

# Frontal Curing of Epoxy Resins: Comparison of Mechanical and Thermal Properties to Batch-Cured Materials

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**ABSTRACT:** The epoxy resin diglycidyl ether of bisphenol F (DGEBF) was cured by the aliphatic amine curing agent Epicure 3371 in a stoichiometric ratio both frontally and in a batch-cure schedule. Glass transition temperatures ( $T_g$ ) were determined using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). DMA also was used for studying the storage modulus ( $E'$ ) and tan delta ( $\tan \delta$ ) of the cured samples. Tensile properties of epoxy samples were tested according to ASTM D638M-93. The properties of the frontally cured epoxy resin were found to be very close to that of batch-cured epoxy resin. Velocity of cure-front propagation was measured for both neat and filled epoxy. Rubber particles (ground tires) were used as a filler. The maximum percentage of filler in the epoxy resin allowing propagation was 30%. Because of convection, only descending fronts would propagate. Advantages and disadvantages of frontal curing of epoxy resins are discussed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1209–1216, 1997

**Key words:** frontal polymerization; frontal curing; propagating fronts; epoxy

## INTRODUCTION

Frontal polymerization is a mode of converting monomer into polymer via a localized reaction zone that propagates, most often through the coupling of thermal diffusion and Arrhenius reaction kinetics. Frontal polymerization was first discovered in Russia by Chechilo and Enikolopyan in 1972.<sup>1</sup> They studied methyl methacrylate polymerization to determine the effect of initiator type and concentration on front velocity<sup>2</sup> and the effect of pressure.<sup>3</sup> A great deal of work on the theory of frontal polymerization was performed.<sup>4–9</sup> Work

was also done with epoxy curing.<sup>10</sup> The literature up to 1984 was reviewed by Davtyan et al.<sup>11</sup>

Pojman and his coworkers demonstrated the feasibility of traveling fronts in a variety of neat monomers at ambient pressure<sup>12–14</sup> and with a solid monomer.<sup>15</sup> Recently, Pojman et al. demonstrated that a thermochromic composite, that is, a material whose color is temperature dependent, could be prepared better via frontal polymerization than with traditional homogeneous methods because the rapid front prevented sedimentation.<sup>16,17</sup> Szalay et al. reported conductive composites prepared frontally.<sup>18</sup> The macrokinetics and dynamics of frontal polymerization have been examined in detail,<sup>19</sup> and applications for materials synthesis considered.<sup>20</sup>

Frontal curing of epoxy resins with amines was first reported in 1975 but without any mechanical characterization.<sup>9,21</sup> White recently developed two continuous curing processes for producing graphite fiber composites with prepregs.<sup>22,23</sup>

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There are potential advantages to using a frontal method, the major ones being the speed at which a sample can be cured, the lack of an autoclave, and the avoidance of charring from thermal run away. In this work we consider the frontal curing of an epoxy resin, EPON 862, with and without filler to determine the quality of the product produced compared to batch curing and the effects of convection on front propagation.

## ACHIEVING FRONTAL PROPAGATION

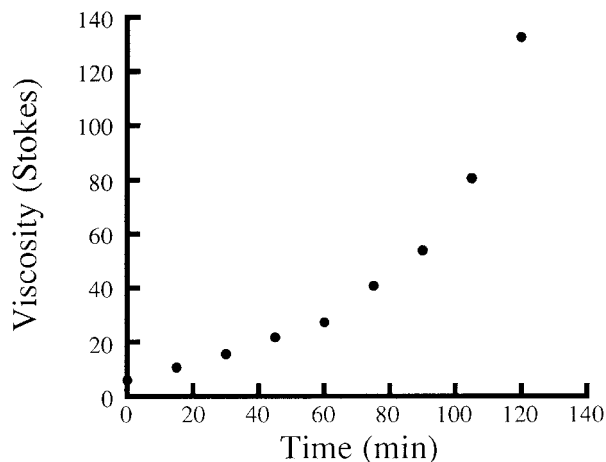
A selection of an epoxy system that will maintain front propagation at room temperature is a difficult problem because several parameters of the system should be satisfied to assure front propagation: low reactivity of the system at room temperature, high effective activation energy, and enthalpy of the cure reactions. The ideal system is one that has an infinite pot life at room temperature but has a high energy of activation so the rate is very high at elevated temperatures. Also, the rate of reaction must be sufficiently high and the exothermicity great enough to overcome heat losses. Thus, small samples with high surface area-to-volume ratios may quench, although a larger sample will support propagation.

We tried several epoxy systems mixed in stoichiometric amount with aromatic amines. However, the reactivity of such systems at room temperature was very low, and we could not ignite the front. Most of the aliphatic amines are very reactive at room temperature, and soon after the front initiation homogeneous curing of the sample occurs. We found the amine curing agent Epicure 3371 is not very reactive at room temperature; the resin gels only after 120 min at room temperature cure (Fig. 1).

The epoxy monomer diglycidyl ether of bisphenol A (DGEBA) was previously cured frontally with a boron trichloride/amine complex ( $\text{BCl}_3\text{—NR}_3$ ) from Ciba-Geigy but only with very large amounts (20–40%).<sup>19</sup> A combination of aliphatic amine and boron trichloride/amine complex was used in the frontal preparation of interpenetrating polymer networks.<sup>24</sup>

## MATERIALS

The epoxy resin diglycidyl ether of bisphenol formaldehyde (DGEBA, EPON 862, Shell) was cured in its stoichiometric ratio with the aliphatic



**Figure 1** Determination of the pot life of EPON 862 with EPICURE 3371.

curing agent (Epicure 3371, Shell). The epoxy equivalent weight of DGEBA was 166–177, as indicated by the manufacturer. The percentage of amine in the total system was 14% by weight. Both components were transparent liquids at room temperature. The two components were mixed with a magnetic stirrer at room temperature. After 10 min of vigorous mixing the resin/amine solution was degassed under vacuum for 5 min.

Tire powder (GF-200 from Rouse Rubber Industries, mean particle size of  $44\ \mu$ ) was used as a filler.

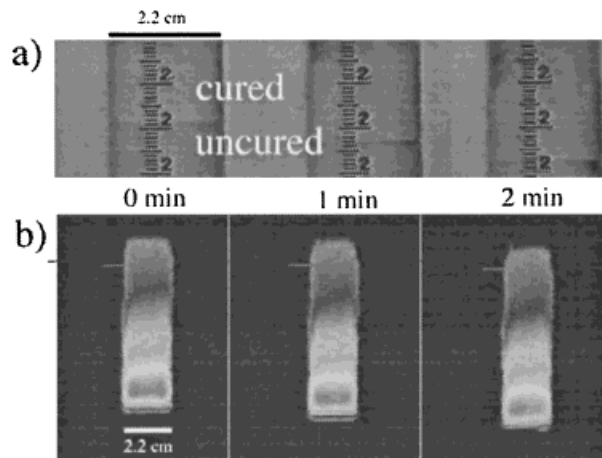
## EXPERIMENTAL PROCEDURES

### Pot Life Determination

An amount of EPON 862 was weighed into a polystyrene cup, and the amine was added. These two were then well blended, and the proper amount was poured into a Gardner viscosity tube. The tube was then placed into a centrifuge to remove bubbles that would interfere with the test. While the tube was in the centrifuge, approximately 0.4 g of Chemie BYK-555 (BYK Chemie Additives and Instruments) was added to the remaining mixture to assist in gas release. The mixture was then placed under a vacuum to degas while viscosity testing proceeded. The viscosity was tested with the Gardner viscosity tube on 15-min intervals for 2 h.

### Preparation of Samples

The prepared epoxy system was poured into glass tubes with an inner diameter 22 mm and a



**Figure 2** (a) Visual images of descending fronts of an EPON 862/EPICURE 3371 front. (b) Infrared images of the same front.

length of 250 mm. Tubes with an inner diameter of 15 mm and a length of 120 mm were used in the part of the work where the influence of amine percentage in epoxy resin on the glass transition temperature values and front velocity were studied. The inside tube wall was treated with a release agent (Fluo-Kem, Aldrich) to aid the removal of cured samples. The front was ignited in the top part of the sample by heating the tube wall with a soldering iron. After ignition, the front propagated downward, and its position was visually determined as a function of time. All frontal experiments were performed at ambient temperature without additional heating.

The schedule for the batch curing was a typical one for epoxy resins cured by aliphatic amines: 24 h at room temperature, 3 h at 70°C, and 3 h at 120°C.<sup>25</sup>

A temperature profile of the front was measured by using a thermocouple (TMQSS-020G-6, Omega) at a point 6 cm below the ignition point where the front had reached a constant velocity. The temporal profile was converted to a spatial one using the front velocity.<sup>13</sup>

Thermal Analysis equipment (DSC 2920, DMA 983, TGA 2050) was used for performing DSC, DMA, and Thermogravimetric Analysis data (TGA). The values of  $(T_g^\infty)_{DSC}$  were defined as the midstep point in the endothermic shift on DSC scans. Samples were 12–22 mg, and the rate of scan was 20°C/min up to 250°C under a nitrogen atmosphere. After completion of the first scan each sample was postcured at 250°C for 35 min and then cooled down to room temperature. The

second scan provided the  $T_g$  of the fully cured epoxy resin  $(T_g^\infty)_{DSC}$ .

TGA was used to measure weight loss of samples with a constant rate of heating (20°C/min) up to 1000°C. Scans were made under nitrogen atmosphere in a platinum pan.

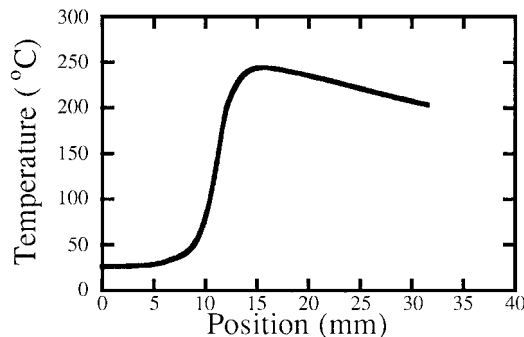
The flexible storage modulus ( $E'$ ) and tangent of mechanical loss angle ( $\tan \delta$ ) were measured by DMA with a constant rate of heating (10°C/min up to 250°C). The size of the samples was 35 × 10 × 3 mm. The frequency of flexible load was equal to 1 Hz during all heating.

Tensile properties of the epoxy resin were tested according to ASTM D638M-93 using an MTS 810 Universal Test Machine (MTS Systems). Dumbbell specimens were cut from cured samples using a jigsaw and their surfaces polished with a whetstone. Four specimens cut from two batch-cured samples and five specimens cut from three frontally cured samples were tested. The samples were loaded in displacement control, and the crosshead loading rate was equal to 5 mm/min.

Infrared images were obtained with a Radiance PM infrared camera (Amber).

## RESULTS AND DISCUSSION

Figure 2 shows a descending front with both visual and infrared imaging. The interface between the gelled and unreacted resin can barely be seen in the visible images, but the larger temperature difference between uncured and cured resin is obvious in the infrared. In the samples filled with rubber particles, no such interface is visible. Infrared imaging cannot reveal the actual front temperature profile because the camera is actually detecting the temperature of the glass. Figure 3



**Figure 3** Temperature profile of a descending front.

shows the spatial temperature distribution in the front determined with a thermocouple.

### Stability of Fronts

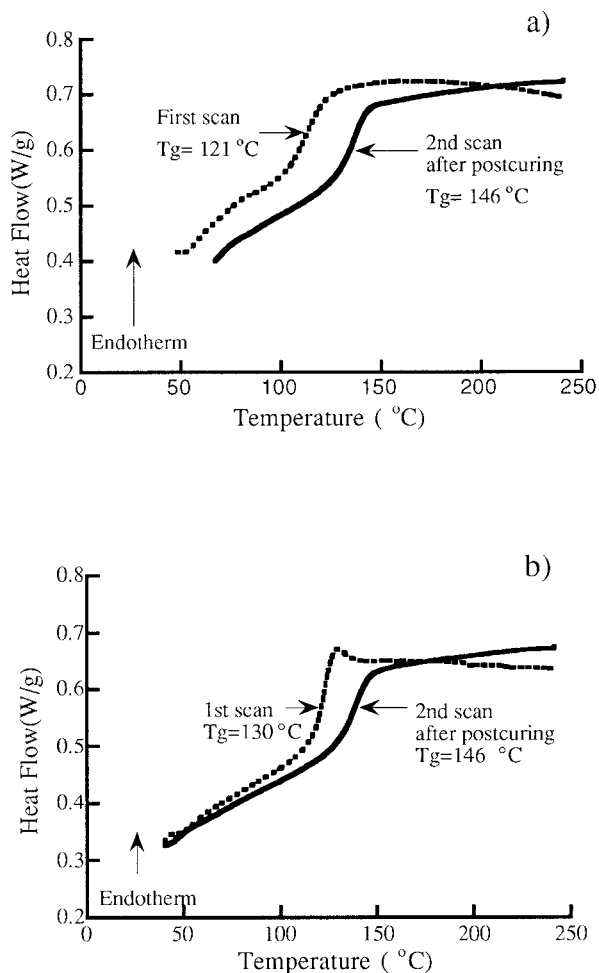
Pojman et al. found that with mono- and diacrylates, ascending, and horizontally propagating fronts were not usually stable, i.e., convection caused by the thermally induced density gradient extinguished the fronts.<sup>13</sup> Bowden et al. recently studied the critical conditions for a convection-free ascending front and found an inverse relationship between front velocity and the viscosity of the unreacted medium.<sup>26</sup> The faster the front velocity, the lower was the initial viscosity necessary to allow convection-free propagation. In our experiments, the resin with or without particles would not allow ascending front propagation. A descending front that was reoriented would stop propagating within a few minutes.

Pojman et al. found that if the rate of heat loss was increased significantly with frontal methacrylic acid polymerization, then the front could lose stability and propagate periodically in a spiral manner.<sup>27</sup> Similar behavior was found with  $\text{BCl}_3$ -amine catalyzed epoxy curing fronts in which the tube was inserted into a room temperature water bath.<sup>19</sup> Such periodic modes of propagation are undesirable for materials synthesis because of the nonuniform product that results. We tested the EPON 862/EPICURE 3371 system that was chilled to  $0^\circ\text{C}$  and then allowed to propagate surrounded by room temperature air. No periodic behavior was observed. A front propagating in a tube immersed in a room temperature water bath was also stable.

An important difference between  $\text{BCl}_3$ -amine and EPICURE 3371 is in their energies of activation. This is why the former has a very long pot life with the resin at room temperature. From the theory of thermal fronts, we know that four factors increase the likelihood of nonuniform propagation: high front temperature, low initial temperature, high energy of activation, and high rates of heat loss.<sup>19</sup> Thus, amine-cured fronts, especially with a filler, should always be stable.

### DSC AND MEASUREMENT OF TEMPERATURE PROFILE RESULTS

Typical DSC scans for frontally cured samples are presented in Figure 4(a). The second scan is for

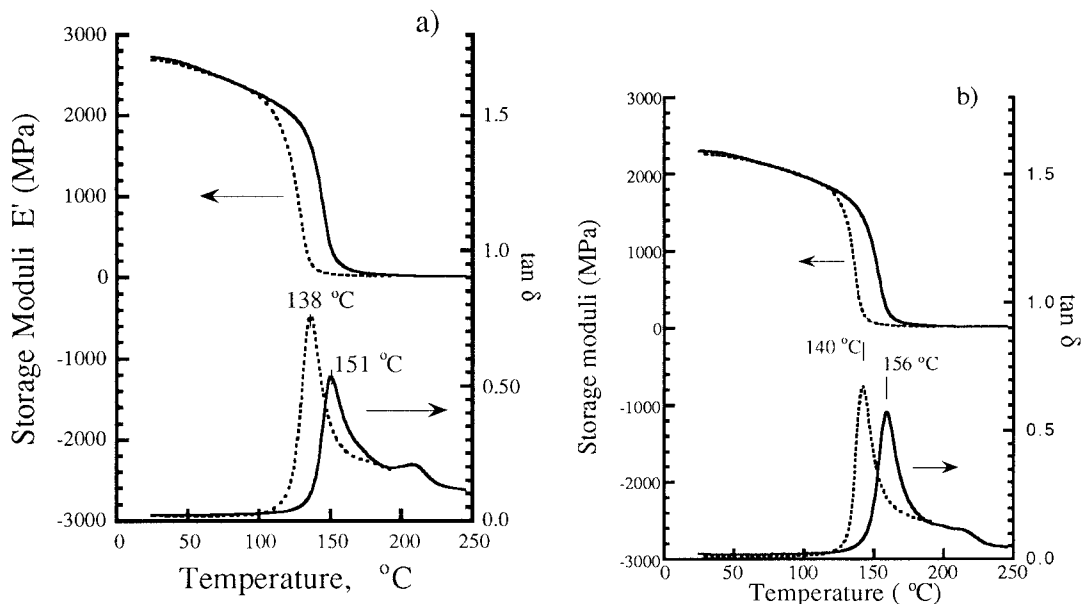


**Figure 4** (a) DSC scans of frontally cured epoxy resin. The glass transition looks like an endothermic step in the heat flow.  $T_g$  is defined as midpoint of the step. Residual heat appears as exothermic deviation in heat flow versus temperature on first scan after glass transition. (b) DSC scans of batch-cured epoxy resin.

fully cured epoxy after postcuring. The scans for batch-cured samples are presented in Figure 4(b).

Both frontally cured and batch samples show similar  $(T_g)_{\text{DSC}}$  values on the first scans (dashed lines), so conversions of the materials also are close.<sup>28</sup> Small differences between  $(T_g)_{\text{DSC}}$  and  $(T_g^\infty)_{\text{DSC}}$  values testify to nearly complete conversion both after frontal and batch curing. This is also confirmed by the small curing exotherms observed on the first scans. The equal  $(T_g^\infty)_{\text{DSC}}$  values for frontal and batch-cured samples indicate that the same epoxy network is created through both curing methods.

However, the first scans of these materials differ after the glass transition. Batch-cured samples have a small endothermic peak while frontal ones



**Figure 5** (a) Dynamical mechanical properties of frontally cured sample. Dashed line: first scan; solid line: scan after postcure. (b) Dynamical mechanical properties of batch-cured sample. Dashed line: first scan; solid line: scan after postcure.

do not. Simon and Gillham noticed that samples, which have vitrified during cure ( $T_g > T_{\text{cure}}$ ), show an endothermic physical aging peak in the vicinity of  $T_g$ .<sup>29</sup> (Physical aging occurs in a material that is in a nonequilibrium state below its glass transition.) From the DSC plots we conclude that frontal samples cured above the glass transition temperature, which is also confirmed by the temperature profile (Fig. 3).

## DMA RESULTS AND TENSILE PROPERTIES

Typical plots of the storage modulus  $E'$  and  $\tan \delta$  as functions of temperature are presented in Figure 5. In the temperature range studied one relaxation is observed that is associated with the glass transition. The maximum of  $\tan \delta$  is considered as the glass transition point and its temperature designated as  $(T_g)_{\text{DMA}}$ . Glass transition

points measured by DMA for frontal and batch-cured samples are very close to each other. The values of storage moduli  $E'$  are very close for batch and frontally cured samples (Table I), which reflects the similar degrees of cure of both samples.

It can be noticed from Table I that  $(T_g)_{\text{DMA}}$  values are greater than  $(T_g)_{\text{DSC}}$  ones. The reason is that DMA samples are larger than the DSC ones, which can lead to a delay in response during the temperature scan.

Measured tensile properties of frontally and batch-cured epoxy resins are presented in Table II. The properties of batch samples are somewhat better than frontal ones because of the higher degree of cure for the batch samples. However, it should be noted that postcuring of the frontally cured samples should produce approximately the same properties in less time than using the batch-cured cycle.

**Table I** DSC and DMA Results of Batch and Frontally Cured Epoxy Resin

Curing Method	$T_g$ DSC (°C)	$T_g^\infty$ DSC (°C)	$T_g$ DMA (°C)	$T_g^\infty$ DMA (°C)	$E'$ at 25°C (GPa)
Frontal	121 ± 2.3	146 ± 1.1	138 ± 6.4	151 ± 2.6	2.40 ± 0.25
Batch	130 ± 3.6	146 ± 1.2	140 ± 2.7	156 ± 3.5	2.35 ± 0.13

**Table II** Tensile Properties of Frontally and Batch-Cured Epoxy Resin

	Strength (MPa)	Yield Deformation (%)	Tensile Modulus (GPa)
Frontal	68.2 ± 0.8	5.15 ± 0.25	2.26 ± 0.06
Batch	75.9 ± 3.6	6.36 ± 0.27	2.36 ± 0.14

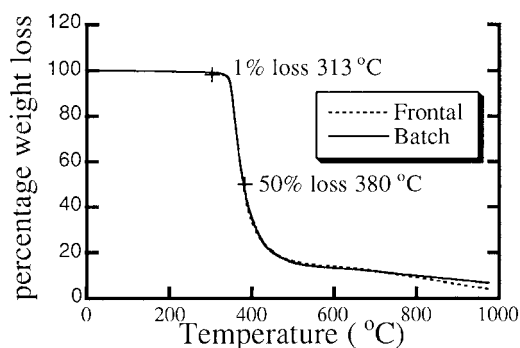
## THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric scans of two epoxies cured in batch and frontal regimes coincide in Figure 6 up to 800°C. Weight loss begins in the vicinity of 313°C, and at 380°C samples lose 50% of their weight.

## INFLUENCE OF AMINE PERCENT ON $T_g$ AND FRONT VELOCITY

It is well known that the epoxy resins cured with the stoichiometric amount of the amine have better physical and mechanical properties than those cured with the nonstoichiometric one.<sup>30</sup> However, the question arises: "Will the epoxy/amine system cured with stoichiometric ratio of the components be the best condition for front propagation?" The answer to this question will depend on how the reactivity and total heat of the epoxy system change with the changing of the amine percentage. The total heat of the curing obviously can only decrease with an excess of any component, whereas reactivity may not.

Let us consider the cure reactions in the epoxy/amine systems. There are two reactions in the curing of amine with the epoxy: between an epoxy



**Figure 6** Thermogravimetric scans of batch and frontally cured epoxy resin EPON 826 + Epicure 3371. Scan rate equals 20°C/min.

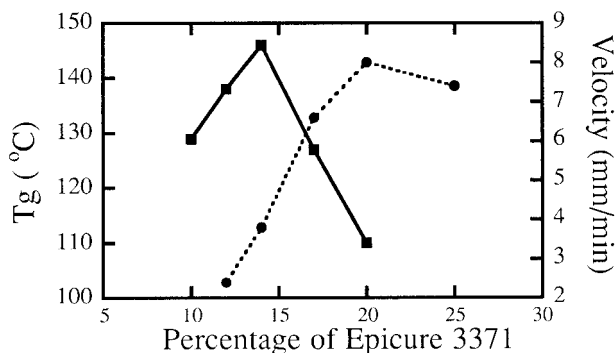
and the primary amine hydrogen to form a secondary amine, and between an epoxy and a secondary amine hydrogen to form a tertiary amine.<sup>28</sup> The rate constant of the first reaction is about two times greater than the second one, although the energies of activation for both reactions are approximately the same.<sup>31</sup> The excess of amine will increase the reactivity of the system up to a ratio of one epoxy group to one primary amine; the front velocity should also increase with increasing of fraction of amine. The experimentally measured dependence of the front velocity upon the amine fraction in Figure 7 confirms this. Amine in excess of 20% decreases the front velocity by decreasing the front temperature. These results are in agreement with earlier works.<sup>9,21</sup>

## INFLUENCE OF FILLER ON FRONT PROPAGATION

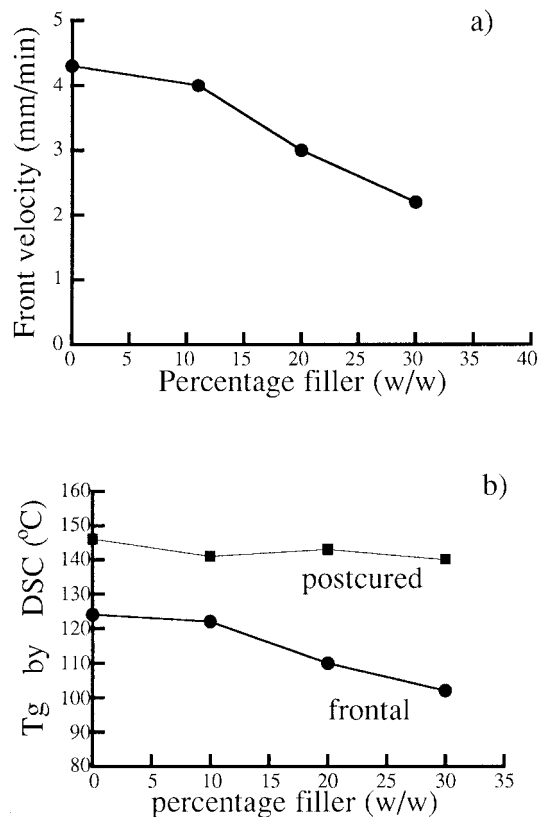
Experiments with tire powder were performed to test the application of frontal curing to filled resins. Inert filler decreases the maximum front temperature, and the front velocity decreases as well. Reduction of the front velocity causes the greater heat losses. This is the main reason of difficulties with front propagation with the filled materials.

Heat losses also depend on the geometry of the system. For tubes with a greater diameter, heat losses are less important than for tubes with a smaller diameter. Therefore, the diameter of the tube will also determine the maximum percentage of filler that allows front propagation. The influence of filler was studied on tubes with inner diameter 22 mm and wall thickness of 1.8 mm.

The front velocity linearly decreases with in-



**Figure 7** Dependence of the glass transition temperature and front velocity of the epoxy resin on variation of amine percentage by weight.



**Figure 8** (a) Influence of filler percentage on front velocity. (b)  $T_g$  of frontally cured epoxy resin filled by tire powder.

creasing amounts of filler [Fig. 8(a)], and the  $(T_g)_{\text{DSC}}$  also decreases [Fig. 8(b)]. These changes are caused by the lowering of the front temperature. Nevertheless,  $(T_g)_{\text{DSC}}$  values remain approximately constant with addition of tire powder, because the epoxy matrix is unaffected by the presence of the particles.

## CONCLUSIONS

We have studied frontally cured epoxy resins using an aliphatic amine curing agent, and for the first time compared the thermal and mechanical properties to those of samples prepared through a traditional batch-curing schedule. We conclude the following: (1) all studied properties of frontally cured epoxy resin are very close to those of batch samples, although the time of curing in former case was much less. (2) The epoxy resin cured frontally is not subject to physical aging in contrast to batch cure because most of the conversion during frontal cure is achieved at temperatures

higher than  $T_g^{\infty}$ . (3) For a specific geometry of the system it was possible to initiate a front in 30% filled epoxy resin. Larger samples could sustain higher fractions. (4) The dependence of the front velocity upon the amine curing agent concentration exhibits a maximum, which is a concentration greater than the stoichiometric amount. Samples formed at the maximum velocity exhibited a lower  $T_g$  than for the stoichiometric amount of amine.

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