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# Application of Cellulose Microfibrils in Polymer Nanocomposites

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Cellulose microfibrils obtained by the acid hydrolysis of cellulose fibers were added at low concentrations (2–10% w/w) to polymer gels and films as reinforcing agents. Significant changes in mechanical properties, especially maximum load and tensile strength, were obtained for fibrils derived from several cellulosic sources, including cotton, softwood, and bacterial cellulose. For extruded starch plastics, the addition of cotton-derived microfibrils at 10.3% (w/w) concentration increased Young's modulus by 5-fold relative to a control sample with no cellulose reinforcement. Preliminary data suggests that shear alignment significantly improves tensile strength. Addition of microfibrils does not always change mechanical properties in a predictable direction. Whereas tensile strength and modulus were shown to increase during addition of microfibrils to an extruded starch thermoplastic and a cast latex film, these parameters decreased when microfibrils were added to a starch–pectin blend, implying that complex interactions are involved in the application of these reinforcing agents.

**KEY WORDS:** Cellulose; crystallites; microfibrils; nanoparticles; composites; nanocomposites; starch; latex; pectin.

## INTRODUCTION

In the early 1990s, researchers at Toyota created polyamide-based nanocomposites in which the addition of Montmorillonite clay to polyamides provided significant increases in dimensional stability, stiffness, and heat distortion temperature [1]. Subsequent work [2–9] has shown that, at relatively low nanoparticle loadings of 3–5%, polymer composites are reinforced because chains within these nanocomposites are restricted to confined domains between sheets of clay. The combination of chain confinement, alignment of nanoparticles (i.e., nanostructure) and strong surface interaction results in improvements in mechanical properties, as well as in decreases in gas and liquid permeability [3].

In the mid-1990s, Favier et al. [10] reported the potential for "all-organic" nanocomposites that are based on polymers reinforced with cellulose nanocrystalline fibrils. They dispersed crystalline cellulose needles (at 3–6% cellulose loadings) in a copolymer acrylate latex film, and increased the dynamic storage modulus by more than three fold. Several groups, especially researchers at CERMAV in Grenoble [10–22], as well as researchers within our group [23] have continued work on the promising hypothesis that natural cellulose nano-scale microfibrils can act in a fashion similar to the clay nanocomposites in reinforcing polymers. *Note*: These crystallites have often been referred to as microfibrils, despite their nano-scale dimensions; a nomenclature that will be continued here.

There are three significant distinctions between clay-reinforced and cellulose microfibril reinforced nanocomposites. (I) In contrast to the "playing card" structure of most clay particulates, typical cellulosic microfibrils are long crystalline "needles"

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ranging in size from 10 to 20 nm in width, with an average aspect ratio of 20–100 (see Fig. 1). (II) Cellulose surfaces provide potential for significant surface modification using well-established carbohydrate chemistry [24]. (III) Sources of cellulose microfibrils, including wood, straw, bagasse, bacteria, and sea animals, are widely diverse, providing a wide range of potential nanoparticle properties.

The promise behind cellulose-derived composites lies in the fact that the axial Young's modulus of the basic cellulose crystalline microfibril is potentially "stronger than steel" and similar to Kevlar, having been reported as 137 GPa [25, 26]. However, no feasible method has been put forth to take full advantage of this remarkable stiffness. More research is needed to characterize the advantages of particular microfibril sources, comparing the effect of fiber source on surface properties, length, and their ability to interact within polymer matrices. For example, during acid hydrolysis of most clean cellulose sources via sulfuric acid (as outlined in Fig. 2), acidic sulfate ester groups are likely formed on the microfibril surface [27–30]. This creates an electric double layer repulsion between the microfibrils in suspension, which plays a big role in their interaction with a polymer matrix and with each other. Additionally, the size of agriculturally-based fibers and microfibrils vary depending on the isolation procedure and cellulose source. For example, preliminary unpublished data from our group suggests that rice straw microfibrils are ~20–25% shorter than cotton. The goal of the present study is to isolate cellulose microfibrils from various cellulose sources, and implement them as reinforcements in polymer gels and films. Mechanical properties will be correlated with variations in microfibril length, charge, and ultimately surface properties.

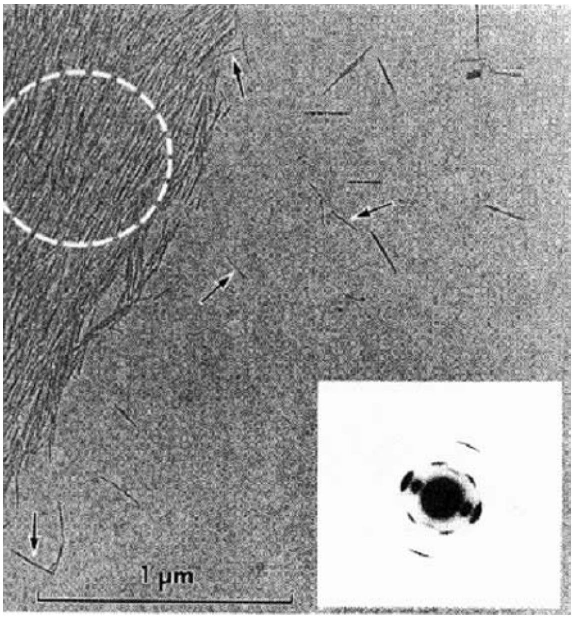

**Fig. 1.** Transmission electron micrograph of cellulose microfibrils showing their needle-like structure. The electron diffraction pattern (inset) confirms their crystalline nature.

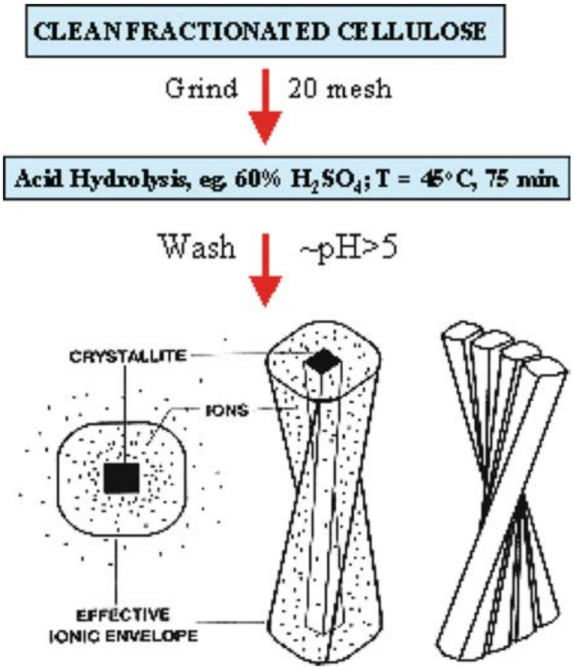

**Fig. 2.** Isolation of crystalline cellulose microfibrils [23], and development of their liquid crystalline microstructure. Sulfuric acid isolation produces a charged outer layer, whereby liquid crystalline alignment develops via charge repulsion.

## MATERIALS AND METHODS

The microfibrils used in this study were derived from softwood dissolving pulp (kindly provided by Rayonier Corp.), cotton (Whatman filter paper #4), and bacterial cellulose from the food source, nata de coco. Microfibril isolation followed the method of Revol et al. [2–4] as modified by Orts et al. [23] and outlined in Fig. 2. Briefly, cellulose sources were ground in a Wiley mill to pass through a 20 mesh. Individual crystallites were isolated by hydrolysis with the following conditions: cellulose concentration of 10% (w/w) in 60% sulfuric acid at 46°C for 75 min. Hydrolysis was completed by adding 5-fold excess water, isolating the microfibrils by centrifugation, and repeating this rinsing step until the pH of the suspension was above 5.0. Under these conditions, the crystallites obtain a charged outer surface on the exposed, outer anhydroglucan residues [27], with charge coverage estimated at 0.2 negative ester groups per $nm^2$.

Starch monofilaments and films were created using Midsol 50 starch (Midwest Grains, Inc., Atchison, KS), or potato starch pregel (Penford Corp., Englewood, CO), as noted. Pectin was obtained from Sigma–Aldrich (St. Louis, MO). Monofilaments were obtained using an in-house, small-scale lab extruder (bore dia. = 3 mm, die dia. = 1 mm and length = 10 cm). Composites were formed by pre-gelatinizing starch, i.e. heating 10% (w/w) starch in water at 95°C for 10 min. Starch and microfibrils are mixed together in a Hobart mixer operated at low setting for 10 min. This mixture was introduced into the extruder, and formed into monofilaments under a "low" and "high" shear mode. Films were created by a similar method except that starch and starch blends were pre-gelatinized at 3% concentration before microfibrils were added. Starch/microfibril slurries were poured onto glass plates, and dried under ambient conditions.

Mechanical testing was performed on an Instron Universal Testing Machine (Instron Corp., Canton, MA). Prior to testing, samples were left to equilibrate at 50% humidity for 24 h. Tensile tests were performed under ambient conditions. Parameters including tensile strength, tensile modulus, and elongation to break were calculated by Instron Series IX software.

Modulated Differential Scanning Calorimetry (DSC) was preformed using a TA Instruments Model 2910 mDSC (TA Instruments, New Castle, DE), equipped with $N_2$ gas purging. Samples of the blended polymer monofilaments with and without micofibrils were hermetically sealed in high volume stainless steel pans (part # 03190218 with *o*-rings, Perkin–Elmer, Norwalk, CT). Pans were heated at a rate of 10°C/min from 30 to 220°C.

## RESULTS AND DISCUSSIONS

The addition of cellulose microfibrils to starch thermoplastic monofilaments has a significant effect on mechanical properties at concentrations as low as 2.1%(w/w). Table I outlines a consistent increase in tensile Young's modulus as a function of microfibril concentration, with greater than a 5-fold increase, relative to a control sample with no cellulose reinforcement, at 10.3% microfibril concentration. The elongation at maximum load (%) also increases as a function of concentration, but above 5% this increase appears to reach a plateau.

**Table I.** Effect of Microfibril Concentration on Mechanical Properties of Wheat Starch Thermoplastic Monofilaments

| % Cotton microfibril | Young's modulus (GPa) | Elongation at max. load (%) |
|---|---|---|
| 0 | $1.39^a$ | $2.7^a$ |
| 2.1 | $5.09^b$ | $3.9^a$ |
| 5.0 | $9.34^c$ | $8.4^b$ |
| 10.3 | $12.45^c$ | $8.8^b$ |

Different superscripts indicate significant differences within a column.

Improvements in the mechanical properties of starch plastics and other polymer with the addition of low concentrations of cellulose microfibrils have been well documented [13–17]. These reports, though, utilize varied cellulose sources, such as sugar beet [16, 17], chitin [20, 21], or tunicin [10, 14, 15, 18]; all of which are potentially longer than cotton microfibrils. For example, reinforcement using tunicin microfibrils, which are derived from the cellulosic mantle of tunicate sea crustaceans, results in outstanding reinforced composites [14, 15]. Tunicin microfibrils are relatively large, highly regular, and are ideal for modeling reinforcement behavior. However, widespread used of tunicin is presently limited by the high costs of harvesting. The positive results in Table I from cotton microfibrils imply that significant reinforcement effects can be realized utilizing cotton microfibrils, which are more widely available.

Table II presents data on the effect of shear (low versus high) during monofilament formation on the mechanical properties of starch-microfibril monofilaments. Most noteworthy is the increase in

**Table II.** Effect of Shear Alignment on Mechanical Properties of Starch Nanocomposites with Cotton Microfibrils Added to Extruded Wheat Starch Thermoplastic

| Sample | Modulus (GPa) | Tensile strength (Mpa) | Elongation at max. load (%) |
|---|---|---|---|
| Starch monofilament | $1.39^a$ | $1.39^a$ | 2.7 |
| With 5% microfibril – low shear | $9.34^b$ | $3.09^a$ | 8.4 |
| With 5% microfibril – high shear | $8.23^b$ | $6.34^b$ | 9.6 |

Different superscripts indicate significant differences within a column.

maximum stress (tensile strength) at the higher shear rate. Shear alignment of microfibrils in a shear field as a function of shear rate was shown by Orts et al. [23] for cotton microfibrils, as well as for microfibrils from a range of other cellulosic sources. This study extends the role of shear-alignment from pure microfibril films to polymer–microfibril composites. Clearly, a more extensive study is required to fully establish the effect of shear on microfibril composites.

Cellulose microfibrils obtained via the isolation treatment outlined in Fig. 2 from three distinct cellulose sources – cotton, soft wood dissolving pulp and bacterial cellulose (nata de coco) – were used to reinforce a starch thermoplastic gel at 5% loading. As outlined in Fig. 3, mechanical properties for the cotton and wood-derived microfibrils are indistinguishable. However, both Young's modulus and % elongation at maximum load are significantly lower for the samples reinforced with bacterial cellulose.

Many factors may contribute to these differences. Isolation techniques have been shown to be critical in affecting polymer reinforcement affects since acid hydrolysis results in surface charges [24, 27]. Although the microfibril isolation technique was essentially identical for the different sources studied, it is possible that the different sources reacted differently to the isolation techniue, resulting in different surface properties. The overriding effect may be the size differences of microfibrils derived from different source. Reinforcement affects are strongly dependent on the aspect ratio [17, 31]. The affect of microfibril size also affects the ability of microfibrils to align within a shear field, and potentially improve mechanical properties as outlined in Table II. Orts et al. [23] used neutron and X-ray scattering data to monitor shear alignment of softwood-derived microfibrils isolated from the same source, but with different sizes and showed that, as the aspect ratio falls below 20, shear alignment of microfibrils, and the ability to maintain this alignment drops significantly. Further work will reveal if the bacterially-derived microfibrils are significantly shorter than the cotton and wood-derived microfibrils, and thus less likely to provide optimal mechanical properties.

Microfibrils were added as reinforcement to industrially relevant latex and starch-pectin blends. In the latex films (Fig. 4), cotton microfibrils at a concentration of 2.5% (w/w) increase maximum load by several-fold, and % elongation at maximum stress by at least 2-fold. These results are not surprising considering the remarkable changes in storage modulus observed by Cavaille and Dufresne [16] and Dufresne [17] for latex reinforced with straw-derived microfibrils.

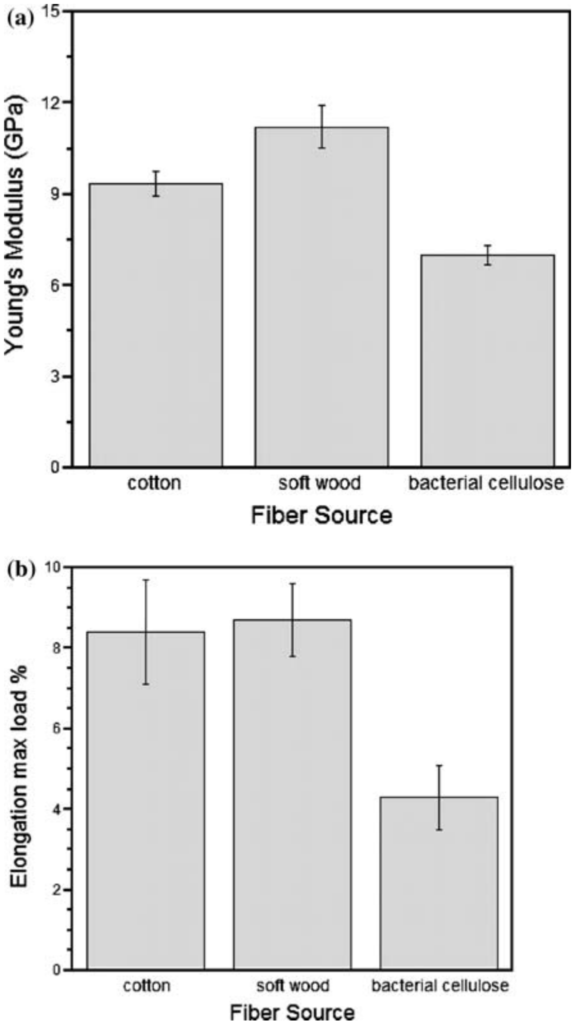

**Fig. 3.** Maximum load (a) and elongation to break (b) of wheat starch thermoplastic monofilaments with the addition of 5% added cellulose microfibrils isolated from cotton, soft wood, and bacterial cellulose.

Analysis of the data in Fig. 5 reveals several trends. First, the mechanical properties of pure pectin and starch films are affected by their blending at 50:50 compositions. Next, the addition of cellulose microfibrils changes the mechanical properties of this control blend. Finally, microfibrils from different cellulosic sources result in films with different mechanical properties. For example, cotton microfibrils reduce the maximum load of the pectin starch blend more than the softwood and bacterial cellulose microfibrils. Modulated DSC was used to

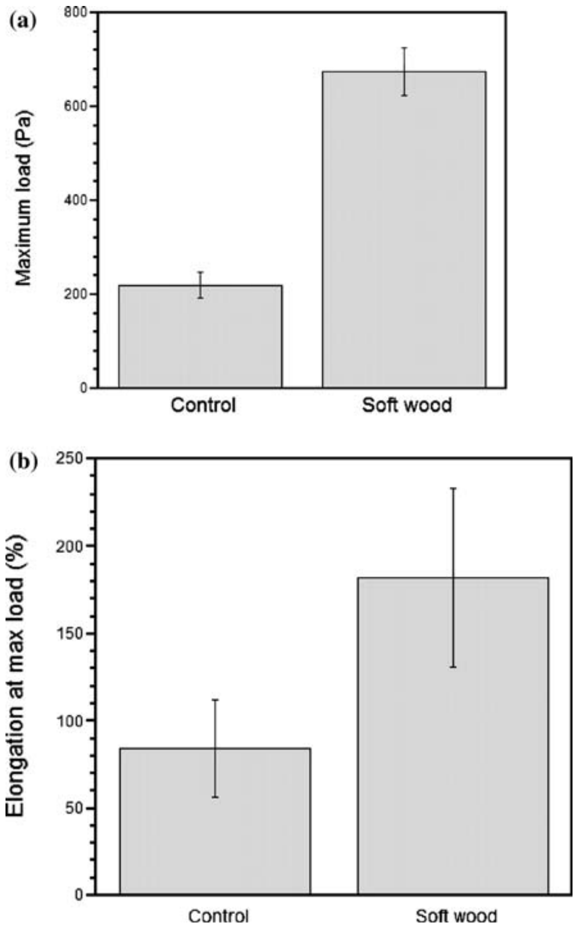

**Fig. 4.** Effect of the addition of 2.5% cotton microfibril to a film cast from latex emulsion. Maximum load (a) and % elongation at maximum load (b) are shown for untreated and microfibril reinforced film as noted.

look for significant changes in the films as a result of blending and cellulose reinforcement (data not shown). Creating the starch–pectin blend significantly altered the melting endotherm; yet, the addition of cellulose microfibrils had no significant effect.

More noteworthy is the decrease in maximum load and stress with the addition of 3% cotton microfibrils to the starch–pectin blend. This result is in direct contrast to the results presented in Fig. 2 for latex films. As pointed out by Angles and Dufresne [15], the addition of microfibrils to multi-component systems can completely change the trends in mechanical properties. Likely, microfibrils have a particular infinity to one particular component over another phase, promoting partitioning and blend immiscibility. DSC, X-ray diffraction, and microscopic structural analyses are being pursued to clarify this. Note that during acid hydrolysis of cellulose, crystalline microfibrils obtain a charged outer surface by the formation of sulfate esters on the exposed, outer anhydroglucan residues [27]. Addition of microfibrils to pectin, an electrolytic polymer, introduces another variable, the interaction of charged polymers with surface-modified and/or charged microfibril crystallites.

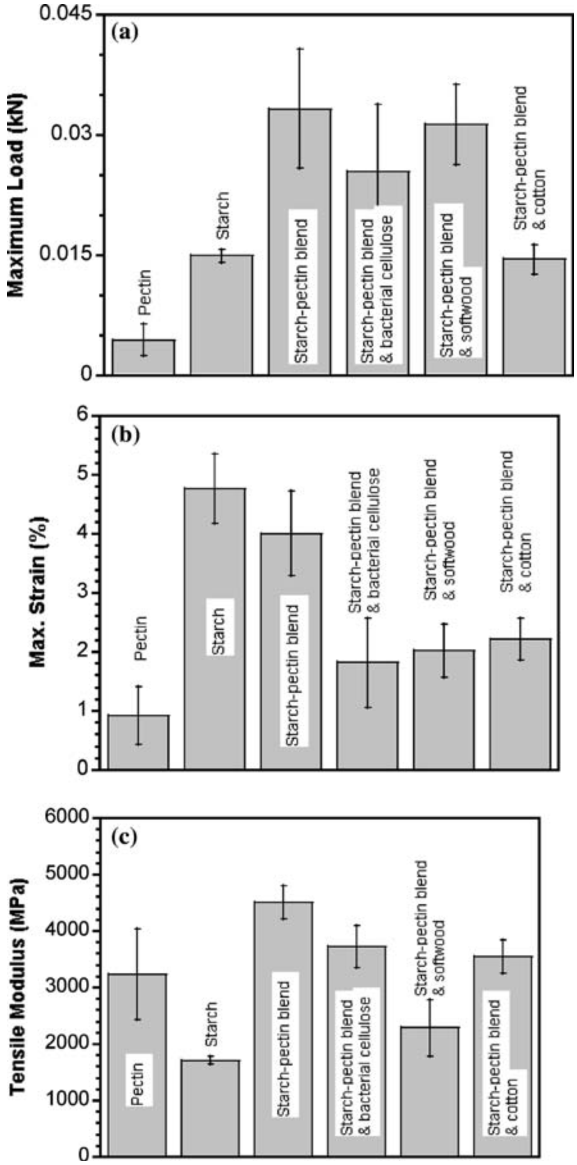

**Fig. 5.** Mechanical properties – maximum load (top), maximum strain (middle) and modulus (bottom) – of 50:50 starch–pectin blended films. Microfibrils derived from various sources, as noted, have been added to the starch–pectin blend at 3% (w/w) concentrations.

## CONCLUSIONS

For starch plastics, the addition of cotton-derived microfibrils at 10.3% (w/w) concentration increased Young's modulus 5-fold, relative to a sample with no cellulose reinforcement. Microfibrils derived from different sources generally had some reinforcement effect; although microfibrils derived from bacterial cellulose did not improve the modulus to the same extent as cotton or soft wood. Differences in size, surface properties, and aspect ratios all may have played a role in these differences. Preliminary data suggests that shear alignment significantly improves tensile strength; however a more complete study with carefully controlled shear rates is required to describe this effect. In particular, tensile strength and modulus increase during addition of microfibrils to an extruded starch thermoplastic and a cast latex film. However, this trend is reversed during addition of the microfibrils to a starch–pectin blend. The complex interactions between electrolytic microfibrils and charged polymers presents a new area of study for these reinforcing agents.

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## REFERENCES

1. A. Okada, M. Kawasumi, A. Usuki, Y. Kojima, T. Kurauchi, and O. Kamigaito (1990) *Mat. Res. Symp. Proc.* **171,** 45.
2. A. Okada and A. Usuki (1995) *Mat. Sci. Eng. C* **3,** 109–115.
3. B. Miller (1997) *Plastics World* 36–38.
4. Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, T. Kurauchi, and O. Kamigaito (1993) *J. Poly. Sci. A, Poly. Chem.* **31,** 983–986.
5. Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, T. Kurauchi, and Kamigaito (1993) *J. Poly. Sci. A, Poly. Chem.* **31,** 1755–1758.
6. Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, T. Kurauchi, O. Kamigaito, and K. Kaji (1994) *J. Poly. Sci. B, Poly. Phys.* **32,** 625–630.
7. T. Lan, P. D. Kaviratna, and T. Pinnavaia (1994) *J. Chem. Mater.* **6,** 573–575.
8. T. Lan, P. D. Kaviratna, and T. Pinnavaia (1995) *J. Chem. Mater.* **7,** 2144–2150.
9. M. Laus, O. Francescangeli, and F. Sandrolini (1997) *J. Mater. Res.* **12,** 3134–3139.
10. V. Favier, H. Chanzy, and J. Y. Cavaille (1995) *Macromolecules* **28,** 6365–6367.
11. P. Hajji, J. Y. Cavaille, V. Favier, C. Gauthier, and G. Vigier (1996) *Polym. Comp.* **17,** 612.
12. D. Dubief, E. Samain, and A. Dufresne (1999) *Macromolecules* **32,** 5765–5771.
13. A. Dufresne, D. Dupeyre, and M. R. Vignon (2000) *J. Appl. Polym. Sci.* **76,** 2080–2092.
14. M. N. Angeles and A. Dufresne (2000) *Macromolecules* **33,** 8344–8353.
15. M. N. Angeles and A. Dufresne (2001) *Macromolecules* **34,** 2921–2931.
16. J. Y. Cavaille and A. Dufresne (1998) in R. V. Greene and S. H. Imam (Eds.), *Biopolymers: Utilizing Natures Advanced Materials*, ACS Publishing, New York.
17. A. Dufresne (1998) *Recent Research Developments in Macromolecules Research* **3,**(Pt. 2), 455–474.
18. V. Favier, H. Chanzy, and J. Y. Cavaille (1995) *Macromolecules* **28,** 6365–6367.
19. V. Favier, G. Canova, S. Shrivastava, and J. Y. Cavaille (1997) *J. Polym. Eng. Sci.* **37,** 1732–1739.
20. A. Morin and A. Dufresne (2002) *Macromolecules* **35,** 2190–2199.
21. M. Paillet and A. Dufresne (2001) *Macromolecules* **34,** 6527–6530.
22. A. Dufresne and M. R. Vignon (1998) *Macromolecules* **31,** 2693–2696.
23. W. J. Orts, L. Godbout, R. H. Marchessault, and J.-F. Revol (1998) *Macromolecules* **31,** 5717–5725.
24. M. Grunert and W. Winter (2000) *Polym. Mat. Sci. Eng.* **82,** 232.
25. I. Sakurada, Y. Nukushina, and I. Ito (1962) *J. Polym. Sci.* **57,** 651.
26. S. A. Wainwright, W. D. Biggs, J. D. Currey, and J. M. Gosline (1982) *Mechanical Design in Organisms*, Princeton University Press, Princeton.
27. J.-F. Revol, H. Bradford, J. Giasson, R. H. Marchessault, and D. G. Gray (1992) *Int. J. Biol. Macromol.* **14,** 170.
28. J.-F. Revol, L. Godbout, and D. G. Gray (1995) US Patent 5,629,055.
29. J.-F. Revol, L. Godbout, X. M. Dong, D. G. Gray, H. Chanzy, and G. Maret (1994) *Liq. Cryst.* **16,**(1), 127.
30. J.-F. Revol and R. H. Marchessault (1993) *Int. J. Biol. Macromol.* **15,** 329.
31. A. Dufresne, J. Y. Cavaille, and W. Helbert (1997) *Polym. Compos.* **18,** 198.