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A DYNAMIC DSC STUDY OF THE CURING PROCESS OF EPOXY RESIN

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Abstract

In order to expand the industrial usefulness of an isothermal time–temperature–transformation (TTT) cure diagram, a method to make it applicable to a solid-state sample involving only resins and a catalyst was studied by using dynamic DSC (DDSC) and cone plate dynamic mechanical analysis (DMA). To estimate how much curing occurred for an industrially used epoxy resin molding compound manufactured in a production process was also studied, together with its position in the TTT cure diagram. The TTT cure diagram proved to be useful for determining the differences between compounds without their dissolution in a solvent, and for estimating their heat history during the production process.

Keywords: DDSC, DMA, epoxy resin, thermosetting polymer, time–temperature–transformation cure diagram

Introduction

A TTT cure diagram is useful in facilitating an understanding of the curing process of a material and its properties after curing. Most diagrams are produced by using torsional braid analysis (TBA). TBA can trace changes in the structure and state for thermosetting polymers, from the initial curing stage to the final curing stage, and even to carbonization. However, TBA has some disadvantages in that it cannot be used for powder samples unless they are dissolved in a solvent, and their absolute modulus values cannot be determined. In order to expand the industrial usefulness of a TTT cure diagram, the purpose of the present study was to prepare a TTT diagram for a powder sample by using DDSC and DMA, and to determine where an industrially used epoxy molding compound is positioned in the TTT cure diagram.

There are three critical temperatures in a TTT diagram: T_{go}, ${}_{gel}T_g$ and $T_{g\infty}$. T_{go} is the glass transition temperature of the uncured reactants. Below this temperature, in principle, they have no reactivity. ${}_{gel}T_g$ is the temperature at which gelation and vitrification coincide. $T_{g\infty}$ is the maximum glass transition temperature. Besides measuring these three critical temperatures, we prepared a TTT diagram by using isothermal DDSC and DMA measurements.

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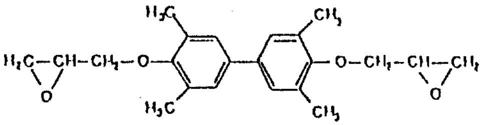
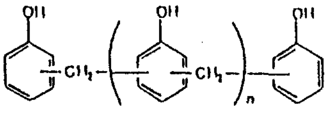
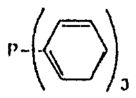
Experimental

For the representative sample, we used 2,2′,6,6′-tetramethylbiphenyl diglycidyl ether (YX, Yuka Shell Co.), phenol novolak (PN, Sumitomo Durez Co.), and triphenylphosphine (TPP, Tokyo Kasei Co.) as the epoxy resin, hardener and catalyst, respectively, at a mass ratio of 64.2/35.1/0.7 (Table 1). They were mixed and heated at 115°C for 3 min on a hot plate and then cooled to room temperature.

Table 1 Chemicals

Name, code and formula	Source and purification
Epoxy Resin (YX)  2,2’,6,6’-tetramethylbiphenyl diglycidylether	Yuka Shell Co. used without further purification
Hardener (PN)  phenol novolak	Sumitomo Durez Co. used without further purification
Catalyst (TPP)  triphenyl phosphine	Tokyo Kasei Co. used without further purification

The DMA experiments were performed on a Rheometrics RDS-II instrument, using the cone plate method. The sample was molded into specimens 25 mm in diameter and 0.4 mm in maximum thickness. The specimens were mounted in the apparatus at the cure temperatures, and the shear stress was applied to them at a frequency of 10 rad s^{-1}. Their storage modulus (G') and loss factor (tan δ) were measured as functions of time.

All experiments relating to DDSC were performed on a TA Instruments DSC 2920 equipped with a modulated DSC and a freezer. The hermetically sealed pans were purged with 30 ml min^{-1} of dry helium. The DSC was calibrated for enthalpy and temperature by using the standard reference indium. The modulated DSC was calibrated for specific heat capacity (C_p) by using linear polyethylene at 150°C. The literature value for C_p was obtained from ATHAS. Each specimen was placed on the sample platform, which was already at the cure temperature. The period of time and the amplitude used during the isothermal measurements were 60 s and ±0.5°C, respectively. T_{go} and $T_{g\infty}$ for the sample were determined by DDSC at 2.5°C min^{-1} and ±0.3°C/60 s^{-1}. The extent of conversion for the samples heated for designated times was calculated on the basis of measurements of residual curing heat by means of DDSC.

Results and discussion

T_{go}=10°C for the sample and $T_{g\infty}$=150°C. Figure 1 shows dynamic mechanical data, G' and tanδ, obtained by curing the sample isothermally at several temperatures. The tanδ curve for 130°C has two peaks. The first peak is associated with gelation and the second peak with vitrification. They suggest that gelation and vitrification take place separately. However, the peak attributed to vitrification is not clear in the 150 and 170°C curves. This means that above $T_{g\infty}$ the sample gels but does not vitrify, and an elastomer (rubber) is formed. The peak attributed to vitrification is not very distinct in the 70 and 90°C curves as compared to the 110 and 130°C curves. The time to gelation was determined from the first peak of tanδ, and the time to formation of the rubber structure (elastomerization) was determined from the time when the modulus started to level off.

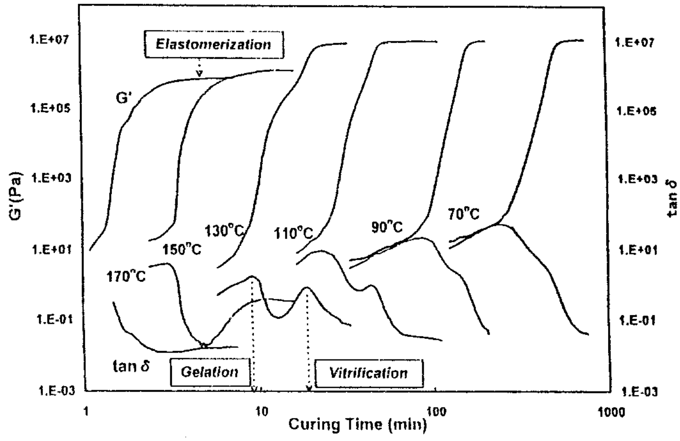


Fig. 1 Dynamic mechanical data (Rheometrics) G', and tanδ obtained by isothermally curing YX/PN/TPP under 10 rad s^{-1} at several temperatures

On the other hand, the time to vitrification was determined by means of DDSC. Figure 2 shows the total heat flow and C_p obtained by curing the sample isothermally at several curing temperatures. A stepwise decrease in C_p is observed. The vitrification time is determined by the time at half the heat capacity change, $t_{1/2\Delta C_p}$. The accurate vitrification time can be determined with the change in C_p, especially at temperatures below 110°C, but it is difficult to measure it above 140–150°C.

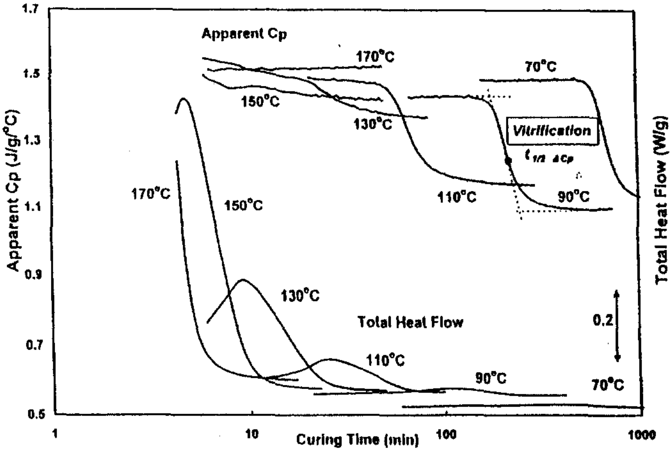


Fig. 2 Total heat flow and heat capacity C_p for the quasi-isothermal curve of YX/PN/TPP at several temperatures with a 0.5°C per 60 s modulation

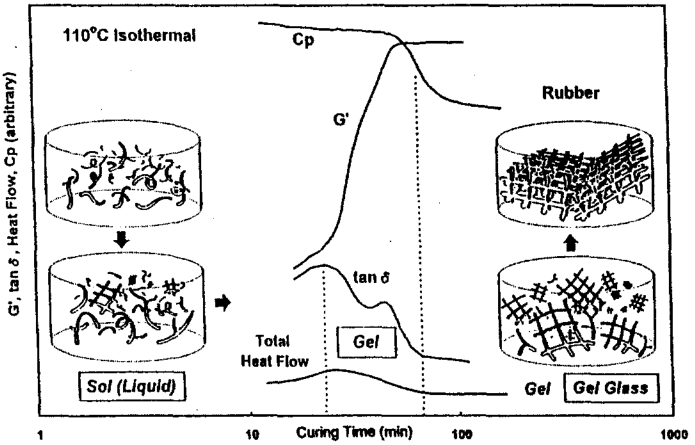


Fig. 3 G', tanδ, total heat flow, and heat capacity C_p for the quasi-isothermal curve of YX/PN/TPP at 110°C and the structrures of YX/PN/TPP at sol (liquid), gel, gel, glass, and rubber states

Figure 3 shows the changes in G', tanδ, total heat flow and C_p when the sample was isothermally cured at 110°C. After tanδ reaches the first peak, the total heat flow shows a peak, and G' increases rapidly, but no significant change is seen in the C_p curve. After the sample begins to vitrify at a frequency of 10 rad s^{-1}, C_p begins to exhibit a stepwise decrease. The vitrification point measured by DDSC appears later than that measured by DMA because of the difference in frequency.

The structures of sol, gel, gel glass and rubber are also shown. The images for the structures are as follows: The sol consists of monomers, oligomers and a limited network structure. If the monomers and oligomers are compared to a solvent and the network structure is compared to a solute, the sol state resembles a solute being dissolved and floating in the solvent. Gel is formed at the gelation point when the network structure begins to expand and the branches of the network are in contact with each other, and the sample transforms from a viscous substance to a visco-elastic one. Therefore, the gel state is similar to a solute being dissolved and expanding in the solvent. The network density then increases with time and the molecular movement begins to freeze at the vitrification point, even though the reaction is not finished. It is in a gel glass state.

When the curing temperature is above $T_{g\infty}$, the cure reaction takes place rapidly and the sample changes into a rubber state. The rubber seems to have only a network structure, without monomers and dimers, so it is like a solute with no solvent.

Figure 4 shows T_g and the extent of conversion *vs.* curing time at 110°C for the sample. The conversion rises linearly with time, but T_g initially remains almost

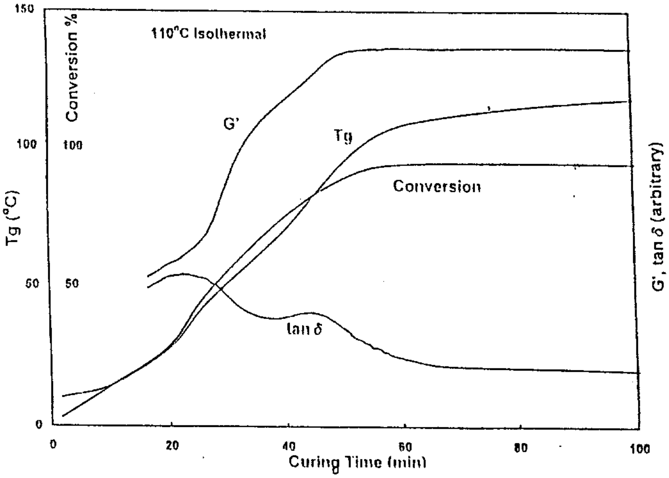


Fig. 4 Extent of conversion, T_g, G', and tanδ *vs.* curing time at 110°C for YX/PN/TPP

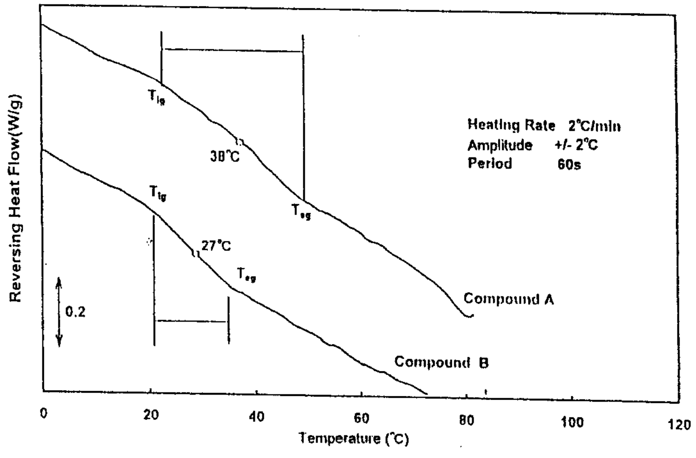


Fig. 5 Reversing heat flow *vs.* temperature for epoxy resin molding Compounds A and B

constant, and rises with time only subsequently. The conversion remains almost constant after 50 min, but T_g increases slightly. Since the network structure density increases with time, it seems that T_g is more sensitive to the change in the network structure than to that in the conversion.

Two kinds of industrially used epoxy resin molding compounds, Compound A and Compound B, which had fillers with the same resin, hardener and catalyst as the above sample, were made under different manufacturing conditions. Figure 5 shows the reversing heat flow *vs*. temperature for Compounds A and B. The extrapolated onset temperature of glass transition, T_{ig}, and the end temperature of glass transition, T_{eg}, for the compounds were measured by DDSC at 2.0°C min^{-1} and ±2.0°C/60 s. T_{ig} is the temperature at the intersection of the straight line formed by extending the baseline on the low-temperature side to the high-temperature side and the tangent drawn to the curve showing a stepped change of glass transition at the point of maximum gradient. T_{eg} is the temperature at the intersection of the straight line formed by extending the baseline on the high-temperature side to the low-temperature side and the tangent drawn to the curve showing a stepped change of glass transition at the point of maximum gradient. As a result, Compound A has a wider T_g range than that for Compound B.

Figure 6 shows the TTT cure diagram for the sample on the basis of these measurements. The gelation curve corresponds to the iso-conversion curves in terms of reaction progress. The positions of the two compounds in the TTT cure diagram were determined. As the temperature of the process was around 110°C, the extent of conversion was determined through the relationship between T_g and conversion at 110°C. The positions of the two compounds were then plotted in the TTT cure diagram. As a result, part of Compound A gelled. Therefore, some parts of Compound A seem to have been in the production process for a longer time than Compound B. It was very difficult to estimate the heat history of the compounds during

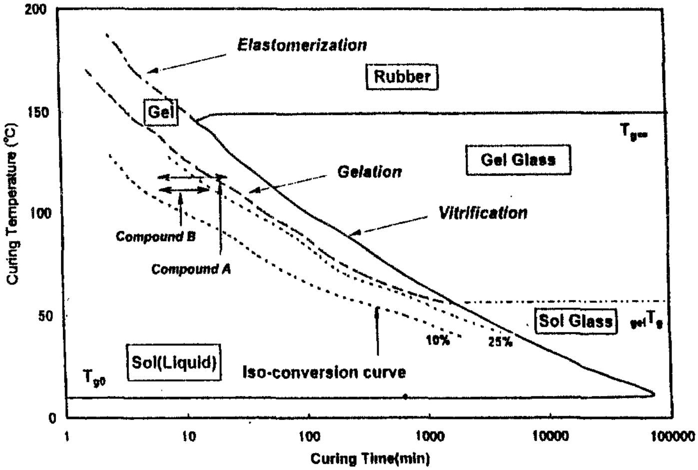


Fig. 6 Time–temperature transformation (TTT) cure diagram for YX/PN/TPP. Locations indicated for Compounds A and B show their curing state on the TTT cure diagram

the manufacturing process, but with the TTT cure diagram it is possible to recognize their differences and to estimate their heat history. It suggests that if a diagram is made for the sample including the fillers and additives in addition to the resins, it will be more accurate.

Conclusions

Through the use of DDSC and DMA, an isothermal TTT cure diagram can be made for a solid-state sample without its dissolution in a solvent. The TTT cure diagram is useful for determining the differences between epoxy resin molding compounds and for estimating their heat history during the production process.

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