

# GLASS TRANSITION TEMPERATURE-LESS (TG-LESS) EPOXY RESIN AS A MATRIX OF HIGH HEAT RESISTANT COMPOSITE

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## 1 Introduction

Epoxy resin has high mechanical and electrical performance with good handling properties. As such, it is one of the most typical and widely used thermosets. These excellent performances are, however, exhibited only below glass transition temperature ( $T_g$ ) of the cured thermosets because they drop drastically above the  $T_g$ . To obtain thermosets that maintain excellent properties even at higher temperature, many researchers have made efforts to form high cross-links in the cured resin or to introduce rigid chemical structures in their backbone. These efforts have been successful, but have led to a reduction in the workability of the thermosets and some limitation in thermal stability. This limitation may be attributed to the fact that the thermoset chemical structure substantially consists of organic compounds. This contrasts with most inorganic materials, such as ceramics and metals, which do not change their properties even at several hundreds of degrees of temperature.

On the other hand, some investigations in the past few decades have been revealed that organic-inorganic hybrids do not exhibit  $T_g$  and maintain a

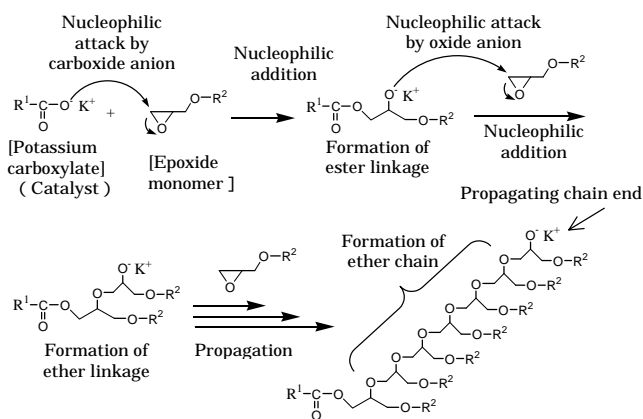
high level of Young's modulus at elevated temperature [1,2]. These hybrids are synthesized by using the common curing reaction of organic thermosets and simultaneous formation of inorganic networks by 'sol-gel' reaction. In the obtained hybrids, Inorganic domains are dispersed at the nanometer level within the organic matrix. It is postulated that the disappearance of  $T_g$  results from the restriction of the motion of organic matrix by the nanometer-sized inorganic domain.

Recent studies from our laboratory revealed that a  $T_g$ -less epoxy resin was easily obtained by curing conventional epoxy resin catalyzed by a salt of alkaline metal and carboxylic acid in spite of absence of inorganic components [3,4]. In this study, we tried to obtain a high heat resistant composite by using  $T_g$ -less epoxy resin as a matrix.

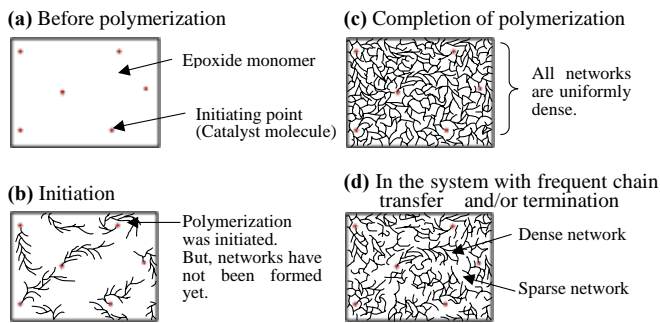
## 2 $T_g$ -less Epoxy Resin

A  $T_g$ -less epoxy resin is easily obtained by curing conventional epoxy resin such as diglycidylether of bisphenol A catalyzed by a salt of alkaline metal and carboxylic acid. In this system, the storage modulus ( $E'$ ) of cured resin does not drop and maintain a high level, in the order of  $10^9$  Pa, as if the cured resin were in a glassy state even at an elevated temperature such as 300 °C as shown in Fig. 3-(b) while the  $E'$  of an ordinary epoxy resin cured by imidazole drops suddenly to low value, in the order of  $10^7$  Pa above its  $T_g$  (ca. 120 °C) as shown in Fig. 3-(a).

$T_g$ -less epoxy resins are cured by the polymerization mechanism shown in Fig. 1. In the first step, addition initiated by nucleophilic attack of a carboxide anion of potassium carboxylate to a carbon atom of epoxy group takes place to form an ester linkage. Next, since a newly formed oxide anion has enough nucleophilicity to open another



**Fig. 1** Polymerization mechanism of  $T_g$ -less epoxy resin catalyzed by potassium carboxylate.

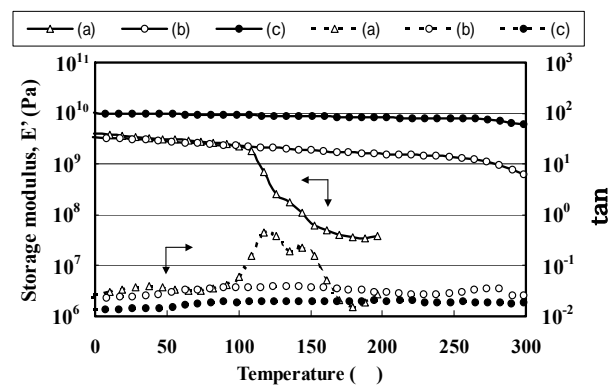


**Fig. 2** Illustration for network formation process during the curing of epoxide anionically catalyzed by carboxylates with alkaline metals or conventional catalysts.

oxyrane ring further, anionic polymerization is brought about to form ether linkages progressively.

This polymerization is similar to living polymerization, for example anionic polymerization of styrene initiated by sodium complex of naphthalene, in terms of the fact that chain transfer is extremely difficult to occur. Moreover, because the polymerization catalyzed by potassium carboxylate is fortunately not so sensitive to  $H_2O$  or air under ordinary curing condition for epoxy resin, this polymerization system can be widely applied to the field of thermosets.

The formation of  $T_g$ -less cured resin is just attributed to this characteristic manner of polymerizing. **Fig. 2** illustrates the network formation process during curing, comparing in  $T_g$ -less epoxy resin and in conventional epoxy resin catalyzed by imidazole. Catalyst molecules are dispersed in epoxy monomers in the initial state as shown in (a). The polymerization of epoxy monomers is initiated from the catalyst molecules as shown in (b). Although the polymerization proceeds linearly because of anionic ring-opening polymerization, cross-linked network is automatically formed with propagating whenever the epoxy monomers are more than 2-functional. In the case of imidazole, chain transfer and/or termination occur frequently during curing. So, the network to be formed should have many defects, which lead to form partially sparse network in dense network as shown in (d). On the other hand, in the potassium carboxylate case, chain transfer and/or termination hardly occur. So, the network to be formed should have few defects and its cross-linking density is uniformly high as shown in (c). The motion of main chain of cured resin corresponding to the micro Brownian movement could be suppressed in the very highly cross-linked network like (c) even at higher temperature. This is precisely the mechanism of  $T_g$ -disappearing.



**Fig. 3** Dynamic viscoelastic behavior of cured epoxy resins and  $T_g$ -less composite reinforced with glass fiber fabrics. (a) Conventional epoxy resin cured by imidazole; (b)  $T_g$ -less epoxy resin cured by potassium carboxylate; (c) Composite using  $T_g$ -less epoxy resin

### 3 Composite using $T_g$ -less epoxy resin

GFRP was prepared by impregnating  $T_g$ -less-type uncured liquid epoxy resin into glass cloths and subsequent pressing and heating them for 2h/120 + 4h/180 . The glass fiber content was 34 vol%. The measurement of dynamic viscoelastic behavior for the obtained GFRP, shown in **Fig. 3-(c)**, revealed that the GFRP could exhibit an excellent mechanical property even around 300 because more than 80% of modulus at 25 was maintained at 250 .

### 4 Conclusion

This study includes the development of a high heat-resistant FRP using  $T_g$ -less epoxy resin, which can be cured by anionic polymerization with potassium carboxylate salt as an initiator. The GFRP with this  $T_g$ -less epoxy resin as a matrix including 34 vol % of glass fiber exhibited high heat resistant property.

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