Multiplexing frequency mode study of packaging epoxy molding compounds using dynamic mechanical analysis

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Abstract

Dynamic mechanical analysis (DMA) measures mechanical properties (modulus and damping) of viscoelastic materials over a spectrum of time (or frequency) and temperature. This paper reports its use to study four epoxy molding compounds (EMC1A, 1B, 2 and 3) for electronic packaging industry using multiplexing frequency (or multiple frequency) mode DMA. The raw epoxy molding compounds were processed under 1 min transfer mold curing (TMC) but different post-mold curing (PMC) conditions. Viscoelastic properties over temperature at fixed oscillatory frequency of the compounds were studied. Specimen EMC1B with longer PMC (4 h) resulted in higher glass transition temperature (T_g) compared to EMC1A (0 h PMC) of the same brand of material. The other two brands of epoxy molding compounds EMC2 and EMC3 behave differently from EMC1 as shown from their T_g variations. It was observed that T_g's of all compounds studied were generally increasing with higher oscillatory frequency DMA temperature sweep. Activation energies (E_a) at T_g relaxation process of compounds were calculated from Arrhenius plots, $\log f$ versus $1/T_g$. Effects of different curing conditions of compounds on E_a were also discussed. It was noticed that EMC1B after 4 h PMC resulted in E_a of about 3.4 times higher than EMC1A (0 h PMC). Application of time–temperature superposition (TTS) technique to the multiplexing frequency mode analysis of the cured epoxy molding compounds was illustrated. Master curves, of modulus as a function of oscillatory frequency of the compounds, were therefore constructed and generated at temperature interval of 20° of each compound. Performance of specimens at specific operating conditions can be predicted and compared. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Dynamic mechanical analysis (DMA) measures complex modulus ($\mathbf{E}^{\star}$), compliance ($\mathbf{J}^{\star}$), and viscosity η in different modes of oscillatory deformation of materials [1]. Deformation modes include flexure, shear, bending, compression and tensile. This technique has been widely used to study dynamic mechanical properties of a variety of materials such as elastomers, thermoplastics, viscous thermosets, composites, ceramics and metals. It is particularly useful for evaluating polymeric materials, which exhibit temperature and time effects on mechanical properties due to their viscoelastic nature. The glass transition (and secondary transitions), cross-linking, creep, and stress relaxation may be investigated. Principal thermoset application include analysis of cross-linking

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and mechanical property development during curing, as well as characterization of cured materials. Polymeric thermoset materials exhibit viscoelastic responses during deformation, which is both time (t) and temperature (T) dependent. Time dependence is therefore related to frequency f by the equation, $t = 1/2\pi f$.

Integrated circuit devices are normally encapsulated with epoxy molding compounds by transfer mold process to protect the devices against mechanical and chemical hazard [2,3]. This paper studies viscoelastic properties of curing of four packaging epoxy molding compounds and applies the time–temperature superposition (TTS) technique [1,2,4–7] to multiple frequency (multiplexing frequency) mode analysis. TTS is based on the observation that time–temperature and frequency–temperature effects in polymers are largely equivalent. That means increasing temperature will shift the same event to shorten experimental time, or increasing the frequency will shift to higher temperatures. Master curves can be constructed to show the behavior of a material over several decades of time, and they can be used to predict or estimate long-term performance in specific operating conditions. The measurement of the activation energy of a glass transition can also be accomplished by making multiple frequency measurements of the loss modulus peak across the temperature range of the transition.

2. Experimental

DMA of four epoxy molding compounds (labeled EMC1A, 1B, 2, and 3) was performed. All samples were transfer mold cured (TMC) for 1 or 2 min followed by different duration of post-mold curing (PMC). They were molded to the same rectangular shapes (1.5 mm × 5 mm × 25 mm) for easy comparison. Treatment conditions of all specimens before DMA are summarized in Table 1. All DMA experiments were performed (Perkin Elmer DMA7) under helium purge environment at a heating rate of 5°C/min. In our experiments, viscoelastic properties of epoxy molding compound were characterized by 3-point bending mode at different steps of frequency (f) from 1 to 50 Hz when sample was being heated. The strain amplitude of all experiments was kept constant

Table 1
Conditions of specimens before DMA study

EMC	TMC (min)	PMC (h)
1A	1	0
1B	1	4
2	2	3
3	2	3

at 1 μm. Storage modulus (E') and tangent of phase angle (δ) were being monitored as functions of temperature at fixed frequency, respectively. Glass transition was detected as a decrease in storage modulus or an increase in loss modulus.

A typical Arrhenius plot, $\log f$ versus $1/T_g$ absolute temperature yields an activation energy (E_a) for the T_g relaxation process. Activation energies of the four epoxy molding compounds were calculated from the slopes $-E_a/R$ of each plot. TTS is an empirical method for predicting material properties beyond the range of laboratory analysis. It allows for the prediction of very long-term and short-term behaviors or behavior at temperature ranges other than original analysis. TTS can be used to extrapolate over the dynamic range of laboratory analysis and predict performances of materials such as polymers and composites over very long time. The procedure for performing TTS involves generating a multiplex data set and shifting the data with respect to a reference curve (chosen as the modulus curve at a specific temperature) to generate a master curve. Shifting the storage modulus relative to the reference curve therefore forms the master curve. Such master curves completely define the viscoelastic properties of a material. The master curves can also be shifted to a higher or a lower temperature, and predictions can be made over very long or short times at the new temperature.

3. Results and discussion

3.1. Viscoelastic property of epoxy molding compounds

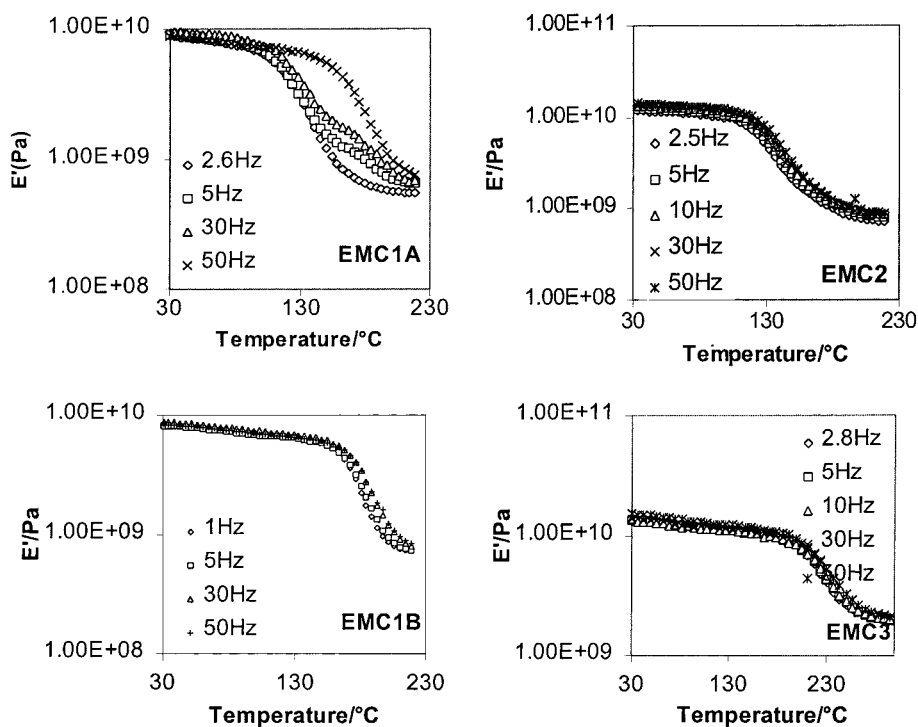Fig. 1 shows the storage modulus (E') plots of all the four specimens as a function of temperature.

Fig. 1. Plots of storage modulus (E') versus temperature of specimens EMC1A, 1B, 2 and 3.

Storage modulus behavior of EMC1A at 50 Hz behaved differently from those at 2.6, 5 and 30 Hz which shows a higher glass transition temperature. The temperature sweep at 50 Hz of EMC1A therefore results in higher degree of cure than at lower frequency modulation. Moreover, EMC1B shows higher T_g and less variation of storage modulus plots compared to EMC1A at all the frequency range. EMC2 and EMC3 behave similar modulus change as functions of temperature except that EMC3 exhibits higher T_g and storage modulus at the rubbery state than EMC2. Fig. 2 shows the tan δ plots of all the four specimens as a function of temperature. Tan δ was seen to shift to higher values with increasing frequency except for experiments at 50 Hz. Multiplexing frequency and the dependency on T_g peak temperature of tan δ are summarized in Table 2. It was observed that T_g increases with respect to the frequency change and EMC1A results in significant T_g shifts following the frequency change compared to EMC1B. Fig. 3 shows plots of T_g (from tan δ) versus different sweeping frequency of the compounds.

Table 2
Dependency of multiplexing frequency and T_g peak temperature of tan δ

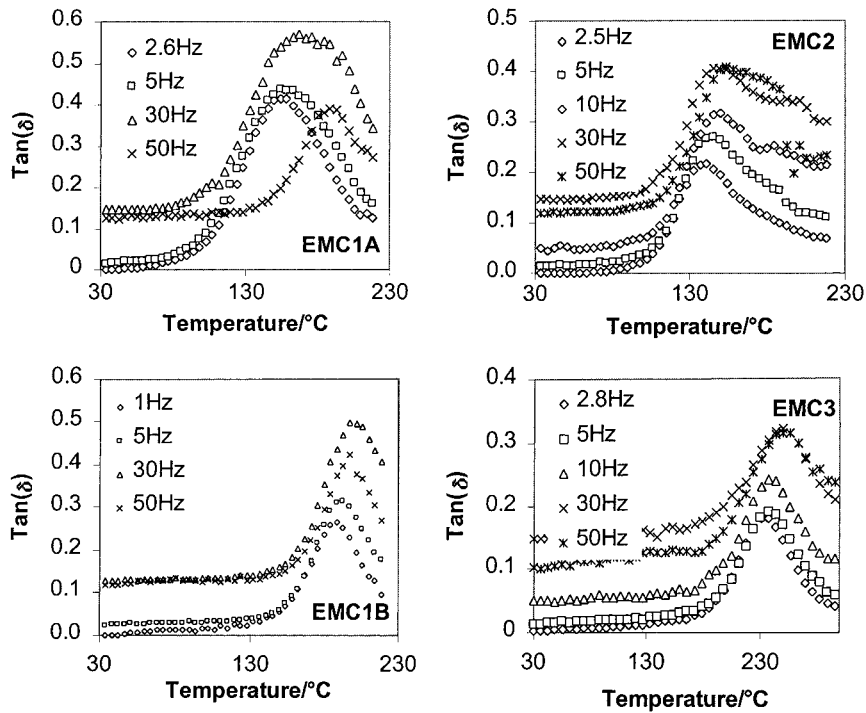| EMC	Frequency (Hz)	T_g^* ($^{\circ}$C)[a]
1A	2.6	154.0
	5	158.0
	30	172.5
	50	190.0
1B	1	187.1
	5	190.8
	30	196.5
	50	202.4
2	2.5	139.2
	5	143.9
	10	146.7
	30	150.0
	50	155.7
3	2.8	233.6
	5	238.4
	10	240.2
	30	248.5
	50	251.6

[a] Peak temperature of tan δ.

Fig. 2. Plots of tan δ versus temperature of specimens EMC1A, 1B, 2 and 3.

EMC1A and EMC1B were processed under the same TMC condition (1 min), but different PMC. EMC1A (0 h PMC) had lower T_g comparing to EMC1B (4 h PMC) at the same frequency value. Moreover, the rate
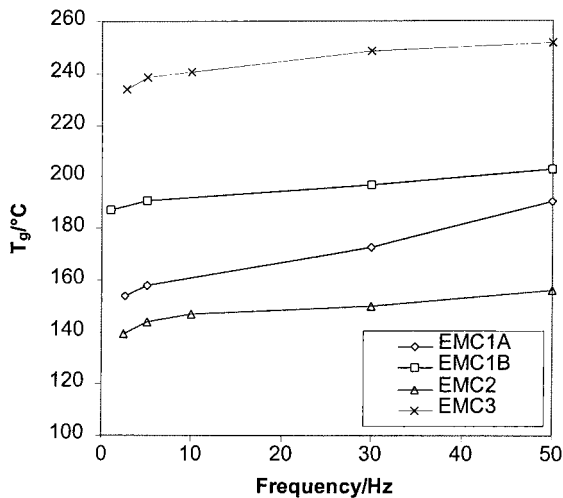

Fig. 3. Plot of T_g versus sweeping frequency of the specimens EMC1A, 1B, 2 and 3.

of T_g increases with respect to frequency is faster for epoxy molding compound EMC1A with no PMC. EMC2 and EMC3 behaved similarly with T_g increased in a simple fashion with increasing frequency. T_g of EMC2 is still slightly increasing from 30 to 50 Hz, while that of EMC3 is not changing much.

3.2. Activation energy of T_g relaxation process of epoxy molding compounds

Fig. 4 is the Arrhenius plot of log f versus $(1/T_g)$ of specimens EMC1A, 1B, 2 and 3, respectively, yielding activation energies (E_a) of 59.1, 203.2, 123.8 and 154.8 kJ mol^{-1} for the T_g relaxation processes. The activation energies are calculated from the slopes of each linear regression line. Coefficients of regression (R) for specimen EMC1A, 1B, 2 and 3 are all >0.91. E_a's of specimen EMC1B with 4 h PMC is larger than 0 h PMC EMC1A, while EMC3 has larger E_a than EMC2. Packaging epoxy molding compounds with further PMC after TMC show higher activation energy values. It is the consequence of further cross-linking of compounds during PMC. It was, therefore, observed
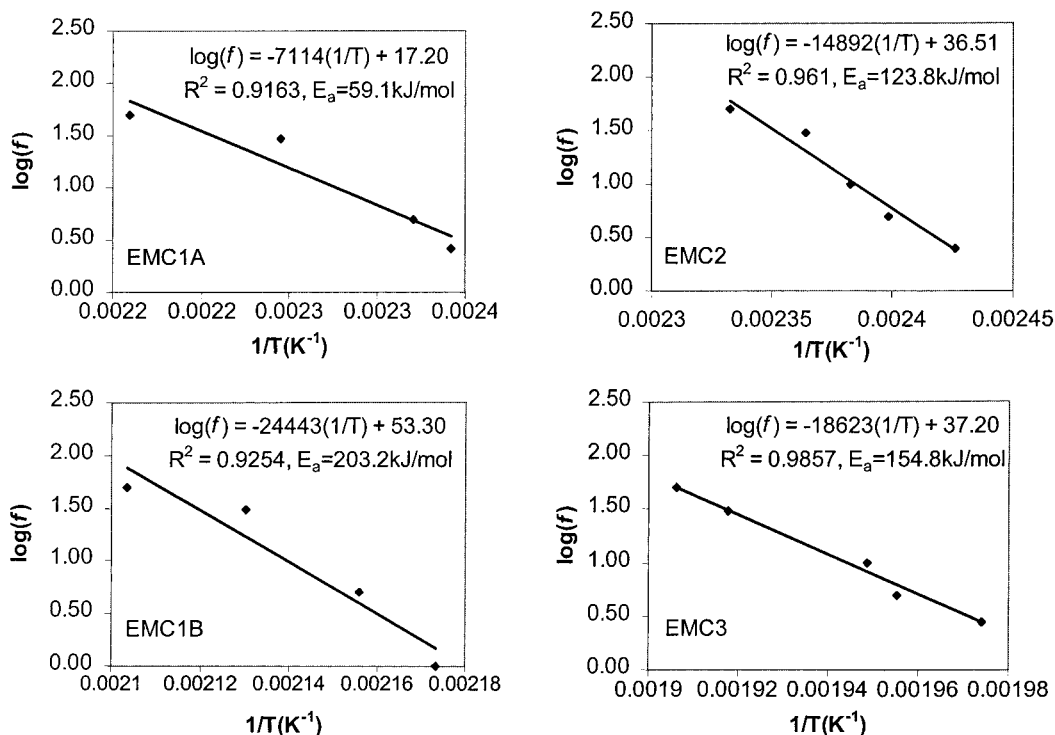
Fig. 4. Arrhenius plots of specimens EMC1A, 1B, 2 and 3.

that E_a of EMC1B after 4 h PMC is about 3.4 times of that without PMC (EMC1A).

3.3. Relationship of T_g and $\ln(E')$ of epoxy molding compounds

Fig. 5 shows the relationship between glass transition temperature and $\ln E'$ (at the rubbery state) of the four cured epoxy molding compounds. EMC1B has higher modulus and T_g compared to EMC1A. This is expected as EMC1B was processed with 4 h PMC that resulted in higher cross-linking reaction. It was also seen that the T_g increase with respect to $\ln E'$ for EMC1A and 1B is almost linear. According to Ogata et al. [5], T_g of epoxy molding compounds is related to the cross-linking density (ρ) at the rubbery state: $T_g = K_1 \log \rho + K_2$, of which ρ can also be calculated from rubbery elastic modulus (E'): $\rho = K_3 E'(T)/T$, where K_1, K_2 and K_3 are constants. Therefore, T_g can be expressed in terms of both cross-linking density (ρ) and modulus (E') at temperatures of the rubbery state. The linear relationship of T_g and $\ln E'$ was also

observed for EMC2. Calculated K_1 for EMC1 and EMC2 are approximately 122 and 74, respectively. These values are comparable to the normal K_1 values (50–110) of most epoxy resin compounds [5]. It is also
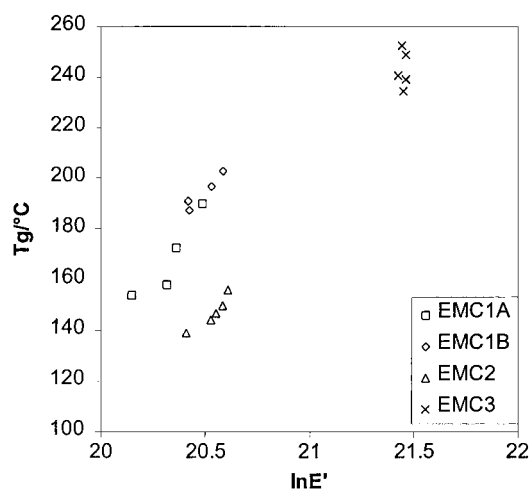

Fig. 5. Plot of T_g versus $\ln E'$ of specimens EMC1A, 1B, 2 and 3.

interesting to note that small increase of E' leads to a significant change of T_g for EMC3.

3.4. Time–temperature superposition application to multiplexing frequency experiments of epoxy molding compounds

The procedure for performing TTS involves data extracted from the multiplexing frequency experiments followed by shifting the data with respect to a reference curve to generate a master curve. Reference curves for epoxy molding compounds EMC1A, EMC1B, EMC2 and EMC3 were chosen to be at temperatures 170, 180, 150 and 220°C, respectively. Therefore, master curves generated for the four compounds are ±20°C of the respective reference curves.

Fig. 6 shows the master curves of the four epoxy molding compounds (E' versus ln f). The curves show that if compounds are subjected to the same oscillatory frequency, higher experimental temperature condition will result in lower modulus of the same brand of material. It is also generally observed that increasing temperatures will shift the same event to shorten experimental time (increasing frequency) or increasing frequency will shift to higher temperature. Moreover, higher experimental temperature conditions lower modulus of EMCs of the same brand of material when they were subjected to same oscillatory frequency. Modulus drop for EMC1B (160–200°C) is larger than EMC1A (150–190°C) at the same frequency. These master curves can also be shifted to a higher or a lower temperature, and predictions can be
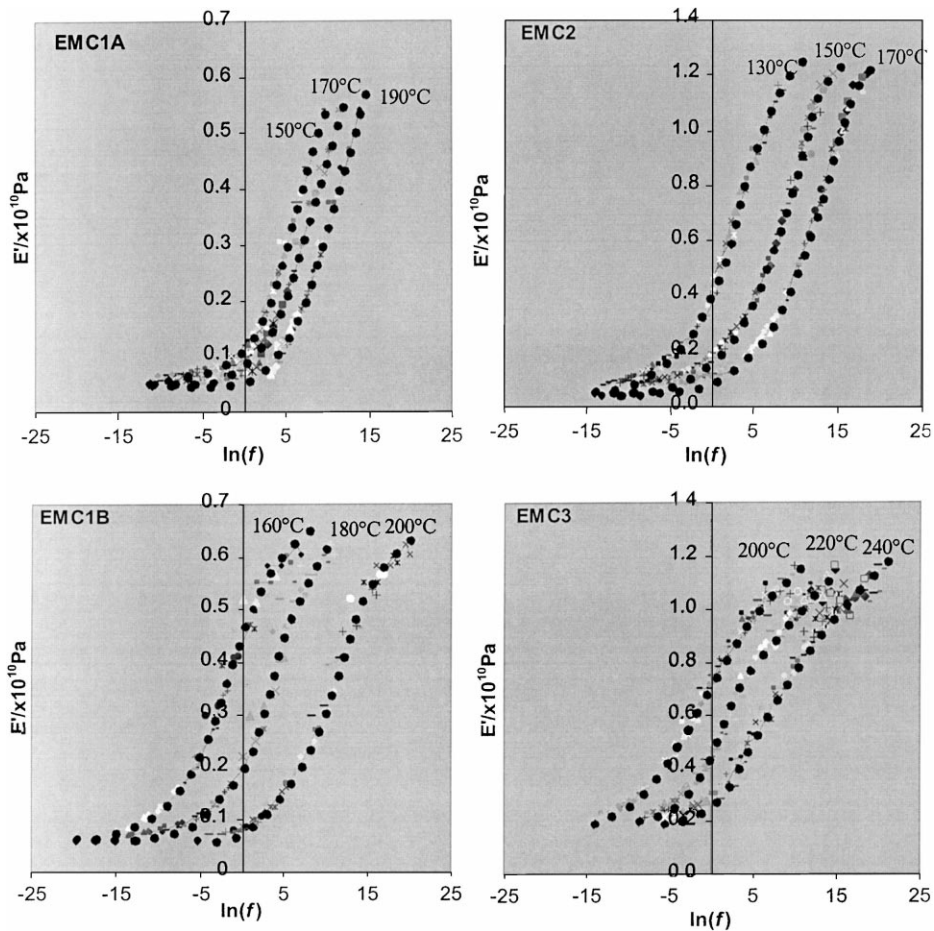

Fig. 6. Master curves of specimens EMC1A, 1B, 2 and 3 generated from TTS.

made over very long or short times at the new temperature. When coupled with a quantitative description of the shift factor versus temperature relationship, such master curves completely define viscoelastic properties of the epoxy molding compounds. The temperature dependence of the shift factor (a_T) was described with the WLF equation [1,6]: $\log a_T = -C_1(T - T_0)/C_2 + (T - T_0)$, where T_0 is the reference temperature, and C_1 and C_2 are constants. For convenience, T_g is usually chosen as the reference temperature; C_1 and C_2 may vary when a different reference temperature is selected. By using $C_1 = 10$ and $C_2 = 47$ [1,6], $\log a_T$ of EMC1A, EMC1B, EMC2 and EMC3 with their selected T_g temperature ranges are approximately equal to -7 to -7.6, -14 to -16, -7.5 to -7.7 and -5.1 to -5.9 at $300°C$, respectively. Shift factor for EMC1A is approximately half that of the EMC1B from the above calculation.

4. Summary

Viscoelastic property of four epoxy molding compounds (EMC1A, 1B, 2 and 3) treated under different transfer and PMC condition was characterized. EMC1B shows higher T_g and less variation of storage modulus plots compared to EMC1A at all the frequency range. EMC3 behave similar modulus change as functions of temperature and exhibits higher T_g and storage modulus at the rubbery state compared to EMC2. Rate of T_g generally increases with respect to frequency and is faster for EMC1A (0 h PMC) compared to EMC1B (4 h PMC). The linear relationship between $\log f$ and $1/T_g$ was observed and T_g relaxation activation energy of each compound was calculated and compared. EMC1B has $E_a \sim 3.4$ times higher than EMC1A. Relationship of T_g versus $\ln E'$ for the compounds were identified as linear and E' of EMC3 is less affected with the change of T_g. Master curves from the TTS of the epoxy molding compounds were generated. It is generally observed that increasing temperature shifts the same event to increasing frequency (or shorten experimental time) from the compounds. EMC1A also shows a lower shift factor than EMC1B.

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