MULTIFUNCTIONAL COMPOSITES FOR IMPROVED POLYIMIDE THERMAL STABILITY

Sandi G. Miller
NASA Glenn Research Center, Cleveland, OH 44135

ABSTRACT

The layered morphology of silicate clay provides an effective barrier to oxidative degradation of the matrix resin. However, as resin thermal stability continues to reach higher limits, development of an organic modification with comparable temperature capabilities becomes a challenge. Typically, phyllosilicates used in polymer nanocomposites are modified with an alkyl ammonium ion. Such organic modifiers are not suited for incorporation into high temperature polymers as they commonly degrade below 200°C. Therefore, the development of nanoparticle specifically suited for high temperature applications is necessary. Several nanoparticles were investigated in this study, including pre-exfoliated synthetic clay, an organically modified clay, and carbon nanofiber. Dispersion of the layered silicate increases the onset temperature of matrix degradation as well as slows oxidative degradation. The thermally stable carbon nanofibers are also observed to significantly increase the resin thermal stability.

KEY WORDS: Nanocomposites, Polyimide, Resin Transfer Molding

1. INTRODUCTION

Over the past decade, primary drivers in the development of high temperature polymers have included increasing resin use temperature and improving processability, specifically melt flow to allow RTM processing. Simultaneously meeting both property advancements is a challenge. Modification of resin chemistry has driven the T_g of some polyimides as high as 400°C.(1) However, such capability often necessitates utilization of highly aromatized structures, resulting in high melt viscosity resins. Melt viscosity can be reduced by modification of the monomer chemistry in the form of aliphatic or ether linkages, or by kinked or twisted structures.(2) Such structures may improve processability, but at the expense of T_g.

The addition of nano-materials to a polyimide is one mechanism by which the T_g or use temperature may be increased. Several groups have reported improved thermal stability of polyimides through dispersion of a layered silicate.(3,4) It has been reported that dispersion of layered silicate clay into a polyimide matrix slows the diffusion of oxygen into the bulk resin, thereby slowing oxididative degradation of the polymer.(5) However, as resin thermal stability continues to reach higher limits, the thermal properties of the clay and organic modifier must be considered. Typically, phyllosilicates used in polymer nanocomposites are modified with an alkyl ammonium ion. Such organic modifiers are not suited for incorporation into high temperature polymers as they commonly degrade below 200°C.

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Literature data suggests that clay modified with a phosphonium ion, specifically tetraphenyl phosphonium bromide (TPPB) may provide the thermal stability necessary for higher temperature applications.(6) Well dispersed clays perform as oxygen barriers; however, the resin use temperature may be pushed to higher temperatures by increasing the thermal conductivity of the matrix. To this end, the resins were also modified with a carbon nanofiber to investigate the effects of these materials on resin thermal stability.

The polyimide matrix used in this study was based on 2,3,3',4'-biphenyltetracarboxylic dianhydride (PBDA), 4,4'(1,4-phenylene-bismethylene) bisaniline (BAX), a triamine, 1,3,5-Tris(4-aminophenoxybenzene), and a 4-phenylethynyl phthalic anhydride (PEPA) endcap. This material will be denoted as BAX-TAB for the purpose of this paper. Literature suggests that the melt viscosity of the BAX-TAB oligomer is amenable to resin infusion methods of processing.(7) Furthermore, the thermal stability of the cured resin exceeds that of commercially available PMR-15.

The purpose of this work is to examine the influence of nano-additives on the thermal stability of the BAX-TAB resin. Effects on processability will follow.

2. EXPERIMENTAL

2.1 Chemicals for resin synthesis Chemicals for TAB synthesis, 4-fluoronitrobenzene, 1,3,5-trihydroxybenzene dehydrate, and hydrazine hydrate, were purchased from Aldrich. 2,2'-Bis(3,4-dicarboxyphenoxy)biphenyl dianhydride (PBDA) was received from Triton Systems Inc. 4,4'(1,4-phenylene-bismethylene) bisaniline (BAX) was received from Maverick Corp., and 4-phenylene phthalic anhydride (PEPA) was received from Imitech Inc.

2.2 Nanoparticles Sodium montmorillonite (Cloisite Na^+) was received from Southern Clay Products. Tetraphenyl-phosphonium bromide (TPPB) was purchased from Aldrich for the purpose of organic modification of Closite Na^+. A proprietary synthetic silicate clay (MSU clay) was supplied by the Pinnavaia group at Michigan State University (MSU). Carbon nanofiber samples, PR-19XT-PS and PR-24XT-PS, were received from Applied Sciences, Inc. All materials were used as received.

Carbon nanofibers PR-19XT-PS and PR-24XT-PS are very fine, highly graphitic, tubular nanofibers with diameters of 150 nm and 100 nm, respectively. The length of the as produced fibers range from 50 – 200 μm. The PS grade carbon nanofiber is produced by pyrolytically stripping the as-produced fiber to remove polyaromatic hydrocarbons from the fiber surface.

2.3 Sample Preparation The TAB synthesis is reported elsewhere.(8) BAX-TAB oligomer synthesis proceeded in a dry, three necked flask, under flowing nitrogen. PBDA (2.6g), and BAX (3.26g) were dissolved in 50 mL dry NMP. The solution was stirred at room temperature for 2 hours. TAB (0.54g) was added and stirred for an additional 2 hours. Finally, PEPA (3.8g) was added and stirring continued overnight at room temperature. The solution was refluxed for 4 hours followed by precipitation of the oligomer into water. The imide powder was filtered and washed with water. The powder was then placed into a beaker of water, stirred for several hours,

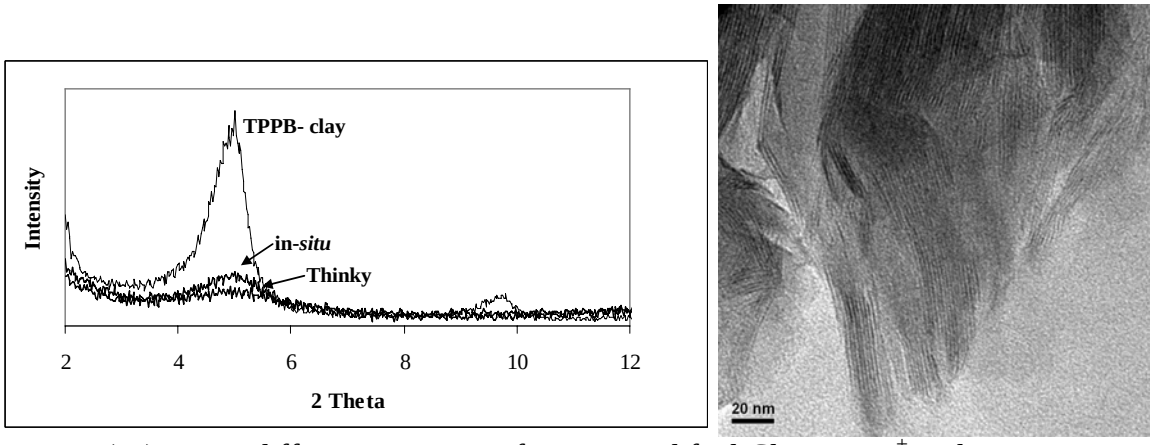
and filtered. The powdered oligomer was dried overnight in vacuum at 100°C. The oligomer powder (1.25g) was weighed out into a 2.54 cm diameter mold and cured for 2 hours at 370°C and 800 psi.

Nanocomposite preparation followed the neat resin synthesis, with the addition of either clay or carbon nanofiber to the oligomer solution. Nanoparticles were added with the PEPA endcap. This initial in-*situ* approach to nanoparticle dispersion did not yield acceptable levels of dispersion in all cases. Therefore, all nanocomposite preparation included preliminary mixing, in NMP, of a specified nanoparticle loading, in a THINKY^{TM} mixer. The THINKY^{TM} mixer simultaneously rotates and revolves the sample container, resulting in a homogenous mixture of materials in a relatively short period to time.

2.4 Characterization The extent of clay layer separation and exfoliation was investigated by wide angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM). Thermal and mechanical properties were determined using thermal gravimetric analysis (TGA) and dynamic mechanical analysis (DMA). The thermal diffusivity of the material was measured using a laser flash technique (Netzsch Instruments, LFA 447) which follows ASTM E1461. Using the diffusivity in combination with the measured heat capacity of a material, the thermal conductivity can be calculated by: $K=C_p\alpha\rho$

3. RESULTS AND DISCUSSION

3.1 Layered Silicate Clay Nanocomposites The dispersion of the clays into the BAX-TAB resin was evaluated by XRD and TEM, as shown in Figures 1a and 1b.



Figures (1a): XRD diffraction pattern of TPPB modified Cloisite Na^+ and nanocomposites, and (1b) TEM of 5wt% TPPB modified clay in the BAX-TAB resin matrix.

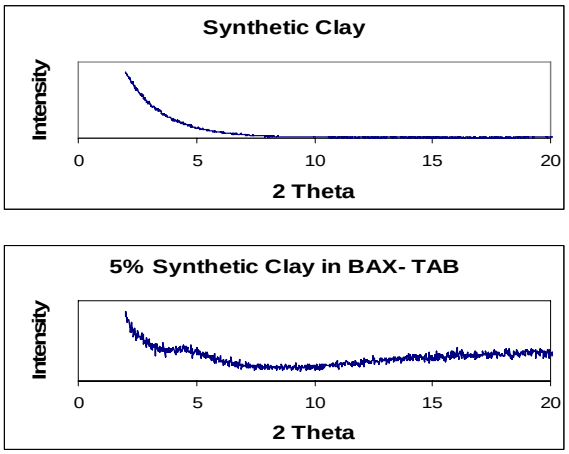
By XRD, the maximum peak height of TPPB clay is at $2\theta = 5.01^{o}$, corresponding to a d_{001} spacing of 1.77 nm. The peak is of a narrow width because the ion-exchange process does not disrupt the stacking registry of a layered silicate tactoid. The space between layers is increased to accommodate the modifier, but the layers remain regularly spaced. When introduced into a resin matrix, the peak broadens and is reduced in intensity. This is due to separation of the outermost clay layers which reduces the number of stacked layers detected in XRD.

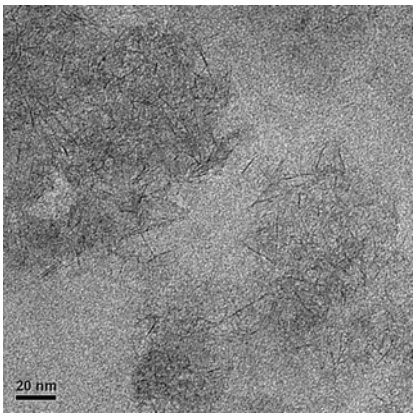
Additionally, the layers may separate by varying distances to accommodate and intercalate a resin, which accounts for the broadening of the peak width. The TEM image shows an intercalated morphology for the TPPB clay nanocomposites, with layer separation averaging 2.15 - 2.50 nm.

As described earlier, the TPPB clay in particular was difficult to disperse in-*situ*. Following addition of the TPPB clay to the BAX-TAB monomer in solution, a diffraction peak was seen by XRD, indicating that there remained several layers of stacked TPPB. Rotating the TPPB clay in NMP in a THINKY^{TM} mixer reduced the clay aggregate size. The clay/NMP solution was then added to the BAX-TAB monomer solution. This procedure yielded improved homogeneity of this mixture, and later of the carbon nanofibers as well.

The TPPB clay was chosen based on literature findings that it may provide thermal stability to a resin.(6) The highly aromatic modifier was desirable for the high processing temperature of the BAX-TAB resin.

The characterization of the MSU synthetic clay nanostructure is pictured in Figures 2a-c. XRD of the MSU-clay shows little evidence of layer stacking, i.e. no d_{001} diffraction peak down to $2\theta = 2^{o}$. A diffraction peak for stacked silicate layers is visible when many layers are stacked at the same repeating distance. Therefore, there may be stacking in the MSU clay, just not in the quantity, or with a registry that is visible by WAXD. However, the "pre-exfoliated" morphology of the MSU clay allows easy dispersion in a resin, as is evidenced by the TEM image of 2c. Here we see several individual platelets throughout the matrix. However, on dispersion in the BAX-TAB resin, followed by resin processing, a diffraction peak at $2\theta = 4.81^{o}$ appears. This indicates some re-aggregation of the clay layers. The clay is synthesized with a surfactant, which is washed off during work-up. However, the Pinnavaia group at MSU has indicated that there may be residual surfactant on the clay. Degradation of that surfactant could account for aggregation of the layers during polyimide processing.(9)





Figures (2a): XRD diffraction pattern of as prepared MSU clay, and (2b) MSU clay nanocomposite. (2c) TEM of 5wt% MSU-clay in the BAX-TAB resin matrix.

The MSU clay was chosen because of its "pre-exfoliated" nature. Many researchers have claimed that optimized exfoliation provides a "tortuous path" for permeation leading to reduced permeability.(10,11) The tortuous path mechanism increases the path length that a permeant must travel to get through a resin. the clay layers should be well separated. The MSU clay, as will be seen later, is not thermally stable. However it is "pre-exfoliated", and therefore it meets a condition for improved barrier performance.

The thermal stability of the TPPB clay is significantly higher than that of the synthetic MSU clay. The temperature at 5% weight loss of TPPB clay is 440°C, compared to 74°C for the MSU clay. Because the TPPB clay itself is thermally stable, and capable of withstanding the BAX-TAB processing temperature of 370°C, the nanocomposite thermal stability is improved over the neat resin. The TGA plot in Figure 3 shows that as degradation proceeds, the rate is slowed by the presence of the TPPB clay. The TPPB nanocomposite provides a 20°C increase in the temperature of 10% weight loss, when compared to that of the neat resin. Although the MSU clay on its own does not demonstrate the same thermal stability as the TPPB clay, it performs equally well in the later stages of degradation. The nanocomposites both reach 30% weight loss at 645°C, whereas the neat resin reaches this weight loss at 620°C. The dispersion of the MSU clay into the polymer is much better than that of TPPB. Past work has demonstrated that dispersion of the nano-clay platelets slows the diffusion of oxygen into the bulk resin.(12) Because the polyimides degrade by an oxidative mechanism, retarding the oxygen permeation slows the resin degradation. Therefore, the low thermal stability of the MSU clay nanocomposite results in a degradation pattern similar to the neat resin temperatures below 600°C. However, as heating time and temperature increase, the nanocomposite weight loss shifts to match that of the TPPB nanocomposite, implying that weight loss is slowed.

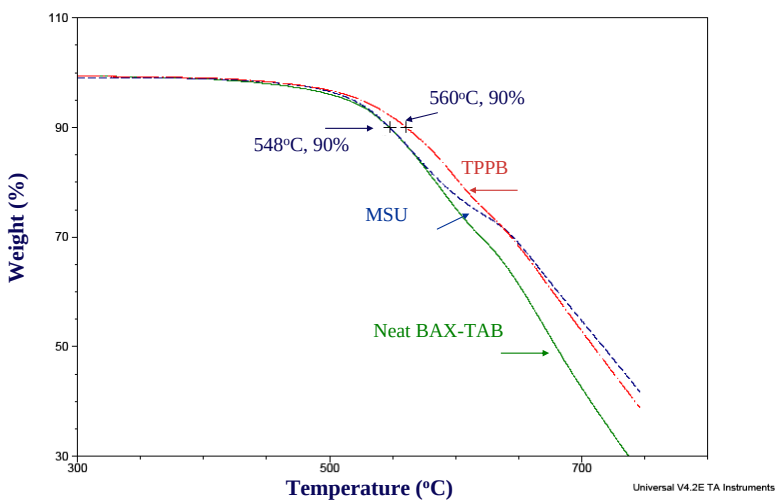


Figure 3: TGA curves of neat resin and clay nanocomposites.

The dynamic mechanical analysis of the BAX-TAB materials (Figure 4) showed an increase in storage modulus below T_g for the MSU nanocomposite. However, both the MSU and the TPPB

clay nanocomposites reduced the resin T_g by 15°C. Such a reduction in T_g has been noted with dispersion of an alkyl ammonium modified clay into a thermosetting polyimide.(13) However, the MSU clay is not organically modified, and the TPPB clay would not be expected to plasticize the matrix. The reason for the decrease in T_g is unclear. One explanation offered is that the nanoparticles increase the resin melt viscosity, thereby affecting crosslink density.

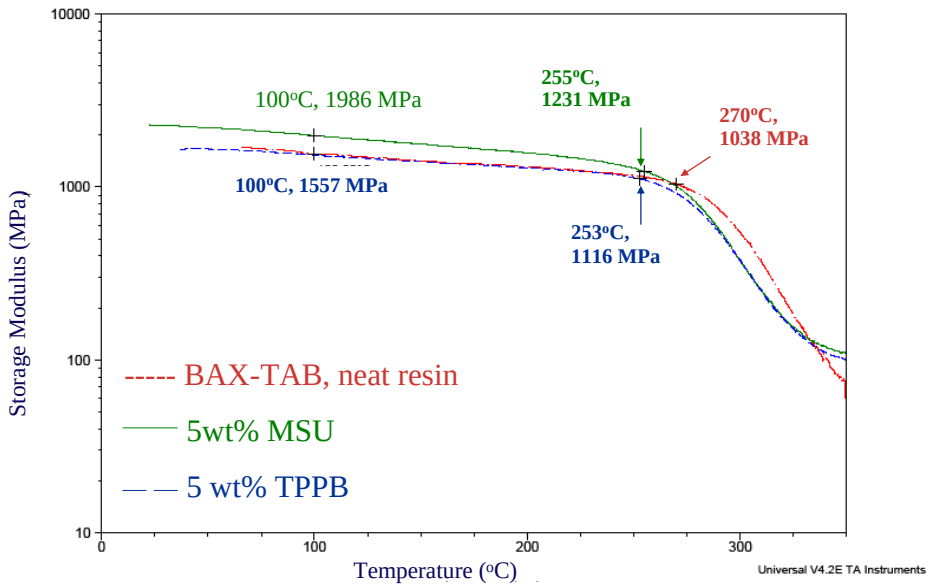


Figure 4: DMA plot of storage modulus for neat resin and clay nanocomposites.

3.2 Carbon Nanofiber Composites The carbon nanofiber dispersion was characterized by TEM, as shown in Figure 5.

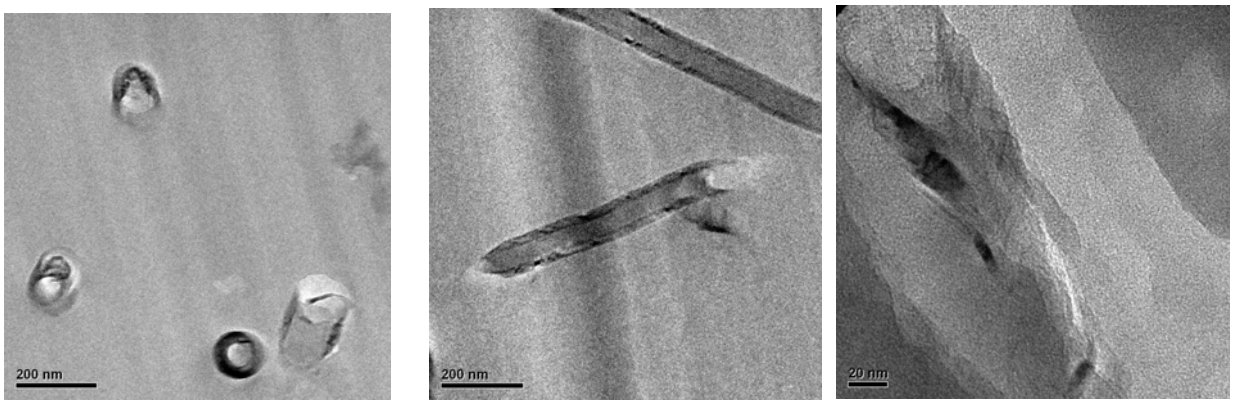


Figure 5: TEM images of PR19XT-PS in BAX-TAB matrix.

Dispersion of carbon nanofibers had a pronounced impact on the thermal stability of the BAX-TAB resin. Figure 6 shows the TGA plot of nanocomposites containing 0.5 wt% PR-19XT-PS,

1.0 wt% PR-19XT-PS 0.5 wt% PR-24XT-PS, and 1.0 wt% PR-24XT-PS. Also included were nanocomposites containing both TPPB clay and CNF. For all nanocomposites there was a 30°C increase in the temperature of 5% weight loss, and a 25°C increase in the temperature at 10% weight loss. This is an improvement when compared to the clay nanocomposites where a 20°C increase in thermal stability was observed. All of the TGA curves show a marked change in the slope of the weight loss curve at approximately 25% to 30% weight loss. This indicates a slowing of the rate of polymer degradation on incorporation of nano-fillers, and should correspond to decreased weight loss in long term isothermal aging studies.

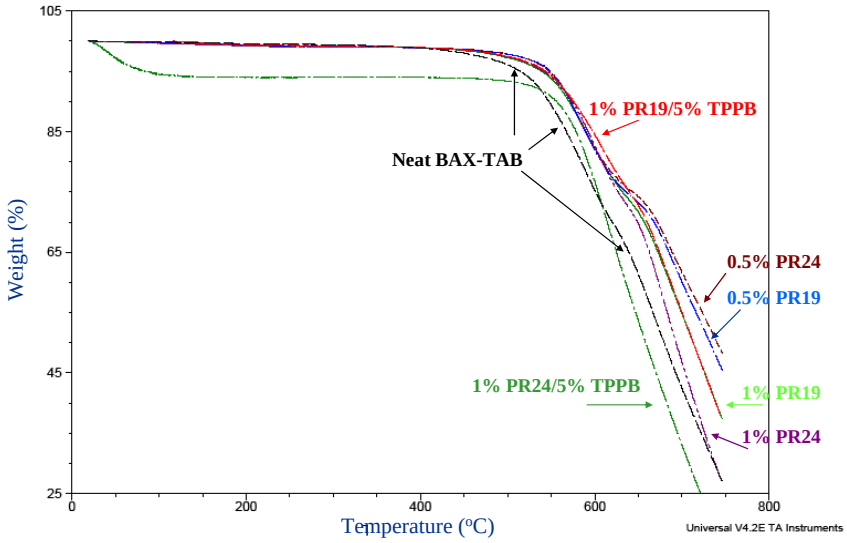


Figure 6: TGA curves of carbon nanofiber nanocomposites.

A comparison of sample weight loss is plotted in Figure 7. The plot illustrates the greater influence the nanofillers have at higher temperatures. At 5% and 10% weight loss there is a 25°C to 30°C increase over the neat resin, at 30% weight loss, the nanocomposites improved the resin stability by up to 50°C. The greatest thermal stability was observed in the samples containing 0.5% PR19 and 0.5% PR24 carbon nanofibers. The sample containing 1% PR24/5%TPPB had exhibited an initial weight loss at low temperatures which may have been due to residual solvent. As a result, the overall weight loss was high for this sample.

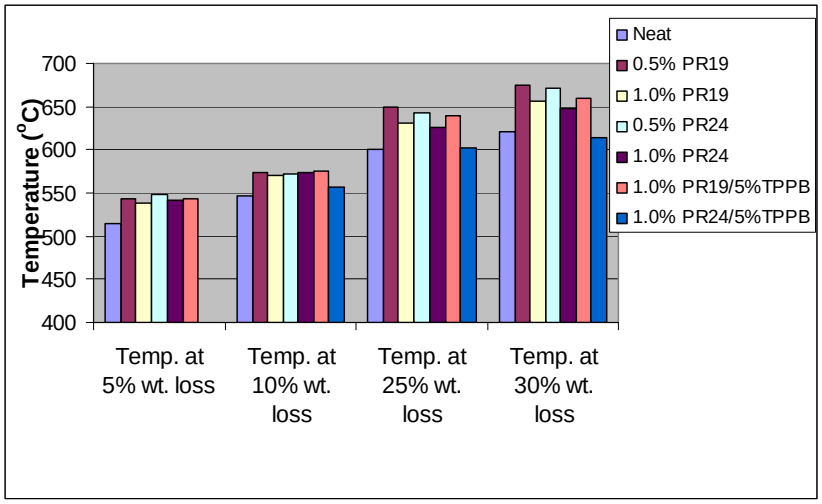


Figure 7: Weight Loss of BAX-TAB nanocomposites

These results agree well with what many researchers have observed when adding a thermally stable nanomaterial, such as CNF, to a resin.(14)

Carbon nanofibers were introduced with the intention of adding multifunctionality to the nanocomposite by imparting thermal conductivity to the resin. However, initial test results, listed in Table 1, show a reduction in thermal conductivity compared to the neat resin.

Table 1: Thermal Conductivity of BAX-TAB nanocomposites.

Nano-filler	Conductivity (W/mK)
none- neat resin	0.252
5 wt% TPPB clay	0.258
5 wt% MSU clay	0.282
0.5 wt% PR24 CNF	0.190
1.0 wt% PR24 CNF	0.169
1 wt% PR19/ 5 wt% TPPB	0.241

The reason for this is unclear and we are continuing to prepare and characterize resins. Because the addition of CNF did have a significant impact on the TGA data, we feel the conductivity may be due to testing methods. The instrument used to measure thermal conductivity, calculated that value from the measured thermal diffusivity through the sample. The test specimen is laid flat in the instrument and heat is applied on one side by means of a laser flash. The diffusion of that heat through the sample is detected. For anisotropic materials, such as carbon nanofibers, obtaining accurate data may require positioning the sample at various orientations. Therefore this work is ongoing.

4. CONCLUSIONS

The addition of both layered silicate clays and carbon nanofibers greatly increased the onset of thermal degradation in BAX-TAB resins. The low thermal stability of the MSU-clay did not negatively impact the nanocomposite thermal properties, and performed equally as well as the TPPB clay at later stages of degradation. The change in thermal stability, as determined by TGA, was greatest with the carbon nanofibers. The thermal conductivity of the nanocomposites is currently being evaluated as the effect of the nano-particles on resin melt viscosity.

5. ACKNOWLEDGMENTS

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