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Mechanical properties of natural rubber nanocomposites reinforced with cellulosic nanoparticles obtained from combined mechanical shearing, and enzymatic and acid hydrolysis of sisal fibers

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Abstract In a previous work (Siqueira et al. 2010b) the preparation of cellulosic nanoparticles from sisal fibers using different processing routes, viz. a combination of mechanical shearing, acid and enzymatic hydrolysis was reported. It was shown that the pre-enzymatic hydrolysis treatment of bleached sisal pulp helps the preparation of well individualized rod-like nanocrystals. An amorphous polymer (natural rubber—NR) was chosen as model matrix to investigate the effect of these nanoparticles on the thermo-mechanical properties of nanocomposites. Both tensile tests and dynamic mechanical analyses showed improved stiffness for all nanocomposites. The enzymatic treatment allowed production of a huge range of cellulosic nanoparticles which provided completely different mechanical properties to NR matrix.

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Introduction

Cellulosic nanoparticles, the generally accepted and overused trade name being nanocellulose, have generated interest from the scientific community because of their biodegradability, strength and other characteristics. Sustainability and green issues continue as top priorities for many businesses and individuals, stimulating the search for non-petroleum based structural materials like bio-nanocomposites that are biodegradable, high performance and lightweight. The extraction or isolation of crystalline cellulosic regions, in the form of nanocrystals, is a simple process based on acid hydrolysis. Different descriptors are used in the literature to designate these crystalline rod-like nanoparticles. It is mainly referred as whiskers, nanowhiskers, cellulose nanocrystals, NCC (nanocrystalline cellulose), monocrystals, microcrystals or microcrystallites, despite their nanoscale dimensions. The terms microfibrils, microfibrillated cellulose (MFC), or nanofibrillated cellulose are used to designate cellulosic nanoparticles obtained by a simple mechanical shearing disintegration process.

Impressive mechanical properties and reinforcing capability of nanocellulose make it ideal candidate for the processing of polymer nanocomposites (Azizi

Samir et al. 2005; Dufresne 2006, 2008; Hubbe et al. 2008). With a Young's modulus of over 100 GPa and a surface area of several hundred $m^2\ g^{-1}$ (Šturcova et al. 2005), it has the potential to significantly reinforce polymers at low filler loadings. However, the dimensions of cellulosic nanoparticles depend on several factors, including the source of the cellulose and the exact preparation conditions. The flexibility and tangling possibility of the nanofibers play an important role (Azizi Samir et al. 2004; Bendahou et al. 2009; Siqueira et al. 2009). It was reported that entangled MFC induces a higher reinforcing effect than straight whiskers, whereas the elongation at break was lower.

In a previous study (Siqueira et al. 2010b) the preparation of cellulose nanocrystals by an acid hydrolysis treatment of MFC (eventually pre-treated with enzymes) was reported. Sisal fibers and two types of commercial cellulases (endoglucanase and exoglucanase) were used. An important range of cellulosic nanoparticles was obtained depending on the treatments and their sequence. The goal of the present study consists in evaluating the reinforcing capability of these nanoparticles. The mechanical behavior of nanocomposite films prepared from these nanoparticles has been investigated in the present study. We choose natural rubber (NR) as the matrix material. The choice of the matrix was dictated by the fact that it is a natural amorphous polymer, often reinforced with nanoparticles and available as latex.

Experimental

Materials

Native sisal fibers (*Agave sisalana*), originating from northeast Brazil, were purchased in Mariana (Minas Gerais, Brazil). Natural rubber (NR) was kindly supplied as latex by Michelin (Clermont Ferrand, France). It contained spherical particles with an average diameter around 1 μm and its solid content was about 60 wt%. The density of dry NR, ρ_{NR}, was 1 g cm^{-3} and it contained more than 98% cis-1,4-polyisoprene. The enzymes used were Celluclast (Cclast) (Novozymes, Denmark) and Ecopulp Energy (Eco) (AB Enzymes, Germany). The enzyme labeled Cclast has mostly an endoglucanase activity while Eco has mostly an exoglucanase activity.

Preparation of nanoparticles

The preparation of sisal cellulose whiskers and MFC was reported in our previous study (Siqueira et al. 2010b). The various treatments performed on sisal bleached pulp and their sequence were easily found in the codification of the specimens, with MFC for the mechanical shearing treatment, AHx for the acid hydrolysis treatment, x being the temperature at which the treatment was performed, and Ey or Cy for the enzymatic hydrolysis treatment carried out with enzyme Eco or Cclast, respectively, y being the enzymatic concentration (wt%). For instance, sample E0.1-MFC-AH45 refers to cellulose nanoparticles obtained by enzymatic hydrolysis of bleached sisal pulp with Ecopulp Energy (concentration 0.1 wt%) followed by mechanical shearing, and acid hydrolysis performed at 45 °C.

Preparation of nanocomposite films

NR latex and aqueous suspension of cellulose nanoparticles were mixed to obtain final dried films around 0.5–1 mm thick and 6 wt% nanoparticle content. The mixture was stirred using a magnetic stirrer for 8 h. Preliminary water evaporation was done using a rotavapor before casting the mixture in Teflon molds. The films were dried in a ventilated oven at 40 °C for 5 days. Further drying was performed in oven under vacuum at 40 °C for 12 h. All mechanical tensile tests were performed the same day to avoid any influence of possible NR oxidation. Nanocomposite films were stored in a conditioned room and dried in oven under vacuum at 40 °C for 12 h before DMA tests. These analyses were performed during the same week.

The codification of the nanocomposite films was as follows: NR-N, where N corresponds to the type of nanoparticle. For instance, sample NR-E0.1-MFC-AH45 refers to NR films reinforced with cellulose nanoparticles obtained by enzymatic hydrolysis of bleached sisal pulp with Ecopulp Energy (concentration 0.1 wt%) followed by mechanical shearing, and acid hydrolysis performed at 45 °C.

Characterizations

The mechanical behavior of natural rubber films reinforced with sisal cellulose nanoparticles was investigated in both the non linear and linear range.

Tensile tests were carried out with a RSA3 (TA Instruments, USA) equipment with a 100 N load cell. Measurements were performed with a cross head speed of 10 mm min^{-1} at 25 °C. The samples were prepared by cutting strips 20 mm long from the films and the distance between jaws was set at 10 mm, whereas the width and the thickness of the samples were measured before each measurement. The initial strain rate was therefore $d\varepsilon/dt = 1.67 \times 10^{-2}\,s^{-1}$. Four samples were used to characterize each nanocomposite.

Dynamical mechanical analysis (DMA) of the nanocomposite films was carried out using the same instrument (RSA3 -TA Instruments, USA- working also in tensile mode). The measurements were performed at a constant frequency of 1 Hz, strain amplitude of 0.05%, in the temperature range −100 to 300 °C, heating rate of 5 °C min^{-1} and distance between jaws of 10 mm. The width of the samples varied from 3 to 5 mm, which was measured before each analysis. Two samples were used to characterize each nanocomposite.

Results and discussion

The non linear and linear tensile mechanical properties of cellulosic nanoparticles reinforced natural rubber (NR) nanocomposite films were measured. The former were studied at room temperature whereas the latter were obtained by varying the temperature over a broad range at a fixed frequency. The cellulose nanoparticle content was fixed at 6 wt% which is expected to be higher than the percolation threshold for all samples. From tensile tests, the Young's modulus (E), tensile strength (σ_R) and strain at break (ε_R) of the neat matrix and related nanocomposites were obtained and results are collected in Table 1.

Apart the unfilled NR matrix, the materials can be separated into four main groups, viz. (i) nanocomposites reinforced with standard MFC, i.e. obtained from only mechanical shearing (NR-MFC), (ii) nanocomposites reinforced with acid hydrolyzed MFC using various hydrolysis times (NR-MFC-AH45, NR-MFC-AH50, and NR-MFC-AH60), (iii) nanocomposites reinforced with nanoparticles obtained by omitting the acid hydrolysis treatment, i.e. mechanically sheared and enzyme hydrolyzed samples (NR-MFC-E0.1 and NR-MFC-C0.1) or enzyme hydrolyzed and mechanically sheared samples (NR-E0.1-MFC, NR-C0.1-MFC and NR-C1-MFC), and (iv) nanocomposites reinforced with acid hydrolyzed MFC that was previously hydrolyzed by enzymes (NR-E0.1-MFC-AH45 and NR-C0.1-MFC-AH45).

It is worth noting that sulfuric acid hydrolysis induces the creation of surface sulfate groups which

Table 1 Mechanical properties obtained from tensile tests for NR matrix and related composites filled with sisal nanoparticles: Young's modulus (E), tensile strength (σ_R) and strain at break (ε_R). The storage modulus (E'_{25}) was obtained from DMA measurements at 25 °C. The filler content for all nanocomposites is 6%wt

Sample	E (MPA)	σ_R (MPa)	ε_R (%)	E'_{25} (MPa)
NR	0.50 ± 0.14	0.56 ± 0.13	576 ± 36	1.2
NR-MFC	102 ± 20	2.3 ± 0.6	5.9 ± 3.1	29.5
NR-MFC-AH45	1.6 ± 0.4	0.52 ± 0.09	478 ± 53	4.5
NR-MFC-AH50	27.8 ± 12.5	3.7 ± 0.5	477 ± 57	64.1
NR-MFC-AH60	109 ± 5	5.1 ± 0.4	364 ± 74	125
NR-E0.1-MFC-AH45	58.2 ± 5.1	6.6 ± 0.6	450 ± 54	196
NR-C0.1-MFC-AH45	61.0 ± 8.9	1.8 ± 0.1	160 ± 25	124
NR-E0.1-MFC	31.7 ± 9.9	2.1 ± 0.1	49.6 ± 5.2	36.4
NR-C0.1-MFC	3.9 ± 0.1	0.81 ± 0.08	349 ± 39	15.5
NR-C1-MFC	1.05 ± 0.01	0.49 ± 0.13	789 ± 28	7.2
NR-MFC-E0.1	2.3 ± 0.4	1.0 ± 0.1	849 ± 11	11.0
NR-MFC-C0.1	0.84 ± 0.06	0.30 ± 0.03	311 ± 20	3.4

density increases with the strength of the treatment. Therefore, the comparison of the reinforcing capability of acid-treated particles with mechanically sheared and/or enzyme-treated charge-free particles is delicate because the interfacial characteristics are different. However, these different characteristics are expected to play a role mainly on ultimate properties but a limited role on the reinforcing capability (linear range).

Acid hydrolyzed MFC

The effect of acid hydrolysis conditions on the mechanical properties of nanocomposite films reinforced with cellulosic nanoparticles can be observed in Fig. 1a, which shows typical stress vs. strain curves. The behavior of the unfilled NR matrix has been added as reference. At room temperature, unfilled NR displays a highly elastic non-linear behavior typically of elastomeric materials. The elongation at break was higher than 500% and tensile modulus lower than 1 MPa. A decrease of the elongation at break and significant increase of both the tensile modulus and strength were observed upon adding nanoparticles.

The effect of acid hydrolysis of sisal MFC can be observed by comparing the tensile behavior of NR-MFC with the one observed for NR-MFC-AH45, NR-MFC-AH50 and NR-MFC-AH60 (Fig. 1a and Table 1). The tensile modulus for the later is similar to the one reported for NR-MFC (around 100 MPa), but the elongation at break is much higher (364% vs. 5.9%). The strength at break is about twice for NR-MFC-AH60 than the one reported for NR-MFC. The possibility of entanglements of MFC probably induces the extreme brittleness of the latter.

Well hydrolyzed nanoparticles, viz. MFC-AH50 and MFC-AH60, induced a higher tensile modulus value to the NR film, i.e. 27.8 and 108.8 MPa, respectively, compared to poorly hydrolyzed nanoparticles, MFC-AH45 (1.6 MPa). Nanoparticles with the highest aspect ratio (MFC-AH60 − L/d = 43) display a higher reinforcing effect than crystalline nanoparticles with a lower aspect ratio (MFC-AH50 − L/d = 30), whereas the strain at break remains relatively high. The heterogeneity of the MFC-AH45 sample is probably the reason of its low reinforcing effect when compared to the neat matrix. By comparing with previous experimental data for NR reinforced with whiskers prepared directly from fibers by acid hydrolysis (Siqueira et al. 2010a) relative Young's modulus values for similar filler content is higher for nanocellulose obtained by hydrolyzing MFC (i.e. MFC-AH60).

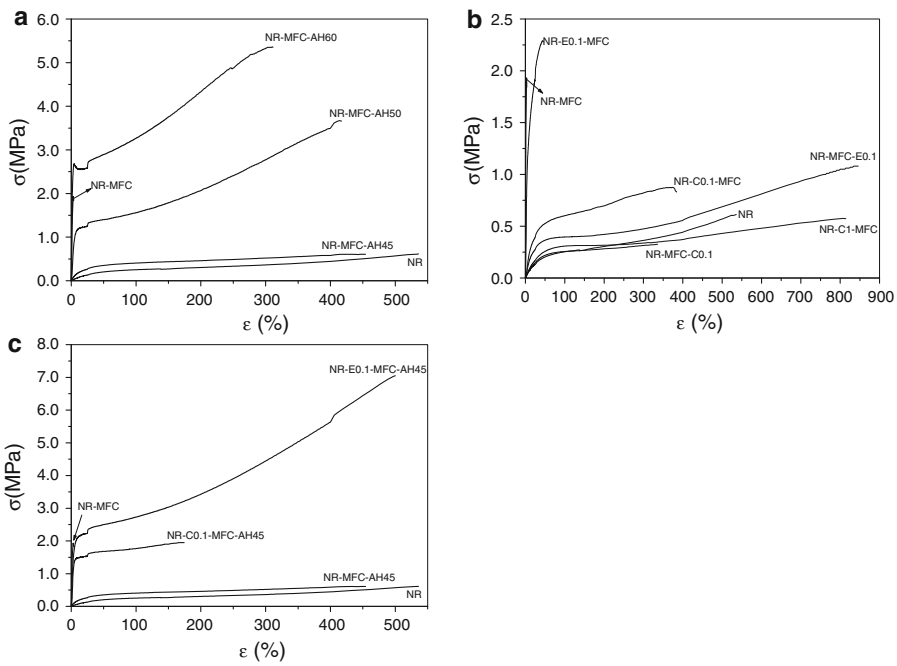

Fig. 1 Typical stress–strain *curves* obtained from tensile tests for NR and NR-nanocomposites films. The filler content for all nanocomposites is 6%wt

Dynamic mechanical analysis measurements were also performed on these materials. Figure 2 shows the evolution of the logarithm of the storage modulus (log E′) (panel a) and tangent of the loss angle (tan δ) (panel b) at 1 Hz as a function of temperature for the NR matrix and nanocomposites reinforced with acid hydrolyzed sisal MFC under different conditions. Working with another latex (poly-styrene-*co*-butyl acrylate), Azizi Samir et al. (2004) did not observed any difference in the reinforcing effect measured by DMA of cellulosic nanoparticles obtained by an acid hydrolysis treatment of variable strength. However, in the present study, significant differences were reported for the relaxed modulus of nanocomposite films reinforced with MFC-AH45, MFC-AH50 and MFC-AH60 (Table 1). These results agree with non linear tensile tests that showed an important dependence of the reinforcing effect depending on the morphology of the filler. An increasing rubbery modulus is observed when increasing the temperature of the acid hydrolysis step. For instance, the relaxed modulus at 25 °C for a film containing only 6 wt%, MFC-AH45 (4.5 MPa), is almost 4 times higher than the one of the neat matrix. However, this value is much higher for nanocomposite films reinforced with the same content of more hydrolyzed nanoparticles. The rubbery storage modulus at 25 °C is 55 times higher for MFC-AH50 (64.1 MPa) and up to 100 times higher for MFC-AH60 (125.3 MPa) compared to the neat matrix.

The temperature position of the tan δ peak (Fig. 2b) is almost independent of the nature of the filler. However, its magnitude strongly decreases upon addition of the cellulosic nanoparticles and strength of the acid hydrolysis treatment. It is obviously ascribed to the concomitant decrease of the storage modulus drop at T_g. However, this relative damping is also generally related to interfacial phenomena (Bendahou et al. 2010) which are expected to be more important when the nanoparticles are more hydrolyzed and therefore when their dimensions decrease. Loss of entanglement possibility upon hydrolysis also probably plays a role. Splitting of the main relaxation peak for NR-MFC was also observed. This phenomenon will be discussed latter.

Enzyme treated MFC

The effect of enzymatic hydrolysis and mechanical shearing for preparing cellulosic nanoparticles on the mechanical behavior of nanocomposites is reported in Fig. 1b. The tensile behavior of unfilled NR and NR-MFC has been added as references. Compared to NR-MFC, the enzymatic treatment (NR-MFC-E0.1 and NR-MFC-C0.1) results in a global decrease of both the tensile modulus and strength but significant increase of the elongation at break. Again this phenomenon is ascribed to the hydrolysis treatment that shortens the nanoparticles and limits the possibility of entanglements.

By comparing the tensile behavior of NR-MFC-E0.1 and NR-MFC-C0.1 with the one of NR-E0.1-MFC and NR-C0.1-MFC, respectively, it clearly appears that the sequence of the treatments, viz. mechanical shearing and enzymatic hydrolysis, has a

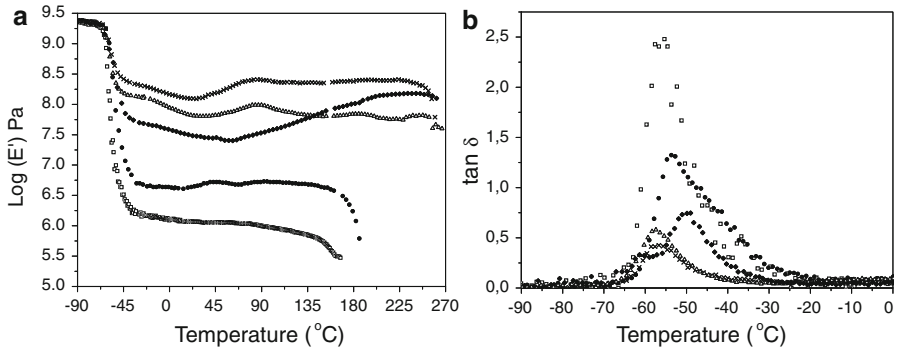

Fig. 2 Evolution of (**a**) the logarithm of the storage tensile modulus E′ and (**b**) loss angle tan δ, vs. temperature at 1 Hz for NR matrix and NR-based nanocomposites films reinforced with 6%wt sisal nanoparticles: NR (*open square*),NR-MFC (*filled diamond*), NR-MFC-AH45 (*filled circle*), NR-MFC-AH50 (*open triangle*) and NR-MFC-AH60 (*times symbol*). The filler content for all nanocomposites is 6%wt

significant impact on the properties of the material. Enzymatic treatment performed before mechanical shearing leads to stiffer materials than when inversing the sequence of the treatments. The difference is more marked with enzyme Eco (exoglucanase) than with Cclast (endoglucanase). The evolution of the elongation at break is more difficult to appraise. In other words, it seems to be more beneficial to first treat the fibers with enzymes and then to mechanically shear the resulting material, than doing the inverse procedure at least under the conditions used in this work. The 0.1 wt% enzymatic hydrolysis treatment of the fibers did not completely destroy the web-like structure of microfibrillated cellulose that influences the stiffness of the material. In contrast, a more hydrolyzed material is probably obtained when the enzymatic hydrolysis is carried out after mechanical shearing. Azizi Samir et al. (2004) also reported a decrease of the Young's modulus when increasing the severity of acid hydrolysis of MFC.

The concentration of enzyme involved in the treatment influences the mechanical properties of nanocomposites, as can be seen by comparing the results obtained for NR-C0.1-MFC and NR-C1-MFC (Table 1 and Fig. 1b). By increasing the enzyme (Cclast) concentration from 0.1 to 1.0 wt% a more hydrolyzed material is obtained. The strong reduction of DP from 263 for enzymatic treated pulp with 0.1 wt% of Cclast to 32 when the sisal pulp is treated with 1.0 wt% of the same enzyme under the same conditions (Siqueira et al. 2010b) confirmed the strong particles' size reduction. A highest as possible DP is desirable for MFC nanofibers, since it is expected to increase the inherent tensile strength of cellulose (Henriksson et al. 2007). Higher Young's modulus and strength values are reported for nanocomposites prepared with nanoparticles treated with the lowest enzyme concentration (0.1 wt%). Indeed, the Young's modulus and strength are 3.9 and 0.81 MPa, respectively, for NR-C0.1-MFC and 1.05 and 0.49 MPa for NR-C1-MFC. However, it is worth noting that the extremely low DP of C1-MFC probably results from the fact that it is no longer crystalline cellulose.

These results show the huge impact of the procedure used to prepare MFC-like nanocellulose with a huge range of strain at break (from 6 to 850%) or Young's modulus (from 0.8 to 101.7 MPa). To our knowledge no study has shown such a comparison proving the outstanding diversity of so-called MFC materials.

It was confirmed by DMA experiments performed in the linear range. Figure 3 shows the experimental data obtained for nanocomposite materials reinforced with enzymatically hydrolyzed and mechanically sheared cellulosic nanoparticles. The behavior of the neat NR matrix and nanocomposite reinforced with only mechanically sheared nanoparticles (NR-MFC) is also reported for comparison. Both the storage modulus (Fig. 3a) and loss angle (Fig. 3b) display important differences depending on the nature of the reinforcing phase. E′ values confirm the conclusions reported for these materials from tensile tests in the non linear range.

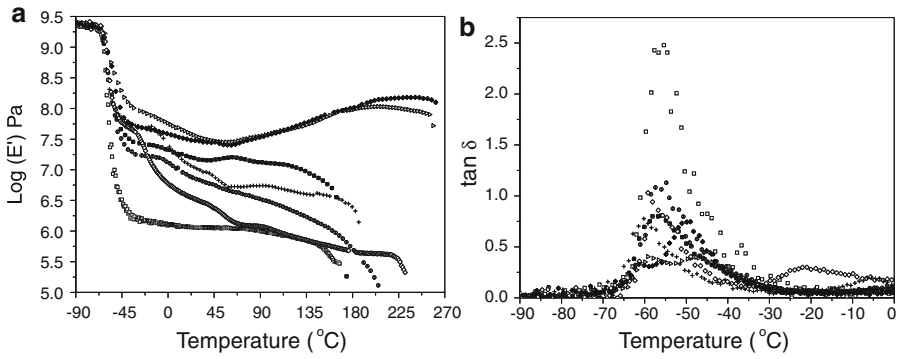

Fig. 3 Evolution of (**a**) the logarithm of the storage tensile modulus E′ and (**b**) loss angle tan δ, vs. temperature at 1 Hz for NR matrix and NR-based nanocomposites films reinforced with 6%wt sisal nanoparticles: NR (*open square*), NR-MFC (*filled diamond*), NR-E0.1-MFC (*right inverted triangle*), NR-C0.1-MFC (*circle with cross*), NR-C1-MFC (*circle with line*), NR-MFC-E0.1 (*positive symbol*) and NR-MFC-C0.1 (*open diamond*).The filler content for all nanocomposites is 6%wt

A peculiar behavior was observed for tan δ for NR-MFC, NR-E0.1-MFC and NR-MFC-C0.1 samples. The main relaxation peak splits into two well-defined peaks. These peaks are located around −60 and −50 °C (or −20 °C for NR-MFC-C0.1). Other researchers (Henriksson 2008; Bendahou et al. 2010) similarly reported the presence of two peaks. Henriksson (2008) attributed this splitting to covalent interactions between the cellulosic surface and the matrix, and possible physically bonded polymer domains in the vicinity of nanosized particles. Strong interactions between MFC and NR due to the presence of residual lignin and hemicelluloses on the surface of the nanoparticles were also suggested (Henriksson 2008). The observation of a similar behavior for NR-MFC and NR-E0.1-MFC composites is an indication that the treatment of MFC with 0.1 wt% cellulase Eco (exoglucanase) did not change the surface of the nanoparticles and the entangled cellulosic network assumed to govern the ultimate properties (Azizi Samir et al. 2004).

When increasing the enzyme Cclast (endoglucanase) concentration from 0.1 to 1 wt%, the rubbery modulus at 25 °C decreases from 15.5 MPa (for NR-C0.1-MFC) to 7.2 MPa (for NR-C1-MFC) in agreement with non linear tensile tests. The nanocomposite prepared with enzyme treated MFC (NR-MFC-C0.1) displays a similar behavior with a storage modulus of 3.4 MPa at 25 °C. The high temperature relaxation peak for NR-C1-MFC shifts to higher temperatures (around −20 °C) compared to NR-C0.1-MFC.

Acid hydrolyzed MFC previously pre-treated with enzymes

The enzymatic hydrolysis treatment performed directly on the bleached pulp, before preparation of MFC by mechanical shearing, not only helps the mechanical homogenization, but also allows the production of homogeneous hydrolyzed suspensions of sisal nanocrystals by acid hydrolysis. As shown in Table 1 and Fig. 1c, the tensile modulus for nanocomposites reinforced with E0.1-MFC-AH45 (58.2 MPa) and C0.1-MFC-AH45 (61.0 MPa) is much higher than for nanocomposites reinforced with MFC-AH45 (1.6 MPa). It is obviously ascribed to the pre-enzymatic hydrolysis of the bleached pulp before mechanical shearing. Enzymes cut the fibers in smaller parts, facilitating microfibrillation and producing MFC with lower diameter and length. This process facilitates the acidic attack since smaller cellulosic particles are more accessible than bigger particles as present in MFC. At the end of the treatment homogeneous nanocrystal suspensions can be obtained, as confirmed by TEM observations. Differences are founded when comparing the strength and strain at break for NR-E0.1-MFC-AH45 and NR-C0.1-MFC-AH45 based nanocomposites. Possible differences in the surface of nanoparticles due to the attack of different enzymes can be responsible for these differences.

DMA experiments confirm the positive impact of enzymatic hydrolysis for the preparation of cellulose

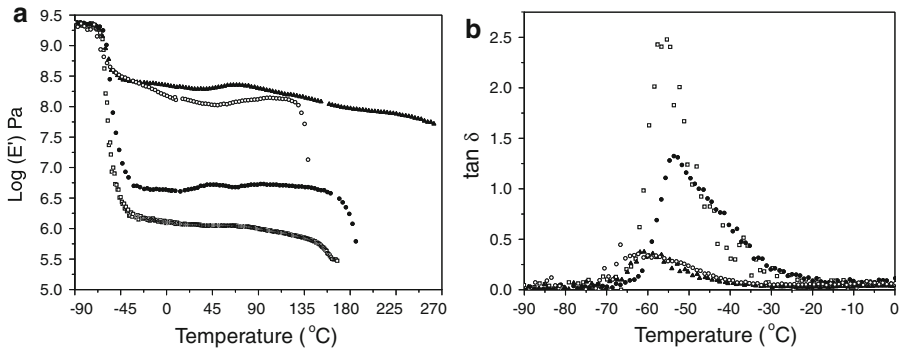

Fig. 4 Evolution of (**a**) the logarithm of the storage tensile modulus E′ and (**b**) loss angle tan δ, vs. temperature at 1 Hz for NR matrix and NR-based nanocomposites films reinforced with 6%wt sisal nanoparticles: NR (*open square*), NR-MFC-AH45 (*filled circle*), NR-E0.1-MFC-AH45 (*filled diamond*) and NR-C0.1-MFC-AH45 (*open circle*).The filler content for all nanocomposites is 6%wt

nanocrystals, as well as the reinforcing effect of these nanoparticles (Fig. 4a). The storage modulus at 25 °C for NR-E0.1-MFC-AH45 (196 MPa) and NR-C0.1-MFC-AH45 (124 MPa) nanocomposites are more than 100 times higher than the one of the matrix (Table 1). These values are higher than those reported for NR reinforced with date palm tree cellulose nanocrystals (Bendahou et al. 2009). A recent study (Bendahou et al. 2010) compared the impact of whiskers and MFC extracted from date palm tree on the mechanical properties of NR films. The Young's modulus value of NR/whiskers nanocomposites (5 wt%) was 16 times higher than the one of NR, while for NR/MFC (5 wt%) nanocomposites it was 70 times higher than the one of the neat matrix.

Another important difference was reported between NR films reinforced with C0.1-MFC-AH45 and E0.1-MFC-AH45. Whereas the rubbery modulus of the former remains roughly constant (around 124 MPa) up to 130 °C, the thermal stability of the latter is observed up to 270 °C. In addition, the magnitude of the tan δ peak is strongly reduced upon 6 wt% C0.1-MFC-AH45 and E0.1-MFC-AH45 addition (Fig. 4b). Actually, the NR-E0.1-MFC-AH45 appeared as the most promising solution for reinforcement with these cellulose nanoparticles.

Conclusions

The reinforcing capability of cellulosic nanoparticles obtained from a combination of mechanical shearing, and enzymatic and acid hydrolysis of sisal fibers was reported. With this aim, nanocomposite materials

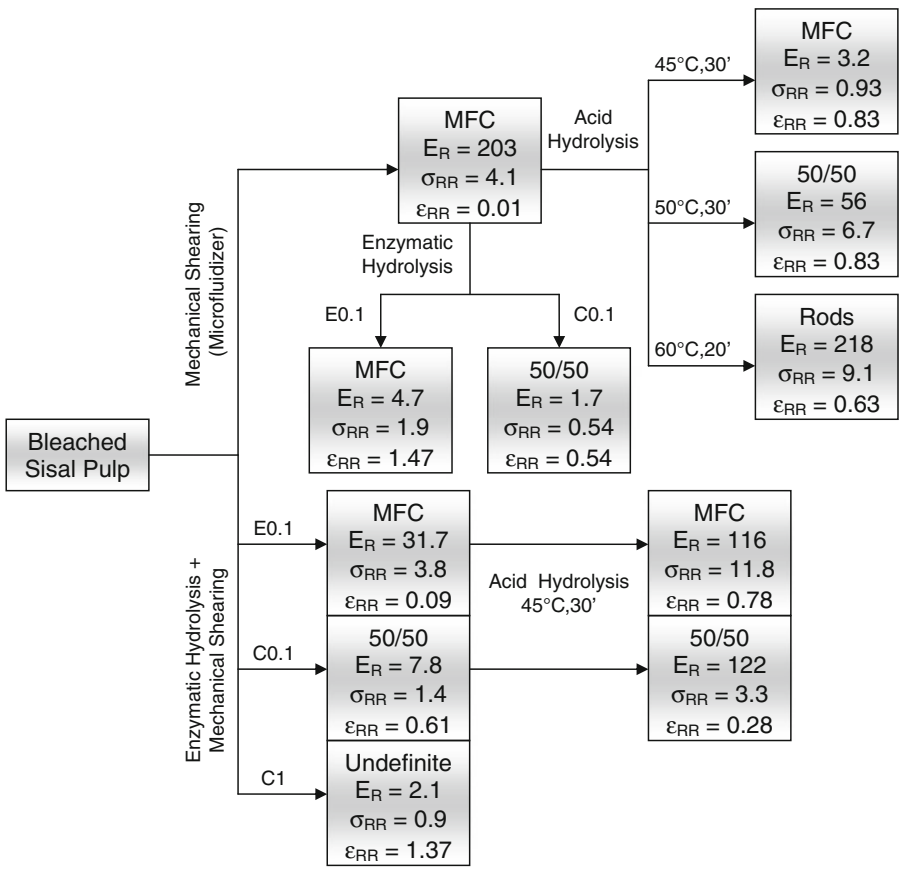

Fig. 5 General scheme of the effect of the various treatments performed on sisal bleached pulp for preparation of cellulose nanoparticles on the appearance of nanoparticles (MFC = MFC-like nanoparticles, 50/50 = mixture of MFC- and rod-like nanoparticles, Rods = well individualized rod-like nanocrystals) and mechanical properties (E_R = relative tensile modulus, σ_{RR} = relative strength, ε_{RR} = relative strain at break). The relative values correspond to the ratio of a given property divided by the one of the unfilled NR matrix

were prepared from these nanoparticles (limiting the filler content to 6 wt%) and natural rubber. The main conclusions are summarized in Fig. 5. It was shown that the acid hydrolysis treatment of MFC tends to drastically increase the elongation at break of the composites, whereas the modulus increases when increasing the temperature of the treatment. Enzymatic treatment performed before mechanical shearing leads to stiffer materials than when inversing the sequence of the treatments. The difference is more marked with exoglucanases than with endoglucanases. Therefore, it seems to be more beneficial to first treat the fibers with enzymes and then to mechanically shear the resulting material, than doing the inverse procedure at least under the conditions used in this work. Acid hydrolysis of these materials increases further the stiffness of the nanocomposites. This study describes an important range of behavior depending on the treatments.

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