JOURNAL OF MATERIALS SCIENCE 39 (2004) 1635–1638

Bio-composites produced from plant microfiber bundles with a nanometer unit web-like network

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Using plant microfiber bundles with a nanometer unit web-like network, a moulded product with a bending strength of 250 MPa was obtained without the use of binders. High interactive forces seem to be developed between pulp fibers owing to their nanometer unit web-like network. In other words, the area of possible contact points per fiber are increased, so that more hydrogen bonds might be formed or van der Waals forces increased. When 2% oxidized tapioca starch, by weight, was added, the yield strain doubled and the bending strength reached 310 MPa. The starch mixed moulded product had a similar stress strain curve to that for magnesium alloy, and three to four times higher Young's modulus and bending strength values than polycarbonate and GFRP (chopped). The mouldings have a combination of environmentally friendly and high strength properties.

1. Introduction

The cellulose microfibril, the basic structural unit of plants, is a bundle of stretched cellulose chain molecules with a 5 nm width [1], and its Young's modulus reaches 134 GPa [2] with a density of 1.5 g/cm^3. Although the strength of microfibrils has not been clarified yet, it can be estimated to be at least 2 GPa based on the experimental results for tensile strength of 1.7 GPa [3], obtained for kraft pulp which mainly consists of cellulose microfibrils where 70 to 80% of microfibrils are distributed parallel to the fiber direction.

The density, Young's modulus and tensile strength are almost equal to those of aramid fiber [4], which is a well-known high strength fiber. Considering that plant fiber is renewable, the most abundant biomass resource on earth, and can be produced in environmentally friendly ways, mouldings of high strength derived from plant resources have properties that make them potentially suitable for wider application in the future. However, despite the high strength of microfibrils, at present the strength of isotropic plant fiber based mouldings such as pulp mouldings and plant fiber reinforced plastic moldings are 80 to 100 MPa [5–12].

To increase the strength of these moulded products using a non-toxic and environmentally-friendly process, we focused on microfibrillated pulp fiber having a nanometer unit web-like network [13–15]. This paper reports for the first time that an environmentally friendly moulded product with a strength comparable to magnesium alloy has been obtained by a combination of microfibrillated pulp fiber and oxidized starch.

2. Experimental procedure

2.1. Materials

The bleached softwood kraft pulp (Lodgepole pine 50%, White spruce 40%, Douglas fir 10% was supplied by Daishowa Paper Co. Ltd. Oxidized starch (Tapioca, D.P.: 290) was a commercial product from Nippon Starch Chemical Co. Ltd. Commercial products of magnesium alloy (AZ91, T6 treated), GFRP (Chopped glass fiber and unsaturated polyester) and polycarbonate were used for the comparison of mechanical properties.

2.2. Microfibrillation

The kraft pulp in a 3% water suspension was defibrated using a refiner and then passed through the micro-gap of a high-pressure homogenizer [13] resulting in a large pressure drop causing shearing and impact forces in the pulp. The homogenizer treatment was repeated up to 30 times to obtain different degrees of microfibrillation. Then, the microdefibrated kraft pulp fiber slurry was subjected to centrifugation to increase the solids content to 10% (wet weight basis).

Original pulp and PFI mill treated pulp (one of the laboratory beaters commonly used to fibrillate and soften pulp) were used as controls. The PFI mill treatment was carried out by changing rotation number from 5×10^3 to 8×10^4 for 10% solid content pulp (wet weight basis).

2.3. Measurement of water retention (WR)

Herrick *et al.* [13] reported that the moisture content after centrifuging microfibrillated pulp slurry (water retention: WR) is an effective way of evaluating the degree of microfibrillation. Thus, the 2% fiber-water slurry was centrifuged at 1,000 G for 15 min and the moisture content of the residual fibers was defined as the "water retention".

2.4. Production of moulding

The 10% solid content fiber slurry was put into a stainless steel die with a porous (30 to 50 μm diameter) metal plate underneath, and gradually pressed at room temperature to a maximum of 5 MPa. This produced a moulded sample with dimensions 100 mm $\times$ 100 mm $\times$ 4 mm. The moisture content of high-pressure homogenizer treated pulp moulding was approximately 100% (dry weight basis). The moulded sample was then dried at 105°C to decrease the moisture content to 2% (dry weight basis) and hot-pressed at 100 MPa and 150°C for 30 min.

Gelatinized oxidized tapioca starch (10% water solution) was mixed well with the 10% solid content 14-pass microfibrillated kraft pulp fibers and then pressed using the die to remove water as described above. The fiber-starch mix was compressed between porous metal plates at 120°C and 20 MPa for 60 min after adjusting the moisture content to approximately 20%.

2.5. Measurement of mechanical properties

Oven-dried samples sized 40 mm $\times$ 8 mm $\times$ 1.5–2.0 mm were prepared from the moulded products. Samples of the commercial magnesium alloy, GFRP and polycarbonate were also prepared. All were subjected to three point bending tests. The span to thickness ratio was 20, and strain velocity was about 5% per min.

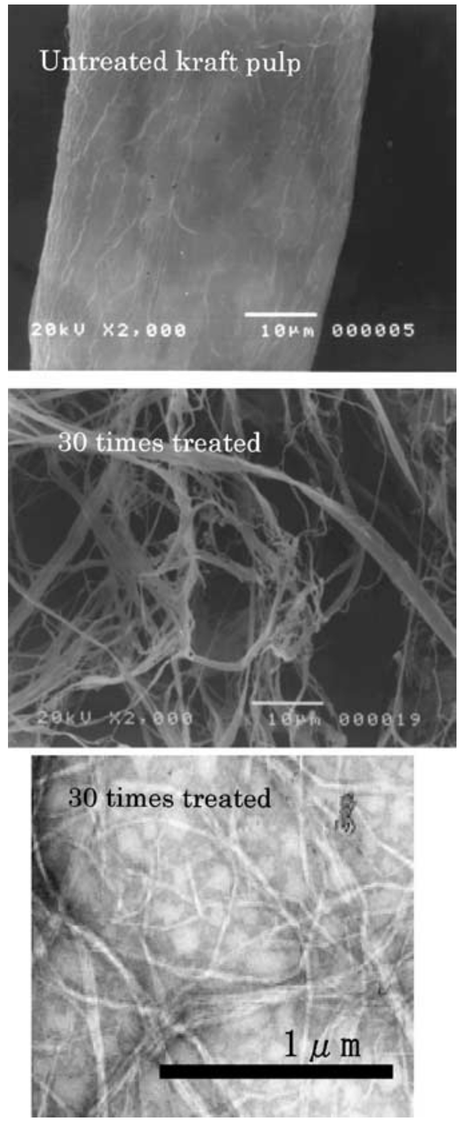

Figure 1 Microfibrillated kraft pulp.

3. Results and discussion

3.1. Microstructure of microfibrillated fibers

The changes in microstructure due to the high-pressure homogenizer treatment are shown by the SEM and TEM images presented in Fig. 1. Pulp fibers were defibrillated and branched to form a web-like structure. After the microfibrillation was repeated 30 times, part of the pulp was reduced to 10 nm widths as shown by the TEM image. As the width of a wood microfibril is considered to be approximately 5 nm [1], part of the pulp was reduced to bundles consisting of 5 to 10 microfibrils, resulting in a very large surface area per fibre.

3.2. Moulded products from microfibrillated fibers

The moulded sample using high-pressure homogenizer treated fiber became increasingly plastic-like in appearance with an increasing number of microfibrillation passes; after 10 passes it became semi-translucent at a thickness of 2 mm. The density of the product increased from 1.25 g/cm^3 for an original pulp moulding to 1.48 g/cm^3 for the moulded product obtained from the 10-Pass microfibrillated pulp fibers.

The mechanical properties of the moulded product are compared as a function of the degree of water retention (WR) as shown in Fig. 2. A common value of WR after beating using a PFI mill for paper making is approximately 150%, which is equivalent to 400 to 500 ml Canadian Standard Freeness. The mechanical properties increased linearly with increasing WR regardless of high-pressure homogenizer treatment and PFI mill treatment. The Young's modulus and bending strength of the microfibrillated pulp moulding (MFPM) increased to 16 GPa and 250 MPa, respectively, without the use of binders. These values are approximately five times those of the original pulp moulding without microfibrillation. The fact that mechanical properties increased against water retention, a measure of the degree of microfibrillation, strongly suggests that high interactive forces are developed between pulp fibers caused by their nanometer unit web-like network. In other words, the area of possible contact points per fiber is increased, so that more hydrogen bonds can be formed or van der Waals forces increased.

However, no further increase in mechanical properties or WR was evident after approximately ten microfibrillation passes. Furthermore, the electron

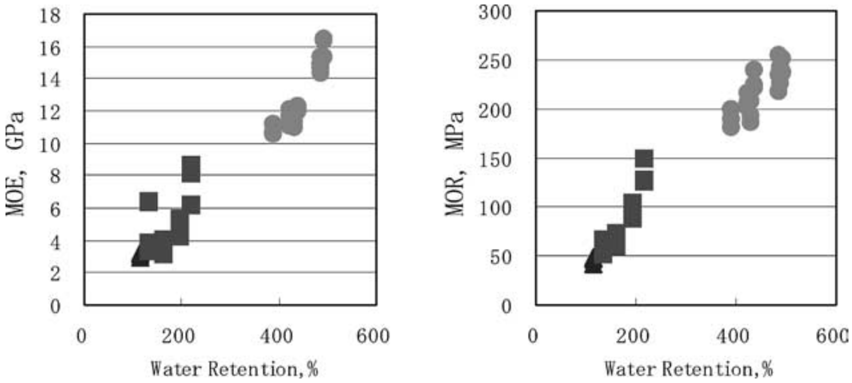

Figure 2 Changes of mechanical properties of kraft pulp mouldings against water retention: ▲, Untreated; ■, PFI mill treatment; ●, High pressure homogenizer treatment.

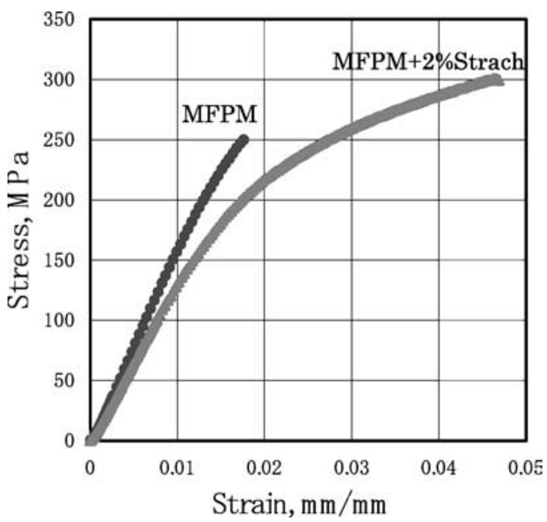

Figure 3 Effect of starch on stress strain curve of microfibrillated pulp moulding (MFPM).

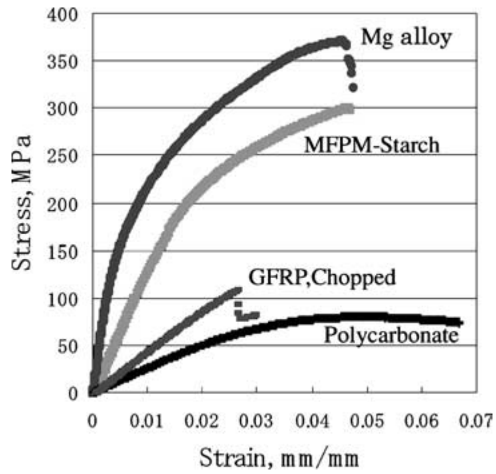

Figure 4 Stress strain curve for starch mixed microfibrillated plant fiber moulding (MFPM-Starch) and various materials.

microscope images indicated that there was a limit in the defibrillation of pulp using the high-pressure homogenizer. Thus, to obtain further increases in the interactive forces among microfibrillated pulp fibers, the effect of addition of oxidized starch as a binder was studied.

When the oxidized starch was added in an amount of 2% by weight to the 14-pass microfibrillated pulp fibers (MFPM-Starch), the yield strain of the moulded product doubled and the bending strength reached 310 MPa as shown in Fig. 3, although the Young's modulus decreased from 16 to 12.5 GPa. The bending strength decreased to 270 MPa at the oxidized starch content of 20%. Considering that the density of the products reached approximately 1.5 g/cm^3 despite the hot pressing at 20 MPa, these results indicate that the added starch may act not only as a binder but also as a plasticizer. Thus the fibers are able to deform during hot pressing in combination with moisture, so that the web like structure of interconnected microfibrils shown in Fig. 1 can produce an increased number of contact points, which prevent the cracks from propagating. This produces a composite capable of absorbing high amounts of work before failure, resulting in very high toughness as shown in Fig. 3.

The stress strain curve for the moulding product made from the microfibrillated pulp fibers (MFPM-Starch) is compared with those for the commercial products magnesium alloy, GFRP and polycarbonate as shown in Fig. 4. The MFPM-starch has a similar stress strain curve to that for magnesium alloy, and three to four times higher Young's modulus and bending strength values than polycarbonate and GFRP. In addition, Fig. 4 indicates that the specific bending strength (the ratio of bending strength to density) for MFPM-starch (density: 1.5 g/cm^3) is equivalent to that of magnesium alloy, an advanced material used for electronic devices due to its high strength and lower density of 1.8 g/cm^3.

4. Conclusions

Using plant microfiber bundles with a nanometer unit web-like network, a moulded product with a bending strength of 250 MPa was obtained without the use of binders. When 2% oxidized tapioca starch, by weight, was added, the yield strain doubled and the bending strength reached 310 MPa. The starch mixed moulded product had a similar stress strain curve to that for magnesium alloy, and three to four times higher Young's modulus and bending strength values than polycarbonate and GFRP. Plants are the most abundant biomass on earth and their basic structural units are microfibrils.

This study indicates that microfibrillated plant fibers with a nanometer unit web-like network might provide one of the most important raw materials for the production of future materials.

Acknowledgments

The authors thank Dr. J. Sugiyama, WRI, Kyoto University for TEM and Mr. K. Bori, Daicel Chemical Industries, Ltd. for the assistance in the preparation of microfibrillated pulp fibers.

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Received 7 May
and accepted 16 September 2003