Chitin Whisker Reinforced Thermoplastic Nanocomposites

ARTICLE *in* MACROMOLECULES · SEPTEMBER 2001

Impact Factor: 5.8 · DOI: 10.1021/ma002049v

2 AUTHORS, INCLUDING:

Alain Dufresne
Grenoble Institute of Technology
313 PUBLICATIONS **15,353** CITATIONS

Macromolecules

Volume 34, Number 19 September 11, 2001

Communications to the Editor

Chitin Whisker Reinforced Thermoplastic Nanocomposites

Michel Paillet and Alain Dufresne*

Centre de Recherches sur les Macromolécules Végétales (CERMAV-CNRS), Université Joseph Fourier, BP 53, 38041 Grenoble, Cedex 9, France

Received December 1, 2000
Revised Manuscript Received May 25, 2001

Chitin, a structural polymer in shellfish, insects, and microorganisms, is, next to cellulose, the most abundant biopolymer. It was reported to possess similar skeletal conformation than cellulose I, including its intramolecular hydrogen bonds.[1,2] Chitin has been known to form microfibrillar arrangements in living organisms. These fibrils are usually embedded in a protein matrix and have diameters from 2.5 to 2.8 nm.[5] Crustacean cuticles possess chitin microfibrils with diameters as large as 25 nm. Chitin microfibrils in arthropod shells and insect cuticles are organized into a helicoid structure that displays a cholesteric pattern in electron micrographs of oblique sections.[3] Marchessault et al.[4] showed that acid-hydrolyzed chitin spontaneously dispersed into rodlike particles that could be concentrated to a liquid crystalline phase and self-assemble to a cholesteric liquid crystalline phase above a certain concentration.[5−7]

By analogy with previous works performed in our Laboratory and which deal with cellulose or starch microcrystal reinforced nanocomposite systems,[8−16] chitin whiskers were used as a reinforcing phase in a thermoplastic matrix. Suspensions of chitin crystallites were prepared as described elsewhere[7] by acid hydrolysis of technical grade material (Kyona Oïl Co., Japan) obtained from squid pen. The object of this treatment was to dissolve away regions of low lateral order so that the water-insoluble, highly crystalline residue may be converted into a stable suspensoid by subsequent vigorous mechanical shearing action.

Samples were first boiled and stirred in a 5% KOH solution for 6 h to remove most of the proteins. This suspension was subsequently kept at room temperature overnight under stirring, filtered, and washed several times with distilled water. Chitin samples were then bleached with 17 g of $NaClO_2$ in 1 L of water containing 0.3 M sodium acetate buffer for 6 h at 80 °C. The bleaching solution was changed every 2 h followed by abundant rinsing the sample with distilled water. After bleaching, the suspension was kept in a 5% KOH solution for 72 h to remove residual protein. The resulting suspension was centrifuged at 3000 trs/min for 20 min.

Chitin whisker suspensions were prepared by hydrolyzing the purified chitin sample with 3 N HCl at the boil for 1.5 h under stirring. The ratio of 3 N HCl to chitin was 30 mL/g. After acid hydrolysis, the suspensions were diluted with distilled water followed by centrifugation (10 000 trs/min for 5 min). This process was repeated three times. Next, the suspensions were transferred to a dialysis bag and dialyzed for 24 h against distilled water until a pH = 6 was reached. The pH was subsequently adjusted to 3.5 by adding HCl. The dispersion of whiskers was completed by a further 2.5 min ultrasonic treatment (B12 Branson sonifier) for every 40 mL aliquot. It was subsequently filtered to remove residual aggregates and kept in a refrigerator until used after adding sodium azoture as protectant against microorganisms. These suspensions display a colloidal behavior, which stability was attributed to the presence of positive charge (NH_3^+) at the surface of the crystallites, resulting from the protonation of amino groups.[4] The solid fraction of this aqueous suspension was determined and was 1.68 wt % after concentration by dialysis against poly(ethylene glycol).

A typical transmission electron micrograph obtained from a dilute suspension of hydrolyzed squid pen chitin is shown in Figure 1. It was achieved with a Philips

* To whom correspondence should be addressed. E-mail: Alain.Dufresne@cermav.cnrs.fr.

10.1021/ma002049v CCC: $20.00
Published on Web 08/11/2001

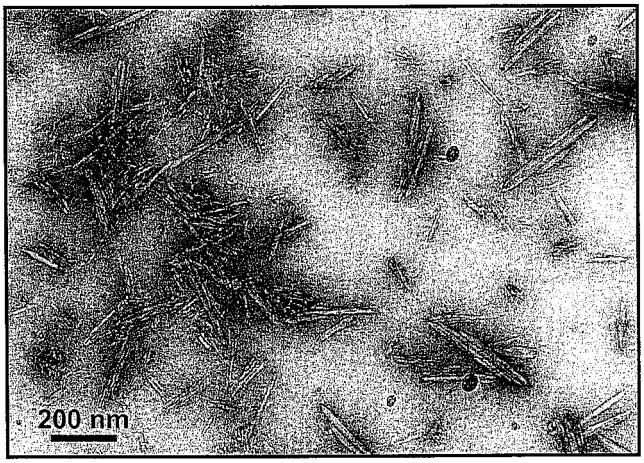

Figure 1. Transmission electron micrograph of a dispersion of hydrolyzed squid pen chitin.

CM200 electron microscope. The suspension is constituted of crystalline fragments of chitin. The preparation shows both individual and aggregated microcrystals in the form of crystallite bundles. The outline of these fragments is roughly defined, most probably because of the presence of remaining protein at the surface. The rodlike individual fragments have a length ranging from about 50 to 300 nm (average value around 150 nm), and they are almost 10 nm in width. These dimensions are similar to what was reported for chitin whiskers obtained from crab shells[5] and for cellulose whiskers prepared from wheat straw.[10] The aspect ratio L/d (L being the length and d the diameter of the filler) of these whiskers is thus around 15.

A latex (average diameter of the particles around 150 nm) obtained by the copolymerization of styrene (34% (w/w)) and butyl acrylate (64% (w/w)) (poly(S-*co*-BuA), and containing 1% acrylic acid and 1% acrylamide, was provided by Elf-Atochem (Serquigny, France). The glass−rubber transition temperature (T_g) of the copolymer was determined from differential scanning calorimetry (DSC) measurements and was found around 0 °C (scanning rate 10 K min^{-1}). The colloidal chitin fragments dispersion was mixed with the latex with various amounts in order to obtain nanocomposite films with a good level of dispersion and with a weight fraction of chitin ranging from 0 to 20 wt %. After stirring, the air in the suspension was removed by vacuum prior to casting in a Teflon mold. Homogeneous and bubble-free 1 mm thick films were obtained by storing the casting at 35 °C, allowing water evaporation and polymer particle coalescence. It was observed from DSC measurements that the T_g of the matrix was not modified upon chitin whiskers addition.

These films were analyzed with a DMTA Metravib SA Mécanalyseur operating with a forced oscillation pendulum. Figure 2 shows the plot of log(G'/Pa) (storage shear modulus, Figure 2a) and tan δ (loss angle tangent, Figure 2b) at 1 Hz as a function of temperature for poly(S-*co*-BuA)/chitin whisker composites. The temperature was varied between 200 and 425 K by steps of 4 K. The curve corresponding to the pure matrix (0% filled composite) is typical of thermoplastic behavior. For temperatures below T_g the copolymer is in the glassy state, and the modulus slightly decreases with temperature but remains roughly constant (around 1 GPa). Then, a rapid decrease in the elastic tensile modulus, by more than 3 decades, is observed, corresponding to the glass−rubber transition. In the terminal zone, the experimental setup fails to measure it.

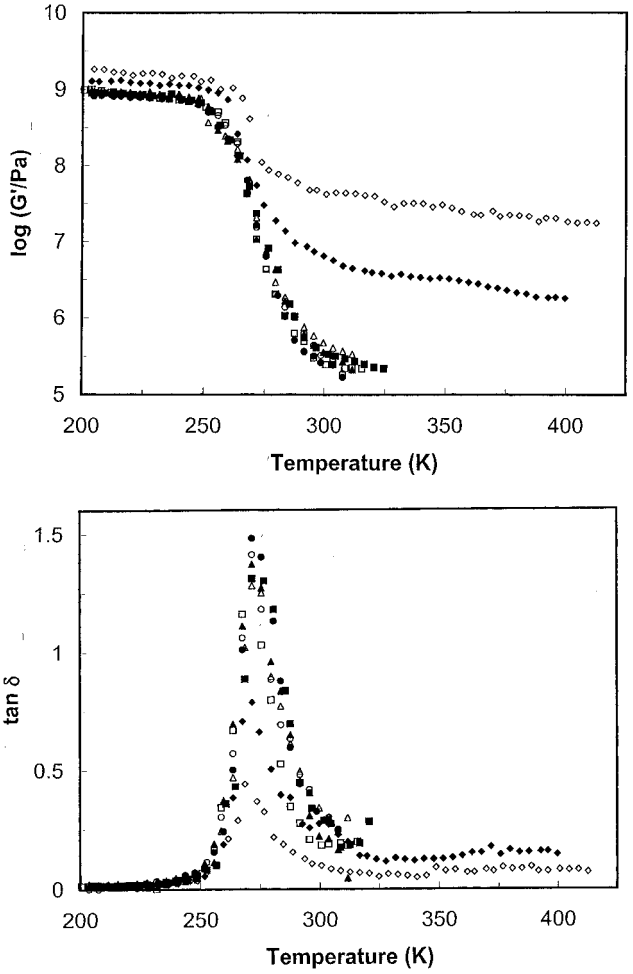

Figure 2. (a) Logarithm of the storage shear modulus G' and (b) loss angle tangent tan δ vs temperature at 1 Hz for squid pen chitin whiskers/poly(S-*co*-BuA) composites filled with 0 (●), 1 (○), 2 (▲), 2.5 (△), 3 (■), 5 (□), 10 (◆), and 20 wt % (◇) of chitin whiskers.

When reinforced by a low weight fraction (lower than 10 wt %) of chitin whiskers, the polymer films did not show any significant improved mechanical properties over the whole temperature range. For higher percentages of chitin whiskers, the composite glassy shear modulus increases up to ∼2 GPa for the 20 wt % filled material.

Above T_g a greater increase in the composite modulus is observed with increasing weight fraction of chitin whiskers. For instance, the relaxed modulus at $T_g + 25$ °C (∼300 K) of a film containing 10 wt % of chitin whiskers is 25 times higher than that of the matrix. For the 20 wt % hydrolyzed squid pen chitin filled composite, the relaxed modulus is increased by more than 160. This reinforcing effect is much less pronounced than the one observed for tunicin—an animal cellulose—whisker filled composites. It was shown that this reinforcing effect strongly depended on the aspect ratio of the cellulose whisker, and therefore on its origin, as well as on the processing technique of the composite.[11,17] For wheat straw cellulose whiskers, with an aspect ratio close to the one of squid pen chitin whiskers, the reinforcing effect was lower than the one reported for chitin whiskers when the films were prepared by a freeze-drying and hot-melting technique of the mixture of the

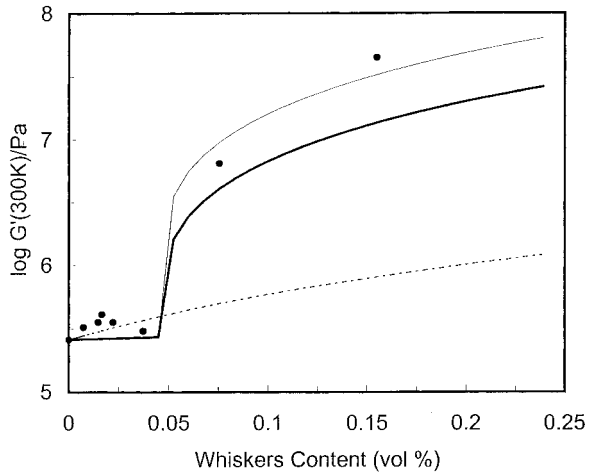

Figure 3. Logarithm of the storage tensile modulus E' at T_g + 25 K (∼300 K) vs volume fraction of squid pen chitin whiskers: comparison between the experimental data (●) and predicted data from the Halpin−Kardos model (dashed line) or from the percolation approach using the experimental (bold continuous line) or adjusted (thin continuous line) G_R value.

suspensions, whereas it was higher for cast and evaporated films. Figure 2b shows that no shift of the main relaxation process is observed in agreement with DSC measurements. A slight decrease of the temperature position of the main relaxation for the highly filled composite (20 wt %) is reported. It is ascribed to a mechanical coupling effect.

The experimental variation of the relaxed storage shear modulus, taken at 300 K (i.e., 25 K above T_g of the matrix), vs whiskers content is plotted in Figure 3. For low whiskers concentration (up to ∼5 vol %), the observed values agree fairly well with those (dashed line in Figure 3) predicted from a classical mean-field approach (Halpin−Kardos model) developed for short fiber composites.[18] However, the experimental data are much higher than the predicted ones for higher volume fraction of chitin whiskers. The advantage of such a mechanical model is to propose a simple analytic expression for the composite modulus, which takes into account the mechanical anisotropy and the geometry of the inclusions and which can be easily extended to a viscoelastic description of the material. It is worth noting that the mean-field approach does not account for the mechanical interaction between the fibers. The Halpin−Kardos 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 can be derived from the micromechanic equations of Halpin−Tsai.[19] This model is described in detail elsewhere.[10] Calculations with this model have been made using the parameters listed in Table 1.

As seen in Figure 3, for low whiskers content the mean-field approach is able to account for the observed data. This indicates that in this composition range the filler−matrix interaction is the main phenomenon involved in the reinforcing effect of chitin whiskers. For higher whiskers content, the model fails to describe the experimental data. To explain the unusually high modulus values of the highly 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.[22] in their adaptation of the percolation concept to the classical phenomenological series-parallel model of Takayanagi et al.[23] At high temperature (i.e., above T_g) the filler modulus, G_R, is far higher than the one of the matrix. It means that all the stiffness of the material is due to infinite aggregates of whiskers, and the elastic shear modulus G'_C of the composite is given by the following equation:

$$G'_C = \psi G'_R \tag{1}$$

where ψ corresponds to the volume fraction of the percolating rigid phase. With v_{RC} being the critical volume fraction of the rigid phase at the percolation threshold and b the corresponding critical exponent, ψ can be written as

$$\psi = 0 \qquad \text{for } v_R < v_{Rc}$$

$$\psi = v_R\left(\frac{v_R - v_{Rc}}{1 - v_{Rc}}\right)^b \qquad \text{for } v_R \geq v_{Rc} \tag{2}$$

The threshold fraction to reach percolation of whiskers strongly depends on the aspect ratio of the dispersed phase and on its orientation in space. For a random orientation, v_{RC} is given by $0.7/f$, with f the aspect ratio of the dispersed phase. In our case, for squid pen chitin whiskers, the aspect ratio is equal to 15 which leads to a percolation threshold close to 4.7 vol %, which corresponds to ∼6 wt % (taking 1.5 and 1.1 for the density of the filler and of the matrix, respectively). According to several studies based on the percolation concepts,[24,25] b takes the value of 0.4 in a three-dimensional system. The stiffness of the chitin whiskers network, different from the one of an isolated whisker, was experimentally measured from a tensile test (with a cross-head speed of 1 mm/min) performed on a β-chitin whiskers sheet and was found equal to 530 MPa. This value was the highest value obtained from several tensile tests, because chitin whiskers sheets were very brittle inducing premature break of the specimen. This highest experimental data are most probably the most

Table 1. Parameters Used for the Halpin−Kardos Modeling

symbol	designation	value
E_{11f}	longitudinal modulus of the chitin whisker	150 GPa[a]
E_{22f}	transverse modulus of the chitin whisker	15 GPa[b]
G_m	shear modulus of the matrix	259 MPa (at 300 K)[c]
G_f	shear modulus of the chitin whisker	5 GPa[d]
ξ_{11}	geometrical parameters of the chitin whisker	30[e]
ξ_{22}	geometrical parameters of the chitin whisker	2[e]
ξ_{12}	geometrical parameters of the chitin whisker	1[e]
ν_f	Poisson's ratio of the whisker	0.3
ν_m	Poisson's ratio of the matrix	0.5 (at 300 K)

[a] Average value of the literature for β chitin.[20] [b] By analogy with cellulose whiskers, it has been taken as the lowest value of the two transverse modulus, which is close to $E_{11f}/10$. [c] Experimental data. [d] Average value of the literature for cellulose.[21] [e] Deduced from the average whisker dimensions (average aspect ratio of 15).

representative data. The shear modulus used for the calculation is therefore close to 0.2 GPa, taking $\nu_f = 0.3$. The tensile modulus of the chitin whiskers sheet is much lower that the value reported for tunicin whiskers sheets for which it was 15 GPa.[8,9] The difference could be partly due to the lower aspect ratio of squid pen chitin whiskers compared to tunicin whiskers (aspect ratio close to 70). Indeed, the tensile modulus of a wheat straw cellulose whiskers sheet (aspect ratio close to 45) was found to be around 6 GPa.[10] The stiffness of the fiber network also strongly depends on hydrogen bonding, which develops between whiskers during the evaporation step. The formation of this network, governed by a percolation mechanism, is influenced by the surface chemical composition of the percolating species. In addition, residual protein remaining at the surface of chitin fragments most probably hinder partly the possible interactions between chitin whiskers.

The calculated curve based on the percolation theory is reported as a bold continuous line in Figure 3. It is lower than the mean-field prediction up a volume fraction of 4.7 vol %. Above this critical percentage, the calculated curve based on the percolation theory increases rapidly, and it clearly appears that the predicted modulus values agree much better than the mean-field approach with the experimental data. This is an indication of the presence of strong interactions between whiskers such as hydrogen bonds, which lead to the formation of a rigid network governed by the percolation threshold. This rigid whiskers network which develops above the percolation threshold by hydrogen bonding allows a thermally stabilization of G' in the rubbery state (Figure 2a). However, the calculation overestimates the relaxed modulus of poly(S-*co*-BuA)-based composites. The experimental data are about 2.4 times lower than the predicted one. This discrepancy can ensue from the underestimation of the chitin network modulus from the tensile test. An attempt was made to fit the calculated curve based on the percolation theory with experimental data, taking the chitin network modulus as an adjustable parameter (thin continuous line in Figure 3). The best fit was obtained with $G_R = 0.5$ GPa, which is close to the experimental value. Therefore, although mainly phenomenological, the model based on percolation concepts is able to take into account the microstructural parameters of the composites.

It is shown in this study that chitin can be used as environmentally friendly particulate filler, and it can be useful for the processing of stiff small-size wares. However, the purification step of chitin has to be optimized in order to remove remaining proteins and to take the best possible advantage of interwhiskers interaction, by favoring the formation of a rigid chitin whiskers network. In addition, the processing and the characterization of nanocomposites based on chitin whiskers with a much higher aspect ratio are also investigated at present, and the results will be published shortly.

Acknowledgment. The technical assistance of Mrs. Audrey Dubois and Mrs. Nathalie Cagnat who contributed to this study is gratefully acknowledged. The authors also gratefully acknowledge Dr. J. L. Putaux for its help in TEM.

References and Notes

(1) Rundall, K. M. *Adv. Insect Physiol.* **1963**, *1*, 257.
(2) Roche, E.; Chanzy, H.; Boudeulle, M.; Marchessault, R. H.; Sundararajan, P. *Macromolecules* **1978**, *11*, 86.
(3) Neville, A. C. In *Biology of Fibrous Composites; Development Beyond the Cell Membrane*; Cambridge University Press: New York, 1993.
(4) Marchessault, R. H.; Morehead, F. F.; Walter, N. M. *Nature* **1959**, *184*, 632.
(5) Revol, J.-F.; Marchessault, R. H. *Int. J. Biol. Macromol.* **1993**, *15*, 329.
(6) Li, J.; Revol, J.-F.; Naranjo, E.; Marchessault, R. H. *Int. J. Biol. Macromol.* **1996**, *18*, 177.
(7) Li, J.; Revol, J.-F.; Marchessault, R. H. *J. Colloid Interface Sci.* **1996**, *183*, 365.
(8) Favier, V.; Canova, G. R.; Cavaillé, J. Y.; Chanzy, H.; Dufresne, A.; Gauthier, C. *Polym. Adv. Technol.* **1995**, *6*, 351.
(9) Favier, V.; Chanzy, H.; Cavaillé, J. Y. *Macromolecules* **1995**, *28*, 6365.
(10) Helbert, W.; Cavaillé, J. Y.; Dufresne, A. *Polym. Compos.* **1996**, *17*, 4, 604.
(11) Dufresne, A.; Cavaillé, J. Y.; Helbert, W. *Polym. Compos.* **1997**, *18*, 2, 198.
(12) Dufresne, A.; Cavaillé, J. Y.; Helbert, W. *Macromolecules* **1996**, *29*, 7624.
(13) Dufresne, A.; Cavaillé, J. Y. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 2211.
(14) Dubief, D.; Samain, E.; Dufresne, A. *Macromolecules* **1999**, *32*, 5765.
(15) Dufresne, A.; Kellerhals, M. B.; Witholt, B. *Macromolecules* **1999**, *32*, 7396.
(16) Anglès, N. M.; Dufresne, A. *Macromolecules*, in press.
(17) Dufresne, A. In *Recent Research Developments in Macromolecules*; Pandalai, S. G., Ed.; Research Signpost: 1998; Vol. 3, pp 455−474.
(18) Halpin, J. C.; Kardos, J. L. *J. Appl. Phys.* **1972**, *43*, 2235.
(19) Tsai, S. W.; Halpin, J. C.; Pagano, N. J. In *Composite Materials Workshop*; Technomic: Stanford, CT, 1969.
(20) Xu, W.; Mulhern, P. J.; Blackford, B. L.; Jericho, M. H.; Templeton, I. *Scanning Microsc.* **1994**, *8*, 499.
(21) Tashiro, K.; Kobayashi, M. *Polymer* **1991**, *32*, 1516.
(22) Ouali, N.; Cavaillé×e2 J. Y.; Perez, J. *Plast. Rub. Compos. Process. Appl.* **1991**, *16*, 55.
(23) Takayanagi, M.; Uemura, S.; Minami, S. *J. Polym. Sci., Part C* **1964**, *5*, 113.
(24) de Gennes, P. G. In *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(25) Stauffer, D. In *Introduction to Percolation Theory*; Taylor and Francis: London, 1985.

MA002049V