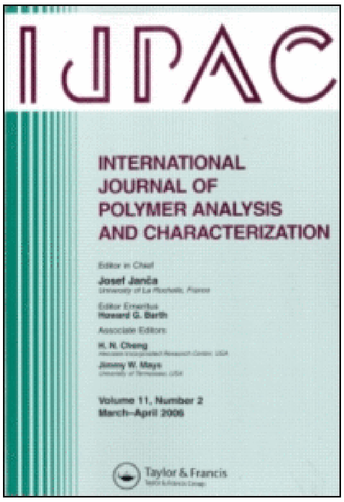

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Characterization of the Network Structure o Epoxy Resins Cured with Active Esters

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Characterization of the Network Structure of Epoxy Resins Cured with Active Esters

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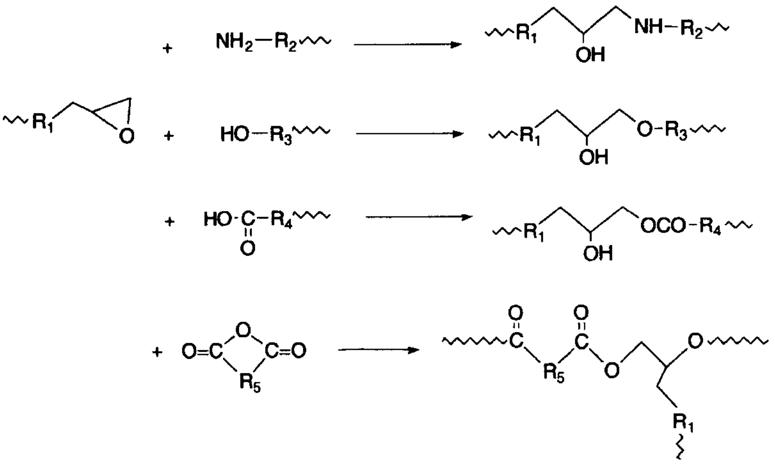
Epoxy resins cured with polyfunctional active esters have no pendant hydroxyl groups but pendant ester groups. Epoxy resins without hydroxyl groups are expected to have high electric resistance, low dielectric constant, and low hygroscopicity. In this paper, the thermal, viscoelastic, dielectric, and hygroscopic properties are described on the epoxy resins cured with active esters in comparison with those of the resins with pendant hydroxyl groups that are cured with conventional curing agents. The network structure of epoxy resins with pendant ester groups is much looser than that of the resins with pendant hydroxyl groups. This is attributed to the lack of hydrogen bonds and to steric hindrance and plasticization of more bulky ester groups in the resins cured with active esters.

KEY WORDS Epoxy resins, cured resins, network structure, active esters

INTRODUCTION

Epoxy groups react with a number of nucleophilic and electrophilic reagents. However, to cure epoxy resins, compounds with active hydrogen atoms, for example, amines, phenols, alcohols, thiols, and carboxylic acids and acid anhydrides are almost exclusively used because of their processability and availability (Scheme I). Most conventional curing agents leave pendant hydroxyl groups in the



SCHEME I

cured resins, which are not favorable for electric and electronic applications. The epoxy resins cured with anhydrides have no hydroxyl groups. They are inferior however, in curability and liberate free acids during storage, which impair the mechanical properties of the cured resins.

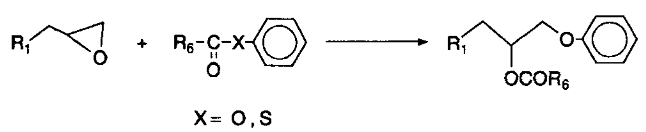
Recently, Nishikubo et al. [1–3] have reported that active esters such as aryl and thioaryl esters of carboxylic acids add to epoxides by using quarternary onium salts as catalyst under mild conditions (Scheme II).

This reaction is not only a novel organic reaction but is also a promising method for epoxy curing, because no pendant hydroxyl groups are left in the cured resins, and only ester groups are formed (Scheme III). The cured resins without hydroxyl groups can be used for applications which require improved electric and lower hygroscopic properties. Furthermore, this curing system is very suitable for the investigation of the effects of hydroxyl groups on the structure and properties of epoxy resins.

In this paper, the various properties and also the network structure of epoxy resins cured with active esters are reviewed in comparison with those resins with pendant hydroxyl groups, which are cured with conventional curing agents.

METHODS

Epicote 828, that is, bisphenol A diglycidyl ether (BADGE) (Scheme IV), was used as an epoxy precursor. Active esters as curing agents were synthesized according to



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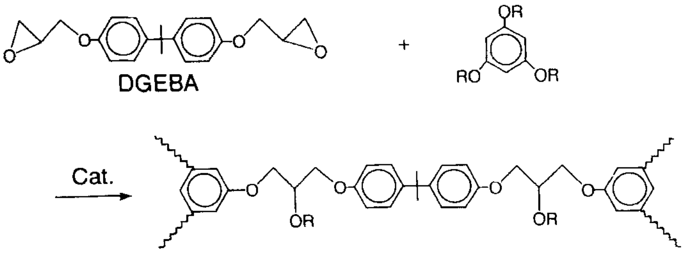
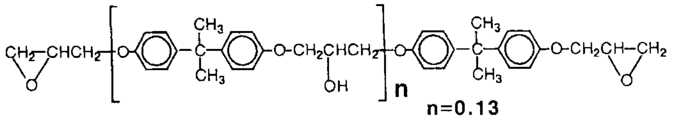


R = —COCH$_3$	(TAB)
—COCH$_2$CH$_3$	(TPrB)
—COCH$_2$CH$_2$CH$_3$	(TBuB)
—COCH(CH$_3$)$_2$	(TiBuB)
—COC(CH$_3$)$_3$	(TPiB)
—COPh	(TBB)

SCHEME III


Bisphenol A diglycidylether (DGEBA)

SCHEME IV

conventional methods. The progress of curing was followed by isothermally recording the exothermic peak due to curing with a Perkin-Elmer DSC System 4.

Glass transition temperature T_g was determined at 5 deg min^{-1} with a Perkin-Elmer DSC System 4 or a Rigaku Thermoflex TMA. Thermal stability of the cured resins was examined with a Rigaku Thermoflex TG. Linear thermal expansion coefficient was obtained at 2 deg min^{-1} with a Seiko TMA/SS.

Viscoelastic properties were measured at 2 deg min^{-1} with a Rheovibron DDV-II at 11 Hz and a Seiko DMS200 at 0.5 Hz. Dielectric properties are recorded at 1 KHz with a Seiko DES200. Water absorption was determined from an increase in weight after a film specimen was immersed in deionized water for predetermined periods of time.

CURING AGENTS AND CATALYSTS

Among six esters of 1,3,5-trihydroxybenzene examined, triacetoxybenzene (TAB) is most effective and the curing reaction proceeds almost quantitatively irrespective of curing temperature [4]. Therefore, this review hereafter deals with the results on the resins cured with TAB.

In addition to quarternary onium salts, triphenyl phosphine (TPP), 1,8-diazabicyclo-[5.4.0] undecene-7 (DBU), and 4-(dimethylamino)-pyridine (DMAP) can be used as catalyst for epoxy curing with active esters [4]. DBU and DMAP, however, also induce ring-opening polymerization of epoxy groups. Addition reaction occurs solely when TPP is used as catalyst. The T_g of the TAB-cured resins is higher than that of the resins cured with quarternary onium salts.

THERMAL PROPERTIES

When the stoichiometric ratio r of acetoxy groups of active ester to epoxy groups of BADGE is varied in the curing systems, the T_g of epoxy resins has a maximum at $r = 1$ (Figure 1) [5]. A maximum is also reported at $r = 1$ for the T_g vs. r curves of the diamine-cured epoxy resins by Galy et al. [6]. When the value of r is smaller than unity, epoxy groups are in excess compared with ester groups. All the ester groups are used when the reaction is completed. The unreacted epoxy groups lead to pendant chain ends, which are mobile and induce the lowering of T_g. However, when r is larger than unity, for example, ester groups are present in excess, unreacted ester groups remain even after completion of the reaction. The distance between cross-links becomes larger; longer chains between cross-links can move more easily than shorter ones resulting in the lowering of T_g.

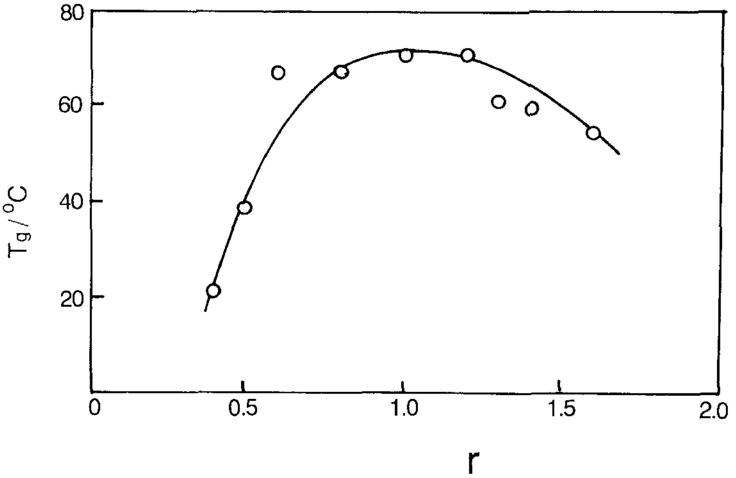


FIGURE 1 Effect of stoichiometric ratio r of acetyl groups of TAB to epoxy groups of BADGE on the glass transition temperature T_g of the epoxy resins cured with TAB.

The T_g of the epoxy resins cured with TAB is lower than that cured with trihydroxybenzene (THB), as described in the following section.

The thermal stability of the epoxy resins cured with TAB increases with increasing r as determined as the starting temperature of weight loss of TG curves (Figure 2) [5].

VISCOELASTIC PROPERTIES

Figure 3 shows the viscoelastic behavior of the epoxy resins cured with mixtures of TAB and THB by varying the ratio THB/TAB [7]. The epoxy resins cured with THB have a cross-link structure similar to that cured with TAB but have free

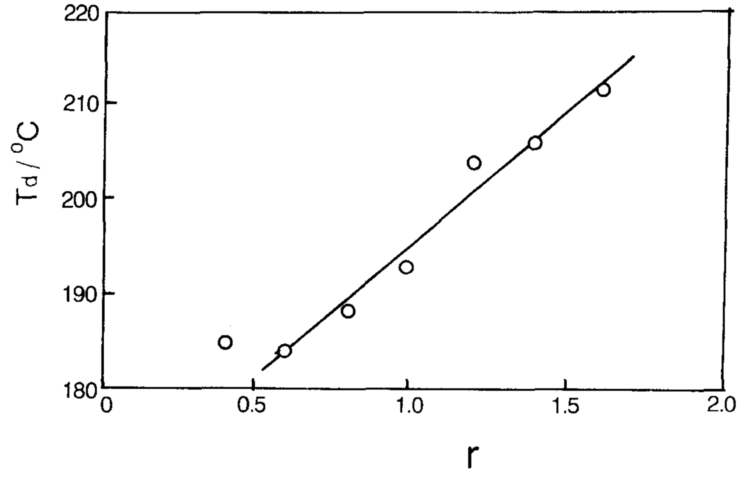


FIGURE 2 Effect of stoichiometric ratio r of acetyl groups of TAB to epoxy groups of BADGE on the decomposition temperature T_d of the epoxy resin cured with TAB.

pendant hydroxyl groups instead of acetyl groups, and the hydroxyl content in the cured resins increases with increasing ratio of THB/TAB in the curing systems (Scheme V).

The α and β' dispersions are observed in Figure 3. The storage modulus (E') curves and also the tan δ peak temperatures T_α values of the α dispersion shift to higher temperature with increasing THB content in the curing systems.

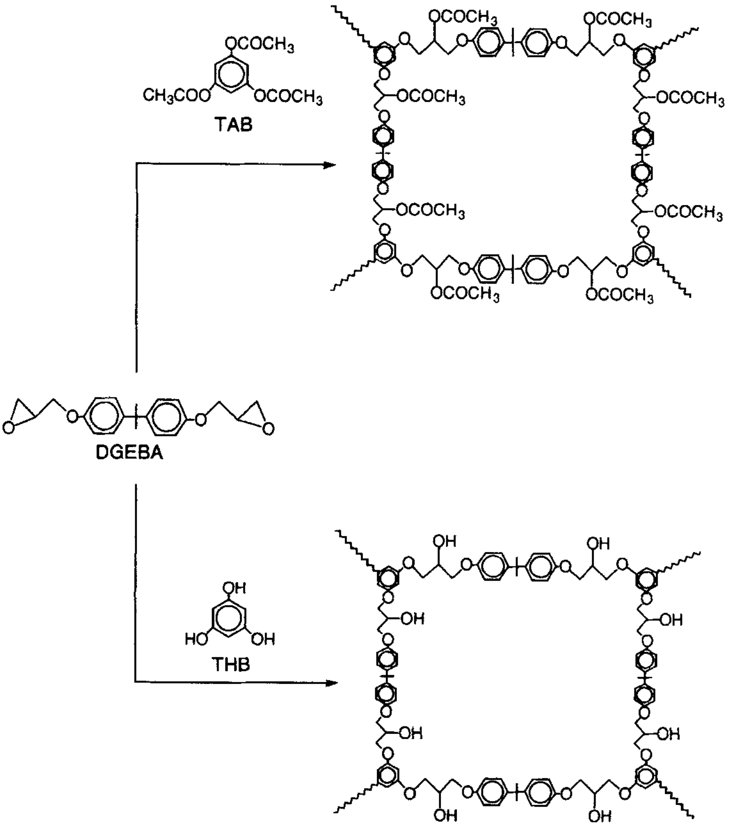
Various viscoelastic parameters are obtained from the curves of Figure 3 and tabulated in Table I together with the density d at 20°C. In Table II, the cross-link density ρ, and the number-average molecular weight between cross-links $\overline{M}_c$ (E') are calculated using the equation of state for rubber elasticity (1) according to the Murayama's method [8]:

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

$$\overline{M}_c(E') = d/\rho \tag{2}$$

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

where $R\Phi$ is the gas constant and d the density at $T_\alpha + 40°\text{C}$. $\overline{M}_c$ (calcd) is



SCHEME V

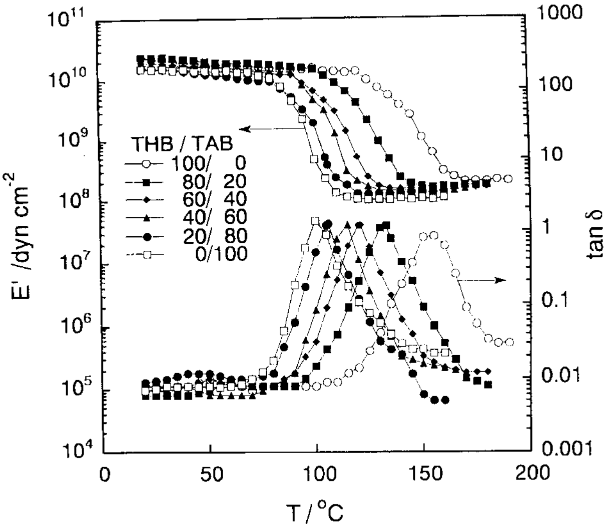


FIGURE 3 Dynamic modulus and loss versus temperature curves of the epoxy resins cured with varying ratios of curing agents, THB/TAB at 11 Hz.

TABLE I

Viscoelastic parameters of the epoxy resins cured with THB/TAB mixtures

THB/TAB (molar ratio)	0/100	20/80	40/60	60/40	80/20	100/0
T_α/°C	101	108	114	121	133	153
d(20°C)/gIIcm^{-3}	1.20	1.21	1.22	1.22	1.23	1.23
E'(20°C)/10^{10} dynIIcm^{-2}	1.51	1.56	1.81	1.92	2.33	2.36
$E'(T_g$ + 40°C)/10^8 dynIIcm^{-2}	1.04	1.30	1.41	1.54	1.70	2.05
$\rho/10^{-3}$ molIIcm^3	1.01	1.24	1.32	1.42	1.53	1.76
M_c/gIImol^{-1}	1132	923	873	812	756	657
Φ	0.48	0.57	0.59	0.61	0.63	0.70

TABLE II

Water absorption and cross-link density of the epoxy resins cured with THB/TAB mixtures

THB/TAB (molar ratio)	k 10^{-2}% h$^{1/2}$	D 10^{-8} cm^2 s^{-1}	Q wt %	ρ 10^{-3} molm^3
0/100	2.72	2.00	0.71	1.01
20/80	2.88	1.60	0.84	1.24
40/60	3.22	1.17	1.10	1.32
50/50	3.53	1.20	1.19	——
60/40	3.76	1.09	1.33	1.42
80/20	4.34	1.01	1.59	1.53
100/0	4.99	0.97	1.87	1.76

calculated by assuming the network structure as shown in Scheme V.

The values of T_α, d(20°C), E', ρ and Φ decrease and $\overline{M}_c$ increases monotonically with the decrease in the ratio THB/TAB.

The T_α values are plotted against the THB content in the curing systems together with the T_g values determined by DSC and TMA in Figure 4. These characteristic temperatures increase monotonically with increasing hydroxyl content in the cured resins.

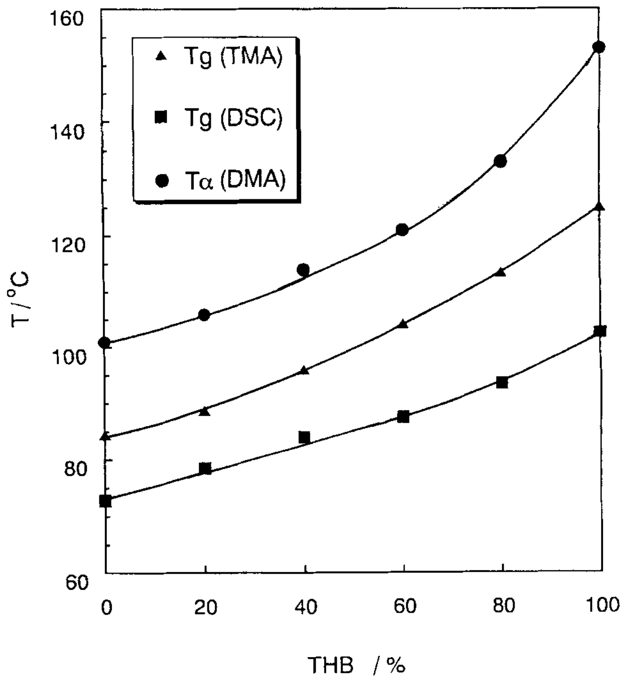


FIGURE 4 T_g and T_α of cured resins versus THB content in the curing agent mixtures.

In the tan δ versus temperature curves in the subzero temperature region, a broad dispersion appears at −50°C for the TAB-cured resin, whereas two peaks (−80°C and 15°C) are observed for the TAB-cured resin (Figure 5) [7]. The tan δ peak at −50°C is usually observed for the epoxy resins cured with conventional curing agents and is attributed to the overlapping of the relaxation of hydroxyl ether segments and that of other parts in the polymer chain [9]. The appearance of two peaks is explained as illustrated in the schematic representation of Figure 6 [9].

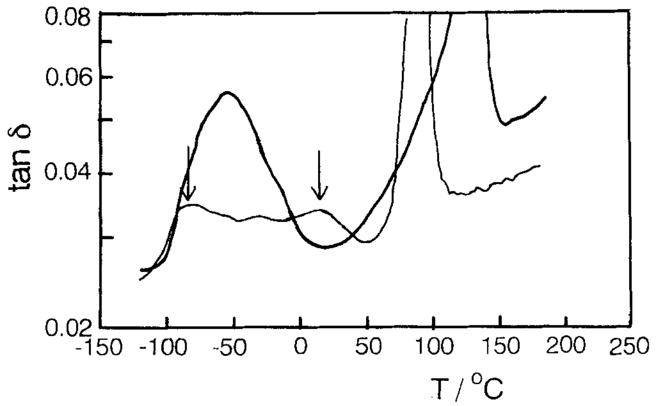


FIGURE 5 Dynamic loss versus temperature curves of the epoxy resin cured with TAB and that with THB at 0.5 Hz. TAB (thinner); THB (thicker).

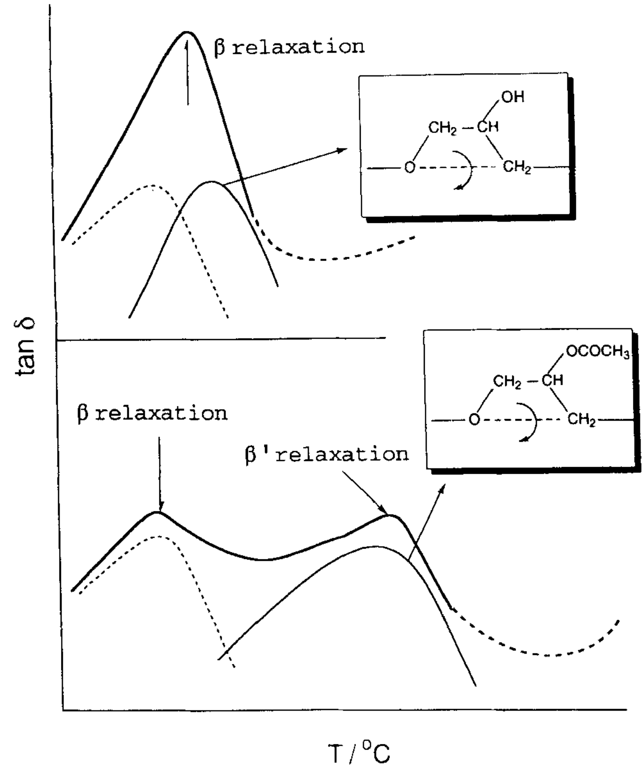


FIGURE 6 A schematic representation of molecular motions at lower temperatures in the TAB-cured epoxy resins.

The peak at 15°C is attributed to the shift of the relaxation of hydroxyl ether segments to higher temperature because the mobility of hydroxyl ether segments is lowered by the acetylation of hydroxyl groups and the peak due to other parts of the chain appears at $-80°C$.

DIELECTRIC PROPERTIES

The dielectric behavior of epoxy resins cured with TAB, phenol novolac resin and a mixture of TAB and phenol novolac resin (50:50) is shown in Figure 7 [10]. The tan δ peak of the β dispersion becomes smaller and shifts to higher temperatures with increasing TAB content in the curing systems. These results are attributed to the decrease in segmental motions induced by the substitution of hydroxyl groups with more bulky acetoxy groups. The dielectric constant ε' of resins cured with phenol novolac resin increases drastically at the tan δ peak temperature due to the β dispersion, whereas the increase in the dielectric constant is less significantly for the TAB-cured resin. The change of dielectric constant is induced by the orientational polarization of local structure. Therefore, the TAB-cured epoxy resins with

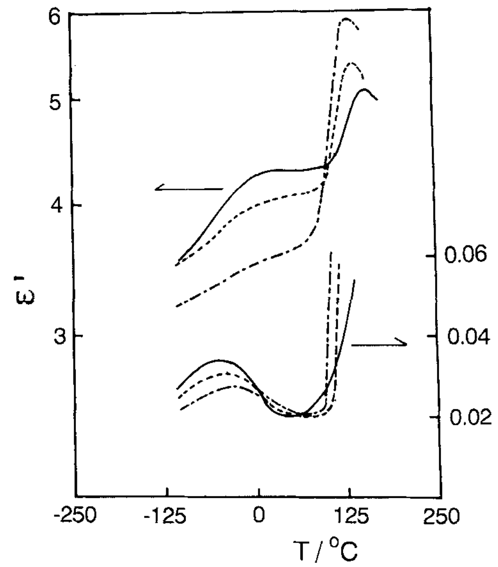


FIGURE 7 Dielectric constant and loss versus temperature curves of the epoxy resins cured with TAB and phenol novolac resin. Phenol novolac/TAB; (100/0) (■), 50/50 (_ _ _ _ _ _ _ _ _). 0/100 (_ · _ · _ · _).

low polarity and local mobility has superior dielectric properties to those cured with conventional curing agents.

HYGROSCOPIC PROPERTIES

The amount of water absorption of the epoxy resins cured with varying ratio of THB/TAB increases with increasing THB content in the curing systems (Fig. 8) [11].

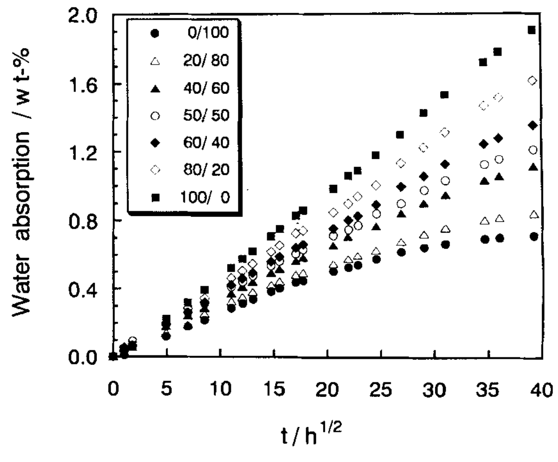


FIGURE 8 Water absorption versus time curves of the epoxy resins cured with varying ratios of THB/TAB.

From the data of Figure 8, the water absorption of the resins and the diffusion of water molecules in the resins are examined using Fick's second law [12].

$$M_t = (4/b)(D/\pi)^{1/2} t^{1/2} \tag{4}$$

$$D = (\pi/3600)(bk/4Q)^2 \tag{5}$$

where M_t refers to the water uptake (wt-%) at time $t(h)$, Q the water uptake at saturation (wt-%), b the thickness of the specimen (cm), D the diffusion coefficient (cm^2s^{-1}), and k the constant representing the rate of uptake ($\%/h^{1/2}$).

From Equations (4) and (5):

$$M_t = kt^{1/2} \tag{6}$$

In Table II, the values of k, D, and Q are tabulated together with the cross-link density ρ. The values of k and Q increase but that of D decreases with increasing THB content in the curing systems. These results indicate that the rate of water absorption and the water uptake at saturation increases with increasing hydroxyl content of the cured resins, whereas the diffusion coefficient increase with increasing acetyl content because the network structure becomes looser by substituting hydroxyl groups with acetyl groups, as will be discussed in the next section.

NETWORK STRUCTURE

As seen from the experimental results mentioned above, the network structure is remarkably affected by the ratio of hydroxyl and acetyl groups in the cured resins. All of the data are explained by assuming that the network structure formed using TAB as cross-linking agent is looser than that induced with THB. In the course of curing, the hydroxyl groups from THB induce association of resulting cross-linked resins, whereas the association is disturbed by the steric hindrance of acetyl groups from TAB.

As the acetyl content increases, molecular interaction becomes weaker due to the decrease in hydrogen bonding and the internal plasticization of acetyl groups, and the molecular chain between cross-links becomes more mobile. These two effects are responsible for the lowering of T_g with increasing acetyl content.

The lowering in density d with acetyl content indicates that the packing of network chains becomes looser. This is also supported by the higher diffusion coefficient D of water molecules in the acetyl-rich resins.

The decrease in modulus E' and the shift of the α dispersion of lower temperatures with decreasing hydroxyl content is attributed to the decrease of hydrogen bonding and the internal plasticization of bulky ester groups.

The shift of the β dispersion due to hydroxyl ether segments to higher temperatures by the substitution of hydroxyl groups with acetyl groups is also evident of the bulkiness of acetyl groups compared with the hydroxyl groups.

The linear thermal expansion coefficient in the rubbery region is not that much affected by the hydroxyl content, whereas in the glassy region it increases with

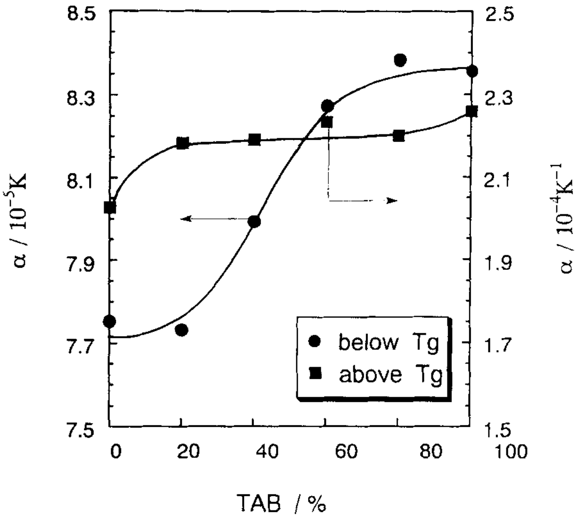


FIGURE 9 Thermal expansion coefficients of the cured resins versus THB content in the curing agent mixtures.

increasing TAB content in the curing systems (Figure 9) [7]. This result supports the fact that stronger intermolecular interaction is caused by hydrogen bonding between hydroxyl groups from THB.

CONCLUSIONS

The epoxy resins cured with polyfunctional active esters have pendant ester groups as distinct from the resins cured with conventional curing agents and containing pendant hydroxyl groups. The substitution of hydroxyl groups with acetyl groups results in lower glass transition temperature, higher β transition temperature, lower density, lower dynamic modulus and dielectric constant, and higher diffusion coefficient of water molecules in the cured resins.

They are attributed to the lack of hydrogen bonding and to the steric hindrance and plasticization of more bulky ester groups in the resins cured with active esters, which result in looser network structure compared with the epoxy resins with hydroxyl groups.

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