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Curing Behavior of Epoxy Resins Using Aminolysis Products of Waste Polyurethanes as Hardeners

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We carried out aminolyses of various rigid polyurethane foams (PUFs) using diethylene triamine and studied application of the aminolysis products as hardners of epoxy resins. Diglycidyl ether of bisphenol A was used for the study on the curing behavior of epoxy resin with the aminolysis product employing differential scanning calorimeter. Curing reaction of the epoxy resin is generally known to be autocatalytic second order reaction. We found that the curing reaction of the epoxy resin with the aminolysis product of rigid PUF did not show autocatalytic characteristics but followed the n-th order kinetics. The activation energy of the curing reaction of the epoxy resin with the aminolysis product of rigid PUF made from sugar based polyol was slightly lower than that of the epoxy resin with aminolysis product of rigid PUF made from amine based polyol.

Introduction

Rigid polyurethane foams (PUFs) of closed cells are widely used in appliances and constructions due to their light weight and superior heat insulation as well as good mechanical properties. Since large of quantities of waste PUFs are inevitably discharged in various stages of manufacture, processing, and after usage, recycling technology of the waste is necessary. Most of recycling technologies of PUFs are based on chemical treatment to get polyols and mechanical grinding for applications as fillers [1-2]. Recently, Imai et al proposed general purpose adhesives based on epoxy resin hardened with chemically recycled waste rigid PUFs [3]. According to Imai and his coworkers, the glycolysis product of waste polyurethane could be used as toughener as well as hardener of epoxy resin.

PUFs are prepared from polymeric 4,4'-diphenyl methane diisocyanate (MDI) and sugar based polyol or amine based polyol [4]. PUFs can be decomposed into their components on heating in some medium. Because urethane, urea, biuret, and allophanate bonds exist generally in PUFs, decomposition reactions of PUFs with decomposers such as glycol and amine would be somewhat complicated. In case of decomposition of PUFs with amine, i.e. aminolysis, it is speculated that several kinds of compounds useful as hardners of epoxy resin will be obtained as shown in Scheme 1. There are many reports in literatures on the curing of epoxy resin with amine or anhydride [5-7], but there is few reports in the literatures on the curing reaction of epoxy resin using decomposition products of PUFs. We prepared various PUFs and aminolysis products of the PUFs using diethylene triamine(DETA) was evaluated as hardener of epoxy resin. For proper applications of the aminolysis products of PUFs, curing behaviors of epoxy resin with aminolysis products as hardeners were studied and are reported in this paper.

Experiment

PUFs were prepared at room temperature using commercial polyols and polymeric MDI. Especially, two types of polyols, a sugar based polyol and an amine based polyol, were used to make PUFs. Table 1 gives a formulation for the preparation of PUFs. Aminolyses of the PUFs were carried out at 180℃ for 4 hours using reagent grade DETA in the environment of nitrogen gas. The ratios of PUF:DETA in the aminolyses were 2:1 by weight. Active hydrogen equivalent weight (AHEW) of the aminolysis product was measured by back titration method using phenyl glycidyl ether. The AHEW value of the aminolysis product of PUF made from sugar based polyol (PUF-I) was 70 g/eq and that of the aminolysis product of PUF made from amine based polyol (PUF-II) was 97 g/eq.

A commercial epoxy resin (YD-128 from Kukdo Chemical Industry Co. the epoxy equivalent weight of which was 187g/eq) was used to study curing behavior. 187 g of the epoxy resin was mixed with 70 g of the aminolysis product of PUF-I or 97 g of the aminolysis product of PUF-II. Exothermic heats of curing reaction of the epoxy resin with aminolysis products were measured during isothermal cure at 60, 70, and 80℃ employing differential scanning calorimeter (DSC, DSC 910 connected with TA-2000). When no more exotherms were observed in DSC, the isothermal cure was stopped and the samples were cooled down to 25℃. In order to determine the residual heat of reaction, the samples were reheated from 25℃ to 240℃ at 10℃/min.

Results and Discussion

Exothermic properties of epoxy resins with the aminolysis products of PUFs as hardeners during curing process were studied employing DSC. For the analysis of exothermic properties, the ultimate heats of cure (QUT) of the resins were obtained from isothermal heat of cure (QT) and the residual heat of cure (QR) determined by reheating the isothermally cured samples from 25℃ to 240℃ as follows;

$$Q_{UT} = Q_T + Q_R \qquad (1)$$

Figure 1 shows DSC thermograms obtained during isothermal cure of the epoxy resin with aminolysis products of PUF-I at different temperatures. Table 2 gives heats of cure for the epoxy resin at various conditions. Degree of cure (C) and rate of cure (dC/dt) at temperature T were obtained from rate of heat generation (dQ/dt) as follows;

$$C = \frac{1}{Q_{UT}}\int_0^t \left(\frac{dQ}{dt}\right)_T dt \qquad (2)$$

$$\frac{dC}{dt} = \frac{1}{Q_{UT}}\left(\frac{dQ}{dt}\right)_T dt \qquad (3)$$

Average values of QUT determined experimentally were used in the analyses with equations (2) and (3).

In Figure 2, plots of dC/dt versus cure time at 60℃, 70℃, and 80℃ for the epoxy resin with DETA as a hardener are shown. It is seen that the rate of cure increases with cure temperature. It is worthwhile to note that the epoxy resin shows maximum in rate of cure due to autocatalytic reactions. Kamal et al proposed a semi-empirical kinetic model to represent the autocatalytic cure of epoxy resin and thermosetting polyester resin as as follows [8];

$$\frac{dC}{dt} = (k_1 + k_2 C^m)(1-C)^n \qquad (4)$$

where m and n are reaction order and m+n = 2 was assumed. Figures 3 and 4 show plots of dC/dt versus cure time for the epoxy resin with aminolysis products of PUFs as hardeners. It is observed that the rates of cure do not show maximum but decrease with cure time. Curing characteristics shown in Figures 3 and 4 imply the curing reaction is the n-th order reaction as follows;

$$\frac{dC}{dt} = k(1-C)^n \qquad (5)$$

Kinetic parameters, k and n in the equation (5), can be determined from the y-axis intercept and the slop in plots of ln(dC/dt) versus ln(1-C). Table 3 gives kinetic parameters for the curing of epoxy resin with aminolysis products of PUFs. Reaction order of the curing reaction of epoxy resin were 2.2～2.4. The rate of cure of the epoxy resin with the aminolysis product of PUF-I was a little bit faster than that of the epoxy resin with the aminolysis product of PUF-II. The activation energy of the curing reaction of the epoxy resin with the aminolysis products of PUF-I was slightly lower than that of epoxy resin with aminolysis products of PUF-II.

Conclusion

The curing reaction of the epoxy resin is generally known to follow autocatalytic second order reraction kinetics. We found that the curing of epoxy resin with aminolysis products of rigid PUFs did not show autocatalytic characteristics but followed the second order reaction. It is speculated that there are many variables affecting the curing behavior of the epoxy resin with aminolysis products of PUFs such as the properties of PUFs as well as amines. Results of further studies on those variables will be reported in the near future.

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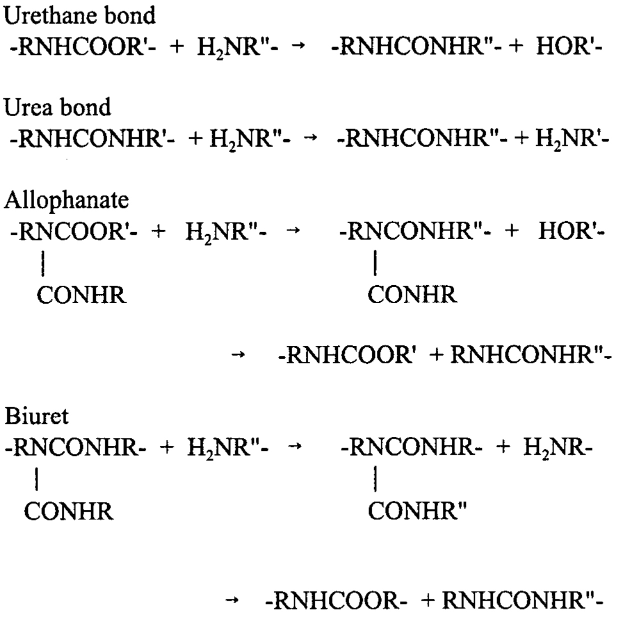

Urethane bond

$-RNHCOOR'- + H_2NR''- \rightarrow -RNHCONHR''- + HOR'-$

Urea bond

$-RNHCONHR'- + H_2NR''- \rightarrow -RNHCONHR''- + H_2NR'-$

Allophanate

$-R\underset{\underset{CONHR}{|}}{N}COOR'- + H_2NR''- \rightarrow -R\underset{\underset{CONHR}{|}}{N}CONHR''- + HOR'-$

$\rightarrow -RNHCOOR' + RNHCONHR''-$

Biuret

$-R\underset{\underset{CONHR}{|}}{N}CONHR- + H_2NR''- \rightarrow -R\underset{\underset{CONHR''}{|}}{N}CONHR- + H_2NR-$

$\rightarrow -RNHCOOR- + RNHCONHR''-$

Scheme 1. Aminolysis reactions of rigid polyurethane foams with an amine.

Table 1. Formulation of Rigid PUFs for Aminolysis Reaction

Chemicals	Composition(by wt.)
Polyol1)	100
Water	1.5
Triethylene diamine2)	0.5
Silicone surfactant3)	1.0
Polymeric MDI4)	1105)

1) PPG-490(sugar based polypropylene glycol) or PPG-640(amine based polypropylene glycol) from Kumho Petrochemical Co. Ltd.
2) 33% (by wt.)
3) Tegostab B 1048 from T. H. Glodschmidt
4) Voranate M-269 from Dow Chemical
5) Isocyanate Index value

Table 2. Heats of cure of the epoxy resins with aminolysis products

Hardner	Cure Temperature (℃)	Q_T (cal/g)	Q_R (cal/g)	Q_{UT} (cal/g)
Aminolysis products of PUF-I	60	51	28	79
	70	55	24	79
	80	61	19	80
Aminolysis products of PUF-II	60	48	31	79
	70	52	22	74
	80	54	15	69

Table 3. Curing kinetic parameters of the epoxy resins with aminolysis products of PUFs

Hardner	Cure Temperature (℃)	n	$k \times 10^3$ (sec^{-1})	Ea (cal/mol)
Aminolysis products of PUF-I	60	2.4	3.6	6012
	70	2.3	4.7	
	80	2.2	6.0	
Aminolysis products of PUF-II	60	2.3	3.4	6074
	70	2.2	4.5	
	80	2.2	5.7	

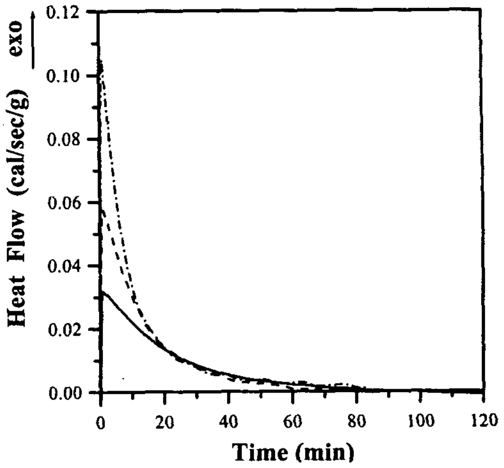

Figure 1. Rate of heat generation versus cure time for the epoxy resin with aminolysis products of PUF made from a sugar based polyol at different temperatures : (—) 60℃ ; (···)70℃ ;(– ·) 80℃

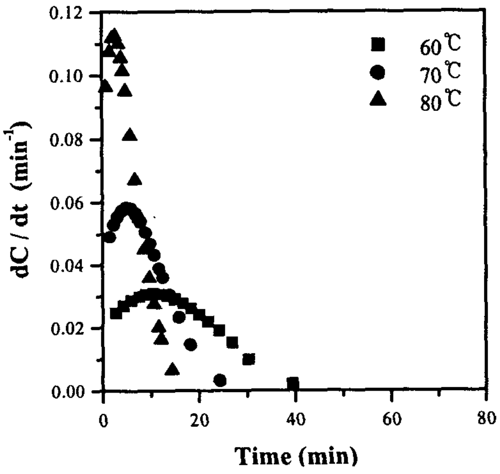

Figure 2. Rate of cure (dC/dt) versus cure time for the epoxy resin with DETA at different temperatures.

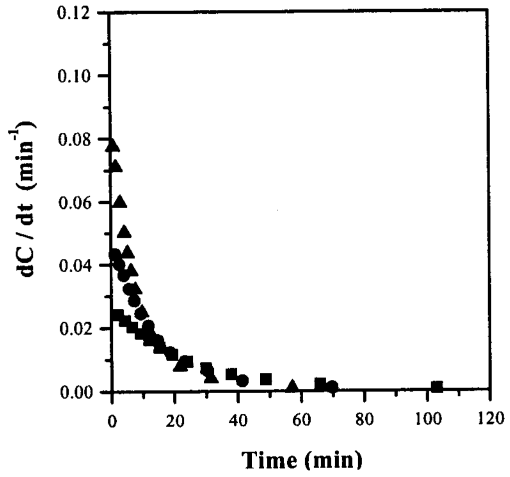

Figure 3. Rate of cure (dC/dt) versus cure time for the epoxy resin with aminolysis products of PUFs prepared from on sugar based polyol at different temperatures. Symbols are the same as in Figure 2.

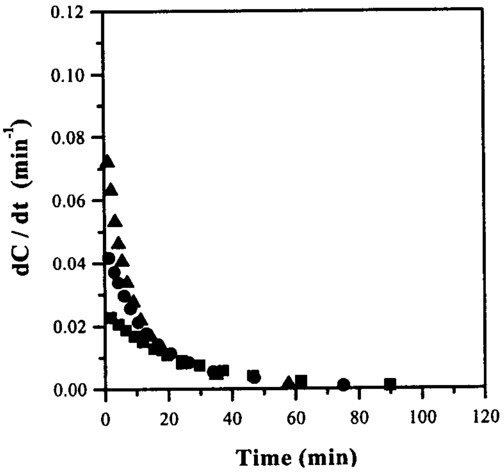

Figure 4. Rate of cure (dC/dt) versus cure time for the epoxy resin with aminolysis products of PUFs prepared from on amine based polyol at different temperatures. Symbols are the same as in Figure 2.