THE DURABILITY OF LIQUID MOLDED CARBON NYLON 6 COMPOSITE LAMINATES, EXPOSED TO AN AGGRESSIVE MOISTURE ENVIRONMENT.

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Abstract

Liquid molding of thermoplastics has been limited by high resin viscosity, high temperature processing requirements, and a short processing window [1]. The processing parameters for vacuum assisted resin transfer molding (VARTM) developed by the authors and previously reported [2] have been adopted to process carbon/nylon 6 composite panels. The material used in this study was casting grade polyamide 6, ε-Caprolactam with a sodium-based catalyst and an initiator.

The present work addresses the effects of moisture exposure on the static and dynamic mechanical properties of carbon fabric-reinforced, thermoplastic polyamide 6 (also referred to as nylon 6 and/or PA6) matrix panels processed using VARTM. The Bao and Yee dual diffusivity model [3] was applied to evaluate the moisture uptake for the C/PA6, fully immersed in distilled water at 100°C. The model shows good correlation with the experimental data in terms of the percentage of moisture absorption with respect to the square root of time. Scanning electron microscopy (SEM) results show that surface defects induced during processing result in matrix micro-cracks after moisture exposure and the fiber matrix interface is compromised. The impact resistance of the material is also lowered due to water ingress. However, the crystallinity and melting peaks are not affected.

1.0 Introduction

Polymer matrix carbon fiber-reinforced composites are widely used in a variety of applications, such as aerospace, mass transit, automotive, and sporting goods. Their use has become popular due to their attractive properties, including high strength to weight ratio, high specific stiffness, and corrosion resistance. However, their susceptibility to environmental degradation, especially hygrothermal aging and ultraviolet (UV) irradiation, depending on the application and formulation of the matrix, has been of major concern.

When exposed to humid environments, polymer-based composite structures can absorb moisture, which affects the long-term structural durability and properties of the composite [4,5]. Since high performance carbon fibers absorb little or no moisture compared to the matrix, the absorption is largely matrix dominated. Moisture penetration is largely dominated by diffusion. Other mechanisms that can contribute are capillarity and transport by micro-cracks [6]. The rate of moisture absorption depends largely on the type of matrix, orientation of the fibers with respect to the direction of diffusion, temperature of the water, and relative humidity [7]. Moisture absorption leads to changes in the thermophysical, mechanical, and chemical characteristics of the matrix by plasticization and hydrolysis [8-10]. Also, moisture wicking along the fiber-matrix interface degrades the fiber-matrix bond, which results in the loss of microstructural integrity. Matrix dominated properties are most strongly affected.

2.0 Kinetics of Water Absorption

A basic study of the existing models of water absorption in composite materials was undertaken, to compare results of the experimental moisture uptake/diffusion data for the condition of the specimens fully immersed in distilled water at 100°C. A number of studies have been conducted on moisture diffusion in composites, and most agree that Fickian behavior adequately predicts the water ingress in these composites [7,11]. These studies have also shown that the most aggressive condition for the composite was full immersion in water at 100° C. The equilibrium absorption was also reached in the minimum time, under 100 h for nylon

6/6 [7]. Most of these studies have been conducted for nonwoven (unidirectional and random chopped fiber) composite materials. Ishak and Berry [7] showed that Fickian absorption adequately modeled the moisture absorption of nylon 6/6 reinforced with short carbon fiber.

Equations 2 and 3 outline the model developed by Crank [12] for diffusion of a substance in one direction only. For an infinitely large plate of thickness h with single phase diffusion, M_t (mass of water absorbed at time t) by M_∞ (mass of water absorbed at saturation) is given by:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0} \frac{1}{(2n+1)^2} \times EXP\left[-\left(\frac{Dt}{h^2}\right)\pi^2(2n+1)^2\right]$$
(2)

This equation is a series solution to Fick's second law, which can then be resolved into two conditions of Dt/h^2 (Equations 3 and 4, respectively):

For $\dfrac{Dt}{h^2} > 0.05$ Equation 2 reduces to

$$\frac{Mt}{M_\infty} = 1 - \frac{8}{\pi^2} EXP\left[-\left(\frac{Dt}{h^2}\right)\pi^2\right]$$
(3)

For $\dfrac{Dt}{H^2} << 0.05$ Equation (2) reduces to

$$\frac{M_t}{M_\infty} = \frac{4}{\pi^{1/2}}\left(\frac{Dt}{h^2}\right)^{1/2}$$
(4)

The diffusivity D can be calculated from the initial linear portion of the absorption curve from Equation (4).

The moisture absorption does not follow the previously described model for woven fabric composites. There have been limited studies on the mathematical modeling of moisture ingress on woven composites [3,13,14]. The transport of moisture in woven composite materials is very complicated, as it is influenced by the matrix material, weave architecture, residual stresses, and the fiber/matrix interface.

Whitney and Browning [14] studied the moisture diffusion of bidirectional graphite composites and proposed a residual stress-dependent model. The basis for the residual stress was the consideration that matrix shrinkage is restricted in both directions, hence large residual tensile stresses may develop after cure. As the diffusion of moisture progresses, the swelling of the matrix relieves the residual stress within the material and slows down the absorption. The linear dependency of diffusion on time proposed improved correlation with the experimental data; however, the fit still showed some discrepancy.

Bao and Yee [3] conducted an extensive study on the diffusion kinetics of moisture in both unidirectional and woven composites. They also found that the diffusion was non-Fickian for the woven composite. They conducted an extensive evaluation of the different models and fits with experimental data, and found that there were discrepancies with the experimental and predicted results. They had also evaluated the stress-dependent model proposed Whitney and Browning [14] and found that the correlation was limited at best. A closer study of the experimental absorption curves showed that there were two distinct linear regions before the equilibrium moisture was reached. They found that the moisture uptake was composed of two processes with different rates: a fast initial rate and then a slower rate. They proposed the following dual diffusivity model, which is the sum of two Fickian processes with different diffusivities.

$$M_t = M_{\infty 1}\left\{1 - \exp\left[-7.3\left(\frac{D_1 t}{h^2}\right)^{0.75}\right]\right\} + M_{\infty 2}\left\{1 - \exp\left[-7.3\left(\frac{D_2 t}{h^2}\right)^{0.75}\right]\right\}$$
(5)

In this model, D_1, $M_{\infty 1}$ and D_2, $M_{\infty 2}$ are the diffusivity and equilibrium uptakes of the fast and slow processes, respectively.

3.0 Experimetal

Carbon Fabric

The carbon fabric used in this study was supplied by US Composites and was a 4 harness satin weave, with a 3K tow size, and an areal density and thickness of 0.02 g/cm^2 and 0.254 mm, respectively. The fabric was washed in acetone to remove lubricants and sizing and then placed in a recirculating oven at 100°C for 1 h to re-move any residual moisture and/or acetone.

Monomer, Activator, and Catalyst (PA6)

AP grade caprolactam monomer was used in this study. The monomer has low levels of moisture (<0.0015% by mass), a low melting point (T_m = 69°C), and low viscosity (4.87 mPa•s at 100°C). Bruggolen C20, hexamethylene dicarbamoyl dicaprolactam, and Bruggolen C10, sodium caprolactamate, both especially developed for AP of caprolactam, were used as the activator and catalyst, respectively. The melt temperature of both C10 and C20 is 60°C. The monomer, catalyst, and activator were supplied by Bruggemann Chemical U.S., Inc., and were used without any further processing or purification. Due to the sensitivity to moisture of the catalyst and activator, they were stored and handled in a dry box with the relative humidity maintained at 8%.

Processing

Twenty 300 x 300 mm layers of the carbon fabric were laid onto the tool surface and bagged and sealed using high temperature film and tacky tape. A thermocouple was positioned at the surface of the top layer of the carbon to record and monitor the tempera-ture. The tool temperature was then raised to 100°C, and a continuous vacuum of 1 atmosphere was applied to the system.

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°C until it was liquid. The catalyst and activator were then added, and the solution was brought to a mol-ten 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°C to polymerize the PA6. For further details on the process the reader is referred to [2].

Moisture Exposure

A significant number of studies have shown that the rate of moisture absorption by polymer matrix composite materials is dependent on the temperature, relative humidity, diffusivity of water in the polymer, and weave architecture of the fabric [3,4,7,14]. These studies have also shown that the maximum (or equilibrium) moisture absorbed by a particular composite material is independent of temperature and relative. At higher temperatures and relative humidity, the maximum amount of moisture absorbed by the material will be reached in a significantly shorter time than exposure to a lower relative humidity and lower temperature.

Since the focus of this study was to evaluate the deterioration in mechanical properties of the carbon fabric-nylon 6 matrix composite, it was decided to expose the material to the most aggressive moisture condition, i.e., immersed in water at 100° C. The specimens were cut from the panels using a diamond saw blade and then polished with 600 grit silicon carbide paper to minimize cracking or debonding of the edges.

The specimens were then dried in a recirculating air oven at 70°C and periodically weighed on a high precision balance with a 0.1 mg resolution, until the weight had stabilized. The dry weight (W_d) of all the specimens was then recorded. The samples were then placed on a rack that prevented them from any contact with each other and fully submerged into a reaction vessel containing boiling water. The temperature of the water was maintained at 100°C using a hot plate and oil bath to maintain even heating. The specimens were taken out at periodic intervals and weighed after excess moisture was wiped off. The percentage weight gain (Equation 1) was monitored as a function of the square root of time.

$$M = \frac{W_i - W_d}{W_d} \times 100$$

(1)

Where M = percentage weight gain; W_i = weight of moist material at a specific time; and W_d = dry weight.

The weight gain was plotted against the square root of time until the equilibrium weight gain M_∞ was reached. The samples were then removed from the chamber. 50% of the samples were put into a container with water at ambient temperature and taken for testing and evaluation, while the rest were placed in a recirculating oven at 70°C to dry. The samples were periodically weighed until the weight had stabilized, indicating that all the moisture had been removed. The samples were placed in a desiccator and taken for testing and evaluation.

4.0 Results and Discussions

Visual observation of the specimens that were exposed to moisture showed that there were areas of whitening of the matrix. The specimens seemed to have maintained structural integrity, and there was no evidence of complete breakdown of the matrix away from the fiber. SEM was conducted to ascertain the damage to the matrix and the fiber/matrix interface. Figure 1 shows cracks that were formed on the surface due to the effects of moisture and heat on the specimens.
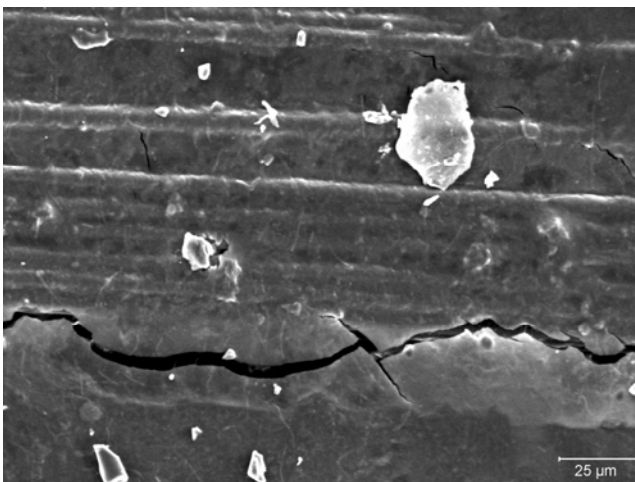

Figure 1. SEM image of carbon/nylon 6 composite surface cracks after 100h exposure to water at 100°C
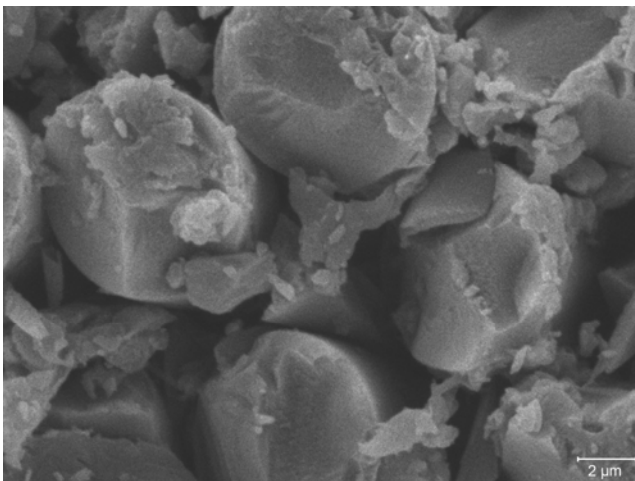

Figure 2. SEM image of carbon/nylon 6 composite showing fiber matrix interface degradation after exposure to water at 100°C for 100 h.

These were probably microcracks, which could not be seen by SEM prior to moisture exposure, that developed due to the residual stresses from the processing of the composite and which were expanded during exposure.

Other processing anomalies, such as surface roughness, stacking faults in the weave, and misaligned fibers, could also contribute to cracks that opened during moisture exposure. Figure 2 shows the effect of the moisture attack on the fiber matrix interface. Figure 3 shows a SEM image of an as-processed sample, and it is evident that the fibers are well coated with the matrix and there is good adhesion of the matrix to the fiber.
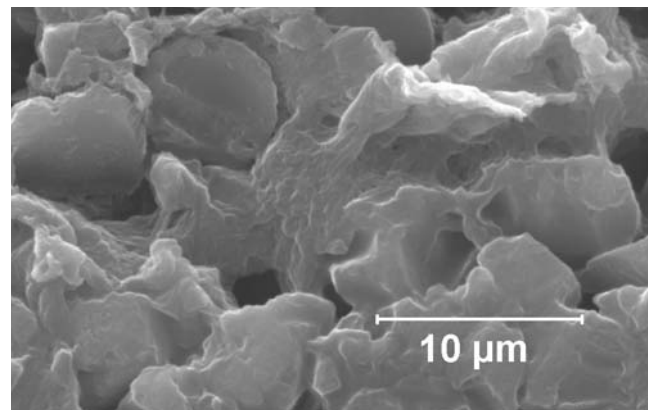

Figure 3. SEM image of carbon/nylon 6 composite showing the fiber matrix interface after processing. Very good wet-out at the filament level is achieved

Water Absorption
Figure 4 shows the moisture absorption curves for the carbon/nylon 6 composites. Closer observation of the figure clearly indicates that for all samples sizes there is a definitive early stage of fast diffusion, followed by a slow (reduced) diffusion rate.

These results are in agreement with the model proposed by Bao and Yee. They showed that there were two distinct linear regions before the equilibrium moisture was reached in bismaleimide matrix woven carbon fiber composites,. Their study found that the moisture uptake was composed of two processes with different rates, a fast initial rate and then a slower rate, which compares well to what is observed in Figure 5. They proposed the dual diffusivity model (Equation 5), which is the sum of two Fickian processes with different diffusivities.

$$M_t = M_{\infty 1}\left\{1 - \exp\left[-7.3\left(\frac{D_1 t}{h^2}\right)^{0.75}\right]\right\} + M_{\infty 2}\left\{1 - \exp\left[-7.3\left(\frac{D_2 t}{h^2}\right)^{0.75}\right]\right\}$$

(5)

In the above model, D_1, $M_{\infty 1}$ and D_2, $M_{\infty 2}$ are the diffusivity and equilibrium uptakes of the fast and slow processes, respectively. As the absorption is described by the sum of two Fickian processes, Equation (4) can be used to determine diffusivity D_1 and D_2 can then be determined from Equation (5).

The curve fit using the Bao and Yee dual diffusion model [2] is shown in Figure 5 for the ASTM D-570 specimens. The dual diffusion model (Equation 5) shows very good correlation with the experimental data obtained in this study, with $R^2 = 0.99$. A Fickian fit is also shown with $R^2 = 0.76$, which shows very poor correlation with the experimental data.

The bidirectional woven fiber arrangement (as in the carbon fabric used in this study) restricts matrix shrinkage in both directions, which could cause surface defects, as described earlier. These defects, especially near the surface, fill up with water very rapidly after immersion. However, this water does not change the local water concentration in the matrix; therefore, the water diffusion in the matrix is independent of the fast diffusion into the defects. Hence, the weight gains can be described by the sum of the two Fickian processes. The slow diffusion process corresponds to the diffusion in the matrix and represents the properties of the composite. The fast diffusion is more a function of the physical flaws of the composite, namely surface defects.
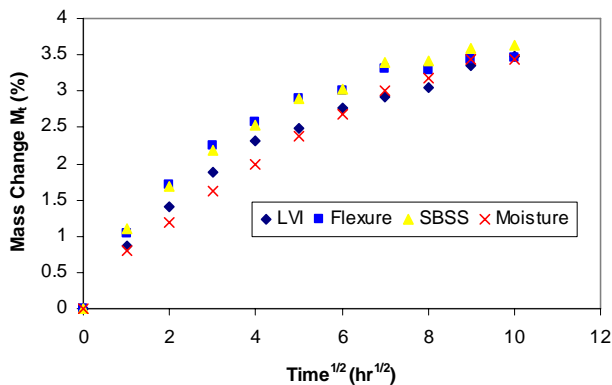

Figure 4. Curve showing percentage of water absorption against the square root of time for the different types of samples immersed in water at 100°C.
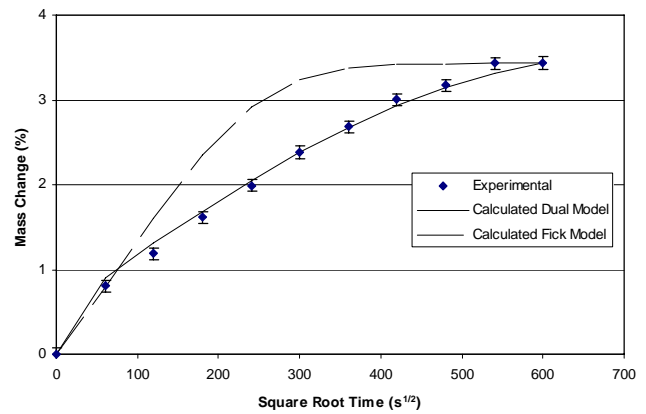

Figure 5. Curve showing percentage of water absorption against the square root of time for the ASTM D 570 samples immersed in water at 100°C compared to the dual diffusivity and Fickian models.

Crystallization Study

A TA Instruments Q100 differential scanning calorimeter (DSC) was used to characterize the thermal behavior of the samples exposed to moisture (M), specimens ex-posed to moisture and then dried (MD), and specimens as processed (D). The specimens were heated from 40 to 250°C at a rate of 10°C/min.

Figure 6 shows the DSC thermograms for the different specimens. A single peak at the melt temperature of 225°C for all three specimens was observed. The crystallinity was determined by comparing the experimental heat of fusion (ΔH) to the theoretical value for a 100% crystalline sample. ΔH was measured by integrating the area under the peaks of the DSC thermograms. All three specimens yielded average ΔH values of 94 J/g, which translated into crystallinity values of 40%. Although various values have been re-ported in the literature for the theoretical ΔH, the value of 230 J/g, referenced from the ATHAS data bank [15], was used as it is the accepted value used by other researchers [16]. There is no apparent influence of moisture absorption on the position (temperature) and shape (crystallinity) of the melting peaks. Russell and Beaumont [17] also found that exposure to boiling water had no significant influence on the structure and morphology of the spherulites of nylon 6 moldings. It can be speculated that although there is plasticization of the matrix and possible changes to the crystal ordering during exposure to moisture, the heating during the DSC study causes the material to dry and recover sufficiently so that the thermograms are the unchanged.
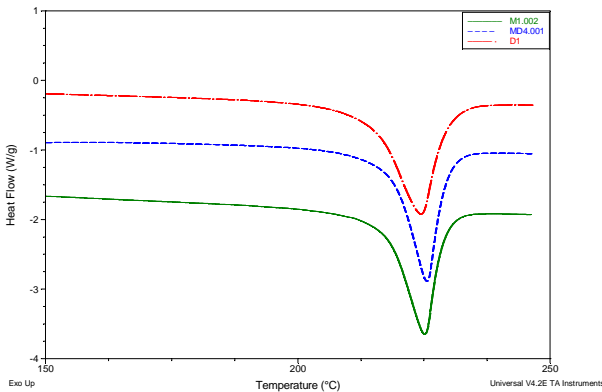
Figure 6. DSC thermograms for samples immersed in water at 100°C for 100 h, after recovery and dry samples.

Impact

Low-velocity impact (LVI) tests were conducted to study the resistance to impact and damage initiation and propagation of the carbon/nylon 6 composite panels exposed to moisture and UV. An instrumented drop weight tower equipped with a load cell of capacity 1590 kg (3500 lbs) was used to conduct the tests. A hemispherical shaped tup of diameter 19.5 mm and mass 0.12 kg was used as the impactor. The total impactor mass, including the tup, was 6.15 kg. The samples were clamped using a pneumatic assist mechanism, such that 76.2 mm diameter of the sample face was exposed to the impactor. Three impact heights, 0.46 m, 0.71 m, and 1.15 m, were chosen in order to capture the dominant failure modes of the plates from incipient to total failure and to analyze the energy absorption mechanism and damage progression. The force-time, energy-time, and load-deflection response of the samples were measured. Damage initiation and progression was monitored.

The failure modes of the three different types of samples, i.e., exposed to moisture (M), exposed to moisture then dried (MD), and as-processed and dried (D), were very different. The samples that were exposed to moisture showed a slight loss in stiffness, as the matrix became more plasticized and the fiber-matrix interfacial bond was compromised. This resulted in a more localized damage zone, as energy transfer/spread was mitigated. The recovered samples (MD) performed marginally better due to the matrix recovering some of its properties; however, the loss in the fiber matrix interface cannot be recovered. Figure 7 shows the force/energy –

time profiles for the samples at the maximum drop height of 760 mm. The maximum energy absorbed by all three samples is approximately the same. However, the dry sample offers some rebound after impact. This implies that the sample is capable of absorbing more energy. The load profiles of the samples show that the failure in the moisture-exposed sample is quite catastrophic, as there is a sharp drop after the maximum load. The dry sample shows that there are damage interactions within the sample at the peak load. These interactions are load transfers from matrix to fiber and delamination. The peak is not sharp, which implies that the sample is capable of withstanding a higher load. Inspection of the failed samples confirm these results, with the dry sample having a larger damage spread compared to the moisture exposed sample. SEM observation, as shown in Figure 8, shows that most of the fibers in the moisture ex-posed samples were not coated with the matrix, while Figure 9, the SEM image of the dry sample, shows that the fractured fibers are still well coated by the matrix. The main mode of failure for the dry samples was tensile face fracture with largely fiber breakage. The moisture exposed sample was a combination of fiber breakage and pull out. The fibers in the dry sample had multiple fractures compared to the moisture exposed samples.
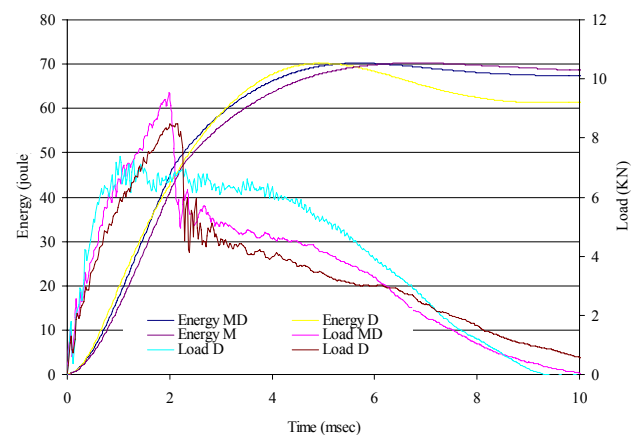

Figure 7. Typical force/energy – time curves for carbon/nylon 6 composite material exposed to moisture at 100°C; M- exposed to moisture, MD- exposed to moisture then dried, D- as processed and dried.
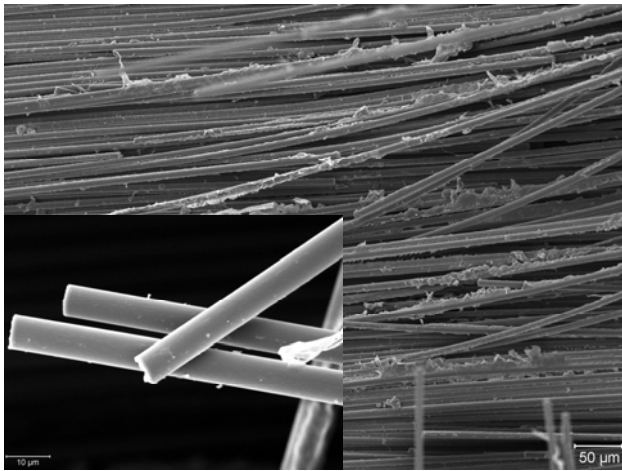
Figure 12. SEM image of moisture exposed sample after low-velocity impact test. Inset shows dry filaments, indicative of the fiber matrix interface attach by the moisture
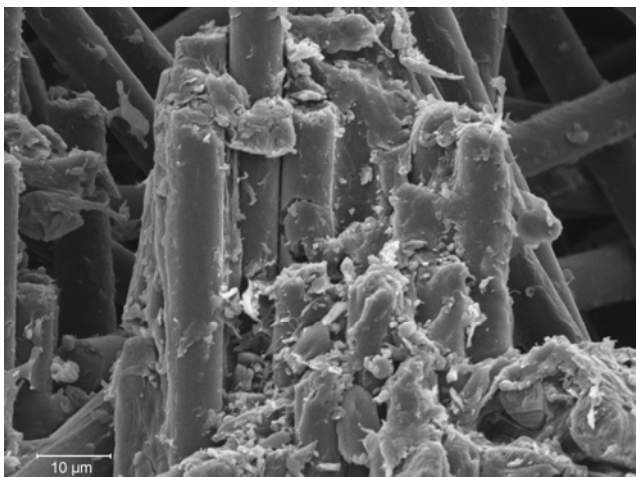

Figure 13. SEM image of as-processed, dry sample after low- velocity impact test. Failure mode is mainly due to fiber breakage, and matrix adhesion to the fiber is clearly evident.

5.0 Summary

The equilibrium moisture content was reached after immersion in distilled water at 100°C for 100 h. SEM images showed that surface defects due to processing have been expanded and the fiber matrix interface was attacked by the water ingress. The dual Fickian model for bidirectional composite developed by Bao and Yee [3] showed good correlation to the experimental results for water absorption.

DSC studies showed that the moisture ingress did not have any influence on the melting peaks or the crystallinity of the composite. Low-velocity impact shows that the damage to the samples exposed to moisture performs much lower than the as-processed dry samples. The main contributing factor to the lowering of the mechanical properties is the plasticization of the matrix and the attack on the fiber matrix interface by the water.

6.0 References

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