

TECHNICAL NOTE: WATER VAPOR TRANSMISSION RATE AND PERMEANCE OF CELLULOSE NANOCRYSTALS/ POLYDIMETHYLSILOXANE HYBRID MEMBRANES MEASURED BY DYNAMIC VAPOR SORPTION

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Abstract. This article describes a fast and reliable method of screening membrane materials designed by measuring moisture vapor transmission rate (WVTR) and permeance of membrane materials using a Payne-style diffusion cell (dry cup) placed in a Dynamic Vapor Sorption (DVS) instrument. The materials were cellulose nanocrystals (CNC)/polydimethylsiloxane (PDMS) hybrid membranes. A casting method was used to fabricate three types of membrane samples. The WVTR and permeance of the samples were measured at two RH (RH) levels of 60% and 80% at 25 °C. The results revealed that the WVTR and permeance of PDMS membrane samples were increased by 34.33% to 39.69% after adding 1 wt% of CNC in the PDMS matrix. WVTR of all samples increased as RH increased from 60% to 80%, but the permeance decreased with increasing RH. The results of all three types of samples showed good consistency in terms of data discrepancy and the trends of WVTR and permeance with RH. Due to the small sample size, the tests could be completed in a few hours at elevated RHs in comparison with the commonly used Mason jar method according to American Society for Testing and Materials (ASTM) E96/E96M-16. Therefore, the Payne cell method in DVS can provide a fast screening of membrane materials.

Keywords: CNC/PDMS membrane, dynamic vapor sorption analyzer, permeance, WVTR.

INTRODUCTION

With the rapid development of gas/vapor selective membrane technology in recent decades, it has been shown that a type of moisture vapor

selective membrane can effectively and efficiently remove moisture from the air. This technology has been applied in the heating, ventilation, and air conditioning (HVAC) systems of some buildings (Kneifel et al 2006; Elustondo and Oliveira 2009). Overall, membrane-based dehumidification systems have shown favorable attributes over conventional dehumidification systems that

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operate by drawing in moist air and passing it through a series of cooling coils, in which water vapor condensation occurs. In contrast, membrane-based dehumidification systems remove the moisture vapor through diffusion without undergoing a phase change and thus consume less energy. Other attributes include simplicity in maintenance and operation, the high selectivity of water vapor and N_2 , ease of scale-up, and low initial cost (Yang et al 2015; Zhao et al 2015; Liang and Chung 2018).

In our recent study (Alikhani et al 2020), the moisture vapor removal efficiency of a commercialized polydimethylsiloxane (PDMS) membrane material was evaluated at four operation parameters (ie temperature, airflow rate, initial RH, and vacuum pressure). It was found that the initial RH of moist air could be dropped by 30% and more in the first 5 min, and then the lowered RH kept constant. In this follow-up study, the PDMS membrane was modified by adding cellulose nanocrystals (CNC). It was expected to improve the permeance of water vapor through the PDMS membrane. In the material development phase, a fast and accurate method to evaluate the water vapor permeance of membrane candidates is necessary since the commonly used Mason jar (dry cup and wet cup) methods in American Society for Testing and Materials (ASTM) E96/E96M-16 Standard Test Methods for Water Vapor Transmission of Materials (ASTM E96/E96M-16 2016) often take weeks to complete each testing run. This technical note aims to demonstrate that a Dynamic Vapor Sorption (DVS) instrument equipped with a Payne-style diffusion cell can be used as a rapid material screening method to study the influence of CNC on water vapor transfer across PDMS membrane materials.

MATERIALS AND METHODS

Materials and Fabrication of Membrane Samples

A CNC suspension at 11.8% solids was made by the United States Department of Agriculture (USDA) Forest Products Laboratory and obtained from the Process Development Center of the

University of Maine (Orono, ME). A PDMS prepolymer and curing agent kit (Dow SYLGARD™ 184 Silicone Elastomer kit) were purchased from Dow, Inc. (Midland, MI).

The pure PDMS membrane samples were prepared by casting the mixture of the PDMS prepolymer and curing agent at the ratio of 10:1 on a flat glass plate and then curing the wet film at 50 °C for 80 min in an oven. They were used as control (Type-I) and substrate for making another two types of samples (Type-II and -III). For making the Type-II and -III samples, a mixed aqueous suspension with a solid ratio of the PDMS prepolymer, curing agent, and CNC at 100:10:1.1 was prepared. The same casting and curing temperature and time were used. Type-II consisted of pure PDMS as substrate and CNC/PDMS composite that was cast and cured on the PDMS substrate. Type-III had a sandwich structure of composite/pure PDMS/composite. The mixture of PDMS prepolymer, curing agent, and CNC was cast on a glass plate and cured firstly. Additional pure PDMS mixture was cast on the composite substrate and cured, followed by the third casting and curing of the PDMS, curing agent, and CNC mixture on the pure PDMS substrate. Self-bonding was formed when casting additional layer(s) on the substrate.

Methods

The water vapor transmission of the membrane samples was measured by sealing a sample in a Payne-style diffusion cell that was placed in a DVS instrument (Model: DVS Advance; Surface Measurement Systems, London, UK). As shown in Fig 1(a), the open area of the Payne cell allowing water vapor to diffuse through the sample was 118.8 mm². A dry cup method was used. Silicon gel beads were placed in the cell to absorb water vapor entered in the cell to maintain a 0% RH. The surrounding environment of the Payne cell was well controlled to desired temperature and RH levels.

For each sample type, three replicates were prepared, which had nominal thickness of Type-I, -II, and -III samples were 130, 100, and 105 μm,

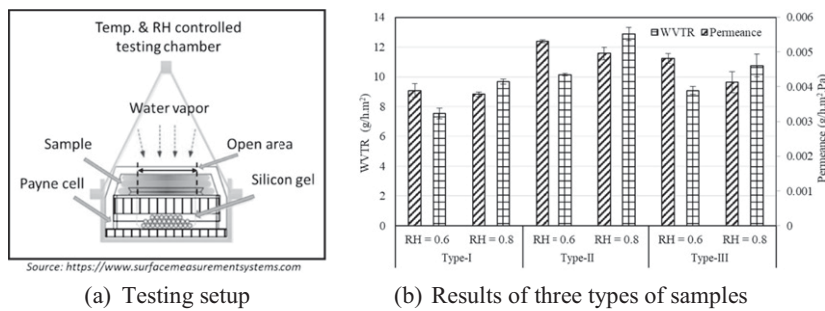


Figure 1. Testing setup and water vapor transmission rate (WVTR) and permeance of three types of samples.

respectively. Before a test started, a predrying process was performed in the test chamber of the DVS instrument by setting the RH was 0%. Then, each sample was first tested at 60% RH (step 1) and then 80% RH (step 2). The temperature was set at 25 C. The increase of mass of the Payne cell assembly with time was recorded simultaneously. It is pointed out that the composite layer of Type-II samples was faced the high RH (60% or 80% RH) side. In this study, the mass of the test assembly was recorded as a function of time. When the curve of mass vs time becomes linear for a certain time period, ie the change of mass with time keeps constant, the steady state is deemed to be achieved. To calculate water vapor transmission rate (WVTR) and permeance, the linear section of the curve in a time period of 3 h was selected to calculate the slope, ie $\Delta m/\Delta t$, for the calculations of WVTR and permeance, Eqs 1 and 2, respectively (ASTM E96/E96M-16 2016):

$$\text{WVTR} = \frac{(\Delta m/\Delta t)}{\text{Area of film}} \left(\text{unit: } \frac{\text{g}}{\text{m}^2 \text{ h}} \right) \quad (1)$$

$$\text{Permeance} = \frac{\text{WVTR}}{\text{Vapor pressure difference}} \left(\text{unit: } \frac{\text{g}}{\text{m}^2 \text{ h Pa}} \right) \quad (2)$$

RESULTS AND DISCUSSION

The results of WVTR and permeance of three types of samples are plotted in Fig 1(b). All test results had a relatively low standard derivation,

indicated by the short error bars in Fig 1(b). For the influence of CNC on WVTR and permeance, Type-II and -III samples with CNC as a nanofiller had high WVTR and permeance values, which were increased by approximately 34.33% to 39.69% compared with Type-I pure PDMS samples, regardless of RH levels. Type-II with an asymmetric two-layer structure had higher WVTR and permeance values than Type-III with a sandwich structure. It is noticeable that the influence of RH on WVTR is opposite to that on permeance for all three types of samples. WVTR increased as RH increased from 60% to 80%; however, permeance decreased as RH increased. The testing results showed good consistency in terms of data discrepancy and the trends of WVTR and permeance with RH in three types of samples tested by using a Payne-cell in DVS. These results also demonstrated that this test method is sensitive to differentiate membrane composition and structure and thus is good to be used to assist membrane development.

CONCLUSIONS

In this study, a Payne diffusion cell coupled with a DVS instrument was used to measure the WVTR and permeance of three types of membrane samples. The addition of CNC increased the water vapor transmission rate of the PDMS membrane significantly. The influence of RH on WVTR and the samples' permeance was the opposite: the former increased with RH, but the latter decreased. DVS shows an advantage for reliably and rapidly screening materials in the

material development phase by assessing moisture vapor transmission under a wide range of RHs.

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