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Sorption of water vapor of EVAL/PAA blend nano-nonwovens modified by layer-by-layer technique

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ABSTRACT

Nonwovens composed of nanofibers of poly(ethylene-co-vinyl alcohol) (EVAL) blended with poly(acrylic acid) (PAA) were prepared by an electrospinning technique and then crosslinked by a heat treatment. A process for adsorbing alternating polyelectrolytes in solutions, termed the ''layer-by-layer (LBL) technique'', was used to coat the nanofibers in the nonwovens. A combination of electrolytes was used: poly(diallyldimethylammonium chloride) (PDDAC) was used as the cationic polymer and poly(sodium 4-styrenesulfonate) (PSSNa) was used as the anionic polymer for the polycation:polyanion combinations. The water content of the modified nanofiber nonwovens increased with the number of LBL treatments at various relative humidities.

Keywords: Electrospinning; Layer-by-layer; EVAL; Poly(acrylic acid); Water vapor sorption

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1. Introduction

Hydrogels are chemically and/or physically crosslinked three-dimensional networks of hydrophilic polymers that have the capacity to retain large volumes of water [1,2]. They consist of both hydrophilic and hydrophobic domains and can allow for the controlled release of bioactive molecules such as drugs, peptides, and proteins [3,4]. The properties of molecule release from the hydrogels depend on the water content of the hydrogels, whereas the water uptake of the hydrogels is determined by the balance between the hydrophilicity and crosslink density of hydrogels.

It is thought that water exists in different states in the hydrogels. There exists water that freezes at a sub-zero temperature, and there also exists water that cannot freeze because of its strong interactions with polar groups. The former is called free water and the latter is called hydration water [5]. Usually, when there is a high level of water uptake, the ratio of free water to hydration water is increased and the mechanical stability of the hydrogel is significantly decreased. For the interaction between the hydrogels and the solute, it is important to maintain a high ratio of hydrated water while allowing a high water content.

Using a pore-filling method, where hydrophilic monomers or polyelectrolytes are grafted inside the pores in porous membranes, is an effective means to raise the ratio of hydrated water to free water [6]. The swelling of the polyelectrolytes is restricted by the hydrophobic inside wall of the porous membrane. As a result, the uptake of the hydration water, and not free water in the membrane increases.

In this study, considering that a nonwoven fabric is a porous material, the gaps between the fibers of a poly(ethylene-co-vinyl alcohol) (EVAL or EVOH)/poly(acrylic acid) (PAA) blend nonwoven were filled up with a polyelectrolyte complex by a layer-by-layer

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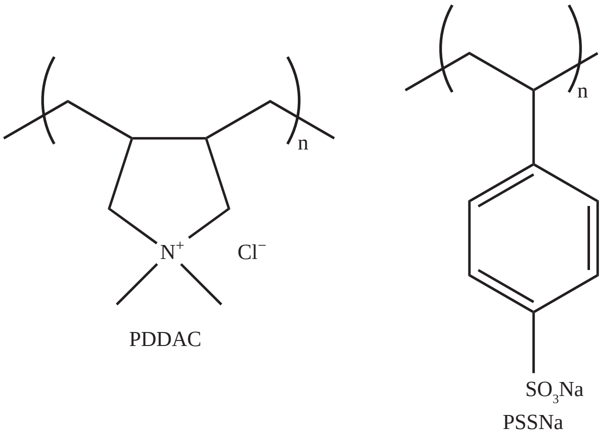


Fig. 1. Polyelectrolytes used.

(LBL) treatment to prepare a novel hydrogel structure. This self-assembly technique based on alternative adsorption of oppositely charged polyelectrolytes allows the construction of a charged multilayer on a base surface [7]. EVAL and PAA were blended to introduce a binding site for the LBL treatment. An electrospinning technique was employed to produce polymer nanofiber nonwovens with a high air gap ratio and a high surface area [8,9]. The ultrathin fibers, termed ''nanofibers'', possessed diameters less than 1000 nm. The nanofiber nonwovens can be used in a broad range of applications, such as separation membranes [10], hydrogels [11], and fuel cell membranes [12]. The sorption of water vapor onto the prepared nanofiber nonwoven, for both water at various relative humidities and liquid water, were studied. The effect of the LBL treatment on the level of water uptake was discussed.

2. Experimental

2.1. Materials

EVAL was kindly provided by Kuraray Co. Ltd. PAA, *N*-methyl-2-pyrrolidone (NMP) and isopropyl alcohol were purchased from Wako Pure Chemical Industries, Ltd. The chemical structures of the polyelectrolytes used in the experiments are shown in Fig. 1. Poly(diallyldimethylammonium chloride) (PDDAC) and poly(sodium 4-styrenesulfonate) (PSSNa) were obtained commercially from Aldrich. These molecules were used without any further purification.

2.2. Fabrication of nanofiber nonwovens

2.2.1. Preparation of polymer solutions

8 wt.% solutions of EVAL and PAA were prepared separately. A 70/30% (v/v) 2-propanol/water solution was made using distilled water to produce a solvent mixture to dissolve the polymers [13]. Both the EVAL pellets and the PAA powder were completely dissolved in the solvent mixture by heating the solution to 80°C. After the dissolution of each polymer, the two polymer solutions were mixed in the range of blend ratio from 0:10 to 10:0 (EVAL:PAA).

2.2.2. Electrospinning

The electrospinning set-up utilized in this study consists of a syringe and blunt-end needle, a grounding electrode (stainless steel sheet on a drum where the rotation speed can be varied), and a high-voltage supply with a low current output (limited to a few μA). A positive voltage (approximately 12.5–37.0 kV) was applied to the polymer solution with the distance between the syringe tip and the target surface being ca. 12 cm. The other spinning conditions were as follows: solution flow rates were 0.05–0.10 mL min^{-1}; spinning chamber temperature was 25°C; and relative humidity was below 15% RH. The resulting fibers were collected on a rotating metal drum to produce a sheet of nonwoven fabric.

2.2.3. Heat treatment of nonwovens

The nonwovens were heat treated at 50–150°C in a dry oven and a vacuum dry oven to crosslink the hydroxyl group of EVAL with the carbonyl group of PAA.

2.3. Characterization of nonwovens

2.3.1. Scanning electron microscopy (SEM)

After the electrospun nonwovens were dried, they were sputter-coated with gold (Au). SEM of the morphologies of the nonwovens was performed on a HITACHI S-300N (HITACHI) electron microscope at an acceleration voltage of 20 kV.

2.3.2. Dilation and weight loss in NMP

In order to investigate the effect of heat treatment, dilation of the nonwoven in 2D directions and weight loss were measured after swelling the nonwoven in NMP, which is considered to be a good solvent for EVAL. The dilation rate was calculated from the area of dilation, S_d, and the initial area, S_i, as follows:

$$\text{Dilation rate}[\%] = (S_\text{d}/S_\text{i})100. \tag{1}$$

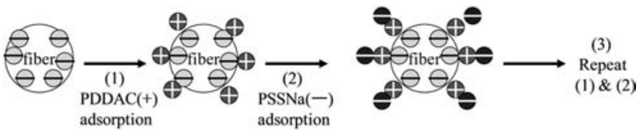


Fig. 2. Schematic diagram illustrating the preparation of the hydrophilic surfaces via LBL coating.

Weight loss was calculated from the initial weight, W_{int}, and the dried weight of nonwoven after extraction from the NMP, W_{ext}, as follows:

$$\text{Weight loss}[\%] = (1 - W_{ext}/W_{int})100. \qquad (2)$$

2.3.3. IR spectroscopy

The IR spectra of the nonwovens before and after the heat-treatment were obtained using an ATR method (attenuated total reflection), and by collecting and averaging 32 scans, at a resolution of 8 cm^{-1}.

2.4. LBL coating of nonwovens

The EVAL/PAA nanofiber nonwoven has sites with negative charge. This is because the LBL structured bilayers were assembled on the EVAL/PAA blend nanofiber surface by alternating adsorption of a positively charged polyelectrolyte, such as PDDAC, and a negatively charged polyelectrolyte, such as PSSNa. The modified nanofiber nonwoven was placed with a filter paper on a separable Buchner type glass funnel. After passing pure water through the funnel to condition the nonwoven, a 1.0×10^{-2} mol dm^{-3} PDDAC solution was passed through the funnel for the adsorption of the positively charged layer. A large amount of pure water was then passed through the funnel to remove the excess polymer solution. Next, for the adsorption of negatively charged layer, a 1.0×10^{-2} mol dm^{-3} PSSNa solution was passed through the funnel before a large amount of pure water was passed in the funnel again to remove the excess polymer solution (see Fig. 2). The adsorption and removal steps were repeated until 0, 2, 4, and 8 bilayers of PDDAC/PSSNa were obtained. The LBL-treated nonwovens were dried for 24 h at 50°C in a vacuum oven to remove the solvent.

2.5. Water vapor sorption of modified nonwovens

The water sorption of the prepared LBL-structured nonwovens was determined using saturation salting methods at 25°C. Potassium chloride (84% RH), sodium chloride (75% RH), sodium bromide (58% RH), and magnesium nitrate (53% RH) were used in this study. The water vapor sorption was calculated from the weights in the wet state, W_w, and in the dry state, W_d, using the following equation

$$\text{Water vaporsorption} = (W_w/W_d)100. \qquad (3)$$

The water uptake of the LBL-structured nonwovens was measured as follows. Nonwovens were weighed in the dry state and then immersed in pure water at 25°C for 24 h. Nonwovens were then removed from the water, tapped with filter paper to remove the excess water on the nonwoven surface, and then weighed in a wet state. Water uptake was calculated from the weights in the wet state, W_w, and in the dry state, W_d, using the following equation:

$$\text{Water uptake}[\%] = (W_w/W_d)100. \qquad (4)$$

3. Results and discussion

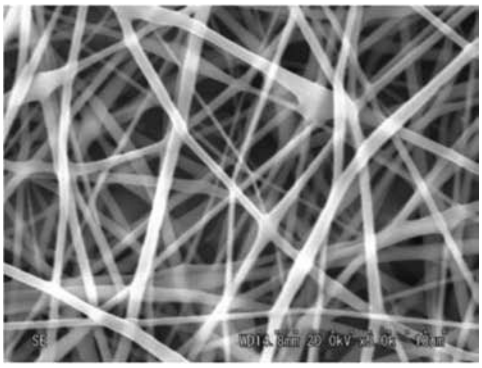
3.1. Electrospinning of EVAL/PAA

Fig. 3 shows SEM images of the spun nonwovens with different blend ratios of EVAL and PAA. The sample names are abbreviated for their blend ratios, for example, EP 64 means that the blend ratio of EVAL to PAA was 6:4. The SEM images indicate that the average fiber diameter of the electrospun samples decreases with an increase in the PAA concentration. The average fiber diameters and spinning productivities are summarized in Table 1. The average fiber diameter decreased from 740 to 98 nm with an increasing PAA blend ratio. Sample EP 100 possessed sharp and smooth fibers (Fig. 3a), while the amount of beaded fibers increased with PAA content (Fig. 3c). Finally, only beads were formed from a pure PAA solution (Fig. 3d), which resulted in a lack of chain entanglement, exhibited by the low average molecular weight (Mw = 25,000) of the PAA used in this study. EP 64 was the most stable for spinning productivity.

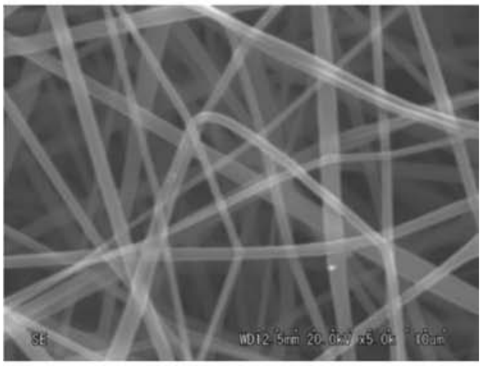
3.2. Heat-treated nonwovens

3.2.3. SEM

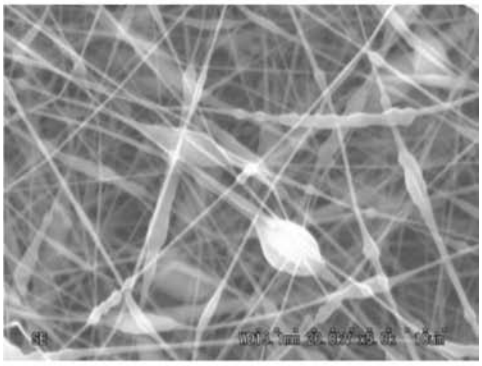
For the hydrogel application of the as-spun blend nonwoven, the PAA component of the nonwoven dissolves into water because PAA is a water-soluble polymer. Therefore, it is necessary to immobilize the PAA component to the nonwoven chemically or physically. Heat treatment to produce an ester bond by a reaction between the hydroxyl group on EVAL with the carboxylic acid on PAA was examined. Fig. 4 shows SEM images of the EP 64 nonwovens before and after heat



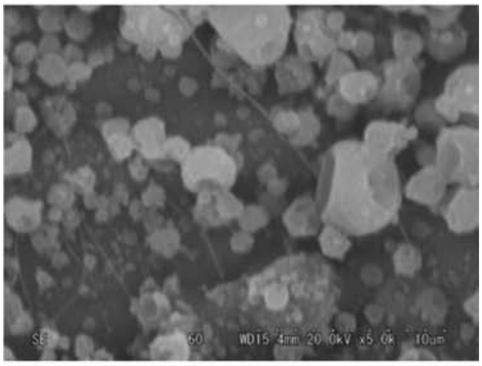
(a) EP 100



(b) EP 64



(c) EP 55



(d) EP 010

Fig. 3. SEM images of as-spun nonwovens.

Table 1
Average fiber diameter and spinning productivity in this study

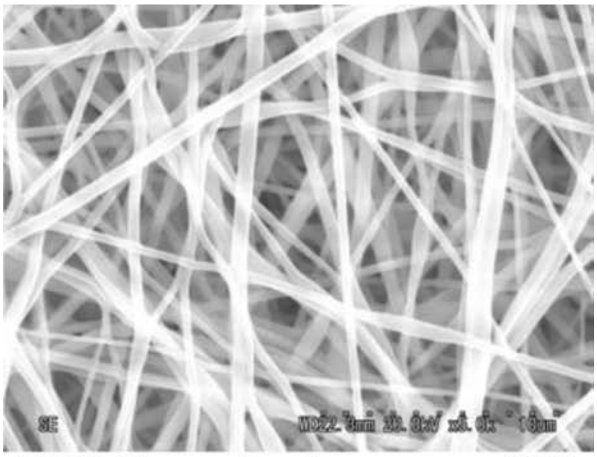
Sample	EVAL:PPA (blend ratio)	Average fiber diameter (nm)	Spinning productivity
EP 100	10:0	740 ± 304	▲
EP 91	9:1	675 ± 186	△
EP 82	8:2	609 ± 212	△
EP 73	7:3	495 ± 235	○
EP 64	6:4	450 ± 167	◎
EP 55	5:5	205 ± 95	○
EP 46	4:6	310 ± 84	△
EP 37	3:7	200 ± 94	△
EP 28	2:8	140 ± 65	△
EP 10	1:9	98 ± 48	▲
EP 010	0:10	Bead form	▲

treatment. Although the nonwovens were pressed between Teflon plates during heat treatment, the shape of the fibers only flattened slightly (Figs. 4a and b). However when the nonwoven was heated at 150°C, the fibers were melted and the nonwoven became a porous film (Fig. 4c).

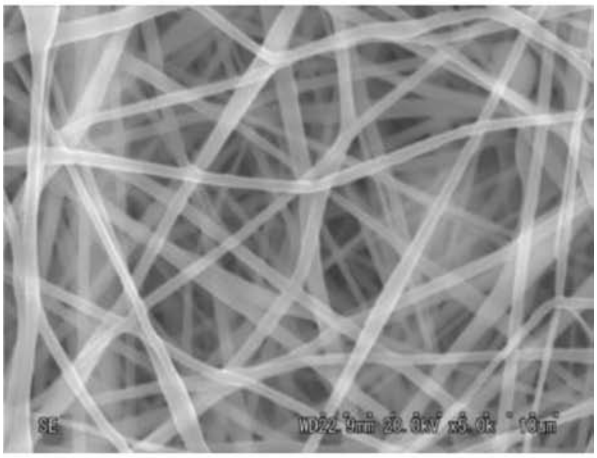
3.2.4. Crosslink of nonwovens

Figs. 5 and 6 show the dependence of the dilation rate on both the temperature and blend ratio of nonwovens in NMP, respectively. The samples heat-treated at temperatures below 80°C were completely dissolved in NMP. The EP 91 and EP 37 samples treated at 90°C were also dissolved in NMP. We believe that the crosslinking reaction did not occur, or that the reaction did not progress. Except for the heat treatments at over 130°C in air, the heat treatment temperature had the same results when conducted under a vacuum and at atmospheric pressure. The dilation rate of the nonwoven decreased with increase in the heat-treatment temperature, while the color of the nonwovens changed from white to yellow for the heat treatments over 130°C in air. The dilation rate decreased with an increase in the PAA content, and the effect of the blend ratio on the dilation rate was more pronounced at lower heat treatment temperatures. This suggests that the degree of crosslinking is controlled by the heat-treatment temperature and the addition of PAA.

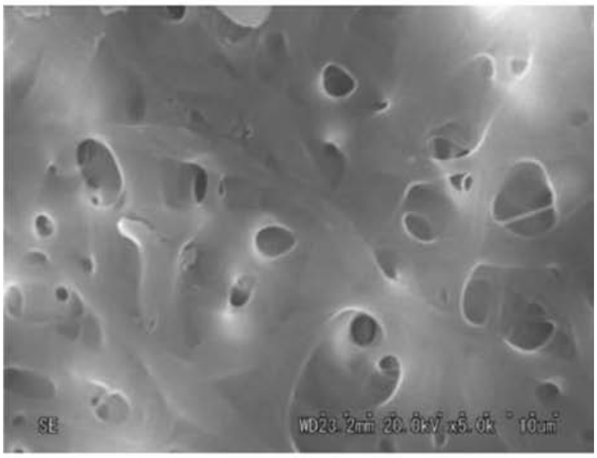
Figs. 7 and 8 show the weight loss of nonwovens in NMP. The weight loss results exhibited the same trends as those of the dilation rate, which indicated that the blend nanofibers were insolubilized by a crosslink reaction between EVAL and PAA. Fig. 9 shows the IR spectra of the nonwoven before and after heat treatment. The peak at 1,710 cm^{-1} shifted to high



(a) EP 64 treated under vacuum at 90°C



(b) EP 64 treated in air at 90°C



(c) EP 64 treated under vacuum at 150°C

Fig. 4. SEM images of heat-treated nonwovens.

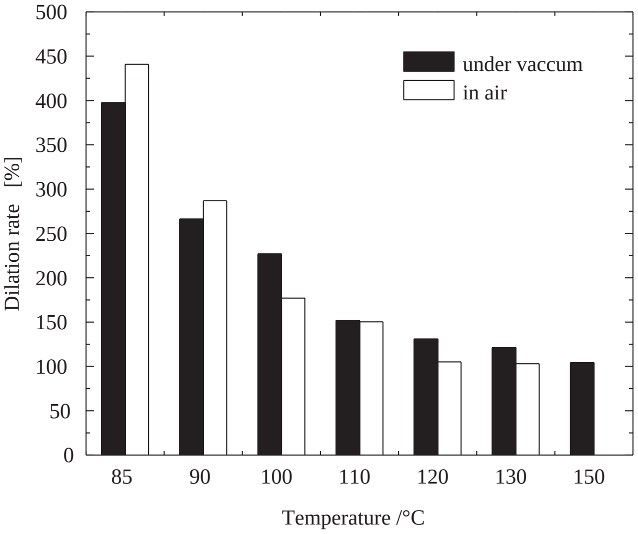


Fig. 5. Temperature-dependence of the dilation rate of EP64 nonwovens in NMP.

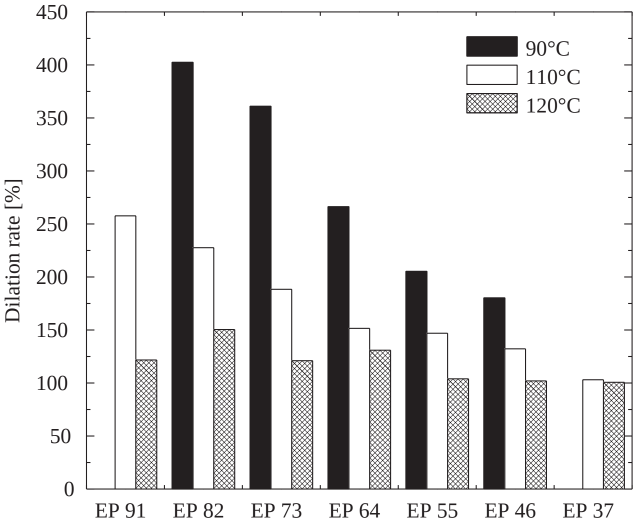


Fig. 6. Effect of blend ratio (EVAL/PAA) of nonwovens in NMP.

wavenumbers with an increase in the heat-treatment temperatures. This peak shift implies that esterification occurs due to the heat treatment [14]. This result is also supported by the variation of the dilation rate and weight loss with varying temperatures. From the above results, the EP 64 nonwoven heat-treated at 90°C under vacuum was selected for LBL coating because this sample has both high electrospinning productivity and sufficient ionic binding sites, such as that on the carboxylic acid group.

3.3. *LBL coating of nonwovens*

Fig. 10 presents the SEM images of the LBL-coated EVAL/PAA nonwovens with various numbers of bilayers of PDDAC/PSSNa. The average diameter of

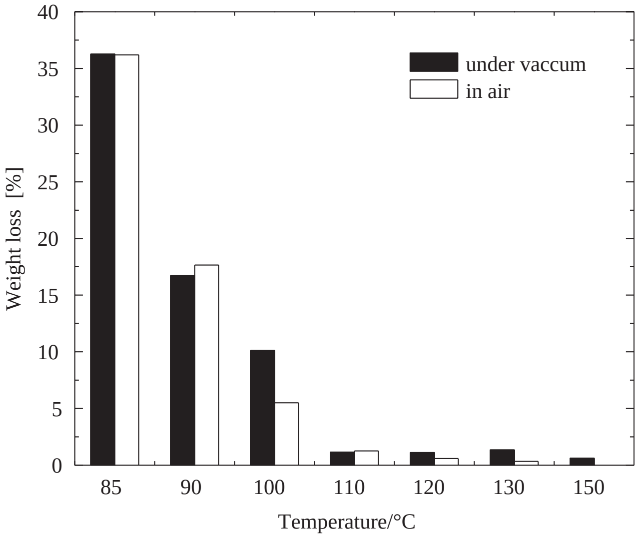


Fig. 7. Influence of heat-treatment temperature on weight loss of EP64 nonwovens.

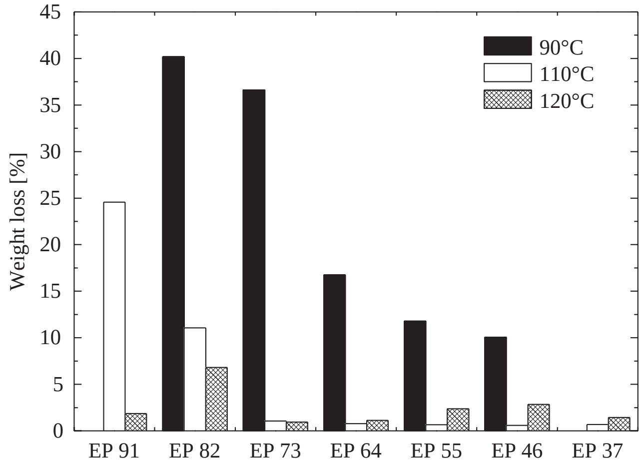


Fig. 8. Influence of blend ratio (EVAL/PAA) on weight loss of nonwovens.

the fibers with the LBL coating was larger than that of the uncoated EVAL/PAA blend nonwovens due to the additional coating of the PDDAC/PSSNa bilayers. It can be seen that the average fiber diameter increased with an increasing number of deposited bilayers. The LBL treatment also changed the surface of the fibers from smooth to rough, which is a result of the polyelectrolytes being adsorbed onto fiber surface. From the SEM images in Figs. 10a and b, the coating appeared to have covered the fiber completely. The nonwoven coated eight times by the LBL coating (Fig. 10c) did not maintain the fiber shape. The PDDAC/PSSNa coatings formed not only on the surface of fibers, but also filled in the air gaps between nanofibers. The EVAL/PAA blend fibers were embedded in the PDDAC/PSSNa coatings and we speculate that the LBL coating had grown to become a 3-dimensional structure between the fibers [15].

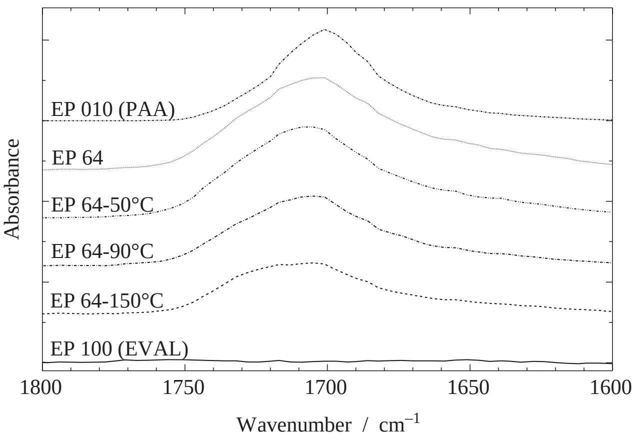


Fig. 9. IR spectra of nonwovens before and after heat-treatment.

3.4. Water content

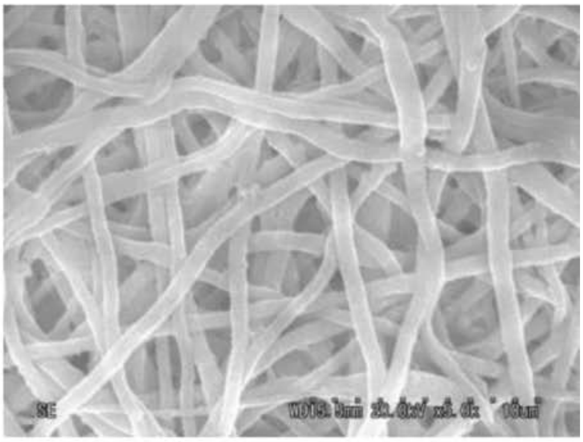
3.4.1. Water vapor sorption of nonwovens

Fig. 11 presents the water sorption of the EVAL/PAA nonwovens coated by LBL with various numbers of bilayers of PDDAC/PSSNa at various relative humidities. The water content increased with the increasing numbers of LBL treatments. This tendency was more pronounced at higher relative humidities. The PDDAC/PSSNa-coated EVAL/PAA nonwovens exhibited a higher degree of hydrophilicity than the uncoated EVAL/PAA blend nonwovens. The water vapor sorption of the nonwoven was enhanced by the LBL coating due to the hydrophilicity of the polyelectrolytes, such as PDDAC and PSSNa.

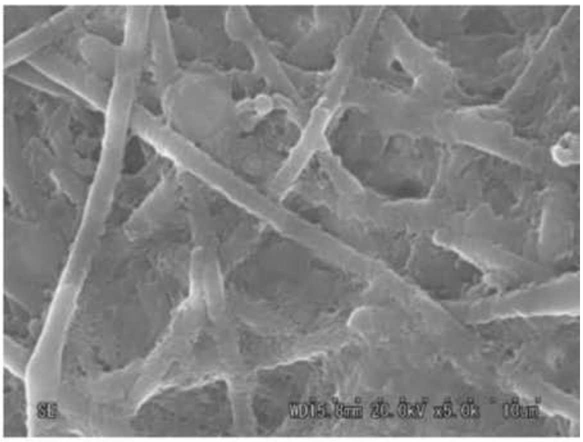
3.4.2. Liquid water uptake of nonwovens

Fig. 12 presents the water uptake of the PDDAC/PSSNa-coated EVAL/PAA nonwovens in liquid water. Little difference was observed in the water content of all the samples since the air gaps inside the nonwoven were filled by polyelectrolytes during the LBL treatment. The EP 100 nonwoven had the largest air gaps between its nanofibers and absorbed liquid water like a sponge while for the LBL-coated samples, the layer of polyelectrolytes on the surface of the nanofiber sorbed the water. For the EP 64 samples treated by LBL, the nonwovens with four LBL treatments showed the highest water content while the sample with eight LBL treatments exhibited a decreased level of water content. This indicated that the LBL treatment enhanced

(a) EP 64; LBL 2 times



(b) EP 64; LBL 4 times



(c) EP 64; LBL 8 times

Fig. 10. SEM images of LBL-treated nonwovens.

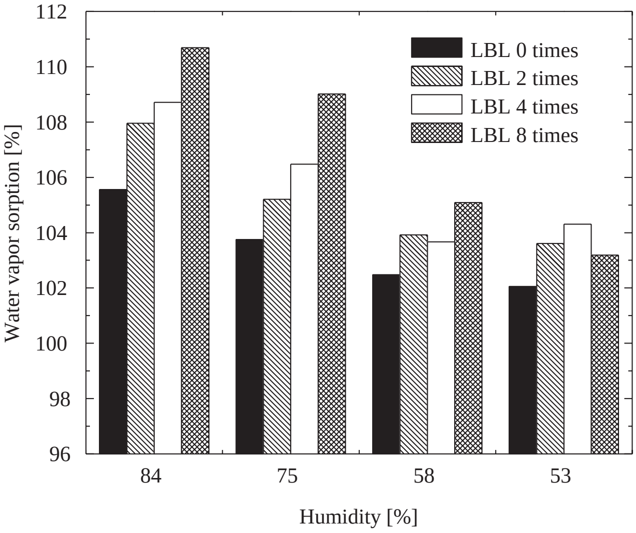


Fig. 11. Water vapor sorption of nonwovens at various relative humidities.

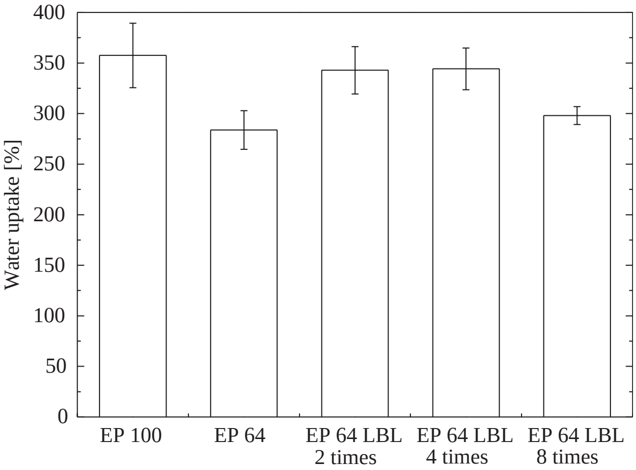


Fig. 12. Water uptake of the nonwovens in water.

the hydrophilicity of the nanofibers and the wettability of the nanofiber surface, while it decreased the water uptake in the air gaps. The air gaps of nonwovens with eight LBL treatments disappeared due to the LBL treatment. The water content of the nonwovens with eight LBL treatments depended on the hydration of the polyelectrolyte multilayers. We believe that the sorption mechanism of water is different for the porous as-spun nonwoven and the LBL-coated nonwoven. The balance between water sorption in the nanofibers coated by the polyelectrolytes (PDDAC and PSSNa) and water uptake in air gaps is important for the enhancement of water content in the LBL-treated blended nanofiber nonwovens.

4. Conclusions

The EVAL/PAA blend nanofiber nonwovens were prepared by an electrospinning method. The average fiber diameter and spinning productivity were controlled by the addition of PAA. The degree of crosslinking was controlled by the heat-treatment temperature and the addition of PAA. A blend ratio of EVAL:PAA = 6:4 and a heat-treatment temperature of 90°C were the optimal conditions, since this sample had a high spinning productivity and a large amount of free binding sites (carboxyl groups) after heat treatment.

The high water content of the blended nanofiber nonwovens modified by a LBL technique was maintained by the hydrophilic polyelectrolyte coating layer. The air gaps between the nanofibers in the nonwovens were filled by the polyelectrolytes PDDAC and PSSNa. Growing layers of both PDDAC and PSSNa by LBL treatment enhanced the hydrophilicity of the nanofibers and the wettability of the nanofiber surface, while it decreased water uptake in the air gaps. The balance between water sorption in nanofibers coated by polyelectrolytes (PDDAC and PSSNa) and water uptake in air gaps is important for the enhancement of water content in the LBL-treated blended nanofiber nonwovens.

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Symbols

S_d	Area of nonwoven after swelling in NMP, cm^2
S_i	Initial area of nonwoven, cm^2
W_{int}	initial weight of nonwoven, g
W_{ext}	dried weight of nonwoven after extraction in NMP, g
W_d	weight of nonwoven in the dry state, g
W_w	weight of nonwoven in the wet state, g

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