



Waterborne acrylic–cellulose nanofibrils nanocomposite latexes via miniemulsion polymerization



Mariem Errezma, Ayman Ben Mabrouk, Sami Boufi*

University of Sfax, Faculty of Science, LMSE, BP1171-3018, Sfax, Tunisia

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ABSTRACT

Waterborne acrylic–cellulose nanofibrils (CNFs) nanocomposite latexes have been successfully synthesized via one-pot miniemulsion polymerization. A cationic copolymer and a low amount of anionic surfactant were used to promote the stabilization process and prevent the aggregation during storage. The effect of the CNFs content and the amount of added copolymer on the particle size and the stability of the dispersion were studied. Evidence of the binding of CNFs onto the polymer particles was supported by FE-SEM observation. Transparent nanocomposite films were obtained by casting after water evaporation and film-formation process. Investigation of the mechanical properties by dynamic mechanical analysis (DMA) and tensile testing revealed an enhancement in both the stiffness and strength of the nanocomposites, which is indicative that the in-situ polymerization in presence of CNFs did not compromise the strong reinforcing potential of CNFs. The synthesized acrylic–CNFs latexes are able to form films with promising properties for application as waterborne coatings.

1. Introduction

Nanocomposites based on nanocelluloses have been the subject of increasing scientific interest during the last two decades [1,2]. The main reason is that a low nanofiller loading (< 10 wt%) is enough to brought beneficial effect on the mechanical properties [3] similar to that observed for composites based on cellulose fibers with a content exceeding 30–50 wt.%. Furthermore, the nanosized dimension of nanocellulose contributed to preserve the optical properties of the polymer matrix.

The high reinforcing potential of CNFs is explained by (i) the high intrinsic mechanical properties of CNFs with modulus and strength around 50–70 and 2–4 GPa, respectively [4,5] (ii) the high aspect ratio of elongated cellulose nanofibrils, (iii) the high crystallinity of CNFs, and (iii) the set-up of an entangled network held-up by strong hydrogen bonding between nanofibril crossings. However, this strong reinforcing effect is tributary of lack of excessive nanofibrils aggregation during the nanocomposite preparation and in most cases, imposes the use of water or hydrogen-bond-forming organic solvents to switch-on the hydrogen bonds among the nanofibers.

The surface modification of cellulose nanofibrils is an alternative to improve the dispersion of CNFs in a polymer matrix or in an organic solvent [6,7]. However, these chemical modifications hinder the potential interactions between nanofibrils through hydrogen-bonding

which is the key parameter driving the reinforcing potential of nanocellulose.

Latex dispersions are widely used for many industrial applications such as coating, waterborne adhesives and additives in cement and concrete composition. The addition of nanocellulose in the form of diluted suspension to a polymer latex was shown to be the most efficient approach to benefit from the strong reinforcing potential of nanocellulose. However, this processing route involved a mixing step, which is a time consuming and required appropriate tool to ensure thorough dispersion of nanosized cellulose fibrils within the latex without any risk of aggregation. The one-pot production of polymer latex in the presence cellulose nanofibrils via in-situ polymerization may facilitate the use of nanocomposite dispersion based on CNFs for application in high performance waterborne adhesive or coatings.

CNFs are nanosized nanocellulose thin flexible fibrils encompassing both crystalline and amorphous domains with typical width in the range of 5–50 nm depending on the extent of fibers disintegration and length within the micron scale [8]. They are mainly obtained through intensive mechanical disintegration actions to breakdown the cell wall of the fibers into nanoscale [9,10]. This can be done via high pressure homogenization [11], microfluidization or highly intensive mechanical grinding, ultrasonication and high speed blender [12].

Miniemulsion polymerization has gained great deal of interest, especially for preparing hybrid nanoparticles [13,14]. In miniemulsion

* Corresponding author.

E-mail address: Sami.Boufi@fss.rnu.tn (S. Boufi).

polymerization, the first step involved the emulsification of the monomer in water by ultrasonication to form finely nanosized monomer droplet stabilized by surfactant. By increasing the temperature, the monomer is decomposed and the polymerization is activated until all the monomer was consumed. Given, the high concentration of monomer droplets, i.e., 10^{12} – 10^{14} per ml, and the absence of free micelles, the droplet nucleation is the main polymer polymerization locus with the consequence that the polymer particles are the replica of the miniemulsion droplets. During the polymerization process, the emulsion is stabilized against coalescence by the addition of a hydrophobic agent that hinders Ostwald ripening and the diffusion of the monomer from a droplet to another. In our previous work, miniemulsion polymerization has been successfully used to produce one-pot nanocomposite dispersion based on cellulose nanocrystals, and starch nanoparticles [15–17]. By the addition of a low amount of a cationic surfactant, the binding degree of the polysaccharide nanoparticles could be controlled, which positively affected the mechanical properties of the nanocomposite film after film-formation as well as the transparency degree. Herein, we pursue our approach to prepare stable nanocomposite dispersion based on CNFs via miniemulsion polymerization. A small amount of a cationic polyelectrolyte and an anionic surfactant were used to promote the binding of negatively charged CNFs onto the monomer/polymer particles and to enhance the colloidal stability of the nanocomposite dispersion.

2. Experimental section

a) Materials

Butylmethacrylate (BMA), 2,2'-azobis(isobutyronitrile) (AIBN), [2 (Acryloyloxy) ethyl]trimethylammonium chloride (AETMC) 80% in water, dioctyl sodium sulfosuccinate (DOSS), hexadecane (HD), 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) and sodium bromide (NaBr) are commercial products supplied by Aldrich and used without further purification. 2-ethylhexyl acrylate (EHA) were purified by vacuum distillation before use. Acetone and ethanol were purchased from Aldrich.

b) Cellulose nanofibrils preparation

The preparation of CNFs from eucalyptus fibers was carried out following the method described in our previous work [18]. Briefly, cellulose fibers were dispersed in 500 mL of distilled water under mechanical stirring. The pH was maintained at 10 by adding a sodium hydroxide solution during all the reaction. Then, TEMPO (0.0625 g) and NaBr (1.25 g) were added in one step to the flask after the stabilization of medium temperature at 4 °C.

Afterwards, the sodium hypochlorite solution (125 mL) was added dropwise for 2 h and while keeping the stable pH at 10. After that, the mixture was stirred at 4 °C for 2 h. When the reaction was complete, oxidized fibers were filtered and washed twice with deionised water.

The carboxylate content of the oxidized cellulose was about 1100 $\mu\text{mol/g}$. The fibre suspension was then dispersed in water at a fibre content of 1–2 wt.% and disintegrated by a high pressure homogenizer (NS1001L PANDA 2K-GEA) with 3 passes at 300 bar and 3 additional passes at 500 bar. A highly transparent CNFs gel was obtained which is indicative of full break down of the cellulose fibre into nanoscale cellulose. The ensuing CNFs were composed of individual nanosized cellulose fibrils with lateral section ranging from 3 to 5 nm as determined from height profile (Fig. 1).

c) Synthesis of poly[2-ethylhexyl acrylate-Co-2(acryloyloxy) ethyl] trimethylammonium chloride]

The cationic copolymer (CAT-COP) was prepared by radical polymerization in ethanol as follows: 0.3 g of EHA and 2.7 g of AETMC in 2 g of ethanol, and 0.03 g of AIBN as an initiator were added in a three-necked flask under a nitrogen atmosphere. The reaction mixture was stirred at 60 °C until complete conversion of the monomers. Then, the resulting polymer was precipitated and washed with acetone and dried in vacuum. For all miniemulsion polymerization reactions, the addition

of the cationic copolymer was made in the form of an aqueous solution at 0.1% concentration.

d) Miniemulsion preparation and polymerization

The emulsion was prepared by mixing the organic phase containing AIBN, hexadecane and butyl methacrylate monomer with the aqueous suspension containing the surfactant and the CNFs suspension. The copolymer was previously added to the CNFs suspension and left under stirring for 1 h to ensure adsorption. The mixture of the two phases was mechanically stirred and then homogenized by ultrasonication during 3 min (Sonics Vibracel Model CV33) at a duty cycle of 60%. During the sonication, the vessel was immersed into an ice bath to prevent heating. Finally, the resulting miniemulsion was flushed with N_2 and the polymerization was carried out at 70 °C for 6 h under gentle magnetic stirring.

e) Preparation of the nanocomposite films:

The nanocomposite films were prepared by simply casting the polymer dispersion synthesized by miniemulsion polymerization in the presence of CNFs in a Teflon mould and leaving at 40–50 °C for several hours until complete evaporation of water and film-formation process. A transparent thin film with thickness in the range of 300–400 μm was obtained.

f) Particle size measurement

The average diameter of polymer particles was determined using dynamic light scattering (Malvern Zetasizer Nano S, Malvern Instruments Ltd., Malvern, UK). The sample was diluted 10 times. The measurements were performed three times for each sample, and the average value was retained as the particle size.

g) ζ -potential measurement

The ζ -potentials were measured at 25 °C using a laser Doppler electrophoresis apparatus (Malvern Nano-Zetasizer ZS, UK). The sample was diluted with KCl solution (to buffer the ionic strength) to about 0.01 wt% of polymer particles. Each measurement was repeated three times.

h) Field-Emission Scanning Electron Microscopy (FE-SEM)

A Weiss scanning electron microscope, operated at an accelerating voltage between 0.75 and 2 kV, was used to capture secondary electrons images of the nanofibrillated surface. A drop of the diluted nanocomposite dispersion (with a solid content of 0.001 wt.%) was deposited on a surface of a silicon wafer and dried at room temperature to remove water. Then, the sample was coated with a thin carbon layer applied by sputtering with a thickness limited to 3–4 nm.

i) Differential scanning calorimetry analysis

DSC measurements were performed on a PYRISTM Diamond DSC (Perkin-Elmer, Waltham, MA) fitted with intracooler cooling system, operating with a heating rate of 10 °C/min within a range of –50 °C to 100 °C under nitrogen atmosphere. The weight of the nanocomposite film samples used for the DSC measurements was around 4 mg. The glass transition temperature T_g refers to the temperature of the inflexion point on DSC thermograms.

j) Dynamic mechanical analysis

DMA experiments were carried out with a PYRISTM Diamond DMA (Perkin-Elmer, Waltham, MA), working with tension mode. Samples were heated from –30 °C to 120 °C with a heating rate of 3 °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 $\text{Tan } \delta = (E''/E')$ were measured as a function of temperature. Sample dimensions were about 20 mm (length) by 7 mm (width) and 0.2 mm (thickness). The main relaxation temperature T_g is defined as the temperature where $\text{Tan } \delta$ reaches a maximum.

k) Mechanical test

In order to study the Tensile strength (σ_{max}), tensile modulus (E) and elongation at break (ϵ_{max}) of the CNFs nanocomposite films, tensile tests were carried out at room temperature using an Universal Testing Machine (Instron TM 1122), fitted with a 500 N load cell and operating at a rate of 10 mm/min. The average of three measured values was taken for each sample, and the measurements were reported as the

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