Fabrication and Characterization of a Novel Polypropylene/Poly(vinyl alcohol)/Aluminum Hybrid Layered Assembly for High-Performance Fibrous Insulation

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ABSTRACT: A novel hybrid layered assembly based on aluminum-coated poly(vinyl alcohol) (PVA) nanofibers supported on a polypropylene (PP) web was fabricated via electrospinning and physical vapor deposition. The PVA nanofibers and coated aluminum were characterized by field emission scanning electron microscopy and transmission electron microscopy. The results indicate that PVA nanofibers approximately 430 nm in diameter and an aluminum coating approximately 37 nm in thickness were successfully embedded on the supporting PP web. Fourier transform infrared spectra and the water vapor transmission rate were used to determine the IR spectral transmission and water vapor transmission through the materials with or without the nanofiber or metal coating, respectively. Compared to the uncoated PP web, the novel hybrid layered assembly showed a significant increase in thermal radiation extinction due to both the radiation reflection of the metal coating and the radiation absorption of the nanofibers without noticeable weight gain or water vapor permeable deterioration. This method represents a simple and practical approach for the production of a lightweight hybrid layered assembly that is highly beneficial in the efficient reduction of heat loss in low-density fibrous insulations without a noticeable deterioration in the water vapor permeability and that could be used for wide applications such as protective clothing, sleeping bags, building construction, and aircraft. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2525–2530, 2008

Key words: nanotechnology; poly(propylene) (PP); radiation; thermal properties

INTRODUCTION

Within the past decade, the incorporation of metal[1–5] or metal oxide nanoparticles[6] into polymer matrices has received more attention for wide applications, such as catalysis, drug and wound dressings, optical information storage, surface-enhanced Raman scattering, and fibrous insulations. For polymeric fibrous materials (e.g., polyester, thinsulate, wool, silk, down, feathers), which are widely usable as thermal insulation[7–11] in cold protective clothing, sleeping bags, building construction, aircraft, and so on, the use of metallic or metalized polymeric fibers has been found to be one of the most efficient ways to reduce heat loss by the improvement of radiation reflection.[12]

Several IR reflective coatings with metals (e.g., aluminum[13]) or metal oxides (e.g., silicon dioxide and titanium dioxide[14]) for polymeric fibrous materials have been fabricated with the sol–gel technique for reduced heat transfer. However, in addition to an accompanied unwanted weight increase of over 20% with metal or metal oxide coatings, the water vapor permeability of the coated fibrous materials also significantly deteriorates because of the blockage by the dense metal or metal oxide coating layer of the permeable pores among the polymeric fibers. As a result, water vapor transport greatly accumulates and condenses in the fibrous insulations, and the total heat loss may significantly increase because of the much higher thermal conductivity of liquid water compared to those of the polymeric fiber and the air in the interfiber void.[15,16] Nanofibers have demonstrated great permeability to water vapor[17,18] because of their extremely large surface-to-volume ratio and large quantity of small pores. Herein, it may be useful to enhance water vapor transfer via the coating of the metal or metal oxide layer onto a conventional polymeric fabric supporting nanofibers instead of its direct coating onto the conventional polymeric fabric.

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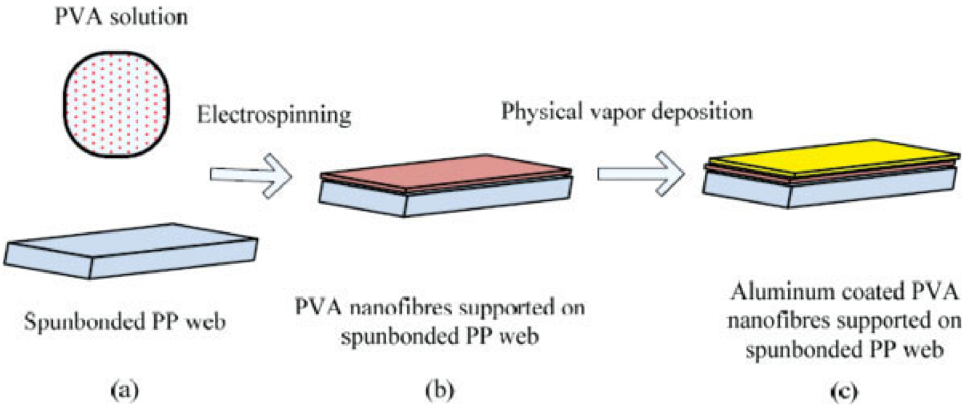

Figure 1 Schematic diagram of the sequential procedure for the production of the PP/PVA/Al hybrid layered assembly: (a) preparation of the stable PVA solution and PP web, (b) electrospinning of the PVA nanofibers onto the PP web, and (c) fabrication of the aluminum-coated PVA nanofibers supported on the PP web. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Moreover, in addition to radiation reflection of the metal or metal oxide layer, the nanofibers may provide extra radiation absorption for further reduced heat transfer.

Electrospinning[19–22] offers a simple, flexible, and low-cost technique for the creation of superfine fibers. For the potential of electrospun nanofibers to be fully realized and further functionalized, it is important to fabricate various fibrous assemblies.[23–25] The combination of the electrospun nanofibers with a metal or metallic oxide coating may be meaningful, as this may provide a simple and practical way to fabricate a novel lightweight hybrid layered assembly, which is expected to be highly resistant to heat transfer but very permeable to water vapor. For this purpose, in this article, we introduce the fabrication of a novel hybrid layered assembly based on aluminum-coated poly(vinyl alcohol) (PVA) nanofibers supported on a polypropylene (PP) web. Field emission scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were carried out to determine the surface morphology and cross-sectional structure, respectively, of the hybrid layered assembly. Fourier transform infrared (FTIR) spectroscopy and water vapor transmission rate (WVTR) measurements were carried out to investigate the thermal radiation and water vapor transport, respectively, through the hybrid layered assembly.

EXPERIMENTAL

Materials

The PP web (weight = 20 g/m^2, thickness = 0.232 mm, porosity = 91%) was provided by China Nonwoven Co. (Shanghai, China). PVA (average molecular weight = 88–103 kg/mol, 98–99%, hydrolyzed) was purchased from Shanghai Chemical Fibres Institute (China) and manufactured by Sigma-Aldrich Company (St. Louis, MO).

Fabrication of the PP/PVA/Al hybrid layered assembly

As shown in Figure 1, the fabrication of the novel PP/PVA/Al hybrid layered assembly was composed two steps, that is, the electrospinning of the PVA nanofibers onto the PP web and the coating of aluminum onto the PVA nanofibers with physical vapor deposition.

We prepared a PVA aqueous solution (10 wt %) by dissolving PVA powder in a distilled-water bath at 80°C under magnetic stirring for 6 h and then cooling it to room temperature with continuous stirring for another 6 h. The solution was inserted into a plastic syringe with a stainless steel nozzle 1.0 mm in diameter. An electric voltage of approximately 20 kV was applied between the nozzle and the collecting electrodes, which were previously covered with a PP web. The electrospinning process is illustrated in Figure 2. The electrospun PVA nanofibers supported on the PP web were then coated with a thin aluminum layer via physical vapor deposition. Here, the sputtering method with a vacuum-sputtering machine (Hong Kong Productivity Council, Hong Kong) was used for physical vapor deposition (PVD) because of the method's low-temperature operation and good industrial applicability.

Characterization of the PP/PVA/Al hybrid layered assembly

Field emission SEM was used to observe the surface morphology of the PP/PVA/Al hybrid layered assembly. TEM images of cross-sectional specimens were obtained with a TECNAI T-12 instrument (FEI Company, Hillsboro, OR) with a 120-kV accelerating voltage. Samples for TEM imaging were prepared as follows. The fibrous assembly specimen was cut into pieces 5 × 10 mm^2, embedded into Spurr resin, and allowed to harden in a convection oven at 60°C for 16 h. The embedded specimen was cross-sectioned

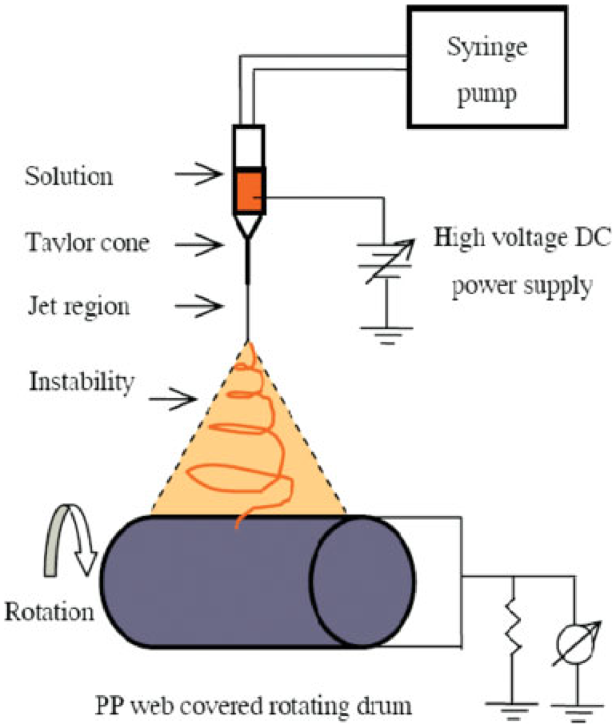

Figure 2 Schematic diagram of the electrospinning process (DC = direct current). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

with a diamond knife and an ultramicrotome. Cross sections with thicknesses of approximately 100–150 nm were collected on copper grids from the microtome boat and dried.

FTIR spectroscopy was carried out with a Nicolet Magna 760 FTIR spectrometer (Thermo Fisher Scientific Inc., Waltham, MA) with a resolution of 2 cm^{-1}. To determine the transmittance percentage (τ_λ), which is the ratio of the transmitted intensity through the thin-film sample ($I_{t,\lambda}$) to the incident intensity before the sample ($I_{i,\lambda}$), directional–directional IR radiation transmission,[26] as shown in Figure 3, through the thin films was performed for five repeated measures:

$$\tau_\lambda = I_{t,\lambda}/I_{i,\lambda} \tag{1}$$

WVTR was measured under an environment with a temperature of 22°C and a relative humidity of 65% with the water vapor transmission dish method according to British Standard BS7209 (1990).[27] The total amount of water vapor transferred through the thin film from the water dish within 24 h was determined.

RESULTS AND DISCUSSION

Figure 4(a,b) shows the field emission SEM images of the PP-web-supported electrospun PVA nanofibers and the aluminum-coated PVA nanofibers, respectively. As shown in Figure 4(a), the electrospun PVA fibers were randomly deposited on the PP web, and the average diameter of the substrate PP fibers was about 22 μm. As shown in Figure 4(b), the average diameter of the electrospun PVA fibers was determined to be approximately 430 nm. Also, the electrospun PVA nanofibers were uniformly coated with aluminum over their upper surface area. Uncoated areas appeared to be the result of fiber touching and interfiber friction. A TEM image of the cross-sectional specimen of the aluminum-coated PVA nanofibers is shown in Figure 4(c). The electrospun PVA fibers can be seen on the right side of the image, and the black-gray area in the image corresponds to the metal coating. The aluminum coating layer was estimated to be approximately 37 nm in thickness, which was much smaller than the supported PP web, which indicated that there was no significant weight or density gain to the functional fibrous assembly.

Figure 5 shows three IR transmittance spectra obtained through the three types of PP webs with or without electrospun nanofibers or metal coating. The spectrum shown in Figure 5(a) corresponds to the IR transmittance spectra through a control PP web without electrospun nanofibers or metal coating. Strong absorption bands at approximately 3080 and 2920 cm^{-1} due to the stretching of CH_2 were observed. Several weak absorption bands in the range 1900–2500 cm^{-1} appeared because of the stretching of C—C. At approximately 1300–1500 cm^{-1}, several medium absorption bands assigned to CH_2 wagging deformation and CH_3 symmetric deformation were also observed. A medium absorption band assigned to CH_2 rocking deformation appeared at approximately 725 cm^{-1}. The spectrum in Figure 5(b) corresponds to the PP web with PVA nanofibers but without the aluminum coating. The spectrum in Figure 5(c) is for a specimen similar to the one in Figure 5(b), but in this case, the nanofibers were coated with aluminum. For the specimen probed in Figure 5(b), a new weak absorption band at approximately 3320 cm^{-1} assigned to the —OH— vibration of the electrospun PVA nanofibers was observed. A new broad band between 400 and 750 cm^{-1} assigned to aluminum appeared in the sample whose spectrum is shown in Figure 5(c).

According to Beer's law,[28] the spectral extinction coefficient to IR for thin films ($\sigma_{e,\lambda}$) can be obtained

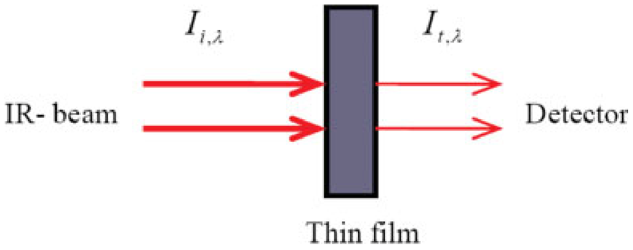

Figure 3 Schematic of the directional–directional IR radiation transmission through a thin film. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

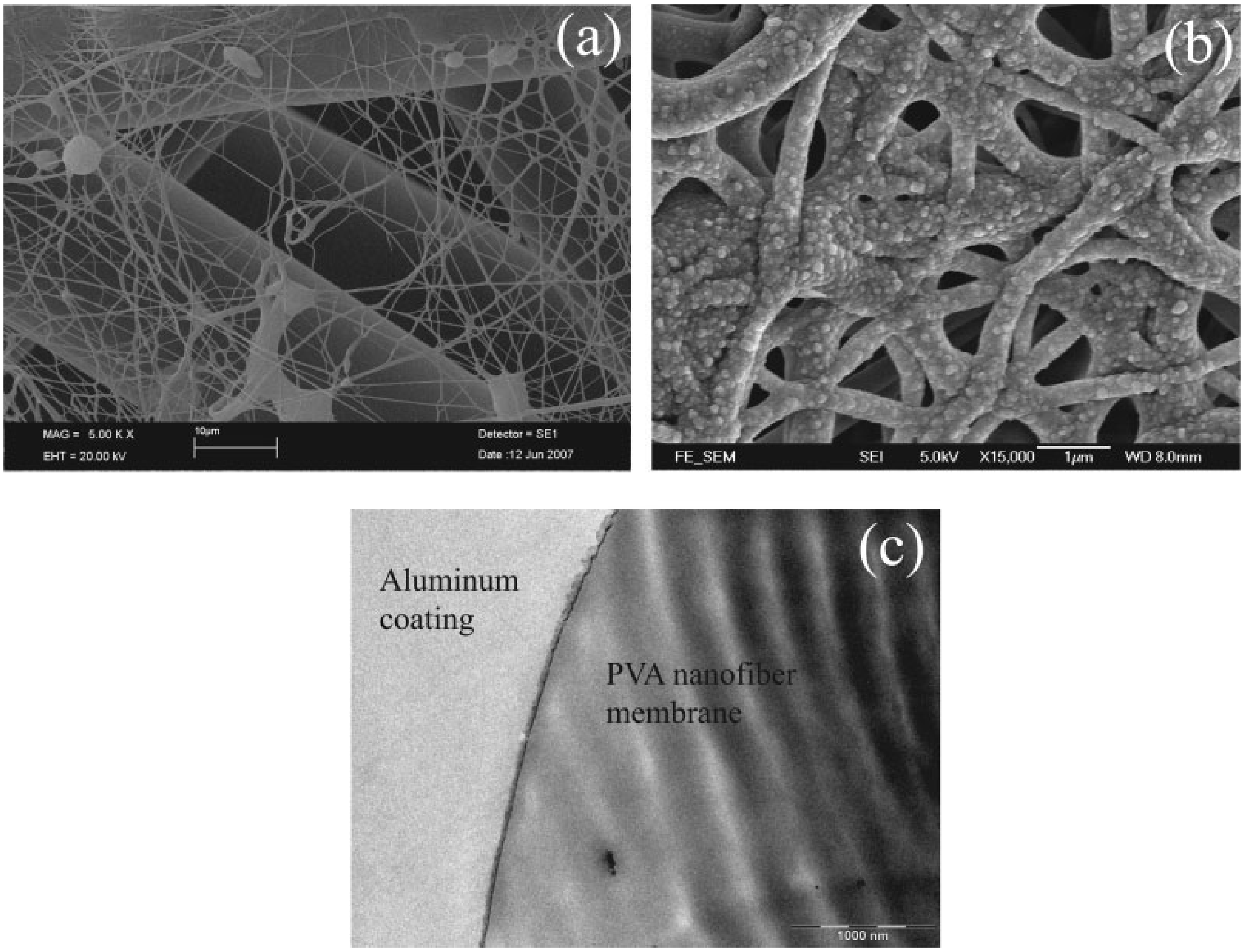

Figure 4 Morphological and structural images of the PP/PVA/Al hybrid layered assembly: (a) field emission SEM image of the PVA nanofibers supported on the PP web, (b) field emission SEM image of the aluminum-coated PVA nanofibers, and (c) TEM image of the aluminum-coated PVA nanofiber membrane.

from the transmittance spectra (τ_λ) and the thickness of the thin films (L) as follows:

$$\sigma_{e,\lambda} = -\ln(\tau_\lambda)/L \tag{2}$$

The $\sigma_{e,\lambda}$'s for the three specimens are shown in Figure 6. As shown, $\sigma_{e,\lambda}$ of the PP webs noticeably increased with the addition of the electrospun PVA nanofibers and further increased with the aluminum coating. Although very few PVA nanofibers were deposited on the PP web, as shown in Figure 4(a), $\sigma_{e,\lambda}$ increased noticeably, as shown by a comparison of the PP webs with and without PVA nanofibers, as shown in Figure 6(a,b), because the finer fibers had better radiation absorption and extinction because of their higher surface-area-to-volume ratio.

A comparison between Figures 6(b) and 6(c) indicated that a further noticeable improvement in the thermal radiation extinction was obtained when aluminum was coated onto the PP-supported PVA

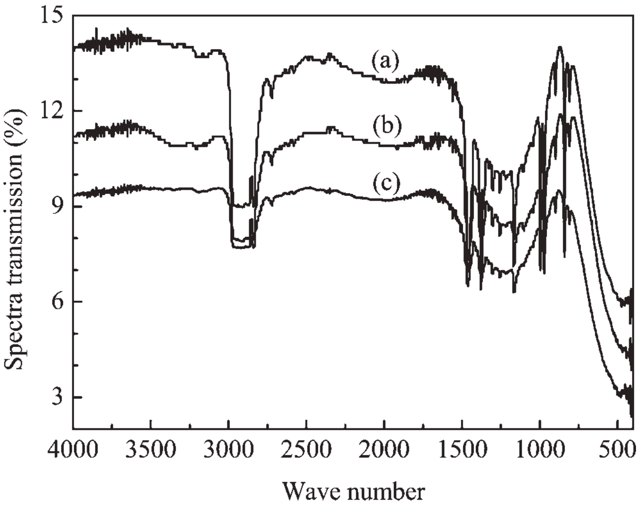

Figure 5 IR spectral transmissions for the (a) uncoated PP web, (b) PP web/PVA nanofibers, and (c) PP web/PVA nanofibers/Al coating.

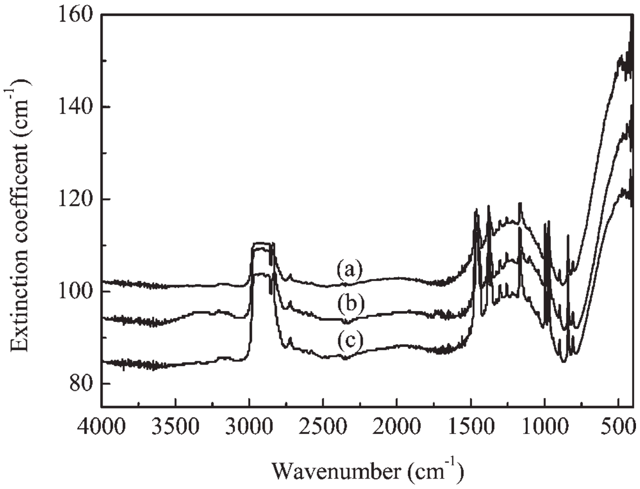

Figure 6 IR $\sigma_{e,\lambda}$'s for the (a) uncoated PP web, (b) PP web/PVA nanofibers, and (c) PP web/PVA nanofibers/Al coating.

nanofibers, although the aluminum coating had a much smaller thickness than the uncoated PP web. This was because even thin metal-coated fibers could efficiently scatter and absorb radiation because the coated fibers acted like little antennae for enhanced electrical conductivity.

To quantitatively compare the extinction coefficients of the three samples with or without nanofibers or the aluminum coating, an apparent Rosseland mean extinction coefficient ($\sigma_{e,R}$) was introduced. The apparent Rosseland mean extinction was determined with the Rosseland approximation:[28]

$$\frac{1}{\sigma_{e,R}} = \int_0^\infty \frac{1}{\sigma_{e,\lambda}} \frac{\partial e_{b,\lambda}}{\partial e_b} d\lambda \tag{3}$$

where $e_{b,\lambda}$ is the spectral black body emissive power e_b is the black body emissive power, and λ is wavelength.

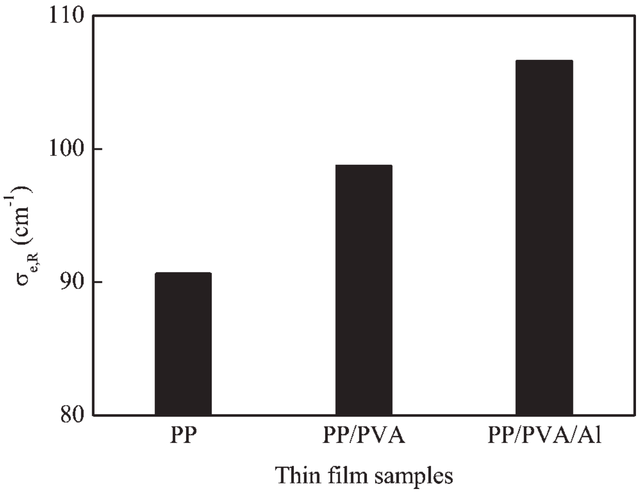

Figure 7 $\sigma_{e,R}$'s for the thin film samples.

TABLE I
WVTR for Three Different Films

Sample	WVTR (g of $H_2O/m^2/h$)
PP web	33.24
PP web/PVA nanofibers	35.27
PP web/PVA nanofibers/ aluminum coating	33.73

The determined results of the $\sigma_{e,R}$'s for the three different samples are illustrated in Figure 7. As shown in Figure 7, $\sigma_{e,R}$ of the uncoated PP web without electrospun nanofibers or the metal coating was 90.6 cm^{-1}, compared to 98.7 and 106.6 cm^{-1} for the PP web/PVA nanofibers and PP web/PVA nanofibers/Al coating assembly, respectively. A significant increase of approximately 18% in $\sigma_{e,R}$, without noticeable weight gain, was achieved for the novel fabricated PP web/PVA nanofiber/Al coating hybrid layered assembly compared to the control PP webs. These results indicate that the use of aluminum-coated nanofibers may provide an effective means of improving the thermal radiation extinction for thermal insulation systems without a noticeable weight gain. Better extinction coefficients can be expected through the optimization of the diameters of the supporting polymer fibers and electrospun nanofibers and the thickness of the aluminum coating.

The WVTRs of the three samples with or without the nanofibers or metal coating are listed in Table I. The novel fabricated PP/PVA/Al hybrid layered assembly had very similar WVTRs to the uncoated PP web. This behavior was expected because the metal coating was deposited on the nanofibers rather than on the PP web, so the porous structure of the system was unaffected. High moisture permeability is advantageous for applications in cold-weather clothing, sleeping bags, and construction because the accumulation of water vapor will result in a great decrease of the thermal insulation performance. With regard to the significant improvement in extinction thermal radiation with little weight gain or blockage of water vapor transmission, the novel fabricated hybrid layered assembly based on aluminum-coated PVA nanofibers supported on a conventional PP web can be expected to be widely applied in high-performance, thermal resistant, moisture-permeable systems for extremely cold environments.

CONCLUSIONS

A novel hybrid layered assembly composed of aluminum-coated PVA nanofibers supported on a PP web was successfully fabricated. The field emission SEM and TEM characterizations revealed that PVA nanofibers approximately 430 nm in diameter and an aluminum layer approximately 37 nm thick were embedded onto the supporting PP web. The measurements of the directional–directional FTIR spectra and WVTR exhibited a significant increase of approximately 18% in $\sigma_{e,R}$ due to both the radiation reflection of the metal coating and the radiation absorption of nanofibers, whereas the water vapor permeability was similar compared to the uncoated PP web. This novel fabricated hybrid layered materials is expected to be highly beneficial for the reduction of thermal radiation transfer in low-density fibrous insulation without noticeable weight gain or a decrease in water vapor permeability for wide applications, such as protective clothing, sleeping bags, building construction, and aircraft.

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