Study of the Epoxy System BADGE ($n = 0$)/1,2-DCH/CaCO$_3$ Filler by DMA and DSC

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ABSTRACT: The influence of an inorganic filler, CaCO$_3$, on the curing kinetics of an epoxy system composed of diglycidyl ether of bisphenol A [BADGE ($n = 0$)], 1,2-diaminecyclohexane (1,2-DCH), and CaCO$_3$ filler was studied by DMA and DSC. Different contents of filler in the range from 10 to 30%, referred to the total weight of the mixture, were tried. It was found that maximum reproducibility of the results and better performance correspond to a filler content of 20%. As usual, the T_g's obtained by DMA and DSC are different at 10–20°C. The results obtained from this study were compared with those corresponding to the system BADGE ($n = 0$)/1,2-DCH without filler; the T_g for this last system is higher than that for the system with filler incorporated, whereas E' and M_c (molecular weight between repetition units) are lower for the system without filler. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 366–370, 2002

Key words: DMA; DSC; BADGE ($n = 0$)/1,2-DCH/CaCO$_3$; glass-transition temperature; E'

INTRODUCTION

Thermoset polymers generally show a behavior between that of an elastic solid (following Hooke's law) and that of a Newton law–dependent viscous liquid. For this reason, these materials are known as viscoelastic and their behavior is determined by a combination of Hooke's and Newton's laws.

Dynamic mechanical analysis (DMA) can be used to study a large number of amorphous or glass materials having different elastic moduli (metals, composites, elastomers, etc.), different geometries (rods, sheets, films, or fibers), and different sizes. Experiments carried out using DMA show that the repetitivity of peak position depends on the material and not on the sample characteristics.

For the present study, the glass-transition temperature (T_g) of the material was measured using DMA and differential scanning calorimetry (DSC).

Dynamic mechanical properties were measured using the isochronous method, in which measurements were performed at constant time or frequency, whereas temperature was changed according to a constant heating rate program.[1]

Practically, the use of DMA in the isochronous mode is equivalent to the choice of a frequency and a scanning program for the experiment. The chosen frequency is usually 1 Hz. The choice of the frequency raises a problem, however, because the use of low frequencies is limited by the need to achieve a sufficient number of cycles to guarantee the reliability of measurements. On the other hand, very high frequencies are also limited by the appearance of mechanical resonance between the sample and the measurement system.

For determination of T_g by DSC, the dynamic mode was used.

EXPERIMENTAL

Materials

The epoxy resin was a commercial BADGE ($n = 0$) (Resin 332; Sigma Chemical Co., St Louis, MO) with an equivalent molecular weight of 173.6 g/equiv, as determined by wet analysis.[2,3] The curing agent was 1,2-diaminecyclohexane (DCH; Fluka Chemie, Switzerland) with an amine hydrogen equivalent weight of 28.5. The inert filler was calcium carbonate (Analema, Spain).

Sample Preparation

Epoxy resin and inert filler were carefully and homogeneously mixed, before the addition of an amount of curing agent equivalent to the epoxy/curing agent stoichiometric ratio. Different percentages of inert filler were tried (10, 15, 20, 25, 30%). These percentages are referred to the total weight of the sample. After mixing, the sample was introduced into a cylindrical frame. The curing reaction was programmed according to a TTT diagram designed for this three-component system.[4] It consists of two stages: (1) 67 min at 50°C and (2) 18 h at 85°C in an oven. After curing, the samples were removed from the frame.

For DMA experiments, 15- to 20-mm-length samples were used. For DSC experiments, samples were 25 to 20 mg in weight and 6 mm in diameter. The samples were sealed, using a press, in aluminum pans before being introduced into the calorimeter.

Differential Scanning Calorimetry (DSC)

A Perkin–Elmer DSC-7 unit (Perkin Elmer Cetus Instruments, Norwalk, CT), under control of a 1020 system controller, was used for calorimetric measurements. Because of the wide range of temperatures necessary for this study (-30 to 250°C), the calorimeter was calibrated using two standards [indium and bidistilled water obtained by the Millipore method (Millipore, Bedford, MA)].

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical properties were measured using a Perkin–Elmer DMA-7 operated in the three-point-bending horizontal measuring system. DMA was calibrated using indium as a standard. Experiments were conducted in a temperature range from 30 to 250°C. Experimental conditions were: dynamic force, 700 mN; static force, 750 mN; and heating rate, 10°C/min. The frequency value used in all the experiments was 1 Hz.

RESULTS AND DISCUSSION

In dynamic mechanical analysis[5] samples were under a variable sinusoidal stress of frequency ω. For a viscoelastic material the resulting strain is also sinusoidal but out of phase with stress at an angle δ because of the energy dissipated as heat. Young's modulus is defined as the quotient between applied stress and the resulting strain per unit length. It is usually convenient to express the sinusoidally varying stress as a complex quantity. Then, the modulus is also complex, and the real part is named the storage modulus E' and the imaginary part is the loss modulus E'', expressed as follows:

$$\frac{\sigma(t)}{\varepsilon(t)} = E^* = E' + E'' \tag{1}$$

The quotient E''/E' is termed the loss tangent (tan δ), which is the ratio of the energy dissipated per cycle to the maximum potential energy stored during a cycle:

$$\tan \delta = \frac{E''}{E'} \tag{2}$$

For a DMA study, T_g can be taken (1) as that corresponding to the maximum of the curve tan δ versus temperature, (2) as the midpoint corresponding to the log E' transition, and (3) as the intersect of the tangents to the log E' curve before the transition and the decrease characterizing the transition.

Several investigators have studied the characteristics of the different assignments of the glass-transition temperature. The most commonly used is that corresponding to the peak in a tan δ versus T plot, but it is also taken as the peak temperature in the E'' versus T plot; however, this temperature is 20–30°C lower than that corresponding to the tan δ peak. This last temperature is very close to that of the E' inflection point decrease, whereas the temperature of the E'' peak is

Table I T_g **Values Calculated Using a DMA for Different Percentages of Inert Filler**

Proportion (%)	T_g (tan δ) (°C)	T_g (E'') (°C)
10	134.7	117.4
15	132.5	117.9
20	149.7	136.0
25	133.5	120.5
30	139.2	116.1

closer to that based on the criterion of intersection of tangents.[6]

For a DSC study, T_g was taken as the temperature at the midpoint between the initial and final heat capacity curves in samples heated at 10°C/min.

Table I shows values of T_g measured by DMA. In this Table, T_g (tan δ) is the temperature corresponding to the peak of the tan δ versus T curve, and T_g (E'') is the glass-transition temperature at the maximum of E'' versus T plot. Analysis of this table shows values similar to those found for some other epoxy systems.[7–11] It can also be observed that temperatures measured at the E'' curve are always lower than those corresponding to the tan δ peaks. Usually, the difference between these values is about 10–20°C. In both cases, the maximum T_g corresponds to a filler content of 20%.

Table II shows T_g values measured by DSC. It can be seen that temperatures in this table are, in fact, 6–23°C different from those corresponding to tan δ peaks. However, as expected, the observed shift with respect to the temperature measured at E'' maximum is less than 10°C. This is in agreement with the fact that temperatures measured at E'' maximum can be considered as values of the standard T_g's, which are very similar to those measured by DSC. The difference between glass-transition temperatures measured by DSC and those measured by DMA were reported by Lee and Peppas,[12] Fraga et al.,[9] Núñez et

Table II T_g **Values Calculated Using a DSC for Different Percentages of Inert Filler**

Proportion (%)	T_g (°C)
10	119.0
15	126.3
20	127.6
25	119.4
30	116.8
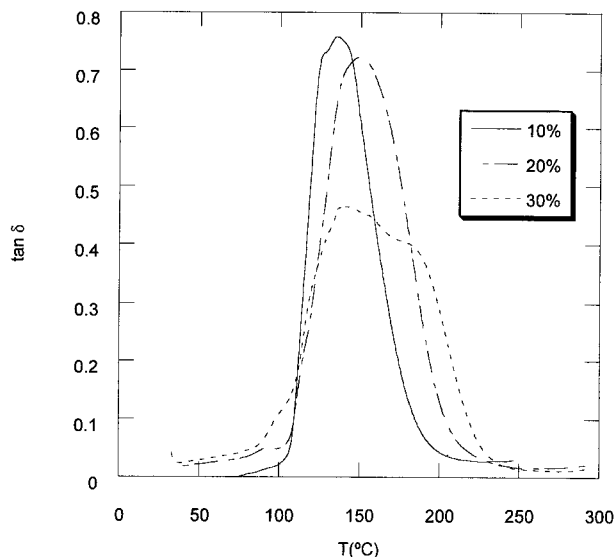
Figure 1 Values of tan δ versus temperature for different percentages of inert filler.

al.,[10,11,13] and Oleinik et al.[14] for this same epoxy system and for similar systems. As can be seen in the above-mentioned tables, T_g drifts toward increasing temperatures up to 20% of filler and then decreases. This can be attributable to the more homogeneous distribution of filler in the material-crosslinked structure corresponding to 20% of filler, as seen in the SEM micrographs corresponding to 20% of filler.[15] At filler concentrations, both greater and lower, different from 20%, calcium carbonate hinders crosslinking, thus causing a decrease in T_g. Figure 1 shows tan δ versus T plots corresponding to filler contents of 10, 20, and 30%. The reason for plotting only these three values was to avoid overlapping of the curves. At the glass-transition region, a decrease in the peak intensities with filler content can be observed. According to Matsuoka,[16] an increase of the number of crosslinking points causes: (1) a decrease of the chain mobility, (2) a loss of a certain amount of free volume, and (3) an increase in T_g. The greater the motion associated with the transition, the greater the intensity of tan δ peaks. Because of this, the decrease of molecular motion, caused by an increase in the filler content, causes a decrease in tan δ peak intensity, as can be seen Figure 1.

Table III shows values of storage modulus (E'), areas under tan δ versus T curves, and glass-transition temperatures (T_g) measured at tan δ peak for different filler contents. It can be observed that for 10 and 15% of filler both T_g and E'

Table III T_g, E', and Area for Different Percentages of Inert Filler

Proportion (%)	E' (10^9 Pa)	Area (°C^{-1})	T_g (tan δ) (°C)
10	0.093	7.0	134.7
15	0.133	6.8	132.5
20	0.331	8.7	149.7
25	0.410	7.3	133.5
30	0.497	7.6	139.2

Table IV   Molecular Weight Values for Different Percentages of Inert Filler

Proportion (%)	M_c (g/mol)
10	252.0
15	255.7
20	229.9
25	254.2
30	245.0

remain constant, thus indicating that at low filler concentration the mechanical properties of the material remain unchangeable. At 20% of filler, both T_g and the area increase, thus causing an increase in damping. Beyond 20% of filler, both the T_g and the area decrease again. However, it is observed that in the transition region, the storage moduli directly increase with filler content. This is in apparent contradiction with a previous statement because the greater damping would correspond to the lower filler content resulting from a greater elasticity. However, this could be justified based on the fact that, when a material is under a sinusoidal stress, the probability of finding a filled zone inside a sample increases with content of filler, thus causing an increase in storage modulus and the material would become less deformable.

During the curing reaction, in the formation of a three-dimensional network, crosslinking takes place through molecular chain covalent bonds. The more crosslinked the polymer, the lower the molecular weight M_c of the repetition units. This means that an increase of filler content, with the consequent loss of crosslinking, causes a decrease in the degree of crosslinking density and thus an increase of molecular weight between repetition units, M_c. Crosslinking increases the glass-transition temperature. Rough estimates of M_c can be made from the shift in T_g using the following equation, proposed by Nielsen[17]:

$$T_g - T_{g0} = \frac{3.9 \times 10^4}{M_c} \qquad (3)$$

where T_{g0} is the glass-transition temperature of the uncrosslinked polymer. This value, calculated using DSC, was 20°C. $T_g - T_{g0}$ is the shift in T_g generated exclusively by crosslinking. Because of this, eq. (3) can use T_g values measured by either DMA or DSC. Table IV shows M_c values calcu-

lated using those T_g's corresponding to the peak of tan δ versus T plots for the different contents of filler. It can be observed that the lowest M_c corresponds to 20% of filler. Analysis of this table together with data shown in Tables I and II leads to the conclusion that the maximum degree of crosslinking is achieved for this filler content, in agreement with findings reported in a previous study.[15]

Table V shows values of T_g, E', and M_c corresponding to the system without filler and with a filler content of 20%, considered to be the optimum value, as reported in a previous study.[15] It may be seen that the 20% filled system shows a higher E', thus indicating a higher damping and a lower deformability. Moreover, M_c is higher for the filled system with the consequent loss of crosslinking because of the limitations imposed by the filler on molecular motion. In a calorimetric study, it was found that the extent of conversion is decreased by the presence of an inorganic filler, CaCO$_3$.[15]

CONCLUSIONS

The behavior of both the storage and loss moduli of an epoxy system BADGE ($n = 0$)/1,2-DCH/CaCO$_3$ filler was studied by DMA and compared with some results obtained by DSC. Because of its greater damping and lower deformability, it was

Table V T_g, E', and M_c for the Epoxy System With and Without Filler

	Without Filler (ref.)	With Filler (20%)
T_g (°C)	162.1	149.7
E' (10^9 Pa)	0.268	0.331
M_c (g/mol)	203.0	229.9

found that the optimum behavior of the three-component system corresponds to a filler content of 20%, referred to the total weight. Epoxy resin and curing agent were at stoichiometric ratio.

Maxima values of T_g for the three-component systems also correspond to a filler content of 20%. Values reported in Tables I–V were obtained from the respective experiments, rather than from Figure 1, where all the experimental curves corresponding to different filler contents are not shown, to avoid overlapping.

REFERENCES

1. Chartoff, R. P. in Thermoplastics Polymers; Turi, E. A., Ed.; Thermal Characterization of Polymeric Materials; Academic Press: San Diego, 1997.
2. Lee, H.; Neville, K. Handbook of Epoxy Resin; McGraw-Hill: New York, 1967.
3. May, C. A. Epoxy Resins: Chemistry and Technology; Marcel Dekker: New York, 1988.
4. Núñez, L.; Fraga, F.; Castro, A.; Núñez, M. R.; Villanueva, M. Polymer 2001, 42, 3581.
5. Wetton, R. E. in Development in Polymer Characterization; Dawkins, J. V., Ed.; Chapman and Hall: London, 1986.
6. Hale, A.; Macosko, C. W.; Bair, H. E. Macromolecules 1991, 24, 2610.
7. Ellis, B.; Found, M. S.; Bell, J. R. J Appl Polym Sci 1996, 59, 1493.
8. Chartoff, R. P.; Weisman, P. T.; Sircar, A. K. in Assignment of the Glass Transition; Seylen, R. J., Ed.; ASTM Spec Tech Publ 1249; American Society for Testing and Materials, 1994; p 88.
9. Fraga, F.; Salgado, T.; Rodriguez Añón, J. A.; Núñez, L. J Therm Anal 1994, 41, 1543.
10. Núñez, L.; Fraga, F.; Castro, A.; Fraga, L. J Therm Anal 1998, 52, 1013.
11. Núñez, L.; Núñez, M. R.; Fraga, F.; Taboada, J.; Villanueva, M. J Appl Polym Sci 1999, 72, 443.
12. Lee, M. C.; Peppas, N. A. J Appl Polym Sci 1993, 47, 1349.
13. Núñez, L.; Villanueva, M.; Fraga, F.; Núñez, M. R. J Appl Polym Sci 1999, 74, 353.
14. Oleinik, E. F. Adv Polym Sci 1986, 80, 49.
15. Núñez, L.; Fraga, F.; Núñez, M. R.; Villanueva, M. J Appl Polym Sci 2000, 75, 291.
16. Matsuoka, S. in Relaxation Phenomena in Polymers; Hanser, C., Ed.; Springer Verlag: Munich, 1992.
17. Nielsen, L. E. J Macromol Sci Rev Macromol Chem 1969, C3, 69.