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GRAPHENE OXIDE AND THERMALLY EXFOLIATED GRAPHENE CYANATE ESTER RESIN COMPOSITES

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ABSTRACT

Recent investigations of cyanate ester resins as high temperature resin materials for space and propulsion applications have brought attention to the need for high temperature composite materials with improved stiffness, strength, hot/wet performance and high maximum use temperatures. The addition of nanocomposite filler materials has been shown to provide property improvement to cyanate ester resins, but often only at high loading levels and with improvement in only one property. Graphene, an allotrope of carbon, is the strongest material yet measured and displays exceptionally high thermal conductivity, electrical conductivity and gas impermeability. Since graphene is an atomically thick monolayer of carbon atoms arranged in a honey-comb lattice, its high surface to volume ratio allows property improvements at lower weight fractions than other composite fillers. The morphology, surface chemical functionality and thermal properties of graphene vary depending on the method of isolation from graphite and subsequent chemical and thermal treatments. Two forms of graphene, graphene oxide and thermally reduced graphene oxide, were dispersed in a commercial cyanate ester resin. The methods of graphene synthesis, isolation and incorporation of graphene into cyanate resin networks will be presented, as will preliminary property investigations of graphene-polycyanurate composites.

1. INTRODUCTION

Graphene, an allotrope of carbon, is an atomically thick monolayer of carbon atoms arranged in a honey-comb lattice. Interest and research of this material has grown rapidly in recent years due to its unusual properties. Graphene is the strongest material measured to date[1] and can display exceptionally high thermal conductivity,[2] electrical conductivity[3] and gas impermeability[4] making it a potential material for multifunctional nanocomposite materials in which the dispersed nanomaterial provides significant improvements in two or more properties. Isolation of individual graphene sheets can be accomplished through both bottom-up (chemical vapor deposition (CVD)[5] and epitaxial growth[6]) and top-down (micromechanical cleavage[7] and graphite oxidation[8],[9]) methods. Bottom-up methods typically produce relatively large graphene

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sheets that are free of defects but since only small quantities of material can be made by these methods they are used for studying the properties of individual graphene sheets. Top-down methods, however, produce relatively large quantities of graphene, with the exception of micromechanical cleavage, which is advantageous for polymeric composite research. The surface chemistry of the graphene sheets is often changed through oxidation to allow exfoliation of the graphene layers. Oxidation results in oxygen functionalities, namely hydroxyl and oxirane groups, incorporated to the surface of the individual graphene sheets and, to a lesser extent functionalization at the edges.[10] Oxygen functionalities improve dispersion in polar solvents and provide potential reactive sites for favorable polymer-filler interactions. The amount of these functionalities can be reduced by thermal treatment thereby affording a degree of control over the amount of oxygen functionalization. Recent investigations of cyanate ester resins as high temperature resin materials for space and propulsion applications have brought attention to the need for high temperature composite materials with improved stiffness, strength, hot/wet performance and high maximum use temperatures.[11,12] Since graphene displays such unusual properties and has been shown to provide property improvement in other polymeric systems, it was of interest to investigate the properties of cyanate ester graphene composites. Graphene oxide and thermally reduced graphene oxide were dispersed in a commercial cyanate resin and the effects of graphene on processability, thermomechanical properties and thermal degradation were investigated.

2. EXPERIMENTATION

2.1 Materials

The dicyanate ester of Bisphenol E (Primaset® LECy) was purchased from Lonza and used as received (Figure 1). Nonylphenol (technical grade) was purchased from Aldrich, and Copper (II) acetylacetonate was purchased from ROC/RIC; both were used as received. Graphite nanoplatelets (xGNP-M-25) were purchased from XG Sciences® and used for oxidation to graphene oxide.

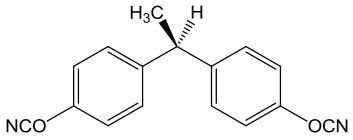

Figure 1. Chemical structure of LECy.

2.2 Graphene Oxide (GO) and Thermally Reduced Graphene Oxide (TRGO) Synthesis

Graphene oxide (GO) was prepared by a modified Hummers oxidation method. In a 2 L Erlenmeyer flask 10 g of xGNP-M-25 graphite nanoplatelets were suspended in a solution of 230 mL of concentrated sulfuric acid and 5.0 g of sodium nitrate. The solution was cooled to 0 °C by placing the flask in an ice bath and 30 g of potassium permanganate was added slowly with stirring which caused the suspension to turn to a thick paste. After the addition of potassium permanganate the solution was warmed to 35 °C and allowed to stir for 30 minutes. After this time 460 mL of de-ionized water was added slowly, which caused the temperature of the suspension to rise to 98 °C. The temperature was held at 98 °C for 15 minutes. The suspension

was then diluted to approximately 1.4 L with water and treated with 150 mL of a 3% hydrogen peroxide solution. The suspension was then filtered through a glass fritted funnel while warm and washed 3 times with a 5% hydrochloric acid solution, once with water and once with acetone.

Thermally reduced graphene oxide (TRGO) was prepared by placing 5.0 g of graphene oxide in a covered graphite boat which was heated in a tube furnace at 800 °C for 5 minutes with flowing nitrogen.

2.3 Composite Sample Preparation

Batches of catalyst comprised of 30 parts by weight nonylphenol to one part by weight of copper (II) acetylacetonate were prepared by mixing the ingredients in a vial and heating to 60 °C while stirring vigorously until complete dissolution took place (typically one to two hours). These batches were retained for up to 30 days.

Composite resins were fabricated by first mixing LECy with 2 parts per hundred by weight of catalyst and 1 wt% GO, TRGO or M-25 graphite. The mixture was then mixed with an IKA T25 Basic high shear mixer for 1 hour followed by ultrasonication for 1 hour. The mixture was partially de-gassed at 90 °C for 30 minutes under reduced pressure (300 mm Hg). To prepare cured samples for TMA, silicone molds made from R2364A silicone from Silpak Inc. (mixed at 10:1 by weight with R2364B platinum-based curing agent) were made by de-gassing for 60 minutes at 95 °C and 300 mm Hg, cured overnight at room temperature, followed by post-cure at 150 °C for 1 hour. The uncured cyanate ester mixture was then poured into the mold. The open mold and sample were then placed under flowing nitrogen at 25 °C and ramped 5 °C/min to 150 °C for 1 hour, ramped 5 °C/min to 210 °C for 24 hours to produce void-free discs measuring approximately 11.5-13.5 mm in diameter by 1-3 mm thick and weighing 200-400 mg. Composite samples for DMA were made using the above procedure with open molds that gave rectangular samples measuring 60 mm x13 mm x 2.5 mm.

2.4 Characterization

DSC was performed on a TA Instruments Q2000 calorimeter under 50 mL/min. of flowing nitrogen. The samples were heated to 350 °C, then cooled to 25 °C and re-heated to 350 °C, all at 10 °C/min. Oscillatory TMA was conducted with a TA Instruments Q400 series analyzer under 50 mL/min of nitrogen flow. The discs were held in place via a 0.2 N initial compressive force with the standard ~5 mm diameter flat cylindrical probe while the probe force was modulated at 0.05 Hz over an amplitude of 0.1 N (with a mean compressive force of 0.1 N) and the temperature was ramped to 350 °C followed by two heating and cooling cycles between 100 °C and 200 °C (to determine thermal lag), and a final ramp to 350 °C all at 10 °C/min for the GO composite samples and 20 °C/min for the M-25 composite and for the neat LECy resin. Linear coefficients of thermal expansion (CTEs) were determined from the dimension change of the cylindrical sample with respect to temperature. All values are reported in ppm/°C at 75 °C. Dynamic mechanical analysis (DMA) was performed with a TA instruments Q800. Rectangular samples with typical dimensions 60 mm x13 mm x 2.5 mm were analyzed in dual cantilever mode and ramped at 5°C/min from 25°C to 350°C at a frequency of 1Hz and amplitude of 10μm. Dispersions of graphene oxide in water were spin-cast on freshly cleaved mica for AFM imaging. AFM images were obtained using a Veco Digital Instruments Nanoscope IV in tapping

mode. SEM images of fractured surfaces were obtained with a FEI Quanta 600 SEM in high vacuum mode. Samples were gold sputtered prior to imaging.

3. RESULTS

3.1 Graphene Oxide Characterization

3.1.1 Graphene Oxide Dimensions

Graphene oxide synthesized by the Hummers method of oxidation was spin cast on freshly cleaved silica and imaged by AFM (figure 2). The graphene sheets varied in both lateral dimensions and shape with an average diameter of approximately 1 µm. Step height scans showed a height of approximately 1 nm which is consistent with previous reports of single layer graphene sheets on flat substrates.[7]

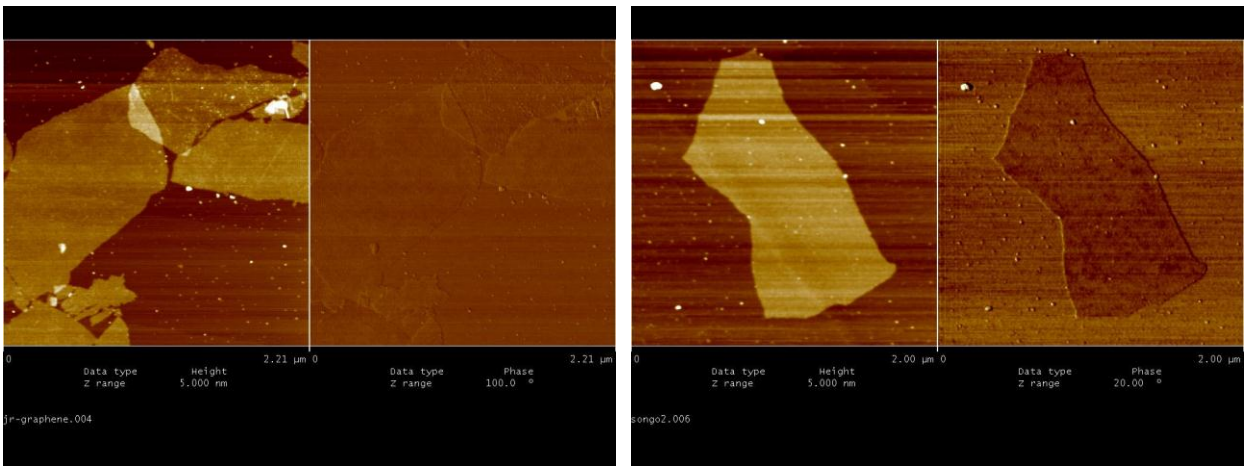

Figure 2. AFM images of graphene oxide on freshly cleaved silica. Images are 2 µm x 2 µm.

The effect of the dispersion method of graphene oxide was also investigated with AFM. It was of interest to examine what effect, if any, high shear mixing and sonication had on the lateral dimensions of GO. The GO collected from the final filtration step after oxidation was layered and paper-like in nature. This material was difficult to disperse in LECy by sonication alone. It was necessary to first break apart the paper-like GO by high shear mixing before further dispersion by sonication. Although time between dispersion and cure was kept to a minimum, reduction in lateral dimensions by either of these methods could potentially have an effect on the degree of settling of GO in the time between dispersion of GO in the uncured liquid monomer and gelation of the surrounding LECy matrix during cure. AFM was performed on GO that was dispersed in water by high shear mixing alone and on GO that was dispersed by sonication alone (figure 3). There was no significant difference between the lateral dimensions of GO dispersed by either method.

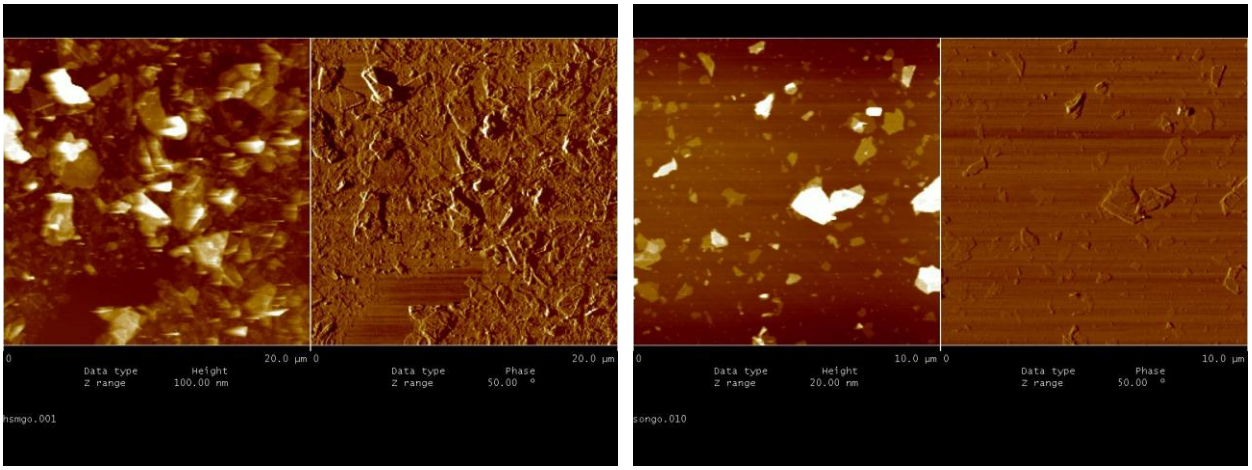

Figure 3. AFM images of graphene oxide dispersed by high shear mixing (left) and sonication (right) in water. Images are 20 µm x 20 µm.

3.1.2 Graphene Oxide Degree of Oxidation

Oxygen functionalities on graphene were expected to have an impact on the nature of the interaction between GO and the surrounding LECy polycyanurate matrix whether it by covalent or non-covalent bonding. Therefore, the relative amount of oxygen functionalities incorporated in the graphene sheets by chemical oxidation was expected to have an effect on final properties of the composite materials. Thermogravimetric analysis (TGA) of GO shows significant weight loss at 200 °C which has been attributed to the removal of oxygen functionalities and restoration of the graphene lattice (figure 4).[13,14] As was expected, weight loss at this temperature was absent for TRGO. Other weight loss event present in TGA are weight loss in the 50-150°C region which is due to evaporation of intercalated water and weight loss above 700 °C which is due to sublimation of the carbon backbone.

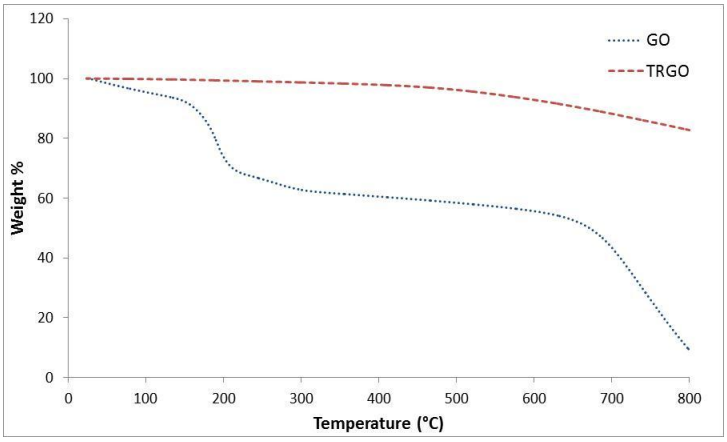

Figure 4. TGA of graphene oxide (GO) and thermally reduced graphene oxide (TRGO) in nitrogen.

The weight loss of between 50-200 °C of approximately 30% is consistent with the weight loss of GO prepared from by the Hummers method from flake graphite.[13] Graphite nanoplatelets (xGNP-M-25 from XG Sciences®), with an average diameter of 25 µm and oxygen content of <1 wt%, were used as the starting material for Hummers oxidation in this study to ensure the greatest degree of oxidation was obtained by this method. However it appears, from TGA data, that the size of the graphite starting material platelets does not have an effect on the final degree of oxidation.

3.1.3 Effect of Graphene Oxide on Cyanate Ester Cure

One of the attractive properties of cyanate ester resins that make them suitable for applications such as filament winding is the wide processing window between the melting temperature of the monomer and the temperature at which the material rapidly cyclotrimerizes to form a gel. Addition of catalysts will produce a resin with a greater degree of cure at a given cure temperature, but will oftentimes decrease this processing window. Hydroxyl-containing compounds, such as phenols, for example, are known to catalyze cyanate ester cure.[15] The practical effect of cyanate ester catalysis is that the temperature at which the maximum rate of cure is achieved is pushed to a lower temperature in effect narrowing the processing window of the system. Although the composites studied here were catalyzed with a transition metal catalyst dissolved in a nonylphenol co-catalyst, further catalysis by the hydroxyl groups could lead to a further decrease in the peak cyclotrimerization cure exotherm. Dynamic DSCs of LECy-GO mixtures reflect this effect to a small extent. The peaks in figure 5 are the cyclotrimerization exothermic events for catalyzed LECy and catalyzed LECy-GO mixtures. The peak temperature

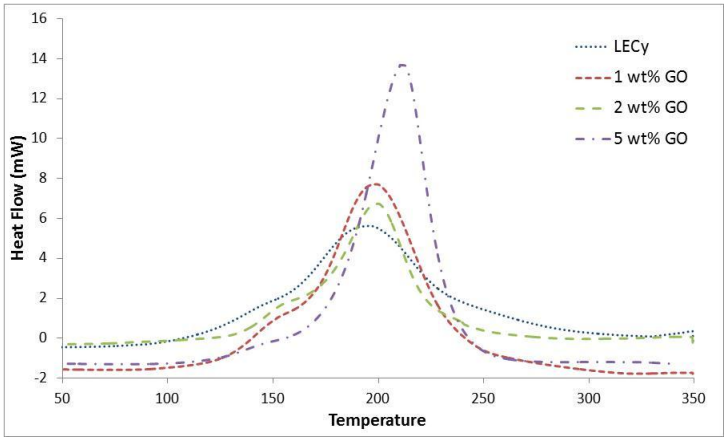

Figure 5. Dynamic Differential Scanning Calorimetry (DSC) of LECy monomer and LECy monomer-graphene oxide mixtures.

exotherm is shifted to a lower temperature and the peak broadened in the LECy samples with GO present. This effect however is small and the catalytic effect is overshadowed in the dynamic DSCs by the transition metal catalyst. Furthermore, the small catalytic effect of GO is not expected, based on the DSCs in figure 5, to have a substantial effect on processability of the resin

3.2 Graphene-Polycyanurate Resin Composite Characterization

3.2.1 Thermomechanical Analysis (TMA)

The glass transition temperatures of 1,2 and 5 wt% GO in LECy and 1 wt% M-25 graphite were determined by oscillatory thermomechanical analysis (TMA) and compared to neat LECy polycyanurate. The samples were subjected to a temperature ramp twice which gave the as-cured T_gs (figure 6) and fully cured T_gs (figure 7). The as-cured T_g of the 5 wt% GO and the 1 wt% M-25 graphite were lower than that of neat LECy polycyanurate and the 1 and 2 wt% GO samples had a T_g slightly higher than LECy (table 1). The slightly higher as-cured T_gs of the 1 and 2 wt% GO samples suggest that GO may catalyze cure giving the material a higher as-cured T_g. The catalytic effect of the 5 wt% may be masked by networked defects introduced by the high loading level or by defects from settling of the GO.

After the first TMA heating cycle, which also functioned as an in-situ post cure, the resins were subjected to a second TMA heating cycle and the fully-cured T_gs were determined. All of the composite materials, with the exception of the 5 wt% GO composite, reached a fully cured T_g close to that of LECy polycyanurate. The lower fully cured T_g of the fully cured 5 wt % GO composite sample is likely due to introduction of network defects and is indicative of poor dispersion at a high loading level.

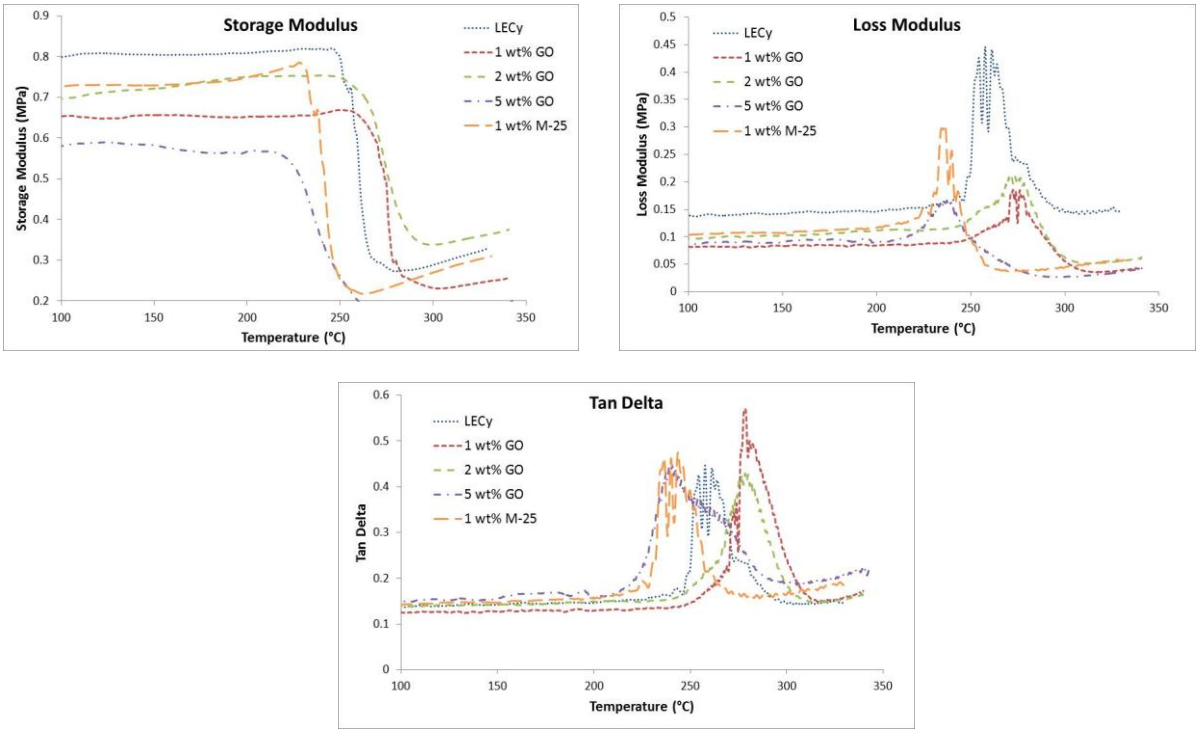

Figure 6. TMA graphs (first heating cycle) of LECy-GO and LECy-graphite composites.

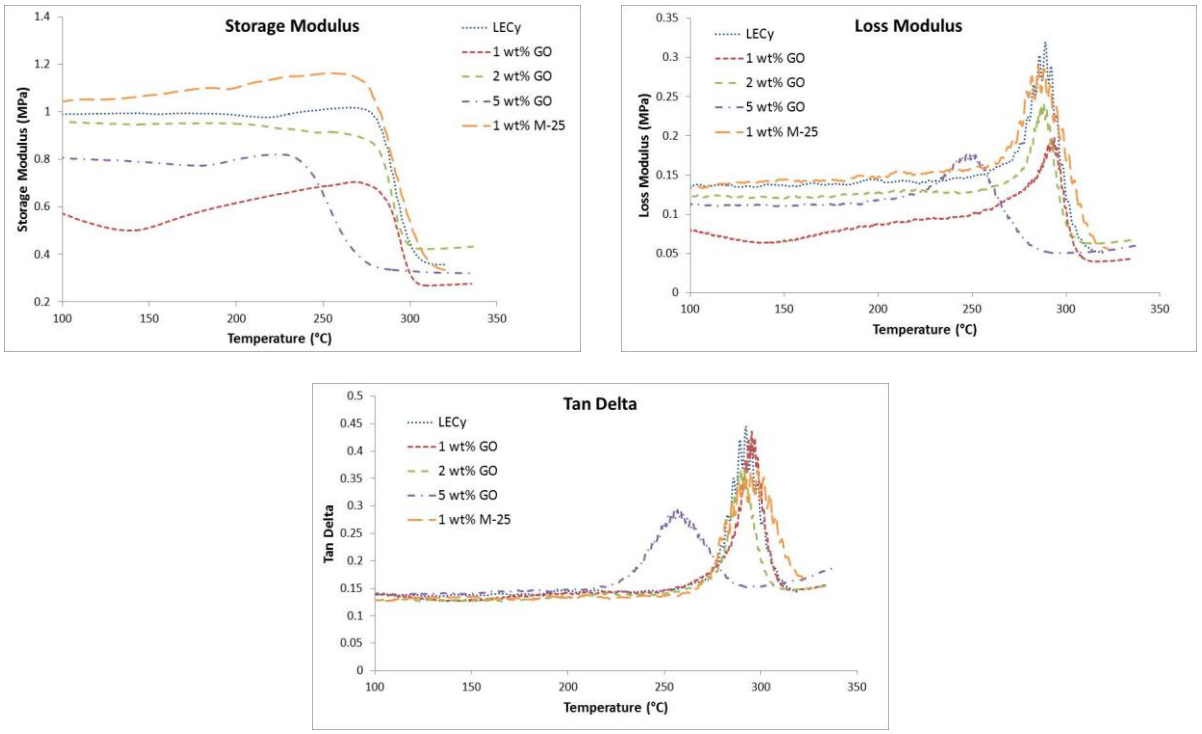

Figure 7. TMA graphs (second heating cycle) of LECy-GO and LECy-graphite composites.

Table 1. Linear coefficient of thermal expansion (CTE) and T_g values for LECy-GO and LECy-graphite composites.

Sample	CTE (ppm/°C)	Loss Modulus Peak (°C)	Tan Delta Peak (°C)	Fully Cured Loss Modulus Peak (°C)	Fully Cured Tan Delta Peak (°C)
LECy	50	254	258	289	292
1 wt% GO	57	276	278	294	295
2 wt% GO	52	275	278	288	290
5 wt% GO	50	236	241	250	257
1 wt% M-25	50	236	244	288	298

3.2.2 Dynamic Mechanical Analysis (DMA)

Glass transition temperatures of graphene and graphite composite materials obtained by the first and second heating cycle in DMA shows similar T_gs for all materials except for the 5 wt% GO composite (figure 7,8). This is consistent with the T_gs obtained from the second heating cycle of TMA. The first heating cycle in DMA does not give an accurate as-cured T_g of the materials because of the slow ramp rate, 5 °C/min, used in the DMA instrument. The ramp rate is actually slow enough that post cure is evident by the tailing of the loss modulus peaks and the bimodal nature of the tan delta peaks. The Tgs of the materials relative to the samples is the same in the second heating cycle but shifted to a higher temperature reflecting the higher degree of cure reached from in-situ post cure in the first heating cycle.

The storage moduli of the fully cured 1 and 2 wt% GO composite materials were greater than LECy in both the first and second heating cycles. Among the fully cured materials, addition of GO resulted in an increase in storage modulus up to 2 wt%. The composites containing 5 wt% GO and 1 wt% M-25 graphite had storage moduli close to that of neat LECy suggesting that any increase in storage modulus imparted by the filler materials were possibly negated by settling.

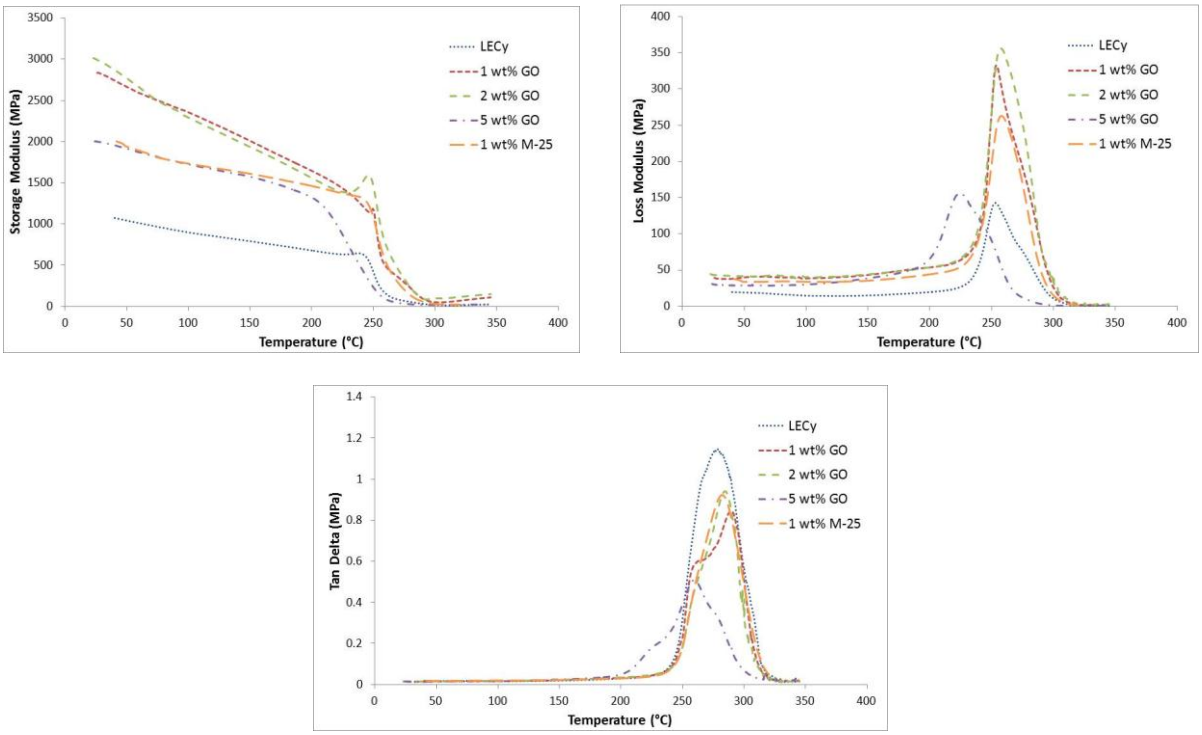

Figure 8. DMA graphs (first heating cycle) of LECy-GO and LECy-graphite composites.

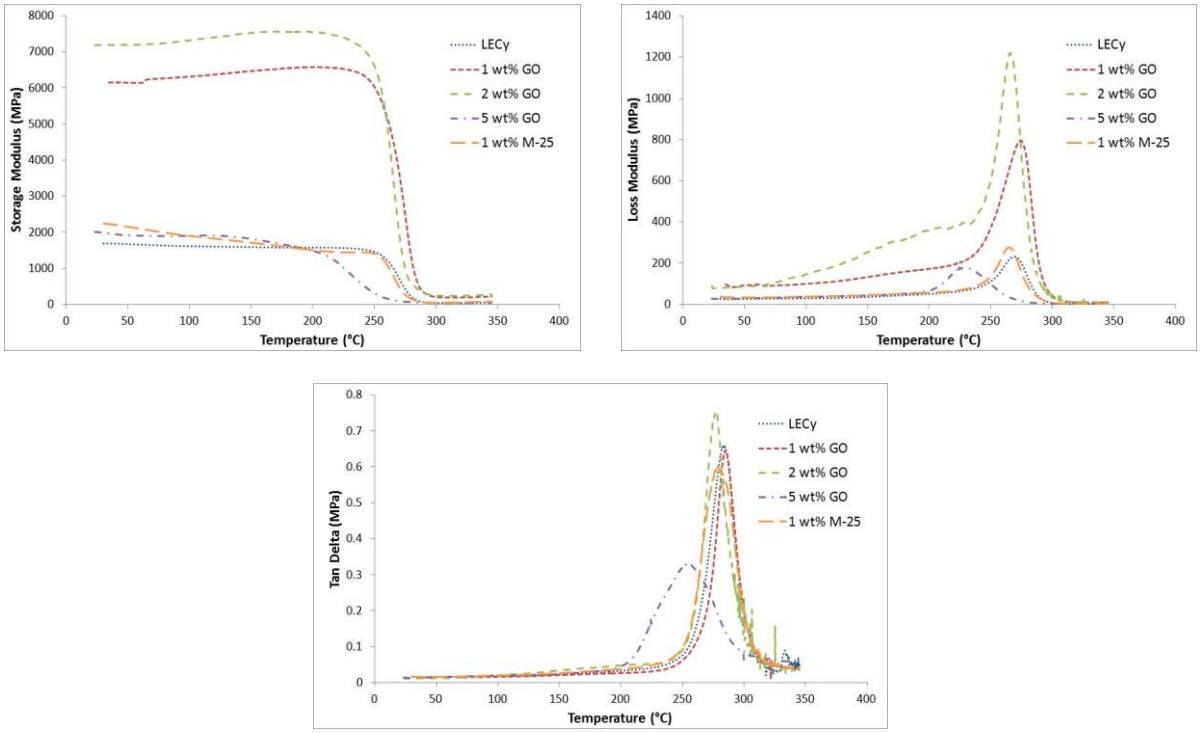

Figure 9. DMA graphs (second heating cycle) of LECy-GO and LECy-graphite composites.

3.2.3 Composite Thermal Stability

Thermogravimetric analysis (TGA) was performed on LECy composite samples containing GO, M-25 graphite and thermally reduced graphene oxide (TRGO). All of the composite materials displayed reduced thermal stability compared to neat LECy. The 5 wt% GO material had the lowest 5 % and 10 % weight loss temperatures in both nitrogen and air (table 2). Greater amounts of GO content generally resulted in poorer thermal stability of the composites. The relation between the different forms of the composite, whether it be graphene oxide, graphite or thermally reduced graphene oxide was less clear. The TRGO composite showed greater thermal stability than LECy in air but degraded at slightly lower temperature in nitrogen.

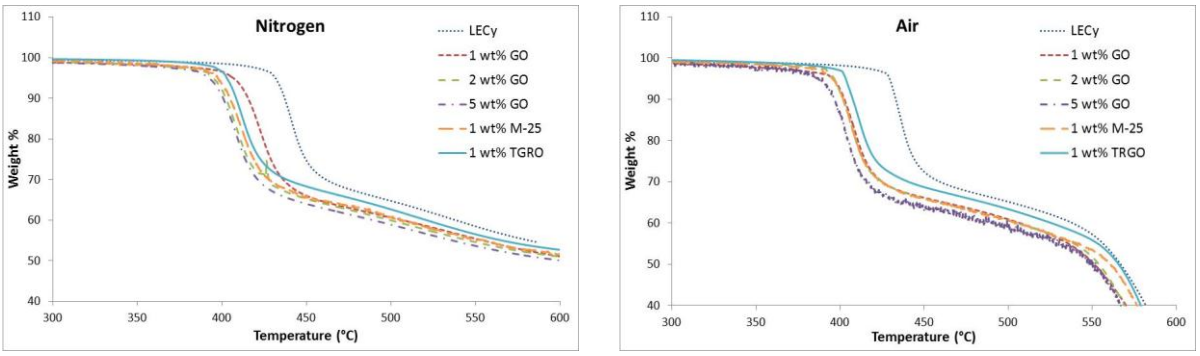

Figure 10. Weight loss vs. temperature for GO, M-25 graphite and TRGO composites in Nitrogen (left) and Air (right) atmosphere.

Table 2. LECy and LECy composite TGA weight loss temperatures and Char yields.

	Nitrogen			**Air**		
Sample	5 % Weight Loss (°C)	10 % Weight Loss (°C)	Char Yield at 600 °C (%)	5 % Weight Loss (°C)	10 % Weight Loss (°C)	Char Yield at 600 °C (%)
LECy	431	437	54	429	433	24
1 wt% GO	405	415	51	394	402	20
2 wt% GO	393	402	51	396	401	13
5 wt% GO	390	400	50	386	396	13
1 wt% M-25	396	404	52	394	402	19
1 wt% TRGO	402	408	53	403	407	19

3.2.4 Graphene Oxide Dispersion

The relative degree of dispersion and approximate GO layer thickness of LECy GO composites was qualitatively characterized using SEM. Although a single GO sheet is below the resolution of the SEM instrument used for imaging, there were some protruding sheets that appeared almost "transparent" by SEM which may have been single sheets (figure 11). The majority of the GO sheets, however, were many-layered. SEM of fractured surfaces also revealed the relative degree of dispersion between the different loading levels of GO composites (figure 12). The 1 wt% GO composite showed good dispersion while the 5 wt% GO composite showed a significant amount of settling and large voids. The presence of settling and voids with 5 wt% GO loading is consistent with the decrease in thermomechanical seen in TMA and DMA.

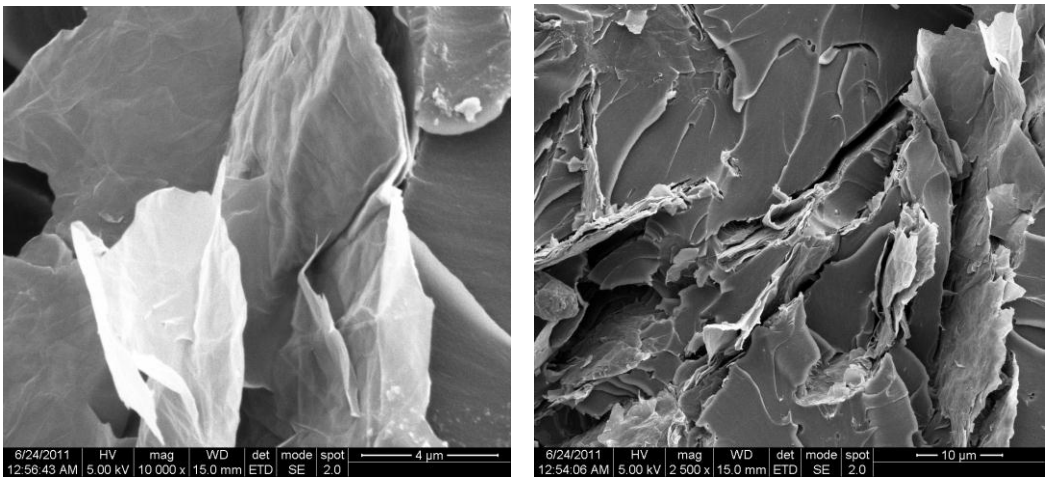

Figure 11. SEM micrographs of the fractured surface of 2 wt% GO LECy composite.

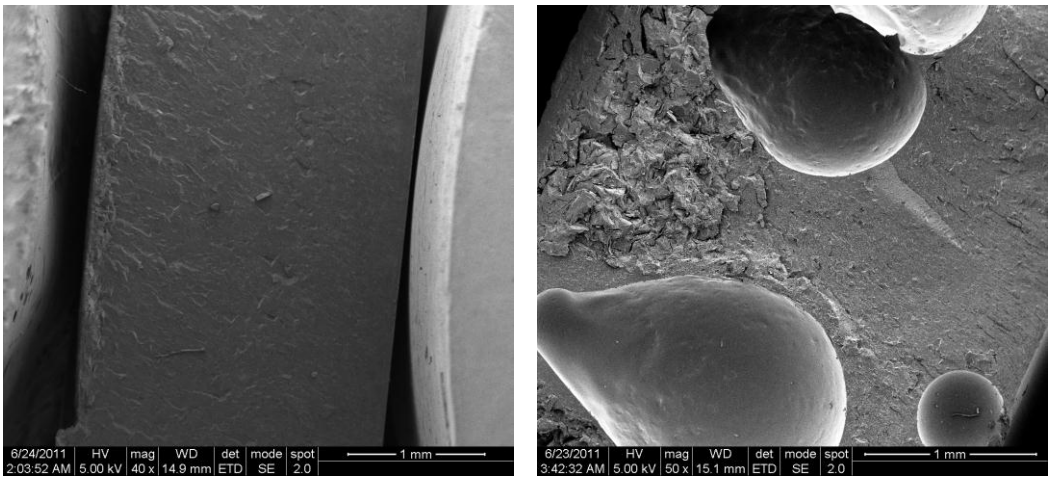

Figure 12. Low magnification SEM micrographs of the fractured surface of 1 wt% (left) and 5 wt% (right) GO LECy composites.

4. CONCLUSIONS

Graphene oxide (GO), synthesized by chemical oxidation, was dispersed in a commercially available liquid cyanate ester monomer, LECy, and cured by a typical cyanate ester resin cure schedule. The results from thermomechanical characterization were compared to composites made containing graphite and thermally reduced graphene oxide (TRGO). The incorporation of GO at low levels, 1-2 weight percent, resulted in a slightly increased as-cured T_g and greater storage modulus than pure LECy polycyanurate. Graphene oxide, graphite and TRGO had no significant effect on processability of the liquid LECy monomer or the T_g of the fully cured composite resin with the exception of 5 wt% GO which resulted in a decrease in T_g. LECy cured with 1 weight percent M-25 graphite and TRGO had no significant difference in fully cured T_g or storage modulus of the fully cured resins. Incorporation of GO, M-25 graphite and TRGO in LECy resulted in a decrease in thermal stability. Dispersion of GO in LECy composites was good at 1 and 2 weight percent, in which the GO sheets were found to be predominantly multiple layers thick, but the 5 weight percent composited showed significant settling which explains the decrease in thermomechanical properties at high loading.

5. REFERENCES

1. Lee, C.; Wei, X. D.; Kysar, J. W.; Hone, J., "Measurement of the elastic properties and intrinsic strength of monolayer graphene." *Science* 321 (2008)**:** 385-388.

2. Balandin, A. A.; Ghosh, S.; Bao, W. Z.; Calizo, I.; Teweldebrhan, D.; Miao, F.; Lau, C. N., "Superior thermal conductivity of single-layer graphene." *Nano Lett.* 8 (2008): 902-907.

3. Du, X.; Skachko, I.; Barker, A.; Andrei, E. Y., "Approaching ballistic transport in suspended graphene." *Nat. Nanotechnol.* 3 (2008): 491-495.

4. Bunch, J. S.; Verbridge, S. S.; Alden, J. S.; van der Zande, A. M.; Parpia, J. M.; Craighead, H. G.; McEuen, P. L., "Impermeable atomic membranes from graphene sheets." *Nano Lett.* 8 (2008): 2458-2462.

5. Liu, W.; Chung, C. H.; Miao, C. Q.; Wang, Y. J.; Li, B. Y.; Ruan, L. Y.; Patel, K.; Park, Y. J.; Woo, J.; Xie, Y. H., "Chemical vapor deposition of large area few layer graphene on Si catalyzed with nickel films." *Thin Solid Films* 518 (2010): S128-S132.

6. Sutter, P. W.; Flege, J. I.; Sutter, E. A., "Epitaxial graphene on ruthenium." *Nature Materials* 7 (2008): 406-411.

7. Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A., "Electric field effect in atomically thin carbon films." *Science* 306 (2004): 666-669.

8. Staudenmaier, L., "Verfahren zur Darstellung der Graphitsaure." *Ber. Dtsch. Chem. Ges.* 31 (1898): 1481-1487.

9. Hummers, W. S.; Offeman, R. E., "Preparation of graphitic oxide." *Journal of the American Chemical Society* 80 (1958): 1339-1339.

10. Lerf, A.; He, H. Y.; Forster, M.; Klinowski, J., "Structure of graphite oxide revisited." *Journal of Physical Chemistry B* 102 (1998): 4477-4482.

11. Guenthner, A. J.; Yandek, G. R.; Mabry, J. M.; Lamison, K. R.; Vij, V.; Davis, M. C.; Cambrea, L. R.; "Insights into moisture uptake and processa-bility from new cyanate ester monomer and blend studies." *Proceedings of SAMPE '10, Vol. 55. Covina, CA: SAMPE International Business Office* 2010, paper 42ISTC-119.

12. Guenthner, A. J.; Lamison, K. R.; Yandek, G. R.; Masurat, K. C.; Reams, J. T.; Cambrea, L. R.; and Mabry, J. M.; "The role of concurrent chemical and physical processes in determining the maximum use temperature of thermosetting polymers for aerospace applications." *Polymer Preprints* 52 (2011): unpaged.

13. McAllister, M. J.; Li, J. L.; Adamson, D. H.; Schniepp, H. C.; Abdala, A. A.; Liu, J.; Herrera-Alonso, M.; Milius, D. L.; Car, R.; Prud'homme, R. K.; Aksay, I. A., "Single sheet functionalized graphene by oxidation and thermal expansion of graphite." *Chemistry of Materials* 19 (2007): 4396-4404.

14. Schniepp, H. C.; Li, J. L.; McAllister, M. J.; Sai, H.; Herrera-Alonso, M.; Adamson, D. H.; Prud'homme, R. K.; Car, R.; Saville, D. A.; Aksay, I. A., "Functionalized single graphene sheets derived from splitting graphite oxide." *Journal of Physical Chemistry B* 110 (2006): 8535-8539.

15. Hamerton, I. (Ed.), *Chemistry and Technology of Cyanate Ester Resins*. London, UK Chapman & Hall, 1994.