

The Effects of Soft Segments on the Physical Properties and Water Vapor Permeability of H₁₂MDI-PU Cast Films

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SYNOPSIS

This research was based on the study of the effects of H₁₂MDI-1, 4BD PU soft segments on the physical properties and water vapor permeability of films cast from solvent evaporation or wet coagulation method. The soft segments studied included polyether, polyester, and polycaprolactone polydiols. The NCO/OH mol ratios of prepolymer were prepared by 2, 3, 4, 5, and 8, respectively. The chain lengths of the soft segments used were: PTMG of molecular weights 650, 1000, 2000, and 2900; PBA of 1000, 2000, and 3000. The results revealed that the polyether-based PU cast films had lower T_g s than the polyester-based PU films. In general, the polyether-based PU films shows the characters of higher water vapor permeability, lower breaking elongation, and higher breaking strength. Films with higher molecular weight soft segments in the polymer chains exhibited lower T_g s, lower breaking strength, higher breaking elongation, and higher water vapor permeability. As the hard segment contents were increased, the films exhibited higher T_g s. Films with higher hard-segment ratios had the highest breaking strength but the water vapor permeability, on the other hand, became lower. Films cast from the solvent evaporation method had higher breaking strength and higher breaking elongation but lower water vapor permeability than films cast from the wet coagulation method. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Segmented polyurethane (PU) is composed of flexible soft segment and rigid hard segment. The variations in the compositions of the soft and hard segments impart PU films a wide range of physical properties. Polyurethane products have been used extensively in making elastomers, coatings, and foams. Recently, PU films with high water vapor permeability were used in breathable coating fabrics,¹⁻³ medical appliances,⁴ and special adhesives. Previous studies of PU were primarily focused on using the aromatic diisocyanates as hard segments while varying the soft segment ratios to investigate the physical and thermal properties. However, PU films based on aromatic diisocyanates have poor light stability and weather resistance, being susceptible to becoming yellowish and chemically degrad-

able.⁵⁻⁷ The research based on the aliphatic diisocyanate series PUs is now becoming a target of interest. J. W. C. Vanbogart et al.⁸ used three types of polydiols: polyester, polyether, and polycaprolactone as soft segments to react with MDI or H₁₂MDI in the synthesis of PUs to study the compositional, mechanical, and thermal properties. Their results indicated that the breaking strength of H₁₂MDI-based PU films was superior to that of MDI-based PUs. C. A. Byrene, N. S. Schneider, and K. C. Frisch⁹ used different isomers of H₁₂MDI in making PU films, in which the relationships between the PU films on the compositions and properties were studied. Other types of aliphatic diisocyanates being studied included HDI, IPDI, TMXDI, PPDI, and XDI.¹⁰⁻¹⁸ These researches were mostly concerned with the study of PU synthesis, properties, and applications.

In the applications of breathable coating fabrics, the water vapor permeability of PU films has become an important element. Previous studies on the water vapor permeability were mostly limited on using the

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aromatic PU membranes.¹⁹⁻²⁴ Studies on the H₁₂MDI-1,4 BD-based PU membranes were relatively few, especially on the compositions and structures of aliphatic PUs in the study of water vapor permeability. This paper studied the soft segments of H₁₂MDI-based PU films, cast from either solvent evaporation or wet coagulation method, on the membranes' physical properties and water vapor permeability.

EXPERIMENT

A two-stage polymerization method was utilized in the synthesis of the H₁₂MDI-based PUs. Polyols and chain extenders were vacuum distilled before use and their —OH and —NCO equivalent weight were determined by titration before subjecting to reactions. At the end of the reactions, all PU resins were diluted to 25% DMF solutions (by weight), and the membranes were obtained by either solvent evaporation or wet coagulation method. The membranes from the solvent evaporation method were obtained by coating the PU solution evenly on a glass plate (ca. 45 × 60 cm), followed by drying the membranes in an oven maintained at 50°C for 72 h. The membranes were then removed and placed in a dessicator

before testing. The membranes from the wet coagulation method were obtained by similarly coating the PU solution on a glass plate, then immediately immersing the glass plate into a water bath maintained at 30°C. After 3 min, the plate was removed from the bath and flushed with cold water, followed by dipping in a warm-water bath for 3 min. The plate was then removed and rinsed with cold water. Finally, the membrane on the plate was dried in an oven kept at 50°C for 24 h.

The samples for molecular weight studies were vacuum dried for 3 days and determined by a Waters GPC instrument. The results are listed in Table I. The physical properties of the membranes were analyzed by stress-strain testings, DSC, and dynamic mechanical studies. Stress-strain testings were performed according to the ASTM D 412 standard method at a crosshead speed of 50 cm/min. with a clamp distance of 3 inches. A V₂ 2A DuPont 9000 instrument was used for DSC measurement, using liquid nitrogen for cooling and with a heating rate of 20°C/min for thermal analysis. Dynamic mechanical data were obtained by using a Rheovibron DDV III apparatus at a frequency of 110 Hz and a constant heating rate of 2°C/min. The temperature range used was -150-+100°C. A LYSSY L80-4000 model was used for membranes' water vapor per-

Table I M_n , M_w/M_n , and T_g of PU of H₁₂ MDI

Composition/Item	M_n for Polyol	NCO/OH Ratio	M_n for PUs	M_w/M_n	T_g (°C) (DSC)	T_g (°C) (Rheovibron)
PEG-H ₁₂ MDI-1,4BD	1000	2	107833	1.705	-44	-39
PPG-H ₁₂ MDI-1,4BD	1000	2	89372	1.804	-36	-23
PTMG-H ₁₂ MDI-1,4BD	650	2	110036	1.712	—	+4.7
PTMG-H ₁₂ MDI-1,4BD	1000	2	121580	1.587	-49	-39
PTMG-H ₁₂ MDI-1,4BD	2000	2	130250	1.590	-70	-71
PTMG-H ₁₂ MDI-1,4BD	2000	3	—	—	-72	-69
PTMG-H ₁₂ MDI-1,4BD	2000	4	—	—	-71	-67
PTMG-H ₁₂ MDI-1,4BD	2000	5	—	—	-70	-69
PTMG-H ₁₂ MDI-1,4BD	2900	2	127833	1.689	-73	-69
PCL-H ₁₂ MDI-1,4BD	1250	2	177854	1.532	-44	-31
PBA-H ₁₂ MDI-1,4BD	1000	2	114013	1.659	-37	-21
PBA-H ₁₂ MDI-1,4BD	2000	2	117426	1.743	-49	-41
PBA-H ₁₂ MDI-1,4BD	2000	3	119320	1.693	-48	-35
PBA-H ₁₂ MDI-1,4BD	2000	4	—	—	-45	-35
PBA-H ₁₂ MDI-1,4BD	2000	5	—	—	-45	-33
PBA-H ₁₂ MDI-1,4BD	2000	8	—	—	—	-25
PBA-H ₁₂ MDI-1,4BD	2000	20	—	—	—	-23
PBA-H ₁₂ MDI-1,4BD	3000	2	152848	1.623	-46	-35
PHA-H ₁₂ MDI-1,4BD	1000	2	93430	1.838	-38	-21

PEG: Polyethylene glycol; PPG: Polypropylene glycol; PTMG: Polytetra-methylene glycol; PCL: Polycaprolactone diol; PBA: polybutylene adipate glycol; PHA: polyhexa-methylene adipate glycol.

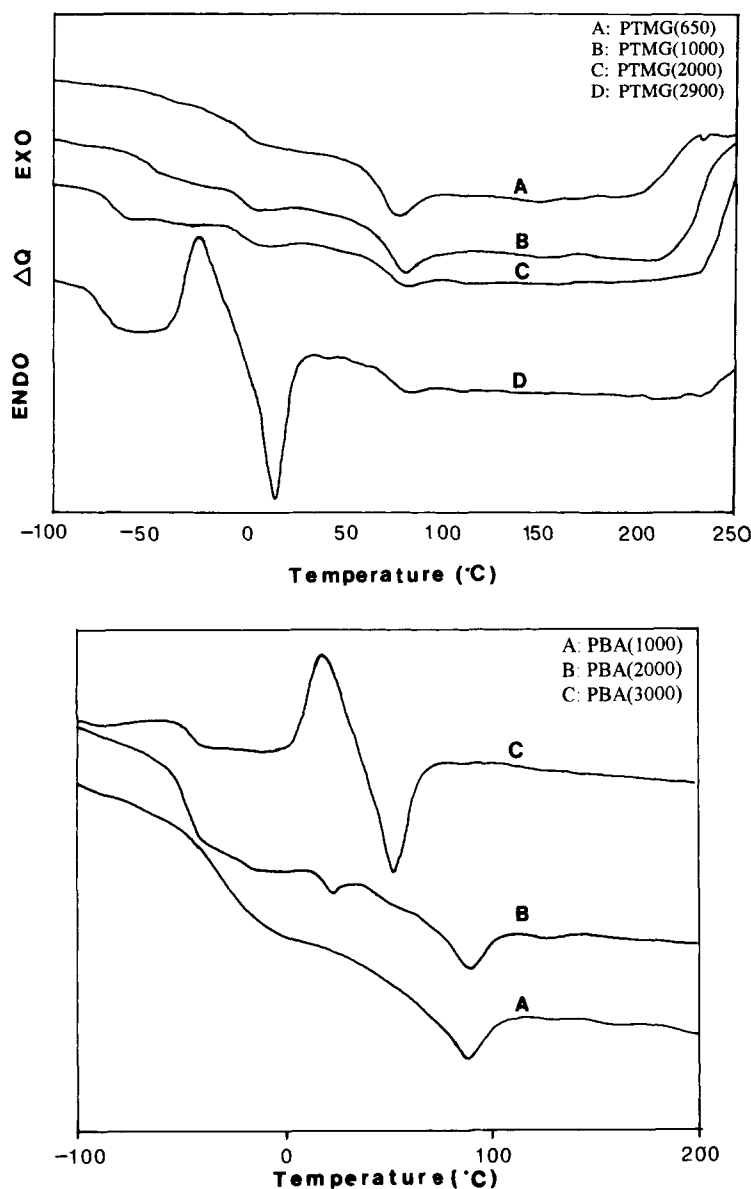


Figure 1 The effect of the molecular weight of polydiol on DSC thermodiagrams of PTMG- and PBA-based PU films.

meability study based on the time transfer method. The testing temperature was 40°C, with a relative humidity at 90% R.H.

RESULTS AND DISCUSSION

DSC

This study describes the properties of PUs using H₁₂MDI as diisocyanate and polyether, polyester, or polycaprolactone as polyol soft segment. Figure 1 shows that as the chain lengths of PTMG and PBA were increased, the T_g s of the PU soft segments were

decreased. Crystallization peaks appeared when the PTMG molecular weight used was 2900 and PBA was 3000. The hard segment T_g s all showed up in the 70–80°C range. Figure 2 was a study of the effects of the soft segment contents on the PU thermal properties. It was found that variations in the soft segment contents exert no significant effects on the soft segments T_g s. The T_g data of the soft segments is summarized in Table I and shows that the ether type PU membranes displayed lower soft segment T_g s in all the six soft segments used: PEG, PPG, PTMG, PBA, PHA, and PCL, in which the PTMG-based PUs had the lowest T_g .

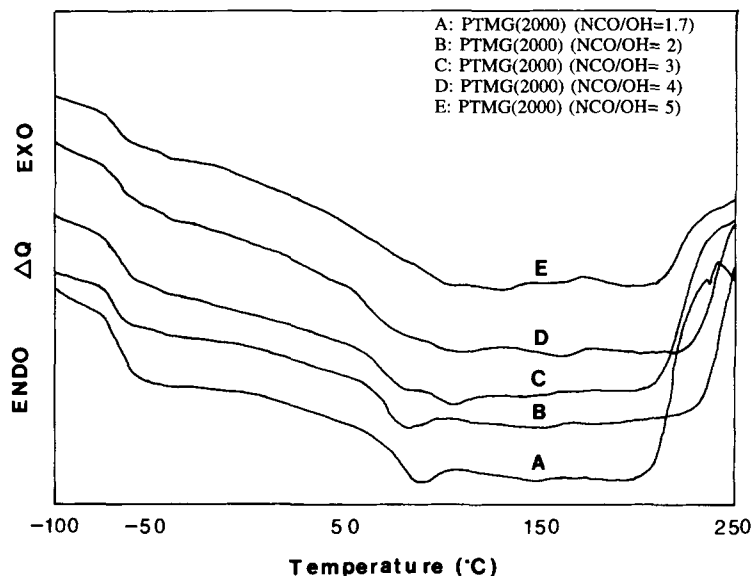


Figure 2 The effect of the content of soft segment on DSC thermodiagrams of PTMG-based PU films.

Rheovibron

The effects of the $\tan\delta$ of H_{12} MDI-based PUs on the soft segment contents and types are shown in Figs. 3, 4, and 5. Figure 3 is the plot of the $\tan\delta$ values of PU membranes vs. PTMG and PBA chain lengths. For the PTMG series PUs, Figure 3 (a) showed that as the chain length of PTMG became longer, the T_g s shown by $\tan\delta$ became lower and the $\tan\delta$ peak

became wider. If the molecular weight of PTMG used was 2900, the crystallization peak of polydiol appeared, which was consistent with the DSC result. As for the PBA series PUs, Figure 3 (b) showed similar chain length effects as the PTMG series, except its polydiol portions did not display distinct peak separation when the molecular weight of PBA used was increased. From the results of the PBA series PU films having higher soft segment T_g s, it is clear

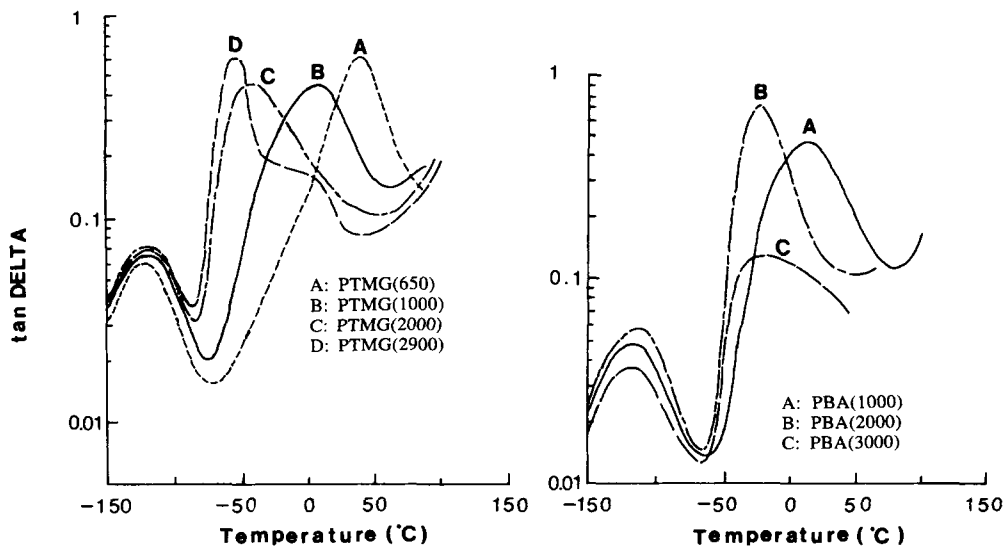


Figure 3 The effect of the molecular weight of polydiol on $\tan\delta$ for the PU films based on different molecular weight of PTMG and PBA.

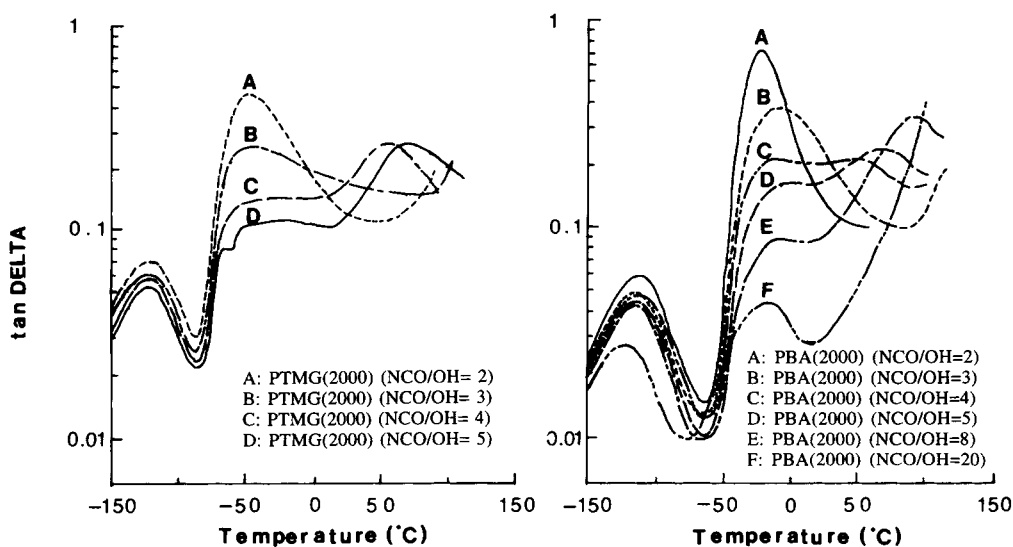


Figure 4 The effect of the content of soft segment on $\tan\delta$ for PTMG- and PBA-based PU films with various NCO/OH ratios.

that the PBA-based PUs are better phase mixing than those of the PTMG-based PUs. Figure 4 is the $\tan\delta$ of the H₁₂MDI series PUs vs. the hard segment contents. It can be inferred from this figure that the

hard segment T_g s remained relatively unaffected, irrespective which polyol, PTMG, or PBA, was used. However, the $\tan\delta$ peaks became wider and the hard and soft segments tend to be phase mixing (or in-

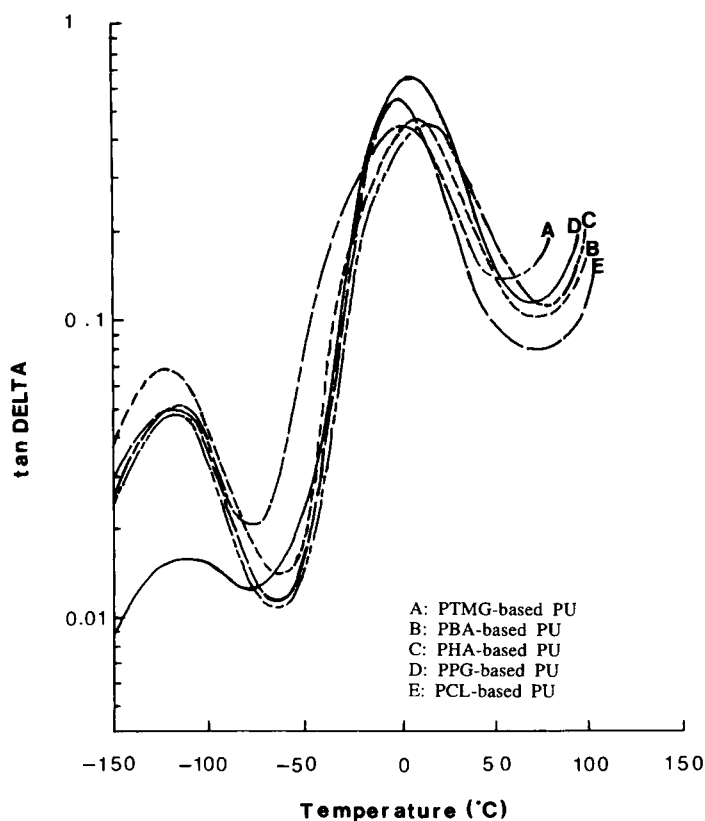


Figure 5 The effect of different types of soft segment on $\tan\delta$ for PU films.

tersegment mixing) as the hard segment contents were increased. Figure 5 is the plot of the $\tan\delta$ of PU membranes vs. the molecular weights of the five polyols including PPG, PTMG, PBA, PHA, and PCL. The molecular weight used for all polyols was 1000 except for PCL, in which molecular weight of 1250 was used. Different soft segments in PUs were found to have different γ transition temperatures: PTMG, -123°C ; PCL, -123 – -115°C ; PBA, -115 – -113°C ; PPG, -119 – -103°C . Another finding from this figure was that the PTMG series PUs exhibited minimum transition temperature as compared to the other series PUs. For PPG series PU containing side groups, the γ transition temperature exhibited a wider temperature range. Figure 6 is the plot of the soft segment T_g s of PU membranes against the polyol chain lengths. It is clear from Figure 6 that the T_g s of PBA series PUs was higher than those of PTMG series PUs. DSC results, however, showed lower T_g s than the Rheovibron data. The T_g s of the PTMG-based PUs are lower than those of PBA series because PTMG has flexible ether chains (—o—) and its ether chains have lower cohesive energy than the corresponding values of PBA series.²⁵ Figure 7 is the plot of the T_g s vs. its hard

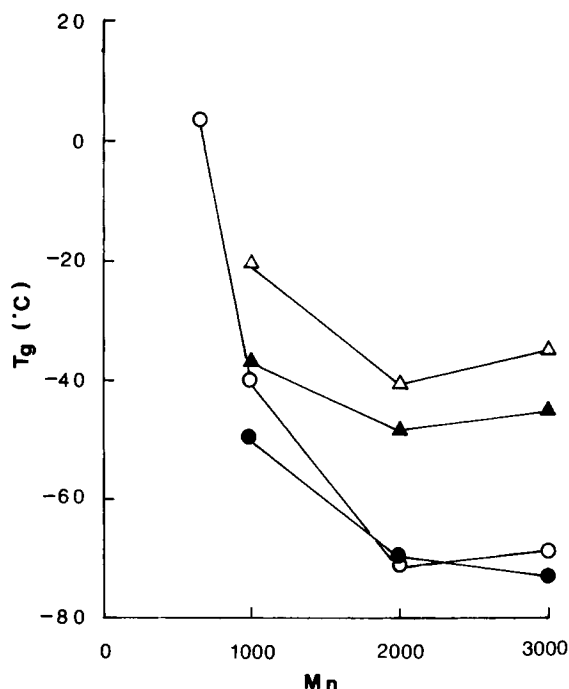


Figure 6 The effect of the molecular weight of polydiol on T_g of soft segment for H_{12} MDI-based PU films. (●): PTMG-based PU film (for DSC), (○): PTMG-based PU film (for Rheovibron), (▲): PBA-based PU film (for DSC), (△): PBA-based PU film (for Rheovibron).

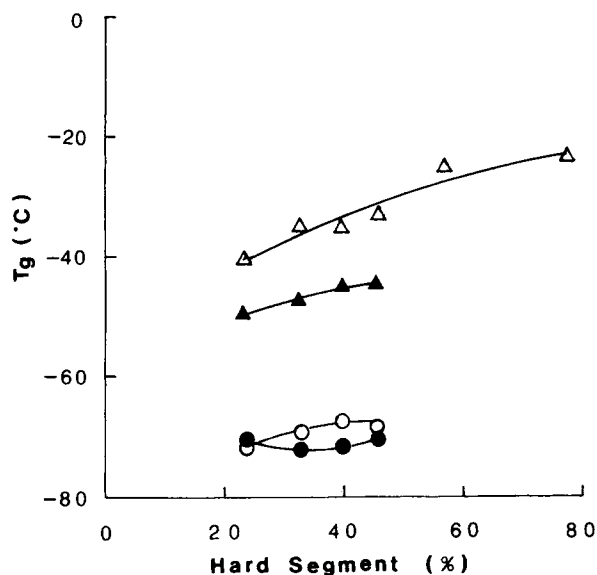


Figure 7 The effect of the content of hard segment on T_g of soft segment for H_{12} MDI-based PU films. (●): PTMG-based PU film (for DSC), (○): PTMG-based PU film (for Rheovibron), (▲): PBA-based PU film (for DSC), (△): PBA-based PU film (for Rheovibron).

segment contents. For the PBA-based PUs, the soft segment T_g s were slightly increased with an increase in the hard segment content. This slight increase in the T_g s apparently arises from the increased molecular rigidity at the soft segment terminals and from the increase in the hydrogen bondings and the change in the domain morphology. For PTMG-based PUs, the T_g s did not change much with an increase in the hard segment content. These results are apparently attributed to the higher flexible ether chains (—o—) and better microphase separation of the PTMG-based PUs.

Stress-Strain Curve

For different soft segments of the H_{12} MDI series PUs, curves of solvent evaporation and wet coagulation membranes are shown in Figure 8. The soft segments of both types of membranes have strong influence on their breaking stress and elongation. Polyester series PU membranes (PBA and PCL) usually have stronger breaking strength but smaller elongation. PHA-based PUs composed of six methylene groups have weaker cohesive energy, weaker breaking strength, and smaller initial modulus. For polyether series PUs, the soft segments, PTMG and PPG, which possess chain flexibility, have lower strength and initial modulus but higher elongation.

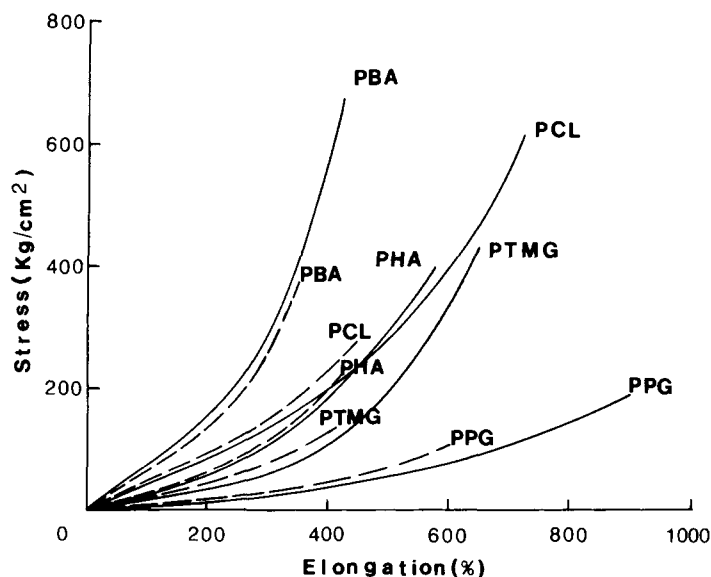


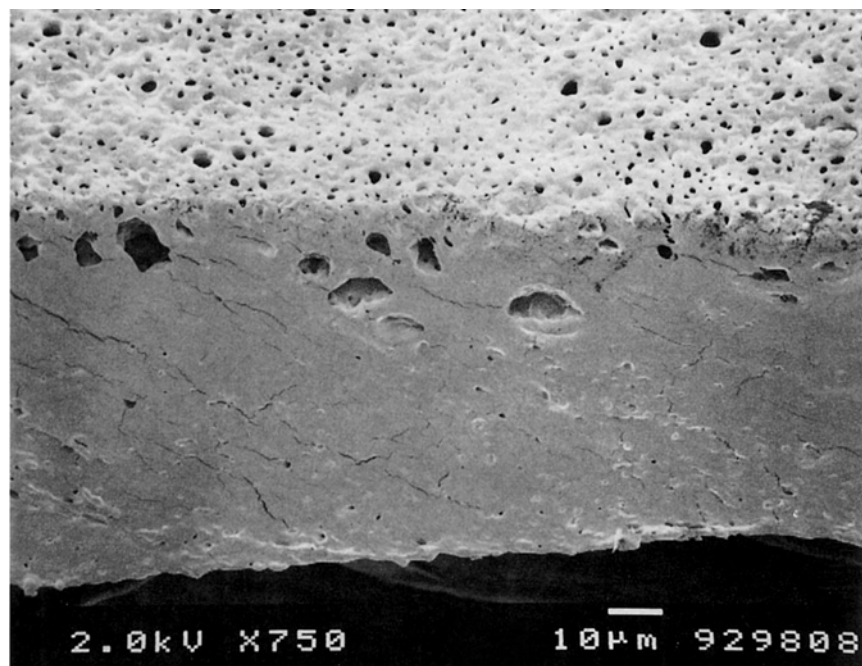
Figure 8 The effect of different types of soft segment on stress-strain curve for the dry casting and wet coagulation PU films. - - - - : Wet coagulation film, — : Dry casting film.

The PPG soft segments possessing side chains are difficult to crystallize, resulting in the lowest breaking strength but the highest breaking elongation. From the results in Figure 8 it is clear that membranes from the wet coagulation method displayed lower breaking stress and elongation than membranes from the solvent evaporation method. These differences in the breaking stress and elongation are presumably resulted from the effects of different casting method. Figure 9 is the SEM pictures of membranes from both casting methods. It is clear from the pictures that membranes from wet coagulation method had microporous surface and the cross-sections of the membranes possessed microporous structures, resulting in lower breaking stress. For the soft segment chain length effects on the PTMG- and PBA-based membranes obtained from the solvent evaporation method, the S-S curve is shown in Figure 10. It was found that higher soft segment chain length will impart its membranes higher breaking elongation, low initial modulus, and low breaking strength. For the PBA series PUs using polyol with molecular weight more than 3000, the soft segment chain length exerts an adverse effect on the breaking stress, elongation, and initial modulus due to crystallization formation on initial stretching. As for the PTMG series PUs possessing higher flexibility, its soft segments are difficult to crystallize on stretching. Zoran²⁶ studied the soft segment chain length effects on the membrane mechanical properties. He found that as the soft segment chain length was increased, the T_g s moved to

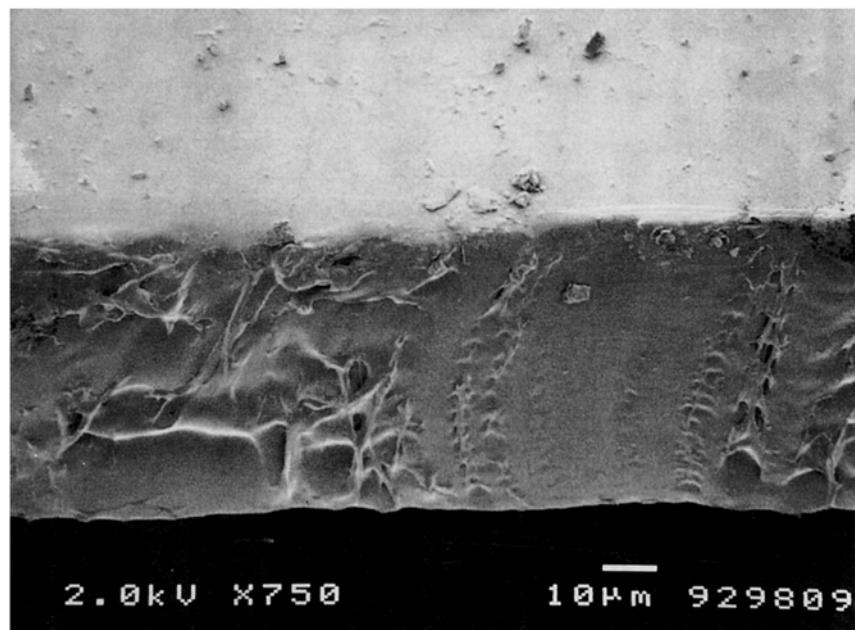
lower temperatures, exhibiting better phase separation. However, as the soft segments were long enough to form crystallization, the mechanical properties of the PU membranes were also improved.

Water Vapor Permeability

For different soft segments of H₁₂MDI series PUs, the curves of water vapor permeability coefficients vs. membranes from solvent evaporation and wet coagulation methods are displayed in Figures 11 and 12. It was found that the soft segments of the PEG membrane cast from the solvent evaporation method had the highest water vapor permeability coefficients, and membranes made from other polyols with decreasing water vapor permeability coefficients were in the order of PCL > PTMG > PPG > PHA > PBA. PEG-based PU membranes could not be obtained from the wet coagulation method, while the water vapor permeability coefficients for other membranes made from wet coagulation method displayed the sequence PCL > PTMG > PBA > PPG > PHA. The membranes of the PEG-based PUs from the solvent evaporation method possess many hydrophilic groups, resulting in very high water vapor permeability coefficient values. Membranes of PTMG-based PUs cast from either method had higher water vapor permeability coefficients than the polyester-based PUs. As for the PCL-based (MW 1250) PU, its molecular chains have both the ether and ester groups, imparting its membrane a



(a) Wet coagulation method.



(b) Dry casting method.

Figure 9 The SEM photographs of PBA-based films. (a) Wet coagulation method. (b) Dry casting method.

higher water vapor permeability coefficient. PBA- and PTMG-based PU membranes cast from both methods with the same thickness but different molecular weights vs. the water vapor permeability are displayed in Figure 13. For PTMG-based PU mem-

branes (from either casting method), its water vapor permeability increased with increasing soft segment molecular weights while the membranes obtained from the wet coagulation method had higher water vapor permeability. For the PBA-based PU mem-

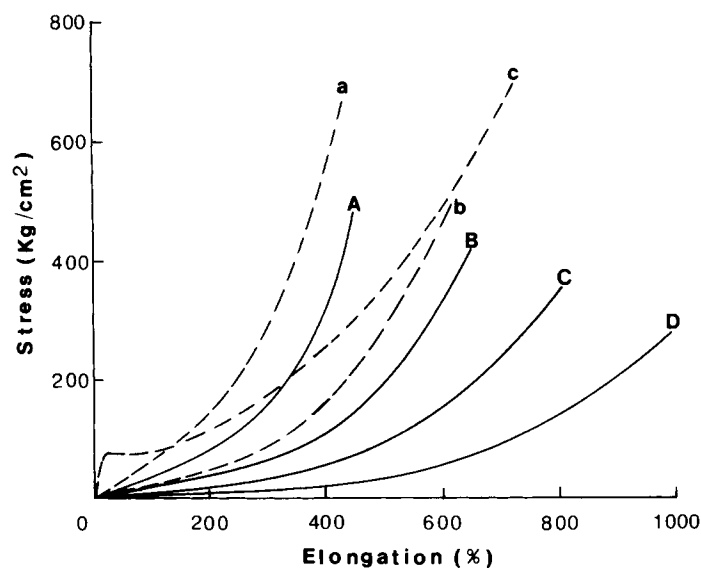


Figure 10 The effect of molecular weight of soft segment on stress-strain curve of PTMG- and PBA-based PU casting films. (A) PTMG (650), (B) PTMG (1000), (C) PTMG (2000), (D) PTMG (2900), (a) PBA (1000), (b) PBA (2000), (c) PBA (3000).

branes, its water vapor permeability from both methods had the highest value when its soft segment molecular weight used was 2000. As the molecular weight used was 3000, its water vapor permeability

became smaller. Membranes with higher molecular weight soft segments possess higher amorphous contents, resulting in higher water vapor permeability. PBA membrane with molecular weight 3000

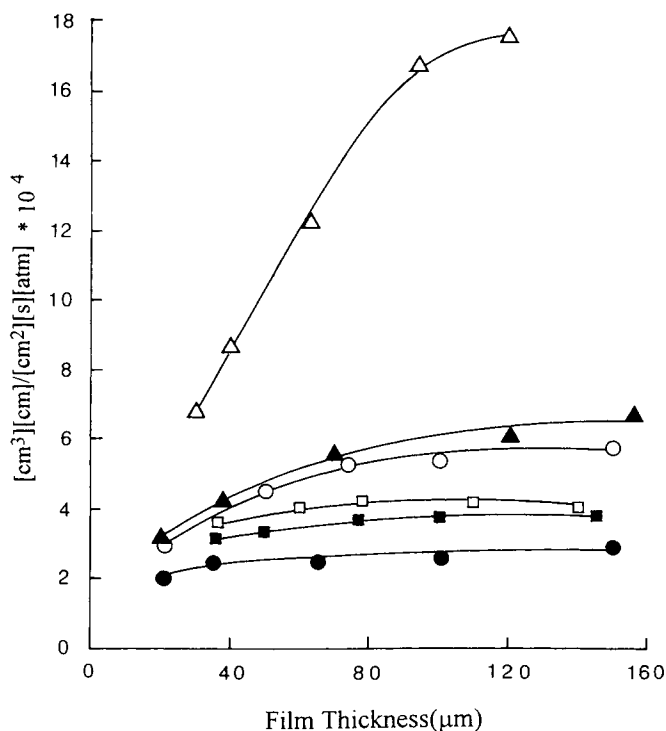


Figure 11 The effect of various soft segment on permeability coefficient for dry casting PU films. (Δ): PEG-based PU film, (▲): PCL-based PU film, (○): PTMG-based PU film, (□): PPG-based PU film, (■): PHA-based PU film, (●): PBA-based PU film.

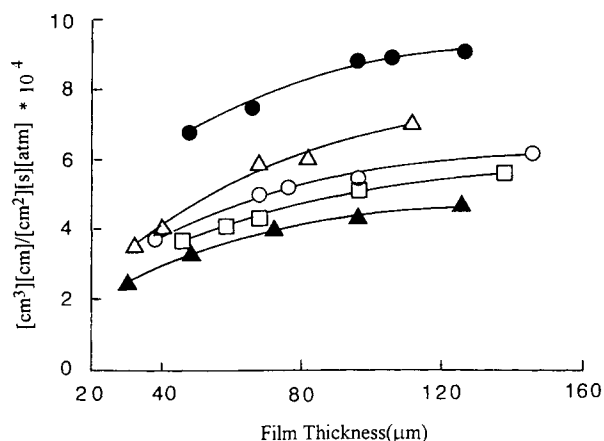


Figure 12 The effect of various soft segment on permeability coefficient for wet coagulation PU films. (●): PCL-based PU film, (Δ): PTMG-based PU film, (○): PBA-based PU film, (□): PPG-based PU film, (▲): PHA-based PU film.

had lower water vapor permeability than PTMG membrane because its longer soft segments will crystallize. The water vapor permeability vs. the hard segment contents of PBA and PTMG-based

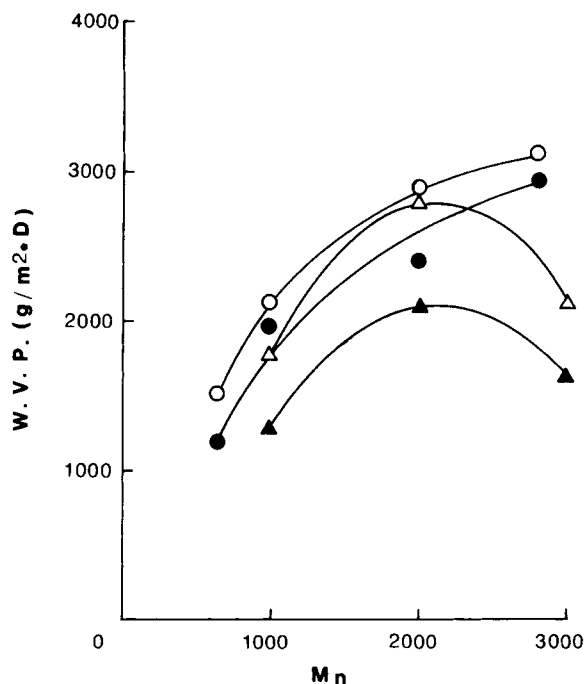


Figure 13 The effect of molecular weight of soft segments on water vapor permeability for PU films. (●): PTMG-based PU films (dry casting method), (○): PTMG-based PU films (wet coagulation method), (▲): PBA-based PU films (dry casting method), (Δ): PBA-based PU films (wet coagulation method).

PU membranes (from both casting methods) is shown in Figure 14. The water vapor permeability of both types of PU membranes decreased with an increase in the hard segment contents. This is because an increase in the hard segment contents will produce greater intersegment mixing, which, in turn, will increase the membrane density. A higher intersegment mixing and membrane density will always induce lower water vapor permeability.

CONCLUSION

This article studies the effects of the soft segment types, chain length, and contents of H₁₂MDI series PUs on the physical properties and water vapor permeability of films cast from either solvent evaporation or wet coagulation method. The conclusions are: (1) for the H₁₂MDI-based PU soft segments, polyester films cast from the solvent evaporation method has higher breaking strength than polyether cast films, of which the PBA-based PU films have better breaking strength but lower breaking elongation. For PBA-based PUs, the films with higher

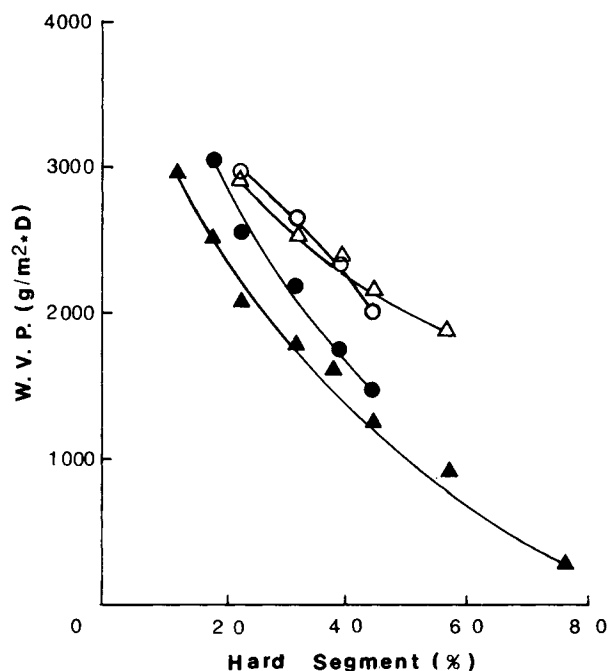


Figure 14 The effect of the content of hard segment on water vapor permeability for PU films. (●): PTMG-based PU films (dry casting method), (○): PTMG-based PU films (wet coagulation method), (▲): PBA-based PU films (dry casting method), (Δ): PBA-based PU films (wet coagulation method).

soft segment contents have higher breaking elongation but the lowest breaking stress. (2) The wet coagulation films have lower breaking strength and elongation than the solvent casting films. The difference in the stress-strain properties is due to the difference in the membrane porosity. (3) For the H₁₂MDI-based PU films, its water vapor permeability values vary with the soft segment types, chain length, contents and film casting methods. For films cast from the solvent evaporation method, the PEG-based PU films have the highest water vapor permeability coefficients. In general, the films cast from the wet coagulation method have higher water vapor permeability values than the films cast from the solvent evaporation method. This difference in the water vapor permeability may be caused by different extent of membrane porosity. Polyether type PU films normally have higher water vapor permeability values than polyester type PU films. Films with higher soft segment chain lengths will also have higher water vapor permeability values. However, if the soft segment crystallizes, the water vapor permeability of the films decreases rapidly.

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