



# Mechanically strong polystyrene nanocomposites by peroxide-induced grafting of styrene monomers within nanoporous cellulose gels



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## ABSTRACT

Nanocellulose is a promising candidate as a "green" reinforcing nanofiller for polymer nanocomposites. Three-dimensionally nanoporous cellulose gels (NCGs) have been demonstrated to exhibit significant dispersibility and compatibilization with hydrophobic polymers. We report a simple and versatile process for the fabrication of NCG/polystyrene (PS) nanocomposites by the *in situ* free radical polymerization of styrene monomers within the NCG. The volume fraction of the NCG in the NCG/PS nanocomposites could be controlled from 10% to 60%. The interconnected nanofibrillar cellulose networks of the NCG were finely distributed and well preserved in the PS matrix after polymerization. Dynamic mechanical analysis revealed a remarkable reinforcement in the tensile storage modulus of the NCG/PS nanocomposites, especially above the glass transition temperature ( $T_g$ ) of the PS matrix. The modified percolation model was in good agreement with the mechanical properties of the NCG/PS nanocomposites. The introduction of the NCG into the PS matrix significantly improved the flexural and tension properties of the NCG/PS nanocomposites.

## 1. Introduction

Nanocellulose is an attractive candidate as a "green" reinforcing nanofiller in both fundamental studies and applied research relating to polymer nanocomposites because of its attractive properties, such as its sustainability, renewability, low density, high specific surface area, high elastic modulus and low coefficient of thermal expansion (Favier, Chanzy, & Cavaille, 1995; Habibi, Lucia, & Rojas, 2010; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011; Siró & Plackett, 2010; Zhu et al., 2016). The most commonly used methods of fabricating nanocellulose-based polymer nanocomposites involve mixing water-soluble or water-dispersive hydrophilic polymers with nanocellulose by simple casting and water evaporation (Anglès & Dufresne, 2000; Azizi Samir, Alloin, & Dufresne, 2005; Favier et al., 1995; Habibi et al., 2010; Mathew & Dufresne, 2002). However, nanocellulose cannot be melted and dissolved in non-polar solvents and has a strong tendency to aggregate in hydrophobic polymer matrices, resulting in inherently poor compatibility and difficulty in processing the generated nanocomposites (Habibi, 2014; Mariano, Kissi, & Dufresne, 2014; Miao & Hamad, 2013; Oksman et al., 2016). Therefore, incorporating nanocellulose into hydrophobic polymer matrices to improve the interfacial compatibility of the nanocellulose with hydrophobic polymers and effectively reinforce the mechanical properties of the polymer is urgently needed.

Various chemical modification and surfactant adsorption methods have been explored to tailor the nanocellulose surface properties through functionalizing the surface hydroxyl groups during the processing of hydrophobic polymer nanocomposites (Bae & Kim, 2015; Bonini et al., 2002; Fox, Capadona, Marasco, & Rowan, 2013; Fujisawa, Saito, Kimura, Iwata, & Isogai, 2013; Oksman, Mathew, Bondeson, & Kvien, 2006; Pereda, Kissi, & Dufresne, 2014; Petersson, Kvien, & Oksman, 2007). For example, the chemical grafting of poly(ethylene glycol) and physical adsorption of polyoxyethylene on the surface of cellulose nanocrystals can improve the thermal stability and mechanical properties of polystyrene (PS) and polyethylene (PE) nanocomposites (Ben Azouz, Ramires, Van den Fonteyne, El Kissi, & Dufresne, 2012; Lin & Dufresne, 2013; Pereda et al., 2014). The direct dispersion of nanocellulose into hydrophobic polymer matrices has also been achieved using a self-assembled nanocellulose template, in which the hydrogen bonding between the nanocellulose was switched "on" or "off" by a solvent-exchange sol-gel process for subsequent filling with a polymer or monomer solution for *in situ* polymerization, such as polyacrylates, polybutadiene and polyurethane (Ansari, Galland, Johansson, Plummer, & Berglund, 2014; Ansari, Skrifvars, & Berglund, 2015; Capadona et al., 2007; Capadona, Shanmuganathan, Tyler, Rowan, & Weder, 2008; Capadona et al., 2009; Dagnon, Shanmuganathan, Weder, & Rowan, 2012; Jonoobi, Aitomäki, Mathew,

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& Oksman, 2014; Mendez et al., 2011; Nakagaito & Yano, 2005, 2008; Nissilä, Karhula, Saarakkala, & Oksman, 2018; Nogi et al., 2006; Shanmuganathan, Capadona, Rowan, & Weder, 2010). In addition, three-dimensionally bacterial cellulose gels have also been examined as candidates for the preparation of polymer nanocomposites after monomer impregnation and polymerization and were found to exhibit extraordinary thermal, optical and mechanical properties (Nogi & Yano, 2008; Quero et al., 2010; Tercjak, Gutierrez, Barud, Domenegueti, & Ribeiro, 2015; Yano et al., 2005).

As an alternative, we have developed a new three-dimensionally nanoporous cellulose gel (NCG) with a typical diameter of approximately 20 nm to reinforce polymer nanocomposites (Cai, Kimura, Wada, Kuga, & Zhang, 2008; Cai, Kimura, Wada, & Kuga, 2009; Cai et al., 2012; Shi et al., 2014). Unlike one-dimensionally cellulose nanowhiskers/nanofibrils, the NCG fabricated by our approach is a transparent monolith with interconnected cellulose nanofibril networks and has high mechanical integrity and size stability in various organic solvents (Shi et al., 2015). Previously, we demonstrated that NCG-based polymer nanocomposites can be accessed from polyacrylate and polyester matrices, including polymethyl methacrylate (PMMA), poly (butyl methacrylate) (PBMA), poly(butyl acrylate) (PBA), P(MMA/BMA), P(MMA/BA), poly( $\epsilon$ -caprolactone) (PCL), poly(L-lactic acid) (PLA) and P(LLA-co-CL) (Li et al., 2014, 2016; Shi et al., 2015). In general, the incorporation of an NCG into a polymer matrix improved the mechanical properties, solvent resistance, and thermal stability of the resulting polymer nanocomposites and decreased their coefficients of thermal expansion.

Polyolefins are the most widely used commodity thermoplastics because of their excellent chemical and physical properties, low cost, superior processability, and good recyclability. Polyolefin composites are a subset of polymer composites that emerged because application requirements were not satisfied by synthesized neat polyolefins (Nwabunma & Kyu, 2008; Stürzel, Mihan, & Mülhaupt, 2016). Inorganic and organic nanoparticles and nanofibers, such as layered silicates, clay, layered double hydroxides, carbon nanotubes and cellulose nanocrystals, have been incorporated to prepare polyolefin nanocomposites with remarkably improved thermal, mechanical and electrical properties (Agarwal, Sabo, Reiner, Clemons, & Rudie, 2012; Bahar et al., 2012; Chung, 2002; Iyer, Flores, & Torkelson, 2015; Iyer, Schueneman, & Torkelson, 2015; Löfgren et al., 2007; Ljungberg, Cavaillé, & Heux, 2006; Oksman et al., 2006; Petersson et al., 2007; Sapkota, Jorfi, Weder, & Foster, 2014; Wang & Sain, 2007). Herein, we report a further exploration of our strategy of fabricating NCG/PS nanocomposites by the *in situ* free radical polymerization of styrene monomers within an NCG. The peroxide-induced grafting of PS chains on the surface of the cellulose nanofibrils can enhance the interfacial affinity between the hydrophilic NCG and the hydrophobic PS matrix. Moreover, the grafted PS nanoparticles are homogeneously dispersed within the NCG/PS nanocomposites, whereas the interconnected cellulose nanofibril networks of the NCG are finely distributed and well preserved in the PS matrix after polymerization. The introduction of the NCG into the PS matrix significantly improved the mechanical properties of the NCG/PS nanocomposites, especially above the glass transition temperature ( $T_g$ ) of the PS matrix. We utilized a modified percolation model to evaluate the reinforcement of the dynamic thermomechanical behavior of the NCG/PS nanocomposites. The modified percolation model was in agreement with the mechanical properties of the nanocomposites. This strategy produces NCG/PS nanocomposites with superior flexural and tension properties and should contribute to the development of new polyolefin nanocomposites and the improvement of their practical exploitation.

## 2. Experimental section

### 2.1. Materials

Cellulose (cotton linter pulp) with a viscosity-average molecular weight ( $M_v$ ) of  $9.2 \times 10^4$  was provided by Sanyou Chemical Fiber Co. Ltd. (Tangshan, China), and dried under vacuum at 105 °C for 24 h prior to use. Styrene was dried over CaH<sub>2</sub> and distilled under reduced pressure. Acetone, benzoyl peroxide (BPO), lithium hydroxide hydrate (LiOH·H<sub>2</sub>O), tetrahydrofuran (THF) and urea were purchased from Shanghai Chemical Reagent Co. Ltd. (Shanghai, China) and used as received.

### 2.2. Fabrication of NCGs

NCGs were fabricated according to our previously described method (Cai & Zhang, 2005; Cai et al., 2008, 2009; Hategekimana, Masamba, Ma, & Zhong, 2015). Briefly, cellulose was dissolved in an aqueous 4.6 wt% LiOH/15 wt% urea solution pre-cooled to -12 °C to form a 6 wt% transparent cellulose solution. The cellulose solution was subjected to centrifugation to remove air bubbles, spread on glass molds at different thicknesses (1, 3, 4 and 6 mm) and coagulated in ethanol overnight. The coagulated solutions were then thoroughly washed with deionized water to produce four thickness-series NCG hydrogels. The thicker hydrogels were compressed under 0.2 MPa at 60 °C to ca. 1 mm to form NCG hydrogels with various pore volumes.

### 2.3. Fabrication of NCG/PS nanocomposites by *in situ* free radical polymerization

The NCG hydrogels were subjected to solvent-exchange with acetone and then impregnated into styrene containing 0.1 wt% BPO as an initiator. The gels were subsequently removed and sealed in glass molds to prevent solution evaporation. The free radical polymerization was allowed to proceed at 60 °C for 24 h, after which the temperature was increased to 80 °C and maintained for 24 h. A reference sample of neat PS was prepared using the same procedure. The volume fractions of the NCG in the NCG/PS nanocomposites were determined gravimetrically as an average of at least three independently prepared samples before and after polymerization. The densities of cellulose and PS are 1.62 and 1.04 g/cm<sup>3</sup>, respectively. The compositions of all nanocomposites are listed in Table 1.

### 2.4. Fourier transform infrared (FTIR) spectroscopy

Infrared spectra were recorded at ambient temperature with an FTIR spectrometer (Nicolet 5700 FTIR Spectrometer, MA) over a wavelength range of 4000 to 400 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup>; 32 scans were collected.

### 2.5. X-ray photoelectron spectroscopy (XPS)

The chemical modification resulting from the grafting of PS chains onto the surface of the cellulose network was further analyzed by XPS. These experiments were performed on an Escalab 250Xi apparatus (Thermo Scientific, USA) operating at 15 kV with a current of 20 mA. Signal decomposition was conducted using Spectrum NT, and the overall spectrum was shifted to ensure that the C–C/H contribution to the C 1s signal occurred at 285.0 kV (Mendez et al., 2011).

### 2.6. Wide-angle X-ray diffraction (WAXD)

WAXD measurements were collected on a WAXD diffractometer (D8-Advance, Bruker, USA) in reflection mode using Ni-filtered Cu K $\alpha$  radiation with a wavelength of 1.542 Å. The voltage was set at 40 kV, and the current was set at 40 mA. The samples were mounted on a solid

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