

건식가공법에 의한 투습성이 우수한 폴리우레탄발포피혁의 제조와 물성

하 창 식·김 영 옥·최 진 석*·조 원 제

부산대학교 고분자공학과, *동성화학공업(주)

(1993년 4월 6일 접수)

Preparation and Properties of Polyurethane Foamed Leather Having Good Permeability to Moisture Vapor by Dry Process

Chang-Sik Ha, Young-Wook Kim, Jin-Seok Choi*, and Won-Jei Cho

Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea

*Dong Sung Chemical Ind. Co. Ltd., 472 Shinpyung-Dong, Saha-ku, Pusan 604-030, Korea

(Received April 6, 1993)

요 약 : 폴리에스터디올과 톨루엔 디이소시아네이트로부터 얻은 우레탄 예비폴리머와 촉매 및 계면활성제를 사용하여, 건식가공법으로 투습성이 우수한 폴리우레탄 발포피혁을 제조하였다. 폴리우레탄 발포피혁의 발포비는 이소시아네이트(NCO) 함량이 증가할수록 또한 계면활성제농도가 감소할수록 증가하였으며 인장강도와 파단신율은 계면활성제의 함량에 따라서는 증가하였으나 NCO 함량에 따라서는 감소하였다. 발포피혁의 발포밀도는 촉진제와 수분의 함량이 증가할수록 감소하였으며 발포밀도가 증가할수록 인장강도와 파단신율은 증가하였다. 투습도는 NCO 함량의 증가에 따라 증가하였다.

Abstract : Polyurethane(PU) foamed leathers having good permeability to moisture vapor have been prepared by foaming a PU prepolymer obtained from hydroxy-terminated polyester diol(HTPD) and tolylene diisocyanate(TDI) with catalyst and surfactant by dry process. Foaming ratio of the PU foamed leathers increased as the NCO contents were increased and the surfactant concentration was decreased. Tensile strength and elongation at break of the PU foamed leathers increased with increasing surfactant concentration but decreased with increasing NCO contents. Foam density of the PU foamed leather decreased with increasing catalyst concentrations and water contents. Tensile strength and elongation at break of the PU foamed leather increased with increasing foam density. Permeability to moisture vapor of the PU foamed leathers increased with increasing NCO contents.

INTRODUCTION

Synthetic polyurethane(PU) leathers have been

prepared by dry or wet process. It was reported that synthetic PU leathers prepared by dry process have substantially no air permeability and their

touch is quite different from natural leather.^{1,2} Synthetic PU leather prepared by wet process has continuous microporous structure and exhibits good air permeability. Instead, a very precise control is required to obtain excellent skin film in wet process. In either the dry or wet process, a larger quantity of organic solvent is released into air or water, which causes environmental problems if no post treatment is conducted for the removal of the released organic solvent. Considerable cost is also needed for the recovery of the organic solvent.

The formation of polyurethane foam used for synthetic leather is more complicated than any of the other urethane applications. In addition to the chemical and physical aspects of the polymerization system, foam formation adds the peculiarities of a colloidal system.^{3,4} For these reasons, relatively little is known in a quantitative sense about the formation of polyurethane foam.

We will focus our study on the preparation of PU foamed leathers having touch, feeling and appearance resembling those of natural leather and a good combination of an excellent moisture permeability and surface scratching strength without any organic solvent. The PU foamed leathers are prepared from three basic components of urethane prepolymer from polyester diol and tolylene diisocyanate(TDI), surfactant, and catalyst by modified dry process, which eliminates the release of solvent and increase the permeability to moisture vapor.

The present article deals with the effects of the composition of urethane prepolymers, NCO content, surfactant concentration and catalyst concentration on the properties of the PU foamed leathers.

EXPERIMENTAL

Materials. The list of materials and their abbreviations or sources is shown in Table 1. The materials were used as received unless otherwise noted. 1,4-BD was degassed at 60°C for 6 hrs under a vacuum of 0.5 mmHg. TDI was kept dry with

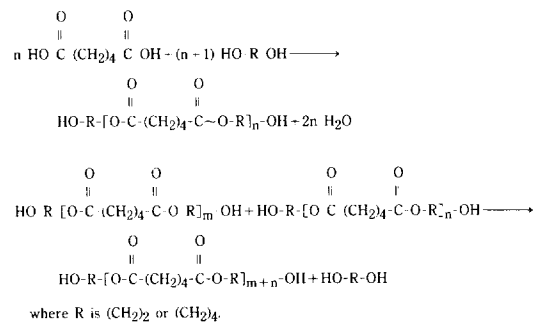
Table 1. Materials and Their Abbreviations or Sources

Materials	Abbreviations	Sources	Remarks
Adipic acid	AA	Junsei	
Ethylene glycol	EG	Junsei	} Urethane Prepolymer
1,4-Butane diol	1,4-BD	Junsei	
Tolylene diisocyanate	TDI	Wako	
Tetra-n-butoxytitane	TBT	Wako	
Dibutyltin dilaurate	T-12	Fluka	Catalyst
Triethylene diamine	DABCO	Junsei	Catalyst
Polysiloxane-polyether copolymer	TEGOSTAB B 8450	Goldschmidt	Surfactant

molecular sieve before use.

Synthesis and Identification of Polyester Diol. Polyester diol was synthesized by the following reaction Scheme I.

A mixture of 4.45 mol of EG and 4.45 mol of 1,4-BD was charged in a 3 l separable flask equipped with a Allihn condenser, reflux condenser, thermometer, and nitrogen inlet. The mixture was agitated and heated to 100°C to react with 6.84 mol of AA. Then, the reaction mixture was kept at 230°C under the nitrogen atmosphere for 4 hrs. 1.5 g of TBT was added to the reaction mixture and further reaction was proceeded for more 2 hrs. When the theoretical amount of water(246.3 g) was condensed, the remained reaction mixture was transesterified by applying vacuum at 200°C for 10 hrs. The polyester diol was further used after removing moisture at 80°C for about 3 hrs under 0.1 mmHg vacuum. The polyester diol synthesized



Scheme I. Synthesis of polyester diol.

was identified on infrared spectra(Shimadzu IR-435) using their films cast on KBr single crystal cell. The acid and hydroxy values of the polyester diol were measured by the JIS-K0078 standard. Moisture content was measured by the Automatic Karl-Fischer moisture Process(Metrohm 658KF) with the JIS-K0068 standard.

Viscosity of the diol was measured with Brookfield viscometer(model RV type).

Synthesis of Urethane Prepolymers : The isocyanate-terminated urethane prepolymer was prepared by reacting a given amount of the polyester diol, as synthesized above, with TDI(2,4-TDI/2,6-TDI=80/20) at 80°C in a 1 ℓ four-necked flask under dry nitrogen. Four PU prepolymers with different NCO contents were prepared, as shown in Table 2. The PU prepolymers were characterized by IR spectra and Brookfield viscosity. The isocyanate content was determined by dibutylamine back-titration analysis(wet method).⁵

Preparation of PU foamed leather(PUFL) : by dry process. The PU foamed leathers were formulated with the viscous urethane prepolymers and required amounts of surfactant(TEGOSTAB B 8450), catalyst, and water. The surfactant concentrations were varied from 0, 0.5, 1.0, to 1.5 pbw(parts by weight) and the catalyst concentrations were varied from 0.5, 1.0, 1.5, to 2.0 pbw, respectively, based on 100 pbw of PUFL. 1/1 mixture of T-12 and DABCO was used for the catalyst. The water content was varied from 0.3, 0.5 to 0.7 php(parts per hundred parts of polyol). The reaction mixture was agitated for 10 sec at 2000 rpm ; whereupon, it was coated on a releasing paper to free-rise and the foam with the initial coating thickness of about 300 μm rose to about 430 to 850 μm high for the above-formulations. Upon completion of the rise, the foam was placed in a mechanical convection oven to cure at 85°C for a specified period. The cure time was adjusted properly according to the reaction profile of each different formulation.

Physical Properties of PU Foamed Leather.

Foam density : The foam density of PU foamed leather was measured according to JIS K-7112. Six

Table 2. Preparation of Urethane Prepolymer for Foamed Leather(PUFL)

	PUFL	I	II	III	IV
Ingredient					
TDI ^{a)}		300	300	300	300
Polyester diol ^{b)}		1240	985	805	670
[NCO]/[OH]		2.78	3.50	4.30	5.14

a) Molecular weight 174.16 g/mol

b) Average molecular weight 2000 g/mol

measurements were averaged.

Foaming ratio and cure time : The foaming ratio was measured based on free rise test using conventional hand mixing methods. The foaming ratio was calculated by the ratio of the maximum rise height to the initial coating thickness of the foam (about 300 μm). The cure time was defined as a measure of the time elapsed for the reaction mixture before foaming to be cured completely after the foam has risen.

Tensile properties : The tensile tests were performed using an Instron tensile tester(Model 11 01). The samples of the dumbell type II size were prepared following the procedure of JIS K-7113. The crosshead speed was 100 mm/min. Five measurements were averaged.

Permeability to moisture vapor : Permeability to moisture vapor was measured at 30°C according to JIS K-6549 method. One side of the foamed leather was exposed to the air of R. H. of 80% and the other side of the leather was let at dry state for 24 hrs. Then, the amount of moisture vapor permeated through the leather at the crosssection (cm²) was defined as the permeability to moisture vapor.

Cell size : The cell size was determined by the optical micrograph. The magnitude was set at ×50.

RESULTS AND DISCUSSION

Characterizations of Polyester Diol and PU Foamed Leather(PUFL). The structure of the polyester diol synthesized for the work was identified by

Table 3. Characterizations of Synthesized Polyester Diol

Characterization	Value
Acid number	0.81
Hydroxyl number	56
Average mol. weight	2000
Water content(%)	0.03
Viscosity(cp/°C)	980/75

IR spectrophotometry. The IR spectra of the polyester diol exhibited characteristic absorption bands at 3200~3600 cm^{-1} (stretching vibration of OH), 2850~3000 cm^{-1} (stretching vibration of aliphatic C-H), 1750 cm^{-1} (stretching vibration of C=O), and 1000~1300 cm^{-1} (stretching vibration of C-O). The acid value and hydroxyl value of the polyester diol were determined using 0.1 N KOH aqueous solution and 1 N KOH aqueous solution, respectively, by equation 1 following the JIS K-0078 standard. The average molecular weight of the polyester diol was determined by equation 2. Table 3 shows the results. The moisture contents and viscosity measured at 75°C are 0.03% and 980 cps, respectively.

$$\begin{aligned} \text{Hydroxyl number} &= 56.1 \times 1000 / \text{equivalent} \\ &\quad \text{weight} \\ &= \text{functionality} \times 56100 / \text{mole-} \\ &\quad \text{cular weight of polyol} \quad (1) \end{aligned}$$

$$\begin{aligned} \text{Molecular weight} &= \text{functionality} \times 56100 / \\ &\quad \text{hydroxyl number} \quad (2) \end{aligned}$$

The PUFL was also characterized by identifying that the characteristic peak of O-H bond around 3200~3600 cm^{-1} was disappeared, while new peaks due to N=C=O around 2250 cm^{-1} and those due to N-H around 3050~3500 cm^{-1} were appeared, on the IR spectrum. The NCO contents of the four synthesized PUFL I, II, III, and IV were determined as 6.0, 8.0, 10.0, and 12.0%, respectively. The Brookfield viscosities of the formulated PUFL before foaming are shown in Fig. 1.

It is seen that the viscosity of the PUFL strongly depends on the NCO contents of the formulated

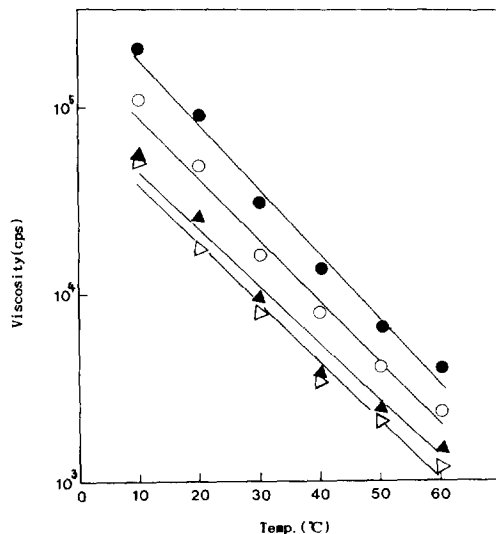


Fig. 1. Semi-log plots of viscosity of the synthesized PU foamed leather (PUFL) with different NCO contents vs. temperature : (●) 6.0%, (○) 8.0%, (▲) 10.0%, (△) 12.0%.

urethane prepolymer before foaming; For a given temperature, the viscosity decreased with increasing NCO contents. The temperature dependence of the viscosity of PUFL is also plotted in Fig. 1. As expected, the viscosity decreases with increasing temperatures.

It should be pointed out that the structure of the polyester diol employed can have a large effect on the physical properties of final foamed leathers. In this work, however, we used only one diol system.

Foam Density.

Effect of Catalyst Concentration : Table 4 shows the effect of catalyst concentration on the rise time and the foam density. In this case, the surfactant concentration and water level were fixed as 0.5 pbw and 0.5 pph, respectively. It is seen that both the rise time and the foam density decrease with increasing catalyst concentration. Here, the rise time is a measure of the time elapsed between the reaction mixture coating on a releasing paper and the completion of the expansion of the foam.⁶

Effect of Water Content : The use of water to control the foam density containing 1.0 pbw catalyst and 0.5 pbw surfactant was investigated. The ad-

Table 4. The Effect of Catalyst Concentration on Rise Time and Foam Density

Catalyst conc. (pbw)	Rise time (sec)	Foam density (g/cm ³)
0.5	120	0.21
1.0	80	0.17
1.5	65	0.14
2.0	50	0.12

Table 5. The Effect of Water Content on Foam Density

H ₂ O(php)	Foam density(g/cm ³)
0.3	0.23
0.5	0.17
0.7	0.14

ded water reacts with isocyanate and produces carbon dioxide as a blowing agent. The water content was varied between 0.3 and 1.0 php and the data are summarized in Table 5. Table 5 shows that the foam density decreases with increasing water content, which is attributed to the formation of more carbon dioxide from the water-isocyanate reaction as water content increases. The foams looked good in that they had good texture and good resilience. The foam using 1.0 php water and above, however, showed cracks. The water content was fixed as 0.5 php, unless otherwise specified, in order to investigate the effects of other experimental variables such as NCO content and surfactant or catalyst concentrations on the properties and cell structure of the PUFL foams.

It should be noted that the utilization of carbon dioxide from the water-isocyanate reaction as a blowing agent is playing an important role in most polyurethane foam applications because of its chlorofluorocarbon(CFC) alternative potentiality. From an environmental standpoint, carbon dioxide is certainly the most attractive of such CFC alternatives in spite of its several drawbacks such as difficult processability, decreased dimensional stability, and increased system cost, since more isocyanate may be needed in the formulation to react

Table 6. The Effects of Isocyanate Contents and Surfactant Concentrations on the Thickness(mm)¹ and the Foam Density(g/cm³)² of the PU Foamed Leathers(PUFL)

PUFL	I	II	III	IV
NCO contents(%)	6.0	8.0	10.0	12.0
Surfactant concentration (pbw)				
0.0	0.54	0.61	0.74(0.16)	0.85
0.5	0.50(0.19)	0.56(0.18)	0.68(0.17)	0.80(0.16)
1.0	0.45	0.53	0.65(0.17)	0.70
1.5	0.43	0.52	0.65(0.17)	0.68

1. Coating thickness : 0.3 mm.

2. The numbers in parentheses denote the foam densities.

with the water added.⁷

Effects of NCO Contents and Surfactant Concentration : The foam density decreases as the NCO contents and the surfactant concentrations increase, but the effects are negligible when compared to those of the catalyst concentration as well as the water level. The foam density was in the range of 0.17 ± 0.02 depending on the NCO contents and the surfactant concentrations(see Table 6).

Foaming Ratio, Cell Structure, and Cure Time.

Effects of NCO Contents and Surfactant Concentration : The nucleation and growth of a cell in preparing a foam is dependent on several factors including the system chemistry and foaming additives.^{8~10} In this work, the effect of NCO contents and surfactant concentration were investigated. A surfactant is capable of stabilizing a cell wall by its unique ability to act at the cell wall interface. It was known that the surfactant decreases the surface tension of the system, increases surface elasticity and surface viscosity to result in smaller cells, stable foams, and reduced deformation of the cell structure.^{11~15}

Table 6 and Fig. 2 show the effect of NCO contents on the thickness of foamed leathers and foaming ratio, respectively. The amount of catalyst was fixed at 1.0 pbw. The foaming ratio increases (but the foam density decreases) with NCO con-

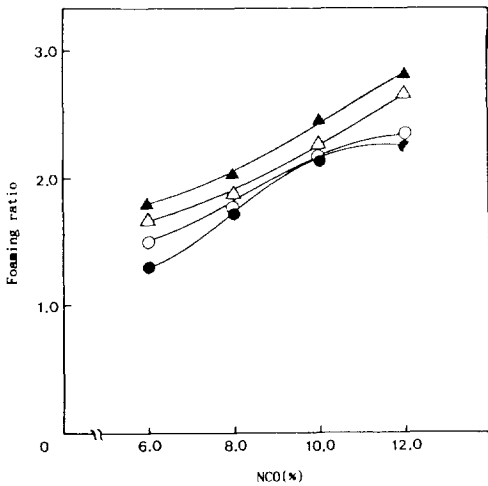


Fig. 2. Plot of foaming ratio of the PU foamed leather with different surfactant concentrations vs. NCO contents : The amount of catalyst was fixed at 1.0 pbw : (▲) 0.0 pbw, (△) 0.5 pbw, (○) 1.0 pbw, (●) 1.5 pbw.

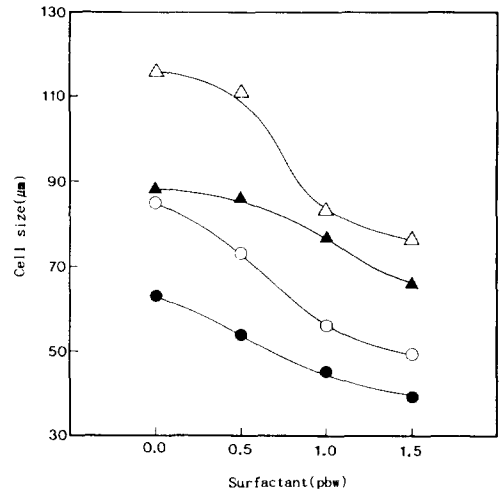


Fig. 3. Plot of cell size of the PU foamed leather with different NCO contents vs. surfactant concentration. The amount of catalyst was fixed at 0.5 pbw : (●) 6.0 %, (○) 8.0%, (▲) 10.0%, (△) 12.0%.

tents and inversely with the surfactant concentration. Fig. 3 shows the effect of NCO contents and surfactant concentration on the cell size of the foamed leathers. It can be seen that the cell size decreases with increasing surfactant concentration but it increases with increasing NCO contents. This effect may be explained by considering the fact that the rising surfactant concentration increases the surface viscosity and in turn the growth of a cell is restricted. Typical cell structure of the foamed leathers were shown in Fig. 4. The cell size ranged from 63 μm to 132 μm. It has been reported that the foam structure and stabilization are strongly governed by the nature of surfactant because it affects the surface tension of the system.¹¹ It was also reported that the initial viscosity of the system is also one of the significant factors in the stabilization of the foam.¹⁸ For example, if the initial viscosity of a prepolymer is high, no surfactant is required, while a prepolymer of lower viscosity necessitates the use of a surfactant as a foam stabilizer.

It should be noted that in the foaming process the relative rates of the gas evolution from the wa-

ter-isocyanate reaction and the viscosity increase caused by the polymerization reaction must be in proper balance to yield stable foams.¹⁶

Effect of Catalyst Concentration : The effect of catalyst concentration on the cure time of the foamed leather is shown in Fig. 5. The surfactant concentration was fixed at 0.5 pbw. The cure time decreases with increasing catalyst concentrations. It was already mentioned that the rise time and the foam density also decreased with increasing catalyst concentration. The foam flowability and reactivity are known to be optimized by catalyst selection. The optimum concentration and kinds of surfactant to prepare a foamed leather was reported to depend on the foaming process, foam pressure, and cure time, etc.^{11,17}

Tensile Properties. The effect of the foam density on the tensile properties is illustrated in Fig. 6. The foam densities referred to in this figure are taken from the data in Tables 4 and 5. As expected, the tensile strength as well as the elongation at break increase with increasing foam density.

The effects of surfactant concentration and NCO contents on the tensile properties are shown in

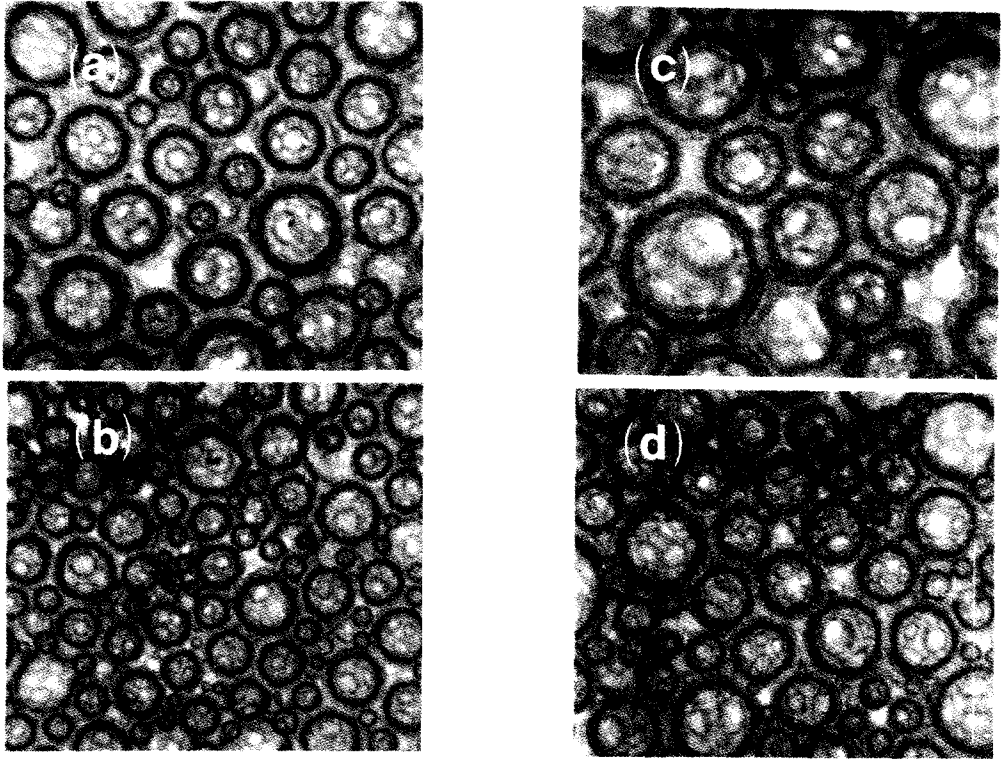


Fig. 4. Typical cell structure of the PU foamed leather : (a) NCO contents of 8.0% and surfactant concentration of 0.0 pbw, (b) NCO contents of 8.0% and surfactant concentration of 1.5 pbw, (c) NCO contents of 12.0% and surfactant concentration of 0.0 pbw, and (d) NCO contents of 12.0% and surfactant concentration of 1.5 pbw.

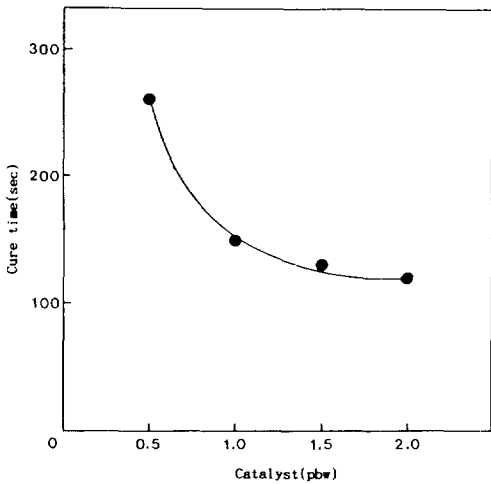


Fig. 5. Plot of cure time vs. catalyst concentration : The surfactant concentration was 0.5 pbw.

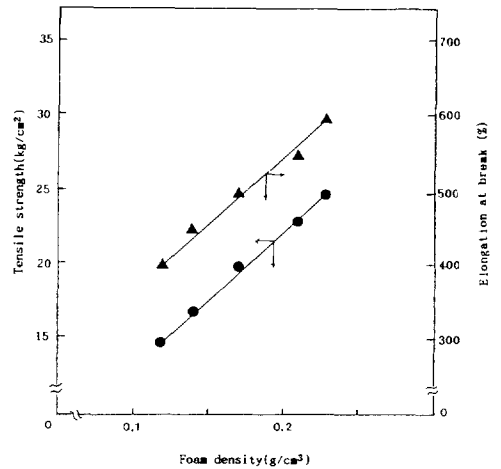


Fig. 6. Plots of tensile strength (●) and elongation at break (▲) of the PU foamed leather vs. foam density (g/cm³).

Figs. 7 and 8. The foamed leather was formulated with constant catalyst concentration(1.0 pbw). The tensile strength and elongation at break of foamed leathers increased with surfactant concentration but decreased with NCO contents. This may be caused by the fact that the cell structure become coarser and the foam ratio becomes higher when the surfactant concentration is lower and NCO contents are higher. In general, the foam ratio decreases with increasing foam density and then the latter is one of the critical factors to govern the physical properties such as tensile strength. Since the effects of NCO contents and surfactant concentrations on the foam density were almost negligible, as already seen in Table 6, however, the results referred to in Figs. 7 and 8 may be described in terms of the cell structure, not the foam density or other factors.

Permeability to Moisture Vapor. The influence of NCO contents and surfactant concentration on the permeability to moisture vapor should also be noted, since the permeability to moisture vapor is the key property needed in synthetic leather.¹ On increasing the surfactant concentration as well as

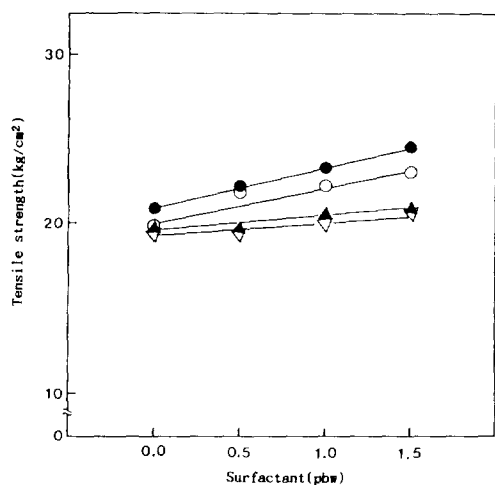


Fig. 7. Plots of tensile strength of the PU foamed leather with different NCO contents vs. surfactant concentration : The amount of catalyst was fixed at 1.0 pbw : (●) 6.0%, (○) 8.0%, (▲) 10.0%, (△) 12.0 %.

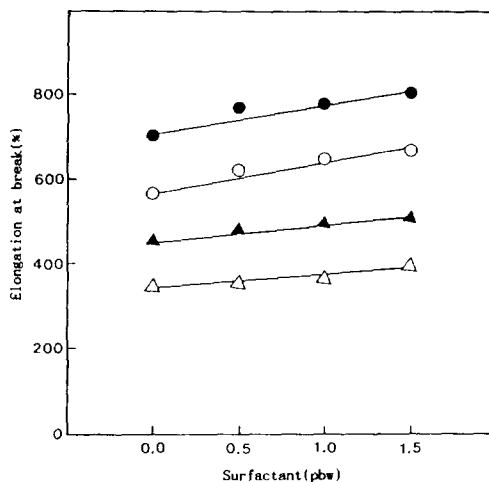


Fig. 8. Plots of elongation at break of the PU foamed leather with different NCO contents vs. surfactant concentration : The amount of catalyst was fixed at 1.0 pbw : (●) 6.0%, (○) 8.0%, (▲) 10.0%, (△) 12.0%.

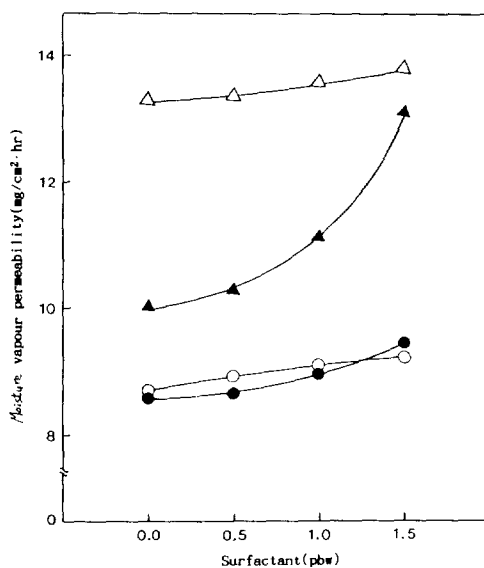


Fig. 9. Plots of permeability to moisture vapor of the PU foamed leather with different NCO contents vs. surfactant concentration : The amount of catalyst was fixed at 1.0 pbw : (●) 6.0%, (○) 8.0%, (▲) 10.0%, (△) 12.0%.

NCO contents, the permeability to moisture vapor increased, as shown in Fig. 9. In this figure, the catalyst concentration was fixed at 1.0 phr.

It may be assumed that the permeability to moisture vapor is also affected by the cell structure of the foamed leather, rather than by the foam density as are the tensile properties. The reason, however, is not clear at present why the permeability to moisture vapor becomes higher as the surfactant concentrations are higher, although the foaming ratio as well as the cell size decreases with increasing surfactant concentrations.

CONCLUSIONS

In this work, polyurethane(PU) foamed leathers by dry process have been prepared by foaming a PU prepolymer, from hydroxy-terminated polyester diol(HTPD) and tolylene diisocyanate(TDI), formulated with catalyst and surfactant. The effects of surfactants, catalysts and NCO contents on the properties of the PU foamed leather were investigated. The important results are summarized as follows.

1. Foam density of the PU foamed leather decreased with increasing catalyst concentrations and water content.

2. Foaming ratio of PU foamed leather increased as the NCO contents increased and the surfactant concentration decreased.

3. The cell size decreased with increasing surfactant concentration but it decreased with increasing NCO contents.

4. Tensile strength and elongation at break of the PU foamed leather increased with increasing foam density.

5. Tensile strength and elongation at break of the PU foamed leather increased with increasing surfactant concentration and decreased with increasing NCO contents.

6. Permeability to moisture vapor of the PU foamed leather increased with increasing NCO contents as well as surfactant concentration.

REFERENCES

1. Kirk-Othmer, "Encyclopedia of Chemical Technology", 3r ed., Vol. 23, John Wiley & Sons, New York (1980), pp. 604-607.
2. *ibid.*, Vol. 14, pp. 231-249.
3. J. H. Saunders, *Rubber Chem. and Technol.*, **33**, 1293 (1960).
4. J. M. Buist, R. Hurd, and A. Lowe, *Chem. & Ind. (London)*, **51**, 1544 (1960).
5. E. J. Malec and D. J. David, "Analytical Chemistry of Polyurethane", Wiley International, New York (1969).
6. I. H. Saunders and K. C. Frisch, "Polyurethanes Chemistry and Technology, Part II-Technology", Interscience Publishers, New York (1964), pp. 84-88.
7. T. W. Bodnar and J. D. Thornsberry, "New Surfactants for Reduced and Non-CFC Blown Rigid Foam Systems", Proc. 33rd Annual Polyurethane Technical/Marketing Conf. Sept. 30-Oct. 3 (1990), p. 52.
8. R. H. Hansen, *SPE J.*, **18**, 77 (1962).
9. A. R. Ingram and H. A. Wright, *Modern Plastics*, **41(3)**, 152 (1962).
10. E. G. Pollard and L. C. Rubens, *U. S. Pat.*, 3,013, 996 (1961).
11. K. Muha and M. E. Harakal, "New Surfactant and Catalysts for All Water Blown MDI Cure Molded Foam", Proc. 33rd Annual Polyurethane Technical/Marketing Conf. Sept. 30-Oct. 3 (1990), pp. 6-10.
12. 今井嘉夫, ポリウレタンフォーム, **1**, 30 (1987).
13. G. Rossmly, H. J. Kollmeier, W. Lidy, H. Schator, and M. Wiemann, *J. Cellular Plastics*, **17**(Nov./Dec.), 319 (1981).
14. H. J. Kollmeier and H. Schator, *J. Cellular Plastics*, **21**(Jul./Aug.), 239 (1985).
15. D. R. Battice and W. J. Lopes, *J. Cellular Plastics*, **23**(Mar.), 158 (1987).
16. I. H. Saunders and K. C. Frisch, *ibid.*, pp. 43-44.
17. H. Yoshimura, S. Okuzono, S. Arai, and D. W. Lowe, "Innovated Tertiary Amine Catalyst Systems for CFC Free All MDI Based HR Foam", Proc. 33rd Annual Polyurethane Technical/Marketing Conf. Sept. 30-Oct. 3(1990), pp. 11-18.