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Interface tailoring through covalent hydroxyl-epoxy bonds improves hygromechanical stability in nanocellulose materials

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ABSTRACT

Wide-spread use of cellulose nanofibril (CNF) biocomposites and nanomaterials is limited by CNF moisture sensitivity due to surface hydration. We report on a versatile and scalable interface tailoring route for CNF to address this, based on technically important epoxide chemistry. Bulk impregnation of epoxide-amine containing liquids is used to show that CNF hydroxyls can react with epoxides at high rates and high degree of conversion to form covalent bonds. Reactions take place inside nanostructured CNF networks under benign conditions, and are verified by solid state NMR. Epoxide modified CNF nanopaper shows significantly improved mechanical properties under moist and wet conditions. High resolution microscopy is used in fractography studies to relate the property differences to structural change. The cellulose-epoxide interface tailoring concept is versatile in that the functionality of molecules with epoxide end-groups can be varied over a wide range. Furthermore, epoxide reactions with nanocellulose can be readily implemented for processing of moisture-stable, tailored interface biocomposites in the form of coatings, adhesives and molded composites.

1. Introduction

The pursuit of high performance materials with minimal environmental impact suggests increased use of biological materials. Greenhouse gases in our atmosphere (carbon dioxide, among others) have reached alarming levels. Plant based materials, which store CO_2 during their life time, could potentially address environmental concerns without hampering industrial growth – contributing to a ‘green’ and more sustainable society. For structural or biocomposite applications, cellulose nanofibrils (CNF) obtained from wood, have attracted wide attention in the past decade due to a combination of high intrinsic mechanical properties (crystal modulus of 138 GPa and strength of 1–6 GPa) and low density (~1.5 g/cm^3) [1,2]. The alternating crystalline and amorphous regions in CNF provide flexibility, allowing them to form physically entangled networks when filtered from water suspensions [3,4]. Films based on CNF (nanopaper) have favorable mechanical and optical properties and have increasingly been investigated for potential use in high-end device applications [5–7].

One of the critical parameters for composite materials development is the interface between constituting components. The interface is more important for nano-scale components, since the available surface is several fold higher compared to micro-scale structures and the material characteristics tend to be dominated by the interface. For instance, cellulose nanofibrils (CNF) from wood have a surface area of up to ~500 m^2/g, as opposed to ~1 m^2/g in micro scale pulp fibers [4]. CNF surfaces are rich in hydroxyl groups, which have strong affinity for water. Under moist conditions, CNF absorb significant amount of water, primarily in the less ordered regions within the fibrils (reducing intrinsic CNF properties) and on the surface. Surface water molecules weaken the fibril-fibril interactions by acting as plasticizers, reducing network stiffness and strength [8]. Moreover, the inherent hydrophilicity makes CNF

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incompatible with hydrophobic polymers used as matrices in composites.

Several surface modification methods have been proposed to address the challenges described [9]. They are generally based on covalent methods such as acetylation [10–12], esterification [13], silylation [14], grafting [15–20] or electrostatic methods based on counter-ions [21–24]. The general strategy is to hydrophobize the CNF surface to increase hygromechanical stability and/or impart better compatibility with hydrophobic polymers. However, covalent reactions are generally done in organic solvent medium, where excess of chemicals are required and the recovery of grafted nanoparticles is tedious and complex. The cost for this type of modification is likely to be high. The electrostatic approach is relatively simple, but relies on the presence of surface charge and cannot be extended to charge-neutral entities.

Hygromechanical stability is a critical problem requiring CNF surface modification. Cunha et al. performed acetylation on nanopaper structure with different porosities and reported a strong decrease (up to 50%) in moisture sorption [11]. Sehaqui et al. used esterification with acid anhydrides to hydrophobize the cellulose surface, obtaining a contact angle of 118.5° (at RH 65%) and strength of 4.4 MPa for water soaked films [13]. Toivonen et al. used base treatment on well mixed CNF/chitosan films to insolubilize the chitosan units, which acted as physical cross links leading to remarkable improvements in mechanical properties of wet gels [25]. However, the properties were lost on exposure to mildly acidic conditions. More recently, *'core shell'* concept, inspired by the high performance of hydrated wood, has been proposed to address hygromechanical stability of CNF based films with water-soluble polymer matrices [26,27]. This concept is interesting since both the components are hydrophilic, and favorable properties rely on nanostructural tailoring including favorable dispersion of nanofibrils in the films.

One route towards more rapid use of cellulose biocomposites is to consider technologies and polymers already used in the composites industry. In a previous study [28], we showed that CNF-epoxy is of interest due to favorable mechanical properties. We suggested covalent bonds between CNF surface hydroxyls and epoxides as a key, although we were unable to prove their existence. The cellulose-epoxy system is of great interest due to the industrial importance of epoxy-based composites, and the potential to use cellulose without costly surface modification.

In the present study, we set out to test the hypothesis of amine-catalyzed covalent link formation between CNF hydroxyls and epoxides. Two critical elements are part of our strategy. A specific mono-epoxide is used in order to have simple reactions and avoid the formation of a crosslinked network or long epoxy homopolymers. The grafted CNF-epoxy films are compared with control samples containing only physical blends of CNF and epoxy oligomers. This makes it feasible to test the covalent grafting hypothesis and also to evaluate the effects of grafting on CNF-epoxy film properties. In the context of new materials, we also evaluate the hygromechanical properties of grafted films. If the specific epoxide used is successfully grafted to the surface, the CNF will be densely coated by small molecules with aromatic rings, and this should have effects on the hydrophilic characteristics of CNF.

A prepreg based concept based on a porous fibril network, potentially prepared by conventional papermaking, is used. The epoxy modification is carried out on the preformed porous 'nanopaper' structure. The processing route has the potential to be scaled up at reasonable cost in line with current industrial processes. The modified prepreg can be used to prepare adhesives, coatings and biocomposites.

2. Materials and methods

2.1. Materials

The mono-epoxide used in this work (1,2-epoxy-3-phenoxypropane or Phenyl Glycidyl Ether or PGE) was obtained from Sigma Aldrich. 2 wt% of 4-dimethylaminopyridine (DMAP, > 99% purity), obtained from Sigma Aldrich was used as catalyst to initiate the reaction.

2.1.1. CNF and CNF network/template

CNF was prepared by enzymatic pretreatment of never-dried pulp containing 13.8% hemicelluloses and 0.7% lignin (supplied by Nordic Paper, Sweden) according to Henriksson et al. [29]. Briefly, the process included enzymatic (Novozym 476) pretreatment of the pulp followed by eight passes through a microfluidizer (Microfluidics Inc., USA). After disintegration, CNF was obtained as a viscous gel with ~1.6% dry weight content.

The CNF gel was diluted to 0.1 wt% (in water) and mixed thoroughly using an ultra-turrax (model D125 Basic, IKA, Germany) at 12000 rpm for 10 min. The suspension was filtered over vacuum using membranes with 0.65 μm pores (Millipore, USA). The wet CNF network obtained after filtration was placed in a solvent bath to exchange the water to solvent. The solvent in the bath was changed at least three times, at intervals of 6–8 h to ensure complete exchange.

2.1.2. PGE grafting

PGE was grafted on a preformed CNF network, by an impregnation based approach. The water in CNF/water network was first exchanged to acetone and the wet CNF/acetone network was used directly for impregnation. CNF/acetone network was impregnated with mono epoxide (PGE) by placing it in a bath containing 50% PGE/acetone solution and the catalyst DMAP (2 wt% with respect to PGE). After 4–6 h of impregnation under mild shaking, the impregnated CNF template was removed from the bath and the acetone was evaporated. Grafting was carried out at 90 °C by placing the dried CNF/PGE network in an oven. After the reaction, free PGE monomers and/or oligomers were removed from the template by washing in acetone for three days. To verify complete removal of free oligomers, the grafted template was refluxed with acetone vapors for five days but no further weight loss was observed. The modified CNF (CNF-g-PGE) had 35 ± 3 wt% of grafted PGE, calculated from weight increase of initial CNF. The obtained films were pressed (Fontijne Presses) for 30 min at 110 °C at a pressure of 50 MPa.

2.1.3. PGE/CNF blending

The control sample with physically blended CNF/PGE was prepared by impregnation of PGE oligomers. PGE (with 2% DMAP as the catalyst) was pre-polymerized at 90 °C, and was then dissolved in acetone (15% solution) to form the impregnating PGE solution. The wet CNF/acetone network was placed in the PGE solution for 6–8 h, and then removed, dried and pressed as earlier. The resulting films had 35 ± 3 wt% of blended PGE in the final material, and are designated as CNF-b-PGE.

As a demonstration, blended films were washed in acetone and 6–8 h of washing was found to be sufficient to remove all the impregnated PGE from the CNF network.

2.1.4. CNF aerogel preparation and impregnation/grafting

To prepare highly porous dried CNF networks (aerogels), the CNF/water template was converted to CNF/ethanol. The solvent exchange was carried out in steps, where 96% ethanol was used for first exchange and pure ethanol after that. The CNF/ethanol