

Effects of Amine Catalysts on Structure of Polyurethane Foams

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ABSTRACT : Effects of catalysts on network structure, hard segment length and distribution of polyurethane foams in the absence of catalysts were investigated. CFC free all MDI-based polyurethane foams were prepared from poly(ethylene adipate)glycol, 4,4'-diphenylmethane diisocyanate, and water. Amine catalysts used were 1,4-diazabicyclo[2,2,2]octane(DABCO), N, N,N',N'-tetramethyl--hexane-1,6-diamine(MR), bis(2-methylamino ethyl)ether(ET), 1,8-diazabicyclo-[5,4,0]-undecene-7(DBU). Dibutyltindilaurate(DBTL) as control was also used. Hard segment components of polyurethane foams were obtained by a selective degradation of polyester chains with 0.01N KOH-methanol solution. The PUFs with DBU catalyst contained more amount of isocyanurate components than other PUFs. On the other hand, the PUFs with ET, MR, DBTL catalysts contained more amount of allophanate and biuret component than the other PUFs.

Keywords : polyester polyurethane foam, amine catalysts, hard segment, molecular distribution, structure of crosslinkage.

I. Introduction

Polyurethanes are a block copolymer with relatively hard segment and long flexible segments. Polyurethanes have high performance properties and various applications in wide fields as elastomers, foams, adhesives, and coating. Polyurethane foams (PUFs) are main products in the polyurethane industry. The process for the manufacture of PUFs comprises two successive primary reactions; a gelling reaction to urethane linkages and

a blowing reaction to produce the urea linkage and carbon dioxide. A variety of catalysts have been induced for the control of these reactions as well as for the improvement of moldability, foam properties, and productivity.^{1,2} The attempt to the reduce CFC material usage is now one of the most important environmental issues nowadays. It is also one of the more attractive attributes of the newly modified all MDI based foam systems which can be produced using only water but without chlorofluorocarbons (CFC) as a blowing agent.^{3,4,5}

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However, these water-blown systems causes many technical problems such as extreme foam hardness, reduced processing range, thick surface skin and poor cure speed. New catalyst systems have been developed and effects of the catalysts on properties as hardness, resilience, and compressive strength were investigated by many groups. However, there are little studies on network structures and hard segment distribution of PUFs.

In our previous paper,^{6,7} effects of hard segment length and distribution, and crosslinking structures, mechanical properties of poly(ethylene adipate)-1,4-butane diol-4,4'-diphenyl methane diisocyanate or 2,4-toluene diisocyanate elastomers were described.

In this article, characteristics of tertiary amine catalysts suitable for CFC free all MDI-polyester based foam systems and effects of the catalysts on the reaction profiles, thermal properties, hard segment length and distribution, and structure of cross-link are discussed.

II. Experimental

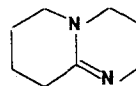
1. Catalysts and Preparation of Foams

Tertiary amines evaluated in this paper were 1,4-diazabicyclo-[2,2,2]-octane (DABCO), 1,8-diazabicyclo-[5,4,0]-undecane-7 (DBU) as acyclic amine, N,N,N',N'-tetramethyl-haxane-1,6-diamine (MR), and bis(2-dimethylaminoethyl)ether (ET) as aliphatic amine. These catalysts which are commercialized as Toyo Cat series were obtained by courtesy of Tosoh Corporation. Dibutyltin dilaurate (DBTL) was also used as a catalyst of organic metal. These catalysts were used as received without purification. Fig. 1 shows



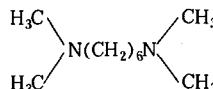
DABCO

1,4-diazabicyclo-[2,2,2]-octane



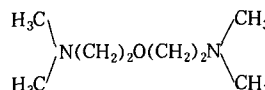
DBU

1,8-diazabicyclo-[5,4,0]-undecene-7



MR

N,N,N',N'-tetramethyl-hexane-1,6-diamine



ET

bis(2-dimethylaminoethyl)ether

 $(C_{11}H_{23}COO)_2Sn(C_4H_9)_2$

DBTL

dibutyltin dilaurate

Fig. 1. Structure of Catalysts.

the catalysts used. The polyurethane foams were prepared from poly(ethylene adipate)glycol (PEA, $M_n=2044$), 4,4'-diphenyl methane diisocyanate (MDI), water as a blowing agent, and silicone compound as a foam stabilizer. PEA and MDI were obtained from Nippon Polyurethane Industry Co. Ltd., Japan. The preparation procedure is shown in Fig. 2. 100 parts of PEA was mixed with 4 parts of water and one part of the foam stabilizer. Amount of the catalyst required by the gel time of preparation reactions during approximately 22 sec was used. The pre-mixture included catalyst and MDI were heated at 40°C and 52°C respectively. MDI was added to the pre-mixture

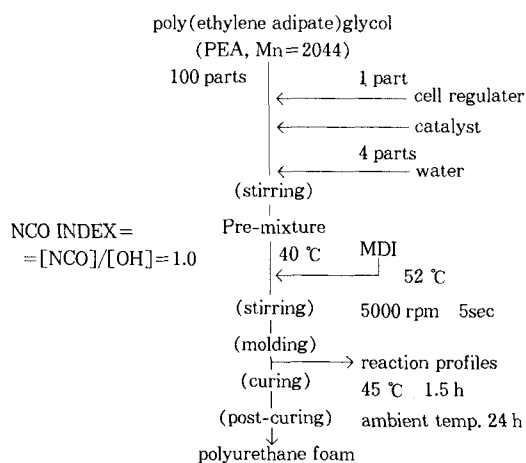


Fig. 2. Preparation Scheme of Polyurethane foams.

ratio), and stirred for 5 sec by means of a homogenizer at 5000rpm. The reaction mixture was poured into the mold. The foam sample was cured at 45 °C during 1.5h and was post-cured at ambient temperature during 24h.

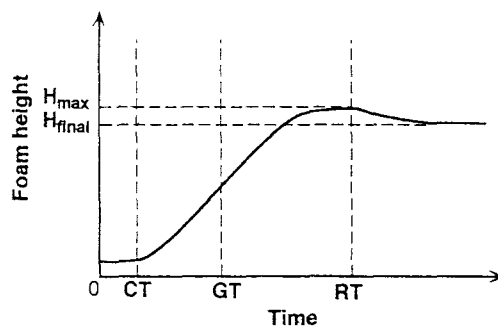
2. Test Methods

2.1. Reaction Profiles

Foam tests were performed on free raise test. The reaction profiles in order to evaluate catalyst were determined using the free rise foam parts. Cream time (CT) is the time until blowing reaction starts after the pre-mixture and MDI were mixed. Gel time (GT) is the time until which stringy products are obtained when small stick is penetrated in the reaction mixture and pulled out. Rise time is the time at which the foam reaches to the maximum foam height (H_{\max}). Fig. 3 shows a schematic profile of foaming reaction.

Foam settling, in other words recession, was calculated by the following equation.

$$\text{Settling}(\%) = \{(H_{\max} - H_{\text{end}})/H_{\max}\} \times 100$$



CT : Cream Time

GT : Gel Time

RT : Rise Time

Rise height = $H_{\max}/\text{Foam weight}$

Settling(%) = $(H_{\max} - H_{\text{final}})/H_{\max} \times 100$

Fig. 3. Typical Rise Profile of Polyurethane Foam.

where, H_{\max} =the maximum foam height (cm), H_{end} =the final foam height (cm). The ratio of the maximum rise height (H_{\max}) to the foam weight (W) to evaluate foaming efficiency was calculated.

2.2 FT-IR Spectra

FT-IR spectra were measured by means of FT-IR spectrometer (JASCO FT-IR 7000, Japan) equipped with ATR.

2.3 Thermal Analysis

DSC thermograms of the PUFs were recorded with the aid of DSC (Rigaku Co. Ltd., Thermplus, DSC-8230, Japan) at heating rate of 10 °C/min from -150 °C to 250 °C under nitrogen atmosphere.

2.4 Observation of Micro-domain Structures

Micro-domain structures were observed by using a polarizing microscope (Nikon, OPTIPHOT2-POL, Japan) equipped with a heating stage (LINKAM, TH-600PM). A sensitive color plate (530nm) was

used for birefringence analysis.

2.5 Measurement of Molecular Weight Distribution of Hard Segments^{6,8}

PUFs were selectively hydrolyzed in order to obtain hard segment components by 0.01N KOH-methanol solution at 50°C for 48h. The hard segment components obtained were analyzed by means of GPC (Shimadzu LC-6A, Japan) equipped with RI detector (Shimadzu RID-6A). Dimethyl formamide (DMF) as a mobile phase was used at flow rate of 1.0mL/min.

III. Results and Discussion

Formation reaction of PUF is constituted of resinification reaction and blowing reaction as next equations.



The reaction profiles of each catalyst at gel time of 22 sec are shown in Table 1. The reaction profile was not obtained in the non-catalyst system

because the reaction was very slow. The rising in the non-catalyst system was not observed. The PUF obtained was leathery. The concentration level of each catalyst required to be the equivalent gel time increased in the order as follows; $\text{ET} < \text{DABCO} < \text{MR} < \text{DBTL} < \text{DBU}$. Catalyst DBU required approximately 1.6 times the concentration level order to equal DBTL at identical gel time, while catalysts MR, DABCO, and ET required about 0.45, 0.41, and 0.21 times respectively. The results shows that catalyst ET had the highest activity per unit weight.

Cream time (CT) value indicates a measure of activity for blowing reaction. CT of the DBU system was 7sec and the smallest in the catalysts evaluated. The order of increase of CT values was $\text{DBU} < \text{ET} < \text{DBTL} < \text{MR} < \text{DABCO}$. CT value of DABCO-system was 12 sec. The results suggest that DBU and ET systems exhibited slower resinification reaction than DBTL system. DABCO and MR systems exhibited delayed CT, as well as a rapid increase in reaction at the later stages of the reaction. Rise time as a measure of formation of CO_2 increased in the order of $\text{DBTL} < \text{ET}, \text{DBU} < \text{MR} < \text{DABCO}$. Settling, on the other hand, is one of the most important factor used to deter-

Table 1. Reaction profile of polyurethane foams

Sample name	Content of catalysts (pbw)	CT ^{*1} (s)	GT ^{*2} (s)	RT ^{*3} (s)	H/W ^{*4} (cm/g)	Settling ^{*5} (%)
NON	-	-	-	-	-	-
DABCO	0.20	12	22	42	0.09	45
DBU	0.80	7	22	31	0.13	0
ET	0.12	9	22	31	0.05	33
MR	0.23	11	22	36	0.07	44
DBTL	0.49	11	22	25	0.11	54

*¹: Cream Time, *²: Gel Time, *³: Rise Time, *⁴: Max height/Foam weight *⁵: (Max height-Final height)/Max height × 100.

mine moldability. This is to say, approximately 5% to 10% settling will assist in producing the most desirable moldability in all MDI foams.³ A large value of settling means that rate of blowing reaction is faster than that of gelling reaction in the system. In other words, gelling reaction and blowing reaction in this system is not balanced. The all catalysts except catalyst DBU have settling value from 33% to 55%. However, catalyst DBU did not display settling. The foaming efficiency, H/W value, increased the order of $ET < MR < DABCO < DBTL < DBU$ between 0.05 and 0.13. These results indicate that DBU system is one of excellent catalysts.

Fig. 4 shows DSC thermograms of PUEs. Glass transition temperature (T_g) of NON-PUF is -30.3°C . T_g of DBU- and DABCO-PUFs is higher than NON-PUF, that is, -24.0°C and -28.3°C respectively. T_g of ET-, MR-, and DBTL-PUF is lower than NON-PUF. Temperature region of glass transition (ΔT_g) of DBU-PUF is 29.3°C , the most broad range in the PUFs evaluated. The order of increase of ΔT_g was $DABCO < DBTL < ET < NON < MR < DBU$. Two endothermic peaks at 48°C and about 150°C in NON-PUF were observed and assigned to melting of soft segments and hard segments respectively. DABCO- and MR-PUFs had exothermic peak at 0°C assigned to recrystallization of soft segments in addition of these two peaks. Broad endothermic transition, which was assigned to various kind of micro-aggregation of hard segments, from about 20°C to 150°C in the other PUFs was observed.

The polarizing micrographs of the sliced PUFs indicate that all PUFs had optical anisotropy. NON-PUF had many small spherulites. The PUFs

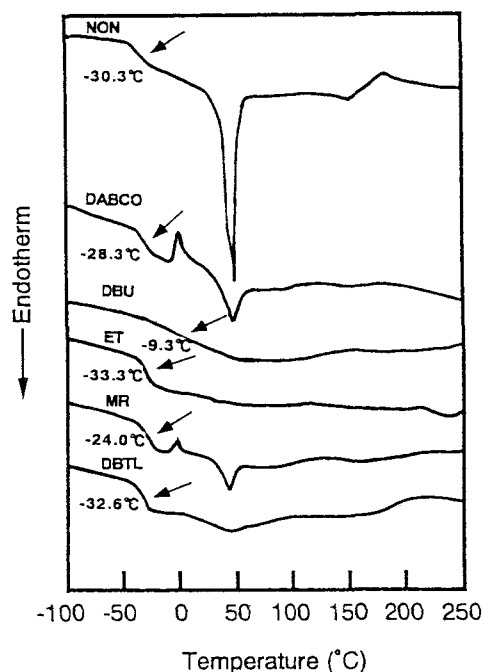


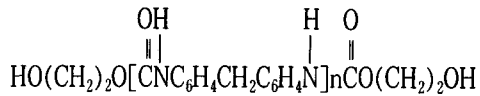
Fig. 4. Effects of Catalysts on DSC Thermograms of Polyurethane Foams.

prepared with catalyst had no spherulites but bright part. These results suggest that DBU-, ET-, and DBTL-PUFs have micro-phase mixture, while NON-PUE has micro-phase separation.

A part of hard segment components obtained by selective hydrolysis of ester groups in DBU-PUF was not be dissolved. FI-IR spectrum had $\nu\text{N-H}$ band at 3300cm^{-1} , $\nu\text{C=O}$ bands at 1709cm^{-1} and 1650cm^{-1} , δNH band at 1543cm^{-1} , and $\nu\text{C-N}$ band at 1421cm^{-1} as characteristic bands of urea and isocyanurate groups.

Fig. 5 shows GPC chromatograms of hard segment components of PUFs. The peaks between retention time of 17min and 20min were assigned to urea hard segments with different chain length as compared with that of model compounds prepared from MDI and MDA. Structure of hard segment

components obtained is as follows;



where $n=1$; urethane reaction between PEA and MDI

$n>2$; urea reaction between MDI and 4, 4'-diamino diphenyl methane (MDA) prepared with H_2O

The peak at 21min was assigned to degradation products of the biuret cross-linkage from the results of model reaction.⁴ The peak at 11min was assigned to isocyanurate derivatives as described in Fig. 5.

Hard segment distribution of NON-PUF was narrower than those of the PUFs with catalysts. NON-PUF contained the reaction residue between PEA and MDI ($n=1$) and biuret crosslinks.

These results lead that isocyanates reacted selectively with the hydroxyl groups of PEA on initial reaction stage because low blowing activity that occurred from different reactivity between water and polymer glycol.

The GPC chromatogram of DBU had most broad peaks in the PUFs used between retention time of 14min and 22min. A many kind of hard segment chain length in DBU system formed due to slow resinification reaction as shown by short CT. No peaks at 11min was attributed to formation of large molecular weight isocyanurate derivatives since DBU-PUF had much insoluble products in the selective degradation.

GPC chromatograms of DABCO-, ET-, MR-, and DBTL-PUFs had also one peak at 11min and

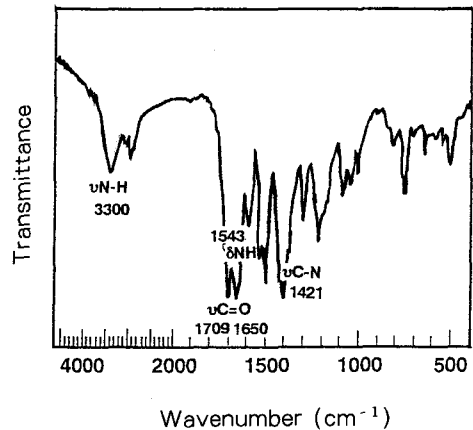


Fig. 5. IR spectrum of insoluble component in DMF.

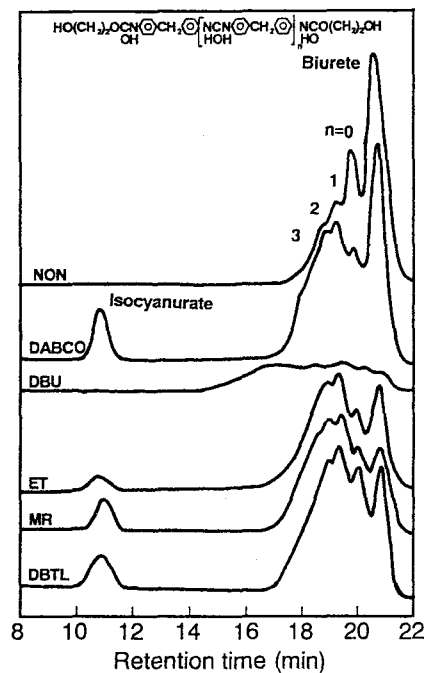


Fig. 6. GPC chromatograms of hard segment of PUFs.

several peaks between retention time of 17min and 22 min. Intensity of the peak at 11min assigned to isocyanurate derivatives increase in the order as follow; $\text{ET} < \text{MR} < \text{DBTL} < \text{DABCO}$. In-

tensity of the peak for biuret linkage decreased in the order of DABCO>ET>DBTL>DBU. From these results, it is indicated that DBU accelerates isocyanurate reaction than biuret reaction, and DABCO, ET, and MR accelerate biuret and isocyanurate reactions.

IV. Conclusion

Effects of catalysts on network structure, hard segment length and distribution of polyurethane foams in the absence of catalysts were investigated. CFC free all MDI-based polyurethane foams were prepared from poly(ethylene adipate)glycol, 4,4'-diphenylmethane diisocyanate, and water. Amine catalysts used were 1,4-diazabicyclo[2,2,2]octane(DBUCO), N,N,N',N'-tetramethyl-hexane-1,6-diamine(MR), bis(2-methylamino ethyl)ether (ET), 1,8-diazabicyclo-[5,4,0]-undecene-7(DBU). Dibutyltindilaurate(DBTL) as control was also used. The PUFs with DBU catalyst contained more amount of isocyanurate components than other PUFs. On the other hand the PUFs with ET, MR, and DBTL catalysts contained more amount of biuret component than the other PUFs.

This study suggests that each catalyst affects

distribution of hard segment length and a kind of crosslinkage and that selection of catalyst is important factors in order to prepare high performance PUFs.

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