



## Poly(vinyl alcohol)/cellulose nanocrystal barrier membranes

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### ABSTRACT

In this study, barrier membranes were prepared from poly(vinyl alcohol) (PVOH) with different amounts of cellulose nanocrystals (CNXLs) as filler. Poly(acrylic acid) (PAA) was used as a crosslinking agent to provide water resistance to PVOH. The membranes were heat treated at various temperatures to optimize the crosslinking density. Heat treatment at 170 °C for 45 min resulted in membranes with improved water resistance without polymer degradation. Infrared spectroscopy indicated ester bond formation with heat treatment. Mechanical tests showed that membranes with 10% CNXLs/10% PAA/80% PVOH were synergistic and had the highest tensile strength, tensile modulus and toughness of all the membranes studied. Polarized optical microscopy showed agglomeration of CNXLs at filler loadings greater than 10%. Differential thermogravimetric analysis (DTGA) showed a highly synergistic effect with 10% CNXL/10% PAA/80% PVOH and supported the tensile test results.

Transport properties were studied, including water vapor transport rate and the transport of trichloroethylene, a representative industrial toxic material. Water vapor transmission indicated that all the membranes allowed moisture to pass. However, moisture transport was reduced by the presence of both CNXLs and PAA crosslinking agent. A standard time lag diffusion test utilizing permeation cups was used to study the chemical barrier properties. The membranes containing  $\geq 10\%$  CNXLs or PAA showed significantly reduced flux compared to the control. The CNXLs were then modified by surface carboxylation in order to better understand the mechanism of transport reduction. While barrier performance improvements were minimal, the chemical modification improved the dispersion of the modified CNXLs which led to improved performance. Of special note was an increase in the initial degradation temperatures of both modified and unmodified systems, with the modified system showing an initial degradation temperature  $>100$  °C higher than the cellulose alone. This may reflect more extensive crosslinking in the modified composite.

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### 1. Introduction

The field of polymer nanocomposites is a rapidly expanding area of research generating new materials with novel properties [1]. Several new materials have been developed within the last decade incorporating nano-sized filler material in polymer matrices. Use of nanomaterials has proven to confer various advantages like improved mechanical, thermal and barrier properties compared to non-filled polymers. These effects are largely due to their high interfacial area, their aspect ratio, their extent of dispersion and percolation, which occurs when the filler particles are present in quantities above the threshold where they start interacting [2]. Nanomaterials, e.g. carbon nanotubes, exfoliated clay, and cellulose

nanocrystals (CNXLs) (Fig. 1) have been successfully employed as fillers in polymer matrices and some systems are being commercialized [3,4].

One application area for these materials is barrier membranes, where the nano-sized fillers impart enhanced mechanical and barrier properties. Research in this area is evolving rapidly to enhance the barrier properties and to overcome certain limitations, e.g. durability, weight, robustness, flexibility and packing volume. Superior barrier membranes find their use in food and biomedical packaging where low permeability to oxygen, aromas, oils, or water are needed [5,6].

While many barrier membranes are designed to prevent the permeation of hydrophilic substances, such as water, other barrier membranes are designed to reduce permeability to hydrophobic substances, such as many toxic chemicals [7]. In this case, the most effective filler material is likely to be an hydrophilic filler. Nanocrystalline cellulose thus has the potential to provide

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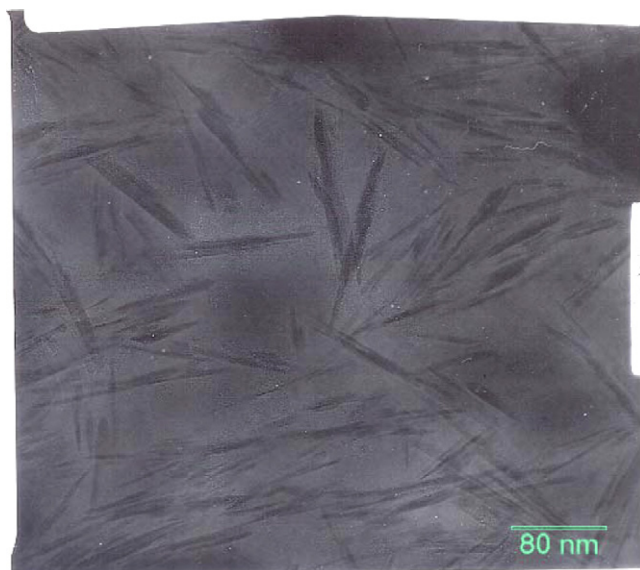


Fig. 1. TEM image of CNXLs from cotton.

improved mechanical, physical and barrier properties to hydrophobes in polymer matrices.

Recently, CNXLs have attracted much attention from researchers for their remarkable reinforcing abilities [8–10]. Cellulose fibers are easily obtained from biomass and are an abundant, renewable, biodegradable resource. Nanocrystalline cellulose is the crystalline portion obtained after acid hydrolysis of cellulose. Typical sizes are 5–10 nm in diameter and 50–200 nm in length [11,12]. Some advantageous properties of CNXLs are their high aspect ratio of around 20–50 (length/width), low density of 1.56 g/cm<sup>3</sup>, high elastic modulus and strength reported to be 145 GPa [10,13,14] and estimated at 7500 MPa, respectively [15]. One example is Orts et al. [9], who obtained cellulose from various sources and added low concentrations to polymer blends to study the reinforcement effect of cellulose. They found 10.3% cellulose fibril content increased the Young's modulus by fivefold in an extruded starch thermoplastic. They also observed complex interactions between the components.

Two major disadvantages of using cellulose as a nanofiller are agglomeration due to high hydroxyl content, i.e. obtaining a good dispersion of cellulose in the polymer matrix, especially in a hydrophobic matrix. Surface compatibility by physical or chemical treatment is usually required when composites are prepared with cellulose and hydrophobic polymers [8].

Zimmermann et al. [10] dispersed cellulose fibers in the hydrophilic polymers poly(vinyl alcohol) and hydroxypropyl cellulose to study their reinforcing effect. Mechanical tests conducted showed a threefold increase in Young's modulus and a fivefold increase in tensile strength compared to the base materials. The elongation at rupture increased 500% with 5 wt% of the fibrils and 300% at 10 or 20 wt% of the cellulose compared to the pure polymer. Borges et al. [16] studied the addition of coupling agent 1,4-butyl diisocyanate, which improved the interaction between cellulose and hydroxypropyl cellulose. With the coupling agent the yield stress increased slightly, the rupture stress and Young's modulus almost doubled, while the % elongation decreased by 10% for membranes with 10 wt% cellulose fibers. Heat treating the same membrane further increased the rupture stress and yield stress by 50% while Young's modulus and % elongation did not improve significantly.

Poly(vinyl alcohol) (PVOH) has been extensively studied as a controlled drug release hydrogel, a membrane material for

chemical separations, barrier membrane for food packaging, pharmaceutical component, manufacturing material for artificial human organs and as a biomaterial [7,17–20]. It is resistant to permeation of solvents and oils and acts as a good barrier against oxygen and aromas. Since PVOH is a hydrophilic polymer, dispersion of hydrophilic CNXLs into the matrix can be successfully achieved by blending an aqueous PVOH solution with an aqueous CNXL dispersion. However, PVOH membranes have poor stability to moisture unless crosslinked [21,22] because the water molecules swell the polymer and disrupt its barrier properties. Crosslinking can be achieved by agents that bind with the hydroxyl groups or by controlled heat treatment [18,23].

Additionally, crosslinking with monoaldehydes and dialdehydes has successfully provided water resistance to PVOH, but the process is not cost effective and leaves undesirable toxic crosslinking agents [23]. Heat treatment, a low-cost method to provide insolubility to membranes, provides crystallinity in PVOH matrices at 200 °C and 10 min treatment time [24]. Temporary insolubility is achieved when PVOH fibers are heat treated with drawing [22]. Another method for crosslinking is by repeated freeze/thaw cycles of PVOH gels, which forms a physically crosslinked PVOH with a three dimensional network. These gels are mechanically strong, but their long-term stability is an issue [23]. Poly(acrylic acid) (PAA) has been successfully used as a chemical crosslinking agent for PVOH [22]. The PVOH/PAA combination has been studied as a hydrogel for biomedical applications [25] and as a separation membrane material [26]. The added PAA creates a highly networked structure and different mesh sizes can be obtained. By controlling the mesh size the size of molecules that can pass through the membrane is controlled [27]. A blend with PVOH/PAA ratio of 80/20 showed the best separation results for a methanol–water pervaporation separation membrane [28]. For an acetic acid–water pervaporation separating membrane a ratio of 75/25 (v/v) was found to be optimum with 40 °C as the optimum temperature [26]. Kumeta et al. [22] showed that using partially neutralized PAA in the range of 5–10 mol% along with heat treatment enhanced the crosslinking reaction between PVOH and PAA.

In this work, crosslinking was accomplished by using heat treatment and adding PAA as a crosslinking agent. The carboxyl group in PAA and the hydroxyl groups of PVOH and CNXLs formed ester linkages along with presumed hydrogen bonding between PVOH and CNXLs. This allows the overall nanocomposite to have effective crosslinking and barrier resistance. The goal is for these barrier membranes to have the ability to prevent permeation of harmful chemicals and to be chemically inert, mechanically strong, tough, flexible and water resistant.

In this study, trichloroethylene (TCE) was chosen as a representative toxic industrial material (TIM) and used to evaluate the barrier properties of the PVOH/PAA/CNXL barrier membranes.

In addition, chemical modification of the CNXLs was performed in order to further explore the mechanism of vapor transport.

## 2. Materials and methods

### 2.1. Theory

We evaluated the transport properties of the membranes using TCE as the permeant in an evaporative flow device: Liquid TCE was contacted to the feed side of the membrane. Its concentration on the permeate side of the membrane was kept at essentially zero by performing the experiment in a hood, where the airflow swept away any permeant from the membrane surface. Thus, the assumptions made for the chemical transport experiments were as follows: (1) Mass transfer occurred in the positive (in this case down) z-direction only. (2) The temperature and relative humidity of the

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