

Cellulose Fiber and Nano-Fiber Composites based on Castor Oil–Polyurethane Matrix

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ABSTRACT

Hybrid cellulose composites comprising woven hemp fabric interspersed with microcrystalline cellulose in a matrix of castor oil based polyurethane. The composites were derived from natural resources except for the diisocyanate required for chain extension and crosslinking, together with likely interfacial bonding with the cellulose components. The composites were characterised using scanning electron and optical microscopy, thermogravimetry and infrared spectroscopy. Mechanical properties measured were creep, recovery and modulated force thermomechanical analysis. Multiplexed frequency was used to obtain activation energy for the glass transition. The composites were semi-flexible, with high tensile strength and toughness, the main damping peak was centred on ambient temperature making the composites suitable for vibration damping application.

Keywords: bio-composite, biomaterial, natural resource, natural fiber, cellulose, urethane

1 INTRODUCTION

Cellulose fibers have high performance intrinsic properties such as modulus and tensile strength, especially considering their density compared with glass fibers. Fibres such as hemp and flax are of high performance after purification treatments to remove non-cellulose constituents such as hemicellulose, pectin, lignin and waxes [1].

Cellulose fibers have provided commercial composites with polypropylene [2,3] and epoxy resins, and their application with biopolyesters, starch and lignin has been investigated [4,5,6,7]. Modulated force mechanical properties are often measured to characterise these composites [8,9]. A matrix derived from natural resources is castor oil based polyurethane [10]. The hydroxy groups of castor oil form urethane groups by reaction with an isocyanate. The exterior hydroxy groups of cellulose are expected to react with isocyanate to provide a strong fiber–matrix interface.

The cellulose content has been increased in the current composites by inclusion of cellulose nano-fibres. A combination of micro-fibers and nano-fibers provides increased fiber volume fraction in the matrix. Nano-fibers

impart increased toughness and reinforce the resin between the micro-fibers. Analogous composites have been formed from combinations such as glass fiber–layered clay and carbon fibers–carbon nanotubes [11].

The aim of this research was to prepare hybrid cellulose composites with woven cellulose fiber and nano-cellulose dispersed in the bio-material matrix. Woven hemp fabric was chosen as the reinforcement, with castor oil based matrix filled with microcrystalline cellulose. Isocyanate crosslinking of the matrix castor oil was performed, with reaction of hydroxyl groups from both cellulose constituents expected to strengthen interfaces.

2 EXPERIMENTAL

2.1 Materials and Nano-composite Preparation

A woven mat of hemp cellulose fibres was used as the primary reinforcement (NZ Hemp Co, Auckland). A scanning electron microscopy image of hemp fibre is shown in Figure 1. The nano-cellulose fibers (microcrystalline cellulose, MCC, Avicel) were dispersed in castor oil using ultrasonication for 10 min. Mixtures containing 5 and 10 %-w/w MCC were prepared, a portion was cured separately and the rest was used to make hemp composites. An excess, to allow for reaction with cellulose hydroxy groups, of methane-4,4'-diphenyldiisocyanate (MDI number 7114 with functionality of 2.2, Huntsman Chemicals, Australia) was stirred into the polyol mixture and the resulting reactive viscose liquid was impregnated into a layer of hemp fabric (a 1:1 composition of resin-MCC and hemp was used in each composite) using steel sheet with a spacer plate, to give composites about 1.5 mm thick, covered with polyethylene film as supports for the curing process. The composites were lightly pressed to give continuous impregnation of the hemp at 23 °C, followed by oven cure at a temperature of 60 °C. The cured composites were removed and stored in zip-lock sealed polyethylene bags. Test specimens were selected and cut from the composite sheets.

2.2 Measurement of properties

Thermal stability and composition were assessed using thermogravimetry (Perkin-Elmer Pyris 1 TGA, 30-850 °C at 10 °C·min⁻¹ under nitrogen with change to air at 700 °C) (Figures 2 and 3). Cure was confirmed using Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer Spectrum 1 with diamond multiple internal reflectance accessory). Overall morphology was recorded using optical microscopy (Nikon Labophot) and FE-SEM (Figure 1). Mechanical properties measured included standard stress-strain tests (Instron 4065, tensile mode at 10 mm·min⁻¹) and modulated force thermomechanical analysis, Perkin-Elmer Diamond DMA, -50 to +120 °C at 2 °C·min⁻¹, 10 μm strain, with a synthetic multiplex frequency combining 1, 2, 4, 10, 20 Hz into a complex frequency. The data for each frequency was resolved from the synthetic frequency by a Fourier transform method included in the instrument software to give storage modulus, loss modulus and tan(δ) at each of the frequencies. Creep and recovery tests were performed in tensile mode with a stress of 0.1 N for 30 min followed by 120 min recovery using a TA Instruments Q800 DMA. Data for both 5 and 10 %·w/w MCC and the corresponding hemp composites are not shown in this paper due to space constraints.

3 RESULTS AND DISCUSSION

Hemp and flax are the two natural fibres with highest strength and modulus. The woven hemp cloth used to make the composites provided the basis for useful composites. Properties were enhanced and filler content increased by the microcrystalline cellulose. The polyurethane (PU) matrix was tough and transparent as used with efficient bonding to the celluloses. Figure 1 shows the relatively rough surface of the hemp fibres.

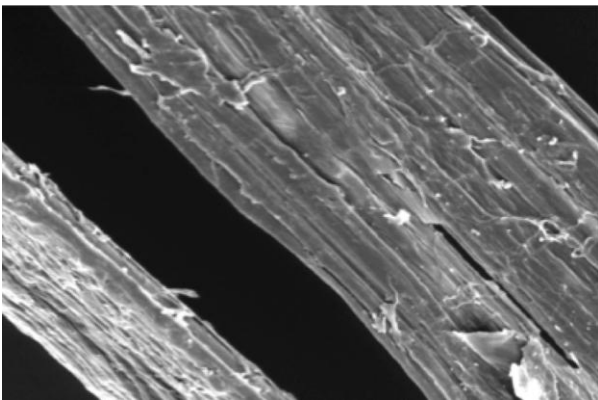


Figure 1: Scanning electron micrograph of raw hemp fiber

Thermogravimetry (Figure 2) did not distinguish decomposition of the cellulose components from the PU matrix. Details in the mass loss curves are revealed by the differential curves shown in Figure 3. The curves for the pure PU and hemp containing composites resolve the most

detailed mass losses. The castor oil polyurethanes were expected to degrade through a reversible reaction of the urethane functional groups, with separate degradation of castor oil and finally degradation of remaining organic species. The pure cellulose in MCC was separately shown to have a single mass loss degradation. When combined with the castor oil PU the degradation occurred with two sharp mass losses. The combined hemp-MCC-PU degradation exhibited some of the mass losses observed in the components with further degradation steps partially resolved. There was no observation of any increased stability of the composites, though moisture loss was not observed due to the protection of cellulose by the more hydrophobic castor oil.

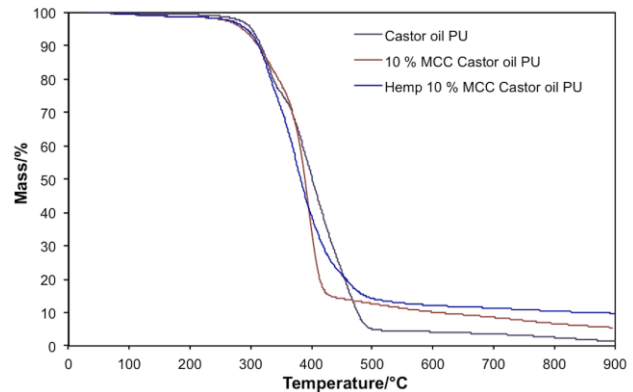


Figure 2: Thermogravimetry of composites

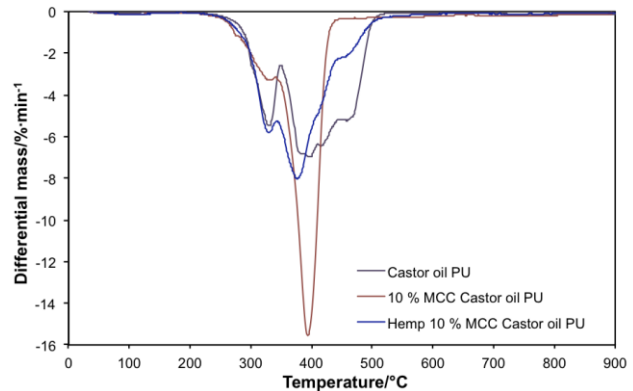


Figure 3: Differential thermogravimetry of composites.

Creep and recovery data is not presented in this paper, however creep and recovery were constrained by MCC filler and inhibited in tensile mode by the hemp cloth, as expected since the woven hemp extended throughout the composite test specimen.

Thermomechanical properties are shown in Figure 4 for the pure polyurethane. The decrease in storage modulus over the glass transition region was dramatic, extending from 7 to 8 GPa to a few MPa. At sub-ambient temperatures the behaviour was mostly elastic. At the glass transition there was a crossover of the storage and loss modulus with tan(δ) becoming greater than 1.0 with

maximum values of 1.2 to 1.6. In this transition region viscoelasticity predominates and excellent damping properties are expected [12]. The peak maxima of the $\tan(\delta)$ curves shift significantly with frequency, the highest temperature peak corresponds to the frequency of 20 Hz.

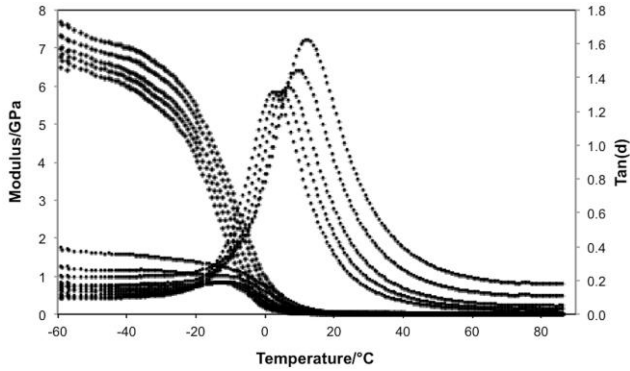


Figure 4: Castor oil mf-TM analysis

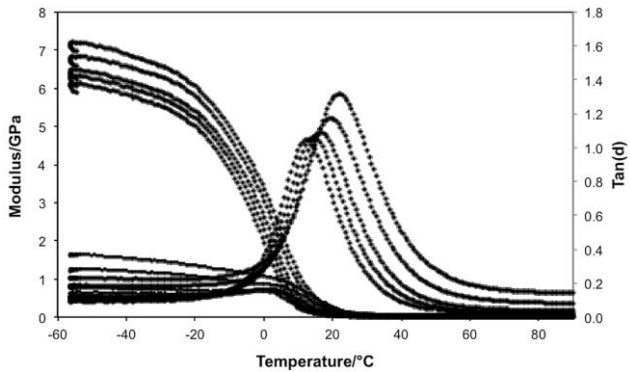


Figure 5: Castor oil with 5 %-w/w MCC mf-TM analysis

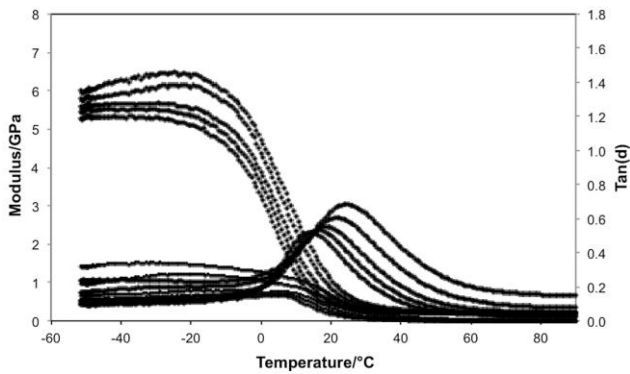


Figure 6: Castor oil hemp composite with 5 %-w/w MCC mf-TM analysis

Figure 5 shows the mf-TM data for 5 %-w/w MCC PU composites plotted on the same scale as the data for the pure PU. The glassy state elastic (storage) modulus was slightly reduced since the filler effect becomes less effective in the glass. Damping was decreased with peak maxima in the range of 1.0 to 1.2, therefore still in a crossover with the loss modulus resulting in predominantly

damping behaviour. The $\tan(\delta)$ peak maxima were shifted to slightly higher temperatures.

Figure 5 allows comparison of the corresponding hemp-MCC PU composite. A further reduction in the glassy state storage modulus occurred, though the modulus gradually increased before reaching the glass transition. The increase may be due to a greater contribution of the hemp fibres as the PU phase became slightly softer. The decrease in storage modulus at the glass transition was similar to that of the MCC-PU and PU. The peak maximum of $\tan(\delta)$ was similar to that of MCC-PU, that is increased from the pure PU. The damping peaks were much reduced when hemp was present with peaks maximum in the range 0.5 to 0.8, thus the hemp composite exhibited predominantly elastic behaviour.

Synthetic multiplexed frequency data for the $\tan(\delta)$ peak temperature at each frequency was used to calculate an Arrhenius activation energy (E_a) for each composition. The peak maximum temperature for $\tan(\delta)$, converted to reciprocal absolute temperature ($1/K$) was plotted with the logarithm of the respective applied frequency. The gradient of the line of best fit is $-E_a/R$ (the gas constant, $R = 3.182 \text{ J/K}\cdot\text{mol}$). The Arrhenius plots are shown in Figure 6. The pure PU gave $E_a = 81 \text{ kJ/mol}\cdot\text{K}$, with 5 %-w/w MCC $E_a = 93 \text{ kJ/mol}\cdot\text{K}$ and with hemp and 5 %-w/w MCC $E_a = 89 \text{ kJ/mol}\cdot\text{K}$. Thus the activation energy for the glass transition according to the $\tan(\delta)$ peak increased slightly with MCC content and was about the same with hemp.

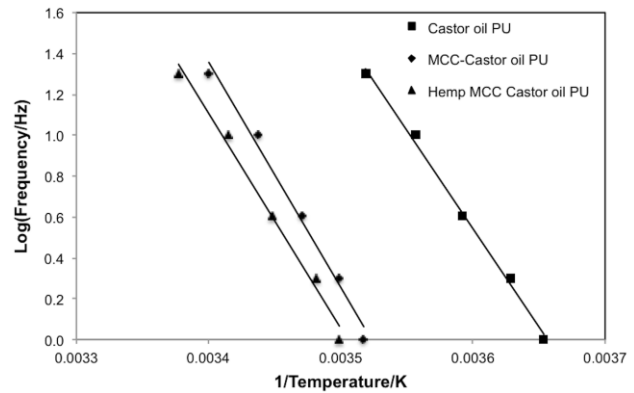


Figure 7: Arrhenius plots from multifrequency mf-TM.

The hemp-MCC-PU composites displayed useful performance in the mechanical analyses. The components were chosen to provide a range of properties contributed by the high strength and modulus hemp, especially when in a long fibre woven cloth. MCC contributed further matrix phase binding and allowed a more highly filled composite than otherwise. Castor oil contributed a trifunctional crosslinking species, efficient dispersion and impregnation of the cellulose components, together with its source as a natural resource. Crosslinking with isocyanate formed the PU and provided a strong interface with the cellulose components, likely arising from interfacial urethane bonds with the cellulose hydroxy groups.

The bimodal combination of cellulose fibre dimensions resulted in complementary properties from the same chemical composition. The nano-cellulose fibers provided thixotropy to the castor oil based reactants. The composites exhibited strength, toughness and a modulus suitable for application as cladding. The appearance can be improved by formation with one or both outer layers laminated with wood veneer, decorative paper board or metal foil. These micro-nano cellulose composites consist predominantly of materials derived from natural resources, they are structurally strong and resistant to water and common cleaning agents over a potential lifetime, while ultimately biodegradable. They can be formed into various shapes using various compression molds, and once cured they retain their shape due to their thermoset chemistry.

4 CONCLUSIONS

Hybrid bio-composites of cellulose fibers and nano-cellulose with a matrix mainly derived from the natural resource, castor oil, were prepared. A high microcrystalline cellulose content was dispersed in the castor oil without appreciable viscosity increase so that impregnation of the hemp cloth was readily performed.

Crosslinking of castor oil with diisocyanate resulted in a polyurethane matrix with potential urethane groups bonding with the surface of the dispersed cellulose phase. Tough, flexible composites were formed with high tensile modulus provided by the woven hemp, matrix stiffening and an increased filler content due to the microcrystalline cellulose. The composites displayed high damping properties extending from sub-ambient across the ambient temperature range.

Further research will extend the thermomechanical frequency range to enable construction of time(frequency)–temperature–superposition mastercurves. Mastercurves will display the elastic and damping property changes with a wide frequency window at constant temperature, indicative of application in damping situations.

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