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THERMAL CONDUCTIVITY OF EXFOLIATED GRAPHITE NANOCOMPOSITES

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Since the late 1990's, research has been reported where intercalated, expanded, and/or exfoliated graphite nanoflakes could also be used as reinforcements in polymer systems. The key point to utilizing graphite as a platelet nanoreinforcement is in the ability to exfoliate graphite using Graphite Intercalated Compounds (GICs). Natural graphite is still abundant and its cost is quite low compared to the other nano–size carbon materials, the cost of producing graphite nanoplatelets is expected to be ~$5/lb. This is significantly less expensive than single wall nanotubes (SWNT) (>$45000/lb) or vapor grown carbon fiber (VGCF) ($40–50/lb), yet the mechanical, electrical, and thermal properties of crystalline graphite flakes are comparable to those of SWNT and VGCF. The use of exfoliated graphite flakes (xGnP) opens up many new applications where electromagnetic shielding, high thermal conductivity, gas barrier resistance or low flammability are required.

A special thermal treatment was developed to exfoliate graphite flakes for the production of nylon and high density polypropylene nanocomposites. X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to assess the degree of exfoliation of the graphite platelets and the morphology of the nanocomposites. The thermal conductivity of these composites was investigated by three different methods, namely, by DSC, modified hot wire, and halogen flash lamp methods. The addition of small amounts of exfoliated graphite flakes showed a marked improvement in thermal and electrical conductivity of the composites.

Keywords: *DSC method, graphite composites, hot-wire method, thermal conductivity, thermal pulse method*

Introduction

Today, thermal management is becoming increasing important in many industries including computer/electronics, automotive, and aerospace. Metals have traditionally been used as the main material in these applications, but have disadvantages compared to polymers and composites such as higher density, greater susceptibility to oxidation/corrosion, and lower design freedom. Thus, developing polymeric materials with high thermal conductivity is of great interest to many industrial sectors.

Most polymers are thermal insulators. Thus, it is necessary to add thermally conductive fillers to achieve suitable thermal conductivity. Plastics with thermal conductivity of 1 to 30 W m^{-1} K^{-1} can be used in heat management applications [1]. Many materials have been investigated to make thermally conductive polymer based composites including metallic fillers, ceramic fillers, and carbon based materials. Some ceramic fillers have high thermal conductivity [2], but are prohibitively expensive and inappropriate for many applications. Metal fillers are more affordable, but suffer the disadvantage of high density. Lighter weight carbon based compounds as conductive fillers are now being investigated including carbon blacks, carbon fibers, graphite, vapor grown carbon fibers (VGCF), and carbon nanotubes.

Carbon blacks are inexpensive and commonly used as fillers to increase electrical conductivity, but often have relatively low thermal conductivity [3]. Vapor grown carbon fibers and carbon nanotubes have excellent thermal conductivity, but their cost is still too high for many applications. The cost of single wall carbon nanotubes is more than $45000/lb, while VGCF are $40–50 per pound. Carbon fibers, having thermal conductivity of 500–1000 W m^{-1} K^{-1} [3], are becoming less expensive and are used in many applications. The conductivity of carbon fiber based composites are reported in the range of 2 to 20 W m^{-1} K^{-1} [4–8]. However, the cost of carbon fiber at $15–20/lb makes these materials unattractive for use as conductive fillers. The thermal conductivity of crystalline graphite could be as high as 3000 W m^{-1} K^{-1}. Natural crystalline graphite is still abundant and its cost is relatively inexpensive compared to other carbon materials. A recently completed study in our group showed the cost of producing graphite nanoplatelets from natural crystalline graphite is expected to be $5/lb or less. This is significantly less expensive than vapor grown carbon fibers or carbon nanotubes.

Graphite nanocomposites can offer advanced properties such as electrical and thermal conductivity at reasonable cost. If the appropriate process condi-

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Table 1 Surface area of carbon materials

Carbon material	Length/μm	Thickness/nm	Aspect ratio	Surface area*/m^2 g^{-1}
xGnP-1	0.86	5–10	86	94±5
xGnP-15	15	5–10	~1500	105±7

*Data from BET measurements using the region between P/P_0 of 0 to 0.2.

tions are applied, graphite nanocomposites offer the potential to produce materials with excellent mechanical, electrical, and thermal properties at reasonable cost, which opens up many new applications. Thus, graphite nanoflakes offer an alternative source for producing nano-scale materials for producing polymer nanocomposites. Since late 1990's, there are multiple reports of intercalated, expanded, or exfoliated graphite nanoflakes that were added to polymer systems to fabricate graphite nanocomposite materials [9–16]. But none of the studies reported the thermal conductivity of these materials.

In this research, a special thermal treatment and process was developed to produce exfoliated graphite nanoplatelets from natural crystalline graphite. Using the exfoliated graphite nanoflakes, composites were fabricated by combining the exfoliated graphite nanoplatelets with nylon 6, nylon 66 and high density polyethylene (HDPE). Transmission electron microscopy (TEM) was used to assess the degree of exfoliation of the graphite platelets and the morphology of the nanocomposites. The thermal conductivity of these composites was measured by three different methods, namely, differential scanning calorimetry, modified hot-wire techniques, and pulsed lamp methods.

Experimental

Exfoliated graphite nanoplatelets

The starting graphitic material used in this research was acid intercalated natural crystalline graphite, Grafguard 160-50A offered from GrafTech. The acid components consist of sulfuric and nitric acid. Nitric acid acts as oxidizer while sulfuric acid acts as an intercalate. The acid intercalated graphite has multiple stage condition, ranging from stage 1 to 5 or higher. By applying rapid heating, exfoliated graphite materials are produced [17]. After the treatment, these graphite flakes showed significant expansion due to the vaporization of intercalated acid in the graphite galleries. The expanded graphite flakes were pulverized by use of an ultrasonic processor. At this point, the average size of the graphite was 15 μm while the thickness was around 10 mm (xGnP-15). By applying a mechanical milling process, the diameter and thickness of the milled flakes became 0.86 μm and 5–10 nm, respectively (xGnP-1). The TEM images of nanoplatelets are shown in Fig. 1. The average diameter of the flakes could be controlled by changing the pulverization and milling conditions and graphite flakes with large aspect ratio were also fabricated. Table 1 summarizes the basic dimensional data of these carbon materials.

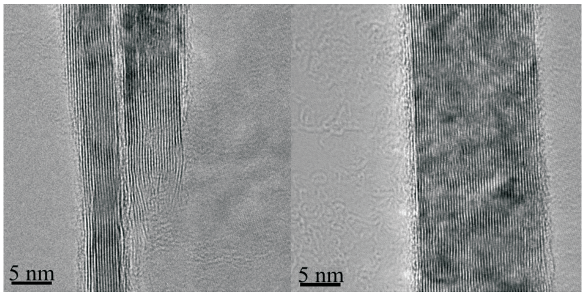

Fig. 1 TEM images of graphite nanoplatelets

Composite fabrication

Melt extrusion was used to blend the exfoliated nanograghite materials in the thermoplastic matrices evaluated in this study. A DSM Micro 15 Compounder, (vertical, co-rotating twin-screw mini-extruder, capacity 15 cc) and a DSM 3.5 cc Injection Molder were used to make composite samples. At first, polymer matrix and reinforcements were mixed in the mini-extruder for 3 min at a screw speed of 200 rpm. Then the mixed system was transferred to the molding cylinder where the material was injected into a mold with the injection pressure of 100 pounds per square inch. The disc shaped sample was removed from the mold immediately after the injection process and cooled on bench at room temperature of 23°C.

Thermal conductivity measurement

Three methods were used to determine the thermal conductivity of the nanocomposites.

DSC method

Differential scanning calorimeters have been used to measure the thermal conductivity of various materials [18–20]. In practice, a quartz disk 6 mm in diameter and 1 mm thick was used as a reference sample. The composite samples were also prepared using the same geometry. Approximately 15 mg of gallium (T_m=29.8°C) was placed on the top surface of a quartz sample, set in the

DSC cell, and heated from 20 to 40°C at 0.1°C min^{-1} ramp rate. This gallium melt was performed twice to ensure intimate contact of the gallium with the sample, and to induce quasi-static thermal equilibrium. The data from the second melt was used for calculations.

Since the melting rate of gallium depends on the heat flow through the quartz disk, the slope of the heat flow *vs*. temperature (q) profile through the melt is indicative of the thermal conductivity (K_x) of the object sample. Because the same quantity of gallium was used for all measurements, and all samples were similar in size, the thermal conductivity of the composite samples may be calculated by the following formula.

$$K_x = q_x^2/q_q^2 \cdot d_x/d_r \cdot K_q$$

where K_x – thermal conductivity of object sample (W m^{-1} K^{-1}); K_q – thermal conductivity of quartz (W m^{-1} K^{-1})=1.37; q_x – heat flow through object sample (W g^{-1} K^{-1}); q_q – heat flow through quartz sample (W g^{-1} K^{-1}); d_x – thickness of object sample (mm) and d_r – thickness of object sample (mm).

The slope of heat flow through quartz was measured for two quartz (as unknown) samples, and averaged to determine q_q. The K_x values were calculated using two samples per composite formulation.

Modified hot-wire method

This method is a transient technique that determines the rate of heat flow from one material to another. In practice, a heating element, supported on a backing, is placed in contact with the material to be evaluated. The temperature of the heating element is monitored, and the rate of temperature increase in at the sensor surface is inversely proportional to the ability of the sample to transfer heat. Using this approach, the thermal conductivity of the specimen can be quickly and non-destructively determined. Measurements were collected by Mathis Instruments Ltd. (Fredericton, NB, Canada) personnel using their TC-30 unit.

Flash method

A halogen flash lamp fires a pulse at the sample's lower surface while the temperature of the reverse surface is measured by infrared detectors. Specific heat is measured by comparing the temperature rise of the sample to the temperature rise of a reference sample of known specific heat. By knowing the density of the sample the thermal conductivity can be calculated. Measurements were collected by the personnel of Netzsch Instruments, Inc. (Burlington, MA, USA) using their LFA 447 unit.

Results and discussion

Figure 2 shows the thermal conductivity data of nylon 66 composites measured by pulsed flash and DSC methods. Both data agreed well up to around 1 W m^{-1} K^{-1}. Above 2 W m^{-1} K^{-1} the DSC method showed much lower values compared to the pulsed method. The DSC method is less sensitive for high thermal conductivity measurement since it relies on the slope of gallium melt curve. As the thermal conductivity of the sample increases, the corresponding change in the slope of the melt curve undergoes a smaller incremental change, making the method less accurate for high thermal conductivity materials at this very slow ramp rate condition. Thus, the DSC method is not an appropriate measurement method for materials with high thermal conductivity such as the graphite filled nanocomposites studied here.

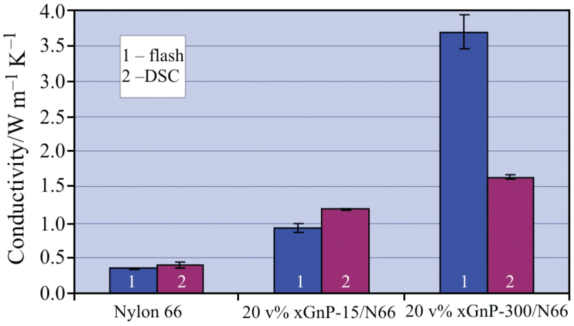

Fig. 2 Thermal conductivity of Nylon 66 composites measured by halogen flash and DSC methods

Figure 3 shows the thermal conductivity data of HDPE/xGnP composites measured by laser flash and hot wire methods. The results obtained from these two methods showed very good agreement. Thus, it was concluded that data obtained from these two method were comparable, at least at 1.2 W m^{-1} K^{-1} or lower level.

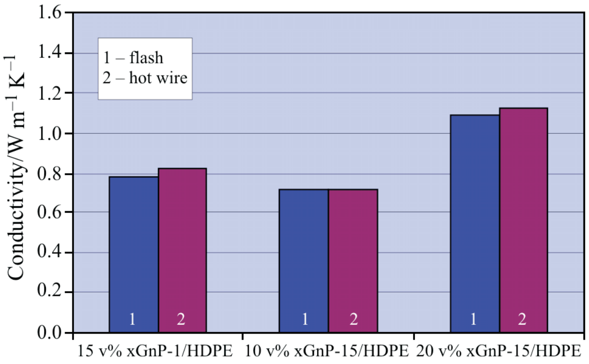

Fig. 3 Thermal conductivity of HDPE composites measured by halogen flash and hot wire methods

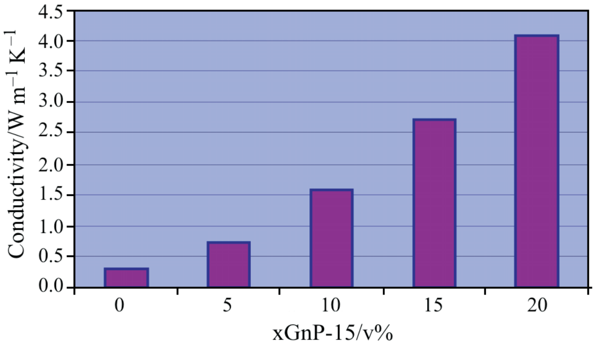

Fig. 4 Thermal conductivity of xGnP-15/Nylon 6 composites measured by halogen flash method

Figure 4 shows the thermal conductivity data of a series of nylon 6/xGnP composites measured by the pulsed halogen flash method. The thermal conductivity increased almost linearly *vs*. the graphite loading and reached more than 4 W m^{-1} K^{-1} at 20 vol% loading level. This value is significantly larger than the control nylon 6 sample.

Conclusions

Three different methods for measuring thermal conductivity were compared. The DSC method gave good results up to 1.5 W m^{-1} K^{-1} but diverged from the pulsed lamp method above 1.5 W m^{-1} K^{-1}. The DSC method should be limited to use for materials having thermal conductivities less than about 1 W m^{-1} K^{-1}. However, the halogen pulsed lamp method and the modified hot-wire method showed good agreement up to 1.5 W m^{-1} K^{-1}.

The halogen lamp flash method revealed that exfoliated graphite nanoplatelet composites with up to 20 vol% xGnP exhibited thermal conductivities of more than 4 W m^{-1} K^{-1} which is significantly higher than the control polymer matrix. Thus, exfoliated graphite nanocomposites offer great promise in applications where thermal management is a priority in performance.

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