Polymer Nanocomposites Reinforced by Cellulose Whiskers

V. Favier, H. Chanzy,* and J. Y. Cavaillé*

Centre de Recherches sur les Macromolécules Végétales,
CNRS and Université Joseph Fourier, BP 53,
38041 Grenoble Cedex 09, France

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There are numerous examples where animals or plants synthesize extracellular high-performance skeletal biocomposites consisting of a matrix reinforced by fibrous biopolymers.[1–3] Cellulose is a classical example of these reinforcing elements which occur as whiskerlike microfibrils that are biosynthesized and deposited in a continuous fashion.[4–5] In many cases, this mode of biogenesis leads to crystalline microfibrils that are almost defect-free, with the consequence of axial physical properties approaching those of perfect crystals. In the present study, we have attempted to mimic biocomposites by blending cellulose whiskers from the mantles of tunicates with synthetic polymer latices. The films cast from such mixtures had a nanocomposite organization whose structure and mechanical properties are described in the present paper.

A batch of edible-grade tunicate *Microcosmus fulcatus,* from the Mediterranean, was obtained from a local fish shop. These sea animals had an overall diameter between 5 and 10 cm with a 1 cm thick cellulose tunic. After anesthetizing with chloroform, the animals were gutted and their tunic was cut into small fragments that were deproteinized by three successive bleaching treatments, following the method of Wise *et al.*[6] The bleached mantles (the "tunicin") were then disintegrated in water, first with a Waring blender (at a concentration of 5% by weight) and then with 15 passes through a Gaulin laboratory homogenizer operated at 400 bar (at a concentration of 1% by weight). The resulting aqueous tunicin suspension was mixed with H_2SO_4 to reach a final acid/water concentration of 55% weight fraction. Hydrolysis conditions were 60 °C for 20 min under strong stirring. A dispersion of cellulose whiskers resulted. After sonication, the suspension was neutralized and washed by dialysis. It did not sediment or flocculate as a consequence of surface sulfate groups created during the sulfuric acid treatment.[7] When concentrated by evaporation, the suspensions displayed typical liquid crystal characteristics.[8]

The suspensions of cellulose whiskers were homogeneously mixed with polymer latices ($T_g = 0$ °C) resulting from the copolymerization of styrene (35% w/w), butyl acrylate (65% w/w), and a small amount of acrylic acid. The suspensions were poured into poly(tetrafluoroethylene) molds and allowed to dry slowly for 1 month at room temperature. Homogeneous and bubble-free 2 mm thick films resulted. These films, cut into strips 35 mm long and 6 mm wide, were analyzed with a DMTA Metravib SA Mécanalyseur operating with a forced oscillation pendulum. The experiments were achieved at a fixed frequency of 0.1 Hz and in a temperature range 200–500 K.

Electron microscopy and electron diffraction analysis on cellulose whiskers was achieved with a Philips EM400T operated at 120 kV. For this, cellulose whisker suspensions were deposited on carbon-coated grids and observed under low-dose conditions, using a 20 μm objective aperture that gave bright-field diffraction contrast images. Microdiffraction on individual cellulose whiskers was performed by the diffraction method of Riecke and Ruska[9] with a probe of 50 nm that required a C2 condenser aperture of 5 μm. Observations on the reinforced films were made on ultrathin sections obtained by cryosectioning. These sections were observed in bright-field diffraction contrast with a Philips CM200 CRYO operated at 200 kV and equipped with a 15 μm objective aperture. The images obtained under low-dose conditions revealed (in black) the cellulose crystallites within the clear polymer matrix. An image of the latex particles was made under low-dose conditions by depositing drops of latex suspensions on carbon-coated grids.

A typical preparation of tunicin crystals is shown in Figure 1A. This sample consists of parallelepiped rods with lengths ranging from 100 nm to several micrometers for widths on the order of 10–20 nm. Upon testing by a microelectron diffraction technique (inset), each element gave a spot diffractogram that corresponded to a section of the reciprocal lattice of cellulose Iβ (here the a^*c^* section) and persisted when the electron probe was scanned along a given rod. As the diffractogram indicated that the cellulose chain axis is along the long dimension of the rods, each rod is therefore a whiskerlike tunicin crystal with no apparent defect. Figure 1B is a low-dose image of the latex particles that were used in this study. Each particle has a diameter of around 150 nm. Some of these particles are individual and have kept their initial spherical shapes. Most of them, however, are coalesced together due to the conditions of sample preparation, viz., room temperature which is 20 K above the T_g of the latex.

Figure 2 corresponds to an ultrathin cryo cross section of a nanocomposite film containing 6% (w/w) of tunicin within the latex. In this image, recorded under low-dose and diffraction contrast conditions, the cellulose crystals are in black within the clear polymer matrix. This image reveals that the cellulose whiskers are distributed throughout the structure, without segregation or association.

When reinforced by a small percentage of tunicin whiskers, the polymer films showed improved mechanical properties which were particularly striking when the films were heated above the glass transition of the polymer. This is illustrated in Figure 3, where part A shows a plot of the shear modulus G as a function of temperature for various whisker/latex compositions ranging from 0 to 14% (w/w). The curve corresponding to the pure matrix is typical for a thermoplastic: below T_g, G remained constant at around 1 GPa and dropped rapidly to 1 MPa during the crossing of the glass–rubber transition temperature. Above this temperature, it behaved as a viscous liquid, with G decreasing rapidly with increasing temperature. The films that contained cellulose whiskers had a slight increase in their G value below T_g, but the drop in G value above T_g was dramatically reduced: only from 1 to 0.1 GPa for a film reinforced by 6% (w/w) whiskers. Above T_g, the reinforced films behaved as rubbers as their G value stayed constant over a wide temperature range. This is illustrated in Figure 3B that corresponds to a film reinforced by 6% (w/w) whiskers for which G keeps a value of 0.1 GPa all the way to 500 K, a temperature at which cellulose starts to decompose.

The variation of the shear modulus G, taken at 325 K (i.e., 50 K above T_g) as a function of the whisker

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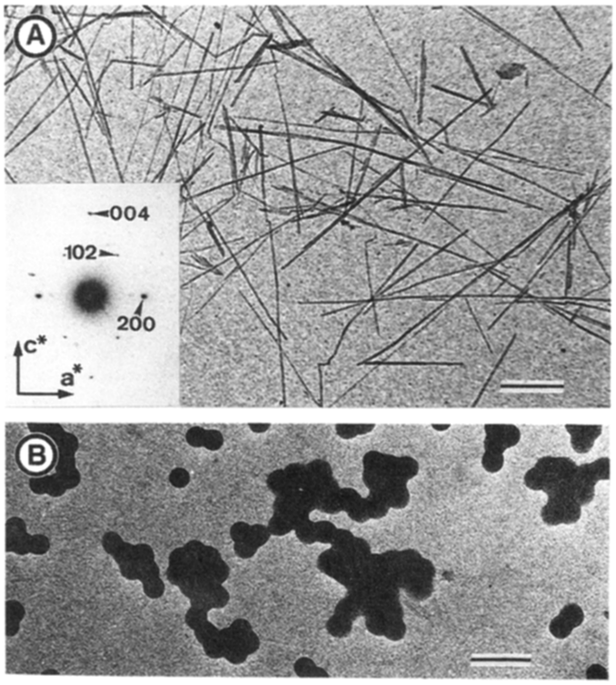

Figure 1. (A) Electron micrograph of rodlike cellulose microcrystals extracted from the mantle of *Microcosmus fulcatus*. Scale bar: 0.5 μm. Inset: typical electron diffractogram recorded on one microcrystal, oriented with its axis vertically. The indexation corresponds to the unit cell of cellulose Iβ defined by Sugiyama *et al.*[22] (B) Low-dose image of the latices that were used for this work. Scale bar: 0.5 μm.

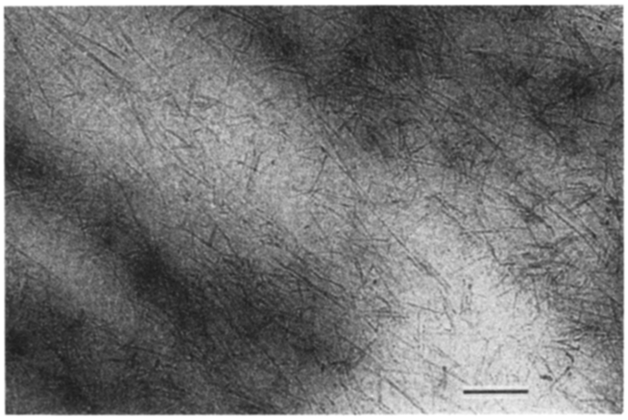

Figure 2. Low-dose images of a cryosection of a nanocomposite film consisting of 6% (w/w) tunicin whiskers in a latex as in Figure 1B. The image, recorded under diffraction contrast bright-field conditions, revealed in black the cellulose whiskers. Scale bar: 0.5 μm.

content, is plotted in Figure 4. The observed values of G (Figure 4) are much higher than those (dashed line in Figure 4) predicted from a classical mean-field mechanical model developed for short-fiber composite. In such an approach, following Halpin and Kardos,[10] the modulus and the geometry of the fibers are accounted for, but one assumes that there is no interaction between the fibers. In particular, the mean-field model is based on the concept that a material made of short fibers, homogeneously dispersed in a continuous matrix, is mechanically equivalent to a superposition of four plies. Within each ply, the fibers are parallel to one another and the mutual orientation of the plies is 0°, +45°, +90°, and −45°. The mechanical properties of each ply are derived from the micromechanic equations of Halpin–Tsai.[11]

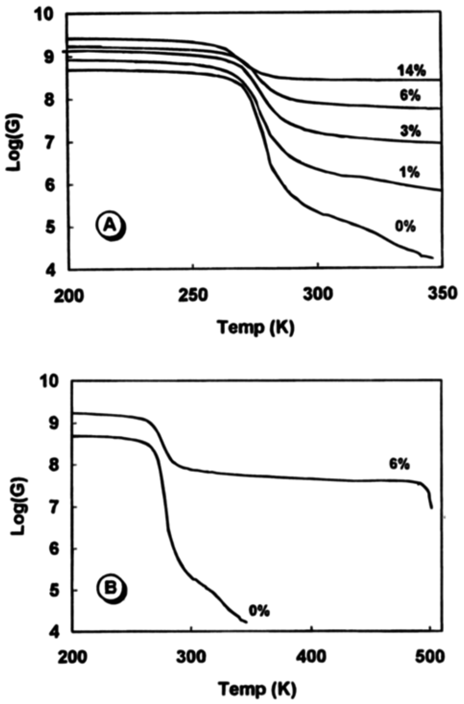

Figure 3. Reinforcement effect as a function of temperature below and above the latex T_g. (A) Log of the shear modulus (Pa) for composites reinforced by weight fractions of cellulose whiskers from 0 to 14%, as a function of temperature in the range 200–350 K. (B) As in A but for temperatures up to 500 K and for a specimen reinforced by 6% (w/w) cellulose whiskers. This specimen is compared with a control sample that does not contain any whisker.

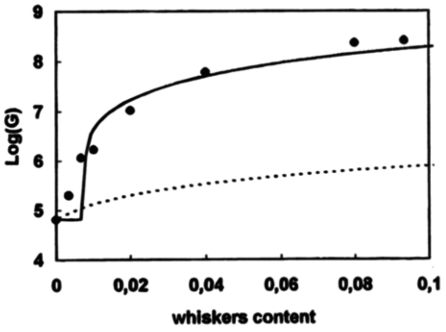

Figure 4. Plot of the log of the shear modulus G (Pa) at 325 K as a function of the volume fraction of cellulose whiskers. Comparison between the experimental (black dots) and calculated data with two different mechanical models: a mean-field model (dashed line) and a percolation model (continuous line).

As seen in Figure 4, the mean-field approach is obviously not able to account for the observed data. In order to explain the unusually high G values of the reinforced films, one needs to invoke (i) a strong interaction between the whiskers and (ii) a percolation effect. The influence of such an effect on the mechanical properties of the films can be calculated following the method of Ouali *et al.*[12] in their adaptation of the percolation concept to the classical parallel-series model of Takayanagi *et al.*[13] The shear modulus of the composite is then given by the equation:

$$G = \frac{(1 - 2\psi + \psi X_r)G_s G_r + (1 - X_r)\psi {G_r}^2}{(1 - X_r)G_r + (X_r - \psi)G_s}$$

where the subscripts s and r refer respectively to the soft and rigid phases; X is the volume fraction of whiskers. In the Takayanagi *et al.* model,[13] ψ is an adjustable parameter. In the Ouali *et al.* model[12] which was used here, ψ corresponds to the volume fraction of the percolating rigid phase. It can be calculated with a simple prediction based on the percolation concept:[12]

$$\psi = 0 \qquad X_r \leq X_c$$

$$\psi = X_r\left(\frac{X_r - X_c}{1 - X_c}\right)^b \qquad X_r > X_c$$

where b is the percolation exponent. According to several studies based on the percolation concepts,[14,15] b takes the value of 0.4 in a three-dimensional system. X_c is the percolation threshold: here $X_c = 1\%$ (v/v) that corresponds to 1.5% (w/w).

The role of percolation of cellulose fibers in paper making is well documented.[16-17] It is, in particular, established that the high mechanical properties of a paper sheet result from the hydrogen-bonding forces that hold the percolating network of the fibers. We believe that it is also the hydrogen-bonding system that is responsible for the unusual mechanical properties of our system when the percolation threshold is reached. A calculated curve based on the percolation theory (solid line in Figure 4) follows the dashed line up to a whisker volume fraction of 1%. Above this percentage, the solid line curve precisely fits the observed G values. We believe that it is also the whisker network that is responsible for the stabilization of G over a large temperature range above T_g. It will be only when the whiskers start to decompose at around 500 K that this stabilization will disappear, inducing a catastrophic decrease of G.

There are a number of literature data that deal with the reinforcement of synthetic polymers with fibrous elements based on cellulose.[18-20] Unlike our nanocomposites, these reinforced structures do not contain homogeneous dispersions of individual cellulose crystals of high axial ratio. Large quantities of cellulosic fillers are therefore required to reach properties comparable to ours.[19] Another approach to the reinforcement of plastics by cellulose is that developed by the group of Nishio,[21] who have prepared networks of regenerated cellulose gels interpenetrated with various water-soluble monomers that are subsequently polymerized. They obtain a significant reinforcement of their composites, even at a relatively low concentration in cellulose. However, their regenerated cellulose is poorly crystalline and does not allow a thermally stable plateau to be reached as that shown in Figure 3B. In addition, their films are water sensitive as opposed to ours which are hydrophobic.

In this paper, laboratory-scale nanocomposite structures were obtained by reinforcing latices with whiskers extracted from rather rare cellulose samples. There are many more common native cellulose or chitin specimens that could also be used to produce similar reinforcement. Both polysaccharides can provide systems of microfibrils with an axial ratio surpassing the above whiskers. These elements could be used directly as reinforcing agents provided that they could be separated from one another and dispersed efficiently within polymer matrices. If this could be achieved, one would expect an even better reinforcing effect at a much lower cellulose concentration.

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