STIFF AND DUCTILE NANOCOMPOSITES OF EPOXY REINFORCED WITH CELLULOSE NANOFIBRILS

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1 Introduction

Polymer-matrix composites have been a material of choice for a long time now. In view of the recent awareness in environmental changes, a considerable effort has been diverted to study materials obtained from bio/renewable sources as a potential substitute to synthetic/petroleum based products. A significant leap in this direction has been the use of plant fibers (jute, sisal etc) as the reinforcing phase in polymer composites. In addition to the green aspect, plant fibers result in increased brittleness, although the strength and stiffness increase favorably.

Epoxy is one of the most widely used class of thermosets, which finds applications in varied fields – adhesives, coatings, as a matrix in composite materials etc. Epoxy composites with glass fibers and natural fibers as reinforcement have been studied extensively. Recently, there has been increased interest in epoxy based nano composites with most of the attention focused on carbon nano tubes [1, 2] and nano cellulose [3-6] as reinforcements. Cellulose nano fibrils extracted from the plant fibers’ cell wall have emerged as a viable alternative for advanced mechanical properties. Cellulose fibrils, composed of crystalline and disordered regions, are the main load bearing structure in the plant cell walls and cellulose crystals have a modulus of 137 GPa [7], which explains the superior mechanical reinforcement of their nano fibrils. It has also been shown that cellulose nano fibrils have a less detrimental effect on the strain to failure resulting in more ductile materials [8]. Small amounts of nano cellulose reinforcements with epoxy matrix are extensively reported in the

literature [9-13]. In this work, an attempt has been made to address the issue of brittleness in epoxy-based composites by using nano fibrillated cellulose (NFC) obtained from commercial pulp. Also, the potential large-scale application of the composite is demonstrated with the preparation a 3D molded nanocomposite shell element.

2 Experimental

2.1 Materials

Diglycidyl ether of bisphenol A (DGEBA), purchased from Sigma Aldrich, was used as the epoxy monomer in this study. A polyether amine, kindly provided by Huntsman Chemicals, was used to cross link the epoxy. NFC was prepared in the lab from commercial pulp; via enzymatic pre-treatment followed by mechanical disintegration by passing through a micro fluidizer, as described by Henriksson et al [14].

2.2 Sample preparation

The NFC obtained after the mechanical disintegration was a gel like suspension with ca. 2 wt% dry content. The gel was further diluted 10 times to approx. 0.2 wt% NFC and this suspension was thoroughly homogenized by mixing with an Ultraturrax (model D125 Basic, IKA, Germany). The dilute suspension was then filtered over vacuum resulting in a template with ca. 80% water content. This template is essentially a porous network of nano fibrils [15]. The open pore network was utilized in the preparation route to impregnate the template with monomers/cross linker followed by curing in situ. Prior to this, water in the template was first exchanged to acetone by placing the network in acetone bath for an extended period of time. To
ensure complete solvent exchange, the acetone in the bath was changed at regular intervals. The epoxy and amine monomer were dissolved in acetone and the template from acetone was placed in the solution. Composites with 20, 40 and 60 wt% of NFC were prepared and the fibril : matrix ratio was controlled by varying the amount of monomers in the impregnating solution. The template was left in the impregnating solution overnight, followed by drying at room temperature and curing at 80 °C for 3 hours and 120 °C for 3 hours. The final weight percent of fibrils in the composite was calculated based on the initial dry weight of the NFC and the final weight of the composite.

2.3 Characterization

Tensile testing was performed using Instron 5944. Prior to testing, the samples were conditioned at 23 °C and 50 % relative humidity. Samples were cut into rectangular strips (40 mm x 5 mm) and tested at a strain rate of 10 %/min. At least 5 replicas of each sample were tested. Tensile modulus was calculated by the slope of the stress-strain curve in the elastic region. The average values and the standard deviation are reported here.

Dynamic Mechanical Thermal Analysis was performed on TA instrument Q800. Temperature ramp between 30 °C and 150 °C was carried out at a speed of 5 °C/min and a frequency of 1 Hz in tensile mode.

Morphology of composite cross sections was studied using Field-Emission Scanning Electron Microscopy (FE-SEM, Hitachi S-4800, Japan). The samples were fractured in the liquid nitrogen to ensure a brittle fracture. The cross sections were then mounted on the sample holder and coated with 10 nm layer of platinum-palladium (Cressington 208HR Sputter Coater) before observation.

3 Results and Discussions

3.1 Mechanical characterization

The characteristic stress-strain curves are presented in Figure 1 and the values of mechanical properties are reported in Table 1. The curve for neat epoxy shows a typical ductile behavior. Elastic region for the material extends up to ca. 1% strain after which the material begins to yield followed by the start of necking at 5% strain until the material fractures at 37.5%. The ultimate tensile strength (UTS) for neat epoxy was 33.2 MPa.

The curves for composites show linear behavior up to ca. 2 %. It seems that no debonding or local damage appears in this region. The plastic region in these curves is dominated by strain hardening unlike in case of the neat epoxy which was dominated by necking. Strain hardening is a characteristic phenomenon in cellulose nanopaper [15, 16] resulting primarily from fibril straightening and the re-aligning of the fibrils along the longitudinal direction which provide additional reinforcement [17, 18]. It is interesting to note that the primary reinforcement in the composite materials occurs in the plastic region, which is evident from the slope of the curves after yielding. The composites with higher NFC content have a stronger strain hardening leading to increased UTS. These observations imply that the characteristic NFC network structure was retained, leading to excellent synergetic properties in the composites.

The composite with 20 wt% NFC loading is particularly interesting because it demonstrates the significant reinforcing effect of NFC with the UTS increased to 90.4 MPa (more than 2 fold increase). Remarkably, even though the stiffness and strength increased significantly, the composite was still ductile and fractured at 23.6 % strain.

The elastic modulus of the composites increased significantly on addition of NFC, from 2.4 GPa for neat epoxy to 10.5 GPa for the 60 wt% composite (Figure 2). The increase was most significant on addition of 20 wt% and 40 wt% NFC, and the increment is somewhat low in the 60 wt% composite. The constantly increasing trend in the stiffness suggests that the fibrils were well dispersed in the matrix and agglomeration was avoided to a large extent. The reduced reinforcing efficiency in the 60 wt% composite suggests that the fibrils were not as well dispersed as in the lower wt% composites.

3.2 Dynamic Mechanical Analysis

The dynamic thermo-mechanical properties of neat epoxy and composites with 20 %, 40 % and 60 % NFC content were studied using a DMTA and are presented in Figure 3.

Figure 3a displays the storage modulus (E’) of the neat epoxy and composites. The storage modulus of the neat epoxy in the glassy state is ca. 1000 MPa and drops rapidly after the onset of glass transition reaching a plateau value of 7 MPa in the rubbery state. The storage modulus of the 60 % NFC composite in glassy state was 4.3 GPa, which is ca. 2
times the value for neat epoxy. The reinforcement potential of NFC is more significant above Tg, where a 20% NFC loading results in a storage modulus of 0.4 GPa, an increase of about 60 times over neat epoxy. The storage modulus in the glassy as well as the rubbery state increased with increasing NFC content, further pointing that the fibrils were well dispersed in the composite. With 60% NFC content, the storage modulus was 4.2 GPa (ca. 4 times that of Neat epoxy) in the glassy state and 1.6 GPa (200 times that of the neat epoxy) in the rubbery state.

The high stability of the composite samples above the glass transition results from the strong network of the cellulose nanofibrils and formation of a percolation network that is attributed to the strong hydrogen bonds between the fibrils. Formation of percolating network and the consequent increase in dynamic mechanical properties has also been reported for composites of cellulose nano whiskers [19, 20].

Figure 4b shows the tan δ vs. temperature curve for the neat epoxy and composite samples. The peak of the tan δ curve is ascribed to the primary mechanical relaxation related to the glass-rubber transition. The glass transition temperature initially decreases when NFC is added to the system and later starts to increase when higher amount of NFC are added (Figure 4). The Tg of the neat epoxy is 68 °C, decreased to 47 °C when 20 wt% NFC is added and then increases again to 73 °C when the NFC content is increased to 60 wt%. The presence of NFC network probably has two competing effects in the composites. On one hand it decreases the cross linking density of the material (decreases the Tg) and on the other hand, the rigid NFC network provides additional hindrance to the mobility of the cross linked polymer chains (increases the Tg). In the 20 wt% composite, the decrease in the cross link density dominates because the low wt% of the fibrils cannot provide enough hindrance to polymer mobility. But, as the NFC content is increased, the NFC network becomes denser and the hindrance effect starts to dominate; thus increasing the Tg of the 40 and 60 wt% composite.

The magnitude of tan δ peak, also, shows a sharp decrease as the NFC content is increased. This is probably because the cellulose nanofibrils induce a certain degree of immobilization to the amorphous epoxy chains, which reduces the effective number of molecules participating in the transition.

3.3 Morphology

The SEM images of the freeze fractured cross section are presented in Figure 5. The 40 wt% and 60 wt% composites cross section show a laminated structure which is very similar to that of an NFC nanopaper [15]. The 20 wt% composite, however, shows a very homogeneous distribution of the fibrils in the composites. It is also apparent that the higher wt% composites had fibril rich regions, indicating some agglomeration. The continuous homogeneous distribution in the 20 wt% composite could also explain the high strain to failure observed during the tensile tests.

3.4 Demonstrator

The possibility to use the NFC/epoxy prepregs for manufacturing of components was verified in a series of manufacturing trials. A photograph of the selected demonstrator component, a protective case for a smartphone, is shown in Figure 6. It was manufactured by vacuum driven compression molding in a steel tool. The manufacturing involved placement of tailor-cut prepreg blanks into the female part of the mold. The blanks alone were however not sufficient to give a homogeneous component. This was caused by a combination of relatively sharp edges in the geometry and a limited drapeability of the prepreg. The problem was circumvented by adding neat epoxy to fill out gaps and fillets. A three-piece metal die, constructed to provide compaction pressure both to horizontal and vertical section of the case, was placed on top of the prepreg stack. The mold, with the die, was covered by several layers - an air and matrix permeable thermoplastic release film was the first layer. The second layer was an absorbing fabric, a so-called breather or bleeder with purpose both to provide a path to evacuate air and to absorb any excess resin during the subsequent compaction and curing. The mold was placed in a vacuum tight bag made from polyamide film and tacky tape. Vacuum was applied to the bag, and kept throughout the curing, to provide compaction force on the metal die. The whole arrangement was finally placed in an oven for curing during 2 h at 80 °C followed by a post-cure for 3 h at 120 °C.

The component manufacturing trials were encouraging since they showed that NFC/epoxy prepregs can easily be used together with
conventional composite manufacturing techniques to make real components. They also revealed that the low drapeability of the current NFC/prepreg is a limiting factor for manufacturing of complex shaped parts. This means that utilization of the full potential of the current material can be achieved for components with relatively flat geometries such as weakly curved panels or sheets.

4 Conclusions

In this study, composites of nano fibrillated cellulose (NFC) in an epoxy resin were successfully prepared. Composites with high NFC content (20 - 60 wt%) were characterized. It was shown that the composites with 20 wt% of NFC showed extremely efficient reinforcement in strength and modulus, and also the ductility was preserved to a large extent. Generally, there was an increasing trend in the strength and stiffness, suggesting a good dispersion even with 60 wt% fibrils.

Dynamic mechanical analysis revealed excellent reinforcement in the rubbery state. The Tg of the material decreased on addition of 20 wt% fibrils and then increased on further addition of NFC.

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References

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Fig. 1. Stress-Strain curves of the neat epoxy and epoxy-NFC composites at 50% relative humidity and 23 °C.

Fig. 2. Dependence of elastic modulus (black triangles) and strength (blue squares) on the NFC content in the composite.

Fig. 3. (a) Storage Modulus and (b) tan δ of neat epoxy and epoxy-NFC composites obtained by DMTA.

Fig. 4. Variation of glass transition temperature with NFC content as observed from the tan δ peak.
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Fig. 5. SEM images of freeze fractured cross sections of the composites.
Fig. 6. Image of the shell molded from Epoxy-NFC prepreg

Table 1. Values of the mechanical properties as obtained from the tensile and dynamic mechanical test.

<table>
<thead>
<tr>
<th>Composite (wt% NFC)</th>
<th>Modulus (GPa)</th>
<th>Strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>Tg (°C)</th>
<th>Storage Modulus (MPa)</th>
</tr>
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<tr>
<td></td>
<td>Avg</td>
<td>stddev</td>
<td>Avg</td>
<td>stddev</td>
<td>Glassy</td>
</tr>
<tr>
<td>0</td>
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<td>0.4</td>
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<tr>
<td>20</td>
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<td>2.0</td>
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<td>2.0</td>
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<tr>
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<td>152.4</td>
<td>7.1</td>
<td>73</td>
</tr>
<tr>
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