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ELASTIC MODULI AND ACTIVATION ENERGIES FOR AN EPOXY/*m*-XDA SYSTEM BY DMA AND DSC

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Abstract

The influence of the resin/diamine ratio on the properties of the system diglycidyl ether of bisphenol A (BADGE *n*=0/*m*-xylylenediamine) (*m*-XDA) was studied. Variation of this ratio resulted in significant effects on the cure kinetics and final dynamic mechanical properties of the product material.

The study was made in terms of storage modulus (E'), loss modulus (E'') and molecular mass between cross-links (M_c) at different ratios. Two geometries (cylindrical and rectangular) were considered. The influence of temperature was studied through the activation energy (E_a), which depends on the epoxy/amine ratio and the geometry of the samples. Glass transition temperatures (T_g) and glass transition temperatures for thermosets with null degree of conversion (T_{g0}) were determined by DSC. T_g decreases when amounts of curing agent greatly in excess of the stoichiometric compositon were used.

Keywords: activation energies, DMA, DSC, elastic moduli, epoxy resin

Introduction

In recent years, epoxy resins have been the subject of numerous technical publications. The interest in these materials originates from the versatility of their possible uses. This fact has encouraged studies of different resin/hardener systems. One of the main characteristics of epoxy polymers is their viscoelasticity, which leads them to behave somewhere between an elastic solid and an ideal viscous liquid. It is well known that the energy applied to an elastic solid is stored in it as potential energy and can therefore be recovered. On the other hand, part of the energy supplied to a viscous liquid is lost as heat, or some other form of dissipated energy. Important information about the viscoelastic behaviour of epoxy resin materials can be obtained by studying the responses of these materials to periodic forces. The strain may be varied sinusoidally as follows:

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$$\varepsilon = \varepsilon_0 \cos\omega t \tag{1}$$

where ε_o is the maximum amplitude of the strain, ω is the frequency, and t is time.

The stress may be given by [1]

$$\sigma = \varepsilon_0 \cos\omega t \left[\frac{\omega}{3} \int_0^\infty E(s) \sin\omega s \mathrm{d}s \right] - \varepsilon_0 \sin\omega t \left[\frac{\omega}{3} \int_0^\infty E(s) \cos\omega s \mathrm{d}s \right] \tag{2}$$

Obviously, the term $\sin\omega t$ is 90° out of phase with the strain. Terms inside brackets are frequency-dependent and define two function. $E'(\omega)$ is the Young storage modulus, and $E''(\omega)$ is the Young loss modulus. Equation (5) may be written as

$$\sigma = \sigma_0 (E' \cos\omega t - E'' \sin\omega t) \tag{3}$$

On the other hand, if we take into account that stress is a sinusoidal function out of phase by an angle δ with the strain, whe have

$$\sigma = \sigma_0 (\cos\omega t + \delta) = \sigma_0 (\cos\omega t \cos\delta - \sin\omega t \sin\delta) \tag{4}$$

Comparison of Eqs (6) and (7) shows that

$$E' = \left(\frac{\sigma_0}{\varepsilon_0} \right) \cos\delta \quad \text{and} \quad E'' = \left(\frac{\sigma_0}{\varepsilon_0} \right) \sin\delta \tag{5}$$

with a quotient

$$\tan\delta = \frac{E''}{E'} \tag{6}$$

This is called the loss tangent; it relates the dissipated and the storage energies in every cycle. At low frequencies, $\tan\delta$ is large for all uncross-linked polymers and in fact becomes inversely proportional to the frequency.

In the transition zone between glass-like and rubber-like consistency, the loss tangent passes through a pronounced maximum for both uncross-linked polymers of high molecular weight and highly cross-linked polymers.

One of the objectives of the present study was to check the influence of sample geometry on the elastic behaviour of the resulting material and to examine whether this geometry affects the formation of the activated complex and hence the material cross-linking from an energetic point of view.

Different series of measurements were made with application of the equation of state for rubber network [4–7], the molecular weights were calculated with an equation proposed by Nielsen [7–10] and values of T_g and T_{go} were measured with a Perkin-Elmer DSC7 instrument.

Murayama and Bell [4] discussed the application of the rubber elasticity theory 40°C above T_g, and Katz and Tobolsky [11] found the results to be in reasonable agreement with elasticity theory.

Experimental

Materials

The epoxy resin used was a diglycidyl ether of bisphenol A (BADGE, n=0) (Resin 332. Sigma Chemical Co.) with *m*-xylylenediamine (*m*-XDA)(Aldrich Chemical Co., 99% pure) as curing agent. Both resin and curing agent were used as received.

This system was chosen in order to supplement previous studies on it [12] and also because of its ease of handling for both low and high viscosity values and the wide ranges of frequencies and temperatures which can be used [13, 14].

Sample preparation

For DSC measurements the sample size was 5–7 mg. Resin and curing agent were carefully mixed inside the calorimeter dry box, at about 5°C, under a nitrogen atmosphere. Samples were sealed in aluminium pans.

For DMA measurements, BADGE, n=0 and *m*-XDA were homogeneously mixed. Curing was performed in a desiccator for 24 h at room temperature, with postcuring for 2 h at 120°C.

Techniques

Differential scanning calorimetry and dynamic mechanical analysis were used.

The key parameters in the present study are the storage modulus (E') and the loss modulus (E''). Both moduli were measured with a DMA7 from Perkin-Elmer. Their ratio (tanδ) is considered in different plots in this paper. Glass transition temperatures (T_g), necessary for some of the calculations, were also determined. In DSC studies, (T_g) was taken at the midpoint between the initial and final heat capacities (Fig. 1). In DMA studies, T_g corresponds to the maximum value in a plot of tanδ *vs.* temperature. Activation energies were determined by considering the variation in T_g with the frequency used in the various DMA experiments. In order to obtain reliable data, different values of the epoxy/hardener ratio were studied.

Mechanical properties were measured with a Perkin-Elmer DMA7, operated in the three-point bending method. The temperature range was 30–250°C, and the heating rate was 10°C min^{-1}. In every series of experiments, the frequency was kept constant and the samples were under a dynamic stress of 700 mN and a

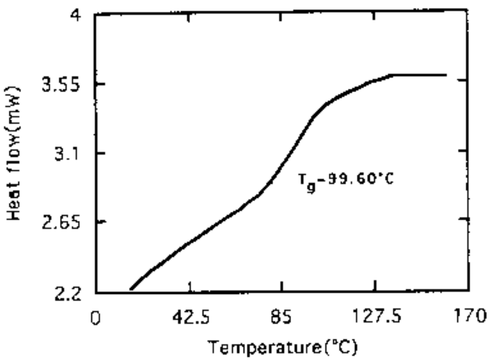

Fig. 1 Heat flow *vs.* temperature plot from which T_g is measured

static stress of 750 mN. Two different geometries (cylindrical and rectangular), and different resin/hardener ratios (100:18, 100:22, 100:24 and 100:26) were used. The constant values for the frequency in the different series of experiments were 1, 5, 10, 15, 20 and 25 Hz.

A Perkin-Elmer DSC7 was used to measure both T_g and the glass transition temperature for thermoset with null degree of conversion (T_{go}). The calorimeter was calibrated in the range of selected temperatures following the procedure given in the Perkin-Elmer DSC7 manual [15]. Two standards (indium and bidistilled water obtained by the Milipore method) were used. The system was continuously under nitrogen. The baseline was periodically adjusted. Temperature ranges were 5–250°C for T_g measurements and –60–250°C for measurements of T_{go}. With regard to the low temperatures necessary for these latter measurements, an Intercooler II was adapted to the DSC7. All experiments were performed at a heating rate of 10°C min^{-1}.

Results

In the present work, values of M_c for the various epoxy/amine ratios studied were determined by using an empirical equation proposed by Nielsen [4–7]:

$$M_c = \frac{3.9\cdot 10^4}{T_g - T_{go}} \tag{7}$$

which takes into account the relationship between the degree of cross-linking and the shift in T_g.

Values of T_g, T_{go} and M_c corresponding to the different epoxy/hardener ratios are listed in Table 1. It can be seen that T_g increases with the amount of hardener up to the stoichiometric ratio (100:22). From this value, the excess of amine makes T_g diminish. The decrease can be attributed to the increasing number of chain ends. The reasoning for this is based on the free volume argument that chain ends have excess free volume associated with them that can facilitate the movement of the molecules and therefore lead to lower values of T_g [16]. The value of T_{go} decreases with the amount of hardener up to the stoichiometric ratio, after which it remains practically constant. M_c values between cross-links for the different epoxy/amine ratios are also listed in Table 1. It may be observed that M_c decreases with the amount of amine up to the stoichiometric ratio, after which it increases with the amount of amine. Similar behaviour was found by Murayama and Bell [4], who report M_c values calculated from the T_g shift.

Figures 1 and 2 illustrate two examples of the way in which T_g and T_{go}, respectively, were determined. Values of T_{go} for epoxy/amine ratios over 100:30 could not be determined with this method, even when starting at temperatures below –60°C.

Table 1 Values of T_g and T_{go}, measured by DSC, and M_c, calculated from Eq.(10), for different resin/hardener ratios

Ratios	T_g/°C	T_{go}/°C	M_c/g mol^{-1}
100:18	99.6	–42.4	275
100:20	122.7	–45.4	232
100:22	128.3	–49.7	219
100:24	117.2	–49.9	233
100:26	110.2	–48.6	246
100:30	93.9	–	–
100:40	71.8	–	–
100:50	55.7	–	–

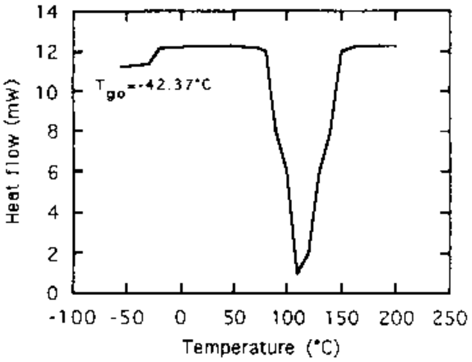

Fig. 2 Heat flow *vs.* temperature plot used to determine the glass transition temperature for thermosets with null degree of conversion, T_{go}

Table 2 Glass transition temperatures (T_g) and storage modulus (E') measured by DMA, as functions of frequency and resin/hardener ratios for cylindrical geometry

Ratio 100:18

f/Hz	T_g/°C	E'/J m$^{-3}\cdot10^6$
1	99.1	43.92
5	102.6	45.88
10	105.1	43.91
15	106.5	44.88
20	106.9	44.88
25	107.3	42.91

Ratio 100:22

f/Hz	T_g/°C	E'/J m$^{-3}\cdot10^6$
1	118.9	48.90
5	121.9	51.92
10	123.6	50.87
15	123.9	52.25
20	125.9	52.92
25	126.0	53.88

Ratio 100:24

f/Hz	T_g/°C	E'/J m$^{-3}\cdot10^6$
1	116.2	48.90
5	119.8	51.92
10	121.4	52.92
15	121.6	54.89
20	123.2	53.88
25	123.5	53.88

Ratio 100:26

f/Hz	T_g/°C	E'/J m$^{-3}\cdot10^6$
1	111.7	44.88
5	115.0	46.89
10	116.3	47.90
15	118.2	50.87
20	118.9	49.91
25	119.1	48.90

Table 3 Glass transition temperatures (T_g) and storage modulus (E') measured by DMA, as functions of frequency and resin/hardener ratios for rectangular geometry

Ratio 100:18

f/Hz	T_g/°C	E'/J m^{-3}·10^6
1	123.1	48.90
5	127.8	52.92
10	129.1	54.88
15	129.7	55.89
20	130.3	56.89
25	131.8	57.90

Ratio 100:22

f/Hz	T_g/°C	E'/J m^{-3}·10^6
1	139.4	53.88
5	140.9	56.89
10	142.8	56.89
15	143.5	60.88
20	144.8	63.89
25	144.8	62.88

Ratio 100:24

f/Hz	T_g/°C	E'/J m^{-3}·10^6
1	137.2	50.91
5	139.1	55.89
10	141.1	57.90
15	142.6	57.90
20	142.7	62.89
25	144.2	62.88

Ratio 100:26

f/Hz	T_g/°C	E'/J m^{-3}·10^6
1	133.6	48.90
5	136.3	56.90
10	139.8	56.90
15	140.3	58.90
20	140.6	60.87
25	142.0	60.87

Table 2 lists values of T_g and E' as functions of the frequency for cylindrical samples corresponding to the various epoxy/amine ratios.

The data in Tables 2 and 3 reveal that both E' and T_g increase with frequency. This behaviour is similar to that reported by Palmese *et al.* [16] and Matsukawa *et al.* [17] from studies of different epoxy/amine systems. It has already been mentioned that T_g increases with the amount of amine up to the stoichiometric value. T_g values corresponding to rectangular geometry are higher than those corresponding to cylindrical geometry. Values of activation energies for the different epoxy/amine ratios and the two geometries are listed in Table 4. These values were calculated by using dynamic mechanical data and an Arrhenius-like equation:

$$f = f_0 e^{-(E_a/RT)} \tag{8}$$

where E_a is the activation energy, R is the gas constant, T is the glass transition absolute temperature and f_0 is a pre-exponential value. The activation energies for the different ratios can be calculated from the slopes of the straight lines obtained from plots of $\ln f$ *vs.* $1/T$.

As may be seen in Table 4, E_a increases with the amount of amine and is greater for rectangular geometry, showing that cylindrical samples are more favourable from an energetic point of view.

Figures 3 and 4 depict typical DMA plots of E' *vs.* T and tanδ *vs.* T for cylindrical and rectangular samples, respectively. Bell [8] and Unsworth *et al.* [9] found similar plots in studies of the thermal degradation of epoxy resins. Fraga *et al.* [12] studied this same epoxidic system at the stoichiometric ratio and obtained plots of similar shape.

Table 4 Activation energies kJ mol^{-1} for rectangular and cylindrical geometries at different resin/hardener ratios

Geometry	Activation energies/kJ mol^{-1}			
	Ratios			
	100:18	100:22	100:24	100:26
Cylindrical	536.2 ± 45.3	689.0 ± 39.2	694.4 ± 35.6	632.9 ± 50.2
Rectangular	630.4 ± 63.4	922.3 ± 70.5	764.0 ± 94.1	827.9 ± 80.5

A study of the tanδ *vs.* T curves reveals a maximum value for tanδ corresponding to T_g, followed by a turndown of the curve. This part of the curve corresponds to the glass transition region. After the sharp drop that the modulus takes in this region, it becomes almost constant in the rubbery plateau region. In this plateau region, the epoxy/amine systems exhibit rubber elasticity and the equation of state for rubber networks [4, 8–10] can be used. For this reason, E' must be meas-

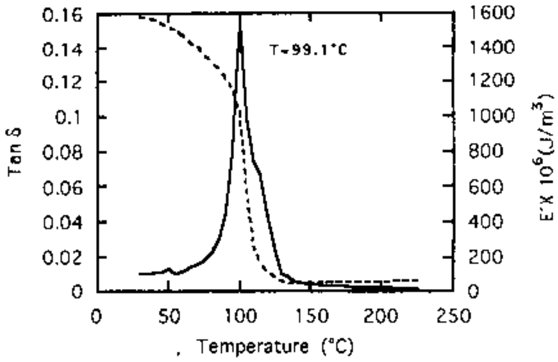

Fig. 3 Tanδ and E' as functions of T corresponding to a cylindrical sample at f=1 Hz. — tanδ; --- $E'\times10^6$ J m^{-3}

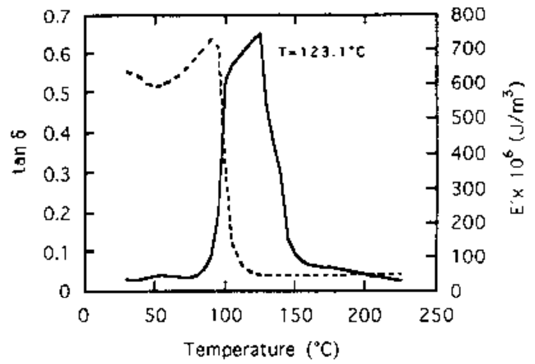

Fig. 4 Tanδ and E' as functions of T corresponding to a rectangular sample at f=1 Hz. — tanδ; --- $E'\times10^6$ J m^{-3}

ured above T_g, and for present purposes E' was measured at T_g+ 40°C. This ensured that the measurements were made in the rubbery plateau region. It can also be seen that the peak corresponding to the rectangular samples is wider than that which corresponds to cylindrical geometry. This is in agreement with the greater values of E_a found for the rectangular samples.

Conclusions

From an energetic point of view, the activation energy values show that cylindrical samples are more favoured than rectangular samples. This means that the activated complex can be obtained more easily, resulting in a more cross-linked material.

This is in agreement with the fact that rectangular samples present higher T_g values, indicating that energy would be stored at higher temperatures. From an economic point of view, it would be necessary to provide a larger quantity of energy to achieve the desired elasticity of the material with the corresponding expense.

References

1 J. D. Ferry, Viscoelastic Properties of Polymers, 3^{a}Ed, Wiley & Sons, New York 1980.
2 D. W. Clegg and A. A. Collyer, The Structure and Properties of Polymeric Materials, The Institute Material, London 1993.
3 L. H. Sperling, Introduction to Physical Polymer Science, Wiley & Sons, New York 1992.
4 T. Murayama and J. P. Bell, J. Polym. Sci., 8 (1970) 437.
5 A. V. Tobolsky, D. W. Carlson and N. Indictor, J. Polym. Sci., 54 (1961) 175.
6 L. R. G. Treolar, The Physics of Rubber Elasticity, Wiley & Sons, New York 1961.
7 L. E. Nielsen, J. J. Macromol. Sci.-Revs. Macromol. Chem., C3 (1969) 69.
8 J. P. Bell, J. Polym. Sci., 6 A2 (1970) 417.
9 J. Unsworth and Y. Li, J. Appl. Polym. Sci., 46 (1992) 1375.
10 C. D. Wingard and C. L. Beatty, J. Polym. Sci., 41 (1990) 2539.
11 D. Katz and A. V. Tobolsky, J. Polym. Sci., A, 2 (1964) 1595.
12 F. Fraga, T. Salgado, J. Rodriguez and L. Núñez, J. Thermal Anal., 41 (1994) 1543.
13 C. A. May, Chemistry and Technology, Marcel Dekker, New York 1988.
14 B. Ellis, Chemistry and Technology of Epoxy Resins, Blackie Academic & Professional, Glasgow 1993.
15 Users Manual 1020 Series DSC7 Thermal Analysis System, Perkin-Elmer Corp. Norwalk, USA 1991.
16 G. R. Palmese and R. L. McCullough, J. Appl. Polym. Sci., 46 (1992) 1863.
17 M. Matsukawa, H. Okabe and K. Matsushige, J. Appl. Polym. Sci., 50 (1993) 67.