EFFECT OF NANOGRAFHTIE ON THERMAL PROPERTIES OF LIQUID MOLDED POLYAMIDE-6 LAMINATES

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Abstract
Anionic polyamide-6 (APA-6) is a thermoplastic polymer that is rapidly polymerized from activated monomer solutions with very low initial viscosity. The advantage of APA-6 is its suitability for liquid infusion of fiber reinforced laminates which is a manufacturing process typically reserved for thermoset resin systems. In this work, pristine graphite nanoplatelets (NGPs) are introduced in the laminates to increase the thermal conductivity of the fibrous preform to enhance polymerization. The effect of NGPs on the polymerization and thermal properties of anionic APA-6 was investigated for concentrations of 0.05, 0.1, 1.0 and 2.0 wt. %. Measurements of the ‘induction time’, the duration of low viscosity during polymerization, were obtained directly through rheological tests and indirectly through differential scanning calorimetry (DSC). NGP concentration was measured to have no effect on the induction time for the concentrations investigated. The presence of NGP showed little to no detrimental effect on polymer properties including crystallinity, thermal stability, conversion efficiency and melt temperature. During polymerization, distinct phases appeared from initially homogeneous NGP/monomer solutions due to settling. The ‘graphite rich’ phase in each sample had an NGP concentration of approximately 9 wt. % which was independent of the nominal NGP concentration.

1 Introduction
Thermoplastic composites are used extensively by automotive, mass transit and other industries. Current applications are generally limited to short fiber composites formed by injection or compression molding processes. To take full advantage of the reinforcement fibers, continuous tapes or other thermoplastic pre-impregnated layers can be stacked and consolidated in an autoclave. Liquid infusion techniques are much more economical compared to autoclave consolidation. The technique can be employed for thermoplastics by significantly reducing either the viscosity of the resin or the flow distance. Liquid molding of APA-6 to produce continuous fiber thermoplastic composites is a novel technology with tremendous potential, yet the technique has only achieved limited industrial adoption[1, 2]. Some of the challenges with the technology arise in the strict thermal requirements of polymerization. If the polymerization occurs just below a critical value of around 150°C, low molecular weight oligomers will be produced which act as imperfections in the polymer[3]. If the polymerization temperature is sufficiently below the critical value, bulk polymer formation can be disrupted entirely. A case study is shown in Fig. 1 when a previously validated[4] vacuum-assisted resin transfer molding (VARTM) process for thin carbon fiber laminates was attempted for a thick glass fiber sample. In this technique, heat is applied from the bottom tool surface alone after infusion. For thick sections of glass fiber, the thermal conductivity of the infused preform was not high enough to ensure complete polymerization at the top surface, thus causing the defect.

This study is an effort to overcome the challenges of APA-6 polymerization with the addition of graphite-based platelets. Excellent thermal conductivity of graphene on the order of 5000 W/m-K[5] and improved conductivity occurring around 1 wt. %[6] make NGPs an ideal choice to improve heat conduction in thick laminates. These nanoparticles as purchased have properties such as specific surface area (13m²/g) and an aspect ratio of (35:1 diameter to thickness) that are beneficial for mechanical enhancement of the final composite matrix[7]. Additionally, carbon reinforcements have been shown to effectively nucleate spherulites during
crystallization of polyamide-6 thus improving interfacial bond strength[8]. This may also be true for NGPs.

Once thermal and contamination issues are addressed, the nature of APA-6 lends itself well to liquid infusion processes. The molten monomer, ε-caprolactam, at 100°C has a very low viscosity of ~10^3 Pa-s. This state endures for a finite time, termed as the ‘induction time’ and is highly dependent on the solution temperature history and the reactivity of the polymerization reagents[3]. To increase the induction time in other studies[4, 9], the fiber preform was infused at a lower temperature and quickly heated to the polymerization temperature, 150°C. The disadvantage of this approach for thick laminates is the danger of insufficient heat transfer causing polymerization to occur at a lower temperature in the center of thick sections and thus causing molecular weight oligomers to be formed instead of high molecular weight polymer[10]. Matched tooling at the proper reaction temperature in conjunction with a relatively slow activator has shown the best promise in current investigations.

The end of the induction time was marked by an exponential increase in solution viscosity and a concurrent exotherm[3]. The coincidence of the heat release with the increase in viscosity allowed for inferred measurements of the induction time to be made using differential scanning calorimetry (DSC) to validate direct rheological measurements of solution viscosity.

With the goal of a long induction time, larger and thicker laminates are more easily filled, however, pre-mixed suspensions of monomer and unmodified filler materials, such as NGPs, are afforded time to separate [11]. In this study, pristine NGPs were allowed to settle during cure to identify the equilibrium concentration of nanoparticles in APA-6. Definite phases appeared after polymerization and were denoted as ‘graphite rich’ and ‘graphite poor’. Local graphite concentration was therefore unknown and was approximated experimentally using thermogravimetric (TGA) analysis. The effect of NGPs on APA-6 was also investigated with DSC analysis to verify that the nanoplatelets can be introduced without penalties to final polymer thermal properties.

2 Experimental

2.1 Materials

Commercially available anionic polymerization grade ε-caprolactam was used without purification (Brueggemann AP-Caprolactam). A Caprolactam magnesium bromide activator and a blocked diisocyanate initiator were also used as-purchased (Bruggolen C1 and C20, respectively). Polar nanographite platelets of 99% carbon with average diameter of 3.5 μm and thickness of 50-100 nm were used as-received (Angstron N008-100-P).

2.2 Sample Preparation

A mixture of ε-caprolactam, activator, and initiator was ground with a mortar and pestle in a glove box with relative humidity <15%. Proportions were combined by weight of ε-caprolactam as 7% activator and 2.5% initiator. The dry powder was combined with NGP platelets in appropriate weight fractions to obtain concentrations of 0, 0.05, 0.1, 1.0 and 2.0 wt. % NGP. The powder mixtures were placed in sealed glass vials and mixed using a vortex mixer until visibly homogeneous. For rheology experiments, some dry powder from each mixture was pressed into a disc of approximately 18mm diameter and 2-4 mm thickness using a pellet press die in the dry glove box. To obtain very small yet homogeneous samples for DSC, the sealed sample vials were heated in a convection oven at 100°C just until all reagents were melted. The vials were promptly removed and homogenized using a vortex mixer until the monomer solution solidified once again. DSC samples of the solidified monomer solution were extracted in the dry glove box to ensure minimal moisture exposure. The vials were sealed loosely and the remaining monomer mixture was polymerized at 150°C in a convection oven for 120 minutes. As-cast nanocomposite samples were machined within 3 hours with a single-flute cutter to obtain 2mm x 3mm x1mm thick chips from both the graphite rich and graphite poor regions, separately, as shown in Fig. 2. Any surface residue was machined away before sample chips were collected. The chips were sealed in plastic sample bags and tested within 48 hours to limit moisture absorption from the air.
2.3 Rheology

Rheological measurements were made using a TA Instruments Advanced Rheometer and a TA AR2000 Controller. Plates were flat aluminum and 25mm in diameter. The purge gas was standard grade compressed nitrogen. The heater temperature was set to 150°C, and once the instrument reached temperature, a portion of a pre-mixed sample pellet was placed between the open plates. The gap was immediately closed to a distance of 200 microns. An isothermal oscillatory time sweep was performed at a frequency of 1 s⁻¹ and 0.5% strain. Time between sample insertion and procedure start was recorded for each run. The rheometer time sweep procedure was allowed to continue past the point where the storage modulus η’ crossed the 10 Pa·s mark, at which the time was recorded. The total induction time was the sum of the two time periods from sample insertion to viscosity rise above 10 Pa·s.

2.4 Thermogravimetric Analysis

A Du Pont Instruments Thermogravimetric Analyzer (TGA 2950) was used for thermal stability analysis. As-cast sample chips were ramped to 600°C at 20°C per minute in nitrogen. Temperature at 10% mass loss T₉₀ and the temperature at the maxima of the derivative of mass with respect to temperature Tₘₐₓ were recorded. Residual mass at 600°C was recorded for all samples for estimation of NGP concentration. A sample of pure NGPs was also run with the same settings and its residual mass percentage was recorded to adjust concentration calculations.

2.5 DSC

Polymerization time and thermal properties were obtained using a TA Instruments DSC and a TA Q100 Controller equipped with a refrigerated cooling system (RCS). Samples of the homogenized and solidified monomer solutions were sealed in hermetic aluminum pans while inside a dry glove box with relative humidity of <15%. Monomer solution samples were brought to thermal equilibrium at 40°C. Time recording was started immediately after the equilibrium step. Temperature was then brought to 150°C in a step fashion, or as quickly as possible, and held at isothermal conditions. Logarithmic heat flow was measured versus time. The time was recorded when the exothermic heat flow signal was greater than 10⁻⁴ mW.

As-cured chips from graphite rich and graphite poor phases were sealed in aluminum hermetic pans. The DSC procedure was as follows: heat from 40°C to 320°C and cool from 320°C to 40°C both at 10°C per minute. Heat of melting ΔHₘ, heat of fusion ΔHₖ and corresponding temperatures Tₘ and Tₛ, respectively were obtained using TA Instruments Universal Analysis software. Heats of melting were compared against the theoretical heat of fusion ΔHₖ for a perfect crystal of APA-6 of 230 J/g from the ATHAS database[12]. Data presented was normalized against the control sample with 0.0 wt. % NGP.

2.6 Polymer Conversion

The mass of 10 as-cast chips from the graphite poor regions was obtained using a Mettler DeltaRange balance (AT261) to 4 significant figures. The chips from were boiled in distilled water for 60 minutes and dried in a convection oven at 120°C for 60 minutes. The final dry mass was recorded. Conversion was calculated as a mass ratio of washed and dried polymer to the initial mass.

3 Results and Discussion

3.1 Qualitative Observations

Homogeneity of the dry powder samples was visibly uniform throughout as can be seen in Fig. 3, although granules could be seen of the dry powder constituents. After melt-homogenization, the samples were completely uniform without any evidence of segregation or settling of the NGPs. There were qualitative differences between the samples during the casting step in the convection oven. Samples with low concentration polymerized uniformly and completely filled the bottom of the flask. As concentration of NGPs increased, there was unreacted monomer surrounding the bulk polymer which over time evaporated away leaving a slightly under-sized sample at the bottom and some residual monomer film on the surface. The simplest explanation for this phenomenon is that there must have been residual moisture adsorbed within the NGPs which can inactivate the monomer anion[13]. In each sample, the NGPs settled to the bottom of the vial. The thickness of the graphite rich layer increased with
increasing nominal concentration. The color of the graphite poor region was mostly homogeneous and darker in color with increasing initial NGP concentration.

3.2 Polymerization Characteristics

Rheological measurements were obtained for all concentrations, 0%, 0.05%, 0.1%, 1.0% and 2.0% and a typical plot of storage modulus $\eta'$ is shown in Fig. 4. It should be noted that the initial monomer viscosity was also essentially unaffected by the nominal concentration of NGP. Further evaluation is necessary to determine more accurately the relationship between monomer solution viscosity and NGP concentration. At 150°C and over several minutes, significant amounts of monomer evaporated despite a very thin gap of 200 microns. Due to this effect, the final polymer formed did not cover the entire disc, which invalidates actual values of viscosity; however, since the viscosity rise is very rapid, the effect on induction time measurements was deemed insignificant. Since moisture contamination was also a possibility in the rheometer which could affect the polymerization rate, DSC data points were taken to validate the rheological measurements.

A typical isothermal cure curve from DSC analysis is shown in Fig. 5. Temperature and logarithmic heat flow are shown. The induction time was taken as the time at which the heat flow was greater than $10^{-4}$ mW. It is clear that the heat rise is very sudden and only visible on a logarithmic scale since the sample mass for DSC is on the order of 10 mg. A plot of all data points obtained by both rheology and DSC analysis for induction time is shown in Fig. 6. Both methods result in a similar average value for induction time with 570 s for DSC and 480 s for rheology. One explanation for this difference is that DSC analysis has tight control on temperature and a very small sample size, whereas the rheology sample size is larger and could self-heat which can accelerate the polymerization rate[14] thereby shortening the induction time. The presence of NGPs in the monomer shows no significant effect on induction time with the utilized methods.

3.3 Thermal Properties

Thermogravimetric analysis was done to determine the effect of NGPs on thermal stability and to estimate the concentration of NGPs in each of the phases. The temperatures of 10% mass loss and maximum loss rate are shown in Table 1 as $T_{90}$ and $T_{\text{max}}$, respectively. The neat APA-6 polymer had higher temperatures for both properties.

For each concentration, the residual mass percent of the graphite poor phase was subtracted from the residual mass of the corresponding graphite rich phase. The total was adjusted by the residual fraction of the pure NGP sample at 600°C, $X_{\text{pure}}$, per Equation (1) and is shown in Table 1 as $C_{\text{NGP}}$. Since residual mass of the graphite poor phase was comparable to that of neat APA-6 as illustrated in Fig. 8, it was assumed that the contribution by mass of NGPs is negligible for further calculations for those samples. In some cases, the residual from pure polymer was higher than the nanocomposite samples indicating that TGA could not be used to determine the graphite concentration of the graphite poor phase.

\[
C_{\text{NGP}}(\text{wt.}) = \frac{R_{\text{rich}} - R_{\text{poor}}}{X_{\text{pure}}} \tag{1}
\]

DSC heat-cool plots were obtained for each sample type. The maxima of the melting and cooling heat flow peaks are recorded in Table 1 as $T_m$ and $T_c$, respectively. The heat of melting was calculated by linear integration of the endothermic peak and is denoted as $\Delta H_m$. Percent crystallinity was calculated as shown in Equation (2) adjusting for NGP concentration in the rich phases and is denoted as $\alpha$ (%).

\[
\alpha(\%) = 100 \times \frac{\Delta H_m}{(1 - C_{\text{NGP}})\Delta H_m} \tag{2}
\]

Crystallinity was normalized by the value for neat APA-6 and plotted in Fig. 9. Heats of fusion $\Delta H_c$ shown in Table 1 were calculated from a linear integral of the cooling exotherm and adjusted for NGP concentration. The heats of fusion shown in Fig. 10 were normalized against the value for the neat APA-6 control sample.

The presence of NGPs shows no significant effect on the melt and solidification temperatures of the graphite poor regions making them comparable to neat APA-6. Graphite rich melt and solidification temperatures are
slightly decreased and increased, respectively for higher nominal concentrations as illustrated in Fig. 11.

4 Conclusions

This work confirms that NGPs do not adversely affect the induction time of APA-6 for liquid infusion and can be used without affecting the final polymer thermal properties. The settling of NGP into distinct phases is a challenge to be addressed through improved dispersion techniques.

- The primary goal of the study was to determine the effect of NGPs on the induction time of APA-6 polymerization. The results of both rheological studies and DSC show no such effect. Monomer viscosity at the start of rheological measurements showed no change with NGP concentration.

- Cast samples of varying nominal NGP concentrations tended to separate into two distinct phases: one graphite rich and one graphite poor. The graphite rich phase had a concentration of approximately 9 wt. % as measured by TGA analysis and was independent of nominal NGP concentration. The graphite poor phase graphite concentration was not measurable with the utilized methods, but noticeable variation in color was visible with higher nominal concentrations corresponding to darker color.

- The presence of unmodified NGPs had no measurable effect on the thermal stability of APA-6 through DSC analysis.

- Crystallinity of as-cast APA-6 was perhaps slightly increased but mostly unaffected by the presence of NGPs for concentrations up to 2.0 wt. %.

6 Acknowledgements

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References


Table 1. Thermal data collected from DSC, TGA, and Conversion %.

<table>
<thead>
<tr>
<th>Sample</th>
<th>TGA</th>
<th>DSC Heating</th>
<th>DSC Cooling</th>
<th>Conversion</th>
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<tr>
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<td>T90 (°C)</td>
<td>Tmax (°C)</td>
<td>R (%)</td>
<td>CNGP (wt. %)</td>
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<td>493</td>
<td>1.12 †</td>
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<td>490</td>
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<tr>
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<td>0.00 †</td>
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<tr>
<td>Graphite Rich-0.05%</td>
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<td>485</td>
<td>10.00</td>
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<td>1.20</td>
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<tr>
<td>NGP Pure</td>
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<td>-</td>
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* Adjusted by weight fraction of NGPs. † No measurable difference from neat APA-6

Fig. 1. The bottom surface of the thick glass fiber reinforced VARTM panel showing good polymerization (left) and the top surface of the sample showing incomplete polymerization due to insufficient heat conduction (right).

Fig. 2. As-cast sample with concentration of 1 wt. % NGP showing the distinctive graphite rich (bottom) and graphite poor (top) regions and the machined chips from each.

Fig. 3. Mixed powder samples from neat to 2 wt. % NGP (left to right) showing homogeneity after hand grinding and vortex stirring.

Fig. 4. Typical complex viscosity during polymerization, $\eta'$ with oscillatory frequency of 1 s$^{-1}$ and 0.5% strain for 0.1 wt. % NGP.
Fig. 5. A typical DSC curve showing temperature (blue) and heat flow (black) for 0.1 wt. % NGP.

Fig. 6. Induction times determined by rheology ◊, DSC ■ and the overall average --- of 500s.

Fig. 7. Temperatures of 10% mass loss and maximum loss rate by TGA.

Fig. 8. TGA curves from both phases: graphite rich (black), graphite poor (grey), and neat *.

Fig. 9. Crystallinity as measured by DSC, adjusted for NGP concentration and normalized by neat APA-6.

Fig. 10. Heat of fusion as measured by DSC, adjusted for NGP concentration and normalized by neat APA-6.
Fig. 11. Temperatures of melting (black) and cooling (blue) as determined by local maxima of DSC peaks.