Structural relaxation in poly(ethyl methacrylate)/nylon fibre composites

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Differential scanning calorimetry (d.s.c.) of composite samples made out of poly(ethyl methacrylate) (PEMA) and nylon fibres with a wide range of fibre volume fractions reveals several interesting features. A decrease in the glass transition temperature of the series as the fibre fraction increases, as well as a decrease of the specific heat increment at the transition are clearly detected; the glass transition (as determined by d.s.c.) even disappears in samples with high nylon content. The effect on the response thermograms of different ageing thermal histories is analysed with the help of a four-parameter model which predicts the qualitative features of the structural relaxation process. The parameters delivered by the fitting of the model to the observed behaviour suggest that the modified response of PEMA when acting as a matrix (when compared to its behaviour as a pure polymer) is caused by a shift of the equilibrium relaxation times with no accompanying widening of the relaxation time distribution. This supports an interpretation of the observed changes in terms of a bulk modification of PEMA in the composites, probably as a consequence of interactions of its molecules with nylon in the process of forming the composites.

(Keywords: structural relaxation; poly(ethyl methacrylate); nylon fibre; composites)

INTRODUCTION

The existence and behaviour of one or more glass transition temperatures (T_gs) in multiphase polymer systems, such as composites and incompatible or partially miscible blends, is a feature of great interest for the relevance it may have as regards the characterization of the interaction among the system's components. Thus, occurrence of a single T_g is often employed as a criterion of compatibility for polymer blends[1,2], and in blends with two T_gs shifts of these with respect to their original positions in the pure component polymers are interpreted as indicators of partial miscibility. Shifts of the T_g with respect to that of the pure matrix polymer have also been detected in polymer composites[3,4]. Such increases or decreases of the T_g could be reflecting the differing mobilities of the chains of the polymer matrix in the neighbourhood of the included phase, and would thus give information on the characteristics of the polymer–reinforcement interface.

The T_g is a parameter that characterizes the kinetics of the process of structural relaxation of amorphous polymers only very poorly. Indeed, its definition in differential scanning calorimetry (d.s.c.) is by no means unambiguous: structural relaxation exhibits different kinetics according to the different physical properties (specific enthalpy, specific volume, refraction index, dielectrical or dynamic-mechanical properties, etc.) employed to monitor it, as each of these probes different molecular species or aggregates.

Structural relaxation in composite materials and blends has attracted some interest[3–9]. In general, the process of structural relaxation can be variously described. For our purposes, it is sufficient to recall that the phenomenological approach bases the analysis of the trend to equilibrium in the glassy state on model equations in terms of a set of internal state variables which is adjoined to the usual equilibrium state parameters of the system; the kinetics of the process is then generated by assigning to the internal state variables relaxation times dependent on the time value and on the distance to equilibrium[10]. The internal variables themselves can be introduced in the models as pure phenomenological parameters, or else arise from statistical mechanical considerations[11,12]. This approach has led to mathematical models with continuous[13–15] or discrete[10] distributions of relaxation times, which have been able to reproduce with remarkable accuracy the results of d.s.c. measurements on amorphous materials subjected to several thermal histories.

Other approaches are based on various physical theories, and they too have been able to account for the most salient facts of the phenomenology of the structural relaxation process; we list here the models of Pérez (which does not employ adjustable parameters)[16,17], Robertson–Simha–Curro[18,19] and Ngai's coupling model[20–22].

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In the present paper our aim is the study of the glass transition of poly(ethyl methacrylate) (PEMA) as a pure polymer and as a matrix in composites with continuous fibre reinforcement of nylon 6. We employ a phenomenological model with adjustable parameters in order to fit the observed behaviour; on the basis of the numerical values of these parameters we interpret the effects of the presence of nylon on the mobility of the PEMA chains. The phenomenon of physical ageing is thus employed to throw light on the interactions between the components of the composite.

EXPERIMENTAL

Sample preparation

Ethyl methacrylate monomer from Fluka was distilled *in vacuo* and bulk polymerized between glass plates for 2 h at 60°C, with 0.03 wt% azobisisobutyronitrile as initiator. Polymerization was then completed 24 h at 90°C. The PEMA thus obtained was dried *in vacuo* at 110°C to constant weight, and then dissolved in toluene at a polymer concentration of 3 wt%. A film of pure PEMA was prepared by casting the solution on a glass plate and drying to constant weight *in vacuo* at 110°C.

Commercial nylon 6 fibres (Compet N 1R69 LO, Allied Fibres, Petersburg, VA, USA) in continuous strands were employed as the reinforcing phase. As-received they were found to contain ~3 wt% moisture, as determined by thermogravimetry in a Du Pont TGA 951 analyzer. Corresponding to water evaporation, a broad peak between 80°C and 130°C was detected, which disappeared in an immediate second scan.

Composite samples were prepared by aligning bundles of nylon fibres on a glass plate, pouring over them the polymer solution and waiting until the solvent had evaporated. This process was then repeated until the matrix polymer completely covered the fibres. The specimen thus produced was then dried *in vacuo* at 110°C to constant weight in order to remove the remaining solvent or monomer.

From the plates thus obtained small pieces were cut and enclosed in aluminium pans for d.s.c. measurements.

As both PEMA and nylon appear to have the same density values (1.14 g cm^{-3}; the figure for nylon was provided by the manufacturer, whereas that for PEMA was taken from references 23 and 24), the volume and weight fractions of reinforcement in the samples are the same. The fibre weight fraction in each sample was determined by thermogravimetry using a piece of the sample and by comparing it with that of the pure PEMA matrix. The samples studied had fibre fractions of 12, 27, 37, 59 and 85%. (These numbers are used in the following to label the samples).

D.s.c. measurements

D.s.c. measurements were performed in a Perkin-Elmer DSC 4 analyzer with a data station 3600, recording about six points per degree centigrade during the heating scans (our figures show, however, only one point per degree). Each measuring scan was followed by another one with empty pans using the same experimental conditions. From both scans, the specific heat as a function of temperature could be determined. The apparatus was frequently calibrated with a sapphire standard. The heating scans took place between 20°C and 130°C, but the specific heats were calculated only for the temperature interval of 35–130°C.

All tests on a given composite specimen were performed on the same sample, and all thermal treatments took place inside the calorimeter.

The experimental procedure consisted of heating the sample to 130°C, and maintaining it at this temperature for 10 min to ensure thermodynamic equilibrium (thus erasing the effects of previous thermal histories). The sample was then cooled at 10°C min^{-1} to the ageing temperature (T_a), and kept at this temperature for the ageing time (t_a). After this time had elapsed, the sample was cooled again at 10°C min^{-1} to 20°C, and finally heated at 10°C min^{-1} from that temperature to 130°C. Heating scans performed after thermal histories without the isothermal (ageing) stage were taken as 'reference' scans.

The thermal histories to which the present study refers used $t_a = 1000$ min and $T_a = 30, 40, 50$°C for the composite samples, and $T_a = 40, 50, 60$°C for the pure PEMA sample.

RESULTS

Figure 1 shows the thermogram (heat flow as a function of temperature) of the reference scans for the pure PEMA and for the composite samples. A decrease in the increment of specific heat at the transition and in the T_g can be clearly seen. *Figure 2* shows the values of the T_g in the reference scans as a function of the fibre content. The T_g was determined as the intercept of the liquid and glass segments of the enthalpy *versus* temperature curves of these scans; as shown later, it coincides with the value of the fictive temperature (T_f) in the glass. *Figure 3* shows the increment of specific heat at the transition, $\Delta c_p(T_g)$, as a function of sample composition, ϕ. The specific heats are calculated from the heat flow curves by comparing them with the thermogram of a sapphire standard obtained in the same running conditions.

Remarkably, the glass transition of PEMA cannot be obtained in samples 59 and 85. Indeed, the values of

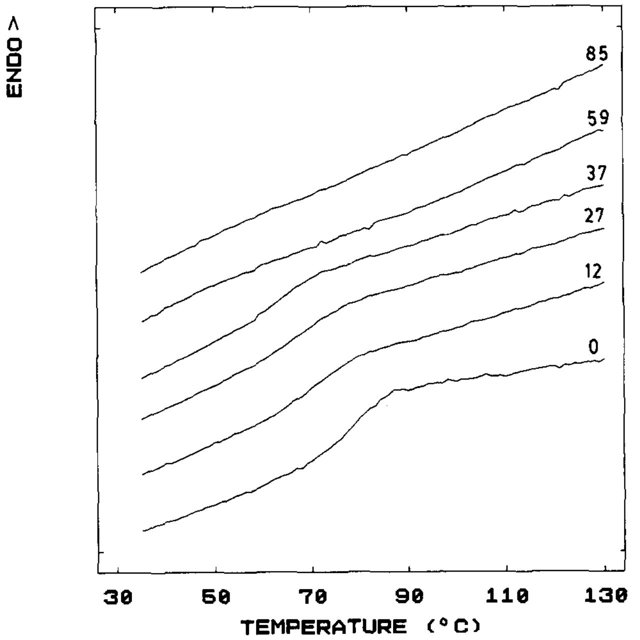

Figure 1 Heating thermogram of the unaged samples. The numbers on the curves are the percentage weight fibre fraction of each sample

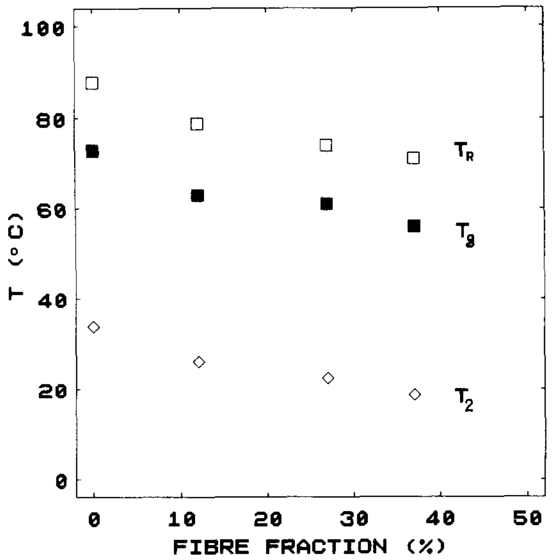

Figure 2 Values of the T_g and of the parameters T_2 and T_R (see text) as a function of sample composition

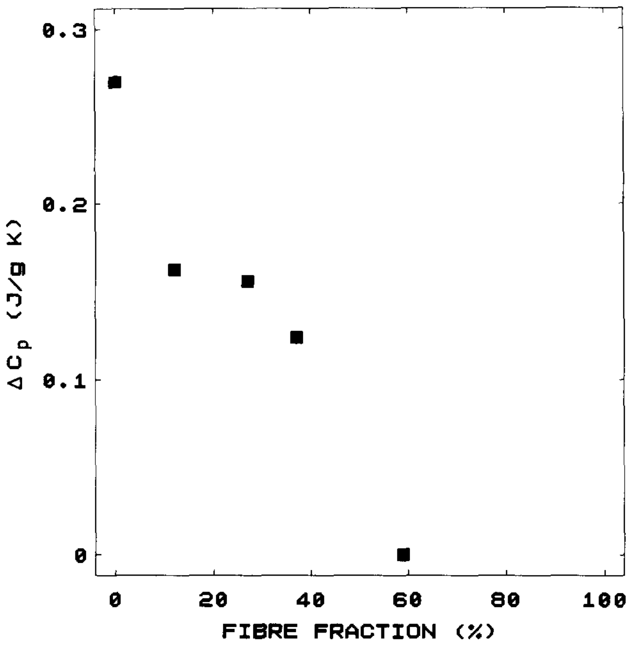

Figure 3 Specific heat increment at the transition as a function of sample composition

$\Delta c_p(T_g)$ in the samples with fibre contents of <0.6 lead to an extrapolation of $\Delta c_p(T_g)=0$ around $\phi=0.6$. In order to exclude the possibility that the transition in these samples had simply shifted to an interval below that available in the measurements, sample 59 was left to age at 30°C for 1000 min. The heating scan made afterwards showed a little peak around 50°C, indicating that the glass transition still takes place in the experimental temperature interval, but with a negligible $\Delta c_p(T_g)$ in the reference scans.

Figure 4 shows the results of scans on the pure PEMA sample, in the unaged case and after ageing at 60°C for 1000 min. The curves start to diverge at low temperature. This means that the process of structural relaxation can be detected for the time-scales corresponding to our measurements even at room temperature. This poses a difficulty for the determination of the curve of specific heat corresponding to the glassy region of the polymer, $c_{pg}(T)$. This function is defined as the ratio between the instantaneous change in enthalpy following a temperature jump and the amplitude of this jump. It can be approximately determined at temperatures below those of the glass transition region. In our case, we determined the shape of the curve of $c_{pg}(T)$ from specific scans, and calculated its slope to be 4.9×10^{-3} J g^{-1} K^{-2}. It was observed that this value is close to that obtained for samples subjected to very long ageing times close to T_g. This is due to the fact that the mobility of the chain segments decreases as the material approaches equilibrium (they are more densely packed), so the samples subjected to the longest ageing times are those whose response to changes in temperature is the closest to the glassy state.

Nylon fibres showed no trace of a glass transition between 30°C and 130°C. This may be due to the high orientation of the chain molecules caused by the spinning process during the manufacture of the fibres. When the same heating scan is repeated after having let the sample melt in the calorimeter pan and having quenched it to room temperature, a glass transition appears in the expected temperature range for nylon (an 'onset' T_g of 45°C and a 'midpoint' T_g of 54°C). Thus, for the purposes of our measurements, it was considered that no glass transition and no physical ageing took place in the nylon phase in our working temperature intervals. The effects of thermal histories on crystallization in nylon were equally considered to be negligible.

The slope of the curve of specific heat of nylon is greater than that of PEMA. As a consequence, the slopes of the $c_p(T)$ curves of the composite samples at temperatures below the glass transition increase with the fibre content. These slopes were calculated as the slopes of the most aged curves, and gave values of 6.1×10^{-3} for sample 12, 6.2×10^{-3} for sample 27, and 7.2×10^{-3} J g^{-1} K^{-2} for sample 37.

The results obtained on samples subjected to different thermal histories are presented in terms of the behaviour

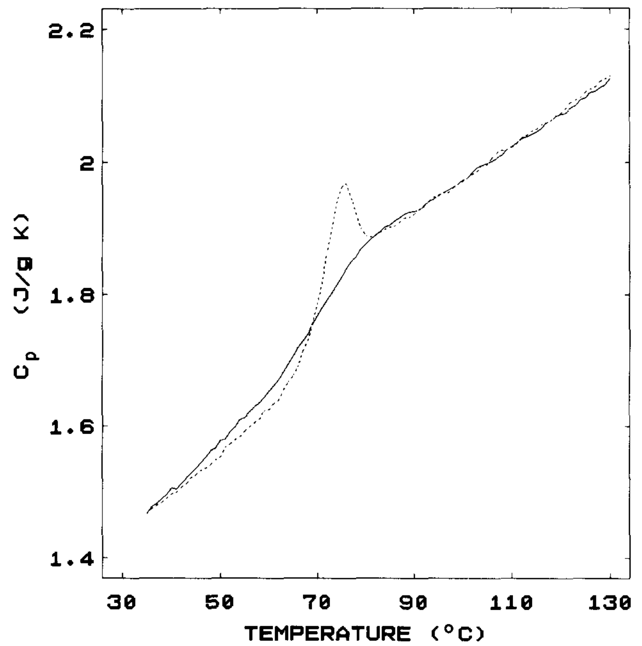

Figure 4 Specific heat of pure PEMA: unaged (——) and aged 1000 min at 60°C (– – –)

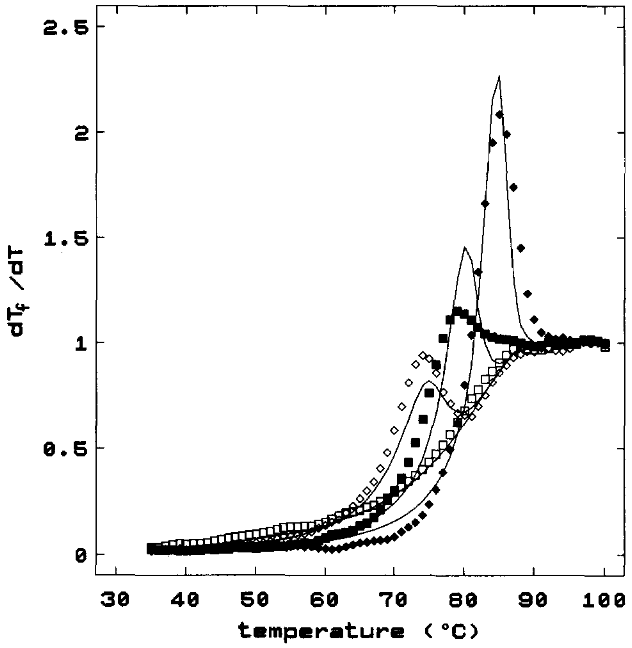

Figure 5 Derivative of the fictive temperature, dT_f/dT, in heating scans of pure PEMA after several thermal histories: unaged (□); aged at $T_a=40°C$ (◇); aged at $T_a=50°C$ (■); aged at $T_a=60°C$ (◆). The full lines represent the thermograms predicted by the model

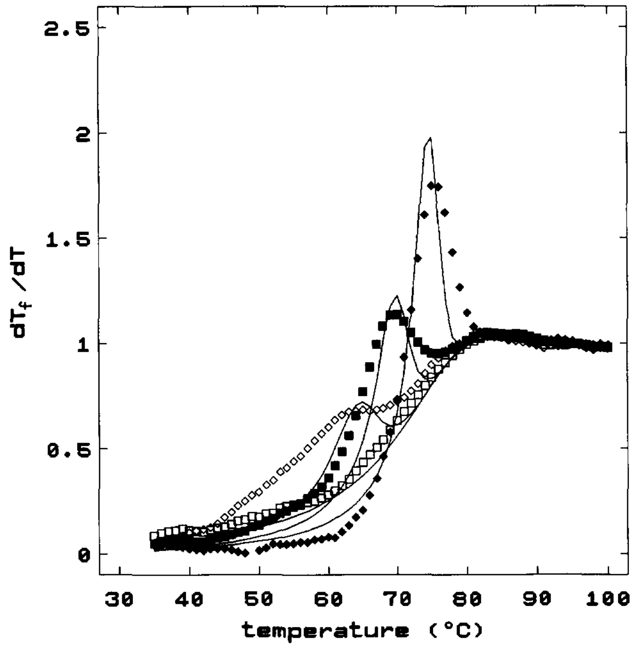

Figure 6 Derivative of the fictive temperature, dT_f/dT, in heating scans of sample 12 after several thermal histories: unaged (□); aged at $T_a=30°C$ (◇); aged at $T_a=40°C$ (■); aged at $T_a=50°C$ (◆). The full lines represent the thermograms predicted by the model

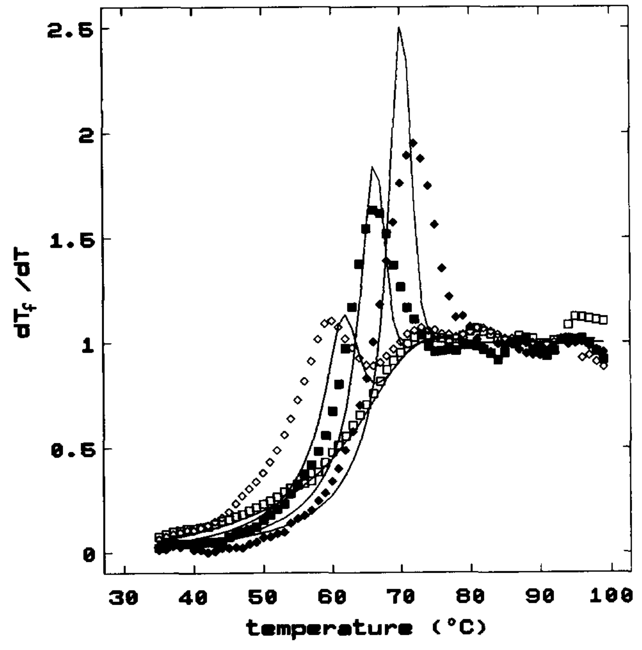

Figure 7 Derivative of the fictive temperature, dT_f/dT, in heating scans of sample 27 after several thermal histories: unaged (□); aged at $T_a=30°C$ (◇); aged at $T_a=40°C$ (■); aged at $T_a=50°C$ (◆). The full lines represent the thermograms predicted by the model

during the scan of the T_f, which characterizes the distance from equilibrium of the glassy state[25]. The T_f is calculated from:

$$\int_{T_f}^{T^*}(c_{pl}-c_{pg})dT=\int_{T}^{T^*}(c_{pe}-c_{pg})dT \qquad (1)$$

where T^* is a temperature high enough in the liquid state for the polymer to be in equilibrium, c_{pl} and c_{pg} are the specific heats in the liquid and glassy state, respectively, and c_{pe} is the experimentally measured specific heat during the scan[14,15]. From equation (1) one obtains:

$$\frac{dT_f}{dT}=\frac{(c_{pe}-c_{pg})(T)}{(c_{pl}-c_{pg})(T_f)} \qquad (2)$$

The derivative dT_f/dT can be considered a normalized specific heat, as in equilibrium $dT_f/dT=1$ [from $T_f(T)=T$] and in the glassy state $T_f(T)=\text{constant}$, and thus $dT_f/dT=0$.

The curves of specific heat in the glassy state were fitted to a straight line, $c_{pg}(T)=G_1+G_2T$. G_2 was determined as explained above, and G_1 was determined so as to make the model curve coincide with the first experimental value of each scan. $c_{pl}(T)$ was equally fitted to a straight line, L_1+L_2T, where now the parameters L_1 and L_2 were obtained from a least squares fit of the experimental points corresponding to the liquid state.

Figures 5, 6, 7 and *8* show the dT_f/dT curves of pure PEMA and of samples 12, 27 and 37 subjected to several thermal histories. In all cases the evolution of the ageing peaks with T_a is in accordance with results from the literature. The temperature of the peak increases with T_a; for lower T_as a small peak shows up in the intermediate zone of the transition, whereas for the higher T_as the peak overlaps the high temperature zone of the transition. The scatter of data on the high temperature part of the curves corresponding to higher nylon contents is due to the normalization leading to dT_f/dT: the small value of the transition Δc_p in these samples magnifies the occasional deviations in the normalized curves.

The results will be interpreted with the aid of the Adams–Gibbs–Vogel model[13]. It employs a structural relaxation function of the Kohlrausch–Williams–Watts type[26–28]:

$$\varphi(t,t_0)=\exp\left[-\left(\int_{t_0}^{t}\frac{dt'}{\tau}\right)^{\beta}\right] \qquad (3)$$

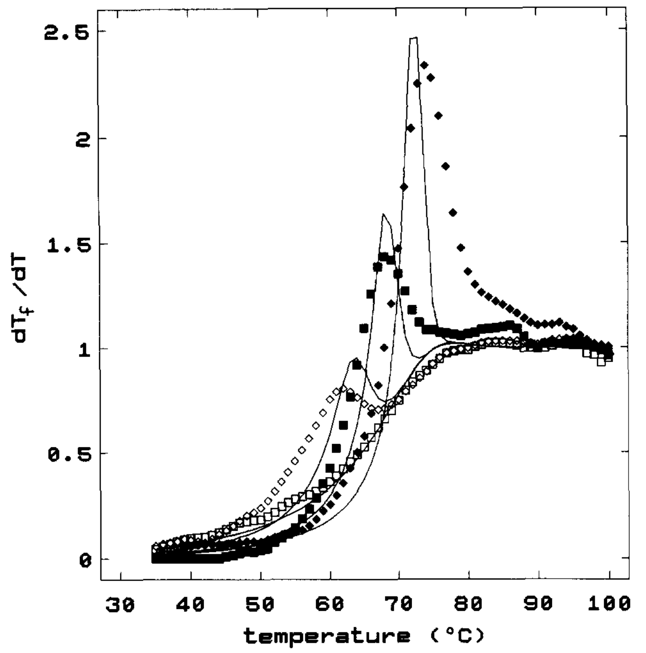

Figure 8 Derivative of the fictive temperature, dT_f/dT, in heating scans of sample 37 after several thermal histories: unaged (□); aged at $T_a = 30°C$ (◇); aged at $T_a = 40°C$ (■); aged at $T_a = 50°C$ (◆). The full lines represent the thermograms predicted by the model

where τ depends on T and T_f as given by:

$$\tau = A \exp\left[\frac{D}{RT(1 - T_2/T_f)}\right] \qquad (4)$$

which, at equilibrium, reduces to Vogel's equation[29]:

$$\tau^{eq} = A \exp\left(\frac{D/R}{T - T_2}\right) \qquad (5)$$

The model equation has four adjustable parameters. Three of them, A, T_2 and D, determine the dependence of the equilibrium relaxation times on temperature. The pre-exponential factor can be replaced by another parameter, T_R, defined[30–32] as the temperature at which the equilibrium relaxation time is 1 s:

$$T_R = T_2 + \frac{D/R}{\ln(1/A)} \qquad (6)$$

The fourth parameter, β, governs the breadth of the distribution of relaxation times.

The way of fitting the values of the four parameters to the experimental dT_f/dT curves by means of a least squares routine is explained in references 30–32. The strong correlation existing between D and T_2 led us to use a value of $D = 12.6\ \text{kJ mol}^{-1}$; this value allowed the best fit to the curves corresponding to the higher T_as.

For each sample and each ageing thermal history a set of best fitting parameters can be obtained, but then — as in other phenomenological models using four parameters[33,34] — the theoretical inconsistency occurs of having different sets of parameter values for a single sample. A self-consistent fit (a single set of parameters for all thermal histories of a single sample) has been determined in the present work by a simultaneous least squares fit of the four experimental scans of each sample. *Table 1* shows the values for the model parameters β, T_2 and T_R thus calculated, and in *Figures 5–8* the model predicted behaviour is superimposed on the experimental results.

DISCUSSION

The change of the glass transition of PEMA in the composite samples with respect to the transition of the pure polymer is of sufficient magnitude to suggest substantial changes in the mobility of the polymer chains when it acts as a matrix in the composite samples. These modifications may originate in a variety of circumstances: interactions at the PEMA–nylon interface, of mechanical or electrostatic nature, or even a different packing of the PEMA molecules when cast in the presence of the nylon phase in the process of preparing the samples may be the cause of different mobility of the chains of PEMA in the vicinity of nylon fibres.

The increment of specific heat in the transition observed on the composite samples diminishes more rapidly than does the amount of PEMA in the samples. That is, a fraction of the PEMA chains does not contribute to the transition as determined by the calorimetric technique. The literature records several cases of multiphase polymer systems in which a part of the disperse amorphous phase does not contribute to the glass transition[1], a fact attributed to the existence of a critical domain size under which the disperse amorphous phase would not be detected by d.s.c. In some incompatible blends as high a fraction as 40% of the sample does not contribute to the specific heat increments of the phases[35]. The same effect has been found in semicrystalline polymers such as polycarbonate and nylon 6, where the Δc_p found experimentally is lower than that expected for the amorphous fraction of material as determined by latent heats of fusion and other techniques[36,37]. Our nylon 6 is itself one such example: as already stated, the fibre does not exhibit any trace of a calorimetric glass transition, although its crystalline content does not exceed 45%. This suggests the presence of amorphous material in disperse intercrystalline domains.

In the case presented here of PEMA/nylon composites layers of PEMA closer to the nylon phase ('interphasic' PEMA) could be in a situation analogous to that described. From the experimental values of $\Delta c_p(T_g)$ the fraction of PEMA not contributing to the glass transition can be estimated:

$$z_{\text{inter}} = 1 - \phi - \frac{\Delta c_p(T_g)}{\Delta c_p^0(T_g)} \qquad (7)$$

with z_{inter} being the volume of PEMA not contributing to the transition per unit volume of composite ('interphasic' PEMA) and $\Delta c_p(T_g)$ and $\Delta c_p^0(T_g)$ being, respectively, the increments of specific heat in the transition in a composite sample and in pure PEMA. The thickness of the PEMA layer affected by the presence of the nylon phase can be estimated by dividing z_{inter} by the surface of nylon per unit volume of composite. The surface of nylon per unit volume of composite, σ, can be calculated from the volume fraction of nylon in the composite and the fibre diameter (in our case 29 μm).

Table 1 Values for the model parameters β, T_2 and T_R

Sample	β	T_2 (°C)	T_R (°C)
0	0.28	33.8	87.6
12	0.27	26.1	78.8
27	0.28	22.4	74.1
37	0.28	18.6	71.2

Table 2 Values of $\Delta c_p(T_g)$, z_{inter}, σ and $z_{\mathrm{inter}}/\sigma$ for samples with fibre fractions $\leqslant 0.59$

ϕ	0	0.12	0.27	0.37	0.59
$\Delta c_p(T_g)$ (J g^{-1} K^{-1})	0.28	0.167	0.161	0.134	0
z_{inter}	–	0.28	0.16	0.15	0.41
σ (cm^2 cm^{-3})	–	166	373	511	814
$z_{\mathrm{inter}}/\sigma$ (μm)	–	17	4	4	5

Table 2 gives the values for the samples with fibre fractions $\leqslant 0.59$. Sample 12 is an exception and has a thickness value of ~ 4 μm. This figure is considerably higher than that of the microdomains opaque to calorimetry referred to in the literature. Thus, rather than the formation of analogues to these domains, our case suggests the existence of a specific interaction of PEMA with nylon which modifies the properties of the former.

This influence of the presence of nylon on the properties of PEMA extends further than the layer close to the fibres; the shift of the temperature interval where the glass transition takes place towards lower values with increasing ϕ suggests that a great fraction of matrix, if not all of it, is affected. Any plasticizing effects of eventual traces of water or solvent must be discarded as being responsible for this shift: their permanence in the samples is highly improbable after the drying process, and they would have been revealed as peaks at temperatures from 80 to 100°C in the heating thermograms.

The displacement of the T_g reflects a change in the structural relaxation process which can be discussed with the aid of the model predictions. The model employed predicts correctly the temperature of the maxima of the ageing peaks for the pure PEMA sample, whereas in samples 27 and 37 the peaks predicted for the varying T_as are closer together than the experimental ones. This feature, a poorer prediction for the multicomponent system than for the pure components, has also been found in miscible[38] and immiscible[39] polymer blends.

It is further interesting to point out that the model correctly predicts the remarkable occurrence of sub-T_g ageing peaks[13,31,32,40–43] in the non-quenched samples of our study, even if the shape and position of these predicted peaks differ somewhat from the experimental ones.

From the characterization of the kinetics of the structural relaxation of our samples in terms of the AGV model, it follows that the decrease of the temperatures at which the transition takes place is due to a decrease of the equilibrium relaxation times — determined by the parameters T_R and T_2, whose values are shifted simultaneously (*Figure 2*) — without change of the form factor β of the relaxation times distribution. These values indicate, indeed, that the form of a plot of τ^{eq} *versus* T [recall equation (5)] is shifted towards lower temperatures as the nylon fraction increases without a change in the shape of the curve itself, as the difference $T_R - T_2$ remains practically constant. The value of the parameter β indicates no broadening of the distribution of relaxation times with an increase of nylon content. The overlapping of the relaxation of successive matrix layers, a mechanism which can cause the relaxation temperatures to shift, would probably lead to a widening of the temperature interval of the transition and of the distribution of relaxation times, and is thus incompatible with our findings. Rather than this hypothesis, some change in the microstructure of the whole matrix (probably arising from the interactions of the PEMA chains with nylon in the process of deposition from the solution) is suggested as being responsible for the different behaviour of PEMA as pure PEMA and as a matrix polymer in the composites studied here.

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