table 3: MFI values of pure PE PE/Cloisite 20A/graphite nanocomposites.**

<table>
<thead>
<tr>
<th>Sample Designation</th>
<th>PCG0-0</th>
<th>PCG1-0</th>
<th>PCG3-0</th>
<th>PCG5-0</th>
<th>PCG3-2</th>
<th>PCG3-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFI (g/10min)</td>
<td>3.98±0.07</td>
<td>3.53±0.07</td>
<td>3.31±0.06</td>
<td>2.67±0.07</td>
<td>3.19±0.05</td>
<td>2.93±0.06</td>
</tr>
</tbody>
</table>
The enhanced barrier properties of the nanocomposites may be explained by the labyrinth or tortuous pathway model. According to this model, the silicate layers of clay inside the intercalated nanocomposites form a staircase-like arrangement which creates a more tortuous path for molecules to traverse the nanocomposite film. It means that in the prepared nanocomposites, the Cloisite 20A layers act as physical barriers against CH₄ molecules transport due to creating of more tortuous paths which offers controlling step against mass transfer.

CONCLUSIONS

In this work, a series of PE nanocomposites containing Cloisite 20A and graphite nanoparticles were prepared and introduced as potential materials for production of polymeric pipes in natural gas transfer systems. For this purpose, some microstructural, mechanical, thermal, electrical and barrier properties of prepared nanocomposites were investigated. The results showed that the nanocomposites had intercalated morphology and significantly improved mechanical properties (i.e. increased Young’s modulus, tensile strength and yield stress and decreased elongation at break) compared to the pure PE. Thermal analysis results demonstrated that the addition of fillers into PE matrix increased slightly the melting points of samples, whereas the MFI values decreased. The enhanced mechanical and thermal properties of the fabricated nanocomposites are advantages for the production of natural gas transportation pipes in practice. The electrical conductivity measurements revealed of creation of conductivity inside the non-conductive PE matrix due to presence of the graphite nanoparticles in the nanocomposites. It seems that the introduced conductive nanocomposites can overcome the problems of creation of static electricity and holes in the conventional polymeric gas transfer pipes. Furthermore, it was found that the addition of clay into the PE matrix could improve the barrier properties of nanocomposites against natural gas in practical gas transportation pipes. In general it was concluded that the prepared reinforced conductive PE/Cloisite 20A/graphite nanocomposites are excellent candidates for production of natural gas distribution and transportation pipes and they can fulfill the main requirements for the ideal pipes.

Acknowledgments

The authors are grateful for the partial financial support provided by the West Azarbayjan Gas Company and Iran Nanotechnology Initiative Council.

Received : Jul. 2, 2018 ; Accepted : Dec. 24, 2018

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