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Molecular Motions in a Polycarbonate Composite as Studied by Thermally Stimulated Recovery and Dynamic Mechanical Analysis

Natália M. Alves[&], João F. Mano*[&] and José L. Gómez Ribelles[§]

[&] Departamento de Engenharia de Polímeros, Universidade do Minho, Campus de Azurém, 4800 Guimarães, Portugal; jmano@u3000.eng.uminho.pt

[§] Departamento de Termodinámica Aplicada, Universidad Politécnica de Valencia, P.O. Box 22012, E-46071 Valencia, Spain; jlgomez@ter.upv.es

SUMMARY: The viscoelastic properties of a short carbon-fibre reinforced polycarbonate are studied in the glassy state and in the glass transition region by means of *Thermally Stimulated Recovery* (TSR) and *Dynamic Mechanical Analysis* (DMA) techniques in the flexural mode. The temperature calibration of the apparatus is discussed. Each thermal sampling experiment is analysed according to a simple Voigt-Kelvin model in which the temperature dependence of the retardation time follows the Arrhenius equation with two adjustable thermokinetic parameters. Non-linear fittings of the experimental data are performed with the corresponding constitutive equation. Both the activation energy and the pre-exponential factor follow the usual trends with temperature and present the well-known compensation phenomena. A divergence between the TSR results of the two materials is found above ≈ 145°C and may be a result of the effect of the interface. The observed movements in the glassy state which are still found to have a cooperative character are analysed according to the Adam-Gibbs theory. Dynamic-mechanical relaxation properties of the composite are reported and analysed in terms of Takayanagi's block model.

1. Introduction

It is well known that, apart from (i) the properties of each component and (ii) the composition and phase morphology, the mechanical behaviour of polymer composites strongly depends on the adhesion quality at the filler/matrix interface. This effect is extremely important because it enables the transfer of the mechanical load imposed on the composite through the filler; the later is usually stiffer than the polymer. The improvement of the adhesion has been the subject of intense work (for carbon fibres see, for example, ref. 1). The layer of a polymer in contact with the filler may have mechanical properties different from those of the rest of the matrix because of interactions with the filler surface, which can be of different types: mechanical immobilisation of the chains, electrostatic forces, chemical bonds, or related to the presence of

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internal stresses, voids or microcracks in the interlayer. Therefore, it is expected that the filler/matrix interface may have strong influence on the viscoelastic properties of polymer composites (see, for example, ref. 2).

Thermally Stimulated Recovery (TSR) is a mechanical spectroscopy related technique which may be used to investigate the viscoelastic properties in polymeric systems, including polymer composites. This technique, also called Thermally Stimulated Creep, has been used for more than 20 years 3-5). During those experiments a static stress is applied to the sample at a temperature T_σ above the temperature range of investigation, where some extension of creep is allowed during a time t_σ. Then, the sample is quenched in order to freeze the resulting strain. Finally, the mechanical recovery (i.e., the decrease of the strain to the corresponding equilibrium value) of the sample is monitored during a constant heating rate (with no stress applied) up to $T > T_\sigma$. Relaxational processes can be detected by sudden decreases of the strain, $\varepsilon(T)$, during heating or by various peaks in $d\varepsilon/dT$ provided they are sufficiently separated from each other. It may be interesting to refer that a technique similar to TSR, called Creep Rate Spectroscopy, was proposed some years ago 6).

The underlying physics of TSR may somewhat be compared with that of other thermally stimulated techniques, such as differential scanning calorimetry (DSC), in which some physical property, intrinsically related with the molecular mobility, is being recorded as the temperature increases or decreases. Such methods have equivalent frequencies of about 10^{-2} - 10^{-3} Hz which are relatively low when compared with the usual frequencies used in dynamical experiments (dielectric or mechanical, for example). This low frequency of the TSR technique is expected to enhance the resolution of the different relaxation processes, increasing the separation of the different "strain steps" in the temperature axis.

Isothermal mechanical creep/recovery experiments have been widely used to characterise the viscoelastic properties of polymeric materials. Despite its non-isothermal character, the TSR technique may also allow to extract valuable information about the dynamics of the polymeric chains while consuming less time. Moreover, from static isothermal or dynamic measurements it is only possible to access the global behaviour of the processes, which are usually described by distributions of characteristic times. By using the *thermal sampling* (TS) procedure, the TSR technique allows to experimentally decompose a complex peak into its individual or elementary components (see the experimental section), enabling analysis of the fine structure of the TSR global spectra.

The TSR experiments reported in literature are usually carried out with torsional stresses. To our knowledge only one work reported TSR experiments under three-point bending$^{7)}$. It is known that the viscoelastic properties depends on the mechanical excitation mode $^{8)}$. In this work, for example, we have used flexural stresses. Moreover, our TSR experiments are performed in the same apparatus as the dynamic mechanical analysis (DMA) experiments. This is a very useful option: two complementary techniques are executed in the same equipment; therefore, the samples are tested under the same conditions (thermal ambience, geometry, stress modes...). For example, the temperature calibration of the apparatus, a procedure often forgotten in this type of experiments, will allow to accurately adjust the temperature axis in both techniques simultaneously.

We present below some TS results on a polycarbonate (PC) and polycarbonate reinforced with short carbon fibres (PC + CF). The experiments cover the glass transition region of the systems. The results are treated by assuming that each TS experiment arises from the thermal stimulated strain release of a single retardation time process. The corresponding thermokinetic parameters are obtained by directly fitting the $\varepsilon(T)$ data with a simple Voigt-Kelvin model. Some DMA experiments are also reported and the comparison between the experimental results of PC and the corresponding composite is carried out on the basis of a simple block model.

2. Experimental

2.1. Materials and preparation of the samples

The materials used in this work were Makrolon 2805 Polycarbonate (PC) from Bayer and PAN-based TENAX HTA 5131 carbon fibres. The fibres were processed without any further surface modifications.

The fibres were cut in 1 inch lengths and fed together with the PC to a Leistritz LSM 30.34 twin-screw extruder. The obtained composite extrudate (PC+CF), with 13.3% volume of carbon fibres, was granulated. The average diameter and the aspect ratio of the fibres in the composite are 7.2 μm and 14, respectively. Tensile bars adapted from ASTM D638M, were injection moulded with PC and PC + CF using a Klockner Ferromatic FM20 injection moulding machine. The processing conditions were chosen in order to enhance fibre orientation in the composite specimens.

The tensile mechanical properties of the materials were tested with an Instron 1122 universal testing machine (for fibres) and with an Instron 4505 universal testing machine (for PC and PC + CF). The mechanical properties obtained are: matrix- E_m = 2483 MPa, σ_m = 55.7 MPa; fibres- E_f = 200 GPa, σ_f = 3.0 GPa; composite- E_c = 9385 MPa, σ_c = 104.9 MPa (E and σ are the Young modulus and the ultimate stress, respectively, and the subscripts m, f and c are for matrix, fibre and composite, respectively).

The samples used in this study (about 18 x 4.36 x 1 mm) were obtained by carefully cutting the extremities of the injection moulded specimens with a diamond saw (Well 3242). The samples were kept at room temperature during at least 6 months before the experiments.

2.2. Equipment

The TSR and the DMA experiments were carried out using a DMA7e Perkin-Elmer apparatus with a controlled cooling accessory. High purity helium was used for purging the sample environment during the experiments, allowing a better thermal contact between the furnace and the sample.

In order to eliminate any deficient calibration of the apparatus thermocouple as well as the thermal gradients between the sample and the thermocouple, the temperature calibration of the equipment was carried out. The method employs the DMA instrument in a penetration mode, in which the displacement of a 3 mm spherical probe tip imposing a 10 mN static force into a small standard metallic sample (in this case Indium, from Goodfellow, 99.99999% purity) is monitored during heating at the same heating rate of the experiments with the polymeric samples (4 $K\cdot min^{-1}$). The onset of the probe displacement curve, due to the melting of the metal, is compared with the theoretical melting point of indium in order to correct the temperature axis of the DMA and TSR experiments. The temperature of the initial creep stage (at T_σ) was corrected using the same procedure at a very low scanning rate (0.2 $K\cdot min^{-1}$).

All the experiments were carried out in a three-point bending mode. The samples were placed over a 15-mm bending platform and a 5-mm knife-edge probe tip provided the mechanical excitation. For the DMA experiments different frequencies were used, between 0.5 and 20 Hz in the temperature range 60 –180°C. In this case a dynamic stress of $4\cdot10^5$ Pa as well as a static stress of $4.8\cdot10^5$ Pa were imposed upon the samples. Each DMA or TSR experiment consumed a different sample.

2.3. TS method

The thermal sampling (TS) experiments were carried out in the "creep-recovery mode" of the equipment mentioned above, with appropriate temperature and stress programs. In these experiments the mechanical stress is applied only in a narrow temperature range within the temperature region where the global process appears. The static stresses were sufficiently small to ensure the studies in the linear regime.

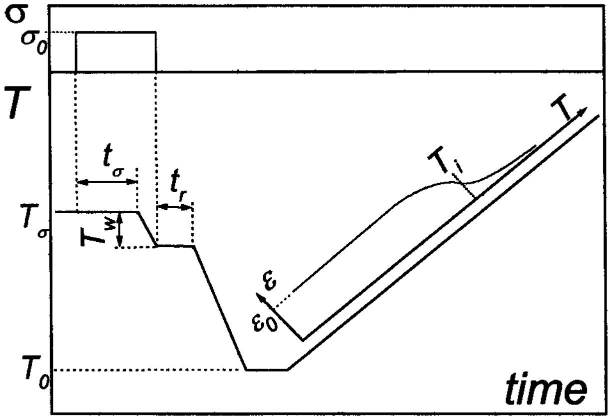

Fig. 1: Scheme of a typical TS experiment

A typical TS experiment is schematically explained in Fig. 1 and may be described as follows: i) a static stress σ_0 is applied at T_σ during a time period t_σ (T_σ varies from experiment to experiment in the region of the global process); ii) the sample is quenched to $T_\sigma - T_w$ (T_w is typically 3 or 4°C) with the mechanical field on; iii) the stress is removed and the mechanical strain is allowed to recover during a period of time t_r (typically 2-4 min); iv) the sample is quenched to T_0, well below the temperature region of the global process (say 50°C below T_σ); and v) the position of the probe tip, always in contact with the sample, is monitored during a controllable heating (typically 4 $\mathrm{K \cdot min^{-1}}$), from T_0 up to a final temperature well above T_σ. For the case of three-point bending experiments on rectangular-section samples, the probe position $y(T)$ can be related to the strain $\varepsilon(T)$ by using simple materials resistance concepts:

$$\varepsilon(T) = \left| \frac{6y(T)h}{l^2} \right| \tag{1}$$

where *h* is the sample thickness and *l* is the sample length. These two parameters are assumed to be constant during the experiment.

3. Results and Discussion

3.1. Thermally stimulated recovery experiments

To execute TSR global experiments, the stress should be applied at a temperature well above T_g in order to activate all relaxational modes characterising the glass transition process. However, the samples studied in this work, even the composite ones, are too soft at those temperatures and any mechanical stress leads to an irreversible flow. Therefore, only TS experiments are reported in this work.

Fig. 2 shows several TS curves corresponding to experiments on PC samples for some T_σ values between 136.7 and 155.2°C (open circles). The same kind of results for PC + CF samples is shown in Fig. 3. The results are expressed as $\varepsilon(T)/\sigma_0$ (a measure of the flexural creep compliance) against temperature. As expected, the curves for the stiff composite material exhibit higher values of $\varepsilon(T)/\sigma_0$ compared with the PC material.

Each TS curve can be analysed as a thermostimulated mechanical recovery process of an elementary mechanism. The Voigt-Kelvin model can be used in order to predict the dependence of the strain upon time or temperature. The corresponding constitutive equation is:

$$\dot{\varepsilon}(t) = \frac{\sigma_0 / E - \varepsilon(t)}{\tau(T)} \tag{2}$$

where σ_0 is the static strain, *E* is the Young modulus of the spring element and $\tau(T)$ is the retardation time of the process, often represented by the Arrhenius equation

$$\tau(T) = \tau_0 \exp(E_a / RT) \tag{3}$$

where τ_0 is a pre-exponential factor and E_a is an apparent activation energy while R is the gas constant. In the Voigt-Kelvin model $\tau = \eta/E$, where η is the viscosity of the newtonian dashpot which is in parallel with the elastic element.

Applying Eq. (2) to the mechanical recovery ($\sigma_0 = 0$) during heating at a constant rate β, the temperature dependence of the strain is

$$\varepsilon(T) = \varepsilon_0 \exp\left[-1/\beta \int_{T_0}^{T} dT'/\tau(T') \right] \qquad (4)$$

where $\varepsilon_0 = \varepsilon(T_0)$.

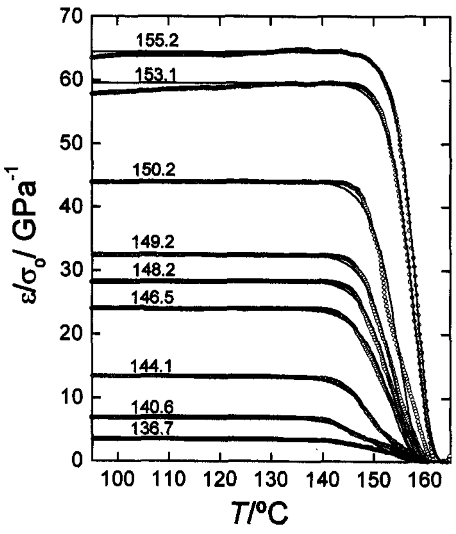

Fig. 2: TS curves of PC in the glass transition region for T_σ values between 136.7 and 155.2°C. The other experimental variables were: $t_\sigma = 4$ min, $T_w = 4$°C, $t_r = 2$ min, $T_0 = 70$°C and $\beta = 4$ K·min^{-1}. The solid lines correspond to the fitting of the experimental results (see text).

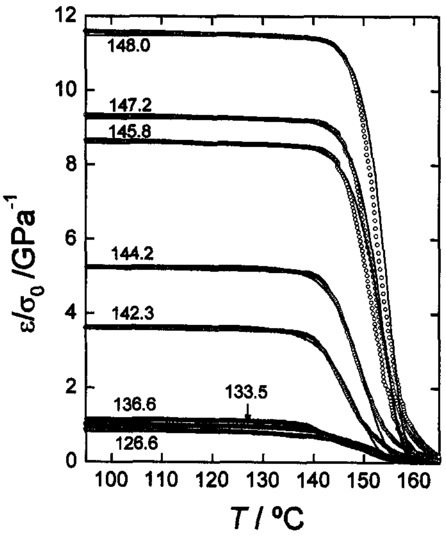

Fig. 3: TS curves of PC + CF in the glass transition region for T_σ values between 126.6 and 148.0°C. The other experimental variables are the same as in Fig. 2. The solid lines correspond to the fitting of the experimental results (see text).

It can be easily seen, from Eq. (4), that $\tau(T) = -\varepsilon(T)/[d\varepsilon(T)/dT]$ is valid. This relation has been used to determine the temperature dependence of the retardation time [9]. The thermokinetic parameters τ_0 and E_a are then easily obtained by a linear fitting of the $\ln(\tau)$ *vs* $(1/T)$ values using Eq. (3). These two consecutive fittings do not necessarily guarantee, from a statistical point of view, the best representation of the experimental curves. Therefore, in this work it was opted to directly fit the experimental results to Eq. (4) assuming that $\tau(T)$ obeys an Arrhenius type behaviour.

Three parameters were obtained for each TS curve: E_a, τ_0 and ε_0. We note that good initial approximations of the ε_0 values are given by the $\varepsilon(T)$ values in the higher landing of the experimental curves. The three adjustable parameters were obtained by minimisation of $\Sigma_i[\varepsilon(T_i) - \varepsilon(T_i,\tau_0,E_a,\varepsilon_0)]^2$ using a non-linear least-squares algorithm (Generalised Reduced Gradient), where $\varepsilon(T_i)$ are the experimental values and $\varepsilon(T_i,\tau_0,E_a,\varepsilon_0)$ are the theoretical ones, obtained from Eq. (4). The low temperature limits used in the fittings were those some 25°C below the onset of the drop of the $\varepsilon(T)$ signal. On the other hand, the high temperature limits were those corresponding to about the half decrease of the initial values. In fact, it was shown that, due to the incomplete isolation of the elementary process with TS experiments the experimental results should diverge from the theoretical prediction [10]; this occurs mainly above the $\varepsilon(T)$ inflection temperature (or temperature of maximum $d\varepsilon(T)/dT$) [5]. Assuming an Arrhenius type dependence of the retardation time we find that the integral in Eq. (4) does not have an explicit analytical solution. An approximate solution may be given by transforming the solution into a quasi-rational expression [11]:

$$-1/\beta \int_{T_0}^{T} dT'/\tau(T') = -E_a/\beta\tau_0\left[E_2(z)/z - E_2(z_0)/z_0\right] \tag{5}$$

where $z = E_a/RT$, $z_0 = E_a/RT_0$ and

$$e^x E_2(x) = 1 - \frac{x^4 + a_1x^3 + a_2x^2 + a_3x + a_4}{x^4 + b_1x^3 + b_2x^2 + b_3x + b_4} + \Delta(x), \quad |\Delta(x)| < 10^{-8} \tag{6}$$

where in our case a_1 = 8.5733287401; a_2 = 18.0590169730; a_3 = 8.6347608925; a_4 = 0.2677737343; b_1 = 9.5733223454; b_2 = 25.6329561486; b_3 = 21.0996530826, and b_4 = 3.9584969228.

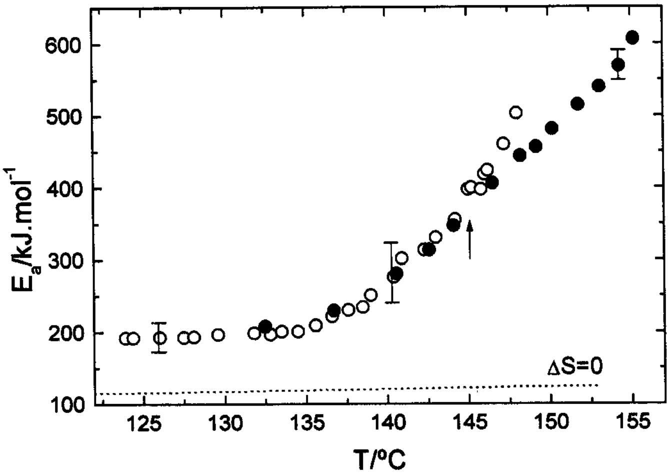

Fig.4 : Temperature dependence of the activation energy values, E_a, for PC (solid circles) and PC + CF (open circles). Dotted line: prediction of the temperature dependence of E_a for the zero-entropy case.

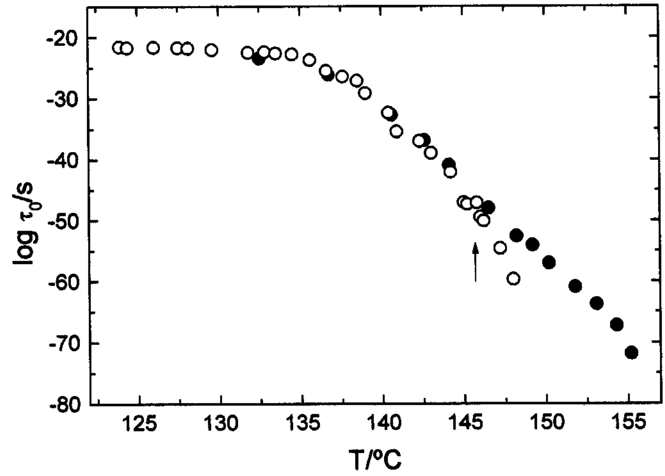

Fig. 5: Temperature dependence of the pre-exponential factor, logτ_0, for PC (solid circles) and PC + CF (open circles).

Figs. 2 and 3 also show the fits obtained (solid lines). The fits can be considered acceptable taking into account the inefficient isolation of elementary modes with the TS experiments on one hand and, the use of a simplified model (Voigt-Kelvin model with Arrhenius dependence of the retardation time) on the other hand.

Figs. 4 and 5 show the temperature dependence of E_a and log τ_0 for the two materials. It was found, mainly for temperatures near the middle of the studied temperature range, that these adjustable parameters could depend, to a certain extent, on the initial values; this is due to the interdependence between the two variables. In fact, as it will be seen later, these variables show a particular behaviour, the so-called compensation phenomenon, which make them somewhat dependent on each other. It is interesting to note that the convergence of the adjustable parameters is less dependent on the initial values for the curves obtained at low and high temperatures.

From Fig. 4 it is seen that the activation energy increases with temperature for both materials, from ~ 190 $kJ\cdot mol^{-1}$ to values above 500 $kJ\cdot mol^{-1}$. Those values are high compared, for example, to the energy of a single covalent bond; for instance, the energy of the C-C σ-bond in ethane is 340 $kJ\cdot mol^{-1}$. However they are often reported in TSR (or in the thermally stimulated depolarisation currents technique, TSDC, the dielectric technique corresponding to TSR) and may be explained on the basis of cooperative conformational rearrangements within the macromolecular segments when the studies are carried out in the glass transition region. The increase of activation energy with increasing temperature indicates that the processes which are being isolated by the TS experiments involve larger polymeric segments or correlation lengths as one approaches the glass transition temperature. Apparently, this increasing cooperativity approaching T_g from lower temperatures is similar to the increase of cooperative rearranging - in the sense of the Adam-Gibbs theory- when approaching T_g from higher values. An interesting picture of the increase of the activation energy near T_g from the low and high temperature sides was observed by us combining dielectric relaxation, TSDC and DSC results 12).

Comparing both materials, Fig. 4 suggests a diverging temperature at ~ 145°C. Above that temperature the activation energies of the PC + CF material become higher than for PC. The corresponding log τ_0 *vs* T representation, shown in Fig. 5, also displays this behaviour. This occurrence may be a result of the effect of the interface between matrix and filler. To discuss this hypothesis, we shall firstly note that the PC chains near the interface interact with the matrix through several points. If the TS experiments are performed at a sufficiently high T_σ, we may isolate processes involving cooperative regions with dimensions larger than the average distance between the interaction points; in this case the resulting ε(T) *vs* T curves should yield larger activation energies. This occurs because those experiments would activate also molecular segments near the interface, besides PC chains in the matrix phase. Such segments have higher hindered mobility, requiring higher activation energies for conformational rearrangements. Above this critical temperature, the activation energy values should increase more rapidly for the composite than for the corresponding pure material; in fact, with increasing temperature, more constrained points are being involved in the motion of the polymer segments. Obviously, we must be aware that more work should be needed in order to confirm this hypothesis. The activation energies obtained for PC (solid symbols in Fig. 4), with values exceeding 630 kJ·mol^{-1} at higher temperatures, may be partially affected by the irreversible flow within the polymeric chains. The occurrence of this effect could also be an alternative explanation for the divergence occurring in results for the two materials at ~145°C. However, it must be emphasised that apparent activation energies in thermoplastics within the glass transition region are usually very high. For example, DSC results carried out in a PC sample in which the dependence of the fictive temperature on the cooling rate was investigated, yield activation energies of about 1250 kJ·mol^{-1} 13).

An interesting behaviour also seen in Figs. 4 and 5 is that observed below ~135°C. The thermokinetic parameters seem to stabilise at values around 190 kJ·mol^{-1}. This observation could be an indication that near and below that temperature region the extension of cooperativity of the isolated processes is vanishing. A simple argument demonstrates that this hypothesis is not correct. Starkweather proposed a procedure to determine the cooperativity extension of relaxational processes derived from the Eyring activated states equations 14). In this treatment it is considered that the activation entropy is zero for localised processes. In such a case the activation energy should lead to

$$E_a = RT\left[1 + \ln(k_B T / 2\pi h f)\right] \tag{7}$$

where f is the frequency of the experiment, k_B is the Boltzmann constant, h is the Planck constant and R is the gas constant. In TSR experiments the frequency may be considered, as $5{\cdot}10^{-3}$ Hz - this value was based on observations of numerous TSDC result 15). The prediction of the activation energy for the zero entropy case is shown in Fig. 4 (dotted line). The considerable difference between this prediction and the experiment results shows that even for the low temperature experiments, the isolated processes have a strong cooperative character.

Another approach can be used in order to discuss the activation energy values at the low temperature side found in Fig. 4. According to the Adam-Gibbs theory the temperature dependence of the characteristic times in the glassy state can be written as:

$$\tau = \tau_0 \exp\left(\frac{B}{TS_c^{glass}}\right) \tag{8}$$

where $B = s_c\Delta\mu/k_B$ (s_c means the configurational entropy of the smallest cooperatively rearranging region and $\Delta\mu$ is the Gibbs energy barrier hindering configurational rearrangement per mol molecules or chain segments) and S_c^{glass} is the configurational entropy of the glassy state. Considering that S_c^{glass} is temperature independent and B is constant, the activation energy in the glassy state is $E_a^{glass} = RB/S_c^{glass}$. In DSC studies in a PC sample it was found that S_c^{glass}=0.0481 J·g^{-1}·K^{-1}, for B=1250 J·g^{-1} [13]. Therefore, these values lead to the activation energy of 210 kJ·mol^{-1} which is consistent with the activation energies found in TS experiments in the glassy state. Note that, in the specific case of PC, the comparison between viscoelastic and calorimetric studies can be reasonably achieved because the relaxation times *vs* temperature curves were found to be quite consistent [13].

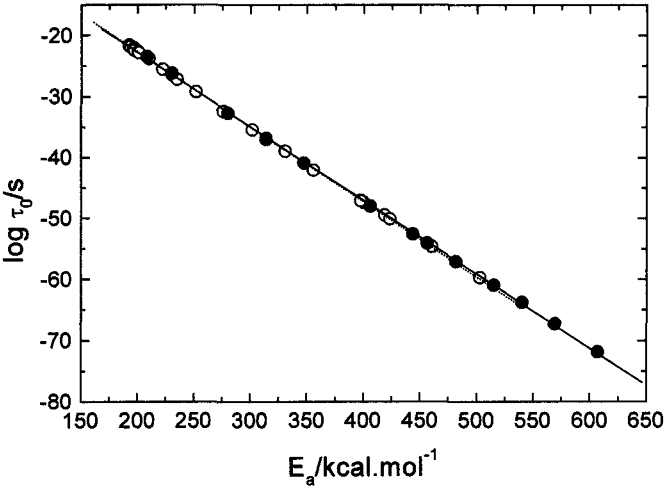

Fig. 6: Compensation plot for PC (solid circles) and PC + CF (open circles). The solid and dotted lines correspond to the linear fitting of the two data set.

The shape of the results shown in Figs. 4 and 5 suggests the existence of a strong correlation between the thermokinetic parameters. In fact, when plotted versus each other, these two parameters show a linear relationship. This behaviour, called compensation phenomenon, has been extensively discussed in literature: it always appears in TSR and TSDC results when the studies are undertaken in the glass transition region. Fig. 6 shows the compensation plot for the two materials.

From the linear fitting of the results two main compensation parameters can be derived - the compensation time τ_c and the compensation temperature T_c:

$$\log \tau_{0,i} = \log \tau_c - E_{a,i} / \ln(10) R T_c \tag{9}$$

Despite the extensive overlap of the two linear representations in Fig. 6, the compensation parameters are found to be somewhat distinct. The compensation temperatures are 158.3°C for PC and 151.0°C for the composite while log τ_c (τ_c in s) yield 1.4 and 2.0, respectively. The practical significance of the compensation parameters is difficult to interpret. In fact, up to now, no consistent theory did offer an unambiguous explanation for their physical origin. Moreover, there are evidences which suggest that the compensation phenomenon itself observed here cannot be considered as a basic feature of the relaxation at the glass transition but is just a mathematical consequence of a fundamental relationship between the activation Gibbs energy and temperature 16). However, it may be interesting to notice that another study using TSR reported a higher compensation temperature and a lower compensation time for a composite system (an epoxy resin reinforced with glass beads) relatively to the corresponding matrix 17).

3.2. Dynamic Mechanical experiments

Some isochronal DMA experiments in the glass transition region were performed in both PC and PC + CF materials in the frequency range 0.5 –20 Hz. The frequency dependence of the temperature position of the maximum of loss modulus, *E''*, was investigated. Assuming a simple Arrhenius dependence, it is possible to estimate an apparent activation energy in this frequency range. We find $E_a \approx 860$ kJ·mol^{-1} and $E_a \approx 760$ kJ·mol^{-1} for the matrix and the composite, respectively. It must be noted that these values are estimates (especially for PC, where the data were of less quality) due to the narrow frequency range. However, as should be expected, the activation energies observed by DMA are somewhat higher than those obtained by TSR because the glass transition is seen at higher temperatures in the former technique.

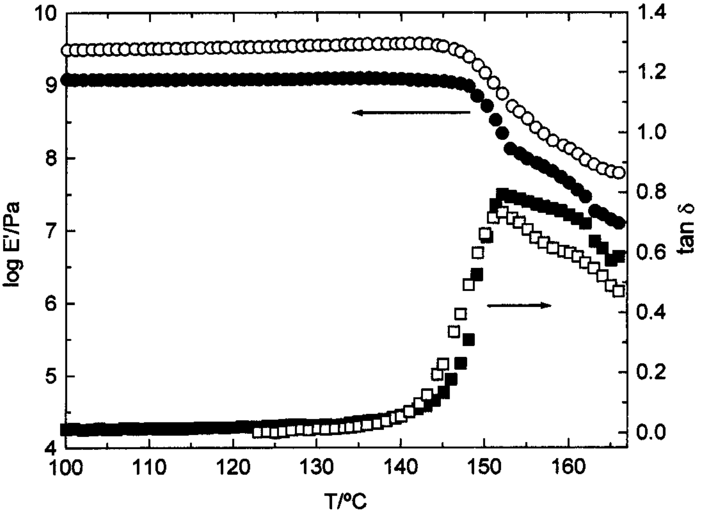

Fig. 7: Storage modulus (circles) and loss tangent (squares) of pure PC (solid symbols) and PC + CF composite (open symbols) obtained at 1 Hz.

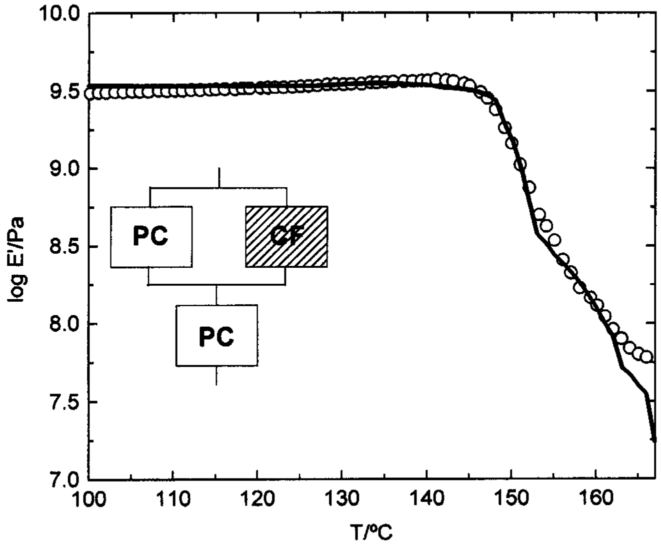

Fig. 8: Storage modulus at 1Hz of the PC + CF composite (open symbols) and model calculation (solid line) with $\lambda=0.4$. See text.

Fig. 7 presents the results of the isochronal dynamic measurements in PC and PC + CF at 1 Hz. The modulus of the composite in the glassy state is nearly three times that of the pure PC. However, the difference increases suddenly near the glass transition temperature suggesting that the effect of the reinforcement is more efficient above T_g. This occurrence should be expected because in this temperature range one observes an increase of the difference between the modulus of the matrix, which is being progressively softer, and the modulus of the fibres, which is approximately constant. The maximum of the loss tangent in the main relaxation region is nearly equal in the composite and in the matrix polymer ($\tan\delta = 0.73$ and 0.79, respectively, in the maximum which appears at 152°C both in the composite and in PC). This behaviour can be explained with the aid of the block model of Takayanagi [18].

The dynamic-mechanical properties of the composite are modelled with a three-block model in which two blocks in a series represent the continuous phase while one block in parallel represents the reinforcing fibre (see the sketch included in Fig. 8). A significant amount of PC is expected to work in series with the rest of the material since the volume fraction of fibre is not very high. The storage modulus and loss tangent of the composite are given by the following equations [19].

$$E' = \frac{(M'E'_m - M''E''_m)(\xi M' + (1-\xi)E'_m) + (M''E'_m + M'E''_m)(\xi M'' + (1-\xi)E''_m)}{(\xi M' + (1-\xi)E'_m)^2 + (\xi M'' + (1-\xi)E''_m)^2} \qquad (10)$$

$$\tan\delta = \frac{(M''E'_m + M'E''_m)(\xi M' + (1-\xi)E'_m) + (M'E'_m - M''E''_m)(\xi M'' + (1-\xi)E''_m)}{(M'E'_m - M''E''_m)(\xi M' + (1-\xi)E'_m) + (M''E'_m + M'E''_m)(\xi M'' + (1-\xi)E''_m)} \qquad (11)$$

with ϕ the volume fraction of fibres, λ the volume fraction of matrix working in series ($\lambda(1-\phi) = \xi$ is the total volume fraction in series); $E'' = E' \cdot \tan\delta$ is the imaginary part of the complex Young modulus; $M' = \varphi E'_f + (1-\varphi)E'_m$; $M'' = \varphi E''_f + (1-\varphi)E''_m$ where $\varphi = \phi/(1-\xi)$. Here the subscript m refers to the properties of PC and the subscript f refers to the dispersed phase. The modulus of the reinforcing fibre was assumed to be 200 GPa constantly and the corresponding loss tangent was assumed to be zero.

Because of the high stiffness of the reinforcing fibre, the loss tangent of the composite turnout to be equal to that of the matrix, even for very low values of the volume fraction of the matrix working in series. For values of λ in the range expected for our composite, the calculated loss tangent curve is nearly independent of this parameter. The value of the storage modulus, on the contrary, highly depends on the value of λ, and this parameter can be determined by fitting the experimental E' data. Fig. 8 compares the model prediction with $\lambda = 0.4$ for the experimental data.

4. Concluding Remarks

In this work the viscoelastic properties around T_g of a short carbon fibre reinforced polycarbonate and unreinforced polycarbonate were studied by means of *Thermally Stimulated Recovery* (TSR) and *Dynamic Mechanical Analysis* (DMA) techniques. From the results obtained we can conclude the following:

(1) It seems possible to carry out TSR experiments with a commercial DMA apparatus. This should lead to a better comparison between the results obtained by both techniques.

(2) The thermal sampling results were described as elementary processes where the temperature dependence of the retardation time follows the Arrhenius equation. The fits of the thermal sampling results assuming a Voigt-Kelvin model are acceptable for both materials. The activation energy increases monotonically with increasing temperature and an opposite trend is observed for the pre-exponential factor. As is usually seen in TSR results in the glass transition region of polymers, the thermokinetic parameters show the compensation phenomena.

(3) Above ≈145 °C a divergence between the E_a *vs* T data of the two materials is detected. The higher values of E_a observed for the composite suggests that this effect may be a result of the interface. On the other hand, at lower temperatures the activation energies approach ≈190 $\mathrm{kJ{\cdot}mol^{-1}}$ for both materials. From the zero-entropy method proposed by Starweather we concluded that the molecular motions isolated by the thermal sampling method at 30 °C below T_g have still a cooperative character. Moreover, it was found that the Adam-Gibbs theory lead to an activation energy for the glassy state of polycarbonate of ≈210 $\mathrm{kJ{\cdot}mol^{-1}}$ which is consistent with the TSR values at low temperatures.

(4) The dynamic mechanical relaxation spectrum of the composite agrees with the one predicted by Takayanagi's block model both in the absolute values of E' and in the fact that the height of the loss tangent peak is nearly unchanged by the presence of 13.3% volume of the reinforcing fibres.

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