Structure and Properties of Cellulose Nanocomposite Films Containing Melamine Formaldehyde

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Received 27 March 2007; accepted 30 May 2007
DOI 10.1002/app.26946
Published online 2 August 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Films of high Young's modulus and low density are of interest for application as loudspeaker membranes. In the present study nanocomposite films were prepared from microfibrillated cellulose (MFC) and from MFC in combination with melamine formaldehyde (MF). The prepared materials were studied with respect to structure as well as physical and mechanical properties. Studies in SEM and calculation of porosity showed that these materials have a dense paper-like structure. The moisture sorption isotherms were measured and showed that moisture content decreased in the presence of MF. Mechanical properties were studied by dynamical mechanical thermal measurements as well as by tensile tests. Cellulose films showed an average Young's modulus of 14 GPa while the nanocomposites showed an average Young's modulus as high as 16.6 GPa and average tensile strength as high as 142 MPa. By controlling composition and structure, the range of properties of these materials can extend the property range available for existing materials. The combination of comparatively high mechanical damping and high sound propagation velocity is of technical interest. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 2817–2824, 2007

Key words: microfibrillated cellulose; biofibers; cellulose nanocomposites; mechanical properties; loudspeaker membrane

INTRODUCTION

Cellulose is synthesized in plants, algae, tunicate sea animals, and some bacteria. Because of its physical properties, cellulose functions as a load-bearing constituent. The extended poly-β(1,4)-D-glucan chains form microfibrils consisting of ordered and less ordered regions.[1] In wood, the lateral dimension for microfibrils is around 3.5 nm. Microfibrils form microfibril aggregates at widths of 20–25 nm.[2] The axial modulus of the cellulose crystal is very high and has been experimentally determined to be 134 GPa.[3]

Cellulose can be disintegrated from wood pulp by treating a pulp suspension in a conventional homogenizer.[4,5] The width of the microfibrillated cellulose (MFC) varies in the range of 10–100 nm[4] and consists of more or less disintegrated microfibril aggregates, referred to as nanofibers within this paper. An image of microfibrillated wood pulp is presented in Figure 1.

Cellulose films based on MFC from wood pulp[6,7] or parenchyma cell walls,[8] and bacterial cellulose (BC),[9] have interesting mechanical properties. Composites, prepared by impregnating the MFC films[10] and BC-films[11] with phenol-formaldehyde, show even better mechanical properties.

The combination of high modulus and low density together with high internal loss makes this kind of material interesting as loudspeaker membranes. BC-films have been studied for this purpose[9,12] and are used in a few commercial products. To our knowledge, however, MFC films and composites have not been studied for this purpose.

In the study by Nishi et al.,[9] the BC-films showed a modulus of 30 GPa, measured by the vibrating reed method, and the sound propagation velocity was estimated to be about 5000 m/s. The damping was as high as 0.04. This damping is comparable to cone paper, which is a conventional membrane material. The modulus for these cone papers is 1.5 GPa and the sound propagation velocity is 1600 m/s[9]. Metals such as aluminum and titanium are also used commercially. They have a modulus of 70 and 110 GPa, respectively. The sound propagation velocity is 5000 m/s but tan δ is only around 0.001.[9]

Ciechanska et al.[12] prepared different films of modified BC with modulus above 4 GPa and sound propagation velocity above 2000 m/s. The damping was not reported but the materials were tested as loudspeaker membranes and were reported to have acoustic properties comparable to titanium diaphragms, although the specific ''metallic'' sound was absent.

The objective of the present work is to study structure-property relationships in high modulus films and

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Contract grant sponsors: Swedish Research Council (MH), Biofibre Materials Centre (LB).

Journal of Applied Polymer Science, Vol. 106, 2817–2824 (2007)

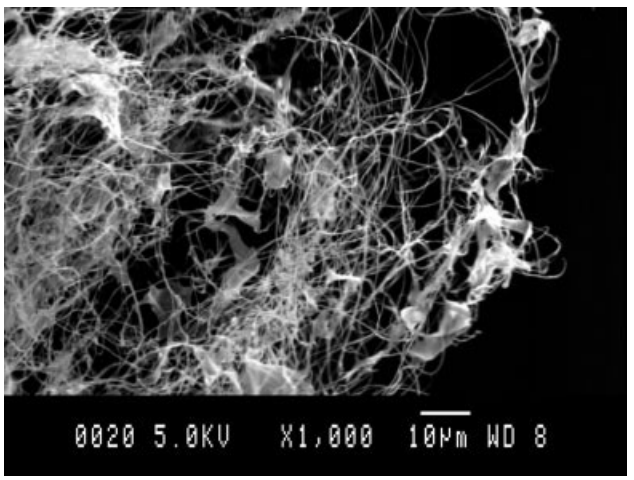

Figure 1 SEM image of freeze-dried MFC. The specimen was coated by a thin layer of carbon.

composites from MFC based on wood. It is of interest to consider whether these films may have sufficient properties to make them candidates for applications as loudspeaker membranes.

EXPERIMENTAL

Preparation of microfibrillated cellulose

MFC was obtained by a combination of enzymatic and homogenisation processing of softwood dissolving pulp (7% hemicellulose) provided by Domsjö Fabriker AB, Sweden. The enzyme used is Novozym 476, manufactured by Novozymes A/S, Denmark. This enzyme is an endoglucanase expected to degrade the cellulose molecules by cutting the chains in the noncrystalline regions. The enzymatic treatment was carried out as follows. The pulp was first beaten 1000 revolutions in a PFI-mill, manufactured by HAM-JERN, Hamar, Norway, to make the cellulose more easily accessible for the enzymes. This was done according to the standardized method EN 25 264-2:1994[13] with one modification: 40 g pulp diluted with water to a total weight of 300 g (13.3% dry content) was used. This was followed by an enzymatic treatment where 3% pulp, by weight, was dispersed in 50 m*M* tris/HCl buffer with pH 7 and 1.5% enzyme by weight of the pulp was added. The pulp was incubated at 50°C for 2 h, washed with deionized water on a Büchner funnel, thereafter incubated again at 80°C for 30 min, to stop the activity of the enzymes, and then washed again. The pulp was finally beaten in a PFI-mill with 4000 revolutions. Finally the pretreated pulp was subjected to the homogenizing action of a slit homogenizer, Laboratory Homogenizer 15*M*, Gaulin Corp., Everett, MA. A 2% pulp suspension was passed 25 times through the slit. This method is based on the work by Henriksson et al.[5] Degree of polymerization (DP) was estimated to 480 from the average intrinsic viscosity after homogenization.[5]

Preparation of MFC films and composites

The method used for preparation of MFC films and composites is based on the work by Nakagaito and Yano[10] MFC, 2 g, was suspended in water at a concentration of 0.5% and stirred for 45 min. The suspension was vacuum-filtrated on a Büchner funnel 18.5 cm in diameter, using Munktell filter paper, grade OOH, Munktell Filter AB, Sweden. After filtration, the wet films were separated by filter paper and then placed between two metal plates and dried at 80°C for 24 h. After drying, the filter papers were separated from the MFC films. This resulted in MFC films with thicknesses of about 70 μm.

The polymer used as matrix in the composites was a water soluble melamine formaldehyde resin Madurit SMW 818 75% WA, provided by Surface Specialties Nordic A/S, Denmark. Dried MFC films were immersed in solutions with a melamine formaldehyde (MF) concentration of 2, 4, and 6%. First the immersed films were kept in vacuum for 20 h and then at ambient pressure for 96 h. After immersion the films were dried at 50°C and then hot pressed at 160°C for 10 min at pressures of 30 MPa. The MF was polymerized at the elevated temperature, resulting in stiff semitransparent films with 5, 9, and 13% MF, respectively.

SEM

The specimens were mounted onto a substrate with carbon tape and coated with a thin layer of gold or carbon. The samples were studied in a JEOL JSM-820 Scanning Microscope with 5 kV acceleration voltage. The cross sections of the films were fracture surfaces from tensile tests.

Density and porosity

Density was measured on films with different MF contents. The films were dried at 80°C for 6 h and weighed. The thickness of the films was measured with a Mitotoyo thickness meter, while the area of the film was measured with a caliper. The pore content was calculated using density for cellulose = 1500 kg/m^3 and density for MF = 1400 kg/m^3.

Moisture sorption

The water sorption isotherms were measured gravimetrically using a Dynamic Vapor Sorption appara-

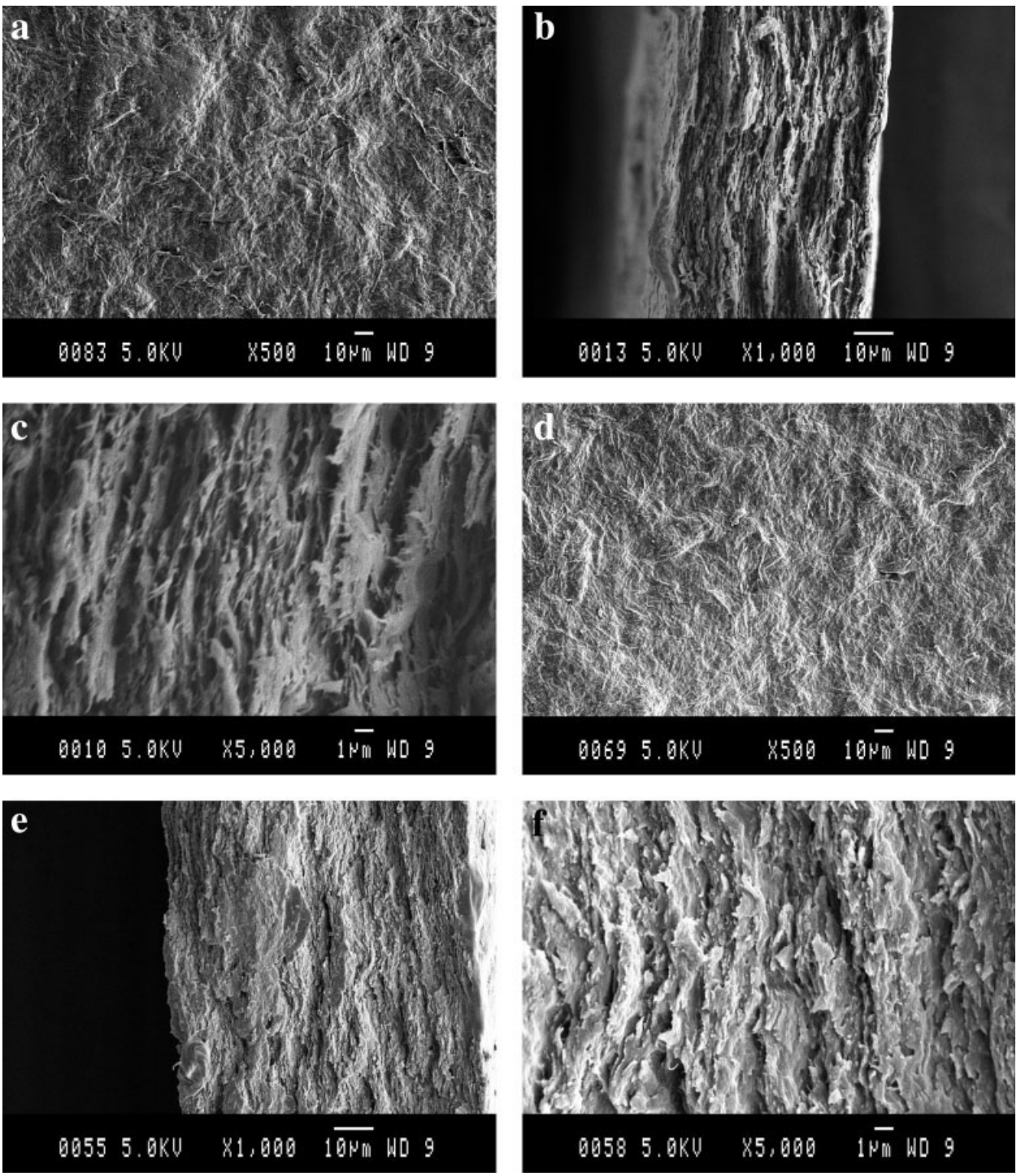

Figure 2 SEM image of the surface (a) and fracture surface (b,c) of MFC film, and surface (d) and fracture surface (e,f) of 9%MF/MFC film. The specimens were coated by a thin layer of gold.

tus from Surface Measurement Systems. The sorption data were obtained by starting at 0% relative humidity (RH) and then increased in 10% RH steps until 90% was reached and thereafter decreased with the same steps until 0% was reached again. Each RH was maintained for at least 500 min, until equilibrium was reached. The temperature was kept at 30°C.

DMTA

DMTA measurements were performed on a Perkin–Elmer DMA 7e in tensile mode. The specimen was a rectangular strip with length of 6 mm, width of 4 mm, and thickness of 70 μm. Temperature scans were performed with a heating rate of 5°C/min and frequency of 1 Hz. The scan was carried out from 25 to 220°C.

The samples were dried prior to testing and the test was performed in nitrogen atmosphere.

Tensile test

Tensile tests of the films were performed with a servo-hydraulic MTS 448 material test system from MTS Systems Corp. equipped with a 500*N* load cell. Specimens of 60 mm length and about 70 μm thickness and 6 mm width were tested with 10% min^{-1} strain rate. The RH was kept at 50% and the temperature at 23°C. The films containing MF were fairly brittle and it was difficult to cut the specimens without introducing flaws at the edges. Some of the specimens, especially the pure MFC films, were not completely flat and when mounted in the tensile test machine the specimen was not completely extended resulting in very low load in the initial part of the test. This part is removed from the final plots and the actual length of the specimen has been taken into account.

RESULTS AND DISCUSSION

During preparation of the MFC the viscosity of the pulp fiber suspension increases dramatically. The Einstein coefficient (and the suspension viscosity) increases dramatically with length/diameter ratio of suspended particles.[14] The viscosity increase is therefore a good measure of the extent of microfibrillation in the suspension. After the MFC is filtrated and dried, a stiff and strong film with some porosity is formed. The mechanical properties of this film are reduced when immersed in water but much of the structure is retained. The nanofibers in the film are not redispersible in water. This is due to the strong interaction between adjacent nanofibers after drying. The interaction is most likely dominated by hydrogen bonding. These porous films can be impregnated by water-soluble monomers or polymers to form composites of high cellulose content.

In previous studies phenol formaldehyde has been used as a matrix material.[10,11] Phenol formaldehyde is water soluble and suitable for impregnation of MFC films but the disadvantage is the dark color of the system. In this study MF was chosen as a matrix material. MF is transparent and in combination with the nanofiber the composites will be semitransparent. The films were impregnated in solutions with different concentrations of MF to make composites with different MF contents. The films were dried and hot-pressed to form composite films. These films were semitransparent, stiff, and brittle. The viscosity of the MF solution increased with increasing MF content. When the films were removed from the solution, some solution remained on the surface and therefore some films had higher MF content at the surface. Films impregnated in MF solutions of the same concentration had similar MF contents.

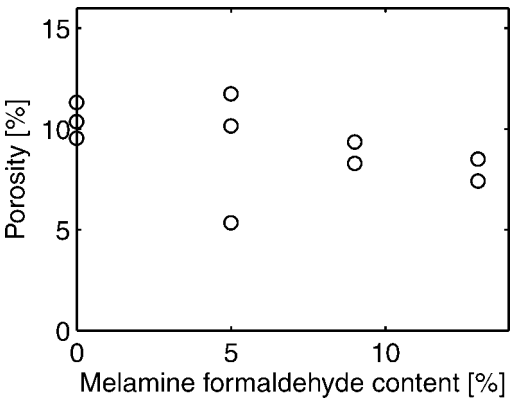

Figure 3 Calculated porosity for the MFC film and MF/MFC films with 5, 9, and 13% MF, respectively.

Figure 2 shows SEM images of film and composite surfaces and cross sections. The images of the cross sections, in particular 2 b, show that the MFC film has a layered structure. This indicates random-in-the-plane fiber architecture. The surface of the MFC film is irregular. The surfaces of the composites are somewhat smoother due to the MF matrix in combination with the applied compression pressure during processing. The density increases with MF content (Table I). This is due to compression during processing of the composites and also due to MF entering and filling some of the porosity during impregnation. Significant porosity is observed in the MFC film (10.5%) but is somewhat lower in the composites (8% porosity at 13% MF content, see Fig. 3). The data scatter for composites with 5% MF is due to local variations in density within one film and between different films for this particular composition. The SEM images together with porosity data show that the MFC films have a

TABLE I
Physical and Mechanical Properties for MFC Film and Composites

MF content (%)	Density (kg/m^3)	Average stress at break (MPa)	Average strain at break (%)	Average Young's modulus (GPa)	Estimated sound propagation velocity (m/s)
0	1340	104	2.6	14.0	3230
5	1360	142	1.4	16.1	3440
9	1360	121	0.91	16.6	3490
13	1370	108	0.81	15.7	3390

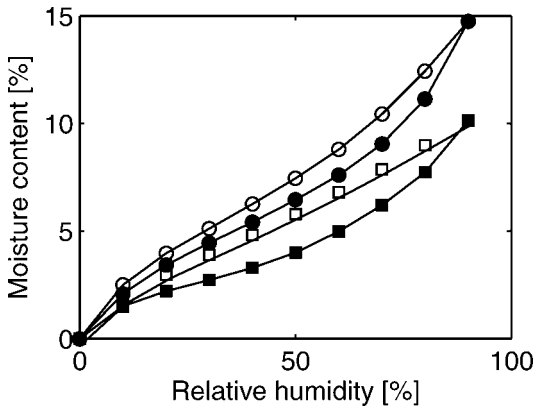

Figure 4 Sorption isotherms. MFC film adsorption (filled circles) and desorption (open circles), and 9%MF/MFC film adsorption (filled squares) and desorption (open squares). Tests were performed at 30°C.

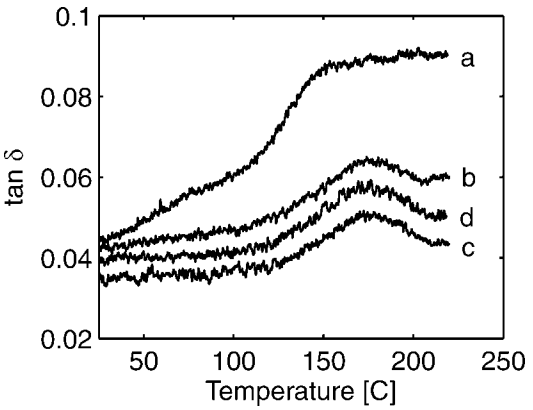

Figure 5 Tan δ as a function of temperature for MFC film and MF/MFC films of different MF contents: (a) MFC, (b) 5% MF/MFC, (c) 9% MF/MFC, (d) 13% MF/MFC.

dense, paper-like structure. The difference compared with conventional paper from pulp fibers is the high density but also the small scale of the constituent nanofibers.

Moisture sorption tests were performed on the MFC film and the 9% MF/MFC film (Fig. 4). At 30°C and 90% RH the equilibrium moisture content is around 15%. This is much lower than data for typical softwoods (containing hemicelluloses) in Scandinavia but within the range observed for various types of cellulose.[15] It is interesting to note that the moisture content is significantly lower for the composite than for the MFC film. Let us assume a hydrophobic matrix and a rule of mixtures sorption behavior. The moisture content of the 9%MF/MFC composite is then expected to be reduced by <10%. In contrast, the desorption data obtained at 50% RH, for instance, shows a reduction of 23%. With adsorption, the difference between data and rule-of-mixtures predictions is even larger. Also, MF is not at all hydrophobic, but adsorbs moisture. The reason for low moisture adsorption in the cellulose nanocomposites is probably due to the interaction between the hydroxyl groups at the cellulose surface and the MF, leaving fewer hydroxyl groups accessible for the water molecules.

The equilibrium water content in a cellulose based material for a certain relative vapor pressure depends on the direction from which equilibrium is approached. This is observed as a sorption hysteresis between the adsorption–desorption curves when moisture content is plotted against relative vapor pressure. The most important reason for this is that a larger number of hydroxyl groups are accessible during desorption as compared with adsorption from the dry state.[15] In the present MF/MFC composite, the hysteresis is greater than that of the MFC film at relative humidities between 20 and 70%.

The MFC film and the composites of different MF-content were subjected to dynamic mechanical thermal analysis (DMTA). At room temperature, the tan δ is around 0.04, which is comparably high and favorable in the context of acoustic membrane applications. The shapes of tan δ curves for the different composites were similar, but the MFC film (Fig. 5) showed a different behavior. For films containing MF, the damping remains constant up to about 120°C. It then increases, with a maximum occurring at 170°C. The increase in damping starts at a lower temperature for the pure MFC film than for the films containing MF. The reason for the high damping of the MFC film is unclear but might be related to nanofiber interactions or greater porosity at very fine scale. All samples, including the MFC film, started to discolor at temperatures slightly below 220°C. This indicates thermal degradation of the cellulose. Although the test is run in nitrogen atmosphere, the test set-up allows for the presence of some oxygen.

The storage modulus for the MFC film and the composites is much higher than the typical 1 GPa range

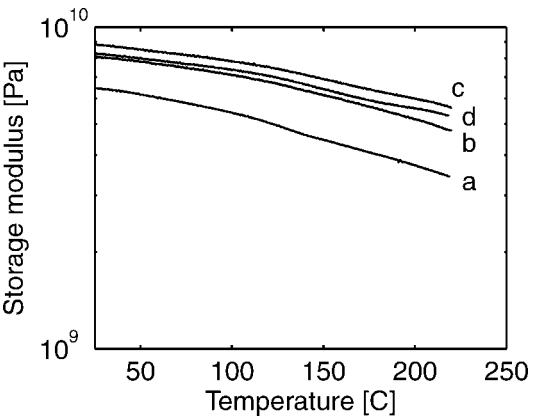

Figure 6 Storage modulus as a function of temperature for MFC film and MF/MFC films of different MF contents: (a) MFC, (b) 5% MF/MFC, (c) 9% MF/MFC, and (d) 13% MF/MFC.

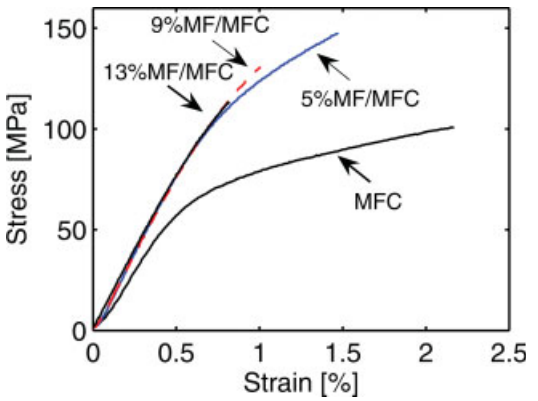

Figure 7 Typical stress–strain curves for MFC film and MF/MFC-films with various MF contents. Information regarding average values for each material, see Figures 8 and 9, and Table I. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

for isotropic polymers, and decreases gradually with increasing temperature (Fig. 6). The storage modulus increases significantly by addition of MF. In the present range of resin content, higher resin content improves the stiffening effect from the MFC by reducing porosity. The difference between samples of 9 and 13% MF is unexpected and will be discussed in connection with the tensile data.

Data from tensile tests are presented in Figure 7 and Table I. The MFC film has a Young's modulus of $E = 14$ GPa, and the 9% MF/MFC composite has $E = 16.6$ GPa. The stiffest specimen showed $E = 19.3$ GPa at 5% MF.

Taniguchi and Okamura[6] also produced MFC films from wood pulp. Their films were reported to have a tensile modulus of 2.7 times the modulus of polyethylene (about 2 GPa). Films from sugar-beet based MFC were reported by Dufresne et al.[8] to have tensile moduli between 1 and 3 GPa. The presence of pectin enhanced Young's modulus, which is much lower than the 14 GPa observed in this present study. Yano and Nakahara[7] also prepared wood-based MFC films, and the Young's modulus was 16 GPa, measured in three-point bending.

Most likely, the low modulus films of Taniguchi and Okamura and Dufresne et al. have high porosity.[6,8] Yano and Nakahara pressed the MFC/water suspension in a porous metal mold and obtained a film density of 1480 kg/m^3. This indicates very low porosity since this value is close to the density of cellulose. In the present study, the MFC-suspension was vacuum filtered and the film was then dried at 80°C for 24 h, compressed between metal plates. Applied pressure is expected to improve interaction and contact area between nanofibers, resulting in higher density. Drying conditions also influence density. Very slow drying of microcrystalline cellulose can produce a material with a density close to cellulose.[16] In addition to density, the modulus of MFC films is controlled by the architecture of nanofibers, i.e., random-in-the-plane or random-in-space.

The results for the composites from the present tensile tests show slightly lower modulus than what Nakagaito and Yano[10] observed. They studied MFC films impregnated with phenol-formaldehyde and the highest reported modulus was 19 GPa measured in three-point bending at a density of 1450 kg/m^3, compared with our 16.6 GPa measured in tension at 1360 kg/m^3. These composites were prepared by similar methods to those in the present study. However, Nakagaito and Yano used 100 MPa pressure, compared with the present 30 MPa. Higher pressure resulted in higher density and hence denser in-plane structure with higher modulus. They also stacked several layers (more homogeneous specimens).[10] Their resin content was slightly higher for the stiffest material, 14% compared with the present 9%. In one specimen of 5% MF, we measured a modulus of 19.3 GPa. On the basis of the available data, our MFC seems to perform as well as that of Nakagaito and Yano.[10] Compared with dark-colored composites, based on phenol-formaldehyde, the present melamine-formaldehyde composites have the potential advantage provided by the transparency of the polymer. This requires a lowering of the porosity.

The large scatter in modulus (Fig. 8) determined from the tensile tests indicates an inhomogeneous structure in our films. This is probably the reason for the unexpected relation between storage modulus for composites with 9 and 13% MF. During processing, the MFC is in a dilute suspension and the nanofibers will entangle and flocculate, resulting in regions of different densities. The pure MFC films were not pressed during processing whereas the composite films were subjected to 30 MPa pressure. The difference in scatter between composites of different MF content reflects differences in structural homogeneity.

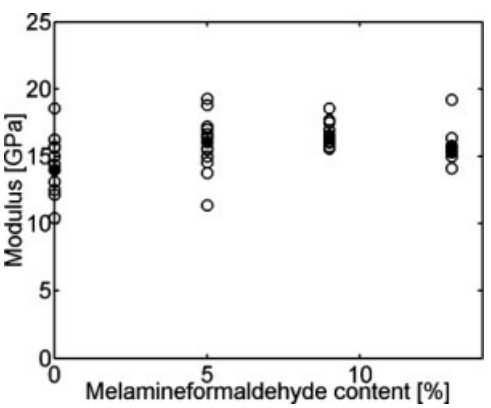

Figure 8 Young's modulus for MFC film and MF/MFC films with different MF contents. Filled circles represent average value.

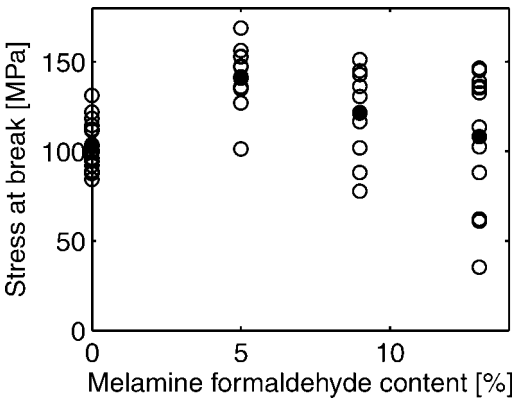

Figure 9 Stress at break for MFC film and MF/MFC films with 5, 9, and 13% MF, respectively. Filled circles represent average values.

The 5% MF/MFC composite shows large scatter in modulus due to large local density variations.

The strength data are of interest in the context of structural homogeneity. Tensile data (Fig. 7) show that composites have increased tensile strength and decreased strain to failure as compared with the MFC film. The average stress at break is highest (142 MPa) for the 5% MF/MFC (Fig. 9) and then it decreases with increasing MF content. The scatter in strength is large and increases for higher MF contents due to embrittlement. There is poor correlation between high modulus and high strength for individual specimens. Since the composites are brittle with low strain to failure, strength is controlled by local defects. In contrast, Young's modulus is determined by the average strain field for the whole specimen at a given load.

The MFC film shows a highly nonlinear stress–strain behavior (see Fig. 6). This reflects deformation mechanisms, which are likely to operate at the scale of individual nanofibers. One may speculate that nanofibers debond from each other, and deform by bending and other complex mechanisms, much like fibers in paper.

The requirements for loudspeaker membranes are high sound propagation velocity (C), e.g., high Young's modulus (E) and low density (ρ), combined with high internal loss. The sound propagation velocity is related to the Young's modulus and density[17] as $C = (E/\rho)^{1/2}$. In this study, the sound propagation velocities have been calculated for the MFC film and composites and are presented in Table I. It is 3230 m/s for the MFC film and 3390–3490 m/s for the composites. This is comparable to those reported in the literature for BC-films.[9,12] In addition, the mechanical damping tan δ of the present materials is as high as 0.04 at room temperature, which is advantageous. The present wood-based MFC films and composites show moduli ten times higher than for cone paper, used conventionally, and the sound velocity is twice as high. A potential advantage for the present wood-based nanocomposite, compared with BC material, is the price. The estimated raw material cost of BC in 2000 was US$ 30/kg, at dry weight basis.[18]

CONCLUSIONS

MFC films were prepared from MFC and composites were prepared by impregnating MFC films with MF, followed by hot-pressing. The films have a dense, paper-like structure with random-in-the-plane fiber architecture. Significant porosity was observed in the MFC film (10.4%) but was somewhat lower in the composites (8.0% porosity at 13% MF content). The MFC films had a modulus of 14 GPa at a density of 1340 kg/m^3 and showed nonlinear stress–strain behavior. By adding MF to the MFC films, the moisture uptake was reduced. The reason for lower moisture adsorption in the MF-based cellulose nanocomposites is probably interaction between the hydroxyl groups at the cellulose surface and the MF, leaving fewer accessible hydroxyl groups. The MF/MFC nanocomposites showed average Young's moduli in tension as high as 16.6 GPa and average tensile strength as high as 142 MPa. The combination of properties attainable with MFC films and composites, including high mechanical damping, demonstrates that these materials have the potential to be used as loudspeaker membranes. Nanocomposite materials based on MFC and MFC combined with polymers can be tailored to reach a wide range of properties not possible with microcomposite materials. In particular, we should learn to control porosity, nanofiber organization and architecture as well as the polymer matrix and its distribution.

Dr. Kjell Jansson at Stockholm University is acknowledged for help with SEM work and Docent Lennart Salmén at STFI-Packforsk is acknowledged for making his DMTA and moisture sorption test equipment accessible to us.

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