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Influences of inorganic fillers on curing reactions of epoxy resins initiated with a boron trifluoride amine complex

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Abstract

Inorganic fillers are widely used for epoxy resins to improve mechanical and thermal properties. However, inorganic fillers may unexpectedly affect the curing reactions of such epoxy resins. In our present study, influences of inorganic fillers on the curing reactions of phenol novolac epoxy resin (EPN) initiated with boron trifluoride ethylamine complex (BF_3MEA) are detailed. The gel times of epoxy resins containing alumina (Al_2O_3) fillers were longer than those of corresponding unfilled epoxy resins, indicating that Al_2O_3 fillers delayed the curing reactions of epoxy resins. Mechanisms were proposed and influences of aluminum hydroxide ($Al(OH)_3$), silica (SiO_2), and aluminum fluoride (AlF_3) fillers were also described. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Epoxy resin; Curing reaction; Inorganic filler

1. Introduction

Epoxy resins are very convenient polymer materials because of their good mechanical, thermal, and electrical properties. Many kinds of epoxy resins are known, including bisphenol-A, bisphenol-F, aliphatic cyclic, and phenol novolac types. There are many systems for curing these epoxy resins, including amine-curing, anhydride-curing and phenol-curing systems. Latent catalysts are also known for a long shelf life of the epoxy resin systems and boron trifluoride ethylamine complex (BF_3MEA) is one of the best known latent catalysts [1,2]. The curing reaction scheme of epoxy resin initiated with BF_3MEA has already been clarified, as shown in Fig. 1 [2].

For industrial use, there are many cases in which inorganic fillers are added to epoxy resin system to ensure better mechanical and thermal properties. On the other hand, inorganic fillers may unexpectedly affect the curing reactions of such epoxy resin systems, for example, the gel times of epoxy resin are generally made longer by containing inorganic filler. However, there are few studies about the mechanism of the phenomena. In this paper, influences of inorganic fillers on curing reactions of phenol novolac epoxy resin (EPN) initiated with BF_3MEA are studied and the mechanisms by which the inorganic fillers make the gel times of epoxy resin longer are clarified.

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2. Experimental

2.1. Materials

Phenol novolac epoxy resin (Fig. 2), EPN (Yuka-Shell), was used. Boron trifluoride ethylamine complex, BF_3MEA (Hashimoto Chemical), was selected as a curing catalyst of the epoxy resin and used without further treatment. Nine kinds of alumina powders (Al_2O_3-a to i), including two spherical-type fillers, were used as fillers. Their shapes and average diameters are shown in Table 1. Aluminum hydroxide powder ($Al(OH)_3$, average diameter: 1.0 μm), crystalline silica powder (cryst-SiO_2, average diameter: 4.0 μm), fused silica powder (fused-SiO_2, average diameter: 7.5 μm), and aluminum fluoride powder (AlF_3, average diameter: 15 μm) were also used as fillers. All the fillers were used after drying for more than 12 h at 130°C.

2.2. Loss of ignition of alumina filler

Alumina fillers are prepared from aluminum hydroxide by condensation with dehydration at quite high temperature, however some groups usually remain in the fillers. The values of weight losses of the alumina fillers on heating at 1100°C for 1 h (loss of ignition (LOI)) can be used as the quantitative representatives of the amount of remaining Al-OH groups in corresponding alumina fillers. The LOI values of Al_2O_3-a to i were estimated, and are shown in Table 1.

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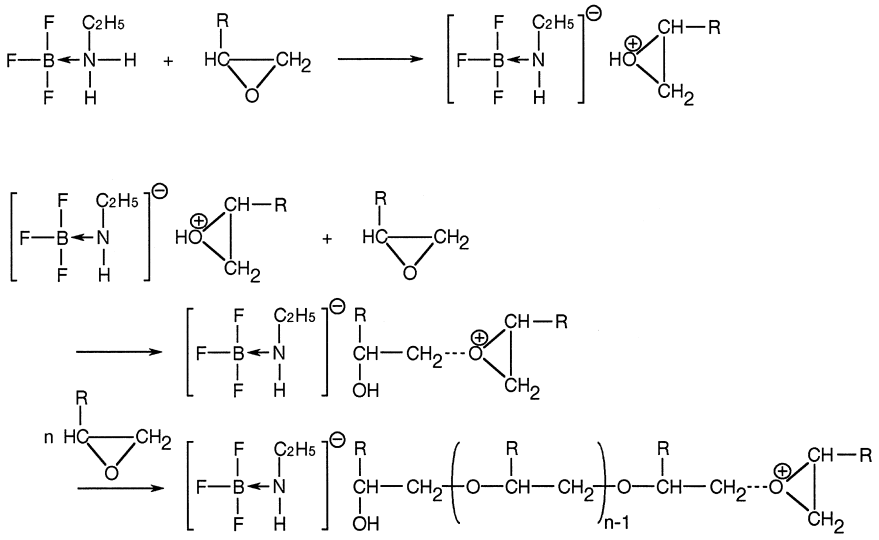

Fig. 1. Curing reaction scheme of epoxy resin initiated with boron trifluoride ethylamine complex.

2.3. Curing reactions and gel time measurement

Typically, a mixture of EPN (50 g) and BF_3MEA (0.5 g) was placed in a stainless steel beaker and heated to 100°C while being stirred mechanically. The temperature was kept at 100°C, dried Al_2O_3-a filler (35 g, 15 vol.%) was added to the beaker slowly for 20 min. Then, the mixture was stirred for another 20 min. It was poured into a glass test tube with a glass bar and cured in an oil bath attached to a gel timer, which make the glass bar turn round slowly and give the gel times as the times when the glass bar stop. In this paper, gel times were the average of two samples.

3. Results and discussion

3.1. Influences of alumina fillers on curing reactions of phenol novolac epoxy resin initiated with boron trifluoride ethylamine complex

Curing reactions of EPN initiated with boron trifluoride ethylamine complex (BF_3MEA) containing an alumina (Al_2O_3) filler were carried out by dipping the test tube filled with the mixture of EPN, BF_3MEA, and Al_2O_3-a filler into the oil bath whose temperature had already be stabilized. At that time, the gel times of the mixtures were also determined. For example, the curing reaction of the mixture of 100 weight parts of EPN and 1 weight part of BF_3MEA containing 15 vol.% Al_2O_3-a filler at 170°C proceeded rather slowly and the gel time was 21 min. In contrast, the curing reaction of the unfilled epoxy resin system under similar conditions proceeded very rapidly and the gel time was 3.4 min, which is approximately 6 times faster than that of the former epoxy resin system.

When the initial weight ratio of BF_3MEA with respect to EPN was increased, the curing reactions of the epoxy resin system proceeded more rapidly. As shown in Fig. 3, the gel times of Al_2O_3-a filled and unfilled epoxy resin systems were close to 4.5 and 2.5 min, respectively, at 170°C as the initial weight ratio of BF_3MEA increased. It was also observed that the presence of Al_2O_3-a filler delayed the curing reactions of the epoxy resin system. On the other hand, when the initial weight ratio of BF_3MEA with respect to EPN was decreased, the curing reactions of the epoxy

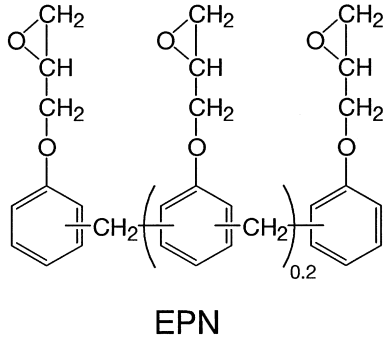

Fig. 2. Structure of phenol novolac epoxy resin (EPN).

Table 1
Shapes, average diameters and LOI values of alumina (Al_2O_3) fillers

Alumina filler	Shape	Average diameter (mm)	LOI[a] (%)
Al_2O_3-a	Random	1.0	0.215
Al_2O_3-b	Random	1.8	0.140
Al_2O_3-c	Random	2.2	0.195
Al_2O_3-d	Random	3.0	0.250
Al_2O_3-e	Random	3.2	0.125
Al_2O_3-f	Random	3.2	0.020
Al_2O_3-g	Random	4.0	0.105
Al_2O_3-h	Spherical	4.0	0.045
Al_2O_3-i	Spherical	10	0.040

[a] Weight loss on heating at 1100°C for 1 h.

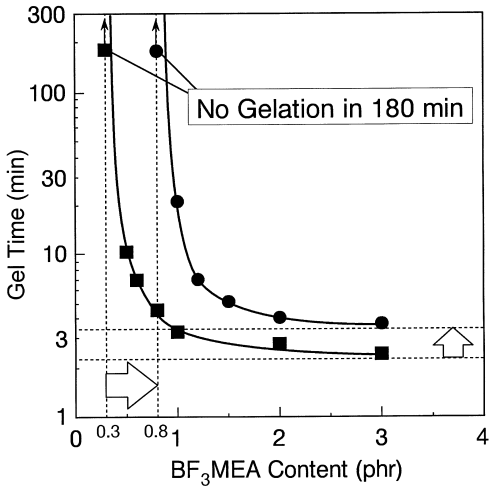

Fig. 3. Gel times of epoxy resin mixtures of phenol novolac epoxy resin (EPN) and boron trifluoride ethylamine complex (BF_3MEA) at 170°C. Effects of containing an alumina (Al_2O_3-a) filler or not (●: Al_2O_3-a filled system; ■: unfilled system). phr: weight parts per 100 weight parts of EPN.

resin system proceeded much more slowly. For example, the curing reaction of the Al_2O_3-a filled epoxy resin system in which BF_3MEA contained 0.8 weight parts per 100 weight parts of EPN proceeded quite slowly and the gelation of the epoxy resin system never occurred during 180 min at 170°C. Similarly, the curing reaction of the unfilled mixture in which BF_3MEA contained 0.3 weight parts per 100 weight parts of EPN proceeded quite slowly and that gelation never occurred either during 180 min at 170°C.

Interestingly, the shapes of the two curves of the Al_2O_3-a filled and unfilled epoxy resin systems in Fig. 3 were very similar to each other. By the addition of Al_2O_3-a filler, the curve of the unfilled epoxy resin system shifted to the directions of higher BF_3MEA content and longer gel time.

Some other alumina fillers (Al_2O_3-b to i) also delayed the curing reactions of epoxy resin system. Table 2 shows the gel times of the EPN/BF_3MEA (100/1, ratio of weight parts) system containing several alumina fillers (runs 1–9). These values were 4.4–21 min, and all were longer than the gel time of the corresponding unfilled epoxy resin system, 3.4 min (run 10).

Table 2
Gel times of EPN/BF_3MEA (100/1 (ratio of weight parts)) systems containing 15 vol.% alumina (Al_2O_3) fillers at 170°C

Run	Alumina filler	Gel time (min)
1	Al_2O_3-a	21
2	Al_2O_3-b	6.8
3	Al_2O_3-c	9.7
4	Al_2O_3-d	8.9
5	Al_2O_3-e	6.0
6	Al_2O_3-f	4.6
7	Al_2O_3-g	6.2
8	Al_2O_3-h	4.4
9	Al_2O_3-i	4.6
10	None[a]	3.4

[a] Without alumina filler.

3.2. Study of model curing systems for the influences of alumina filler on the curing reactions of epoxy resin

Al_2O_3 fillers delayed the curing reactions of epoxy resin system. There might be two possible mechanisms, which cause this phenomenon. One is the decrease of propagation reaction speed, and the other is inhibition of the propagation reaction, for example, the chain-transfer reaction. When the epoxy resin system contained 15 vol.% Al_2O_3 filler, the densities of EPN and BF_3MEA decreased to 85% with respect to the corresponding unfilled epoxy resin system. This might lead to the decrease of propagation reaction speed and make the gel time of epoxy resin longer. Because of Al-OH groups remaining in the Al_2O_3 filler, the chain-transfer reaction of growing cation with the Al-OH groups might also occur, as shown in Fig. 4. If the chain-transfer reaction occurred, the propagation reaction would be inhibited and the gel time of the epoxy resin system would become longer. Model systems were constructed to clarify if these two possible mechanisms were true or not.

First, the curing reactions of epoxy resin systems at lower temperature were tried to examine the model of the slow propagation reaction by decreasing the densities of EPN and BF_3MEA. Fig. 5 shows the gel times of the epoxy resin systems at 150 and 170°C. The gel times at 150°C were longer than those at 170°C. By decreasing the reaction temperature, the curve of the epoxy resin system shifted to the direction of longer gel time.

Next, the reactions of epoxy resin containing only 0.75 vol.% of $Al(OH)_3$ filler were tried to examine the model of chain transfer reaction by Al-OH groups remaining in the Al_2O_3 filler. There were also Al-OH groups in the mixture, but they had less influence on the densities of EPN and BF_3MEA. Fig. 6 shows the gel times of the 0.75 vol.% $Al(OH)_3$ filled and unfilled epoxy resin systems at 170°C. The gel times of the $Al(OH)_3$ filled epoxy resin were longer than those of corresponding unfilled epoxy resin systems, especially at low BF_3MEA content. By adding a small amount of $Al(OH)_3$ filler, the curve of the epoxy resin system shifted to the direction of higher BF_3MEA content.

Because shifts to both directions of higher BF_3MEA content and longer gel time were observed in Fig. 3, the influences of Al_2O_3 filler were thought to be from both the decrease of propagation reaction speed and inhibition of the propagation reaction by the chain-transfer reaction as described above. In this case, the propagation reaction speed should be the same in all cases of 15 vol.% Al_2O_3 filled systems and the chain-transfer reaction would occur more easily by using Al_2O_3 filler with high LOI value which had more Al-OH groups remaining. Fig. 7 shows the relationship between the gel time of EPN/BF_3MEA (100/1, ratio of weight parts) system containing 15 vol.% Al_2O_3 filler at 170°C and the LOI value of the corresponding Al_2O_3 filler.

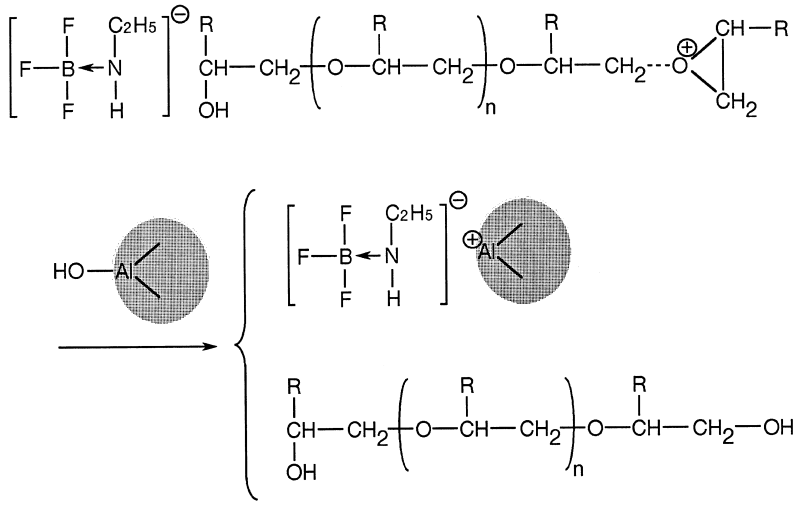

Fig. 4. Scheme of possible chain-transfer reaction of growing species with Al-OH groups remaining in the alumina filler.

As expected, the gel time was longer if the LOI value was higher. The expected gel times of this system which give the curve in Fig. 7 were estimated by following assumption. From the result of Fig. 3, the shift amount of the curve to the direction of higher BF_3MEA content was approximately 0.5 phr, when the 15 vol.% Al_2O_3-a filler (LOI: 0.215 %) was used. Assuming that the shift amount was in proportion to the LOI value of the corresponding Al_2O_3 filler, the expected gel time of the 15 vol.% Al_2O_3 (LOI: *L*%) filled system with 1 phr of BF_3MEA was equal to the gel time of the 15 vol.% Al_2O_3-a filled system with *C* phr of BF_3MEA given by following equation:

$$C = 1 + 0.5\{(0.215 - L)/0.215\}$$

All gel times estimated were very close to the curve in Fig. 7, which supported both proposed mechanisms.

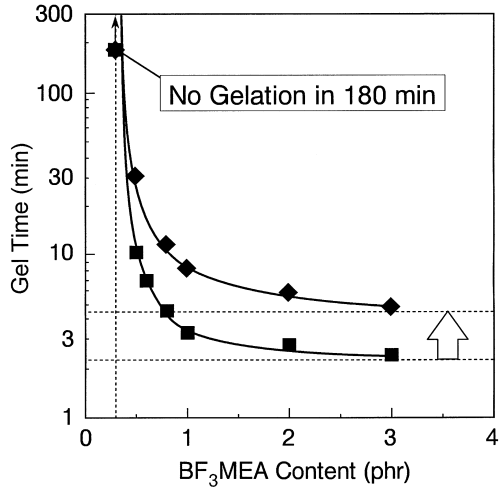

Fig. 5. Gel times of epoxy resin mixtures of phenol novolac epoxy resin (EPN) and boron trifluoride ethylamine complex (BF_3MEA). Effects of reaction temperature (◆: 150°C, ■: 170°C). phr: weight parts per 100 weight parts of EPN.

3.3. Influences of inorganic fillers on curing reactions of phenol novolac epoxy resin initiated with boron trifluoride ethylamine complex

Inorganic fillers besides alumina filler also delayed the curing reaction under similar conditions. The gel times of EPN/BF_3MEA (100/1, ratio of weight parts) system containing 15 vol.% crystalline silica (cryst-SiO_2) filler and fused silica (fused-SiO_2) filler were 4.4 and 4.6 min, respectively, at 170°C. These were longer than that of the corresponding epoxy resin system, but close to the value of the shortest gel time in the Al_2O_3 systems. The result indicated that the chain-transfer reaction occurred quite slowly with the Si-OH groups which generally remain in the SiO_2 filler. The gel time of EPN/BF_3MEA (100/1, ratio of weight parts) system

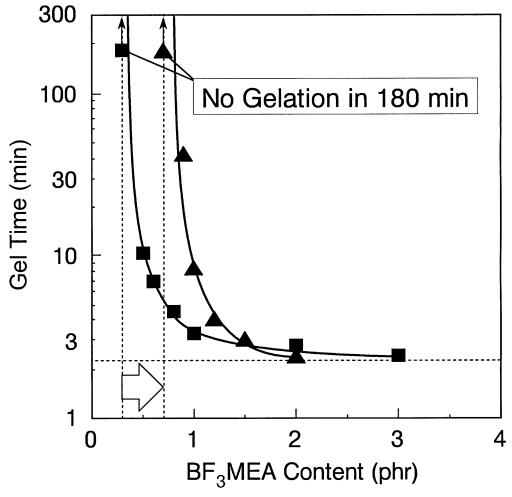

Fig. 6. Gel times of epoxy resin mixtures of phenol novolac epoxy resin (EPN) and boron trifluoride ethylamine complex (BF_3MEA) at 170°C. Effects of aluminum hydroxide ($Al(OH)_3$) filler (▲: $Al(OH)_3$ filled system, ■: unfilled system). phr: weight parts per 100 weight parts of EPN.

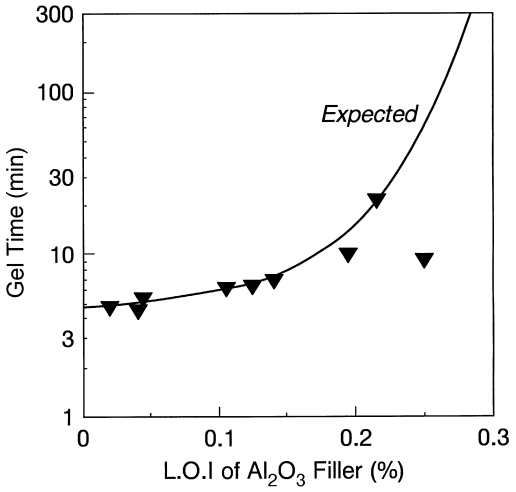

Fig. 7. Gel times of epoxy resin mixtures of phenol novolac epoxy resin (EPN) and boron trifluoride ethylamine complex (BF_3MEA) at 170°C. Effects of LOI of alumina filler. EPN/BF_3MEA: 100/1, ratio of weight parts. LOI: weight loss on heating at 1100°C for 1 h.

containing 15 vol.% aluminum fluoride (AlF_3) filler was 8.3 min at 170°C, indicating that the chain-transfer reaction also occurred. The chain-transfer reaction might occur with Al-OH groups which remain in AlF_3 filler because AlF_3 is from aluminum hydroxide and hydrogen fluoride by condensation with dehydration.

4. Conclusions

Influences of inorganic fillers on curing reactions of EPN initiated with boron trifluoride ethylamine complex (BF_3MEA) were clarified. Alumina fillers increased the gel time of the EPN/BF_3MEA system, indicating that the fillers delayed the curing reactions. Model studies led to two mechanisms: (1) that the propagation reaction of epoxy resin became slower by decreasing the densities of EPN and BF_3MEA; and (2) that the chain-transfer reaction of growing species occurred with Al-OH groups remaining in alumina filler. Aluminum hydroxide, silica and aluminum fluoride fillers also delayed the curing reactions of epoxy resin systems.

References

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