Starch Nanocrystal Fillers in an Acrylic Polymer Matrix

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Summary: Aqueous suspensions of nanocrystals can be obtained by acid hydrolysis of native waxy maize starch granules. The disruption of waxy maize starch granules by 2.2N HCl hydrolysis has been followed by scanning and transmission electron microscopy and laser granulometry. The mechanical properties of composite materials made of poly(styrene-co-butyl acrylate) filled with starch nanocrystals were characterized by dynamic mechanical analysis. These nanocrystals appeared to be an interesting reinforcing phase in a thermoplastic matrix.

Keywords: acid hydrolysis; filler; nanocomposites; starch nanocrystals; waxy maize starch

Introduction

The growing interest in degradable products has led scientists to develop the use of biopolymers for applications in which synthetic polymers or mineral fillers were traditionally used. In this context, research has been devoted to cellulose and especially to cellulose which revealed to be an interesting model filler in various polymer matrices [1]. By analogy with cellulose whiskers, studies have been performed on starch. Starch is a natural and biodegradable polysaccharide presents in higher plants as an energy storage polymer. Starch granules are mainly composed of two polysaccharides consisting of α-linked D-glucosyl units: amylose (a mostly linear macromolecule) and amylopectin (a 4-5% branched macromolecule). The granules exhibit an onion-like structure of alternating amorphous and semi-crystalline growth rings. It is accepted that the partial crystallinity of native starch granules is due to a clustered organization of

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amylopectin side chains [2]. Aqueous suspensions of nanocrystals can be obtained after several weeks of hydrochloric acid hydrolysis (also called “lintnerization”) of native starch granules [2,3]. In a previous work, semi-crystalline residues obtained by this treatment on potato starch appeared to be an interesting reinforcing phase in poly(styrene-co-butyl acrylate) [4]. As it has been recently shown [5], crystalline nanoplatelets with a well-defined morphology can be obtained from the lintnerization of amylopectin-rich “waxy” maize native starch granules. The present work focuses on studying the evolution of starch granules morphology during acid treatment as well as the influence of selected parameters of the acid hydrolysis (nature and concentration of acid, time of hydrolysis, temperature) on the disruption of such starch granules. The insoluble residues were characterized by scanning and transmission electron microscopy (SEM and TEM), as well as laser granulometry. The mechanical properties of composite materials made of poly(styrene-co-butyl acrylate) (poly(S-co-BuA)) filled with starch nanocrystals were also analyzed by dynamic mechanical analysis (DMA).

Experimental

Waxy maize starch nanocrystals. 10 g of native amylopectin-rich (99 wt%) waxy maize starch granules (Waxylis™, Roquette S.A., Lestrem, France) was mixed with 200 mL of diluted acid (2.2N HCl or 1.5-4M H_2SO_4) in order to reach a weight concentration of 5 wt% [3-6]. Then, the suspensions were put in a thermostated atmosphere (35°C or 40°C) and continuously stirred at 100 rpm. After different times of hydrolysis, the insoluble residues were washed by successive centrifugations in distilled water until neutrality and mechanically treated by Ultra Turrax (IKA, Staufen, Germany) during 5 min at 13000 rpm in order to disperse the aggregates formed during centrifugation. The resulting aqueous suspensions were stored at 4°C. The yield of hydrolysis Y was calculated as the ratio of the dry weight of insoluble residue after hydrolysis to the dry weight of native granules.

Poly(styrene-co-butyl acrylate). We used a latex of a copolymer of styrene (34 wt%) and butyl acrylate (64 wt%) stabilised by 1% acrylic acid and 1% acrylamide, with a glass-rubber transition temperature (Tg) around 0°C. The latex contained particles with an average diameter of 200 nm.

Composite film processing. The starch nanocrystals suspensions treated by Ultra Turrax were mixed with the polymer latex in fractions varying from 0 to 50 wt%. The mixtures were freeze-dried, heated at 90°C during 10 min and hot-pressed during 1 min at 2 MPa (300 psi) to obtain films about 1 mm thick.

Electron microscopy. Scanning electron microscopy was performed with a JEOL JSM-6100 (Tokyo, Japan) instrument. Transmission electron microscopy observations were made with a Philips CM200 (Eindhoven, The Netherlands) microscope operated at 80 kV. Particles were negatively stained with 2 %(w/v) uranyl acetate.

Laser granulometry. Laser granulometry measurements were done using a Malvern Mastersizer (Orsay, France). The dispersions were characterized using the median particle size d_{50}, which divides the size distribution into two equal halves.

Dynamic mechanical analysis. Dynamic mechanical tests were carried out using a RSA2 spectrometer from Rheometrics (Piscataway, New Jersey, USA) working in the tensile mode. The samples were thin rectangular strips with dimensions about 25x7x0.7 mm^3. The setup measured the complex tensile modulus E*, that is displayed as the storage component E' and the loss component E". Measurements were performed in isochronal conditions at 1 Hz and the temperature was varied between 200 and 400 K by steps of 3 K with a soak time of 30 s.

Results and discussion

Hydrolysis kinetics. First, hydrolysis was performed using the conditions of lintnerization defined by Robin *et al.* [3]: 2.2N HCl at 35°C, during 2 to 40 days. When Y is plotted versus time, three phases are distinguished (Figure 1a) corresponding to different stages of granule disruption. During the first 4 days, the yield rapidly drops to 38 wt%, which roughly corresponds to the relative crystallinity of the native granules [7]. Considering that α(1-6) links are more reactive than α(1-4) and that acid diffusion is favoured in disorganized regions, the amorphous growth rings are rapidly dissolved during this first stage. From 4 to 14 days, the yield decreases more slowly to 10 wt%.

During this stage, the acid gets enough time to diffuse in the semi-crystalline growth rings and preferentially dissolves the α(1-6) branching points. The yield finally reaches 0.5 wt% during the remaining 26 days. Crystallites containing mostly α(1-4) links and some residual α(1-6) links are slowly hydrolyzed.

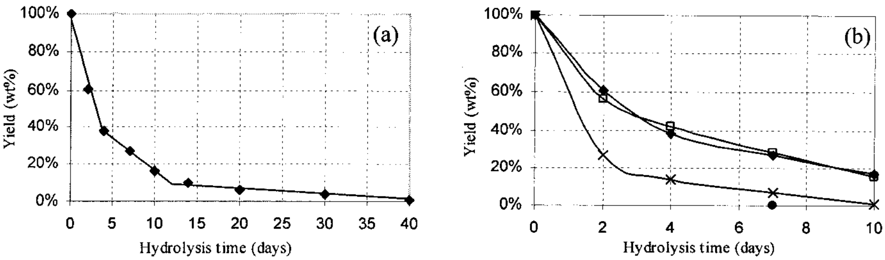

Figure 1. Evolution of the yield of hydrolysis Y versus time of (a) 2.2N HCl at 35°C, (b) 2.2N HCl at 35°C (♦), 3M H_2SO_4 at 35°C (□) and 40°C (x).

We have restricted our examination of the effect of others parameters on the H_2SO_4 hydrolysis to the first stages of acid treatment (2, 4, 7 and 10 days for the nature of acid and temperature, 7 days for the acid concentration). By comparison with 2.2N HCl treatment, a 3M H_2SO_4 hydrolysis is needed to obtain the same evolution of yield (Figure 1b) as already shown by Muhr *et al.* [8]. In addition, a higher temperature (40°C) accelerates the disruption of the granules (Figure 1b). Like for temperature, an increase in acid concentration dramatically accelerates the degradation. Yields of 43.7, 28.6 and 0 wt% were respectively obtained for 1.5M, 3M and 4M H_2SO_4 at 35°C during 7 days. A 4M concentration leads to a complete dissolution of starch.

Evolution of the insoluble residue morphology. The major fraction of native waxy maize starch consists of 10-15 μm polyhedral granules (Figure 2a). After 2 days of HCl treatment, the granule surface is rougher. As the acid hydrolysis progresses, pits develop, which may correspond to erosion or a collapse of the faces (Figures 2a-c). This phenomenon is faster with H_2SO_4 (not shown). Figure 2c suggests that the edges are more resistant than the faces. The initial morphology of granules is lost after 10 days. Aliquots of native and hydrolyzed granules were manually sheared in conical tubes. Broken native granules present a radial fibril-like fracture surface (Figure 2d). This structure has already been described for starches from other

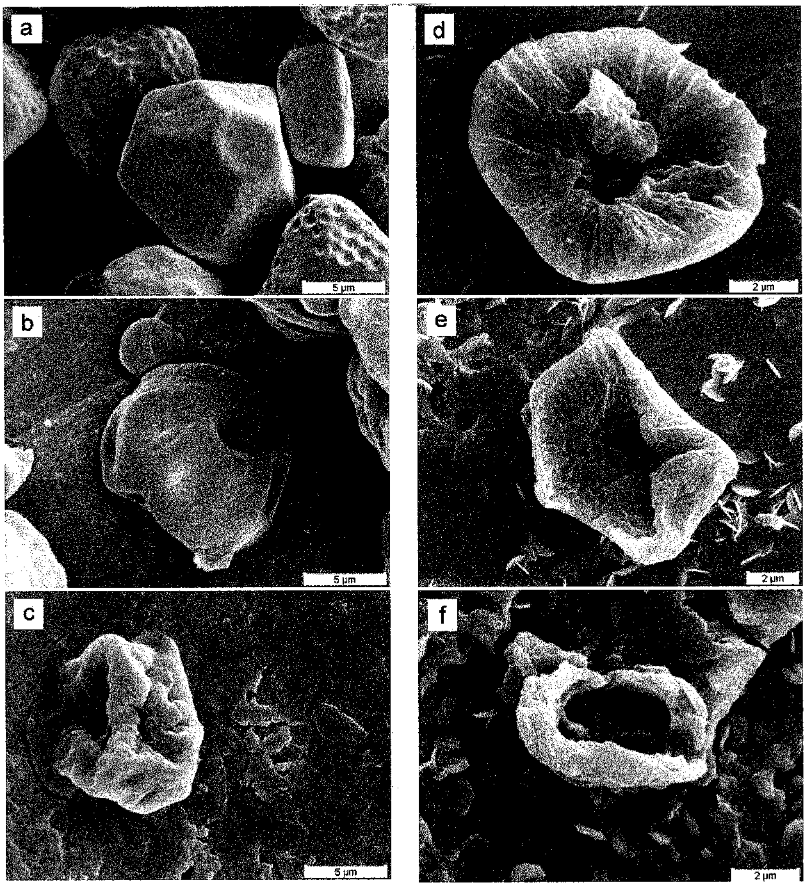

Figure 2. SEM pictures of native waxy maize starch granules (a,d) and residues obtained after 2 days (e), 4 days (b,f) and 7 days (c) of 2.2N HCl hydrolysis. Some samples were broken by manual shearing in a conical tube before (d) or after hydrolysis (e,f).

botanical origins [9-15]. Irregular cavities can be observed at the hilum of the granules (Figure 2d). When the granules are dried, cracks may develop at the central region which is assumed to be less organized than the rest of the particle [16]. After 2 days of hydrolysis, both radial fibril-like organization and 250-400 nm thick concentric layers are observed (Figures 2e,f). This illustrates the onion-like structure of alternating amorphous and semi-crystalline layers also shown by TEM [17]. After 4 days, only fragments of the outer growth rings are observed, confirming that they are more resistant than the inner region. These results are consistent with a radial diffusion of the acid to the less resistant granule core. This diffusion may be favoured by the existence of pores running from the surface to the hilum. This degradation mechanism is comparable to that of α-amylase enzymatic hydrolysis of potato starch granules [18,19].

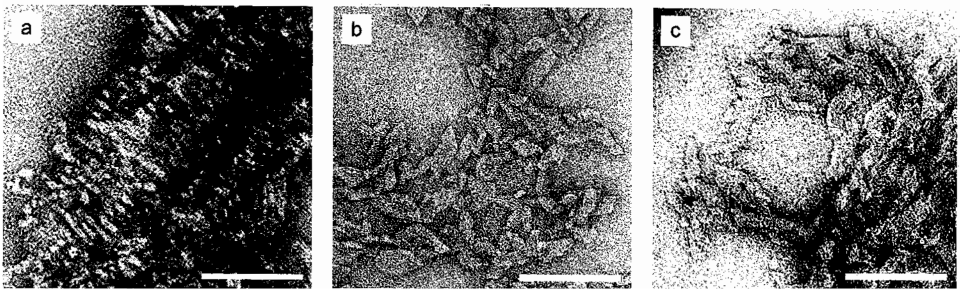

Figure 3. TEM pictures of negatively stained nanocrystals after (a) 4 days and (b) 14 days of 2.2N HCl hydrolysis, (c) 14 days of 3M H_2SO_4 hydrolysis. Scale bar: 100 nm.

After a few days of 2.2N HCl hydrolysis, TEM pictures show fragments containing ordered stacks of lamellae oriented edge-on (Figure 3a). They are assumed to correspond to the organization of amylopectin in the semi-crystalline growth rings: amorphous lamellae containing α(1-6) branching points alternating with crystalline lamellae consisting of double-helices of amylopectin side-chains [5,10,11]. The thickness of the crystalline lamellae measured from the pictures is about 6-7 nm and the combined thickness of crystalline and amorphous lamellae is about 9-10 nm. These data are consistent with those from previous works [10,11,17,20,21]. Such ordered fragments are seen during the first 10 days of hydrolysis. This shows that in the first phase of hydrolysis, the semi-crystalline growth rings are also partially susceptible to hydrolysis. From 7 days of hydrolysis, some parallelepiped platelets (20 nm × 50 nm) are observed, which correspond to separated lamellae seen in planar view [5]. Typical images of such platelets obtained after 14 days of hydrolysis are shown Figure 3b. Aggregates of platelets with similar shapes were also observed in a sample treated for 14 days with 3M H_2SO_4 (Figure 3c). The fact that the yield of hydrolysis rapidly gets lower than the relative crystallinity of native starch granules (about 40% [7]) and that it drops to 0.5 wt% after 40 days of hydrolysis suggests that the crystalline platelets are dissolved by the acid after being separated.

Table 1. Evolution of the median size d_{50} of the insoluble residue during 2.2N HCl and 3M H_2SO_4 hydrolysis for 5 min of Ultra Turrax treatment.

Time of hydrolysis (days)	2	7	10	14	20	40
d_{50} (μm), 2.2N HCl	14.4	11.4	8.3	8.0	7.2	6.3
d_{50} (μm), 3M H_2SO_4	13.7	8.0	5.6	5.3	5.6	-

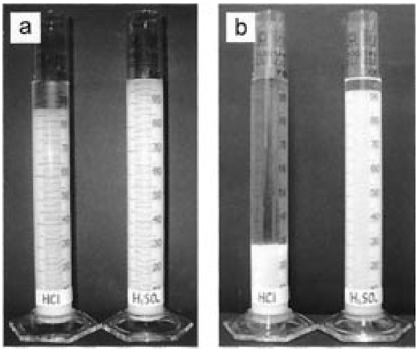

Figure 4. Comparison of the sedimentation properties of HCl (left tube) and H_2SO_4 (right tube) hydrolysis residues suspended in water: (a) after 5 min ; (b) after 60 min.

Table 1 shows the regular decrease of the median particle size d_{50} measured by laser granulometry in 0.02 wt% suspensions after different times of 2.2N HCl or 3M H_2SO_4 treatment. This decrease is consistent with the disruption of the granules observed by microscopy techniques. However, the sizes measured after 2 weeks of hydrolysis (8.0 μm for HCl and 5.3 μm for H_2SO_4) are in apparent contradiction with the dimensions of the nanometric platelets observed by TEM (Figures 3b,c). In fact, both techniques bring complementary data on the same sample but at different scales. Laser granulometry clearly detects micrometric objects that are composed of the nanometric units shown by TEM. That d_{50} does not vary much after 14 days of acid treatment which suggest that flocculation occurs in the suspensions. While the hydrolysis severs an increasing number of α(1-6) branching points, the platelets that should be more separated tend to re-agglomerate by electrostatic interaction. The formation of sulfate-ester groups on the surface of the nanocrystals during a H_2SO_4 hydrolysis should limit this flocculation and produce more stable suspensions. This was confirmed by comparing the sedimentation properties of suspensions obtained using each acid (Figure 4). One other possible reason for improved stability in the case of H_2SO_4 hydrolysis may be due to the lower particle.

Mechanical behaviour of composite materials. The evolution of the logarithm of the storage tensile modulus E' as a function of temperature has been studied for poly(styrene-co-butyl acrylate) films reinforced by starch nanocrystals obtained from 2.2N HCl hydrolysis at 35°C. The influence of filler concentration is displayed in Figure 5 after 7 days of hydrolysis. The curve corresponding to the unfilled matrix is typical of an amorphous thermoplastic behavior.

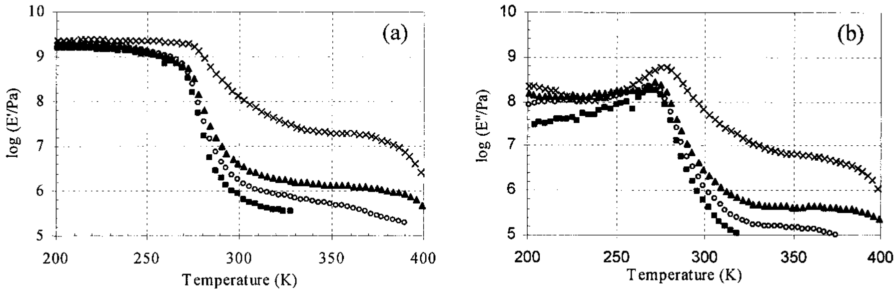

Figure 5. (a) Logarithm of the storage modulus E' and (b) logarithm of the loss modulus E" versus temperature at 1 Hz for composite materials filled with 0 (■), 10 (○), 30 (▲) and 50 wt% (X) of starch nanocrystals obtained from 2.2N HCl hydrolysis at 35°C during 7 days.

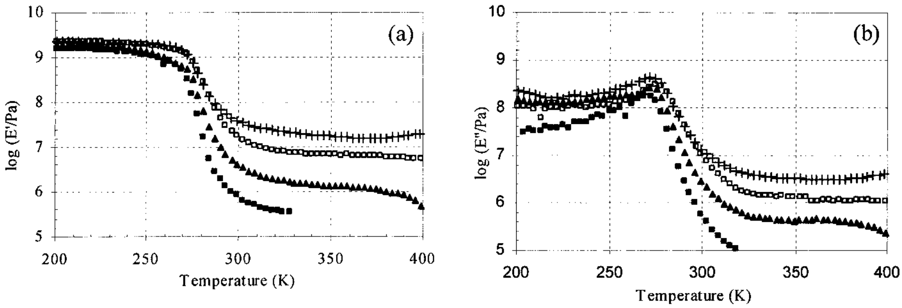

Figure 6. Logarithm of the storage modulus E' (a) and logarithm of the loss modulus E" versus temperature at 1 Hz for composites materials filled with 0 (■) and 30 wt% of starch fillers obtained from 2.2N HCl hydrolysis at 35°C during 7 days (▲), 14 days (□) and 40 days (+).

For temperatures below Tg (273 K), the copolymer is in the glassy state and the storage modulus E' (around 2 GPa) slightly decreases with temperature. Then, E' decreases rapidly by more than 3 decades. This sharp drop is associated with the glass-rubber transition of the polymer. In the terminal zone, E' decreases with temperature until irreversible flow of the material. For temperatures above Tg, the composite modulus of the 50 wt% filled material is about 100 times higher than that of the matrix. In addition, the flowing of the composite films appears at higher temperature that for the unfilled matrix. The plot of log(E') versus temperature for poly(S-co-BuA) reinforced with 30 wt% starch nanocrystals obtained for different times of hydrolysis is displayed in Figure 6a. The storage modulus increases with increasing times of hydrolysis, i.e. with a decrease of the size of the nanocrystals aggregates (Table 1). In fact, for a given starch content, the lower the size of particles, the higher the dispersion of the filler among the matrix, what leads to a higher storage modulus. Figures 5b and 6b show that no shift of the main relaxation (associated with T_g) is observed.

Conclusions

Agglomerates of semi-crystalline starch nanoplatelets were obtained after acid hydrolysis of waxy maize starch granules under variable conditions. Starch nanocrystals obtained after 40 days of 2.2N HCl hydrolysis appear to be an interesting filler in a poly(S-co-BuA) matrix. The mechanical properties of the composite materials are substantially improved by increasing the amount of filler. The problem is that such a filler obtained with a yield of 0.5% and suspensions are not stable. Further experiments (tensile tests, Differential Scanning Calorimetry and Thermo Gravimetric Analysis) have to be carried out in order to investigate the origin of the reinforcing effect of starch filler and the influence of the morphology of nanoplatelets.

Further work will consist in preparing stable suspensions of starch nanocrystals, in shorter time and with a higher yield. We have shown that H_2SO_4 hydrolysis produces more stable suspensions and that an increase of the temperature and/or acid concentration accelerates the degradation of starch granules. A design of experiments is in progress in order to optimize H_2SO_4 hydrolysis, taking into account different selected parameters: hydrolysis time, temperature, acid concentration, starch concentration and stirring.

Acknowledgments

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