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Dielectric studies of three epoxy resin systems during microwave cure

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Abstract

Dielectric properties of three curing epoxy resin systems at an industrial microwave frequency, 2.45 GHz, were measured over a temperature range lower than the cure temperature. Extent of cure, which is determined by DSC, is used to describe the progress of the polymerization. It has been found that, normally, the real and the imaginary part of the complex dielectric constant increased with temperature and decreased during microwave cure. The changes of the dielectric properties during the reaction are related to the decreasing number of the dipolar groups in the reactants and the increasing viscosity. The Davidson–Cole model can be used to describe the experimental data. The Zong model is applicable to polymeric materials at high microwave frequencies and can be used to calculate the parameters of the Davidson–Cole model. The epoxy resins exhibit one γ relaxation, which can be described by the Arrhenius rate law. The evolutions of the parameters in the models are discussed.
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Keywords: Microwave processing; Epoxy resin; Dielectric properties

1. Introduction

Epoxy resin is one of the most versatile materials used in such areas as general purpose, electrical, and aerospace. In the general-purpose area, the diglycidyl ether of bisphenol A (DGEBA) epoxy resin is the preferred material and has been used as pipers, adhesives, protective coatings, and electrical insulations. Compared with conventional thermal heating, microwave heating of epoxy resins has many advantages, e.g. shortening processing time, saving energy, and improving properties [1–3]. The study of the dielectric properties during the curing process of epoxy resin has both fundamental and practical interests. It provides useful information about details of the curing reactions and, thus, has been developed as a nondestructive testing technique to monitor the curing processes. Studies on the dielectric properties of neat DGEBA epoxy resins [4–9] and reacting systems [10–14] of DGEBA and curing agents have received considerable attention. One main relaxation, α, and two secondary relaxations, β and γ, were found in DGEBA [4]. The structural α relaxation, which takes place at low frequencies and high temperature, was due to the micro-Brownian motions of polymer chains [5–7,11–13]. The secondary β process, occurring at higher frequencies and lower temperature, was assigned to a smaller section of the polymer chain than the α process, e.g. the hydroxyether group $-CH_2-CHOH-CH_2-O-$ [10]. The secondary γ relaxation, which is found located at higher frequencies than the β process, was the motion of individual groups of atoms, such as, epoxy groups, amine groups, and hydroxyl groups [5,11–14]. The evolution of the dielectric constant and the dielectric loss factor during cure is related to the disappearance of dielectric dipoles in the reactants [15–18] while the changes in the relaxation time depend on the viscosity of the reacting mixture [19–23].

Until now, the studies on DGEBA epoxy resins primarily focus on measuring dielectric properties as a function of frequency at a constant temperature. However, microwave heating apparatus usually operates at a constant frequency, e.g. 2.45 GHz for all domestic microwave ovens. The Federal Communications Commission (FCC) allocated a number of microwave frequencies for Industrial, Scientific and Medical applications (ISM), among which 2.45 GHz is the major operating frequency worldwide. In order to improve industrial applications of microwave processing of

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Table 1
Properties of the epoxy resin and curing agents

Name	Chemical structure	Epoxy/amine equivalent weight	Density @ 25 °C (g/ml)
DGEBA	CH_3, O, O, CH_3, O, O	171–175	1.16
DDS	H_2N, NH_2, O, S, O	62	1.33
Jeffamine D-230	H_2N, CH, CH_2, O, CH_2, CH, NH_2, x=2.6, CH_3, CH_3	60	0.948
mPDA	H_2N, NH_2	27	1.14

epoxy resins, understanding the dielectric properties and relaxation during cure at an ISM microwave frequency is essential. In the present paper we focus on the dielectric analysis of the curing systems of DGEBA and three different curing agents at 2.45 GHz over a temperature range. The dielectric properties changing with the reaction were fit by two models and the evolutions of dielectric parameters, e.g. dielectric strength, shape parameter, and relaxation activation energy, were analyzed.

2. Experimental

2.1. Materials

The epoxy resin used in this study was DGEBA (DER 332 by Dow Chemical). The curing agents were 3,3-diaminodiphenyl sulfone (DDS by TCI America), a difunctional primary amine (Jeffamine D-230 by Huntsman), and *m*-phenylenediamine (mPDA by Sigma-Aldrich). The chemical structures and properties of DGEBA and the curing agents are shown in Table 1.

2.2. Sample preparation

All of the materials were used as received without further purification. In preparing neat DGEBA/DDS epoxy resins, stoichiometric DGEBA and DDS (2.79:1 by weight) were mixed in a glass beaker. The mixtures were well stirred by hand in a 130 °C oil bath until the DDS was completely dissolved (in approximately five minutes). Finally, the resins were degassed at 0.02 bar at 100 °C for 5 min. In order to prepare neat DGEBA/Jeffamine epoxy resins, DGEBA was first preheated in a glass beaker at 50 °C to melt any crystals present and then a stoichiometric Jeffamine (weight ratio of DGEBA/Jeffamine 2.88:1) was added. The mixture was stirred for 5 min with a magnetic bar at room temperature and degassed at 0.02 bar at room temperature for 5 min. To prepare neat DGEBA/mPDA epoxy resins, stoichiometric DGEBA and mPDA (6.4:1 by weight) were mixed in a glass beaker. The mixtures were well stirred with a magnetic bar at 65 °C for 5 min and then degassed at 0.02 bar at room temperature for 5 min.

2.3. Measurements

A single-frequency microwave processing and diagnostic system was used to heat the epoxy resins and assess their dielectric properties. Details of the experimental equipment can be found in the literatures [24,25]. The degassed epoxy resins were poured into a Teflon holder. The Teflon holder with a fluoroptic temperature probe was located at the position of the highest electric field for the TM012 cavity mode at 2.45 GHz. The fresh DGEBA/DDS samples were heated to react at 145 °C for specified reaction time periods, e.g. 1, 5, and 20 min, with the exception of those for the 0% cured epoxy resin, which were heated to 100 °C. The curing temperatures for the DGEBA/Jeffamine and DGEBA/mPDA systems were 90 and 110 °C, respectively, and the peak temperatures for the unreacted epoxy resins were 80 and 90 °C, respectively. Thereafter, the single frequency microwave curing system was switched to become a low-power swept frequency diagnostic system. Measurements of temperature and dielectric properties using the swept frequency method were made during free convective cooling of the samples. The cooled samples were analyzed

Table 2
DSC results of the curing DGEBA/DDS system

Reaction heat (J/g)	432	387	395	324	249	168	203	72
	448	436	415	350	253	299	153	109
	419	403	360	362	269	262	58	63
	439	370	330	370	294	222	57	64
	429	365	363	290	308	297	319	157
Extent of cure (%)	0	9	14	22	37	42	64	79
Standard error (±%)	1	3	3	3	3	6	11	4

with a Differential Scanning Calorimeter (DSC) to determine the residual heat of reaction per gram and, thus, the extents of cure. The experimental DSC results and calculated extents of cure of the three systems are shown in Tables 2–4.

3. Results and discussion

The changes in the dielectric properties of the curing DGEBA epoxy resins at 2.45 GHz are shown as plots of the dielectric constant (ε') and the dielectric loss factor (ε'') against temperature in Fig. 1. Normally, the dielectric properties decrease as the extent of cure increases and increase with temperature. However, the dielectric loss factor of low extents for DGEBA/Jeffamine and DGEBA/mPDA systems decreases at temperatures over 70 °C, exhibiting one relaxation. The relaxation, occurring in three reacting systems with or without showing peak ε'' value, should be the γ relaxation due to the high frequency used in this study [11–14]. To interpret the relaxation, one should know the dielectric behaviors of all involved dipolar groups, which are, however, too complicated to differentiate. Since the dipolar groups within the reacting system and their dynamics are substantially similar, the dielectric properties of the reacting system reflect the combination of all the dipolar groups involved in the reaction.

DGEBA reacts with amines via a ring-opening mechanism. Three-step reactions occur during cure [26]. In the first step, an epoxy group reacts with a primary amine to form a hydroxyl group and a secondary amine. In the second step, the formed secondary amine reacts with another epoxy group to produce a hydroxyl group and a tertiary amine. The third step is etherification, which is reaction of a hydroxyl group formed during the reaction and an epoxy group to form an ether crosslinking epoxy. However, etherification is insignificant for stoichiometric mixtures [23]. In this study, it is assumed that the reaction is between the amine hydrogens and the epoxy groups. The curing reaction of epoxy resins with amines is illustrated in Fig. 2. The progress of the reaction is defined in terms of extent of cure. The viscosity of the reacting systems rise as the polymerization goes on [23] and two distinguishable transitions, i.e. the gelation and the vitrification, are crossed. The γ relaxation in this experiment is the motion of individual groups of atoms, which should include: epoxy and amine groups with the unreacted DGEBA and curing agents; dipolar groups with the intermediate products and final polymers, e.g. –OH, –NH–, and =N– [11–14]. As the reaction goes on, epoxy dipoles disappear, amine dipoles change to –NH– and =N–, and new dipoles, such as hydroxyl groups, appear. Overall, the total number of the dipolar groups within the reacting system is stable. Taking into account decreasing dielectric properties during cure, it is reasonable to suppose that the contribution of different dipolar groups to the relaxation is different. The unreacted epoxy groups, –O–, and amine groups, $-NH_2-$, within the reaction system are the main driving forces for the apparent combined γ relaxation observed in this study. The disappearance of the epoxy and amine groups during the reaction is one reason accounting for the changes of the dielectric properties. Other researchers reported similar results [15–18]. However, it may not be the only reason. According to the classical Debye theory, the dielectric dipoles are regarded as spheres in a continuous medium having a macroscopic viscosity [27]. Schonhals and Schlosser studied the dielectric relaxation in polymeric solids and argued that the environment with high viscosity hindered the diffusion process of dipolar groups, causing the dielectric behavior of polymers far from ideal Debye materials [28]. In this study the transitions from liquid to gel and then to solid during the cure reactions was observed for the three systems. The increasing viscosity of the reacting systems should hinder the mobility of the dipolar groups associated with the relaxation and cause the relaxation time to increase [19–23]. The two reasons

Table 3
DSC results of the curing DGEBA/Jeffamine system

Reaction heat (J/g)	260	296	298	222	177	160	119	62
	313	253	229	185	208	143	125	44
	299	238	192	205	156	161	82	50
Extent of cure (%)	0	10	18	30	38	47	63	82
Standard error (±%)	5	6	11	4	5	2	5	2

Table 4
DSC results of the curing DGEBA/mPDA system

Absorbed heat (J/g)	467	488	319	311	211	89	72
	492	370	297	215	192	93	60
	477	403	302	223	198	112	81
Extent of cure (%)	0	11	35	47	58	79	85
Standard error (±%)	2	7	1	6	1	1	1

accounting for the evolution of the dielectric constant and the dielectric loss factor are a decrease in the number of the dipolar groups in the reactants and an increase in the viscosity during the reaction.

Several empirical models were proposed to describe the dielectric properties of materials, e.g. the Debye model [27], the Cole–Cole model [29], the Davidson–Cole model [30], the Havriliak and Negami model [31], and the Zong model [14]. The Davidson–Cole model can be used to describe the dielectric behavior of the three systems. The Davidson–Cole model [30] is given by:

$$\varepsilon * -\varepsilon_\infty = \varepsilon' - j\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)}{(1 + j\omega\tau)^n} \tag{1}$$

$$\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)\cos(n\theta)}{(1 + (\omega\tau)^2)^{n/2}} \tag{2}$$

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\sin(n\theta)}{(1 + (\omega\tau)^2)^{n/2}} \tag{3}$$

$$\theta = \arctan(\omega\tau) \tag{4}$$

where ε^* is the complex dielectric constant; ε' is the dielectric constant, ε'' is the dielectric loss factor; j is the imaginary unit; ω ($=2\pi f$, f is the oscillator frequency in Hz) is the radial frequency of the electric field in s^{-1}; τ is the relaxation time in s; ε_0 is the static frequency dielectric constant; ε_∞ is the high frequency dielectric constant, and n is the shape parameter with a range of $0 \le n \le 1$. The shape of Cole–Cole plot of the Davidson–Cole model is a straight line at high frequencies and a semicircle with center on the horizontal ε' axis at low frequencies. The straight line can be represented by the Zong model [14]:

$$\varepsilon * -\varepsilon_\infty = \frac{(\varepsilon_0 - \varepsilon_\infty)}{(j\omega\tau)^n} \tag{5}$$

$$\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)\cos(n\frac{\pi}{2})}{(\omega\tau)^n} \tag{6}$$

$$\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\sin(n\frac{\pi}{2})}{(\omega\tau)^n} \tag{7}$$

Kauzman defined relaxation to be the time lag in the response of a system to a change in the physical forces (temperature, electric field, magnetic field, stress, etc.) to which it is subjected [32]. The dielectric relaxation time is an indication of the average amount of time required for a collection of dipoles in an electromagnetic field to revert to a random orientation once the field is removed. The dominant γ relaxation in this experiment should fit the Arrhenius rate law [32]:

$$\tau = A\,e^{\left(\frac{E_a}{RT}\right)} \tag{8}$$

where E_a is the activation energy in J/mol, R is the gas constant in J/mol K, T is the temperature in K, and A is the relaxation time in the high temperature limit in s.

The Zong model, simpler than the Davidson–Cole model, is applicable to linear dielectric complex plane plots, e.g. DGEBA/DDS systems, DGEBA/Jeffamine epoxy resins over 30% extent of cure; DGEBA/mPDA epoxy resins over 47% extent of cure. Compared with Jeffamine and mPDA, DDS has a rigid chain which hinders the relaxation of dipolar groups (see Table 1). Therefore, the dielectric behavior of DGEBA/DDS epoxy resins at low extents under 2.45 GHz is similar to that of polymers, which can be described by the Zong model, while that of DGEBA/Jeffamine and DGEBA/mPDA epoxy resins at low extents is similar to that of low molecular weight chemicals, such as glycerol, which can be described by the Davidson–Cole model. In a word, the Zong expression is applicable to polymeric materials at high frequencies. Furthermore, it can be used to calculate the parameters in the Davidson–Cole model for three systems even if it can not describe all the experimental data. The values of the parameters, n, ε_∞, and E_a, and a relation between (ε_0–ε_∞) and A, can be calculated using Eqs. (5)–(8) even for DGEBA/Jeffamine and DGEBA/mPDA at low extents [14]. For the GEBA/DDS system, the values of (ε_0–ε_∞) is taken from the literature [13] and then A was determined. The values of ε_0 for DGEBA/Jeffamine and DGEBA/DDS systems were modified until the calculated dielectric data fit the experimental ones well. The comparison of the experimental data with the calculated data is shown in Fig. 1. The difference between the actual and theoretical values is caused by the calculation error based on the approximation functions and the experimental error due to fluctuation of measured data including temperature, resonant frequency, half-power frequency bandwidth, DSC samples.

The parameter ε_0 represents the equilibrium behavior while ε_∞ represents the instantaneous behavior. Therefore, (ε_0–ε_∞) is the effective moment of the orienting dipoles [31]. The γ relaxation strength ($\varepsilon_0 - \varepsilon_\infty$) was found to decrease during the polymerization of the three systems (see Fig. 3), which is consistent with the decreasing number of the epoxy and amine groups of the reactants. Researchers at

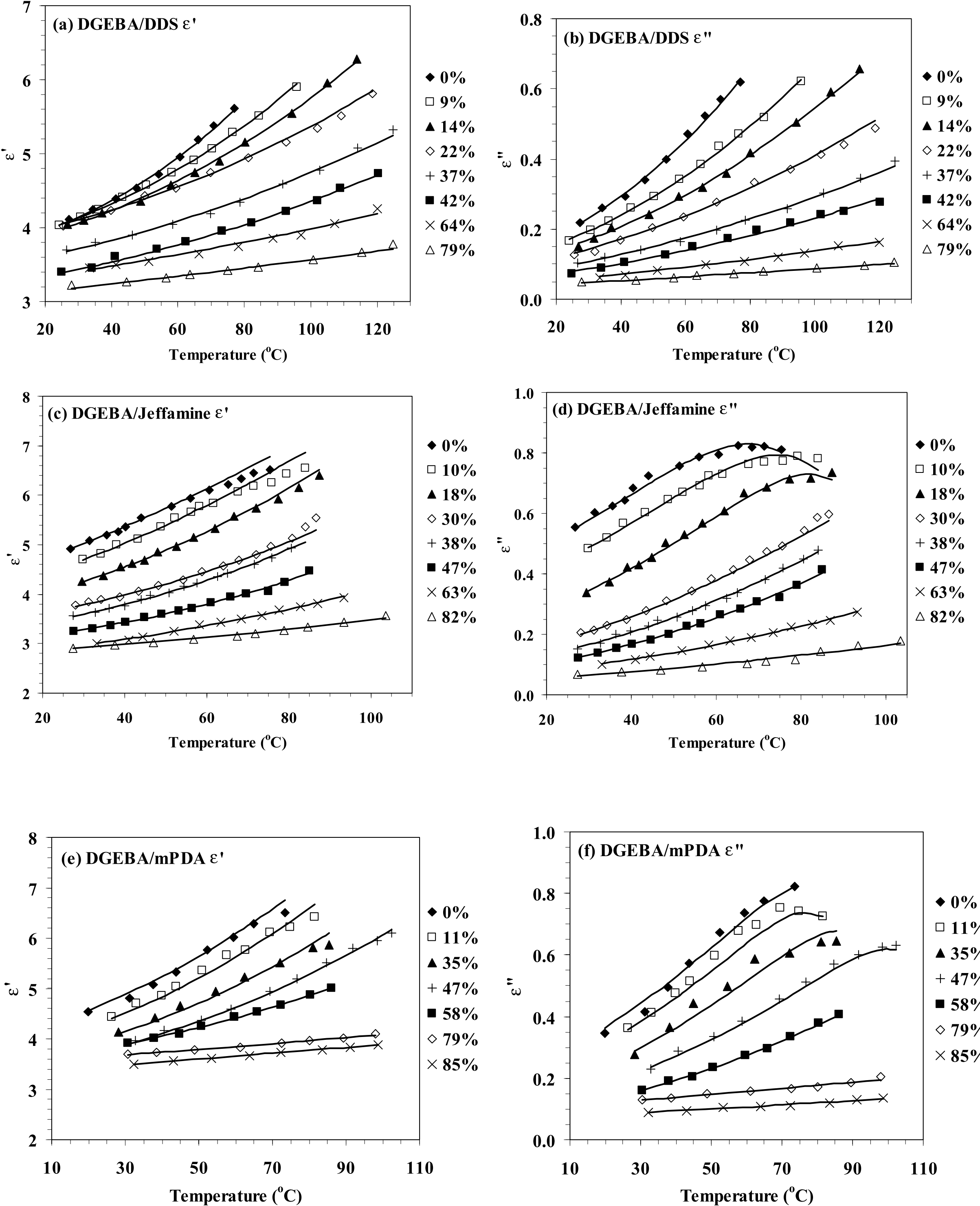

Fig. 1. Temperature dependence of the dielectric constant (ε') and the dielectric loss factor (ε'') at 2.45 GHz for the systems of DGEBA and three curing agents at different extents of cure (%): (a) DDS ε'; (b) DDS ε''; (c) Jeffamine ε'; (d) Jeffamine ε''; (e) mPDA ε'; (f) mPDA ε''. The curves represent the calculated data; the points represent experimental data.

University of Pisa reached same results for similar reacting systems [11,13] while Sheppard and Senturia reported that the relaxed dielectric constant ε_∞ deceased as the reaction progressed and could be linearly related to the extent of cure for DGEBA/DDS reacting system [17]. In addition, the relaxation strength was found to diminish with increasing molecular weight of DGEBA prepolymers [7].

Fig. 4 shows the shape parameter n as a function of extent of cure for the three systems. As the reaction goes on, n decreases from 0.18 down to 0.07. The three systems have

Step 1

R—NH2 + [epoxide]—R1 → R—NH, R1, OH

Step 2

R—NH, R1, OH + [epoxide]—R2 → R—N, OH, R2, R1, OH

Fig. 2. DGEBA epoxy resin curing mechanism.

same trend. The parameter describes the skewness of the dispersion of the relaxation times, which increases as n ranges from unity to zero. The value of n for an ideal Debye material is unity while that for polymeric solutions is around 0.5 [33]. The relaxation time is mainly connected with the mobility of the dipolar groups for the γ relaxation. During the reaction the motion of dipolar groups is hindered by the medium with increasing viscosity caused by curing epoxy resins. Therefore, the parameter n decreases. The rationale is similar to the argument that n is connected with the local chain dynamics of a polymer and deceases in the range 0.5–0 with an increase of hindrance of orientational diffusion in the polymer [28]. Another similar result is that the parameter n for DGEBA prepolymers decreases as the molecule weight increases [7].

The activation energy of the γ relaxation for all three systems first increases, and then decreases during cure (see Fig. 5). The activation energy is the mean value of a distribution of activation energies [32] and changes with the

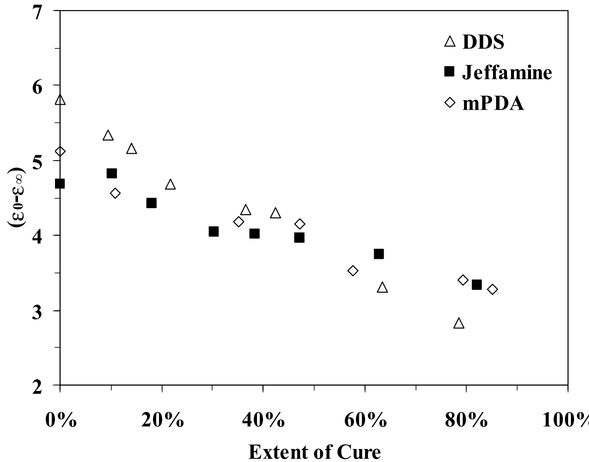

Fig. 3. Relaxation strength (ε_0–ε_∞) as a function of extent of cure for the systems of DGEBA with three curing agents. The dashed lines are the guide for the eye.

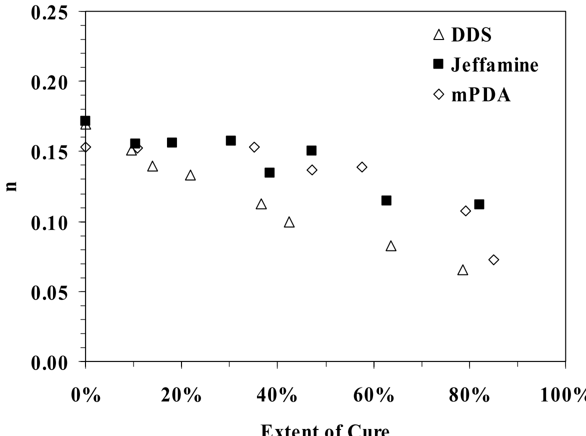

Fig. 4. Shape parameter n versus extent of cure for the three systems.

polymerization [19]. The phenomenon of increasing activation energy is consistent with the fact that the viscosity increases as the polymerization progresses. However, after the extent of cure reaches around 50–60% the activation energy start to decrease. It may be explained by that the hindrance ability of the existing polymer chains may be weaker than that of dipoles in the reactants and thus less energy is needed for dipolar groups to relax after the peak point. Inasmuch as the gel point for the DGEBA/DDS system is 58% [23], the peak during 50–60% extents may be related to the gel point of the curing system.

The relaxation time increases as the reaction proceeds. For instance, the calculated γ relaxation time at 80 °C has been reported as a function of the extent of cure in Fig. 6. This is consistent with Kauzman's study on relaxation on polymers [32]. The main reason for the remarkable increase of the relaxation time during the reaction is the rise of the medium viscosity [23]. Furthermore, it is shown in Fig. 6 that the relaxation time of DGEBA/DDS system is about two decades larger than that of DGEBA/Jeffamine and DGEBA/mPDA systems. This confirms the argument that the dielectric behavior of DGEBA/DDS system at low

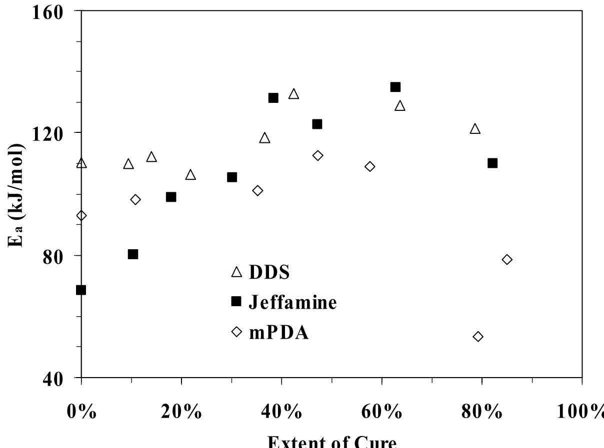

Fig. 5. Activation energy E_a versus extent of cure for the three systems.

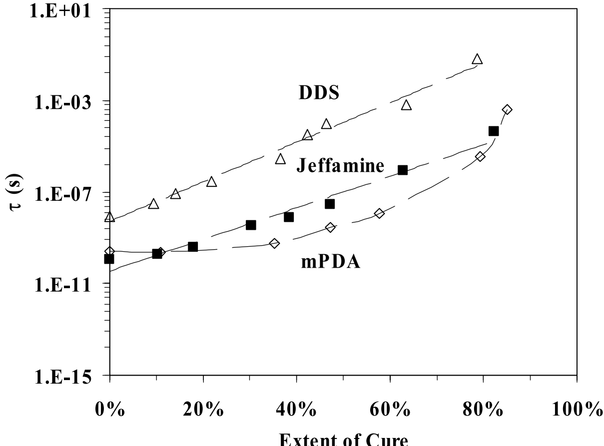

Fig. 6. Calculated relaxation time versus extent of cure for the three systems at 80 °C. The dashed lines are the guide for the eye.

extents is more like that of polymers than that of DGEBA/Jeffamine and DGEBA/mPDA systems.

Fig. 7 shows the calculated dielectric constant versus extent of cure for the three isothermal curing systems, i.e. DGEBA/DDS at 145 °C, DGEBA/Jeffamine at 90 °C, and DGEBA/mPDA at 110 °C. The dielectric constant exhibits a linear relation to the extent of cure and may be a convenient dielectric quantity to in situ monitor the polymerization. This agrees with the results the study on another DGEBA curing system [15].

4. Conclusions

The dielectric properties of the curing systems of DGEBA epoxy resin with three curing agents, i.e. DDS, Jeffamine D-230, and mPDA, as a function of temperature at 2.45 GHz have been investigated. The progress of the reaction is defined in terms of extent of cure. Generally, the

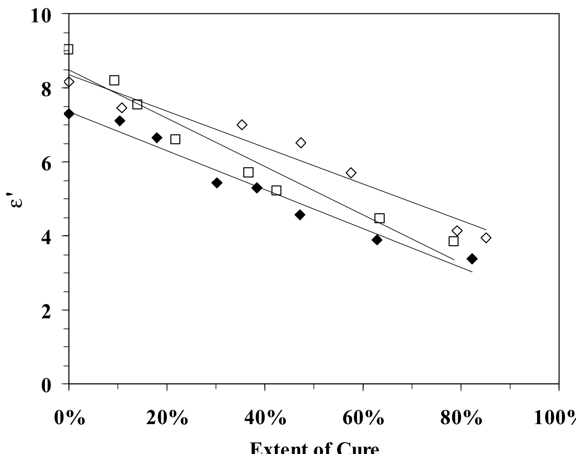

Fig. 7. Calculated dielectric constants (ε') versus extent of cure for the three systems. (□) DGEBA/DDS system curing at 145 °C; (♦) DGEBA/Jeffamine system curing at 90 °C; (◇) DGEBA/mPDA system curing at 110 °C.

real and the imaginary part of the complex dielectric constant increased with temperature and decreased as the extent of cure increased. The two reasons accounting for the evolution of the dielectric quantities are a decrease in the number of the dipolar groups in the reactants and an increase in the viscosity. The Davidson–Cole model can be used to describe the experimental data. The Zong model is applicable to polymeric materials at high microwave frequencies and can be used to calculate the parameters in the Davidson–Cole model. The γ relaxation has been identified and can be described by the Arrhenius rate law. The evolution of the parameters in the models is discussed. The relaxation strength decreases during cure mainly because the number of the epoxy and amine groups in the reactants decreases. The main reason for the facts that the shape parameter decreases, the activation energy and the relaxation time increases, is increasing viscosity of the reacting system. The dielectric constant may be used to real-time monitor the DGEBA curing reactions.

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References

[1] Zong L, Zhou S, Sgriccia N, Hawley MC, Kempel LC. J Microwave Power 2003;38:49.
[2] Fu B, Hawley MC. Polym Eng Sci 2000;40:2133.
[3] Wei J, Hawley MC, Delong JD, Demeuse M. Polym Eng Sci 1993;33:1132.
[4] Pochan JM, Gruber RJ, Pochan DF. J Polym Sci: Polym Phys 1981;19:143.
[5] Casalini R, Fioretto D, Livi A, Lucchesi M, Rolla PA. Phys Rev B 1997;56:3016.
[6] Koike T. Polym Eng Sci 1993;33:1301.
[7] Koike T, Tanaka R. J Appl Polym Sci 1991;42:1333.
[8] Simpson JO, Bidstrup SA. J Polym Sci Part B: Polym Phys 1993;31:609.
[9] Sheppard NF, Senturia S. J Polym Sci Part B: Polym Phys 1989;27:753.
[10] Domenici C, Levita G, Marchetti A, Frosini V. J Appl Polym Sci 1987;34:2285.
[11] Butta E, Livi A, Levita G, Rolla PA. J Polym Sci Part B: Polym Phys 1995;33:2253.
[12] Casalini R, Livi A, Rolla PA, Levita G, Fioretto D. Phys Rev B 1996;53:564.
[13] Gallone G, Capaccioli S, Levita G, Rolla PA, Corezzi S. Polym Int 2001;50:545.
[14] Zong L, Zhou S, Sun R, Kempel LC, Hawley MC. J Polym Sci Part B: Polym Phys 2004;42:2871.
[15] Livi A, Levita G, Rolla PA. J Appl Polym Sci 1993;50:1583.
[16] Carrozzino S, Levita G, Rolla P, Tombari E. Polym Eng Sci 1990;30:366.
[17] Sheppard NF, Senturia SD. Polym Eng Sci 1986;26:354.

[18] Eloundou JP, Gerard JF, Pascault JP, Kranbuehl D. Macromol Chem Phys 2002;203:1974.

[19] Lane JW, Seferis JS, Bachmann MA. Polym Eng Sci 1986;26:346.

[20] Lane JW, Seferis JS, Bachmann MA. J Appl Polym Sci 1986;31:1155.

[21] Kortaberria G, Arruti P, Mondragon I. Polym Int 2001;50:957.

[22] Lairez D, Emery JR, Durand D, Pethrick RA. Macromolecules 1992; 25:7208.

[23] Simpson JO, Bidstrup SA. J Polym Sci Part B: Polym Phys 1995;33: 55.

[24] Jow J. PhD Dissertation, Michigan State University, East Lansing, MI, 1988.

[25] Zong L, Charvat GL, Kempel LC, Hawley MC. 26th AMTA Symp, Stone Mountain, GA, Oct 2004.

[26] Lee H, Neville K. Epoxy resins: their applications and technology. New York: McGraw-Hill; 1957, p. 41.

[27] Debye P. Polar molecules. New York: Dover; 1945.

[28] Schonhals A, Schlosser E. Colloid Polym Sci 1989;267:125.

[29] Cole KS, Cole RHJ. Chem Phys 1941;9:341.

[30] Davidson DW, Cole RHJ. Chem Phys 1951;19:1484.

[31] Havriliak S, Negami S. Polymer 1967;8:161.

[32] Kauzmann W. Rev Mod Phys 1942;14:12.

[33] Viovy JL, Monnerie L, Brochon JC. Macromolecules 1983;16:1845.