

Preparation and Characterization of HDPE/Silane-Modified Nanoclay Composites for Application in Fuel Storage

Mukul R. Jain

Global TS Manager, Nano Specialty Inc

Chhavi Jain, Sunil Shah, and R C Jain

Vardhman Technologies

ABSTRACT

Organophilic nanoclay that was prepared by surface modification of Montmorillonite clay with quaternary ammonium compound was further treated with a surface modifier (silane). Subsequently, different composites were obtained by blending 5 wt % of clay, nanoclay, or silane-treated nanoclay with high-density polyethylene (HDPE) using Brabender Plasticorder. The morphology of the prepared composites was analyzed by using scanning electron microscopy (SEM). In addition, the effect of the surface modifier on the dispersion of clay platelets in the polymer matrix was studied by elemental mapping using energy dispersive X-ray spectroscopy (EDX). Results indicate that the use of silane significantly improves the dispersion of nanoclay, resulting in enhanced mechanical properties. Furthermore, the effect of surface modification on the barrier properties of the nanocomposites was analyzed by determining the long-term permeation rate of xylene and gasoline in blow-molded containers made of HDPE, HDPE/clay composite, HDPE/nanoclay composite, and HDPE/silane-treated nanoclay composite at 23 and 50°C. Of all the composites, the composite with 5 wt.% silane-modified nanoclay showed the best barrier performance. In particular, the barrier property of HDPE/silane-treated nanoclay nanocomposite was found to be 20-folds higher than that of HDPE container. These results suggest the enhanced performance of containers made of HDPE/silane-modified nanoclay for fuel storage in automotive applications.

KEYWORDS: fuel, nanocomposites, HDPE, organo-clay, montmorillonite clay, barrier properties

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INTRODUCTION

Clay-reinforced polymer nanocomposites are a new class of functional materials composed of nano sized clay particles dispersed in a polymer matrix. The enhanced functionalities of these nanocomposites are due to the very high surface area of clay platelets available for the interaction with the polymer molecules.^[1, 2] Nanoclays are layered-silicates, in which the six tetrahedral silicon rings that are surrounded by oxygen at its vertices share alternate edges with the octahedral aluminums. The sharing of alternate edges leads to a configuration with six octahedral aluminums in a ring. More precisely, two out of the three octahedral sites are occupied by aluminum, leaving the third octahedral site vacant. The six-membered silicon tetrahedral sheets are located on both sides of the octahedral aluminum sheet. The gap between two

of these triple sheets is called interlayer spacing. Here, the substitution of Al^{3+} for Si^{4+} ions results in a need for charge compensation. This is often accomplished by an external positive ion, such as calcium or sodium.^[3, 4, 5] In principle, the performance of the composite mainly depends on the dispersion of the clay platelets in the polymer matrix and the resulting structure of the nanocomposites, namely, flocculated, intercalated, or exfoliated structures. In general, the high dispersion of clay platelets through exfoliation of individual clay platelets in the polymer matrix is considered to have better properties.

Meanwhile, high-density polyethylene (HDPE) is being extensively used as a polymer in these nanocomposites owing to its moderate cost and high strength to weight ratio.^[6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17] It is one of the widely used

polymers for industrial applications. However, it does not have a polar group on its backbone to interact with the polar clay surface. Therefore, the wetting properties of HDPE are often improved by using quaternary ammonium or phosphonium compounds. In addition, silane surface modifiers are also used for this purpose. The silane tends to condense on the clay surface by forming a covalent bond. Subsequently, the other organic part diffuses into the organic phase, thereby improving the miscibility of the inorganic phase with the organic phase. The anchoring of the organic part of silane compound to the HDPE molecules further strengthens the inorganic-organic bonds. In this study, we have analyzed the improvement in the dispersion of clay platelets as a result of surface treatment with quaternary ammonium compound and silane by elemental mapping using energy dispersive X-ray spectroscopic (EDX) analysis. In addition, the morphology of the prepared nanocomposites was observed by using scanning electron microscopy (SEM). The effect of the surface treatment of the nanoclay on the viscous behavior of the polymer matrix was analyzed by determining the melt flow index (MFI) of the various nanocomposites with different compositions of nanoclay. Furthermore, the tensile strength and impact strength of the composites were evaluated to understand their mechanical property. The long-term barrier property of the containers made of HDPE, HDPE/clay composite, HDPE/nanoclay composite, and HDPE/silane-treated nanoclay composite was determined by estimating their permeation rate towards xylene and gasoline 23 and 50°C.

EXPERIMENTAL

Materials

Montmorillonite (raw) clay and amino propyl triethoxy silane, which was used as the surface modifier in this study, were purchased from Kuver Enterprises, Baroda, India. Analytical grade reagents of xylene and quaternary ammonium compound (hexadecyl trimethyl ammonium bromide) were obtained from Sulab Chemicals, Baroda. HDPE was purchased from Reliance Industries Ltd., Mumbai, India, while gasoline and 91 Octane (MG91) was purchased from IOCL, Mumbai, India.

Preparation of HDPE/Clay Nanocomposite

The raw clay, organoclay, and silane-treated organoclay samples used in this study were first dried at 100°C for 12 h using a conventional oven. Subsequently, all the three different clay samples were blended with HDPE by using a Brabender plasticorder (Figure 1) at 180°C for 10 min, at a speed of 80 rpm. The blended mixture was cut into small pellets using a pelletizer. The pellets thus obtained were dried overnight at 100°C. The test specimens were subsequently prepared by using injection molding process (Polymechplast Machines Ltd.). The temperature of the mixing zone was maintained in the range of 180-205°C, with an injection pressure of 80%.

Table 1. Composition of HDPE/Clay blends

Composition	Raw clay content	Organoclay content	Silane concentration
H _{5r} C	5 %	-	-
H _{1m} C	-	1 %	-
H _{3m} C	-	3 %	-
H _{5m} C	-	5 %	-
H _{7m} C	-	7%	-
H _{10m} C	-	10%	-
H _{5m} C-1S	-	5%	1%
H _{5m} C-3S	-	5%	3%
H _{5m} C-5S	-	5%	5%



Figure 1. Photograph of the Brabender Plasticorder used in this study

The composition used for preparing the blends and the corresponding coding are summarized in Table 1. The percentage of raw clay and organoclay listed in Table 1 is with respect to HDPE, while the percentage of silane is with respect to the organoclay content.

Preparation of Blow-Molded Containers

In this study, blow-molded containers of capacity 10 and 22 liters were made of HDPE, HDPE/blended clay composite, and HDPE/modified-nanoclay composite, by using Battenfeld blow molding machine.

Evaluation of the Prepared Nanocomposites

Elemental mapping-energy dispersive x-ray spectroscopic (EDX) analysis

The elemental composition of the different samples prepared in this study and the distribution of clay in the polymer matrix was analyzed by using EDX (JEOL JSM

6380 LV) equipped with INCA X-Sight (Oxford instruments), operated at an accelerating voltage of 20 kV and energy resolution of 85 eV. The samples under study were kept at a distance of 10-15 mm from the detector, at a takeoff angle of 35°. In order to prevent false elemental identification, special care was taken to attach the sample to the sample holder in such a way that they are actually positioned outside the sample holder. The EDX-SEM elemental mapping analysis was carried out on cryogenically broken samples, sputter coated with platinum (JEOL, JFC 1600, auto fine Coater) prior to the analysis. This was carried out to minimize the effects of electrostatic charging. The EDX spectra thus obtained were mapped for aluminum and silicon atoms in the clay platelets.

Scanning electron microscopy analysis

Morphological analysis of the cryogenically broken samples was performed using field-emission scanning electron microscope (JEOL JSM 6380LV INCA X-Sight), operated at an accelerating voltage of 20 KV. Prior to analysis, the surface of the samples was coated with platinum (JEOL, JFC 1600, auto fine Coater), in order to minimize the effects of electrostatic charging.

Melt Flow Index (MFI)

The MFI of HDPE and its composites with organoclay and raw clay were measured as per ASTM 1238 standard by using a MFI tester (Poly Plast, India). In the typical experiment, the MFI of HDPE and HDPE/clay nanocomposites was measured at 190°C at a pressure of 2.16 kg. The MFI value was determined by averaging the values of 10 readings.

Tensile strength and elongation at break

The tensile strength of the nanocomposites was measured as per the ASTM D638 standard (type 4) using universal testing machine (Hounsfield, UK), at a crosshead speed 100 mm/min with a load of 5 kN, maintaining a gauge length of 25 mm. The reported tensile strength was determined by averaging the values of five samples.

Impact strength

The impact strength of the HDPE/clay nanocomposites was measured as per the ASTM D256 standard, using an impact tester (CIPET). The notched samples for the Izod impact strength were prepared with a special notch cutting tool, using a two-joule energy hammer at the striking velocity of 3.46 m/sec. The average of five readings has been reported as the impact strength of the sample.

Barrier property of blow-molded containers

The barrier property of the blow-molded containers was evaluated by using two different hydrocarbon fluids, namely, AR grade xylene and MG91 gasoline. In the typical experiment, the weight loss of xylene was monitored in 10 liter capacity blow-molded containers for up to 21 d and 180 d at 23 and 50°C. In case of MG 91 Gasoline, the weight loss

was monitored in 22 liter capacity blow-molded containers for up to 180 d at 23 and 50°C. Four different types of blow-molded containers were included in the study, namely, HDPE, HDPE/clay composite, HDPE/organoclay nanocomposite, and HDPE/silane-treated organoclay nanocomposite.

RESULTS AND DISCUSSION

Energy Dispersive X-Ray Spectroscopy Analysis

Figures 2(a), 2(b), and 2(c) show the EDX elemental mapping of H_5rC , H_5mC , and H_5mC_5S , respectively. As mentioned earlier, the samples were broken under liquid nitrogen and the broken surface was coated with platinum using a vacuum coater. The green and red dots in the EDX spectra correspond to the aluminum and silicon atoms, respectively, which in turn represent the dispersion of clay platelets in the polymer matrix. The agglomerated bunches of dots seen in the EDX spectra indicate the presence of flocculated clay tactoids. In particular, the EDX spectrum of HDPE/clay composite shows high level of agglomerated bunches of dots, indicating the poor dispersion of clay platelets in the polymer matrix. On the other hand, the EDX spectrum of HDPE/surface-modified clay composite showed improvement in the dispersion of dots and reduction in the agglomerated bunches of dots, implying better clay dispersion and high exfoliation level of the clay platelets. It is a well-known fact that the performance and properties of the nanocomposite mainly depend on the dispersion of nanoclay. Therefore, a nanocomposite with higher exfoliated structure of clay platelets is expected to exhibit better performance. [18, 19, 20, 21, 22] The surface treatment of organoclay with silane increases the interface strength, thereby facilitating better dispersion of the clay platelets. This in turn improves the overall performance of the prepared nanocomposite.

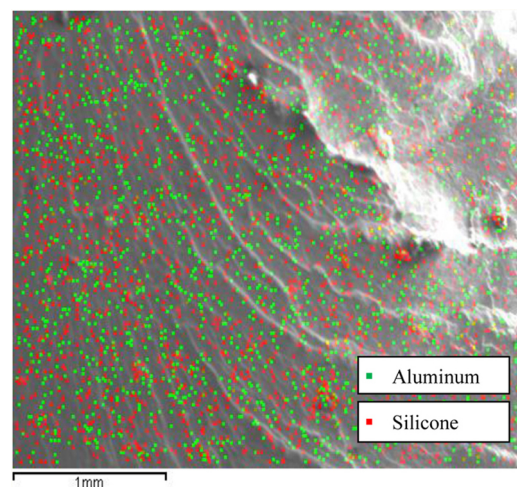


Figure 2: (a). EDX elemental mapping analysis of H_5rC