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Waxy Maize Starch Nanocrystals as Filler in Natural Rubber

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Summary: Starch nanocrystals obtained from acid hydrolysis of waxy maize starch granules consist in crystalline nanoplatelets about 6–8 nm thick with a length of 20–40 nm and a width of 15–30 nm. New nanocomposite materials, i.e. natural rubber (NR) filled with waxy maize starch nanocrystals were processed by casting. Dynamic mechanical analysis has shown that starch nanocrystals were a good reinforcing agent for NR at temperatures higher than the glass transition temperature of NR. Tensile tests have shown that until a weight fraction of 20 wt%, this new filler presented the advantage to reinforce natural rubber without decreasing significantly the strain at break of the material. These properties may be due to both the morphological nature of starch nanocrystals, and the formation of a percolating starch nanocrystals network within the NR matrix, resulting from hydrogen bonding forces between starch aggregates.

Keywords: filler; mechanical properties; nanocomposites; natural rubber; starch; starch nanocrystals; swelling behaviour

Introduction

In a context of both biomass valorization and nanocomposite materials development, starch nanocrystals obtained by acid hydrolysis of potato and waxy maize starch granules have been used as filler in a synthetic polymeric matrix and appeared to be an interesting reinforcing agent [1,2]. Starch nanocrystals consist in crystalline nanoplatelets about 6–8 nm thick with a length of 20–40 nm and a width of 15–30 nm [3]. In order to lift the problem of availability, a previous work consisted in optimizing the preparation of nanocrystals from waxy maize granules with the view to extend their use in nanocomposite applications [4]. The focus of this work was to process new nanocomposite materials, i.e. natural rubber filled with waxy maize starch nanocrystals. These materials were characterized in terms of morphology, swelling behaviour and mechanical properties.

Experimental

Waxy Maize Starch Nanocrystals

The preparation of waxy maize starch nanocrystals by sulphuric acid (H_2SO_4) hydrolysis of native waxy maize starch granules (Waxylis™, Roquette S.A., Lestrem, France) was optimized and described previously [4]. Such nanocrystals are generally observed in the form of aggregates (Figure 1) having an average size around 4.4 μm, as measured by laser granulometry [4].

Natural Rubber

Natural rubber (NR) was kindly supplied as NR latex by the Technical Center MAPA (Liancourt, France). It contained spherical particles with an average diameter around 1 μm.

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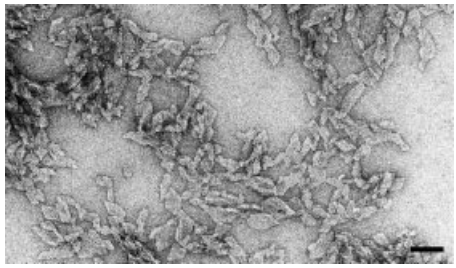

Figure 1.
TEM picture of negatively stained waxy maize starch nanocrystals (scale bar: 50 nm).

Composites Processing

The aqueous suspension of starch nanocrystals and the latex were mixed in various proportions in order to obtain composite films with weight fractions of dry starch nanocrystals (w_s) ranging from 0 to 50 wt% (labelled L100 to L50). Then, the mixtures were degassed under vacuum, cast in Teflon moulds, evaporated at 40 °C for 6–8 hours and finally heated at 60 °C under vacuum for two hours. Resulting films were conditioned at room temperature in dessicators containing P_2O_5 salt during about one week.

Swelling Behaviour

The kinetics of water and toluene absorption was determined for squared samples ($10 \times 10 \times 0.2$ mm^3). The water uptake (WU) as well as toluene uptake (TU) were calculated as $WU(\%) = \frac{m_t - m_0}{m_0} \times 100$ where m_0 and m_t are the weights of the samples before and after a time t of immersion, respectively. The diffusion coefficients were calculated using the following equation: $\frac{m_t - m_0}{m_\infty} = \frac{2}{L}\left(\frac{D}{\pi}\right)^{1/2} t^{1/2}$, where m_∞ is the weight of the sample at the equilibrium, $2L$ the thickness of the film, and D the diffusion coefficient[5].

Mechanical Properties

Dynamic mechanical tests were carried out with a spectrometer RSA2 from Rheometrics working in the tensile mode. Measurements were performed on thin strips ($25 \times 7 \times 0.7$ mm^3) in isochronal conditions at 1 Hz. The temperature was varied between 200 and 450° K by steps of 3° K. Tensile tests were performed using an Instron 4301 testing machine working with a cross-head speed of 10 mm.min^{-1}. Dumbbell shaped specimens 4 mm wide, 7 mm long (L_0) and about 1 mm thick were used. Successive tensile tests consisted in stretching the sample up to a given elongation $\Delta L_1 = 10$ mm (cycle 1), then releasing the force down to the initial force of 1.5 N, and stretching again the material up to $\Delta L_2 = 2\Delta L_1$(cycle 2), and so on.

Results and Discussion

Swelling Behavior of Composite Materials

The diffusion coefficients of toluene were estimated for all compositions (Figure 2a). The unfilled NR matrix displayed the highest toluene diffusion coefficient. Adding starch nanocrystals to the NR matrix resulted in a significant decrease of the toluene diffusivity. In the case of the immersion in distilled water, the effect of the addition of starch nanocrystals is the opposite (Figure 2b). The unfilled NR matrix displayed the lowest water diffusion coefficient, and adding starch nanocrystals to NR resulted in an increase of the water diffusivity. For both solvents, a discontinuity is observed around a weight fraction of 10 wt%.

All these results seem to show that above 10 wt% starch nanocrystals could form a three-dimensional network, in agreement with TEM observations (Figure 1), that allows reducing the swelling capability of the matrix by toluene. The formation of this network was already reported for rod-like polysaccharide fillers [6]. It was assumed to result from the establishment of strong hydrogen bonds between particles that can form during the water evaporation process. The structure of starch nanocrystals is completely different but one can assume that above a given volume fraction, starch nanoparticles clusters can connect to form a continuous infinite and open network.

The reduction of swelling upon starch nanocrystals addition could also be due to possible interactions between starch and

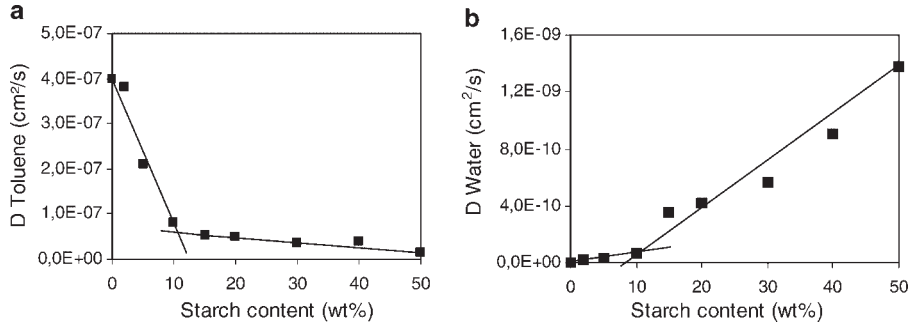

Figure 2.
Evolution of the diffusion coefficients of (a) toluene and (b) water vs. starch content.

natural rubber, thereby preventing the swelling of the polymeric chains located in the interfacial zone. However, similar experiments carried out with chemically modified particles and DSC experiments have shown that interactions between starch nanocrystals and natural rubber were quite weak [5].

Contrarily to toluene swelling experiments and as expected, the formation of a continuous polar network of starch nanocrystals within the NR matrix seems to favour the swelling of the films by water.

Mechanical Behavior of Composite Materials

The curve of log(E′/Pa) corresponding to the unfilled matrix is typical of a fully amorphous high molecular weight thermoplastic behaviour (Figure 3a). When adding starch nanocrystals, the glassy modulus of the composite increases up to 3 GPa for the 30 wt% filled material. Above T_g, a higher increase of the storage modulus is observed by increasing the weight fraction of starch nanoparticles. For instance, the relaxed modulus at room temperature (25 °C) of nanocomposite films containing 10, 20 and 30 wt% of filler is about 10, 75 and 200 times higher, respectively, than the pure matrix. No significant improvement of the thermal stability of composites was induced by adding starch nanocrystals within the NR matrix. Actually, the matrix displays a rather high thermal stability and starch begins to degrade at about the same temperature at which NR starts to totally disentangle and flow.

The curve of tan δ displays a peak located in the temperature range of the glass transition of natural rubber [5]. This relaxation process, labelled α, is associated with the anelastic manifestation of the glass-rubber transition of the polymer and involves cooperative motions of long chain sequences. Both the temperature position (T_α) and the magnitude of the peak (I_α) decrease when adding starch nanocrystals. The decrease in T_α becomes significant for the 20 wt% starch reinforced material for which T_α decrease from −56 °C for the unfilled NR down to −61 °C. This is attributed to (i) the broadening of the glass-rubber transition zone towards lower temperatures reported from DSC measurements [5], and (ii) a classical mechanical coupling effect (the shift of the tan δ peak results from the strong decrease of the modulus drop upon filler addition). The reduction of the magnitude of I_α when increasing the starch nanocrystals content, results from (i) the decrease of the number of mobile units participating to the relaxation process, and (ii) the decrease of the magnitude of the modulus drop associated with T_g.

It was suspected from swelling experiments that a percolating starch nanocrystals network within the NR matrix may form, resulting from hydrogen bonding forces between starch aggregates. This phenomenon, induced during the evaporation step of the material processing, should most

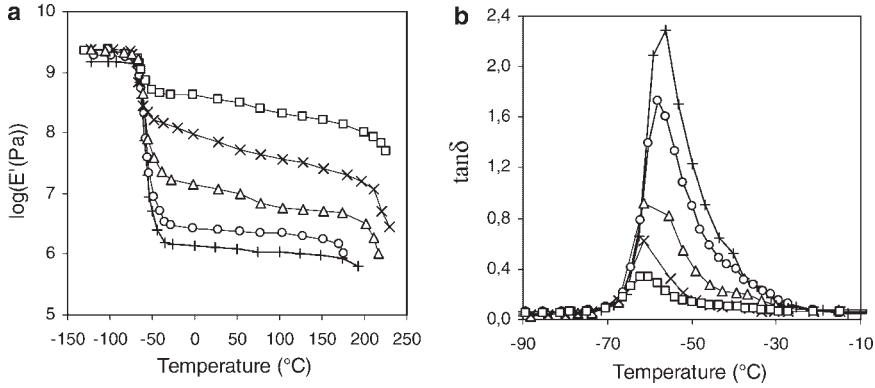

Figure 3.
(a) Logarithm of the storage tensile modulus E' and (b) tanδ vs. temperature at 1 Hz for waxy maize starch nanocrystals/NR nanocomposite films: L100 (+), L95 (○), L90 (Δ), L80 (×), and L70 (□).

probably affect the mechanical properties of the composites in the linear range.

Tensile tests show that the samples exhibit an elastic nonlinear behaviour typical of amorphous polymer at $T > T_g$ (Figure 4). As expected, the strain at break decreases and the tensile modulus as well as the stress at break increases with increasing starch content. Considering the ultimate properties, a good compromise between the increase of the strength and the decrease of the strain seems to be reached for a starch content around 20 wt% [7].

The reinforcing effect of starch nanocrystals was compared to the one of classical fillers for natural rubber published in the literature such as clays, organoclays, carbon black and chitin whiskers. Starch nanocrystals are clearly a good substitute for carbon black since the addition of only 10 wt% of starch nanoparticles to NR induces a reinforcing effect similar, in terms of stiffness, to the one observed with 26.6 wt% carbon black [8]. In addition, high starch nanocrystals contents up to 20 wt% seem to preserve the elastic behaviour of NR-based composites, contrarily to carbon black. However, starch nanocrystals are not so competitive than organoclays [8]. Compared to chitin whiskers, starch nanocrystals-based composites display a lower tensile modulus but higher ultimate properties (both higher strength and strain at break) for 5 wt% filler content [9].

For the unfilled NR matrix, the tensile module continuously increases during successive cycle (Figure 5). This phenomenon is ascribed to the strain-induced crystallisation of natural rubber [10]. Such a continuous increase is observed for low starch contents (up to 5 wt%). This means that the behaviour of the poorly filled nanocomposite films is mainly governed by the one of the matrix. It could be ascribed to the absence of a continuous nanocrystals network within the NR matrix.

For highly filled nanocomposite materials (starch content higher than 5 wt%) the tensile modulus decreases during the first

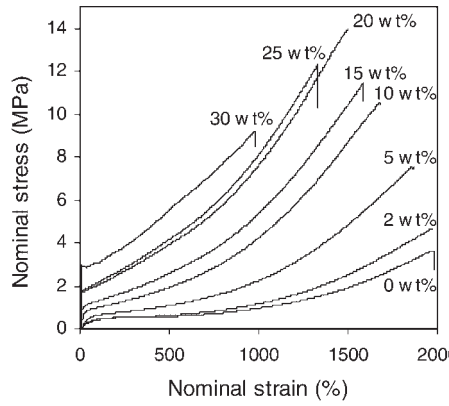

Figure 4.
Typical nominal stress vs. nominal strain curves of waxy maize starch nanocrystals/NR nanocomposite films at room temperature.

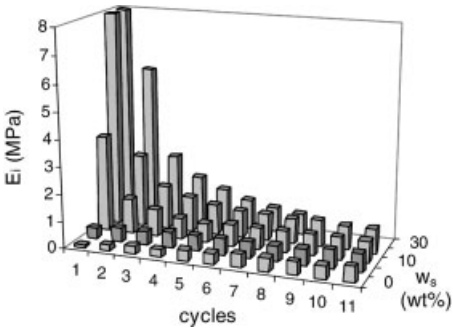

Figure 5.
Evolution of the nominal tensile modulus E_i measured for each successive tensile test cycle i NR reinforced with a given weight content of waxy maize starch nanocrystals (w_s).

five cycles. The higher the starch content is, the stronger the modulus drop is. This modulus drop during the early successive tensile experiments could be ascribed to the progressive disruption of the continuous starch nanocrystals network. The higher the starch nanoparticles content is, the closer the continuous network is and the stronger the effect of the disruption is. Furthermore, it was already shown that the addition of filler (carbon black for instance) decreases the ability of NR to crystallize [11]. After the fifth cycle, the modulus remains roughly constant. This should mean that complete disruption of the continuous starch network was achieved and that no strain-induced crystallization of the film occurred at this stage. It is also observed that for a given cycle, the modulus increases with the starch content. This reinforcing effect agrees with both DMA and tensile tests results.

Regardless the composition, the shrinkage increases for each additional successive tensile cycle. This could be ascribed to both the strain-induced crystallization that leads to the formation of crystallized domains corresponding to irreversible extended chains and to the proportionally increased elastic component to the total compliance. When increasing the starch nanoparticles content, the shrinkage becomes more important, i.e. the residual elongation decreases for a given cycle. The presence of the filler induces a higher elastic behaviour of the material and decreases at the same time its viscoelasticity.

Conclusion

Waxy maize starch nanocrystals appeared to be a potential substitute of carbon black as filler in natural rubber at temperatures higher than the glass transition temperature of NR. Until a weight fraction of 20 wt%, this new filler presents the advantage to reinforce natural rubber without decreasing significantly the strain at break of the material. For instance, it was shown that the addition of 20 wt% of waxy maize starch nanocrystals in natural rubber allows reducing the diffusivity of toluene by 8, increasing the storage modulus and the strength at break by 75 and 4, respectively, and decreasing the strain at break by only 25%.

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