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PREPARATION AND PROPERTIES OF EPOXY RESINS CURED WITH SILYL ESTERS OF PHENOL NOVOLAK AND CRESOL NOVOLAK

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Abstract

The curing agents of epoxy resin, trimethylsilyl ethers of phenol novolak (TMSPN) and cresol novolak (TMSCN) were prepared by refluxing phenol novolak and cresol novolak respectively, with the mixture of hexamethyldisilazane and chlorotrimethylsilane in THF. The curing reaction of epoxy resin with these curing agents and the thermal properties of cured resins were examined. The T_g values of epoxy resins cured with TMSPN were a little higher than those cured with TMSCN. The maximum of T_g is 118°C for TMSPN-cured epoxy resin against 112°C for TMSPN-cured epoxy resin. The water adsorption of hydrophobic epoxy resins cured with TMSPN was a little lower than those cured with TMSCN. The clear decrease of water adsorption is attributed to the difficulty of the micro-void formation caused by the more tight primary structures of TMSPN. The water adsorption at 25°C containing trimethylsilyl groups is about one-tenth of that of epoxy resins cured with conventional curing agents and even one-half of that of the epoxy resins cured with active esters. The low water adsorption is attributed to the presence of trimethylsilyl groups, which are more hydrophobic than ester groups, and to the absence of hydroxyl groups of the cured resins.

Keywords: cresol novolak, DSC, dynamic mechanical properties, epoxy resins, glass transition temperature, phenol novolak, trimethylsilyl group, water adsorption

Introduction

Epoxy resins contain two or more epoxy groups in a molecule. Their backbone may be aliphatic, cycloaliphatic, or aromatic. The epoxy groups react with curing agents to yield insoluble and infusible three dimensions networks. Curing agents have two or more reactive group in a molecule, which can react with epoxy groups. The epoxy prepolymer and the curing agent determine the properties of cured epoxy resins. Because of the versatility of their properties, epoxy resins are used in a variety of applications such as coatings,

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laminates, composites, bondings, and adhesives. To fulfill a demand for high-performance epoxy resins, novel curing agents are still being sought.

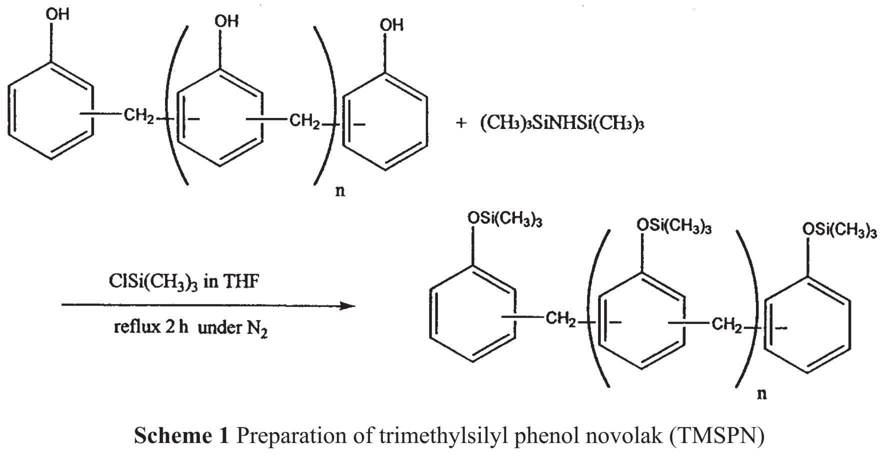
We have studied curing reaction of epoxy resins with various active esters and properties of cured resins [1–3]. Epoxy resins cured with active esters have tertiary ester groups in the cured resins, whereas epoxy resins cured with conventional curing agents, active hydrogen compounds possess hydroxyl groups after curing. Epoxy resins having no hydroxyl groups show excellent electric properties and low water adsorption [3]. In this paper, trimethylsilyl ethers of phenol novolak and cresol novolak were prepared as curing agents, and the reaction of these curing agents and the properties of cured resins were examined.

Experimental

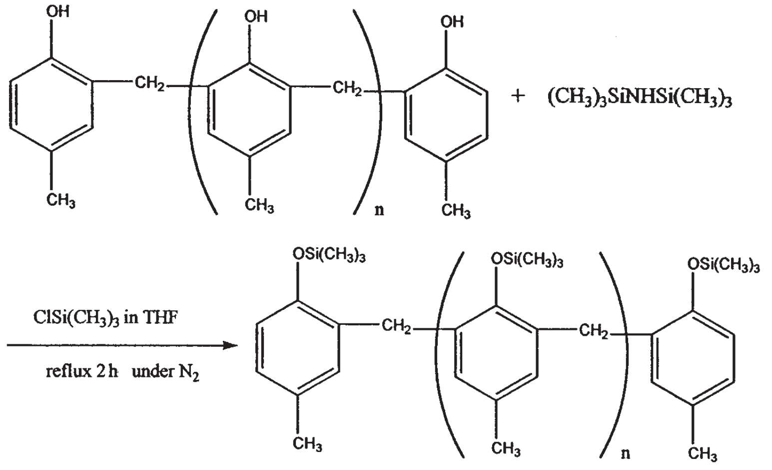
Trimethylsilyl phenol novolak (TMSPN) was prepared by refluxing phenol novolak (1.8 g; 2.54 mmol), hexamethyldisilazane (4.0 mL; 19.1 mmol) and chlorotrimethylsilane (0.2 mL; 1.58 mmol) in THF (40 mL). Chlorotrimethylsilane was added to lower the reaction temperature [4]. The product was yellow viscous liquid. Trimethylsilyl cresol novolak was prepared in the similar method. Bisphenol A diglycidyl ether (BPDGE) was cured with TMSPN or TMSCN using tetra-*n*-butyl phosphonium bromide as catalyst at 100°C. Glass transition temperature (T_g) was determined at 5°C min^{-1} with SEIKO DSC 120. The sample was sealed in an aluminum container. Dynamic mechanical properties were measured at 1 Hz at 2°C min^{-1}, with SEIKO DMS 210.

Results and discussions

The yield of TMSPN was 72% and that of TMSCN was 78%. It was confirmed that the trimethylsilylation occurred completely by IR and ^{1}H-NMR.



Scheme 1 Preparation of trimethylsilyl phenol novolak (TMSPN)



Scheme 2 Preparation of trimethylsilyl cresol novolak (TMSCN)

The T_g values of cured resins are plotted against *r*, the ratio of the epoxy groups of BPDGE to the trimethylsilyl groups of TMSPN (or TMSCN) (Fig. 1). When the value of *r* is smaller than unity, epoxy groups are in excess compared with trimethyl groups. All the trimethyl groups are used up when the reaction is completed. The unreacted epoxy groups lead to mobile pendant chain ends, which induced the lowering of T_g [5]. On the other hand, when *r* is larger than unity, trimethylsilyl groups are in excess, unreacted trimethylsilyl groups remain even after completion of the reaction. The longer distance between cross-links can move more easily than shorter ones resulting in a lowering of T_g. The T_g values of epoxy resins cured with TMSPN are a little higher than those cured with TMSCN, because of the more tight primary structure of TMSPN. The maximum of T_g at r=1 is 118°C for TMSPN-cured resin and 112°C for TMSCN-cured resin.

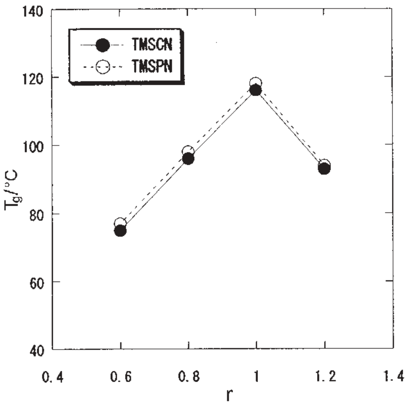


Fig. 1 T_g *vs.* *r*, the ratio of the epoxy groups of BPDGE to the trimethylsilyl groups of TMSPN (or TMSCN) for TMSPN (or TMSCN) cured epoxy resins.
Curing agent: ○ – TMSPN; ● – TMSCN

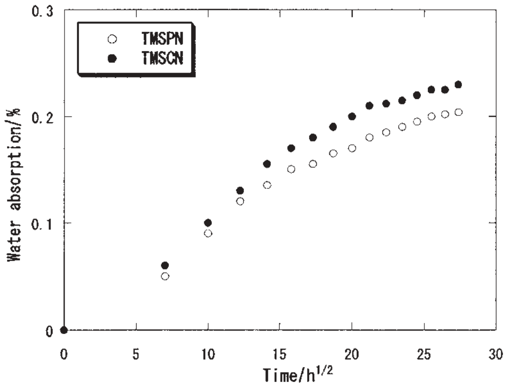


Fig. 2 Water adsorption of epoxy resins. Curing agent: ○ – TMSPN, ● – TMSCN

The water adsorption was determined using immersing dried specimens in deionized water at 25°C, and the mass increase of specimens was weighed at predetermined intervals. The water adsorption was plotted *vs*. the immersed time in Fig. 2. From these data, the water adsorption of the cured resins and the diffusion of water molecules in the epoxy resins are determined using Fick's second law.

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

$$D=(\pi/3600)\,(bk/4Q)^2$$

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

Table 1 The water adsorption and diffusion of the epoxy resins

	Curing agent	TMSPN	TMSCN
Rate of water uptake	$k\cdot10^2$/% h$^{-1/2}$	0.902	1.03
Diffusion coefficient	$D\cdot10^8$/cm^2 s^{-1}	1.03	1.05
Water uptake	Q/mass%	0.197	0.223

The values of k, D and Q are shown in Table 1. The water adsorption of the epoxy resins containing trimethylsilyl groups at 25°C is about one-tenth of that of epoxy resins cured with conventional curing agents, which have hydroxyl groups, and even one-half of that of the epoxy resins cured with active esters [3]. This low water adsorption is attributed to the presence of silyl groups, which is more hydrophobic than ester groups, and to the absence of hydroxyl groups. The water uptake at saturation and the diffusion coefficient of TMSCN are higher than those of TMSPN. The network structure of TMSCN is looser than that of TMSPN due to the methyl groups attached to aromatic nuclei that include more voids in cured epoxy resins. Therefore, the diffusion of water molecules in the polymer network is easier in TMSCN than in TMSPN, and the water adsorption of TMSCN becomes higher than that of TMSPN. TMSPN has more restricted configuration and becomes more tight structures than TMSCN. Therefore, micro-void formation of TMSCN occurs more easily. The micro-void formed in TMSPN-cured epoxy resin is more inflexible and less water is adsorbed.

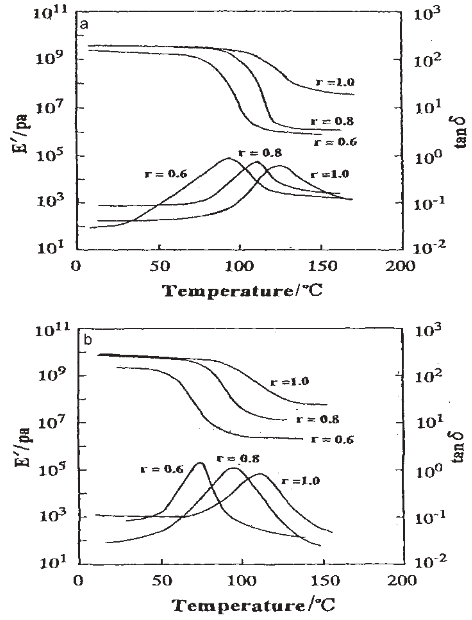


Fig. 3 Viscoelastic properties of epoxy resins cured with TMSPN and TMSCN.
a – TMSPN-cured epoxy resins; b – TMSCN-cured epoxy resins

The temperature dependence of the storage modulus (*E*') and the tan δ of resins cured with TMSPN and TMCPN shows the behavior of the typical network polymers (Fig. 3a and Fig. 3b). As *r* approaches to unity, the storage modulus *E*' *vs.* temperature curves and the peak temperature curves of tan δ shift to higher temperature. These results show the more complete network formation as observed for T_g values. The small peaks appeared at lower temperature region due to the relaxation of cured resins. The peaks of tan δ for TMSCN-cured epoxy resin (r=1) is 113°C and that for TMSPN-cured epoxy resin is 128°C. The effect of more tight primary structure of TMSPN also appears in the thermomechanical curves.

Conclusions

Silyl esters of phenol novolak (TMSPN) and cresol novolak (TMSCN) are used for the curing of epoxy resins. The T_g of the TMSPN-cured epoxy resin is 118°C, while the T_g of the TMSCN-cured one is 112°C. The water adsorption of the TMSPN-cured epoxy resin is lower than the TMSCN-cured one. The difference is attributed to the more tight primary structure of TMSPN than TMSCN.

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