

Role of Reinforcing Material in Ion Exchange Membranes Prepared by the Paste Method

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Synopsis

Ion exchange membranes prepared by the paste method contain polyvinylchloride cloth as a reinforcing material, which is necessarily used to endow the membranes well-balanced properties: electrochemical and mechanical properties. The role of the reinforcing material was studied in terms of the membrane structure.

INTRODUCTION

Nowadays, ion exchange membranes are practically used in various ways. These membranes generally contain a reinforcing material, which is necessarily used to make the membrane properties well-balanced, especially to endow the membranes toughness and dimensional stability. However, the role of the reinforcing material has been little studied so far.

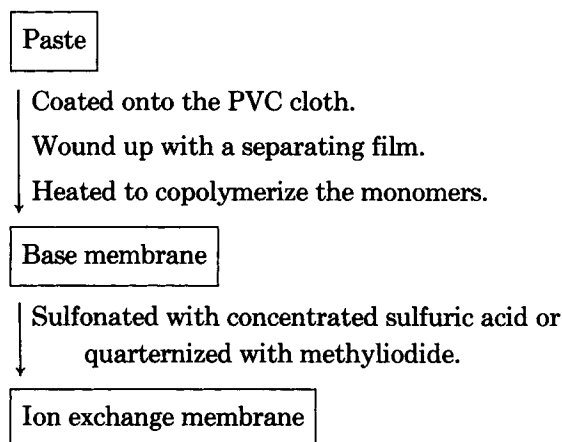
We have already reported the preparative method of ion exchange membranes, the past method.^{1,2} The paste is prepared by mixing fine powder of polyvinylchloride (PVC), a monomer with a functional group suitable to introduce the ion exchange group, divinylbenzene (DVB) as the crosslinking agent, a radical polymerization initiator, and others. The paste is coated onto a PVC cloth and the monomers are copolymerized. The monomer mixture is soaked even into the PVC cloth and copolymerized there. Subsequently, the ion exchange group is introduced onto the resultant resin component. Here, it is noteworthy that the resin component separates out of the gelled PVC phase during the copolymerization and is finely and continuously dispersed in the PVC phase. Therefore, the ion exchange membrane consists of two phases of PVC and the ion exchange resin component, finely and closely intertwining together.³⁻⁷ Also, the ion exchange resin component is finely and continuously dispersed even in the PVC cloth.⁷ However, the structural change of the PVC cloth during the preparative process is still obscure. Then, this paper is concerned with the structural change of the PVC cloth in order to understand the role of the PVC cloth as the reinforcing material.

EXPERIMENTAL

Membranes

The membranes used were the cation exchange membranes, Neosepta CL-25T and CH-45T and the anion exchange membrane, Neosepta AF-4T and their base membranes. These membranes were prepared by the paste method

(Tokuyama Soda Co., Ltd.).^{1,2} The outline of the paste method is shown as follows.



The pastes for the cation exchange membrane and the anion exchange membrane consist mainly of styrene (St)-DVB-benzoylperoxide (BPO)-PVC powder and 4-vinylpyridine (4-VP)-DVB-BPO-PVC powder, respectively. Then the cation exchange membrane was prepared by sulfonating the styrene unit in the base membrane and the anion exchange membrane was prepared by quarternizing the 4-vinylpyridine unit in the base membrane. Table I shows the properties of the ion exchange membranes.

X-Ray Diffraction

Wide-angle x-ray diffraction was measured by the use of Rotaflex PU-200PL (Rigaku Denki Kogyo Co., Ltd.) with nickel filtered Cu-K α radiation ($\lambda = 1.54$ A). The crystallinity index was measured by an empirical ratio, as proposed by D'Amato et al.⁸ In order to examine the orientation of the crystalline

TABLE I
Properties of the Ion Exchange Membranes of Na⁺ or Cl⁻ Form

	Cation exchange membrane		Anion exchange membrane
	Neosepta CL-25T	Neosepta CH-45T	Neosepta AF-4T
Ion exchange capacity, meq/g dry membrane	1.6	2.0	2.1
Water content, g H ₂ O/g dry membrane	0.24	0.30	0.30
Thickness, mm	0.16	0.16	0.15
Burst strength, kg/cm ²	4	4	6
Electric resistance, ^a cm ²	2.5-3	2-2.5	2-2.5
Transport number ^b	> 0.98	> 0.98	> 0.98

^a Measured in a 0.5N NaCl solution at 25°C.

^b Measured by electrodialysis in a 0.5N NaCl solution at 25°C and current density of 2A/dm².

phase, the azimuthal change in the intensity of the 110 reflection for PVC was measured by the x-ray diffractometer equipped with a versatile specimen holder.⁹

RESULTS AND DISCUSSION

It is beyond question that the PVC cloth as the reinforcing material is effective to make the ion exchange membranes tough and dimensionally stable. The keypoint is how much the properties of the PVC cloth remain after the process to prepare the ion exchange membranes, especially regarding the crystallinity.

The base membranes for Neosepta CL-25T, CH-45T, and AF-4T have fairly good transparency and the base membrane for Neosepta AF-4T is pale yellow owing to the coloration of the 4-VP-DVB resin component. The PVC cloth in the base membranes is not visible to the naked eye, owing to the membrane structure consisting of the two phases of PVC and St-DVB or 4-VP-DVB resin component, finely and continuously intertwining together.³⁻⁷ Also, it can reasonably be presumed that some amount of St-DVB or 4-VP-DVB should graft polymerize onto PVC, as previously reported.¹⁰ The formation of the graft polymer should be effective to enhance the cohesiveness between the two phases of PVC and the St-DVB or 4-VP-DVB resin component. It also means

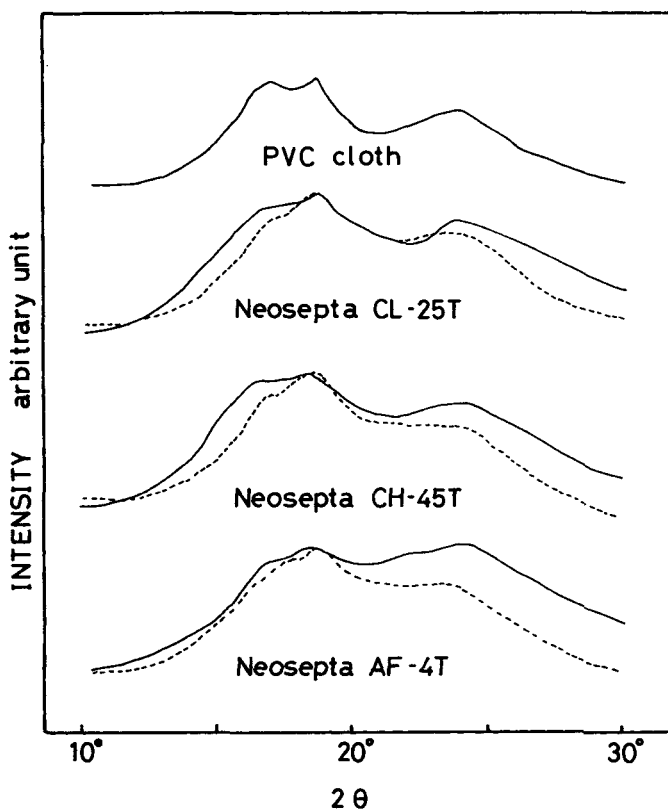


Fig. 1. X-ray diffraction diagrams: (—) ion exchange membrane and (---) base membrane.

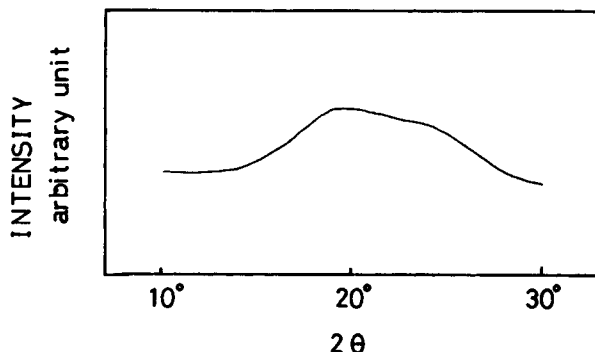


Fig. 2. X-ray diffraction diagram of the sheet-shaped composite prepared from the paste for Neosepta CL-25T with no PVC cloth.

that the PVC cloth as the reinforcing material is quite cohesive to the other part of the membrane. On the other hand, it is well known that PVC is crystalline to some extent.^{8, 11-14}

Figure 1 shows the x-ray diffraction diagrams of the PVC cloth, the ion exchange membranes, and their base membranes. The crystallinity of the PVC cloth is rather low and no sharp peak can be observed. However, two relatively clear peaks can be observed at $2\theta = 16.4^\circ$ and 18.4° , which are assigned to 200 and 110 planes, respectively.¹² The peaks of the base membranes are more obscure than those of the PVC cloth and those of the ion exchange membranes are even more obscure. However, the peak positions of all the samples are nearly identical. Here the peaks can be attributed to the crystalline phase of the PVC cloth in comparison with the x-ray diffraction diagram of the sheet-shaped polymer composite prepared by the polymerization of only the paste for Neosepta CL-25T, with no PVC cloth (Fig. 2).

Table II shows the d-spacing of the 110 plane. No significant difference can be observed in the data. This means that the crystalline part of the PVC cloth is not deformed during the process to prepare the membranes. Table III shows the crystallinity index of the membranes. The order is the PVC cloth > Neosepta CH-45T > Neosepta CL-25T > Neosepta AF-4T, regarding both the base membranes and the ion exchange membranes. The difference between each combination of the ion exchange membranes and their base membranes is not significant. This means that the introduction of the ion exchange group is ineffective on the crystallinity index. It is reasonable that the value of the

TABLE II
The d-Spacing of the 110 Plane of the Membranes

Sample	d-Spacing (Å)	
	Base membrane	Ion exchange membrane
Neosepta CL-25T	4.79	4.82
Neosepta CH-45T	4.79	4.82
Neosepta AF-4T	4.79	4.79

d-spacing of the PVC cloth: 4.82 Å.

TABLE III
The Crystallinity Index of the Membranes

Sample	Crystallinity index (%)	
	Base membrane	Ion exchange membrane
Neosepta CL-25T	29.8	30.4
Neosepta CH-45T	33.4	33.9
Neosepta AF-4T	25.1	22.0

Crystallinity index of the PVC cloth: 40.6%.

PVC cloth is largest because the other samples contain the amorphous components other than the PVC cloth: the St-DVB resin component, the 4-VP-DVB resin component, or the ion exchange resin component. It is unclear why the values of the Neosepta AF-4T and its base membrane are smaller than those of the others, but it could probably be attributed to the larger affinity of 4-VP-DVB for PVC than that of St-DVB.

Figure 3 shows the patterns of the change in the diffraction intensity at $2\theta = 18.4^\circ$ when the sample was rotated in the range of the azimuth ($\Omega = 0-90^\circ$), which is the polar angle between the 110 reflection and the meridia. The minimum point of the intensity is observed at $\Omega = 45^\circ$ for all the samples and is reasonable because the fiber of the PVC cloth crosses vertically and the

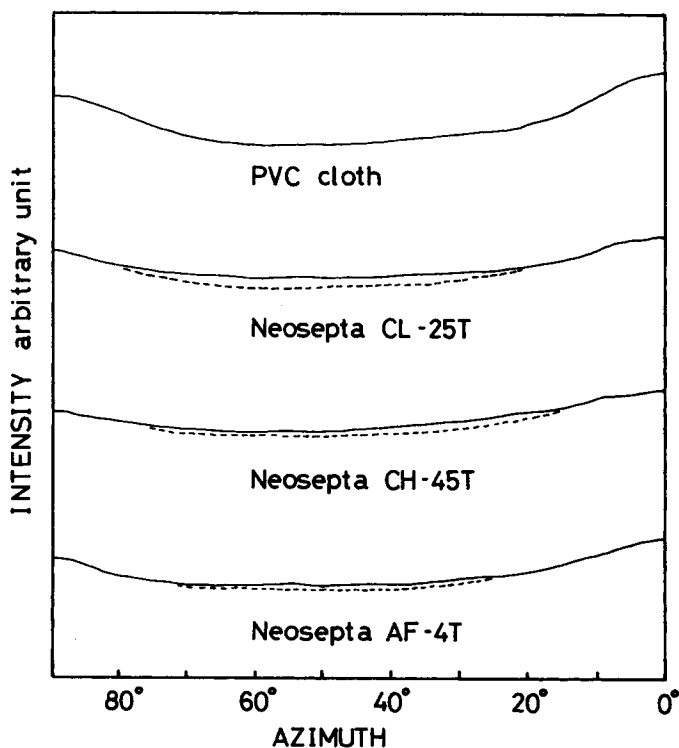


Fig. 3. Azimuthal change in the diffraction intensity at $2\theta = 18.4^\circ$. (—) ion exchange membrane and (---) base membrane.

fiber directions are consistent with $\Omega = 0^\circ$ and 90° . Therefore, the diffraction intensity is minimum at $\Omega = 45^\circ$. Here the difference between the intensities at $\Omega = 0^\circ$ or 90° and $\Omega = 45^\circ$ is related to the orientation degree of the crystallites to the fiber direction and the larger the difference, the larger the orientation degree. Also, the intensities at $\Omega = 0^\circ$ are relatively stronger than those at $\Omega = 90^\circ$, and this is reasonably understandable as follows: the former are ascribed to the warp and the latter the woof. The orientation degree of the base membranes is smaller than that of the PVC cloth and this means that the copolymerization of the monomers in the PVC cloth deteriorates the orientation, probably because soaking and copolymerization of the monomers make the drawn amorphous part of the PVC cloth relaxed and more voluminous. Furthermore, the introduction of the ion exchange group deteriorates the orientation even more, probably owing to the introduction of the ion exchange group which makes the amorphous part more voluminous. The results described above show that the monomers are absorbed into the amorphous part of the PVC cloth and copolymerize there, and this is the reason why the orientation degree of the crystallites decreases. However, the crystalline part itself remains clear. It is impossible presently to discuss the change in the structure of the PVC cloth in relation to the properties of the ion exchange membranes.

We can conclude that the crystalline structure of the PVC cloth remains to some extent in the ion exchange membranes and that is why the PVC cloth is effective in endowing the membranes with their well-balanced properties, especially the toughness and the dimensional stability. Also, the PVC cloth has the appropriate affinity for the monomers, and therefore the tight structure of the membranes results from the copolymerization of the monomers. Thus, excellent ion exchange membranes can be prepared by using PVC cloth as very suitable reinforcing material.

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Received September 22, 1986

Accepted December 9, 1986