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The effect of amine/epoxy ratio on the fracture toughness of tetrafunctional epoxy resin

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Summary

The effect of amine/epoxy ratio on the fracture toughness(K_{Ic}) of tetrafunctional epoxy resin was investigated. K_{Ic} value was measured by single-edge notch-bend test. The K_{Ic} value of the tetrafunctional epoxy resin increased with increasing the amount of amine curing agent. This result was explained with the structural viewpoint of the epoxy network. The network structure of the tetrafunctional epoxy was analyzed with dynamic thermomechanical measurement and *in-situ* near IR technique.

Introduction

Epoxy resin is a thermoset material used in various industrial fields such as adhesive, matrix for composites, electrical materials, protective coating materials and so on. This is attributed to the fact that epoxy resin has many advantages over common thermoset like high mechanical properites, high electrical properties and good processibility and such properties are easily controlled by changing the formulation(1-5).

It is well known that the network structure of thermoset resin is closely related to the mechanical properties such as modulus and fracture toughness and so on. Among the properties of tetrafunctional epoxy resin, its brittleness is thought to be closely related to the network structure like crosslinking density(6). This brittle characteristic has limited the application fields of tetrafunctional epoxy resin. In general, the increase of crosslinking density of epoxy resin induces the decrease of fracture toughness. However, it is not simple especially in case of tetrafunctional epoxy resin whether the increase of amine/epoxy ratio directly leads to the decrease of fracture toughness or not. Although the network structure of epoxy resin depends on such factors as amine/epoxy ratio, curing cycle, and functionality of epoxy, the amine/epoxy ratio is the most important factor in determining the network structure of epoxy resin. Especially, the tetrafunctional epoxy resin forms very complicated network structure with changing the amine/epoxy ratio because tetrafunctional epoxy resin undergoes very complicated cure reactions.

In this study, it was our primary objective to investigate the effect of amine/epoxy ratio on the fracture toughness of tetrafunctional epoxy resin. The characterization of network structure of tetrafunctional epoxy resin with different amount of amine curing agent was tried by dynamic mechanical thermal analyzer(DMTA) and *in-situ* near IR technique.

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Experimental

Materials

N,N,N',N'-tetraglycidyl-α,α'-bis-(4-aminophenyl)-p-diisopropylbenzene (abbreviated as TGBAP) and α,α'-bis-(4-aminophenyl)-p-diisopropylbenzene (abbreviated as BAP) were used as an epoxy resin and a curing agent, respectively. These materials were supplied by Shell Chemical Company and used as supplied without further purification. The chemical structures of TGBAP and BAP were illustrated in Fig. 1. The physical properties of these materials were represented in previous paper(7).

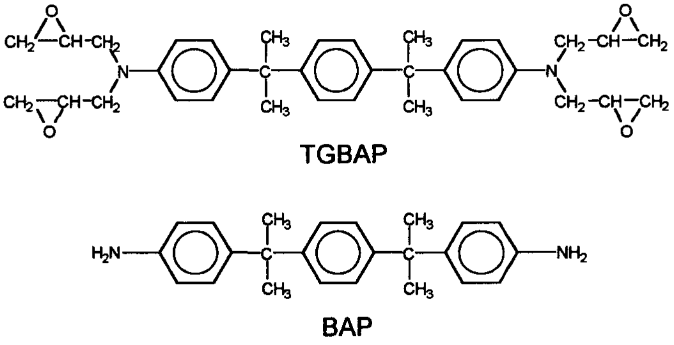


Fig. 1 Chemical structures of TGBAP and BAP

Sample casting

The tetrafunctional epoxy resin systems were made by melt casting. The amount of curing agent was varied as 20, 30, 40, 50, 60, and 70 phr. Each molten mixture was cast and cured for 2 hrs at 180℃ and for 4 hrs at 200℃, consecutively.

Measurements

The dynamic mechanical properties of cured epoxies were determined by DMTA (Rheometrics Scientific Co. MKIII). The dynamic mechanical thermal analysis was performed by bending mode with 1 Hz frequency and the heating rate was 3℃/min.

Fracture properties of the cured epoxy specimens were measured by single-edge notch-bend(SENB) test using an universal testing machine model Instron 4201 according to ASTM E399. The dimension of SENB specimen used in this study was 5x10x45 mm. This bar was notched with a 250 μm radius notching cutter followed by liquid nitrogen cooled razor blade tapping to introduce a sharp crack. The test was carried out at room temperature and crosshead speed was 10 mm/min. 5 specimens were tested in this study.

In-situ near IR analysis was performed by Bomem DA-8 equipped with liquid nitrogen cooled InSb detector. The spectrum was obtained by transmittance technique with resolution of 4 cm^{-1} and 10 coaddition. Each spectrum was collected at 180 °C in every 2 min.

Results and discussion

The fracture toughness (K_{Ic}) of the tetrafuctional epoxy resin with different amount of BAP was given in Fig. 2. K_{Ic} value was calculated according to the method represented in previous paper(8).

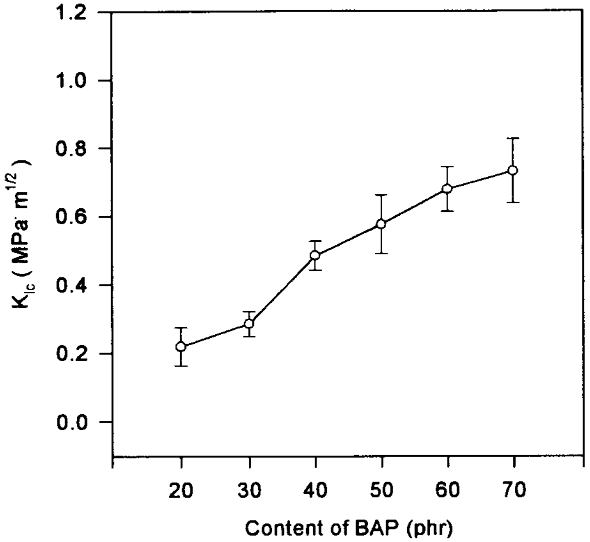


Fig. 2 Fracture Toughness of tetrafunctional epoxy resin as a function of the content of BAP

It was observed that K_{Ic} values of the tetrafunctional epoxy resins increased with increasing the amount of BAP.

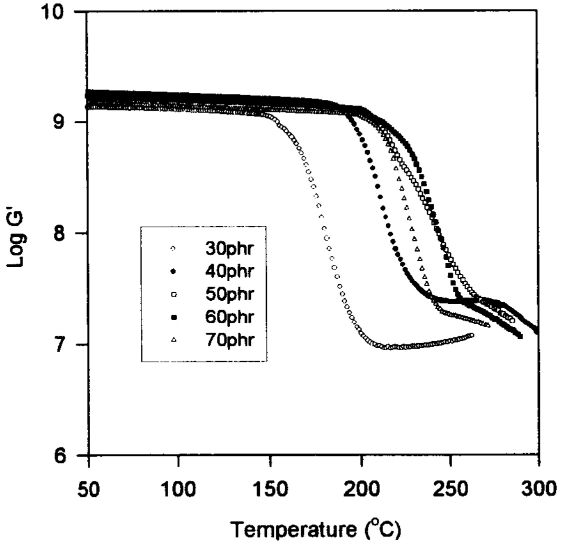


Fig. 3 Dynamic storage modulus(G') of tetrafunctional epoxy resin with increasing the content of curing agent

This result is interesting in fact that the increase of the amount of curing agent does not simply induce the decrease of fracture toughness of the tetrafunctional epoxy resin. In order to explain this result, it is necessary to analyze the K_{Ic} values with the structural veiwpoint of epoxy network. The structural analysis of the tetrafunctional epoxy resin was performed by DMTA.

Fig. 3 and 4 show dynamic mechanical properties of the tetrafunctional epoxy resin with different amount of BAP. In case of 20 phr, the specimen was too brittle to endure the dynamic mechanical measurement.

As represented in Fig. 3, rubbery plateau was observed only at 30 and 40 phr cases but it was not clearly detected in other cases. This rubbery plateau was thought to be appeared due to the conflicting phenomena such as the increase of stroage modulus by progress of unfinished cure reaction and decrease by temperature effect. This implies that the curing of 30 and 40 phr cases were not completely finished. The uncomplete cure reaction of above two cases was confirmed by DSC measurement(99.8 J/g for 30 phr, 45.3 J/g for 40 phr).

Especially, 50 phr system showed different feature compared with the other cases. It showed obvious shoulder in storage modulus curve and different slope. This shoulder was also observed in bending tanδ curve(Fig. 4).

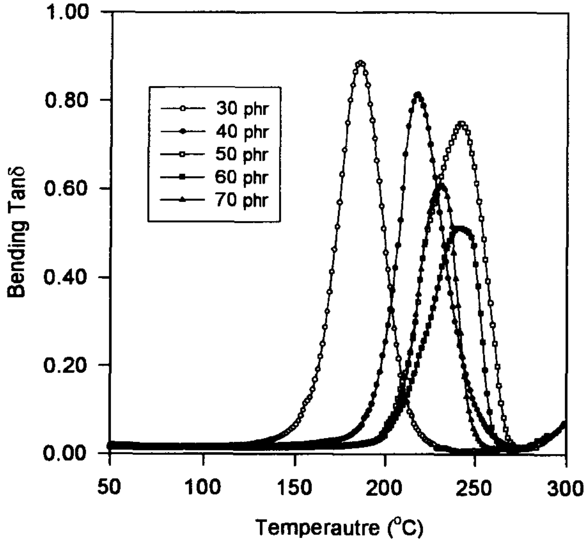


Fig. 4 Damping of tetrafunctional epoxy resin with increasing the content of curing agent

The glass transition temperature (T_g) and width at half height for each epoxy system determined by tanδ peak displayed in Fig. 4 were summarized in Table I. From the Table I, T_g value of epoxy resin shows its maximum at 50 phr case. When the amount of BAP more than 50 phr was included, the T_g value of epoxy resin decreased. This fact implies that the stoichiometric value of amine to epoxy ratio exists between 50 and 60 phr cases. In TGBAP/BAP system, calculated stoichiometric amount of BAP was located between 50.6 and 57.3 phr.

What is worthwhile to note is that the width at half height broadens as the amount of BAP increases up to 50 phr. The increase of the width at half height means the range of temperature at which the different network segment gains mobility increases. This broadening resulted from the heterogeneous network structure due to the various kinds of reaction occurred in epoxy curing.

Table 1. Thermomechanical properties of tetrafunctional epoxy resin as a function of curing agent content.

Sample codes	T_g (°C)	Width at half height (°C)
30	185.6	28.4
40	218.0	29.3
50	241.2	38.5
60	240.9	32.2
70	230.1	24.6

Considering the Table I, 50 phr case has the most heterogenous network structure in TGBAP/BAP system. To explain this result, the curing reactions of 30, 50 and 70 phr cases were investigated by *in-situ* near IR.

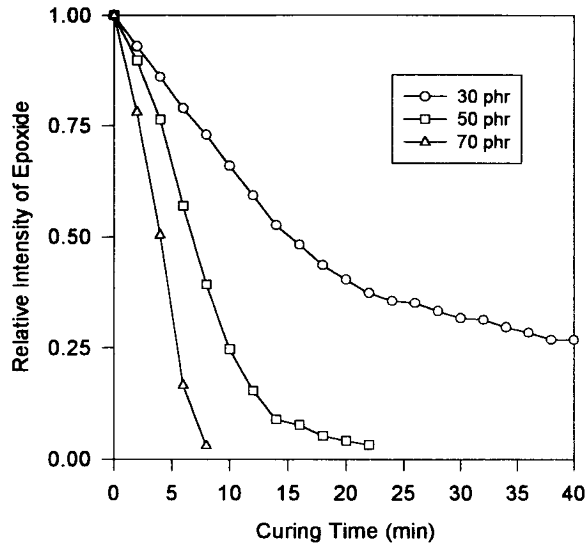
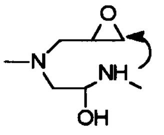


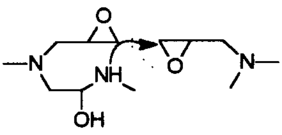
Fig. 5 The relative intensity of epoxide group as a function of curing time (cured at 180 °C)

The integrated intensities of epoxide and amine functional groups of each case as a function of curing time were given in Fig. 5 and Fig. 6, respectively. The band at 6046 cm^{-1} assigned to epoxide overtone and the band at 6663~6560 cm^{-1} due to NH_2 and NH overtone were used in this study.

From Fig. 5, when curing time was 8 min, the degree of conversion of 50 phr was two times larger than that of 30 phr. This means that chain mobility of 50 phr case was less than that of 30 phr. However, in Fig. 6, NH group of 50 phr case began to reduce after 8 min and it disappeared faster than 30 phr case. In TGBAP/BAP system, there are two kinds of reaction related to NH group.



intramolecular



intermolecular

Intramolecular reaction is kinetically favored when the chain mobility is reduced by the formation of rigid network. It was reported that when the diglycidylamine based epoxy, as a model compound of tetrafunctional epoxy resin, was cured with amine, cyclization reaction occurred most easily in stoichiometric case(9). Considering this fact, it could be known that intramolecular reaction of 2° amine with epoxide occured more easily in 50 phr case than 30 phr case. The ring structure formed by intramolecular cyclization induces the reduction of crosslinking density. The reduction of crosslinking density generally brings about the increase of K_{Ic} value of the epoxy resin.

The T_g of 50 phr case showed high value, in spite of the reduction of crosslinking density. This is attributed to the fact that although crosslinking density decreased due to the formation of ring structure, most of functional groups were consumed so only few unreacted functional groups were left in this case. This fact was also confirmed by Fig. 5 and 6. They show most of functional group was consumed in 50 phr case.

When BAP was 70 phr, most of epoxide group disappeared after 10 min. In this case, 1° amine group was completely consumed, but large amount of 2° amine group remained. This means that in case of 70 phr, most of network structure was developed through the reaction of 1° amine and epoxide groups and with this reason the width at half height of BAP 70 phr case become narrow. Therefore, $\overline{M}_c$ of this case must be large because NH linkage was left unreacted in network. As a result, K_{Ic} value of 70 phr case is greater than the other cases. However, comparing the T_gs of 70 and 50 phr case, it was expected that the mechanical properties of 70 phr case were not so good as those of 50 phr case.

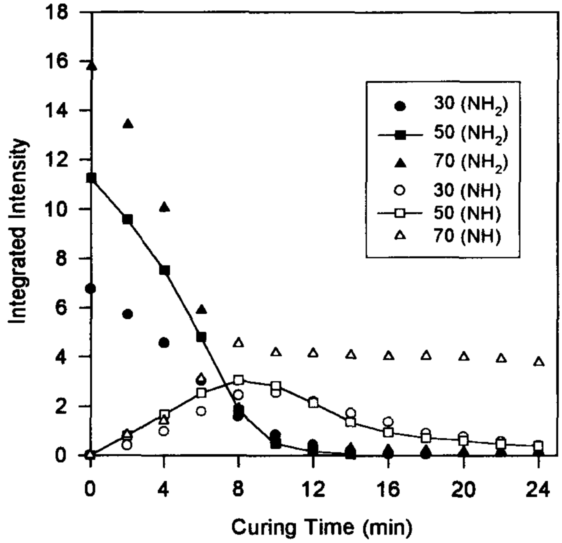


Fig. 6 The integrated intensity of amine group as a function of curing time (cured at 180 °C)

When the epoxy was cured with less than equivalent value, it was observed that large amount of epoxide group remained until 1° and 2° amine groups disappeared completely. This unreacted epoxide group was expected to be consumed by hydroxyl group formed by curing reaction. However, as previously metioned, 30 and 40 phr cases undergo incomplete cure reaction, so a lot of unreacted epoxide group remained in network structure. This unreacted epoxide group induces the nonuniform stress distribution, consequently microscopic stress concentration. Therefore, the breakage of chain around unreacted epoxide easily happened due to this stress concentration. In addition, this broken chain bring about an additional stress concentration, as a result, K_{Ic} value decreased. This stress concentration will be much alleviated as the amine/epoxy ratio approaches to stoichiometric value and the K_{Ic} value simply increases.

Conclusion

The K_{Ic} value of tetrafunctional epoxy resin increased with increasing the amount of curing agent. In this study, the stress concentration effect due to unreacted epoxide group and the decrease of crosslinking density through intramolecular cyclization and unreacted 2° amine group were considered as important factors affecting the K_{Ic} value of tetrafunctional epoxy resin. The T_g of the tetrafunctional epoxy resin increased as the amount of curing agent approached to 50 phr and then decreased. The decrease of T_g in excessive curing agent case was ascribed to the fact that most of NH lingkage was left unreacted in network structure, consequently crosslinking density was reduced. When the amount of curing agent was 50 phr, tetrafunctional epoxy resin showed the most complicated network structure due to the easiness of intramolecular cyclization. Considering the K_{Ic} and T_g value, 50 phr was the best formulation in this study.

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