



# Cellulose nanofibrils/polyvinyl acetate nanocomposite adhesives with improved mechanical properties



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## ABSTRACT

Cellulose nanofibrils (CNFs) are nanoscale cellulose produced from renewable resources with strong reinforcing potential when included in a polymer matrix. In this work, the effect of the addition of CNFs on the properties of waterborne polyvinylacetate (PVA) adhesive was investigated. Adhesive formulations with different contents in CNFs from 1 to 10 wt.% was prepared by simple mixing of PVA dispersion with CNFs suspension in water. The viscosity of the adhesive increased with the addition of CNFs, namely over a content of 5%. Shear strength of wood joints at dry as well as wet conditions was improved by CNFs inclusion. Adding 10% of CNF to the PVA adhesive increased the shear strength by about 2 folds compared to the neat adhesive. This strengthening effect was explained by the strong reinforcing impact brought by CNFs inclusion in the PVA matrix. The addition of CNFs also improved the water resistance of PVA adhesive and strongly enhanced the mechanical performance in wet conditions, namely over 7% of CNF content.

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## 1. Introduction

Adhesives based on waterborne Polyvinyl acetate (PVA) have been one of the mostly used adhesive in wood industries for more than five decades (Stoeckel, Konnerth, & Gindl-Altmutter, 2013). It is also widely used in the formulation of waterborne adhesive for porous materials including paper, board, textile, ceramic, foils and the like (Conner, 2001). Adhesive based on PVA offer numerous advantages such as good adhesion to wood and paper substrates, easy processing using simple mixing methods, excellent stability over time, and cost-effective production due to the relatively low cost of PVA dispersion (Jaffe, Rosenblum, & Daniels, 1990). Moreover, polyvinyl acetate adhesives have a low degree of toxicity and have been approved for use in food and drug packaging. Despite these numbers of attributes, PVA suffers from two main drawbacks: first, PVA has very poor performance in wet conditions, and secondly, mechanical performance of PVA adhesive deteriorates with increasing temperature and loses its bonding resistance capacity over 70 °C.

The shortcoming of PVA adhesive in wood originated mainly from the structural properties of the polymer itself. Indeed, PVA is an amorphous polymer with a  $T_g$  not far from room temper-

ature (around 40 °C). Accordingly, as the temperature goes over 40 °C, large-scale cooperative motion of polymer chains are possible, resulting in a strong drop in the modulus of the polymer which inevitably leads to a decrease in the cohesive energy of the adhesive. Furthermore, the sensitivity of PVA adhesive to water results from the plasticizing effect of water on polyvinyl alcohol used as colloidal protective for PVA and as a tackifier for the adhesive on polyvinyl alcohol used as colloidal protective for PVA and as a tackifier for the adhesive. One way to reduce this effect is to achieve a controlled thermosetting of PVA by copolymerization with crosslinkable monomers such as hydroxyl ethyl acrylate, *N*-methylol acrylamide (Brown & Frazier, 2007) and *N*-isobutoxy methyl acrylamide. However, these monomers result in the release of formaldehyde (Brown, Loferski, & Frazier, 2007), which is now classified as carcinogen. The crosslinking can also be achieved by blending PVA dispersion with thermosetting resins or hardeners such as ureaformaldehyde, melamine-formaldehyde (Kim & Kim, 2005), and phenol-formaldehyde resins (Lopez-Suevos & Frazier, 2006). However, these latter require hot pressing or extended pressing at ambient temperatures, and exhibit reduced storage stability. Another alternative to alleviate the shortcoming of PVA adhesive is the resort to nanotechnology by the inclusion of nanoparticles. Examples of nanoparticles that have shown a beneficial effect on the properties of PVA adhesives include carbon nanotubes (Maksimov, Bitenieks, Plume, Zicans, & Meri, 2010), nano-aluminium oxide (Kaboarani & Riedl, 2012), graphene

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(Khan, May, Porwal, Nawaz, & Coleman, 2013) cellulose nanocrystals (Aydemir, Gündüz, Aşık, & Wang, 2016; Kaboorani et al., 2012) or nanoclays (Kaboorani & Riedl, 2011).

Cellulose nanofibrils (CNFs), which is simply cellulose broken down to nanoscale, has become a subject of intense research during the last decade (Kalia, Boufi, Celli, & Kango, 2014) with promising application in broad fields of innovative materials (Klemm et al., 2011), including nanoreinforcement in polymer based nanocomposites (Boufi, Kaddami, & Dufresne, 2014), strength additives for paper (Gonzalez et al., 2013; Boufi et al., 2016), packaging with enhanced barrier properties, drug delivery (Kolakov, Peltonen, Laukkanen, Hirvonen, & Laaksonen, 2012), adsorbents for water treatment (Maatar, Alila, & Boufi, 2013; Maatar & Boufi, 2015), functional membranes (Sehaqui, Zhou, & Berglund, 2011), nanostructured foams (Mohammed Alia & Gibson, 2013), coating additives (Grüneberger, Künniger, Zimmermann, & Arnold, 2014).

The increasing interest in CNFs has been motivated by properties of CNFs such as their nanoscale dimensions, biodegradable character (Vikman, Vartiainen, Tsitko, & Korhonen, 2015), relative easy production (Boufi & Chaker, 2016), high yield without post purification treatment, cost effectiveness, high aspect ratio, light weight and sustainability. Besides, according to the current knowledge, nanocellulose is classified as a non-toxic material (Vartiainen et al., 2011), completely biodegradable and without adverse effects on health or on the environment. These benefits contributed to facilitate the use of CNF and eliminate safety concerns, commonly encountered for mineral and carbon nanofillers.

Considering the strong reinforcing potential of CNFs when incorporated in a polymer matrix, the inclusion of CNF in PVA adhesive might contribute to improve the performance of wood joints bonded with PVA in humid conditions and at elevated temperatures. Moreover, since both of PVA binder is in the form of a waterborne polymer dispersion, the use of CNFs gel as reinforcement in PVA adhesive should be easy to process by a simple mixing route. However, to the best of our knowledge, the application of CNF for PVA wood-adhesive reinforcement has been the subject of only one reported work by Lopez-Suevos, Eyholzer, Bordeanu, and Richter (2010). In this work, The effect of CNFs addition on viscoelastic properties of PVA based nanocomposites was analysed by DMA and the suitability of the CNFs to prepare PVA adhesives for wood bonded assemblies was evaluated. However, although a huge reinforcing effect was noted when CNFs were added to PVA, almost no effect on the shear strength of the adhesive at room temperature was noted for PVA adhesive with CNFs content up to 3%. Only a moderate enhancement in heat resistance by about 20% was noted with adhesive containing 3% CNFs. A possible reason for this moderate enhancement is the low CNF content. For this reason it is necessary to explore the effect of CNFs on PVA adhesive over a larger content, which is the aim of the present work. The impact of CNF inclusion up to 10 wt% (based on dry solid content) on the bond strength of PVA adhesives at room and elevated temperatures as well as the effect on wet adhesion were investigated.

## 2. Materials and methods

### 2.1. Materials

Commercial polyvinylacetate (PVA) latex from Vinavil (Vinavil 2150 H) containing polyvinyl alcohol as emulsifying and stabilizing agent was used in liquid form with the following characteristics: pH=5 and solid content: 50–52%. Polyvinylalcohol (PVOH) with 98% hydrolysis degree (Selvol 323) from Sekisui. Dibutyl phthalate (DBP) from Aldrich. Beech wood, from local producer was used to make wood joints. It was conditioned at 25 °C and 50% relative humidity for several months to reach constant moisture content.

Commercial bleached Eucalyptus pulp (eucalyptus globulus) in the form of dry sheets was used as a starting material for the preparation of CNF.

### 2.2. Preparation of CNF suspension

Fibres were first pretreated by TEMPO-mediated oxidation to facilitate the disintegration process and produce CNF with high yield. The oxidation was carried out at pH 10 following the method reported previously (Boufi & Gandini, 2015). In brief, Cellulose fibres (2 g) were suspended in 200 mL water. TEMPO (30 mg) and NaBr (250 mg) were added to the suspension. Then 50 mL of a commercial NaClO solution (12°) was added dropwise to the cellulose suspension at a temperature around 5 °C, kept constant throughout the oxidation reaction. The pH was maintained around 10 by the continuous addition of a 0.1 M aqueous solution of NaOH. The oxidation was stopped by adding ethanol (20 mL) and the pH was adjusted to 7 by adding 0.1 M HCl. After thorough washing with water to remove salt, suspension of 1.5 wt% of pretreated fibres were homogenized in a high pressure homogenizer (NS1001L PANDA 2 K-GEA, Italy) applying six shear cycles (3 × 300 bar; 3 × 600 bar). A thick transparent CNF gel was obtained after six passes.

The morphology of the CNF analysed by AFM showed long and thin individual fibrils with lateral section ranging from 2 to 4 nm as determined from height profile (Fig. 1B).

### 2.3. Preparation of CNF/PVAc adhesives

Formulations of PVA adhesive with different contents of CNFs were prepared by mixing appropriate amounts of CNF suspension (with solid content 3.2%) to PVOH solution during 15 min using inclined blade impeller at 1000 rpm. Then PVA dispersion, DBP and water was added to the mixture and stirred for 15 min with gentle mechanical stirring to obtain homogenous viscous adhesive composition. DBP was added as a coalescing promoter to ensure the efficient coalescence of polymer particles, namely in presence of CNFs. The formulation of all adhesive was given in Table 1.

Samples of nanocomposite films were prepared by casting the CNF–PVA adhesive composition on Teflon sheets followed by drying at 45 °C for 3 days. The film was conditioned at room temperature and 50% relative humidity for at least one week prior to analysis.

### 2.4. Fabrication and tests of wood joints

Test samples for bond strength evaluation were prepared according to NF EN 205 standard. Beech wood was cut into (150 × 20 × 5) mm specimens that were glued with the adhesives and compressed under a static pressure of 1 MPa at ambient temperature for 2 h. Then all bonded specimens were conditioned at temperature of 25 °C and relative humidity of (50 ± 5) % for 7 days in order to reduce internal stresses in the bond joint and ensure equilibrium moisture content.

Bond strength was tested in a tensile machine and the shear strength  $T$ , N/mm<sup>2</sup>, can be calculated by using Eq. (1). The measurements were replicated five times for each sample and average values are reported.

$$T = \frac{F_{\max}}{lB} \quad (1)$$

where  $F_{\max}$  is the maximum force at break,  $B$  is the width of tested bonded surface, mm,  $l$  is the length of tested bonded surface, mm.

Samples prepared as previously mentioned were immersed in water at ambient temperature for 24 h and then tested in the wet

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