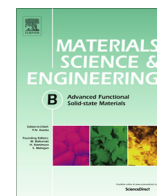




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# Investigating the mechanical and barrier properties to oxygen and fuel of high density polyethylene–graphene nanoplatelet composites

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## ABSTRACT

Graphene nanoplatelets (GnP) of different sizes were investigated for their ability to modify high density polyethylene (HDPE) for potential fuel system applications, focusing on compounding via melt mixing in a twin-screw extruder. Mechanical properties, crystallinity of the polymer, and permeation to oxygen and fuel were assessed as a function of GnP concentration. The surface of GnP acted as a nucleation site for the generation of HDPE crystallites, increasing the crystallinity. The flexural properties were improved, clearly influenced by platelet size and quality of dispersion. A sharp, 46% decrease of the impact resistance was observed, even at low GnP concentration (0.2 wt.%). With a 15 wt.% GnP-M-15 (platelets with a 15  $\mu\text{m}$  diameter), a 73% reduction in oxygen permeation was observed and a 74% reduction in fuel vapor transmission. This correlation was similar throughout the GnP concentration range. The smaller diameter platelets had a lesser effect on the properties.

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## 1. Introduction

Polymer composites are a growing area of interest, especially for the auto industry, for light weighting and fuel efficiency purposes. In particular, some thermoplastics like polyethylene or polypropylene offer low cost and ease of processing (via injection molding or extrusion), and adding fillers can improve their thermo-mechanical properties, thermal or electrical conductivity, or generate better barrier properties [1]. The properties of a composite material tend to not only depend on the properties of its constituents (matrix and filler) but also on the properties of the interface/interphase between them [2]. This is particularly true for nano-composites, as the surface area of the interface increases with a size reduction of the filler (at iso-volume concentration). Recently, the development of particles with an anisotropic shape (like rods, tubes, platelets, or even stars) has triggered a high level of interest because of the possibility to generate anisotropic properties, usually at low concentration [3].

Auto manufacturers are constantly looking for an improvement in vehicle fuel economy. This can be done by light weighting, but also by reducing the fuel evaporative emissions (hydrocarbon vapors that escape from a vehicle fuel system), which requires the use of light materials with optimal barrier properties for the manufacture of fuel lines and fuel tanks. Currently, fuel tanks have

a layered structure made of a film with high barrier properties, such as polyamide 6 (PA 6) or ethylene vinyl alcohol (EVOH), sandwiched between layers of a semi-crystalline thermoplastic such as high density polyethylene (HDPE). An adhesive layer of maleic anhydride grafted polypropylene insures good adhesion between them. Producing a fuel tank with a layered structure is not straightforward at the industrial scale, and EVOH is a relatively expensive thermoplastic that is sensitive to the ambient humidity level, as moisture greatly affects its barrier properties [4]. Moreover, while EVOH is an excellent barrier against diffusion of pure hydrocarbon based fuel, the barrier properties are reduced with fuel blends containing ethanol which are slated for increases. Standards set by the California Air Resources Board for low emission vehicles (LEV) state that no more than 2 g of hydrocarbons can be emitted during 24 h per car. However, future regulations for LEV II decrease that amount to 0.5 g, and even stricter partial zero emissions reduce the value to 0.054 g. Fuel tank designs will need to be modified to reach these standards.

The advent of platelet shaped nanoparticles offers a promising new alternative to the multilayer approach. Because of their impenetrable nature and their platelet morphology, the addition of platelet shaped nanoparticles forces gases that penetrate the polymer to follow a tortuous path, which slows down their diffusivity, as shown in Fig. 1. For example, nanoclay based polymer composites have been extensively investigated, with a large focus on montmorillonite composites. Nanoclays are layered silicates with Van Der Waals attraction forces between the layers, which

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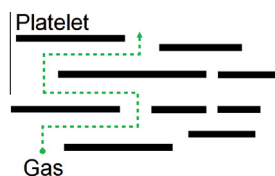


Fig. 1. Tortuous path created by platelet shaped nanoparticles in a polymer matrix.

can be overcome relatively easily in order to intercalate the polymer matrix between the layers [5–7]. Sharp improvements of the toughness of polypropylene have been reported with the addition of nanoclays [8,9], as well as an improvement of the barrier properties of the hosting polymer matrix [10,11].

Like layered silicates, graphene possesses a platelet-like structure, which induces the same mechanism regarding barrier properties. Additionally, graphene has high electrical and thermal conductivities, whereas layered silicates do not. This means that graphene-based nanocomposites could offer more versatility if the concentration, dispersion and orientation of the graphene platelets are such that they lead to the generation of a percolated network [12]. While manufacturing pristine, highly crystalline, single layer graphene can be accomplished in a bottom-up approach via chemical vapor deposition [13], this process is not applicable for the production of industrial quantities at a cost effective price. Graphene nanoplatelets (GnP), made of a few stacked layers of graphene, can be produced in a cost effective, industrially robust process using a top down approach by intercalating bulk graphite with sulfuric acid, rapidly heating to induce expansion and then mechanically or ultrasonically reducing the GnP size [14]. GnP produced by this method contains oxygen functional groups at the edges of the platelets, with relatively few defects on the surface. The GnP thickness is less than 10 nm, and their diameter can be controlled between several hundred of nanometers up to 80  $\mu\text{m}$ .

Previous investigations with this material has focused on its combination with thermoplastics like polypropylene [15], low [16] and high [17] density polyethylene, and thermosets such as epoxy [18] or vinyl ester resins [19], but the main focus of was mechanical reinforcement and electrical and thermal conductivity. The barrier properties of similar systems, especially regarding fuel, have not been investigated extensively. Literature has shown that at the same loadings of GnP and nanoclays, the GnP composites will exhibit better permeation resistance to oxygen [20]. Recent studies have shown that incorporating graphene materials at extremely low concentrations of less than 1 wt.% has actually resulted in an increase in permeation due to voids at the interface of the filler and the polymer, however higher concentrations would be expected to result in enhanced barrier properties [21].

Assessing the barrier and the mechanical properties of HDPE-GnP composites as an alternative material for fuel tanks is the focus of this investigation.

## 2. Materials and methods

### 2.1. Materials

High density polyethylene (HDPE) was supplied by INEOS Olefins and Polymers USA under the trade name K46-06-185 and was used as received. It has a density of  $0.946 \text{ g}\cdot\text{cm}^{-3}$  (ASTM D4883) and a melt index ( $190 \text{ }^\circ\text{C}/21.600 \text{ g}$ ) of  $4.2 \text{ g}/10 \text{ min}$  (ASTM D1238). Three grades of graphene nanoplatelets (GnP-M-15, GnP-M-5 and GnP-C-750) were obtained from XG Sciences (Lansing, Michigan, USA). Grades GnP-M-15 and GnP-M-5 have a surface area of  $120\text{--}150 \text{ m}^2\cdot\text{g}^{-1}$ , an average thickness of 6 nm, and an average diameter of  $15 \text{ }\mu\text{m}$  and  $5 \text{ }\mu\text{m}$ , respectively. Grade GnP-C-750

has a surface area of  $750 \text{ m}^2\cdot\text{g}^{-1}$ , an average thickness of 6 nm, and a diameter comprised between  $300 \text{ nm}$  and  $1 \text{ }\mu\text{m}$ . All samples were heated for 1 h at  $450 \text{ }^\circ\text{C}$  in an air circulating oven to remove any trace volatile compounds remaining from the manufacturing process.

### 2.2. Nanocomposite processing

A co-rotating, twin-screw, DSM 15 cc extruder was used to process all of the nanocomposites. The melt temperature was set to  $210 \text{ }^\circ\text{C}$  and the twin-screws were rotating at  $40\text{--}50 \text{ rpm}$ , maintaining a constant shear force of approximately 6000 N. HDPE and GnP, in the dry state at room temperature, were manually mixed by hand and then transferred to the extruder and allowed to mix for 5 min. The composite was then transferred to a Daga Micro-injector. The temperature holding barrel for the injector was set to  $210 \text{ }^\circ\text{C}$ , the mold was set to  $110 \text{ }^\circ\text{C}$  and the pressure for the injection molding was 150 psi (1.0 MPa). Different molds were used to manufacture the flexural and Izod impact resistance test specimens. Neat HDPE and HDPE-GnP composites were processed under the same conditions. The range of GnP concentration was varied from 0.2 wt.% up to 30 or 40 wt.%, depending on the viscosity of the melt. Film samples for oxygen permeation testing were made by compressing two flexural specimens together between two mirror-finished platens, heated to  $180 \text{ }^\circ\text{C}$  and maintained at  $180 \text{ }^\circ\text{C}$  for 5 min in a heated Carver press. A pressure of 550 psi was applied. The whole assembly was contained within a vacuum bag made with a polyamide film during pressing to avoid the generation of bubbles in the HDPE-GnP film. This resulted in films with thicknesses from 150 to  $200 \text{ }\mu\text{m}$ . The same procedure was used to make films for fuel permeation testing, by compressing two Izod test specimens under vacuum. The thickness of those films was typically higher, between 0.5 and 1.0 mm.

### 2.3. Testing procedures

A UTS SFM-20 testing machine was used to measure the flexural properties of the composites according to ASTM D790 using a 100 lb load cell and a displacement speed of  $0.05 \text{ in}\cdot\text{min}^{-1}$ . The thickness to span ratio was 1/16. 10 specimens were tested for each composite system.

Izod impact specimens were notched with a motorized tooth notcher 24 h prior to testing, and then tested with a TMI impact apparatus and a 1 lb hammer (ASTM D256). 10 specimens were tested for each composite system.

The crystallinity level was measured by Differential Scanning Calorimetry (DSC) with a TA Instruments Q2000 differential scanning calorimeter. Samples were first heated with a rate of  $20 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$  to  $160 \text{ }^\circ\text{C}$ , and held at  $160 \text{ }^\circ\text{C}$  for 5 min before being cooled down to  $40 \text{ }^\circ\text{C}$  with a rate of  $20 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ . This erased any thermal history of the specimens before assessing the influence of the GNP particles on the crystallinity of HDPE. The samples were then reheated to  $160 \text{ }^\circ\text{C}$  with a rate of  $20 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ . The crystallinity of the HDPE matrix can be calculated according to Eq. (1):

$$x\% = \frac{1}{1 - \text{wt.}\% \frac{\delta H_m}{\delta H_m^0}} \quad (1)$$

where  $x\%$  is the crystallinity,  $\delta H_m$  is the melting enthalpy of the sample, and  $\delta H_m^0$  is the theoretical melting enthalpy of pure crystalline HDPE, which is estimated by Mirabella et al. to be  $288 \text{ J/g}$  [22]. Three specimens were tested for each composite system.

Permeation to oxygen was measured using a Mocon OX-TRAN 2/20 ML. Films were conditioned for 6 h prior to testing. The resulting oxygen transmission rate was normalized with respect to film thickness.

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