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Reinforcing Mechanisms of Starch Nanocrystals in a Nonvulcanized Natural Rubber Matrix

Patrice Mélé,^{*,†} Hélène Angellier-Coussy,[‡] Sonia Molina-Boisseau,[§] and Alain Dufresne^{||}

[†]LEPMI/LMOPS UMR5279 CNRS UJF INP Grenoble Université de Savoie, 73376 Le Bourget du lac, France

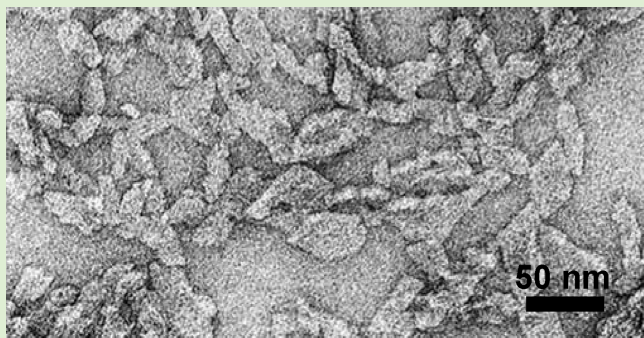
[‡]UMR IATE, Université Montpellier 2, Place Eugène Bataillon, 34095 Montpellier Cedex, France

[§]Centre de Recherches sur les Macromolécules Végétales (CERMAV-CNRS), ICMG, affiliated with Université Joseph Fourier, BP 53, 38041 Grenoble Cedex 9, France

^{||}The International School of Paper, Print Media and Biomaterials (Pagora), Grenoble Institute of Technology, BP 65 - F-38402 Saint Martin d'Hères Cedex, France

S Supporting Information

ABSTRACT: A phenomenological modeling approach was developed to try to understand the reinforcing mechanism of starch nanocrystals in a nonvulcanized natural rubber matrix. Natural rubber was not cross-linked to maintain the biodegradability of the biosourced materials. Nonlinear dynamic mechanical experiments highlighted the significant reinforcing effect of starch nanocrystals and the presence of the Mullins and Payne effects. Two models were used to predict the Payne effect considering that either filler–filler (Kraus model) or matrix–filler (Maier and Göritz model) interactions are preponderant. The use of the Maier and Göritz model demonstrated that phenomena of adsorption and desorption of NR chains on the filler surface governed nonlinear viscoelastic properties, even if the formation of a percolating network for filler contents >6.7 vol % was evidenced by the Kraus model.



INTRODUCTION

Unfilled elastomers are known to exhibit linear viscoelastic behavior at shear strains up to 10–20%.¹ To enhance the mechanical properties of elastomers, most of them are reinforced with fillers, notably carbon black, silica, or clays such as montmorillonite.^{2,3} It has been shown that unlike unfilled elastomers, reinforced materials exhibit a nonlinear viscoelastic behavior at shear strains as low as a few percent, generally described in terms of Mullins or Payne effects. The Mullins effect or “stress softening effect” is characterized by a pronounced lowering of the storage modulus (or stress) when elastomers are sheared a second time.⁴ The Payne effect characterizes the decrease in the real part of the elastic modulus with increasing strain amplitude. This nonlinear behavior has been first evidenced for natural rubber filled with carbon black² and has been confirmed by many authors for reinforced synthetic elastomers.^{1,5–9} This behavior is of great practical importance and essential for tire applications. It has been related to usage properties, and, in particular, to the rolling resistance or the wet skid resistance of tires.¹⁰ Various mechanisms have been proposed in the literature to explain the origins of the reinforcement of elastomers. They include molecular surface slippage or rearrangements, particle displacements, interparticle chain breakage, strong and weak surface binding, and other network particle surface phenomena.⁸

During the last decade, the increase in fossil energy costs and environmental issues has resulted in the development of biodegradable materials from renewable resources. In parallel, polymer nanocomposites have attracted considerable interest in both academia and industry, owing to their outstanding mechanical properties like elastic stiffness and strength while using only a small amount of nanoparticles. The enhanced properties include not only mechanical performances but also barrier resistance, flame retardancy, as well as optical and electrical properties. In this context, waxy maize starch nanocrystals have been used as filler in a nonvulcanized natural rubber (NR).^{11,12} The NR matrix was not cross-linked to keep the biodegradability and recyclability of such biosourced materials. Waxy maize starch nanocrystals appeared to display interesting barrier properties and to be an effective reinforcing filler for NR at temperatures higher than T_g of the matrix. Dynamic mechanical analysis performed in the linear viscoelastic region has shown that the relaxed modulus at room temperature of nanocomposites containing 10, 20, and 30 wt % (around 6.7, 13.4, and 20.1 vol %) of filler was about 10, 75, and 200 times higher, respectively, than the one of the unfilled

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matrix. It was also shown that up to a content of 20 wt % (13.4 vol %), starch nanocrystals led to an effective reinforcing effect of the NR matrix without decreasing the elongation at break of the materials.²

Polysaccharides are good candidates for renewable nanofillers because they have partially crystalline structures conferring interesting properties. Recent reviews have been published on cellulose nanoparticles,^{13–16} which is by far the most studied polysaccharide for such application. The literature in this field is growing very fast, and it is now a commercial product. However, there is no doubt that increasing works start to be done and will be done in the near future on starch nanoparticles. A recent review reports the advances published in the field of starch nanoparticles.¹⁷ It was outlined that the literature is significantly lacking in a comprehensive explanation of the reinforcing mechanism of starch nanocrystals, contrary to cellulose nanocrystals, for instance. Similar to the latter, the reinforcing effect of starch nanocrystals is generally ascribed to the formation of a hydrogen-bonded percolating filler network above a given starch content corresponding to the percolation threshold. However, this assumption is difficult to prove because the connecting particles should be starch clusters or aggregates with ill-defined size and geometry. The focus of the present work was to complete our knowledge on the reinforcing mechanism of starch nanocrystals by using a modeling approach.

EXPERIMENTAL SECTION

Materials. The materials used in the present study are constituted of waxy maize starch nanocrystals and NR latex.¹² Starch nanocrystals were obtained by sulphuric acid hydrolysis of native waxy maize starch granules (Waxyliis, Roquette S.A., Lestrem, France).¹⁸ They consist in platelet-like objects having a thickness of 6–8 nm, a length of 40–60 nm, and a width of 15–30 nm.¹⁹ The latex of NR LA-TZ (MAPA, France) had a dry content of 61.58% and a NR dry content of 60.1%, with a d_{50} value of 0.81 μm . Nanocomposite films were obtained by casting according to the following procedure. First, the aqueous suspension of waxy maize starch nanocrystals and the NR latex were mixed in desired proportions to obtain dry films 1 mm thick. Then, the mixtures were stirred and degassed on a rotavapor during about 10 min. After that, the preparations were cast in Teflon molds and evaporated at 40 °C in a ventilated oven for 6–8 h and finally heated to 60 °C under vacuum during 2 h. Films were stored over P_2O_5 until they were tested.

Dynamic Mechanical Analysis. Dynamic measurements were performed by using a DMA 450+ device supplied by 01 dB-Metavib company (Limonest, France). For tests performed in the linear domain, dynamic tensile measurements provided the complex Young's modulus (E^*) and the damping factor ($\tan \delta$) as a function of the temperature (ranging from –125 to 220 °C) for a single frequency (1 Hz). For experiments in the nonlinear region, specific shear jaws for films, supplied by 01 dB-Metavib Company, are used. This setup provided the complex shear modulus (G^*) and the damping factor ($\tan \delta$) as a function of the double strain amplitude (DSA) from 0.1 to 100%. Tests were performed at room temperature (25 °C) and at the same frequency (1 Hz).

The samples shapes have been optimized as a function of the stiffness of the used load cell (150 N, $K \approx 10^6$ N/m), the characteristics of the DMA 450+, and the dimensions of the tensile or shear jaws.

Samples were codified in the following parts of this Article as Lx-cy, where x was the weight percentage of NR and y indicated the cycle number (Table S1 of the Supporting Information). The volume fraction of starch nanocrystals was calculated for each formulation from the weight percentage of starch nanocrystals by considering a density

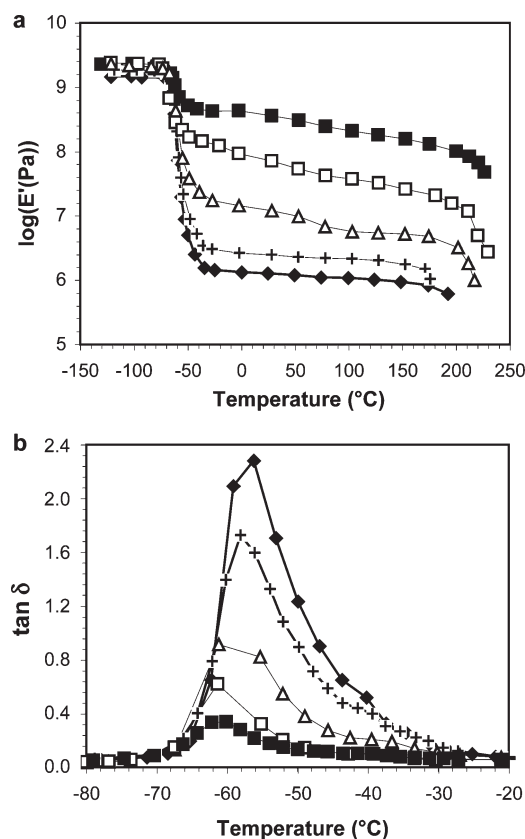


Figure 1. (a) Logarithm of the storage tensile modulus E' and (b) tangent of the loss tangent angle $\tan \delta$ versus temperature at 1 Hz for NR filled with different waxy maize starch nanocrystals contents: (◆) 0, (+) 5, (△) 10, (□) 20, and (■) 30 wt %.

of starch nanocrystals of 1.55 $\text{g} \cdot \text{cm}^{-3}$ and a density of dry NR of 1 $\text{g} \cdot \text{cm}^{-3}$.¹²

RESULTS AND DISCUSSION

Reinforcing Effect of Starch Nanocrystals. Dynamic mechanical measurements were performed at 1 Hz for NR films filled with starch nanocrystals up to 30 wt % in the linear domain. The plot of the logarithm of the storage modulus, $\log(E')$, and damping factor, $\tan \delta$ versus temperature are displayed in Figure 1. Starch nanocrystals displayed a significant reinforcing effect, in particular on the rubbery plateau of the nonvulcanized NR polymer (Figure 1a). This reinforcing effect was attributed to the formation of a percolating starch nanocrystals network through hydrogen linkages between starch nanoparticles clusters (Figure 2).¹² In an previous study, toluene swelling measurements showed that toluene uptake values decreased continuously when increasing the starch nanocrystals content, with a rupture of behavior around 10 wt %, that is, 6.7 vol %.¹² This confirmed the formation of a percolating starch nanocrystals network that could be governed by a percolation mechanism, with a threshold value around 10 wt % (i.e., 6.7 vol %).¹²

The evolution of $\tan \delta$ with temperature highlighted a peak related to the main relaxation (or T_α) of NR (Figure 1b). The addition of starch nanocrystals led to not only the decrease in the magnitude of this peak but also to the shift of its maximum toward lower temperatures, in particular for filler contents higher than 10 wt %. Similar results have been observed for polymers or

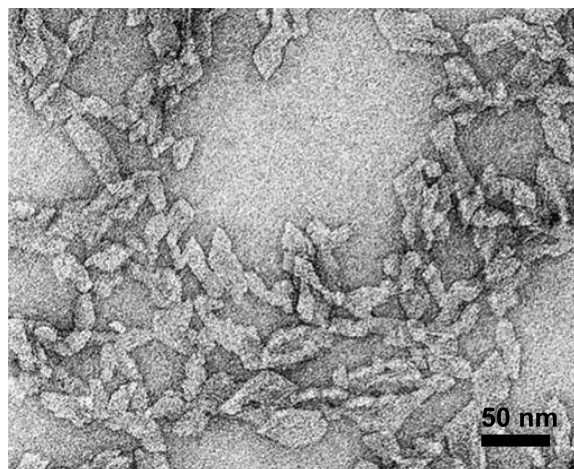


Figure 2. Transmission electron micrograph of negatively stained waxy maize starch nanocrystals.

elastomers reinforced by classical fillers, such as silica and carbon blacks, and have been related to a phase inversion phenomenon occurring for filler volume higher than the percolating threshold.^{20,21}

To complete this study, nonlinear dynamic mechanical experiments were then performed, at 25 °C, that is, at $T_g + 85$ °C (Figure 3). The plot of the storage shear modulus G' versus the DSA, γ , confirmed the reinforcing effect of starch nanocrystals in the nonvulcanized NR matrix, regardless the volume fraction of nanocrystals. The storage shear modulus of natural nanocomposites increased with increasing filler content, in the whole range of deformation. It can be noted that the magnitude of this effect was amplified for low values of strain (corresponding to the parameter G'_0), in agreement with previous experimental results on vulcanized rubbers reinforced by either silica^{8,22} or carbon blacks.²³

The curves of the loss moduli, $G'' = f(\gamma)$, presented a broad maximum when increasing the deformation, especially for filler contents higher than 10 wt %. The evaluation of this property is extremely important because it is related to the dissipative energy during one cycle of deformation per volume unit, U_v in the linear viscoelastic field. This parameter is proportional to G'' through the following expression

$$U_v = \pi G'' \gamma^2 \quad (1)$$

where G'' is the loss modulus (Pa) and γ the strain magnitude.

In the nonlinear case, no equivalent expression exists. Accordingly, in the next following part of this paper, it will be assumed that U_v is proportional to the loss modulus and the square of the shear amplitude.

On the basis of the evolution of G'' as a function of the filler content (Figure 3b), U_v increased thus with the volume fraction of filler, in particular for deformations lower than 3 to 4%. In this region, it can be proposed that this parameter was governed by the square of the strain amplitude γ^2 . For deformation higher than 3 to 4%, the decrease in $G'' = f(\gamma)$ led to a reduction in the slope of the evolution of U_v as a function of γ : this parameter tends then toward a constant value, showing the reduction of the reinforcing effect induced by starch nanocrystals.

The dissipative phenomena can also be analyzed with the variation of the damping factor, $\tan \delta (= G''/G')$ versus strain amplitude. $\tan \delta$ is besides preferred by many searchers because it is independent of the sample shape and has been related to

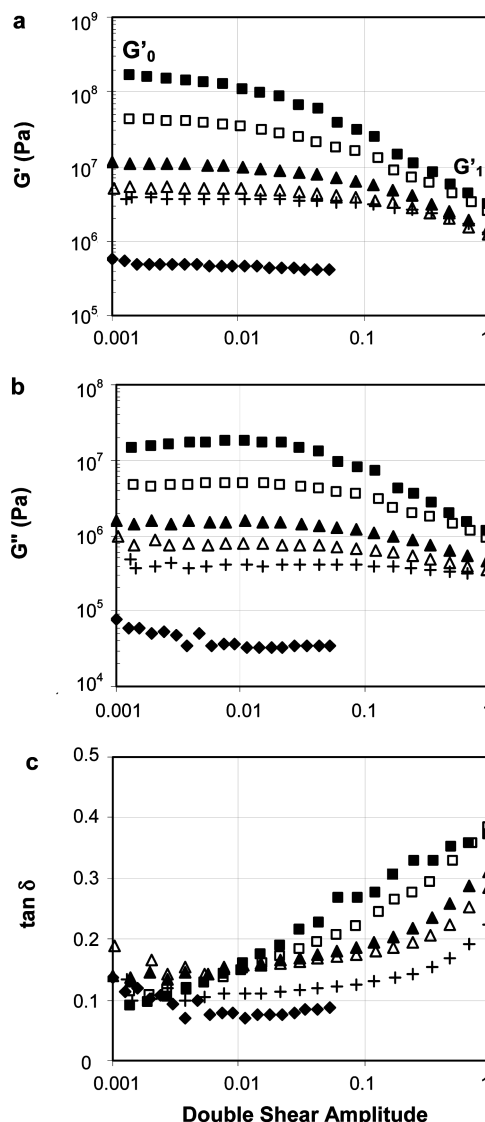


Figure 3. Variation of (a) the storage shear modulus G' , (b) the loss shear modulus G'' , and (c) $\tan \delta$ as a function of the double shear amplitude γ , at 25 °C, for NR filled with different waxy maize starch nanocrystals contents: (◆) 0, (+) 5, (△) 10, (▲) 15, (□) 20, and (■) 30 wt %.

different properties in the field of tires, in particular to wet grip or to rolling resistance of tires.¹⁰ The evolution of $\tan \delta$ versus the strain amplitude for the different nanocomposites was superimposed in Figure 3c. This parameter increased with the particle content, in particular for deformations higher than few percents. The decrease in G'' with increasing deformation was compensated by the important reduction of $G' = f(\gamma)$. Increasing the filler content tended to increase the dissipative phenomena, especially for large deformations.

Mullins Effect. Three successive tensile cycles were performed for each sample to demonstrate the presence or not of the Mullins effect in our specific natural nanocomposites, characterized by a stress softening effect. For the unfilled NR matrix, curves corresponding to the successive cycles were perfectly superposed, to a few percent (6–8%) (Figure 4a). For nanocomposites, a significant decrease in G'_0 can be observed between the first and the second cycle, for films reinforced with 30 wt % starch nanocrystals (Figure 4b).

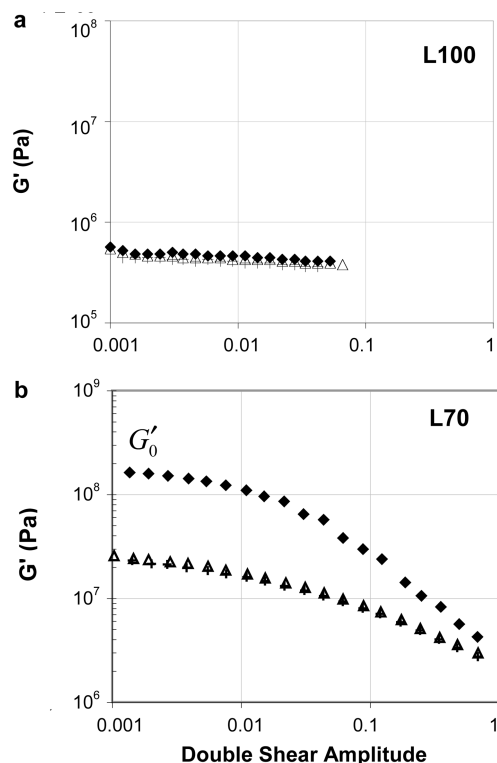


Figure 4. Variation of the storage shear modulus G' as a function of the double shear amplitude γ for (a) unfilled NR (L100) and (b) NR filled with 30 wt % waxy maize starch nanocrystals (L70), at 25 °C, for three successive cycles: (◆) cycle no. 1, (△) cycle no. 2, and (+) cycle no. 3.

This evolution was characteristic of the Mullins effect often reported for filled vulcanized elastomers.²⁴ No further evolution was observed between cycles 2 and 3. The magnitude of the drop of G'_0 between the first and the second cycle was quantified by calculating $\Delta G'$ (%) through the following expression

$$\Delta G' = \frac{G'_{01} - G'_{02}}{G'_{01}} \times 100 \quad (2)$$

where G'_{01} (MPa) and G'_{02} (MPa) are the storage modulus measured at a strain amplitude of 0.1% for the first and the second cycles, respectively. Data are collected in Table S2 of the Supporting Information.

The magnitude of the Mullins effect significantly increased with increasing filler content, as already shown by many authors for filled elastomers. It is worth noting that this increase was almost proportional to the filler content. Mullins suggested that the stress softening of filled elastomers is due to a disentanglement of the chains network with the breakdown of interactions between the filler particles and the rubber matrix.^{24,25} From Table S2 of the Supporting Information, it can be seen that the intensity of the Mullins effect appeared to be more dependent on the filler content than the presence or not of a percolating nanoparticles network; that is, this stress softening effect can also be linked to the slippage of polymer chains on the particle (or network) rather than surface breakdown of the particle network.

Payne Effect. The typical features generally associated with the Payne effect, that is, strain dependence of the viscoelastic properties of filled NR are illustrated in Figure 3. Unfilled NR displayed a linear viscoelastic behavior, with no change in dynamic moduli with strain amplitude, whereas the storage modulus of

nanocomposites decreased with increasing deformation from a maximum value, G'_0 , down to a value, G'_1 , corresponding to the storage modulus at 100% of deformation. Note that unlike cross-linked filled elastomers, where a plateau at high strain amplitude is generally reached, the viscoelastic behavior of nonvulcanized rubber reinforced with starch nanocrystals did not achieve this limit. It can be, however, observed that the magnitude of the Payne effect increased with increasing filler content, as already shown by many authors for vulcanized elastomers reinforced with carbon black,²⁶ silica,^{8,27,28} or even soy spent flakes.²⁹

As already observed for synthetic elastomers, such as SBR filled with silica,⁸ the nonlinear effect was observed even at low starch nanocrystals content, well below the percolation threshold (close to 10 wt %). This result suggested that the strain dependence of the viscoelastic properties of filled nonvulcanized NR could not be only related to the development of filler–filler interactions. The critical strain amplitude, where the nonlinearity effect appeared, was moreover gradually shifted toward smaller values of deformation with increasing the starch nanocrystals content. This result can be particularly highlighted with the increase in the $\tan \delta$ value with increasing particles content for a constant deformation level. As a result, the nonlinear viscoelastic behavior displayed by NR/starch nanocrystals nanocomposites could not only be related to the formation or the development of a percolating network of fillers. The magnitude of this phenomenon seems to also depend on the specific surface between polymer and particles, in agreement with Sternstein and Zhu works.²⁹ These authors postulated that the decrease in both the storage and loss moduli with increasing strain was related to filler–polymer interactions including the aspects of trapped topological entanglements. To contribute to the understanding of the nonlinear viscoelastic behavior of these NR/waxy maize starch nanocrystals nanocomposites, we developed a phenomenological modeling to discriminate its possible origin(s).

Modeling of the Payne Effect. Two main groups of theories can be found in literature for modeling the Payne effect. They are based on either filler structure models or on matrix–filler bonding and debonding models.²⁷

In filler structure models, the filler–filler interactions are considered to be preponderant. The variations of moduli with strain depend on the agglomeration and deagglomeration mechanisms of the filler network.² Assuming van der Waals interactions between particles, Kraus proposed that contacts are continuously broken and reformed under a periodic sinusoidal strain.³ According to this author, the evolutions of the storage shear modulus and loss shear modulus are described by the following expressions

$$\frac{G' - G'_\infty}{G'_0 - G'_\infty} = \frac{1}{1 + \left(\frac{\gamma}{\gamma_c}\right)^{2m}} \quad (3)$$

and

$$\frac{G'' - G''_\infty}{G''_0 - G''_\infty} = \frac{2 \left(\frac{\gamma}{\gamma_c}\right)^m}{1 + \left(\frac{\gamma}{\gamma_c}\right)^{2m}} \quad (4)$$

where G'_∞ is equal to $G'(\gamma)$ for very large strain, G'_0 is equal to $G'(\gamma)$ for very low strain, γ_c is a characteristic shear strain amplitude,

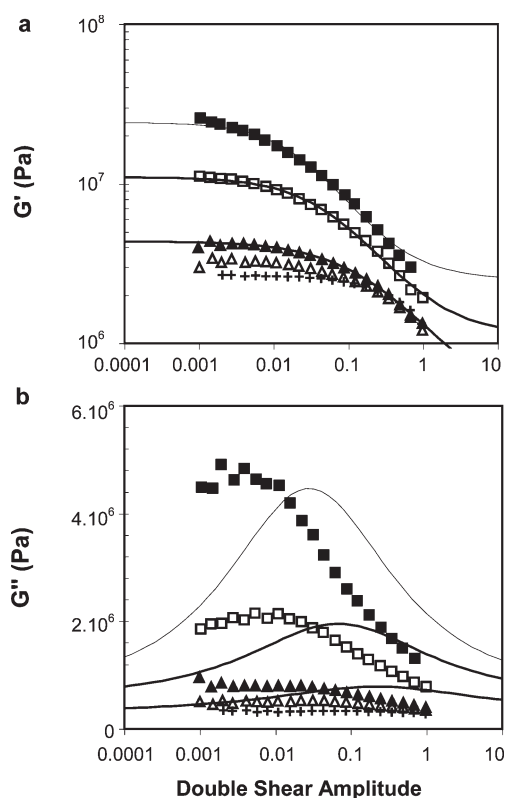


Figure 5. Variation of the experimental (a) storage shear modulus G' and (b) loss shear modulus G'' as a function of the double shear amplitude γ for cycle no. 2 of NR filled with different waxy maize starch nanocrystals contents: (+) 5, (Δ) 10, (\blacktriangle) 15, (\square) 20, and (\blacksquare) 30 wt %. Solid lines represent the calculated moduli using the Kraus model (eqs 3 and 4).

$G'_0 - G'_\infty$ is reduced to half of its zero-strain value, and m is a fitting parameter related to filler agglomerate structures.

The comparison between experimental and theoretical data obtained with Kraus model is proposed in Figure 5. Fitted values are given in Table S3 of the Supporting Information. To remove the influence of the Mullins effect in simulations, the samples were “demullinised”; that is, simulations have been done on cycle no. 2 or 3. The Kraus model well-described the variations of $G' = f(\gamma)$ for starch nanocrystals content higher than 10 wt % corresponding to the percolation threshold content. This result was consistent with the assumptions of this model. However, differences can be noted between experimental and theoretical values of the dissipative modulus, G'' versus strain amplitude (Figure 5b). Fitted values were in fact shifted toward higher deformations compared with experimental variations. As a result, the interest of using Kraus model lied with the confirmation of the formation of the filler network for nanoparticle contents higher than 10 wt %. This local phase inversion explains then the increase in the elastic properties at low deformation for filler content higher than the percolating threshold. Its limit was to be unable to predict (i) the elastic properties of the lowest filled materials and (ii) the dissipative properties of the different nanocomposites.

Accordingly, additional simulations were then performed, taking into account the influence of the matrix–filler mechanisms on the viscoelastic properties of nanocomposites. These models are based on the idea that the adsorbed polymer at the

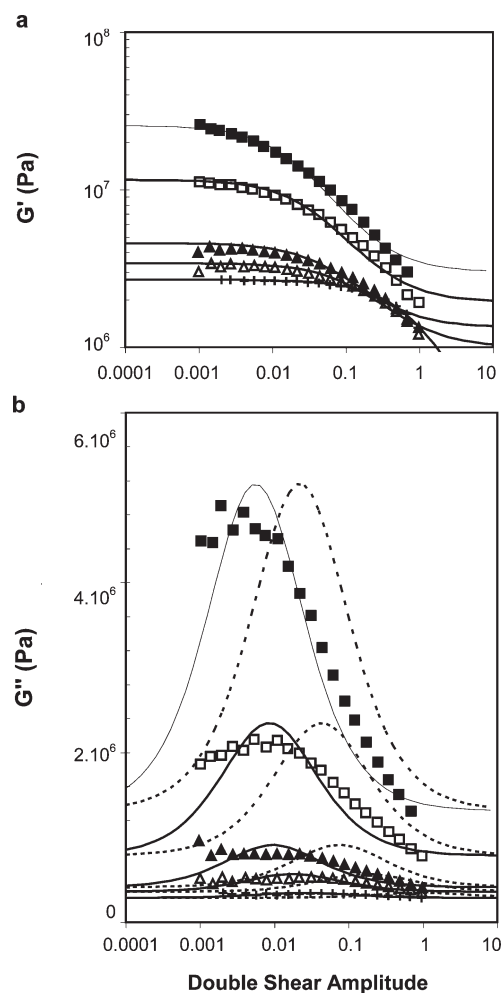


Figure 6. Variation of the experimental (a) storage shear modulus G' and (b) loss shear modulus G'' as a function of the double shear amplitude γ for cycle no. 2 of NR filled with different waxy maize starch nanocrystals contents: (+) 5, (Δ) 10, (\blacktriangle) 15, (\square) 20, and (\blacksquare) 30 wt %. Dashed lines and solid lines represent the calculated moduli using the Maier and Göritz model (eqs 5 and 6) and the modified Maier and Göritz model (eq 7), respectively.

filler surface could act as a reinforcing phase and affect the macroscopic behavior.³⁰ One of the most commonly used model, in this field, is that of Maier and Göritz,³¹ where the following expressions described the variations of the real and imaginary parts of the shear modulus, G^* , as a function of the strain amplitude

$$G' = G'_{st} + \frac{G'_{i0}}{1 + c\gamma} \quad (5)$$

and

$$G'' = G''_{st} + G''_{i0} \frac{c\gamma}{(1 + c\gamma)^2} \quad (6)$$

where G'_{st} corresponds to the contribution of “stable” links, G'_{i0} is related to the “instable” links, G''_{st} is associated to the internal friction, and G''_{i0} refers to slippage of polymeric chains segments.

A comparison between experimental and simulated data is proposed in Figure 6. A good agreement between experimental and fitted values can be observed for G' , regardless of the volume

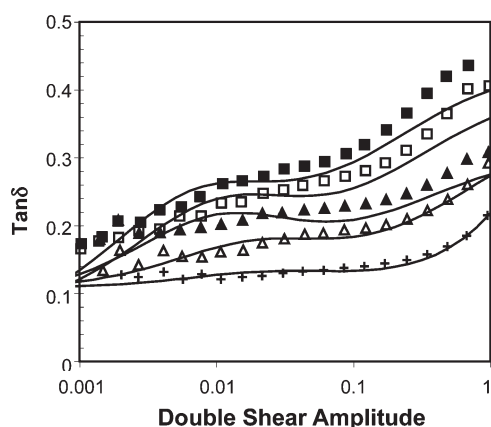


Figure 7. Variation of the experimental damping factor, $\tan \delta$, as a function of the double shear amplitude for cycle no. 2 of NR filled with different waxy maize starch nanocrystals contents: (+) 5, (Δ) 10, (\blacktriangle) 15, (\square) 20, and (\blacksquare) 30 wt %. Solid lines represent the calculated damping factor values using the modified Maier and Göritz model for calculating the loss moduli (eq 7).

fraction of filler or the DSA. For the variations of G'' for nanocomposites versus the strain magnitude, some discrepancy can be, however, detected. These differences can originate from the difficulty to define the inflection point of $G' = f(\gamma)$. A higher sensitivity is indeed detected on the curves of $G'' = f(\gamma)$. To minimize this feature, a new variable, called α' , has been added in eq 6. This variable can be considered as a sensibility probe for the variations of the dissipative part G'' as a function of γ . Equation 6 becomes

$$G'' = G''_{st} + G''_{i0} \frac{\alpha' c \gamma}{(1 + \alpha' c \gamma)^2} \quad (7)$$

Values of this parameter are listed in Table S4 of the Supporting Information. The integration of such a variable in the phenomenological Maier and Göritz' model allowed then to account for the experimental evolution of G'' as a function of the amplitude of deformation, γ , whatever the filler content (Figure 6b). It can be moreover observed that its values decreased with the amount of particles, meaning that the shift between experimental and fitted values of $G'' = f(\gamma)$ gradually decreased (Table S4 of the Supporting Information).

As a result, the evolution of the damping factor, $\tan \delta$, as a function of the strain amplitude was then predicted regardless of the filler content (Figure 7). The differences between experimental and theoretical data observed for very small deformations ($\gamma = 0.1\%$) were due to the low values of dynamic load recorded versus time. The prediction of $\tan \delta$ versus strain amplitude was in fact important for applications in the tires field because this parameter has been related, for example, to their rolling resistance. This modeling showed moreover that the nonlinear viscoelastic behavior of NR/starch nanocrystals nanocomposites was mainly governed by filler–polymer interactions. The phenomena of adsorption/desorption or slippage of NR chains on the filler surface appeared to be predominant, even if a percolating network occurred for particle contents >10 wt %.

CONCLUSIONS

Nonlinear dynamic mechanical experiments confirmed the significant reinforcing effect of waxy maize starch nanocrystals in

a nonvulcanized NR matrix. For example, reinforcing NR by 6.7 vol % of starch nanocrystals allowed us to increase the relaxed modulus at room temperature by a factor 10. The presence of both Mullins and Payne effects was highlighted for all nanocomposites, even for low filler contents. A phenomenological modeling approach was developed to try to understand the reinforcing mechanisms of starch nanocrystals and to discriminate the possible origins of the nonlinear viscoelastic behavior of NR/starch nanocrystals nanocomposites.

Two models were used to predict the Payne effect: (i) the Kraus model considering that filler–filler interactions are preponderant and (ii) the Maier and Göritz model that is based on matrix–filler interactions. It was demonstrated that phenomena of adsorption/desorption or slippage of NR chains on the filler surface governed the nonlinear viscoelastic properties of nonvulcanized NR/starch nanocrystals nanocomposites, even if the formation of a percolating network for filler contents >6.7 vol % (10 wt %) was evidenced.

The approach proposed in this Article is now being applied to other nanocomposites to separate the relative contributions of filler–filler to filler–polymer interactions from their nonlinear viscoelastic behavior.

ASSOCIATED CONTENT

S Supporting Information. Corresponding values of weight fraction (w_f) and volume fraction (v_f) of starch nanocrystals. Relative amplitude of the Mullins effect for NR/starch nanocrystals nanocomposite films. Fit parameters of storage shear modulus by Kraus model and loss shear modulus by the modified Kraus model. Fit parameters of storage shear modulus by Maier–Göritz model and loss shear modulus by the modified Maier–Göritz model. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*Tel: +33 (0)4 79 75 94 34. Fax: +33 (0)4 79 75 86 14. E-mail: Patrice.mele@univ-savoie.fr.

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REFERENCES

- (1) Chazeau, L.; Brown, J. D.; Yanyo, L. C.; Sternstein, S. S. *Polym. Compos.* **2000**, 21, 202–222.
- (2) Payne, A. R.; Whittaker, R. E. *Rubber Chem. Technol.* **1971**, 44, 440–478.
- (3) Kraus, G. J. *Appl. Polym. Sci.: Appl. Polym. Symp.* **1984**, 39, 75–92.
- (4) Mullins, L.; Tobin, N. R. *Rubber Chem. Technol.* **1957**, 30, 555–571.
- (5) Stenberg, B.; Jansson, J. F. *J. Appl. Polym. Sci.* **1981**, 26, 3773–3778.
- (6) Drozdov, A. D.; Dorfmann, A. *Polym. Eng. Sci.* **2002**, 42, 591–604.
- (7) Bokobza, L. *Macromol. Mater. Eng.* **2004**, 289, 607–621.
- (8) Gauthier, C.; Reynaud, E.; Vassoille, R.; Ladouce-Stelandre, L. *Polymer* **2004**, 45, 2761–2771.

- (9) Fathallah, T. Développement d'un outil d'analyse transdisciplinaire permettant la caractérisation couplée des propriétés mécaniques dynamiques et électriques de différentes classes de matériaux. Ph.D. Thesis, University of Savoy, 2009.
- (10) Locatelli, J. L.; De Puydt, Y.; Serra, A. In *Eurofillers '99*; Wiley-VCH: Weinheim, Germany, 2001.
- (11) Angellier, H.; Molina-Boisseau, S.; Dufresne, A. *Macromolecules* **2005**, *38*, 9161–9170.
- (12) Angellier, H.; Molina-Boisseau, S.; Lebrun, L.; Dufresne, A. *Macromolecules* **2005**, *38*, 3783–3792.
- (13) Azizi Samir, M. A. S.; Alloin, F.; Dufresne, A. *Biomacromolecules* **2005**, *6*, 612–626.
- (14) Hubbe, M. A.; Rojas, O. J.; Lucia, L. A.; Sain, M. *BioResources* **2008**, *3*, 929–980.
- (15) Habibi, Y.; Lucia, L. A.; Rojas, O. J. *Chem. Rev.* **2010**, *110*, 3479–3500.
- (16) Siró, I.; Plackett, D. *Cellulose* **2010**, *17*, 459–494.
- (17) Le Corre, D.; Bras, J.; Dufresne, A. *Biomacromolecules* **2010**, *11*, 1139–1153.
- (18) Angellier, H.; Choïnard, L.; Molina-Boisseau, S.; Ozil, P.; Dufresne, A. *Biomacromolecules* **2004**, *5*, 1545–1551.
- (19) Putaux, J. L.; Molina-Boisseau, S.; Momaur, T.; Dufresne, A. *Biomacromolecules* **2003**, *4*, 1198–1202.
- (20) Mélé, P. Relations entre l'architecture et le comportement mécanique de systèmes hétérogènes à matrice polymère. Habilitation à diriger des recherches. University of Savoy, France, 2004.
- (21) Mélé, P.; Marceau, S.; Brown, D.; de Puydt, Y.; Alberola, N. D. *Polymer* **2002**, *43*, 5577–5586.
- (22) Cassagnau, P. *Polymer* **2003**, *44*, 2455–2462.
- (23) Frohlich, J.; Niedermeier, W.; Luginsland, H. D. *Composites, Part A* **2005**, *36*, 449–460.
- (24) Mullins, L. *Rubber Chem. Technol.* **1969**, *42*, 449–460.
- (25) Marckmann, G.; Verron, E.; Gornet, L.; Chagnon, G.; Charrier, P.; Fort, P. *J. Mech. Phys. Solids* **2002**, *50*, 2011–2028.
- (26) Wang, M. J. *Rubber Chem. Technol.* **1999**, *72*, 430–448.
- (27) Ladouce-Stelandre, L.; Bomal, Y.; Flandin, L.; Labarre, D. *Rubber Chem. Technol.* **2003**, *76*, 145–159.
- (28) Mélé, P.; Da Silva, C.; Marceau, S.; Brown, D.; De Puydt, Y.; Alberola, N. D. *Macromol. Symp.* **2003**, *194*, 185–190.
- (29) Sternstein, S. S.; Zhu, A. J. *Macromolecules* **2002**, *35*, 7262–7273.
- (30) Berriot, J.; Montes, H.; Martin, F.; Mauger, M.; Pyckhout-Nintzen, W.; Meier, G.; Frielinghaus, H. *Polymer* **2003**, *44*, 4909–4919.
- (31) Maier, P. G.; Göritz, D. *Kautsch. Gummi Kunstst.* **1996**, *49*, 8–21.