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The Evaluation of the Flexural Strength of Cured Epoxy Resins from Heat Capacity Data

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The flexural strength of epoxy resins cured at different temperatures and times was investigated and compared to the heat capacities obtained during thermal analysis. Theoretical and experimental results indicated that the change in heat capacity at the glass transition temperature of epoxy resins decreases with increasing cure time and temperature. Further, for the given epoxy resin composition, it was determined that those samples with higher ΔC_p values have higher flexural strength than those with lower ΔC_p values.

Epoxy resins show a strong co-relation between flexural strength and measured heat capacities. Since the measurement of heat capacity by the Differential Scanning Calorimetry technique is simple and reproducible, it presents a means of evaluating the flexural properties of epoxy resins which will result from any known set of cure conditions.

KEY WORDS Epoxy resin, heat capacity, flexural strength, Differential Scanning Calorimetry, glass transition temperature.

INTRODUCTION

Conventionally, heat capacity is used to represent the quantity of heat needed to increase the temperature of a unit mass of a material by a unit of temperature. Previous work¹ indicated that the heat capacity of amorphous solids at constant pressure increases smoothly with temperature, but increases discontinuously at the glass transition temperature. In the region above T_g , the heat capacity continues to increase at a slower rate.

In 1963, Simha and Boyer² proposed the following relationship:

$$\Delta C_p T_g = K \quad (1)$$

where T_g is the glass transition temperature, K is a proportionality constant, ΔC_p is the change in heat capacity at T_g and it is defined as:

$$\Delta C_p = (C_p)_l - (C_p)_g \quad (2)$$

where $(C_p)_l$ and $(C_p)_g$ are the heat capacity of a material at the states above and below T_g .

Equation 1 indicates that a polymer material with a low value of ΔC_p has a high glass transition temperature. Because the glass transition temperature is an important structural characteristic of polymers, and the fact that the measurement of heat capacity is relatively simple and practical using such computer operated, well-instrumented equipment as a Differential Scanning Calorimetry, information about the relationships between the heat capacity and the mechanical properties of polymers will be studied in this work.

Among the variety of polymers, epoxy resins are the commonly used thermoset polymers and possess the typical crosslinked structure. For this reason epoxy resins were selected as the test samples in this experiment.

Based on the above ideas, the following studies have been made: 1. The effects of cure temperature and time on the values of heat capacity. Since the values of heat capacity are affected by the extent of curing, it is possible to vary the heat capacity by controlling the cure conditions. 2. Investigation of the effect of controlling the cure conditions on the flexural strength of the cured resins. 3. Developing the relationship between heat capacity and flexural strength of cured epoxy resins.

THEORETICAL CONSIDERATION

When a material is heated, the heat energy, ΔH , of absorption (or evolution) is proportional to the change in entropy, ΔS , of its molecules:

$$\Delta H = T\Delta S \quad (3)$$

Since the heat energy ΔH can also be expressed in the following form, we may write:

$$\Delta H = C_p m \Delta T \quad (4)$$

where C_p is the heat capacity, m is mass, ΔT is the change in temperature. Thus, the heat capacity of a sample can be expressed as the function of entropy change of its molecules.

$$C_p = \frac{T\Delta S}{m\Delta T} \quad (5)$$

When a crosslinked polymer is heated to the rubbery state, due to the molecular motions, the polymer segments between two crosslinked points move from one position to another position. According to statistical thermodynamics,³ the entropy of molecular motions in the rubbery state can be expressed as:

$$\Delta S = -0.5 kN(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \quad (6)$$

where α is elongation ratio, k is Boltzmann's constant, N is the number of segments in polymer chain and x, y, z , are the coordinates of the crosslinking point.

The heat capacity of an epoxy resin can therefore be expressed as:

$$C_p = \frac{-0.5 kN(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3)}{m\Delta T} \quad (7)$$

The number of segments in chain can be expressed as M_c , the average molecular weight between two crosslinks.³

$$\rho = \frac{NM_c}{\tilde{N}} \quad (8)$$

where ρ is density of the polymer, \tilde{N} is the Avogadro constant.

There is a relationship among the gas constant R , Boltzmann's constant k , and the Avogadro constant \tilde{N} :

$$R = k\tilde{N} \quad (9)$$

From the theory for polymers during the rubbery state,³ the shear modulus G , of a polymer with a crosslinked network in the rubbery state, may be expressed as:

$$G \cong \frac{\rho RT}{M_c} \quad (10)$$

Inserting Equations 8, 9 and 10 into Equation 7, results in:

$$C_p = \frac{G}{2 m\Delta T} (\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \quad (11)$$

The shear modulus of a material can be expressed in terms of E , the Young's modulus and γ , the Poisson ratio. For isotropic material, γ is approximated to 0.5, and the statement for G becomes:

$$G = \frac{E}{2(1+\gamma)} = \frac{E}{3} \quad (12)$$

This yields the relationship between the heat capacity and the elastic modulus of the material. Putting Equation 12 into Equation 11 yields:

$$C_p = -\frac{E}{6 m\Delta T} (\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) \quad (13)$$

Equation (13) shows that the heat capacity of a polymer is negatively proportional

to its elasticity modulus and the segment configuration in the structure. From Equation 2, the change in heat capacity at the glass transition temperature is written as: $\Delta C_p = (C_p)_1 - (C_p)_g$, which may be rewritten using Equation 13,

$$\Delta C_p = -\frac{E}{6 m \Delta T} (\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3) - (C_p)_g \quad (14)$$

From the above result, it can be seen that the change in heat capacity of cured epoxy resins is a function of their chain stiffness or the density of crosslinking and the elastic modulus.

In a similar fashion, the work reported here will attempt to show the relation between flexural strength and changes in measured heat capacity. Based on these results, the heat capacity can be used to evaluate mechanical properties and vice versa.

EXPERIMENTAL METHOD

1. Sample Preparation

The epoxy resin used in this experiment was D.E.R. 331, the curing agent was Ureamid 125. Both were provided by the ADCHEM FASTENERS Inc.

The specimens were made by casting carefully mixed epoxy resin compositions in aluminum moulds. These were cured in a thermostatically controlled oven. The cure temperatures used were 125°C, 150°C, 175°C and 200°C. The cure times used were 10, 20, 40, 60, 90 and 120 minutes. The cured specimens were cut into the required sizes for testing in the flexural test equipment.

The ratio of curing agent to resin was held at a ratio of 1:4 on a weight basis.

2. The Measurement of Heat Capacity

The heat capacities of all specimens were measured by the Differential Scanning Calorimetry, DSC-2C, Perkin-Elmer. The details of the experimental procedure are described in the literature.⁴ The data on heat capacity were calculated according to the following Equation:

$$\frac{\partial H}{\partial t} = m \Delta C_p \frac{\partial T}{\partial t} \quad (15)$$

or

$$\Delta C_p = \frac{1}{m} \times \frac{\partial H}{\partial t} \bigg/ \frac{\partial T}{\partial t} \quad (16)$$

where C_p is the heat capacity, m is mass of the specimen. $\partial H/\partial t$ and $\partial T/\partial t$ are the heat flow rate and heating rate of the DSC. In this work, $\partial T/\partial t$ is selected to be

set at 20°C/min., and $\partial H/\partial t$ is read from the chart recording output of the DSC. The results were tabulated and presented in Table I.

3. Flexural Test

Flexural tests are customarily performed in accordance with the ASTM D7900 Equation (1). The experimental procedure used in this work also followed ASTM test procedure and, therefore, followed the literature.⁵ The tests were conducted in a three point loading device attached to a tensometer as shown in Figure 1, a single load being applied at the midpoint of specimens of uniform dimensions. The specimens were rectangular beams of the following linear dimensions 127 mm × 12.7 mm × 6.4 mm. The results of flexural strength were calculated according to following formula⁵:

$$\text{Flexural strength} = \frac{3 PL}{2 bd^2} \quad (17)$$

where b is width, d is thickness, L is the distance between two supports, and P is load. S. I. units were used throughout.

RESULTS AND DISCUSSION

1. Effects of Cure Temperature and Time on the ΔC_p Values

According to Equation (13), the ΔC_p value is negatively proportional to segment configuration or the chain mobility. For cured epoxy resins, the chain mobility is

TABLE I
Experimental data of epoxy resins (D.E.R. 331)

$(C_p)_g$ (J/g K)	$(C_p)_r$ (J/g K)	C_p (J/g K)	T_g (°C)	$\Delta C_p T_g$ (J/g)	M_c (g/mole)
1.44	1.66	0.22	110	24.20	330
1.44	1.68	0.24	104	24.96	348
1.45	1.72	0.27	97	26.16	371
1.47	1.75	0.28	93	26.04	386
1.47	1.77	0.30	88	26.40	406
1.47	1.80	0.33	85	28.05	419
1.48	1.82	0.34	83	28.22	429
1.50	1.86	0.36	80	28.80	443

$(C_p)_g$ and $(C_p)_r$ are the heat capacities at the glassy state and rubbery state respectively.

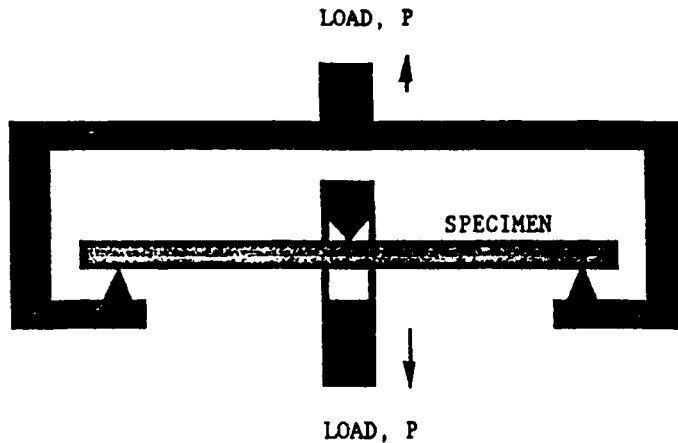


FIGURE 1 Schematic representation of the three-point loading device of flexural testing.

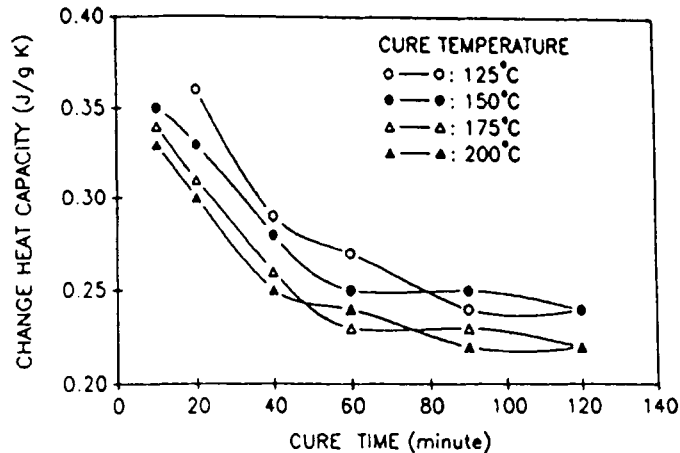


FIGURE 2 The effects of cure temperature and time on the ΔC_p values of cured epoxy resins.

dependent on the density of crosslinking in the network. The density of crosslinking is affected by the cure temperature and time. The main influence of cure temperature and time on the epoxy resins is its effect on the reaction kinetics of the mechanism through which the network is developed.⁶ High cure temperatures and long cure times result in a high conversion during the crosslinking reaction and a high crosslinking density. Consequently, this reduces the heat capacity of the samples.

Figure 2 shows the experimental results of the ΔC_p of epoxy resins which were cured under different curing conditions. The results proved that both the cure temperature and the cure time have effects on the ΔC_p values. The effects are apparent: the ΔC_p values decrease with the increase of the cure temperature and cure time. The ΔC_p value of epoxy resins changes from 0.36 to 0.22 J/g K when the cure temperature is changed from 125°C to 200°C and the cure time is from 10 minutes to 120 minutes. The ΔC_p values drop rapidly from 0.36 to 0.25 J/g K

at early stage, eg. cure times from 10 minutes to 60 minutes and cure temperatures from 125°C to 200°C. However, the ΔC_p values change very slowly after cure time longer than 60 minutes and at cure temperature above 150°C. The value measured in this test, for example, only changed from 0.25 to 0.22 J/g K when testing was continued from 60 minutes to 120 minutes at 200°C. The maximum value of ΔC_p in this example is at the cure condition of 125°C for 20 minutes. The lowest value appears to cure temperature from 175°C to 200°C, when the cure time is longer than 60 minutes.

These results can be explained from the stand point of density of crosslinking. When the cure time is from 10 minutes to 60 minutes, the extent of the curing reaction, or the density of crosslinking of the epoxy, changes from low to high.⁶ The unreacted epoxy groups in the mass rapidly decrease during this time. The ΔC_p values are also shown to have decreased. It was considered that after 60 minutes treatment the epoxies had been fully cured. During these tests, the ΔC_p values change very smoothly with n steps being noted. Low temperature and short cure time produce a low density of crosslinking in the network. In this network of low density of crosslinking there are more segment movements in the chains, and the ΔC_p values are larger. The cure reaction proceeds quickly at higher cure temperatures, and the measured ΔC_p changes are evident. Prolonged cure time and increasing cure temperature will stabilize the cured structure.

Table I shows the values of ΔC_p , T_g , the glass transition temperature, and M_c , the number-average molecular weight between crosslinks. The values of M_c were calculated according to the following equation which is given by L. Nielsen.⁷

$$T_g - T_{go} = \frac{3.9 \times 10^4}{M_c} \quad (18)$$

where T_{go} is the glass transition temperature of the uncrosslinked polymer. In this experiment, the T_{go} value of the resin was determined to be -8°C .

According to the data listed in the Table I, the values of M_c increase with the decrease of ΔC_p . This result indicates that the epoxy resins with a high density of crosslinking structure have low ΔC_p values. This result also supports the above explanation, since a low value of M_c means a high density of crosslinking network and low chain mobility.

2. Relationships Between ΔC_p Values and Mechanical Properties

The superior mechanical properties of cured epoxy resins only appear after the formation of their crosslinked structure. The network parameters which affect the mechanical response of a crosslinked epoxy are network defects and topography. Network defects in the form of unreacted groups serve as sites for crack initiation and propagation. Topography defects, such as notches and scratches, lower the mechanical properties.

Figure 3 shows the results of flexural tests on epoxy resins with different known ΔC_p values. The apparent phenomenon in place here is that a decrease in ΔC_p value is noted with an increase of flexural yield strength. When the flexural strength changes from 46 to 58 MPa, the value of ΔC_p goes from 0.36 to 0.25 J/g K in a

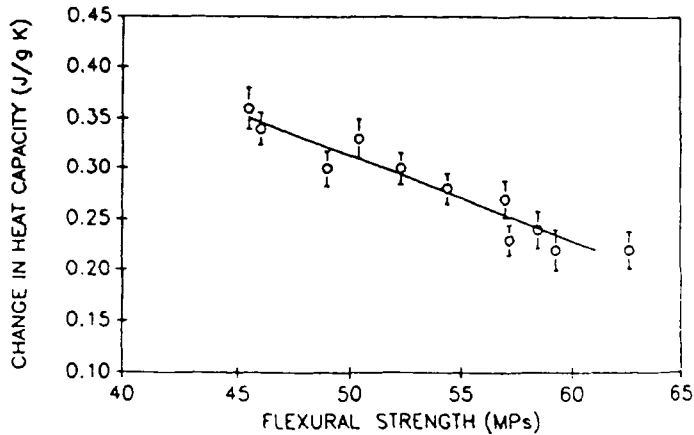


FIGURE 3 The variation of the change in heat capacity with flextural strength of cured epoxy resins.

smooth, gradual curve. Over this range, the curing extent and the density of crosslinking of epoxies increases gradually. When the flexural strength rises above 60 MPa, the ΔC_p values are low, about 0.25 to 0.22 J/g K. From Table I, we can see that samples with this value are fully cured and have the high density of a crosslinked network.

It can also be seen that the ΔC_p values drop more rapidly in the range from 0.36–0.25 J/g K at the start of the curing process than at other stages. Correspondingly, the flexural strength is clearly increasing. This phenomenon is due to the fact that, at this stage, the chain mobility in the structure is rapidly reduced, and the density of crosslinking increases from a low to high value.

The above results indicate that epoxies with lower ΔC_p values have the higher flexural strengths than those with higher ΔC_p values.

Within experimental error, the relationship between the change in heat capacity, ΔC_p , and the flexural yield strength, E , can be summarized by the linear equation:

$$\Delta C_p = -8.4 \times 10^{-3} E + 0.73 \quad (19)$$

where ΔC_p is in J/g K and E is in MPa.

The equation can be used to evaluate the flexural strength of cured epoxy resins from a knowledge of their heat capacity.

It is generally known that the mechanical strength of cured epoxy resins increases with the extent of crosslinking (or cure). Cured epoxy resins with high concentration of low-molecular-weight molecules show brittle behavior. However, beyond a certain stage of cure, the mechanical behavior becomes insensitive to the subsequent changes in cure time and temperature or the degree of crosslinking. At very high cure temperatures the mechanical strength shows a significant decrease in value due to the oxidation and degradation reactions which are known to occur at or above these temperatures.

These facts are important when manufacturing composites which have an epoxy resin as the matrix. Clearly the performance of the composite is contingent upon

carrying out the curing step under conditions which will furnish the matrix and matrix-reinforcing phase bonding in an optimal way. The contribution of the matrix is very important in composite production and composite performance.

CONCLUSION

The relationship between the ΔC_p values and the cure extent, as well as the flexural strength of cured epoxy resins, has been investigated. From the results it is apparent that the ΔC_p value is a convenient parameter for obtaining valuable information about the structure and properties of cured epoxy resins. The following conclusions are drawn:

1. The cure temperature and time influence the value of the change in heat capacity of epoxy resins. For example, increasing cure temperature and time reduces the values of the change in heat capacity. Epoxy resins with low value of ΔC_p have high curing extent and a high density of crosslinking in the network. The ranking of specimens by heat capacity of any given epoxy system, which has been cured by different treatments, is simple, rapid and reproducible.

2. The flexural strengths of epoxy specimens with lower values of ΔC_p are higher than those of specimens with higher ΔC_p values.

3. Based on above results, the ΔC_p value of epoxy resins can be used to evaluate their cure extent and the resulting flexural properties. The equation $\Delta C_p = -8.4 \times 10^{-3} E + 0.73$ links the two parameters for this particular epoxy system.

4. Since the measurement of heat capacity using the DSC is simple and practical, it is possible to use heat capacity data to evaluate the flexural strength of epoxy resins after different known cure treatments.

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