Thermal Properties of Epoxy Resin Cured with Imidazole

INTRODUCTION

Imidazoles are widely used as curing agents for epoxy resins. They provide good electrical and mechanical properties to cured resins.[1] Epoxy resins cured with imidazoles are used widely as sealing materials for semiconductor devices, printed circuit boards, or powder paints.[2]

The curing mechanism of epoxy resin with imidazole consists of two steps.[3] The first step is the substitution reaction of protone of the first position of imidazole to epoxide. The second step is the ring opening reaction of epoxide by the catalyst which was produced in the first step. Epoxy resins cured with imidazoles have ether-type bonds which adhere molecules to each other to form the macromolecule. The thermal properties of the cured resin, which have ether-type bonds, are somewhat different from the resin cured with curing agents other than imidazoles.

One of the most important characteristics of the resin cured with imidazoles is heat resistance. The resins cured with imidazole do not show a sharp fall of the modulus at about the glass transition temperature (T_g) compared to the resins cured with curing agents other than imidazole. T_g and heat deflection temperature (HDT) are the most widely used methods for determing the heat resistance of the cured resins.

The higher HDT of epoxy resins cured with imidazoles can be easily obtained with the addition of a large amount of filler. The curing mechanisms of epoxy resins with imidazoles have been described by many authors.[4-9] The increase in HDT of silica-filled epoxy resin-cured imidazoles is known.[10]

In this paper, we describe the thermal properties of epoxy resins cured with imidazole and compare them with epoxies cured with curing agents other than imidazoles.

EXPERIMENTAL

Materials

Diglycidyl ether of bisphenol A was used as epoxy resin. The epoxy resin used here is manufactured by Yuka Shell Epoxy Co., Ltd. (Tokyo) under the trade name Epikote #828. The equivalent weight of Epikote #828 was 187, and the viscosity was 12,500 centipoises at 25°C. Three kinds of curing agents, 2-ethyl-4-methylimidazole(2E4MZ) and benzyldimethyl-amine(BDMA) as catalytic curing agents, triethylenetetramine (TETA) as primary aliphatic amine, and methyltetrahydrophthalic anhydride(Me-THPA) as acid anhydride, were used for the experiments. From the maximum T_g for the resins cured with 2E4MZ, BDMA, or TETA, amounts were determined 3 phr (per hundred resin) for 2E4MZ or BDMA and 13 phr for TETA. Me-THPA was used near stoichiometric amounts in the presence of 2E4MZ as catalytic curing agents, 89.7 phr of Me-THPA and 0.2 phr of 2E4MZ were used.

A fused silica manufactured by Denki Kagaku Kogyo Co., Ltd. (Tokyo), under the trade name DF F-44, was used as filler and resulted in improvement of thermal properties of the cured resins. Chemical composition of the fused silica used here is: SiO_2; above 99.5%, Al_2O_3; under 2000 ppm, Fe_2O_3; under 1000 ppm.

The suitable amounts of epoxy resin, curing agent, and a fused silica were fully mixed by an agitator. The mixtures were cast between two glass plates with adhered cellophane and then were cured to form test pieces.

The curing in two steps was employed sequentially. Curing conditions were as follows: 1st cure; 75–120°C/2–6 h, 2nd cure; 150°C/2 h.

Apparatus and Procedure

HDTs of the cured resins were measured by using a Heat Deflection Tester 148-HDP (made by Yasuda Seiki Seisakusho Co., Osaka) according to ASTM D648-56. The size of a test piece was:

125 mm (length) × 6.4 mm (width) × 12.7 mm (thickness). A test piece was placed on the bridge which was set at the span of 100 mm in the silicon oil bath. Then, the weight of 1273 g was loaded on the test piece. The test piece immersed in the silicon oil bath was heated at the rate of 2°C/min. The bending lengths of a test piece were measured. HDT is defined as the temperature at which the bending length of a test piece has reached 0.26 mm. The ridigity and the loss modulus of the cured resins were measured by using a fully automated torsional pendulum-type viscoelastic tester RD-1100AD (made by Rhesca Co., Ltd., Tokyo) at the heating rate of 3°C/min in a vacuum over the temperature range of 25–250°C. The size of the test piece used for the measurement was 50 mm (length) × 1.7 mm (width) × 1.7 mm (thickness). T_g's of the cured resins were obtained from the peak of a loss modulus measured by RD-1100AD.

RESULTS AND DISCUSSION

Relationships between the Concentration of Silica and HDT or T_g

Fused silicas are used as fillers to improve physical properties, especially thermal properties of cured resins. Relationships between the concentration of a fused silica and T_g's or HDTs of cured resin with various curing agents are shown in Figures 1 and 2, respectively. T_g of the resin cured with 2E4MZ was superior to resins cured with curing agents other than 2E4MZ. Moreover, T_g values of the cured resins are not influenced by the amounts of fused silica. On the other hand, HDT values of the resin cured with 2E4MZ increases as the concentration of fused silica increases. HDT of the resin cured with BDMA decreases slightly as the concentration of fused silica increases and then increases. However, the T_g of resins cured with TETA or Me-THPA are not influenced by the amounts of fused silica used.

It is assumed that this peculiar phenomena for HDTs of the resin cured with 2E4MZ or BDMA depend on the structure of the cured resins.

Epoxy resins are converted by means of cross-link reactions into a three-dimensional network held together by covalent bonds.[11]

The catalytic curing agents 2E4MZ or BDMA serve as initiators for resin homopolymerization, whereas the polyfunctional curing agents as TETA or Me-THPA are used in stoichiometric amounts and function as comonomers or reactants in the polymerization of epoxy resin.

Epoxy resins cured with 2E4MZ or BDMA have ether-type bonds. HDTs of resins cured with 2E4MZ increase exceedingly as the concentration of fused silica increases, but changes of HDTs for resins cured BDMA is very small.
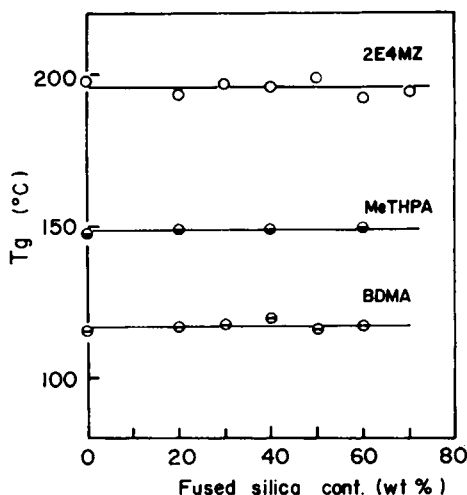

Fig. 1.   Relationship between the concentration of fused silica and T_gs of resin cured with various curing agents.
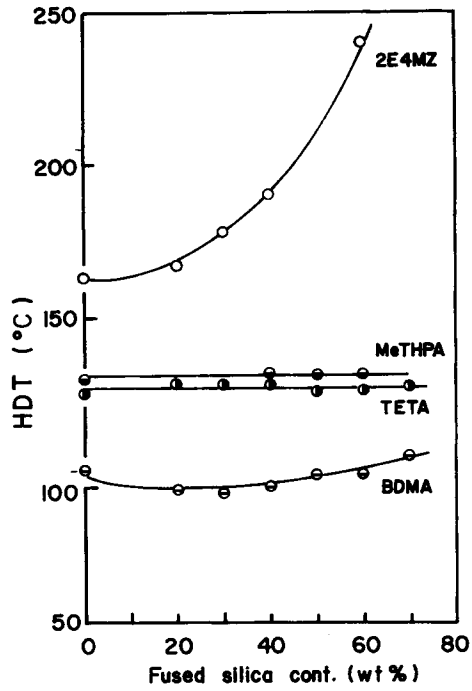
Fig. 2. Relationship between the concentration of fused silica and HDTs of resin cured with various curing agents.
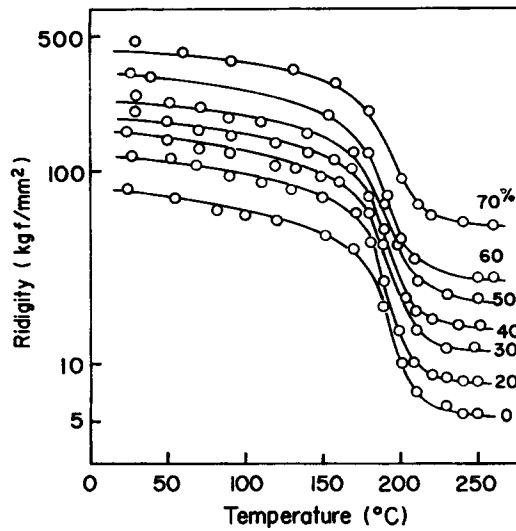

Fig. 3. Temperature dependence of rigidity for cured resin containing fused silica. Curing agent: 2E4MZ. Curing conditions: 75°C/2 h + 150°C/4 h.

Ridigity of Cured Resin

In order to confirm the increasing phenomenon in HDT, the rigidity of resins cured with various curing agents were measured. Plots of the rigidity obtained at various contents of fused silica against temperatures are shown in Figures 3 and 4. Percentage in figures refer to the concentration of fused silica in weigh percent of mixtures. Figures 3 and 4 show the rigidity of resins cured with 3 phr of 2E4MZ and BDMA, respectively. Moreover, the spectrum of resins cured with TETA or Me-THPA was omitted, because they showed nearly the same identical spectrum with Figure 4.

Figures 3 and 4 showed different spectra. The rigidity of the resin cured with 2E4MZ fell slightly at about T_g. On the other hand, the rigidity of the resins cured with BDMA fell sharply at about T_g.

HDT is defined as the temperature, at which the bending length (12.5 × 6.25 mm) of a test piece of the cured resin on the bridge, the span of which is 100 mm, has reached 0.26 mm when loaded with a weight of 1,273 g. The bending modulus (E) of the cured resin is expressed as follow:

$$E = \frac{L^3 \times F}{4 \times bd^3 \times \text{bending length}} \tag{1}$$

where L is the length of the span, and b and d are the height, and the width of a test piece, respectively. F is a loading weight. By bringing all variables other than E and the bending length in the formula (1) together into the constant K, the formula (1) becomes as follow:

$$\text{Bending length} = \frac{K}{E} \tag{2}$$

This means that the bending length is inversely proportional to the bending modulus. The bending modulus, when the bending length has reached 0.26 mm, was calculated at about kg/mm^2 by formula (1). Thus, the definition of HDT is the temperature, at which the bending modulus of a test piece has reached 100 kg/mm^2. On the other hand, T_g is defined as the
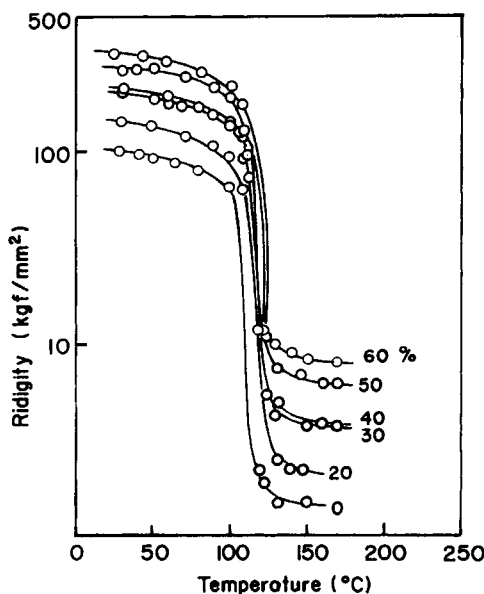

Fig. 4. Temperature dependence of rigidity for cured resin containing fused silica. Curing agent: BDMA. Curing conditions: 100°C/6 h + 150°C/4 h.
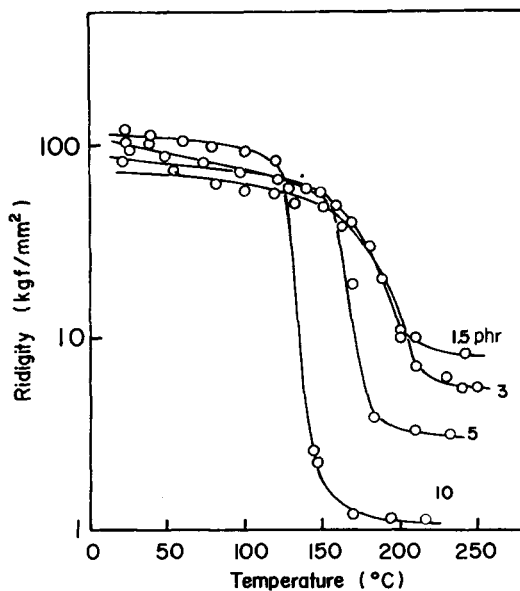
Fig. 5. Temperature dependence of rigidity for resin cured with various amounts of 2E4MZ. Curing conditions: 75°C/2 h + 150°C/4 h.
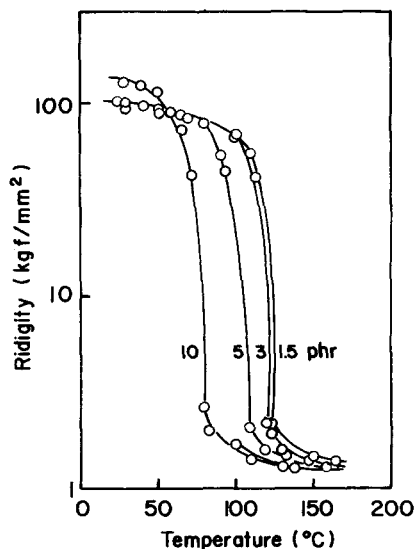

Fig. 6. Temperature dependence of rigidity for resin cured with various amounts of BDMA. Curing conditions: 100°C/6 h + 150°C/4 h.

temperature at which the bending modulus decreases sharply in relationship to temperature and bending modulus. The rigidity (G) related to the bending modulus (E) as follows:

$$E = 2G(1 + \nu) \tag{3}$$

where ν is Poisson's ratio.

Therefore, HDT is determined as the temperature, at which the rigidity of the cured resins reach about 38 kg/mm^2, because the Poisson's ratio for the cured epoxy resin is about 0.3.[12] In Figure 2, the temperature at which the rigidity reaches about 38 kg/mm^2 increases as the concentration of fused silica increases. The above phenomenon was not observed in Figure 3. The resins cured with BDMA also have ether-type bonds in their structure. However, different spectra were observed for the rigidity of cured resin which did not contain fused silica. Plots of the rigidity obtained at various amounts of 2E4MZ and BDMA against temperature are shown in Figures 5 and 6, respectively. Curves of the rigidity for the cured resin were divided clearly into three parts, namely a glassy plateau region, a glass transition region, and a rubbery plateau region. The rigidity in the rubbery plateau region for the resin cured with 2E4MZ increases as the amounts of 2E4MZ decreases and the resin cured with BDMA does not change.

The heights of rubbery plateau region are in proportion to the molecular weights between cross-link points (M_c). Therefore, it is assumed that M_c for the resin cured with 2E4MZ increases as amounts of 2E4MZ decrease, whereas that for the resin cured with BDMA does not change with varying amounts of BDMA.

We conclude from the results described above that the slow changes in rigidity for the silica-filled resins cured with 2E4MZ depend on the molecular weight between cross-link points in the same manner as the type of bonds in their cured structures.

CONCLUSIONS

HDTs, T_gs, and the rigidity of resins cured with various curing agents were measured. 2-Ethyl-4-methylimidazole (2E4MZ) and benzyldiamine (BDMA) as catalytic curing agents and triethylenetetramine (TETA) and methyltetrahydrophthalic anhydride (Me-THPA) as polyfunctional curing agents were used for the experiments.

HDTs of resin cured with 2E4MZ increase as amounts of fused silica increase, whereas resin cured with TETA or Me-THPA they do not change with amounts of fused silica. HDTs of resin cured with BDMA changed slightly with varying amounts of fused silica.

It is concluded that the increase in HDT of silica-filled resins cured with 2E4MZ depend on the slow change of the modulus at about T_g, because HDT is defined as the temperature at which the bending modulus has reached 100 kg/mm^2.

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MASAYUKI ITO
HAJIME HATA
KAZUO KAMAGATA

Research and Development Center,
Shikoku Chemicals Corp.,
25-1 Miyako, Namegawa, Hiki-gun
Saitama 355, Japan