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Nanocomposites of Chitin Whiskers from *Riftia* Tubes and Poly(caprolactone)

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ABSTRACT: Nanocomposite materials were obtained from a colloidal suspension of high aspect ratio β chitin whiskers as the reinforcing phase and poly(caprolactone) as the matrix. The chitin whiskers, prepared by acid hydrolysis of *Riftia* tubes, consisted of slender parallelepiped rods with an aspect ratio close to 120. A procedure was optimized to prepare a latex of poly(caprolactone). After mixing and stirring the two aqueous suspensions, solid films were obtained by either freeze-drying and hot-pressing or casting and evaporating the preparations. An amorphous poly(styrene-*co*-butyl acrylate) latex was also used as a model matrix. The thermal and mechanical properties of the resulting films were evaluated. The reinforcing effect of chitin whiskers is discussed on the basis of different types of mechanical models, and it is concluded that these whiskers form a rigid network assumed to be governed by a percolation mechanism. The formation of this network allows the thermal stabilization of the material for temperatures higher than the melting temperature of the poly(caprolactone).

Introduction

Trends in solid waste management, rapid changes in legislation, and the growing worldwide interest in degradable products have led scientists to increase activities on the development and design of environmentally friendly materials. Much research is therefore carried out on poly(caprolactone) (PCL), a biodegradable polymer, mainly with the view to increase its mechanical properties.^{1–9} PCL is a semicrystalline thermoplastic polymer which is used for instance to make suture thread. A classical way to improve the mechanical behavior of a material is the addition of fillers to process a composite material. This was the choice made in this study. Yet the material can be no longer biodegradable, and thus the advantage of using a biodegradable polymer is lost. In this respect, a natural filler such as chitin would be a much better choice as the reinforcing phase for PCL.

Chitin, a structural polymer which can be found in exoskeleton of crustacean, cuticle of insects, and cell wall fungi, is, next to cellulose, the most abundant biopolymer.¹⁰ Although it does not occur in organisms producing cellulose, it is often considered as a cellulose derivative since it is also a polysaccharide.¹¹ Indeed, chitin has the same backbone than cellulose, but the 2-hydroxy has been replaced by an acetamide group, resulting in mainly β -(1 \rightarrow 4)-2-acetamido-2-deoxy-D-glucopyranose structural units (GlcNAc).¹¹ Chitin has been known to form microfibrillar arrangements in living organisms and can be used for medical applications since it is safe for the human body.¹⁰ These fibrils are usually embedded in a protein matrix and have diameters from 2.5 to 2.8 nm.¹² Crustacean cuticles possess chitin microfibrils with diameters as large as 25 nm. Many reviews have been written which outline chitin, mainly from crab and shrimp shells, and its derivative's usefulness in such areas as pharmaceutical and biomedical applications, paper production, textile finishes,

photographic products, cements, heavy metal chelating agents, membranes, hollow fibers, and waste removal.^{10,13–15}

In a previous preliminary work, the preparation technique and the characterization of chitin microcrystals, or whiskers, obtained from squid pen were reported.¹⁶ Their aspect ratio L/d (L being the length and d the diameter) was estimated around 15 from transmission electron microscopy. Composite films were processed by casting and evaporating a mixture of an aqueous suspension of microcrystals and an aqueous suspension of polymer (latex) containing spherical particles of poly(styrene-*co*-butyl acrylate), poly(*S-co*-BuA). It was found that these whiskers bring a reinforcing effect, especially at $T > T_g$ of the matrix, and improve the thermal stability of the composite. This effect was discussed on the basis of the theoretical model of Halpin–Kardos. It was concluded that the reinforcing effect observed does not seem to be only due to the geometry and the stiffness of the whiskers. The formation of aggregates or clustering of fillers within the thermoplastic matrix is also to be accounted for. Other studies on nanocomposites filled with cellulose whiskers led to the same conclusion.^{17–22}

The chitin whiskers are obtained in suspension in water. Therefore, the obtaining of a good level of dispersion of the filler within the polymer matrix requires the use of either an aqueous suspension, that is to say a latex, or an aqueous solution of the polymer. PCL being insoluble in water, the former method was investigated. The aim of this study is to describe the processing of a latex of PCL and of an aqueous suspension of chitin whiskers used for the processing of nanocomposites. Then, the mechanical properties of these materials are investigated.

Experimental Section

***Riftia* Tubes.** The chitin was obtained from tubes secreted by a vestimentiferan worm called *Riftia*. The tubes were kindly provided by J. Ravaut and F. Gaill from the Laboratoire de Biologie Cellulaire et Moléculaire du Développement, Univer-

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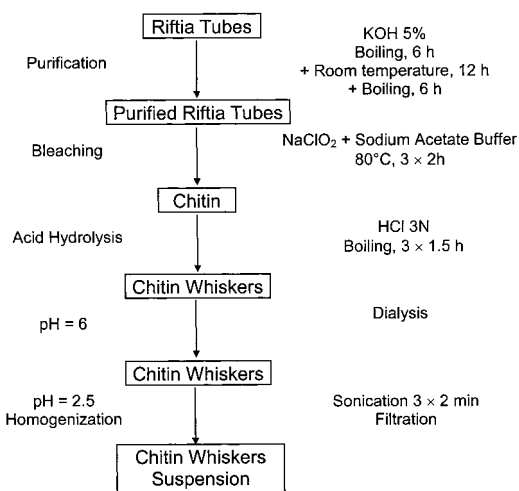


Figure 1. Chemical and mechanical treatments of *Riftia* tubes for the preparation of chitin whiskers.

sité Pierre et Marie Curie, Paris, France. They were collected during different missions on the East-Pacific Ridge at a depth of 2500 m. They occurred as unbleached tubes around 2 cm in diameter. These samples were chosen because of their high degree of crystallinity and of the expected high aspect ratio of the constituting whiskers upon hydrolysis. The chitin of *Riftia* is constituted of β -chitin.

Deproteinization of the Chitin. The technique used for the purification of the chitin and the preparation of the whiskers is similar to previous published procedures^{16,23} but differs slightly owing to the source of chitin. The whole treatment is reported in Figure 1 and is described below. Tube fragments were first stirred by boiling for 6 h in a 5 wt % aqueous KOH solution. Then, the specimens were rinsed with distilled water and filtered under vacuum on a 1 μ m pore size Blutex nylon net. The resulting paste was dissolved in the same solution and stirred at room temperature overnight. Finally, the first step was performed again. Between each KOH treatment, the rinsing and filtering procedure was repeated.

Following this treatment, chitin samples were bleached with 17 g of NaClO₂ in 1 L of distilled water mixed with 27 g of NaOH in 75 mL of acetic acid completed with 925 mL of distilled water. The suspension was heated at 80 °C for 2 h under stirring. This procedure was repeated three times with rinsing by centrifugation at 11 200 tr min⁻¹ (20 335g) (Sigma 6K15) for 15 min at 10 °C between each step.

Chitin Whiskers. The chitin whiskers suspension was prepared by hydrolyzing the purified chitin sample with 3 N HCl at the boil under stirring for 1.5 h. After acid hydrolysis, the suspensions were diluted with distilled water followed by centrifugation and decanting the supernatant. Repeating this process three times with the residue, the whiskers were obtained by removing the amorphous parts of the microfibrils.

The suspensions were dialyzed for 2 h in running water and then overnight in distilled water. An additional dialysis for 12 h changing the distilled water every 2 h was performed until a pH = 6 was reached. The dispersion of whiskers (0.15 wt %) was completed by three successive ultrasonic treatments for 2 min each (Branson Sonifier B12) for every 40 mL aliquot.

It was subsequently filtered to remove residual aggregates. Next, the pH was adjust at about 2.5 by adding HCl. This suspension displays a colloidal behavior, which stability was attributed to the presence of positive charge (NH₃⁺) at the surface of the crystallites resulting from the protonation of amino groups.²⁴ After concentration by dialysis against poly(ethylene glycol) with a number-average molecular weight (M_n) of 35 000 g mol⁻¹, the solid fraction of this aqueous suspension was 0.22 wt %. It was stored at 6 °C after adding chloroform to avoid bacterial developments until used.

Polycaprolactone. The poly(caprolactone) (PCL), with a number-average molecular weight (M_n) of 80 000 g mol⁻¹, was

provided as white granules by Aldrich Chemical Co. Since no studies were done before on PCL latex, the whole experimental procedure was established. However, the preparation of aqueous suspensions of PCL nanoparticles for pharmaceutical applications was described in the literature by spanish research groups.^{25–27} These works were taken as a starting point for the fabrication of the latex. It is worth noting that in these previous works the amount of surfactant used to stabilize the nanoparticles suspension was greater than the one of the polymer. In materials applications this amount has to be reduced. Moreover, an attempt was performed to increase the concentration of the polymer in the solvent compared to the published procedure.

The preparation of the latex requires the use of a surfactant in order to obtain a stable suspension. It was kindly supplied by BASF. It was constituted by a bloc copolymer of about 70 wt % poly(ethylene oxide) and 30 wt % poly(propylene oxide) (PEO–PPO–PEO) with a number-average molecular weight (M_n) around 13 000 g mol⁻¹. It is called poloxamer 407 and commercialized under the trademark Lutrol F127.

Poly(styrene-*co*-butyl acrylate). A commercial latex of poly(styrene-*co*-butyl acrylate) (poly(S-*co*-BuA)) was kindly supplied by Elf-Atochem, Serquigny, France, to prepare nanocomposites with an amorphous matrix. It was obtained by the copolymerization of styrene (34 wt %) and butyl acrylate (64 wt %) and contained 1% acrylic acid and 1% acrylamide. The aqueous suspension contained spherical particles with an average diameter of \sim 150 nm. Its glass–rubber transition was around 0 °C. It was filtered twice under vacuum on a 1 μ m pore size Blutex nylon net in order to remove possible particle aggregates.

Nanocomposite Films Processing. The colloidal microcrystalline dispersion was mixed with the suspension of latex in various amounts in order to obtain composites films with a weight fraction of chitin compared to the mass of polymer ranging between 0 and 10%. The different mixtures were calculated to obtain around 1.5 g of dried matter, thereby producing films ranging between 0.5 and 1 mm thick. Two processing techniques were used.

On one hand, the films were processed by freeze-drying and molding a mixture of the two aqueous suspensions. Hot-pressing was performed with a carver laboratory press at 21 bar and at 100 °C. Films were allowed to slowly cool at room temperature. This processing technique was used only for PCL. On the other hand, after mixing and stirring, the mixture was degassed under vacuum in order to remove the remaining air and cast in a Teflon mold stored at 75 °C for PCL and 35 °C for poly(S-*co*-BuA). A nanocomposite film results by water evaporation and particles coalescence. These temperatures were chosen because they are higher than either the melting temperature (T_m) of PCL or the glass–rubber transition temperature (T_g) of poly(S-*co*-BuA). In both cases, the air can be eliminated more easily during evaporation. For the last processing technique (evaporation), films with high whiskers content were difficult to obtain since the amount of water in the mixture was too high.

The chitin volume content was calculated taking 1.5 g cm⁻³ for the density of crystalline chitin, 1.146 g cm⁻³ for the density of PCL, and 1.1 g cm⁻³ for the density of poly(S-*co*-BuA). Sample compositions and their designations are presented in Table 1. The weight fraction of chitin was expressed on a dry basis of unfilled matrix (chitin/matrix) whereas the volume content was given with respect to the composite volume (chitin/chitin + matrix).

Microscopies. Transmission electron microscopy (TEM) observations were made with a Philips CM200 electron microscope. A droplet of a dilute suspension of microcrystalline chitin was deposited and allowed to dry on a carbon-coated grid. The accelerating voltage was 80 kV.

For the images of the mixing of latex and whiskers, a droplet of a dilute suspension was deposited on a perforated carbon film (NetMesh). The excess of liquid was absorbed with a filter paper. Then, the grid was quickly quenched in liquid ethane from a quick freezing platform Leica EM-CPC ("cryo" micro-

Table 1. Codification, Processing Technique, Composition, Glass–Rubber Transition Temperature (T_g), Melting Temperature (T_m), and Degree of Crystallinity (χ_c) of the Various Chitin Whisker Filled Composites

sample	matrix	processing technique	chitin content (wt %) ^a	chitin content (vol %) ^b	T_g (°C)	T_m (°C)	χ_c (%) ^c
PCL1	PCL	as-received	0	0	−60.0	69.0	58.0
PCL2	PCL	hot-pressing	0	0	−62.3	63.0	50.6
E0	PCL	water evaporation	0	0	−62.0	65.0	55.9
E0.5			0.5	0.38	−59.6	64.0	37.2
E1			1	0.77	−57.3	67.6	47.7
E2.5			2.5	1.87	−61.0	62.4	48.3
P0	PCL	freeze-drying and	0	0	−62.5	62.0	45.6
P0.5		hot-pressing	0.5	0.38	−62.4	63.0	45.3
P1			1	0.77	−62.1	62.4	42.9
P2.5			2.5	1.87	−62.6	62.4	42.6
P5			5	3.68	−62.0	63.2	40.7
P10			10	7.36	−63.0	61.6	42.9
A0	poly(S-co-BuA)	water evaporation	0	0			
A0.5			0.5	0.33			
A1			1	0.67			
A2.5			2.5	1.64			
A5			5	3.64			

^a Expressed on dry PCL basis [chitin/PCL]. ^b Taking 1.5, 1.146, and 1.1 g cm^{−3} as the density of chitin, PCL, and poly(S-co-BuA), respectively. ^c Degree of crystallinity calculated taking $\Delta H_\infty = 136$ J g^{−1}.²

copy). The sample was put on the stage Gatan 626 cooled with liquid nitrogen.

The atomic force microscopy (AFM) observations were achieved with a Digital 3100 IIIa microscope. A droplet of a dilute suspension of whiskers was deposited on a cleaved flake of mica. Then, the water was evaporated by warming with an infrared lamp.

Infrared Spectroscopy. Measurements were performed with a Fourier transform infrared (FT-IR) spectrometer (Perkin-Elmer 1720 X).

Differential Scanning Microscopy (DSC). Differential scanning calorimetry (DSC) was performed with Perkin-Elmer DSC7 equipment, fitted with a cooler system using liquid nitrogen. Each sample was heated from −120 to 120 °C at a heating rate of 20 °C min^{−1}. The melting temperature (T_m) was taken as the peak temperature of the melting endotherm while the glass transition temperature (T_g) was taken as the inflection point of the specific heat increment at the glass–rubber transition.

Dynamic Mechanical Analysis. Dynamic mechanical tests were carried out with a spectrometer RSA2 from Rheometrics working in the tensile mode. The value of 0.05% for the strain magnitude was chosen so as to be in the domain of the linear viscoelasticity of the material. The samples were thin rectangular strips with dimensions about 25 × 4 × 1 mm³. The setup measures the complex tensile modulus E^* , i.e., the storage component E' and the loss component E'' . Measurements were performed in isochronal conditions at 1 Hz, and the temperature was varied between 150 and 450 K by steps of 3 K. The time allotted to reach thermal stabilization between each thermal step, termed “soak time” in the RSA2 software, was stated at 30 s in most of the experiments.

Results and Discussion

Poly(caprolactone) Latex. Previous works^{25–27} dealing with the preparation of aqueous suspensions of PCL nanoparticles for pharmaceutical applications were taken as a starting point for the fabrication of the latex. In these works, a large amount of surfactant (125 wt % on dry basis of PCL) was used to obtain these suspensions. We have tried to decrease this amount by a trial and error procedure varying systematically the surfactant concentration and performing a visual examination of the resulting suspension. The criterion for the optimization of the formulation was to obtain a stable polymer suspension using the lower amount of surfactant. Attempts were performed with surfactant concentrations ranging from 100 down to 2 wt % (on a dry basis

of PCL). At the same time, attempts were also made to increase the polymer concentration in the suspension and preserve the stability of the latex. The optimized formulation was obtained with 15 wt % of poloxamer 407, corresponding to 13 wt % on the dry film basis. A stable polymer suspension resulted, and the stability of this latex was held for several weeks when stored at 6 °C. Finally, the experimental procedure for the PCL latex preparation is described below.

The solution of PCL was first obtained by dissolving 0.5 g of polymer in 125 mL of acetone at boil. A 75 mg sample of surfactant was dissolved in 125 mL of distilled water under mechanical stirring at room temperature. After mixing, the two solutions were stirred, and acetone and part of the water were evaporated at 30 °C using a rotavapor. The aqueous suspension with a solid fraction around 20 wt % contained spherical particles with an average diameter of ~150 nm.

Chitin Whiskers. Under low stirring, the suspension of chitin microcrystals prepared by acid hydrolysis of the tubes of *Riftia* displays a colloidal behavior when observed in polarized light between cross nicols. It is ascribed to the formation of birefringent domains. This colloidal behavior was previously observed for cellulose microcrystals suspensions.²¹ In the case of chitin, this is due to the presence of positive charges (NH₃⁺) at the surface of the whiskers, resulting from the protonation of amino groups.²⁴

Transmission electron (Figure 2a) and atomic force (Figure 2b) micrographs were obtained from a dilute suspension of chitin whiskers. The suspension is constituted of individual chitin fragments consisting of slender parallelepiped rods that have a broad distribution in size. These fragments have a length ranging from 500 nm up to 10 μm, and they are weakly distributed in width (around 18 nm). The dimensions of the whiskers were averaged on 240 representative items. The length distribution of these microcrystals has a typical histogram shown in Figure 3. Very long whiskers were not accounted for because they are most probably only partially hydrolyzed. The average length was found around 2.2 μm. More than 75% of the whiskers have a length below 3 μm. The average aspect ratio (L/d , L being the length and d the diameter) of these whiskers is therefore around 120.

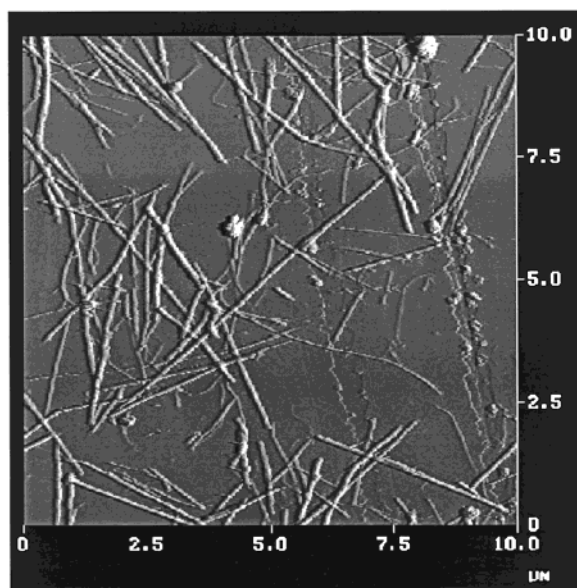
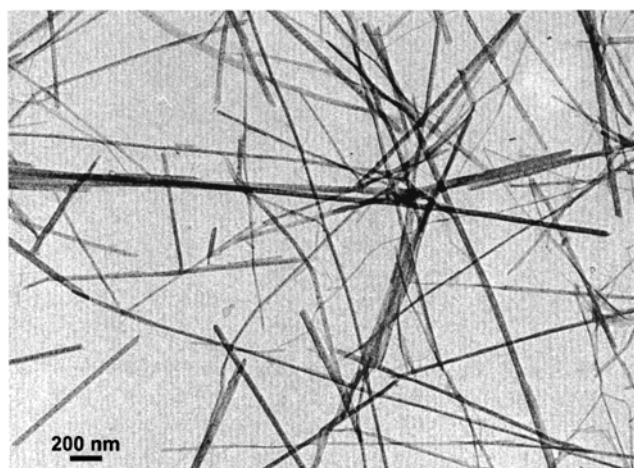


Figure 2. (a, top) Transmission electron and (b, bottom) atomic force microscopy micrograph from a dilute suspension of chitin whiskers from *Riftia* tubes.

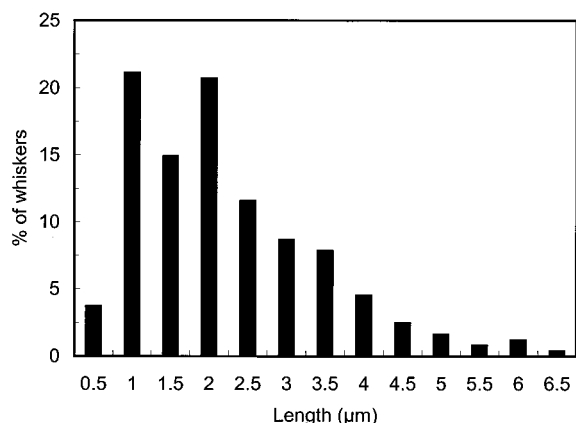


Figure 3. Length distribution of chitin whiskers, extracted from *Riftia* tubes and hydrolyzed with a chlorhydric acid solution.

An infrared spectrum was carried out on a film of chitin whiskers obtained from the evaporation of the whiskers suspension in order to display the absence of residual proteins on the chitin fragments (Figure 4). In the carbonyl region, this spectrum presents two strong absorption peaks at 1630 and 1560 cm^{-1} characteristic

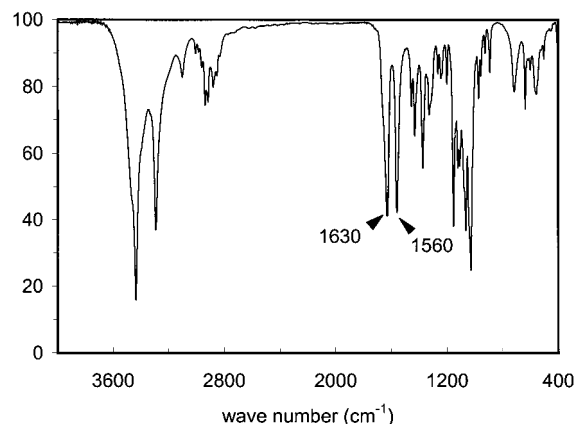


Figure 4. Fourier transform infrared spectrum taken from a film of chitin whiskers obtained from the evaporation of the whiskers suspension.

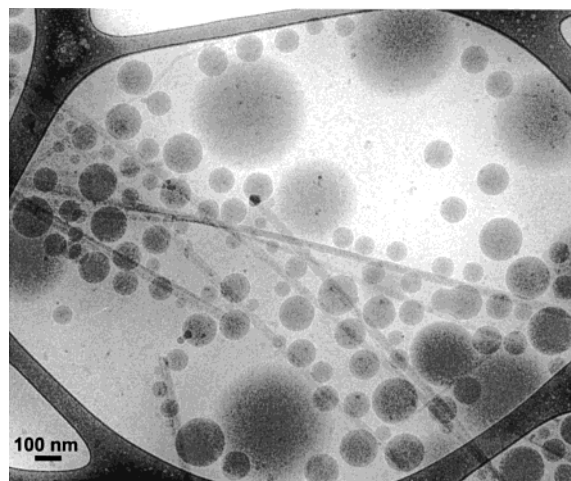


Figure 5. Transmission electron micrograph from a mixture of poly(caprolactone) latex and dilute suspension of chitin whiskers from *Riftia* tubes.

of anhydrous β -chitin. The absence of the peak at 1540 cm^{-1} corresponding to the proteins²⁸ proves that the successive treatments were strong enough to eliminate all the proteins and to obtain pure chitin.

Mixture of Chitin Whiskers and PCL Latex. A "cryo" transmission electron micrograph was obtained from the mixture of the PCL suspension and of the whiskers dispersion (Figure 5). The latex consisted of well-individualized spheres with a diameter ranging from 50 to 300 nm. The average diameter of the spheres, which display the more precise contour, is around 150 nm.

Thermal Analysis. All the samples were analyzed using differential scanning calorimetry (DSC) in order to determine their thermal properties. Results are collected in Table 1. The glass-rubber transition, the melting point, and the degree of crystallinity of the as-received PCL were found around -60 $^{\circ}\text{C}$, 69 $^{\circ}\text{C}$, and 58%, respectively. These values agree with previously reported ones.² When hot-pressed no significant change is observed, except a slight decrease of both the melting temperature and the degree of crystallinity for the hot-pressed sample. It is worth noting that the crystallinity of semicrystalline polymers is strongly dependent on the thermal history of the sample.

For all the chitin whiskers/PCL composites, both T_g and T_m seem to be almost independent of the whiskers concentration. However, for a given composition, T_m is

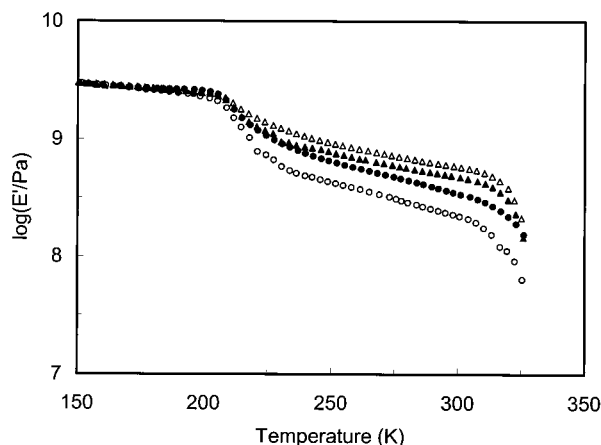


Figure 6. Logarithm of the storage tensile modulus E' vs temperature at 1 Hz for evaporated chitin whiskers/poly-(caprolactone) nanocomposites filled with 0 (●), 0.5 (○), 1 (▲), and 2.5 wt % (△) of chitin whiskers.

systematically lower for the hot-pressed samples than for the evaporated ones. This means a decrease of the size of the crystalline domains for the formers. In addition, the degree of crystallinity seems to globally decrease with the whiskers content for both kinds of processing. The heat of fusion used to calculate the degree of crystallinity for each composite was normalized with respect to the mass of PCL. For composites, the PCL crystallizes in the presence of whiskers, which display a high specific area. During crystallization, the whiskers are most probably first ejected and then occluded in intercrystalline domains, hindering the crystallization of the polymer. It is worth noting that, for a given composition, the degree of crystallinity is systematically lower for the freeze-dried and hot-pressed materials than for the evaporated ones. This should most probably influence the mechanical behavior of these composites. The degree of crystallinity of the E0.5 sample is very low compared to other composites since it was quenched in liquid nitrogen as it came out of the oven. This composition will display a specific behavior afterward.

Mechanical Analysis. Dynamic mechanical analysis measurements were performed for unfilled matrices and up to 10 wt % filled composites. The mechanical behavior of both evaporated and hot-pressed materials will be discussed separately and then compared. The mechanical properties of nanocomposite films with a model amorphous poly(*S-co-BuA*) matrix filled with chitin whiskers from *Riftia* tubes will be also investigated.

The values of the glassy storage modulus of the composites were normalized at low temperature at the average measured value for all the samples. It corresponds to 3 GPa for the chitin whiskers/PCL films and to 1 GPa for the chitin whiskers/poly(*S-co-BuA*) films. Indeed, the measurements of the sample dimensions were not very precise since both polymers were in the rubbery state and were rather soft at room temperature. Moreover, the film thickness was sometimes not very constant and homogeneous along these samples.

Evaporated Chitin Whiskers/PCL Nanocomposites. Figure 6 shows the isochronal evolution of the logarithm of the elastic tensile modulus ($\log E'$) at 1 Hz as a function of temperature for evaporated films filled with 0 and up to 2.5 wt % whiskers. At low temperature, E' slightly decreases with temperature but remains roughly constant. At higher temperature, a rapid de-

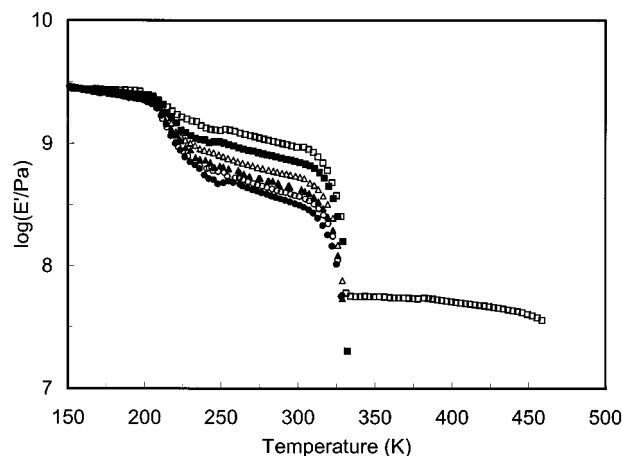


Figure 7. Logarithm of the storage tensile modulus E' vs temperature at 1 Hz for hot-pressed chitin whiskers/poly-(caprolactone) nanocomposites filled with 0 (●), 0.5 (○), 1 (▲), 2.5 (△), 5 (■), and 10 wt % (□) of chitin whiskers.

crease in the elastic tensile modulus is observed in the range 210–230 K. This modulus drop occurs in the glass–rubber transition temperature previously determined by DSC. It is ascribed to a relaxation process which can be therefore associated with the anelastic manifestation of the glass–rubber transition of the polymer. This mechanism involves cooperative motions of long chain sequences. The temperature position of this relaxation remains constant whatever the concentration of filler may be.

Above this temperature range, the storage modulus tends to roughly stabilize, which value corresponds to the rubbery modulus. The rubbery modulus of a semi-crystalline polymer is known to depend on the degree of crystallinity of the material. The crystalline regions of PCL act as physical cross-links for the elastomer. In this physically cross-linked system, the crystalline regions would also act as filler particles due to their finite size, which would increase the modulus substantially. An increase of the rubbery modulus is observed with increasing the whiskers content. The peculiar behavior reported for the 0.5 wt % whiskers filled composite (E0.5) can be most probably related to the DSC observations and could be ascribed to the lower degree of crystallinity of the PCL matrix. The relaxed modulus increases from 0.35 GPa for the unfilled matrix up to 0.59 GPa for the 2.5 wt % filled composite whiskers at room temperature. This modulus increase cannot be ascribed to an increase of the crystallinity of the matrix, since a slight decrease of χ_c upon whiskers addition was reported from DSC measurements. This phenomenon could be therefore due to a reinforcing effect of the chitin whiskers obtained from *Riftia* tubes. The modulus drops irretrievably with the breakup of crystalline domains around 330 K, whatever the whiskers content maybe. This disastrous decrease of the mechanical properties was previously observed for nanocomposite films obtained from tunicin—an animal cellulose—whiskers and from a semicrystalline poly(hydroxyoctanoate) (PHO) matrix.²⁹

Hot-Pressed Chitin Whiskers/PCL Nanocomposites. The evolution of $\log E'$ as a function of temperature at 1 Hz for hot-pressed films filled with 0 up to 10 wt % whiskers is displayed in Figure 7. The behavior of the hot-pressed unfilled PCL is roughly similar to the one reported for the evaporated matrix. By adding chitin whiskers, an increase of the rubbery modulus is ob-

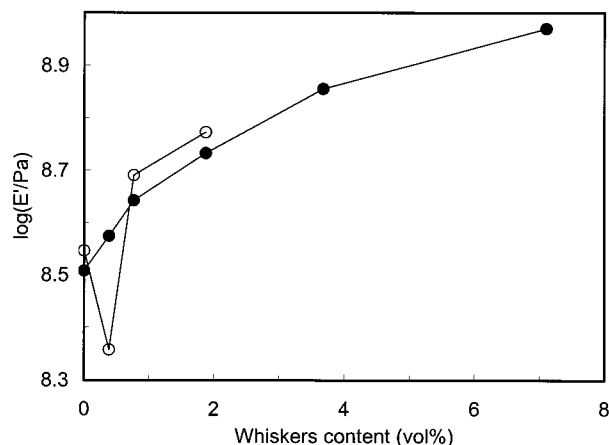


Figure 8. Evolution of the logarithm of the relaxed tensile modulus estimated at 298 K vs chitin whiskers content for hot-pressed (●) and evaporated (○) chitin whiskers/poly(caprolactone) nanocomposites. The solid lines serve to guide the eye.

served again. It increases from 0.32 GPa for the unfilled matrix up to 0.93 GPa for the 10 wt % filled composite whiskers at room temperature. At higher temperature again, the modulus drops irretrievably around the melting temperature of PCL.

For the 10 wt % whiskers filled composite the modulus drops at T_m and stabilizes subsequently surprisingly around 42 MPa at higher temperature up to 460 K. At this temperature, the sample was broken near the jaws most probably because of the damages induced by the tightening. Indeed, for the same composition the breakup of the sample corresponding to the end of the plateau occurred at different temperatures from one experiment to another. Since the matrix becomes a viscous liquid from T_m , this phenomenon can only be explained by the formation of a stable rigid phase. So, the degradation temperature of this rigid phase must be higher than 460 K. In previous studies on squid pen chitin whiskers¹⁶ or cellulose whiskers/poly(S-*co*-BuA) nanocomposites,^{17–22} the formation of a rigid network of whiskers was observed. The formation of this network within the amorphous matrix was ascribed to strong interactions between microcrystals. For cellulose whisker based composites, the relaxed modulus remains remarkably constant up to 500 K, a temperature where cellulose starts to degrade.¹⁷

A stabilization of the mechanical properties above the melting temperature of a semicrystalline matrix was also previously observed for tunicin whiskers/PHO nanocomposites, but only using a suitable in situ thermal treatment.²⁹ It consisted of increasing the time allotted to reach thermal stabilization ("soak time") between each thermal step (3 K). A stabilization of the storage modulus above T_m was reported for a "soak time" of 2000 s, whereas it was not observed for a lower "soak time". For chitin whiskers/PCL nanocomposites filled with 5 wt % whiskers, an experiment was run with a "soak time" of 60 s and a temperature increment between each measurement of 1 K. Above T_m , a weak stabilization of the modulus around 16 MPa was observed (results not shown) for this composition and these experimental conditions.

Influence of the Processing Technique. Figure 8 shows the evolution of the storage relaxed modulus at 298 K vs chitin whiskers content for both hot-pressed and evaporated nanocomposite films. Except for the

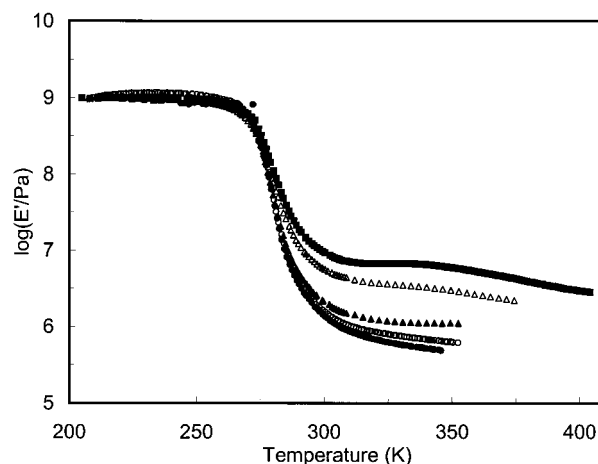


Figure 9. Logarithm of the storage tensile modulus E' vs temperature at 1 Hz for evaporated chitin whiskers/poly(styrene-*co*-butyl acrylate) nanocomposites filled with 0 (●), 0.5 (○), 1 (▲), 2.5 (△), and 5 wt % (■) of chitin whiskers.

evaporated nanocomposite film filled with 0.5 wt % whiskers, a similar continuous increase of the modulus is observed for both processing techniques. For a given composition, the modulus of the evaporated nanocomposite films is higher compared to the hot-pressed one. In cellulose whiskers filled poly(S-*co*-BuA) composites similar results were reported.²² This phenomenon was ascribed to both the morphology of the composite and the fact that different interactions between whiskers can establish. During water evaporation and polymer particles coalescence the mobility of the whiskers is higher since the mixture of the two aqueous phases is less viscous than the melt polymer. Stronger interactions can result between whiskers within the solid evaporated polymer film.

For chitin whiskers filled PCL composites, this hypothesis seems not to be the only explanation, since the matrix is semicrystalline. First, the modulus is higher for the evaporated unfilled matrix than for the hot-pressed one. This difference is ascribed to the higher degree of crystallinity of the former. In addition, if specific interactions are able to occur in the evaporated nanocomposite films, this should result in a different evolution of the modulus as a function of the composition. This is not observed in Figure 8, since the gap between the two sets of experimental data remains constant, at least up to 2.5 wt %. To try to elucidate the nature of the interactions between whiskers in the chitin microcrystals filled PCL composites, nanocomposite films with an amorphous matrix were processed and characterized. They were obtained from the same chitin whiskers suspension and a model poly(S-*co*-BuA) latex previously used as the matrix in cellulose whiskers filled composites.^{17,21,22}

Evaporated Chitin Whiskers/Poly(S-*co*-BuA) Nanocomposites. The evolution of the logarithm of the storage tensile modulus ($\log E'$) at 1 Hz as a function of temperature for poly(S-*co*-BuA) films filled with 0 up to 5 wt % whiskers is displayed in Figure 9. It is first observed that the modulus drop above T_g is much higher than the one reported for chitin whiskers/PCL composites. This is ascribed to the fully amorphous nature of the poly(S-*co*-BuA) matrix. Both the tensile rubbery modulus and the thermal stability of the film increase with the whiskers content. The relaxed modulus is increased by about 1 decade from 0.6 MPa for the

unfilled matrix up to 6.8 MPa for the 5 wt % whiskers filled composite at 330 K. These values remain roughly constant up to 346 K for the unfilled matrix and 404 K for the 5 wt % whiskers filled composite. This behavior is similar to what was observed for chitin whiskers extracted from squid pens filled poly(S-*co*-BuA) composites.¹⁶ However, these last whiskers had a 10 times lower aspect ratio. The main difference leads in the fact that no reinforcing effect was observed with squid pen chitin whiskers below 5 wt %, whereas a significant modulus increase is observed with *Riftia* tubes chitin whiskers from 1 wt %.

This reinforcing effect is lower than for nanocomposites filled with tunicin whiskers with an aspect ratio close to 70 for which the rubbery modulus gain was about 3 decades upon 6 wt % whiskers addition.^{17,29} For these materials, the high reinforcing effect was explained by the formation of a rigid network within the polymer matrix, cellulose whiskers being linked through hydrogen bonds. For chitin whiskers, the possible interactions between microcrystals are most probably weaker.

Modeling of the Mechanical Behavior. In the linear domain, a wide range of theoretical formulas are available for predicting the mechanical behavior of composite materials in terms of microstructure and fiber and matrix properties (see for example ref 30). Although these methods give satisfactory predictions of the mechanical properties for fiber reinforced polymers, particularly moduli, they are usually only applicable to unidirectional fiber reinforcement. More rigorous calculations are also difficult to perform and often require adjustable coefficients to be achieved. In the present study, two theoretical models have been used. The first one is based on a mean field approach and the second one on a percolation approach.

Mean-Field Approach. The theoretical model of Halpin–Kardos³¹ gives, in a relatively easy way, the elastic tensile modulus E_c of composites reinforced by randomly dispersed short fibers. In this approach, fibers are supposed to be dispersed in a continuous matrix, and no interactions between fibers are taken into account. The properties of the composite depend on the mechanical properties of the parent components as well as on the size, shape, mechanical anisotropy, and volume fraction of the fibers. The composite is assimilated to a “quasi-isotropic” material framed by four layers of oriented plies (at 0°, 45°, 90°, and –45°). It is noteworthy that when the mechanical behavior is mainly elastic (i.e., the imaginary part of the complex modulus is negligible), $E_c \sim E_c$. The mechanical properties of a single ply (unidirectional short fibers) are given by the Halpin–Tsai micromechanics equations (“self-consistent” approach).³² This model is described in detail elsewhere.²¹

Between T_g and T_m of PCL, the mechanical behavior of the chitin whiskers/PCL systems was predicted from this classical mean field approach. Both experimental and predicted (as a dashed line) variations of the relaxed tensile modulus, taken at 298 K, are plotted against the whiskers content (vol %) in Figure 10a. The characteristics of the fiber have the following values: $L/d = 120$ (estimated from TEM and AFM), Poisson's ratio $\nu_f = 0.3$ (chitin being crystalline over the whole temperature range), stiffness in the fiber direction $E_{11f} = 150$ GPa (average value from literature),³³ stiffness perpendicular to the fiber direction $E_{22f} = 15$ GPa (by analogy with

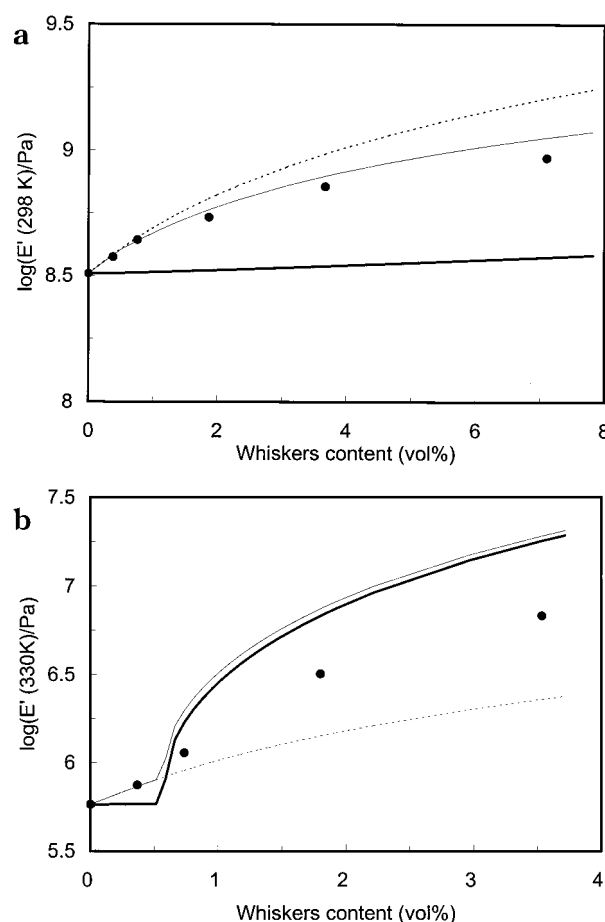


Figure 10. Logarithm of the storage tensile modulus E' at (a) 298 K for hot-pressed chitin whiskers/poly(caprolactone) nanocomposites and (b) 330 K for evaporated chitin whiskers/poly(styrene-*co*-butyl acrylate) nanocomposites. Comparison between the experimental data (●) and predicted data from the Halpin–Kardos model (dashed line), from the percolation approach (bold continuous line) or from the “hybrid” percolation model (thin continuous line).

cellulose whiskers, it has been taken as the lowest value of the two transverse modulus, which is close to $E_{11f}/10$), and in-plane shear modulus $G_f = 5$ GPa (average value of the literature for cellulose³⁴). For the matrix, the following parameters were used at 298 K: $\nu_m = 0.4$ (this value results from a mixing rule, taking $\chi_c \sim 50\%$, the matrix being composed of a rubbery amorphous part, $\nu_a = 0.5$, and a crystalline part, $\nu_c \sim 0.3$), and $E_m = 0.32$ GPa (experimental data observed for the unfilled matrix at 298 K). It appears that the predicted modulus values agree with the experimental data up to about 1 vol % but overestimate the rubbery modulus for higher concentrations.

Both experimental and predicted (as a dashed line) evolutions of the storage tensile rubbery modulus, taken at 330 K, for chitin whiskers filled poly(S-*co*-BuA) composites are plotted as a function of the whiskers content (vol %) in Figure 10b. Same parameters as previously presented were used for the fiber. For the matrix, the following parameters were used at 330 K: $\nu_m = 0.5$ (the amorphous matrix being in the rubbery state), and $E_m = 0.6$ MPa (experimental data observed for the unfilled matrix at 330 K). For this system it is observed that the predicted modulus values fits again the experimental data up to about 1 vol % but strongly underestimate the rubbery modulus for higher concentrations. It appears that the mean field approach is only

valid at low whiskers content (<1 vol %) for both matrices.

Previous published works on cellulose whisker based nanocomposites involved the percolation concept to account for the reinforcing effect.^{17,19,22,29} The reinforcing effect of cellulose whiskers was ascribed to 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 allows a thermally stable plateau to be reached.

Percolation Approach. The term percolation for the statistical geometry model was introduced in 1957 by Hammersley.³⁵ It is a statistical theory, which can be applied to any system involving a great number of species likely to be connected. It was observed for the tunicin cellulose and the squid pen chitin that the material can be thought to have achieved percolation, beyond a critical volume fraction, or threshold concentration, which depend on the mean length of the fibers.

The influence of such an effect on the mechanical properties of heterogeneous systems can be well predicted following the method of Ouali et al.³⁶ in their adaptation of the percolation concept to the classical series-parallel model of Takayanagi et al.³⁷ This model was successfully used to predict the mechanical behavior of heterogeneous materials, such as polymer blends³⁸⁻⁴¹ and nanocomposite structures.^{16,17,22,29,42-44} The general outlines will be briefly described.

In this approach, the elastic tensile modulus E_c of the composite is given by the following equation:

$$E_c = \frac{(1 - 2\psi + \psi v_R) E_S E_R + (1 - v_R) \psi E_R^2}{(1 - v_R) E_R + (v_R - \psi) E_S} \quad (1)$$

The subscripts S and R refer to the soft and rigid phase, respectively, and v_R corresponds to the volume fraction of filler (rigid phase). The adjustable parameter, ψ , involved in the Takayanagi et al. model corresponds in the Ouali et al. prediction 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

$$\begin{aligned} \psi &= 0 & \text{for } v_R < v_{RC} \\ \psi &= v_R \left(\frac{v_R - v_{RC}}{1 - v_{RC}} \right)^b & \text{for } v_R \geq v_{RC} \end{aligned} \quad (2)$$

where $b = 0.4$.^{45,46} For a 3D network, v_{RC} depends on the aspect ratio L/d of the fiber as $v_{RC} = 0.7/(L/d)$.⁴⁷ For chitin whiskers obtained from *Riftia* tubes, the aspect ratio close to 120 leads to a value of $v_{RC} = 0.58$ vol %, i.e., around 0.8 wt %.

The stiffness of the chitin microcrystals network, different from the one of an isolated whisker, was experimentally measured for a film of chitin whiskers obtained from the evaporation of the suspension in a Teflon mold. The mechanical behavior of this filler was characterized using both high strain tensile tests and dynamic mechanical analysis. In both cases, the film was allowed to dry at 110 °C for 20 min. Indeed, water is expected to reduce the interactions between the microcrystals and therefore the stiffness of the film. In addition, this should be more representative of the

behavior of the chitin whiskers within the hydrophobic matrix. The average value for the whiskers sheet modulus obtained from these various experiments was around 2 GPa. For comparison, the tensile modulus of a film of cellulose whiskers ranges between 5 and 15 GPa depending on the source of cellulose.^{17,22,42} For chitin whiskers extracted from squid pen, it was found around 0.5 GPa.¹⁶ In this last previous work, the presence of residual proteins on the surface of the whiskers was reported. It is worth noting that the interactions between cellulose microcrystals are expected to be stronger than between chitin whiskers. Indeed, the hydrogen bonds are allowed to develop between two hydroxyl groups in cellulose and between an amino and a hydroxyl group in chitin. The former is expected to be more energetic.

The calculated curves based on the percolation theory are reported as bold continuous lines in parts a and b of Figure 10 for chitin whiskers filled PCL and poly(S-co-BuA), respectively. It clearly appears that this model fails to describe the mechanical properties of both the chitin whiskers filled PCL (Figure 10a) and poly(S-co-BuA) (Figure 10b) nanocomposites.

For chitin whiskers/poly(S-co-BuA) systems, the calculated curve based on the percolation theory is lower than the dashed line representing the mean field approach prediction up to a whiskers volume fraction of 0.58%. This concentration corresponds to the theoretical percolation threshold for rigid-rod-like particles with an aspect ratio close to 120. For this composition, a sharp modulus increase results from the percolation model. The experimental evolution is smoother most probably due to the fact that the prediction does not account for the distribution of the whiskers lengths. Above the percolation threshold, the qualitative evolution of the relaxed modulus is quite well described by the model. However, the experimental data are overestimated. It is worth noting that the percolation approach was found to be suitable to fit the experimental moduli of cellulose whisker filled poly(S-co-BuA) composites.^{17,22,29,42,44} This was ascribed to the presence of strong interactions between cellulose whiskers such as hydrogen bonds, which lead to the formation of a rigid network. A possible explanation for the failure of the percolation approach when applied to the chitin whisker based nanocomposites results from the weakness of inter-chitin microcrystals interactions compared to cellulose. During the nanocomposite film formation, the interactions between whiskers are most probably hindered by the presence of viscous polymer chains. These interactions can establish more easily when forming a whiskers film directly from a chitin aqueous suspension.

For the PCL matrix based composites, the predicted data are much lower than those obtained from the mean field approach (Figure 10a). This is due to the fact that the mechanical behavior of the "soft" phase (PCL: 0.32 GPa at 298 K) is not much lower than the one of the "rigid" phase (chitin whiskers network: 2 GPa). Indeed, when the mechanical properties of the two phases are close on each other, the influence to the rigid percolating phase is negligible at low filler concentration. In fact, the predicted mechanical properties seem to be equivalent to those of a homogeneous composite filled with an apparent filler content lower than the real one. Actually, no sharp jump of the predicted modulus is observed in the vicinity of the percolation threshold, contrary to what is reported for the amorphous matrix (Figure 10b).

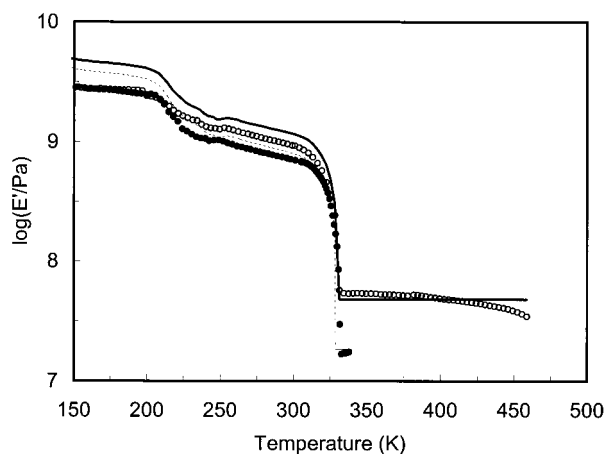


Figure 11. Logarithm of the storage tensile modulus E' vs temperature at 1 Hz. Comparison between the experimental data for composites filled with 5 (●) and 10 wt % (○) of chitin whiskers and predicted data from the “hybrid” percolation model for composites filled with 5 wt % (dashed line) and 10 wt % (continuous line) of chitin whiskers.

According to this hypothesis, an attempt was made to fit the experimental data of chitin whiskers/PCL composites with a specific parallel model (“hybrid” percolation model). It is constituted by the combination of a percolating whiskers fraction and a homogeneous domain. The effect of the former, which volume fraction is equal to Ψ of the percolation model, is negligible in this composition range. The latter, which volume fraction is equal to $1 - \Psi$, corresponds to the Halpin–Kardos model. This model is equivalent to a mean field model, considering only the nonpercolating fraction of microcrystals. For higher whiskers content, the whiskers percolating volume fraction should be no longer negligible. The prediction of the mechanical behavior of the chitin whiskers/PCL nanocomposites from the “hybrid” percolation model is reported as a thin continuous line in Figure 10a. A rather good agreement between experimental and predicted data is observed, despite ignoring the high length distribution of the whiskers in the model.

Above the melting temperature of the PCL matrix, the classical mean-field approach fails to describe the stabilization of the mechanical properties at high whiskers content. In this temperature range, the “hybrid” percolation model described above is equivalent to the percolation model, since the matrix becomes a viscous liquid, which mechanical properties are negligible.

Figure 11 shows the plot of experimental and predicted modulus from “hybrid” percolation model for the 5 and 10 wt % whiskers filled PCL over a wide temperature range. This model allows accounting for the mechanical stabilization of the material for temperatures higher than T_m of the matrix. This phenomenon is ascribed to the formation of a percolating chitin whiskers network within the matrix. In addition, the formation of this entangled chitin whiskers network should most probably hinder the flow of PCL chains because it was observed that even at high temperature the dimensional stability of the sample is preserved. The hydrogen bonding responsible of the cohesion of the material at high temperature is yet weaker than in the case of cellulose. It is assumed by analogy with the poly-(S-co-BuA) matrix based composites that the chitin network is only partially formed below T_m . However, it is observed that, at temperature higher than T_m of PCL,

the hybrid model perfectly fits the experimental data. This model involves the experimental modulus of the whiskers film obtained from the evaporation of the whiskers aqueous suspension. Therefore, it seems that above T_m the whiskers interactions are completely restored.

Conclusion

Nanocomposite structures were prepared from poly-(caprolactone) as the matrix and chitin microcrystals, or whiskers, as the reinforcing phase. The chitin whiskers were obtained from tubes secreted by *Riftia*, a vestimentiferan worm. They were extracted from the raw material by a chemical treatment leading to purified chitin, followed by an acid hydrolysis and a mechanical treatment in order to obtain a colloidal aqueous suspension of chitin microcrystals. Individual chitin whiskers consisted of slender parallelepiped rods with an aspect ratio close to 120 and a diameter of 18 nm. A procedure was optimized to obtain a latex of poly-(caprolactone) using a copolymer of poly(ethylene oxide) and poly(propylene oxide) as the surfactant. A stable aqueous suspension with a solid fraction around 20 wt % containing spherical particles with an average diameter around 150 nm was prepared.

After mixing the two aqueous suspensions, nanocomposite films were obtained by either casting and evaporating or freeze-drying and hot-pressing the mixture. A significant reinforcing effect was observed at $T > T_g$ of the matrix. This effect can be described in this temperature range by a “hybrid” percolation model, equivalent to a mean-field model, considering only the nonpercolating fraction of microcrystals. The relatively weak interactions between whiskers, compared to cellulose, result in a partially formed microcrystals network within the rubbery matrix. At high temperature ($T > T_m$) and above 5 wt % whiskers, the network is allowed to restore resulting in the stabilization of the mechanical properties over a large temperature range.

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