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NETWORK STRUCTURE AND GLASS TRANSITION OF EPOXY RESINS CURED WITH ACTIVE ESTER

S. Nakamura and M. Arima

DEPARTMENT OF APPLIED CHEMISTRY, FACULTY OF ENGINEERING, KANAGAWA UNIVERSITY, KANAGAWA-KU, YOKOHAMA 221, JAPAN

The effect of network structure on the glass transition temperature (T_g) was examined by differential scanning calorimetry, thermomechanical analysis and dynamic thermomechanometry for epoxy resins cured with mixtures of curing agents consisting of an active ester, 1,3,5-triacetoxybenzene (TAB), and a polyfunctional phenol, 1,3,5-trihydroxybenzene (THB). Free hydroxyl groups are formed from THB after curing, whereas acetyl groups are left from TAB. The T_g value of cured epoxy resins decreased with increasing TAB content in the curing agent, which is attributed to the looser network structure induced by the steric hindrance of acetyl groups from TAB in the curing reaction and also to the weaker intermolecular interaction and the internal plasticization of acetyl groups from TAB.

Keywords: epoxy resins, glass transition, network structure

Introduction

Polyfunctional active esters such as aryl and thioaryl esters of carboxylic acids are effective for epoxy curing, and not hydroxyl but ester groups are left in the cured resins [1]. The glass transition temperature (T_g) of the epoxy resins cured with active esters are lower than those cured with conventional curing agents [2].

We intended to examine the effect of network structure on the T_g of epoxy resin cured with an active ester, 1,3,5-triacetoxybenzene (TAB) by differential scanning calorimetry, thermomechanical analysis and dynamic thermomechanometry in comparison with that cured with a polyfunctional phenol, 1,3,5-trihydroxybenzene (THB), which is assumed to have similar crosslink structure but has free hydroxyl groups after curing.

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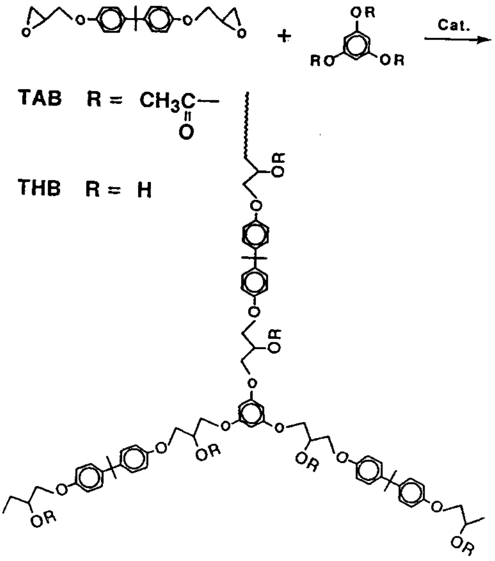
Experimental

Bisphenol A diglycidyl ether was cured with THB/TAB mixtures using tetrabutylphosphonium bromide as catalyst at 150°C for 3 h and then at 170°C for 2 h.

Free hydroxyl groups are formed from THB, whereas acetyl groups are left from TAB after curing as seen in Scheme 1.



T_g was determined at 5 deg·min^{-1} with Perkin-Elmer DSC System 4. Linear thermal expansion coefficient was obtained at 2 deg·min^{-1} with Seiko TMA/SS. Dynamic mechanical properties was measured at 2 deg·min^{-1} with Rheovibron DDV-II at 11 Hz and Seiko DMS 200 at 0.5 Hz.

Results and discussion

The α and the β' dispersions were observed in the dynamic mechanical curves of cured resins at 11 Hz (Fig. 1). The storage modulus (E') at the glass transition region and also the dispersion peak temperature ($T\alpha$) of tan δ shift to higher temperature with increasing THB content in the curing mixture.

Various parameters were calculated from the dynamic mechanical data using the equation of state for rubber elasticity [3].

$$E' = 3\Phi\rho RT \tag{1}$$

$$\overline{M}_c = d/\rho \tag{2}$$

$$\Phi = \overline{M}_c\,(\text{calcd.}) / \overline{M}_c(E') \tag{3}$$

where Φ is the front factor, ρ the crosslink density, R the gas constant, d the density at T_α + 40°C and $\overline{M}_c$ the number-average molecular weight between cross-

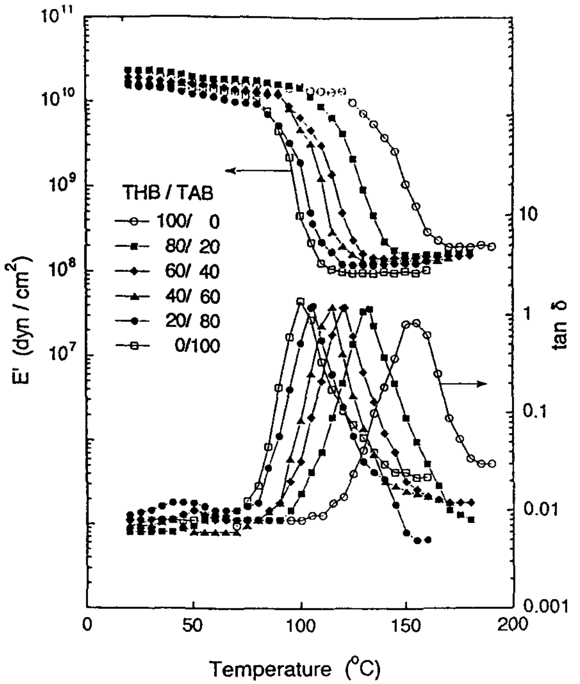


Fig.1 Dynamic mechanical curves of epoxy resins cured with various ratios of curing agents, THB/TAB (11 Hz)

The results of calculation are tabulated in Table 1 together with the results of dynamic mechanical measurements. The values of T_α, d, E', ρ and Φ decrease and M_c increases monotonically with the decrease in the ratio THB/TAB, which reflects the difference of network structure. Namely, the network structure is remarkably affected by the ratio of hydroxyl and acetyl groups in the cured resin.

The lowering of d with increasing TAB content indicates that the packing of molecular chain becomes looser. The decrease in E' with increasing TAB content is attributed to the decrease of hydrogen bonding and the internal plasticization due to acetyl groups.

Table 1 Dynamic mechanical properties of cured resins

THB/TAB (molar ratio)	0/100	20/80	40/60	60/40	80/20	100/0
T_α/°C	101	106	114	121	133	153
d(20°C)/g·cm^{-3}	1.20	1.21	1.22	1.22	1.23	1.23
E'(20°C)/ 10^{10}dyn·cm^{-2})	1.51	1.56	1.81	1.92	2.33	2.36
E'(T_α+40°C) / 10^{-8}dyn·cm^{-2}	1.04	1.30	1.41	1.54	1.70	2.05
ρ/ mol·dm^3	1.01	1.24	1.32	1.42	1.53	1.76
$\overline{M}_c$/g·mol^{-1}	1132	923	873	812	756	657
Φ	0.48	0.57	0.59	0.61	0.63	0.70

1 dyn·cm^{-2} = 0.1 Pa

The T_g values obtained by DSC and TMA and the T_α values obtained by dynamic mechanical measurements increase monotonically with increasing hydroxyl content in the cured resin (Fig.2).

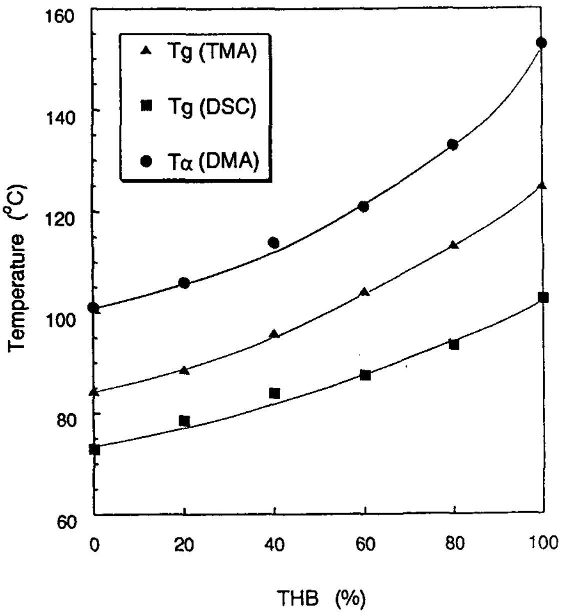


Fig.2 T_g and T_α of cured resins *vs*. THB% in the curing agent

In the course of curing, the hydroxyl groups from THB induces aggregation of resulting crosslinked resins, whereas the aggregation was disturbed by the steric hindrance of acetyl groups from TAB. Consequently, the network structure becomes looser with increasing TAB in the curing mixture, resulting in the decrease in *d* an ρ.

As the hydroxyl content decreases, molecular interaction becomes weaker due to the decrease in hydrogen bonding and the internal plasticization of acetyl groups, and the molecular chain between crosslinks becomes more mobile. This weaker interaction is also proved by the decrease in *E*'.

These two effects are responsible for the lowering of T_g.

The linear thermal expansion coefficient above T_g was not so much affected by the network structure, whereas that below T_g decreased with increasing THB content, which supports the stronger intermolecular interaction due to hydroxyl groups from THB (Fig. 3).

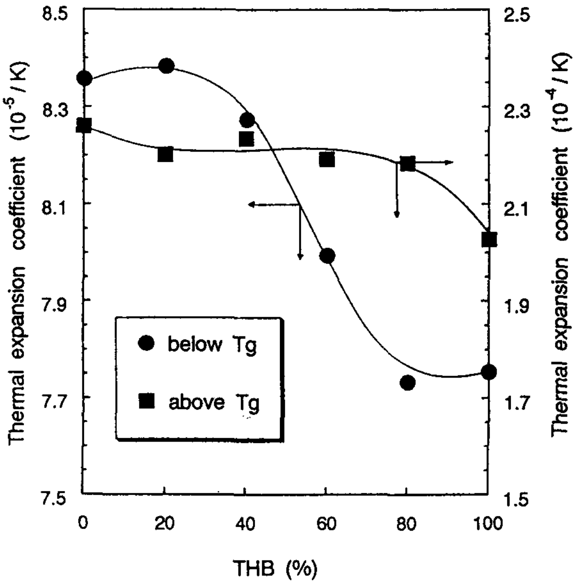


Fig. 3 Thermal expansion coefficient of cured resins *vs.* THB% in the curing agent

In the dynamic mechanical curve obtained at 0.5 Hz, a broad dispersion was observed at –50°C for THB-cured resin, which is attributed to the overlapping of the relaxation of hydroxy ether segments and that of other parts in the polymer chain [4]. Two peaks (–80°C and 15°C) and a shoulder (–30°C) appeared for TAB-cured resin (Fig. 4). The appearance of a peak at 15°C is explained by the shift of the relaxation of hydroxy ether segments to higher temperature because the mobility of hydroxy ether segments is decreased by the acetylation of hydroxyl groups [4].

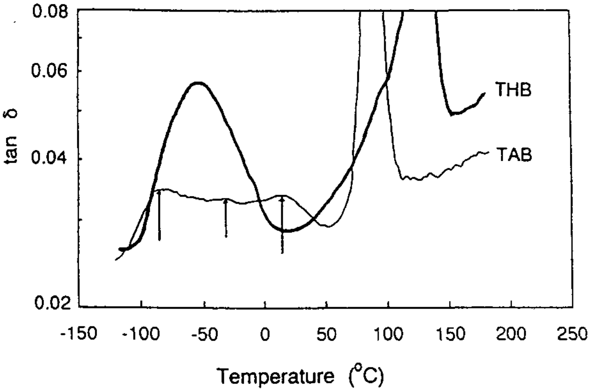


Fig. 4 Dynamic mechanical curves of epoxy resins cured with TAB and THB (0.5 Hz)

Conclusion

The T_g of epoxy resins decreases with decreasing ratio of THB/TAB in the curing mixture. The lowering of T_g is attributed to the following two effects.

1) The hydroxyl groups from THB induces aggregation of resulting crosslinked resins, whereas the aggregation was disturbed due to the steric hindrance of acetyl groups from TAB. Therefore, the network structure becomes looser with increasing TAB, and the decrease in *d* and ρ is resulted.

2) The intermolecular interaction becomes weaker by substituting hydroxyl groups with acetyl groups. Furthermore, acetyl groups result in internal plasticization. These effects decrease the *E*' value.

References

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Zusammenfassung — Mittels eines simultanen TG-DTA/FT-IR Systemes wurde ein Versuch zur Abschätzung des Mechanismus der thermischen Zersetzung von Polymeren unternommen und beschrieben. Zur Bestimmung des Types flüchtiger Substanzen, die in bestimmten Stadien der Zersetzung aus Poly(ethylen-terephthalat) und Poly(butylen-terephthalat) entstehen, wurden die FT-IR-Spektren bei verschiedenen Temperaturen und die Differenzspektren aus Subtraktion der Spektren bei verschiedenen Temperaturen in einem Spektrenverzeichnis gesucht. Die quantitative Analyse der freigesetzten Gase wurde unter Verwendung der spezifischen Gasprofile an den spezifischen Absorptionsbanden durchgeführt. Die kinetischen Parameter wurden anhand der TG- und der spektroskopischen Kurven für verschiedene Temperaturen geschätzt.