

# Dynamic Mechanical Analysis of Bismaleimidodiphenyl Methane and Diallylbisphenol-A Crosslinked Polymers

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## Synopsis

Crosslinked compositions prepared from bismaleimidodiphenyl methane and diallylbisphenol A in the weight ratio of 0.99 to 1.31 have been subjected to dynamic mechanical thermal analysis (DMTA). The glass transition temperatures of all these fully cured compositions are above 300°C. The stoichiometry of the reactants in the above range does not change the thermal degradation pattern of these crosslinked polymers. DMTA shows that there is a very small decrease in storage modulus at room temperature with increasing amount of diallylbisphenol A. The glass transition temperature decreases slightly as the amount of diallylbisphenol A increases; the  $T_g$  range is 330–339°C.

## INTRODUCTION

Earlier research on high temperature polymers concentrated primarily on thermal stability and paid little attention to processability and price. However, for a polymer to be successful as a structural matrix, it must exhibit a favorable combination of processability, performance characteristics, and price. A desirable high temperature polymeric system for composites and adhesives applications must exhibit adaptability to conventional processing techniques at low temperature and pressure and should exhibit good mechanical properties, acceptable repairability, durability, and cost-effectiveness.

Recent work on high temperature polymers shows that polyimides provide higher temperature capability than do epoxy resins.<sup>1</sup> The severe conditions (high temperatures and pressures) required for processing of polyimides has limited their use. In addition, many polyimide compositions are based upon condensation chemistry, which tends to result in the formation of voids in cured compositions, be they composites, adhesives, or coatings. In general, it is very difficult to fabricate high quality structural components using these materials.

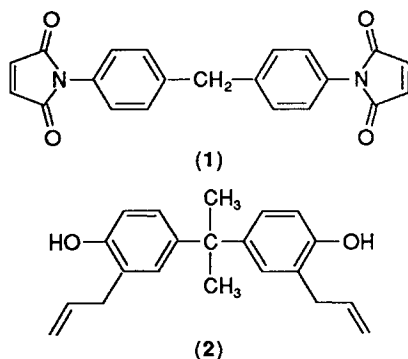
Bismaleimide compositions provide void-free composites. These materials have temperature capability higher than that of epoxies but lower than that of polyimides. Composite materials based on graphite-filled bismaleimide display good thermal mechanical properties. However, most commercially available systems lack good weatherability and are very brittle. Zahir and Renner<sup>2</sup> have reported bismaleimide diallylbisphenol A compositions that offer easy processability and high glass transition temperature- ( $T_g$ ) cured networks. The physical properties of these polymers indicate that they are suitable for high performance composite applications.<sup>3,4</sup> It was found that higher ratios of the

bismaleimide component provided better overall physical properties of the cured composition. However, higher ratios of diallylbisphenol A offered lower viscosity and hence easier processability. In this study we investigated the effect that changing the ratio of reactants has on the modulus and the  $T_g$  of the cured compositions.

## EXPERIMENTAL

### Materials

Bismaleimidodiphenyl methane (**1**) was obtained from Ciba-Geigy Corporation. It is a commercial-grade yellow powder containing greater than 85% of theoretical maleimide double bond content. Diallylbisphenol A (**2**) is also a Ciba-Geigy product. It is a commercial-grade amber-colored viscous liquid at room temperature and its hydroxyl content is typically greater than 0.62 eq/100 g (0.66 eq/100 g theoretical).



Scheme 1.

### Sample Preparation

Bismaleimide **1** and diallylbisphenol **2** (Table I) were heated in a beaker at 150°C with continuous stirring to obtain a homogeneous melt. The melt was placed in aluminum pans at 150°C for 1 h and then at 240°C for 5 h.

TABLE I  
Properties of Selected Compositions

ID	Wt ratio <sup>a</sup>	$T_g(\tan \delta)$ (°C)	$T_d$ (TGA) (°C)
A	1.31	339	435
B	1.18	336	416
C	1.07	332	413
D	0.99	330	419

<sup>a</sup> Weight ratio of bismaleimide to diallylbisphenol A.

### Thermal Characterization

Thermal decomposition of the polymers was studied with a DuPont 990A thermal gravimetric analyzer (TGA); the initial softening points were determined with a DuPont 943 thermal mechanical analyzer (TMA) employing the penetration mode with a heating rate of 10°C/min.

The tensile storage modulus,  $E'$ , and loss tangent,  $\tan \delta$ , were determined using a Polymer Laboratories Dynamic Mechanical Analyzer (DMTA) in the dual-cantilever beam mode. The sample was subjected to small amplitude oscillating flexure at 0.1, 1.0, and 10 Hz while the temperature was increased from 50 to 400°C at 1°C/min.

### RESULTS AND DISCUSSION

Polymerization of (1) and (2) proceeds via more than one mechanism to produce highly crosslinked networks.<sup>3-5</sup> The TMA of sample A (Table I) showed a small transition at 340°C (Fig. 1); the temperature may correspond to the glass transition temperature of the network. Heating the sample for longer times (6 h) did not raise this transition temperature. The same composition when cured for shorter intervals of time had shown lower temperature transitions (Fig. 2). Differential scanning calorimetry displayed no detectable exotherm after the samples were cured for 5 h. Hence 5 h was selected as the cure time for additional comparisons.

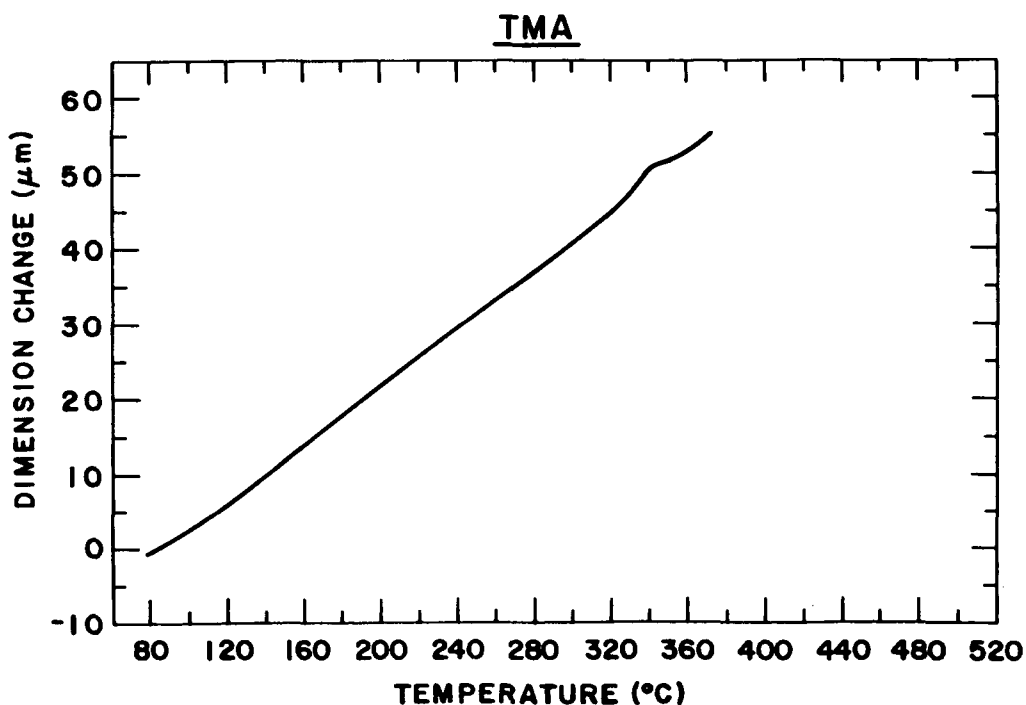


Fig. 1. Thermal mechanical analysis of composition A (Table I).

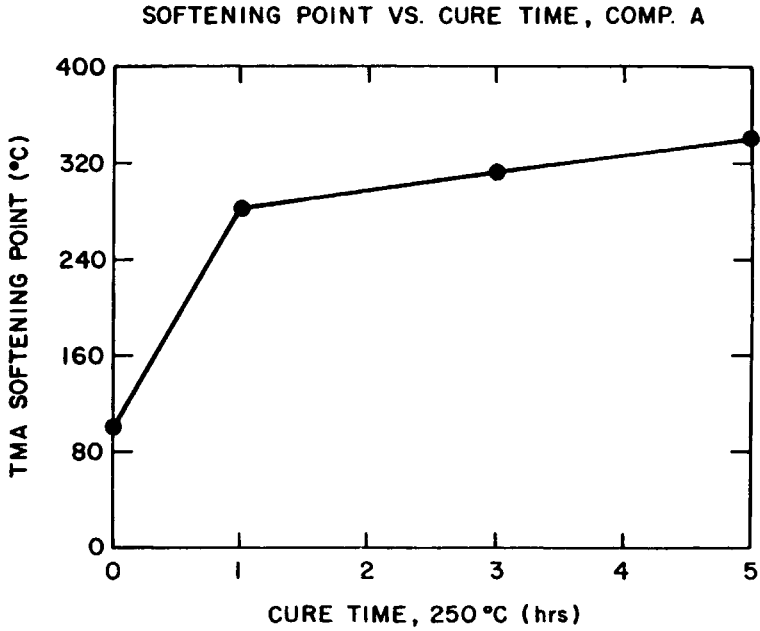


Fig. 2. Softening points (TMA) of composition A cured for various time intervals.

Since the materials are highly crosslinked and show only small transitions in TMA, dynamic mechanical measurements were undertaken for a more detailed investigation of glass transition behavior. Tensile storage modulus is

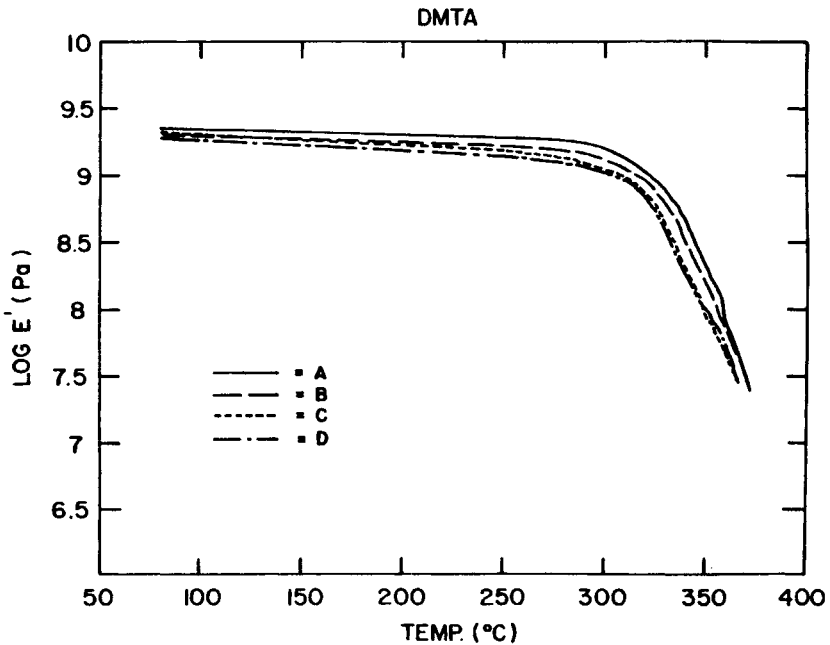


Fig. 3. Dynamic mechanical thermal analysis ( $\log E'$  vs. temperature) of compositions A-D.

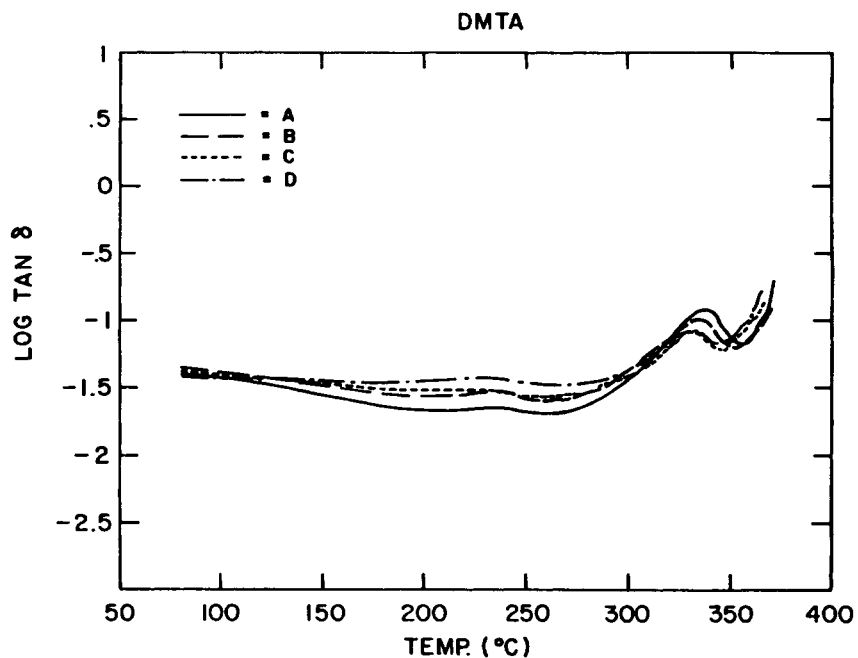


Fig. 4. Dynamic mechanical thermal analysis ( $\log \tan \delta$  vs. temperature) of compositions A-D.

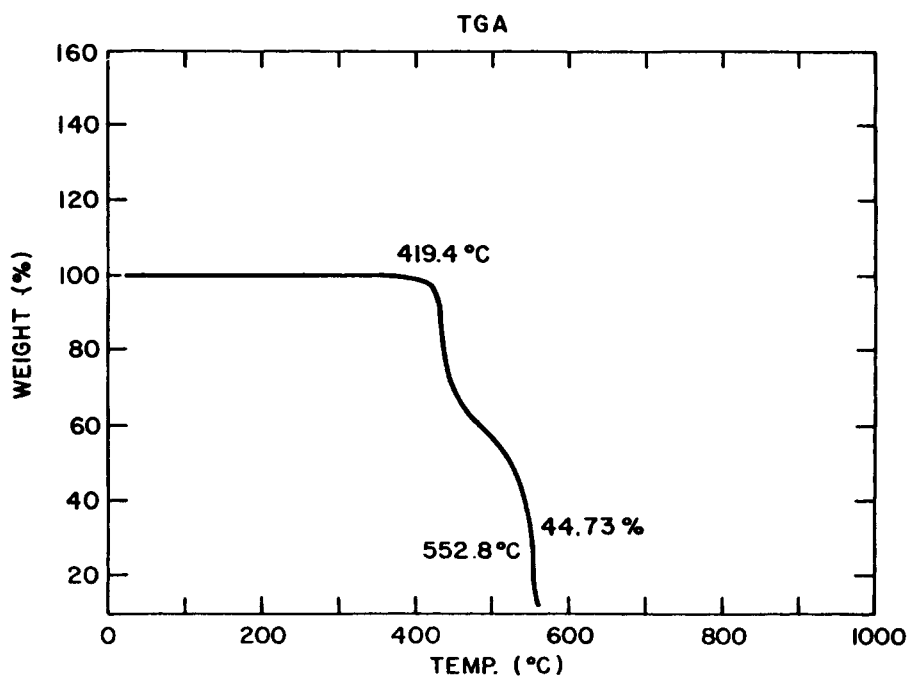


Fig. 5. Thermal gravimetric analysis of composition D in air.

found to decrease only slightly below  $T_g$  with increasing amount of diallylbisphenol A (**2**) (Table I). Similarly,  $T_g$  (as approximated by the location of the loss tangent maximum at 1 Hz) decreases only slightly with increasing amounts of (**2**) (Table I).

The loss tangent shows a broad, shallow maximum centered at about 230°C. The height of this maximum increases with decreasing bismaleimide/diallylbisphenol ratio; simultaneously, the principal transition centered at 330 to 340°C becomes broader and shallower (Figs. 3 and 4). These changes suggest that the network becomes more heterogeneous as the amount of bismaleimide is reduced. The cure of these compositions involves a number of reactions, and more than one type of network may be formed.<sup>5</sup>

It is possible that some additional reaction may take place during the measurement of dynamic mechanical properties; how much is difficult to assess. The compositions are exposed to temperatures above the postcure temperature of 240 for about 90 min before  $T_g$  is reached. It should be noted, however, that DSC reveals no remaining exotherm after the normal cure schedule and that addition of a 1-h bake at 300°C to the normal bake schedule did not change the transition temperature observed in TMA. Samples run to temperatures above  $T_g$  in the dynamic mechanical experiment tended to exhibit some thermal degradation (the sharp increase in loss tangent and drop in modulus at temperatures above about 360°C coincides with the onset of visible degradation of the samples).

Thermal degradation of the compositions was not appreciably affected by the change in reactant ratio (Table I). A TGA obtained in air on the composition with the highest amount of diallylbisphenol A (Sample D, Table I) is shown in Figure 5. There is no weight loss up to approximately 400°C. Up to approximately 550°C, nearly 45% of the polymer is left as residue.

## CONCLUSIONS

In the weight ratio of 0.99–1.31 of bismaleimide to diallylbisphenol A, the glass transition temperature of the fully cured polymer is essentially independent of the reactant ratio. The thermal stability in air also does not change with the change in composition. Thermal stability and high modulus retention at elevated temperatures indicate that these compositions are potentially suitable for high performance composites, adhesives, and coatings.

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