Preparation of Poly(styrene-*co*-hexylacrylate)/Cellulose Whiskers Nanocomposites via Miniemulsion Polymerization

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ABSTRACT: A stable aqueous nanocomposite dispersion containing cellulose whiskers and a poly(styrene-*co*-hexylacrylate) matrix was prepared via miniemulsion polymerization. We were able to prepare a stable dispersion with a 20 wt % solid content and a cellulose whiskers content ranging from 1 up to 5 wt % based on polymer content. To avoid particle agglomeration leading to coagulum formation, the addition of a low amount of reactive silane, i.e., methacryloxypropyl triethoxysilane revealed to efficiently stabilize the dispersion. The nanocomposite dispersion was characterized using dynamic light scattering, transmission electron microscopy, and atomic force microscopy. Films obtained by casting followed by water evaporation and particle coalescence were analyzed by differential scanning calorimetry, dynamic mechanical analysis, and tensile testing. At 5 wt % whiskers loading, an enhancement by 500% of the storage modulus above the glass transition was determined. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 2946–2955, 2009

Key words: cellulose whiskers; nanocomposite; miniemulsion polymerization

INTRODUCTION

The research activity on polymeric nanocomposite materials has been intensely expanded during the past decade.[1–3] Among the interesting properties offered by nanocomposites, one can cite:

- Increased modulus at very low filler concentration
- Lower density of the overall composite material
- Decreased permeability to gases, water, and hydrocarbons (barrier effect)
- Better surface and optical properties

Since the first report of reinforcement of a polymer matrix using cellulose whiskers obtained by acid hydrolysis of cellulosic substrates,[4] cellulose whiskers have been used extensively as model fillers in various polymeric matrices.[5,6] Thanks to their nanometric scale and monocrystalline structure, whiskers do not display any surface or bulk defects leading to an elastic modulus estimated to be about 134 GPa,[7] close to the theoretical modulus of cellulose chains, and a very high strength in the order of 7 GPa.[8]

One of the main drawbacks of cellulose whiskers is their poor dispersibility/compatibility with nonpolar solvents or resins. Thus, the application of cellulose whiskers or nanocrystals as a reinforcing phase, requiring a good dispersion level, has been mostly limited to polymer matrices which are either water soluble, such as polyvinyl alcohol, polyoxyethylene or plasticized starch, or as an aqueous polymer dispersion, such as natural rubber latex or synthetic copolymer.[5,4,7,9,10] To overcome this problem and broaden the type of possible polymer matrices, the surface energy of cellulose whiskers should be reduced either by chemical surface modification or surfactant coating. The former approach was successfully adopted for different reagents like alkenyl succinic anhydride,[11] isocyanates,[9] maleated polypropylene,[10] and chlorosilane.[12] Even though such a treatment improved the nanofiber dispersion in organic solvents such as toluene and cyclohexane, the performance of the ensuing nanocomposites based on the modified whiskers were found to decrease significantly compared with unmodified whisker nanocomposites. This loss of performance

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was ascribed to the destruction of the three-dimensional network formed by whiskers through hydrogen bonding. This later is known to contribute to the overall reinforcing effect through a mechanical percolation effect of the nanoparticles in the composites made with unmodified nanofibers.[13]

A miniemulsion is defined as an aqueous dispersion of relatively stable oil droplets, composed of monomer, water, surfactant and hydrophobic compounds, with a size ranging from 50 to 300 nm. A miniemulsion is produced using a shearing system, i.e., a high-speed homogenizer or ultrasonicator. It is rather stable with respect to aggregation and sedimentation and exhibits greater shear stability than conventional emulsions.[14,15,16] The surfactant concentration should be high enough to provide adequate droplet stability against coalescence but without exceeding the Critical Micelle Concentration. A hydrophobic costabilizer (such as hexadecane and cetyl alcohol) is generally added to reduce the diffusional degradation by Ostwald ripening of the miniemulsion droplets,[17] and the subsequent propagation reaction occurs primarily in submicrometer monomer droplets. Each of those droplets can be regarded as an individual nanophase reactor. The high concentration of particles, i.e., 10^{12}–10^{14} per mL, and the absence of free micelles favor droplet nucleation over homogeneous or micellar nucleation. Thus, the droplets become the primary loci of particle nucleation, and one can expect that the particle number does not change during polymerization.

Recently, miniemulsion polymerization has been found to be a particularly attractive way to obtain nanocomposite particles, and it is the subject of numerous theoretical and experimental studies.[18–21] Weili et al.[22] prepared asymmetric nanocomposite particle pairs of polystyrene and silica via a one-step miniemulsion polymerization. Zhou et al.[23] synthesized SiO_2/polystyrene/TiO_2 multilayer core-shell hybrid microspheres via miniemulsion polymerization using a cationic initiator and emulsifier. Zhaohui and Yulin[24] synthesized a stable water-based polystyrene nanoclay composite suspension via miniemulsion polymerization. A novel polystyrene-encapsulated laponite hybrid system in the form of an aqueous dispersion was developed by Qunhui et al.[18] with up to ca. 5 wt % of clay loading via a miniemulsion polymerization approach.

Nanocomposites based on cellulose whiskers can be obtained by mixing a diluted suspension of the whiskers with a latex dispersion followed by water evaporation to obtain a thin film. However, even though a high reinforcing effect was noted for the ensuing material, this approach is time consuming as it involves two steps, the first one mixing of a diluted whiskers suspension with a solid content not exceeding 0.5 wt % to avoid aggregation, and the second one casting of the dispersion giving rise to a thin film after water evaporation and polymer particle coalescence. Because of the necessity to work with a low solid content after mixing with whiskers suspension, the film thickness cannot exceed 100–200 μm. Moreover, it has been reported that the topological dispersion of whiskers in the nanocomposite film obtained from mixing whiskers suspension with a latex strongly depends on the processing technique and conditions. Heterogeneous composites with numerous locally oriented domains of whiskers are likely to occur after film formation.[19] Polymerization in emulsion with cellulose whiskers present reduces the processing time, and may also result in better homogeneous dispersion of the nanowhiskers in the final material due to whisker-droplet interactions.

In this work, the preparation of a nanocomposite dispersion based on cellulose whiskers and a poly (styrene-*co*-hexylacrylate) matrix via miniemulsion polymerization is investigated. The ensuing nanocomposite dispersion could be used in the form of a thin film after water evaporation and particle coalescence, or in agglomerated form to obtain granules that could be further transformed by other techniques such as extrusion or injection. We expect that this new approach, which enables the dispersion of cellulose whiskers in a polymeric matrix without the necessity to isolate them from water in which they form a stable suspension, will allow us to prepare stable dispersions with a relatively high solid content combined with a homogenous distribution of the nanofibers within the matrix. It also allows for the generation of a premixed dry cellulose nanoparticles/polymer mixtures that can be fed to an extruder. This is expected to result in extruded nanocomposites with improved nanoparticle dispersion, and thus improved mechanical performance, over the use of two separate dry feeds.

EXPERIMENTAL

Materials

Styrene (St) and 2-Ethyl Hexylacrylate (EHA) were purified by vacuum distillation before use. Benzoyl peroxide, Sodium Dodecyl Sulfate (SDS, surfactant), γ-methacryloxypropyl triethoxysilane (MPS), octamethylcyclotetrasiloxane (TSi), and acrylic acid, were products from Aldrich and used without further purification.

Alfa hydrolysis

Bleached soda pulp was obtained from the Tunisian annual plant esparto (*Alfa tenassissima*). It was first submitted to a treatment with a NaOH solution (5 wt %) for 1 h at 70°C under mechanical stirring.

TABLE I
Recipe for the Miniemulsion Polymerization of
Styrene-ethylhexylacrylate in Presence of
Cellulose Whiskers

Component	Added (g)	Percentage in total (wt %)	% With respect to monomer
Styrene-ethylhexylacrylate	3.2/1.6	20.3	100
Octamethylcyclotetrasiloxane	1.2	5	25
Benzoyl peroxide	0.25	1	5.2
Cellulose whiskers	0–0.25	0–1	0–5
SDS	0.1	0.4	2
Water	17–16.75	72–72.8	

The fibers were subsequently filtered and rinsed with distilled water. The NaOH treatment was repeated until the solution did not discolor significantly. A subsequent bleaching treatment at 80°C for 2 h was used to whiten the alfa fibers. The bleaching solution contained equal parts of aqueous chlorite (1.7 wt % $NaClO_2$ in water) and an acetate buffer (27 g NaOH and 75 mL glacial acetic acid, diluted to 1 L using distilled water). The alfa content was approximately 5 wt %, and the bleaching step was repeated two times. The fibers were again filtered and rinsed with distilled water between each treatment step. The fibers were subsequently dried for 24 h at 40°C in a convection oven. The dried treated fibers were ground to a fine powder and dispersed in 65 wt % sulfuric acid at a concentration of around 4 wt %. This suspension was held at 60°C under mechanical stirring for 15 min to allow for hydrolysis. The dispersion was subsequently diluted with an equal part of cold water and washed by successive centrifugations at 10,000 rpm and 10°C until a turbid supernatant became visible (three times). Dialysis against distilled water was performed to remove free acid in the dispersion. This was verified by neutrality of the dialysis effluent. Complete dispersion of the whiskers was obtained by a sonication step using a Branson sonifier. The dispersions were stored in the refrigerator after filtration over a No. 2 fritted glass filter to remove residual aggregates and addition of several drops of chloroform. Determination of the whisker content was done by weighing aliquots of the solution before and after drying.

Miniemulsion preparation and polymerization

The miniemulsion preparation conditions are reported in Table I. The oil phase contained 1.2 g of TSi and 0.7 g of benzoyl peroxyde in 4.8 g of a mixture of styrene (3.2 g) and ethylhexylacrylate (1.6 g) monomer. The aqueous phase was prepared by adding 0.1 g of SDS in 20 g of a cellulose whiskers suspension in water at room temperature. When polymerization was conducted in presence of γ-MPS, the silane was added to the whiskers suspension before SDS addition. Subsequently, the pH was adjusted to 4 by adding acetic acid, and the whiskers suspension was kept for 2 h to ensure silane hydrolysis. The pH was then restored to 7 before adding the monomers. When present, the acrylic acid was added to the whiskers suspension immediately before sonication.

A miniemulsion was obtained by mixing both solutions (the described mixed oil phase and the aqueous phase) followed by 15 min of sonication in a sonication bath at 25°C. Upon completion of the sonication, the as-prepared miniemulsion was polymerized at 70°C for 3 h under mechanical stirring with a half-moon shaped Teflon stirrer at 300 rpm under an inert N_2 atmosphere.

Film processing

The nanocomposite film was prepared by casting the dispersion in a Teflon mould and allowed to dry slowly at 40°C under air convection. A typical time of around 24 h was found to be sufficient to prepare a cohesive film with a thickness in the range 300–400 μm (dry state).

Size determination

The average diameter of polymer particles was determined using dynamic light scattering (Malvern Zetasizer Nano S, Malvern Instruments Ltd., Malvern, UK). The latex was diluted with 5×10^{-3} M KCl solution (to buffer the ionic strength) to about 1 wt % of polymer particles. Each measurement was repeated three times, and the average value was retained as the particle size.

Transmission electron microscopy

Transmission electron micrographs of cellulose whiskers were taken with a Philips CM200 transmission electron microscope with an acceleration voltage of 80 kV. Nanowhiskers were deposited from an aqueous dispersion on a microgrid (200 mesh, Electron Microscopy Sciences, Hatfield, PA) covered with a thin carbon film (200 nm), etched under an

air atmosphere to make it hydrophilic. The deposited nanowhiskers were subsequently negatively stained with an aqueous 2% uranyl acetate solution.

Cryogenic transmission electron microscopy of the synthesized latexes was performed on a Jeol 2100F TEM operating at a 100 kV acceleration voltage. The emulsions were diluted with deionized water, and one drop of the latex was placed on the porous carbon coated side of a 200-mesh copper grid. Water was removed, and the grid was immediately dropped in liquid nitrogen cooled liquid anhydrous 2-methylbutane. Samples were kept under liquid nitrogen cooling until transfer to the cryoTEM holder for analysis.

Atomic force microscopy

An atomic force microscope (AFM) from Digital Instruments having a NanoScope III controller with a MultiMode head was used to examine the surface of the samples. Analyses were performed in Tapping Mode in air under moderate conditions for recording phase images. Silicon cantilevers with a resonance frequency of about 200–400 kHz and a spring constant of 12–103 N/m were used for imaging. The trace and retrace signals were set identical before image capture, and no filtering was used during scanning. The images presented are raw, unprocessed data, except for flattening in some cases. Samples were prepared by depositing a drop of a dispersion of whiskers in water onto freshly cleaved mica. Water was removed before imaging by holding the sample in silica gel at ambient conditions for several hours.

Differential scanning calorimetry

Differential Scanning Calorimetry (DSC) was performed on a DSC Q100 (TA Instruments, New Castle, DE) fitted with a manual liquid nitrogen cooling system. Conditioned film sections were placed in hermetically closed DSC crucibles. Samples were tested in the range -50 to $100°C$ at a heating rate of $10°C/min$ under a nitrogen atmosphere. Sample weight was between 2 and 5 mg. The glass transition temperature, T_g, mentioned in the text refers to the temperature of the inflexion point on DSC thermograms.

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was conducted in tension mode using a PYRIS^{TM} Diamond DMA (Perkin-Elmer, Waltham, MA). Temperature scans were run from -80 to $100°C$ at a heating rate of $1°C/min$ at a frequency of 1 Hz and an amplitude of 10 μm. The storage (E') and the loss (E'') moduli and the loss factor Tan $\delta = (E''/E')$ were measured

as a function of temperature. Sample dimensions were about 20 mm (length) by 10 mm (width) and 0.1–0.4 mm (thickness). The main relaxation temperature T_α is defined as the temperature where Tan δ reaches a maximum.

Tensile testing

The mechanical behavior at large deformations for the unfilled matrix, and the nanocomposites was analyzed with an Zwick Universal Testing machine with a load cell of 500 N. Experiments were performed with a cross head speed of 10 mm/min at constant temperature, 23°C. The specimens were thin rectangular film (50 × 10 × 0.5–0.3 of length, width, and thickness, respectively).

RESULTS AND DISCUSSION

Miniemulsion polymerization

Even though miniemulsion polymerization is not as widely used as emulsion polymerization, this technique proved to be more effective in preparing stable nanocomposite particles in water. Contrary to emulsion polymerization, where the particles are first generated by homogenous or micellar nucleation, in miniemulsion polymerization the monomer droplets, generated by sonication, are stabilized by a surfactant and a highly water-insoluble material that prevents Ostwald ripening. The ensuing monomer droplets become the principle locus of particle nucleation. The large surface area of the droplets guarantees that most of the surfactant is adsorbed on their surface so that little free surfactant is available to form micelles or to stabilize aqueous phase polymerization.

Adopting the recipe presented in Table I, stable dispersions without any coagulum trace were obtained up to 4 wt % whisker content relative to the polymer content. The evolution of the particle size versus whisker content is shown in Figure 1. However, one can note a continuous increase in the particle size upon whiskers addition. At 5 wt % whisker loading, the particle size exceeds six times the average size of dispersion droplets in the miniemulsion without any whiskers, and a coagulum exceeding 20 wt % of the initial amount of the monomers starts to appear.

In the absence of the whiskers, the polymer particle size (95 nm) does not exceed 110% of the droplet size generated by sonication and kept for 2 h at room temperature (size equal to 87 nm). This result indicates that the droplets constitute the locus where the polymerization occurs and that they are stable enough against Ostwald ripening during the polymerization.
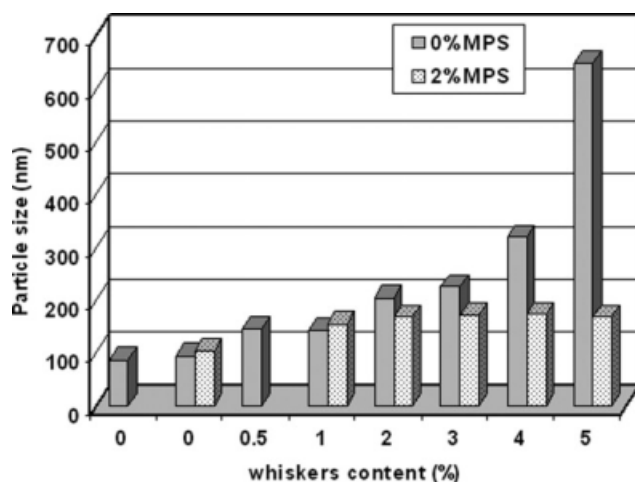
Figure 1 Average particle size obtained from dynamic light scattering analysis versus nanocrystals content of the latex prepared by miniemulsion polymerization.

To reduce the negative effect of the whiskers, which seems to favor particle agglomeration, two reactive monomers were added in a low amount to the aqueous phase (about 2 wt % based on the monomer weight). These monomers bear polar groups and are expected to accumulate on the surface of the polymer particles after copolymerization with monomers, where they are in contact with the aqueous phase. By adding this reactive monomer, we aim to produce polymer particles bearing on their surface polar groups able to anchor onto the whiskers through hydrogen bonding. The first approach consisting in the addition of acrylic acid up to 4 wt % based on the monomer was found to be unsuccessful in preventing coagulation above 4 wt % whiskers loading, even though it yielded dispersions with a lower average particle size (370 nm in the presence of 3 wt % acrylic acid against 600 nm without acrylic acid). However, in the presence of 2 wt % of MPS, a different behavior is noted as shown in Figure 1. The particle size of the ensuing dispersion is maintained roughly constant at 170 nm up to 5 wt % whisker content and a coagulum-free dispersion was obtained. It is worth to note that MPS was added to the whiskers suspension at pH 4 and kept under stirring for 2 h to ensure complete hydrolysis of the ethoxy silane groups. Indeed, our previous work[20,21,25] studying silane hydrolysis in the presence of water, has shown that such conditions ensure silane hydrolysis within 2–3 h and limit silanol self-condensation, which would generate oligomeric species linked through siloxane bridges. Thus, the added silane is mainly in the form of hydrolyzed monomers that will generate silanol-functionalized latex particles on which cellulose whiskers could be anchored through physical interaction with the silanol groups. This hypothesis is further sup-

ported by TEM observation later in this article. It worth noting that miniemulsion polymerization is reported to be the most appropriate method to prepare silanol-functionalized latex particles by copolymerization of MPS with styrene and acrylate or methacrylate monomers.[16,26–28]

The idea that silanol groups will promote nanofiber attachment on the polymer particles is based on our previous work on the interaction of silane coupling agents with cellulose substrates.[26] It was shown that these compounds display a high affinity for the cellulose surface which favors their adsorption onto cellulose substrates through Van der Waals interactions and hydrogen bonding of the silanol groups with the surface hydroxyl groups. Further moderate heat treatment of the fibers results in the chemical grafting of the silane coupling agent through a condensation reaction of silanol with the surface hydroxyl groups but may also result in self-condensation of silanol groups generating siloxane bridges.[29]

Throughout the rest of our work, different nanocomposite dispersions were prepared in the presence of 2% MPS to avoid particle agglomeration.

The effect of the presence of whiskers on the polymerization kinetics was also analyzed. Results shown in Figure 2 indicate the same trend of conversion versus time in the absence and in the presence of 2 or 3 wt % of whiskers. These results disagree with those reported for miniemulsion or emulsion polymerization in the presence of inorganic particles or nanoclay. It was shown that the presence of those particles reduces both the final monomer conversion and the reaction rate.[28,29] If one excludes any possible interaction between the growing radicals and the nanofibers, and no agglomeration of droplets is induced by the nanofibers, then we would expect no
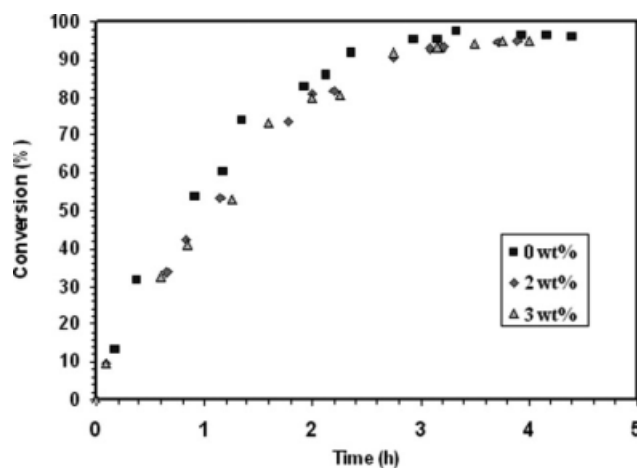
Figure 2 Conversion versus time curves for polymerization of styrene and EHA obtained in the presence, and in the absence of cellulose nanocrystals (polymerization was carried in presence of 2% MPS based on monomer content).
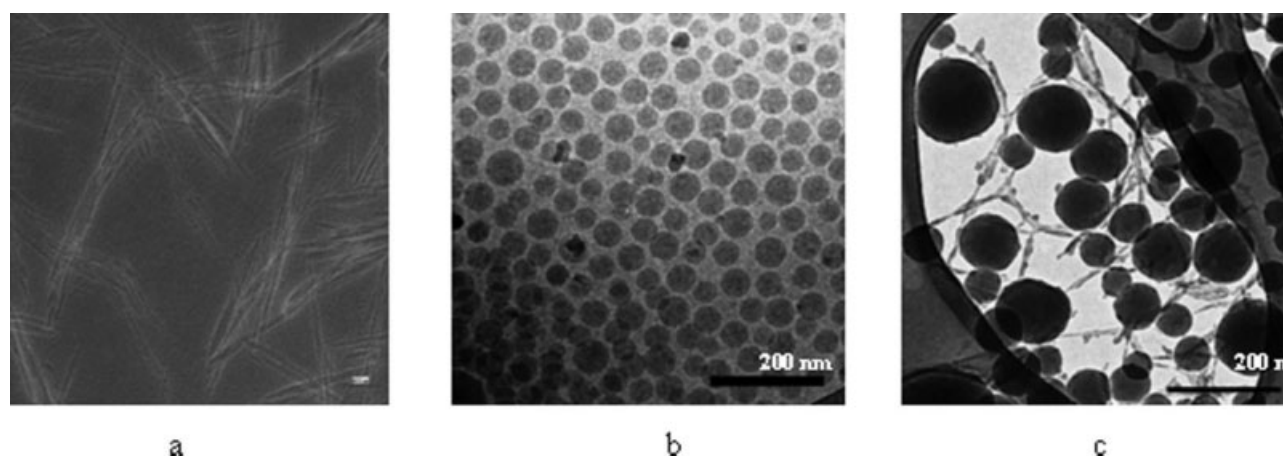
Figure 3 Transmission electron micrographs (TEMs) of (a) cellulose nanowhiskers obtained from alfa fibers, (b) the whisker-free polymer dispersion particles, and (c) the nanocomposite dispersion containing 2 wt % whiskers in the presence of MPS.

effect on the reaction kinetic considering that the monomer droplets constitute the main locus of the polymerization reaction. The increasing size of the droplets with increasing whisker content however indicates some interaction between the droplets and the whiskers. Droplet agglomeration is thus expected to occur later in the reaction, when most of the droplet is polymerized such that the reaction kinetics remains largely unaffected.

TEM observation

Figure 3 shows a TEM micrograph of whiskers and polymer dispersions with different whisker contents. The whiskers in suspension (Fig. 3, panel a) revealed a needle-like structure with a tendency to partial agglomeration by alignment of the whiskers along their longest axis. The average length and width of alfa whiskers were estimated to be around 200 ± 20 and 10 ± 2 nm, respectively, which gives an aspect ratio around 20. TEM observations of polymer droplets and nanocomposite particles were carried out on a thin film of a stabilized dispersion in 2-methylbutane by removing water and quench-freezing the liquid dispersion using liquid nitrogen as described in the Experimental Section. In the absence of whiskers, uniform individual polymer particles were obtained with an average size ranging from about 90 to 110 nm (Fig. 3, panel b), which is in agreement with values determined from dynamic light scattering (DLS) measurements. The dispersion containing 2 wt % whiskers (in the presence of 2 wt % MPS) shows discrete particles with larger diameters ranging from 120 to 170 nm (Fig. 3, panel c). It can be seen that a high proportion of the whiskers are linked to the polymer particle surface, probably through physical (may also be chemical) interaction with the silanol groups located on the surface of the particles.
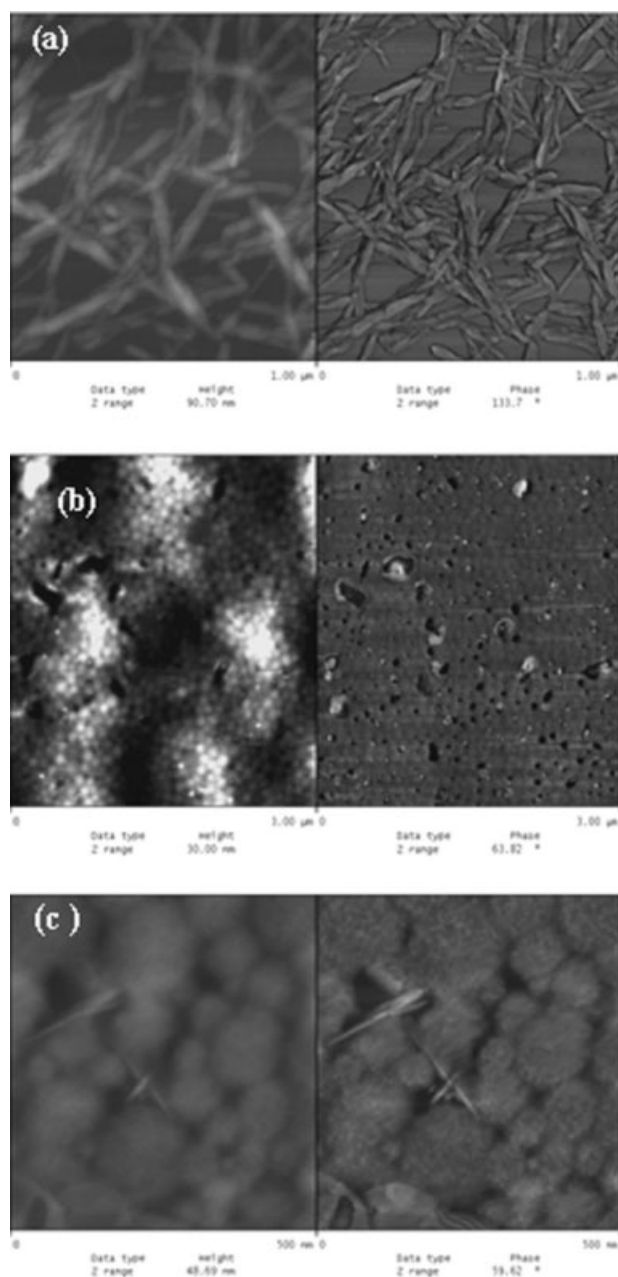
Indeed, given the condition under which the silane was used (addition suspension of whiskers for 2 h at pH 4–5), a high hydrolysis level of the silane will occur, thus favoring the accumulation of the silanol groups on the particle surface after copolymerization with styrene and acrylate monomer due to their hydrophilic character.

AFM analysis

The AFM imaging of cellulose whiskers [Fig. 4(a)] revealed a rounded shape wider than observed through TEM analysis. These images are similar to those reported by Kvien et al.[30] despite the different source of cellulose. The AFM image of the whisker-free polymer dispersion [Fig. 4(b)], taken just before particle coalescence, shows spherical monodisperse polymer particles. Figure 4(c) shows the nanocomposite dispersion containing 1 wt % of whiskers prepared in the presence of 2 wt % MPS, during the coalescence process. It can be seen that the polymer particles are more heterogeneous in size, with some nanofibers (in a relatively individual form) dispersed within the matrix.

Thermal analysis

The DSC traces for the nanocomposite films containing various whisker contents are shown in Figure 5, and data are collected in Table II. A single glass-rubber transition around 26–30°C is observed, in agreement with the main relaxation temperature values observed by DMA analysis (see later). The presence of a single glass transition and the value of the T_g close to that evaluated from the Fox relation (equal to 25°C for St/HEA 66/34 wt %) is indicative of the statistical distribution of St and HEA within the macromolecular backbone. The value of T_g and

Figure 5 DSC traces showing the glass transition for the neat matrix and nanocomposite films reinforced with 0, 2, 3, 4, and 5 wt % whiskers in the presence of 2 wt % of MPS.
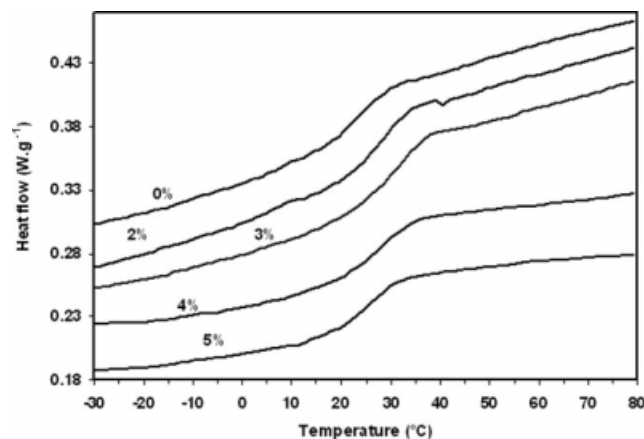

Figure 4 AFM topography, and phase image of (a) cellulose whiskers after drying on a mica surface (b) the whisker-free latex dispersion and (c) the nanocomposite dispersion containing 1 wt % whiskers.

coalescence of polymer particles occurred before DMA analysis. Results depicted in Figure 6(a,b) show that below T_g, the tensile storage modulus of the nanocomposites were roughly equivalent to the one obtained for the neat matrix up to a 2 wt % whiskers content. Above this concentration, E' was slightly enhanced and attained 1 and 1.5 GPa for a 3 and 5 wt % whiskers loading, respectively. This behavior is in agreement with other work and can be explained by the relatively low difference between the elastic tensile modulus of the whiskers and that of the glassy matrix thus resulting in a limited reinforcing effect. On the contrary, above T_g, a significant increase in the storage modulus, especially at high whiskers content, is noted. At 50°C, the storage modulus attained 3.5, 7.5, 19, and 98 MPa with 0.5, 1, 3, and 5 wt % whiskers loading respectively, compared with 0.1 MPa for the neat matrix.

The significant enhancement of the reinforcing effect, namely above 1 wt % whiskers is the consequence of the relatively high aspect ratio of cellulose whiskers obtained from alfa (around 20) combined with the small size of the reinforcing particles which results in reinforcement through percolation at low whiskers fractions.

the specific heat increment (ΔC_p) is found to be independent of the filler content, indicating that the nanofiber incorporation within the matrix does not result in any rigidification effect by restricting polymer chain mobility.

DMA analysis

Nanocomposite films were obtained by casting nanocomposite dispersions in a Teflon mold. The cast dispersions were then left to dry at 40°C until

TABLE II
Glass Transition Temperature and Specific Heat Increment Obtained From DSC Measurements for Nanocomposite Films Reinforced with Different Whisker Contents

Whisker content (wt %)	T_g (°C)	ΔC_p (J/g K)
0	30	0.068
2	28	0.06
3	26	0.05
4	26	0.05
5	28	0.06
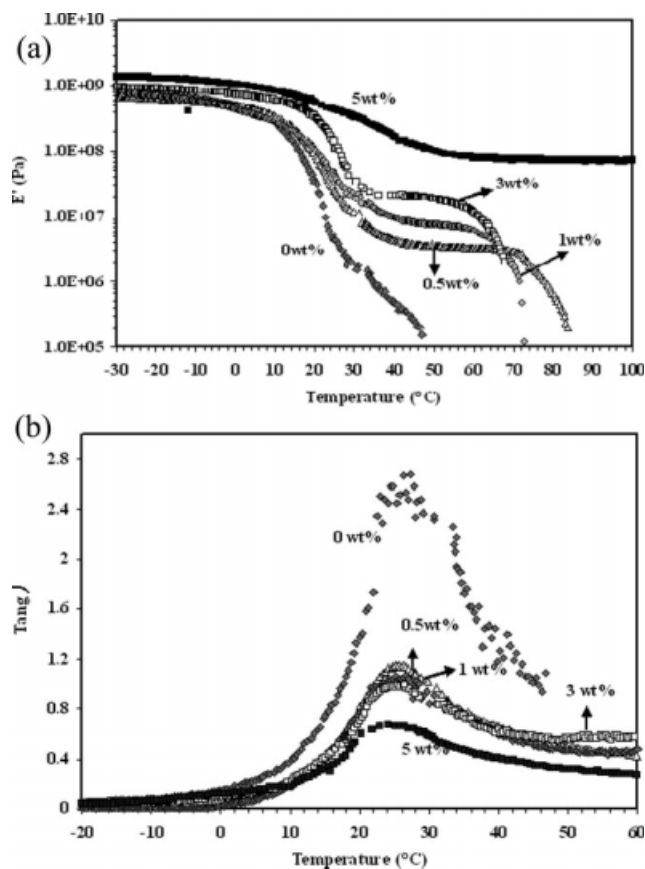
Figure 6 Evolution of (a) the storage tensile modulus E', and (b) loss angle tangent Tan δ versus temperature at 1 Hz for nanocomposites film reinforced with different whiskers content in presence of 2 wt % of MPS.

The percolation threshold is calculated to occur around 3.5 vol % using the following relation $P_t = 0.7/L/d$.[31] Above this critical concentration, a rigid percolating whisker network through strong whisker/whisker hydrogen bonds interactions is expected to form. The formation of this continuous network can be affected by the polymer particle size. Indeed, the particles act as impenetrable domains to whiskers during the film formation due to their high viscosity. Thus, the small polymer particle size and the good interaction between the whiskers and the polymer particles contribute for the percolation attainment at lower nanofibers fractions. This result is in line with the results reported by Azizi et al.[6] Moreover, we note that the rubbery plateau is maintained over a wide temperature range in the presence of the whiskers, even at a very low content of 0.5 wt %. When we report the storage modulus E' at 40°C versus whiskers content, it can be seen that above 3 wt % whiskers content, E' increases more rapidly than the trend observed for whiskers contents below 3 wt %. This effect may be due to the generation of a relatively dense three dimensional network between the nanofibers through percolation. Further

investigation to better understand this phenomenon and correlate it with the preparation method of the nanocomposite dispersion is currently under investigation.

For all the nanocomposites as well as the neat matrix, the tanδ trace exhibits a well-defined relaxation (α relaxation) around 26°C associated with the cooperative motions of long chain sequences. The presence of whiskers results in a notable drop in the magnitude of the α relaxation accompanied with a broadening in the Tan δ peak but without a shift in the position of α relaxation. These two effects are often observed in cross-linked polymers[32] and are indicative of reduced polymer chain mobility resulting from the nanofibers, which act as physical entanglements. This result is in tune with the enlargement of the rubbery plateau observed. The constant position of the glass transition temperature is in agreement with DSC results. However, both T_g and the specific heat increment (ΔC_p) were found to be independent of whisker content, indicating absence of chain mobility restraint. This discrepancy may be due to the localization of the nanofibers on the particle surface in the miniemulsion, thereby preventing them to be perfectly homogeneously dispersed within the polymer matrix after water evaporation and particle coalescence.

Tensile tests

The high strain mechanical behavior of films obtained from neat matrix samples as well as from composites reinforced with different whisker contents was characterized by tensile tests. This
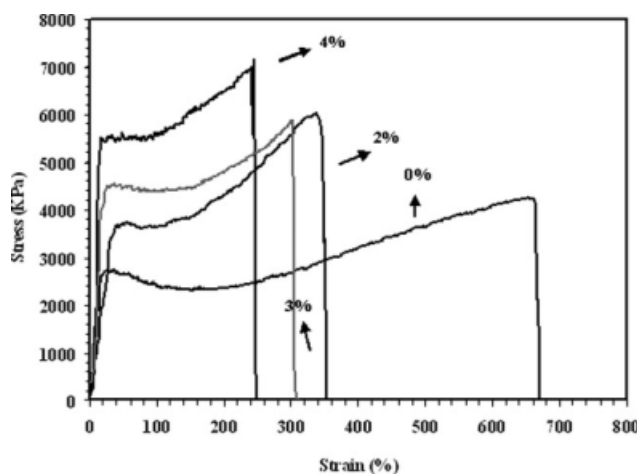
Figure 7 Typical tensile stress vs. strain curves for the neat matrix and nanocomposite films reinforced with different whiskers content (T = 22°C, crosshead speed = 10 mm min⁻¹). The whisker contents are indicated in the figure.

Whisker content (wt %)	Strain at break (%)	Yield stress (MPa)	Tensile strength (MPa)
0	680 (10)	2.7 (0.1)	4.2 (0.2)
2	360 (10)	3.7 (0.2)	6 (0.3)
3	300 (10)	4.5 (0.25)	5.9 (0.3)
4	240 (10)	5.5 (0.3)	7 (0.35)

analysis was performed at a constant temperature maintained around 20°C to avoid fluctuation and scatter in the results due to the T_g value being close to 26°C. Figure 7 shows the stress-strain curves obtained for the four films. The strain at break, yield stress, and tensile strength were determined from the curves, and the results are presented in Table III. The unfilled matrix is characterized by a yielding behavior and extensive deformation reaching about 700% before breaking. Nanofiber incorporation results in a significant increase in both the yield stress and tensile strength with a drop in the strain at break. Likewise, a reduction of the plastic deformation domain with an increasing whisker content is clearly visible (Fig. 7). These effects arise from the strong filler–filler interactions but also from interactions between the filler and the matrix. As the whiskers content increases, the behavior of the nanocomposite film becomes filler-dominated, whereas it is mainly governed by the matrix below the percolation threshold. From Table III, we can notice an enhancement in the yield stress by about 100% for a 4 wt % whiskers loading, compared with the unfilled matrix.

CONCLUSIONS

A stable aqueous nanocomposite dispersion based on cellulose whiskers and a poly(styrene-co-hexylacrylate) matrix was successfully prepared by *in situ* polymerization of styrene and EHA in the presence of the cellulose whiskers via miniemulsion polymerization. The nanocomposite dispersion was characterized using DLS, transmission electron microscopy (TEM) and AFM. In the absence of any added reactive monomers, a continuous increase in the particle size upon whisker addition is observed, which results in significant coagulum formation above 5 wt % of cellulose whiskers. The addition of a low amount of reactive silane, i.e., MPS was found to be efficient to stabilize the dispersion and avoid coagulum formation up to a 6 wt % whiskers content. Indeed, the addition of 2 wt % of MPS, based on monomer content, revealed to be efficient to prevent particle coagulation and to effectively sta-

bilize the nanocomposite dispersion. Homogenous distribution of the cellulose whiskers within polymers particles in presence of the silane coupling agent was confirmed by CryoTEM analysis.

This approach provides an efficient way for the production of water-based polymer nanocomposites containing up to 6 wt % of cellulose nanocrystals without the necessity to isolate the nanofibers from water, a medium in which they are stable. Nanocomposite films obtained by the casting/evaporation technique of these nanocomposite dispersions were analyzed by DSC, DMA, and tensile testing. The DMA analysis shows a significant increase in the storage modulus above T_g, with larger improvements obtained for higher whisker contents. The significant enhancement of the reinforcing effect, namely above 1 wt % whiskers is the consequence of the relatively high aspect ratio of cellulose whiskers extracted from alfa (around 20) and the small polymer particle size before film drying. The DSC analysis revealed a quasi constant value of T_g of the matrix and specific heat increment (ΔC_p) regardless the filler content indicating that the nanofibers incorporation within the matrix does not bring about any restriction in chain mobility. The characterization of the high strain mechanical behavior for the nanocomposite films shows a significant increase in both the yield stress and tensile strength with a drop in the strain at break with the whiskers incorporation.

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