



Influence of ionic interactions between nanofibrillated cellulose and latex on the ensuing composite properties



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ABSTRACT

The hydrophilic nature of nanofibrillated cellulose (NFC) impedes its easy incorporation in hydrophobic thermoplastic matrices. This introduces difficulties in composites compounding and achieving the sufficient NFC dispersion within the matrix. The use of matrix in latex form increases the range of applied plastics. However, poor NFC/matrix interfacial adhesion may still result in lower performance composites. The use of ionic interactions is aimed at providing strong interactions at the NFC/matrix interface after film casting and simultaneously the composite homogeneity. In this work, cationic and anionic latexes of poly[styrene-co-(2-ethylhexyl acrylate)] were synthesized via miniemulsion polymerization. The composites were produced by incorporating 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-oxidized NFC (up to 5 wt.%) into the latexes, followed by film casting of the ensuing formulations. NFC/latex interactions were examined in terms of the NFC dispersion in the matrix and the ensuing composite mechanical properties. Both elastic modulus and ultimate strength increased for the composites comparing to the neat matrices. The use of cationic latex produced non-stable aqueous dispersions and non-homogeneous composite films, deduced from scanning electron microscopy and tensile experiments. On the contrary, stable aqueous dispersions and homogeneous composites were prepared using anionic latex. X-ray photoelectron spectroscopy revealed differences in chemical composition of the composite top and bottom surfaces.

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1. Introduction

Nanofibrillated cellulose (NFC) is a material extracted from cellulose fibers (found, for example, in wood or plants) using biochemical and mechanical treatments. Due to its natural origin, relatively high strength and ability to form transparent products, NFC has a great potential for application in composite materials. The main concern in this context is to replace petroleum-based plastics with bio-based polymers [1,2].

Dimensions of NFC depend strongly on cellulose source and the production process. Typically, NFC has a diameter of 5–50 nm and a length of several micrometers [3,4]. Dry cellulose fibers can be disintegrated to small fragments using mechanical methods. However, this leads to the damage of nanofibrils, resulting in a material with low degree of polymerization and aspect ratio and, hence, relatively poor mechanical properties. Thus, NFC is commonly produced by disintegration of fibers in water medium, which loosens the hydrogen bonding between the nanofibrils and prevents their reverse coagulation after separation. The preliminary enzymatic [5–7] or oxidation treatments [8,9] are commonly performed to facilitate the NFC isolation. Since cellulose possesses high water holding capacity, the resulting material appears in the form of gel even at low NFC concentration (e.g., 0.125 wt.%, [7]) and is commonly used without drying to avoid hornification [10].

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The main challenge of NFC use in composites is associated with cellulose hydrophilic nature and the hydrophobic characteristics of most thermoplastics, which induces difficulties in composites compounding and achieving the good dispersion of nanocellulose filler within the matrix [11]. A way to increase the range of applied polymer matrices is to use polymers in the form of latex. Thus, one of the options for composites production is mixing the NFC suspensions with waterborne latexes, followed by casting evaporation.

Latex is usually produced through the emulsion polymerization process. In conventional emulsion polymerization, water-insoluble monomer is polymerized in surfactant micelles, localized in water. The monomer in this case needs to travel through aqueous phase to reach the micelles. The polymerization of very hydrophobic monomers is thus difficult [12]. The other possible process to synthesize latex is *via* miniemulsion polymerization. Within such process, high shear forces are primarily applied to split the emulsion into nanometric/submicron monomer droplets. Surfactant and costabilizer are used to retard monomer diffusion into larger droplets. In such system, the droplet specific surface area is very large due to the small droplet size. Thus, most of the surfactant is adsorbed at the droplet surface and little surfactant is present in the form of micelles. Consequently, the polymerization reaction proceeds mostly in the monomer droplets, which can yield faster kinetics and therefore lower polymerization times [13].

A number of studies were reported on the use of NFC [14–20] or other type of nanocellulose – nanocrystalline cellulose (NCC) [19,21–27] to reinforce latex composites. In these works, NFC or NCC had mainly physical or van der Waals interactions with the polymer matrix. Ben Mabrouk et al. [28] showed the production of polybutylmethacrylate latex *via* miniemulsion polymerization, containing cationic surfactant and negatively charged NCC (due to the presence of sulfate ester groups after sulfuric acid hydrolysis). It was reported that the electrostatic interactions between the positively charged particles and negatively charged NCC ensured the anchoring between these two components.

In this work the above concept of ionic interactions between latex particles and nanocellulose filler is employed in order to produce NFC-reinforced latex composites. The latexes with positively and negatively charged particles were synthesized *via* miniemulsion polymerization, assisted by cationic and anionic surfactants. 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO)-oxidized NFC (negatively charged due to the presence of carboxylate ions) was produced and incorporated thereafter into the latexes. The composite films were prepared by casting. The composites were examined from the point of view of composites homogeneity, as well as the reinforcing effect of the incorporated NFC.

2. Experimental

2.1. Materials

Bleached softwood bisulfite pulp (Quality 2100) was obtained from Domsjö Fabriker AB, Sweden. The alpha-cellulose content of 93% and the DP of 780 were specified by the supplier. The monomers of styrene ($\geq 99\%$) and 2-ethylhexyl acrylate (2-EHA, 98%) were obtained from Sigma–Aldrich and were further distilled under vacuum and kept refrigerated under nitrogen gas atmosphere. Luperox A75, containing 75% of benzoyl peroxide and the remainder water, TEMPO (98%), sodium bromide ($\geq 99\%$), sodium hypochlorite solution (13%), tetradecyltrimethylammonium bromide (TTAB, $\geq 99\%$), sodium dodecylsulfate (SDS, $\geq 99\%$), 1-hexadecanol ($\geq 99\%$) and hydroquinone ($\geq 99\%$) were the products of Sigma–Aldrich and were used without further purification.

2.2. Nanofibrillated cellulose production

Bleached softwood bisulfite pulp was soaked in water for 4 h and dispersed in a standard disintegrator for 10,000 revolutions according to ISO 5263-1:2004 standard. TEMPO-mediated oxidation was performed as reported previously [29] with slight modifications. Briefly, TEMPO/NaBr/NaClO (0.1/1/5 mmol/g of cellulose, respectively) system was used. First, TEMPO and NaBr were mixed with the cellulose aqueous suspension. Then, the pH of NaClO water solution was adjusted to 10 using HCl and added to the above suspension. The concentration of the obtained cellulose suspension was 1 wt.%. The reaction was carried out at 25 °C at a controlled pH of 10 ± 0.1 , kept constant by the addition of NaOH. When the decrease of pH was no longer observed, indicating that no longer creation of carboxyl groups is taking place, the pH was lowered to 7. The oxidized cellulose was filtered and washed on a Büchner funnel with a nylon sieve of 1 μm mesh size and redispersed in deionized water at 1.50 wt.%. The obtained suspension was passed 60 times through Supermasscolloider grinder (model MKZA6-2, disk model MKG-C 80, Masuko Sangyo Co., Ltd., Japan). The morphological properties of the produced NFC and the rheological and structural characterization of its aqueous suspensions were reported previously [30,31].

2.3. Latex synthesis

Two latexes of poly[styrene-*co*-(2-ethylhexyl acrylate)], hereafter denoted as P[S-*co*-(2-EHA)], with cationic (TTAB) or anionic (SDS) surfactants were synthesized *via* miniemulsion polymerization, as summarized in Table 1. First, a pre-emulsion of the surfactant and costabilizer in water was prepared by heating the above components at 70 °C for 1 h under mild stirring. Then, the monomers were added and the resulting product was emulsified in an ice bath by ultrasound using Branson sonifier 250 for 5 min at a duty cycle of 70% and a micro tip limit of 4. The polymerization reaction was performed under inert nitrogen gas atmosphere by mixing the prepared emulsion with the initiator (benzoyl peroxide), stirring at 150 rpm and heating at 70 °C for a period of time, defined from the monomer conversion analysis. As a result, statistical copolymer was obtained.

2.4. Composites fabrication

The produced TEMPO-oxidized NFC suspension was degassed under atmospheric pressure of 5 kPa for 24 h to remove air trapped in the fibrous network. The composite dispersions of NFC and latex, with cellulose to polymer fraction ranging from 0 to 5 wt.%, were prepared by blending the above components using 4-bladed stainless steel stirrer at 200 rpm. Composite films were prepared by casting the prepared dispersions in Teflon molds for 48 h at

Table 1
Formulations for the miniemulsion polymerization of P[S-*co*-(2-EHA)].

Product	Role	Quantity (g)	
		Latex C	Latex A
TTAB	Surfactant	0.20	–
SDS	Surfactant	–	0.17
1-Hexadecanol	Costabilizer	0.44	0.44
Water	Medium	24.00	24.00
Styrene	Monomer	8.23	8.23
2-Ethylhexyl acrylate	Monomer	4.00	4.00
Luperox A75 ^a	Initiator	1.00	1.00

^a Luperox A75 is used as a source of benzoyl peroxide (75%, remainder water).

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