Liquid Molding of Carbon Fabric Reinforced Nylon Matrix Composite Laminates

Selvum Pillay, Haibin Ning, Uday K. Vaidya, and Gregg M. Janowski

Department of Materials Science and Engineering, The University of Alabama at Birmingham, 254 BEC, 1150 10th Avenue South, Birmingham, AL, 35294.
Corresponding Author's e-mail: uvaidya@uab.edu

ABSTRACT: This manuscript describes the processing techniques and processing windows used to produce carbon fiber reinforced, nylon matrix composite panels. Anionic polyamide 6 resin (casting grade) was polymerized *in situ* after infusion. Careful time and temperature control were necessary to obtain total fiber impregnation with subsequent complete polymerization. These advances will permit the use of affordable thermoset manufacturing processes such as Vacuum Assisted Resin Transfer molding (VARTM) or Resin Transfer Molding (RTM) to produce thermoplastic-matrix composite structures. The processing parameters, methodology and limitations of using VARTM for nylon matrix composites are highlighted. Static and low velocity impact response of the panels are presented and compared to traditional thermoplastic and thermoset composites. DSC scans show full polymerization of the resin was achieved. SEM evaluation show full wet-out of the preform was achieved at both the macroscopic and microscopic level. The properties of the panels produced using the process developed has been equivalent to, or superior, compared to reported values of other carbon thermoset composite panels manufactured using VARTM.

KEYWORDS: VARTM, reactive resin, Nylon, PA6.

INTRODUCTION

The use of thermoplastic composites has gained steady favor over traditional materials such as steel in structural and semi-structural applications. The current US market for such materials is in excess of one billion pounds per annum, half of which is consumed by the automotive industry [1, 2]. This utilization is driven by specific strength, damping, corrosion resistance, and impact resistance. However, these composites are limited to products that can be manufactured using traditional thermoplastic processes like injection molding, compression molding and extrusion. These processing techniques typically result in short fiber lengths and cannot use continuous fiber woven fabrics. Recent developments in processing and materials technology strive to improve the mechanical properties, especially in impact, of thermoplastic composites, which require maximum fiber length (3, 4). Thermoplastic resins, like PEEK, PEKK, reinforced with woven fabric can be processed using an autoclave under very high temperatures and pressures, a very expensive processing approach. Vacuum assisted resin transfer molding (VARTM) has been very well developed and is now a proven low-cost manufacturing technique for thermoset

resin composites. VARTM offers a closed mold system that allows zero Volatile Organic Compounds (VOC's), and it uses a single sided tool, which reduces cost. Unfortunately, the high melt viscosity of thermoplastic resins generally precludes the use of VARTM due to poor impregnation or mold fill.

Thermoset infusion techniques can be used for thermoplastics by either significantly lowering the viscosity of the resin or reducing the flow distance. By accomplishing this, the advantages of thermoplastics over thermosets of cost, faster cycle times, superior impact properties, and recyclability can be brought to composite materials and structures.

There has been substantial interest recently in liquid molding of thermoplastic resin composites using the matrices anionic polyamide 12 (5, 6), cyclic PBT (7, 8), and anionic polyamide 6 (9, 10). The current study will utilize polyamide 6 (PA6), a well known commodity thermoplastic resin that has been used extensively for nylon casting applications. In this research, a process is developed for the use of PA6 as an effective matrix for infusion into a carbon fabric preform. Mechanical property data will be presented that indicates that these composites possess high modulus, tensile strength, and impact resistance.

MATERIALS AND PROCESSING

Caprolactam monomer, Bruggolen C10 catalyst, and Bruggolen C20P activator were used to form the polyamide 6 resin and were supplied by Bruggemann Chemical U.S., Inc. This system is used extensively by the polymer casting industry to cast near-net-shapes. The short polymerization times make the system ideal for casting. The monomer is melted ($T_m = 69^\circ C$) in two parts, one containing the initiator and one containing the catalyst. The two parts are then either mixed and poured into the mold or mixed via an injection head and injected into the mold. Reaction injection molding of nylon block copolymers were first done by H. Mooji, DSM, Netherlands. (11).The 3K tow size, 4 harness satin weave carbon fabric with an areal density of 0.02 g/cm^2 was supplied by US Composites.

The carbon fabric was washed with acetone to remove the lubricants and sizing. Twenty layers of the carbon fabric were placed between two layers of porous Teflon cloth and then laid onto the tool surface. The preform was then bagged and sealed using high temperature bagging film and tacky tape.

The viscosity of the resin is a function of the levels of catalyst and initiator, temperature, and time. Various combinations were investigated to achieve both full wet-out of the preform and full polymerization. The caprolactam was heated to $100^\circ C$ until it was liquid. The catalyst and activator were then added, and the solution was brought to a molten state. The catalyst is sensitive to moisture, and the caprolactam oxidizes rapidly at these temperatures. Therefore, storage and processing must be done in a dry nitrogen environment. The resin was then infused into the preform via an infusion line. Once the resin reached the end of the preform, the infusion line was clamped off, and the temperature was raised to $150^\circ C$ to polymerize the nylon. PA6 anionically polymerized from solution has a higher degree of crystallinity compared to the same material crystallized from the melt. (10).

DSC scans were conducted to establish the degree of polymerization. Scans on initial samples showed a number of peaks at temperatures ranging from $70^\circ C$ to $220^\circ C$. This implies that there

was a large percentage of the monomer in the system and full polymerization was not achieved. Figure 1 shows a DSC scan of a fully polymerized panel. Only one sharp peak is observed at $220^{\circ}C$, the melting temperature of PA6. The sharpness of the peak indicates a high degree of crystallinity, which is characteristic of PA6 anionically polymerized from solution.

One limitation of using liquid molding techniques for thermoplastic resin is the high melt viscosity. This leads to poor wet-out of the fibers both macroscopically (tows) and microscopically (filament). The viscosity of the Caprolactam, initiator and catalyst at $100^{\circ}C$ is low enough that macroscopic (a function of the flow) and microscopic (due to capillary action) wet-out is achieved. The SEM images shown in Figure 2 show the wet-out at the filament level. It can be observed that the fiber is completely coated by the resin in both the cross sectional and the longitudinal view of the fibers.
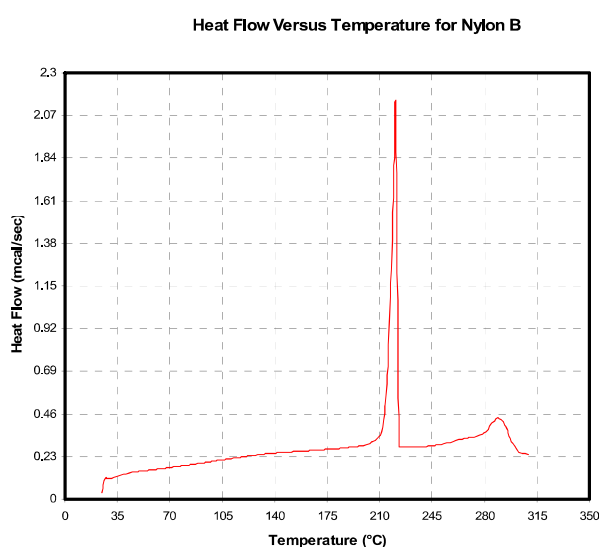

Figure 1: DSC scan of carbon /PA6 samples. Note the sharp peak at $220^{\circ}C$ and no peaks lower than $220^{\circ}C$, which implies full polymerization.
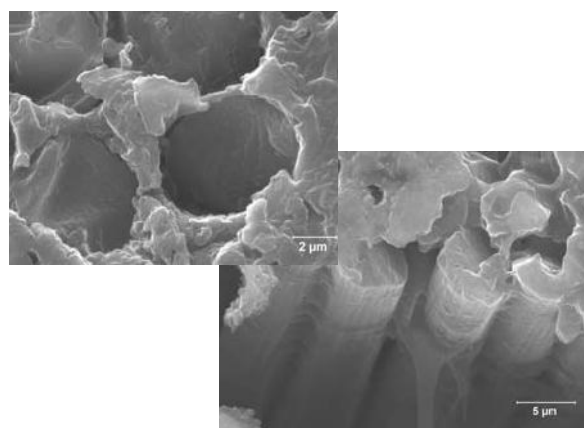
Figure 2. SEM image showing cross section and longitudinal carbon filaments and PA6 resin. The filaments are fully wet-out with resin.

MECHANICAL TESTS

Tensile

Tensile tests were conducted according to ASTM D 3039M using samples of dimensions 12.5 x 250 mm cut from the panel. The sample ends were tabbed with an epoxy glass material, dimensions 12.5 x 63 x 0.85 mm, with the tab ends tapered to 5°. The tabs were bonded to the sample using a Three Bond™ thermoplastic adhesive. Samples were tested in a servo-hydraulic tensile test machine at a displacement rate of 2 mm/minute with a gage length of 120 mm. The change in length of the sample was measured using a clip-on extensometer, which was detached prior to failure.

The average modulus and ultimate tensile strength (UTS) values were 64.86 GPa and 822 MPa, respectively. The modulus was marginally lower than reported values for carbon/ epoxy (V_f = 50%) of 70 GPa. However, the UTS is above the reported value of 600 MPa. The sample failed within the gage, and failure was mainly fiber dominated. Figure 3 shows a typical failed sample.

Figure 3. Typical failed sample in tension, failure occurred in the gage.

Flexure

Three point bend tests were conducted according to ASTM D 790M. Samples of dimension 10 x 80 x 4 mm were prepared from the panel. The tests were conducted on a SATEC power screw universal test machine. The support span was set at 64 mm, and the rate of cross head motion was 1.7 mm/minute. The average flex modulus and flex strength was 45 GPa and 490 MPa, respectively. The mode of failure was tensile face fracture and delamination.

Impact

Low velocity impact (LVI) tests were conducted using a Dynatup 8250 impact-testing machine equipped with a load cell of capacity 1590 kg (3500 lbs). A hemispherical shaped head tup of diameter 19.5 mm and mass 0.12 kg was used. The total mass including the tup mass, impactor and the holding bolts was 0.24 kg for the hemispherical impactor. The samples were clamped using a pneumatic assist mechanism, such that 76.2 mm (3") diameter of the sample face was exposed to the impactor. The force-time, energy-time and load-deflection response of the samples were measured. Damage initiation and progression was monitored.

Figure 4 illustrates a typical force-time-energy curve for the carbon / nylon composite sample. The energy to peak load and the peak force were normalized with respect to the thickness. The average values of E/t and F/t were 62097.95 J/m and 1873.306 kN/m, respectively. The failure mode was observed to be primarily tensile fracture of the back surface. Figure 5 shows the tensile face of an impacted sample. The impact energy absorbed by the carbon / PA6 samples were found to approximately 27% greater than reported values for rubber toughened SC15 epoxy / carbon samples.
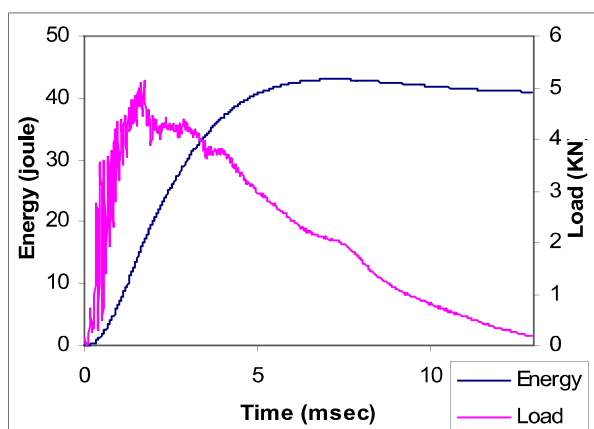
Figure 4 Typical Force / Energy – Time curve for carbon / PA6 composite sample.

Figure 5 Tensile face of typical impacted sample.

SUMMARY

Vacuum Assisted Resin Transfer Molding, a method that is well established for thermosets, has been effectively used to infuse carbon fabric performs with PA6 resin. The processing parameters were established to provide a low viscosity of the resin for a long enough time for full wet-out of the preform and good fiber impregnation. The method was significantly modified to accommodate the differences of the thermoplastic resin, especially with regard to temperature and moisture control. The DSC scans showed that the resin was fully polymerized. The sharp peak in the scan is an indication of a high degree of crystallinity. The SEM images show that macroscopic and microscopic fiber impregnation was achieved.

The preliminary impact, tensile and flexure data show that the thermoplastic composite possesses properties equivalent to or superior to thermoset composites. When compared to reported values, the ultimate tensile strength is superior using the PA6 resin. The impact data shows that the PA6/carbon panel is superior to SC 15, a specially developed thermoset resin for impact. Further tests need to be conducted and compared to equivalent carbon/epoxy composites for meaningful comparisons.

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