

# Characterization of Epoxy Foams

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**ABSTRACT:** Epoxy foams were prepared from the commercial system (LY 5054 epoxy resin, HY 5054 amine as curing agent, and DY 5054 siloxane as foaming agent) supplied by Ciba-Geigy. From the differential scanning calorimeter results the optimal epoxy–amine ratio was determined. A maximum  $T_{g\infty}$  value of 85°C was found for an epoxy–amine ratio of 100:35 by weight. In this system, the siloxane reacts with the amine releasing hydrogen that acts as the real foaming agent. The density decreased from 490 to 215 kg/m<sup>3</sup> as the epoxy:blowing agent ratio increased from 100:1 to 100:3 by weight of the reactive mixture. Under the synthesizing conditions, the glass transition temperature

( $T_{g\infty}$ ) of the foam did not vary significantly as the blowing agent increased. The modulus and compressive strength of the foam exhibited a power-law dependence with respect to density of the form:  $E \propto (\rho)^n$ , where  $n=1.8$ . Scanning electron microscopy analysis verified that the foam have a closed cell structure. The relation between composition, final morphology, density, and properties of the foam was analyzed. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2992–2996, 2003

**Key words:** foam; mechanical properties; epoxy; blowing agent

## INTRODUCTION

Among the newer materials, structural thermoset foams have caught attention, because they combine good mechanical resistance with a low weight.<sup>1–3</sup> As well, they are extensively used by several industries. i.e., automotive, aeronautic, etc.<sup>1</sup>

In particular, epoxy foams have been recently developed due to their high thermal and chemical stability. Some technical papers of the Ciba-Geigy Company have proved that these foams can be used as matrices of composite materials.<sup>4</sup>

This subject has been partially studied in mixtures of epoxy systems with different organic solvents (hexane or cyclohexane) as the physical blowing agent. In this case, as the exothermic crosslinking reaction take place the solvent is evaporated, making the mixture blow. Using a chemical foaming agent is another alternative, in which a gas is released during the crosslinking reaction. By changing the amount of chemical foaming agent, it is possible to produce foam with different densities and properties. This is a simple, easy, and economic method for production of epoxy foam.

The aim of this work is to find the optimum composition of the epoxy–amine reactive system and the study of the relationship between composition, final morphology, density, and properties of the foam.

## EXPERIMENTAL

### Materials

The chemical system used in this work was kindly supplied by Ciba-Geigy, Basel, Switzerland). Epoxy resin (LY5054) were heated to 80°C and degassed by vacuum overnight before use. The siloxane (HY5054) and amine (DY5054) were used as received.

### Preparation of epoxy foams

The epoxy foams were synthesized with a ratio of epoxy:amine:blowing agent of 100:25–50:1–4 respectively. All possible combinations were done keeping a constant temperature of 50°C, and maintaining the foaming process free.

During the foaming process, two parallel reactions occur. A scheme of the same is shown in Figure 1. In the first reaction, the blowing agent (siloxane) reacts with amino hardeners releasing hydrogen. The hydrogen gas acts as expanding agent and the system foams out. The second reaction is the typical addition reaction between the epoxy–amine groups.<sup>5</sup>

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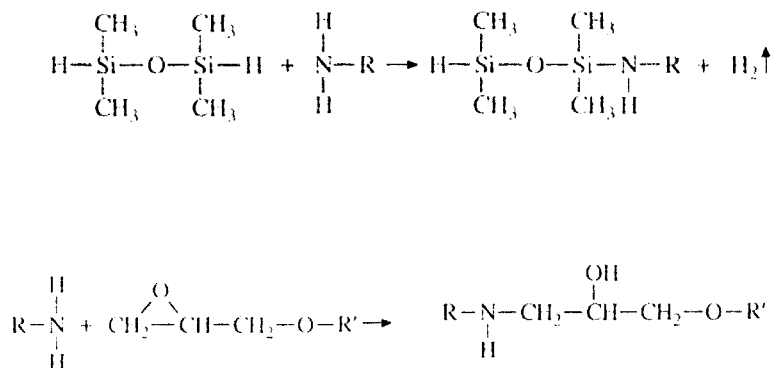


Figure 1 Scheme of the possible reactions in the epoxy:amine:siloxane system.

### Testing methods

The glass transition temperature ( $T_g$ ) was determined using a differential scanning calorimeter (Shimadzu DSC 50) at a heat rate of  $10^\circ\text{C}/\text{min}$  in nitrogen atmosphere.

A set of thin tubes (2 mm diameter) containing epoxy-amine mixtures were immersed in an oil bath kept at constant temperature. Gelation times,  $t_{\text{GEL}}$ , were measured by gently pulling a thin wire, immersed in the sample, taking  $t_{\text{GEL}}$  as the time at which the whole tube was lifted up by pulling the wire.

The apparent density of the epoxy foams was determined using cylindrical specimens with a size of  $25 \times 25$  mm (diameter and height, respectively). A compressive test was performed with an INSTRON machine following the test procedure ASTM D-1621-94. The displacements were calculated from the reading obtained with a linear variable differential transducer.

The scanning electron microscopy (SEM) photographs of the polished surface of the different foam were taken with a scanning electron microscope Philips model SEM 505. The samples were previously coated with gold. Micrographs were magnified and regions containing about 100 bubbles were analyzed. This led to the determination of the size distribution, as  $n$  (number of bub-

bles) vs  $D$  (diameter) for each formulation. The average diameter of the bubble was calculated<sup>6</sup>:

$$D_p = \frac{\sum nD}{\sum n} \quad (1)$$

## RESULTS AND DISCUSSION

### Selection of the optimum epoxy-amine relation

The glass transition temperature ( $T_g$ ) of the system without blowing agent was measured for different epoxy:amine ratios. Figure 2 shows  $T_g$  values for different weight ratios of epoxy:amine: 100:25–50. The optimum epoxy-amine ratio was found to be 100:35. With this ratio, a maximum  $T_g$  of  $85^\circ\text{C}$  was measured. A high  $T_g$  value is obtained as a result of a high crosslinking density and thus a higher rubber modulus and a major thermal stability of the foams are expected.

Gelation times for the 100:35 system at different curing temperatures are shown in Figure 3. An activation energy of  $60.5$  kJ/mol was obtained for the selected system using the following correlation:

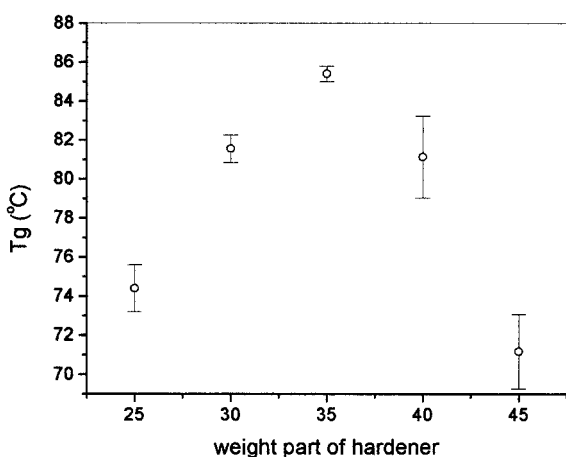


Figure 2  $T_g$  values for different epoxy:amine ratios.

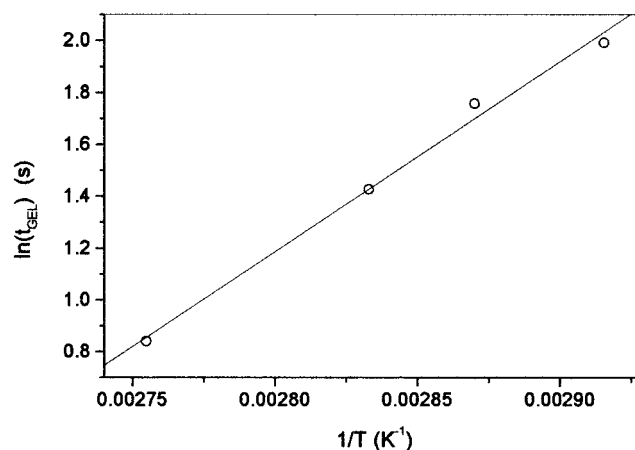


Figure 3 Gelation times for the 100:35 epoxy:amine system at different temperatures.

**TABLE I**  
 **$T_{g\infty}$  of the Epoxy Foam with Different Amounts of Foaming Agent<sup>a</sup>**

Epoxy:amine:siloxane (weight part)	$T_{g\infty}$ initial (°C)	$T_{g\infty}$ half (°C)	$T_{g\infty}$ end (°C)
100:35:1.25	92	98	104
100:35:1.50	92	98	103
100:35:1.75	90	97	103
100:35:2.00	92	97	104
100:35:2.50	92	99	104

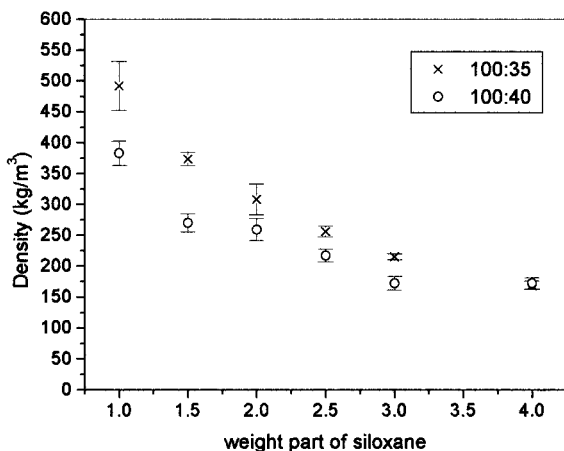
<sup>a</sup>  $T_{g\infty}$  initial or “onset” value is the temperature obtained in the first slope change,  $T_{g\infty}$  half is the temperature in the middle of the change, and  $T_{g\infty}$  is the temperature at the end of the change in the glass state.

$$\ln(t_{\text{GEL}}) = \ln(A) - \frac{Ea}{R \times T} \quad (2)$$

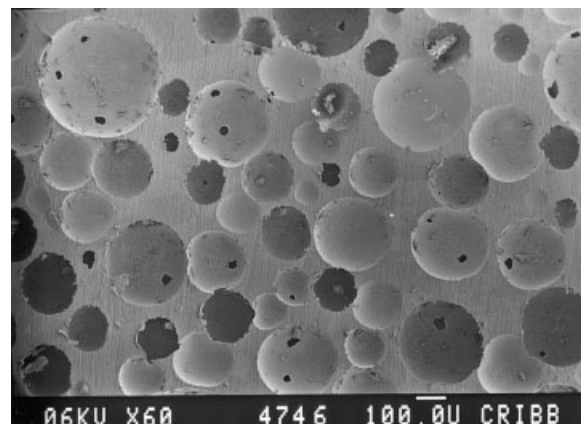
where  $Ea$  is the activation energy (kJ/mol),  $R$  is the gas constant (kJ/mol K),  $T$  is the foaming temperature (K), and  $t_{\text{GEL}}$  is the gelation time (s). It is important to point out that the gelation time is a very important variable when these materials are being processed.

#### Characterization of epoxy foams

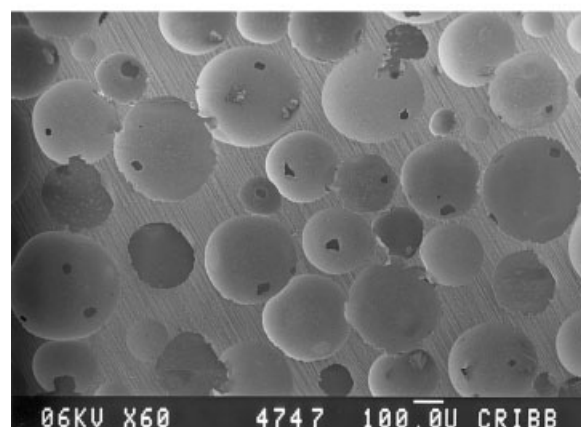
Table I shows glass transition temperature values for complete conversion ( $T_{g\infty}$ ) measured for different foams with a epoxy:amine ratio 100:35. The results show that the siloxane does not affect in an important way the  $T_{g\infty}$  values, and as a consequence, no change in the crosslinking density is expected. Figure 4 shows the density results for the 100:35 and 100:40 systems with different amounts of siloxane. The lower amount of amine, the higher foam density. For low concentrations of blowing agent, the increase of the amine content results in low density foam, probably because the blowing agent must react with the amine to produce



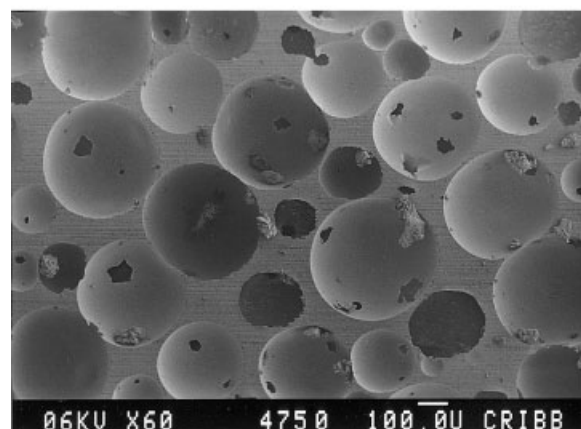
**Figure 4** Foam density variation with amount of blowing agent for different epoxy:amine ratio.



(a)



(b)



(c)

**Figure 5** SEMs of epoxy foams with different amount of polysiloxane. (a) 100:35:1, (b) 100:35:2, and (c) 100:35:3

hydrogen gas. For the both epoxy–amine ratios, as the blowing agent content increases, the foam density tends to similar values. This result is consistent with the reaction between amine and siloxane being responsible for the foaming process.

Figure 5 shows the SEM microphotograph of the

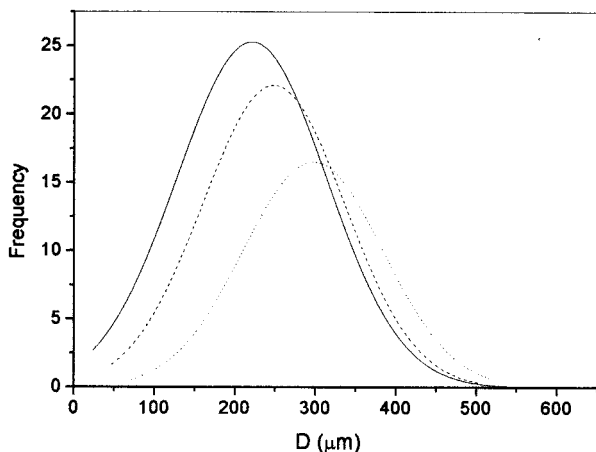


Figure 6 Size distribution of cell for different polysiloxane content (a) 100:35:1, (b) 100:35:2, and (c) 100:35:3

foam with different quantities of polysiloxane (1–3 weight part). All the bubbles are spherical with few contact points between them, as it is characteristic of high density foams. The foam is composed of big bubbles with small bubbles around them. Figure 6 show the bubble diameter distribution. The average diameter increases from 239 to 309  $\mu\text{m}$  for 1 to 3 weight part of polysiloxane. However, the width of the curves (a measure of the dispersion of the distribution) are similar for all samples.

The apparent modulus and compressive strength as a function of foam density are shown in Figures 7 and 8, respectively. As the amount of foaming agent increases, the mechanical properties and the density decrease. The experimental data can be fit with a power-law expression with respect to the foam density,<sup>7</sup> as follows:

$$E = A\rho^n \tag{3}$$

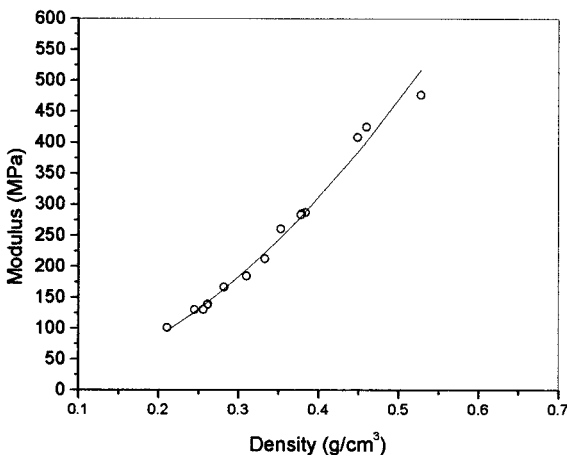


Figure 7 Density dependence of the modulus in compression.

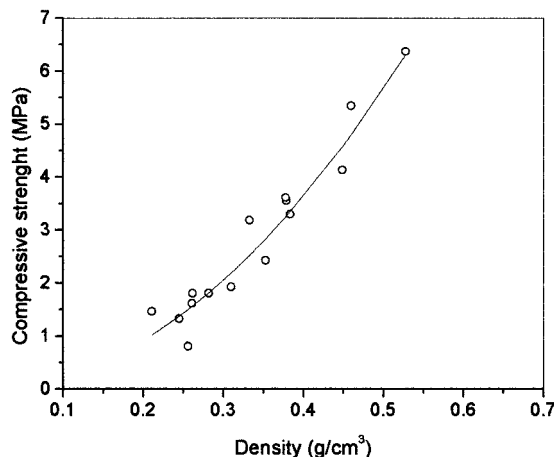


Figure 8 Density dependence of the compressive strength in compression.

$$\sigma_c = B\rho^p \tag{4}$$

where  $E$  (MPa) and  $\sigma_c$  (MPa) are the modulus and compressive strength of the foam, respectively,  $\rho$  is the foam density ( $\text{g}/\text{cm}^3$ ),  $A$  and  $B$  are constants related to the physical properties of the resins, and  $n$  and  $p$  are density exponents related to the structure and deformation mechanics of cellular material.<sup>7</sup> Over the range of density analyzed, a good fit of modulus and compressive strength is obtained for values of density exponent  $n$  and  $p$  of 1.8 and 1.84, respectively, and  $A=1586$  and  $B=28.1$ . The parameters  $n$  and  $p$  in eqs. (3) and (4) are similar. These parameters are different in low-density foam (i.e., polyurethane foam)<sup>7</sup> but not necessarily in the high-density foams. Low-density foam could collapse due to the bending of the wall cell. For high-density foam, the cell wall has high rigidity and thickness, and the properties will depend on the matrix properties.

### CONCLUSIONS

The optimum epoxy–amine weight ratio for the unfoamed system was 100:35, taking into account the obtained  $T_g$  values.

Low amine content produces foams with higher densities, suggesting that the reaction between the amine and siloxane generates the blowing agent.

Similar  $T_{g\infty}$  values were obtained with different percentages of blowing agent for the same epoxy:amine ratio, suggesting that crosslinking density is independent of the blowing agent content.

SEM analysis indicates that the foam structure is a closed cell one. When the quantity of blowing agent increases, the size of the cell increases, while the density, the compression strength, and the modulus decreases.

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