폴리올과 촉매에 따른 경질 폴리우레탄 폼의 물성 연구

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Effect of Polyols and Catalysts on Properties of Rigid Polyurethane foam

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INTRODUCTION

Polyurethane gets to be produced through the reaction of polyether polyol or polyester polyol composing a soft segment to a compound of the diisocyanate family composing a hard segment, and a catalyst, a surfactant, a blowing agent and the like are added to it for any application and improvement of physical property thereof. Various kinds of polyols are used depending upon the molecular structure, the molecular weight, the functional group and the OH-value thereof, and it has a direct effect on the physical property of polyurethane.[1~4] Polyester polyol is preferably used owing to the high strength of its ester structure. Results of studying the physical property of the foam manufactured by using it are being reported.[5, 6]

Catalysts used in manufacturing rigid polyurethane foam are broadly classified into metal-family catalysts and tertiary amine-family catalysts according to kinds of substances thereof. Also, their type can be divided into the blowing type, the gelation type, the balance type, the MDI trimerization type and the delayed type according to roles of catalysts, wherein the balance type of catalyst plays both roles of the blowing type and the gelation type. Accordingly, a variety of catalysts are developed and sold on the market.

However, there are not many reports having systematically discussed any correlation between functionality or OHV of polyols and catalysts and foaming behavior or physical property of foam in manufacturing foam actually. Therefore, this study is to identify an effect that each catalyst and polyol have on the reaction velocity and the physical property in manufacturing rigid polyurethane foam.

EXPERIMENTAL

The materials used in this study were obtained from commercial sources. For the synthesis of the rigid polyurethane foams, diisocyanate, polyols, blowing agents, and catalysts were used. Polymeric 4,4-diphenylmethane diisocyanate(PMDI) was supplied from BASF Co.(Seoul, Korea) and was used as a diisocyanate. The average functional group of PMDI was 2.9 and NCO content was 31±5 wt%. The equivalent weight and viscosity of PMDI were 133.5g mol^{-1} and 450 ~ 650cps, respectively.

The foaming reaction was carried out as follows: The premixed master solution containing polyol, catalyst, water, silicon surfactant, and blowing agent along with the isocyanate were held at 25±1℃. Fixed amounts of the premixed master solution and isocyanate were vigorously mixed together at 3,000rpm for a period of 30 seconds. The solution was then rapidly transferred to a 2 liter polyethylene vessel kept at 25±2℃, and then observed reaction rate(gel time), reaction temperature.

RESULTS AND DICUSSION

1. Effect depending upon polyol structure

Table 1 show the effect that the functional group of polyol had on the gel time, the density, the compressive strength and Tg of the foam in case the molecular weight of polyol was similar to that of the conventional polyol. As the functional group of polyol was increased respectively to 4 and 4~5 from 3, the gel time got to be faster respectively to 240 seconds and 210 seconds from 342 seconds. This is because any increase in the functional group also causes the caloric value to be increased at the time of polymerization and thereby the rate of reaction is increased, like the case with any increase in the OH-value of polyol.

Table 1. The effect of the functional group of polyol on the gel time, the density, the compressive strength of the PUF.

	PUF 2-280	PUF 2-320	PUF 3-290	PUF 3-400	PUF 3-670	PUF 4~5-360	PUF 4~5-510
Maximum rxn. temp. (℃)	59	72	55	65	93	52	65
Gel time (sec.)	115	62	342	281	245	345	275
Density (kg/m^3)	88	90	106	108	126	108	125
Compressive strength (kg$_f$/cm$^{2)}$	9.60	10.28	8.33	10.48	15.26	10.87	16.05

In order to identify that the cause of the increase in the compressive strength of the foam according as the functional group is increased at the same density was the increase in the degree of crosslinking, Tg was measured by using DSC. As shown in Figure 1, Tg has a tendency to get increased to 126℃ and 159℃ from 63℃ according as the functional group is increased. It can be known from the above result that though the effect that any increase in the functional group of polyol has on the density of the foam is not so great, it causes the degree of crosslinking in the foam to be increased and thereby the compressive strength of the foam is increased.

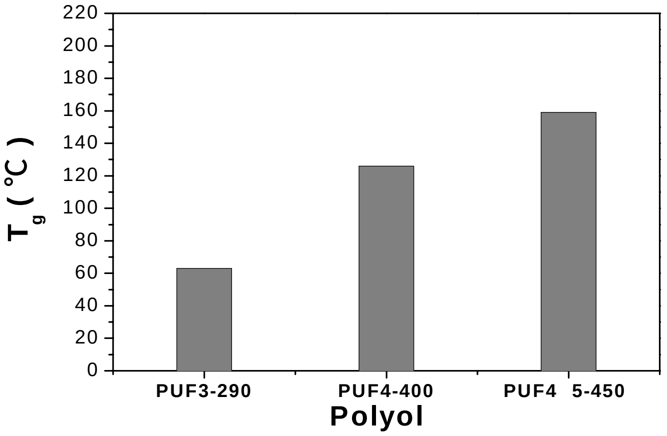


Figure 1 – Effect of functionality of polyol on the glass transition temperature (Tg) of PUF.

2. Effect depending upon catalyst

The result of catalyst effect was shown in Fig. 2 and Table 2. As the amount of the catalyst was increased in the order of 0.5, 1, 1.5 and 2pbw, G/T got to be faster. As the content of PC-5 was increased, the density and the compressive strength had a tendency to be enhanced. However, since PC-5 did not affect the cross-linking degree of foam, Tg showed similar values.

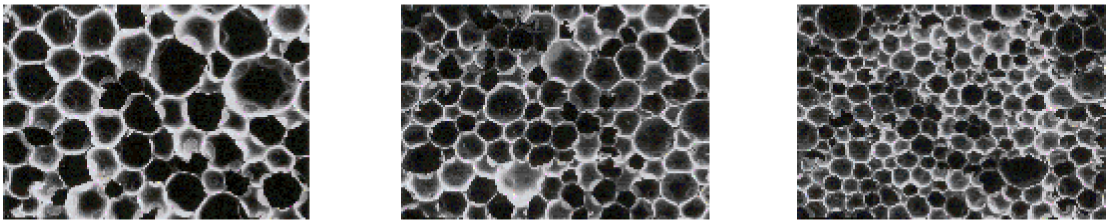
As the amount of triethylenediamine was increased from 0.5pph to 2.0pph, the density was little changed from 112.77kg/cm^3 to 116.39kg/cm^3 so that it was almost fixed, but the compressive strength was increased from 10.29kgf/cm^2 to 12.66kgf/cm^2. This is because as the content of the catalyst was increased, the cell size got decreased, as shown in the result of SEM in Fig. 2. Like

Table 2. The effect of the catalyst on the gel time, the density, the compressive strength of the PUF.

	Content	**Density**	**Gel time**	**Compressive strength**	**Tg**
Pentamethyl diethylene triamine	0	119.4	1115	11.90	119
	0.5	104.45	222	10.23	
	1	128.89	115	15.50	121
	1.5	157.59	78	21.24	
	2	189.25	70	29.83	123
Dimethylcyclohexylamine	0	106.12	918	9.67	120
	0.5	94.08	205	8.71	
	1	92.22	124	8.96	122
	1.5	93.08	92	9.22	
	2	95.44	73	9.96	120

Triethylenediamine/ dipropyleneglycol	0	119.4	1115	11.90	119
	0.5	112.77	244	10.29	
	1	112.62	131	11.54	118
	1.5	113.2	86	11.85	
	2	116.39	64	12.66	123

the case of triethylenediamine, it can be seen that as the amount of dimethylcyclohexylamine was increased in the order of 0.5, 1, 1.5, 2pbw, the density was little changed in the order of 94, 92, 93 and 95kg/m^3,, but the compressive strength was continuously increased.



(a) (b) (c)

Figure 2. Scanning Electron Micrograph of polyurethane foams with 33LV content ;
(a) 0.5pph,(113kg/m^3) (b) 1 pph(113kg/m^3), (c) 2 pph(116kg/m^3)

CONCLUSION

In this study, we evaluated the effect that the structure of polyol had on the gel time, the reaction temperature, the density, the compressed strength and Tg of the foam and the cell structure.

As the functional group of polyol was increased, the reaction temperature, the density, the compressed strength and Tg of the foam were also increased. Also, even at the same density, the compressed strength and Tg of the foam were increased as the functional group and the OH value of polyol were increased, and the cell structure was finely formed as the functional group and the OH value of polyol were increased.

It was found out that in the case of all catalysts, as the amount thereof was increased, there was little variation in the density and cross-linking degree of foam but the compressed strength was increased.

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