

Nonrigid Microporous PVC Sheets: Preparation and Properties

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ABSTRACT: The non-rigid microporous PVC films are prepared by mono-axially stretching nonporous sheets containing fillers which show an average particle size of 2 to 10 μm . The nonporous PVC film is generated from paste-like PVC. The influence of recipe components on the mechanical properties, morphological behavior and permeability to water vapor and water was investigated as well as the influence of the stretching ratio. Filled PVC pastes exhibit higher values for viscosity than those of pure polymer mixtures. For processing the compounded paste by means of a doctor blade a low viscosity is required meaning the amount of filler is limited by the resulting paste viscosity. Due to dewetting, the filler ini-

tiates the holes of the microporous system during the stretching process. Empirically, a minimum of about 15 vol % filler particles are necessary in order to achieve an interconnected air hole system. Varying the components PVC, plasticiser and filler, PVC membranes could be prepared with high water vapour permeability and high waterproofness simultaneously. To utilize the membranes commercially a continuous preparation process was developed. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2119–2126, 2010

Key words: porous structure; PVC films; monoaxial stretching; porous films

INTRODUCTION

Microporous materials (films, sheets, membranes, or coatings) are applied in the separation technology, for personal care items, in the building industry as well as for manufacturing high-performance fabrics providing breathability and waterproofness. Well-established polymer materials for manufacturing microporous membranes are Polyurethane, Polytetrafluoroethylene, and Polyolefins. Several widely differing techniques were developed for preparing microporous polymer structures. Such techniques range from innumerable variations of classical phase separation to incorporation of solid particles in a substrate which are subsequently leached out to ion plasma treatment, to sinter polymer powders and to stretch an inhomogeneous polymer matrix. All these methods were commercially utilized. For instance, stretching thermoplastic sheets is well-established for PTFE^{1–3} or Polyolefins.^{4–14} The effects of fillers, polymer mixtures, and process parameters on the forming of the microporous system are intensively investigated.

Some of the techniques are useful for preparing microporous structures of PVC:

A. Phase inversion method:

The classical phase inversion method involves the use of at least three components a polymer, a solvent, as well as a nonsolvent for said polymer. For preparing a microporous structure of PVC, a process was developed, that comprises forming a colloidal dispersion of latex of a vinyl chloride polymer in which the polymer is in aqueous colloidal suspension in a water-soluble organic solvent for the polymer. The heated dispersion causes the colloidal polymer particles to cohere, thus forming a microporous product.¹⁵

Besides the thermally initiation, the isothermal method is possible. The membrane was prepared from a polymer solution and a subsequent treatment with a nonsolvent. Also PVC copolymers and blends were investigated.^{16–19} The disadvantage of the phase inversion processes is that at least two solvents are imperative. The large amount of solvent used in the preparation of solutions must be subsequently extracted. It is also apparent that the process requires a relatively high degree of process control to obtain structures of desired configuration. For these reasons, procedures are not applicable for large quantities or a continuous roll-to-roll process, respectively.

B. Using porogen fillers:

Leaching of inorganic fillers: The incorporation of leachable particles into the polymer matrix is useful to prepare microporous structures. Suitable porogen

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TABLE I
Labeling of Fillers Used

Materials	Supplier	Labeling	Chemical material	Particle size [μm]	
				d_{50}	d_{98}
Omyafilm 704	OMYA GmbH	CC-2	CaCO_3	2	10
Minex 7	Quarzwerte GmbH	SO-1	SiO_2 , Al_2O_3 , K_2O , nephelinsyenit	5	16
Dow Corning 9506 Powder	Dow Corning Corp.	SX-1	Polysiloxane	3	15
SLM 444,232	Wacker Chemie AG	SX-2	Polysiloxane	2,2	
SLM 444,123	Wacker Chemie AG	SX-3	Polysiloxane	2,2 bimodal	18
Zonyl MP-1200	Du Pont	CF-1	PTFE-powder	2,5-4,5	9
Nanoperl	SOVITEC GmbH	SO-K	Glass beads	24	180
Nanoperl NP2-P1	SOVITEC GmbH	SO-K2	Glass beads	2	8
Nanoperl NP3-PO	SOVITEC GmbH	SO-K4	Glass beads	4,44	16

fillers can be inorganic salts like CaCO_3 .²⁰ The fillers were mixed into the coating compound homogeneously. The CaCO_3 containing resin film is prepared by coating a substrate, evaporating the solvent and curing. The polymer film has to immerse in an acid to remove the CaCO_3 .

The size of porogen particles will affect the size of pores while the polymer to porogen ratio is directly correlated to the amount of porosity of the final structure. This approach allows the preparation of structures with regular porosity. However, the method is limited by a small thickness range.

Using decomposable porogens: In contrast to inorganic salts described earlier, porogen molecules (e.g., diamino hexane, amino butane) decompose during heating. In Ref. 22, an additional extraction of the decomposition products is recommended.²¹⁻²³

Our effort relates to microporous PVC film that may be continuously prepared by a facile roll-to-roll process, avoiding organic solvents or additional leaching, respectively. This work describes a method for generating a microporous PVC membrane using an inhomogeneous polymer matrix that is created by adding certain fillers to a PVC paste, followed by forming a thin film with subsequent solidification. During stretching, the resulting film voids are built at the interface between polymer and solid filler. Due to increasing extension, the holes are enlarged and merge with neighboring air holes building an interconnecting pore system. Most important are the properties of the filler to realize this concept successfully. Low wettability and no chemical reaction of the filler to the PVC matrix are required. Therefore, the influence of amount, particle size, and chemical composition of certain fillers on the forming of the microporous system was investigated. In addition, it was searched for the main factors to control the moisture permeability as well as water resistance.

To utilize the described technique commercially, a continuous preparation process was developed.

EXPERIMENTAL

Materials

The PVC types used in this study were low to medium molecular weight emulsion type PVC homopolymers of a fine particle size supplied by Vinnolit GmbH & Co. KG and Vestolit GmbH & Co. KG. The characteristics and suppliers of the fillers are given in Table I. DINP (Palatinol N, Gebr. Overlack; Chemische Fabrik GmbH) and derivatives of citric acid (Citrofol AHII, Citrofol BII, Jungbunzlauer Austria AG), DINCH (BASF AG), DOP (BASF AG), and an epoxydised high-oleic sunflower isopropyl ester (EHOSiPE; Pilot Pflanzenöltechnologie Magdeburg e.V.) were used as plasticiser.

Preparation

A typical plastisol was prepared from 100 parts of polyvinyl chloride resin, 45 parts of plasticiser, 2 parts of a Ca/Zn stabilizer, and 19.5 vol % filler in relation to the total volume. The components were mixed to a homogeneous plastisol using a high-speed mixer and ground using a roller grinding mill until the maximum particle size did not exceed 40 μm . Before the coating process, entrapped air was removed from the paste by vacuum. To form thin PVC sheets, the plastisol was coated onto release paper in two layers by means of an on-roll-knife coater. Every layer was gelled separately at temperatures of about 180°C for at least 3 min. The film thickness was maintained at about 120 μm .

The resulting PVC film was stretched in various ratios, mainly 1 : 2.0 upto 1 : 4.5 using a monoaxial stretching unit with short gap stretching facilities. Depending on the stretching ratio, the thickness of

the microporous PVC films was reduced to almost 50 μm .

All experiments using DINP or citric acid esters were carried out on a continuous coating plant (Herbert Olbricht GmbH&Co.KG). At least 20 m \times 0.4 m compact foil was prepared. It was tailored to 0.15 m width before stretching on a "Teach-Line mono-axial stretching unit MDO" (Dr. Collin GmbH).

Scanning electron microscopy

A Philips Electron Optics XL 30 ESEM scanning electron microscope was used to observe the surface and cross sections of the PVC membranes. The cross sections of the samples were prepared by cutting the PVC film while freezing in liquid nitrogen. All samples were gold sputtered.

Tensile strength and elongation at break

The tensile strength of the film and the elongation at break were measured by using the testing device 2020TH Allround-Line by Zwick & Roell according to DIN 53504-S2. At least five samples were tested and averaged.

Water vapor permeability and waterproofness

Water vapor permeability was measured according to the Herfeld method. To measure the water vapor permeability, a glass vessel of approximately 45 mm height and 6 mm in diameter covered by a removable metal screw cap was used. The screw cap had a circular opening of 1000 mm^2 . The glass vessel, filled with 50 cm^3 water, was covered with the round sample (O 60 cm) and sealed with the metal screw cap. The vessel was weighted and placed into a desiccator that was filled with dried silica gel. After annealing the desiccator at 38°C for 24 h, the vessel was weighted again. The measurement was repeated after 24 h. Starting from the average mass loss, the water vapor permeability could be calculated. Note that no movement of the air in the desiccator occurs.

Due to an intended application of the films as membrane in the clothing or shoe industry, a higher temperature of 38°C was applied during measurement. The humidity was set 0%/100%.

The measurement was carried out in triplicate and averaged. Variations of the single values from the average were less than 5%.

The numerous existing measurement methods for water vapor permeability cause difficulties in comparing with given values from literature or product data sheets. Therefore, some commercially available breathable membranes were analyzed with the method described earlier obtaining maximum values of 2200 $\text{g}/\text{m}^2\text{d}$. The values obtained from these

breathable membranes should help to assess the materials manufactured during the course of research work.

The waterproofness was measured according to DIN EN 20811. Each sample was measured five times and averaged.

RESULTS AND DISCUSSION

Forming a microporous system

Effect of filler nature and size

The microporous system of filled and stretched PVC films was investigated using scanning electron microscopy. The surface as well as the cross sections of the microporous PVC films were observed. The results showed that the critical point is the building of air holes at the surface. Sometimes holes occurred in the cross section whereas the surface was compact. The fillers were enclosed by the polymer. Otherwise, if a porous surface had been detected, in either case the bulk material showed interconnected pores. Because of this fact and the difficulties preparing cross sections of these flexible and soft films, mostly the SEM of the surface was used to appreciate the formation of pores.

The particles were completely embedded into the polymer matrix, if mineral-based fillers had been applied, e.g., CaCO_3 (CC-2) or SiO_2 (SO-1). The desired effect of separation between filler and plastic could not be observed. In contrast to thermoplastic polyolefin materials, where calcium carbonate filled systems usually create microporous sheets,⁴⁻¹¹ in case of nonrigid PVC these fillers were not suitable.

The application of fillers based on polysiloxane (SX-1, SX-2, SX-3), glass spheres (SO-K, SO-K2, SO-K4), or PTFE (CF-1), respectively, led to dewetting followed by hole-forming. Figure 1 shows the surface structure of PVC sheets containing different fillers at a stretching ratio 1 : 3.4. It is quite evident there are high requirements to the filler to prepare PVC membranes bearing predefined pore dimensions as well as close pore size distribution. Figure 1(A,B) show the surface of polysiloxane filled PVC sheets. The polysiloxane filler SX-1 tended to form agglomerates, causing the dispersibility in the PVC paste to be rather low. The formed pores show dimensions of more than 20 μm . On the other hand, polysiloxane filler SX-2 had a superior dispersibility in PVC paste. Every single particle was enclosed by the polymer and agglomeration was not observed. Using this filler, pore dimensions less than 10 μm could be realized. Caused by the close average size distribution and the spherical particles of SX-2, the pore shape and size were uniform. A wide average size distribution gave different pore dimensions side by side as shown in Figure 1(C). The PVC sheet was

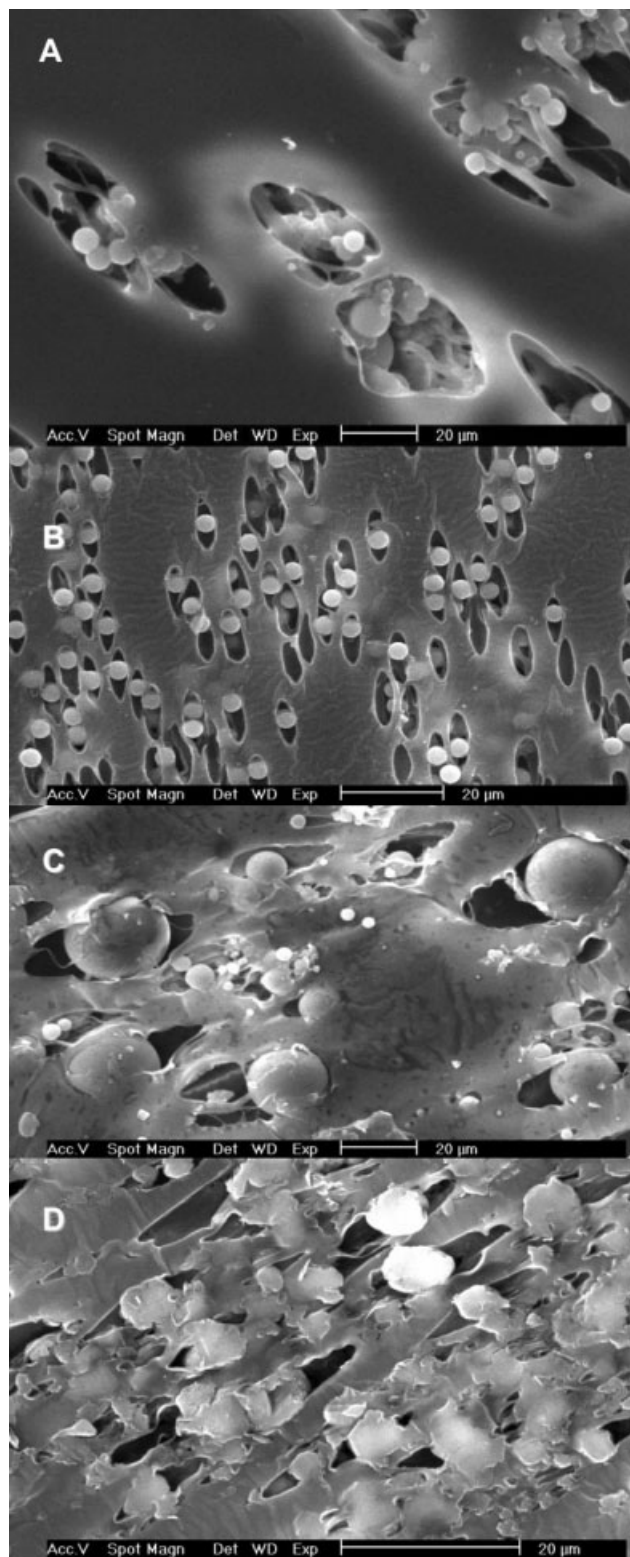


Figure 1 Scanning electron micrographs of surface of PVC sheets bearing various fillers after stretching; The PVC plastisol contained 19.5 vol % filler and DINP as plasticiser; 1A, filler SX-1; 1B, filler SX-2; 1C, filler SO-K; and 1D, filler CF-1.

filled with glass beads (SO-K). The surface of a PVC membrane containing pulverized PTFE particles is shown in Figure 1(D). Despite the rough particle surface, the polymer matrix was separated from the particle and formed voids while stretching. By contrast attempts using pulverized glass particles were not successful in creating microporous structures. It is believed that a interconnected pore system cannot be produced with an amount of filler less than 15% by volume.⁶ Thus, 19.5 vol % filler were used for the present investigations.

Effect of stretching ratio

Due to the excellent behavior of the polysiloxane filler SX-2, it was used to investigate the influence of the stretching ratio on the pore size. It became apparent that the stretching ratio influences the maximum pore size (Fig. 2). Results from water vapor permeability (Fig. 3) gave cause for assumption that the interconnection of pores starts at a minimum stretching ratio of about 1 : 1.5. The formed pores enlarge with increasing stretching ratio. The pores on the surface of the PVC membrane that is shown in Figure 2 were measured. The average values range from $0.6 \mu\text{m} \times 2.8 \mu\text{m}$ to $6.0 \mu\text{m} \times 12 \mu\text{m}$ (width \times length; see Table II).

Shape and average size of the pores were not influenced by the used PVC or plasticiser. Combinations of three different PVC and four plasticizer systems were investigated. Using the same filler and process parameters, the surface and cross section of the PVC sheets showed similar properties.

Moisture permeability and waterproofness

Both the permeability for water and for water vapor was limited by the pore system's geometry on the one hand and the hydrophobicity of the recipe components PVC, plasticizer, and filler from which the membranes were prepared on the other hand. The influence of the recipe components was investigated by varying the one single component at a time. Figure 3 illustrates the changes of the water vapor permeability and the waterproofness when PVC types are varied. The values were obtained for membranes prepared with a plasticiser mixture of derivatives of citric acid and glass beads as filler. In Figure 3, the plotted test values were obtained for stretching ratios ranging between 1 : 1 (compact sheet) and 1 : 4.5 (350% strain). It is obvious that the moisture permeability as well as the waterproofness depend on the PVC type. In case of PVC having a high amount of emulsifier (PVC 1), the waterproofness decreased to nearly zero at already low strain (160%). Using a PVC type with a low content of emulsifier (PVC 2), the waterproofness remained at a high level. PVC 3

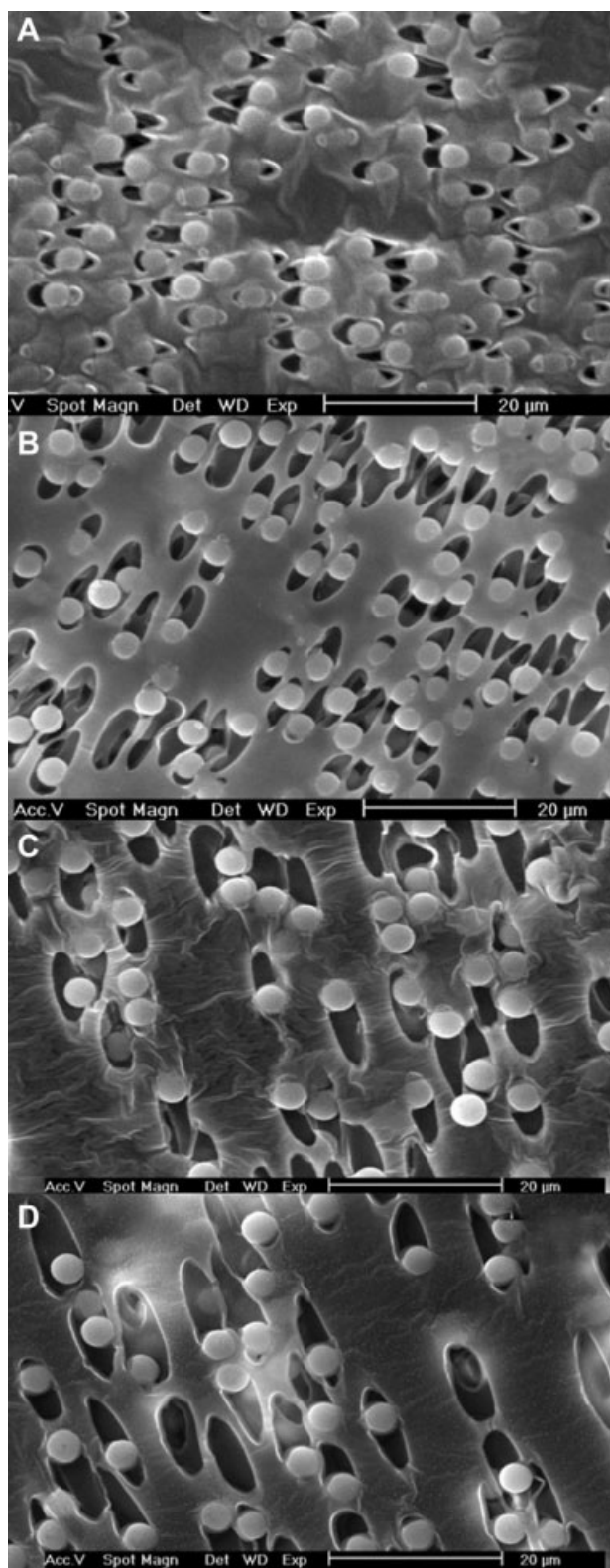


Figure 2 Scanning electron micrographs of surface of PVC sheets that were stretched in a different ratio; The PVC plastisol contained 19.5 vol % filler SX-2 and DINP plasticizer; Stretching ratios: A, 1 : 2.0; B, 1 : 2.5; C, 1 : 3.5; and D, 1 : 4.0.

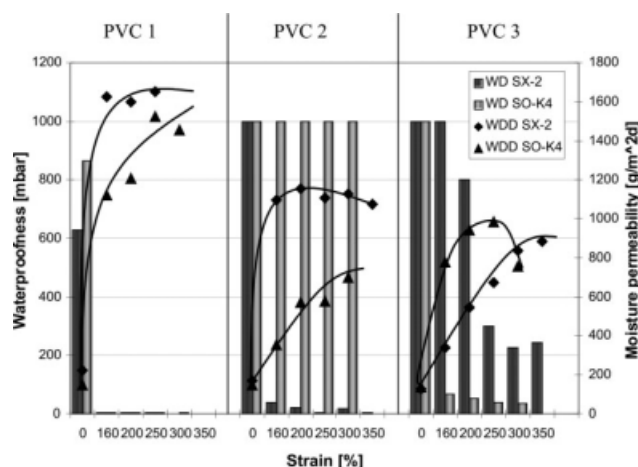


Figure 3 Waterproofness and moisture permeability of membranes obtained from PVC 1, PVC 2, and PVC 3 at different stretching ratios 19.5 vol % filler (SX-2, dark; SO-K4, light) and a mixture of citric acid esters as plasticiser were used.

was a hydrophobic PVC type containing an amount of emulsifier ranging between those of PVC 1 and PVC 2. Membranes prepared from PVC 3 to increase strain showed a continuously decreasing waterproofness. At the maximum value of 900 g/m²d moisture permeability, the waterproofness was still up at about 250 mbar. The highest moisture permeability of about 1500 g/m²d could be achieved using the more hydrophilic PVC 1. PVC 2 had a maximum moisture permeability of about 700 g/m²d. Using the polysiloxane filler instead of glass beads, the maximum moisture permeability increased to 1700 g/m²d (Fig. 3). In membranes prepared from PVC containing a high amount of emulsifier, the waterproofness could not be improved neither by variations of the filler nor of the plasticiser. In contrast to that the waterproofness of membranes produced from PVC types containing medium and low amounts of emulsifier could be controlled by the type of fillers used. In any case, the polysiloxane filler caused a decrease of the waterproofness below 100 mbar even if a low stretching ratio was applied. Using a suitable PVC type and glass filler, a waterproofness of upto 1000 mbar can be obtained, but the moisture permeation does not reach as high values as the polysiloxane filler does.

TABLE II
Maximum Pore Size that was Obtained by SEM on the Membrane Surface

Stretching ratio	Maximum pore size [μm]
1 : 1.8	2.8
1 : 2.0	3.8
1 : 2.9	6.6
1 : 3.4	12.0

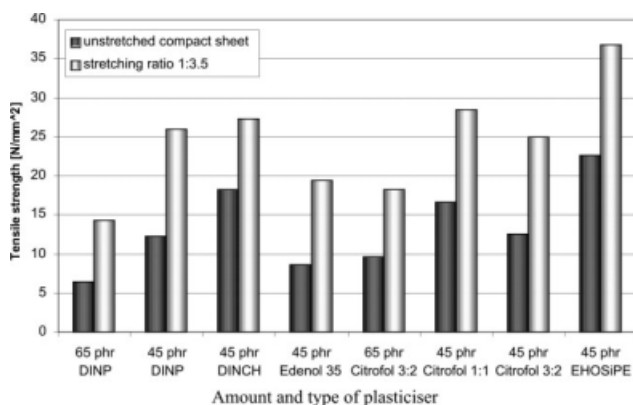


Figure 4 Tensile strength of PVC sheets containing various plasticiser.

Mechanical properties of the PVC sheets

The mechanical behavior is important for both the preparation process, especially stretching and the performance characteristics of the membranes. Thus, the tensile strength was measured twice, before and after the stretching process.

The mechanical properties of the PVC membranes were mainly influenced by the type and the content of the plasticiser. In general, the tensile strength dropped with increasing plasticiser content. A compact PVC sheet (PVC 1) containing 65 parts of plasticiser (DINP) showed a tensile strength of 6 N/mm², whereas the same sheet containing 45 parts of plasticiser showed a tensile strength of 12 N/mm². Due to the improved mechanical strength and a lower shrinkage, 45 parts of plasticiser were used for further investigations. Varying the type of plasticiser, the tensile strength could be controlled in the range between 8 N/mm² (epoxidised linseed oil) and 23 N/mm² (Edenol 35). Stretching the PVC sheets caused an increase of the tensile strength upto 25–30 N/mm² using DINP, derivatives of citric acid, or DINCH and more than 35 N/mm² using EHOSiPE (Fig. 4).

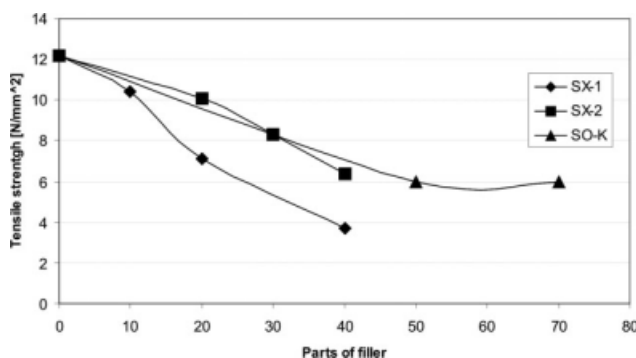


Figure 5 Tensile strength of PVC sheets in dependence of the amount of fillers.

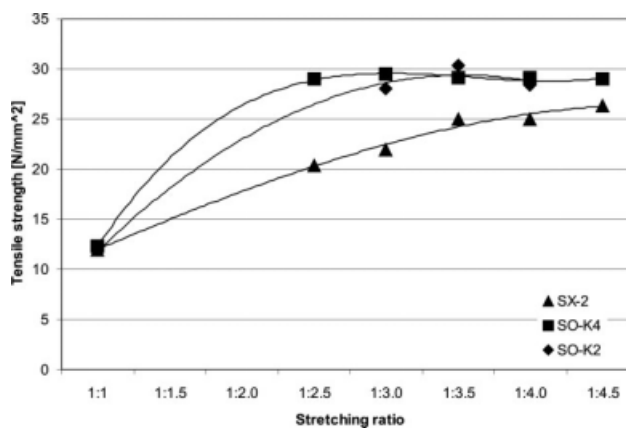


Figure 6 Tensile strength of PVC sheets in dependence of the stretching ratio.

Furthermore, the tensile strength depended on the amount of filler (Fig. 5), the stretching ratio (Fig. 6), and the PVC type (Fig. 7). PVC sheets were prepared using plastisols from PVC 1 and 65 parts DINP to investigate the influence of the amount of filler. At least 15 vol % particles of 2.5 μm mean size are necessary to achieve an interconnecting pore system. This value is given in literature for preparing microporous polyolefin sheets.⁶ The higher the amount of filler used the higher the connected pore volume, but the higher the paste viscosity and the worse the mechanical properties of the sheets. In case of PVC sheets, the optimum filler content was 19.5 vol %. That equates to 35 parts of polysiloxane fillers and 65 parts of glass filler, due to the different densities. In Figure 5, there is shown the decrease of the tensile strength for 100- μm thick compact PVC sheets using polysiloxane fillers (SX-1, SX-2) as well as glass beads (SO-K). Starting from 12 N/mm² for the unfilled PVC sheet, the tensile strength using 19.5 vol % SX-2 filler (8 N/mm²) as well as 19.5 vol % SO-K filler (6 N/mm²) was quite low. The tensile strength for the filled systems could be improved upto 12 N/mm² by optimizing of the recipe. For example, the PVC sheets containing PVC 2, 19.5 vol % filler

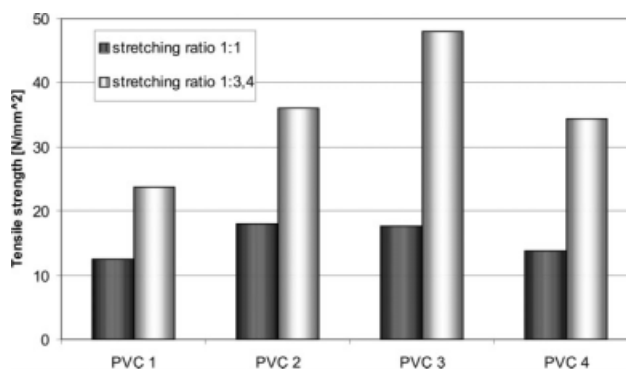


Figure 7 Tensile strength of PVC sheets containing different PVC types.

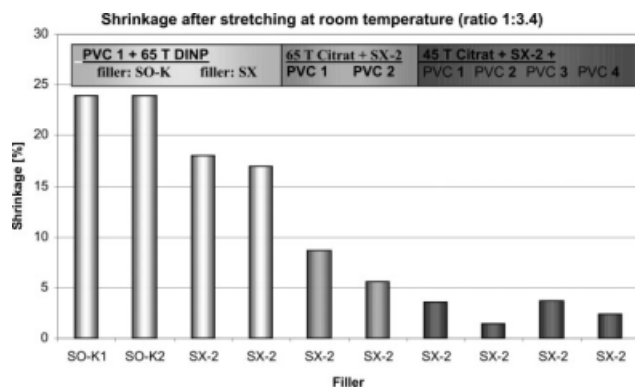


Figure 8 Differences in shrinkage of PVC sheets in dependence of fillers, PVC type, and plasticiser.

(polysiloxane or glass beads), and derivatives of citric acid as plasticiser (45 parts) gave tensile strengths of about 18 N/mm² for the compact sheets and values in the range of 25 and 30 N/mm² for the stretched sheets (Fig. 7). Especially, the values of the polysiloxane filled systems were depending on the stretching ratio while the glass filled systems reached the maxima at low stretching ratios of 1 : 2.5 (Fig. 6).

The differences between various PVC types were less for the compact films but became significant after stretching. For instance, the highest tensile strength obtained in films prepared from PVC 3 increased from 18 (compact) to 48 N/mm² (stretched). By contrast, PVC 1 showed only half the value of PVC 3 after stretching.

All the investigated compact PVC foils showed sufficient tensile strength to tolerate stretching ratios of at least 1 : 3.0.

Shrinkage of the PVC sheets

To obtain microporous PVC membranes, the compact films were stretched with a ratio of upto 1 : 4.5. After the stretching process, the membranes were able to relax which involved shrinkage of the membranes. Figure 8 shows the effect of the various recipe components on the shrinkage. The bars one to four in the bar chart visualize the influences of the filler. Four different fillers were incorporated into a PVC paste containing 65 parts of plasticiser. In comparison to glass beads, membranes filled with polysiloxane particles showed a lower shrinkage. The used particle size did not have a significant effect on the shrinkage. A considerable decrease in shrinkage can be obtained by varying the plasticiser. In comparison to membranes containing DINP (3rd bar, ~17%), membranes with the plasticiser citric acid ester showed a lower shrinkage (5th bar, ~8%). Furthermore, a decrease in shrinkage was achieved by minimizing the amount of plasticiser from 65 parts down to 45 parts (bar 5 and 7) as well as by optimizing

the PVC (bars 7 to 10). Using an ideal composition of the PVC paste, membranes can be produced that show less than 2% shrinkage after stretching upto 1 : 3.5.

Continuous preparation

The aim was to develop a continuous process for preparation microporous films that is not restricted by the use of solvents or subsequent leaching. This could provide for a two step roll-to-roll process. First step was the preparation of the compact PVC sheet via common plasticiser PVC coating. The PVC plastisol was coated onto release paper in two layers by means of an on-roll-knife coater. The PVC sheet was delaminated and stretched continuously after gelification at temperatures of 180°C for 4 min.

CONCLUSIONS

The research work succeeded in the generation of microporous membranes via incorporation of fillers in PVC pastes, producing thin films by spread-coating and gelification, and subsequent stretching of the resulting filled compact film. Polysiloxane as well as glass beads were proved as suitable fillers. Moisture permeability and water resistance were mainly affected by recipe components, especially the PVC type and the type of filler as well as stretching ratio.

Using filler particles having a mean particle size of about 2–3 μm and a maximum particle size below 10 μm, membranes could be obtained with a microporous system that is both permeable to moisture and water resistant. The moisture permeability was variable in the range from 700 to 1700 g/m²d. Depending on the PVC type and filler water resistance was achieved upto 1000 mbar.

Required performance characteristics, like low shrinkage (<2%) and high tensile strength (>20 N/mm²) were succeeded via improvement of the recipe.

Thus, a simple process was developed to produce nonrigid, breathable PVC membranes, that is not restricted by the use of solvents or subsequent leaching. This could provide for a two step roll-to-roll process. First step was the preparation of the compact PVC sheet via common plasticiser PVC coating, second step was the stretching process. Both techniques are commonly used in various applications. Therefore, it is to believe that the process will be commercially applicable.

References

1. Gore, R. W. U.S. Pat. 3,953,566 (1973).
2. Gore, R. W. U.S. Pat. 3,962,153 (1973).
3. Rudolph, C. DE Pat. 195 44 912 A1 (1995).

4. Brady, A. K.; Burnett, J. J.; Klug, L. C. DE Pat. 697 17 146 T2 (1996).
5. Stopper, R. S.; Jacobs, L. R. DE Pat. 698 25 881 T2 (1998).
6. Kundu, P. P.; Choe, S. J Macromol Sci Polym Rev 2003, 43, 143.
7. Kim, K.-J.; Kwon, S.; Kim, H.; Kundu, P. P.; Kim, Y.-W.; Lee, Y.-K.; Lee, B. H.; Choe, S. J Appl Polym Sci 2003, 87, 311.
8. Kim, K.-J.; White, J. L.; Shim, S. E.; Choe, S. J Appl Polym Sci 2004, 93, 2105.
9. Nago, S.; Mizutani, Y. J Appl Polym Sci 1996, 61, 31.
10. Nago, S.; Nakamura, S.; Mizutani, Y. J Appl Polym Sci 1992, 45, 1527.
11. Nago, S.; Mizutani, Y. J Appl Polym Sci 1998, 68, 1543.
12. Kundu, P. P.; Biswas, J.; Kim, H.; Shim, S. E.; Choe, S. Adv Polym Technol 2004, 23, 230.
13. Kwon, S.; Kim, K. J.; Kim, H.; Kundu, P. P.; Kim, T. J.; Lee, Y. K.; Lee, B. H.; Choe, S. Polymer 2002, 43, 6901.
14. Nago, S.; Mizutani, Y. J Appl Polym Sci 1993, 50, 1815.
15. Rainer, N. B.; Wilson, P. A. U.S. Pat. 3,674,722A (1970).
16. Kang, J. S.; Kim, K. Y.; Lee, Y. M. J Appl Polym Sci 2002, 86, 1195.
17. Babu, P. R.; Gaikar, V. G. J Appl Polym Sci 2000, 77, 2606.
18. Hirose, S.; Yakusawa, E.; Nose, T. J Appl Polym Sci 1981, 26, 1039.
19. Islam, M. A.; Stojcheva, R. N.; Dimov, A. J Membr Sci 1996, 118, 9.
20. Kenkyusho, S. C. JP 22,618,37A (1989).
21. Eydal, A. M.; Hajdu, K.; Hazan, B.; Edelstein, D. J Appl Polym Sci 1992, 46, 1613.
22. Baniel, A.; Eydal, A.; Edelstein, D.; Hajdu, K.; Hazan, B.; Ilan, Y.; Zamir, E. J Membr Sci 1990, 54, 271.
23. Eydal, A. M.; Hajdu, K.; Hazan, B.; Edelstein, D. J Appl Polym Sci 1992, 46, 1621.