Bio-nanocomposites based on cellulose microfibril

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The objective of this study was to develop a new process to manufacture high-strength biocomposites exploiting the unusually high-strength properties of cellulose microfibrils [1, 2]. Most of the studies that have been carried out heretofore were based on film casting techniques of composite fabrication as a way to assure good dispersion of cellulose whiskers or fibrils in the matrix. Some of the studies tried different methods but attained reduced reinforcements due to poor dispersion of cellulose.

Here, a novel method to obtain composites by lamination of phenolic resin impregnated sheets of microfibrillated cellulose was proposed. The concept was based on utilizing microfibrillated cellulose (MFC), a cellulose morphology obtained through microfibrillation of kraft pulp fiber by mechanical processesses of refining and high-pressure homogenization [3, 4]. The treatment confers drastically large surface area to the material, characterized by a nano-scalar, web-like networked fibrils and microfibrils, which have the potential to increase interactive forces between reinforcing elements and matrix in a composite. When the mechanical properties of MFC-based composites were compared with those of non-fibrillated kraft pulp-based composites, there were no significant differences in Young's modulus, around 18-19GPa. However, the ultimate strength of MFC composites achieved 370MPa, a value 1.4 times higher than that of pulp composites [5]. The higher strength was an effect of the larger yield strain resulting in enhanced toughness of MFC composites. The work of fracture is a consequence of the highly extended surface area of networked nano-scalar fibrils, which generates an increased bond density resulting in a crack delaying mechanism. As a consequence of the nano-scalar dimensions of the fibrils, fracture sites will be smaller and more widely distributed in the material volume. The nanostructured material failure is therefore delayed and the strength is increased. Such a deforming behavior makes MFC-based composites as strong and tough as commercial magnesium alloy.

The degree of fibrillation of pulp fibers was evaluated concerning its effect on the mechanical properties of the final composites [6]. It was found that the strength of composites dependency on fibrillation level is not linear. There was no change in strength for composites prepared using pulp treated by refiner up to 16 passes, however, a sudden increase occurred when the treatment attained 30 passes through the refiner (Fig.1). SEM observations revealed that fibrillation of the fibers surface solely did not increase fiber interactions. Only the complete fibrillation of the bulk of the fibers resulted in an increment of mechanical properties, and additional fibrillation by homogenization treatment led to a linear increase of strength. Microfibrillation eliminates defects or weaker parts of the original fibers that would act as the starting point of cracks, but also increases interfibrillar bond densities creating a structure that favors ductility. Such ductility contributes to the material failure delay resulting in increased strength of the composites.

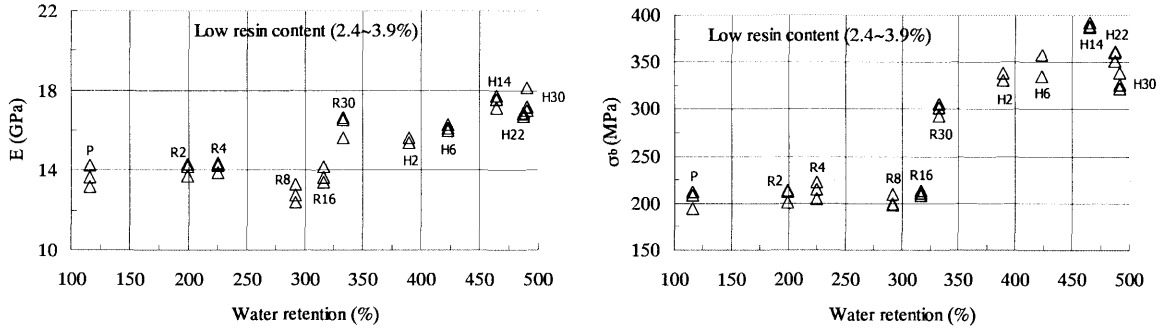

Fig. 1 Young's modulus and bending strength of composites vs. water retention of fibrillated kraft pulp with resin contents between 2.4 to 3.9%. P refers to non fibrillated pulp, plots labeled R relate to kraft pulp treated by refiner only, and those labeled H refer to kraft pulp additionally treated by homogenizer after 30 passes through the refiner. Numerals denote the number of passes through the refiner or homogenizer.

The effect of fiber content on the mechanical properties of MFC composites was also assessed. The

relationship was not linear, exhibiting a linear raise in Young's modulus at fiber contents up to 40wt% and lowering the increasing ratio at higher contents. This tendency in reinforcement was also shown by the CTE measurements, the thermal expansion decreased rapidly, about 6 times from the CTE of PF resin to values similar to e-glass (10ppm/K) at fiber contents above 60wt%. The fast decrease in CTE can be attributed to the much larger Young's modulus of cellulose microfibril (138GPa [1]) compared to the PF resin (5GPa) and to the extremely low CTE of cellulose microfibril (0.1ppm/K [7]). Effective reinforcement of mechanical properties as well as thermal expansion restraint could be attained at fiber contents from around 50% up, demonstrating the effective reinforcing capability of cellulose microfibrils and the advantages of microfibrillation.

Finally, in order to compare the effect of different cellulose morphologies on the mechanical properties of composites, bacterial cellulose (BC) was used as reinforcement, and compared with those of MFC composites [8]. The singular structure of BC pellicles, with dimensionally uniform, somewhat straight, and continuous fibrillated structure was considered as a perfect model of the ultimate microfibrillated cellulose. The strength of BC-based composites was slightly higher than that of MFC-based composites, nevertheless the modulus exceeded by about 1.5 times, achieving 28GPa. On the other hand BC composites exhibited very limited yield strain showing a brittle fracture behavior. Such characteristics were attributed to the continuity of the BC structure comprised of continually connected straight fibrils which are stiff and do not deform under stress. Another reason for the high modulus could be the in-plane orientation of fibrillar elements through compression of BC pellicles [9]. When composites were made using fragmented BC, the mechanical properties became very similar to that of MFC composites as in terms of modulus, strength and ductility, which is an indication that the geometrical arrangement of BC fibrils is responsible for the higher Young's modulus. From these results, it was concluded that although the Young's modulus achieved by MFC composites was not a match for the modulus of BC composites, MFC has the advantage of resulting in composites with high work of fracture. This toughness is likely due to the micro-scalar structure of loose and entangled networked fibrils that deforms when the composite is subjected to stress, resulting in large elongation and strength as opposed to the straight and continuous structure of BC fibrils.

Microfibrillation of plant fibers is definitively one of the most prominent means to exploit the remarkable mechanical properties of cellulose in the fabrication of high-strength and tough composites.

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