



Pressure sensitive adhesive property modification using cellulose nanocrystals

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ABSTRACT

The impact of cellulose nanocrystals (CNCs) as a property modifier for pressure sensitive adhesives (PSAs) was investigated. Stable CNC/poly(*n*-butyl acrylate-co-methyl methacrylate) latex nanocomposites with different CNC loadings ranging from 0.25 to 1 wt% (based on monomer weight) were synthesized by both an *in situ* seeded semi-batch polymerization and a blending technique. The PSA films obtained from both techniques demonstrated a concurrent enhancement of shear strength, tack, and peel strength with increasing CNC content. However, the performance enhancement for the PSAs prepared via the *in situ* technique was substantially greater: increases of up to 3.8x for tack, 6x for peel strength and 20x for shear strength for the *in situ* technique compared to increases of up to 2.4x for tack, 1.5x for peel strength and 6.4x for shear strength for the blending technique. The difference in mechanical performance of the CNC/PSA films synthesized via the *in situ* technique vs. blending was a result of better interaction of CNCs with the polymer matrix during both latex synthesis and film formation.

1. Introduction

Pressure sensitive adhesives (PSAs) are viscoelastic materials which adhere instantly to a substrate with light pressure and are easily removed without leaving an adhesive residue [1]. PSAs find application in a wide range of products such as tapes, labels, protective films and medical products. PSA performance depends on the polymer's microstructural properties such as molecular weight distribution, glass transition temperature (T_g) and gel content which are mainly influenced by monomer composition and reaction conditions [2,3]. Acrylic-based PSAs typically consist of a low T_g monomer such as butyl acrylate (BA, $T_g = -54^\circ\text{C}$) and a high T_g monomer such as methyl methacrylate (MMA, $T_g = 115^\circ\text{C}$). The low T_g monomer encourages flow and wetting of the substrate, which potentially increases adhesive strength to the PSA while the high T_g monomer can be used to tune the T_g to the desired application temperature [1].

The performance required of PSAs is determined by the desired application. The mechanical performance of PSAs is usually evaluated by tack, peel strength, and shear strength. Tack is greatly influenced by the wetting capability of the PSA to the substrate, and it reflects how quickly a PSA sticks to a substrate under short contact. Peel strength measures the bond strength between a PSA and a substrate after

applying the pressure necessary to wet the substrate. Shear strength is a measure of the internal or cohesive strength of the PSA. A balanced combination of tack, peel strength, and shear strength is required for optimal mechanical performance [1].

PSAs are produced through hot melt, solution, and emulsion polymerization techniques [4]. Emulsion polymerization is preferred to solution polymerization due to the use of water in the reaction medium instead of organic solvents, for environmental reasons [5]. Higher molecular weight polymers are more easily achievable by emulsion polymerization compared to solution-based methods due to the high polymer concentration at the locus of polymerization (i.e., the polymer particles). The solvent-based polymers are often limited to lower molecular weights due to the presence of unwanted chain transfer reactions as well as a lower local polymer concentration throughout the polymerization.

Although water-based PSA production is more environmentally friendly, the adhesive performance, particularly shear strength, is typically inferior to that of its solvent-based counterpart. Surfactants, commonly added to emulsion-based PSA formulations, reduce PSA performance due to the migration of ionic surfactant molecules from the bulk latex to the PSA film surface during the drying process [6–8]. In addition, during the drying process, each latex particle contains its

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own discrete gel network (each particle is separate) and relies on the entanglements of chain ends extending beyond the latex particle boundaries to improve cohesive strength. On the other hand, solvent-based PSAs are not limited by the compartmentalized particle morphology as in emulsion polymerization and can therefore form a continuous gel network, which leads to better mechanical performance [9,10].

In order to modify the mechanical performance of PSA films produced by emulsion polymerization, one can, for example, add microstructural modifiers such as crosslinkers and chain transfer agents to the reaction formulation. However, the improvement of one property (e.g., shear strength) often occurs at the cost of declining performance in another (e.g., tack). Nonetheless, various approaches have been undertaken to overcome this performance conundrum [11–14].

Fillers, including inert and reinforcing types, are usually added to a polymer matrix to reduce cost, and perhaps improve chemical resistance, and mechanical performance [15]. For PSA films, a number of nanofillers such as carbon nanotubes, nanoclay, nanosilica, and nanoTiO₂ have been shown to positively influence composite material properties [16–23]. For instance, the addition of surface modified carbon nanotubes at small amounts (0.3 wt%) greatly improved the viscoelastic properties and adhesion energy of emulsion-based PSAs by 65 and 85%, respectively [16]. Attempts to improve the adhesive properties of emulsion-based PSAs using nanosilica have also been reported [22]. Increased nanosilica content resulted in increases of tack of 250 and 300% at 2 and 4 wt% nanosilica loadings, respectively. However, the peel strength showed a maximum at 2 wt% nanosilica loading and worse performance at 4 wt% loading compared to the base case, while shear strength worsened at 2 wt% loading and increased at 4 wt% loading.

One interesting nanomaterial is cellulose nanocrystals (CNCs). CNCs are rod-like nanoparticles most commonly extracted from plant-based products (e.g., wood pulp) via controlled acid hydrolysis [24]. Strong acids, such as sulfuric acid and hydrochloric acid, readily break down the more accessible disordered regions in the cellulose microfibrils while the crystalline domains remain largely intact. When sulfuric acid is used, some of the hydroxyl groups on the CNC surface are substituted with anionic sulfate half-ester groups and this consequently makes the CNCs colloidal stable as dispersions in water. In addition, the presence of hydroxyl groups on the CNC surface offers reactive “handles” for further surface functionalization such as esterification, etherification, silylation, or polymer grafting, which can improve CNCs’ compatibility and dispersibility, and facilitate their incorporation into different polymer matrices [25]. High axial elastic modulus, high aspect ratio, low density, renewability and non-toxicity of CNCs make them ideal candidates as nano-reinforcing materials for polymer matrices [26].

The use of CNCs as a property modifier has been investigated in a wide range of natural or synthetic polymers such as natural rubber (NR) [27,28], cellulose acetate butyrate (CAB) [29], poly(lactic acid) (PLA) [30,31], polyurethane [32,33], acrylic films [34–36], and epoxy emulsions [37]. There are different processing techniques to incorporate CNCs into polymer matrices such as blending, *in situ* reaction (e.g., grafting), melt mixing, and in aqueous or non-aqueous media. The appropriate processing technique is determined by the nature of the polymer and the final application [38,39].

For aqueous polymer systems, aqueous CNC dispersions can be added to water-soluble polymers (e.g., polyvinyl alcohol (PVA)), hydrodispersible polymers (e.g., carboxymethyl cellulose (CMC)) or polymer latexes through blending and *in situ* reaction techniques [40–42]. Favier et al. [34] prepared the first CNC nanocomposite over 20 years ago, spurring an entirely new research thrust. In their seminal work, CNCs and latex were combined via the blending technique. The mechanical measurements showed that the storage modulus of the styrene/butyl acrylate (35/65% w/w) copolymer matrix was significantly improved with CNC loadings as low as 1 wt%. Subsequent efforts using the same

copolymer system investigated the effect of CNCs obtained from wheat straw [35,43] or tunicin [43]. The resulting nanocomposites displayed noticeably enhanced mechanical properties even at low CNC contents. The strong hydrogen bonding ability between CNCs (and mechanical percolation) was proposed as the governing mechanism behind the formation of a rigid network in the nanocomposite films. More recently, Vatansver et al. [44] reported the synthesis of CNC reinforced poly (BA-co-MMA) via blending with different CNC contents up to a maximum of 3 wt%. The thermal, barrier, and mechanical properties (e.g., tensile strength) of the nanocomposites were enhanced with increasing CNC content. However, in none of the above cases was adhesive performance measured.

Aqueous CNC dispersions can be incorporated in a polymer composite through *in situ* emulsion polymerization, which is also economically favourable. The synthesis of stable CNC/latex dispersions was reported via miniemulsion polymerization by adding a reactive monomer, γ -methacryloxypropyl triethoxysilane (MPS), to the polymerization formulation [45,46] or by tailoring CNC-surfactant interactions [47]. It was reported that the addition of CNCs improved the storage modulus of nanocomposite films in the rubbery state [45,46] and could be used to tailor the polymer molecular weight and the latex size and surface charge [47], respectively. Most recently, partially disintegrated nanocellulose fibres (different from the well-defined CNCs used here) were added to a suspension polymerization of 2-ethyl hexyl acrylate for adhesive applications [48].

We recently reported on an *in situ* batch emulsion polymerization technique for the incorporation of CNCs into a latex polymer [49]. Having overcome a number of stability challenges, an approach using CNCs in a seed formulation is proposed. In this study, we successfully synthesized CNC/latex nanocomposites via *in situ* seeded semi-batch emulsion polymerization for application as PSAs. The impact of CNC loading on the mechanical and adhesive performance of the PSA films is evaluated and compared to CNC nanocomposite films obtained via blending.

2. Experimental methods

2.1. Materials

n-Butyl acrylate (BA) and methyl methacrylate (MMA) monomers, sodium dodecyl sulfate (SDS) anionic surfactant, potassium persulfate (KPS) initiator, allyl methacrylate (AMA) crosslinking agent, 1-dodecanethiol (NDM) chain transfer agent, and hydroquinone (HQ) inhibitor were all purchased from Sigma Aldrich. All the above chemicals were reagent grade and were used as received. Tetrahydrofuran (THF, HPLC grade) was obtained from EMD Chemicals. Poly (vinylidene fluoride) (PVDF) membrane filters with a pore size of 5.0 μ m were purchased from EMD Millipore. Distilled deionized (DDI) water was used throughout all experiments. CNCs were obtained from CelluForce (Windsor, QC, Canada). Ashless Whatman filter paper (grade 542) was purchased from Fisher Scientific. Nitrogen gas was purchased from Linde Canada. Melinex[®] 453 polyethylene terephthalate (PET) films were obtained from Tekra.

2.2. Aqueous CNC dispersion preparation

A specified amount of spray dried CNC (0.25–1 wt% based on total monomer weight) was dispersed into the required amount of DDI water and stirred with a magnetic stir bar for 2–4 h depending on the CNC concentration until it appeared to be well-dispersed according to visual inspection. Afterwards, the dispersion was sonicated using a Sonic Dismembrator Ultrasonic processor (500 W with 65% amplitude) for 15 min in an ice bath to avoid overheating. Finally, the CNC dispersion was filtered through ashless Whatman 542 filter paper by vacuum filtration.

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