

Mechanical Properties of Nanocomposites from Sorbitol Plasticized Starch and Tunicin Whiskers

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ABSTRACT: Nanocomposite materials were obtained using sorbitol plasticized waxy maize starch as matrix and tunicin whiskers as the reinforcement. The effect of filler load (0–25 wt % whiskers) and the relative humidity levels (0–98%) on the mechanical behavior of the films are discussed for linear and nonlinear deformation. The performance of the films is explained, based on the morphology and structural behavior of the composite materials (Mathew and Dufresne, *Biomacromolecules* 2002, 3, 609). The nanocomposites exhibit good mechanical strength due to the strong interaction between tunicin whiskers, matrix, plasticizer (sorbitol), and water, and due to the ability of the cellulose filler to form a rigid three-dimensional network. The evolution of T_g as a function of relative humidity level

and filler load is studied in detail. A decrease in crystallinity of the amylopectin phase is observed at high filler loads, due to the resistance to chain rearrangement imposed by the whiskers. The mechanical strength increased proportionally with filler loads, showing an effective stress transfer from the matrix to the whiskers. An even distribution of whiskers (as determined by SEM) and plasticizer in the matrix contributes to the mechanical performance. The mechanical properties of the nanocomposites showed a strong dependence on relative humidity conditions. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 4065–4074, 2008

Key words: plasticized starch; biopolymers; nanocomposites; tunicin whiskers; thermomechanical properties

INTRODUCTION

Biopolymers are increasingly studied and used for applications in which synthetic polymers are currently used. Ecological, social, and economical factors drive the present urge to develop biodegradable and recyclable materials. Several biodegradable systems are developed with this view in mind.^{1–8} Starch has been used as biodegradable additive in many commercially available products in the past and several high-performance composite materials were developed using a thermoplastics starch matrix and different cellulosic fillers.^{9–13}

It is well known that native cellulose, when subjected to strong acid hydrolysis, readily break down into microcrystalline or nanocrystalline cellulose.¹⁴

The length of the constitutive microcrystals is dependent on the sample origin. They can be as short as about a tenth of a micron, for cotton and wood cellulose, or as long as several microns for tunicates or seaweeds such as *Valonia*.¹⁵ The average width is typically between 5 and 20 nm. The use of highly crystalline nano whiskers, which have high aspect ratio and axial mechanical properties, can lead to good mechanical performance.^{16–22} It was shown that the unusual mechanical properties of tunicin whiskers based nanocomposites were due to a mechanical percolation phenomenon.^{12,13,16,17} Above the percolation threshold, cellulose whiskers form a rigid three-dimensional network within the matrix, resulting from strong interactions between whiskers. This hydrogen-bonded network induced a thermal stabilization of the composite up to 500 K, the temperature at which cellulose starts to decompose.

However, in our earlier reports on glycerol plasticized starch/tunicin whiskers composites a relatively low reinforcing effect was reported upon the addition of tunicin whiskers.²³ This unexpected low mechanical performance was due to the accumulation of the main plasticizer toward the cellulose/amylopectin interfacial zone, which interferes with hydrogen-bonding in the system.²⁴ The coating of the cellulose whiskers by plasticizer hindered the stress

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transfer at filler/matrix interface, resulting in poor mechanical properties. Therefore, further studies are taken up with a different plasticizer to understand the possibilities of creating an efficient filler/matrix interface, which will not interfere with the stress transfer mechanism. We have also investigated in detail the possibilities of using different polyols as the plasticizer for starch and were reported earlier.²⁵

Composites were developed from waxy maize starch and an aqueous suspension of tunicin whiskers using 33 wt % sorbitol as the plasticizer and the choice of sorbitol was based on its higher molecular weight compared with glycerol (182 vs. 92 g mol⁻¹). The morphological investigation of these composites were reported earlier by us.²⁴ The studies showed that sorbitol having a higher molecular weight and the larger amount of alcohol groups to interact with starch, has been successful in hindering the diffusion of the plasticizer to the filler surface. The effect of relative humidity and filler load on the glass-rubber transition temperature (T_g), morphology, water uptake, and crystallinity of the system was also reported in detail.²⁶ The SEM studies of these nanocomposites revealed an even distribution of the filler in the matrix and no evidence of preferential migration of plasticizers toward the cellulose surface was observed. It was found that crystallinity of the system increased continuously on the addition of tunicin whiskers. The glass transition temperature of the plasticized starch matrix was found to increase slightly up to about 15% whiskers loading, after which it decreased. In the present work, the mechanical performance of this system is investigated in both the linear and nonlinear ranges as a function of both the moisture and the whiskers contents. The complexity of this system arises from the presence of starch, cellulose, main plasticizer (sorbitol), and water, giving rise to competitive interaction and the high specific surface area of tunicin whiskers ($\sim 170 \text{ m}^2 \text{ g}^{-1}$).

EXPERIMENTAL

Film processing

The preparation of cellulose microcrystals (or whiskers) from tunicate (a sea animal) and of the starch gels preparation from waxy maize starch are described elsewhere.²⁶ Cellulose whiskers consist of slender parallelepiped rods that have a broad distribution in size. They have a length ranging from 500 nm up to 1–2 μm 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

+ sorbitol + water + colloidal cellulose whiskers suspension) were mixed to obtain composite films with a homogeneous dispersion and with different compositions. The sorbitol 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). A homogeneous mixture was obtained by stirring in a preheated autoclave reactor at 160°C for 5 min. After mixing, the air remaining in the suspension was removed under vacuum (~ 300 mbars) 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. Six relative humidity (RH) atmospheres at 20–25°C were used, namely 0, 31, 43, 58, 75, and 98% RH. Samples were conditioned 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 was around 10^{-4}). The specimen was a thin rectangular strip ($\sim 30 \times 5 \times 0.5$ mm) conditioned at the previously mentioned relative humidities. Measurements were performed in isochronal conditions at 1 Hz, and the temperature was varied in steps of 3 K/min between 150 and 510 K. In the present work, results are displayed through the storage modulus, E' , and the loss factor, $\tan \delta$.

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 100N. The specimen was a thin rectangular strip ($\sim 30 \times 5 \times 0.5$ mm), conditioned at the relative humidities mentioned earlier. The gap between pneumatic jaws at the start of each test was 20 mm. The stress–strain curves of conditioned samples were obtained at room temperature at a cross-head speed of 10 mm min⁻¹. Mechanical tensile data were averaged over at least six specimens and the results had good reproducibility in all cases.

RESULTS AND DISCUSSION

Dynamic mechanical analysis (linear range)

Dynamic mechanical analysis of the unfilled and filled (up to 25%) starch materials was performed to

TABLE I
Glass-Transition temperatures (T_g) and the Melting
Temperatures (T_m) of Tunicin Whiskers/Plasticized
Starch Nanocomposites Conditioned at Different
Moisture Conditions (From DSC)

RH (%)	Cellulose (wt %)	T_g (K)	T_m (K)
0	0	286.2	–
	5	289.3	–
	10	291.7	–
	15	290.87	–
	20	286.5	–
	25	283.5	–
31	0	266.7	–
	5	276.5	–
	10	275.9	429.07
	15	287.5	430.06
	20	284.5	425.04
	25	280.3	421.26
43	0	245.4	419.5
	5	240	415.6
	10	244.4	422.21
	15	242.2	412.04
	20	243.7	416.45
	25	241.6	416.16
58	0	242.7	415.79
	5	241.5	413
	10	241	414.39
	15	247.89	410.6
	20	243.5	405.7
	25	238.5	411.07
75	0	221.5	418.19
	5	222.7	401.57
	10	226	406.41
	15	221.1	400.42
	20	219.4	403.32
	25	220.5	406.95
98	0	208.3	396.09
	5	211.4	397.84
	10	216.8	408.75
	15	223.8	399.33
	20	220.3	396.79
	25	218.5	403.11

study the thermomechanical behavior of these systems. The effects of both water and filler contents on the linear mechanical properties were analyzed. In Table I, the temperatures of glass-rubber transition (T_g) and melting endotherm (T_m) previously obtained from DSC measurements²⁵ are given for clarity and ease of comparison.

Plasticized starch matrix

The plots of the storage tensile modulus (E') and loss angle tangent ($\tan \delta$) at 1 Hz as a function of temperature for the sorbitol plasticized starch matrix conditioned at various RH are given in Figure 1(a,b), respectively. At low temperature ($T < 220$ K), the polymer is in the glassy state and no noticeable change in the storage modulus value with variation in moisture content is expected. However, it is well

known that the exact determination of the glassy modulus value depends on the precise knowledge of the sample dimensions. At room temperature, most of the samples were soft (especially for highly moist films) and it was difficult to obtain a constant and precise thickness along these samples. For the ease of comparison of the effect of water content on the modulus evolution, the modulus at 150 K was normalized at 1 GPa for all the samples. At higher temperatures, a decrease of the storage of modulus is observed. This modulus drop appears in the glass-rubber transition zone previously determined by DSC (see Table I).²⁶ It is therefore ascribed to an energy dissipation phenomenon involving cooperative motions of long amorphous sequences likely to rotate and translate.

This relaxation process is displayed in Figure 1(b) in the concomitant maximum of the loss angle tangent. The temperature position of this main relaxation process decreases as the moisture content increases, in agreement with DSC results,²⁶ owing to the plasticization effect of water. It decreases from 292 down to 235 K as the relative humidity increases

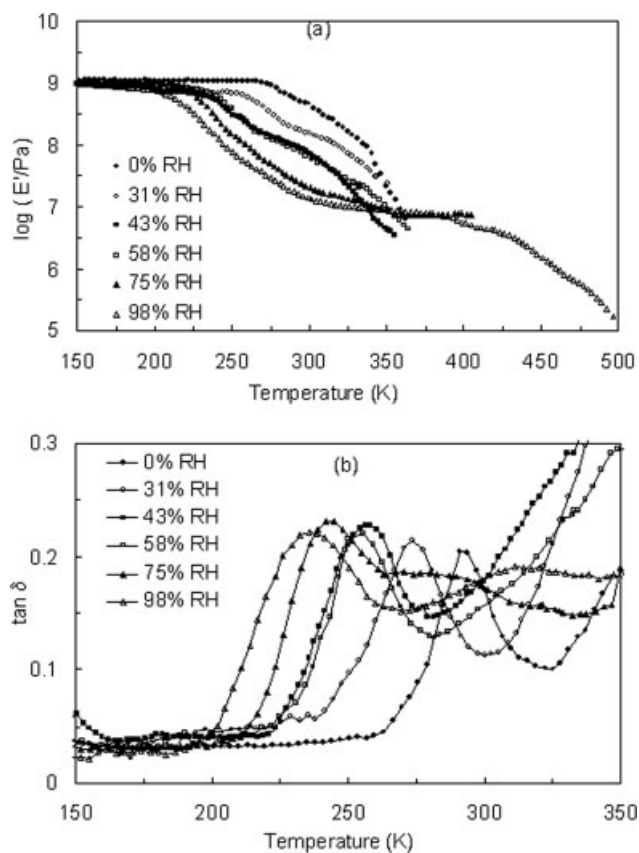


Figure 1 (a) Logarithm of the storage tensile modulus E' and (b) loss angle tangent $\tan \delta$ versus temperature at 1 Hz for sorbitol plasticized starch matrices conditioned at different RH. E' at 150 K was normalized at 1 GPa for all the samples.

from 0 to 98% RH. This behavior reflects the lower energy requirement for molecular motion to occur in the presence of bound water. At higher RH levels, water-water bridges loosen the H-bonded network and relaxation occurs at lower temperatures. Similarly to what was observed for glycerol plasticized waxy maize starch,²¹ no significant difference is reported for the temperature position of the main relaxation process when samples are conditioned at either 43 or 58% RH. This was ascribed to the fact that the water and total plasticizer contents were very close for these two materials. The main difference between glycerol and sorbitol plasticized starch was the presence of a double T_g for the former and a single one for the latter.^{21,23,24} From dynamic mechanical analysis, two successive maxima of $\tan \delta$ were clearly identified for the glycerol plasticized starch.²³ These two relaxations processes were ascribed to the glass-rubber transition of glycerol and amylopectin-rich domains. The single T_g observed for sorbitol plasticized starch is not an unequivocal indication of a homogeneous system. The presence of one glass transition temperature for the majority of binary, ternary, and quaternary polymeric systems is usually attributed to the close proximity of the T_g s of the component phases.^{26,27} It is worth noting that the T_g of pure sorbitol is ~ 273 K while that of glycerol is ~ 198 K. The glass-rubber transition of sorbitol and sorbitol plasticized amylopectin are in close proximity and it could explain the single peak. It is also important to note that the temperature position of the main relaxation (as well as the T_g values) of sorbitol plasticized matrix falls between the two transitions reported for glycerol plasticized waxy maize starch.^{23,24}

Concerning the magnitude of the main relaxation process of the plasticized starch matrix, no significant change is observed as a function of the moisture level, despite the fact that an increasing part of the amylopectin chains crystallize with increasing RH level. However, it is observed that for semicrystalline materials (43% RH conditioned samples and up) the width of the main relaxation process is higher than for amorphous materials. This can be ascribed to a broader distribution of the relaxation times of amorphous amylopectin chains in the presence of crystalline domains and is indicative of positive interaction between the different phases in the plasticized matrix.

On increasing temperatures above T_g , the measurement of the storage modulus becomes difficult for dryer samples because of their brittleness. The E' value for 0 and 31% RH conditioned samples should reach a plateau around 1 MPa typical of fully amorphous materials. A broader temperature range can be investigated for moister samples (75 and 98% RH conditioned materials). The inherent progressive dehydration of the material due to the temperature

increase is not sufficient to weaken it. For these moist samples, the relaxed modulus stabilizes around 10 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 starch sample, the higher the crystallinity.^{28–30} This behavior was reported for our materials also.^{25,26} The crystalline regions of amylopectin act as physical crosslinks for the elastomer. In this physically crosslinked system, the crystalline regions also is expected to act as filler particles because of their finite size, thus increasing the modulus substantially. The reinforcing effect of the crystallites within the matrix is also attributed to the size of the crystalline domains, which is related to the melting temperature, and to their size distribution. As reported earlier, for the 98% RH conditioned composites, the crystallinity of the material is higher than for the samples conditioned at 75% RH.²⁶ This can contribute to an increase of the relaxed modulus. At the same time the amorphous matrix becomes softer with increase in the water content which will decrease the relaxed modulus. These two effects compensate each other and the rubbery modulus is found to be of similar magnitude for both samples. In the final zone, the tensile modulus steadily decreases with increasing temperature due to irreversible chain relaxation [Fig. 1(a)].

Plasticized starch/tunicin whiskers composites

Figure 2 shows the evolution of $\log(E'/\text{Pa})$ [Fig. 2(a)] and $\tan \delta$ [Fig. 2(b)] versus temperature at 1 Hz for sorbitol plasticized starch/tunicin whiskers nanocomposites conditioned at 98% RH. The storage modulus at 150 K was normalized again at 1 GPa for all the samples. This is justified by the fact that at the initial temperature used for these studies the difference in modulus between the crystalline cellulose and that of the glassy phased starch matrix was not high enough to easily appreciate a reinforcing effect.

No significant change of the temperature position of both the modulus drop [Fig. 2(a)] and loss angle tangent maximum [Fig. 2(b)] upon whiskers addition is reported. Our previous DSC measurements²⁶ displayed a slight increase of T_g up to about 15 wt % whiskers loading and a decrease of T_g at higher whiskers content. The main difference measured is the magnitude of the main relaxation process, which is strongly reduced upon whiskers addition. The magnitude of this relaxation process, which is related to the magnitude of the modulus drop, depends upon both the number of mobile entities and their contribution to the compliance. Therefore, the reduction of the magnitude of the relaxation process may be, at least partially, due to the decrease of

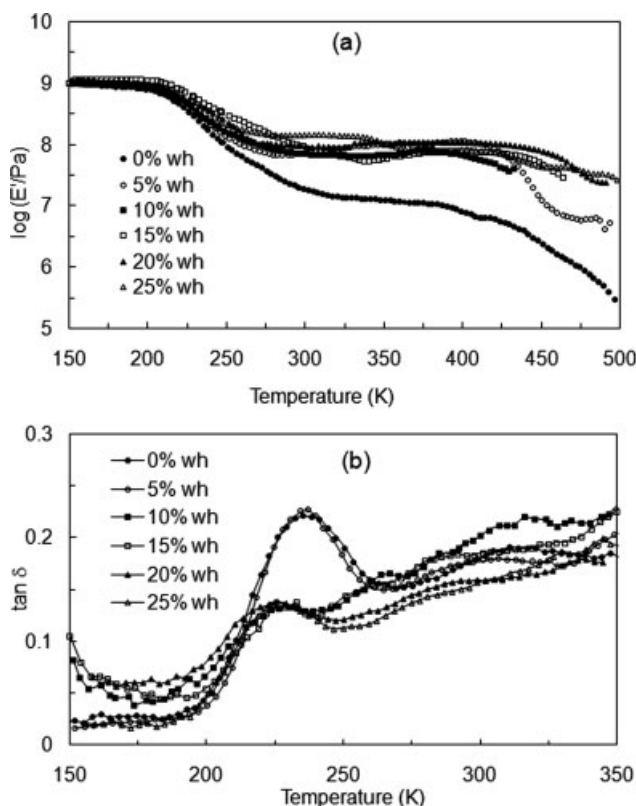


Figure 2 (a) Logarithm of storage tensile modulus E' and (b) loss angle tangent $\tan \delta$ versus temperature for sorbitol plasticized starch matrices with different whiskers content, conditioned at 98% RH. E' at 150 K was normalized at 1 GPa for all the samples.

matrix material amount, responsible for damping properties. It is also observed that the modulus drop is reduced for the films that contained cellulose whiskers. For instance, the relaxed modulus of a film containing 15 wt % of whiskers (around 186 MPa at 350 K) is more than eight times higher than that of the matrix (around 22 MPa at 350 K). This reinforcing effect should be higher at increasing temperature because the modulus of composites decreases gradually with temperature whereas the one of the unfilled matrix drops sharply.

After the relaxation around 230 K, the composite modulus decreases progressively up to ~ 400 K, where after the modulus decreases more rapidly. The mechanical behavior in this temperature range is similar for 5–25 wt % whiskers filled samples. They all exhibit an ill-defined plateau region in the temperature range of 300–400 K.

The modulus of glycerol plasticized starch cellulose whiskers composites was significantly lower than for sorbitol plasticized starch/tunicin whiskers composites.²⁴ The plasticizer was found to accumulate at the cellulose/amylopectin interface, reducing the ability of the cellulose whiskers to form a strong

network, resulting in a relatively low modulus. In this sorbitol plasticized system, the modulus is roughly 15–20 times higher than the corresponding glycerol plasticized system. The absence of transcrystallization of plasticizer at the cellulose/amylopectin interface was proved by DSC and WAXS studies.¹⁴ Also, crystalline domains were found to develop in the matrix during the water evaporation step, contributing to the enhanced modulus.

The $\tan \delta$ curve [Fig. 2(b)] passes through a maximum around 230 K, corresponding to the relaxation of amylopectin domains. The peak shows a decrease in intensity as the whiskers content goes above 5 wt %, showing a decrease in the number of relaxing species involved in the transition. The decrease in mobility of the system by the introduction of whiskers may be the reason for this decrease in peak height. However, one must note that the temperature positions of the $\tan \delta$ peak remain constant for filler loads up to 15 wt %, whereas for higher filler contents, a shift to lower temperatures is measured. This is indicative of a decrease in the crystallinity in the system. The presence of a large amount of whiskers (above 15 wt %) in the gelatinized starch decreases the mobility of the amylopectin chains, and restricts the ability of starch to crystallize during evaporation step. This decrease in crystallinity of starch at higher whiskers content results in a lowering of T_g . The same trend was observed in DSC analysis and is explained in detail in the first part of this work.²⁶

In Figure 3, the $\log E'$ (normalized in 1 GPa at 150 K) and $\tan \delta$ curves of composites with 75% RH are presented. A modulus drop is seen for the composites around 235 K whereas the modulus remains almost constant up to ~ 450 K. The modulus drop is less in the case of composites and the magnitude of the storage modulus in the rubbery domain increases from 21 to 1870 MPa as the whiskers content increases from 0 to 25 wt %. The $\tan \delta$ curves [Fig. 3(b)] exhibit a single peak. The $\tan \delta$ peaks remain almost constant at ~ 240 K, so there is no measurable phase-separation. In the case of glycerol plasticized composites, a disastrous decrease in modulus was observed at low temperatures, except for highly filled material.²⁴ Such a decrease does not occur in the sorbitol plasticized system, and the modulus increases steadily with an increase of whisker content from 10 to 25 wt %. This again shows that there is no hindrance for the matrix-filler adhesion by transcrystallization of the plasticizer at the interface between the matrix and the filler. This leads to an efficient stress transfer from the matrix to the filler. The absence of the reinforcing effect at 5% whiskers may be due to the fact that the concentration of whiskers is not sufficient enough to form a reinforcing network in the system.

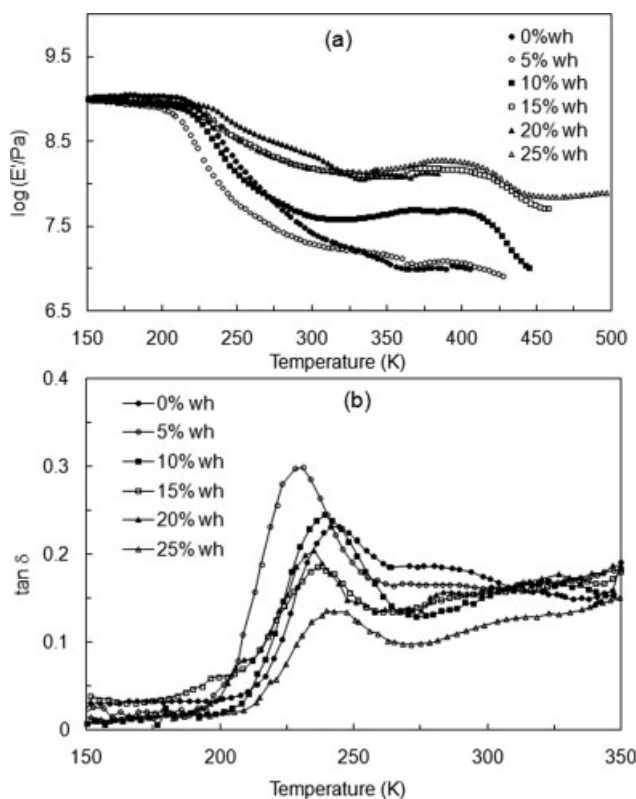


Figure 3 (a) Logarithm of storage tensile modulus E' and (b) loss angle tangent $\tan \delta$ versus temperature for sorbitol plasticized starch matrices with different whiskers content, conditioned at 75% RH. E' at 150 K was normalized at 1 GPa for all the samples.

In Figure 4–7, the $\log E'$ and $\tan \delta$ curves of the composition at 58, 43, 31, and 0% RH, respectively, are given. For 58% RH, a gradual drop in modulus as the temperature increases is measured, marking the relaxation of the amylopectin phase. In the rubbery plateau region (~ 300 – 430 K), where the modulus remains almost constant, we can see an increase in mechanical strength with increase in filler content. The $\tan \delta$ curves [Fig. 4(b)] also show a maximum around ~ 255 K for all filler loads. The relaxation peak intensity decreases with filler load, indicating an increase in stiffness of the matrix upon whiskers addition.

In the case of 43% RH, an improvement in storage modulus with addition of whiskers is observed [Fig. 5(a)]. One can clearly see that the unfilled plasticized matrix behaves as a viscoelastic liquid above 300 K, as the modulus drops drastically with temperature. The composites (with 5–20% whiskers), however, display a more gradual modulus drop around 300 K, after which the modulus remains almost constant up to 475 K. The modulus is 180 MPa for unfilled matrix, 350 MPa for 5 wt % whiskers and 1370 MPa for 25 wt % whisker composites. Also, around 380 K, a slight increase in modu-

lus was observed due to progressive dehydration of the material.

The $\tan \delta$ plot of the composites conditioned at 43% RH as a function of temperature, is given. The decrease in peak height with filler addition is a direct result of decrease in molecular motion in the system due to increased whisker interactions.

In Figure 6, the $\log E'$ and $\tan \delta$ plots of composites conditioned at 31% RH are given. The glass transition modulus drop is largest for unfilled system, and decreases with increasing whiskers content. At 350 K, the modulus of 25 wt % whiskers filled samples is about 17 times (79 MPa) higher than that for the unfilled samples (47.5 MPa).

The $\tan \delta$ curve [Fig. 6(b)] also shows a peak at ~ 270 K corresponding to the glass-rubber transition of the amylopectin rich region. No significant change in temperature position occurs with increasing whisker content.

The storage modulus and loss factor of the composites conditioned 0% RH is shown in Figure 7. It can be seen that the modulus drop is gradually reduced as the content of cellulose whiskers increased. The

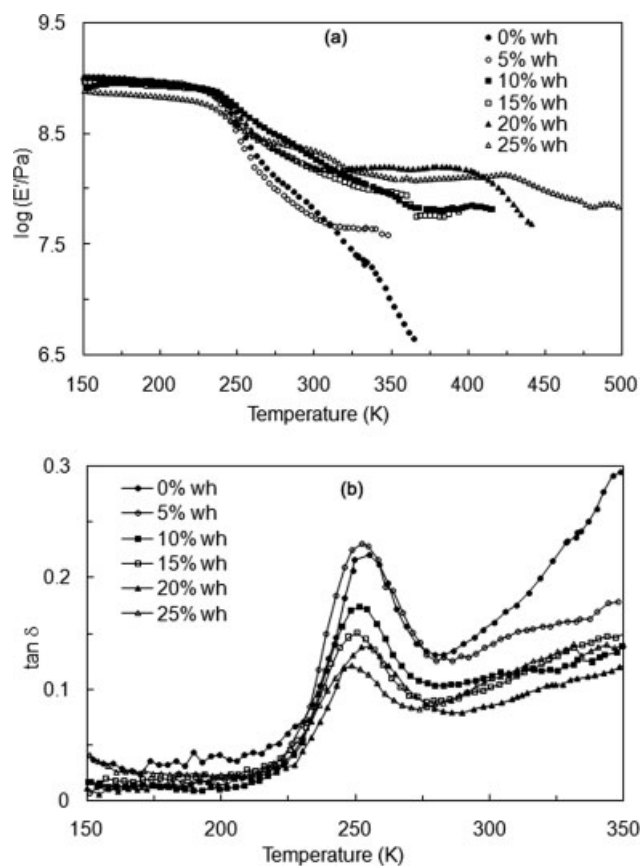


Figure 4 (a) Logarithm of storage tensile modulus E' and (b) loss angle tangent $\tan \delta$ versus temperature for sorbitol plasticized starch matrices with different whiskers content, conditioned at 58% RH. E' at 150 K was normalized at 1 GPa for all the samples.

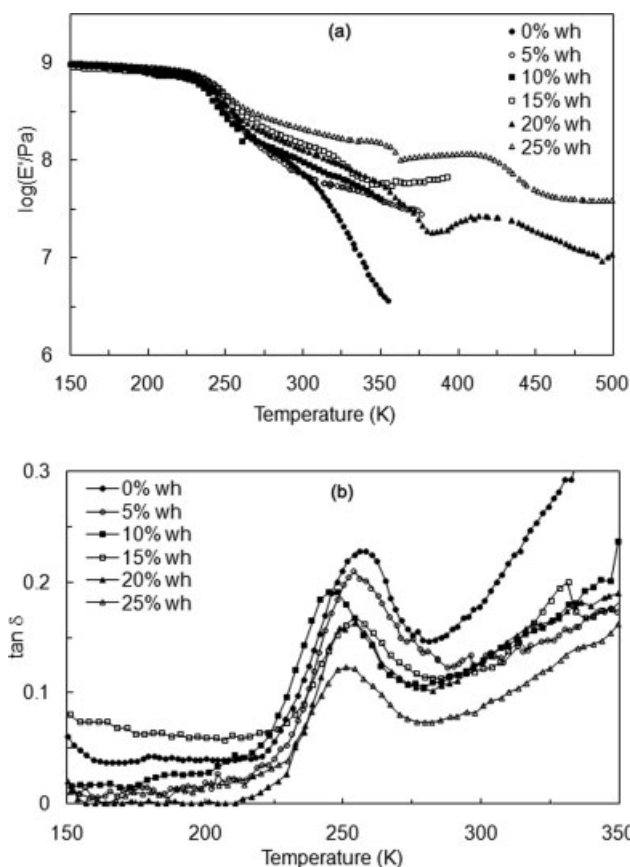


Figure 5 (a) Logarithm of storage tensile modulus E' and (b) loss angle tangent $\tan \delta$ versus temperature for sorbitol plasticized starch matrices with different whiskers content, conditioned at 43% RH. E' at 150 K was normalized at 1 GPa for all the samples.

relaxed modulus at 350 K for composites with 25 wt % whiskers is 1100 MPa, whereas it has a value for the matrix of 53 MPa, a behavior in line with the other RH levels. In Figure 7(b), no significant change in the temperature position of the $\tan \delta$ maxima is observed as the whiskers content increases.

It can be seen that the $\tan \delta$ peak height decreases as the filler content increases, showing a reduction in the number of relaxing species involved in the relaxation process. The resistance to participate in the relaxation process is directly proportional to the filler loading and is attributed to the resistance offered to polymer chain relaxation by the percolating tunicin whiskers network. It can also be seen that modulus increase in all the cases with increase in filler loading. In addition to the reinforcing effect, an increase in thermal stability also was observed with addition of whiskers. The storage modulus drop at glass transition occurs at higher temperatures as the filler load increases. This phenomenon is more prominent at low RH levels. Added moisture in the composite reduces the whisker-matrix interactions and the matrix can relax at lower temperatures.

As the filler content increases, failure occurs at higher temperatures. At 20% whiskers and above, the modulus drops only around 500 K, when cellulose degradation occurs.

Tensile tests (nonlinear range)

The nonlinear mechanical behavior of sorbitol plasticized starch matrix and tunicin whiskers filled composites was analyzed at room temperature.

Plasticized starch matrix

The stress-strain curves of unfilled starch matrix at 31, 43, 58, and 75% RH are given in Figure 8 (at 0% RH and 98% RH the unfilled samples were too weak to be tested). It can be seen that the tensile strength remains almost constant around 4 MPa for 43 and 58%, and decreases to 3 MPa at 75%, whereas at 31% RH the tensile strength is about 8 MPa. Arvanitoyannis and coworkers have reported a decrease in tensile strength with increased crystallinity for corn starch films, due to embrittlement of the sample.³¹ In

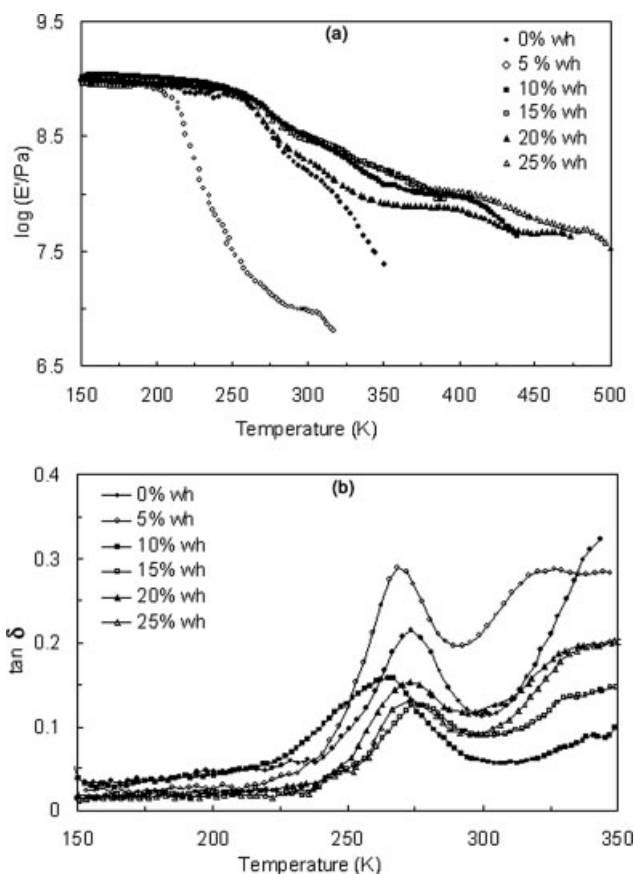


Figure 6 (a) Logarithm of storage tensile modulus E' and (b) loss angle tangent $\tan \delta$ versus temperature for sorbitol plasticized starch matrices with different whiskers content, conditioned at 31% RH. E' at 150 K was normalized at 1 GPa for all the samples.

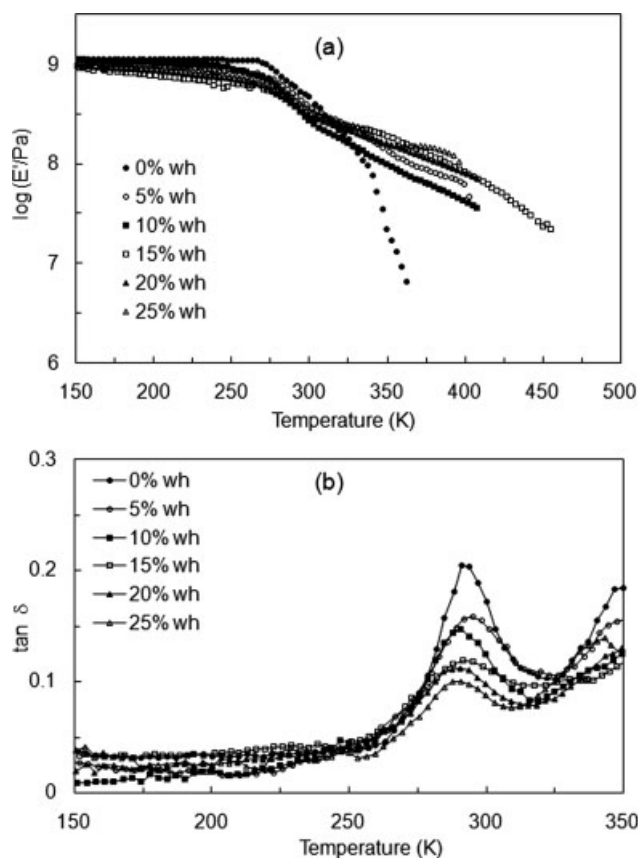


Figure 7 (a) Logarithm of storage tensile modulus E' and (b) loss angle tangent $\tan \delta$ versus temperature for sorbitol plasticized starch matrices with different whiskers content, conditioned at 0% RH. E' at 150 K was normalized at 1 GPa for all the samples

the case of sorbitol plasticized matrix, increasing crystallinity is also expected to cause embrittlement. The reduction in tensile strength is observed, albeit on a limited scale. The elongation at breaks increases as the RH level increases from 31 to 75% due to plasticization of the amylopectin chains by sorbed

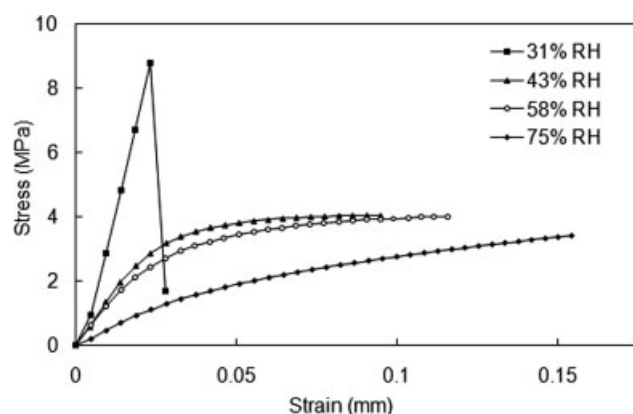


Figure 8 Effect of moisture level (RH %) on the stress-strain curves of unfilled sorbitol plasticized matrix.

water. At 31% RH, the plasticization by water is less and the almost all molecular mobility can be attributed to the 33% of sorbitol. The elongation at break is governed by the ability of polymer chains to slip over one another under an applied load. The plasticizing effect of the water makes the polymer chains flexible and extendable, resulting in the measured increase in maximum elongation.

The Young's modulus (slope of the stress-strain curve) increases for the unfilled matrix, as the RH level decreases. For 31% RH the modulus is measured to be 350 MPa, and at 75% RH, it drops to 48 MPa. The modulus values are in agreement with the storage modulus values measured at room temperature using DMA. As was noted before, the modulus values for sorbitol-plasticized starch are substantially higher than values found for the glycerol plasticized system.

Plasticized starch/cellulose whiskers composite

The mechanical behavior of the composites conditioned at (0 to 98% RH) was determined, as a function of filler load. Stress-strain curves of the composites conditioned at 75% RH are given in Figure 9, as representative curves. The elongation at breaks remains almost constant around 16–18%. The large amount of water present in the system plasticizes the matrix, and the elongation at break is largely independent of filler load. This shows that the flexibility of the system and chain extensibility is governed by the plasticizer content. The strength increases gradually with increased filler load, showing that the whiskers are the load bearing entity in the composites.

In Figure 10, the tensile strength, Young's modulus and elongation at breaks are plotted a function of whiskers content, for different RH condition. It can be seen, that at a given filler load, the tensile

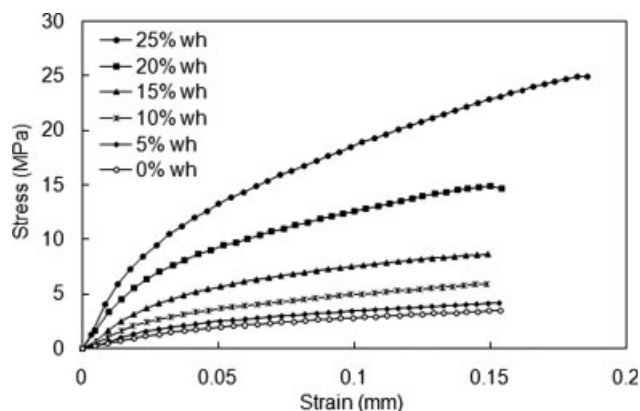


Figure 9 Effect of filler loading on the stress-strain curves of sorbitol plasticized matrix/tunicin whiskers composites conditioned at 75% RH.

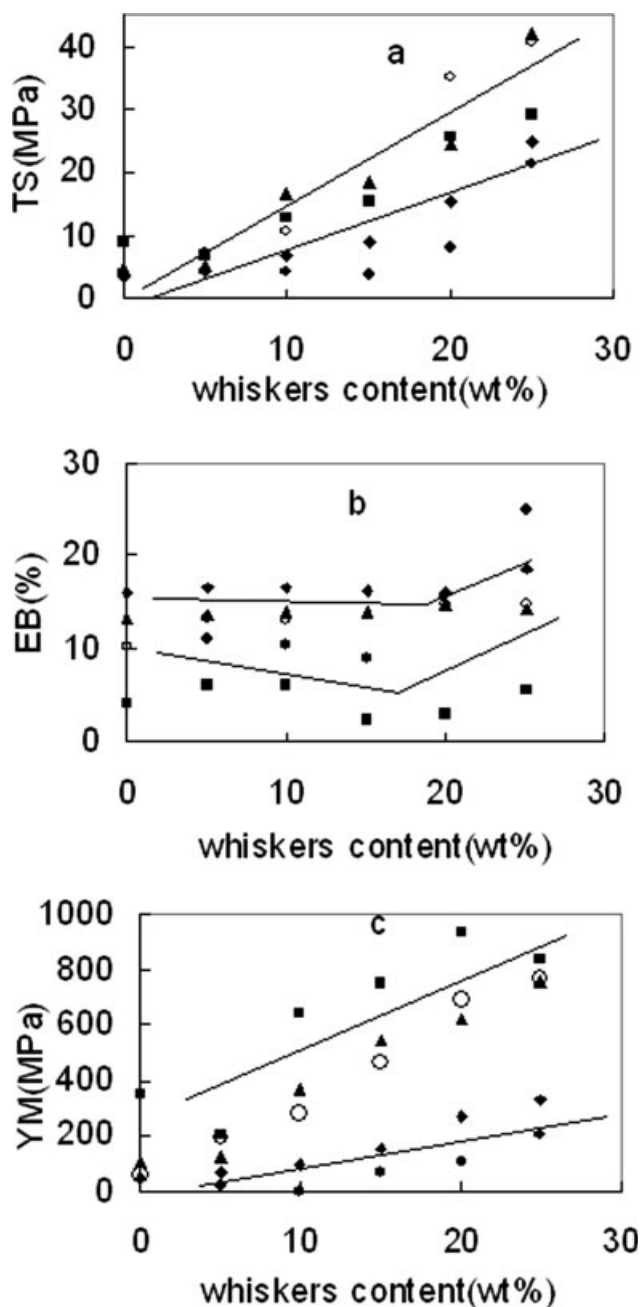


Figure 10 (a) Tensile strength, (b) Elongation at break, and (c) Young's modulus as a function of cellulose content in sorbitol plasticized starch/tunicin whiskers composites at 31 (■), 43 (○), 58 (▲), 75 (◆), and 98 (●). Solid lines serve to guide the eye.

strength and Young's modulus increase as the RH level decreases from 98 to 31%.

The tensile strength [Fig. 9(a)] shows a consistent increase above 10 wt % whiskers, at all RH levels. The strength is highest at 25% whiskers. When the effect of moisture on strength is considered, it can be seen that the tensile strength is higher for samples conditioned at low RH level (31 and 43%).

The elongation at break is low for all samples, irrespective of filler content and moisture level. The

matrix is more or less rigid, without much possibility for extension. This confirms our earlier conclusions that there are strong H-bonding interactions between the plasticizer, matrix, and fillers.

The Young's modulus as a function of whiskers content also shows a marked increase with filler loading. The Young's modulus is also found to increase with a decreasing water uptake. For example, the Young's modulus increases from 208 MPa (98% RH) to 838 MPa (31% RH) for 25 wt % whisker composites. The plasticization by water thus appears to have a very significant effect on the composite performance. In addition, at higher RH levels (above 75%), a thin layer of water molecules may accumulate at the amylopectin/cellulose whisker interface, restricting efficient stress transfer between the matrix and filler. It was also shown earlier through contact angle measurements that the water has more affinity to cellulose than to starch and agrees with the assumption that water can accumulate at the interface.²³

It is worth comparing the tensile strength and modulus with the glycerol plasticized tunicin whiskers composites. In glycerol plasticized system, at 25wt% whiskers, only a limited increase in modulus was observed.²⁴ The Young's modulus of sorbitol plasticized starch is as high as 950 MPa (for 20%wh at 31% RH) while the maximum values for the glycerol plasticized system was only ~ 300 MPa (for 25%wh at 35% RH). The maximum tensile strength observed was ~ 15 MPa (for 25 wh at 35% RH) where as in sorbitol plasticized system tensile strength reached up to ~ 42 MPa (for 25% wh at 58% RH). The maximum elongation at break observed for glycerol plasticized starch was 15% (for 0% whiskers at 35% RH) and decreased further with the addition of whiskers, compared with sorbitol plasticized starch which showed a maximum of 25% elongation (for 25%wh at 98% RH). This enhanced performance of sorbitol plasticized system can be explained as follows.

In the glycerol plasticized system, transcrystallization of plasticizer in the cellulose/amylopectin interface was demonstrated, effectively decreasing fiber-matrix adhesion. The sorbitol plasticized system did not show this transcrystallization phenomenon (evidenced by DSC and WAXS). This leads to improved fiber-matrix adhesion and effective stress transfer between the matrix and filler.

In the sorbitol plasticized system, crystallites may be formed during evaporation as well as sample conditioning. Since these starch rich phases are below their T_g , one explanation for the increase in modulus is the crystallinity of the starch phase.^{25,32} In sorbitol plasticized systems, the higher modulus is the combined outcome of the presence of crystallites that act as fillers and crosslinks³² as well as the

reinforcing effect of the tunicin whiskers network. In the case of glycerol plasticized system only the latter is prominent.

CONCLUSIONS

Nanocomposite materials were obtained from sorbitol plasticized waxy maize starch and tunicin whiskers. Their mechanical performance was studied in nonlinear and linear range. The unfilled matrix exhibited a one step decrease of storage modulus and a loss angle tangent peak, showing the relaxations associated with amylopectin rich domains. For all RH levels, the modulus increased gradually with filler load, and above $\sim 5\%$ whiskers, a significant improvement is observed. The tensile strength and Young's modulus are high at lower RH levels, and elongation at break remains constant, irrespective of RH and filler content. This shows that a good fiber-matrix adhesion is present in the system favoring effective stress-transfer at the fiber/matrix interface. The large number of H-bonds between the matrix and the plasticizer checks the elongation at break and improves the modulus of the composite.

The composite system can be considered as a rigid network of plasticizer, amylopectin, and whiskers by hydrogen bonding, in addition to the individual network formed by the reinforcing whiskers. The result is enhanced mechanical properties and improved thermal stability.

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