PROCESSING METHODS OF HIGH DENSITY POLYETHYLENE-EXFOLIATED GRAPHENE NANOPlateLET NANOCOMPOSITES FOR AUTOMOTIVE FUEL TANKS APPLICATIONS

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Abstract
Melt mixing followed by injection molding was used to manufacture high density polyethylene (HDPE) – exfoliated graphene nanoplatelet (GnP) nanocomposites. In order to further enhance the composite properties (mechanical and barrier), different processing techniques were explored including microlayer coextrusion and solution mixing with sonication followed by extrusion. Multiple modifications to the nanocomposite constituents were investigated, including cryo-milling of the HDPE pellets and coating of the platelets with a wax or polyolefin elastomer before extrusion processing. In each case, mechanical properties (Izod impact and flexural) and barrier properties (permeation to oxygen) were assessed to evaluate the relationships between morphology, processing and properties.

Results showed that through simple melt mixing of HDPE and GnP, there was a clear increase in stiffness, a decrease in Izod impact resistance, and a 50% decrease to both oxygen and fuel permeation with a 5 wt. % GnP composite. Microlayer coextrusion yielded a high alignment of the nanoplatelets in the direction of the flow and resulted in improved permeation resistance at low GnP concentration, but did not result in a further improvement of barrier properties at concentrations above 5 wt. %. Cryo-milling the HDPE pellets into a powder resulted in a minor decrease in mechanical properties and a 35% decrease in oxygen permeation. A wax coating on the platelets before melt extrusion resulted in an increase in Izod impact resistance, a decrease in flexural modulus and an increase in oxygen permeation. A polyolefin elastomeric coating of the GnP resulted in retaining the flexural properties and with a slight improvement to the Izod impact resistance and the barrier properties.

I. Introduction

Lightweight composites with enhanced barrier properties offer a potential way to reduce the weight and increase the fuel efficiency of automotive vehicles when used for the manufacture of the fuel tank and line system. Currently polymer fuel tanks are made using a layered structure with a barrier polymer such as ethylene vinyl alcohol (EVOH) sandwiched between high density polyethylene (HDPE). It is necessary to have an EVOH layer because oxygen and fuel can easily permeate through HDPE, causing fuel loss. In adding Graphene nanoplatelets (GnP) to the HDPE matrix, a tortuous path is created due to the large aspect ratio of the platelets as
depicted in Figure 1. This idea has previously been studied with nanoclays and resulted in a significant decrease in the transmission of oxygen through the composite [1].

![Platelet Gas](image)

**Figure 1. Tortuous path created by GnP in a polymer matrix.**

Previous work has been completed on the addition of GnP to HDPE via simple melt extrusion and injection molding of composites, which resulted in a reduction in the oxygen transmission rate of up to 55% with a 7.5%wt. GnP composite, but a decrease of 50% in impact resistance [2]. In order to be viable for use in fuel tanks, the impact resistance loss needs to be recovered and the barrier properties further enhanced, leading to multiple process techniques being explored. An important factor for optimal barrier properties is the alignment of the platelets. A microlayer co-extrusion die offers a way to achieve ideal alignment in an extrusion process [3]. In this process, the die takes a stream of polymer and cuts it in half vertically, repositions the two ribbons into a vertical stack, then compresses the stack to the original thickness, creating a layered system. Each stage effectively doubles the number of layers in the system, as presented in Figure 2. Repetition of the process results in multiple layers, and should result in a high alignment of the GnP.

![Cut in half Stack and press](image)

**Figure 2. Microlayer co-extrusion process.**

Another major factor for property enhancement is the dispersion of the platelets. It has been previously shown that coating the GnP in a low molecular weight wax improves the dispersion in a polyolefin matrix [4]. Alternatively, processing the HDPE and GnP through a solution based mixing stage could improve the dispersion. The large difference in the coefficient of thermal expansion between the GnP and HDPE could create voids during the cooling process, which may be eliminated by coating the GnP with an elastomer [5]. Coating the GnP with an elastomer could also help to recover a portion of the lost impact resistance when GnP is added to the matrix as the elastomer would help absorb energy and undergo plastic deformation.

**II. Materials and Methods**

**II.1 Materials**

HDPE (grade K46-06-185) with a density of 0.946 g.cm\(^{-3}\) was supplied by INEOS Olefins & Polymers USA in pellet form and used as received. Two grades of Graphene nanoplatelets (GnP) from XG Sciences (Lansing, MI, USA) were used – M-15 and M-25. Both grades have an average thickness of 6 nm and surface area of 120-150 m\(^2\).g\(^{-1}\), however their average diameters...
are 15 and 25 microns respectively. The platelets were heated at 450 °C in air for one hour to remove any volatile compounds remaining after the manufacturing process. Two grades of wax were used to coat the platelets, a low molecular weight (500 g.mol\textsuperscript{-1}) paraffin wax provided by Sigma Aldrich and a higher molecular weight (800 g.mol\textsuperscript{-1}) wax (Sasolwax H1 by Sasol) more stable at higher temperatures. A polyolefin ethylene-octene copolymer elastomer (Engage 8200 provided by Dow Chemicals) was also used as a coating.

II.2 Manufacturing Processes

Multiple manufacturing processes were used and compared. For melt extrusion a co-rotating, twin screw DSM Micro 15 cc extruder was used, with the melt temperature of the HDPE at 210 °C. Materials were allowed to mix for 5 minutes at 6000 N of shear force (40-50 rpm) and then transferred to a micro-injector barrel with the temperature also set to 210 °C. The melt was then injection molded into the desired mold, which was heated at a temperature of 110 °C, with a pressure of 150 psi.

As a pre-processing step, solution mixing was investigated with the GnP dispersed in xylene via light sonication (20W) for 30 minutes, followed by the addition of HDPE pellets and heating the solution to boiling for 1 hour under reflux conditions with magnetic stirring. Upon cooling to room temperature, the composite precipitated out and then was dried under vacuum at 80 °C overnight and then processed through the DSM. A second approach consisted of cryo-milling the HDPE pellets using liquid nitrogen and a Mikro-Bantam mill with a 0.02 inch filter. Ultrasonication of the HDPE powder and GnP was done in xylene to coat the HDPE particles with GnP, using a low power setting (20W) to avoid reduction in the platelet size.

A third pretreatment step investigated was coating the platelets. The coating material was dissolved in xylene and then GnP was dispersed using mild sonication (20W). This was repeated for the two olefin waxes and the polyolefin elastomer. The three resulting dispersions were then dried at 80 °C overnight in a vacuum oven and then processed in the DSM microextruder at various concentrations with HDPE.

Large scale extrusion was performed using a Leistritz extruder with 25 mm co-rotating twin screws and a module multi-layer slit die provided by Premier Dies Corporation, which yields a 16 layer structure. The extruder and die were set to 200 °C with a screw rotation speed of 20 rpm and yielding a melt pressure from 2000-2300 psi depending on the GnP concentration. Upon exiting the die, the extrudate was cooled with a 3-roll chill stack set to 100 °C, and finally collected on a spool at a rate of 2 feet per minute.

II.3 Mechanical Testing

A UTS SFM-20 from United Calibration Corp was used to measure flexural properties according to ASTM standard D790. A 100 lb. load cell was used with a thickness to span ratio of 1/16. The crosshead speed was a constant 0.05 inch.min\textsuperscript{-1}. Izod impact resistance was measured following ASTM D256. A 1 lb. hammer was used with TMI impact equipment. Specimens were notched after injection molding and allowed to relax for 24 hours before testing.

II.4 Permeation of Oxygen

Thin films of the composite were made using a heated Carver Press. The press was heated to 210 °C and materials were pressed between mirror-finished steel plates under vacuum with the use of a vacuum bag. For injection molded composites, two flexural samples were used to make the films. HDPE powder obtained by the cryo-milling and sonication was pressed directly. The samples obtained with the multi-layer slit die did not need to be pressed with the Carver press
as a film was directly produced. The films were tested with a Mocon OX-TRAN 2/20 ML to determine the oxygen transmission rate through the sample. The reported rate was then normalized to the thickness of the sample, which was measured with calipers before testing.

II.5 Morphology of composites with Scanning Electron Microscopy

The structure of the composites, coating of the HDPE powder and coating of the GnP were characterized by Scanning Electron Microscopy (SEM) with a Zeiss EVO LS25 microscope under high vacuum using secondary electron mode. A 3 nm layer of tungsten was deposited on the surface using a Leica EM MED020 sputter coater to eliminate sample charging.

III. Results and Discussion

III.1 Microlayer Co-extrusion Composites

In previous work the baseline for melt extrusion mixing of HDPE and GnP was investigated [2]. While enhanced barrier properties were achieved, further improvement is necessary for the use of a HDPE-GnP composite in fuel tanks and fuel lines. Since it was previously established that the oxygen and fuel transmission rates follow a similar pattern, fuel permeation testing was omitted to save time [2]. One problem in the HDPE-GnP composites is the lack of perfect alignment of the platelets. When using a microlayer co-extrusion process, the alignment of the platelets would theoretically be ideal. Films of 0, 2, 5, 10 and 15 weight percent GnP-M-25 were produced. Figure 3 shows the comparison in morphology for a film compressed from a thicker specimen to a desired thickness compared to a microlayer co-extrusion film. In the compressed film, there is noticeable misalignment of the GnP with respect to the flow direction. In the microlayer co-extrusion film, there is a very high degree of alignment of the GnP, exactly as theorized. Figure 4 shows a comparison of the oxygen transmission rates corresponding to pressed films made with DSM specimens and the films made with microlayer co-extrusion. When using the multilayer die, an increase in the transmission rate for the neat polymer was noticed, probably because of a difference in crystallinity. However the relative improvement of the barrier properties at a weight concentration of 2% was much better. As the weight content of GnP increased, both processes led to similar values of the transmission rate. This suggests that at low concentrations, the alignment of the GnP is very important. However, the enhancement of the barrier properties at high concentrations is still limited by the quality of dispersion, which is a common problem for many carbon based nanoparticles [6].

![Figure 3. Comparison of the morphology between films made using microlayer co-extrusion film and a Carver press film from injection molded samples.](image)
III.2 Solution dispersions of HDPE and GnP-M-15 in xylene

In order to explore better dispersion of the GnP in the HDPE, a solution dispersion approach was investigated. Since boiling xylene dissolves HDPE well, addition of the GnP to this solution may yield a better dispersion. Concentrations of 2, 5, and 10 weight percent of GnP-M-15 in HDPE were made with this method. Once the dispersion was dried to remove all of the xylene, it was processed though the DSM for the production of flexural and impact specimens. Two films were produced, one via compressing two flexural samples in the Carver press and one through compression molding of the material obtained by solution dispersion with no further processing. Figure 5 shows the mechanical properties of the solution dispersion (red) along with the previously established regular melt mixing values (blue). The flexural properties remained similar for all concentrations for both modulus and strength. At a weight content of 10% GnP, a slight improvement in the modulus was observed. There is an improvement in the impact resistance ranging from 11% to 24% depending on concentrations, suggesting that there may be a slight improvement in the overall GnP dispersion throughout the matrix. The results corresponding to oxygen transmission can be seen in Figure 6. When processed through the DSM, the solution dispersion yields similar results as the melt mixing in terms of oxygen transmission rate. However, as shown with the 7.5% wt. GnP data, if the solution dispersion is compression molded directly after drying, there is a 40% reduction in the oxygen transmission rate compared to DSM mixing. When the material is reprocessed through the DSM, the major advantages of the solution mixing are lost due to misalignment, agglomeration and size reduction of the platelets.
Figure 5. Mechanical properties HDPE-GnP-M-15 composites: solution dispersion versus melt mixing
**III.3 Cryo-milled HDPE-GnP-M-15 composites**

In order to improve the platelets dispersion and consequently the barrier properties of the composite, a cryo-milled HDPE was used instead of its pellet form. Two different processing techniques were employed. Melt extrusion was done with the powder to make flexural and impact specimens, and the Carver press was used to compress a film from two flexural specimens. Additionally, sonication of the HDPE powder and GnP in xylene was investigated, and a compression molded film was made from the dried powder. The comparison of the flexural properties obtained with the melt mixing using HDPE powder (red) or pellet (green) form is displayed in Figure 7. Compared to a use of HDPE in the pellet form, there was a decrease of the flexural modulus and strength; however it was still higher than the neat pellet resin. There is a negligible difference in the IZOD impact resistance between the powder and the pellet form of HDPE. In terms of the barrier properties, sonication and compression molding of HDPE powder and GnP-M-15 yielded the same results as compressing a film from injection molded flexural samples. Both ways of processing the HDPE powder yielded a 35% reduction in the oxygen transmission rate through the composite when compared to the melt extrusion of the HDPE pellet composites, as shown in Figure 8, and a 65% reduction compared to the neat resin. Little additional improvement was found with the sonication process due to lack of uniformity in the GnP coverage on the powder particles and agglomerations of the platelets were still detected, as seen in the SEM images of Figure 9. Methods for overcoming these problems are currently being investigated.

*Figure 6. Oxygen transmission rates of through HDPE-GnP-M-15 composites: solution dispersion versus melt mixing.*
Figure 7. Mechanical properties of the melt extrusion of 5% wt. GnP-HDPE powder versus GnP-HDPE pellets.
Figure 8. Barrier properties of the sonication and melt extrusion of 5% wt. GnP and HDPE powder composites compared to GnP and HDPE pellet composite.

Figure 9. SEM images of HDPE powder coated with GnP-M-15 after sonication in xylene and drying.

III.4 Wax coating the GnP

It has previously been shown that a wax coating can increase the dispersion of carbon nanoparticles in a polymer matrix due to the better interaction between the wax and matrix, and similar results should be expected [4]. Two waxes compatible with HDPE were used: a paraffin wax produced by Sigma Aldrich and a low molecular weight polyethylene wax produced by Sasol that is more stable at the melt mixing processing temperature. The ratio of GnP to was was 80:20. After drying, the coated GnP platelets were processed with HDPE pellets using the same DSM procedures. The resulting mechanical properties are shown in Figure 11. A significant decrease of up to 26% in flexural strength and 37% in modulus were observed for 5% weight paraffin coated GnP samples relative to the unmodified GnP. The Sasol wax also yielded
a decrease, but was better than the paraffin wax with only a 15% decrease in flexural strength and 19% decrease in flexural modulus. However, a noticeable increase in impact resistance of up to 26% was measured for both waxes. The decrease in flexural properties may be due to the wax coating reducing the reinforcing effect of the GnP. The load transfer from the HDPE matrix to the GnP may not be as effective. On the contrary, the presence of the wax allows for some plastic deformation under the high speed loading during impact testing. This can be seen in SEM images of the impact fracture surfaces presented in Figure 10. The “cell structure” existing in the HDPE – GnP composite that was previously reported and is re-presented in part d was still present in parts a-c, but there was noticeable plastic deformation as well, revealed by the elongated filaments of matrix protruding from the surface. This explains the increase in impact resistance. Figure 12 shows that there is minimal effect on the barrier properties with the Sasol wax. An increase of the transmission rate of up to 45% was even obtained with the low molecular weight paraffin wax. While the wax coating helped improve the impact resistance, it did not have a positive effect on the barrier properties.

Figure 10. SEM images of the fracture surface after Izod impact test a) overview of 5% wt. Sasol wax coated GnP-HDPE, b) higher magnification of same composite, c) “cell” structure and plastic deformation of composite, and d) 5% wt. unmodified GnP-HDPE composite.
Figure 11. Mechanical properties of the 5% wt. wax coated GnP – HDPE composites.
Figure 12. Barrier properties of the 5% wt. wax coated GnP-M-15 and HDPE composites.

III.5 Elastomer coating the GnP

Elastomer coating of GnP was investigated as a potential way to overcome the difference in the coefficient of thermal expansion between the GnP and HDPE, as well as a possible route to improving impact resistance when GnP is added to the HDPE matrix. Produced in a similar way to the wax coated GnP-HDPE composite sample, the elastomer (Engage 8200 from Dow Chemical) was deposited as the surface of the GnP particles by sonication in xylene at a ratio of 1:1 and then dried. The corresponding mechanical properties are shown in Figure 13. A decrease relative to the unmodified platelets was observed regarding the flexural properties. However, the values were still equivalent to those of the neat HDPE. The impact resistance was positively influenced by the elastomeric coating, yielding a 13% increase at a loading of 2% wt. elastomer coated GnP and a 34% increase at a 5% wt. loading. The reason for this increase is the increased amount of plastic deformation present when a higher amount of elastomer is used, which can clearly be seen in Figure 14. The “cell structure” with a platelet present at the center of each cell is visible, and the extensive plastic deformation resulting from the addition of the elastomer is clearly seen, especially compared to part d of Figure 11. As shown in Figure 15, the barrier properties are slightly improved compared to the unmodified GnP nanocomposites, but were not as improved as cryo-milled composites or compressed solution dispersion material, suggesting that the dispersion is only marginally improved with the polyolefin elastomer coating.
Figure 13. Mechanical properties of the elastomer coated GnP-M-15 and HDPE composites. Note: the weight percent mean there is equal parts GnP and elastomer. i.e. 5% GnP, 5% elastomer, and 90% HDPE.
Figure 14. SEM images of the fracture surface after Izod impact test a) overview of 5% wt. elastomer coated GnP in HDPE, b) higher magnification of same composite, c) and d) “cell” structure and plastic deformation of composite.

Figure 15. Barrier properties of the elastomer coated GnP in HDPE.
IV. Conclusions

This study aimed at improving the barrier properties of HDPE-GnP nanocomposites, obtained by melt mixing and injection molding, by using alternative manufacturing processes and engineering the surface of the GnP particles. Additionally, the influence of such changes on the mechanical properties was examined as well. While each method yielded positive results, there were drawbacks associated with each. With a microlayer co-extrusion process, a high alignment of platelets was achieved and a significant increase in barrier properties at low GnP concentrations was measured, but as the GnP content increased, the same level of barrier properties was approached regardless of the processing method. This was attributed to agglomeration issues. When using the solution mixing process, the flexural properties were identical to melt mixing, but the Izod impact resistance was improved. If the dried solution mixture of HDPE/GnP is pressed into a film, a significant decrease in the oxygen transmission rate is obtained. However, once processed through the DSM, the benefits generated by the solution processing were nullified. Cryo-milling the HDPE into a fine powder resulted in an increase in barrier properties, had a negligible effect on impact resistance and decreased flexural properties. A wax coating on the GnP before melt processing with HDPE resulted in an improved impact resistance, but a negative impact on the barrier and flexural properties. An elastomeric coating of the platelets also yielded improved impact resistance and a marginal improvement in barrier properties, but a decrease in flexural properties. Overall, obtaining outstanding barrier properties without affecting the mechanical properties of HDPE-GnP nanocomposites using melt mixing extrusion and injection molding processes is very challenging. Current research is focused into combing a few of these methods to create synergistic effects.

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VI. Bibliography


