Thermal Conductivity, Electrical Conductivity and Mechanical Properties of Polypropylene/Graphene and Polystyrene/Graphene Nanocomposites

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Abstract

In recent years, many studies have been conducted regarding polymer nanocomposites, namely polymers doped with various forms of graphene. The impact toughness, tensile strength, and thermal conductivity of Polypropylene/Graphene and Polystyrene/Graphene nanocomposites were compared at different Graphene concentrations varying from 5% to 25%. The electrical conductivity of Polypropylene/Graphene nanocomposites of the same composition was also determined. The goal of these tests was to find an optimal composition that enhances the electrical and thermal conductivity as well as tensile strength of polypropylene without compromising the impact toughness for the potential application of a battery anode. At 10% loading of GNP, an over 100% increase in thermal conductivity and a 60% increase in tensile strength were achieved with only a 4% loss to impact strength. The electrical conductivity increased from 260 S/m at 10% loading of GNP to 2 \( \times 10^7 \) S/m at 15% loading of GNP. The results conclude that the nanocomposites with a load between 10% GNP and 15% GNP by weight displayed ideal material characteristics.

1. Introduction

Polymer nanocomposite research often has many different objectives, but a common goal of creating materials with improved properties in any of many possible categories. Flame retardancy, electrical and thermal conductivity smoke suppression, tensile strength, impact strength, glass transition temperature, melting point, elasticity, etc; there are applications where each of these properties may be deemed more valuable. The addition of additives to create a nanocomposite is the most common way to alter these properties. However, it is not without drawbacks, and not very predictable [2]. Thus, experimental research is necessary.

Usually, the addition of additives will disrupt at least partially the matrix of the polymer [1]. This is a good example because creating disruptions is a good technique for fire retardancy and smoke suppression, as the combustion may hit a very small layer of non-combustible graphene nanoparticles (GNPs), slowing combustion [1]. However, this same layer may be a point of weakness in terms of impact strength, where it may break along that layer.

Our research dealt with this issue among others. The earlier stages of our project attempted a composite using Polystyrene (PS). PS is a polymer with a density of 1.052 g/cm³ and a molecular weight of the repeat unit of 104.15 g/mol [15]. The PS did not handle the disruption acceptably, and the result was a brittle
material with few possible useful applications.

In this research, we originally proposed to use graphene as a fire retardant by synthesizing it with polystyrene into a nanocomposite. Graphene is a 2-dimensional layer of carbon that has outstanding properties of high thermal conductivity, superior mechanical stiffness, and large specific surface area [13]. There is previous research that used functionalized graphene oxide and obtained improved fire safety data using a masterbatch-melt blending approach, but we used pure graphene nanoparticles in this research. We expected that addition of high graphene content into polystyrene can effectively improve fire safety and mechanical property of the nanocomposite. To determine the most effective graphene/polystyrene concentration ratio, several samples with different concentrations were prepared and tested.

Our project goal from the very beginning was to use GNPs in unusually high doses in a nanocomposite to improve properties. Preliminary research suggested up to 40 wt% GNPs could be added to a polymer nanocomposite for some potentially extraordinary properties.

Initial testing with polystyrene produced a very brittle material, so much so that it was difficult even to create molds of for testing. In response, we decided to try polypropylene (PP) as our principal polymer. Polypropylene has a low glass transition temperature which allows it to act more like a fluid at room temperature, making it better suited for these kinds of composites [3]. PP has a density of 0.86 g/cm³ and a molecular weight of the repeat unit of 42.08 g/mol [15]. PP has a crystalline structure as opposed to the amorphous structure of PS. The difference in the degree of crystallinity attributes to higher heat resistance and sharper melting points. Moreover, a highly crystalline structure is prone to being more brittle due to the compactness and static organization of the molecules [16].

The result was immediate improvement and a promising material. We then created samples of the same graphene concentrations as the PS nanocomposites but conducted with PP, and were able to compare the two materials afterwards. We successfully improved properties in tensile strength and thermal and electrical conductivities without noticeable detriment to impact toughness.

2 Experimental Section
2.1 Materials
XGNP-H-5

Graphene Nanoplatelets were purchased from XG Sciences. The nanoplatelets have an average particle diameter of 5 microns. Polypropylene pellets were purchased from Amco Plastic Materials Inc. Polystyrene pellets were purchased from Amco Plastic Materials Inc.

Both the PP and PS nanocomposites were prepared in the following loadings of GNPs by weight: 0%, 5%, 10%, 15%, 20%, and 25% using a Brabender mixer filled to its capacity of 200g run at 256 °C for twenty minutes. The nanocomposites were then pelletized by hand and molded to meet the various testing standards using the appropriate molds and a Carver Hot Press at 256 °C and compressed to 6000 psi for five minutes.

2.2 Experimental Methods
2.2.1 IZOD Impact Toughness Test

The nanocomposites were molded into the appropriate ASTM D256-10e1 standard mold with dimensions 64 x 12.7 x 3.2 mm with a notch in the center and then tested on a Testing Machines Inc. Monitor Impact Tester that records the maximum energy absorbed by the sample in J/m [4].
2.2.2 Tensile Strength Test

The nanocomposites were molded into the appropriate ASTM D638-14 standard dogbone shaped mold and tested on an Instron 5542 Single Testing Column System. A plot of force versus stroke is returned and from that the Young’s modulus is calculated [5].

2.2.3 Thermal Conductivity Test

Thermal conductivity of the samples was measured on a Unitherm Model 2022 Thermal Conductivity Instrument using the ASTM E1530 Guarded Heat Flow Meter Method. The thermal conductivity tests were performed at 25 °C and recorded in W/(m*K) [6].

2.2.4 Electrical Conductivity Test

The Electrical conductivity of the samples was measured by cutting portions of the nanocomposite into 1 cm2 blocks and attaching two wire probes to each end and using an EC meter to read the conductivity.

Table 1. Various compositions of nanocomposites after mixing the polymer and graphene for both PP and PS.

<table>
<thead>
<tr>
<th>% GNP</th>
<th>% Polymer (PP and PS)</th>
<th>Weight GNP (g)</th>
<th>Weight Polymer (g)</th>
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<tr>
<td>0</td>
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<td>0</td>
<td>200</td>
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<tr>
<td>25</td>
<td>75</td>
<td>50</td>
<td>150</td>
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3. Results and Discussion

The polymers, once combined with graphene powder, turned from clear/translucent white to black throughout at every concentration due to the natural black/grey color of graphene. This can be assumed to mean the GNP's were present on the surface covering the polymer and within the matrix itself [7].

Five samples of each concentration of GNP’s for both nanocomposites were prepared for the IZOD impact test for consistency. After the test was performed, the average impact strengths were recorded in J/m and averaged with their respective errors.

Using the results from Table 1, impact strength of PP/GNP and PS/GNP nanocomposites were plotted for comparison with their respective concentrations in Figure 1.

Both concentrations were found to have an overall decreasing trend in impact strength. This trend may be due to the incorporation of graphene in the polymer matrix, disrupting the crystal structure. It is important to note that the shape of the molds for this test included a notch in the middle along the edge to propagate fracturing the material. Thus, the combination of the disruption and the shape of the molds are possible contributors to this decrease.

Beyond a load of 10 wt% GNP, fluctuation in impact strength is present in both nanocomposites – more so in PS. This can be attributed to experimental error such as surface deformities in some of the samples. Most notably, the PS/GNP composites undergo a 48% reduction in impact strength when GNP concentration is increased from 5 to 10%. On the contrary, the impact strengths of the
PP/GNP nanocomposites were reduced by only 8.6%.

Similarly, five dogbones samples of each concentration of GNPs for both nanocomposites were molded for tensile testing. Stress (extension %) and strain (MPa) were recorded every 0.1 seconds. 45 to 50 data points from the elastic region – the region before the material begins to yield – were plotted on a stress versus strain graph. The slope of the line these points created is known as the elastic or Young’s modulus [8]. The moduli for each sample were calculated and then averaged for each concentration with their respective errors.

The elastic moduli for both nanocomposites were then plotted against each other for comparison in Figure 2.

The polystyrene nanocomposite immediately starts a trend in decreasing elastic modulus as GNP concentration is increased. A study done by Qiu et al. suggested that adding a small concentration of functionalized graphene oxide (FGO) (1 wt%) to polystyrene increased the tensile strength by 23.3% [9]. At such small concentrations, good dispersion of FGO in the polymer matrix occurs. However, when increased to 5 wt% FGO, the tensile strength decreased significantly [9], which is also apparent in the results of this research. As concentration increases past a certain point – in this case being 5 wt% – GNPs start to reaggregate as part of their nature to self-assemble; Thus, dispersion becomes poor [10].

On the other hand, the PP nanocomposites had a gradual and steady increase in elastic modulus as GNP loading increased. Although the modulus for PP is lower than PS, it steadily increases as GNP concentration is increased. The explanation of this phenomenon is somewhat complex and beyond the scope of this research. Simply put, GNPs have a restrictive effect on the movement of the polymers molecular chains, thereby increasing its modulus [11]. Compared to pure PP, GNP loading of 10% increased the modulus by 1.5 times its original value. GNP loading of 25% increased the modulus by almost 3 times its original value.

The thermal conductivity tests were performed at 25 °C and recorded in W/(m*K). The GNP loadings of the molds for PP composites for this test were 0, 7.5, 13.5, 20, 26.5 and 32 GNP wt%
respectively. The PS nanocomposites were consistent with the previous tests with the addition of 30 and 35 GNP wt%. After the results were obtained, trendlines were given to the set of points in order to establish a trend between GNP loading and thermal conductivity, illustrated in Figure 3.

![Thermal Conductivity Test](image)

**Figure 3.** Thermal Conductivity for both PP/GNP and PS/GNP nanocomposites.

This test resulted in a linearly correlated relationship between GNP loading and thermal conductivity in both cases. Pure PP and PS started with a thermal conductivity of 0.223 and 0.153 which are consistent with their literature values of 0.22 and 0.13 at 25 °C respectively [12]. According to the trendline, PS with 30 wt% GNP loading, compared to pure PS, increased thermal conductivity four-fold while PP at the same loading of GNP increased its original thermal conductivity five-fold.

Electrical conductivity for the PP/GNP nanocomposites were performed for a variety of different frequencies. However, for the sake of consistency, the data for 100 mHz will be used for comparison between the various graphene concentrations. Each sample had an area of 1 cm². Resistances along with their corresponding frequencies were recorded and compiled for comparison in Figure 4. The natural logarithm of electrical conductivity was compared to the GNP content in order to establish an overall trend between them.

![Electrical Conductivities at 100 mHz](image)

**Figure 4.** The natural log of Electrical conductivities and Polypropylene with different GNP concentrations at 100 mHz.

The electrical conductivity for the PP/GNP nanocomposites have a sharp spike from 10 to 15 wt%, increasing it from 260 to 2×10⁷ S/m. This means that around these concentrations, the nanocomposites reached their percolation threshold in that pseudo-circuits were formed within the composites structure.

4. Conclusion

The influence by addition of graphene nanoparticles(GNPs) into polypropylene(PP) and polystyrene(PS) matrix is deeply studied in this research. Our primary goal of this research has changed from studying PP/GNP nanocomposite to comparing the properties of PP/GNP and PS/GNP after we figured out that PS/GNP nanocomposite will have a limited use due to its brittleness.

As shown in Figure 1, an overall decreasing trend is found in both PP/GNP and PS/GNP nanocomposites from IZOD impact strength due to possible incorporation of graphene in both polymers. From tensile testing, it is found that PP/GNP has a increasing trend while
PS/GNP has a decreasing trend. Especially, increasing the graphene content in PS/GNP to 5 wt% of graphene significantly lowered. The increase in graphene concentration has a linear increase in thermal conductivity for both PP and PS nanocomposites.

When choosing the optimal concentration of GNP, IZOD Impact test becomes a deciding factor. Based on the analysis from all tests, it’s suggested that the most applicable concentration for PP/GNPs is 10 wt% because when the wt% increases from 5 wt% to 10 wt% thermal conductivity has a steady increase by 28.6% from 0.35 W/m*k to 0.45 W/m*k and elastic modulus also increases by 8.2% from 16.88 MPa to 18.38 MPa. In contrast to other trends, decreasing trend is shown in IZOD tests. Impact strength significantly drops by 28% from 19.62 J/m to 14.22 J/m when the concentration changes from 10 wt% to 15 wt%. Electrical conductivity test showed a huge increase from 10 to 15 wt%, which remains consistent with the optimal range of GNP content chosen. A possible application of the nanocomposite could be a battery anode because of its high electrical conductivity, corrosion resistance [14], and high impact and tensile strength.

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References