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Plasticized Starch/Tunicin Whiskers Nanocomposite Materials. 2. Mechanical Behavior

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ABSTRACT: In a previous work [*Macromolecules* 2000, 33, 8344], nanocomposite materials were obtained using glycerol plasticized starch as the matrix and a colloidal suspension of tunicin—an animal cellulose—whiskers as the reinforcing phase. The mechanical behavior of resulting films was characterized in both the linear and the nonlinear range. The effects of the filler and water contents were evaluated, and the results were discussed on the basis of the knowledge of the structural morphology reported in the first part of the paper. The reinforcing effect of tunicin whiskers strongly depended on the ability of cellulose filler to form a rigid network, resulting from strong interactions between whiskers such as hydrogen bonds, and therefore on the moisture content. It was shown that increasing water content induced the crystallization of amylopectin chains and the accumulation of plasticizer in the cellulose/amylopectin interfacial zone. Both phenomena strongly interfere with hydrogen-bonding forces likely to hold the percolating tunicin whiskers network together.

Introduction

Recent trends in solid waste management and rising interest in biodegradable products have influenced the policy of developing environmentally friendly materials. Accordingly, thermoplastic starch is gaining attention as a cheap and totally biodegradable component in film processing. The development of starch-based materials is increasing in different field applications such as the food industry, packaging, encapsulation, paper coating, binders, and biodegradable plastics.^{1–4} An attractive way to increase the mechanical performances of such materials while preserving their biodegradable and bioassimilable nature is the use of cellulosic fillers as a reinforcing phase. Improved thermomechanical properties and a decrease of the water sensitivity of composite materials obtained from a starch matrix filled with cellulose microfibrils were reported in previous works.^{5,6}

In the first part of the present paper,⁷ the structural analysis of nanocomposite materials obtained from glycerol plasticized starch as the matrix and a colloidal suspension of cellulose whiskers as the reinforcing phase was detailed. The cellulose whiskers were prepared from tunicin—an animal cellulose—and consisted of slender parallelepiped rods. Their regular shape, high aspect ratio, and monocrystalline nature justify their identification as whiskers and make tunicin whiskers to be an ideal model systems. The objective of the processing and characterization of starch/cellulose whiskers systems was therefore to understand the phenomena involved in the improvement of starch properties by the incorporation of cellulose microfibrils.^{5,6} Tunicin whiskers were extensively used as model fillers in several kinds of polymeric matrices, including synthetic^{8–11} and natural ones.^{12–14} Casting mixtures of tunicin whiskers suspensions and lattices led to composites with drastically enhanced mechanical properties, especially at $T > T_g$ of the matrix, by virtue of the formation of a cellulose whiskers network, even when the whisker

volume fraction was only a few percent. The formation of this rigid network, resulting from strong interactions between whiskers was assumed to be governed by a percolation mechanism.^{8,10} This hydrogen-bonded network induced a thermal stabilization of the composite up to 500 K, the temperature at which cellulose starts to decompose.

Structural features such as a transcrystallization phenomenon of a semicrystalline poly(hydroxy alkanoate) (PHA) on cellulose whiskers were found to hinder the mechanical percolation of cellulose whiskers and the formation of a rigid network within the polymer matrix during the film formation by evaporation.¹³ This resulted in a disastrous decrease of the mechanical properties of the semicrystalline PHA composite filled with tunicin whiskers as soon as the melt temperature of the matrix was reached.

It was shown in the first part of this paper⁷ that the glycerol plasticized starch/tunicin whiskers systems were complex due to the presence of four components (starch, cellulose, main plasticizer (glycerol), and water). Competitive interactions between these components were reported. The unfilled matrix appeared as a complex heterogeneous system composed of glycerol- and amylopectin-rich domains. An accumulation of both plasticizers (glycerol and water) in the cellulose/amylopectin interfacial zone was evidenced by differential scanning calorimetry and X-ray diffraction. The specific behavior of amylopectin chains located near the interface probably led to a transcrystallization phenomenon of amylopectin on the surface of the cellulose whiskers.

All these factors make the present system largely more complex than in the previous studies.^{8–14} This should result in difficulties to analyze experimental thermomechanical spectra and lead to multiple interpretations. Previous mechanical and dielectric studies performed on polysaccharides have revealed relaxation processes in three temperature ranges:¹⁵ (i) low temperatures (glassy state), attributed to secondary relaxations of small-scale molecular motions or rotation of the methylol group; (ii) intermediate temperature, at-

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tributed to the glass–rubber transition and to relaxation involving the motion of bound water; (iii) high temperatures (rubbery state), attributed to water loss and chain stiffening. Nevertheless, this above-mentioned interpretation of the viscoelastic spectra can be largely modified due to the complexity of the present system, which needs a particular evaluation and no extrapolation from the pure phases. In addition, the interfacial phenomena in starch/cellulose whiskers composites are assumed to be noticeable owing to the high specific area of tunicin whiskers ($\sim 170 \text{ m}^2/\text{g}$). For instance, in a 25 wt % tunicin whiskers filled composite the specific area is of the order of $425\,000 \text{ cm}^2$ of filler surface/ cm^3 of material.

In the present study, the mechanical behavior of glycerol plasticized starch/tunicin whiskers composites is analyzed in both the linear and the nonlinear range. The effect of the filler and water contents is evaluated. Results are discussed on the basis of the knowledge of the structural morphology reported in the first part of the paper.⁷

Experimental Section

Film Processing. The preparation of cellulose microcrystals (or whiskers) from tunicate (a sea animal) and as the starch gels preparation from waxy maize starch are described in the first part of this work.⁷ Cellulose whiskers consist of slender parallelepiped rods that have a broad distribution in size. They have a length ranging from 500 nm up to $1\text{--}2 \mu\text{m}$, and they are almost 10 nm in width. The average aspect ratio (L/d , L being the length and d the diameter) of these whiskers was estimated to be close to 70. Waxy maize starch is almost pure amylopectin (amylose content is lower than 1%) and was kindly supplied by Roquette S.A. (Lestrem, France). The starting products (starch + glycerol (Prolabo, 98% purity) + water + colloidal cellulose whiskers suspension) were mixed in order to obtain composite films with a homogeneous dispersion and with different compositions. The glycerol content was fixed at 33 wt % (dry basis of starch matrix). The cellulose whiskers content was varied from 0 to 25 wt % (cellulose/starch + glycerol). The mixture was carried out in a stirred preheated with boiled water autoclave reactor at 160°C for 5 min. In these conditions, the temperature of 160°C is reached about 10 min after mixture casting. After mixing, the air remaining in the suspension was removed under vacuum ($\sim 300 \text{ mbar}$), and the mixture was cast in a Teflon mold and stored at 70°C under vacuum to allow water evaporation.

Films were conditioned at several relative humidities as was explained in part 1 of this work.⁷ Four relative humidity (RH) atmospheres at $20\text{--}25^\circ\text{C}$ were used, namely 35, 43, 58, and 75% RH. Conditioning was achieved for at least 2 weeks to ensure the equilibration of the water content in the films with that of the atmosphere (stabilization of the sample weight).

Dynamic Mechanical Analysis (Linear Range). Dynamic mechanical tests were accomplished using a Rheometrics RSA2 spectrometer in the tensile mode. Test conditions were chosen in such a way that the measurements were in the linear viscoelasticity region (the maximum strain ϵ was around 10^{-4}). The specimen was a thin rectangular strip ($30 \times 5 \times 0.5 \text{ mm}$) conditioned at the previously mentioned relative humidities. The setup measured the complex tensile modulus E^* , i.e., the storage component E' and the loss component E'' , as well as the ratio of the two components, i.e., $\tan \delta (= E''/E')$. In the present work, results are displayed through E' and $\tan \delta$. Measurements were performed alternatively at five frequencies, i.e., 0.1, 0.316, 1, 3.16, and 10 Hz. Between each isothermal measurement, the temperature was varied by steps of 3 K between 150 and 510 K.

Tensile Tests (Nonlinear Range). The nonlinear mechanical behavior of the starch-based composites was analyzed using an Instron 4301 testing machine in tensile mode, with a load cell of 100 N capacity. The specimen was a thin

rectangular strip ($\sim 30 \times 5 \times 1 \text{ mm}$), conditioned at the relative humidities mentioned above. The gap between pneumatic jaws at the start of each test was adjusted to 20 mm.

The stress–strain curves of conditioned samples were obtained at room temperature at a strain rate $d\epsilon/dt = 8.3 \times 10^{-3} \text{ s}^{-1}$ (cross-head speed = 10 mm min^{-1}). The true strain ϵ can be determined by $\epsilon = \ln(L/L_0)$, where L and L_0 are the length during the test and the length at zero time, respectively. The true stress σ was calculated by $\sigma = F/S$, where F is the applied load and S is the cross-sectional area. S was determined assuming that the total volume of the sample remained constant, so that $S = S_0 L_0/L$, where S_0 is the initial cross-sectional area. Stress vs strain curves were plotted, and the tensile or Young's modulus (E) was measured from the slope of the low strain region in the vicinity of $\sigma = \epsilon = 0$ ($[d\sigma/d\epsilon]_{\epsilon=0}$).

Ultimate mechanical properties were also characterized. The true ultimate stress, or true stress at break, $\sigma_b = F_b/S$, where F_b is the applied load at break, was reported for each tested sample. Ultimate elongation was characterized by the true ultimate strain, or true strain at break, $\epsilon_b = \ln[1 + (\Delta L_b/L_0)]$, where ΔL_b is the elongation at break. Mechanical tensile data were averaged over at least three specimens.

Results and Discussion

Samples Composition. The glycerol composition (33 wt %) of the plasticized starch/tunicin whiskers composites processed in our previous work⁷ was expressed on the dry basis of starch matrix in order to maintain a constant glycerol content within the matrix regardless of the cellulose content. The cellulose content was expressed on the plasticized starch matrix basis (glycerol + starch). As is well-known, starch and cellulose are highly hygroscopic materials and water is an intrinsic constituent of polysaccharides. In the first part of this paper,⁷ the water content of the various samples conditioned in different relative humidity atmospheres was evaluated by thermogravimetric analysis (TGA). It varied from 3 up to about 40 wt % [water/(starch + glycerol + cellulose)] as the relative humidity increased from 0 to 98% RH. Taking into account this water content, it changes the actual composition of the specimen, especially in highly moist conditions. The actual compositions of the various starch/cellulose composites conditioned at different water activities were evaluated and are collected in Table 1. It must be noticed that the amount of both glycerol and water correspond to the overall total of plasticizer within the material, which is also reported in Table 1. For some formulations, it represents up to half of the total specimen weight. Throughout this work, tunicin whiskers contents will be expressed on water free glycerol plasticized starch matrix basis.

Dynamic Mechanical Analysis (Linear Range). Dynamic mechanical measurements were performed on all the samples (plasticized starch matrix and related cellulose whiskers filled composites up to 25 wt %) in order to display the thermomechanical behavior of these systems. The effects of both the water content within the films and the filler loading on the thermomechanical properties were evaluated. For the sake of clarity and ease of comprehension, a summary table (Table 2) on key DSC parameters obtained in our previous work⁷ is added.

Plasticized Starch Matrix. Figure 1 shows an isochronal plot of $\log(E/\text{Pa})$ (storage tensile modulus, Figure 1a) and $\tan \delta$ (loss angle tangent, Figure 1b) at 1 Hz as a function of temperature for glycerol plasticized starch conditioned at various relative humidities. $\tan \delta$ was plotted on a linear scale, and the temperature range was

Table 1. Composition of the Starch/Tunicin Whiskers Composites Conditioned at Different Water Activities

cellulose (%) ^a	RH (%)	S/G/C ^b (%) ^c	"dry" matter (%) ^d	cellulose (%) ^e	starch (%) ^f	glycerol (%) ^g	water (%) ^h	plasticizer (%) ⁱ
0	0	67/33/0	97.2	0	65.1	32.1	2.8	34.9
	35	67/33/0	92.3	0	61.8	30.5	7.7	38.2
	43	67/33/0	84.1	0	56.3	27.8	15.9	43.7
	58	67/33/0	83.1	0	55.7	27.4	16.9	44.3
	75	67/33/0	76.4	0	51.2	25.2	23.6	48.8
3.2	0	64.8/32/3.2	94.8	3.0	61.4	30.4	5.2	35.5
	35	64.8/32/3.2	89.0	2.8	57.7	28.5	11.0	39.5
	43	64.8/32/3.2	84.2	2.7	54.6	26.9	15.8	42.7
	58	64.8/32/3.2	81.4	2.6	52.7	26.0	18.6	44.6
	75	64.8/32/3.2	75.3	2.4	48.8	24.1	24.7	48.8
6.2	0	62.8/31/6.2	94.8	5.9	59.5	29.4	5.2	34.6
	35	62.8/31/6.2	89.7	5.6	56.3	27.8	10.3	38.1
	43	62.8/31/6.2	82.3	5.1	51.7	25.5	17.7	43.2
	58	62.8/31/6.2	82.2	5.1	51.6	25.5	17.8	43.3
	75	62.8/31/6.2	75.0	4.7	47.1	23.3	25.0	48.3
16.7	0	55.8/27.5/16.7	94.1	15.7	52.5	25.9	5.9	31.8
	35	55.8/27.5/16.7	90.6	15.1	50.6	24.9	9.4	34.3
	43	55.8/27.5/16.7	84.0	14.0	46.9	23.1	16.0	39.1
	58	55.8/27.5/16.7	80.3	13.4	44.8	22.1	19.7	41.8
	75	55.8/27.5/16.7	79.9	13.3	44.6	22.0	20.1	42.1
25	0	50.25/24.75/25	96.4	24.1	48.4	23.9	3.6	27.5
	35	50.25/24.75/25	91.2	22.8	45.8	22.6	8.8	31.4
	43	50.25/24.75/25	86.7	21.7	43.6	21.5	13.3	34.8
	58	50.25/24.75/25	84.4	21.1	42.4	20.9	15.6	36.5
	75	50.25/24.75/25	81.3	20.3	40.9	20.1	18.7	38.8

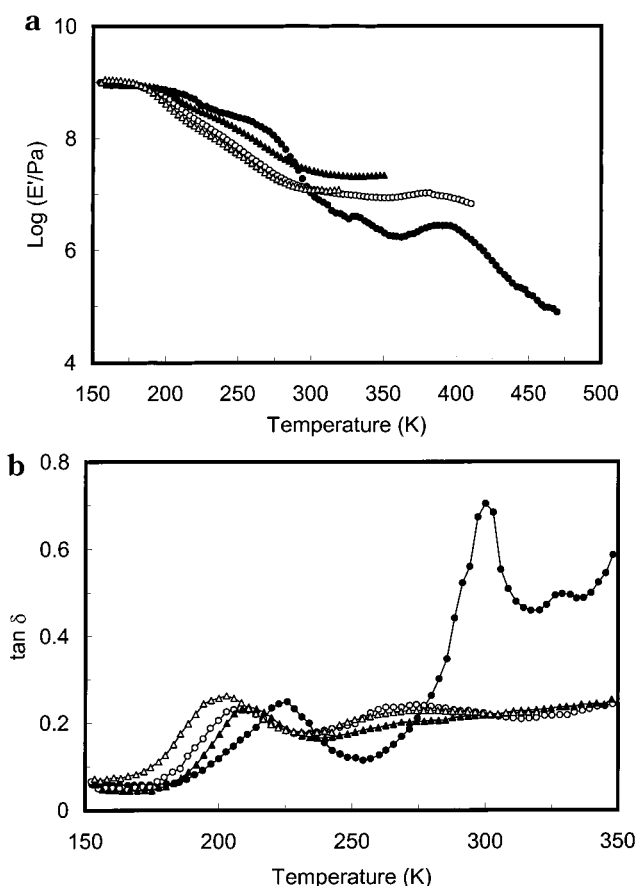
^a Expressed on water free plasticized starch matrix basis [cellulose/(glycerol + starch)]. ^b S = starch, G = glycerol, C = cellulose. ^c Theoretical values based on water free materials. ^d Expressed on wet basis [(starch + glycerol + cellulose)/(starch + glycerol + cellulose + water)]. ^e Expressed on wet basis [(cellulose)/(starch + glycerol + cellulose + water)]. ^f Expressed on wet basis [(starch)/(starch + glycerol + cellulose + water)]. ^g Expressed on wet basis [(glycerol)/(starch + glycerol + cellulose + water)]. ^h Expressed on wet basis [(water)/(starch + glycerol + cellulose + water)]. ⁱ Expressed on wet basis [(glycerol + water)/(starch + glycerol + cellulose + water)].

Table 2. Glass–Rubber Transition Temperatures Associated with the Midpoints of the Transitions of Glycerol-Rich ($T_{g,1}$) and Amylopectin-Rich ($T_{g,2}$) Domains and Melting Temperatures (T_m) of Tunicin Whiskers/Plasticized Starch Nanocomposites Films Conditioned at Different Moisture Contents

RH (%)	cellulose (wt %)	$T_{g,1}$ (K)	$T_{g,2}$ (K)	T_m (K)
35	0	225.5	300.0	
	3.2	208.0	296.0	
	6.2	208.5	307.0	
	16.7	210.5	298.0	
	25	212.5	313.0	
43	0	190.5	274.0	405.5
	3.2	186.0	280.0	405.0
	6.2	183.0	328	404.0
	16.7	190.5	330.0	405.0
	25	192.5	331.0	407.5
58	0	186.0	271.5	430.0
	3.2	185.5	245.0	431.5
	6.2	185.0	336.0	438.0
	16.7	188.5	350.0	433.0
	25	184.0	327.5	442.5
75	0	175.5	260.0	429.0
	3.2	183.0	238.0	429.0
	6.2	181.0	336.0	429.0
	16.7	180.0	336.5	429.5
	25	191.0	337.0	431.5

restricted to 150–350 K. At higher temperatures, broad dispersion regions of $\tan \delta$ were observed.

For low temperatures, it was difficult to observe any change in the storage modulus with variation of the moisture content. As is well-known, the exact determination of the glassy modulus depends on the precise knowledge of the samples dimensions. In this case, and especially for highly moist samples, the films were soft, and it was very difficult to obtain a constant and precise thickness along these samples. To minimize this effect, the samples were frozen in liquid nitrogen prior to the experiments to accurately measure their dimensions. Furthermore, starch being in the glassy state, the modulus should be almost independent of the moisture conditions. To be able to compare the effect of water content on the drop of the elastic tensile modulus, E' at

**Figure 1.** (a) Logarithm of the storage tensile modulus E' and (b) loss angle tangent $\tan \delta$ vs temperature at 1 Hz for glycerol plasticized starch matrices conditioned at 35 (●), 43 (○), 58 (▲), and 75% RH (△). E' at 150 K was normalized at 1 GPa for all the samples.

150 K was normalized at 1 GPa for all the samples. In this temperature range, the tensile modulus slightly decreases with temperature but remains roughly constant.

At higher temperatures, a two-step decrease of the storage modulus is observed (Figure 1a). Such two-step decreases of the modulus for starchy materials were also reported by other authors.^{15–17} These two modulus drops appear in the glass–rubber transition zones previously determined by DSC⁷ (see also Table 2). In the first part of this work,⁷ the unfilled plasticized starch matrix appeared as a complex heterogeneous system composed of glycerol-rich domains dispersed in an amylopectin-rich continuous phase. Each phase exhibited its own glass–rubber transition ($T_{g,1}$ and $T_{g,2}$ in Table 2). The two observed modulus drops are therefore ascribed to energy dissipation phenomena involving cooperative motions of long amorphous sequences likely to rotate and translate in different surroundings. They are displayed in Figure 1b in the concomitant relaxation processes where the loss angle tangent passes through two successive maxima. The temperature position of these two relaxations processes decreases as the moisture content increases, in agreement with DSC results,⁷ owing to the plasticizing effect of water (see also Table 2). It decreases from 225 to 203 K for the low-temperature relaxation process and from 300 to 275 K for the high-temperature relaxation process, as the relative humidity increases from 35 to 75% RH. The former will be labeled α_1 and the latter α_2 throughout this work. No significant difference is reported for the temperature position of both relaxation processes when samples are conditioned at either 43 or 58% RH. This is most likely due to the fact that the water and total plasticizer contents are very close for these two materials (see Table 1).

It is worth noting that, except the above-mentioned temperature depression, the general appearance of the α_1 relaxation process is unaffected by the moisture content (Figure 1b). The magnitude and the half-height width of the corresponding $\tan \delta$ peak remain roughly similar whatever the water content may be. On the contrary, the appearance of the α_2 relaxation process is significantly affected as the relative humidity level changes from 35 to 43% RH. Its intensity is strongly reduced, and its half-height width is increased in moister condition. The intensity mainly depends on the magnitude of the modulus drop, and the half-height width is representative of the size distribution of mobile entities participating in the relaxation process. These significant changes are most probably due to the crystallization of the plasticized starch matrix in moist conditions.¹⁶ Indeed, DSC and X-ray diffraction showed that for low water content (up to 35% RH) glycerol plasticized starch was fully amorphous, whereas at increasing moisture content the material was semicrystalline.⁷ In this way, the transition from the glassy to the rubbery state is done in an extensive temperature domain, being difficult to detect and results in a weaker modulus drop. The general appearance does not change further with increasing water content, and no significant change is observed for the α_2 relaxation peak as the moisture conditioning increases from 43 to 75% RH.

This is an indication that only the amylopectin chains located in the amylopectin-rich continuous phase, whose glass–rubber transition is ascribed to the α_2 relaxation process, are able to crystallize. In addition, it is worth noting that for the 35% RH conditioned sample (amorphous starch) the magnitude of the low-temperature modulus drop, associated with the α_1 relaxation process, is much lower than the one corresponding to the high-

temperature modulus drop, associated with the α_2 relaxation process. This observation confirms the hypothesis expressed in the first part of the paper⁷ that the heterogeneous glycerol/starch system should be visualized as a blend of glycerol-rich domains embedded in an amylopectin-rich matrix. Obviously, this morphology is also valid for higher moisture content but cannot be directly supported from dynamic mechanical measurements because of the growth of crystalline domains in moist conditions, which disturb the relaxation processes associated with the amorphous part of the material.

Isothermal thermomechanical measurements were also performed alternatively at five frequencies, i.e., 0.1, 0.316, 1, 3.16, and 10 Hz in the vicinity of both the α_1 and α_2 relaxations. Between two measurements, the temperature was raised by 3 K. The α_1 and α_2 relaxations were frequency-dependent, and from the isochronal measurements, the apparent activation energy, E_a , was estimated. Assuming that if the relaxations are considered as Arrhenius processes, the relaxation time of these relaxations $\tau = 1/2\pi f$ can be expressed as

$$\tau = \tau_0 \exp\left(\frac{E_a}{RT}\right) \quad (1)$$

It follows the values reported in Table 3 for the plasticized starch matrix conditioned at different relative humidities. The very high values of the apparent activation energies, E_a , ranging between 132 and 161 kJ/mol for the α_1 relaxation and between 222 and 307 kJ/mol for the α_2 relaxation, as well as the very low related preexponential times, τ_0 , are typical of main relaxations associated with the glass–rubber transition. It is worth noting that the values reported for the α_2 relaxation process are rough estimates because of the ill-defined temperature position of the $\tan \delta$ maxima. However, a decrease of the apparent activation energy with increasing water content is observed for both relaxation processes. This expected effect of the moisture content is related to the fact that water acts as a plasticizing agent toward relaxing amylopectin chains. The purpose of the plasticizer is to depress the T_g of polymers by hindering intermolecular interactions and thus favoring intermolecular motions. The efficiency of the plasticizer is closely related to its compatibility with the polymeric matrix.

The general difficulty in interpreting the mechanical spectra of complex systems is due to the presence and superimposition of different kind of relaxations, arising from the various constituents, such as amylopectin, glycerol, and water.^{15–24} For instance, Butler and Cameron¹⁵ have announced different possible causes of secondary relaxations in starch, such as (i) rotation of hydroxyl groups, (ii) rotation of the methylol group, (iii) localized motions of the chain backbone, including liberation of the glucose units about the (1–6)- α linkage, and (iv) a boat–chair interconversion of the glucose unit. A low-temperature relaxation process reflecting an increase of mobility of water in starch was also reported.^{15,19} As the bound water becomes mobile, motions of the hydroxyl groups of starch would likely begin, thus facilitating the local structural relaxation processes.¹⁹

The existence of a dual hydration regime, involving H-bonding of the water molecules to the polysaccharide at low hydration degrees and formation of water–water associations at higher water contents, was also reported

Table 3. Apparent Activation Energy, E_a , and Preexponential Factor, τ_0 , of the Main Relaxations Associated with the Glass–Rubber Transitions of Glycerol-Rich (α_1) and Amylopectin-Rich (α_2) Domains of the Starch/Tunicin Whiskers Composites Conditioned at Different Water Activities

relaxation	RH (%)	cellulose (wt %)	E_a (kJ mol ⁻¹)	τ_0 (s)	relaxation	RH (%)	cellulose (wt %)	E_a (kJ mol ⁻¹)	τ_0 (s)
α_1	35	0	161	3.3×10^{-39}	α_2	35	0	307	1.9×10^{-54}
		3.2	160	3.8×10^{-39}			3.2	209	2.5×10^{-38}
		6.2	163	1.0×10^{-39}			6.2	202	5.9×10^{-36}
		16.7	165	8.2×10^{-40}			16.7	121	8.0×10^{-22}
		25	156	1.2×10^{-38}			25	166	1.2×10^{-28}
	43	0	144	1.1×10^{-37}		43	0	260	5.2×10^{-51}
		3.2	139	3.1×10^{-37}			3.2	148	6.9×10^{-31}
		6.2	136	1.3×10^{-36}			6.2	146	4.6×10^{-29}
		16.7	141	2.8×10^{-37}			16.7	216	4.1×10^{-39}
		25	138	5.2×10^{-37}			25	298	3.2×10^{-51}
	58	0	150	1.1×10^{-38}		58	0	222	6.1×10^{-43}
		3.2	136	1.4×10^{-36}			3.2	176	5.0×10^{-36}
		6.2	144	5.2×10^{-38}			6.2	261	1.1×10^{-51}
		16.7	141	3.0×10^{-37}			16.7	284	3.6×10^{-54}
		25	144	5.6×10^{-38}			25	235	2.4×10^{-43}
	75	0	132	7.0×10^{-36}		75	0	249	1.7×10^{-49}
		3.2	132	7.2×10^{-36}			3.2	250	1.0×10^{-49}
		6.2	132	5.4×10^{-36}			6.2	248	2.7×10^{-49}
		16.7	132	5.6×10^{-36}			16.7	174	1.1×10^{-35}
		25	122	2.5×10^{-34}			25	275	5.3×10^{-52}

by Scandola et al.¹⁸ At very low levels of hydration, the water molecules interacting with the hydroxyl groups of the polysaccharide contributed to the formation of a more diffuse and stronger H-bond network than that existing in the “dry” polymer. As a consequence, the molecular motion displayed through the low-temperature relaxation of the “dry” polysaccharide was shifted toward higher temperatures, reflecting the higher energetic requirement for the molecular motion to occur in the presence of bound water. At higher hydration levels, the loss of specificity of the binding sites, i.e., formation of water–water bridges, caused a loosening of the H-bond network.

At increasing temperatures above T_g in the range 300–400 K, the storage modulus of the 35% RH conditioned sample tends to roughly stabilize (Figure 1a). The asymptotic value, close to 1 MPa, is typical of a fully amorphous material. In the temperature range 365–390 K an increase of the storage modulus is observed due to the progressive dehydration of the material. Water mobilization and loss are displayed through broad dispersion regions of the loss factor $\tan \delta$ (not shown). In the terminal zone, the elastic tensile modulus becomes lower and lower with temperature, and the experimental setup failed to measure it, due to irreversible chain flow (Figure 1a).

By increasing the moisture conditioning up to 43% and 58% RH, the relaxed modulus increases up to 10 and 20 MPa. The rubbery modulus is known to depend on the degree of crystallinity of the material. It is well-known that the higher the moisture content of the sample, the higher the crystallinity ratio is.^{19,27,28} The crystalline regions of amylopectin 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. It must be noticed that the reinforcing effect of the crystallites within the matrix is probably also attributed to the size of the crystalline domains and to their size distribution. For higher moisture conditioning (75% RH), the crystallinity of the material does not evolve anymore.⁷ This should result in a stabilization of the relaxed modulus, but in the same time the amorphous matrix becomes softer with

increasing the water content, resulting in a global lowering of the relaxed modulus. At 43% RH, the rubbery modulus of the plasticized starch drops irreversibly with the breakup of crystalline domains, around 410 K, which corresponds to the melting temperature determined by DSC⁷ (see also Table 2). For higher moisture content, it was observed that the melting temperature was higher (around 430 K).⁷ However, from dynamic mechanical measurements the rubbery modulus drops at lower temperatures (around 355 K at 58% RH and around 325 K at 75% RH). This is ascribed to the weak cohesion between crystalline domains due to the softening of the starch amorphous material under highly moist conditions. Indeed, the high content of plasticizers (water and glycerol) acting as internal lubricants prevents the stiffening of the non-crystalline domains at temperatures higher than T_g .²⁹

Plasticized Starch/Cellulose Whiskers Composites. The evolution of $\log(E/\text{Pa})$ and $\tan \delta$ vs temperature at 1 Hz is plotted in Figure 2 for glycerol plasticized starch/tunicin whiskers composites conditioned at 35% RH. In Figure 2a again, the storage tensile modulus at 150 K was normalized at 1 GPa for all the samples. This is justified by the fact that in this temperature range the difference between the elastic modulus of the cellulose whiskers and that of the starch matrix was not high enough to easily appreciate a reinforcing effect.

No significant change of the temperature position of the two modulus drops and $\tan \delta$ maxima upon whiskers addition is reported, in agreement with previous DSC results.⁷ Isothermal measurements were also performed on composites conditioned at 35% RH in the range 0.1–10 Hz in the vicinity of the α_1 and α_2 relaxations. The corresponding apparent activation energies, E_a , and related preexponential times, τ_0 , as calculated from the frequency dependence of the $\tan \delta$ peaks are reported in Table 3. These values are not significantly different from the one obtained for the unfilled starch matrix conditioned at 35% RH, and the apparent activation energy remains almost constant upon whiskers addition.

As is usually done in such multifrequency studies²⁵ and according to the time–temperature superposition principle, an attempt was made to superimpose the E'

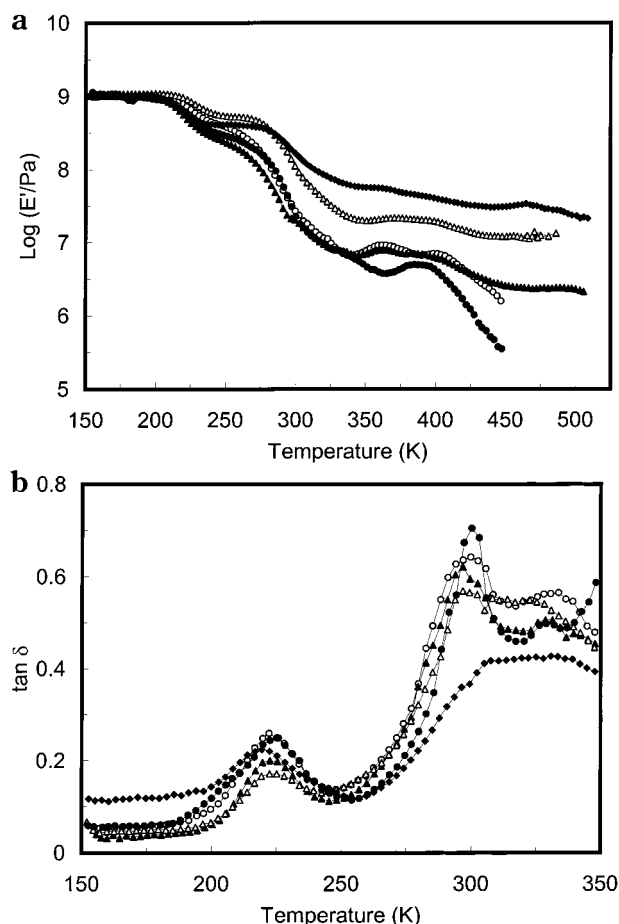


Figure 2. (a) Logarithm of the storage tensile modulus E' and (b) loss angle tangent $\tan \delta$ vs temperature at 1 Hz for glycerol plasticized starch/tunicin whiskers composites filled with 0 (●), 3.2 (○), 6.2 (▲), 16.7 (△), and 25 wt % (◆) of cellulose whiskers and conditioned at 35% RH. E' at 150 K was normalized at 1 GPa for all the samples.

and $\tan \delta$ curves by simply shifting them along the frequency scale to produce a master curve over an enlarged range of frequencies at a reference temperature T_0 (not shown). In principle, a vertical shift $\rho T / \rho_0 T_0$ should also be applied to account for the change in polymer density $\rho - \rho_0$ between T and T_0 . Actually, this correction was very small on the restricted temperature range under consideration, and vertical shifts were neglected. The reliability of shifting E' and $\tan \delta$ curves was established by the use of the same shift factor for both sets of data.

In the main α relaxation region, associated with the glass–rubber transition (but above T_g), the temperature dependence of the horizontal shift factor a_T is expected to obey the well-known Williams–Landel–Ferry (WLF) equation:²⁶

$$\log a_T = \log\left(\frac{f_0}{f}\right) = \log\left(\frac{\tau}{\tau_0}\right) = -\frac{C_1^T(T - T_0)}{C_2^T + (T - T_0)} \quad (2)$$

where f_0 and f are the frequencies of the motions at temperatures T_0 and T , respectively, τ_0 and τ are the corresponding molecular mobility relaxation times defined as the inverse of the frequency of the maximum in $\tan \delta$, $(2\pi f_0)^{-1}$ and $(2\pi f)^{-1}$, respectively, and C_1^T and C_2^T are the values of the viscoelastic coefficients at the reference temperature T_0 . It is usual to consider as the

Table 4. Experimental Viscoelastic Coefficients and Apparent Activation Energy, E_a , Calculated from Eq 3 of the Starch/Tunicin Whiskers Composites Conditioned at 35% RH

cellulose (wt %)	T_0 (K) ^a	$C_1^{T_0}$	$C_2^{T_0}$ (K)	E_a (kJ mol ⁻¹)
0	300	3.4	18.8	314
3.2	296	4.0	32.4	206
6.2	307	2.4	22.4	193
16.7	298	1.4	23.3	122
25	313	3.1	50.4	116

^a Choosing T_0 as the glass–rubber transition temperature determined from DSC experiments.⁷

reference temperature the glass–rubber transition temperature determined from DSC experiments. The corresponding temperature was assigned to the T_g of amylopectin-rich domains previously determined for the plasticized starch matrix.⁷

It is obvious that the WLF equation, based on the free-volume concept, provides a reasonably good description of the viscoelastic behavior in the high-temperature region but is not quite as valid as the temperature decreases near T_g . In fact, the WLF equation is assumed to be valid within the interval $T_g < T < (T_g + 100^\circ\text{C})$. Outside of this interval, the use of the Arrhenius equation may yield more accurate results. According to eq 2, $C_1^{T_0}$ and $C_2^{T_0}$ can be conveniently determined from plots of $(T - T_0)/\log a_T$ vs $(T - T_0)$. The values of the viscoelastic coefficients can be derived from the slope and intercept with the y -axis of this straight line. The corresponding coefficients are collected in Table 4 for the glycerol plasticized starch/tunicin whiskers composites conditioned at 35% RH. The viscoelastic coefficients were not calculated for samples conditioned in moister atmospheres because the WLF equation is assumed to be only valid for amorphous polymers. The $C_1^{T_0}$ and $C_2^{T_0}$ values range between 1.4 and 4.0 and between 18.8 and 50.4 K, respectively. No trivial evolution of these coefficients with whiskers loading is reported, except a global increase of $C_2^{T_0}$ with increasing cellulose content. The observed viscoelastic coefficients are much lower than the “universal” constants reported by Williams, Landel, and Ferry (17.4 and 51.6 K, respectively).²⁶

From the WLF equation, an apparent activation energy for viscoelastic relaxation can be calculated.²⁵ At high temperatures it can be calculated as

$$E_a = 2.303RT_g^2 \frac{C_1^g}{C_2^g} \quad (3)$$

The corresponding apparent activation energies, E_a , as calculated from eq 3 are reported in Table 4. A good agreement is reported with apparent activation energies previously determined (Table 3).

For the films that contained cellulose whiskers, the magnitude of the two-step modulus drop is strongly reduced (Figure 2a). For instance, the relaxed modulus of a film containing 25 wt % of whiskers (around 48 MPa at 365 K) is about 20 times higher than that of the matrix (around 2.5 MPa at 365 K). However, this reinforcing effect is very low compared to experimental data reported in previous works for either synthetic^{8–10} or natural^{12–14} matrices filled with tunicin whiskers. For instance, the relaxed modulus of a film containing only 6 wt % of whiskers was 1000 times higher than that of the matrix when a synthetic copolymer of styrene and butyl acrylate was used as the matrix.^{8–10} This high

reinforcing effect 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, besides the geometry and stiffness of the whiskers. The discrepancy between these previous observations and the present results shows that the plasticizer agents (glycerol and water) most probably hinder the formation of the hydrogen-bonded cellulose network within the matrix. In the first part of this paper,⁷ an accumulation of plasticizer in the cellulose/amylopectin interfacial zone was evidenced. This plasticizer accumulation should probably interfere with hydrogen-bonding forces likely to hold the percolating network of the whiskers together.

This unexpected result seems to disagree with previous experimental data reported for glycerol plasticized starch filled with cellulose microfibrils.⁵ For these systems, a strong increase in the composite modulus was observed. The relaxed modulus was increased by 2 decades, even with filler content as low as 3.85 wt %. This obvious preposterousness and conflicting results could be explained from the sole difference between the two kinds of filler, that is, the flexibility. Cellulose whiskers are stiff and straight well-defined objects, whereas cellulose microfibrils are flexible and hairy fibers. Therefore, in composites filled with cellulose microfibrils, the reinforcing effect occurs most probably both from the formation of the hydrogen-bonded cellulose network within the matrix and from a tangling effect. In composites filled with cellulose whiskers, only the former phenomenon is likely to occur. This observation represents an interesting contribution to the knowledge of the behavior of cellulose microfibril filled composites, since up to now cellulose whiskers were undoubtedly used as a model cellulosic filler to account for the behavior of cellulose microfibrils.

In addition to this comparatively weak, but significant, reinforcing effect, an increase of the thermal stability of the starch matrix upon tunicin whiskers addition is also observed (Figure 2a). Whereas the glycerol plasticized starch matrix behaves as a viscous liquid at temperature higher than ~400 K, the films that contain 6.2 wt % tunicin whiskers and up behave as rubbers as their storage modulus value stays almost constant over a wide temperature range. E' keeps a constant value all the way to 500 K, the temperature at which cellulose starts to decompose. This phenomenon was also reported for amorphous matrices filled with tunicin whiskers and was ascribed to the rigid whisker network that was likely to develop above the percolation threshold by hydrogen bonding.^{8–10,12}

In the temperature range 150–350 K, the two relaxation processes (α_1 and α_2) are displayed through two maxima in $\tan \delta$ curves (Figure 2b). The magnitude of both relaxations decreases as the whiskers content increases. This phenomenon is ascribed to both the decrease of the relaxing entities participating in the relaxation process and to the concomitant lowering of the modulus drop upon whiskers addition.

Figures 3–5 display the evolution of the storage tensile modulus, E' , on a logarithmic scale and the loss angle tangent, $\tan \delta$, on a linear scale for glycerol plasticized starch/tunicin whiskers conditioned at 43, 58, and 75% RH, respectively, in the temperature range 150–510 K. The temperature range of the evolution of $\tan \delta$ was limited to 150–350 K to focus attention on the double main relaxation processes of the amylopec-

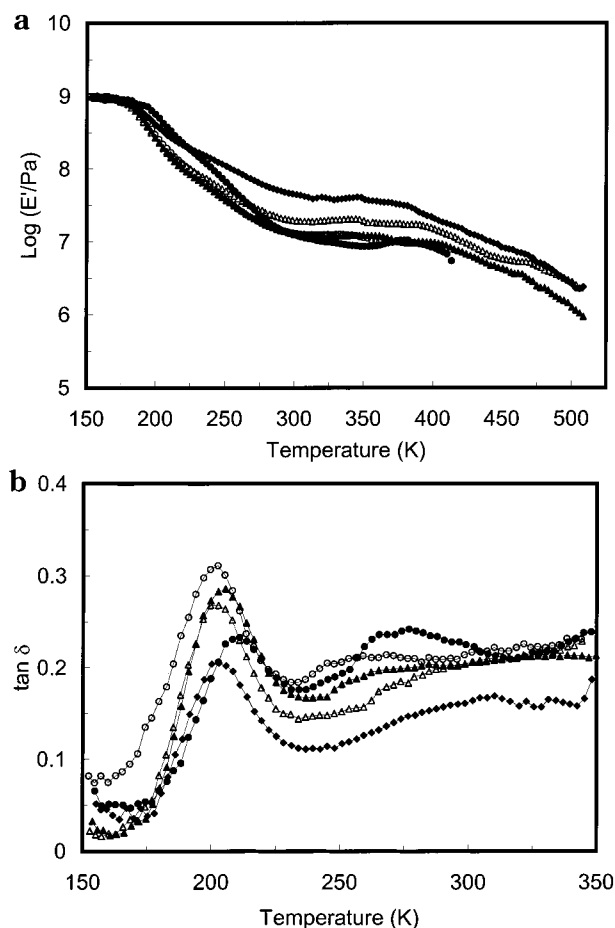


Figure 3. (a) Logarithm of the storage tensile modulus E' and (b) loss angle tangent $\tan \delta$ vs temperature at 1 Hz for glycerol plasticized starch/tunicin whiskers composites filled with 0 (●), 3.2 (○), 6.2 (▲), 16.7 (△), and 25 wt % (◆) of cellulose whiskers and conditioned at 43% RH. E' at 150 K was normalized at 1 GPa for all the samples.

tin–glycerol system. The isochronal $\log E'$ vs temperature curves were normalized as previously at 1 GPa at low temperature. Isothermal measurements were also performed on these composites in the frequency range 0.1–10 Hz and in the vicinity of the α_1 and α_2 relaxations. The calculated apparent activation energies, E_a , and related preexponential times, τ_0 , are reported in Table 3. No significant evolution of these values is observed when the whisker loading varies for a given moisture content. Nevertheless, similarly to what was observed for the unfilled starch matrix, the apparent activation energy decreases as the moisture content increases for a given whiskers content, displaying the plasticizing effect of water for these systems.

Regarding the 43% RH conditioned sample (Figure 3a), the reinforcing effect upon whiskers loading seems to be much lower than for the composites conditioned at 35% RH (Figure 2a). This can be partly ascribed to the fact that the starch matrix is no longer fully amorphous, as was the case at 35% RH, but semicrystalline.⁷ The storage tensile modulus at 365 K of the 43% RH conditioned unfilled matrix is around 9 MPa, whereas it is around 2.5 MPa for the 35% RH conditioned one. A simple mixing rule allows to account for the lower relative reinforcing effect with the semicrystalline matrix. The relaxed modulus at 365 K of the 25 wt % whiskers filled composite conditioned at either 35 or 43% RH is nearly independent (~50 MPa) of the

moisture content. This is ascribed to the fact that at high filler content the stiffness of the material arises from the percolating network of cellulose whiskers and is almost independent of the stiffness of the matrix. At low filler content (0 and 3.2 wt %), the rubbery modulus drops irretrievably with the breakup of crystalline domains, around 410 K, which corresponds to the melting temperature determined by DSC.⁷ For higher whiskers loading (6.2 wt % and up), the modulus drop is not so sharp, and E' decreases progressively up to 500 K, the temperature at which cellulose starts to decompose. This is an indication that for these samples a weak percolating cellulose whiskers network probably forms. Compared to the 35% RH conditioned samples, one can imagine that both the crystallization of the matrix and the accumulation of plasticizer in the cellulose/amylopectin interfacial zone that occur when the specimens are conditioned in moister atmospheres hinder the hydrogen-bonded filler network formation.

For the 43% RH conditioned materials, the α_1 relaxation process appears to be stronger than the α_2 one (Figure 3b), contrary to what was observed at 35% RH (Figure 2b). This is due to the involvement of amylopectin chains located in the amylopectin-rich domains in the crystalline zones. The temperature position of the α_1 relaxation process slightly decreases upon whiskers addition (Figure 3b). Its magnitude first increases strongly for the 3.2 wt % filled composite compared to the unfilled matrix and then decreases progressively up to a value lower than that of the unfilled matrix for the highly filled sample (25 wt %). This can be ascribed to a relocation of the main plasticizer (glycerol) and to an increased mobility of amylopectin chains in glycerol-rich domains. This results in a decreased mobility of amylopectin chains in amylopectin-rich domains displayed through both a decrease of the magnitude and an increase of the temperature position of the α_2 relaxation process. The shift of the α_2 relaxation toward higher temperatures in the presence of whiskers is due to the shift of the glass-rubber transition temperature of amylopectin-rich domains previously reported from DSC measurements (see also Table 2).⁷

When the glycerol plasticized starch/tunicin whiskers are conditioned in moister atmospheres (58% RH, Figure 4), a surprising and unexpected result is observed. Except for the highly filled sample (25 wt %), the rubbery modulus decreases upon whiskers addition. The rubbery modulus at 355 K (just before the irretrievable modulus drop) of the unfilled matrix is around 22 MPa, reflecting the higher crystallinity of this sample compared to the 35 and 43% RH conditioned plasticized starch. When filled with 3.2 wt % of whiskers, it decreases to about 4 MPa for the same temperature. The highly filled composite (25 wt %) displays a relaxed modulus close to 100 MPa in this temperature range. The most probable explanation of the decrease of the modulus upon low content whiskers addition is that the accumulation of plasticizer near the cellulose/amylopectin interface should probably be enhanced under moister conditions. Indeed, the increased molecular mobility ascribed to the plasticizing effect of water should most probably induce a higher diffusivity of the plasticizer toward the cellulose surface. The tunicin whiskers are therefore isolated of each other by a plasticizer film preventing any contact and hydrogen bonds formation. This phenomenon is evidenced through the irretrievable modulus drop of the composite at 350–

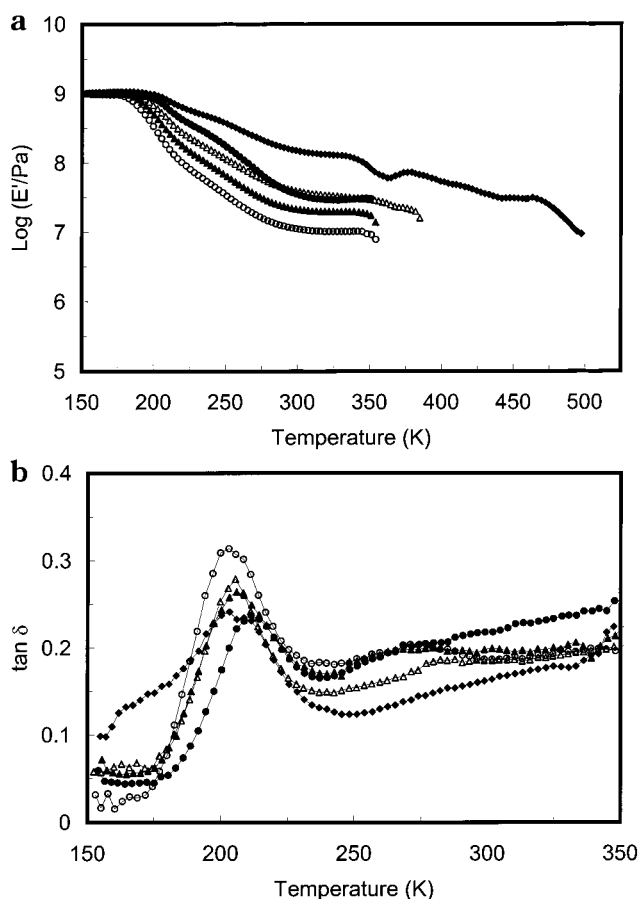


Figure 4. (a) Logarithm of the storage tensile modulus E' and (b) loss angle tangent $\tan \delta$ vs temperature at 1 Hz for glycerol plasticized starch/tunicin whiskers composites filled with 0 (●), 3.2 (○), 6.2 (▲), 16.7 (△), and 25 wt % (◆) of cellulose whiskers and conditioned at 58% RH. E' at 150 K was normalized at 1 GPa for all the samples.

390 K. In addition, the presence of this coating plasticizer film prevents any contact between the starch matrix and the reinforcing phase, hindering the stress transfer required for a reinforcing effect to be observed. The system is therefore equivalent to a starch matrix filled with very low modulus particles, assimilated to empty spaces. It is only when the whiskers loading becomes sufficiently high (25 wt %) that amylopectin/cellulose and cellulose/cellulose interactions are likely to occur, inducing both a reinforcing and a thermal stabilization effect. The same trend as at 43% RH is observed for the two main relaxations processes (Figure 4b).

Figure 5a shows the isochronal plot of $\log(E'/\text{Pa})$ at 1 Hz as a function of temperature for glycerol plasticized starch filled with tunicin whiskers conditioned at 75% RH. For this material, one can think again that an isolating plasticizer film or coating should form at the cellulose/amylopectin interface. However, a transcrystallization phenomenon of amylopectin on cellulose whiskers was evidenced for these highly moist materials.⁷ It was displayed through an extra peak in the X-ray diffraction pattern for 16.7 and 25 wt % filled composites. This crystalline coating was supposed to be constituted of a glycerol/amylopectin complex. It is assumed to weakly transfer the stress from the matrix to the filler as displayed by the low reinforcing effect observed for these composites. In addition, the cellulose network could probably form within the material from the

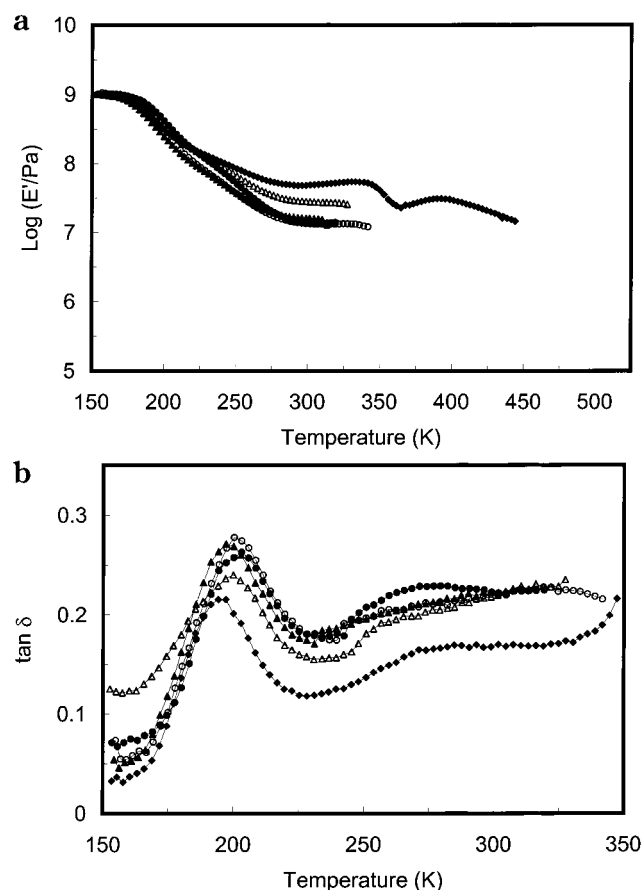


Figure 5. (a) Logarithm of the storage tensile modulus E' and (b) loss angle tangent $\tan \delta$ vs temperature at 1 Hz for glycerol plasticized starch/tunicin whiskers composites filled with 0 (●), 3.2 (○), 6.2 (▲), 16.7 (△), and 25 wt % (◆) of cellulose whiskers and conditioned at 75% RH. E' at 150 K was normalized at 1 GPa for all the samples.

formation of interwhiskers links through transcrystalline layers grown on cellulose surface. This results in a disastrous decrease of the mechanical properties of these composites at relatively low temperature, except for the highly filled material for which direct cellulose/cellulose contacts are likely to occur.

Compared to the 43 and 58% RH conditioned specimens, the increase of the magnitude of the α_1 relaxation process upon the addition of low fractions of tunicin whiskers is not so strong for the 75% RH conditioned composites. The $\tan \delta$ maximum sharply decreases for the 16.7 and 25 wt % filled samples. This is due to a decrease of the number of relaxing species involved in the α_1 relaxation process. The missing entities, which do not participate to this relaxation process in the highly filled samples, could be involved in the probable starch/glycerol transcrystalline layer.

Tensile Tests (Nonlinear Range). The nonlinear tensile mechanical behavior of both the unfilled glycerol plasticized starch matrix and related tunicin whiskers filled composites was analyzed at room temperature. The effects of both the water content within the films and the filler loading on the high strain properties were evaluated.

Plasticized Starch Matrix. The tensile modulus of unfilled starch–glycerol matrix films, derived from the initial slope of the stress–strain plots, is plotted in Figure 6a (it corresponds to a cellulose whiskers content equal to zero) for the various moisture conditions. It

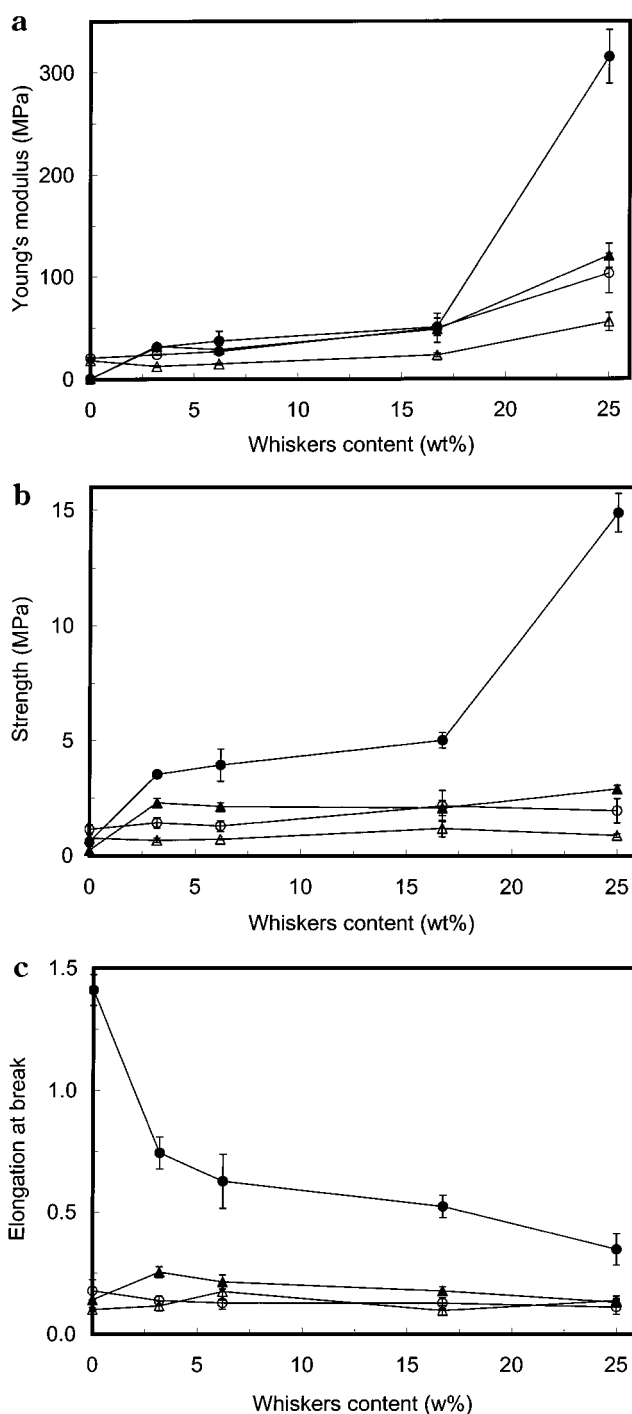


Figure 6. (a) Young's modulus, (b) tensile strength, and (c) elongation at break vs cellulose content of glycerol plasticized starch/tunicin whiskers composites conditioned at 35 (●), 43 (○), 58 (▲), and 75% RH (△) (the solid lines serve to guide the eye). Average values and 95% confidence interval of at least three tests are reported.

ranges between 0.24 and 20 MPa depending on the water content. It is worth noting that at room temperature the glycerol plasticized starch matrix is in the glass–rubber transition zone, as measured by DSC.⁷ The modulus value is therefore strongly sensitive to any temperature fluctuation. Because the moist starch films contain both amorphous and crystalline regions, the measured moduli are average values reflecting the contributions of each phase. Crystalline domains act as both filler and cross-links on the mechanical properties. These values are in agreement with storage tensile

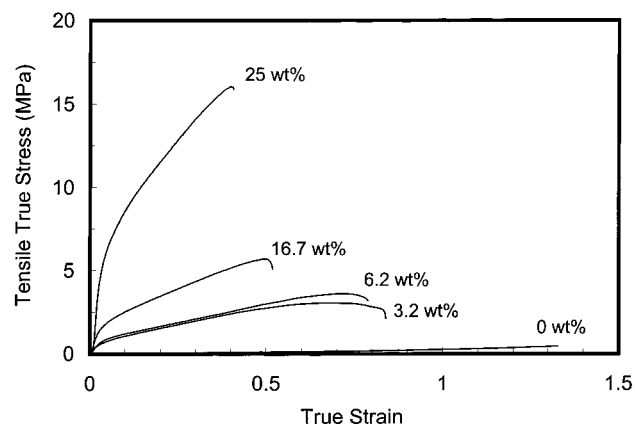


Figure 7. Typical true stress vs true strain curves of glycerol plasticized starch/tunicin whiskers composites conditioned at 35% RH ($T = 25\text{ }^{\circ}\text{C}$, $d\epsilon/dt = 8.3 \times 10^{-3}\text{ s}^{-1}$). The tunicin whiskers contents are indicated in the figure.

moduli measured at room temperature (Figure 1a). However, they are much lower than the ones reported from tensile tests in a previous work for glycerol plasticized potato starch (50–100 MPa),⁶ but it is well-known that the tensile modulus greatly depends on the experimental conditions, such as strain rate and temperature.

The ultimate properties of unfilled starch–glycerol matrix films are reported in Figure 6b,c (it corresponds to a cellulose whiskers content equal to zero) for the various moisture conditions. The true stress and true strain were calculated as described in the Experimental Section. It must be noticed that the fracture of the drier materials (up to 58% RH conditioned composite) occurred in a rather brutal way, whereas the 75% RH conditioned specimen exhibited tearing before break, resulting in a gradual decrease of the tensile stress. The tensile strength was defined for these materials as the highest stress measured before tearing. The 35% RH conditioned sample (amorphous material) displays a typical rubberlike behavior with a high strain at break ($\sim 140\%$). As the water content increases, starch is likely to crystallize, and the elongation at break strongly decreases (up to $\sim 18\%$ at 43% RH). No significant difference is reported for moister specimens. The strength of the material is almost moisture independent and ranges between 0.25 and 1 MPa.

Plasticized Starch/Cellulose Whiskers Composites. The mechanical behavior of the plasticized starch based composites (conditioned at 35, 43, 58, and 75% RH) was analyzed at room temperature as a function of the cellulose whiskers content. Typical stress vs strain curves for the glycerol plasticized starch/tunicin whiskers conditioned at 35% RH are shown in Figure 7. As for the unfilled matrix, the fracture of the drier materials (up to 58% RH conditioned sample) occurred in a rather brutal way, whereas the 75% RH conditioned specimen systematically torn before break resulting in a gradual decrease of the tensile stress. For the 25 wt % filled composite the tearing of the film occurred regardless of the moisture conditions, except at 35% RH.

The tensile modulus of glycerol plasticized starch/tunicin whiskers composite films is plotted in Figure 6a for the various moisture conditions. No significant reinforcing effect is observed regardless of the moisture content up to 16.2 wt % tunicin whiskers. It is only when the cellulose content reaches 25 wt % that an increase in the modulus is observed. This result seems to

disagree with previous dynamic mechanical data, which showed a reinforcing effect at room temperature for lower cellulose content. The ineffective reinforcing effect of cellulose whiskers in the starch matrix, as measured from tensile tests, could originate from the fact that dynamic mechanical measurements involve weak stresses. The possible interactions between percolating cellulose whiskers and between the filler and the matrix are not damaged. Under higher stress, as used for tensile tests, these interactions seem to be destroyed. This observation agrees with the previous structural analysis of these composite materials which shown an accumulation of plasticizer at the cellulose/amylopectin interface.⁷ The formation of this soft interphase most probably prevents any effective stress transfer at the filler/matrix interface when the material is loaded. For highly filled composites (25 wt %), the whiskers concentration is high enough to allow some direct interwhisker interactions. A sparse cellulose whiskers percolating network is most likely to form owing to the high specific area of tunicin whiskers. The higher modulus increase with increasing whiskers loading is observed for the less plasticized material (35% RH conditioned sample), for which the relocation of the plasticizer is assumed to be more restricted. For this specimen the modulus value increases from 51 to 315 MPa as the cellulose whiskers content increases from 16.7 to 25 wt %. At intermediate moisture content (43 and 58% RH), the highly filled composite displays very close modulus values due to similar plasticizer content (see Table 1).

The evolution of the tensile strength and ultimate strain vs whiskers content is plotted in parts b and c of Figure 6, respectively, for glycerol plasticized starch/tunicin whiskers composites conditioned at various moisture conditions. The ultimate properties of the materials seem to be almost composition-independent in moist conditions (43% RH and up). No significant evolution for both the tensile strength and the elongation at break is reported, regardless of the whiskers loading. On the contrary, the strength of the composite conditioned at 35% RH increases as the cellulose content increases. For these materials, a decrease of the ultimate strain vs whiskers content is reported. The much higher values of the elongation at break for the 35% RH conditioned specimen compared to other conditioning conditions is most likely mainly due to the amorphous state of this material.

Conclusions

Nanocomposite materials were obtained from glycerol plasticized waxy maize starch as the matrix and a suspension of tunicin—an animal cellulose—whiskers as a model reinforcing phase. Their mechanical behavior was analyzed in both the linear and the nonlinear range. The effect of moisture content on the glycerol plasticized starch matrix was first reported. A two-step decrease of the storage modulus and concomitant relaxation processes where the loss angle tangent passes through two successive maxima are observed. These two relaxations are associated with the glass–rubber transitions of glycerol-rich (at lower temperature) and amylopectin-rich domains (at higher temperature). The relative magnitude of these relaxation processes and their evolution with water content show that the starch matrix is composed of glycerol-rich domains dispersed in an amylopectin-rich continuous phase and that only the amylopectin chains located in the amylopectin-rich

domains are able to crystallize in moist conditions. A decrease of the thermal stability of the starch matrix is also reported for increasing moisture content.

A relatively very low reinforcing effect is reported upon the addition of tunicin whiskers. This observation could be explained by competitive interactions between the components and by a plasticizer accumulation in the cellulose/amylopectin interfacial zone. This plasticizer accumulation phenomenon, enhanced in moist conditions, most probably interferes with hydrogen-bonding forces that are likely to hold the percolating cellulose whiskers network within the matrix. In highly moist conditions, a possible transcrystalline zone around the whiskers originates from the amylopectin chains located in the glycerol-rich domains. In addition, the coating of the cellulose whiskers by a soft plasticizer-rich interphase hinders the stress transfer at the filler/matrix interface when the material is submitted to a high strain tensile test, resulting in poor mechanical properties of composite materials.

These results disagree with previous experimental data reported with glycerol plasticized starch filled with cellulose microfibrils. An interesting contribution of this work is to display that tunicin whiskers cannot still undoubtedly used as model cellulosic filler to account for the behavior of cellulose microfibrils. In microfibril filled composites, a tangling effect most probably contributes to the previously reported reinforcing effect.

From the knowledge of the structural morphology and of the detailed experimental mechanical behavior of plasticized starch/tunicin whiskers composites, the modeling of the mechanical properties of these complex materials will be discussed in the near future. In addition to some practical applications, this forthcoming study can help to understand some physical properties such as geometric and mechanical percolation effects.

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