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The transport properties of polymer membrane-fabric composites

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Breathable waterproof fabrics used in this study were prepared by polyurethane coating and polytetrafluoroethylene (PTFE) laminating processes. Outer garments manufactured from these materials can improve wearer comfort by increasing the transport properties of the fabrics. Water vapor permeability, water resistance, water repellency, air permeability, and the other characteristics were measured to evaluate the changes of transport properties with various finishing methods. In the case of the coated fabrics, wet coating A type had high water vapor permeability and low waterproof value, but dry coating A type showed opposite results. Air permeability at low pressure and airflow rate with differential pressure up to 350 kPa were different according to finishing methods. Significant differences in transport properties appeared as the coating methods or amounts of coating solution added to base fabrics were changed. Water vapor permeability and air permeability decreased, and water resistance increased with the amount of coating dope. On the other hand, the transport properties of laminated fabrics were relatively uniform regardless of two or three layers although some tactile properties might have been changed with laminated layers.

1. Introduction

Human beings rely on the evaporation of sweat to remain comfortable and prevent overheating in hot environments and during exercise. In some situation, the evaporation rate from wet skin is less than the rate of sweat secretion. So accumulated water vapor may condense inside the inner clothing of a wearer undertaking arduous exercise in a cold and wet climate. Perspiration-soaked clothing loses much of its insulative value and the wearer thus bears an increased risk of body chill or even hypothermia, when he ceases activity. This condensation problem is particularly acute in the popular garments manufactured from coated and laminated fabrics because the standard polymers have generally low water vapor permeability [1, 2]. The perception of discomfort in the active case depends on the degree of skin wetness due to perspiration, and how long the wetness persists after activity stops. Therefore, liquid water transport in fabrics plays an extremely important role in garment comfort [3]. Especially, the ability of an outerwear fabric to transmit water vapor emitted from the body as insensible perspiration and evaporated sweat is an important factor in assessing the comfort of clothing assemblies.

It is generally known that breathable fabrics easily transport water vapor through the fabric structure while they have resistance to the passage of water [4]. The principle of this particular function is the enormous difference in size between water vapor molecules (approximately 0.4 nm in diameter) and rain droplets which usually exceed 100 μm in diameter [2, 5]. These materials are classified roughly into three types: (a) high yarn count and closely woven fabrics made of fine fibers combined with water repellent treatment and calendering, (b) microporous membrane laminated fabrics, and (c) resin-coated fabrics with a microporous layer. In these materials, it is very important to keep the comfortable microclimate inside the clothing for the active sportswear, and this function can be promoted by increasing the transport properties of fabrics.

The transport properties of water and moisture through fabrics have been discussed from various points of view. Woodcock [6] developed the moisture permeability index, and allowed to predict the ranges of environment and metabolic activity in which thermal equilibrium can be maintained, and replaced the single environmental temperature or heat loss given by the older clo formula of Gagge *et al*. [7]. The clo is a useful clothing insulation unit and a clo value of 1.0 is the insulating value of the ordinary man's suit ensemble warn at spring weather (21°C, 50% RH). Mechanisms of moisture transport at various levels of moisture content were investigated [8], and the contribution of fiber surface properties and fabric pore structure to liquid transport and retention phenomena were discussed. The significance of them with wetting and transport properties of fabrics was confirmed [9]. Recently, the introduction of the comfort is important in many fields of clothing

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and textiles, so the relationship between these transport properties and comfort properties have been considered [3, 10, 11].

In this study, various characteristics of breathable waterproof fabrics were measured to evaluate the changes of transport properties with various breathable waterproof finishings, and these changes were analyzed with many parameters of fabric construction and finishing methods. Furthermore, the correlation among the characteristic values was investigated and the database for manufacturing more comfortable and efficient breathable waterproof fabrics was made.

2. Experimental

2.1. Materials

The specimens used in this study were prepared by coating and laminating processes, and classified according to the coagulation method, shape of knife, and the number of laminating layer. Table I shows the classification and the characteristics of the materials used in this study. The coated fabrics were manufactured by direct coating with polyurethane. The breathable waterproof properties of the fabrics were obtained by micro-porous structure through wet- or dry-coagulation process except A type in dry coating, which was manufactured by the combination of hydrophilic and hydrophobic polyols with diisocyanate components to produce optimum moisture vapor transmission properties. It showed no evidence of voids or microporous structure [12, 13].

The laminated fabrics were prepared by 2-and 3-layer laminating with base fabric, poly (tetrafluoroethylene) (PTFE) membrane and knitted lining. The functional component of these laminates was a thin and micro-porous membrane made from solid PTFE sheet by a novel drawing and annealing process [14]. The unfinished fabrics were also used to compare with finished ones in this study.

2.2. Weight, thickness, and microstructure of membrane

The weight in mass per unit area was measured before and after finishing, and then the weight increase upon coating or laminating process was calculated. Thickness was measured with KES-FB3 compression tester at 49.03 Pa. The surface of coated and laminated fabrics was observed using a Scanning Electron Microscope (JSM-5400, Japan), and the samples were coated in conventional manner with a thin layer of gold palladium to prevent charging.

2.3. Measurement of water transport properties

Water vapor permeability was measured by the permeation cup method (JIS 1099 A-2) to determine the transport property of water vapor emitted from the body, and it was calculated by the following equation.

$$\text{Degree of water vapor permeability (g/m}^2\text{/day)} = \frac{(a_2 - a_1)}{S} \times 2.4 \quad (1)$$

where, a_2-a_1: weight changes of permeation cup with the specimen and water per 1hour (mg/h), S: area of permeation (mm^2).

TABLE I Characteristics of the specimens

No.	Construction of base fabric				
	Fiber contents	Yarn count (denier)	Fabric count (warp × filling/m)	Thickness (mm)	Weight (g/m^2)
WA[a] 1	Nylon	80 × 80	5197 × 4016	0.28	83.6
WA 2	Nylon	70 × 70	4961 × 3504	0.14	66.9
WA 3	Nylon	70 × 320	8425 × 2598	0.54	166.8
WB[b] 1	Nylon	70 × 140	6654 × 2677	0.32	119.1
WB 2	Nylon	70 × 320	5827 × 2047	0.52	124.5
WB 3	Nylon	140 × 200	2992 × 1890	0.41	105.8
WB 4	Nylon	210 × 200	2480 × 2047	0.19	98.2
DA[c] 1	Nylon	70 × 160	4567 × 2992	0.29	89.4
DA 2	Nylon	70 × 320	5827 × 2047	0.52	124.5
DA 3	Nylon	400 × 470	2283 × 1378	0.63	173.0
DB[d] 1	Nylon	70 × 160	4449 × 2835	0.53	108.0
DB 2	Nylon	70 × 320	5472 × 2165	0.53	134.3
DB 3	Nylon	70 × 160	6496 × 2756	0.25	96.9
DB 4	Nylon	400 × 470	2283 × 1378	0.63	173.0
2L[e] 1	Nylon	70 × 70	3819 × 3701	0.23	81.1
2L 2	Nylon	70 × 144	4646 × 2677	0.36	95.5
2L 3	Nylon	380 × 150	2402 × 2323	0.37	135.3
2L 4	Nylon	80 × 240	5354 × 2165	0.47	143.2
3L[f] 1	Nylon	70 × 70	3819 × 3701	0.28	98.0
3L 2	Nylon	80 × 84	4724 × 3819	0.24	95.9
3L 3	Nylon	80 × 200	4291 × 2756	0.29	104.0
3L 4	Nylon	70 × 140	4331 × 3071	0.28	107.2

[a]WA: wet coating/floating knife type.
[b]WB: wet coating/roll over knife type.
[c]DA: dry coating/floating knife type.
[d]DB: dry coating/roll over knife type.
[e]2L: base fabric/PTFE membrane.
[f]3L: base fabric/PTFE membrane/knitted lining.

Measurement of waterproofing was carried out on hydrostatic head tester of Mullen type with high range of water pressure in accordance with ASTM D 751. In hydrostatic head test, one face of the fabric is in contact with water which is subjected to a steadily increasing pressure until water penetrates the fabric. The values of the pressure at the appearance of the third water drop through the fabric were recorded.

Water repellency was estimated by the contact angle between the fabric surface and certain liquid drop, and showed the degree of liquid splash on fabric surface. This test was carried out using contact angle meter in accordance with ASTM D 5725 at standard condition, and the distilled water (surface tension 76 mN/m) was used as the test liquid.

2.4. Measurement of air permeability properties

Air permeability was measured with Automated Perm Porometer APP-1200A in accordance with ASTM D 737. We determined the airflow rate and resistivity with increasing pressure, and the Frazier analysis was also made [15]. This method determines the volume of air that can penetrate through a textile with a pressure differential of 125 Pa.

3. Results and discussion

3.1. Pore structure

The microstructure of the membrane was observed to analyze the relationship between the transport properties and pore structure of the membrane. The SEM photographs of breathable waterproof fabrics manufactured by coating processes are shown in Fig. 1. There were some differences in microstructure according to the finishing methods. In the case of most breathable waterproof fabrics, the surfaces of the microporous barrier are interconnected by a vast network of holes and passage ways. In wet-coagulation process, the solvent used to dissolve polyurethane could be replaced by water from the water-side surface in coagulation bath, so the pore structure was formed in membrane. On the other hand, in dry coated fabrics, the pore structure was formed by volatile solvent in dry coagulation process. But the specimens manufactured by dry coating-A method had unique morphology, which showed no evidence of voids or microporous structure, but they had water vapor permeability by absorption-diffusion-desorption mechanism.

The functional component of laminated fabrics was a thin and micro-porous membrane made from solid PTFE sheet. The film made from fine powder PTFE is stretched simultaneously in two directions at right angles near the melting point, and then annealed and

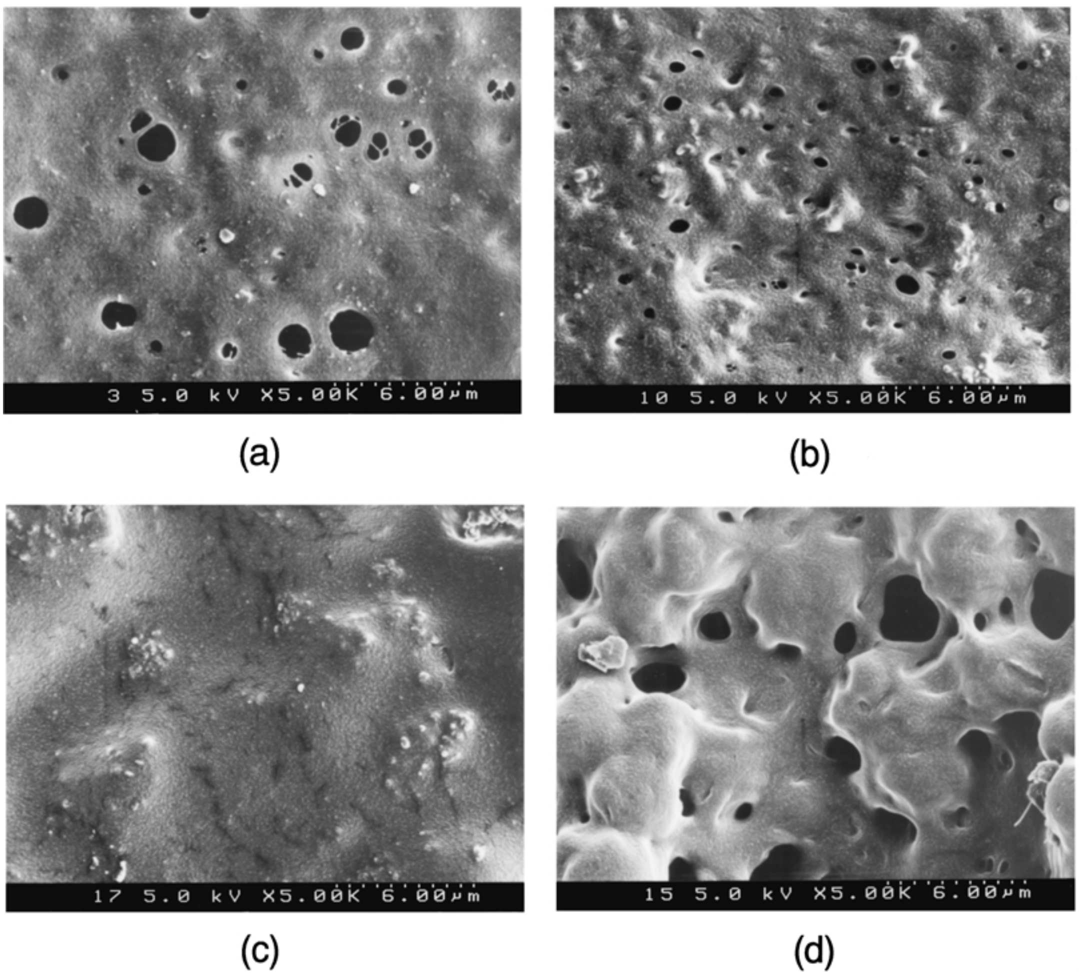

Figure 1 SEM photographs of the membrane surface with various breathable waterproof finishings (5,000×): (a) Wet coating A, (b) Wet coating B, (c) Dry coating A, and (d) Dry coating B.

TABLE II The constructive values and t-values before and after finishing

Characteristics	Finishing method	Mean values		T-values from paired t-test			
		Before	After				
Weight (g/m^2)	WA	105.76	116.97	−2.524			
	WB	111.90	156.94	−4.699[a]	−3.509[a]		
	DA	128.94	186.57	−14.680[b]			−7.285[c]
	DB	128.05	166.09	−8.122[b]	−9.454[c]		
	2L	113.78	144.62	−4.116[a]			
	3L	101.26	176.97	−23.038[c]		−5.737[c]	
Thickness (mm)	WA	0.315	0.266	2.805			
	WB	0.360	0.341	0.466	1.351		
	DA	0.479	0.389	1.457			2.828[a]
	DB	0.485	0.391	1.920	2.631[a]		
	2L	0.357	0.340	1.030			
	3L	0.270	0.467	−10.283[b]		−2.125	

[a] $p < 0.05$: significant at 0.05 level.
[b] $p < 0.01$: significant at 0.01 level.
[c] $p < 0.001$: significant at 0.001 level.

cooled rapidly [16]. Orientation at elevated temperature causes fibrillation and produces a matrix of particles bound together by the resulting fibrils.

3.2. Constructive properties

The constructive characteristic values were measured and the results were used for analyzing paired t-test, and Table II shows the mean and t-values with various breathable waterproof finishings. The weight of all specimens increased after finishing. The increase in weight showed some differences with coating methods (Table II), and the weight increases of dry coating A method were remarkably higher than those of any other coating processes because of the nonporous membrane. On the other hand, we confirmed that coating dope added to wet coating A type was relatively low, and it might affect the transport properties.

Thickness decreased with coating processes. It is due to the compactness of fabrics that is caused by penetration of coating solution into the fabric interstices during various coating processes. In order to achieve good mechanical adhesion of the coating to the smooth fabric surface, the polymer spreading solution must penetrate deep into the fabric interstices. There were not significant differences with coating processes in thickness, but this compactness of the fabrics would influence not only stiffness in mechanical properties, but also intrinsic transport performance of base fabrics. Laminated fabrics showed similar aspect with coated fabrics except for the case of 3-layered fabrics, which showed prominent increase in weight and thickness with attachment of the knitted lining. In the case of laminated fabrics, adhesive droplets were added between them in order to overcome the well-known 'non-stick' property. The low surface energy of this polymer makes it very difficult to bond their surfaces with other substrates, so this surface inertness makes fluoropolymers unsuitable for use in areas involving adhesive bonding. Any penetration of finishing dope did not occur compared with coating methods.

3.3. Water transport properties

Water vapor molecules are generally thought to travel through microporous membrane using the micro-pores incorporated into their structure, and the transport properties are affected by the driving force of water vapor. Fig. 2 shows the mean values of water vapor permeability with various finishings on breathable waterproof fabrics. Generally, in the case of coated fabrics, significant differences in water vapor permeability appeared as the coating methods and amounts of coating solution were changed. Those of wet coating-A and dry coating-B type were relatively high, but the dry coating-A type with non-porous membrane showed the lowest value. So these two methods would be appropriate when high moisture permeability is required, but the problems of waste water and air pollution also have to be considered, because the environmental issue has been growing. In dry coating A type, the molecular structures of those solid polymers have to be considered to know how they can transmit water vapor. All polymers consist of a series of long flexible chains held together in a three-dimensional network by weak attractive forces which may be reinforced by stronger chemical bonds. The serviceable temperature range of most flexible polymer

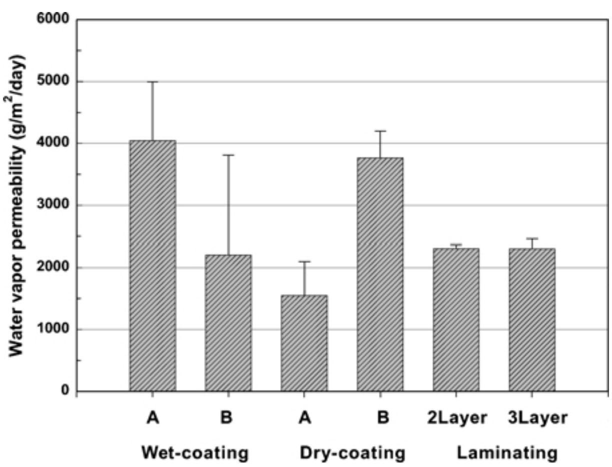

Figure 2 Water vapor permeability with various breathable waterproof finishings.

films and coatings lies well above their glass transition temperatures, so the molecular chains are in constant thermal motion and will tend to kink and fold randomly along their lengths. This chain movement prevents perfect close packing of the molecules, and very tiny holes or intermolecular pores are formed throughout the polymer structure. Intermolecular pores are much smaller than micropores and invisible even by scanning electron microscope because of the resolution limit of the SEM. Dry coated fabrics have some permeability although they are not susceptible to 'pumping through' effects observed with some microporous structures.

Water vapor permeability was in inverse proportion to the increase of coating dope. On the other hand, those values of laminated fabrics were very uniform regardless of whether two or three layers were used, because the functional component used in these laminated fabrics was the same material. Accordingly, in the coating processes, the proper water vapor permeability required by the consumer could be obtained by controlling the coating methods and the amount of coating dope.

Fig. 3 shows the variations of water resistance with breathable waterproof finishing. An area of concern for outdoor apparel and equipment manufacturers is the resistance of the outer fabric layer to water penetration. These water resistant fabrics provide the desired comfort of protecting the wearer from the penetration of water through the fabric. Microporous fabrics provide an effective solution to this problem. In the case of coated fabrics, the water resistance increased with the amount of coating dope in high correlation. Especially, dry coating A type of fabrics showed somewhat high resistance to water, because they are exceptionally impermeable to wind and rain although moisture permeability is not enough for comfortable materials. All of the laminated fabrics showed higher values than 98.07 kPa, which surpassed the values required in active sports wear.

If the fabrics were wetted by rain or water drop and the water layer was formed on the surface of the fabric, water vapor and air permeability might decrease. Therefore, water repellency was also a very important factor in breathable waterproof fabrics. In order to determine the relative hydrophilicity or hydrophobicity of the specimens, contact angle measurements were made

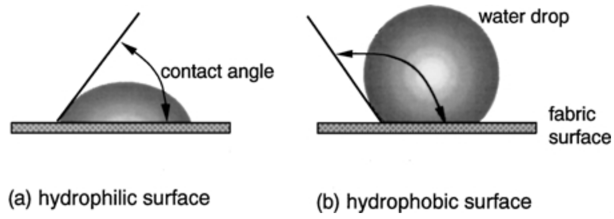

Figure 4 The behavior of water drop on fabric surfaces.

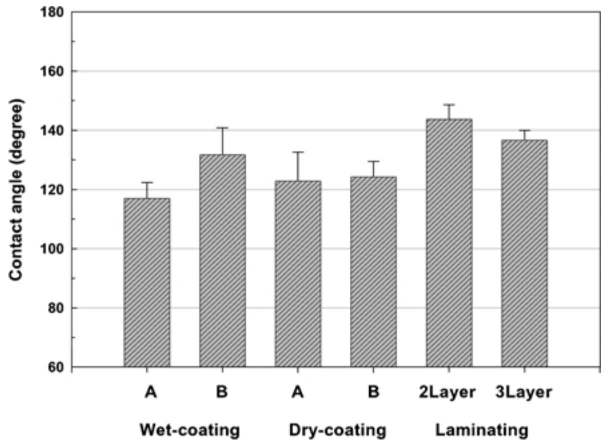

Figure 5 Contact angle between water drop and fabric surface with various breathable waterproof finishings.

with drops of pure water placed on the surface of the fabrics. Two examples are given in Fig. 4 to illustrate textiles exhibiting hydrophilic behavior, where the contact angle is less than 90 degrees, and hydrophobic behavior, where the contact angle is greater than 90 degrees. The results of water repellency are shown in Fig. 5. All of them were greater than 90 degrees. And the contact angle hysteresis, as evident by comparing the difference between advancing and receding contact angle measurements of liquid drops on the textile surfaces, did not occur, because liquids and solids did not chemically interact. Therefore, no water layer could be formed on the surface of the fabric, and water vapor permeability might be promoted. Any significance in different finishing methods was not shown in water repellency, but surface treatment of the base fabric was related to the performance.

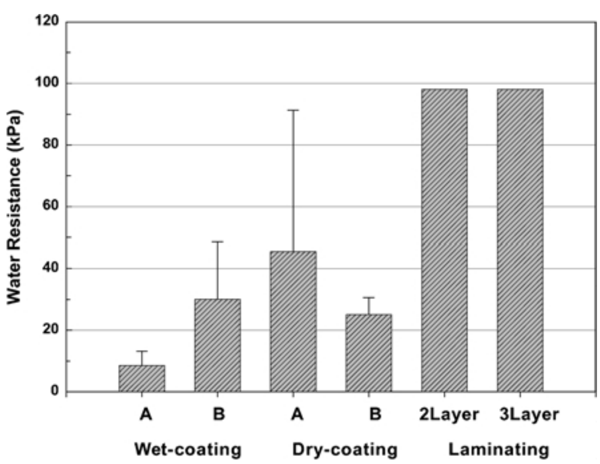

Figure 3 Water resistance with various breathable waterproof finishings.

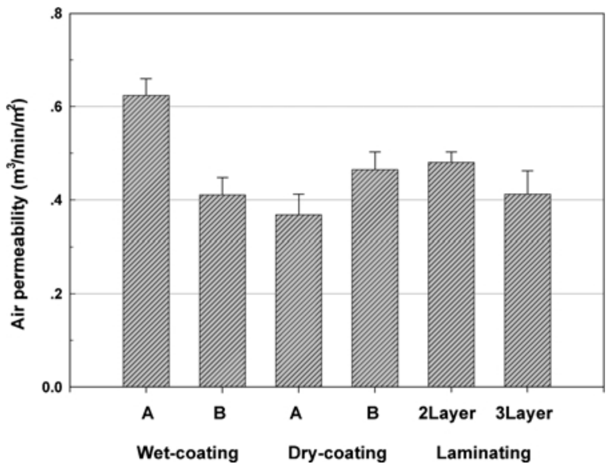

Figure 6 Air permeability from Frazier analysis with various breathable waterproof finishings.

3.4. Air permeability properties

Moisture and air movements through a textile fabric are sometimes considered together under the topic of fluid flow. Airflow through a fabric occurs when the air pressure is different on the two sides of the fabric. Air permeability is the rate of airflow through the fabric where a different air pressure is on either surface of the fabric. Fig. 6 shows the results of air permeability with Frazier analysis. The rate of airflow is adjusted so that a prescribed pressure is achieved between the two sides of the fabric. The prescribed pressure was 12.7 mm of water, which is equivalent to 125 Pa. The results showed

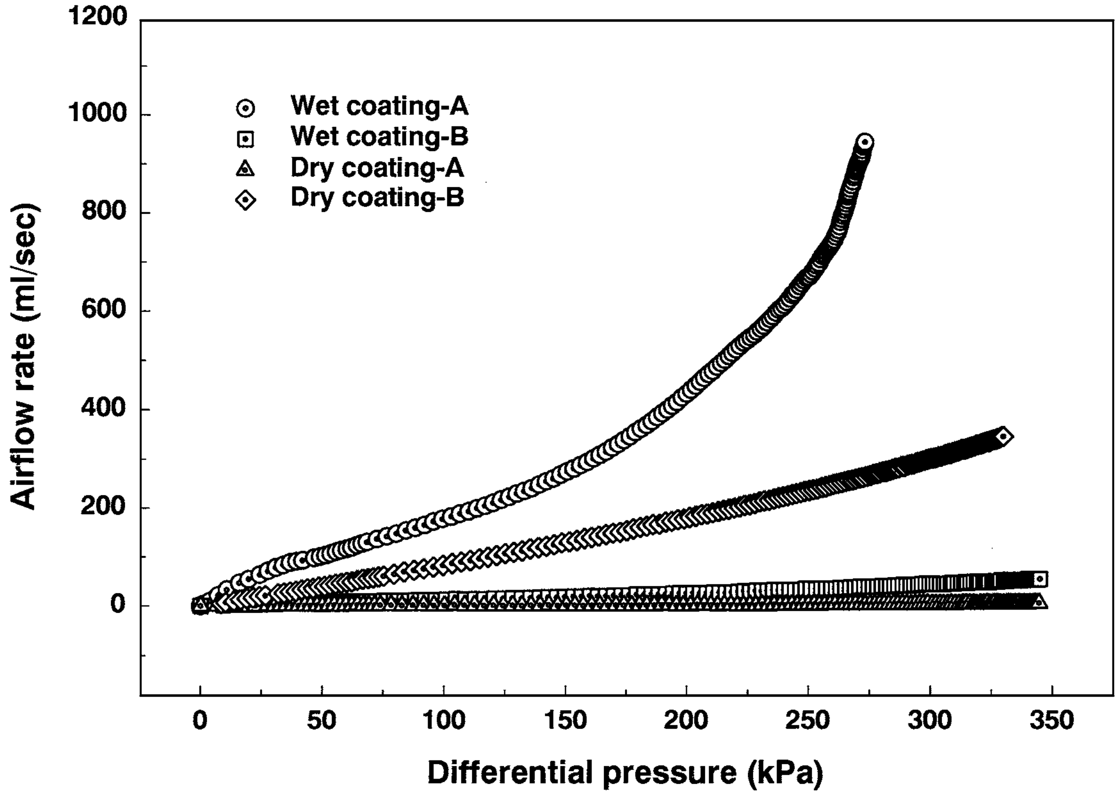

Figure 7 Airflow rate with differential pressure in breathable waterproof fabrics manufactured by coating processes.

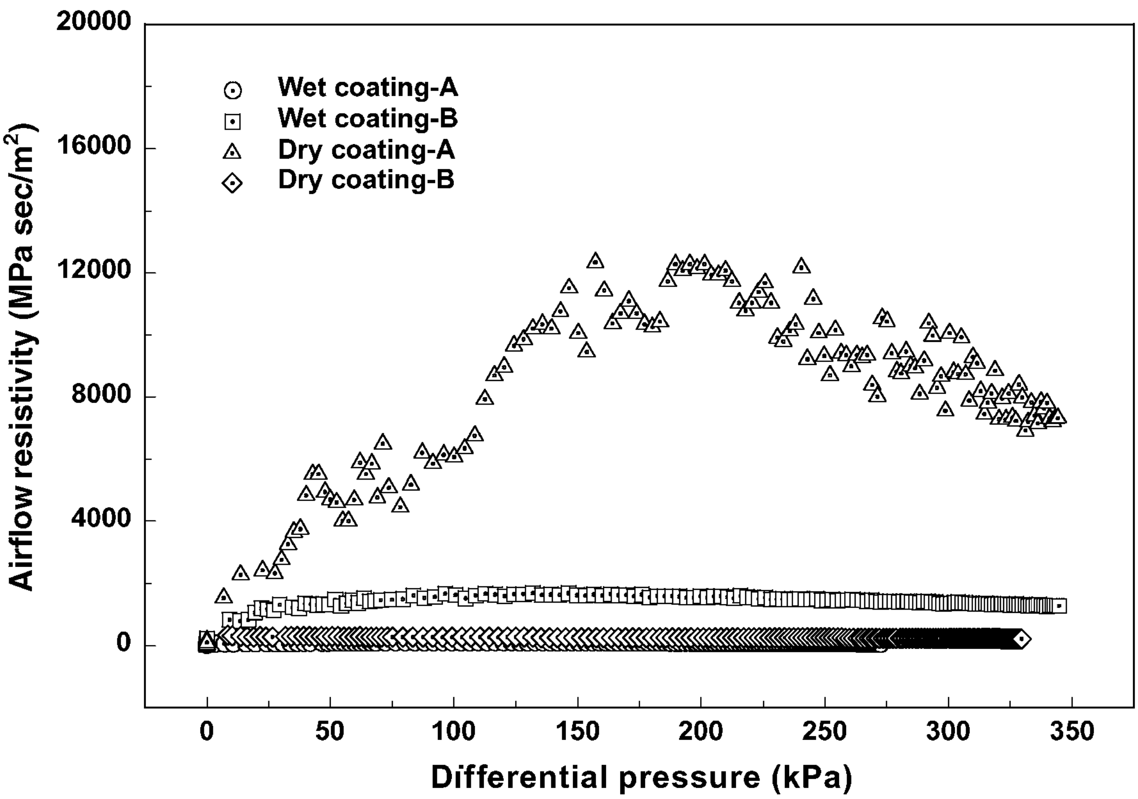

Figure 8 Airflow resistivity with differential pressure in breathable waterproof fabrics manufactured by coating processes.

very low permeability, because the pressure difference was relatively low level to polymer membrane-fabric composites. The air permeability decreased with weight increase and showed the high correlation ($r = 0.994$). In addition, we measured the airflow rate and airflow resistivity as the differential pressure increased from 0 to 344.7 kPa, and the results are shown in Figs 7 and 8. Generally, the results of airflow were similar to diffusion of moisture vapor through a fabric. The fabrics manufactured by wet coating-A type significantly showed high increase of airflow rate with differential pressure up to 206.8 kPa, and it was due to the contribution of large and irregular pore structures. The amount of coating solution was also the lowest of four kinds of coating methods. Airflow rate of dry coating A type was remarkably low, and those of wet coating-B type and laminated fabrics were at a similar level. On the other hand, air flow resistivity of dry coating A type showed very high values, and it was caused by non-porous structure compared to the other materials. Usually, air permeability increases as fabric interstices increase in number and size, but air permeability was rarely influenced by base fabric constructions in these polymer membrane-fabric composites

4. Conclusions

Breathable waterproof fabrics manufactured by different coating and laminating processes were investigated to define the variations of water and air transport properties. The pore structures of fabric surface showed the significant morphology change with breathable waterproof finishings, and these differences revealed some related transport properties. Especially, dry coating A type showed non-porous structure, but had some permeability performances. Laminated fabrics showed uniform values in water vapor permeability and waterproof properties, but those properties of coated fabrics were significantly changed with coating methods. Wet coating A type had high water vapor permeability and low waterproof value, but dry coating A type showed opposite results. Airflow rate gradually increased, and airflow resistivity decreased with differential pressure, but wet coating B, dry coating A, and laminated fabrics were not much changed up to 350 kPa.

The correlation between weight increase and transport properties was very high only in coated fabrics, especially, air permeability and waterproof were closely related with amount of coating dope. Therefore, the properties of the fabrics manufactured by coating method could be altered according to the amount of coating dope added on base fabrics. So the control of dope amount in this process is very important to the transport properties.

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