MECHANICAL, THERMAL AND ELECTRICAL PROPERTY ENHANCEMENT OF GRAPHENE-POLYMER NANOCOMPOSITES

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Abstract

In this work, NanoXplore’s proprietary graphene nanoplatelets, heXo-G V20, are melt-extruded into thermoplastics LLDPE, HDPE and TPU. Graphene is shown to effectively increase the stiffness and the strength of a matrix TPU. The flexural and tensile moduli increase with loading levels of graphene whereas the tensile strength increases at low loading levels, but does not further increase at higher graphene concentrations.

A ten fold increase in thermal conductivity was achieved by adding heXo-G V20 graphene to LLDPE matrix. The thermal conductivity percolation threshold was reached at 10% loading. At 1% loading of graphene the onset of the decomposition temperature and maximum weight loss temperatures were shifted by about 50°C, significantly improving the thermal stability of the PE matrix.

Fourteen orders of magnitude increase in electrical conductivity of HDPE was obtained at 30% loading of graphene.

Excellent EMI shielding of 40 dB was achieved with 20 wt% addition of graphene in a TPU matrix.

Introduction

Graphene, a 2D monolayer, hexagonal lattice of carbon, has gained a reputation for its outstanding properties such as mechanical strength, thermal and electrical conductivity. Translating these properties into real-life applications however has been difficult with the key challenge being the large-scale production of high-quality low-cost graphene (Nazarpour, 2016). Despite this, more and more products based on graphene are starting to appear and many promising applications are expected to make their way into the market in the next couple of years. Notable applications of graphene which provide a value-added solution are in EMI shielding, geothermal pipes, thermal interface materials and structurally reinforced 3D printed and automotive parts.

There is an increasing demand to produce light polymer composites for structural applications such as automotive and aerospace. High strength to weight ratio, toughness, corrosion resistance and creep resistance is achieved by adding fillers such as glass fiber, carbon fiber and carbon black. In addition, enhanced mechanical strength, improved thermal and electrical conductivity of polymer composites are highly desired. Polymers are not inherently thermally conductive with thermal conductivity values between 0.1 and 0.3 W/m·K. Increasing the thermal conductivity of polymers, however will allow, for example, to partially replace metals and ceramics in heat transfer devices which can lead to considerable cost and energy savings. Adding thermally conductive additives such as boron nitride or graphene is a method to increase the thermal conductivity of polymers, while retaining their mechanical properties and flexibility.

Most plastics are inherently electrically insulating materials. However, adding carbon-based additives such as carbon black and carbon fiber to polymers can impart antistatic, electric dissipative or conductive properties. Examples include automotive parts which can be painted with electrostatically or electrically conductive plastics as jacket covers for high-power transmission cables. Recently, it has been shown that carbon nanotubes and graphene, will impart higher electrical conductivity to plastic compounds in comparison with the conventional carbon-based additives (Gkourmpis, 2016).

Plastics with conductive fillers can also be used for EMI (Electromagnetic interference) shielding. At the moment, the most common way to shield electromagnetic radiation is by reflection from the metallic sheets. Such shielding is known as the Faraday cage effect operating from DC to high frequency. However, the problem associated with these systems is poor mechanical flexibility, bulkiness, corrosiveness and poor tuning of shielding effectiveness. An alternative EMI shielding solution is
the loading of a polymer matrix with a conductive filler such as graphene (Thomassin, 2013).

Materials and Methods

Materials

The graphene used is NanoXplore’s proprietary heXo-G V20 with the following characteristics: 20 nm thickness and 50 µm average flake size.

The polymer resins used are listed in Table 1.

Table 1. Trade name and description of thermoplastic resins

<table>
<thead>
<tr>
<th>Polymer matrix</th>
<th>Trade name</th>
<th>Description</th>
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<tbody>
<tr>
<td>LLDPE</td>
<td>NovaPol PI-2024-A</td>
<td>Injection molding resin</td>
</tr>
<tr>
<td>HDPE</td>
<td>HDPE 5502</td>
<td>Blow molding resin</td>
</tr>
<tr>
<td>TPU</td>
<td>Urethane Texin 1209</td>
<td>Aromatic polyether based</td>
</tr>
</tbody>
</table>

Methods

Compounding of thermoplastics

The heXo-G V20 and TPU, LLDPE and HDPE thermoplastic resins were compounded in a 25-millimeter co-rotating twin screw extruder Coperion ZSK25WLE (40 L/D). The extruder was operated at 200 rpm and the barrel temperature profile of 200°C from the feeding zone to die head. The extrudates were cooled in a water bath, dried and pelletized.

Injection Molding

Tensile and flexural bars were molded using an Arburg 370A injection molding machine to test according to ASTM D638 and ASTM D790.

Characterization

Differential scanning calorimetry (DSC) was performed using a Pyris 1 differential scanning calorimeter (Perkin Elmer) with a thermal analysis controller TAC 7/DX UN under nitrogen gas. Samples were heated from 0°C to 400°C at a rate of 20°C/min.

Thermogravimetric analysis (TGA) was performed using a TA QA 500 at a heating rate of 10°C/min from room temperature to 1000°C.

Tensile tests were conducted using a Tensile Tester (Zwick Roell Z030) with a preload of 6 N according to ASTM D638 Type I. The speed of the test was 50 mm/min. Five specimens were tested for each composition.

Flexural tests were performed using a flexural tester (Zwick Roell Z030) according to ASTM D790. The loading speed was 5.08 cm/min. Five specimens were tested for each composition.

The Modified Transient Plane Source (MTPS) technique according to ASTM D7984 was used to measure the thermal conductivity.

Hot-pressed sheets with a thickness of 0.45 mm were used to measure the conductivity of the nanocomposites in three different techniques. A homemade 4-probe setup was used to measure sheet conductivity with a needle spacing of 2.6 mm. Current was applied on the two outer probes using a Keithley 237 instrument as the current source and voltage was recorded from the two inner probes by an Agilent 3458A multimeter.

A commercial dielectric spectroscopy system (Novocontrol Alpha-A analyzer) was used to measure dielectric response and bulk conductivity in a frequency range of 0.1 Hz to 300 kHz according to ASTM D150. Samples were cut in circular shape (40 mm diameter).

In addition, bulk conductivity of the samples was measured using a two-electrode setup composed of a Keithley 6517A electrometer, a Keithley 2010 multimeter and a Trek high voltage amplifier. Samples were similar to those used in dielectric spectroscopy and the applied field was from 0.1 V/mm to 5 kV/mm depending on the conductivity of each nanocomposite.

In order to characterize the EMI SE in X-band frequency, a network analyzer (Agilent N5245A) connected with WR-90 rectangular waveguide was employed. The specimens were prepared with a hot press into a rectangular mold and then placed between two parts of the waveguide. The S-parameters of each nanocomposite were achieved over the X-band frequency.
Results and Discussion

Mechanical Properties

Graphene is considered the world’s strongest material with a tensile modulus of 1 TPa and strength of 130 GPa. Also, it is considered to be an ultralight material with a weight of 0.77 mg/m² (Lee, 2008). The addition of graphene in a polymer matrix increases the modulus and this enhancement is more pronounced in elastomers and low modulus thermoplastics, which can be attributed to the large stiffness difference between polymer resin and filler (Kim, 2010).

In order to understand the influence of graphene on mechanical properties, heXo-G V20 graphene was melt extruded and dispersed in the TPU matrix. The results indicate that the addition of graphene to TPU leads to an enhancement in the stiffness and strength of the resin.

As seen in Figure 1, the tensile and flexural moduli are significantly enhanced with the addition of graphene in TPU at all loading levels of graphene. At 1% graphene loading, the tensile and flexural modulus increase by 12% and 7% respectively compared to the base resin TPU. At 5% graphene loading, there is an increase of tensile modulus of 70% and flexural modulus of 40%.

![Figure 1. Tensile and flexural modulus of graphene-filled TPU with respect to graphene loading](image)

The tensile strength, representative of the reinforcement effect, demonstrate a different trend with graphene loading. With the addition of 1 wt.% graphene, the tensile strength of the TPU matrix increases by 7 wt.%. At 5 wt.% loading, the tensile strength does not further increase and remains at 7 wt.%. This might be attributed to aggregation of graphene sheets at higher graphene loading levels due to Van der Waal interactions. The enhancement in mechanical properties is expected to be more pronounced when there is a stronger affinity of graphene and resin leading to better dispersion and preventing graphene particle aggregation.

Thermal Conductivity and Stability

In addition to the improvements in mechanical properties, thermal conductivity is also enhanced in graphene-filled composites due to the inherently high thermal conductivity of graphene and its high surface area. Graphene has over 100-fold anisotropy of heat flow between the in-plane and out-of-plane directions. The high in-plane conductivity is attributed to covalent sp² bonding between carbon atom whereas the reduction in the out-of-plane is due to the Van der Waal forces (Pop, 2012).

Pristine, high quality graphene has very high thermal conductivity which ranges from 4840-5300 W/m-K in the in-plane direction (Gkoumpis, 2016). Despite its potential, once graphene is incorporated into a polymer matrix, the thermal conduction enhancement is not as dramatic as expected. Graphene dispersion and interactions in a polymer matrix, purity and exfoliation of graphene as well as orientation of filler all play a role in the overall thermal conductivity.

In Figure 2, the out-of-plane thermal conductivity is plotted versus graphene loading levels. Upon examination, two linear relationships appear to exist, with one having smaller slope of 0.02 W/K-m-% graphene at low loading, and the other one having a higher slope of 0.04 W/K-m-% at high loading. The turning point is observed around a loading of graphene of 10 wt.%. This loading level corresponds to the percolation threshold. The maximum thermal conductivity of 2.32 W/K-m was obtained at 50 wt.% graphene, which corresponds to a ten-fold increase.
Graphene added to the polyethylene also improved the thermal stability of the matrix as measured by the thermogravimetric analysis (TGA). The onset of the decomposition temperature and maximum weight loss temperatures were about 50°C higher (data not shown here).

**Electrical Conductivity**

Similar to thermal conductivity, electrical conductivity is also very much dependent on loading level of graphene and increases rapidly when the threshold level is reached.

In Figure 3, the electrical conductivity data of graphene-filled HDPE is plotted with respect to the concentration of graphene. Moreover, different electrical characterization methods are compared. At higher graphene loading levels, there are large discrepancies between the electrical conductivity values measured by each of the methods. The four-probe method measures the in-plane electrical conductivity which is about 100 times higher than that obtained by the 2-probe method which measures the out-of-plane conductivity. The difference is due to the anisotropy of the graphene particles and their orientation. As shown in Figure 3, at low loading levels (<15 wt. %), the conductivity of the composite is essentially that of a dielectric medium and the polymer remains insulating. As the loading level is increased to 15 wt.%, a percolation threshold is achieved where the conductivity starts to increase rapidly as a function of loading level of graphene. This is when a continuous network of conductive filler is formed throughout the insulating matrix. Fourteen orders of magnitude increase in electrical conductivity of HDPE was obtained at 30 wt.% loading level.

In Figure 4, the electrical conductivity of an HDPE and LLDPE are compared with two different crystallinity values. The higher crystallinity of LLDPE of 47.5 wt% leads to a lower percolation threshold level compared to the HDPE with a lower crystallinity of 27.8 wt%.

**EMI Shielding**

Due to the dimensional structure of graphene, the percolation threshold can be achieved at low loading level which makes graphene a viable candidate for EMI shielding materials. The benefits of a conductive polymer composite include weight reduction, good
mechanical properties, corrosion resistance and design flexibility.

EMI shielding results were obtained on TPU and graphene-filled TPU plaques of 0.5 mm and 2 mm thickness for examined frequencies in the X band. The shielding effectiveness is measured in terms of reduction in magnitude of incident power upon transition across the shield. The shielding mechanisms include absorption loss, reflection loss and multiple internal reflections (Thomassin, 2013).

For a graphene loading of 5 wt% in TPU and 0.5 mm thickness, 16 dB shielding effectiveness was achieved. When the loading is increased to 20 wt% for the same thickness of 0.5 mm, 31 dB was measured. When both the loading level is increased to 20 wt% and the thickness to 2 mm, 40 dB was obtained, which corresponds to an attenuation of 99.99%. Evidently, the higher the graphene loading and thickness of TPU plaques, the more effective the EMI shielding since there is an increase in both absorption and reflection losses. More specifically, when graphene is exposed to an electromagnetic field, the dipole moments in the polymer and filler change their direction to the direction of the electromagnetic field, which leads to electromagnetic wave energy reduction. Moreover, the EMI shielding is also highly dependent on graphene dispersion (filler-polymer interaction) and alignment of graphene particles.

**Conclusions**

Graphene can be used as an added-value multifunctional additive for thermoplastics in many potential commercial applications. In this study, it was demonstrated that NanoXplore’s graphene-enhanced polymers significantly enhances mechanical, thermal and electrical properties of commercial polymers. At moderate loading levels of graphene, the moduli triple, there is a ten-fold increase in thermal conductivity and fourteen order of magnitude increase in electrical conductivity.

However, there are still technical challenges to be addressed. For example, there needs to be an improvement of the dispersion of graphene in the polymer matrix by the further functionalization of graphene and by the addition of compatibilizers to avoid the agglomeration of graphene, which occurs at higher graphene loading levels. Moreover, the improvement of the quality, aspect ratio and alignment of graphene particles during processing is crucially important. Also, by tuning the structure-property relationships of graphene-polymer composites, the thermal and electrical percolation threshold of graphene can be reduced as well as the loading levels in commercial polymers. Despite these issues, there is enormous potential of graphene as an advanced lightweight additive due to both its functionality and tunability.

**References**


Nazarpour, S. and Walte. R.S., 2016, Graphene Technology from Laboratory to Fabrication. Wiley-VCH.
