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NANOCELLULOSE REINFORCEMENT OF TRANSPARENT COMPOSITES

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ABSTRACT

In this work, we evaluate the impact of nanocellulose reinforcement on transparent composite properties. Due to the small diameter, high modulus, and high strength of cellulose nanocrystals, transparent composites that utilize these materials should show improvement in bulk mechanical performances without a corresponding reduction in optical properties. In this study composites were reinforced using dispersed nanoparticles as well as continuous architecture developed from hydrogel-based processes. Poly(methyl methacrylate) and Bisphenol F resin systems were integrated with nanocellulose of varying crystallinity, fiber size, and surface functionalization. Mechanical performance was determined from dual cantilever dynamic analysis, tensile, and charpy tests following ASTM standards. Optical properties were evaluated for transmittance and scattering behavior, and compared to baseline studies of aqueous and organic solvent dispersions.

1. INTRODUCTION

Polymer nanocomposites are an increasingly developing area in composites manufacturing because of improvements the nanoparticles add to the system. There is interest in developing nanoparticles that result in advanced composite performance for a wide variety of applications. In comparison to other possible nanomaterials, nanocellulose has distinct advantages. Nanocellulose fibrils show high strength and modulus values in the range of 10GPa and 100-160 GPa, respectively [1]. They are also easily processed and easily modified resulting in low production costs [2] and may be readily dispersed in thermoplastics through solvent-based methods such as electrospinning to provide mechanical reinforcement [3].

Previous studies have demonstrated optically clear thin film polymer composites reinforced with nanocellulose [4]. The current study extends these concepts towards a processing technique that yields bulk composites with improved mechanical properties and minimal impact on optical quality. Addressing the problems with manufacturing nanocellulose composites is the main focus of this study. The complications arise in properly keeping the cellulose well-dispersed in a three-dimensional structure and avoiding agglomerations. Any agglomerations will weaken the mechanical properties and degrade optical performance. This study overcomes these obstacles by using sol-gel and aerogel procedures to template the nanocellulose network prior to introducing the matrix [5].

2. EXPERIMENTATION

2.1 SAMPLE PREPARATION

2.1.1 Resin Formulations

Several resins and curing agent formulations were evaluated to backfill the sol-gel and aerogel structures. It was determined that to backfill effectively, the resin recipe had to be low in viscosity, have a high volatilization pressure, have a pot life of at least four hours, and cure below 140 ˚C. The low viscosity allows the resin and curing agent to move through the small pore network structure of the sol-gel and aerogel. The high volatilization pressure is important to minimize monomer loss from the resin mixture while under vacuum. The long pot life allows adequate time for the resin to penetrate into the network system. The limited cure temperature minimizes thermal degradation of cellulose. Using these parameters, we downselected the resin mixtures to two for this study.

The first resin mixture consisted of EPON 862, a Bisphenol F based epoxy, and Epikure W, an aromatic amine curing agent. This system was evaluated under all of the mechanical tests reported here. However, the Epikure W curing agent adds a very dark brown color to the system, compromising the optical transmittance such that its utility was limited to testing mechanical performance and optical scattering. The second resin mixture consisted of a Low-Vis Spurr embedding epoxy resin (vinylcyclohexane dioxide and diglycidyl ether polypropyleneglycol) that exhibited very little color after cure and was therefore used for optical analyses.

2.1.2 Cellulose NanoFibril Sol-Gel

An aqueous dispersion of nanofibrilated cellulose (NFC) was prepared by using the TEMPO oxidation technique [6]. TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical) is an oxidation mediator that selectively oxidizes the C-6 carbon of glucose monomers in the cellulose polymer chain. The resulting cellulose chains are functionalized with carboxylic acid groups. These groups generate enough interfibril repulsion to push chains apart with less mechanical force than required by other methods of producing cellulose fibrils. The resulting filaments average about 20 nm in diameter and can be microns long.

A sol-gel producing method utilizing concentration gradients was used to solvent exchange acetone with the water in the NFC dispersion. The NFC dispersion was poured into a glass container at an amount to obtain the desired thickness. During solvent exchange, the sol-gel retained its geometric properties. It was important to use the appropriate container and amount of solution to obtain the desired sample size. The NFC dispersion demonstrated shear thinning behavior and was therefore stirred at high velocity to reduce viscosity and better enable it to adopt the shape of the container. The dispersion was then placed under reduced pressure to expel gas absorbed during mixing, which was evident by visible bubbles.

The purpose of exchanging from water to acetone is that acetone provides higher volatility while also maintaining the spatial network of the cellulose nanofibrils through interactions with hydroxyl groups of the cellulose. The acetone was layered on the top of the NFC solution in a manner that did not affect the surface of the NFC dispersion. Because of the miscibility of water

and acetone, the solvents gradually exchanged until equilibrium was reached. After several hours the liquid top layer was removed and a new acetone layer was added. This was done two times a day for a week until a rigid disc formed. This final disc was an NFC-acetone sol gel.

Once the sol-gel was created, the NFC network was backfilled with resin. The epoxy resin system was mixed according to manufacturer guidelines and poured on top of the sol-gel. A weight was used to keep the NFC-acetone sol-gel fully immersed during the backfill.

The submerged sol-gel was placed under vacuum with pressure adjusted to maintain a consistent stream of acetone bubbling from the setup. The sol-gel, during this part of the processing, was always fully immersed to avoid introducing voids to the sample and subsequent collapse of the gelled structure. While submerged under vacuum, the departure of acetone pulled in the epoxy mixture. After four hours under reduced pressure, dependent on the pot life of the resin mixture, the epoxy backfilled cellulose sol-gel was removed, placed in a Teflon dish, and then cured. Curing temperature and duration were determined based on the resin and curing agent mixture. The EPON 862 and Epikure W backfilled cellulose sol-gels were cured at 120˚C overnight under a nitrogen purge. The Low-Vis Spurr embedding epoxy backfilled composites required overnight curing at 70˚C under nitrogen purge.

2.1.3 Cellulose Freeze Dried Aerogels

Cellulose nanofibril aerogels were produced from an aqueous dispersion through a freeze-dry process. With the aerogel disc fabricated, the epoxy resin system was driven into the open pore network of the cellulose system using a vacuum oven and the method described in section [2.1.2]. The aerogel was kept submerged in a resin mixture and put under vacuum. This pulled out the air that previously occupied the voids and replaced it with epoxy resin system. The backfilled aerogel was then removed from the excess resin mixture and cured at the specified temperature and duration.

2.2 OPTICAL TESTING

2.2.1 Testing Procedure

A Gardener Haze-Gard Plus was used to analyze the transmittance, haze, and clarity of specimens. Transmittance is the percentage of light transmitted through the sample. Haze and clarity are measures of the amount of transmitted light that is scattered more than 2.5˚ and less than 2.5˚, respectively, versus the incident beam. The machine took two separate readings from circular areas 3.5 mm in diameter and determined a percentage for comparison. Each specimen was cleaned thoroughly prior to testing. The process was repeated at least three times and results averaged for each sample.

2.3 MECHANICAL TESTING

2.3.1 Dual Cantilever Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA) was used to characterize temperature dependent mechanical properties. Samples were prepared by cutting a section of the fully cured epoxy backfilled sol-gel and aerogel into a rectangle that was 13mm in width and at least 35 mm in length. The piece was then ground down to a uniform thickness between 2.5-3 mm. The grinding process was also used to make the final width uniform to 12-13mm. The specimen was clamped tightly in a dual cantilever fixture using a torque wrench set at 0.56 N-m. The length of sample being measured in this fixture was 7.6 mm.

The temperature was equilibrated at -50˚C for 5 minutes and then ramped to 250˚C at a rate of 3˚C per minute while flexure was conducted at 1 Hz with amplitude of 12 μm. This temperature range was broad enough to encompass the glass transition temperature and glassy and rubbery region plateaus for all the specimens.

2.3.2 Conventional Instron Tensile Testing

Tensile testing was performed on an Instron 1125 load frame using digital image correlation (DIC) to provide accurate measurements of strain. Testing was done with a 5 kN load cell at a load rate of 1.27 mm per minute. The data was taken from the camera strain software and the load cell to establish the stress-strain relations.

Based on the ASTM Standard D 3039, samples were cut in dogbone geometry with a gage length of 20 mm, thickness of 3.2mm, and width of 2.5mm. The samples were cut using a water jet and the thickness and widths measurements were recorded over an average of three points along the gage length. One side of the tensile specimen was speckled with paint for DIC.

2.3.3 Izod Impact Testing

Impact testing was performed using an Instron POE 2000 Izod Impact Tester with a head speed of 1.8 m/s (6 ft/s). Specimens were cut to create uniform square cross-sections of about 9.6 mm^2 and lengths that fit into the testing equipment based on the ASTM Standard D 256. Each specimen condition was tested at least three times.

3. RESULTS

3.1 Optical Testing

The Low Vis Spurr epoxy backfilled cellulose sol-gel composite tested was about 6.5 mm thick and about 1.2wt% nanofibrilated cellulose in the epoxy. The optical measurements were 49% transmittance, 26% haze and 46% clarity. While the sample had been polished and cleaned, some of the surface defects were too deep to grind out, which may have compromised optical testing. The most noticeable was a small concave area on the bottom surface.

Previous studies in our laboratory using cellulose solutions and thin films using dispersions of cellulose nanocrystals in solvents and polymers have indicated that optical properties noticeably degrade with increased nanocellulose concentration and sample thickness. Similar behavior is evident in the current study as well. However, the difference between the neat epoxy and the

backfilled cellulose sol-gel network are negligible. It is clear that the introduction of cellulose into an epoxy system will have little effect on the optical qualities. It is also evident that the thickness and slight discoloration affect the optical properties more than the cellulose in comparison to the trends established before on thinner samples.

The epoxy-filled cellulose aerogel was not used in the optical measurements due to the poor properties it exhibited. The aerogels appear to promote agglomeration of nanofibrils during the freeze-drying process, which allows for high transparency but significant scattering. This effect is not seen in the cellulose sol-gel processing, because the acetone takes up the hydroxyl groups that are associated with the van der Waals forces from nanofibril to nanofibril.

3.2 Mechanical Testing

3.2.1 Dual Cantilever Dynamic Mechanical Analysis

Figure 1 illustrates the dual-cantilever dynamic mechanical analysis data, which highlights the glassy region, glass transition drop, and rubbery plateau of each sample. There are two important characteristics shown from the data collected. In the glassy region, there is little difference between samples of neat epoxy, the cellulose sol-gel backfilled with epoxy, and the cellulose aerogel backfilled with epoxy. However, there is an increase in storage modulus in the rubbery region with the addition of cellulose. The other note-worthy discovery is that using the sol-gel backfilling procedure, there is a large drop in glass transition temperature. This drop may be attributed to the presence of acetone in the exchange procedure. Residual acetone may be present, plasticizing the epoxy; or the acetone may be interacting with the epoxy or curing agent, reducing cure conversion. It is unlikely to be caused by the NFC itself since addition of the same weight percentage of NFC using the aerogel method did not cause much change to glass transition temperature.

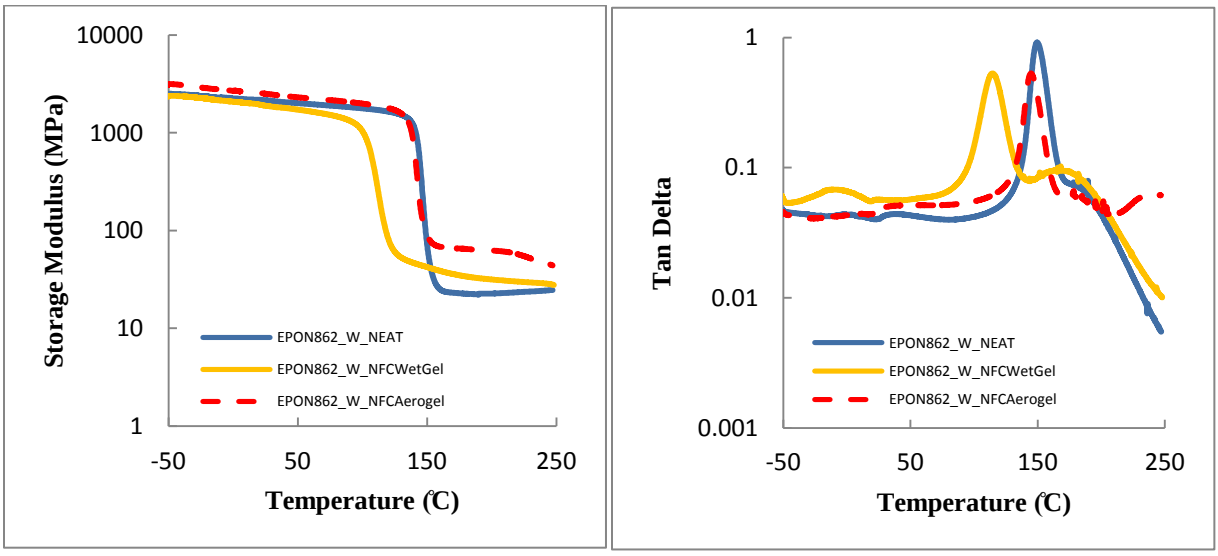

Figure 1: DMA-derived data for NFC-epoxy composites showing temperature dependent (a) storage modulus and (b) tan delta

In the rubbery region, there are large differences in modulus between the epoxy samples and the backfilled cellulose specimens. The neat epoxy sample has a modulus of about 23 MPa at its rubbery plateau. The storage moduli of the epoxy backfilled cellulose sol-gel and cellulose aerogel are 32 MPa and 63 MPa which are a 42% and a 178% increase in modulus, respectively. With the addition of the nanocellulose networks into the neat epoxy, storage modulus was increased in the rubbery region. As the matrix epoxy becomes amorphous in the rubbery region, the high strength and high modulus nanocellulose does not undergo a phase change and therefore boosts mechanical properties in the composite. The backfilled sol-gel exhibited a large reduction in glass transition temperature, about 30°C, relative to the neat epoxy, while there was little difference in glass transition between the neat and the backfilled cellulose aerogel. This discrepancy was also clearly evident in the tan delta curves shown in Figure 2.

3.2.2 Conventional Instron Tensile Testing

Tensile tests were performed on neat epoxy and epoxy backfilled cellulose aerogels. The stress-strain relationships are displayed in Figure 2. The neat epoxy was ductile and failed at a large strain and high stress. The addition of the cellulose aerogel network increased the elastic modulus. Taking the modulus to be the slope of the stress-strain relation between the optimal range of 0.001 and 0.003 strain, the backfilled cellulose aerogel and neat epoxy moduli were approximately 169 GPa and 113 GPa, respectively. The addition of cellulose increased the elastic modulus by 50%. The large surface area of the cellulose allowed the network to transfer its properties to the neat epoxy, and the high modulus of the nanocellulose network was able to improve the modulus of the matrix epoxy.

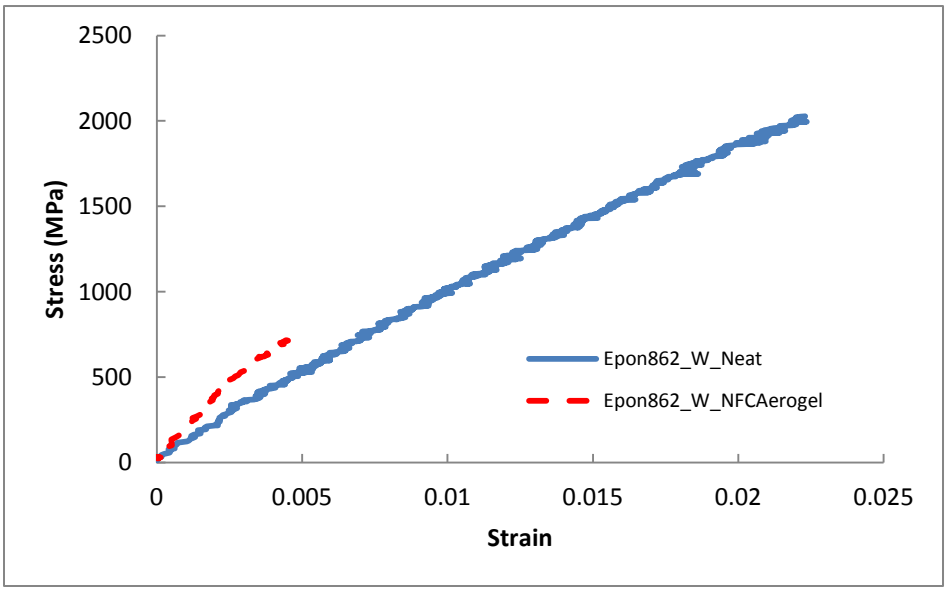

Figure 2: Stress-Strain Relations of Composite Samples in Tension

The addition of cellulose to the neat epoxy decreased the ultimate failure stress and strain by a substantial amount. The cellulose aerogel network created stress concentrations in the epoxy system at the weak bonding sites at cellulose agglomerations. The van der Waals interaction at the cellulose associations are not strong enough to endure the stress and strain the cured epoxy can alone.

3.2.3 Impact Izod Testing

The data from the POE 2000 tests was used to calculate the comparative impact characteristics of energy to break and impact resistance. Failure was achieved in every test, but according to the averages and standard deviations seen in Table 1, there was a large discrepancy between each type of sample and between the specimens within the sample condition. A substantial reduction in impact resistance, about 20x, was noted for aerogel-reinforced epoxy, possibly resulting from brittle fracture of the cellulose network. A much smaller reduction, about 20%, occurred with the NFC templated from the gel state, indicating that the tendency towards brittle fracture was substantially reduced by generating a finer network.

The impact testing highlighted the negative effects that cellulose has as reinforcement. The addition of cellulose decreased the important characteristics of the neat epoxy in the impact testing. While the sample geometries (shape, and ratios of dimensions) used for this test were based on the ASTM standard, each dimension was smaller than the minimum stated in the ASTM due to small sample sizes. Due to this, forces in addition to impact, such as bending, are expected to affect the sample and may influence the data quality. It is worth noting that several individual NFC-reinforced samples exhibited impact performance that exceeded that of the neat epoxy, suggesting motivation for reevaluating these materials in larger sizes.

Table 1: Impact Izod Testing Data Readout and Calculations

Sample Name	**Total Energy (mJ)**	**Cross Sectional Area (mm^2)**	**Izod Energy per Cross Section (J/m^2)**	**Impact Resistance (J/m)**
EPON862_W_NFCAerogel	3.5 (43%)	10.24 (6%)	344 (50%)	1.00 (50%)
EPON862_W_NFCWetgel	53 (45%)	9.45 (6%)	5650 (42%)	17.40 (43%)
EPON862_W_NEAT	66 (2%)	9.45 (3%)	7010 (4%)	20.91 (2%)

4. CONCLUSIONS

In this study, neat epoxy was compared to epoxy reinforced with nanocellulose networks. This was accomplished in two ways, by freeze-drying NFC dispersions to form aerogels, and by creating an NFC sol-gel and exchanging the solvent with epoxy. Backfilling the cellulose aerogels resulted in the highest increase in mechanical properties but at the price of increasing stress concentrations and eliminating the optical transparency due to the agglomerations. The cellulose sol-gel backfilling method improved mechanical properties compared to the neat epoxy but not at the same degree as the aerogel process. The sol-gel method also allowed for optical transparency unlike the aerogel method. Further improvement in optical performance can be expected following more rigorous polishing procedures and more refined processing techniques to limit surface inconsistencies.

Mechanical properties show promise with increases in elastic and storage moduli, but there is a need to develop processing and testing procedures to improve glass transition temperature differences and impact resistance. The addition of cellulose networks into epoxy resin systems exhibited an enhancement in rubbery region storage modulus and tensile elastic modulus. The problems listed have to do with the processing techniques currently utilized in composite manufacturing. A decrease in the glass transition temperature of the sol-gel composites occurs because of the use of acetone in the process. This can be inferred because it is the only difference between the cellulose aerogel and cellulose sol-gel procedures. The impact testing samples are much smaller than requested by the ASTM standard and better processing can increase the thickness of finished specimens.

5. REFERENCES

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