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Improvement of Starch Film Performances Using Cellulose Microfibrils

Alain Dufresne* and Michel R. Vignon

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

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 a myriad of α-(1→6)-linked branch points. The most commercially important starch comes from corn, wheat, rice, potatoes, tapioca, and peas. 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.

Starch has received considerable attention during the past two decades as a biodegradable thermoplastic polymer and as a biodegradable particulate filler. Indeed, products from agricultural sources, such as starch, offer an attractive and cheap alternative in developing degradable materials. Starch is not truly thermoplastic as most synthetic polymers. However, it can be melted and made to flow at high temperatures under pressure and shear. If the mechanical shear becomes too high, then starch will degrade to form products with low molecular weight. Addition of water or other plasticizers enables starch to flow under milder conditions and reduces degradation considerably. However, the thermomechanical stability is strongly reduced by the addition of plasticizers.

By itself, starch is a poor choice as a replacement for any plastic. It is mostly water soluble, difficult to process, and brittle. In principle, some of the properties of starch can be significantly improved by blending it with synthetic polymers. Physical incorporation of granular starch or starch derivatives as a functional additive and filler into synthetic polymers during processing has been largely used since the first announcements of using starch in combination with synthetic polymer either as starch gel blends with ethylene acrylic acid copolymers by Westhoff et al.[1] or as particulate starch dispersions in polyolefins by Griffin.[2] More recently, increasing interest in developing new and inexpensive biodegradable materials has led to a substantive amount of research in polymer blends containing starch.[3−8] However, the mechanical properties of films are generally reduced by incorporation of starch. Like most of the polymers, starch is immiscible with most of the synthetic polymers at the molecular level. Grafting of synthetic polymers on starch is known to improve some of its properties, but although the grafting of starch with synthetic polymers has been known for

30 years, very few processes have led to full-scale commercialization.

Another way of using starch in the material field is the processing of starch microcrystals, which can be obtained as an aqueous suspension. This filler brings a great reinforcing effect to a polymeric matrix, as shown previously.[9]

In this work, an attempt was made to improve the thermomechanical properties and to decrease the water sensitivity of starch-based systems, preserving the biodegradability of the material. An alternative way to palliate these restrictions is the use of cellulose as a natural and biodegradable filler. Natural cellulose fibers are gaining attention as a reinforcing phase in thermoplastic matrixes. Its low density, a highly reduced wear of the processing machinery, and a relatively reactive surface may be mentioned as attractive properties, together with their abundance and low price. In addition, the recycling by combustion of cellulose composites is easier in comparison with inorganic filler systems. Nevertheless, such fibers are used only to a limited extent in industrial practice, which may be explained by difficulties in achieving acceptable dispersion levels.

Cellulose fibers are constituted of long threadlike bundles, called microfibrils, of cellulose molecules stabilized laterally by hydrogen bonds between hydroxyl groups of adjacent molecules. Cellulose microfibrils can also be found as intertwined microfibrils in parenchyma cell wall, in particular from potato pulp. They can be extracted from this biomass by a chemical treatment, leading to purified cellulose, followed by a mechanical treatment in order to obtain a homogeneous suspension due to the individualization of the microfibrils. This suspension has been used afterward to process composite materials with a high level of dispersion, by mixing with an aqueous suspension of gelatinized starch as matrix.

Potato pulp was purified according to the treatment displayed in Figure 1. After the removal of starch granules, the remaining pulp is traditionally pressed and dried to be marketed as cattle feed. This byproduct was provided, as pellets, by Avebe Co. (Haussimont, France). The pellets were hydrated into water and ground in a Waring blender apparatus for 10 min. The potato slurry was then poured on a 0.25 mm sieve and washed with water, to remove most of the remaining starch granules.

The alkali extraction with sodium hydroxide (NaOH) solution allowed the solubilization of pectins, residual starch, and hemicelluloses, which were then removed by filtration and finally rinsed with distilled water. The resulting insoluble residue was bleached with a sodium chlorite ($NaClO_2$) solution, as already described for sugar beet.[10,11] At this stage, the different cell walls are individualized, as shown in Figure 2A, but the microfibrils are still associated within the cell wall.

To extract and individualize the microfibrils from the cell walls, a mechanical treatment is required. The insoluble bleached cellulosic pulp was suspended in distilled water (2 wt %) and disintegrated for 15 min in a Waring blender. The suspension was then homogenized by 15 passes through a Manton-Gaulin laboratory homogenizer, described elsewhere by Dufresne et

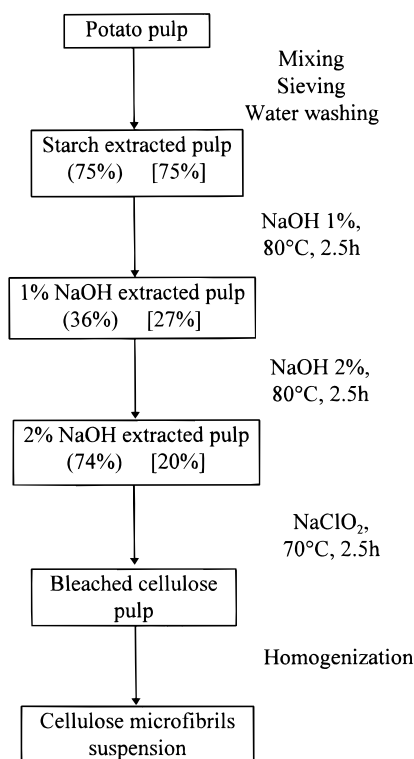* To whom correspondence should be addressed (e-mail: dufresne@cermav.cnrs.fr).

Figure 1. Chemical and mechanical treatments of potato pulp. Data in parentheses correspond to the yield of insoluble residue recovered at each step, and data in square brackets refer to the cumulative yield from starting material.

al.,[11] and operated at 500 bar at a temperature that was controlled at 90−95 °C. The effect of the homogenization treatment with the Manton-Gaulin apparatus is well displayed in Figure 2B, which shows a transmission electron micrograph (TEM) of individualized cellulose microfibril preparation. The resulting suspension is constituted of cellulose microfibrils that have a length around a few micrometers with a width ∼2−4 nm.

Composite materials were processed from potato cellulose microfibrils, potato starch as matrix, and glycerol as plasticizer. The cellulose microfibril suspension (3.3 wt %/wt) was first mixed with a solution of gelatinized starch (3.1 wt %/wt). The amount of each part was adjusted in order to obtain the required cellulose/starch content in the dry film. The cellulose filler content was varied from 0 to 40 wt %. Glycerol was added as plasticizer, and its content was expressed in percent of the total dry weight of cellulose + starch. The amount of glycerol was varied between 0 and 30 wt %. For example a film referred to as 10% cellulose, 90% starch, and 30% glycerol, contains respectively 0.2, 1.8, and 0.6 g of each component. These suspensions were homogenized with a T25 Ultra-turrax, but microbubbles were generated, which can be removed by pumping the suspension under vacuum prior to casting in a Teflon mold and storing at 37 °C.

Dynamic mechanical tests were carried out with a Rheometrics spectrometer RSA2 working in the tensile mode. This material being hygroscopic, all the samples were heat-treated in situ at 400 K for 10 min, immediately before experiments. Owing to the thickness of the samples (∼200 μm), this time is sufficient to remove most of the moisture. To maintain a constant water content during the measurements, the experiments were performed under nitrogen flow. The plot of $\log(E'/\text{Pa})$ (storage tensile modulus) versus temper-
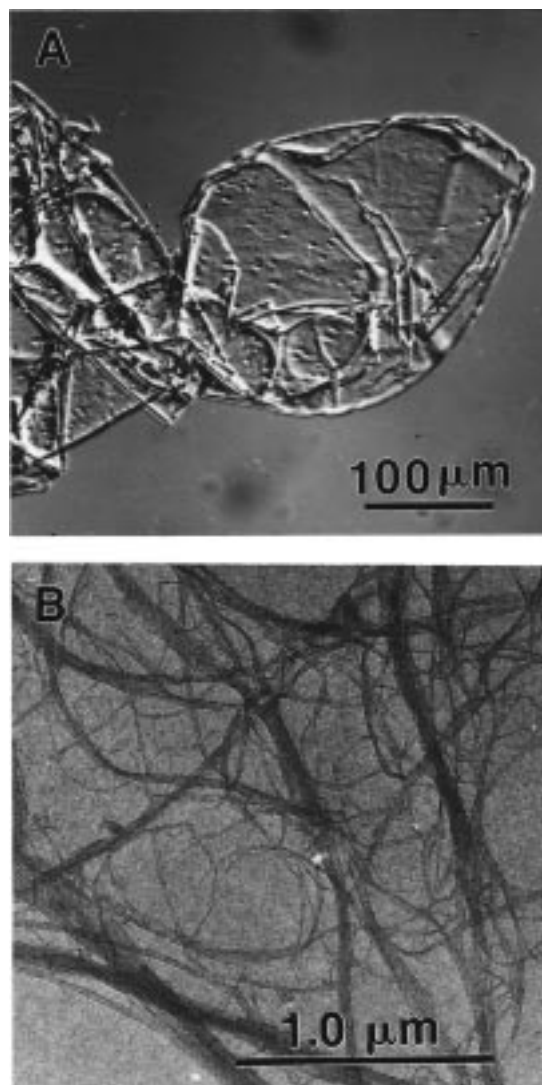

Figure 2. (A) Optical micrograph in Nomarski contrast showing individualized potato cell wall. (B) Transmission electron micrograph showing individualized cellulose microfibrils after high-pressure mechanical treatment.

ature at 1 Hz is displayed in Figure 3, for the pure starch film, the 30 wt % glycerol-plasticized film, and the plasticized system filled with 5 and 10 wt % cellulose microfibrils. It is clear that the pure starch does not exhibit any glass−rubber transition over the whole explored temperature range, contrarily to the plasticized system, which shows a modulus drop around 250 K. For temperatures below T_g, the starch/cellulose microfibril composite modulus does not vary significantly, with respect to the filler content. However, above T_g a great increase in the composite modulus is observed (around 2 decades), even with filler content as low as 5 wt %. The modulus drop of the 5 wt % filled composite at the glass−rubber transition of the plasticized starch matrix is strongly decreased compared to the unfilled plasticized matrix one and appears as an ill-defined relaxation process. It is worthy to note that this amount of cellulose in the plasticized system refers to the starch + cellulose content. In fact, this amount represents only 3.85 wt % of the total system starch + glycerol + cellulose. Moreover, the relaxed modulus remains practically constant up to 380 K. With increasing volume fraction of cellulose microfibrils (5−10 wt %), no evolution of the rubbery modulus is observed, but
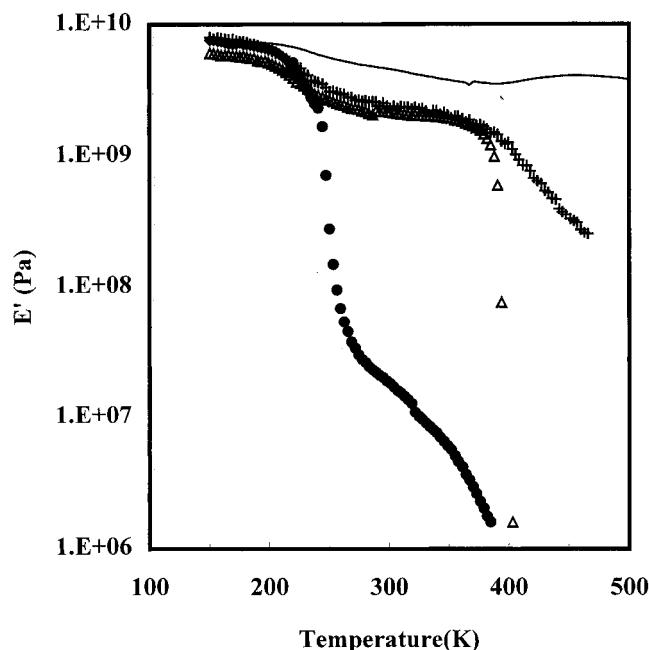
Figure 3. Storage tensile modulus E' versus temperature at 1 Hz for pure starch (—) and 30 wt % glycerol-plasticized starch filled with 0 wt % (●), 5 wt % (△), and 10 wt % (+) cellulose microfibrils.

the terminal zone occurs at a higher temperature and the modulus decrease associated with the macromolecules flow is more progressive. Therefore, the thermomechanical behavior of the plasticized starch film is strongly enhanced by addition of a few percent of cellulose microfibrils.

Although starch, with three hydroxyl groups per monomer, is a hygroscopic material, there are very few studies of water absorption by starch-based systems. The kinetics of water absorption was determined for various cellulose microfibril contents, using either unplasticized or 30 wt % glycerol-plasticized starch as matrix. In classical sorption kinetics experiments, the mass of sorbed penetrant is measured as a function of time. The specimens used were thin rectangular strips with dimensions of 10 mm × 10 mm × 0.2 mm. The films were supposed to be thin enough so that the molecular diffusion was considered to be one-dimensional. Samples were first dried overnight at 100 °C. After weighing, they were conditioned at 25 °C in a desiccator containing sodium sulfate in order to ensure a relative humidity (RH) ratio of 95%. They were then removed at specific intervals and gently blotted with tissue paper to remove the excess of water on the surface, and the water uptake was calculated as follows:

$$\text{water uptake (\%)} = \frac{M_t - M_0}{M_0} \times 100 \qquad (1)$$

where M_t and M_0 are the weights at time t and before exposure to 95% RH, respectively.

Two well-separated zones were displayed during water uptake experiments. At lower times (zone I: $t <$ 200 min), the kinetics of absorption is fast, whereas the long-time kinetics of absorption is slow and leads to a plateau (zone II). It was observed that the behavior was Fickian. The water uptake at equilibrium is plotted in Figure 4 versus composition for the unplasticized system and the 30 wt % glycerol-plasticized starch matrix as
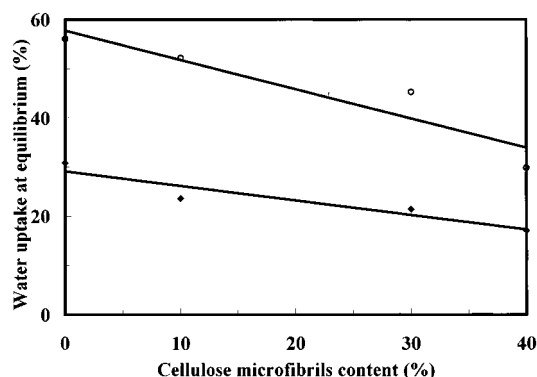

Figure 4. Water uptake at equilibrium versus cellulose content for 0% (◆) and 30% (○) glycerol plasticized starch matrix composites.

well. It is clear that the water uptake is much higher for the plasticized polymer than it is for the unplasticized one. For instance, the unfilled system absorbs around 55% water when it is plasticized, whereas the weight percentage increase at equilibrium is only 30% for pure starch. Therefore, the starch is all the more sensitive to the water uptake as the glycerol content is high. Moreover, increasing the cellulose content decreases the water uptake. The water uptake decreases linearly with the microfibril content. It reaches around 30% and less than 20% for the glycerol-plasticized and unplasticized starch matrix, respectively, filled with 40 wt % cellulose. These results are in agreement with the fact that starch is more hydrophilic than cellulose. However, the linear dependence of the water content at equilibrium versus cellulose composition shows that starch/cellulose interfaces do not influence the water uptake. This phenomenon allows us to envisage new applications to starch as a natural and biodegradable material, which were restricted up to now. Indeed, its mechanical behavior is strongly dependent on the moisture content, which is difficult to control.

The present study has dealt with a method of thermal stabilization and water uptake decrease of starch-based materials, preserving the aptitude of processing of plasticized materials and biodegradability. With this aim, cellulose microfibrils were used as a cheap and environmentally friendly filler. They were extracted from potato parenchyma cell wall by a chemical treatment leading to purified cellulose, followed by a mechanical treatment in order to obtain a homogeneous suspension due to the individualization of the microfibrils. This suspension was used afterward to process composite materials with a high level of dispersion, by mixing with an aqueous suspension of gelatinized potato starch as matrix. It is worthy to note that any agricultural residue can be used as a source to process cellulose microfibrils. It was found that a strong increase in the thermomechanical stability can be obtained with only a few percent of filler, whereas the water sensitivity linearly decreases with the cellulose microfibril content. Another problem that limits the use of starch as material is its brittleness due to the anarchical growth of amylose crystals with time. It was shown that crystallization of amylose can be oriented by the presence of cellulose.[12] A more detailed study on the mechanical behavior of these composite materials, depending on the glycerol, cellulose microfibrils, and relative humidity content will be published shortly.

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