Ultra selective ionic liquid/nanocellulose blend membranes for CO_2 capture

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Introduction

Bio-based materials represent the most sustainable alternative to synthetic plastics. Nanocellulose fibrils (NFCs) are a renewable bio nanomaterial, typically obtained from mechanical or chemical treatment of cellulosic sources. Thanks to their high aspect ratio, good mechanical properties, ability to form hydrogen bonding and bio-based origin, NFCs are considered one of the most promising candidate for the processing of polymer nanocomposites (Dufresne 2013). Recent study revealed that the unique hydrophilic nature of nanocellulose membranes leads to exceptional gas separation properties under humid conditions. CO_2/N_2 selectivity as high as 500 has been achieved (Ansaloni et al. 2017), although with limited CO_2 permeability. In an attempt to increase the CO_2 permeability of NFCs, novel hybrid membranes have been fabricated by adding CO_2-philic ionic liquid owing good compatibility with cellulosic materials.

Material and Methods

Three ILs have been chosen and blend membranes with interesting properties have been fabricated and tested. . The proportion of ionic liquids used were 20% [Emim][OAc], 34% [Emim][OAc], 30% [Bmim][NO_3] and 30%[Bmim][DCA]. Self-standing MFC-based membranes prepared by solution casting technique. Single gas humid permeation tests were carried out to screen the better performing IL. 1-Ethyl-3-methylimidazolium acetate [Emim][OAc] was screened due to superior separation performance, CO_2 chemical-physical sorption capability and cellulose dissolution capacity. Thin film composite membranes were prepared using vacuum filtration technique on a commercial PDMS membrane. The self-standing membranes were used for single gas humid permeation tests and other techniques including FTIR, XPS, TGA, water and high-pressure gas sorption were also used to characterize the membranes. The thin film composite membranes were used for mixed gas humid permeation tests.

Results and Discussion

Good compatibility of [Emim][OAc] with nanocellulose has led to the achievement of homogeneous hybrid films, as observed through SEM imaging (Figure 1). The CO_2 sorption analysis has highlighted that the CO_2 solubility in the matrix increases proportionally to the [Emim][OAc] amount in the hybrids. Additionally, the surface C-N ratio (determined by XPS) also decreases rapidly from 82.8% in pure MFC films to 26.8% and 19.4% in the films of blends containing 20% and 24% [Emim][OAc],

respectively. This leads to an increase in CO_2 permeability retaining high selectivity due to the increased CO_2 solubility, decreased diffusional resistance and increased surface adsorption resulted from the increased nitrogen content in the blend membranes. On the other hand, all the ILs contained membranes have better water solubility than pure NFC membranes, corresponding to the polarity of ILs as seen in Figure 2. Membranes containing 34% [Emim][OAc] have the strongest tendency of water sorption even at low activity. Increasing water activity leads to a hybrid-swollen matrix due to hydrophilicity of both nanocellulose and the IL (Dai et al. 2016). The CO_2 permeability increases multiple folds with increasing relative humidity while inheriting the selectivity arising due to the tortuous network formed by cellulose nanofibrils. Thus, most membranes of this kind conveniently outstripped the Robeson upper bound as shown in Figure 3(a).

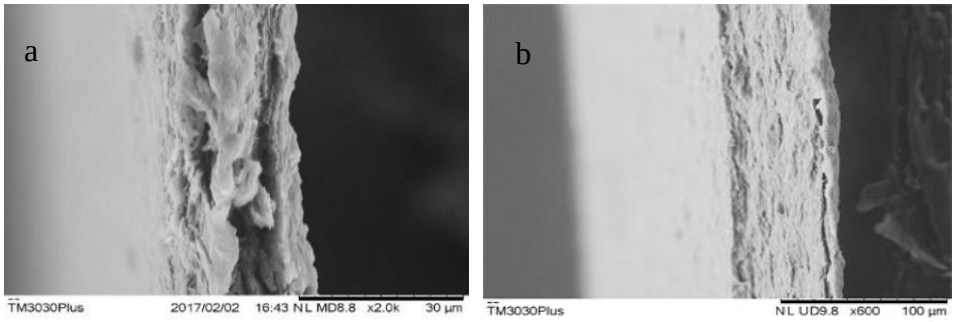


Figure 1. Cross sectional SEM image of NFC/IL blend containing . (a). 20%[Emim][OAc] (b). 50% [Emim][OAc]

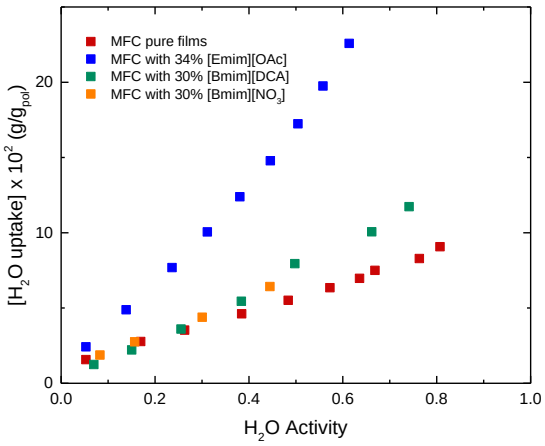


Figure 2. Water uptake capacities of different IL containing MFC films measured at 35°C as a function of water activity

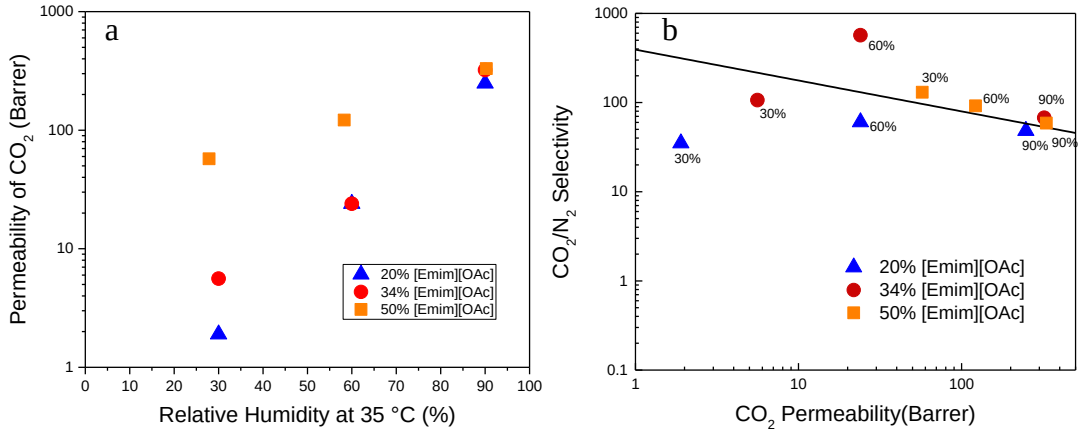


Figure 3. (a). Mixed gas CO_2 permeability with 1.7 bar feed pressure as a function of RH at 35°C. (b). Mixed gas permeation performance (35°C, 1.7 bar feed pressure) of hybrid membranes in Robeson plot

Conclusions

Ultra selective [Emim][OAc]-based hybrid blend membrane with nanocellulose has been successfully fabricated and tested. High compatibility of ionic liquid and nanocellulose resulted in the achievement of homogeneous blends, and a clear relationship between the IL content and the CO_2 permeability has been clearly identified. The study demonstrates one of the highest CO_2 selectivities obtained in physical and chemical sorption room temperature ionic liquid-based membranes.

References

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