A Study on Novel Waterproof and Moisture-Permeable Poly(vinylidene fluoride) Micropore Membrane-Coated Fabrics

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ABSTRACT: The feasibility of PVDF (polyvinylidene fluoride), as a novel waterproof and moisture-permeable material, to substitute PTFE (polytetrafluoroethylene) for manufacturing civil high-performance textiles was discussed. The work was focused on the design of casting solution composition (including solvent, additives, and polymer), possible methods to produce durably binded coated micropore membrane fabrics as well as their influences on membrane properties. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 801–807, 2001

Key words: PVDF membrane; coated fabrics; waterproof and moisture-permeable finishing; high-performance fabrics

INTRODUCTION

In recent years, the development of new technology and processes for textile finishing, for example, coating, laminating, and high-performance fabrics were produced.[1,9] Yet these performances were at the cost of losing wearing comfort to a certain extent, for the coating or laminate introduced will block or close tiny openings among fibers, and so affects the heat and moisture exchange between human body and atmosphere, and results in uncomfortable wearing.

To meet with the comfortable wearing requirements, which are important to military and civil textiles, waterproof and moisture-permeable fabrics were developed.[2,5,7] Of all the waterproof and moisture-permeable mechanisms, the micropore mechanism is the most important, which realizes the two contradicting properties, i.e., waterproofing and moisture-permeability by the huge size difference among pores, moisture molecules, and raindrops. Usually, when the diameter of pores is between 0.2–20 μm, passage of raindrop is prevented, while the moisture molecule can pass through easily.

The famous PTFE-laminated fabric, i.e., Gore-Tex fabric,[3,4,6] is the typical representative of the micropore mechanism, and is considered worldwide the most advanced waterproof and moisture-permeable fabric. But normal methods are not available for PTFE fabrics manufacturing, and special processes and equipment are needed, for example, two-dimensional drawing equipment, critical temperature, tension control, etc. Also, because of its expensive price, it is impossible for PTFE fabrics to be used widely as civil textiles.

Many researchers have been tried to produce novel waterproof and moisture-permeable fabrics integrating excellent performances like PTFE, and yet with low cost. But so far no product has

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been put forward to totally substitute PTFE. Different from other research, a totally new material has been used in this research to make the target fabrics, i.e., PVDF (polyvinylidene fluoride). PVDF has good mechanical strength and environmental resistance. Although its hydrophobicity is less than PTFE, its processibility is much better than PFTE, especially by means of phase inversion processing.[13] Therefore, the PVDF micropore membrane is a good candidate to substitute PTFE as a novel waterproof and moisture-permeable fabric.

EXPERIMENTAL

Material

The materials used were: PVDF (provided by Shanghai Organic Fluoride Institute, China); *N*,*N*-dimethyl formamide (DMF), *N*,*N*-dimethy acetamide (DMAc), LiCl, PEG-400, PEG-1000, PEG-2000, PEG-4000, etc., were of chemical reagent, and provided by Tianjin Chemical Reagent Manufactory, China; Polyurathane (PU) adhensive (provided by Ultex Company, USA); etc. Fabric: polyester.

Experimental Methods

PVDF, solvent, and additives were put in a flask and agitated at 70–90°C for 1–2 h until totally dissolved. Then the polymer solution was degassed and casted onto a glass plate or directly coated on fabrics with a coating machine (Werner Mathis AG LTF 97885, Switzerland). After a certain preevaporation time, the glass plate or fabric was immersed into a gelation bath (cold water) to undergo phase inversion. After the solution transformed into micropore membrane, it was rinse with fresh water for 12–24 h.

Membrane Characterization[10,11,17,18]

Porosity (Pr) measurement was $Pr = (W_0 - W_1)/W_0 \times 100\%$, where W_0 is the weight of the wet membrane, and W_1 is the weight of dry membrane.

Mean Pore Size

If all pores inside the membrane are of the same size and round, straight passages vertical to the membrane surface, the mean pore size is corresponding to the filtered liquid (pure water) volume passed through the membrane within a certain time interval and under suitable testing pressure. The PVDF membrane was compacted with distillated water under 0.1 MPa pressure for c.a. 20 min, and when the flux was stable, the accurate time (t) required for collecting 10 mL water through a specially sized membrane was measured. The expressions used to calculate Flux (F) and mean pore size (r_f) are:

$$F = Q/A \times t$$

$$\overline{r_f} = \sqrt{(2.90 - 1.75\,Pr) \cdot 8 \cdot \mu \cdot I \cdot F/Pr \cdot \Delta P}$$

where Q is the volume of filtered water (l); t is the time (h); A is membrane size (m^2); F is the flux (l/m^2 · h); μ is the viscosity of filtered liquid, i.e., water in this research (Pa · s); I is the membrane thickness (m); ΔP is the testing pressure (MPa); and Pr is the porosity of the membrane (%).

Moisture Permeability

According to National Standards: GB/T 12704-91.

$$Wvt = 24 \cdot \Delta m/S \cdot t$$

where Wvt is the water vapor transmission rate (g/m^2 · 24 h); Δm is the difference of weights before and after testing (g); S is the size of tested sample (m^2); and t is the testing time (h).

Hydrostatic Pressure

The sample was placed and fixed onto the Hydrostatic Pressure Tester holder and pressure was exerted on it. The pressure was relieved when a third water drop appeared on the fabric surface. The related digital reading was recorded as the hydrostatic pressure.

Microscopic Photography

The wet membrane was immersed into 60% glycerol solution for 12 h. Then the morphology of the membrane cross-sections was observed on a photographic microscopy or SEM. The photoes were then taken and developed.

RESULTS AND DISCUSSION

Though usage of PVDF in the field of waterproof and moisture-permeable finishing has not yet

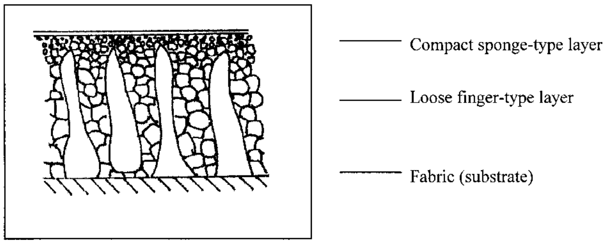

Figure 1 Design of half-sponge and half-finger structure of PVDF micropore membrane fabric.

been reported, the widely used PVDF distillation membrane[6] implies the possibility of PVDF as feasible waterproof and moisture-permeable finishing.

The greatest advantage of PVDF over PTFE is its good processibility, i.e., easily dissolved in some organic solvents (DMF, DMAc, etc.) and it produces micropore membranes by simple phase inversion, which greatly reduces the processing difficulty and cost. In this study, the polymer PVDF was precipitated from an even casting solution into the asymmetric pore structure when immersed in a gelation bath (cold water), and the casting solution was, in most cases, composed of polymer, solvent, and nonsolvents (additives).

Usually, asymmetric pore structure, i.e., different pore shape or size along the vertical section of membrane, is produced by this method. Two typical pore structures are sponge-type and finger-type. Different structures exhibit respective properties. Moreover, there are many factors influencing the pore structures, for example, composition of casting solution (including the type and concentration of polymer, solvent, and additives), preevaporation time, membrane thickness, gelation conditions, etc. Adjusting the above parameters, a intermediate structure, i.e., half-sponge and half-finger structure (or tight skin layer and the finger-like sublayer) can also be obtained, which is the one intentionally prepared in this research, as shown in Figure 1.

Table I Influence of Solvents on Membrane Properties

Solvent	Pr	F_{Dry}	$\overline{r_{f\mathrm{Dry}}}$	Wvt
DMF	72.7	27	0.9	2385
DMAc	73.4	71	1.35	2016

The additive used was PEG-1000 and the preevaporation time was 1 min.

Pr: Porosity of membrane (%); F_{Dry}: Flux of dry of membrane (l/m^2 · h); $\overline{r_{f\mathrm{Dry}}}$: pore size of dry membrane (μm); Wvt: Water vapor transmission rate (g/m^2 · 24 h), the following same symbols have the same meanings and units.

It is obvious that the upper sponge structure of the membrane (tight skin layer, with tiny pore size, less than 1 μm) is able to resist the penetration of water drop/rain drop effectively while the finger-like substructure, which is of a much bigger pore size (several μm), possesses small resistance to the dissipation of moisture/perspiration molecules. Therefore, a good combination of waterproof and moisture-permeable functions is obtained with this special membrane structure.

Effects of Solvents

Generally, the greater the solubility parameter difference between polymer and solvents, the faster the polymer will precipitate and is more favorable for finger-type pores to be formed.

There are many kinds of solvents for PVDF casting solution, for example, DMF, DMAc, NMP, DMSO, etc., but because of the high price of NMP

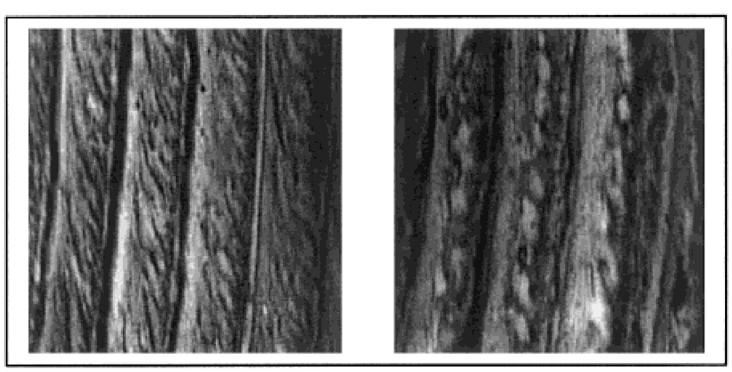

Figure 2 Influence of DMF and DMAc on pore structure (microscopic photoes, 100×).

Table II Relations Between PVDF Viscosity and Membrane Properties

Samples	PVDF Viscosity	Pr	F_{Dry}	$\overline{r_{f\text{Dry}}}$	Wvt
1#	161	73.4	25	0.94	2098
2#	882	66.35	8	0.49	2208

The additive was PEG-1000, preevaporation time was 2 min, and the unit of viscosity was mpa · s. Concentration of both PVDF solutions is 12%.

and inability of DMSO, the choice was made between DMF and DMAc.

The porosity of the DMF membrane was a little bit lower than that of DMAc (Table I). But the flux and mean pore size of DMF dry membrane were lower, meaning better waterproof properties.

The higher Wvt value of the DMF membrane indicated better moisture permeability and possible evener pores and more effective moisture-permeable passages.

Compared by the microscopic photoes (Fig. 2), the structures below compact surficial layer were even, fine, and condensed finger-type pores for the DMF membrane, with sponge-type pores for the DMAc. Because the former structure coincided with the hypothetical pore model, DMF was selected as the suitable solvent.

Selection of PVDF Molecule Weight

As a matrix of micropore membrane, PVDF molecule weight had considerable influences on pore size, porosity, waterproofing and moisture permeability, coatability of casting solution on fabrics, etc. Table II shows relations between different PVDF molecule weights (expressed by spinning viscosity) and membrane properties.

Data listed in Table II reveal that lower porosity, mean pore size, and flux of dry membrane or better waterproof ability were obtained by higher viscosity PVDF (2#). In addition, a higher Wvt value, and so a better moisture permeability were also found on the 2# membrane. Low molecular weight and low viscosity PVDF solution usually resulted in solution leakage during coating as well as difficulty to cast smooth, strong membrane on a glass plate even though the PVDF concentration was as high as 15%. Accordingly, higher molecule weight PVDF (2#) was selected.

As in the micrographs cf. (Fig. 3), loose, wide fingers corresponds to low molecule weight PVDF membrane, while there was an even, fine, and condensed half-sponge and half-finger structure to the high molecule weight PVDF, which also fits in with the hypothetical model.

Influence of Additives on Membrane Properties

Additives are nonsolvent substances to the casting solution. They will not react with polymer or solvent, but can easily be dissolved in solvent as well as gelation agent (water). As an important composition of casting solution, additives intensively influence pore structure morphology and solvent evaporation or exchanging rate, which are the major factors dominating membrane properties.

The additives used in the PVDF solution were listed in Table III.

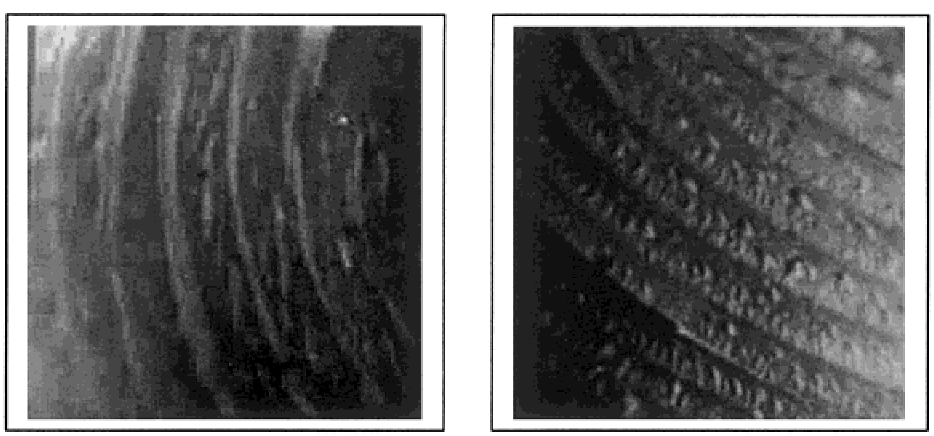

Figure 3 Influence of PVDF molecule weight on pore structure (microscopic photoes, 100×).

Table III Influence of Different Additives on Membrane Properties

Additives	PEG-400	PEG-1000	PEG-2000	PEG-4000	LiCl
Pr	69.2	69.5	64.3	65	70.2
F_{Dry}	0	0	30	47	0
$\overline{r_{f\mathrm{Dry}}}$	—	—	0.91	1.23	—
Wvt	1890	1985	1835	1760	2008

The dosage of additives was 1 g/10 g PVDF.

Among all the additives studied, LiCl, PEG-1000, and PEG-400 had higher porosity and *Wvt* value, and so better moisture permeability. And their dry membrane flux was 0 under testing pressure, much lower than those of PEG-2000 and PEG-4000, indicating better waterproof abilities.

Pore structures (Fig. 4) of LiCl, PEG-400, and PEG-1000 are mainly of the finger-type, and the pores are long, thin, and condensed, nearly penetrating through the whole section, which account for their better moisture permeability. PEG-2000 and PEG-4000 formed wide and uneven sponge-type structure with large and loose pores, i.e., unfavorable for the waterproof and moisture permeable properties. Accordingly, it is concluded that LiCl, PEG-400 and PEG-1000 are better additives.

Research on the Binding of PVDF Micropore Membrane and Fabrics

In general, binding fastness between micropore membrane and fabrics depends on two factors;

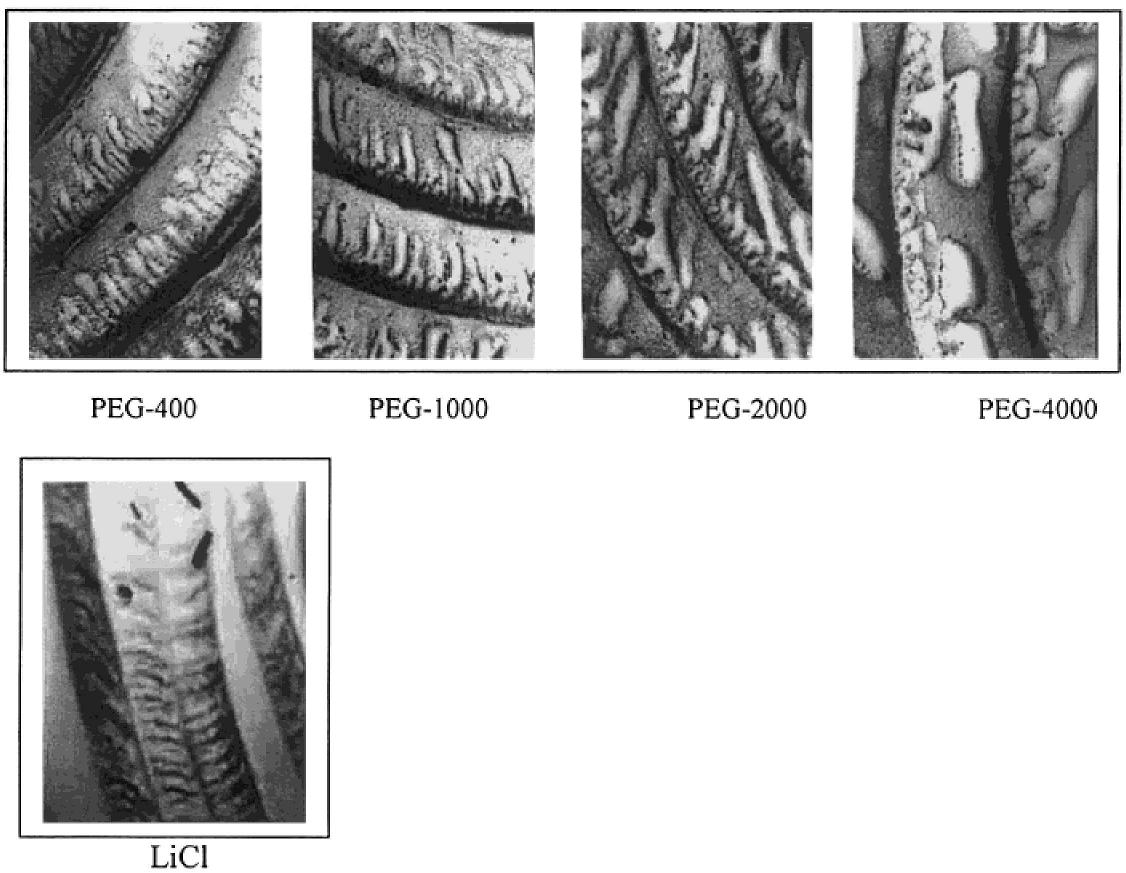

Figure 4 Impact of different additives on pore structure (microscopic photoes, 100×).

Table IV Property Comparision of Different Waterproof and Moisture-Permeable Fabrics

Coated Fabrics	PTFE-I	PU-I	PU-II	PTFE-II	PVDF
Moisture permeable mechanism	Micropore	Micropore	Stepping stone	Micropore	Micropore
Waterproof ability (hydrostatic pressure)	Over 13 m	About 2 m	Over 13 m	Below 0.5 m	6.36 m
Water vapor transmission (*Wvt*)	1572	1629	998	2108	1968
Thickness of coated fabrics (μm)	360	171	132	282	134

one is a mechanical anchor, and the other is a chemical fixation.

By means of the phase inversion process, a layer of PVDF micropore membrane had been formed onto polyester fabrics. But PVDF has low surface tension, and so is hard-to-bind material. In addition, both have nearly no reactive groups, and so except for the weak mechanical anchor, there is no chemical fixation between them so that they are easily separated when being rubbed. Furthermore, the PVDF membrane produced by the phase inversion process has only low strength and is easily to be damaged by exterior action.

Various methods have been tried to accomplish durable binding, for example, modification of PVDF membrane (oxidation/hydrophilic treatment[14,15]), formula adjustment of PVDF solution (addition of adhesives[12]), modification of polyester fabrics (alkali/amine treatment in one bath, plasma treatment,[8,16] etc.), as well as selection of appropriate adhesives. It has been found that the most feasible method is as follows. First, a very thin layer of PU (polyurethane) adhesive was precoated and dried onto the substrate. Then PVDF solution was coated and underwent phase inversion and drying. Finally another thin nonporous and hydrophilic PU coating was applied, dried, and cured to provide protection for the unstable micropore membrane surface. The prepared fabric had been conferred with acceptable fastness and fairly good waterproof and moisture-permeable properties, as shown in Table IV.

PTFE-II–laminated fabrics had the best moisture permeability but the lowest hydrostatic pressure (Table IV). PU-II–coated fabrics had very high hydrostatic pressure but the lowest *Wvt* value, due to its nonporous coating. PU-I–coated fabric was of medium *Wvt* and hydrostatic pressure corresponding to their large-sized sponge-type pore structure (Fig. 5). PTFE-I laminate's nonconcentric, intersecting, and web-like pore structure (Fig. 5) illustrated its excellent hydrostatic pressure and better moisture permeability. Table IV also showed PVDF-coated fabric pos-

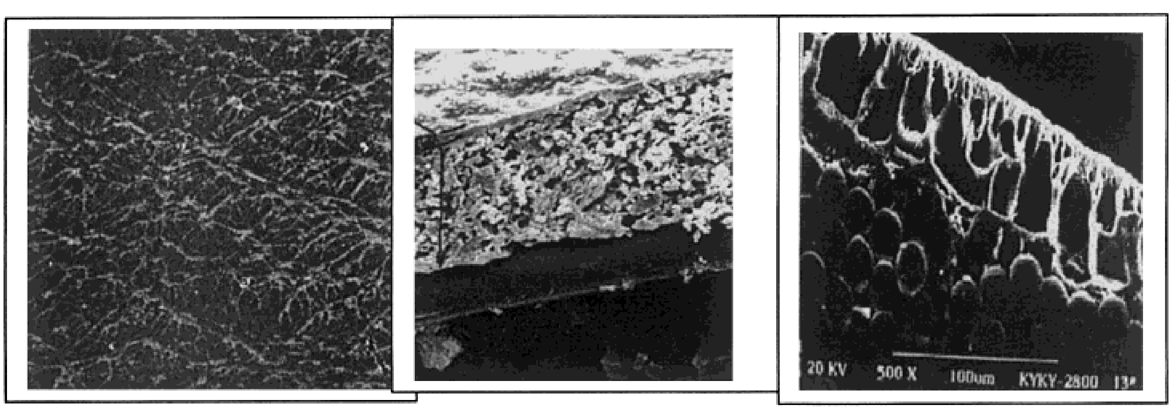

Figure 5 SEM photoes of different membrane pore structures.

Table V A Membrane Parameters' Comparison Between PVDF and PTFE

Membrane Parameter Membrane	Pore Size (μm)	Thickness (μm)	Porosity (%)
PVDF	0–1	20–40	80.4
PTFE	0.2	25.4	82

sessing a 6 m of hydrostatic pressure; Although lower than PTFE-I or PU-II, it is enough for applications in civil textiles. Besides, higher *Wvt* value and fairly good moisture permeability had been obtained on PVDF fabrics. These advantageous properties of PVDF-coated fabrics might have resulted from their half-sponge and half-finger micropore structure (Fig. 5), which fitted in well with the hypothetical model.

And among the 134-μm thickness of the PVDF-coated fabrics, the PVDF membrane occupied 23 μm, and so the whole fabric was fairly light and thin. The pore size and porosity of PVDF was approaching the PTFE level as well (Table V).

CONCLUSION

A PVDF micropore-coated fabric with acceptable waterproof and moisture-permeable performances has been developed. Results of membrane characterization showed that the pore size, porosity, and membrane thickness of the PVDF micropore membrane is approaching the PTFE level. Besides, with appropriate processes, a durable fixation between the membrane and fabric was possible. Therefore, a novel PVDF waterproof and moisture-permeable membrane-coated fabric is feasible.

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