Journal of Thermal Analysis, Vol. 48 (1997) 623-634

THERMALLY STIMULATED CREEP STUDY OF BISMALEIMIDE/CARBON FIBER COMPOSITE

*Ph. Ponteins**,**, *B. Medda**, *Ph. Demont*** *and C. Lacabanne***

*Division Avion, Aérospatiale, 31060 Toulouse Cédex 03
**Laboratoire de Physique des Polymères, Université Paul Sabatier, 31062 Toulouse Cedex, France

Abstract

The correlation between structure/microstructure and thermomechanical properties has been investigated by the Thermally Stimulated Creep (TSC) technique in a high performance thermostable thermoset matrix composite. The high resolving power of this technique allows us to analyse the α retardation mode. The kinetics of molecular movements liberated at the glass transition has been investigated by the technique of fractional loading: the analysis of each elementary process gives the real compliance and the retardation time as a function of temperature. The values of the activation parameters show the existence of a compensation phenomenon which characterizes the microstructure. It also gives access to the loss compliance of the composite material as a function of temperature and frequency. The predictive calculation of loss compliance has been validated by the results obtained by dynamic mechanical analysis (DMA).

Keywords: bismalleimide/carbon fiber composite, DMA, kinetics, TSC

Introduction

The structural optimization planned on the second generation supersonic aircraft requires reducing the weight of the various aircraft parts by using new or improved composite materials. These materials must of course be carefully characterized before being validated on transport aircraft whose mission will be to accumulate 80 000 flight hours over more than 25 years of operation.

One of the major limiting factors in the use of polymeric matrix composites is the effect of long term exposure to high service temperature. So, it is necessary to develop new techniques of investigation to predict the thermomechanical properties and to establish correlations between structure/microstructure and thermomechanical properties.

Thermally Stimulated Creep [1] has been applied to the analysis of cooperative movements liberated around the glass transition temperature. The high resolving power of this spectroscopy has allowed us to characterize the microstructure of the polymeric matrix by studying the distribution of retardation times governing the viscoelastic behavior. From the obtained data, we have calculated the loss compliance of the composite material as a function of temperature and frequency.

0368–4466/97/ \$ 5.00

John Wiley & Sons Limited
Chichester

The investigated material is a bismaleimide/carbon fiber composite [2, 3]. It has been shown that carbon fiber reinforced bismaleimide/BMI exhibits a number of characteristics, such as high glass transition temperature and excellent thermal stability, which suggest that these materials are good candidates for use in aerospace application. To improve toughness [4], tensile strength and elongation at break, the base BMI resin was modified by the addition of copolymers such as allyls, diamines, epoxies and elastomers.

Materials and method

Materials

The aromatic nature and high crosslink density of the cured network confers an excellent thermal stability on Bismaleimides matrix composite [5]. In order to improve its behaviour after impact, which is the major drawback of these networks, Bismaleimides are reacted with allylphenol which reduces the crosslink density by increasing the distance between crosslinks. There are three principal temperature regimes associated with the cure reactions, namely (a) 100–200°C range, (b) 200–300°C range (c) 300–350°C range. As illustrated in Fig. 1, in regime (a), the 'ene' reaction occurs slowly and there is evidence that it may be reversible. At high temperature (200–300°C), the 'ene'-BMI double-bond crosslinking polymerization (Diels-Alder reaction) occurs as indicated in Fig. 1. In regime (c), in the 300–350°C range, further cure occurs as the specimen cure temperature exceeds the T_g of the resin.

The polymerization is achieved by curing in autoclave. The lay-up of the sample comprises two unidirectional plies. After polymerization till a conversion degree of 90%, a volume fiber content of 66% is obtained. Samples having dimensions of 70×5×0.2 mm have been prepared for Thermally Stimulated Creep experiments.

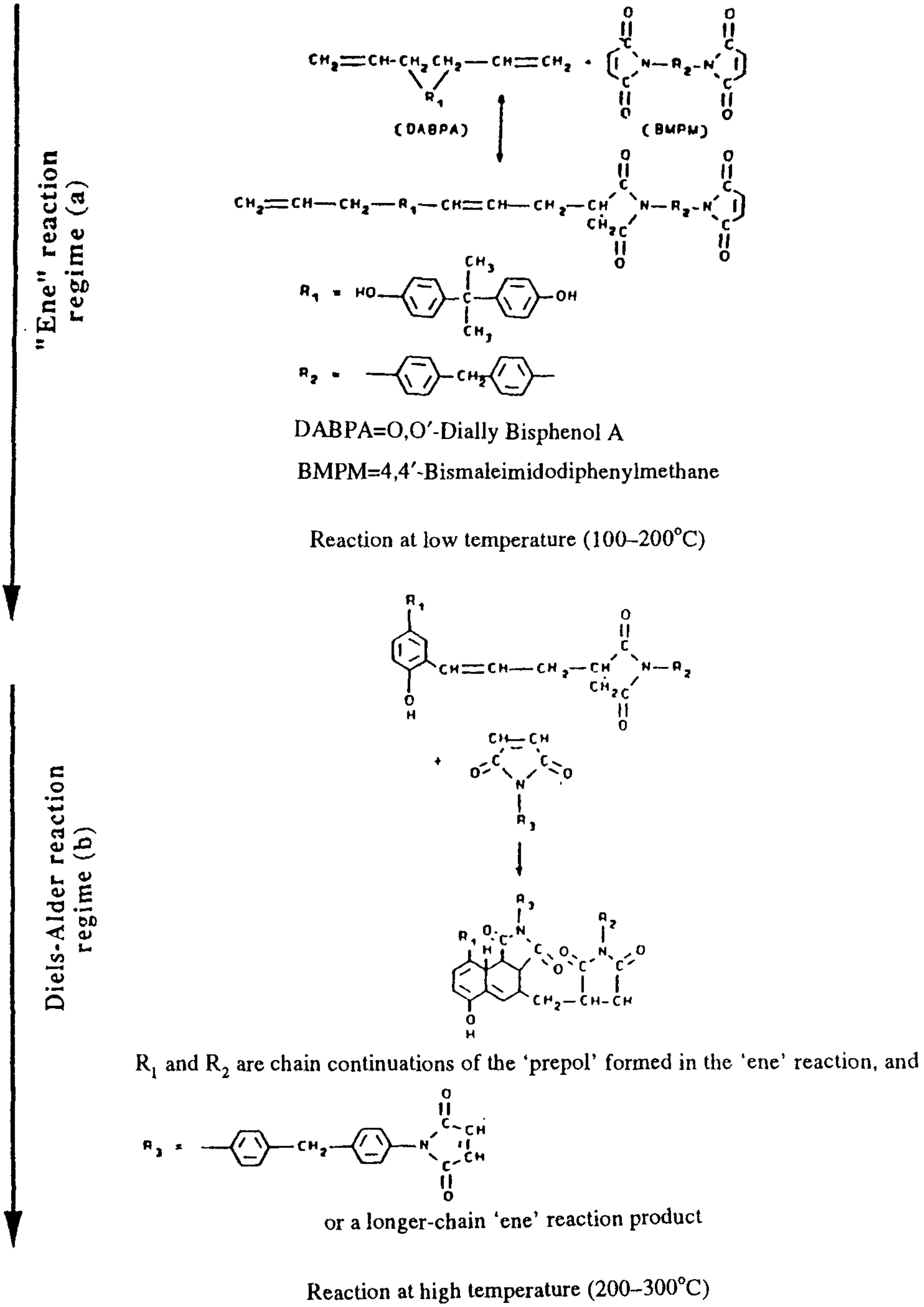
For dynamic mechanical analysis (DMA), the test specimens have the following lay-up: [0]16. The dimensions are 70×10 mm (0°//to 70 mm).

Thermally stimulated creep

Principle

The principle of Thermal Stimulated Creep (TSC) [1, 6] is the following:

A static shear stress of torsion is applied to the sample at a given temperature for two minutes. Then the sample is quenched in order to freeze this configuration. The stress is removed and after two minutes, the temperature is increased at a rate of 7°C min^{-1}. Then the sample returns to equilibrium and the complex TSC spectrum is recorded. It shows the rate of change of the deformation γ° as a function of temperature. For the purpose of comparison, it has been normalized by the applied stress.



DABPA=O,O′-Dially Bisphenol A

BMPM=4,4′-Bismaleimidodiphenylmethane

Reaction at low temperature (100–200°C)

R_1 and R_2 are chain continuations of the 'prepol' formed in the 'ene' reaction, and

or a longer-chain 'ene' reaction product

Reaction at high temperature (200–300°C)

Fig. 1 The principle chemical reactions which occur during the polymerization of the BMI network

Experimental

Complex TSC spectrum

The complex TSC spectrum with a load temperature T_σ is shown in Fig. 2. The static shear stress ($\sigma=131$ MPa) was applied for 2 min. The rate of change of the deformation γ° was recorded during the sample warm-up from 220 to 320°C.

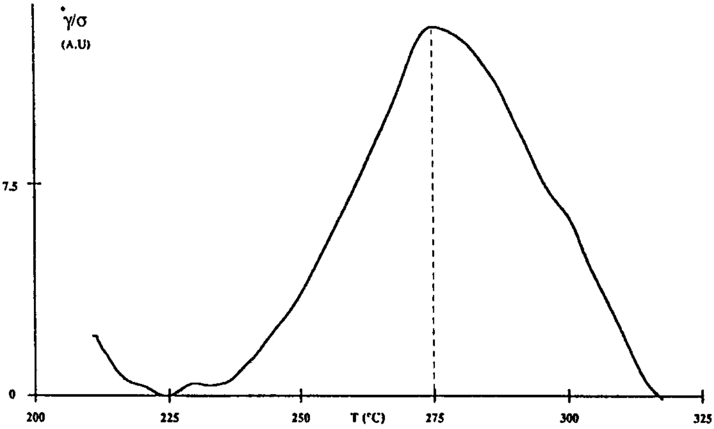


Fig. 2 TSC complex spectrum of bismaleimide/carbon fiber composite. $T_\sigma=300$°C, $\sigma=131$ MPa

This spectrum corresponds to the high temperature retardation mode. The maximum of this spectrum is located at about 275°C which is very close to the glass transition temperature of the matrix ($T_{g,DSC}=240$°C). Therefore we may associate this retardation mode with the molecular movements liberated at the glass-transition.

Fine structure of the complex TSC spectrum

The spectrum obtained with the previous protocol is generally complex. It corresponds to a discrete distribution of retardation times. The fractional loading technique was applied to resolve experimentally the complex spectrum into elementary spectra and to analyse the macromolecular mobility liberated at T_g.

$T_{1\sigma}-T_{2\sigma}=\Delta T_\sigma$ is the stress window and the temperature difference between two successive applications of stress is the loading step. Fractional loading experiments are performed as follows: a stress σ is applied at $T_{1\sigma}$ for a time $\Delta t_\sigma=2$ min; the temperature is then lowered by ΔT to $T_{2\sigma}$ ($\Delta T=10$°C) under stress. At $T_{2\sigma}$, the stress is removed and the specimen is permitted to recover partially for $\Delta t_\sigma=2$ min. The sample is then quenched to $T_0 << T_{2\sigma}$ and viscoelastic strain ($\gamma<10^{-3}$) is frozen in. A linear heating run at 7°C min^{-1} is then performed, during which the decay of the frozen-in strain $\gamma(t)$ is recorded. The temperature dependence of its derivative $\gamma^\circ(t)$ constitutes an elementary spectrum.

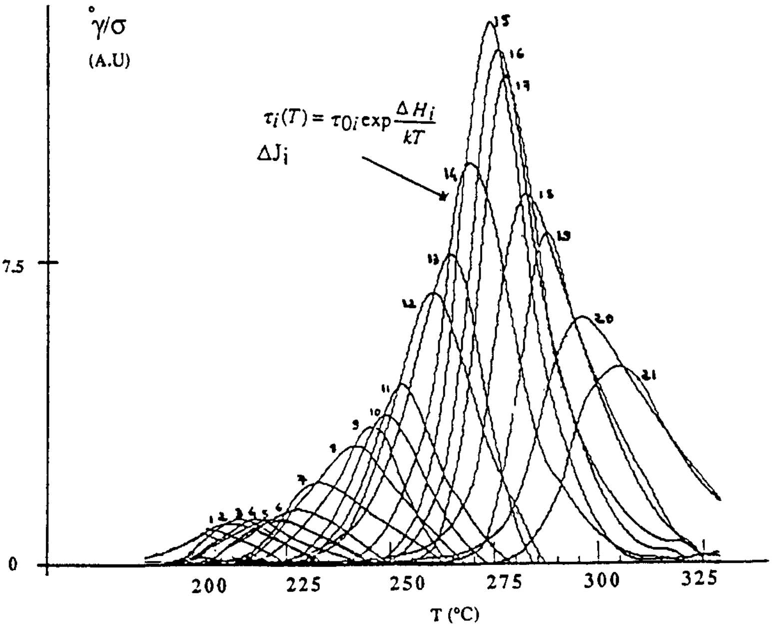


Fig. 3 Elementary peaks obtained by technique of fractional loading with $\Delta T = 5$°C, T_σ was varied from 205 to 305°C by steps of 5°C. $\sigma = 131$ MPa

The stress window is shifted by 5°C from 205 to 305°C. Thus we observe a series of elementary spectra as shown in Fig. 3.

Each fractional loading response is investigated using an analysis method derived from Bucci-Fieschi-Guidi treatment [7] where a single retardation time for each elementary recovery process is assumed. The retardation time τ_i associated with each elementary process 'i' as a function of temperature T is given by:

$$\tau_i(T) = \left|\frac{\gamma_i(T)}{\mathring{\gamma}_i(T)}\right| \tag{1}$$

where γ_i is the deformation for the process 'i' and $\mathring{\gamma}_i(T)$ is the rate of change of deformation of the process 'i'.

In the BMI matrix composite, the retardation times follow an Arrhenius law.

$$\tau_i(T) = \tau_{0i}\exp\frac{\Delta H_i}{kT} \tag{2}$$

where k is the Boltzmann constant, τ_{0i} is the preexponential factor and ΔH_i is the activation enthalpy.

The analysis of each elementary spectrum 'i' givens ΔH_i and τ_{0i}. The values of these parameters are reported in Table 1.

From $\mathring{\gamma}_i(T)$ we can deduce ΔJ_i, the variation of the real compliance J_i for each i process.

Table 1 Activation parameters deduced from the technique of fractional loading

Peak n^r	T_{m_i}	ΔH_i/eV	τ_{io}/s
1	217	2.98	$5\cdot10^{-29}$
2	219	3.03	$3\cdot10^{-30}$
3	222	3.19	$2\cdot10^{-31}$
4	223	3.33	$5\cdot10^{-33}$
5	227	3.33	10^{-32}
6	232	3.42	$4\cdot10^{-33}$
7	240	3.74	$7\cdot10^{-36}$
8	244	4.03	$3\cdot10^{-38}$
9	248	4.07	$2\cdot10^{-38}$
10	252	4.15	$8\cdot10^{-39}$
11	259	4.2	$7\cdot10^{-39}$
12	261	4.4	10^{-41}
13	269	5	$2\cdot10^{-45}$
14	273	5.2	$8\cdot10^{-47}$
15	277	5.7	$3\cdot10^{-51}$
16	279	5.51	10^{-49}
17	282	5.3	$2\cdot10^{-47}$
18	287	5	10^{-43}
19	295	4.5	$4\cdot10^{-40}$
20	301	4	10^{-34}
21	306	3.7	10^{-31}

We can associate an equivalent frequency f_{ieq} to $\tau_i(T_{m_i})$ by the following relationship:

$$f_{ieq} = \frac{1}{2\pi\tau_i(T_{m_i})} \tag{3}$$

where T_{m_i} is the maximum temperature of the peak, i. Since $\tau_i(T_{m_i})\approx100$ sec, the equivalent frequency of TSC appears to be low: $f_{ieq}=5\ 10^{-3}$ Hz for a scanning rate of 7°C min^{-1}.

Considering the fact that the window is only 5°C, the global TSC curve corresponds to an isofrequency at 5 10^{-3} Hz. It can be directly compared with the spectra deduced from dynamic mechanical analysis.

Dynamical mechanical analysis

Dynamical mechanical analysis was performed to validate the predictive calculation of the complex compliance. We used a torsion excitation mode with a fre-

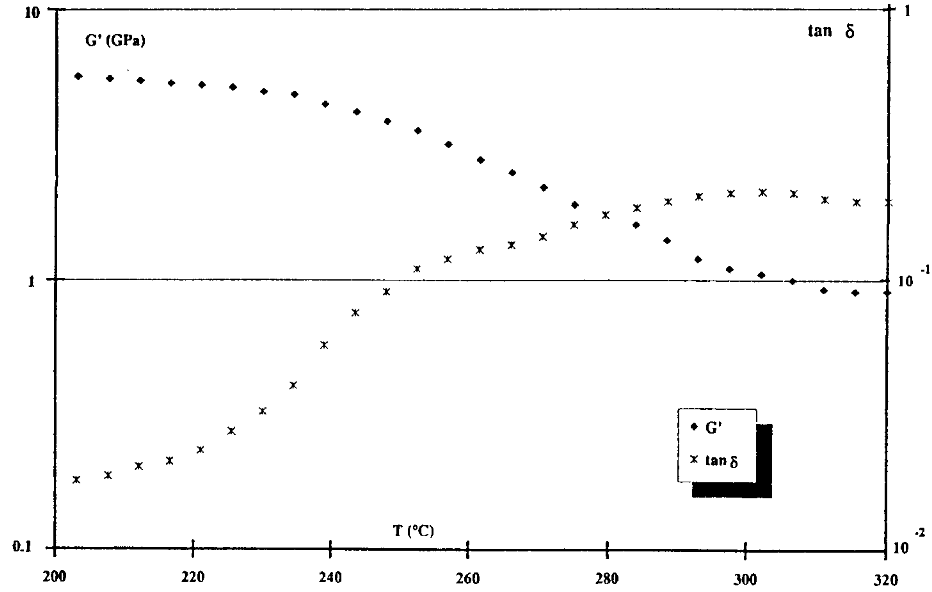


Fig. 4 High temperature spectra of DMA

quency of 1 Hz. The variations of the G' modulus and tan(δ) as a function of temperature were recorded (Fig. 4) on a RHEOMETRICS-RDC 7700 Dynamic Mechanical Analysis.

Discussion

High temperature retardation mode

Because of the high fiber content (66%), the glass transition temperature can't be located precisely by DSC. The TSC technique clearly shows the viscoelastic region associated with T_g. The high crosslink density of cured network provides a high T_α value, higher than for other thermosets studied by TSC technique until now. We have reported in Table 2 some T_α values recorded by the TSC technique for comparison.

Table 2 T_α values of polymeric matrix composites recorded by TSC technique

TGDDM-DDS composite	Cyanate epoxy composite	BMI composite
250°C	208°C	275°C

The good thermomechanical behaviour of the BMI matrix composite is due to the stability of imide heterocycle nucleus. The Diels-Alder reaction creates a compact network with complex chemical links. It is interesting to study the molecular mobility in order to verify if the BMI composite follows universal law found for other conventional polymeric matrix composite.

Distribution of the activation enthalpies

This study has been completed by analysing the variation of activation enthalpies as a function of T_{m_i} (Fig. 5). From 217°C to about 277°C, the apparent activation enthalpy increases gradually with temperature.

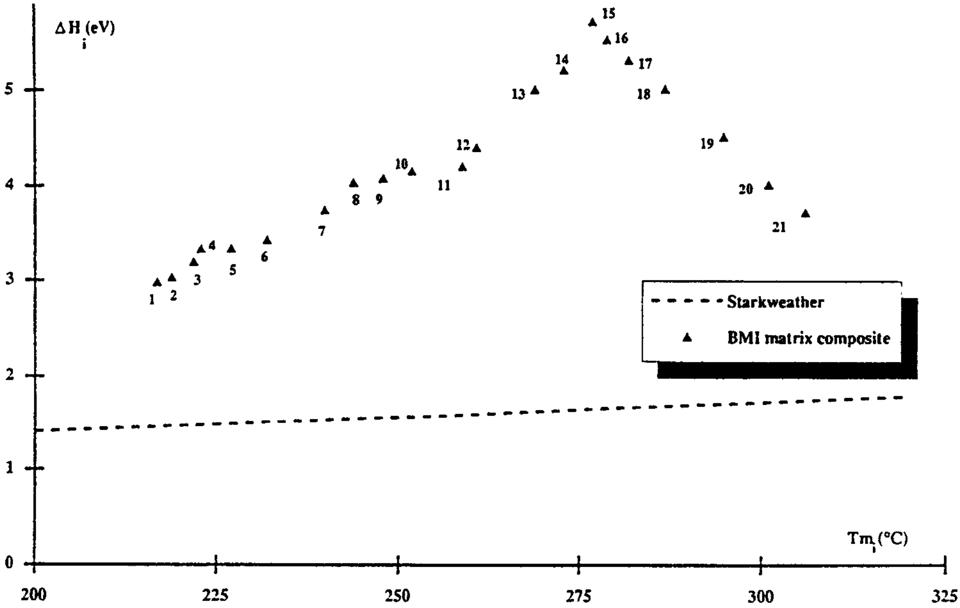


Fig. 5 Apparent activation enthalpy ΔH_i of α retardation mode of BMI/carbon fiber composite as a function of the temperature of the TSC maximum T_m. The dotted line is the Eyring-Starkweather $\Delta S=0$ prediction (Eq. (4))

Starkweather has developed a procedure [8, 9] to analyse the nature of viscoelastic relaxations. Thus, the Eyring activation enthalpy ΔH_E can be deduced from:

$$\Delta H_E = kT\left[1+\ln\frac{kT}{2\pi h f_{eq}}\right]+T\Delta S \tag{4}$$

where h is the Planck constant and ΔS is the activation entropy.

According to Eyring Starkweather theory and Eq. (4):

- if $\Delta S=0$, the molecular movements are localized,
- if $\Delta S>0$, the molecular movements are complex and cooperative.

The dashed line in Fig. 5 is calculated using Eq. (4) with $\Delta S=0$. It characterizes localized movements. From 217°C, i.e. temperature range that includes α mode, the data lie far from the relationship derived from Eq. (4). This observation shows that the movements liberated at the BMI matrix composite glass transition are delocalized and cooperative.

The study of the activation parameters allows us to characterize the chain dynamic liberated at the glass transition and the microstructure of the polymeric matrix composite.

The high values of the activation enthalpies show that the material studied is thermostable. Nevertheless, the activation enthalpies are less high than Cyanate-Epoxy matrix composite ones, for example (for the high retardation mode of a Cyanate-Epoxy matrix composite we have $3<\Delta H_i<6.9$ eV). According to the Hoffman-Williams-Passaglia theory, the high activation enthalpies correspond to movements of long sequences located in the matrix. The relatively low values of the activation enthalpies, compared to other polymers with high T_g, show that the microstructure of the BMI composite is very compact, with crosslinks very close to each others.

Compensation equation

We have reported on Fig. 6 the variation of log τ_{0i} as a function of ΔH_i. It is clear that log τ_{0i} varies linearly with ΔH_i for the elementary peaks 1 to 15 constituting the α retardation mode, so that

$$\tau_{0i}(T)=\tau_c \exp\left(-\frac{\Delta H_i}{kT_c}\right) \tag{5}$$

where T_c is the compensation temperature and τ_c is the compensation time.

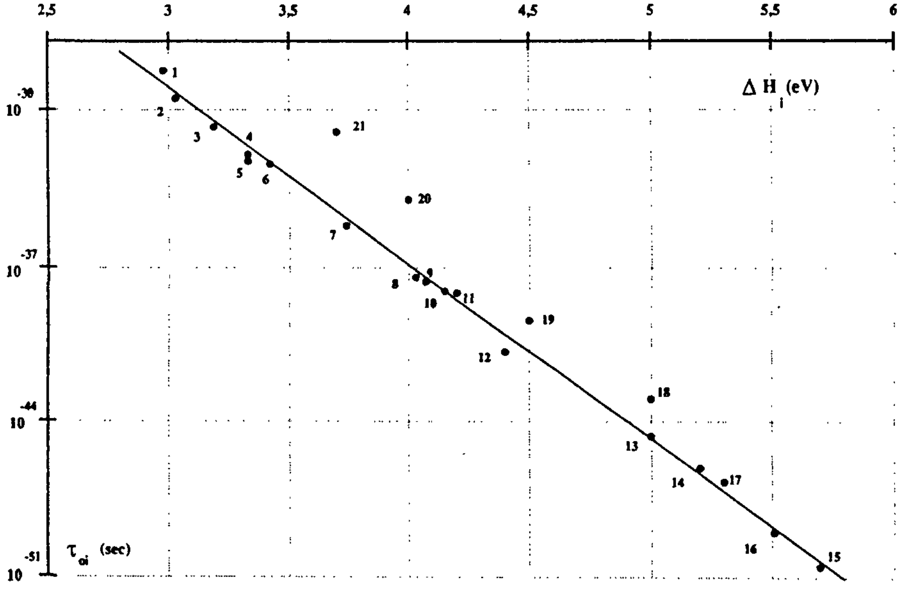


Fig. 6 Compensation diagram where log τ_{0i} is plotted *vs.* ΔH_i

From the solid line of Fig. 6

$$T_c = 365^\circ\text{C}$$
$$\tau_c = 3.2 \cdot 10^{-6}\ \text{sec}$$

In the other words, the retardation times of the elementary processes constituting the α retardation mode follow the compensation equation:

$$\tau_i(T) = \tau_c \exp\left\{\frac{\Delta H_i}{k}\left(\frac{1}{T} - \frac{1}{T_c}\right)\right\}$$

The compensation parameters (τ_c, T_c) characterize the microstructure of the composite.

This behaviour has been observed in many other polymers. So the BMI matrix composite follows a phenomenological law established on conventional polymers [10]. According to previous data [11], the α retardation mode described by the compensation law has been attributed to hierarchically correlated movements. The low value of the compensation time is due to the rigidity of carbon fibers. The BMI network without carbon fibers presents a higher τ_c (0.17 sec).

The high value of the compensation temperature must also be attributed to carbon fibers.

Prediction of the complex compliance

The Kelvin-Voigt model represents creep behaviour to a first approximation. It gives the variation of the anelastic complex compliance as a function of temperature and frequency. Then, the loss compliance is given by the following relationship:

$$J_i''(\omega, T) = \frac{\Delta J_i \omega \tau_{0i} \exp(\Delta H_i/kT)}{1 + [\omega \tau_{0i} \exp(\Delta H_i/kT)^2} \qquad (6)$$

So the ΔJ_i and ΔH_i values deduced from TSC analysis allow us to calculate $J''_i(\omega, T)$.

Then, by making the summatiom over all the elementary processes, the loss compliance of the composite material can be calculated as a function of angular frequency ω and temperature using the equation:

$$J''(\omega, T) = \Sigma_i \frac{\Delta J_i \omega \tau_{0i} \exp(\Delta H_i/kT)}{1 + [\omega \tau_{0i} \exp(\Delta H_i/kT)^2} \qquad (7)$$

Figure 7 shows the variation of the loss compliance as a function of temperature at a frequency of 1 Hz. Note that the anelastic behaviour of the material can be predicted at different sollicitation frequencies.

From the shift of the maximum, we can also calculate an average activation enthalpy, ΔH_{av}, by making the assumption that the frequency-temperature dependence follows an Arrhenius law.

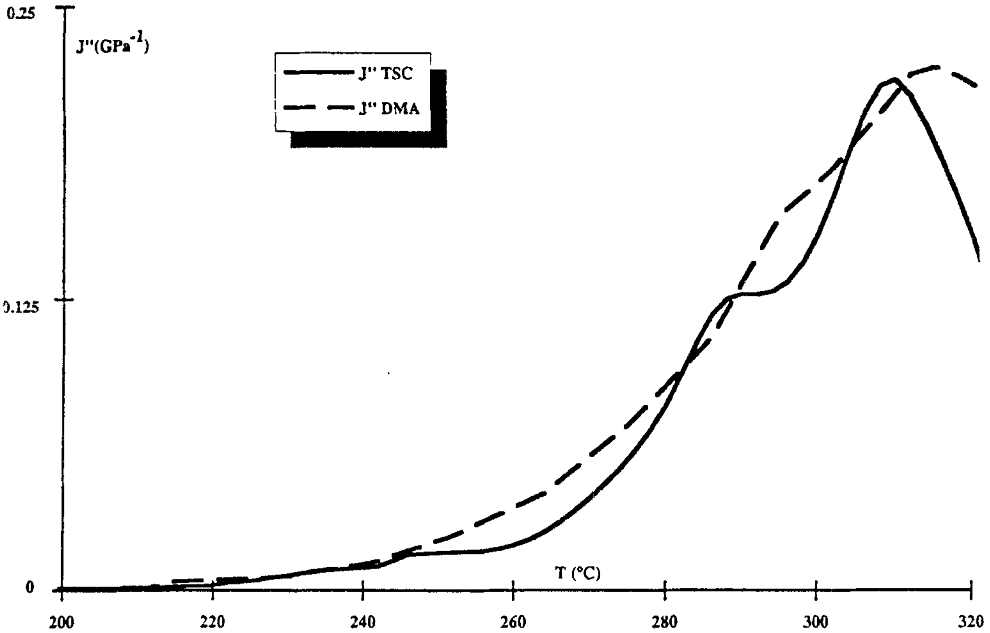


Fig. 7 Prediction of loss compliance as a function of temperature. Comparative study with DMA

$$f = f_0 \exp\left(\frac{-\Delta H_{av}}{kT}\right) \tag{8}$$

The calculation gives $\Delta H_{av}=5.3$ eV.

So we can predict the anelastic behaviour of the material as a function of temperature and frequency.

In order to validate the predictive calculation of the loss compliance, we have compared this spectrum with results obtained in DMA (Fig. 7).

From the $G'(T)$, $\tan\delta(T)$ spectra and $J''(T)=G''(T)/[G'^2(T)+G''^2(T)]$ equation, we have calculated the spectrum corresponding to the variation of J'' as a function of temperature. The comparison of the two $J''(T)$ spectra (Fig. 7) shows that the predictive calculation of the loss compliance is coherent with the DMA results.

Conclusions

A bismaleimide/carbon fiber composite has been investigated by TSC. The molecular mobility liberated around the glass transition temperature is characterized by a distribution of retardation times following an Arrhenius equation. The corresponding parameters-activation enthalpy and preexponential factor obey a compensation law. In other polymeric materials, such a phenomenological behavior has been associated with hierarchically correlated movements. This analysis allows us to predict the variation *vs.* temperature and frequency of the viscoelastic complex compliance. Those results are in good agreement with experimental data from DMA in the frequency range where they are available.

References

1 J. C. Monpagens, D. G. Chatain, C. Lacabanne and P. G. Gautier, J. Polymer Sci., 15 (1977) 767.
2 R. J. Morgan and R. J. Jurek, Polymer, 34 (1993) 813.
3 H. D. Stenzenberger, Composite structures, 24 (1993) 219.
4 S. P. Wilkinson, T. C. Ward and J. E. Mc. Grath, Polymer, 34 (1993) 870.
5 R. J. Morgan, R. J. Jurek, A. Yen and T. Donnellan, Polymer, 34 (1993) 835.
6 L. Michel, Thesis n°140, Paul Sabatier University Toulouse, 1990, France.
7 C. Bucci, R. Fieschi and G. Guidi, Phys. Rev., 146 (1966) 816.
8 H. W. Starkweather, Macromol., 14 (1981) 1277.
9 H. W. Starkweather, Macromol., 32 (1991) 2443.
10 C. Lacabanne, A. Lamure, G. Teyssedre, A. Bernes, M. Mourgues, J. Non Cryst. Solids, 172–174 (1994) 884.
11 J. Boye, J. J. Martines, C. Lacabanne, P. Perret and B. Chabert, Polymer, 33 (1992) 323.