

USE OF EXFOLIATED GRAPHITE FILLER TO ENHANCE POLYMER PHYSICAL PROPERTIES

Bryan W. Debelak University of Dayton, 300 College Park, Dayton, OH 45469, USA
Khalid Lafdi University of Dayton, 300 College Park, Dayton, OH 45469, USA

Abstract

Exfoliated graphite filled polymers, having three different particle sizes labeled as small, medium and large flake, were prepared with exfoliated graphite concentrations from 0.1-20% by weight. After sieving, the particles were reduced to nanometer size through exfoliation, shear mixing, and ultrasonication, which further breaks and delaminates them. The electrical, thermal, mechanical and tribological properties of the nanoparticle filled polymers were measured. In addition, light, and scanning electron microscopy characterization were performed. Compared with the pure polymer, the polymers filled with 20% wt. exfoliated graphite have seen a significant reduction in electrical resistivity from 1.5^8 to 0.5 Ohm-cm. The thermal conductivity for the polymers containing 20% wt exfoliated graphite has also been drastically improved, increasing from 0.2 to 5 W/m-K. The flexural modulus achieved a maximum increase of 3.8 GPa which is a 60% above the value for the pure polymer (2.4 GPa).

1. Introduction

Polymers with nanoparticle additives have attracted considerable attention in recent years because of their highly sought after multifunctional characteristics. Pure materials are inevitably limited in applications by their inherent properties. Polymeric materials are typically limited in applications due to their inherent low thermal conductivity, low thermal stability, high electrical resistivity, and ductile mechanical properties. However, polymers may be attractive because they have high strength to weight ratios, are inexpensive, and are easy to process. The addition of a nanometric additive into polymers may drastically enhance their properties and consequently its multifunctionality.

To increase the tribological performance of polymers, several solid lubricant additives have been commercially used including graphite flakes, molybdenum disulfide, antimony trisulfide, copper sulfide, calcium chloride, and polytetrafluoroethylene (PTFE) [4-6,13]. Graphite is a particularly attractive solid lubricant since it is abundant, cost effective and can provide improved wear resistance.

Graphite is a naturally occurring, or synthetically produced, crystalline form of carbon that is highly conductive (with an electrical conductivity of 10^4 S/cm at ambient temperature). The attractive physical properties and lubricating effect of graphite flakes has been correlated to its crystalline structure. A derivative form of graphite called expanded graphite, or “exfoliated” graphite could be a superior filler for producing multifunctional polymers. Exfoliated graphite is usually obtained by rapid heating and vaporization of a gas within a graphite intercalation compound (GIC).

It should be emphasized that the size, aspect ratio, and degree of dispersion of the graphite nanoparticles for the composite materials having the same composition, but prepared through different methods, (such as epoxy/EG), are radically dependent on the extent of shearing exerted on the material, which is due to the fact that although exfoliated graphite itself can endure large compression stress, it can be readily fragmented in the course of shearing. Recent publications that have studied exfoliated graphite filled polymers have reported percolation thresholds of electrical conductivities from 0.75 to 2 wt% and maximum electrical conductivities between 10^{-4} S/cm to 0.5 S/cm [1,3,14]. There have also been several attempts to use graphite flakes as a solid lubricant additives for polymers. Li et al. studied epoxy and graphite composites and showed that the friction coefficient can drop from 0.48 to 0.25 as graphite content increases from 0 to 30 vol. %, but further addition of graphite will have little affect on modifying the friction coefficient [8]. Xian and Zhang fabricated polyetherimide/graphite composites with graphite content varying from 0-20% by volume [13]. The results showed a continual decrease in the wear rate with increasing graphite content. The use of exfoliated graphite and the investigation on the size of flake has not yet been investigated for the tribological properties. There also has been limited testing to determine the relationship between mechanical properties and exfoliated graphite loading levels, though, through the publications already available, a similar trend seems to be developing.

To alleviate much of the high costs and complex processing associated with carbon nanotubes and even nanofibers, exfoliated graphite is easy to manufacture and only costs a few dollars per pound. This study is intended to be a complete investigation of the physical and tribological properties of exfoliated graphite filled polymers as function of filler dimension (particle size and their degree of expansion) and its concentration within the polymer. The size of the exfoliated graphite particles and its affect on polymer properties has yet to be investigated in literature. For the tribological properties, the effect of expanding graphite before implementation as a lubricant has not been studied. The size of the particle alone may have a significant impact on property variations. A comprehensive set of data which relate the concentration of additives to physical properties will be studied.

2. Experimental

2.1. Materials preparation

The graphite used in this study was natural flake graphite which has an average diameter of 500 μm . The polymer used for the matrix material was EPON Resin 862.

Exfoliated graphite was prepared as the follows: a mixture containing nitric and sulfuric acid and natural graphite was used. The intercalated graphite compound was subjected to sudden heat treatment temperature of 900°C and rapid expansion then occurred. During this study, three kinds of exfoliated graphite filled polymers, having different graphite particle sizes, were prepared. The graphite flakes are classified as small, medium, and large.

Materials containing polymer and exfoliated graphite concentrations of 0.1, 0.5, 1, 2, 4, 8, 12, 16, and 20% were prepared. After the mixing process of exfoliated graphite and polymer is completed, the mold with the mixture was loaded in a hydraulic press to cure. The curing conditions for the molds are pressed under 675 psi at 250°F for 2 hours and then at 350°F for 2 more hours. To assist the dispersion of the filler in the polymer, resistivity scan was used to evaluate the resistivity value in the cured sample, 64 data points were obtained using four probe measurements. All samples had shown consistent resistivity value with standard deviation less than 4%.

2.2. Materials Characterization and Physical Properties

A positive byproduct caused by the exfoliation of graphite is the increase in surface area. Here, the surface area of the exfoliated graphite was characterized on the MICROMERITICS Accelerated Surface Area and Porosimetry System (ASAP 2010).

Reflective light optical microscopy was performed to investigate the dispersion of the graphite nanoparticles throughout the polymer matrix. It was also used to investigate the surfaces of the samples after tribological testing. Scanning Electron Microscopy was also performed on the samples to examine the degree of exfoliation achieved by the graphite nanoparticles as well as the microstructure of the exfoliated graphite nanoparticles within the matrix.

The electrical resistivity of the exfoliated graphite filled polymers was measured at room temperature using a standard four-probe method. The polymer samples were cut into specimens of $20 \times 10 \times 3 \text{ mm}^3$ for testing. For the samples with lower filler contents, the resistivity was out of the detectable range of the four-point resistivity probe. The electrical conductivity could then be found because by taking the resistivities reciprocal.

Thermal conductivity of the additive filled polymers was measured on the LFA 447 Nanoflash diffusivity instrument. The sample dimensions were approximately $10 \times 10 \times 1 \text{ mm}^3$. The tests conformed to ASTM E1461. Measurement of the thermal diffusivity, specific heat and density allows the calculation of the thermal conductivity.

Thermomechanical analysis (TMA) was conducted using a TA instruments TMA Q400. The sample dimensions were approximately $10 \times 10 \times 1 \text{ mm}^3$. The samples were tested in the temperature range from room temperature to 250°C in a nitrogen environment at atmospheric pressure, at a heating rate of 2°C/min. One of the benefits of this test is that coefficients of thermal expansion (CTE) can be easily measured by TMA.

The mechanical properties of the polymers were studied using the three-point flexural test according to ASTM D790-00. The three-point flex test utilizes a sample size of $38 \times 10 \times 3 \text{ mm}^3$. A span ratio (length to thickness) of 8:1 was used. Flexural testing was conducted using an Instron load frame with a crosshead speed of 0.5 in/min.

The wear tests were performed on a pin-on-disc climate tribometer. In order to maximize the effects of wear to achieve clear results, the exfoliated graphite filled polymers were chosen as the material for the pin, and stainless steel was selected for the counter surface, or disk.

The mass added for the normal force was 175g. The rotational speed of the disk was 300 rpm while the linear speed was 0.2 m/s. The test temperature was 25°C, 60% relative humidity. The tests were performed for 90

minutes. The friction coefficient between the exfoliated graphite filled polymer test samples and the steel disk is recorded directly through the instrument and plotted as a function of time. The volume loss of material lost from the specimens was calculated by measuring the thickness before and after the wear tests.

3. Results and Discussion

Following the above procedure, the surface area of the three sizes of exfoliated graphite particles were measured and summarized in Table I. The results from the surface area analysis showed: small flake had a value of 16.02 m²/g, medium was 15.61 m²/g, and large was 15.35 m²/g. Thus, the surface area may be related to the extent of exfoliation as well as the particle size.

Table 1. Surface area of exfoliated graphite.

Exfoliated graphite	Small	Medium	Large
Surface area (m ² /g)	16.02	15.61	15.35

As shown in Figure 1, the worm-like structure is observed for all three graphite sizes. The small flakes are the longest and thickest, indicating a lower aspect ratio. The large flakes are the smallest and thinnest; however, they may have a higher aspect ratio. At high magnification, the nanosheets from the exfoliated graphite can be observed clearly. There are many hole-like spaces between the nanosheets, which is caused by the greatly expanded volume.

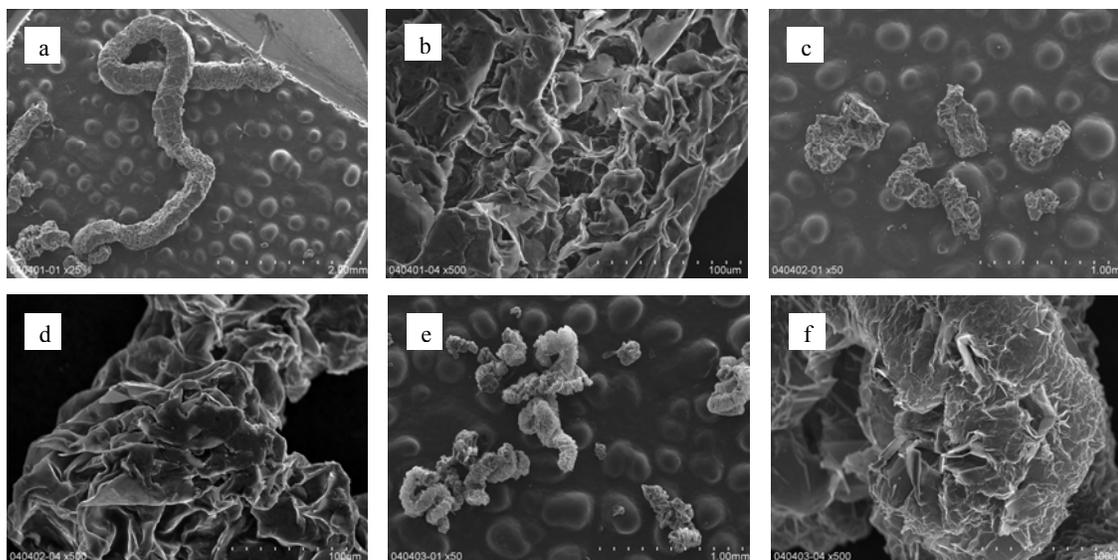


Figure 1. Microstructure of exfoliated graphite morphology: (a) & (b), small; (c) & (d), medium; and (e) & (f), large.

To investigate the microstructure of the exfoliated graphite nanoparticles further, higher magnification imaging was carried out (Figure 2). We can observe a porous-like structure with very straight and polygonal graphene walls that have failed to break apart. This elucidates to the fact that graphene planes are thin enough to show some flexibility.

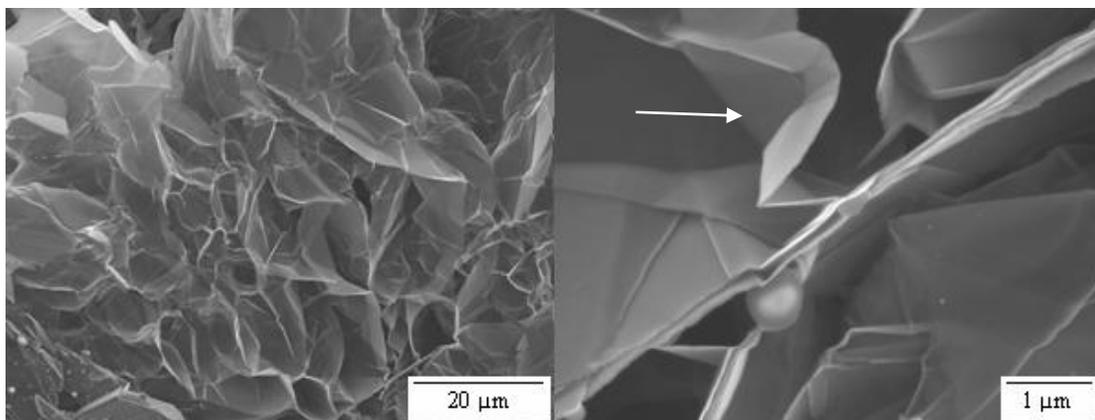


Figure 2. High magnification SEM micrographs of exfoliated graphite nanoparticle.

Exfoliated graphite filled polymers were prepared and light microscopy (LM) was carried out (Figures 3a-c). The dark spots in these images are artifacts that developed during polishing. However, the exfoliated graphite particulates appear uniformly dispersed (arrow in Figure 3).

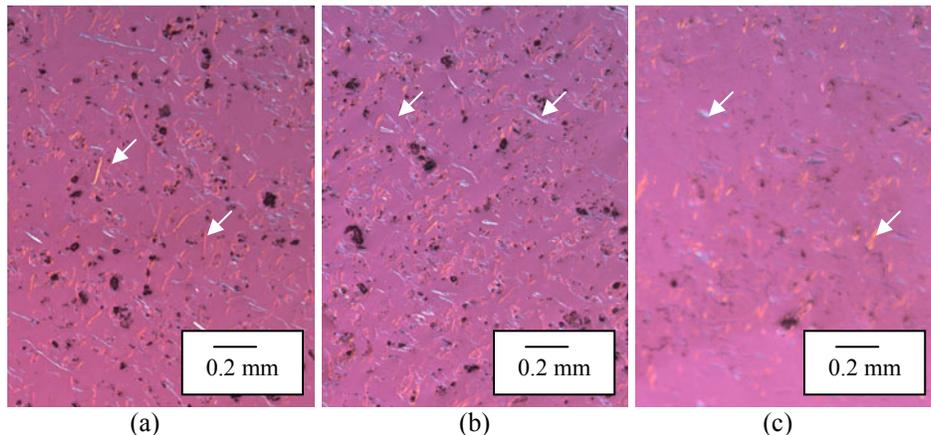


Figure 3. Light microscopy micrographs of exfoliated graphite filled polymers, (a) small (b) medium (c) and large flake, with similar graphite loading level (8 wt%).

3.1. Electrical properties

As already emphasized, one of the goals of making exfoliated graphite filled polymers is to develop highly conductive materials without sacrificing polymers inherent high strength to weight ratio. Figure 4 shows the electrical resistivities of the exfoliated graphite filled polymers versus the graphite filler concentration for the three different graphite size filled polymers, large, medium, and small graphite additives. Lower filler percentages are not presented because they were out of the detectable range of the instrument used to measure electrical resistivity. Like most polymers, the epoxy used for the matrix material is not electrically conductive and its room temperature volume resistivity in a dry state is as high as 1.5^8 Ohm-cm [12]. It is shown that the electrical resistivity of the exfoliated graphite filled polymers decreases with increasing exfoliated graphite concentration. The addition of graphite significantly lowers the resistivity of the polymer with a sharp transition from an electrical insulator to an electrical semiconductor. At 8 wt% of exfoliated graphite, for all three sizes, the resistivity for the polymer systems is already nearly four orders of magnitudes lower than the baseline polymer. When the polymers were filled with 20 wt% of exfoliated graphite, for the three sizes, the resistivities reached levels that were between six to eight orders of magnitude lower than baseline. The augmentation of the electrical resistivity can be attributed to the nanoscale dispersion of graphite nanosheets within the polymer and the formation of conducting networks.

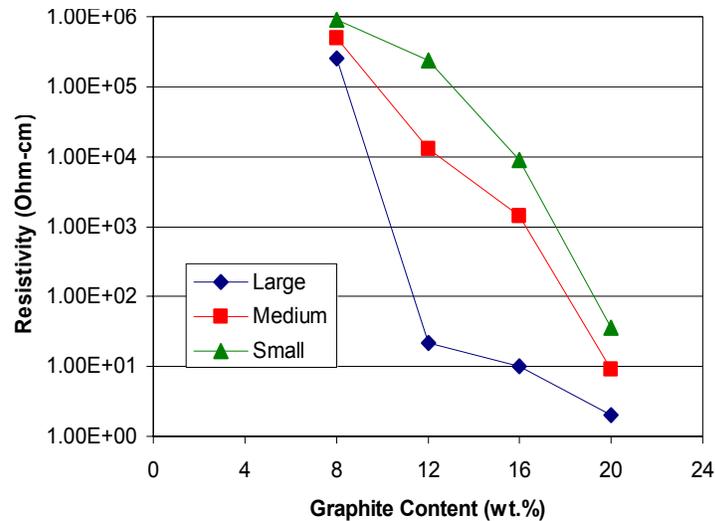


Figure 4. Electrical resistivity of exfoliated graphite filled polymers with different graphite sizes as a function of the graphite content.

As can be seen from Figure 4, the three sets behave rather differently as should be expected. The large graphite flake filled polymers showed the lowest resistivities at each graphite concentration, followed by medium and small, respectively. The large flakes also produced the highest rate of decrease in resistivity with initial increase in concentration. While the rate of change of decrease for large flakes after 12 wt % seemed to level off somewhat, the medium and small flake conductivities continued to decrease at a continually increasing rate. The lowest electrical resistivity values for large, medium, and small flake were 2, 9, and 36 Ohm-cm respectively. The trends show that the electrical resistivity decreased along with increasing the particles size. Clearly, the electrical conductivity critically depends on how the graphite is processed, exfoliated, and dispersed in the polymer matrix. The differences in behaviors of electrical resistivities can be mainly attributed to the fact that the aspect ratios of the three different graphite sizes differ, since the electrical properties of carbon based materials increases with grain and crystallite size. In our case, the particle size in filled polymers represents the graphene domain that forms a conducting network, responsible for property improvement.

3.2. Thermal Properties

By analogy to the electrical properties data, the thermal properties of the additive filled polymers should be highly improved after the addition of exfoliated graphite. Figure 5 shows the thermal conductivities of the exfoliated graphite filled polymers versus the graphite filler content for the large, medium, and small flake graphite. As with the electrical conductivity, it can be seen that the thermal conductivities for the three particulate sizes increase with higher graphite concentration. The data seems to illustrate a different percolation threshold for each composite system. The large graphite flake polymers have a threshold at 3 wt%, while medium and small have thresholds at 6 and 10 wt% respectively. With the addition of just 4 wt% of large particles graphite into polymers, the thermal conductivity was 0.868 W/m-K which is nearly a 300% increase over the baseline polymer (0.219 W/m-K). The large flake systems increase nearly linearly with increasing graphite content while both medium and small systems increased at an increasing rate. At 20 wt% graphite the three exfoliated graphite filled polymers had very similar thermal conductivity values. At 20 wt% all of the series were about 4.3 W/m-K, about 2000% increase over pure polymer. These results show that the mean carbon free path and conductive network produced by adding the graphitic filler strongly improves the transport routes necessary for high thermal conductance.

The best results for the thermal conductivity of exfoliated graphite filled polymers were compared against carbon nanofiber composites and high heated-treated (HHT) nanofiber composites thermal conductivities found in literature [10] and is shown in Figure 6. The large flake polymers proved to be superior as a conductive filler than carbon nanofibers or HHT carbon nanofibers. The maximum thermal conductivity of 4.3 W/m-K was 1031% higher than the carbon nanofiber composites and 53% higher than the HHT carbon nanofiber composites. Exfoliation of the graphite flake into sheets produces a highly conductive material with a higher aspect ratio than typical carbon nanofiber. This elucidates as to why the thermal conductivity is greater for exfoliated graphite.

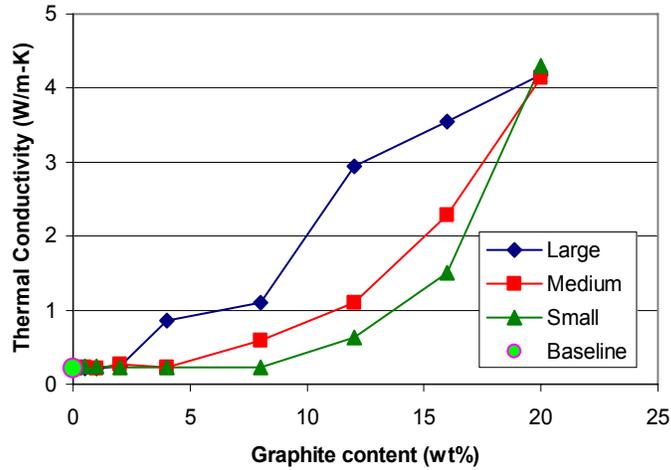


Figure 5. Thermal conductivity of exfoliated graphite filled polymers with different graphite flake sizes as a function of the graphite content.

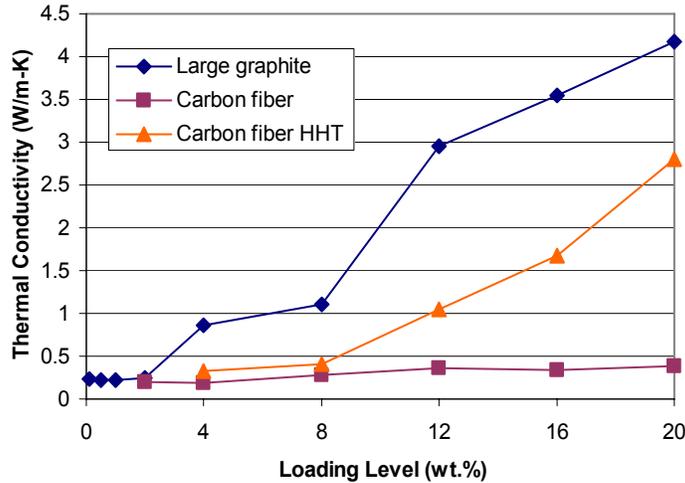


Figure 6. Thermal conductivity comparison of graphite flake filled polymers versus carbon nanofiber and HHT carbon nanofiber composites.

Figure 7 shows the coefficient of thermal expansion (CTE) of the exfoliated graphite filled polymers with different particle sizes as a function of the graphite content. The CTE results reveal almost identical curves, all decreasing with increasing graphite content, yet they are just offset from each other. The exfoliated graphite is able to lower the CTE's of the polymer simply through the rule of mixture. Exfoliated graphite has a lower CTE value than the pure polymer, mixing them together will create a system that results in a compromise between the two materials. The large flakes give the lowest CTE values at each graphite loading level, followed by medium and small, respectively. This can be attributed to the exfoliated graphite phase whereby interfacial surface area-to-volume ratio increases as the flake size gets larger, and thus the aspect ratio. The CTE of the large flake below the transition temperature, with only 4 wt% graphite filler, achieved a decrease to 57 $\mu\text{m}/(\text{m}\cdot^\circ\text{C})$ which is a 25% decrease from the baseline polymer (71 $\mu\text{m}/(\text{m}\cdot^\circ\text{C})$). This demonstrates that at low graphite loading, the polymer with the small nanoparticle filler lowers the expansion effects of the system.

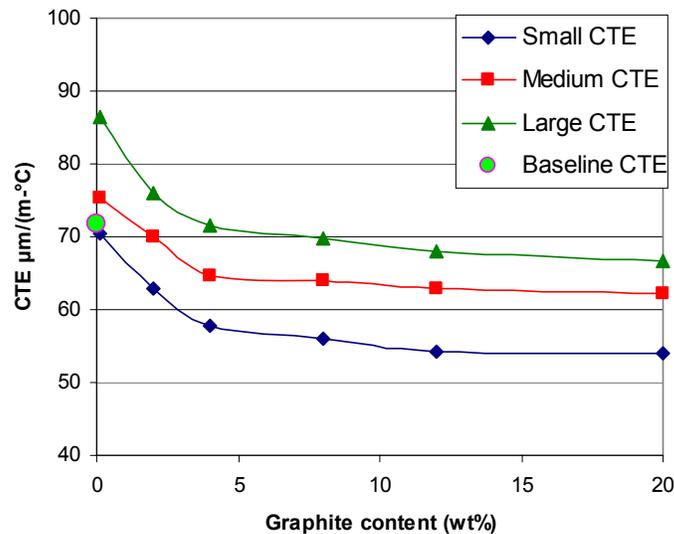


Figure 7. CTE measurements of exfoliated graphite filled polymers with different particulate sizes as a function of the graphite content.

3.3. Mechanical Properties

The measurements for flexural modulus and strength of the exfoliated graphite filled polymers versus exfoliated graphite concentration are shown in Figure 8. In general, the flexural modulus increases with the increase of graphite content for all three graphite size systems within an acceptable standard deviation, which is the typical characteristic for inorganic filled composites [9]. The presence of rigid graphite sheets increased the modulus of the polymer. The flexural modulus of the small flake filled polymers with a graphite content of 20 wt% is 3.84 GPa which is a 60% increase from the baseline polymer (2.40 GPa). It is interesting to note that with the initial addition of all three graphite sizes there seems to only a slight increase in modulus, and just as seen with electrical conductivity, there seems to be threshold for graphite content after which the modulus increases at a faster rate.

On the other hand, the flexural strength for all three graphite sizes showed their largest increase in strength with minimal graphite content. The flexural strength of the large flake polymers with 0.1 wt% of graphite filler achieved the greatest increase of 0.172 GPa which is a 87% increase from the baseline neat polymer (0.092 GPa). From this point, further increase of graphite content causes a decrease in flexural strength reaching as low as 0.0364 GPa for small particle with 12 wt% graphite, which is a 153% decrease from the pure polymer. This trend of decreasing in strength is mainly due to the poor mechanical strength of graphite crystallites because of their easy shear and glide of 001 plane of graphene layers. It might be possible that the monomers and polymers might not be able to diffuse into the closed cavities inside the exfoliated graphite. This phenomenon may cause the graphite sheets around cavities to overlap each other and form an accumulation during processing. The aggregates of graphite sheets may result in poor mechanical properties of the polymer systems [2].

It has been reported that strength decreases from 3% to 175% below the baseline values with the addition of graphite filler into a polymer [3,7,11]. This drop in mechanical properties seems to be related to processing conditions, a shorter sonication time, may lead to bundles of poorly exfoliated groups of graphite rather than dispersed. Typically, if the exfoliated graphite is well dispersed throughout the matrix, a rise in the flexural modulus should be prevalent.

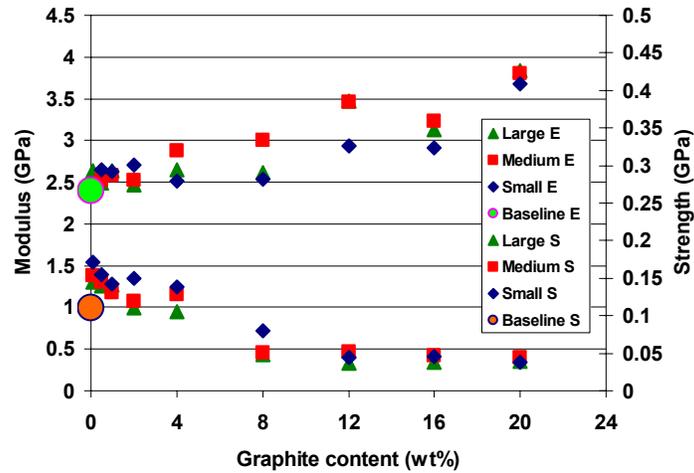


Figure 8. Flexural strength and flexural modulus of the exfoliated graphite filled polymers with different graphite sizes as a function of the graphite content.

4. Conclusions

To overcome the current polymer limitations, exfoliated graphite filled polymers were fabricated and proven to significantly enhance the physical and tribological properties of the base polymer. A lightweight, highly conductive polymer was successfully made by monitoring the dimensions and degree of exfoliation of the filler. We investigated different filler concentration ratios from 0 to 20%. The electrical resistivity of the polymers was measured and showed a transition from an insulating to a conducting polymer. There was an improvement in the electrical resistivity by as much as eight orders of magnitude. Similarly, the thermal conductivity demonstrated great improvement, nearly 2000% increase compared to the base polymer. The excellent conductivities achieved in the polymers can be attributed to the dispersion of graphitic sheets throughout the polymer, forming a unique conductive network. The increase of exfoliated graphite concentration also demonstrated a reduction in the CTE values due to the rule of mixture.

The electrical and thermal conductivities achieved by the exfoliated graphite filled polymers were proven to be higher than carbon nanofiber and HHT nanofiber based polymer composites. Not only can exfoliated graphite produce higher conductivities in polymers, they are also significantly more cost effective and easy to manufacture than current methods of manufacturing nanofibers or nanotubes.

The addition of exfoliated graphite gradually increased the modulus of the base polymer after the percolation threshold was achieved. However, the strength seemed to reduce within an increase in concentration due to slip in the graphite planes and to a lack of interface between graphite and polymer.

It was demonstrated that an increase of exfoliated graphite concentration led to a significant decrease of the wear rate. For each of the three sets, the addition of graphite resulted in a nearly linear decrease of the wear rate. Higher aspect ratio of the large flake graphite directly exhibit both high thermal, electrical and modulus properties coupled with low thermal expansion properties contributed to greater wear resistance.

References

- [1] Chen G.H., Wu D.J., Weng W.G., Yan W.L., Preparation of polymer/graphite conducting nanocomposite by intercalation polymerization. *J. of Appl. Polym. Sci.*, 82, 2506 (2001).
- [2] Chen G.H., Wu D.J., Weng W.G., Wu D.J., Yan W.L., Preparation of polystyrene/graphite nanosheet composite. *Polymer*, 44, 1781 (2003).
- [3] Du X.S., Xiao M., Meng Y.Z., Hay A.S., Synthesis and properties of poly(4,4'-oxybis(benzene)disulfide)/graphite nanocomposites via in situ ring-opening polymerization of macrocyclic oligomers. *Polymer*, 45, 6713 (2004).
- [4] Friedrich K., Reinicke R., Zhang Z., Wear of polymer composites, in: G.W. Stachowiak (Ed.), Proceedings of the Institution of Mechanical Engineers, vol. 216. *Part J: Journal of Engineering Tribology*, 415 (2002).
- [5] Jacko M.G., Lee S.K., "Encyclopedia of Chemical Technology", fourth ed. 1992, vol. 4, p 523.
- [6] Hager A.M., Davies M., in K. Friedrich (Ed.), "Advances in Composite Tribology", Composite Materials Series 8, Elsevier, Amsterdam, 1993, p. 107.
- [7] Li J., Kim J.K., Sham M.L., Conductive graphite nanoplatelet/epoxy nanocomposites: Effects of exfoliation and UV/ozone treatment of graphite. *Scripta Materialia*, 53, 235 (2005).
- [8] Li X., Gao Y., Xing J., Wang Y., Fang L., reduction mechanism of graphite and MoS₂ in epoxy composites. *Wear*, 257, 279 (2004).
- [9] Matsuo Y., Hatase K., Sugie Y., Preparation and Characterization of Poly(vinyl alcohol)- and Cu(OH)₂-Poly(vinyl alcohol)-Intercalated Graphite Oxides. *Chem. Mater.*, 10, 2266 (1998).
- [10] Matzek M.D., Carbon Nanocomposites: Physical Properties and Osteoblast adhesion studies. Thesis. April 2004
- [11] Pan Y.X., Yu Z.Z., Ou Y.C., Hu G.H., A new process of fabricating electrically conducting nylon 6/graphite nanocomposites via intercalation polymerization. *J. Polym. Sci. Part B*, 38, 1626 (2000).
- [12] Product Bulletin: EPON Resin 862. Resolution Performance Products. March 2005
- [13] Xian G., Zhang Z., Sliding wear of polyetherimide matrix composites: II. Influence of graphite flakes. *Wear*, 258, 783 (2005).
- [14] Zheng W., Lu X., Wong S.C., Preparation of polymer/graphite conducting nanocomposite by intercalation polymerization. *J. of Appl. Polym. Sci.* 91, 2781 (2004).