

# Torsional Braid Analysis and Gelation in Thermoset Resins

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## Synopsis

The origin of the two damping maxima observed during curing of thermoset resins by torsional braid analysis has been studied using a standard epoxy resin. The first peak is not caused by gelation of the resin, but is due to certain flow phenomena prior to gelation. This first peak always occurs at approximately the same viscosity and is observed only when a fiber braid is used as support. It is therefore, in principle, not possible to detect gelation by torsional braid analysis. The second (vitrification) peak is correct, but it is indicated somewhat too early.

## INTRODUCTION

Torsional braid analysis (TBA) is a special kind of mechanical spectroscopy developed by Gillham.<sup>1</sup> It is widely accepted to characterize the curing behavior of thermoset resins. A fiber braid support is impregnated with resin and forced into torsional vibrations. Resin related transitions during curing are then detected by monitoring time-dependent changes in damping characteristics at constant temperature.

Two damping maxima are observed by TBA during isothermal monitoring of thermoset cure. The first is attributed to gelation of the resin, and the second to vitrification (the transition from the liquid or rubbery state to a glass). These data are the basis for TTT (Time-Temperature-Transformation) diagrams<sup>2-4</sup> and are recommended for quick and convenient evaluation of processing parameters.

Some uncertainty, however, arises from the nature of the first TBA peak, which is attributed to gelation of the resin. Gelation on a molecular level according to Flory is the incipient formation of an infinite network during curing. At this point the system changes its macroscopic properties, and the formation of insoluble material is observed. However, for practical purposes gelation is often defined on a macroscopic scale as the time to reach a definite viscosity.

The assumption that the first TBA peak is due to gelation is supported only by a rough correlation between TBA-peak times and gel time data obtained by other methods. The data reported in the literature, however, are somewhat conflicting. In some cases good correlation between TBA and other methods has been reported,<sup>5</sup> but in others considerable deviation.<sup>6</sup> Unfortunately, an experimental check as to whether this first TBA peak is in fact due to gelation has never been reported in the literature.

This, of course, must be confirmed if these data are to be used for processing criteria. Thus an experimental study was carried out to clarify the origin of the first TBA peak.

## EXPERIMENTAL

The material used was a standard commercial epoxy (Epikote 828) cured by 4,4'-diamino-diphenylsulfone (Ciba-Geigy). The resin was first degassed under vacuum at 120°C, mixed with a stoichiometric amount of DDS (NH/epoxy ratio = 1/1) and stirred until a clear solution was obtained. It was then quickly cooled and stored in a freezer to prevent further reaction. The glass transition temperatures were measured by DSC (20°C/min, midpoint). TBA measurements were performed using a commercial instrument supplied by Plastics Analysis Instruments (Princeton, NJ).

## RESULTS

The study reported here is based on the following concept: If the first TBA peak is in fact due to gelation, then the degree of cure or the glass transition temperature at the first TBA maximum must remain constant, independent of cure temperature. According to Flory, gelation depends only on the functionality and stoichiometry of the components, but not on experimental conditions such as cure temperature.

The measurements were performed as shown in Figure 1. A test run was first carried out up to vitrification to assure that both TBA peaks could be well resolved and identified. The experiment was then repeated until the first maximum was reached, then quenched and analyzed. It was repeated again (with a new sample), run to the second maximum, and again quenched for analysis.

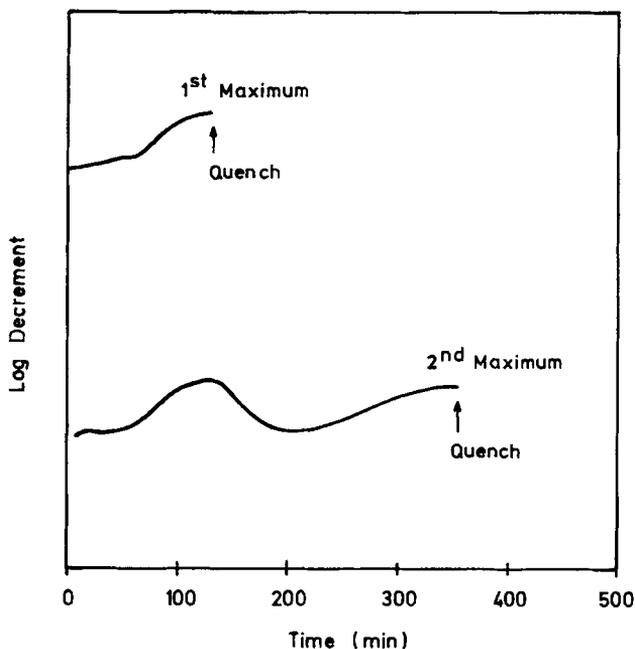


Fig. 1. Basic concept to clarify the origin of the TBA maxima.

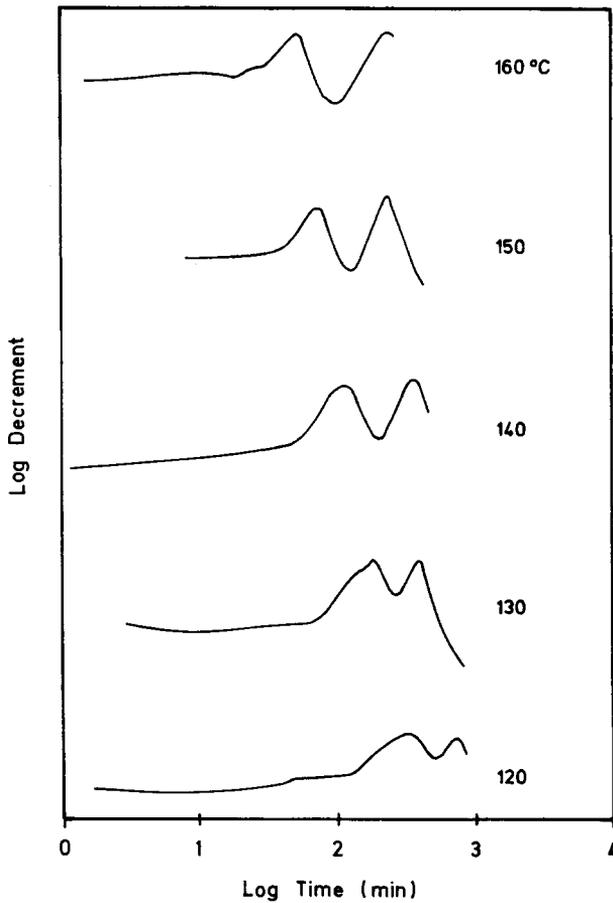


Fig. 2. Isothermal TBA traces using a glass fiber braid as resin support.  $T = 120\text{--}160^\circ\text{C}$ .

Due to the small sample size, the glass transition temperature obtained by DSC was used to characterize the degree of cure. This is allowed because the glass transition temperature of a given system depends only on the degree of cure.

If the first TBA maximum is caused by gelation, then all samples quenched at the first maximum should have the same glass transition temperature. In contrast, the glass transition temperatures of the samples quenched at the second (vitrification) peak should depend on cure temperature. They should thus increase with increasing cure temperature.

Figure 2 shows the complete TBA traces over the whole temperature range studied ( $120\text{--}160^\circ\text{C}$ ). In all cases, both TBA maxima are well resolved and sufficiently narrow providing easy determination of the maxima as points for quenching during the subsequent runs.

Figure 3 shows the glass transition temperatures of the samples after quenching. The glass transition temperatures of the samples quenched at the second (vitrification) peak increase as expected with increasing cure temperature. However, they are in general about  $10\text{--}15^\circ\text{C}$  higher than glass transition temperatures determined by other methods or criteria such as DSC or  $G''$

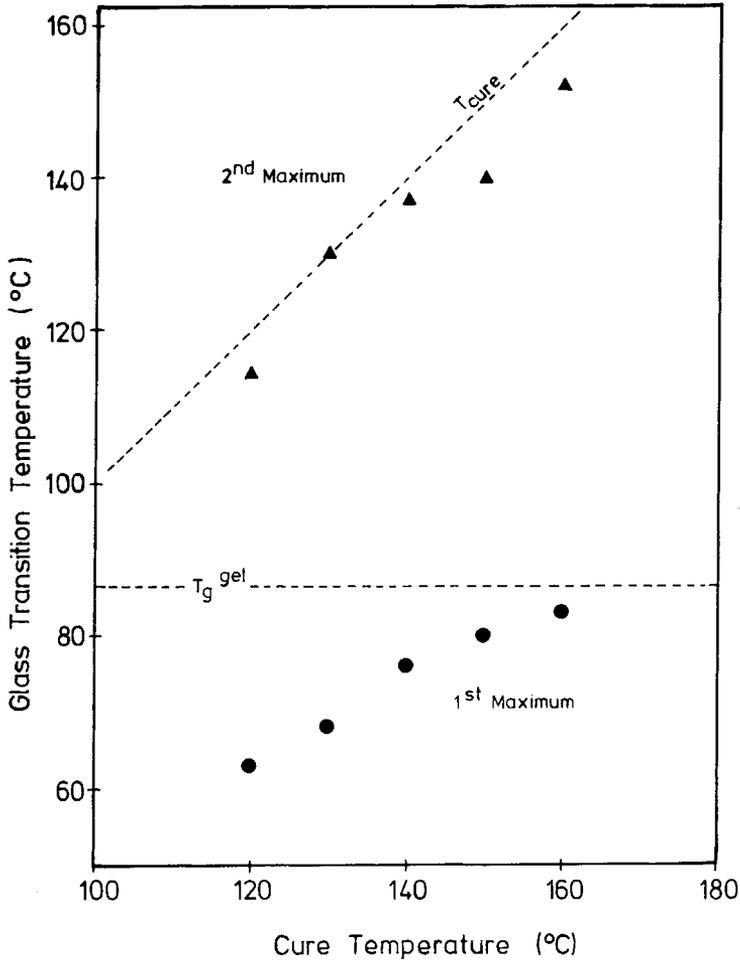


Fig. 3. Dependence of the glass transition temperatures at both TBA maxima on cure temperature.  $T = 120\text{--}160^\circ\text{C}$ .

maximum (loss modulus). Thus vitrification is indicated somewhat too early by TBA using damping maximum. These deviations, however, are not severe and can be tolerated.

However, the glass transition temperatures of the samples quenched at the first TBA maximum (the gelation peak) also depend on the cure temperature and are always lower than the true glass transition temperature at gelation ( $T_{g\text{ gel}} = 86^\circ\text{C}$ ), which was known from a different study.<sup>7</sup>

This result cannot be incidental, because it is well reproducible, and experiments with two other commercial resins led to the same results. The glass transition temperatures at the first TBA peak are always lower than the true glass transition temperature at gelation. These data indicate that the first TBA peak is not caused by gelation, but rather due to an event which always occurs prior to gelation when the resin is still a viscous liquid.

In order to confirm this, a control experiment was performed in which a silicone rubber hose (1 mm inside diameter) was used in place of the fiber

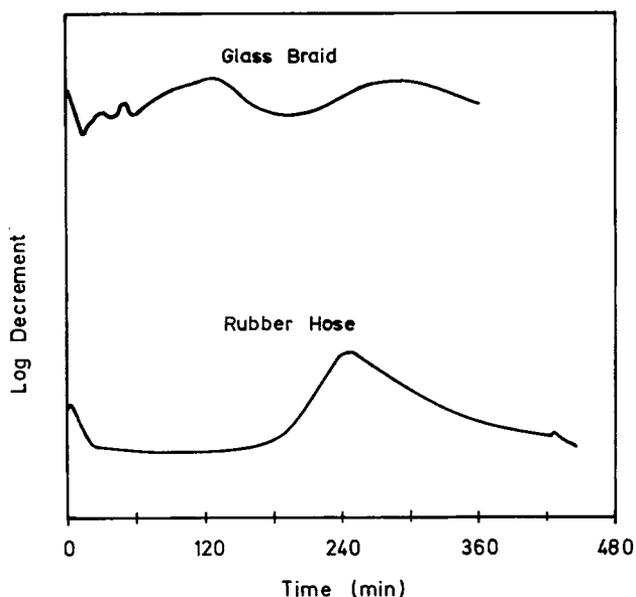


Fig. 4. Comparison of the TBA traces with fiber braid and rubber hose as resin support.  $T = 140^{\circ}\text{C}$ .

braid as the resin support. If this TBA peak is related to gelation, it must be present with both the rubber hose and the fiber braid, because gelation is independent of the experimental arrangement. The results are shown in Figure 4.

When the glass braid is used as the resin support, both TBA peaks are present. With the rubber hose, however, the first peak disappears and only the second (vitrification) peak is observed. Its shift to shorter times compared to the braid experiment is due to resin advancement during sample preparation (epoxy conversion 13.5%), so the time to reach vitrification is shortened.

It can be concluded from the data discussed so far that the first TBA peak is not related to gelation of the resin itself. It seems to be an event specific for the composite from both the fiber braid and the resin. Because of some concern that this peak might be more viscosity related,<sup>8</sup> the increase in viscosity with time was followed. The corresponding increase in  $T_g$  was obtained from DSC by sampling at certain time intervals.

By comparison with the corresponding  $T_g$ -time curves the end points of the viscosity curves could be chosen so that the glass transition temperatures (and therefore the epoxy conversions) were the same as those in the TBA experiments. The results are shown in Figure 5.

All of the curves shown in Figure 5 end at approximately the same viscosity (6000–8000 mPa s), independent of the temperature. The somewhat different times compared to the TBA times may be due to differences in reactivity, because another resin batch was used. Thus the first TBA peak is not related to gelation of the resin, but represents an isoviscous state during curing.

The results obtained here indicate that the first TBA peak may be explained by certain flow phenomena of the resin between the fibers during

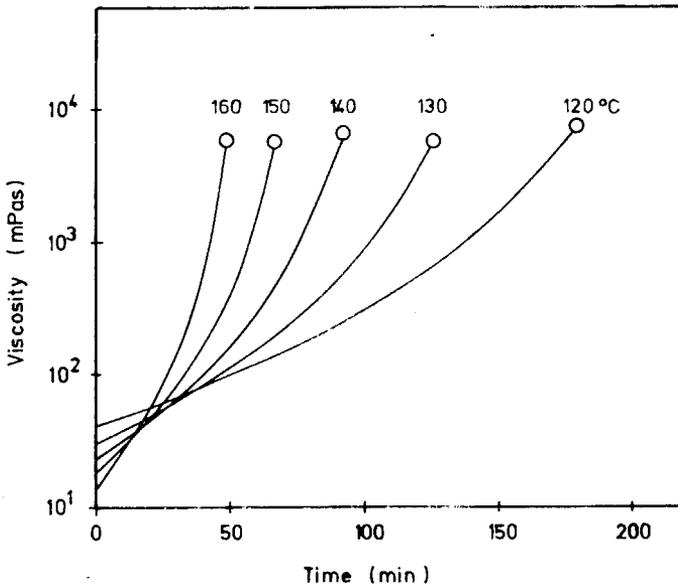


Fig. 5. Isothermal viscosity changes during curing. (End points chosen such that the glass transition temperatures are equal to the corresponding glass transition temperatures at the first TBA maxima.)  $T = 120\text{--}160^\circ\text{C}$ .

oscillation. If the resin-impregnated glass braid is forced into vibration, the liquid resin can reduce mechanical stresses by flow processes between the fibers. These flow processes are viscosity-dependent and decrease with time.

At a certain time, however, a state is reached where the relaxation time for viscous flow becomes equal to (half) the period of oscillation. At this point the viscous flow ceases, and the whole oscillating system from glass braid and resin changes its damping characteristics. This change gives rise to the observed maximum in damping.

The observed dependence of the glass transition temperature at the first TBA maximum on cure temperature (Fig. 3) may be explained in the same way. The viscosity decreases (at comparable degree of cure) with increasing cure temperature; so a higher conversion is required to compensate for this and to once again reach the viscosity limit where the flow phenomena are inhibited.

### CONCLUSION

From the data reported here it may be concluded that it is in principle not possible to detect gelation by torsional braid analysis. The first TBA maximum, which previously had been interpreted as gelation, represents an isoviscous state. It is caused by certain flow phenomena of the resin between the fibers and therefore can only be observed using a fiber braid as support. The interpretation of the second peak (vitrification) is correct, although it is indicated somewhat too early, such that the glass transition temperatures at the second TBA maximum are still about  $10^\circ\text{C}$  lower than the cure temperatures.

### References

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