Communications to the Editor

New Nanocomposite Materials: Microcrystalline Starch Reinforced Thermoplastic

Alain Dufresne,* Jean-Yves Cavaillé, and William Helbert

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

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Starch is a natural, renewable, biodegradable polysaccharide produced by many plants as a storage polymer. It usually has two major components and appears as a mixture of two glucosidic macromolecules very different in structure and properties: largely linear amylose of molecular weight between one thousand and one million, consisting of α-(1→4)-linked D-glucose and amylopectin, having the same backbone as amylose but with myriad α-(1→6)-linked branch points. Native starch occurs in the form of discrete and partially crystalline microscopic granules that are held together by an extended micellar network of associated molecules. It is well-known that native starch granules contain more or less concentric "growth rings" or shells or layers that are readily visible by optical or electron microscopy.[1] Molecular chains of amylose are almost perpendicular to these growth rings and to the surface of the granule.[2] This onion-like structure has been attributed to chemical differences between the layers,[3] differences in the density of deposition of molecules of starch,[4] and differences in crystallinity.[5] Acid treatment is needed to reveal the concentric lamellar structure of starch granules, and it has been shown that these lamellae, around 5000 Å thick, have subspacing of a few hundred angstroms.[4] The object of this treatment is 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.[6]

By analogy with previous works performed in our laboratory and which deal with cellulose microcrystal reinforced nanocomposite systems,[7−9] starch microcrystals, which are mainly formed of amylose, were processed by acid hydrolysis of the amorphous domains of potato starch granules obtained from Sigma (Ref. 9005-25-8). They occur as a finely divided white powder, insoluble in water. Starch granules (50 g) were first mixed with 1 L of 2.2 N hydrochloric acid (820 mL of water and 180 mL of 36% hydrochloric acid). The microcrystal suspension (5% w/w of solid component in water) was stored at 35 °C for 15 days. This time allows us to remove most of the amorphous zones without damaging the crystalline zones. The suspension was stirred every day in order to ensure the homogeneity of the suspension. It was then diluted with an equal volume of distilled water and washed by successive centrifugation (4000 trs/min) until acid free. At this step, crystals are broken into microcrystals, which change the refractive index of the solution so that the suspension becomes opaque. The dispersion of microcrystals was completed by a further 3 min ultrasonic treatment (B12 Branson sonifier). It was then kept in a refrigerator until used after adding sodium azoture as protectant against microorganisms. The solid fraction of this aqueous suspension was determined and was around 1.5%. A typical electron micrograph obtained from the dilute suspension of hydrolyzed starch is shown in Figure 1. It was achieved with a Philips CM200 electron microscope. An ultrasonic treatment prior to drying the suspension on the electron microscope grids considerably reduced the aggregation of the microcrystals. The suspension is constituted of starch fragments which have a homogeneous distribution in size. Each fragment is constituted of associated microcrystals which are not clearly identified. The microcrystals are a few tens of nanometers in diameter.

A latex obtained by the copolymerization of styrene (34% (w/w)) and butyl acrylate (64% (w/w)), and containing 1% acrylic acid and 1% acrylamide, was provided by Elf-Atochem (Serquigny, France). The aqueous suspension contained spherical particles with an average diameter around 150 nm and had a 50% (w/w) solid fraction. The glass−rubber transition temperature (T_g) of the copolymer is around 0 °C. The colloidal microcrystalline dispersion was mixed with the suspension of latex with various amounts in order to obtain composite films with a weight fraction of starch ranging from 0 to 60%. After stirring, the preparations were freeze-dried and hot-pressed. Hot-pressing was performed with a Carver Laboratory Press at 138 bar during 30 min at 90 °C.

Dynamic mechanical tests were performed on all the samples (pure matrix to 60% starch microcrystals filled composites). They were carried out with a spectrometer RSA2 from Rheometrics working in the tensile mode. The plot of log(E'/Pa) (storage tensile modulus) versus temperature at 1 Hz is displayed in Figure 2. The temperature was varied between 200 K and 380 K by steps of 3 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 2 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 elastic tensile modulus becomes lower and lower with temperature and the experimental setup fails to measure it.

At the filler concentrations considered, there are of the order of 200 000 to 400 000 cm^2 of filler surfaces/cm^3 of material. Therefore, neglecting the likely agglomeration of the filler, the interparticle separations are of the order of the particle diameters. This should have an effect on conformational properties and will certainly result in significant increases in the T_g of the

* To whom correspondence should be addressed (e-mail: dufresne@cermav.grenet.fr).

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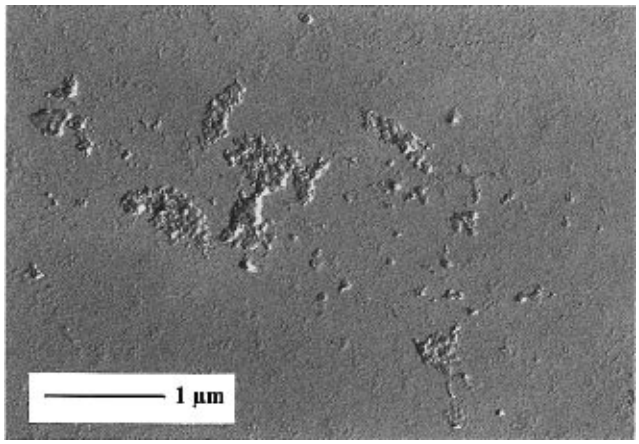

Figure 1. Transmission electron micrograph from a dilute suspension of hydrolyzed starch.

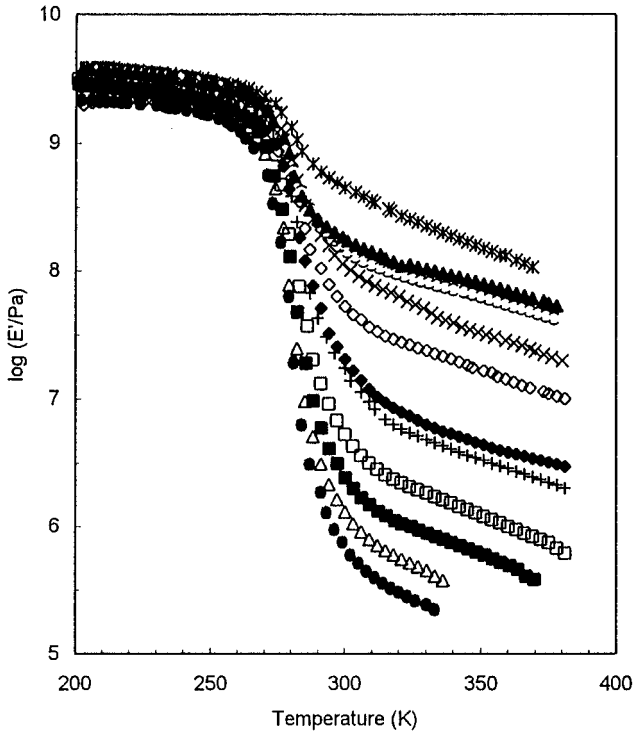

Figure 2. Storage tensile modulus E' versus temperature at 1 Hz for composites filled with 0% (●), 5% (△), 10% (■), 15% (□), 20% (+), 25% (◆), 30% (◇), 35% (×), 40% (○), 45% (▲), and 60% (*) (wt/wt) of starch microcrystals.

matrix phase. However, the first observation that should be emphasized is that the temperature position of the modulus drop associated with T_g remains almost constant whatever the concentration of filler may be. This anomalous behavior was observed elsewhere,[9−11] and based on the concept of interphase an explanation was given by Theocaris and Spathis.[12]

For temperatures below T_g, the composite modulus increases up to 4 GPa for the 60% filled material. However, the exact determination of the glassy modulus depends on the precise knowledge of the sample dimensions. In this case, at room temperature, the composite films were soft and it was very difficult to determine precisely the thickness of these samples. In order to minimize this effect, the samples were frozen in liquid nitrogen prior to any experiment to accurately measure their dimensions.

Above T_g a greater increase in the composite modulus is observed with increasing volume fraction of microcrystalline starch. For instance, the relaxed modulus at $T_g + 50$ °C (∼325 K) of a film containing only 30% starch is 100 times higher than that of the matrix. For the 60% microcrystalline cellulose filled composite, the relaxed modulus is increased by about a thousand.

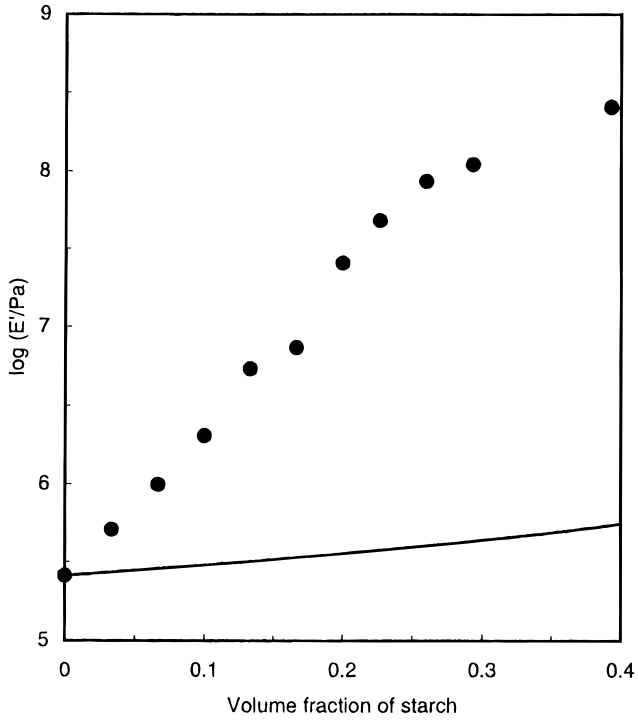

Figure 3. Evolution of the logarithm of the relaxed tensile modulus E' estimated at 325 K versus starch content. Filled circles represent the experimental data, and the solid line represents the calculated moduli using the generalized Kerner prediction (eq 1).

Figure 3 shows the evolution of the logarithm of the relaxed modulus (estimated at 325 K) versus the starch content. A wide range of theoretical formulas are available for predicting the mechanical behavior of composite materials in terms of microstructure and filler and matrix properties (see, for example, ref 13). Although these methods give satisfactory predictions of the mechanical properties for fiber reinforced polymers, particulary 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. More generally speaking, the macroscopic behavior of a heterogeneous material depends on three main parameters, namely (i) the behavior of each phase, (ii) the spatial arrangement of the phases, and (iii) the interface properties.[14−16]

For polymers containing nearly spherical particles, the Kerner equation[17] or the equivalent equation of Hashin and Shtrikman[18] can be used to calculate the modulus of a composite if there is some adhesion between the two components. For materials in which rigid spheres are dispersed in an elastomeric phase, the so-called regular systems, the Kerner equation can be greatly simplified. Halpin and Tsai[19−21] have shown that it can be put in a more general form. The Kerner equation can be generalized still further according to Lewis[22] and Nielsen[23] to

$$\frac{M}{M_1} = \frac{1 + AB\nu_2}{1 - B\Psi\nu_2} \tag{1}$$

where M is any modulus and the subscripts 1 and 2

refer to the continuous and dispersed phases, respectively. The constant A accounts for factors such as the geometry of the filler phase and the Poisson ratio of the matrix and is therefore strongly dependent on the morphology of the material. It is related to the generalized Einstein coefficient k_E by

$$A = k_E - 1 \tag{2}$$

The constant B takes into account the relative moduli of the filler and matrix phases. It is defined by

$$B = \frac{M_2/M_1 - 1}{M_2/M_1 + A} \tag{3}$$

Its value is therefore near 1.0 for fillers much more rigid than the polymer matrix. The factor ψ is a reduced concentration term dependent upon the maximum packing fraction v_m of the filler. It is generally given by the following function which fulfills the necessary boundary conditions

$$\psi = 1 + \left(\frac{1 - v_m}{v_m^2}\right) v_2 \tag{4}$$

The Kerner equation and its modifications were derived for spherical particles in a linearly elastic matrix. However, this does not imply that it may be applied only below T_g. Indeed, it is well-known that the behavior of polymers is not purely elastic, but in fact viscoelastic. For this reason, it is usual to modify the relationships for elasticity by introducing viscoelastic moduli, i.e. under their complex form $E^*(i\omega,T)$. However, at the temperature at which calculations will be performed (325 K), this is not necessary, because the storage modulus E' is about 10 times higher than the loss modulus E''. Therefore, the error made in taking E as E' is around 10%. The result for the calculation is shown in Figure 3 as a solid line, taking $v_m = 0.74$ (maximum packing fraction for a face-centered cubic packing type), $k_E = 2.50$ (value of the Einstein coefficient for dispersed spheres[20]), and $E'_1 = 0.26$ MPa (experimental data observed for the pure matrix at 325 K). It is obvious that the calculated moduli from this model do not fit the experimental moduli of the real systems. This means that the material cannot be considered as consisting of spherical particles dispersed in a continuous matrix.

The present study has dealt with the preparation technique of new nanocomposite materials consisting of microcrystals obtained from potato starch dispersed in a synthetic polymer matrix. These materials were processed by freeze-drying and molding a mixture of aqueous suspensions of starch microcrystals and thermoplastic polymer latex with a weight fraction of microcrystals ranging from 0 to 60%. It was found that this filler brings a great reinforcing effect, especially at temperatures higher than the T_g of the synthetic matrix. Starch can therefore be used as an economic and environmentally friendly particulate filler, and it can be useful for the processing of stiff small-size wares. Classical models for polymers containing nearly spherical particles based on a mean field approach do not allow us to explain this reinforcing effect. It is probably due to the morphology of these nanocomposite systems which will be discussed in the light of aggregates formation and percolation concepts in the near future. The processing of cheaper, reinforced, and fully biodegradable composites based on poly(hydroxybutyrate) is also being investigated at present, and the results will be published shortly.

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