# TPX / Siloxane Blend Membrane for Oxygen Enrichment

J. Y. LAI and G. J. WU, *Department of Chemical Engineering, Chung Yuan University, Chung Li, Taiwan, Republic of China,* and S. S. SHYU, *Department of Chemical Engineering, Central University, Chung Li, Taiwan, Republic of China*

## Synopsis

The effects of composition, molecular weight, and milling temperature on homogeneity, gas permeability, selectivity of oxygen/nitrogen, and mechanical strength of the TPX/siloxane blend membranes were studied. By adjusting the blending conditions and hence controlling the homogeneity, the gas permeability of TPX membrane was significantly improved without loss of oxygen/nitrogen selectivity. The oxygen permeability of $1.57 \times 10^{-8}$ $cm^3$ (STP) $cm/cm^2$ s cm Hg and the oxygen/nitrogen permeation ratio of 6.92 can be obtained under the condition of TPX (MX-001)/siloxane (75,000 MW) = 9/1 at 65°C milling temperature. This membrane possesses 133 $kg/cm^2$ tensile strength and 92% elongation. The morphology of the blend membranes was studied.

## INTRODUCTION

Poly(4-methyl-pentene-1) (TPX) is a potentially useful membrane material for oxygen enrichment, because of its excellent mechanical strength, high oxygen-nitrogen selectivity, and fairly high gas permeability. The oxygen permeabilities ($P_{O_2}$) and oxygen permeability to nitrogen permeability ratios ($P_{O_2}/P_{N_2}$) of most TPX membranes are in the ranges of $2.6–3.9 \times 10^{-9}$ $cm^3$(STP) $cm/cm^2$ s cm Hg and 2.7–4.15, respectively.[1-3]

It has been reported that silicone rubber is more permeable to gases than most of other membranes.[4] However, its $P_{O_2}/P_{N_2}$ permeability ratio is only about 2; consequently, silicone rubber cannot be used to enrich the oxygen from the air to more than 30%.[4] Thus the development of other types of membrane is needed. Among various approaches, the development of a composite membrane is one solution to improve the performances of these simple membrane. Ward et al.[5] prepared the copolymer membranes of dimethyl–siloxane/polycarbonate, resulting in an increase of the $O_2/N_2$ selectivities of siloxane membrane. Kawakami et al.[6] utilized plasma deposition of vinylpyridine onto siloxane substrate to improve the gases selectivity of siloxane membrane with loss of gas permeability. Lai and Wei[7] utilized the γ-ray irradiation-grafted vinylpyridine onto TPX and significantly improved the $P_{O_2}/P_{N_2}$ ratio up to 7.5 without loss of gas permeability by adjusting the tightness of TPX membrane before grafting. Furthermore, the properties and performances of a composite membrane can also be improved by blending two or more polymers.[8-15]

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The present study is to investigate how the gas permeability of TPX membrane may be improved by blending with polydimethylsiloxane. The effects of composition, kind of TPX, molecular weight of siloxane, and milling temperature on homogeneity, gas permeability, selectivity of oxygen and nitrogen, and mechanical strength of the blend membranes were studied. The blend membrane homogeneity, which plays an important role on the gas permeability and permselectivity, was determined by microscopy and Rheovibron study.

## EXPERIMENTAL

### Materials

Poly(4-methyl-pentene-1) (TPX, MX-001 and RT-18) were supplied by Mitsui Co. $T_m$'s are 235 and 240°C, tensile strength, 140 and 235 kg/cm$^2$, elongation, 120 and 25, hardness, 35 and 85, and softening temperature, 147 and 173°C for TPX (MX-001 and RT-18) from Mitsui Co. catalog, respectively. Polydimethylsiloxane with 75,000 and 100,000 MW and high gum was obtained from Polyscience Co. Cyclohexene was supplied by Ferak Berlin Co. Oxygen and nitrogen of 99.9% purity were used.

### Membrane Preparation

The casting solutions were prepared by different compositions of TPX and siloxane (MW 75,000 and 100,000 and high gum) to a total 5 wt % of solute in cyclohexene and were agitated and milled at different temperature (55, 65, 75°C) for 30 min. The membrane was formed by casting the solution onto a glass plate which was preheated to the same temperature as the casting solution to a certain predetermined thickness by using a Gardner knife. The glass plate was evaporated for 40 min at a predetermined temperature of 90°C in a well-circulated oven. Then the glass plate with the membrane was immersed in 4°C water for 2 h. The membrane was then peeled off and dried in vacuum for 24 h to remove solvent residue. The membrane thickness was 30 $\mu$m in average.

## GAS PERMEABILITY TEST OF MEMBRANE

The apparatus for measuring the permeability of the gas through the membrane is shown in Figure 1. The gas permeability was determined by the following equation:

$$P = q \cdot l/(p_1 - p_2) \cdot A \cdot t$$

where $P$ = gas permeability [cm$^3$(STP) cm/cm$^2$ s cm Hg], $q/t$ = volume flow rate of gas permeate [cm$^3$(STP)/s], $l$ = membrane thickness (cm), $p_1$ and $p_2$ = pressures on the high pressure side and lower pressure side of the membrane, respectively (cm Hg), and $A$ = effective membrane area (cm$^2$).

### Microscope and Rheovibron

An optical microscope of Olympus PHM and a scanning electron microscope (SEM) of Cambridge S150 MK2 were used to study the homogeneity of the prepared blend membranes.

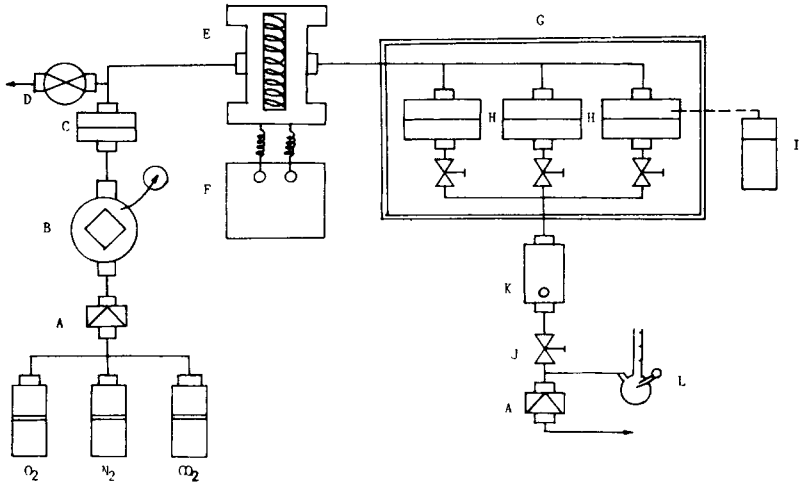



Fig. 1. Gas permeation apparatus: (A) check valve; (B) regulator/pressure gauge (0–11 kg/cm$^2$); (C) gas filter; (D) vent; (E) heater; (F) temperature controller; (G) thermoisolator; (H) membrane cell SS filter holder 50 mm OD; (I) digital thermometer TX-500; (J) shut-off valve; (K) flowmeter R-2-15-AA; (L) soapfilm meter.

A direct reading viscoelastometer, Rheovibron DDV-II-C of Toyo Baldwin Co., was used to study the homogeneity by determining the $T_g$ change of the blended membranes.

### Measurement of Tensile Strength

The tensile strength measurement of TPX and blended TPX membranes were carried out on the Toyo Baldwin type Tensilon/UTM-III-100 instrument at various temperature. The membranes were tested by ASTM method[16] for their tensile strengths and elongations in their dry states.

## RESULTS

### Effect of Milled Temperature

Because of the problem of bubble formation above 75°C, the milling temperatures in this study were in the range of 55–75°C. Figure 2 depicts that as the milling temperature increases the gas permeability decreases and the oxygen/nitrogen permeability ratio increases. This trend appears to hold for siloxane with different molecular weight blend with TPX (RT-18).

### Effect of Composition

The oxygen permeabilities and permeability ratios of oxygen and nitrogen of TPX (MX-001) membranes[7] were in the range of 2.91–7.14 $\times$ $10^{-9}$ cm$^3$(STP) cm/cm$^2$ s cm Hg, and 2.7–4.4, respectively. Table I shows that the gas permeabilities were significantly improved without loss of $P_{O_2}/P_{N_2}$, compared to pure TPX membrane, for the blended membranes containing less than 20 wt % of siloxane. As shown in Table I, as the wt % of siloxane increases,

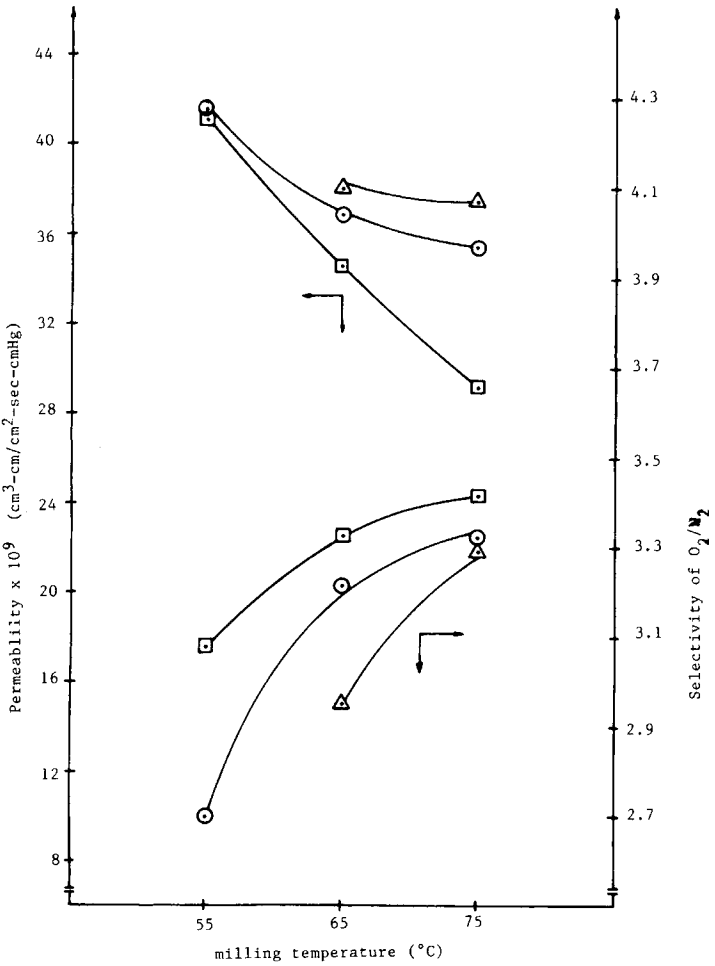



Fig. 2. Effect of milling temperature and polydimethylsiloxane MW on gas permeabilities and permeability ratios of polyblends membrane. TPX (RT-18)/Siloxane = 7/3: (□) 75,000 MW; (○) 100,000 MW; (△) high gum.

oxygen and nitrogen permeabilities increase and $P_{O_2}/P_{N_2}$ decreases. It appears that the less siloxane contents the more homogeneity it shows. In Figure 3(C), the morphology of TPX/siloxane (= 6/4) blend shows an obvious phase separation in contrast to the pure TPX (MX-001) [Fig. 3(A)]. As the content of silicone rubber decreases, the morphology of TPX/siloxane blend tends to be more homogeneous [Fig. 3(B)]. Figure 4 depicts two distinct transitions of TPX/siloxane, indicating incompatibility between the two polymers. One is the low-temperature transition which is produced by silicone phase; the other is high-temperature transition which is caused by TPX. When the content of silicone rubber decreases to 10 wt %, both $T_g$'s shift inwardly. This may indicate that molecular mixing occurs between silicone rubber and TPX. The dynamic data (mechanical behavior) is consistent with the morphological observation shown in Figure 3(B). The same results were found for using TPX

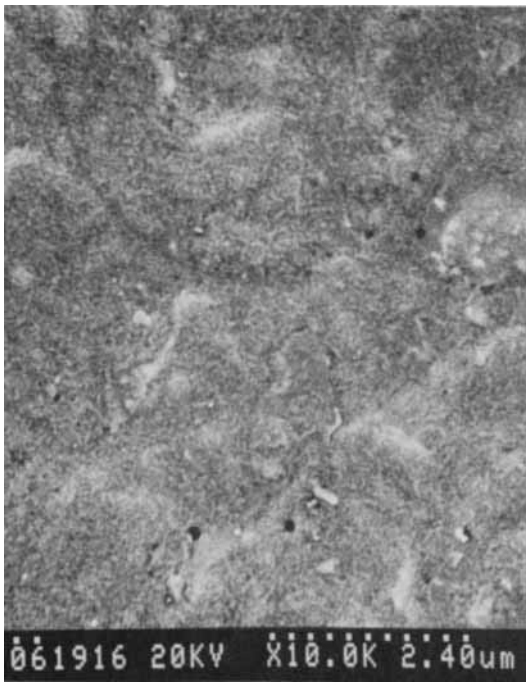
TABLE I
Effect of Composition of Polyblends Membrane on Gas Permeabilities and Permeation Ratios[a]

| Composition (wt % of siloxane) | MW of Polydimethyl-siloxane | Gas permeability ($P \times 10^9$) ($cm^3$ cm/$cm^2$ s cm Hg) | | Permeation ratio |
|---|---|---|---|---|
| | | $O_2$ | $N_2$ | $P_{O_2}/P_{N_2}$ |
| 100 | — | 60.00 | 30.00 | 2.00[4] |
| 40 | 75,000 | 40.70 | 14.00 | 2.93 |
| 30 | 75,000 | 23.68 | 7.01 | 3.56 |
| 20 | 75,000 | 20.73 | 3.79 | 5.50 |
| 10 | 75,000 | 15.73 | 2.52 | 6.92 |
| 30 | 100,000 | 24.39 | 8.02 | 3.19 |
| 30 | high gum | 24.44 | 9.08 | 2.78 |
| 0 | — | 2.91 | 0.66 | 4.40[7] |

[a] Operating pressure = 20 psig; operating temperature = 25°C; milled at 65°C, TPX used is MX-001.

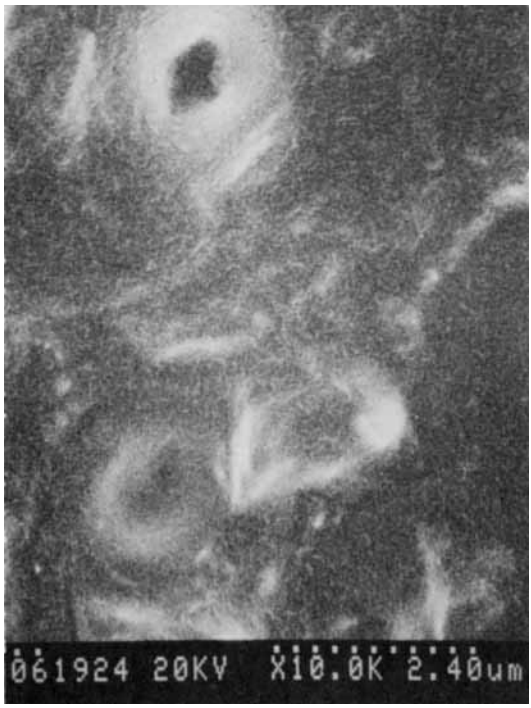

(A)

Fig. 3. Microphotographs (×10000) of the polymer blends: (A) pure TPX (MX-001); (B) the polymer blend of 10 wt % siloxane content; (C) the polymer blend of 40 wt % siloxane content.




(B)

Fig. 3. (*Continued from the previous page.*)




(C)

Fig. 3. (*Continued from the previous page.*)

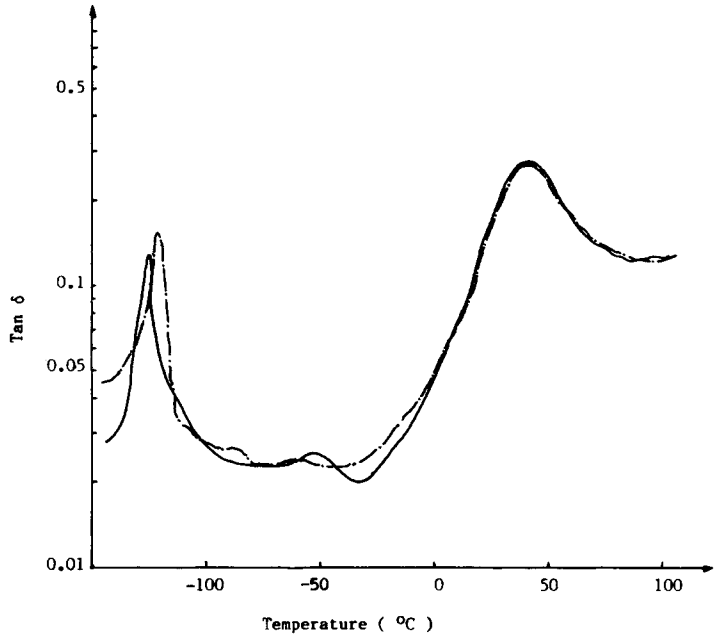


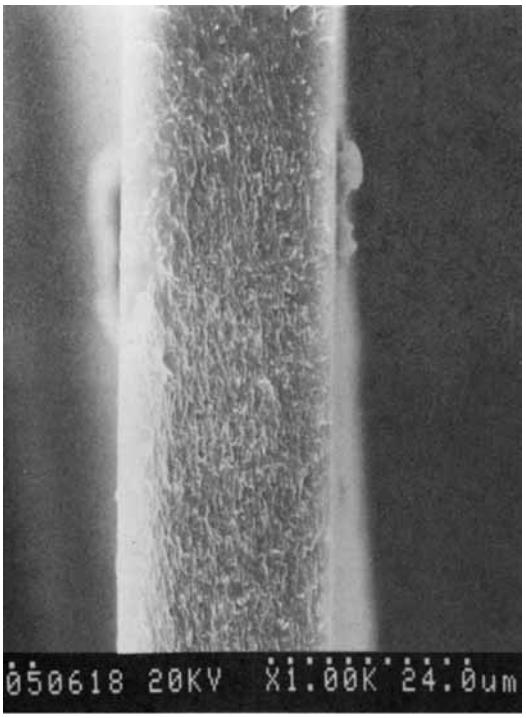

Fig. 4. Tan $\delta$ vs. temperature for polyblends membranes: (———) TPX (MX-001)/siloxane (100,000 MW) = 6/4; (—·—·) TPX (MX-001)/siloxane (100,000 MW) = 9/1.

(MX-001) blended with different molecular weights of siloxane, i.e., 75,000, 100,000 and high gum.

## Effect of Molecular Weights of Siloxane and Different Kind of TPX

The molecular weight of siloxane does not have a marked effect on both the oxygen permeability and the $P_{O_2}/P_{N_2}$ of the membrane blended with TPX (MX-001). The oxygen permeabilities are in the range of 23.68–24.44 $\times 10^{-9}$ $cm^3$(STP) cm/$cm^2$ s cm Hg for the membranes blending TPX (MX-001) with all different molecular weight siloxanes in the ratio of 7:3. In the blended membrane with same weight ratio [TPX(MX-001)/siloxane], the oxygen/nitrogen permeability ratio increases slightly as the molecular weight of siloxane decreases. In the case of using TPX (RT-18) to mix with siloxane, the similar results were observed (shown in Fig. 2).

Because of the large pendant group on TPX, the density of the crystalline region is lower than that of the amorphous region in TPX. This indicates that the crystalline region has more free volume than the amorphous region does. The inherent viscosities ($\eta$) of MX-001 and RT-18 of TPX were measured by Ubellohde Viscosimeter and the ratio was $\eta_{MX\text{-}001}/\eta_{RT\text{-}18} = 1/1.3$. TPX (MX-001) has lower molecular weight and more branching chain than TPX (RT-18) does. The morphologies of these two types of TPX are shown in Figure 5. From the scanning electron microscopy, it is obvious to see the morphology of TPX (MX-001) is more homogeneous and denser structure than that of TPX (RT-18). Therefore, TPX (RT-18) is expected to be higher $O_2$ permeability and lower selectivity of oxygen and nitrogen. The morphology data are



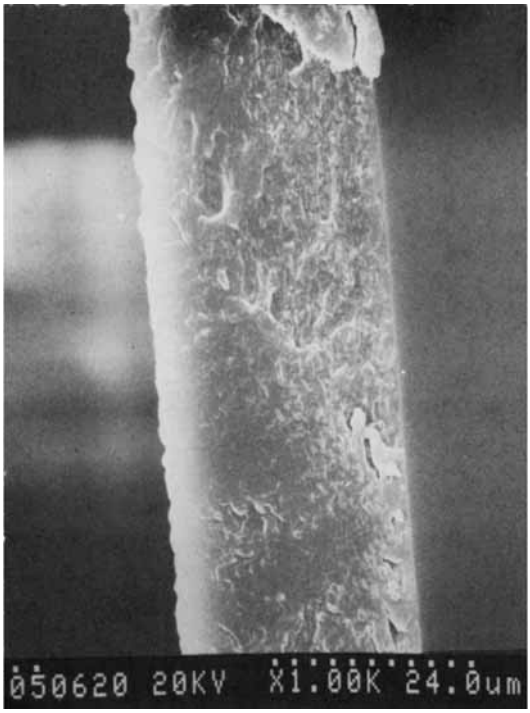

(A)

Fig. 5. Microphotographs (×1000) of the cross section of: (A) pure TPX (MX-001); (B) pure TPX (RT-18); (C) TPX (MX-001) blend with 10 wt % siloxane (100,000 MW).

consistent with the oxygen permeability to TPX (RT-18) blend membranes showing 30–56% higher than that of the TPX (MX-001) blend membranes. Figure 5(C) shows that the cross section of TPX (MX-001)/siloxane (100,000 MW) = 9/1 membrane is quite homogeneous. Furthermore, the TPX (MX-001)/siloxane (100,000 MW) membrane is more porous than the pure TPX (MX-001) membrane is [Fig. 5(A)]. This explains the higher gas permeability of blended membranes.

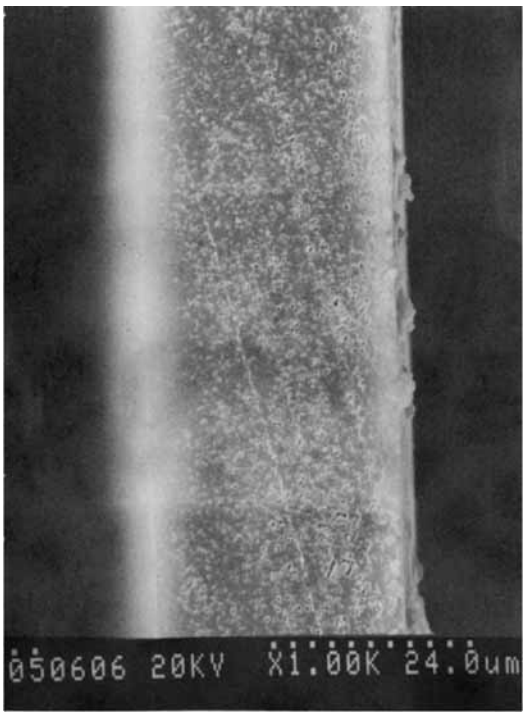
## Mechanical Strength of Membrane

The tensile strength and elongation of pure TPX (MX-001) membrane are 200 kg/cm$^2$ and 75%, respectively. The tensile strength and elongation were not appreciably different from polyblend membranes containing 75,000 and 100,000 MW and high gum of polydimethylsiloxane in this study. Figure 6 shows that, as the wt % of siloxane increases, the tensile strength decreases and elongation increases. The tensile strength and elongation are 133 kg/cm$^2$ and 92%, respectively, for TPX (MX-001) : siloxane = 9 : 1 membrane, which possesses the highest oxygen/nitrogen permeability ratio. Comparing to 4-vinylpyridine $\gamma$-ray grafted TPX membrane,[7] this blend membrane possesses higher elongation and lower tensile strength.




(B)

Fig. 5. (*Continued from the previous page.*)




(C)

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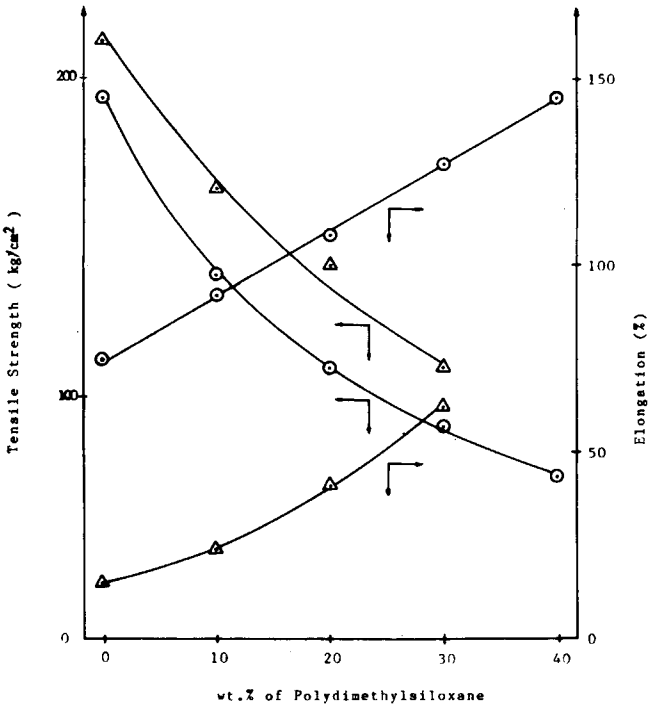


Fig. 6. Effect of composition on tensile strength and elongation of polyblends membrane: (○) TPX (MX-001)/siloxane (100,000 MW); (△) TPX (RT-18)/siloxane (100,000 MW).

## DISCUSSION

The occurrence of a microphase separation in a blending polymer is well documented. It is known that the microphase separation can be decreased by increasing the milling temperature.[17] The results of this study show that as the milling temperature increases the gas permeability decreases and $P_{O_2}/P_{N_2}$ increases. This could be explained by the fact that the homogeneity of the blend membrane increases because of a dense packing of polymer molecules. The increasing TPX/siloxane interaction is a result of an increase of the milling temperature. Furthermore, as the homogeneity of the blended membrane improved, the gas permeability decreased, and oxygen/nitrogen permeability ratio increased.

It is observed that the poor membrane formed when membranes are prepared by TPX (RT-18) without or with low siloxane content. The results of the present study suggest that TPX (RT-18) should not be blended with less than 30 wt % siloxane for reasonable elongation.

It is interesting to point out that both the oxygen and nitrogen permeabilities of any of the blended membranes prepared in this study fall within the range of the lower and upper limits of the permeabilities of the pure materials, namely, the oxygen and nitrogen permeabilities of pure TPX and siloxane. However, for a given change of the TPX content in a TPX/siloxane-blended membrane, the contents of decrease of oxygen permeability and nitrogen permeability are not proportionally the same. This could result in a situation in which the $O_2/N_2$ permeability ratio of the blended membrane is larger

than the $O_2/N_2$ permeability ratio of either pure material. The results shown in Table I is an example of an enhancement of the permeability ratio of $O_2/N_2$ without having the oxygen permeability of the blended membrane higher than that of pure siloxane.

Although the oxygen permeability of TPX(RT-18)/siloxane membrane is about 30 wt % less than that of polydimethylsiloxane membrane,[4] TPX(RT-18)/siloxane membrane has a higher $P_{O_2}/P_{N_2}$ than siloxane membrane has. The gas permeability and $P_{O_2}/P_{N_2}$ are higher than that of pure TPX membrane[1-3,7] and membranes by plasma deposition of vinylpyridine onto siloxane membrane substrate.[6]

## CONCLUSION

By adjusting composition, molecular weights of TPX and siloxane, and milling temperatures, the oxygen permeabilities of TPX/siloxane blend membranes can be varied from 1.57–4.11 $\times 10^{-8}$ $cm^3$(STP) $cm/cm^2$ s cm Hg. The oxygen/nitrogen permeability ratios are in the range of 3.08–6.92. The gas permeabilities of the blend membranes decreased but $P_{O_2}/P_{N_2}$ increased with increasing milling temperature. By increasing the siloxane content, the oxygen permeability of the blend membrane increases; on the other hand, the $P_{O_2}/P_{N_2}$ ratio decreases as the siloxane content increases.

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