DEVELOPMENT OF MULTI-SCALE BIOCOMPOSITES FROM FLAX, NANOCELLULOSE AND EPOXY BY RESIN INFUSION

S Phillips¹, P. Kuo², C. Demaria¹, L. Lessard¹, M. Sain² and P Hubert¹*
¹ Department of Mechanical Engineering, McGill University, Montreal, Canada,
² Faculty of Forestry, University of Toronto, Toronto, Canada
* Corresponding author (pascal.hubert@mcgill.ca)

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1. Introduction

Bio-based composite materials are increasingly gaining acceptance as viable alternatives to conventional composites. In parallel with their development, there have been significant advancements in the understanding of nano-modified composites. This includes the use of bio-based nano-modifiers such as nanocellulose (NC) which is promising due to its abundance, low cost and excellent mechanical properties [1]. Advancement in these two areas raises the possibility of producing novel multi-scale biocomposites which could mimic the hierarchical structure of highly efficient materials found in nature. Some studies have already shown noticeable increases in mechanical properties by making use of hierarchical structures in biocomposites using conventional manufacturing processes [2]. However, it is clear that these conventional processes fall short in producing biocomposites of similar complexity to those found in nature and therefore must be adapted.

As a step in this direction, the current paper considers the resin infusion process as a base in producing multi-scale biocomposites from flax and nanocellulose. The aim was to produce a hierarchical biocomposite with markedly improved impact and interlaminar shear properties over the single-scale composite. This paper begins with a description of the fabric treatment process followed by the manufacturing of multi-scale plates by the resin infusion process. The results from void analysis, drop-weight impact testing and short beam testing are then discussed.

2. Sample manufacturing

2.1 Materials

The selected constituent materials for the multi-scale composite were the following; twill weave flax fabrics, NC and a conventional epoxy resin suitable for resin infusion (Araldite LY1564/Aradur 3486). The flax fabrics were kindly supplied by Lineo NV and the NC was derived from softwood at the University of Toronto. The NC production from softwood pulp consisted of two parts; chemical treatment (to remove lignin, hemicellulose and other impurities) and mechanical treatment to defibrillate. The chemical treatment process was used that described in the work published by Alemdar and Sain [3]. After the chemical treatment, the bleached pulp with 2% consistency was fed to a high shear defibrillator for 10 passes.

2.2 Fabric chemical treatment

It is well know that hydrophilic cellulose-based fibres such as flax benefit from chemical treatment in order to render them more compatible with hydrophobic resin systems [4]. In this study, all fabrics were treated with a 1% concentration of gamma-glycidoxypropyltrimethoxysilane in a solution of 60% ethanol and 40% distilled water (pH between 3.5 and 4). The treatment process was carried out a room temperature for 2 hours followed by vacuum oven drying.

2.3 Laminate manufacturing

For the laminate manufacturing, an aluminum tool plate was employed with a conventional vacuum bagging arrangement for the resin infusion process (Figure 1). The tool was placed on a hot plate to
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facilitate accelerated curing of the resin. A distribution media (AirTech® Resinflow 60) was incorporated in the layup that was cut two centimeters short of the preform end to avoid race tracking. The distribution media was incorporated to encourage thru-thickness flow of the resin and consequently better distribution of the NC in the laminate.

**Figure 1:** Bagging arrangement for resin infusion laminate manufacturing

Two methods were developed that incorporated the NC into the multi-scale composite. The first involved grafting the NC directly onto the flax fibre surface during the treatment process (labelled MS (Grafted) in Table 1). This method involved compacting in a dry state in the resin infusion pre-filling stage. This method was accomplished by adding an aqueous NC solution to the silane solution during the treatment process. The mass ratio of NC to flax fibre was selected as 10%. To better distribute the NC in the silane bath, spacers made up of glass fibre screen were placed in between the flax fabrics during the treatment process. The silane bath was then allowed to evaporate at room temperature until the fabrics were dry (about 48 hours). Following this treatment process, it was noted that the NC tended to agglomerate on the surface of the fabrics and agglomerations could be observed on the cured laminates (Figure 2).

**Figure 2:** Scanned surface of cured laminate using grafting technique; note agglomerations of nanocellulose are clearly visible

The second method involved modifying the standard resin infusion procedure so that the aqueous NC solution could be incorporated directly in the ply stack by wet-layup prior to bagging (labelled MS (Wet-layup) in Table 1). The stack was then heated to 80 °C for one hour to evaporate the bulk of the water. During the pre-filling stage some moisture remained which resulted in softening and lubrication during the compaction of the preform. Following this procedure, the consumables were placed and a vacuum hold was applied for 24 hours in order to eliminate residual moisture. The mass ratio of NC to flax fibre for this method was selected as 7%. This ratio was lower than the grafting method as it was the maximum amount of aqueous NC solution that could be feasibly spread on the dry fabrics.

Following the above preparations for the NC the epoxy resin (Araldite LY1564/Aradur 3486) was mixed by hand with the hardener for 5 minutes. This was followed by a 45 min debulk at 4.5 kPa of pressure. The resin was then infused with a filland post-fill outlet vacuum pressure of 50 kPa as controlled by a vacuum regulator. This high outlet pressure was selected to avoid additional degassing of the resin during processing. The inlet was clamped at the point the resin reached the end of the preform. The tool heating was commenced after 15 minutes had elapsed during the post-fill stage. A cure temperature of 50±5 °C was selected for a curing period of 16 hours. The heating and cooling rate resulting from the hot plate was 0.7±0.1 °C/min. Sample data from a thermocouple installed on the vacuum bag (and insulated using sealant tape)
during the curing stage for this setup is shown in Figure 3.

Figure 3: Sample thermocouple data from tool plate setup during curing stage

To investigate the influence of the NC on mechanical properties, three panels measuring 150 x 330 mm² were manufactured by each of the above two methods. An additional six panels that did not incorporate NC were also manufactured for comparison. For three of these panels, the preforms were saturated with tap water and subjected to the same 80 °C one hour drying and 24-hour debulk as the NC wet-layup technique (labelled SS (Wet) in Table 1). This was done to achieve the same lubricating and softening effect of the water so that a better comparison could be made with the multi-scale composite manufactured by the wet-layup technique where an aqueous NC solution was spread on the fabrics. The other three panels were compacted in a dry state (labelled SS (Dry) in Table 1).

Table 1: Test matrix for laminate manufacturing

<table>
<thead>
<tr>
<th>Panel</th>
<th>m_NC/m_flax (%)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS (Dry)</td>
<td>0</td>
<td>Dry flax preform</td>
</tr>
<tr>
<td>MS (Grafted)</td>
<td>10</td>
<td>Grafted NC onto flax preform</td>
</tr>
<tr>
<td>SS (Wet)</td>
<td>0</td>
<td>Wet flax preform</td>
</tr>
<tr>
<td>MS (Wet-layup)</td>
<td>7</td>
<td>Wet NC layup onto flax preform</td>
</tr>
</tbody>
</table>

* mass ratio of NC to flax fibre

During the infiltration of the panels, there were clear differences in the flow behaviour for the different preparation methods. Most striking was the difference in infusion time. For the SS (Wet) composite, the infusion took approximately 15 minutes whereas for the MS (Wet-layup) technique the infusion time took about 20 minutes for approximately the same porosity and ambient temperature. In addition, the flow front pattern was much more erratic for the processes that incorporated NC (Figure 4). For the MS (Grafted) method, there was not even a clear flow front and large pockets of dry spots remained unfilled when the resin reached the end of the preform. These areas gradually filled radially until the preform was completely saturated.

Figure 4: Infusion of flax fabric after MS (Wet-layup) preparation; note the rapidly advancing flow front in the distribution medium indicating low in-plane and thru-thickness permeability of the modified fabric

In addition to differences during processing the final laminates showed distinct differences. Most apparent was changes in thickness and consequently fibre volume fraction as calculated based on the areal weight of the flax fabrics (Figure 5).

Figure 5: Fibre volume fraction for single- and multi-scale nanocellulose, flax and epoxy composites manufactured by a modified resin infusion process

It is evident from Figure 5 that the processes that begun with wetting of the preform with water reached significantly higher fibre volume fractions than those that were dry upon initial compaction for the same consolidation pressure. The single- and multi-scale composites made from an initially wet
preform reached fibre volume fractions of 40.6±0.8 and 39.7±1.1% respectively. In contrast, the single- and multi-scale composite manufactured without initially wetting the preform reached fibre volume fractions of merely 31.9±0.4 and 28.7±0.4% respectively. Lubrication and softening effects have been observed previously for cellulose-based reinforcements especially upon exposure to a polar wetting fluid [5, 6]. The reason for the lower fibre volume fraction achieved by the multi-scale (Grafted) technique compared to the single-scale (Dry) technique was likely due to the agglomeration of NC at the fabric surface and the resultant resistance to yarn nesting during compaction.

3. Mechanical characterization

Subsequent to the manufacturing of the samples, they were subjected to a mechanical characterization. Nano-modifiers such as NC can improve the interlaminar properties since they provide reinforcement in a region of the composite which would otherwise be devoid of fibres [2, 7-9]. For this reason, the following properties were investigated; void content, interlaminar strength and drop-weight impact resistance. For the purposes of comparing mechanical properties, the single-scale (Dry) properties were used as reference for the multi-scale (Grafted) composites and the single-scale (Wet) case was used as reference for the multi-scale (Wet-layup) composites.

3.1 Void analysis

In the current paper, the percentage of voids in the laminates was used as an indicator of the quality of the composite. Void analysis was carried out by optical microscopy and image analysis due to the inappropriateness of the commonly used resin-burn off technique (ASTM D2734) for composites reinforced with cellulose-based fibres. Samples with a length of 2 cm were cut with a tile saw 1 cm from the outlet where the highest void content was thought to occur due to the low resin pressures that occur near the outlet. Due to the limited field of view of the microscope, a minimum of 60 images were necessary for each sample which were then assembled in a freeware image editing software, ImageJ. Upon examination of the images, it was noted that the contrast of the voids with the rest of the composite was very low. To better distinguish them, they were highlighted manually and filled in with black pixels. The images were then converted to 8-bit greyscale and a threshold function was applied to isolate the filled in regions whose area was finally measured by the software. The results are summarized in Figure 6.

<table>
<thead>
<tr>
<th>Sample cross-section</th>
<th>Void %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS (Dry)</td>
<td>0.7±0.6</td>
</tr>
<tr>
<td>SS (Wet)</td>
<td>0.3±0.3</td>
</tr>
<tr>
<td>MS (Grafted)</td>
<td>11.3±2.7</td>
</tr>
<tr>
<td>MS (Wet-layup)</td>
<td>1.0±0.5</td>
</tr>
</tbody>
</table>

**Figure 6:** Cross-sections of single-scale and multi-scale composite manufactured by resin infusion

The microscopy results provided valuable insight about the consequences of the two methods explored to incorporate NC. Most obvious was the difference in overall void content. The grafting technique resulted in significant higher void content. More critical was the nature of these voids. As can be seen in Figure 6, the voids were both large inter-yarn voids and smaller elongated inter-ply voids. The latter void morphology was deemed most critical since the NC was primarily intended to improve interlaminar properties.

The multi-scale composites produced by the wet-layup technique, showed much more reasonable void contents as well as a better fibre volume fraction as shown in Figure 5. Thus, the multi-scale composites produced by this technique were expected to result in superior mechanical properties compared to the grafted technique simply based on the quality of the composites.

3.2 Interlaminar strength

One of the most often studied properties that is known to be void sensitive is interlaminar shear
strength [10, 11]. Interlaminar shear strength (ILSS) was obtained by the short beam test carried out in accordance with ASTM D2344 on a MTS Insight load testing machine with a 5kN load cell. Although this is a controversial method to obtain ILSS (due to the complex stress state involved) it was deemed appropriate for comparative purposes. A load rate of 0.5 mm/min was applied and the span to depth ratio was set to 4. The sample geometries are given in Table 2. The samples were cut on a diamond tile saw and the edges were sanded using 240 grit sand paper.

The impact test, where is the specimen width at centre span. The calculated interlaminar shear for this processing method led directly to voids and consequently a reduction in interlaminar properties. Thus, the processing method led directly to voids and consequently a reduction in interlaminar properties. Therefore, even if the NC led to an increase in ILSS, the importance of proper incorporation of these nano-fibres to produce high quality composite parts cannot be underestimated. For the case of the single- and multi-scale cases that began with a wet preform, there was not a significant difference in ILSS as determined from short beam strength.

Table 2: Measured sample geometries for short beam strength specimens (± standard deviation)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Thickness (mm)</th>
<th>Width (mm)</th>
<th>Length (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS (Dry)</td>
<td>4.51±0.06</td>
<td>8.79±0.28</td>
<td>28.5±0.1</td>
</tr>
<tr>
<td>MS (Grafted)</td>
<td>5.01±0.07</td>
<td>9.99±0.11</td>
<td>30.5±0.2</td>
</tr>
<tr>
<td>SS (Wet)</td>
<td>3.54±0.07</td>
<td>7.38±0.32</td>
<td>22.1±0.1</td>
</tr>
<tr>
<td>MS (Wet-layup)</td>
<td>3.62±0.1</td>
<td>8.28±0.10</td>
<td>22.9±0.1</td>
</tr>
</tbody>
</table>

This configuration resulted in a mode of failure of interlaminar shear for both systems as observed under a microscope. The interlaminar shear strength was calculated from:

\[
ILSS = 0.75 \cdot \frac{P}{h \cdot w}
\]

where \( P \) is the maximum observed load during the test, \( h \) is the specimen thickness at centre span and \( w \) is the specimen width at centre span. The calculated ILSS values are summarized in Figure 7.

![Figure 7: Interlaminar shear strength for single- and multi-scale composite manufactured by resin infusion; incorporation of nanocellulose fibres did not lead to a increase in interlaminar shear strength](image)

The results indicated that the incorporation of the NC did not lead to an increase in interlaminar shear properties. In the case of the grafted technique, it led to a 35% decrease in ILSS. However, there was also a 10% decrease in fibre volume fraction so part of this decrease was likely due to this fact. Nonetheless, the microscopy results indicated a large presence of interlaminar voids for this processing technique which is in agreement with this large decrease in interlaminar properties. Therefore, even if the NC led to an increase in ILSS, the importance of proper incorporation of these nano-fibres to produce high quality composite parts cannot be underestimated. For the case of the single- and multi-scale cases that began with a wet preform, there was not a significant difference in ILSS as determined from short beam strength.

3.3 Drop tower impact

Automotive applications have been sighted as a major market for bio-based composites due to their low cost and relatively good mechanical properties [12]. Consequently, impact properties are of importance. The influence of NC on the impact properties was investigated in accordance with ASTM 7136. Five samples were tested with a ply sequence of [(45/-45)/(0/90)]S and dimensions of 4.5 x 100 x 150 mm3. The same sample cutting procedure was used as for the short beam samples presented in the preceding section. The impact energy was selected as 7J based on initial trials with spare specimens. This corresponded to a height of 11.6cm for the 1.6cm diameter hemispherical impacting head. The total weight of the impact head and test frame crosshead was 6.143 kg. The velocity at the point of impact was measured with an Instron optical gate and the force was monitored by a 22kN-capacity Instron® force transducer. The specimens were installed in the fixture outlined in ASTM D7136 and were impacted on the tool side. Representative force histories for the various samples are presented in Figure 8a. The velocity, displacement and energy histories were then determined as outlined in ASTM D7136 (based on
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Figure 8 provides much insight into the extent of damage induced in the single- and multi-scale composite manufactured by the various techniques. The force histories revealed that the single-scale composites were able to carry more load before experiencing damage in comparison to the multi-scale composites. The SS (Dry) and SS (Wet) laminates reached maximum loads of 1932±53N and 1761±35N respectively. The reason for the higher load for the dry case was likely due to its larger thickness. In contrast, the MS (Grafted) and MS (Wet-layup) reached loads of only 1450±145N and 1507±64N. The high amount of error for the MS (Grafted) technique was likely due to the non-uniformity of NC as illustrated in Figure 2.

The velocity data indicated that more elastic recovery occurred for the single-scale composites and consequently a higher velocity was achieved on the rebound of the impacting head. The maximum velocity after the rebound was over 30% higher for the SS (Dry) case compared to the MS (Grafted) case. Similarly, the maximum velocity was over 10% higher for the SS (Wet) case compared to the MS (Wet-layup) case. This higher rebound velocity led to a greater increase in displacement of the impacting head as indicated in Figure 8c.

Finally, the energy absorption history indicated a lower amount of recovered energy (i.e. the difference between the peak and final energy) for the multi-scale composites. As can be seen in Figure 8d, after the impact event the recovered energy was almost 50% higher for the SS (Dry) case compared to the MS (Grafted) case. Similarly, a decrease of 20% was recorded for the MS (Wet-layup) case compared to the SS (Wet) case. This decrease in energy recovery was presumably due to a greater dissipation of energy in damaging the multi-scale composites. These results imply that between the two methods explored for incorporating the NC, the wet-layup technique led to superior impact properties.

Following the testing of the samples, the extent of damage was evaluated by measuring the impact dent depth and the maximum damage diameter (Figure 9).
Figure 9: Dent depth and maximum dent diameters of single-scale and multi-scale flax, nanocellulose and epoxy composites after being impacted by 1.6cm diameter hemispherical striker head with 7J of impact energy

It can be seen from Figure 9, that the extent of the damage was generally greater in the case of the multi-scale composites as was suggested by Figure 8. For roughly the same fibre volume fraction, the depth of the dent was over twice as large for the multi-scale composite manufactured by the grafting technique. This was likely due to the significant amount of interlaminar voids as observed in Figure 6. Similarly, a distinct increase in dent depth was noted for the multi-scale composite manufactured by the wet-layup method suggesting that the addition of the nano-cellulose did not contribute to an improvement in interlaminar properties.

In terms of damage modes, cracks were observed on the bag-side of all samples. However, in the case of the multi-scale composite, there were dramatic signs of delamination as well (especially in the case of those manufactured by the grafting technique). This further suggests that the NC incorporated by both methods led to a decrease in interlaminar properties. Representative damage areas for all types of samples are shown in Figure 10.

Figure 10: Representative bag-side damage areas after drop-weight impact testing for single- and multi-scale composites manufactured from flax, nanocellulose and epoxy by resin infusion; (a) single-scale (Dry), (b) multi-scale (Grafted), (c) single-scale (Wet) and (d) multi-scale (Wet-layup)

4. Conclusions

Multi-scale composites based on flax, epoxy and nanocellulose were developed using the resin infusion process. Two methods to incorporate the NC were explored; a grafting technique based on a silane treatment and a wet-layup of aqueous NC solution in the resin infusion pre-filling stage. Void analysis revealed that the silane-based grafting technique led to a high amount of interlaminar voids and consequently a reduction in short beam and drop-weight impact properties. Conversely, the wet-layup technique did not lead to interlaminar voids. However, a marked decrease in impact properties was still noted for this method in drop-weight impact tests. Overall, the incorporation of NC by the studied methods did not lead to an improvement in interlaminar properties. This study highlights the link between the incorporation of nano-modifiers such as NC in composite manufacturing processes and the final quality of the composite part.
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