Journal of Thermal Analysis, Vol. 40 (1993) 705-710

INFLUENCE OF THE COMPENSATION PHENOMENA OF POLYMERIC MATRIX COMPOSITES

C. Lavergne, A. Dufresne, D. Chatain and C. Lacabanne*

SOLID STATE PHYSICS LABORATORY, URA CNRS 74, PAUL SABATIER UNIVERSITY, 118 ROUTE DE NARBONNE, TOULOUSE, FRANCE

Thermally Stimulated Creepe and Current (TSCr and TSC) have been used for investigating the interface/interphase in DGEBA-DDA matrix and glass beads composites. In all samples, a complex α retardation/relaxation mode is observed near the glass transition of the matrix. A study of the fine structure has shown that, for the elastic processes, the activation enthalpies are ranging from 2 and 8 eV, while for the dielectric ones, they are restricted between 0.5 and 1.5 eV. Moreover, for a given activation enthalpy, the preexponential factor τ_0 and the activation entropy ΔS are characteristic of matrix filler interface.

Keywords: compensation phenomena, kinetics, TSC, TSCr

Introduction

Since the last decades, composite materials have been widely studied. In particular, special attention has been paid to the interfacial problems. As the stress transfer capacity is strongly linked to physical properties of the interfacial region, a better knowledge of this zone is necessary for the improvement of composites. The aim of this work is to study the influence of interfaces on the pp of composites. The aim of this work is to study the influence of interfaces on the properties of DGEBA-DDA matrix and glass beads composites. For this purpose, the TSCr and TSC spectroscopies have been applied. In this paper, the materials and methods will be presented first. Then, the obtained data by the TSCr/TSC spectroscopy will be exposed.

---

* At present in I. R. C. of Biomedical Materials, Queen Mary and Westfield College, Mile End Road, E1 4NS London, UK.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Materials and methods

Thermally Stimulated Creep and Current (TSCr and TSC) spectroscopies were used to study the retardation/relaxation spectra of the composites.

The transition spectra were characterized by Differential Scanning Calorimetry (DSC).

The matrix of the composites was prepared by mixing a DGEBA (diglycidyl ether of bisphenol A) prepolymer and DDA (dicyandiamide) hardener [1]. The amine to epoxy ratio was 0.6. The volumic fraction of filler was 20%. The interface was realized by a surface pretreatment (of the glass) with the A1100 an amino-silane coupling agent. The interphase was obtained by coating beads with an elastomeric interlayer prepared from a prepolymer derived from reacting CTBN (carboxyl terminated butadiene acrylonitrile) copolymer and DGEBA to produce an epoxide terminated prepolymer.

Three samples have been investigated: DGEBA-DDA matrix (M)
matrix + silane treated beads (MBS)
matrix + elastomer coated beads (MBE)

Results

Complex TSCr and TSC spectra

Figures 1 and 2 show the variation of the inverse of the viscosity η^{-1} and the dynamic conductivity σ *vs*. temperature. The TSCr and TSC spectra have been recorded in the same experimental conditions for the three samples. These spectra have been associated with the α mode which is the inelastic/dielectric manifestation of the glass transition of the DGEBA-DDA matrix previously studied by DSC. The maximum temperature T_α is situated around 140°C in TSCr and 100°C in TSC. We can observe that, independently from the experimental procedure, T_α and T_g vary in the same way (Table 1): for the silane treated beads, they are shifted towards higher temperatures while for the elastomeric coated filler, they are at a lower temperature compared with an untreated system.

Table 1 Transition/retardation/relaxation temperature for M, MBS and MBE

	M / °C	MBS / °C	MBE / °C
T_α(TSCr)	142	145	139
T_α(TSC)	105	106	90
T_g(DSC)	144	147	135

Fine structure of TSCr/TSC spectra

The TSCr/TSC fractional techniques allow us to resolve such complex spectra into elementary processes [2] characterized by single relaxation times τ obeying an Arrhenius equation $\tau(t) = \tau_o\exp(\Delta H / kT)$, where τ_o is the preexponential factor and ΔH the activation enthalpy. So, on a compensation diagram $\lg\tau_o(\Delta H)$, the experimental points associated with the elementary peaks are aligned. For comparison, the results obtained by the TSCr and TSC techniques are exhibited in

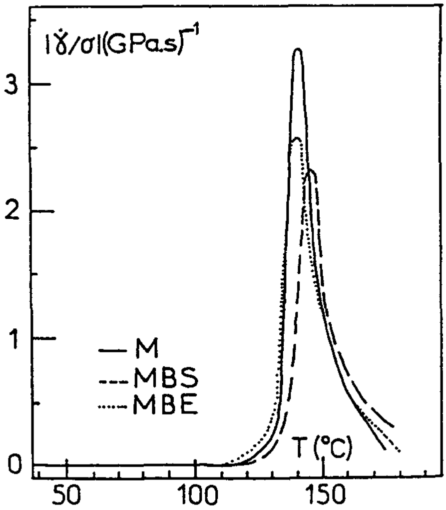

Fig. 1 Complex TSCr spectra

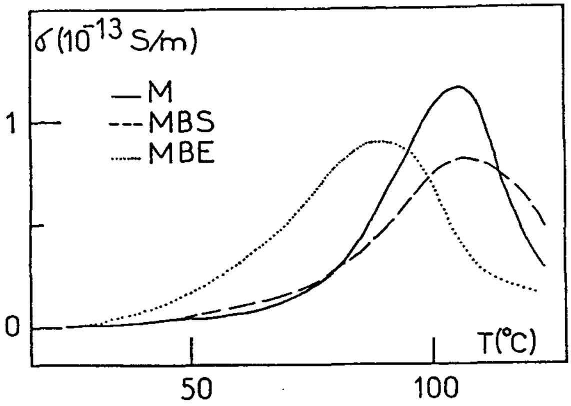

Fig. 2 Complex TSC spectra

Fig. 3. Then, it appears that for the inelastic processes, the activation enthalpies are ranging from 1 to 8 eV while for the dielectric ones, they are restricted between 0.5 and 1.5 eV. As the lower enthalpies correspond to the molecular mobility of interfacial regions, TSC is more sensitive to emphasize the differences specific of the interface/interphase as shown in Fig. 4.

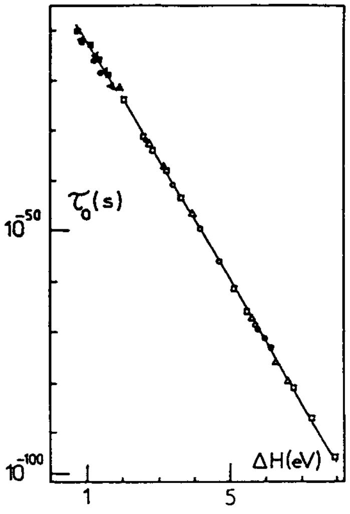

Fig. 3 Variation of τ_0 *vs.* ΔH for M(□, ■), MBS (Δ, ▲, MBE (o, •) respectively for TSCr and TSC

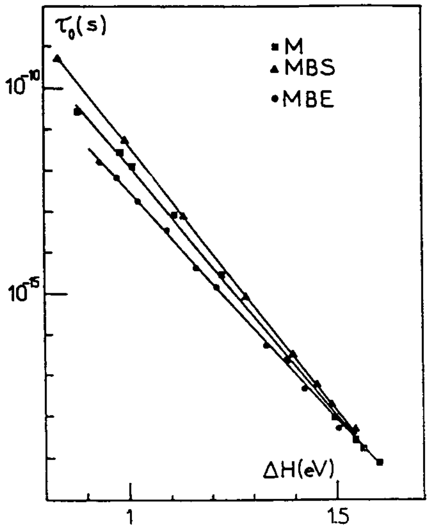

Fig. 4 TSC compensation diagram of M (■, MBS (▲, MBE (•)

At high enthalpies, the compensation lines converge. At lower enthalpies, a significant shift is observed. The DGEBA-DDA matrix has been taken as a reference: the compensation line corresponding to the MBS composite is situated at upper values of τ_o. Activation entropies (ΔS) can be deduced from τ_o with the Eyring equation $\tau_o = h/kT \exp(-\Delta S / k)$, where h is the Plank constant, and k the Boltzmann constant.Then, according to the equation, the activation entropies ΔS have lower values than for the matrix. On the contrary, for the MBE composite, a decrease of τ_o and therefore an increase of ΔS is observed.

Discussion

The α retardation/relaxation mode associated with the glass transition of the matrix corresponds to cooperative motions of long chain sequences. For the MBS composite, the α peak is shifted towards higher temperatures (Figs 1 and 2). This phenomenon traducts a decrease of the molecular mobility in the vicinity of the bead. It may be attributed to a rigidification of the interfacial region, due to the existence of strong linkages introduced by the silane coupling agent between filler and matrix [3]. In the case of the MBE composite, T_α is shifted towards lower temperatures. The polyepoxy network is then slightly plasticized by the elastomeric coating. This result, in accordance with Gerard [4] suggests a reduction of the reticulation density.

The study of the fine structure of the α mode shows the existence of a single compensation phenomenon (Fig. 3). The lowest ΔH values recorded in TSC indicate the existence of more localized motions of chain segments than in TSCr. With this last technique, the involved sequences are longer. So, the TSC spectroscopy is more suitable for studying the influence of the interfaces.

As shown in Fig. 4, the compensation lines converge at high enthalpies. According to the model of Hoffman-Williams-Passaglia [5], the activation enthalpy is indicative of the length of the mobile unit. So it's logical to think that high enthalpies correspond to movements of long chains situated in the bulk matrix. Moreover, in this zone, the lowest values of ΔH observed for the composites reveal a restriction of the movements propagation, due to the presence of the filler. In the low enthalpy region, the slope of the compensation line is modified according to the nature of the interface. Indeed, in the MBS composite, ΔS is decreased. The Boltzmann equation $S = k\ln W$ suggests a decrease of the number of accessible sites in motion at the glass transition. Then, the physical linkages between the filler and the matrix are strong enough to reduce movements of mobile sequences. On the contrary, for the MBE composite, the observed increase of the entropy suggests more numerous accessible sites and a greater mobility of the polyepoxy network partially interpenetrated by the elastomeric coating.

Conclusions

This TSCr/TSC study of model composites has shown the existence of an α retardation/relaxation mode. It has been assigned to the inelastic/dielectric manifestation of the glass transition of the matrix. The analysis of its fine structure has revealed a single composition phenomenon. The presence of the filler significantly modifies the molecular mobility of the interfaces: it decreases in the MBS composite while it increases in the MBE one.

References

1 N. Amdouni, University Thesis, Lyon 1989.
2 C. Lacabanne, D. Chatain and J. C. Monpagens, J. Macromol. Sci. Phys., B13, 4 (1977) 537.
3 N. Nishiyama, K. Horie, R. Shick and H. Ishida, Polym. Comm., 31 (1990) 380.
4 J. F. Gerard, Polym. Eng. Sci., 28 (1988) 568.
5 J. D. Hoffman, G. Williams and E. Passaglia, J. Polym. Sci., Part C,14 (1966) 173.

Zusammenfassung — TSCr und TSC wurden zur Untersuchung der Grenzfläche/Grenzphase in einer DGEBA-DDA Matrix und in Glaskugelverbundstoffen. Bei allen Proben wird in der Nähe des Glasumwandlungspunktes der Matrix eine komplexe Verzögerung/Relaxation beobachtet. Eine Untersuchung der Feinstruktur ergab, daß die Aktivierungsenthalpie für die elastischen Prozesse zwischen 2 und 8 eV liegt, während sie für die dielektrischen auf 0.5 und 1.5 eV beschränkt bleibt. Weiterhin sind präexponentieller Faktor τ_0 und die Aktivierungsentropie ΔS bei vorgegebener Aktivierungsenthalpie charakteristisch für die Matrixfüllstoffgrenzfläche.