



Protein-mediated interfacial adhesion in composites of cellulose nanofibrils and polylactide: Enhanced toughness towards material development

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ABSTRACT

The role of animal protein, casein, as compatibilizer and eco-friendly dispersant in composites comprising cellulose nanofibrils (CNF) and polylactic acid (PLA) was investigated. The effect of casein-mediated surface modification of PLA was validated with dynamic adhesion experiments that considered the contact area according to JKR approximation. In fact, a remarkable increase by ~50% in the work of adhesion between CNF and PLA was observed after casein adsorption. It is likely that the improved adhesion gave rise to an enhanced dispersion of CNF and PLA within the composite matrix. Moreover, the mechanical properties of the respective nanocomposites were significantly improved. When compared to protein-free CNF/PLA nanocomposites, the systems containing casein indicated an enhanced extensibility (by 130%) and tensile toughness (by 60%) whereas tensile strength and Young's modulus were improved to a limited extent (6 and 12%, respectively). Finally, it is demonstrated that the surface modification of PLA with casein improves the compatibility between CNF and PLA, which is a prerequisite for the feasible preparation of 3D shaped cellulose-based packaging materials by direct thermoforming.

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1. Introduction

Environmental concerns are the main reasons for the growing interest in sustainable and renewable packaging materials [1]. Paper and paperboard have already established a firm position in global packaging market accounting for one third of the total market by volume [2]. However, the limited ability to form 3D shapes, moisture sensitivity and poor barrier properties are some of the main challenges that remain for full utilization of paper materials in packaging. The ability of a material to adopt defect-free 3D shapes depends on its ability to undergo plastic deformations and is described as formability, which is strongly associated with the toughness. This is challenging for fiber-based systems while their barrier and moisture resistance can be improved by introducing coating layers [3].

The main features of paper and paperboard to meet the requirements of 3D forming were recently studied by Vishtal et al. [4–6]. For instance, a combination of high-consistency treatment and subsequent low-consistency refining of fibers was proposed to improve the toughness of fiber networks [7], where both extensibility and strength were improved significantly, by 320% and 270%, respectively. Spraying of a gelatin [8], agar [9] or their combination [10] on pre-formed fiber networks was shown to improve their formability. In addition, building a polyelectrolyte multilayer on the surface of the fibers by the layer-by-layer technique resulted in paper suitable for 3D forming [11,12]. Hydroxypropylated cellulose was used to enable highly extensible and translucent paper [13] and thermoplastic paper was produced from partly derivatized dialcohol cellulose by using conventional papermaking techniques [14]. Recently, it was

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found that the paper toughness can be improved significantly by adding PLA latex to the fiber suspension prior to its consolidation as a fiber network [15–17]. It should be mentioned that the mixing between the fibers and PLA is significantly improved when PLA is introduced as a latex, consisting of micro-particles dispersed in water. Moreover, this avoids issues related to aggregation of hydrophilic cellulose fibers in the organic solvents that otherwise need to be used. Related approaches appear promising for adoption at industrial scales.

Poly(lactic acid) (PLA) is one of the most promising thermoformable polymers owing to its biodegradability, relatively low cost and good processability. Therefore, a combination of PLA and natural fibers is an attractive method for producing high-performance bio-based composites. However, the performance maximization of such composites relies on a homogeneous dispersion and interfacial adhesion of the fibers within the polymer matrix [18]. In fact, the compatibility of hydrophilic lignocellulosic fibers with less polar polymers is one of the main challenges in green composite manufacturing. Several approaches have been proposed to address this challenge, including surface functionalization of PLA [19] and/or fibers [20–22] as well as facilitating dispersion by addition of surfactants [23] and plasticizers [24]. Yet, the compatibility remains as a critical issue since the properties of the composite may not be improved as much as could be expected. Moreover, the mentioned approaches are often tedious and may include hazardous chemicals, which limits or prevents their industrial implementation. Therefore, the utilization of bio-based dispersants, such as proteins, would potentially afford an environment-friendly method for the preparation of PLA/cellulose composites.

Abundant and low cost agricultural products such as proteins are amphoteric polymers containing hydrophobic and hydrophilic residues and therefore they can display affinity with a wide range of surfaces. For example, when proteins come into contact with a hydrophobic surface they readily adsorb by allowing their hydrophobic residues to come close to the substrate while leaving the more hydrophilic groups exposed to the surrounding environment [25]. Milk proteins, such as caseins, can act as dispersion aids for the inorganic constituents such as colloidal calcium phosphate (CCP) which is not soluble in water [26]. It was shown that casein surrounds the CCP with a stabilizing shell to form a water-soluble micelle. We recently investigated the affinity of PLA with the vegetable and animal proteins (casein, gelatin, soy protein isolate, and hydrolysate) [27]. The obtained results indicated that the surface energy of PLA increased upon protein adsorption and the application of casein at pH 8 suggested an improved compatibility between cellulose nanofibrils (CNF) and PLA. Moreover, casein has been utilized as a dispersant in composite systems comprising PLA and cellulose nanocrystals (CNC) [28]. Casein was extensively used as a wood adhesive before 1930's and its affinity to cellulose has been proposed to be driven by the interactions between the hydroxyl groups of cellulose and the peptide bonds of casein [29]. It is also important to note that from the application point of view the utilization of casein proteins is relatively straightforward, as only a mild heating treatment is required to disrupt the casein micelles and facilitate their adsorption onto cellulose surface.

In this work, the ability of casein to compatibilize cellulose nanofibrils (CNF) and PLA was explored. In detail, the effect of the incorporated protein on the work of adhesion between the CNF and PLA were studied by evaluation of the adhesion energy using the micro-adhesion measurement apparatus (MAMA). Finally, the mechanical properties of the CNF-PLA composite films were investigated and their suitability for 3D thermo-forming is discussed.

2. Experimental section

2.1. Materials

Bleached softwood kraft pulp (cellulose 80.3%, xylan 10.4%, glucomannan 8.4% and total lignin <0.9%) was provided by Stora Enso. Casein sodium salt from bovine milk (C8654) was obtained from Sigma–Aldrich (US). Poly (lactic acid) (PLA) Ingeo 3052D was purchased from NatureWorks LLC and was used for the preparation of model surfaces in the contact adhesion studies. According to the supplier, the glass transition temperature (T_g) of this PLA resin is in the range of 55–60 °C. A commercial PLA latex (Landy PL-3000, Miyoshi Oil & Fat Co., Ltd., Japan) was used to make the composite films. The mean particle size of 1.2 μm for the PLA latex was determined by DLS. The PLA latex was weakly anionic with a charge density of 49 $\mu\text{eq/g}$ (conductometric titration). According to the manufacturer the minimum film-forming temperature (MFFT) of PLA latex is 20 °C.

2.2. Preparation of nanofibrillar cellulose (CNF)

First, wood fibers were washed to Na-form in order to ease the defibrillation process, according to a procedure described by Swerin et al. [30]. The charge density of the fibers used was 27 $\mu\text{eq/g}$ (conductometric titration). Next, mechanical refining using Valley beater was performed until the SR value reached ~85 units. This ensured fiber accessibility and fibrillation efficiency. Finally, diluted fibers (solids contents <1 wt%) were disintegrated by a high-pressure microfluidizer (M110P, Microfluidics corp., Newton, MA, USA) after six passes. The prepared aqueous dispersions of CNF were stored at 4 °C until use.

2.3. Preparation of denatured protein solution

Prior to utilization, casein was dispersed in Milli-Q water and dialyzed using a 1 kDa mesh membrane tube (SpectraPor, Spectrumlabs) and freeze-dried. Purified casein was dissolved in 10 mM bicarbonate buffer at pH 8 to yield a desired concentration and mixed with a magnetic stirrer for 2 h. After mixing, the solution was heated for 30 min at 45 °C to induce the thermal denaturation of the protein. Finally, the casein solution was filtered with an Acrodisc syringe GHP filter with a pore size of 0.45 μm (Sigma-Aldrich, U.S.A.) to remove any solid particles and degassed. To avoid the chemical and/or physical degradation of casein in aqueous solution, freshly made solutions were used in the experiments.

2.4. Preparation of working surfaces for contact adhesion measurements

PDMS hemispherical caps were prepared from poly(dimethylsiloxane) (184 silicone elastomer, Dow Corning, USA) and a curing agent (184 curing agent silicone elastomer, Dow Corning). Curing agent was added to PDMS in a 1:10 ratio (parts per weight) under vigorous stirring after which the mixture was deaerated in a vacuum for 1 h. Then hemispherical droplets of the reaction mixture were placed on a glass slide treated with fluorodecyltrichlorosilane (Sigma-Aldrich) and then cured for 1 h at 105 °C to produce caps with a radius of approx. 1 mm. The cured caps were extracted in heptane for at least 12 h to remove the unreacted monomer. To obtain PLA-coated PDMS caps, the surfaces of the cured and extracted PDMS caps were covered with a thin layer of PLA by solvent casting (about 30–40 μl of 1 wt% PLA dissolved in THF). After 4 h of solvent evaporation, the samples were dried overnight under vacuum at 50 °C. Finally, denatured casein was adsorbed from 1 g/l buffer solution (pH 8) onto PLA-coated PDMS

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