Preparation of Epoxy Hardeners from Waste Rigid Polyurethane Foam and Their Application

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SYNOPSIS

Aliphatic amines were used as decomposer to decompose waste rigid polyurethane and polyisocyanurate foams, and the obtained decomposed products were directly used as curing agent of epoxy resin. Effects of the decomposing condition including amine type, foam–decomposer ratio, and reaction temperature on the decomposition reaction and properties of the decomposed products were investigated. Using amines with low molecular weight could enhance decomposition reaction rate and total amine number and lessen viscosity of the obtained decomposed products. Viscosity of the decomposed products decreased with increase of reaction temperature, but increased with increment of foam–decomposer ratio. Shear strength of adhesives consisting of decomposed products and epoxy resin was measured, and their thermal properties were analyzed. The adhesives could be cured completely over 60°C and their shear strength enhances with adding coupling agent in the adhesive system. The adhesives have good thermal stability and show satisfactory shear strength with more than 15, 15, 7, and 3 MPa at 25, 60, 100, and 150°C, respectively. The results demonstrate that the obtained adhesive systems can be used as structural adhesive.

INTRODUCTION

Polyurethane foams have shown considerable growth in the airplane, automobile, furniture, packaging, and construction industries over the past 40 years due to their good properties. Clearly, the recycling of waste polyurethane foams has become a global issue with the increase of the waste from these systems.

Several recycling techniques for polyurethane have been described in the technical and scientific literature.[1-10] The recycling technologies of polyurethanes can be classified into physical recycling, chemical recycling, and energy conversion. The chemical reclaiming is generally employed to obtain recycled polyols and amines. But it is very difficult and complicated to separate and purify polyols and amines from the decomposed products.

Substances containing amino groups and other groups are always produced in decomposition reaction of polyurethane. To simplify the process of treating the waste and avoid the intricate separation, a method using decomposed products which were obtained by glycolysis of waste rigid polyurethane foam directly as one component of epoxy adhesive has been developed.[11] This method, in which amines and other products (including polyol, etc.) in the obtained mixture of decomposed products were designed to function as hardener of epoxy adhesive and additives (or plastisizer) respectively, has been verified to be efficient and has been also applied in construction of roads. Since some amount of decomposer still exists in final product after decomposing reaction, the remaining decomposer with low molecular weight causes damage to applied materials on mechanical strength and heatproof to a certain extent.

The chemical compounds containing amino group can be also used to decompose polyurethane foam chemically.[12,13] They can clearly hardened epoxy resins. It can be estimated that using amines to replace glycols as decomposer of waste polyurethane foam will greatly improve mechanical and heat-resistant properties of the materials consisting of the decomposed products and epoxy resin.

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In this study, aliphatic amines were chosen as decomposer to aminolyse the waste rigid polyurethane foam and polyisocyanurate foam. The decomposed products were directly employed as hardener of epoxy resin. Effects of decomposing condition including amine type, the ratio of foam–decomposer, and temperature on decomposition reaction and properties of decomposed products were investigated. The bonding strength of adhesive consisting of epoxy resin and the decomposed products was measured and their thermal properties were analyzed.

EXPERIMENTAL

Materials

1. Rigid foams (provided by INOAC Corporation):
   a. Polyurethane foam (Foam A) composed of polymeric diphenylmethane diisocyanate (MDI) and polyether polyol (hydroxyl value (OHV) = 345 mgKOH/g, MW = 650, functionality $f = 4$)
   b. Polyurethane foam (Foam B) composed of polymeric MDI and polyether polyol (OHV = 457 mgKOH/g, MW = 510, $f = 4.4$)
   c. Polyisocyanurate foam (Foam C) composed polymeric MDI and modified by polyester polyol (OHV = 315 mgKOH/g, MW = 356, $f = 2$)
   d. Polyurethane (Foam D) composed of toluene diisocyanate (TDI) and polyether polyol (OHV = 430 mgKOH/g, MW = 391, f = 3)
2. Diethylene triamine (DETA), provided by Kanto Chemical Co. Inc.
3. Triethylene tetramine (TETA), provided by Kanto Chemical Co. Inc.
4. Tetraethylene pentamine (TEPA), provided by Kanto Chemical Co. Inc.
5. 4,4′-Methylenedianiline (MDA), DAM-L, provided by Nippon Polyurethane Industry Co., Ltd.
6. Bisphenol A epoxy resin, DER 331J, provided by Dow Chemical Co. Ltd.
7. Silicone coupling agent, SH-6040, provided by Toray-Dowcorning Co. Ltd.

Decomposition of Rigid Foams

Aliphatic amine was added into a 500-mL four-neck flask equipped with a reflux condenser, a thermometer, and a stirrer. Waste rigid foam with about 3 m/m diameter, which was ground in HORAI Pulverizer, was continuously added into the reactor at constant temperature. The decomposition reaction proceeded until the foam was completely dissolved. The period from adding foam to complete dissolving of the foam was named as the reaction time.

Preparation of Epoxy Adhesives

Epoxy adhesives were obtained by mixing epoxy resin with the decomposed products which contain amino groups. In some cases, amounts of coupling agent, which is usually used in preparation of epoxy adhesives, were added to the adhesives mentioned above. After mixing, the adhesives were coated on two piece of aluminum alloy sheets and the bonded samples were cured with contact pressure at different curing condition.

Measurements

1. Total amine number of the decomposed product was measured by acetic acid–perchloric acid method using COMTILE-900 Auto-Titrator.
2. Viscosity of the decomposed product was measured by using Contraves Rheomat 115.
3. Gel permeation chromatogram (GPC) of the decomposed product was obtained by using Shimadzu LC-4A. The chromato-column was Shodex KF (801, 803, 8025) and the mobile phase was tetrahydrofuran.
4. Content of MDA in the decomposed product was analyzed by using Shimadzu LC-6A. The chromato-column was Unisil NQC18 and mobile phase was 0.1M ammonium acetate–acetonitrile (65/35).
5. As the characteristics of bonding strength of adhesives, shear strength of adhesives at different temperature was measured by using SHIMADZU AGS-5KNB Testing Machine according to Japanese Industrial Standard (JIS) K 6850. Aluminum alloy was used as testing sheet. The crosshead speed was 50 mm/min.
6. The thermogravity property of cured samples was measured by using TG/DTA 220 of Seiko Instruments Inc. The heating rate was 20°C/min.
7. The dynamic viscoelasticity was analyzed by using DMS 200 of Seiko Instruments Inc. The heating rate was 3°C/min.

RESULTS AND DISCUSSION

Decomposition Reaction of Rigid Foam

Polyurethane foam and polyisocyanurate foam can be dissociated into their components.[12,13] Because diverse chemical bonds such as urethane, urea, biuret, and allophanate exist in the foams, the decomposition reaction of foam in chemical reagent is complicated. It becomes difficult and tiresome to analyze different components in the obtained decomposed product qualitatively and quantitatively. The models of dissociation reaction of polyurethane foams in aliphatic amine such as DETA can be depicted as following:

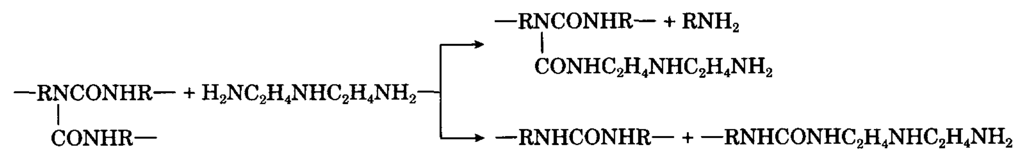
1. Urethane bond

$$\text{—RNHCOOR'— + } H_2NC_2H_4NHC_2H_4NH_2 \longrightarrow \text{—RNHCONH}C_2H_4NHC_2H_4NH_2 \text{ + —R'OH}$$

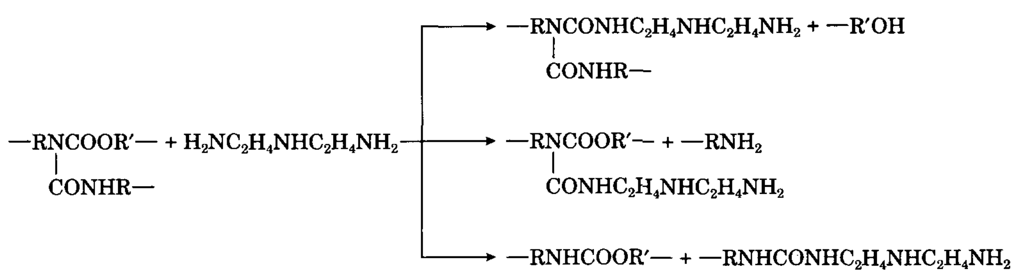
2. Urea bond

$$\text{—RNHCONHR'— + } H_2NC_2H_4NHC_2H_4NH_2 \longrightarrow \text{—RNHCONH}C_2H_4NHC_2H_4NH_2 \text{ + —R'}NH_2$$

3. Biuret bond



4. Allophanate bond



A large quantity of active groups which can react with epoxy resin is generated in the decomposition reaction, and the groups can be used as hardener of epoxy resin. GPC curve of the decomposed product of foam A is shown in Figure 1. The result explains that there are a lot of components with molecular weight ranging from 100 to 1000 in the obtained decomposed product. Compared with the decomposed product obtained by using glycol,[11] the decomposed product in this study has lower molecular weight. It demonstrates that amine is a more efficient decomposer than glycol and decomposes polyurethane foam more completely than glycol.

Effects of various amines on decomposition reaction are shown in Table I. It could be found that when a lower molecular weight of amine is used in the decomposition reaction, the decomposition reaction rate and the total amine number of the obtained decomposed products increase and the viscosity of decomposing system decreases for the same reaction temperature.

The rate of decomposition reaction of polyurethane foam is related to the basicity of decomposers.[12,13] DETA, whose concentration of active hydrogen atom is equal to 4.85 N/100 g and higher, has the strongest basicity among the three kinds of amines. It makes the decomposition reaction of polyurethane foam faster, more complete, and leads a lower viscosity of decomposed product. The fact that the decomposed product obtained when DETA was used as decomposer has the highest total amine number and the lowest viscosity certainly has some relationship to the highest concentration of amino groups and the lowest viscosity of this amine among the three amines. The lower the molecular weight

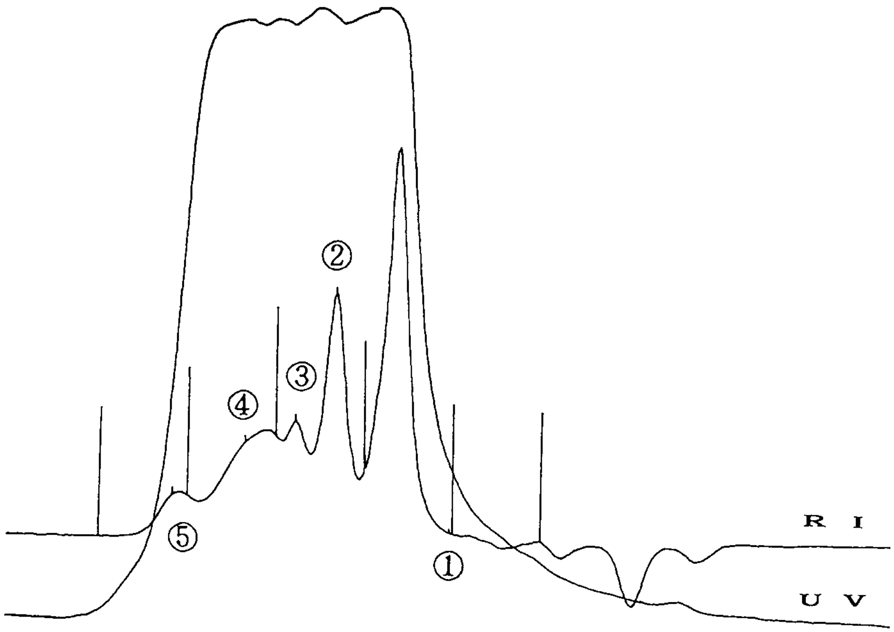


Figure 1 GPC curve of the decomposed product from foam A with the molecular weight distribution. Foam A-DETA (weight ratio) = 2/1; reaction condition: 170°C × 70 min. ① M_n = 100; ② M_n = 250; ③ M_n = 330; ④ M_n = 500; ⑤ M_n = 1000.

of amine, the better the efficiency of decomposing reaction and the properties of the final decomposed products.

The effects of temperature on decomposition reaction rate and properties of final decomposed products are listed in Table II. The decomposition reaction took place at 150, 160, 170, and 180°C, respectively, and DETA was used as decomposer.

From the results shown in Table II, it was found that reaction rate increases (that is, reaction time, which was taken to dissolve completely the waste polyurethane foam, shortens) with rise of reaction temperature. Increasing reaction temperature had little or no effect on total amine number but greatly decreased the viscosity of the final decomposed product. It is clearly advantageous to practical application of the decomposed product.

Compared with the case of using glycol as decomposer, using amine can make decomposition reaction possible to proceed at a lower temperature, to need a shorter time, and to increase total amine number of the obtained decomposed product. This is in correspondence with the results of GPC experiments.

Increasing foam–DETA ratio is certainly advantageous for a treated quantity of waste polyurethane foam, but it leads to an increase in the viscosity of the decomposed product as shown in Table III. Contrary to the case of using glycol as decomposer, raising the foam–DETA ratio decreases total amine number of the decomposed product. It is because the former is a process of producing amino groups

Table I Effects of Amines of Decomposition Reaction of Foam A and Properties of the Obtained Decomposed Products

	DETA	TETA	TEPA
Foam A–amine	2/1	2/1	2/1
Temp. (°C)	170	170	170
Time (min)	70	100	150
Total amine number (mg/g)	415.5	360.8	342.6
Viscosity (Pa s, 60°C)	1.9	18.4	96.9

Table II Effect of Reaction Temperature on Decomposing Reaction of Foam A and Properties of the Decomposed Products

	150°C	160°C	170°C	180°C
Foam A–DETA	2/1	2/1	2/1	2/1
Time (min)	130	100	70	40
Total amine number (mg/g)	408.8	417.0	415.5	420.1
Viscosity (Pa s, 35°C)	153	63.8	35.7	21.9

Table III Effects of Foam A–DETA Ratio on Properties of the Decomposed Products

Foam A–DETA	1.0/1	1.5/1	2.0/1	2.5/1	3.0/1	4.0/1
Total amine number (KOHmg/g)	728.3	631.6	415.5	400.4	263.9	212.1
Viscosity (Pa s, 60°C)	0	0.5	1.9	—	13.9	203.8

by consuming glycol, but the latter is a process of consuming amino groups of DETA gradually, though aromatic amino groups are also produced in the decomposition reaction.

The information of decomposition reaction of foams A, B, C, and D and properties of their decomposed products are listed in Table IV. It is clear that the decomposition rate of various foams and the properties of their final decomposed products appear to be different. It is predicted to have a relationship to raw materials used and chemical structures of the foams.

That the decomposition rate of foam C is the highest could be attributed to type of foam, polyisocyanurate foam modified by polyester polyol. Generally polyester polyurethane decomposes easier than polyether polyurethane due to its ester group. Ester group and urethane groups in foam C can be simultaneously decomposed in amine media, while it is difficult to dissociate ether groups in foams A, B, and D. That the decomposed product D has the lowest viscosity might be due to the TDI type of foam.

Shear Strength and Thermal Properties of Adhesives Consisting of the Decomposed Products and Epoxy Resin

The bonding or shear strength of adhesive made up of decomposed product A and epoxy resin at different curing conditions were measured and results are shown in Figure 2.

It can be found that shear strength of the adhesive increases with curing time and reaches the maximum value about 18 MPa at 100°C for 2 h and 80°C for 5 h. The sample cured at 60°C has shear strength about 16.5 MPa after curing for 15 h. This shows that although the sample cured at 60°C may reach the maximum value of strength, it would take a longer time and make practical application difficult. It was difficult for the adhesives to be cured completely and reach their highest strength when cured at room temperature. Since amino groups produced in decomposition reaction are basically aromatic, the adhesives composed of the decomposed products must be cured at elevated temperatures.

Compared with adhesives consisting of epoxy resin and the decomposed products obtained through using glycol as decomposer, the new adhesive system only needs lower curing temperature and has higher shear strength.[11] It could be attributed to DETA used as decomposer. Unlike diethylene glycol (DEG), which could hardly react with epoxy resin, DETA can easily react with epoxy resin at room temperature. Though some amounts of DEA and DETA remain, respectively, in their decomposed products, excess DETA can cure epoxy resin while excess DEG cannot react with epoxy resin and exists in final product only as an additive. The excess DEG might affect strength and thermal properties of materials.

Effect of coupling agent on shear strength of the adhesive is presented in Figure 3. Shear strength increases with an increment in coupling agent. It demonstrates that the coupling agent can apparently

Table IV Decomposition Reaction of Different Waste Foams and the Properties of the Decomposed Products

	Foam A	Foam B	Foam C	Foam D
Foam–DETA	2/1	2/1	2/1	2/1
Temperature (°C)	170	170	170	170
Time (min)	70	60	40	60
Total amine number (KOHmg/g)	416	410	418	358
Viscosity (Pa s, 30°C)	72.4	203	135	4.5
Content of MDA (wt %)	0.99	0.58	1.14	—
Decomposed product	A	B	C	D

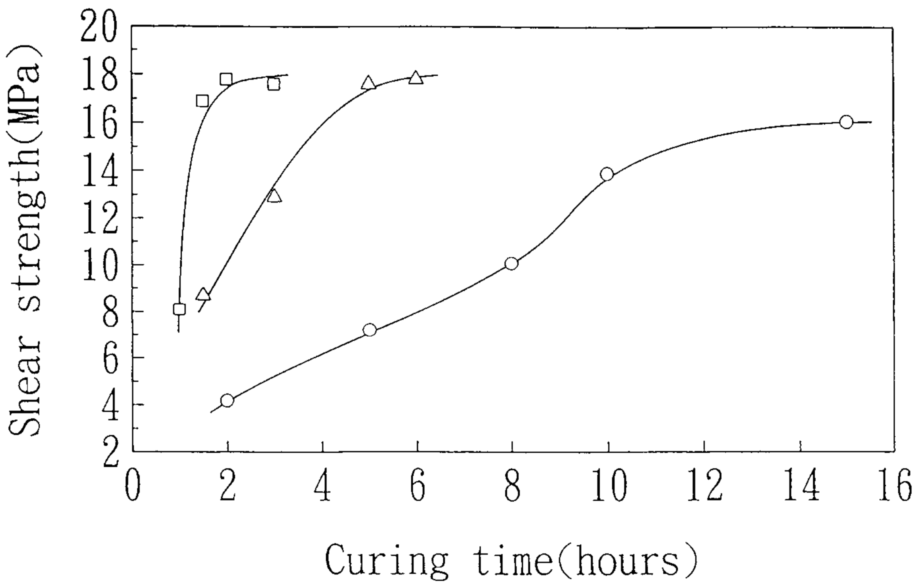


Figure 2 Relationship between curing time and shear strength of adhesive made up of decomposed product A and epoxy resin at various curing temperatures. Decomposed product A–epoxy resin–coupling agent (weight ratio) = 30/100/1.3. (○) 60°C, (△) 80°C, (□) 100°C.

improve shear strength of the adhesive just like other epoxy adhesives.

Table V shows shear strength of different adhesives consisting of epoxy resin and the decomposed products from various rigid foams at different temperatures. Compared with the adhesive consisting of epoxy resin and DETA, the adhesives demonstrate much more satisfactory shear strength at various temperatures. This fact is due to MDA, polyurethane oligomers with amino groups, and polyether polyol in the decomposed products, which were produced in decomposition reaction and existed in the decomposed product. MDA is a aromatic amine and shear strength of adhesives composed of aro-

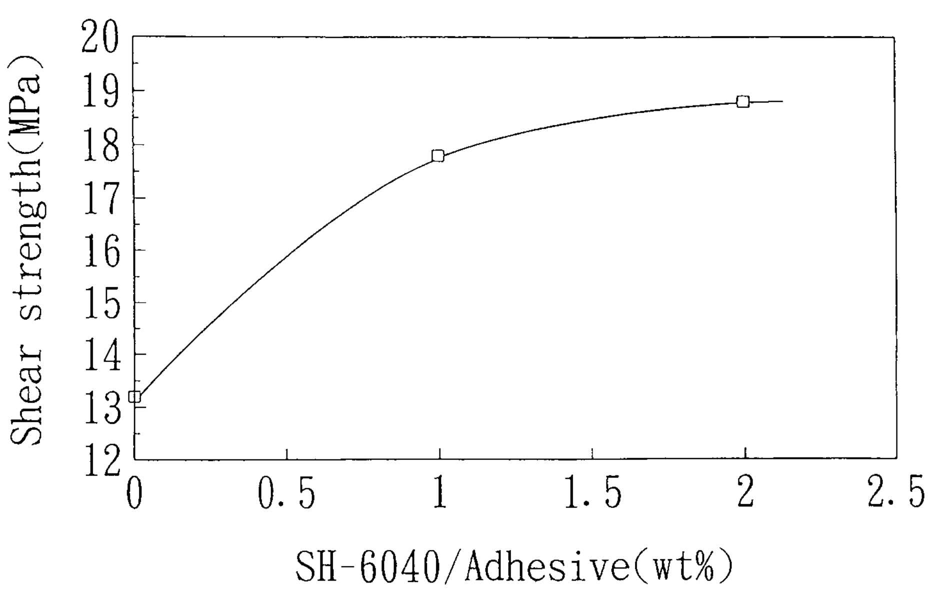


Figure 3 Relationship between content of coupling agent and shear strength of adhesive consisting of decomposed product A and epoxy resin. Decomposed product A–epoxy resin (weight ratio) = 30/100; curing conditions: 100°C × 3 h.

Table V Shear Strength of Adhesives Composed of Epoxy Resin and the Various Decomposed Products

Epoxy Resin DER 331J (g)	Decomposed Product (g)					SH-6040 (g)	Shear Strength (MPa)			
	A	B	C	D	DETA		25°C	60°C	100°C	150°C
100	30	—	—	—	—	1.3	17.8	17.2	8.6	3.0
100	—	30	—	—	—	1.3	15.9	19.6	7.4	4.0
100	—	—	30	—	—	1.3	19.8	16.0	13.2	4.5
100	—	—	—	40	—	1.4	14.8	12.6	4.0	—
100	—	—	—	—	15	1.2	10.7	8.4	7.0	—

matic amine is usually higher than that of adhesives composed of aliphatic amines. Polyurethane oligomers and polyols could be considered as additives or toughened agents, and they reduce brittleness of epoxy resin. The results above explain that this kind of adhesive can be used as a structural adhesive.

Thermal degradation temperatures and glass transition temperatures of the materials consisting of epoxy resin and various decomposed products are shown in Figures 4 and 5. Except for materials made of decomposed product C, the thermal degradation temperatures and glass transition temperatures of the materials range from 342 to 362°C and from 62 to 80°C, respectively, and are basically similar to that of the material made up of epoxy resin and DETA. The material consisting of epoxy resin and decomposed product C has the highest thermal degradation temperature and glass transition temperature and is principally equal to that of material consisting of epoxy resin and MDA. It relates to the highest concentration of MDA in the obtained decomposed product as shown in Table IV.

CONCLUSION

Aliphatic amines can be employed to decompose rigid polyurethane and polyisocyanurate foams, and

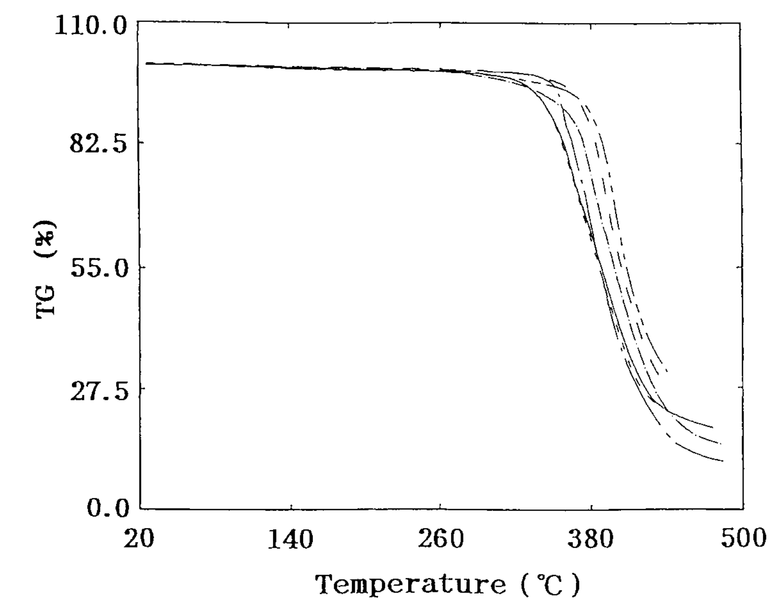


Figure 4 Thermogravity of materials consisting of epoxy resin and various decomposed products. Curing conditions of samples: 100°C × 3 h. Composition ratio (weight ratio) of materials and thermal degradation temperature: (– – —— –) MDA–epoxy resin = 20/100, 381°C, (— — —) decomposed product C–epoxy resin = 30/100, 373°C, (— • —) decomposed product D/epoxy resin = 40/100, 362°C, (——) DETA–epoxy resin = 15/100, 352°C, (------) decomposed product B–epoxy resin = 30/100 344°C, (———) decomposed product A–epoxy resin = 30/100, 342°C.

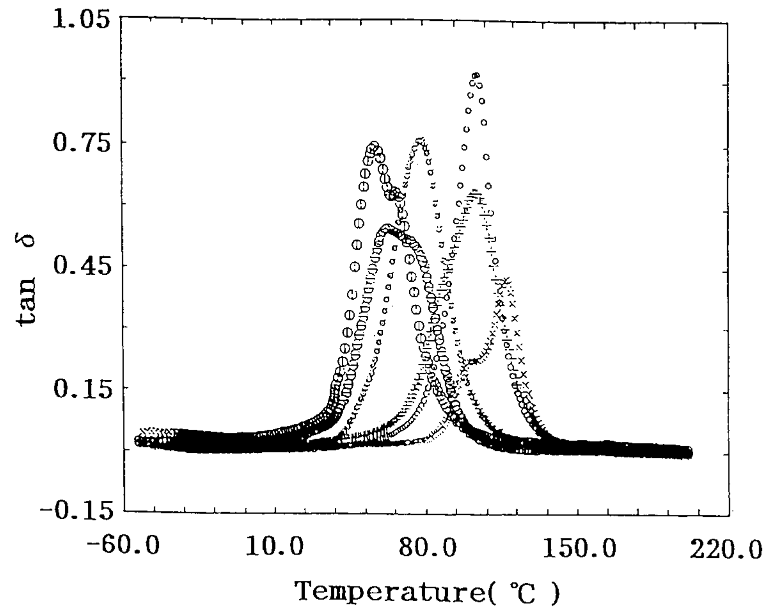


Figure 5 Glass transition temperatures of materials consisting of epoxy resin and various decomposed products. Curing conditions of samples: 100°C × 3 h. (×) DETA–epoxy resin (weight ratio) = 15/100, T_g = 113.6°C, (○) MDA–epoxy resin (weight ratio) = 20/100, T_g = 103.6°C, (+) decomposed product C–epoxy resin (weight ratio) = 30/100, T_g = 103.9°C, (ơ) decomposed product A–epoxy resin (weight ratio) = 30/100, T_g = 79.1°C, (⊖) decomposed product D–epoxy resin (weight ratio) = 40/100, T_g = 69.3°C, (⦶) decomposed product B–epoxy resin (weight ratio) = 30/100, T_g = 62.3°C.

the obtained decomposed products could be efficiently used as curing agents of epoxy resin. Using amines with lower molecular weight enhances decomposition reaction rate, increases total amine number, and reduces viscosities of the decomposed products. The viscosity of decomposed products could be lessened by increasing reaction temperature. But increasing foam–decomposer ratio enhances viscosity of decomposed products. The adhesives consisting of the decomposed products and epoxy resin can be cured over 60°C. The shear or bonding strength of the adhesives can apparently be improved by adding a silicone coupling agent. The adhesives have satisfactory shear strength of more than 15, 15, 7, and 3 MPa at 25, 60, 100 and 150°C, respectively, and excellent thermal degradation temperatures that are basically the same as conventional epoxy adhesives.

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