

FORMABLE NANOCOMPOSITE MEMBRANES FOR ENERGY RECOVERY VENTILATORS

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Keywords: Nanofiber, Nanocomposite, Electrospinning, Membrane, Energy recovery ventilator

ABSTRACT

An energy recovery ventilator (ERV) is a mechanical device that recovers ventilation energy by transferring heat and moisture between building exhaust and fresh air supply systems. The ERV core designed by dPoint Technologies is comprised of flat water vapor permeable membranes. A water vapor-transporting polymer is coated on the microporous substrate. It provides higher selectivity for water vapor over other gases and zero air crossover to prevent cross contamination from the two air streams, higher durability in wet and freezing conditions, and less susceptibility to degradation by mold and bacteria than those of hygroscopic-coated papers. In this report, formable nanocomposite membranes are discussed as a next-generation ERV material. The nanocomposite membranes have a multi-layered structure; polyester (PET) microfibers/polytetrafluoroethylene (PTFE) microporous film/polyacrylonitrile (PAN) nanofibers/polyurethane-polyethylene oxide (PU-PEO) film. The PU-PEO film fabricated by gravure rolling served as a functional water vapor selective layer. Electrospinning was used to deposit non-woven nanofibers on the PTFE film with 3D interconnected pores and an ultra-high surface area per volume. The PAN nanofibrous layer is believed to function as a framework for the PTFE film to support the PU-PEO coating, a diffusion barrier against gas contaminants utilizing the tortuous path through the 3D interconnected porous structure, and a thermal barrier to protect the PET layer from a high-temperature molding process. The PAN nanofibers with the area density between 0.12 and 0.40 g/m² did not obstruct water vapor transport of the nanocomposites but were significantly effective in protecting air-crossover of the shaped membranes. Furthermore, the water vapor transport performance of the shaped membranes increased up to 30% compared to those of the flat nanocomposite membranes, resulting from the multi-dimensional transfer of the energy across the shaped membrane. This pilot study confirms the potential of the nanofiber-sandwiched, formable composite membranes that function more efficient energy recovery of an ERV core.

1 INTRODUCTION

An energy recovery ventilator (ERV), also called an enthalpy exchanger, is a mechanical device used in building ventilation systems that consists of an enclosure, fans to move air streams, ducting, an enthalpy exchanger filters, control electronics, and other components. It processes the recovery of energy from building exhaust by transferring heat and moisture between the exhaust and fresh air supply systems [1-3]. According to the International Energy Agency reports in 2012, a residential/commercial building sector utilized approximately 115 EJ globally, accounting for 32% of global energy demand, 30% of energy-related CO₂, 66% of halocarbon and 25-33% of black carbon emissions [4]. Thus, a high-efficiency ERV can make a significant impact on energy loss with ventilation, greenhouse effect, and air pollution. It was reported that up to 65% of energy associated with treating supply air (heating, cooling, humidification, and dehumidification) can be saved by using the high-efficient ERV [5]. In hot and humid climates ("cooling condition" in Fig. 1a), the incoming

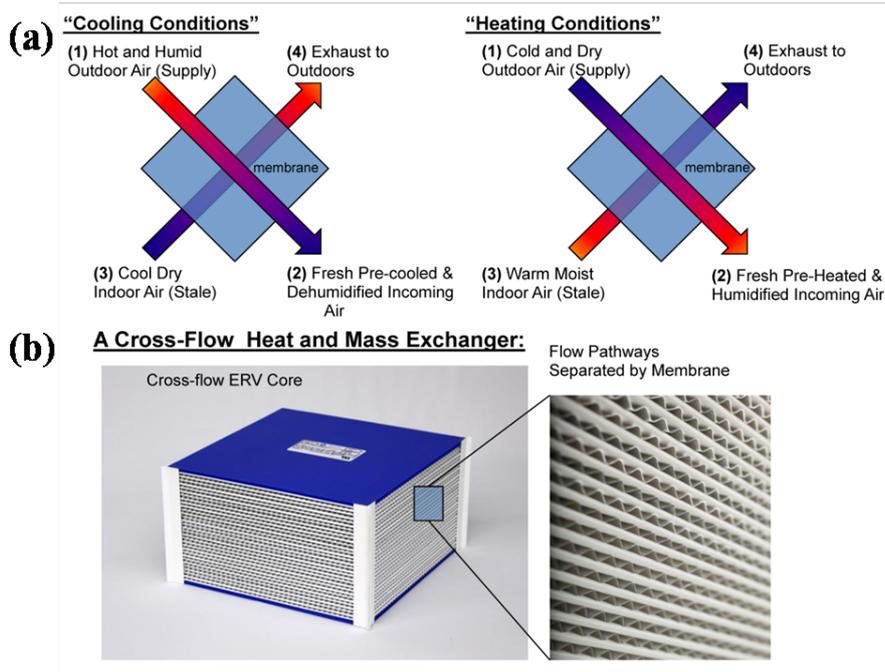


Figure 1: (a) Illustration of an energy recovery ventilator (ERV) core transferring heat and moisture between building exhaust and fresh air supply systems and (b) photographs of an ERV core (right) and water vapor permeable membrane layers (left) designed by dPoint Technologies [1].

air is hot and humid, but the exhaust air is cool and dry. By passing the cool and dry air over one side of a permeable membrane and the hot and humid incoming air over the opposing side, the exhaust air can be used to pre-cool and dehumidify the incoming air, reducing the energy consumption load on an air conditioner. In cold and dry climates ("heating condition" in Fig. 1a), on the other hand, incoming cold and dry air is pre-heated and humidified with warm and relatively humid exhaust air, reducing the energy consumption load on a heating system. The use of an ERV also improves indoor air quality and comfort through energy efficient ventilation. An ERV device tends to regulate humidity levels, which may reduce the likelihood of mold, bacteria, and fungi growth. Recycling water vapor from the exhaust air stream in the "heating condition" climates raises humidity levels, thereby reducing skin irritation, dryness, and respiratory symptoms caused by dry air [1,2].

A key component in the ERV system is an ERV core which transfers the heat and moisture between the two air streams. Two most common types of an ERV core are a planar-type and a rotating wheel-type device. The planar-type core uses membrane plates that are comprised of planar, water-permeable membranes supported with spacers and/or frames. The plates are stacked, sealed, and configured to accommodate incoming and exhaust streams. The spacers maintain proper sheet spacing as well as defining airflow channels for wet and dry streams on opposite sides of each membrane sheet. The enthalpy wheel-type core uses a rotating wheel which picks up heat energy and releases it into the colder air stream between the two streams. The wheel-type ERV uses desiccants to transfer moisture. They have moving parts which may require extra maintenance and allow contaminant crossover between the air streams. Benefits of the planar plate-type ERV core designs are that they are readily scalable because the quantity as well as the dimensions of the membrane plates can be adjusted for different end-use applications, and they have efficient vapor transportation without moving parts and are selective for water vapor over gases and contaminants [1,2].

The ERV core designed by dPoint Technologies is comprised of water permeable membrane layers (Fig. 1b). The ERV membrane should be thin enough to allow the adequate exchange of heat between the two streams, driven by a temperature gradient. The membrane should be also water permeable to allow moisture to pass through the material, driven by vapor pressure differential and water concentration gradients between the two streams. Another requirement is that the membrane should be

impermeable to air and contaminant gases, to prevent the mixing and crossover of contaminants from the exhaust air to the fresh supply air stream through the membrane. However, there is still potential for crossover contamination resulting from leakage in the ERV assembly and/or passage of the gases and contaminants through the membrane [1-3].

This study explored the development of a next generation ERV membrane with high heat and moisture transport, to improve the efficiency of energy recovery and savings while maintaining a high quality of indoor air. A nanofiber technology and a polymer solution coating were applied to current, commercialized, microporous polymer membranes to make them formable into a multi-dimensional structure, thereby increasing their functionality while maintaining zero air- crossover performance of the membranes. A layer of nanofibers generated by electrospinning was attached to the membranes. A variety of methodologies has been used for nanofiber production, including drawing, template synthesis, phase separation, self-assembly, and electrospinning. Electrospinning has drawn increasing interest in various industry applications due to its relative simplicity, feasibility for mass production, and adaptability to utilize a wide range of polymers. When an electric potential is applied to a polymeric solution, the charged polymer liquid forms a cone shaped droplet (Taylor cone) at the tip of a spinneret nozzle. When an electrostatic force overcomes the surface tension of the liquid droplet, an electrospun jet forms and undergoes a series of whipping, stretching and elongation, and solidified nanofibers are deposited on the grounded target (Fig. 2a). Electrospinning produces a non-woven nanofibrous structure with 3D interconnected pores (Fig. 2b) and a high surface area per volume (Fig. 2c) [2,3,6,7].

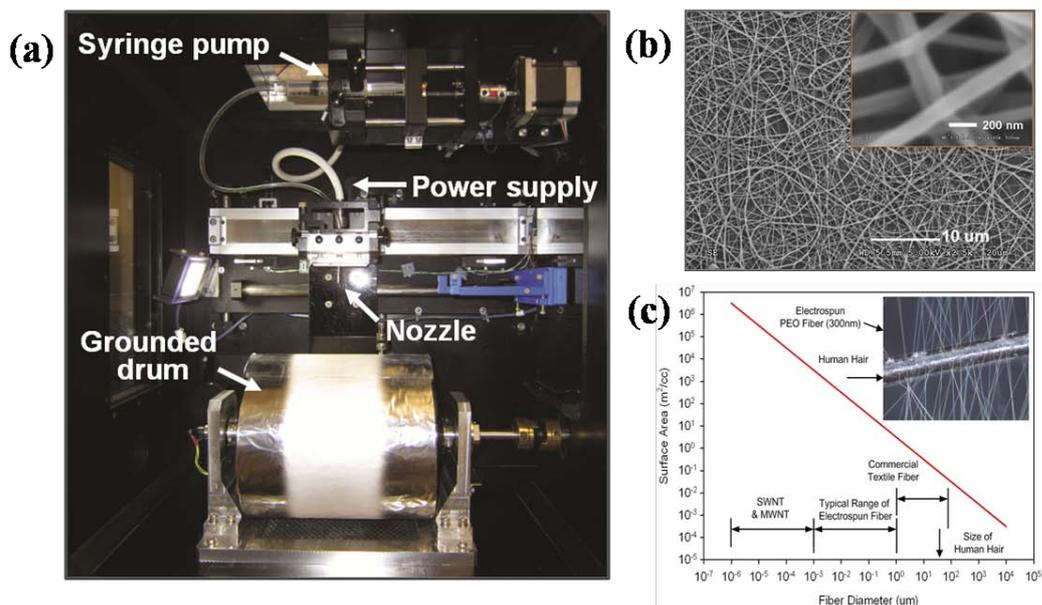


Figure 2: (a) Electrospinning system for nanofiber fabrication [6], (b) SEM micrograph of electrospun poly(vinyl alcohol) nanofibers, and (c) relationship of fiber diameter to surface area (Inset: optical microscope image of poly(ethylene oxide) nanofibers and human hair) [7].

2 MATERIALS AND METHODOLOGY

2.1 Materials for membrane fabrication

Two commercially available microporous films were used as a basic substrate to fabricate a formable ERV membrane. They have a double-layered structure; a microporous polytetrafluoroethylene (PTFE) layer (top) and a non-woven polyester (PET) microfibrillar layer (bottom); Each of the films was referred to as 125-PTFE and 137-PTFE. Polyacrylonitrile (PAN, Mw: 150,000) was purchased from Sigma-Aldrich Canada for the fabrication of nanofibers.

Dimethylformamide (DMF) from Fisher Scientific Canada was used to prepare a PAN solution for electrospinning. A polyurethane-polyethylene oxide dispersion in water (PU-PEO; Permax 230) was purchased from Lubrizol, USA. A polycarbodiimide solution (Picassian XL-702, Stahl, USA) was used to cross-link the PU-PEO solution.

2.2 Membrane fabrication

A 10 wt% PAN solution in DMF was filled in a 10 mL disposable syringe (BD, USA) with a needle (PrecisionGlide™ 18G 1½, BD, USA). The syringe pump ejected the solution at a rate of 0.08 mm/min, and a voltage of 23 kV applies at the needle tip. The grounded drum rotated at a rate of 0.50 m/min to collect electrospun nanofibers. The syringe moved horizontally to deposit the nanofibers uniformly on a microporous PTFE film attached to the drum. The spinning distance between the tip and the drum was 20 cm. A gravure roller was used to coat a PU-PEO solution on the surface of a PTFE film with and without electrospun PAN nanofibers. Four different types of the membranes were fabricated, referred to as 125-PTFE-PU, 125-PTFE-PAN-PU, 137-PTFE-PU, and 137-PTFE-PAN-PU depending on the type of a PTFE film and the presence of a PAN nanofiber layer. An area density of a PAN nanofibrous layer and a PU-PEO coating layer was calculated by measuring the dimension of the membrane and weighing the each layer of the membranes. For a forming process, a mold was pre-heated to 65 °C in a closed chamber environment at 135 °C. The sample was pleated between the mold by a hydraulic compress machine for 30 and 45 sec.

2.3 Scanning electron microscopy

An each layer surface of the membranes was examined using scanning electron microscopy (SEM; Hitachi S-3000, Japan) at an operating voltage of 5.0 kV. The surface was coated by gold sputtering.

2.4 Pressurized air crossover

Pressurized air crossover was tested as previously reported [1,3]. Samples (18cm × 5 cm) were placed in a counter flow test module with an active area of 45.6 cm². Air-crossover was measured by applying and maintaining a static air pressure (3 psi) on one side of the membrane, while the opposing side of the membrane was exposed to atmospheric pressure. The air flow through the membrane material was measured using a flow meter. The pressurized air crossover is a direct indication of the level of defects or porosity in the membrane, as it measures air flow through pores in the membranes. Defect free films have zero crossover in this test.

2.5 Oxygen crossover

Oxygen crossover was measured in the same module as the pressurized air crossover test, as previously reported [1,3]. A pure nitrogen stream (2000 cc/min) flowed over the surface of one side of the membrane. A dry air stream (2000 cc/min and 500 cc/min) flowed over the opposing membrane surface. The module outlets on both streams were open to atmosphere, such that differential pressure between the two streams was minimized and only diffusive transport and not convective transport occurred through the membrane. An oxygen sensor was placed at the outlet of the nitrogen stream to measure the oxygen concentration. Since the concentration of oxygen in dry supply air is known, and the nitrogen stream contains no oxygen at the inlet, the percentage of oxygen passing through the membrane by diffusion can be reported as

$$\chi_{O_2} (\%) = (C_{O_2,2} / C_{O_2,3}) \times 100 \quad (1)$$

where C refers to the percent concentration of oxygen (O₂) at points 2 and 3, in a counter-flow test module, with point 2 at the nitrogen-side outlet (measured by the sensor), and point 3 at the air-side inlet. The oxygen transport provides an indication of the overall selectivity of the membrane material, specifically the level of defects in the dense coating layer. This crossover testing is similar to exhaust air transport ratio (EATR) testing.

2.6 Water vapor transport

Dynamic water vapor transport was measured using a testing station as reported previously [3]. The sample was kept in the sample test module used for the air/oxygen crossover test. The flow rate, temperature, and relative humidity of each inlet gas stream were controlled, and the outlet temperatures and relative humidity of each gas stream were measured via a Labview© interface. The gases were supplied and directed in counter-flow over the opposing surfaces of the membrane. The membrane active area in the test jig was 45.6 cm², and the length of the flow pathway was 16cm. All gas lines were heat traced into a temperature controlled oven, where the module and humidity probes were located, such that all measurements were isothermal and that no condensation might occur within the membrane module and on the humidity probes. During a 'standard' vapor transport test, a first gas stream was supplied at 50 °C and 0% relative humidity to the inlet on one side of the membrane. A second gas stream was supplied to the inlet on the other side of the membrane at 50 °C and ~50% relative humidity at the same flow rate as the first gas stream. The water content and temperature of the two streams were measured and recorded at the outlets, using calibrated Vaisalla humidity probes (HMT221). From these values, a mass balance could be completed on the system to determine the mass flow of water vapor through the membrane (kg/min). Water flux was calculated by dividing the mass flow by the membrane area over which the transport has occurred (kg/m²/day). The water flux of the membranes was measured before and after a forming process.

3 RESULTS AND DISCUSSION

3.1 Fabrication of nanocomposite membranes

Fig.3 shows SEM micrographs of each layer surfaces of the PTFE substrates. The two PTFE substrates possessed similar non-woven PET microfibrous layer structures on the bottoms. The fibers had the uniform size of diameters, approximately 20 um (Fig. 3a). The 125-PTFE film was found to have a less porous structure than a 137-PTFE film as shown in Fig. 3 b and c, respectively. The 125-PTFE film is composed of sub-micrometer size pores (dark area) and 3D interconnected micropores (bright area). Conversely, the 137-PTFE film showed to have relatively uniform, 3D interconnected micropores throughout the overall surface. A 10 wt% PAN solution in DMF was electrospun into the randomly deposited nanofibers on the PTFE substrate (Fig. 4a). PAN is a synthetic, semicrystalline polymer with the linear formula (C₃H₃N)_n. PAN was chosen because it has been used for ultra-filtration membranes, and it has thermal stability (up to 300 °C), resistance against chemical cleaning agents and alkaline solutions, high strength and elastic modulus, and capability to absorb many different metal ions [8, 9]. Using a gravure rolling machine, a 21% PU-PEO solution in a binary solution of water and ethanol (70/30 wt%) was coated on the surface of the PAN nanofibers. Fig. 4b shows the continuous, homogeneous, planar PU-PEO surface without the trace of the PAN nanofibers, confirming that the PAN nanofibers were completely impregnated and coated by the PU-PEO solution. In this study, the PU-PEO coating was placed to function a water vapor permeable layer on the top surface of the membranes. A PU-PEO polymer has traditionally been used in "breathable" apparel applications. In the presence of water vapor, the PU-PEO polymer sorbs water into the "soft" PEO blocks of the polymer and creates "capillary channels" through which water can migrate, driven by a concentration gradient. The "hard" polyurethane segments provide mechanical integrity to the polymer film [2,10]. The four types of the membranes were named after 125-PTFE-PU, 125-PTFE-PAN-PU, 137-PTFE-PAN-PU, and 137-PTFE-PAN-PU depending on the PTFE substrate type and the presence of the PAN nanofibers. Each of the membranes were formed into a pleated shape. Fig. 5 shows photos of the pleated 137-PTFE-PAN-PU nanocomposite membrane.

3.2 Pressurized air and oxygen crossover

The pressurized air of 3 psi was forced to flow on one side of the membranes to measure air crossover indicating the levels of defects in the membranes. The graph in Fig. 6 summarizes the pressurized air crossover measurements of all membrane samples before and after the forming process for 30 and 45 sec. The PTFE/PAN/PU membranes containing the PAN nanofibers with the areal density of 0.25 ± 0.4 g/m² were selected for this air crossover test. The 125-PTFE based membranes

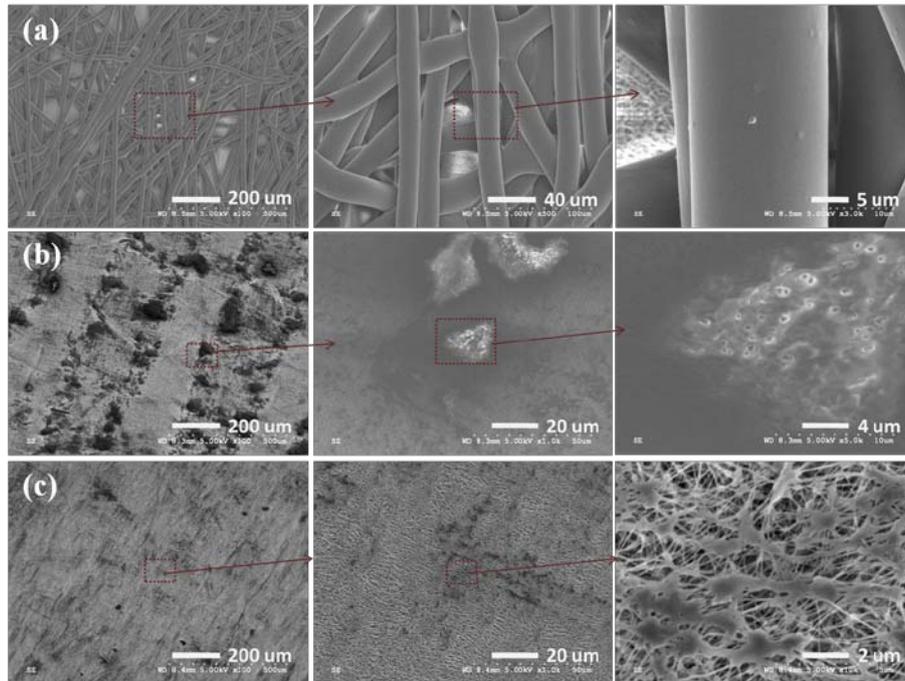


Figure 3: SEM micrographs of (a) PET microfibers (bottom surface of PTFE substrate), (b) 125-PTFE microporous film, and (c) 137-PFPE microporous film.

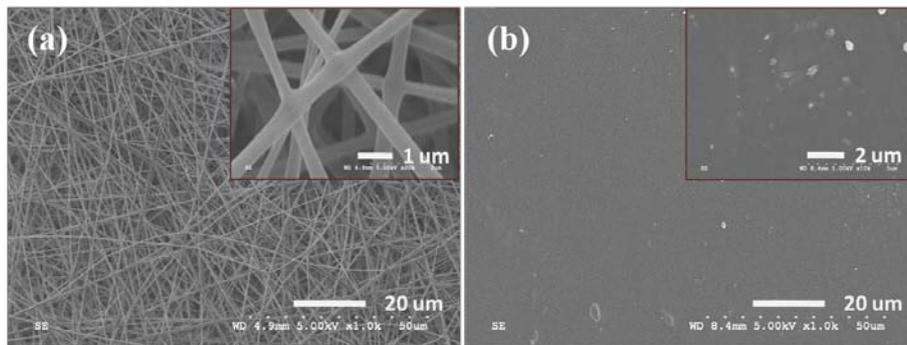


Figure 4: SEM micrographs of electrospun PAN nanofibers (a) deposited on PU-PEO film (b) coated on microporous PTFE substrate.

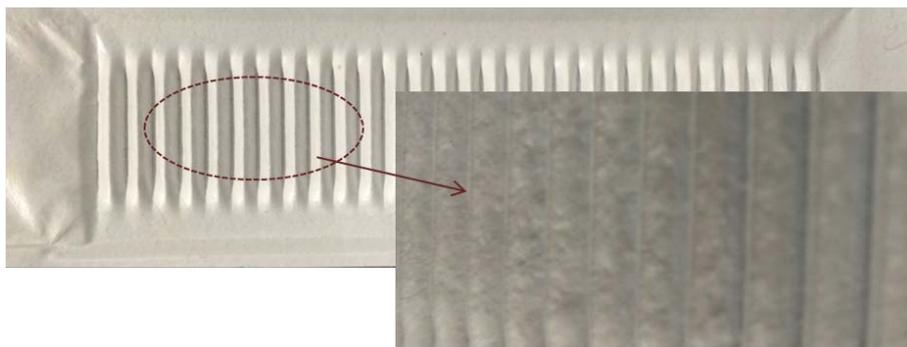


Figure 5: Photos of pleated PET/PTFE/PAN/PU-PEO membrane after forming process.

and the 137-PTFE based PTFE membranes did not show a significant difference of the pressurized air crossover. However, the addition of the PAN nanofiber layer between the PTFE substrate and the PU-PEO coating layer resulted in a substantial decrease of the air crossover amount. Furthermore, it was confirmed that the double coating step produced almost zero air crossover except the 125-PTFE-PU and the 137-PTFE-PU membranes formed with 45 sec compression. In the case of the oxygen crossover test, all of the membrane samples had less than 1% of oxygen crossover in both flow rates except the single coated 137-PTFE-PU membrane after forming for 45 sec. The oxygen crossover of the membrane was $1.55 \pm 0.71\%$ and $4.53 \pm 2.48\%$ at the 2000 cc/min and 500 cc/min rates, respectively. From these gas crossover results, it can be concluded that the PAN nanofiber layer is substantially effective to reduce defects and open pores on the pleated membranes. The double coating step resulted in almost zero air crossover of the pleated PTFE/PAN/PU nanocomposite membranes even after 45 sec forming process.

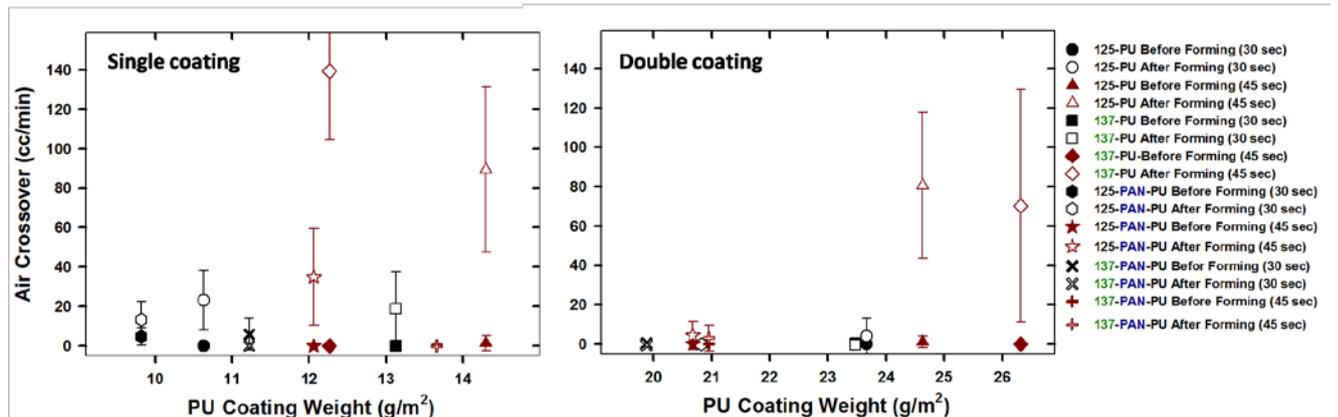


Figure 6: Pressurized air crossover of four different types of membranes before and after forming process for 30 and 45 sec. The membranes containing PAN nanofibers with the areal density of $0.25 \pm 0.4 \text{ g/m}^2$ were selected for the pressurized air crossover test.

3.3 Water vapor transport

Fig 7. shows the result of dynamic water vapor transport of the PTFE-PAN-PU nanocomposite membranes depending on the PU-PEO areal density. The water vapor flux of the membranes decreased with the PU-PEO areal density. The increase of the PU-PEO thickness obstructed the diffusion of water vapor molecules passing through the membrane. The forming process significantly increased the water vapor flux of the pleated membranes up to $25 \text{ kg/m}^2/\text{day}$. Approximately 30% increase of the water vapor transport, compared to the values of the plain PTFE-PAN-PU membranes, resulted from the enlarged surface area for water vapor permeation. A conventional ERV core with flat polymer membranes requires spacers to support the membranes which generally block heat and moisture transfer. The proposed formable membranes in this study can be shaped and attached to one another to provide self-supporting layers and core structures. The multi-dimensional transfer of energy across the shaped membranes can increase an enthalpy-exchanging surface area per volume and results in more efficient energy recovery of the ERV core with more compact size than the conventional ERV core. The effect of the PAN nanofiber layer on the water vapor transport was evaluated as shown in Fig. 8. The water vapor flux of the flat PTFE-PAN-PU membranes was measured depending on the areal density of the PAN nanofibers ranging from 0.12 g/m^2 to 0.35 g/m^2 . It was found that the PAN layer did not obstruct the diffusion of the water vapor molecules passing through the membranes.

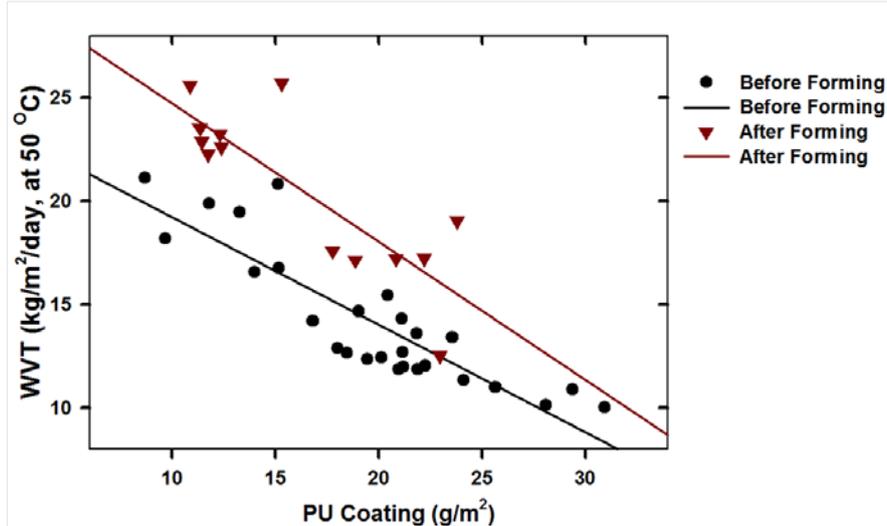


Figure 7: Water vapor transport of PTFE-PAN-PU nanocomposite membranes before and after forming process. The membranes with pressurized air crossover less than 16 cc/min were selected for the water vapor transport test.

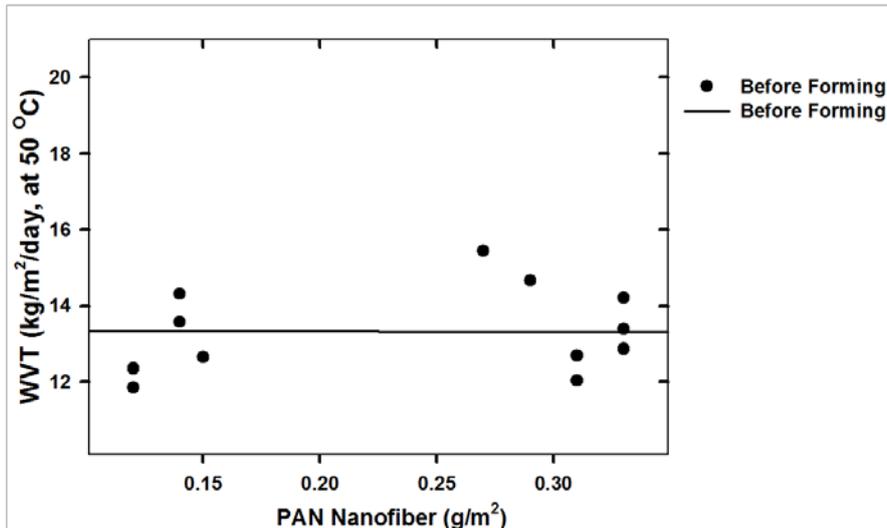


Figure 8: Water vapor transport of PTFE-PAN-PU nanocomposite membranes vs. PAN nanofiber areal density. The flat, double-coated membranes with pressurized air crossover less than 16 cc/min were selected for the water vapor transport test. The areal density of the PAN nanofibers ranged between 0.12 g/m² and 0.35 g/m².

4 CONCLUSION

The formable PTFE-PAN-PU nanocomposite membranes for an energy recovery ventilator were successfully fabricated. The electrospun PAN nanofibers played a significant role to prevent air and oxygen gas from passing through the membranes, while not obstructing water vapor transport performance. The maximum water vapor flux of the pleated membranes at 50 °C reached to approximately 25 kg/m²/day, up to 30% increase compared to that of the flat nanocomposite membranes. This is attributed to the multi-dimensional transfer of the energy across the enlarged surface of the shaped membranes. This pilot study confirms the potential of the nanofiber-sandwiched, formable composite membranes functioning more efficient energy recovery of an ERV core.

ACKNOWLEDGEMENTS

This work was financially supported by a Natural Science and Engineering Council Canada–Collaborative Research and Development (NSERC-CRD) grant and MITACS Elevate Postdoctoral Fellowship Program grant sponsored by dPoint Technologies Inc.

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