TSC Study of Secondary Dielectric Relaxations in a Polyepoxy Matrix Composite

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ABSTRACT: Two thermal analysis techniques—Differential Scanning Calorimetry and Thermostimulated Current—have been used to characterize a mica/glass fiber-reinforced composite; the matrix is a novolac epoxy resin. The glass transition temperature of the composite as determined by DSC is 80°C. Below the glass transition temperature, two complex relaxation modes γ and β, respectively situated at −90 and −40°C, have been observed. The analysis of the fine structure shows that they are constituted of elementary processes characterized by relaxation times following compensation laws. Because the compensation temperature corresponding to the γ mode is located in the vicinity of the glass transition, it has been assigned to cooperative movements precursors of the glass transition. The mobile units might be the phenyl rings in the bisphenol A. Considering its dependence upon water content, the β mode has been related to the molecular mobility of bound water. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 135–139, 1997

Key words: secondary dielectric relaxations; polyepoxy matrix composite

INTRODUCTION

In the electrical industry, the failure of critical materials used for electrical power delivery can induce the reduction or even the interruption of production. To avoid these failures, the French distribution of electricity searches for preventive maintaining. Alternator insulators used in power station belong to those critical materials because they are submitted to numerous stresses like mechanical stresses, high electric field, and humidity. So the detection of structural changes, leading to long-term dielectric failure, is an important chalenge.

The ThermoStimulated Current (TSC) technique is widely used to characterize composites.[1,2] It gives information on dielectric relaxations and for composites on the interface effects.[3] Experiments are performed at a very low equivalent frequency (10^{-3} Hz), which allows separatation of the relaxation modes. Moreover, the fractional polarization, which is a specific procedure of TSC technique, gives access to new parameters such as activation enthalpy and entropy, and to the distribution of relaxation times. Finally, when compensation phenomena occur, the related parameters, obtained from the fractional polarization analysis, give additional information on the relaxation's origin.

In this work, the Differential Scanning Calorimetry has been used to determine the glass transition temperature. The dielectric relaxations of the composite have been studied by using TSC and fractional polarization techniques, in the tem-

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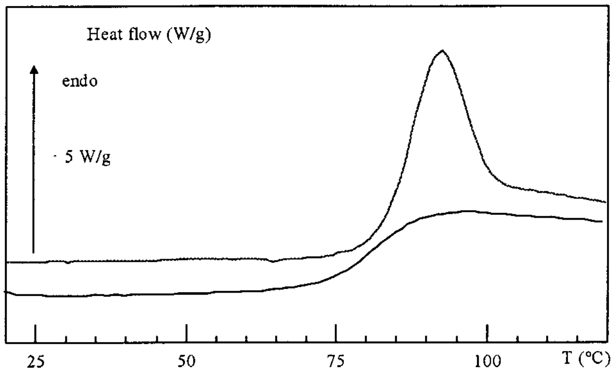

Figure 1 DSC of the novolac composite.

perature range corresponding to secondary relaxations.

MATERIAL AND METHODS

Material

The material is a composite constituted by mica paper, glass fiber, and a thermoset: the novolac epoxy resin. The novolac is a binding resin with good insulating performances.

Methods

Differential Scanning Calorimetry (DSC)

The thermograms were recorded on a DSC7 from Perkin–Elmer. The sample has been enclosed in an aluminum pan, the reference being constituted by an empty pan. The sample weight was 43 mg, the temperature varying from 20 to 120°C at a scanning rate of 20°C/min.

Thermally Stimulated Currents (TSC)

The TSC sample was cut to obtain a disk of 1 cm diameter and 1 mm thickness. The sample was clamped between two capacitor plates and polarized for 2 min under a 200V voltage at a temperature of 30°C. Then it was quenched down to −150°C to freeze the dipolar entities oriented by the static electric field. The sample was short circuited, and the current was recorded by heating the sample at a scanning rate of 7°C/min.

RESULTS AND DISCUSSION

Differential Scanning Calorimetry (DSC)

Thermograms obtained for the novolac composite are shown in Figure 1. On the first temperature scan an endothermic peak is observed at 91°C. For the second scan, this peak desappears, and a classical heat capacity step is observed. The glass transition temperature was defined as the midpoint of the heat capacity step, i.e., 80°C. The endothermic peak corresponds to the manifestation of physical aging, well known in amorphous polymers.[4] It is associated with physical bonding break formed during annealing at temperatures below the glass transition. Heating above the glass transition temperature erases the chemical history, and so the aging. That is why the endothemic peak desappears in the second scan.

Complex TSC Spectrum

The composite TSC spectrum is presented in Figure 2. Two relaxation modes labeled β and γ are observed in order of decreasing temperature. The β mode is located at −40°C and the γ mode at −90°C. An additional mode located at 30°C can be observed in Figure 2. Complementary studies show that this mode is polarization temperature dependent. It corresponds to the low temperature component of the peak associated with the glass transition, which is located at a higher temperature (80°C).

Elementary TSC Spectra

To eliminate water, the sample used for this study was pumped out for 15 h under a secondary vacuum. The elementary spectra obtained by fractional polarization are shown in Figure 3. The fractional polarization method consists in applying the electric static field in a narrow temperature range selecting a narrow distribution of relaxation times. For example, the first spectrum was obtained by applying the field at $T_p = -120°C$ for 2 min. This allows one to only orient the units having a relaxation time lower than 2 min. The temperature was then lowered until $T_d = T_p - 5°C$, the field was cut off, and the sample was short circuited during $T_d = 2$ min. So units with short relaxation times can relax. Then the sample was quenched until $T_o = T_p - 40°C$ under short circuit. The depolarization current was recorded by using the same protocol as the complex spectrum. Thus, we obtained an elementary spectrum composed by a single peak; this spectrum can be analyzed with the hypothesis of a unique relaxation time.

A series of elementary spectra was obtained by

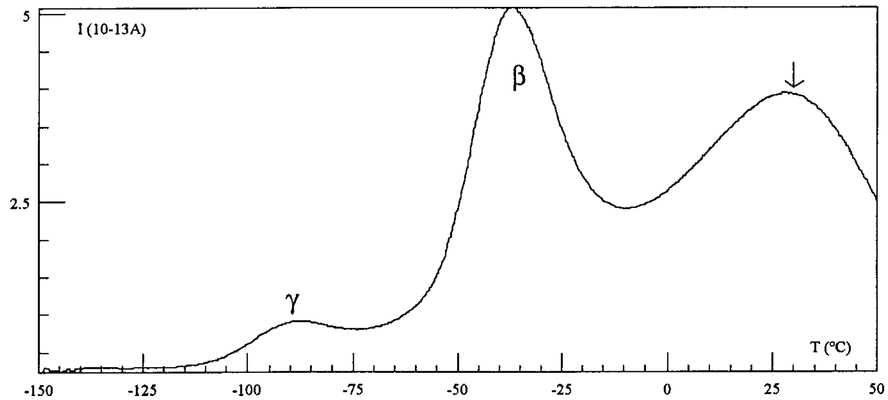

Figure 2 TSC complex spectrum.

shifting the polarization window along the temperature axis from −120 to −5°C, in steps of 5°C. The elementary spectra envelope is slightly different from the global spectrum. The maximum of the β mode corresponds to the elementary spectrum number 18, located at $T_m = -30°C$. However, analysis of elementary peaks confirms the existence of only two relaxation modes, as observed on the complex spectrum.

Analysis of Elementary Spectra

For each elementary peak the temperature dependence of the relaxation time is given by the Bucci Fieschi Guidi equation[5]:

$$\tau_i(T) = \frac{1}{\beta I_i(T)} \int_T^{\infty} I_i(T)\, dT$$

where $\tau_i(T)$ is the relaxation time at a temperature T for the elementary process i, $I_i(T)$ is the depolarization current, and β is the scanning rate.

The Arrhenius diagram of the relaxation time distribution is plotted in Figure 4. Each line has been obtained from the analysis of one peak. The linear dependence of τ_i vs. T^{-1} shows that all processes obey an Arrhenius equation:

$$\tau_i(T) = \tau_{oi} \exp \frac{E_{ai}}{kT}$$

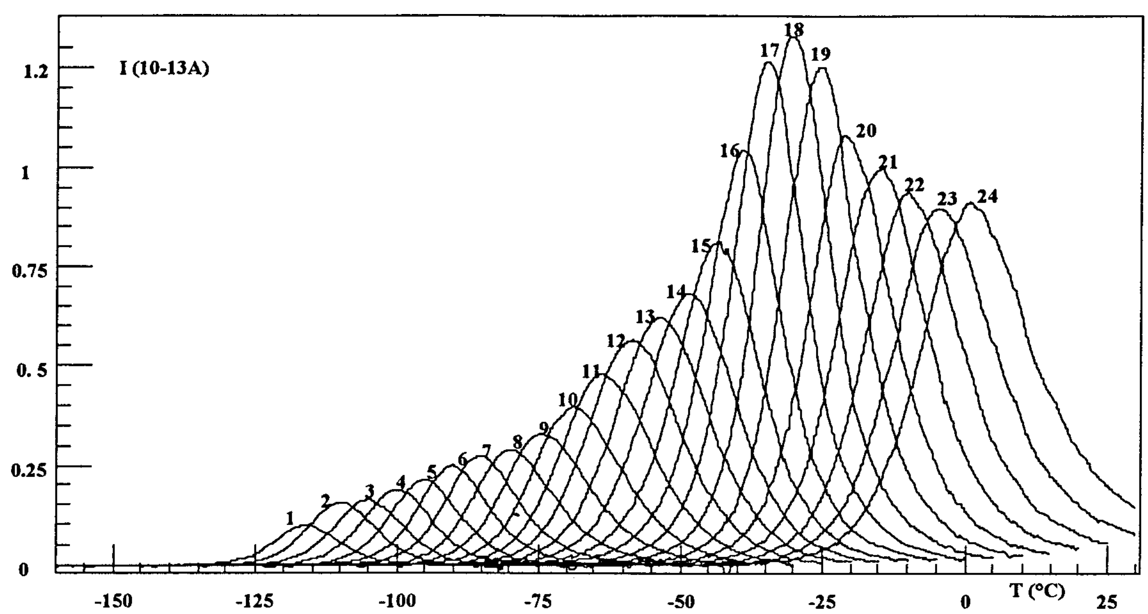

Figure 3 Elementary spectra of the novolac omposite.

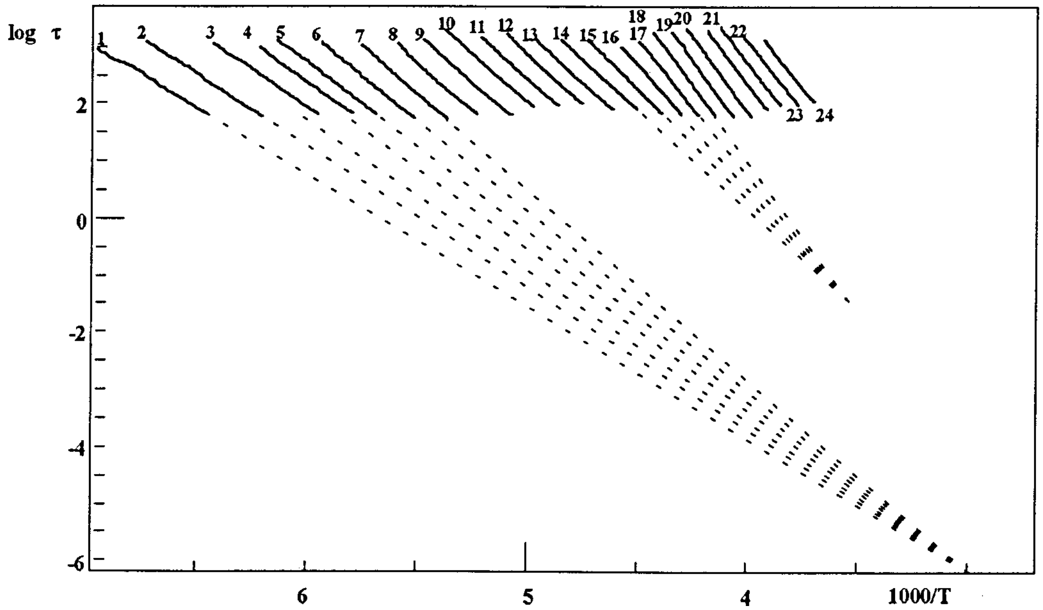

Figure 4 Arrhenius diagram.

where τ_{oi} is the preexponential factor, and E_{ai} is the activation energy.

The dependence of the Arrhenius parameters can be precised by drawing the variation of log τ_{oi} as a function of E_{ai} (cf. Fig. 5). In the Arrhenius diagram (Fig. 4), some straight lines (1 to 7 and 14 to 18) converge towards the same point. Correspondingly, a linear dependence between log τ_{oi} and the enthalpy is observed in the compensation diagram (Fig. 5). Both representations reveal compensation phenomena. This result shows that the variation of one of the activation parameters is compensated by the variation of the other. In the activated states theory, the compensation effect is described by a relation between entropy and enthalpy. From the Hoffman, William, Passaglia model, one compensation phenomenon is due to cooperative movements. The entities with increasing length relax with increasing activation energies. So compensation phenomena may be associated with cooperative mo-

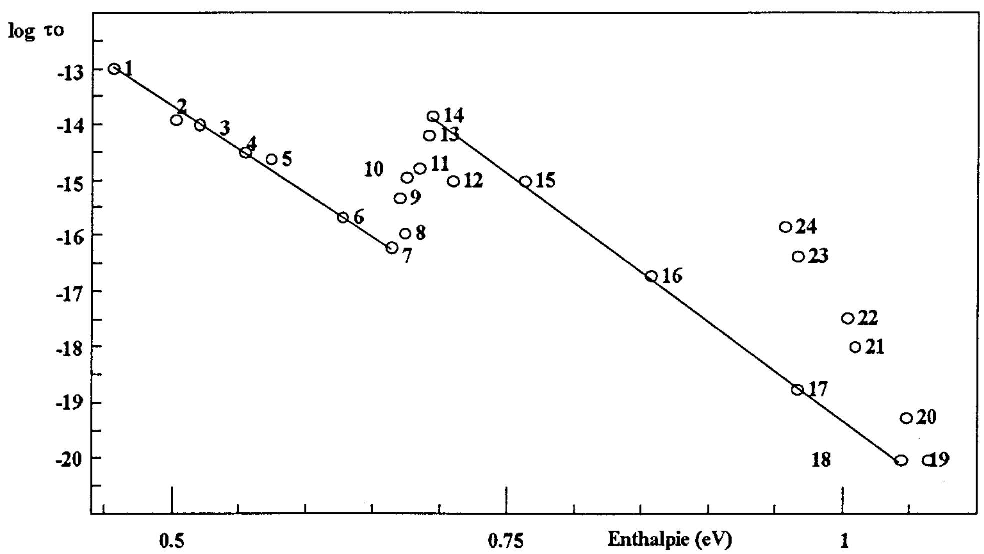

Figure 5 Compensation diagram.

tions and are generally indicative of a transition in the corresponding temperature range.

In the Arrhenius diagram, two compensations are observed. They appear in the same temperature range than the two modes ever observed in the complex spectrum.

For the elementary processes numbered 1 to 7, corresponding to the γ mode, the compensation parameters are:

$$T_{c1} = 61°C \text{ and } \tau_{c1} = 6\ 10^{-7} \text{ s.}$$

For the second compensation associated with the β mode, the compensation parameters are:

$$T_{c2} = 9°C \text{ and } \tau_{c2} = 3\ 10^{-2} \text{ s.}$$

DISCUSSION

The TSC study of the novolac resin can be compared with the high and low temperature analysis of a similar composite reported by M. Goel et al.[6] and M. Topic and Z. Katovic.[7] At low temperature, they have observed two relaxation modes labeled β_1 and β_2 at −115 and −86°C. The glass transition temperature of the novolac was 61°C. By analyzing the fine structure they have shown that the β_2 mode followed a compensation law with T_c = 35°C. These authors have attributed the β_2 mode to motions of phenyls and shown that the presence of water influences this motion. The TSC study of a composite gives a global response that can be not only due to each component but also to their interfacial arrangement. At low temperature, the movements are localized. So the interfacial polarization effects can not be considered and the thermoset linked to its environment gives the major response. All modes are of a dipolar nature.

On the complex spectrum, two relaxation modes appear. The fractional polarization and the analysis of the fine structure will help us to determine the origin of these modes.

The β mode located at −40°C is sensitive to hydration. We have verified that its amplitude increases with hydration level. The analysis of its fine structure showed that it obeys a compensation law. The compensation temperature (9°C) is near the glass melting temperature. Thus, it is logical to think that this mode is due to motions of bound water.

The γ mode, located at −90°C, is close to the β_2 mode observed by Topic et al.[7] The analysis of the fine structure showed that it obeys a compensation law like the β_2 mode, and that its compensation temperature is 61°C. As for the β_2 mode,[7] the compensation temperature is below the glass transition temperature. So this mode can be associated with cooperative movements precursors of the glass transition. As for the β_2 mode, the mobile units could be the phenyl rings in the Bisphenol A.

CONCLUSION

The TSC curve recorded in the temperature range of −150–30°C showed two peaks at temperatures $T_m(\gamma) = -90°C$ and $T_m(\beta) = -40°C$. A better insight has been obtained by using the fractional polarization method. The whole spectrum has been decomposed in 24 elementary peaks. Each of the obtained peaks has been analyzed and the variations of the corresponding relaxation times have been determined. Moreover, variation of the Arrhenius parameters have shown the existence for two compensations phenomena. The compensation temperature of the γ mode allows attributing it to precursor movements of the glass transition. As for the β mode varying with the hydration level, it is associated with bound water. Our results are in good agreement with the Goel and Topic results.

REFERENCES

1. A. Dufresne and C. Lacabanne, *Polymer,* **36,** 441 (1995).
2. C. Maggana, G. Spathis, P. Pissis, A. Kanapitsas, C. G. Delides, and A. S. Vatalis, Proc. ISE8, 1994.
3. T. Tanaka, S. Hayashi, and K. Shibayama, *J. Appl. Physiol.,* **48,** (1977).
4. B. Fruth and G. Lipak, Proc. Sixth Int. Symp. on High Voltage Eng., New Orleans, LA, 1989, p. 21.
5. C. Bucci, R. Fieschi, and G. Guidi, *Phys. Rev.,* **148,** 816 (1966).
6. M. Goel, P. S. Viswanathan, and P. Vasudevan, *Polymer,* **19,** 905 (1978).
7. M. Topic and Z. Katovic, *Polymer,* **35,** 5536 (1994).