Thermoplastic Starch−Waxy Maize Starch Nanocrystals Nanocomposites

Hélène Angellier,[†] Sonia Molina-Boisseau,[†] Patrice Dole,[‡] and Alain Dufresne*[,§]

Centre de Recherches sur les Macromolécules Végétales (CERMAV), ICMG-CNRS, affiliated with Université Joseph Fourier, BP 53, 38041 Grenoble Cedex 9, France, UMR INRA/FARE, BP 1039, 51687 Reims Cedex 2, France, and Ecole Française de Papeterie et des Industries Graphiques de Grenoble (EFPG-INPG), BP 65, 38402 St Martin d'Hères Cedex, France

Received October 21, 2005; Revised Manuscript Received November 28, 2005

Waxy maize starch nanocrystals obtained by hydrolysis of native granules were used as a reinforcing agent in a thermoplastic waxy maize starch matrix plasticized with glycerol. Compared to our previous studies on starch nanocrystals reinforced natural rubber (NR) [*Macromolecules* **2005**, *38*, 3783; **2005**, *38*, 9161], the present system presents two particularities: (i) thermoplastic starch is a polar matrix, contrarily to NR, and (ii) the chemical structures of the matrix and the filler are similar. The influence of the glycerol content, filler content, and aging on the reinforcing properties of waxy maize starch nanocrystals (tensile tests, DMA) and crystalline structure (X-ray diffraction) of materials were studied. It was shown that the reinforcing effect of starch nanocrystals can be attributed to strong filler/filler and filler/matrix interactions due to the establishment of hydrogen bonding. The presence of starch nanocrystals leads to a slowing down of the recrystallization of the matrix during aging in humid atmosphere.

Introduction

Among naturally biodegradable polymers using renewable resources, starch is probably the most promising material. It is a versatile biopolymer with immense potential, low price, and abundant availability, not depending on fossil sources, for use in the nonfood industries. The most commercially important sources of starch come 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. The semicrystalline structure of native starch is attributed to the short-chain fraction of amylopectin arranged as double helices and packed in small crystallites.[1,2]

Starch has received considerable attention during the past three decades as a biodegradable thermoplastic polymer or as biodegradable particulate filler. Starch is not truly thermoplastic, but it can be converted into a continuous polymeric entangled phase by mixing with enough water or nonaqueous plasticizer (generally polyols, such as glycerol). The resulting material can be manufactured using technology already developed for the production of synthetic plastics, thus representing a minor investment. However, the hydrophilic nature of thermoplastic starches makes them susceptible to moisture attack and resultant changes in dimensional stability and mechanical properties. In addition, retrogradation and crystallization of the mobile starch chains lead to an undesired change in thermomechanical properties.

One way for the development of new and inexpensive biodegradable materials is to blend destructured starch with synthetic[3−7] or natural polymers.[8−11] However, the mechanical properties of films are generally reduced by incorporation of starch. Like most polymers, starch is immiscible with most 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 alternative is the reinforcement of thermoplastic starch with mineral or cellulosic fillers. Mineral fillers as talc,[12] kaolin,[13] and clay[14−17] hold polar groups allowing an easy association with thermoplastic starch. The use of cellulosic fillers as reinforcing agent in thermoplastic starch leads to preserve the biodegradability of thermoplastic starch. Studies have been carried out on fibers from different botanical sources,[18−20] microfibrilles[21,22] and whiskers.[23,24] In the case of the use of tunicin whiskers,[24] it was shown that the reinforcing effect was very low due to the migration of glycerol at the thermoplastic starch/tunicin whiskers interface. Contact angle measurements clearly showed that both glycerol and water displayed a higher affinity for the cellulose whisker surface than for amylopectin.

In this context, waxy maize starch nanocrystals, obtained by hydrolysis of native granules, have been used as a reinforcing agent in thermoplastic starch. Waxy maize starch nanocrystals have shown interesting reinforcing and barrier properties in natural rubber.[25,26] Comparatively to natural rubber, this system presents two particularities: (i) thermoplastic starch is a polar matrix and (ii) the chemical structures of the matrix and the filler are similar.

The first objective of the present work was to study the influence of glycerol on the reinforcing properties of waxy maize starch nanocrystals. The second objective was to study the influence of filler content on mechanical and structural properties of the composite films. Finally, it was important to check if the reinforcing effect of starch nanocrystals was still valid after retrogradation of the matrix. Thereby, the influence of the presence of waxy maize starch nanocrystals on the aging of thermoplastic starch has been briefly studied.

* Corresponding author. E-mail: Alain.Dufresne@efpg.inpg.fr.
[†] ICMG-CNRS.
[‡] UMR INRA/FARE.
[§] EFPG-INPG.

10.1021/bm050797s CCC: $33.50
Published on Web 01/17/2006

Mechanical properties were investigated by tensile tests and dynamic mechanical analysis. The structure of the materials has been analyzed using X-ray diffraction.

Experimental Section

Waxy Maize Starch Nanocrystals. The preparation of waxy maize starch nanocrystals (labeled WN) by sulfuric acid (H_2SO_4) hydrolysis of native waxy maize starch granules (Waxylis, Roquette S. A., Lestrem, France) was optimized and has been described previously.[27] Such nanocrystals are generally observed in the form of aggregates having an average size around 4.4 μm, as measured by laser granulometry.[27]

Film Processing. Thermoplastic starch was processed by casting, from the mixing of native waxy maize starch granules, glycerol (Aldrich, purity ≥ 99%) and distilled water. Waxy maize starch contains more than 99 wt % of amylopectin macromolecules. A quantity of 5.5 g of a mixture of starch and glycerol was first dispersed in 35 g of distilled water. Then, the mixture was heated at 150 °C for 10 min in a reactor, under pressure and mechanical stirring. The reactor was cooled with water. When the temperature of gelatinized starch reached 40 °C, the suspension of waxy maize starch nanocrystals was added in desired quantities. After that, the mixture was stirred for 10 min before being cast in a Teflon mold. Finally, the mixture was evaporated in a nonventilated oven at 40 °C for 24 h. It was necessary to decrease the temperature of gelatinized starch before adding waxy maize starch nanocrystals, otherwise starch nanocrystals also gelatinize. Solid films having a thickness of about 250 μm were obtained. Composite films were stored at 43% RH (K_2CO_3 saturated solution) for one week before being tested (time 0). In the case of accelerated aging, samples were stored in 88% RH atmosphere (KCl saturated solution) for one week (time 1) or two weeks (time 2). After aging in a humid atmosphere, samples were re-stored at 43% RH for a few days before being tested.

The content of glycerol was relative to the matrix. A glycerol weight fraction of 20 wt % means that 1.1 g of glycerol was mixed with 4.4 g of starch granules and 35 g of water. The filler weight content was relative to the total mass of starch and glycerol. The composition of the different thermoplastic starch/waxy maize starch nanocrystals films is detailed in Table 1.

Dynamic Mechanical Analysis (DMA). Dynamic mechanical tests were carried out using a Rheometrics RSA2 spectrometer working in the tensile mode. Test conditions were chosen in such a way that the measurements obey the laws of linear viscoelasticity (the strain equaled 5×10^{-4}). The specimen was a thin rectangular strip ($30 \times 6 \times 0.25$ mm^3). The setup measured the complex tensile modulus E^*, i.e., the storage component E' and the loss component E''. The ratio between the two components, $\tan \delta = E''/E'$, was also determined. Measurements were performed at 1 Hz, and the temperature was varied by steps of 3 °C between −150 and +200 °C.

Tensile Tests. The nonlinear mechanical behavior of starch nanocrystals filled composites was analyzed using an Instron 4301 testing machine working in tensile mode. Dumbbell shaped specimens 4 mm wide, 7 mm long (L_0) and about 1 mm thick were used. The initial gap between pneumatic jaws was adjusted to 10 mm. Force (F) vs elongation (e) curves were obtained for each sample at room temperature and with a cross-head speed of 10 mm·min^{-1} (initial strain rate $d\epsilon/dt = 2.4 \times 10^{-2}$ s^{-1}).

The nominal strain (ϵ_{nom}) and the nominal stress (σ_{nom}) were calculated by $\epsilon_{nom} = e/L_0$ and $\sigma_{nom} = F/S_0$, respectively, where S_0 is the initial cross-section. Stress versus strain curves were plotted, and the Young's modulus (E) was measured from the slope of the low strain region.

Ultimate mechanical properties were also characterized. The stress at break (σ_b) and the elongation at break (ϵ_b) were reported for each sample. Mechanical tensile data were averaged over at least five specimens.

X-ray Diffraction. Films were submitted to X-ray radiation for 2 h at room temperature and humidity (about 56% RH) using a Philips PW3830 generator operating at the Ni-filtered Cu Kα radiation wavelength ($\lambda = 1.542$ Å). Diffraction patterns were recorded on Fuji imaging plates read by a Fuji BAS 1800 II Phospho-Imager. The profiles of the diffraction patterns were obtained using the Scion Image software.

Table 1. Composition and Codification of Waxy Maize Starch Nanocrystals/Thermoplastic Starch Composite Films

sample	glycerol content (wt %)	filler content (wt %)	glycerol (g)	starch granules (g)	starch nanocrystals (g)
TPS20	20	0	1.1	4.4	0
TPS20-5	20	5	1.05	4.18	0.28
TPS20-10	20	10	0.99	3.96	0.55
TPS20-15	20	15	0.94	3.74	0.82
TPS25	25	0	1.38	4.12	0
TPS25-2	25	2	1.35	4.04	0.11
TPS25-5	25	5	1.31	3.92	0.28
TPS25-10	25	10	1.24	3.71	0.55
TPS25-15	25	15	1.17	3.51	0.82
TPS30	30	0	1.65	3.85	0
TPS30-5	30	5	1.57	3.66	0.28
TPS30-10	30	10	1.49	3.47	0.55
TPS30-15	30	15	1.40	3.28	0.82

Table 2. Tensile Properties (Nominal Values) of Thermoplastic Starch Films Plasticized with Different Ratios of Glycerol: Young Modulus (E) and Stress (σ_b) and Strain (ϵ_b) at Break

sample	E (MPa)	σ_b (MPa)	ϵ_b (%)
TPS20	49	2.4	182
TPS25	11	1.02	297
TPS30	0.46	0.26	551

Results and Discussion

Influence of Glycerol Content on the Mechanical Properties of Thermoplastic Starch-Waxy Maize Starch Nanocrystals Composites. Three glycerol contents were taken into account for the study, viz., 20, 25, and 30 wt % (Tables 1 and 2). Some tests have been performed with lower glycerol contents (12 and 17 wt %), but when adding starch nanocrystals, films became brittle and difficult to characterize. The mechanical properties of films stored for one week at 43% RH were analyzed by tensile tests and DMA.

First, experiments were conducted on unfilled matrixes. Tensile tests showed a different behavior depending on the glycerol content (Figure 1). Tensile properties are reported in Table 2. We observe that the increase in glycerol content leads to a more ductile behavior: the strain at break increases, whereas the stress at break decreases. Similar results have already been shown for potato starch,[28] amylose isolated from potato starch and waxy maize starch,[29] and for other polyols such as sorbitol.[30] It is a typical behavior of a ductile polymer/plasticizer system.[28] Glycerol plays the role of internal lubricant, enhancing the softening and mobility of the noncrystallized phase at room temperature.

The influence of glycerol on the viscoelastic properties has been studied by DMA. Figure 2a presents the isochronal evolution (1 Hz) of the relative logarithm of the storage modulus, defined as the ratio between the actual modulus and the modulus in the glassy state. We have chosen this representation in order to lift the problems of measurement of sample dimensions. At low temperatures, no significant variation of E' is observed. For

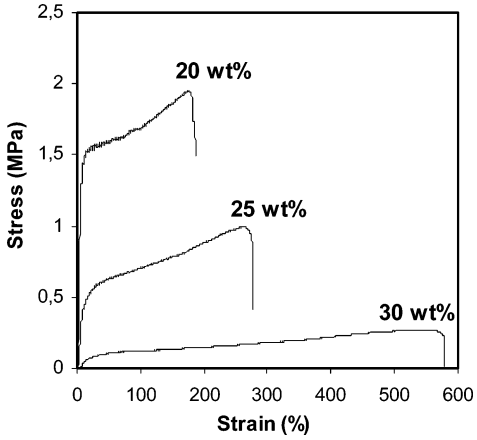

Figure 1. Typical curves of stress (MPa) versus strain (%) for thermoplastic starch plasticized with different glycerol contents and stored at 43% RH for one week. Glycerol contents are indicated in the Figure.

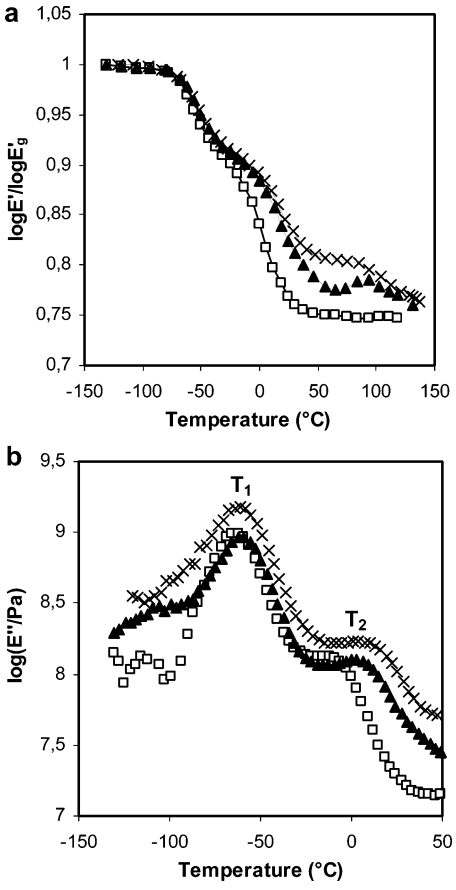

Figure 2. Evolution of (a) log E'/log E'_g where E'_g is the storage modulus of materials in the glassy state, and (b) log E'' versus temperature at 1 Hz for unfilled thermoplastic starch plasticized with 20 wt % (×), 25 wt % (▲), and 30 wt % (□) glycerol, and stored at 43% RH for one week (time 0).

temperatures higher than −75 °C, we observe a two-step storage modulus drop. This has been already reported by other authors.[15,24,28] Here, we see that the increase in glycerol content leads to a decrease of the elastic modulus of the materials, corroborating the results of tensile tests. The rubbery storage modulus values estimated at 50 °C (E'_{50}) are collected in Table 3.

The two-step modulus drop is associated with two concomitant successive maxima of the loss modulus E'', around −60 (T_1) and 0 °C (T_2) (Figure 2b). Temperatures and intensities

Table 3. Storage Modulus at 50 °C (E'_{50}) and at T_2 + 50 °C (E'_{T_2+50}), Temperatures (T_1 and T_2), and Magnitude (I_1 and I_2) of α_1 and α_2 Relaxations Measured from the Curve of log(E'') and tan δ Respectively, for Thermoplastic Waxy Maize Starch Plasticized with 20, 25, and 30 wt % Glycerol

sample	E'_{50} (MPa)	E'_{T_2+50} (MPa)	T_1 (°C)	T_2 (°C)	I_1	I_2
TPS20	170	158	−61.2	10	0.225	0.298
TPS25	61	57	−62.2	3	0.243	0.392
TPS30	31	33	−62.2	−12.4	0.250	0.461

of the two relaxations α_1 and α_2 were measured from the curve of the logarithm of E'' and tan δ versus temperature, respectively, and are collected in Table 3. We show that T_1 does not depend on the glycerol content, whereas T_2 decreases when the glycerol content increases. Table 3 also reports the rubbery modulus estimated at T_2 + 50 °C (E'_{T_2+50}). These values are close to E'_{50} because E' roughly stabilizes in this temperature range. We also observe that intensities I_1 and I_2 increase when the glycerol content increases. This increase is more significant for α_2 relaxation because of the more pronounced drop of storage modulus.

Previous studies have shown that unplasticized thermoplastic starch presents a unique relaxation α around 50 °C.[15,28] When starch is plasticized with glycerol, it has been shown that the plasticized starch/glycerol system is heterogeneous. A phase separation results in glycerol-rich domains (α_1 relaxation) and starch-rich domains (α_2 relaxation).[15,24,31] For plasticized waxy maize starch and since the magnitude of the second drop of E', associated with α_2 relaxation, was more significant than for α_1, it was deduced that glycerol-rich domains are included in a continuous amylopectin-rich phase.[24]

The influence of glycerol on the position and intensity of both relaxations is the same as the one of water.[23,24] The plasticizer content does not influence the relaxation of plasticizer-rich domains (for the given range of concentrations). However, an increase of the plasticizer content leads to a higher mobility of amylopectin chains and thereby to their relaxation at lower temperatures.

Second, the influence of the glycerol content on the reinforcing effect of waxy maize starch nanocrystals has been investigated using tensile tests performed at room temperature. Rigorously, the reinforcing effect of given filler should be studied at a constant temperature value with respect to T_g (T_g + ΔT = constant). In our case, the glass transition temperature varies depending on the composition of the sample, whereas the temperature at which the tensile tests were performed remains constant. Thereby, data shall be interpreted with precaution. All of the results are collected in Table 4. No modulus value is reported for sample TPS20-15. These materials were very brittle, and the determination of the modulus was very hazardous because of the small number of experimental points and the sigmoid shape of the stress−strain curve. We show that the relative reinforcing effect of waxy maize starch nanocrystals is more significant when the glycerol content is high. The addition of 10 wt % starch nanocrystals allows increasing the stress at break and the Young modulus of thermoplastic starch plasticized with 30 wt % glycerol by 10 and 54, respectively, whereas these values are increased by only 6 and 7 for materials plasticized with 20 wt % glycerol. Furthermore, the decrease of the strain at break is lower in the case of highly plasticized systems.

The effect of the introduction of rigid and crystalline particles is more significant in systems containing a high plasticizer

Table 4. Mechanical Properties of Thermoplastic Starch Reinforced with 5, 10, and 15 wt % Waxy Maize Starch Nanocrystals and Plasticized with 20, 25, and 30 wt % Glycerol, at Time 0 (Nonaged Materials): Young Modulus (E) and Stress (σ_b) and Strain (ϵ_b) at Break

sample	E (MPa)	σ_b (MPa)	ϵ_b (%)
TPS20	49 ± 12	2.4 ± 0.5	182 ± 52
TPS20-5	298 ± 54	13.2 ± 3.3	8.2 ± 1.5
TPS20-10	333 ± 54	13.6 ± 1.6	8.6 ± 1.5
TPS20-15	-	7.6 ± 2.9	4.5 ± 1.4
TPS25	11 ± 3.6	1.0 ± 0.1	297 ± 64
TPS25-2	75 ± 17	3.3 ± 0.4	122 ± 31
TPS25-5	80 ± 3.5	3.6 ± 0.4	97 ± 18
TPS25-10	82 ± 30	4.2 ± 1	57 ± 21
TPS25-15	241 ± 46	9.8 ±1.4	20 ± 8
TPS30	0.46 ± 0.3	0.26 ± 0.1	551 ± 80
TPS30-5	3.4 ± 1.1	1.3 ± 0.5	236 ± 40
TPS30-10	25 ± 14	2.7 ± 0.5	89 ± 21
TPS30-15	44 ± 5	3.6 ± 0.3	82 ± 13

content, i.e., more amorphous and displaying a lower T_g value. However, it is important to keep in mind the true properties of materials. On the first hand, we show that the Young modulus of thermoplastic starch plasticized with 30 wt % glycerol and reinforced with 15 wt % starch nanocrystals (TPS30-15) is lower than the one of the unfilled matrix plasticized with only 20 wt % glycerol (TPS20) (Table 4). On the other hand, we note that the addition of starch nanocrystals in systems containing a low plasticizer content leads to brittle materials and, therefore, to the decline of the mechanical properties (see TPS20-15 for example). Therefore, a good compromise for the following study is a glycerol content of 25 wt %.

Influence of the Filler Content on the Structural and Mechanical Properties of Thermoplastic Starch/Waxy Maize Starch Nanocrystals Composites. The influence of the filler content on the structural and mechanical properties of nanocomposite materials has been studied for films plasticized with 25 wt % glycerol. Four filler contents have been considered, viz., 2, 5, 10, and 15 wt %. The use of higher filler contents leads to brittle materials, difficult to manipulate and characterize. An eventual percolation phenomenon, as shown in natural rubber around 6.7 vol % (i.e., 10 wt %),[25,26] will be difficult to evidence.

Structural properties of non aged materials (one week at 43% RH) have been analyzed by X-ray diffraction (Figure 3). As native waxy maize starch granules, waxy maize starch nanocrystals present the A-type crystalline structure (WN) characterized by two peaks at $2\theta = 10.1°$ and 11.5°, a strong intensity peak at 15.3°, a double peak at 17.1° and 18.2°, and a last strong intensity peak at 23.5°.[32] Thermoplastic starch is characterized by a broad hump centered on 19°, revealing that the material is fully amorphous (TSP25). This shows that the crystalline structure of native starch granules has disappeared during the processing by casting. When adding starch nanocrystals in thermoplastic starch, we observe the apparition of the typical peaks of A-type. The magnitude of the peaks increases when the filler content increases, revealing that the crystalline structure and probably the crystallinity of starch nanocrystals are preserved during the processing method described in the experimental part.

The diffraction profiles of the various composite films do not result from a simple mixing rule of the diffractograms of the two pure components, i.e., $I = w_{WN}I_{WN} + (1 - w_{WN})I_{TPS}$ where I, I_{WN}, and I_{TPS} are the diffracted intensity at each angle for a given composite film, starch nanocrystals, and thermoplastic starch, respectively, and w_{WN} is the weight content of

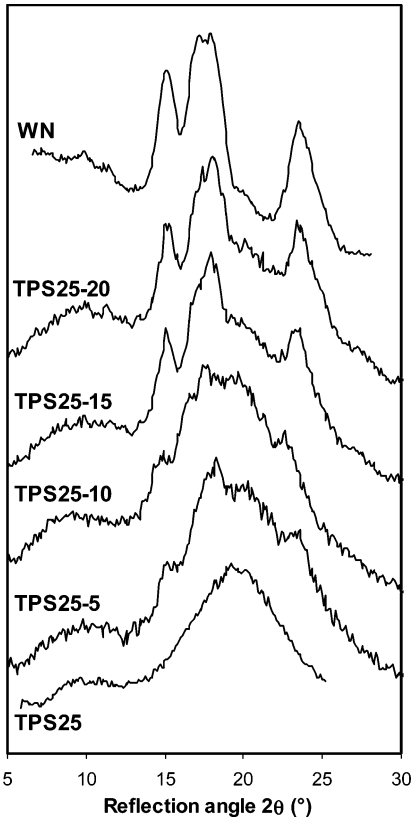

Figure 3. X-ray diffraction patterns of waxy maize starch nanocrystals (WN) and of thermoplastic starch plasticized with 25 wt % glycerol and filled with different weight fractions of waxy maize starch nanocrystals.

starch nanocrystals. For experimental data, the intensity of peaks characteristic of A-type is stronger than according to the calculation. Qualitatively, it was deduced that the degree of crystallinity of the composite films is higher than the one brought by the filler. It is probable that crystallization occurs at the interface between filler and matrix.

The mechanical properties of thermoplastic starch plasticized with 25 wt % glycerol and filled with starch nanocrystals have been investigated by tensile tests performed at room temperature and dynamic mechanical analysis. The typical curves of stress versus strain for materials filled with 5, 10, and 15 wt % nanocrystals and stored at 43% RH for one week are presented in Figure 4. The unfilled matrix (TPS25) is a viscoelastic material, characterized by a low Young modulus (11 MPa) and a low stress at break (1 MPa). Because of the high degree of polymerization of amylopectin, macromolecules are able to entangle, leading to a high strain at break ($\epsilon_b = 297\%$). As expected, the addition of nanocrystals allows the Young modulus and the stress at break to be increased significantly but leads to a drastic decrease of the strain at break (Table 4).

The reinforcing effect of starch nanocrystals in thermoplastic starch is difficult to compare with other fillers because of the various botanical sources of starch, the type and the plasticizer content, and the processing method which differs according to the authors. Furthermore, mechanical properties strongly depend on the humidity of the atmosphere during the processing step[34] and experimental testing conditions, such as strain rate and size of the samples. However, it is interesting to compare the reinforcing effect of starch nanocrystals to those of tunicin whiskers, because of the organic nature of both fillers and similar nature of the matrix material used, viz., glycerol plasticized waxy maize starch. The reinforcing effect of waxy maize starch

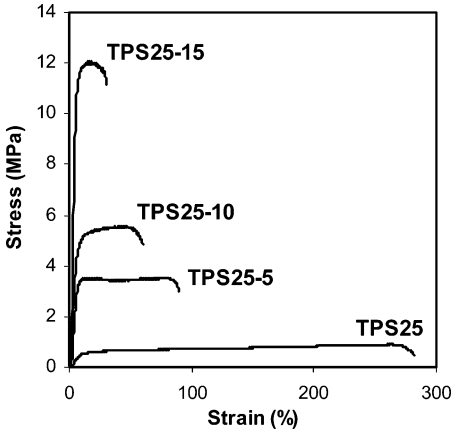

Figure 4. Typical curves of stress (MPa) versus strain (%) for waxy maize thermoplastic starch plasticized with 25 wt % glycerol/waxy maize starch nanocrystals composite films stored at 43% RH for one week.

Table 5. Comparison of the Relative Mechanical Properties of Natural Rubber (NR) and Nonaged Thermoplastic Starch (TPS25) Reinforced with 5, 10, and 15 wt % Waxy Maize Starch Nanocrystals (WN): Relative Young Modulus (E_R) and Relative Stress (σ_{bR}) and Stain (ϵ_{bR}) at Break

sample	E_R	σ_{bR}	ϵ_{bR}
NR-5	2.5	2.0	0.9
NR-10	7.5	3.0	0.9
NR-15	19.2	3.1	0.8
TPS25-5	7.3	3.6	0.3
TPS25-10	7.5	4.2	0.2
TPS25-15	22	9.8	0.07

nanocrystals in thermoplastic starch is higher than the one of tunicin whiskers.[24] This result is surprising since tunicin whiskers appear as rodlike nanoparticles with a high aspect ratio that should result in a higher reinforcing capability than nanoplatelet-like starch particles. Anglès and Dufresne[24] have shown, using contact angle measurements, that glycerol and water had a greater affinity with cellulose than with thermoplastic starch. It resulted in a migration of both plasticizers toward the cellulose/thermoplastic starch interface, leading to the formation of a soft interphase around the filler and inhibition of the percolating phenomenon between cellulose whiskers and, thereby, to the absence of reinforcing effect of tunicin whiskers in a thermoplastic starch. In our case, since the chemical nature of the filler and the matrix is the same, glycerol and water should display about the same affinity for both components. For this reason, we assume that the migration of the glycerol toward the interface is limited, making possible the establishment of direct strong interactions between starch nanocrystals.

It is also interesting to compare the reinforcing effect of starch nanocrystals in thermoplastic starch plasticized with 25 wt % glycerol to the one reported for the same filler in natural rubber (NR).[26] Table 5 presents the relative properties which were calculated as the ratio between the value observed for the nanocomposite and the one observed for the unfilled matrix. We note that the reinforcing effect of starch nanocrystals is more significant in thermoplastic starch than in natural rubber. Relative modulus and relative strength are both higher using thermoplastic starch as matrix whereas the relative elongation at break is significantly lower. The higher reinforcing effect observed with thermoplastic starch becomes more significant considering the difference between the room temperature at which tests were performed and the glass transition temperature of the materials. Indeed it is higher in the case of natural rubber

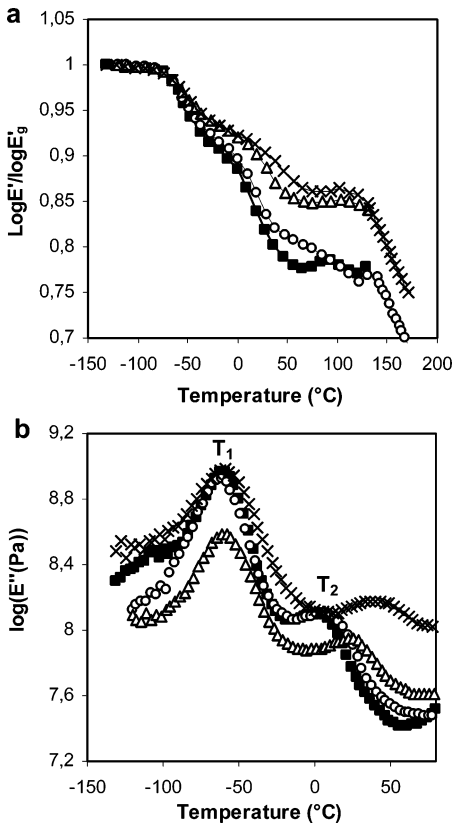

Figure 5. Evolution of (a) log E'/log E'_g where E'_g is the storage modulus of materials in the glassy state, and (b) log E'' versus temperature at 1 Hz for thermoplastic starch plasticized with 25 wt % glycerol, reinforced with 0 (■), 5 (○), 10 (△), and 15 wt % (×) starch nanocrystals and stored at 43% RH for one week (time 0).

($T_g = -60$ °C for NR) than in the case of thermoplastic starch that displays two T_gs associated with glycerol-rich and starch-rich domains around −62 and +3 °C as measured from DMA experiments (Table 3). In addition, the high-temperature relaxation process shifts toward higher temperatures when the starch nanocrystals content increases as it will be evidenced later. Concerning the lower values of relative elongation at break for thermoplastic starch filled materials, the comparison is more ambiguous since it could be ascribed to the higher T_g of these systems compared to NR and/or to the possible stronger filler/matrix adhesion. Weak filler/matrix adhesion was reported for starch nanocrystals reinforced NR,[25] whereas it is expected to be stronger when using thermoplastic starch as a matrix material.

For NR-based composites, it was shown that a percolating network may establish between starch nanocrystals during the evaporation step of the latex of natural rubber due to hydrogen bonds.[25,26] In the case of thermoplastic starch-based materials, we have shown previously that the establishment of such interactions between starch nanocrystals may also be possible. Furthermore, we assume that strong interactions may also appear between the filler and the chains of amylopectin. These filler/matrix interactions may explain at least partially the drastic decrease of the strain at break when adding starch nanocrystals in thermoplastic starch. It is also possible that the reinforcing effect of starch nanocrystals in thermoplastic starch may be favored by an eventual crystallization at the filler/matrix interface.

Dynamic mechanical analysis has been performed on samples stored at 43% RH for one week (nonaged). Figure 5a presents the evolution of the relative logarithm of the storage modulus versus temperature. We observe that the magnitude of the two-

Table 6. Storage Modulus at 50 °C Calculated by Assuming that $E'_g = 1$ GPa for All of the Samples (E'_{50}) and Temperatures (T_1 and T_2) and Magnitude (I_1 and I_2) of α_1 and α_2 Relaxations for Thermoplastic Waxy Maize Starch Plasticized with 25 wt % Glycerol and Reinforced with 5, 10, and 15 wt % Starch Nanocrystals

sample	E'_{50} (MPa)	T_1 (°C)	T_2 (°C)	I_1	I_2
TPS25	11.6	−62.2	3	0.243	0.392
TPS25-5	19.5	−61.3	4−7	0.197	0.361
TPS25-10	55	−61.2	25.4	0.171	0.267
TPS25-15	83	−59.3	39.8	0.156	0.232

step modulus drop is reduced when filling thermoplastic starch with waxy maize starch nanocrystals. Since the exact determination of the glassy modulus depends on the precise knowledge of the samples dimensions which are difficult to precisely set at room temperature before measurement, the elastic modulus at 50 °C (E'_{50}) of composites has been here calculated assuming that the storage modulus in the glassy state, E'_g, equals 1 GPa for all the samples. Thereby, E'_{50} was obtained by the following equation: $E'_{50} = 10^{9x}$ where x is the value of $\log E'/\log E'_g$ at 50 °C (Table 6). Because the elastic modulus is almost constant in the temperature range 50−100 °C, the error made by measuring E' at a constant temperature whereas T_g varies is low.

Both α_1 and α_2 relaxations are still observed in Figure 5b. When the filler content increases, the temperature position of the low-temperature relaxation, T_1, remains roughly constant whereas the temperature position of α_2, T_2, increases significantly. Both relaxation magnitudes, I_1 and I_2, decrease at the same time (Table 6).

The decrease in I_1 and I_2 is logical for two reasons. (i) It is directly linked to the diminution of the magnitude of the two-step modulus drop (Figure 5a). (ii) When the filler content increases, the proportions in both glycerol and amylopectin comparatively to the total sample decrease. This leads to a diminution of the number of glycerol molecules and amylopectin chains that participate to α_1 and α_2 relaxations. The fact that T_1 does not vary means that starch nanocrystals do not disrupt the mobility, i.e., the relaxation, of glycerol-rich domains. For thermoplastic potato starch plasticized by more than 30 wt % glycerol and reinforced with clay, it was reported that T_1 decreases continuously when increasing the filler content.[14] The increase of the relaxation temperature of amylopectin-rich domains (T_2) when adding starch nanocrystals is opposite to what was observed in the case of clay reinforcement.[14] It means that starch nanocrystals reduce the mobility of amylopectin chains. Starch nanocrystals have the opposite effect than those of glycerol (Table 3). The increase of T_2 may be due to a direct contact between starch nanocrystals and amylopectin-rich domains. This would confirm the presence of interactions between the filler and the matrix due to hydrogen bonding forces. The fact that the value of T_2 is close to room temperature for TPS25-10 and TPS25-15 could explain the brittleness of the samples reported from tensile tests.

Influence of Filler on the Aging of Thermoplastic Starch/Waxy Maize Starch Nanocrystals Composites. The evolution of the crystalline structure of unfilled thermoplastic waxy maize starch upon aging has been studied by X-ray diffraction (Figure 6a). The diffraction pattern at room temperature of the unfilled and nonaged matrix (storage for one week at 43% RH) is

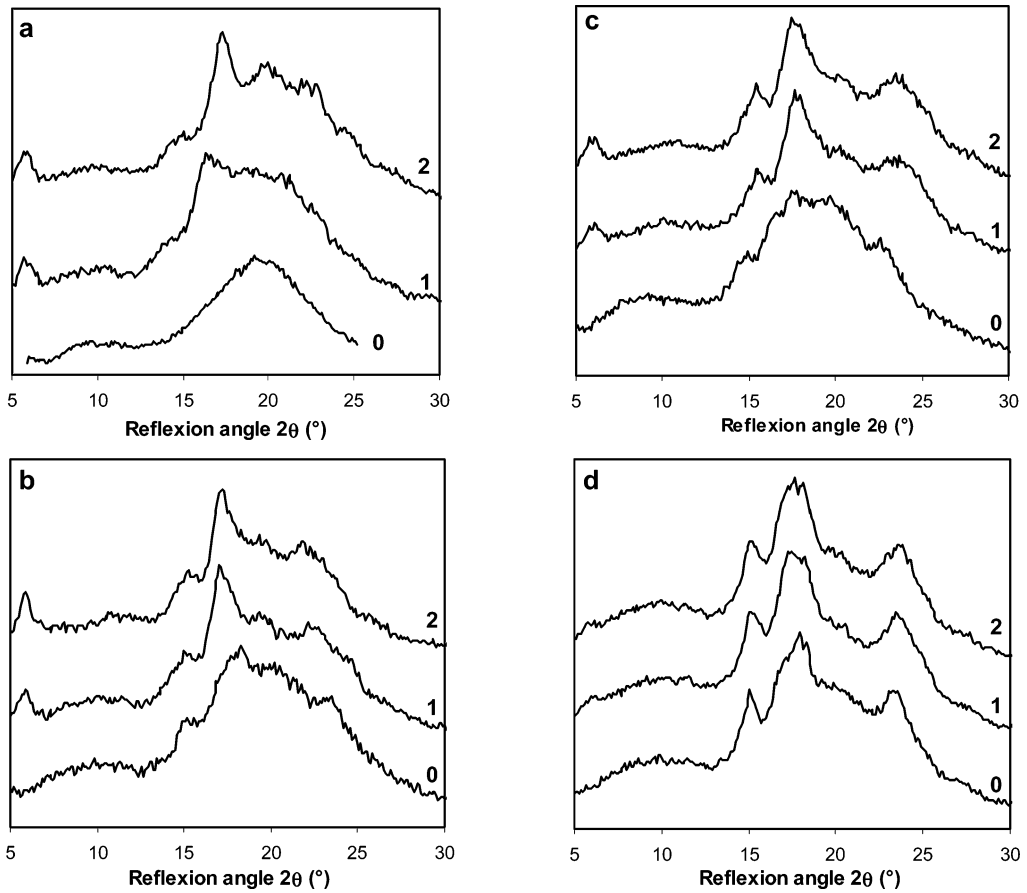

Figure 6. X-ray diffraction patterns of thermoplastic waxy maize starch plasticized with 25 wt % glycerol: (a) unfilled matrix, and composites filled with (b) 5 wt %, (c) 10 wt %, and (d) 15 wt % waxy maize starch nanocrystals, for aging times 0 (1 week at 43% RH), 1 (1 week at 88% RH), and 2 (2 weeks at 88% RH).

characterized by a broad hump centered on 19°, revealing that the material is completely amorphous, as already mentioned. During the storage in humid atmosphere (88% RH), we observe the apparition of a B-type amylose allomorph diffractogramm.[32] The B-type is notably characterized by strong magnitude peaks at 5.6° and 17.1°. This evolution is known for all starch gels.[32] As for potato starch films, the intensity of the peaks increases, whereas their width decreases during aging in humid atmosphere, revealing that both the crystallinity and the size of the crystallites increase. The final degree of crystallinity depends on the capability of the chains to form crystallites and on the molecular mobility during re-crystallization.[34]

Two types of reorganization of amylopectin may occur. Above the glass transition temperature of the material, amylopectin can form inter- and intramolecular double helices. The intermolecular double helices are formed between two lateral segments of two different molecules of amylopectin. This type of crystallization may be responsible for the change in the crystalline type and the evolution of crystallinity during time.[35]

The originality of the present work is to study the evolution of the crystalline structure of materials filled with starch nanocrystals during storage in a humid atmosphere. We show that the introduction of such nanocrystals leads to the disappearance of B-type peaks, and to the apparition of peaks characteristic of the A-type (Figure 6b−d). The crystalline A-type is easily recognizable thanks to a peak located at 15.3°, a shoulder at 18.2° of the peak at 17°, a large peak around 24°, resulting from the superposition of the peaks at 22° and 24° of B-type and of the peak at 24.5° of A-type. For a starch nanocrystals content of 15 wt %, there are no evident peaks of B-type anymore (Figure 6d). However, when observing more attentively the diffraction patterns, we note in Figure 6d: (i) the apparition of a peak of weak intensity at 5.6°, (ii) the increase in the magnitude of the peak at 18.2°, and (iii) a broadening of the peak at 23.5°. These observations show that the recrystallization of the matrix in B-type occurs, but very slowly.

We have shown that the relaxation temperature T_2 of the amylopectin-rich domains was equaled to 25.4 and 39.8 °C for nonaged materials filled with 10 and 15 wt % nanocrystals, respectively, whereas it was equaled to 3 °C for the unfilled matrix. These differences explain why the recrystallization in B-type at room temperature is slowed, even inhibited, when adding starch nanocrystals. When the α_2 relaxation temperature (associated with the glass transition of amylopectin-rich domains) is close to or higher than the room temperature, polymer chains do not have enough mobility to reorganize and recrystallize.[36]

We have shown that starch nanocrystals disturbed the retrogradation of amylopectin chains, probably due to the variation of T_g. Here, the question is to know if nanocrystals allow slowing down the evolution of mechanical properties of starch materials during aging. Aged samples have been characterized by tensile tests carried out at room temperature.

The evolution of the mechanical properties of filled materials during the storage in a humid atmosphere is similar to the one of the unfilled matrix: aging is characterized by an increase in both the Young modulus and the stress at break and a decrease of the strain at break (Figure 7). The diminution of the composite's elasticity is less significant than those of the unfilled matrix because the strain at break of filled materials at time 0 is already low. All of the mechanical properties are listed in Table 7.

Contrarily to the unfilled matrix, mechanical properties of filled materials change significantly and continuously during

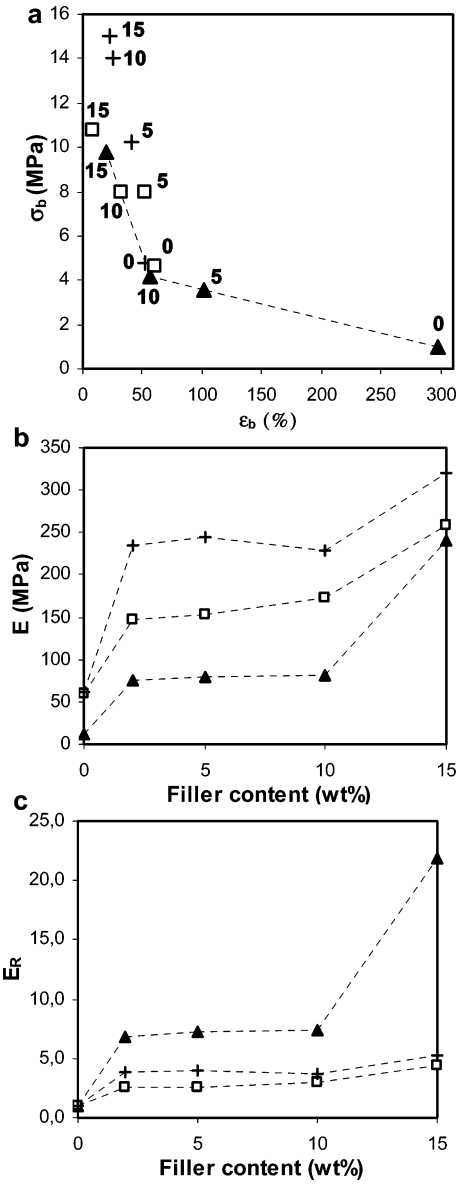

Figure 7. Evolution of (a) stress at break (σ_b) versus strain at break (ϵ_b), (b) of Young modulus (E) and (c) relative Young modulus versus filler content for thermoplastic waxy maize starch plasticized with 25 wt % glycerol unfilled matrix (0) and composites filled with 5 wt % (5), 10 wt % (10), and 15 wt % (15) starch nanocrystals. Values are reported for three aging times: time 0 (▲), time 1 (□), and time 2 (+).

the two weeks of aging (Figure 7a). It is probable that they have not have reached their limit values even after two weeks of aging. This result confirms X-ray diffraction analysis: the presence of starch nanocrystals induces a slowing down of the aging by recrystallization of the matrix.

The mechanical properties of nonaged thermoplastic starch filled with 10 wt % starch nanocrystals are similar to those of the aged unfilled matrix. The reinforcement with filler contents lower than 10 wt % is only interesting for a use in dry atmosphere. Mechanical properties of filled materials are higher than those of the unfilled matrix, event after aging. The use of filler contents higher than 10 wt % results in high modulus and stress at break values (after aging), with a strain at break remaining constant around 20%.

Figure 7b shows that the storage at 88% RH of unfilled thermoplastic starch leads to an increase in Young modulus due to the intermolecular reorganization of the lateral chains of

Table 7. Stress (σ_b) and Strain (ϵ_b) at Break and Young Modulus (E) Given with Their Standard Deviations for Thermoplastic Waxy Maize Starch Plasticized with 25 wt % Glycerol and Filled with Different Contents of Nanocrystals[a]

sample	aging	E (MPa)	σ_b (MPa)	ϵ_b(%)
TPS25	time 0	11 ± 3.6	1.0 ± 0.1	297 ± 64
	time 1	59 ± 11	4.6 ± 0.7	61 ± 11
	time 2	61 ± 2.6	4.8 ± 0.3	52 ± 3.5
TPS25-2	time 0	75 ± 17	3.3 ± 0.4	122 ± 31
	time 1	147 ± 13	7.6 ± 0.7	57 ± 13
	time 2	234 ± 28	9.7 ± 0.7	44 ± 4
TPS25-5	time 0	80 ± 3.5	3.6 ± 0.4	97 ± 18
	time 1	154 ± 20	8.0 ± 0.7	52 ± 8.5
	time 2	245 ± 29	10.2 ± 0.7	41 ± 8
TPS25-10	time 0	82 ± 30	4.2 ± 1	57 ± 21
	time 1	173 ± 22	8.0 ± 0.4	33 ± 3.5
	time 2	229 ± 33	14 ± 1.2	26 ± 5
TPS25-15	time 0	241 ± 46	9.8 ± 1.4	20 ± 8
	time 1	259 ± ?	10.8 ± -	9 ± ?
	time 2	320 ± 33	15 ± 1.7	23 ± 3.1

[a] Values are given for the three aging times defined in the Experimental Section.

amylopectin, as already mentioned. The double helices aggregate and form crystalline regions in the material,[37] leading to the reduction in the mobility of amylopectin chains and acting as physical cross-links.[38] We consider that these intermolecular crystallites reinforce the materials. We have mentioned that the recrystallization may also occur at the intramolecular scale. The presence of intramolecular crystallites results in a reduction of intermolecular interactions and of the cohesion of the matrix and thereby in cracks.[38] It is an additional reason for the diminution of the strain at break for aged samples. Further aging (time 2) does not lead to a significant evolution of the properties compared to time 1.

Figure 7c, representing the evolution of the relative Young modulus versus the filler content for the three times of aging, clearly corroborates that the reinforcing effect of waxy maize starch nanocrystals is the most significant for the nonaged materials. For aged materials, the reinforcing effect of starch nanocrystals is in competition with the recrystallization of the matrix.

Conclusion

We have shown that the relative reinforcing effect of waxy maize starch nanocrystals in nonaged thermoplastic starch is the most significant for a high glycerol content.

The mechanical properties of thermoplastic waxy maize starch plasticized with 25 wt % glycerol and reinforced with waxy maize starch nanocrystals are clearly higher than those of the unfilled matrix, even after aging of the material. This reinforcing effect is attributed to the establishment of strong interactions not only between starch nanocrystals but also between the filler and the matrix and probably to a crystallization that may occur at the filler/matrix interface.

The filler/matrix interactions were underlined by the study of the thermomechanical properties of nanocomposite films (DMA). Two relaxations, labeled α_1 and α_2, were observed around −60 and 0 °C for thermoplastic waxy maize starch plasticized with 25 wt % glycerol. It was shown that the low-temperature relaxation, corresponding to the one of glycerol-rich domains, is influenced by neither the glycerol content nor the filler content. It was also shown that the temperature of the second relaxation, corresponding to the one of amylopectin-rich domains, increases up to temperatures close to room temperature when the glycerol content decreases and/or the filler content increases. The reduction in the molecular mobility of amylopectin chains at room temperature for filled materials has been explained by the establishment of hydrogen bonding forces between starch nanocrystals and thermoplastic starch.

A highly interesting result was that the reduction in the mobility of polymer chains at room temperature in the case of filled materials led to a considerable slowing down of the recristallization in B-type of thermoplastic starch during its storage in humid atmosphere. It resulted in a slower evolution of the mechanical properties of filled materials compared to the unfilled matrix.

One of the interests of the use of starch nanocrystals in such an application could be the possibility of adjusting the properties of thermoplastic starch and controlling their evolution during time.

It is obvious that similar properties could be achieved with amylose films. However, this would be to the detriment of the slowing down of the retrogradation of the matrix. All of these results allow us to think that the reinforcement of thermoplastic starch with waxy maize starch nanocrystals presents numerous interests and that further studies should be conducted.

Acknowledgment. The authors are grateful to Mr. Michel Serpelloni (Roquette Frères S.A., Lestrem, France) for the supply of waxy maize starch.

References and Notes

(1) Sarko, A.; Wu, H.-C. H. *Staerke* **1977**, *30*, 73.
(2) Imberty, A.; Chanzy, H.; Perez, S.; Buleon, A.; Tran, V. *Macromolecules* **1987**, *20*, 2634−2636.
(3) Arvanitoyannis, I.; Biliaderis, C.; Ogawa, H.; Kawasaki, N. *Carbohydr. Polym.* **1998**, *36* (2/3), 89−104.
(4) Ratto, J. A.; Stenhouse, P. J.; Auerbach, M.; Mitchell, J.; Farell, R. *Polymer* **1999**, *40* (24), 6777−6788.
(5) Sen, A.; Bhattacharya, M. *Polymer* **2000**, *41* (26), 9177−9190.
(6) Averous, L.; Fringant, C. *Polym. Eng. Sci.* **2001**, *41* (5), 727−734.
(7) Sharma, N.; Chang, L.; Chu, Y.; Imail, H.; Ishiaku, U.; Ishaki, Z. *Polym. Degrad. Stabil.* **2001**, *71*, 381−393.
(8) Carvalho, A. J. F.; Job, A.; Alves, N.; Curvelo, A. A. S.; Gandini, A. *Carbohydr. Polym.* **2003**, *53* (1), 95−99.
(9) Coffin, D. R.; Fishman, M. L. *J. Appl. Polym. Sci.* **1994**, *54* (9), 1311−1320.
(10) Arvanitoyannis, I.; Nakayama, A.; Aiba, S.-I. *Carbohydr. Polym.* **1998**, *36* (2/3), 105−119.
(11) Fishman, M. L.; Coffin, D. R.; Konstance, R.; Onwulata, C. *Carbohydr. Polym.* **2000**, *41* (4), 317−325.
(12) Bhatnagar, S.; Hanna, M. A. *Starch/Stärke* **1996**, *48* (3), 94−101.
(13) Carvalho, A. J. F.; Curvelo, A. A. S.; Agnelli, J. A. M. *Carbohydr. Polym.* **2001**, *45* (2), 189−194.
(14) Park, H. M.; Lee, W. K.; Park, C. Y.; Cho, W. J.; Ha, C. S. *J. Mater. Sci.* **2003**, *38* (5), 909−915.
(15) Wilhelm, H.-M.; Sierakowski, M.-R.; Souza, G.; Wypych, F. *Carbohydr. Polym.* **2003a**, *52* (2), 101−110.
(16) Wilhelm, H.-M.; Sierakowski, M.-R.; Souza, G.; Wypych, F. *Polym. Int.* **2003b**, *52* (6), 1035−1044.
(17) Pandey, J. K.; Singh, R. P. *Starch/Stärke* **2005**, *57* (1), 8−15.
(18) Wollerdorfer, M.; Bader, H. *Ind. Crops Prod.* **1998**, *8* (2), 105−112.
(19) Curvelo, A. A. S.; Carvalho, A. J. F.; Agnelli, J. A. M. *Carbohydr. Polym.* **2001**, *45* (2), 183−188.
(20) Averous, L.; Fringant, C.; Moro, L. *Starch/Stärke* **2001**, *53* (8), 368−371.
(21) Dufresne, A.; Vignon, M. R. *Macromolecules* **1998**, *31* (8), 2693−2696.
(22) Dufresne, A.; Dupeyre, D.; Vignon, M. R. *J. Appl. Polym. Sci.* **2000**, *76* (14), 2080−2092.
(23) Anglès, M. N.; Dufresne, A. *Macromolecules* **2000**, *33* (22), 8344−8353.
(24) Anglès, M. N.; Dufresne, A. *Macromolecules* **2001**, *34* (9), 2921−2931.

(25) Angellier, H.; Molina-Boisseau, S.; Lebrun, L.; Dufresne, A. *Macromolecules* **2005**, *38* (9), 3783−3792.
(26) Angellier, H.; Molina-Boisseau, S.; Dufresne, A. *Macromolecules* **2005**, *38* (22), 9161−9170.
(27) Angellier, H.; Choisnard, L.; Molina-Boisseau, S.; Ozil, P.; Dufresne, A. *Biomacromolecules* **2004**, *5* (4), 1545−1551.
(28) Lourdin, D.; Bizot, H.; Colonna, P. *J. Appl. Polym. Sci.* **1997**, *63* (8), 1047−1053.
(29) Myllärinen, P.; Partanen, R.; Seppala, J.; Forssell, P. *Carbohydr. Polym.* **2002**, *50* (4), 355−361.
(30) Gaudin, S.; Lourdin, D.; Le Botlan, D.; Ilari, J. L.; Colonna, P. *J. Cereal Sci.* **1999**, *29*, 273−284.
(31) Stading, M.; Rindlav-Westling, A.; Gatenholm, P. *Carbohydr. Polym.* **2001**, *45* (3), 209−217.
(32) Katz, J. *Z. Phys. Chem.* **1930**, *150*, 37−59.
(33) Follain, N.; Joly, C.; Dole, P.; Bliard, C. *J. Appl. Polym. Sci.* **2005**, *97* (5), 1783−1794.
(34) Rindlav-Westling, A.; Stading, M.; Hermansson, A.-M.; Gatenholm, P. *Carbohydr. Polym.* **1998**, *36* (2/3), 217−224.
(35) Van Soest, J. J. G.; Knooren, N. *J. Appl. Polym. Sci.* **1997**, *64* (7), 1411−1422.
(36) Myllärinen, P.; Buléon, A.; Lahtinen, R.; Forssell, P. *Carbohydr. Polym.* **2002**, *48* (1), 41−48.
(37) Putaux, J. L.; Buléon, A.; Chanzy, H. *Macromolecules* **2000**, *33* (17), 6416−6422.
(38) Van Soest, J. J. G.; De Wit, D.; Vliegenhart, J. F. G. *J. Appl. Polym. Sci.* **1996**, *61* (11), 1927−1937.

BM050797S