

Determining the role of interfacial transcrystallinity in composite materials by dynamic mechanical thermal analysis

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(Revised 19 February 1995)

The ability of this research group to obtain specimens of isolated transcrystalline layer by microtoming, reported in this paper for the first time, has opened a window for a range of characterization techniques. Here, the interfacial transcrystallinity in aramid fibre-reinforced nylon 66 microcomposites is studied using dynamic mechanical thermal analysis. The results show that the viscoelastic energy damping of the transcrystalline layer, $\tan \delta_{tc} = 0.064$, is smaller while the elastic modulus, $E'_{tc} = 4.6$ GPa, is higher compared with the crystallized matrix. Moreover, the magnitude of the energy damping by the transcrystalline layer could be used in a rule-of-mixtures expression to calculate the energy damping of an aramid fibre-reinforced nylon 66 microcomposite. It is also shown that the activation energy for relaxation, corresponding to the energy barrier for polymer chain movement, increases in the presence of reinforcement and transcrystallinity.

(Keywords: transcrystallinity; dynamic mechanical thermal analysis; nylon 66; aramid fibre; viscoelastic properties)

INTRODUCTION

Recently, the crystallization behaviour of nylon 66 in the presence of aramid fibre reinforcement was investigated under isothermal and non-isothermal conditions by both hot-stage microscopy and differential scanning calorimetry^{1,2}. A focal issue of that work was the finding that the fibres behaved as a giant nucleating site enhancing the rates of both nucleation and crystallization of the nylon matrix. In fact, it was observed that the high nucleation density along the fibre resulted in the growth of a thick and uniform transcrystalline (tc) layer on the fibre surface.

The presence of a thick interfacial layer, namely the tc layer, calls for an extension of the classical interfacial stress transfer models, because now they ought to consider, in addition to the level of bonding and the shear stress of a sharp interfacial boundary, the elastic properties of a thick interfacial layer.

An important role of the transcrystalline interface, as shown by our recent studies, is to diminish the processing-related residual thermal stresses that degrade the

performance of some composite materials. It has been claimed that such stresses, which result from differential shrinkage of the constituents upon cooling from the processing temperature, are highest for semicrystalline thermoplastic matrices, due to a large amount of crystallization-associated matrix shrinkage on top of the thermal strains³. Yet, our recent results suggested that in carbon fibre-reinforced poly(ether ether ketone) the presence of transcrystallinity improved the static strength by more than 20% and prolonged the fatigue life by more than three orders of magnitude^{4,5}. The explanation given proposed that the thermal stresses were relieved due to preferred orientation of the transcrystalline layer relative to the fibre, thereby conferring additional rigidity to the matrix in that direction⁴. Based on existing tc models, it was proposed that an effective preferred orientation would be that in which the *c*-axis of the crystallite (the polymer chain direction) was aligned parallel to the fibre direction^{6,7}.

The question of the effect of the tc layer on the mechanical performance of composites is not solved yet because of two main reasons. One is the absence of a reliable experimental technique for analysis of the transcrystalline structure. The other is the inability in most cases to isolate the contribution of the tc layer from that

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of the crystalline matrix when comparing with a control of amorphous matrix.

As we are gradually improving the capability in our laboratory to produce isolated tc specimens, we feel that both the question of the structure and the effect of the tc layer can be addressed and solved soon. The first example is given by this paper where the effect of the tc layer on the mechanical performance is evaluated by dynamic mechanical analysis (d.m.t.a.).

D.m.t.a. is one of the most important techniques used to evaluate the mechanical behaviour of composite materials. It is the most powerful method for studying structure-property relationships in that the damping behaviour of these materials is directly related to molecular structure⁸⁻¹¹ and interfacial interactions¹²⁻¹⁸. Estimation of the magnitude of the damping at the interfaces will, therefore, enable us to obtain information relating to the tc layer.

EXPERIMENTAL

Materials and processing

Pellets of nylon 66, obtained from Nilit, Israel, were used for the matrix. The polymer was characterized by the following weight- and number-average molecular weight values: $M_w = 32\,500$ and $M_n = 16\,800$, calculated from the intrinsic viscosity in formic acid and from end-group analysis, respectively. Single filaments of aramid Kevlar 29 (Du Pont) were used as reinforcement. The filaments were retrieved from 1000 filament, 1500 denier yarns with a proprietary rope processing finish (1500-1000-R 80-961). Two sets of samples were prepared for measurement via d.m.t.a., i.e. microcomposites and strip specimens microtomed from them.

Unidirectional microcomposites were produced by aligning single filaments accurately on a nylon film, using a special fibre micropositioning device to align the fibres¹⁹. The nylon films, and the microcomposites produced from them, were prepared by pressing, using a Carver press with minimal applied pressure. Kapton polyimide sheets (Du Pont) coated with respective layers of Freekote 44 and Freekote HMT release agents (Hysol) were placed between the nylon films and the press plates. Under these conditions, no surface transcrystallization was observed. Pressing was performed at 290°C for 16 min followed by either quenching in ice-water (quenched sample) or cooling at 2°C min⁻¹ to 250°C for a 3 h isothermal treatment, terminated by ice-water quenching (crystallized sample). Both thermal treatments resulted in the same degree of crystallinity of 39%².

The microcomposite sample contained 20 filaments positioned at an average centre-to-centre distance of 200 µm. The microcomposites used for the experiments were 140 µm thick and 3 mm wide, and the nominal volume fraction of fibres was 0.54%. The water content of the samples was 1.9% (determined by drying to constant weight in a vacuum oven at 80°C for 40 h).

Strip specimens of 100 µm width were cut from the microcomposite samples according to the scheme presented in Figure 1a, using a microtome (McIlwain Tissue Chopper, The Mickle Laboratory Engineering Co. Ltd, Surrey, UK). Selecting strips from the inter-fibre regions enabled us to get strips which contained two tc layers from two adjacent fibres. Figure 1b is a photomicrograph of a strip specimen containing two

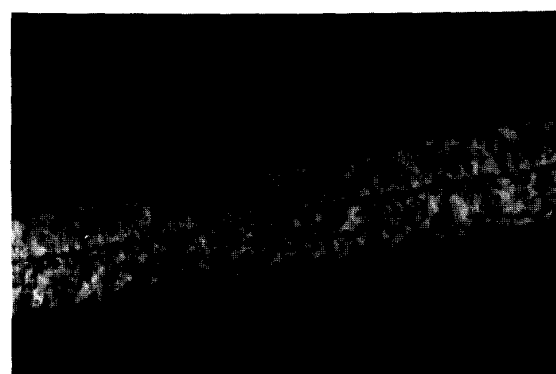
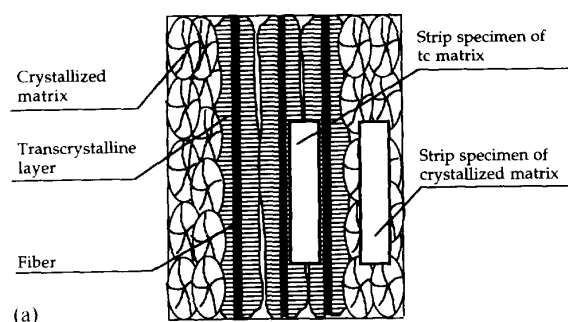


Figure 1 (a) Schematic description of how strip specimens were produced and (b) photomicrograph of a strip specimen containing a double transcrystalline layer ($\times 100$)

adjacent tc layers. On the basis of the cylindrical geometry of the 40 µm thick transcrystalline layer and the width and thickness of the strip, the nominal volume fraction of transcrystallinity in each strip specimen was around 36%. For comparison of the d.m.t.a. results, identical strips of crystallized and quenched matrix were also sliced, and used as controls.

Dynamic mechanical tests

Tensile dynamic mechanical tests were conducted under nitrogen using a dynamic mechanical thermal analyser (DMTA, model MKII, Polymer Laboratories Ltd, Loughborough, UK). The microcomposites were tested at a frequency of 1 Hz in a temperature range of -150 to 250°C, at a heating rate of 3°C min⁻¹ and under a constant tensile load of 1 N. For the strip samples, due to their small dimensions, a frequency of 5 Hz and a constant tensile load of 0.1 N were applied. The activation energy evaluation tests were performed at various frequencies (0.3, 1, 3, 10, 20 and 30 Hz) in a temperature range of 0-150°C and at a heating rate of 1°C min⁻¹. The specimen clamping procedure followed exactly that recommended in the Operators' Manual, to ensure optimum clamping pressure. That procedure resulted in a clamping torque of 40 and 20 cN m for the microcomposite and strip specimens, respectively.

The d.m.t.a. equipment used here is designated for testing of single fibres too, and so its precision is sufficient for microcomposites and strip specimens. The results of the microcomposites and strips presented here are an average of two and three runs, respectively. It was found that the errors in the location and magnitude of

the glass transition temperature signal were $\pm 1^\circ\text{C}$ and $\pm 3\%$, respectively. Also, the DMTA software could produce smoothed experimental traces and exact values such as those of *Tables 1* and *2*.

RESULTS AND DISCUSSION

Energy damping

Energy damping in viscoelastic polymers results from inelastic movement of molecular chain segments in the amorphous regions, whereby the applied elastic energy is dissipated as heat. In a transition region, where the free volume reaches a critical level, the damping peaks to a high value due to the initiation of molecular motion. The α -damping peak, corresponding to the glass transition temperature, T_g , is of greater magnitude than the damping peaks at lower temperatures. This transition is concerned with a diffusional motion of main-chain segments in the non-crystalline regions, under the structural restraint of the neighbouring molecular chains in the crystalline regions. The β -transition and, in some cases, the γ -transition, appear below the α -peak, and reflect secondary transitions.

The mechanical relaxation behaviour of polyamides has been studied extensively²⁰⁻²². The origin of the α -transition peak is believed to result from rupture of hydrogen bonds between polymeric chains, which give rise to the motion of long-chain segments in the amorphous region. The origin of the β -transition is attributed to segmental motion that involves amide groups in the amorphous region, which are not hydrogen bonded to other amides on a nearby chain. The γ -transition is thought to be associated with the small-scale reorientational motion in the amorphous region of the methylene units between the amide group²⁰.

The experimental results, presented in *Figures 2* and *3a* and *b*, showed that isothermal crystallization and/or the addition of fibres reduced the absolute measured values of the loss tangent at all temperatures when compared with the quenched and/or unfilled matrix, in agreement with ref. 20. Correspondingly, the α -transition parameters exhibited significant sensitivity to the morphological differences as shown in *Table 1*, which summarizes the data of the α -transition. The α -peak temperature, which refers to the T_g , is shifted to a higher temperature in the crystallized material. The shift is by 7.7 and 4.1°C for the neat matrix and the microcom-

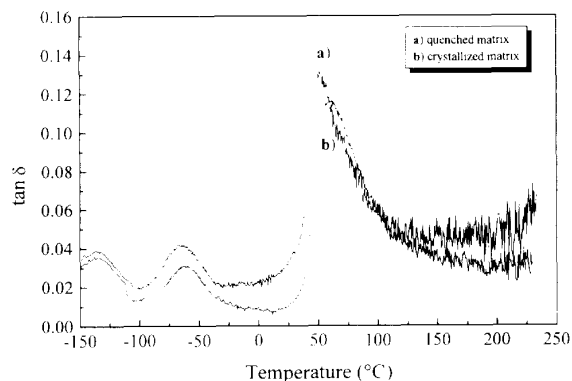


Figure 2 Loss tangent curves of quenched and crystallized nylon 66 matrices

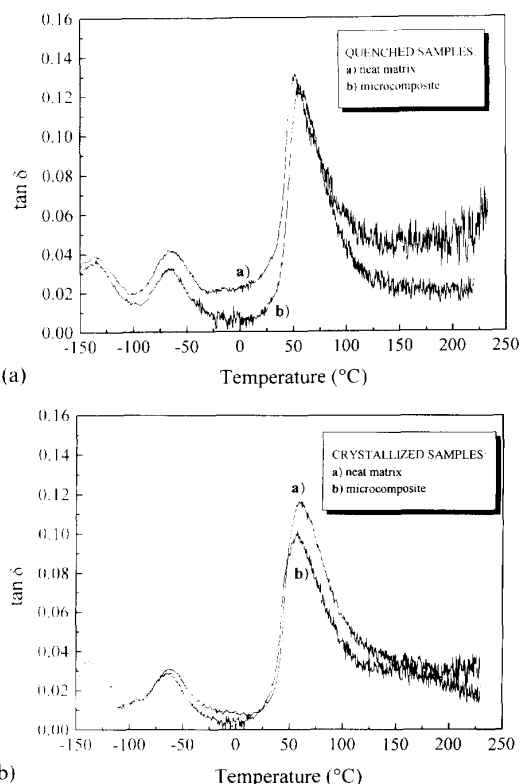


Figure 3 Loss tangent curves of nylon 66 and microcomposite specimens: (a) quenched samples; (b) crystallized samples

posites, respectively. It is pointed out that the morphological difference between the quenched and crystallized materials (which had equal degrees of crystallinity) amounted to a crystal size difference, whereby quenching resulted in a relatively large number of small crystallites². Evidently, larger crystallites lead to reduced mobility of the molecular chains in the amorphous phase.

As mentioned before, the magnitude of the damping peaks is a useful tool for obtaining information about the molecular structure of the material. The amplitude of the α -peak is a measure of the viscoelastic nature and must therefore be expected to reflect factors such as crystallinity and the presence of the fibres, which restrain segmental mobility. It is seen in *Figure 2*, which compares the d.m.t.a. traces of the neat matrix, that the magnitude of the α -peak in the quenched sample is higher than in the crystallized sample. These results sustain the claim that the smaller, imperfect spherulites of the quenched polymer impose lower restraints than the more perfect, larger spherulites of the crystallized one. A similar behaviour has been observed in other studies with a variety of polymers, e.g. nylon 66, nylon 6^{20,21}, poly(ethylene terephthalate) (PET)^{23,24} and polyethylene²⁵. The damping peaks were, also, found to be affected by the morphology^{10,26}.

Because the fibres act in a similar way to crystallinity, i.e. to increase the constraint, they would be expected consequently to raise T_g and to lower the energy damping. *Figures 3a* and *b* show that the amplitude of the loss tangent in microcomposites is smaller than in the corresponding neat polymers, implying that the fibre imposes an additional restriction on the movement of

Table 1 D.m.t.a. data from quenched and crystallized nylon 66 matrices and their microcomposites

Material	Temperature at α -peak ($^{\circ}\text{C}$)	Exptl $\tan \delta$ at α -peak	Calc. $\tan \delta$ at α -peak	ΔE (kcal mol $^{-1}$)
Quenched matrix	51.2	0.1318	-	81.68
Crystallized matrix	58.9	0.1169	-	91.00
Quenched microcomposite	53.2	0.1243	0.1311	92.43
Crystallized microcomposite	57.3	0.1018	0.1163	107.24

polymer chains. It is expected that the effect of the fibre will depend on the fibre-matrix bond strength because strong bonding is essential to activation of the fibre restraint through the stress transfer mechanism at the interface, whereas poor bonding results in energy dissipation at the interface^{14,18,20,27}. However, the effect of the fibres on the glass transition temperature is ambiguous, and it can be seen in *Table 1* that the T_g of the quenched nylon is raised by addition of fibres while that of the crystallized samples is lowered. This conflicting behaviour is evident in the scientific literature, occasionally by the same authors, and can be attributed to the fact that the addition of fibres has a concomitant effect on the degree of crystallinity. For example, the addition of unsized Kevlar 49 fibres to PET elevated T_g by almost 4°C , while in the presence of sized fibres T_g and the degree of crystallinity were depressed significantly, which was attributed to the possibility that the sizing formulation could act as a plasticizing agent for the PET²⁸. The same authors later claimed that, in contrast with the results obtained in their previous study, where fibre reinforcement produced a depression in the degree of crystallinity (and T_g), no effect on the ultimate degree of crystallinity was observed²⁹. Thus, the values in *Table 1* probably do not reflect the net influence of the fibres on T_g , because the sized fibres might have produced concomitant changes in the degree of crystallinity.

The damping term of a composite, $\tan \delta_c$, can be estimated by using the rule of mixtures, as suggested by Nielson³⁰, who claimed that for reinforcement of low damping $\tan \delta_c$ is given simply by the proportional contribution of the matrix according to its relative content:

$$\tan \delta_c = (1 - V_f) \tan \delta_m \quad (1)$$

where V_f is the volume fraction of the reinforcement and the subscripts c and m refer to the composite and matrix, respectively. *Table 1* presents the $\tan \delta_c$ values for both the quenched and crystallized microcomposites. The calculations are based on the respective $\tan \delta_m$ of *Table 1* and on a value of $V_f = 0.54\%$. It is seen that the experimental values for the quenched and crystallized microcomposites are 5.5 and 12.5%, respectively, lower than the prediction. In the absence of a significant change in the degree of crystallinity with the addition of fibres, this deviation could be attributed to an additional restraining effect imposed by the fibre, possibly the tc layer whose effect is demonstrated below.

The effect of the tc layer on the damping characteristics is expected to result from the fact that its crystalline structure is more ordered and oriented. Hence, its presence is expected to result in further restriction of molecular chain movement. In fact, the application of equation (1) to predict the $\tan \delta$ values of a variety of short

and continuous fibre-reinforced polymers has resulted in overestimations^{20,31}, and it was concluded that the presence of the reinforcement led to a greater reduction in $\tan \delta_c$ than would be expected from simple consideration of volume fraction due to a 'shell' of material around the fibre, possessing modified properties that restrict molecular motion²⁰. Similarly, it has been claimed that equation (1) does not take into account the changes in matrix stiffness within the interphase due to chemical modification of the structure in epoxies^{15,17} and due to transcrystallinity in thermoplastics³². Hence, in our case, it is proposed that equation (1) will be modified to account for the presence of transcrystallinity by including an additional term as follows:

$$\tan \delta_c = (1 - V_f - V_{tc}) \tan \delta_m + V_{tc} \tan \delta_{tc} \quad (2)$$

where $\tan \delta_{tc}$ is the damping and V_{tc} is the volume fraction of the tc layer. Assuming that the fibres of radius r are coated by a constant and uniform coaxial tc layer of thickness t , and for a given fibre volume fraction V_f , it can be easily shown that:

$$V_{tc} = V_f (2rt + t^2)/r^2 \quad (3)$$

A unique achievement of the experimental work here was the ability to obtain, by microtoming, strip specimens which comprised a relatively high proportion of transcrystallinity (36%), and to use them for d.m.t.a. testing (*Figure 1*). Because the dimensions of the tc specimens were different from those of the original specimens reported in *Table 1*, the tc strip specimens were tested with two new sets of microtomed strips of similar dimensions of quenched and crystallized neat polymer. The noise with the strip specimens was higher than with the microcomposites, therefore the d.m.t.a. software was used to smooth the experimental traces. The results are presented in *Figure 4* and *Table 2*, and it is apparent that the differences between the three samples are much higher than the experimental error. The anticipated additional restraint of the tc layer is evident from the lower $\tan \delta$ of the tc specimen. Taking the volume fraction of transcrystallinity in the tc specimen to be 36% of the crystallized matrix, and applying the rule of mixtures (as expressed by equation (2) for $V_f = 0$), it is possible to calculate that for 100% transcrystallinity $\tan \delta_{tc} = 0.064$. If this value is used with the experimental value of $t = 30 \mu\text{m}$ in the combined equations (2) and (3), it will result in $\tan \delta = 0.1062$, which is in good agreement with the experimental value of 0.1018 given in *Table 1*.

Modulus characteristics

Figures 5a and *b* present the storage modulus, E' , as a function of temperature for the two specimen sets. As expected, the stiffness (expressed by E') was affected

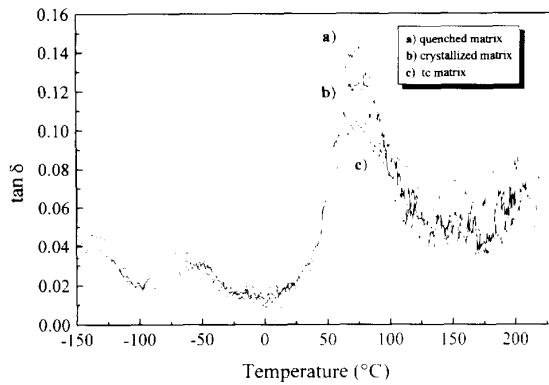


Figure 4 Loss tangent curves for strip specimens of quenched, crystallized and tc matrices

Table 2 Experimental values of loss tangent of strip specimens

Material	Tan δ
Quenched matrix	0.1418
Crystallized matrix	0.1270
Tc matrix	0.1041

by the same factors that affected the energy damping. Thus, the same factors that restricted movement of the molecular chains, i.e. crystallinity, reinforcement and transcrystallinity, increased the elastic modulus. Accordingly, it is seen that the crystallized material exhibits a higher modulus than the quenched, and those of the microcomposites are higher still. For example, at 25°C the storage moduli are 2125, 2750, 3075 and 3250 MPa for the quenched and crystallized neat polymer and microcomposites, respectively. Similar thermal treatment and reinforcement effects have been reported in the literature for other systems^{10,15,20,27}.

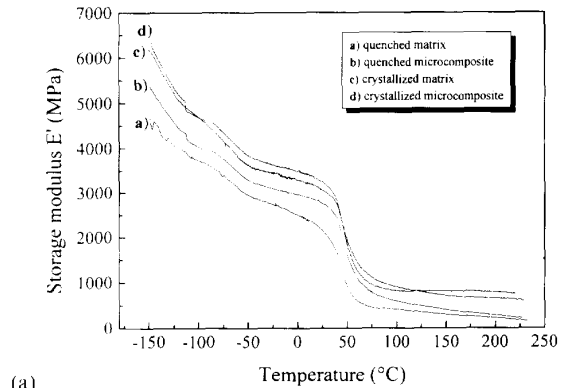
The results of the strip specimens in Figure 5b emphasize the prominent effect of transcrystallinity. At 25°C the storage modulus of the tc sample (with $V_{ic} = 0.36$) was 3255 MPa compared with 2480 and 2250 MPa for the crystallized and quenched samples, respectively. Applying the rule-of-mixtures approach to the storage modulus at 25°C (by analogy to the procedure for the loss tangent above), a value of $E'_{ic} = 4633$ MPa for 100% transcrystallinity is obtained. This implies that the stiffness in the fibre direction of the transcrystalline layer is double that of the bulk crystallized matrix.

Frequency dependence

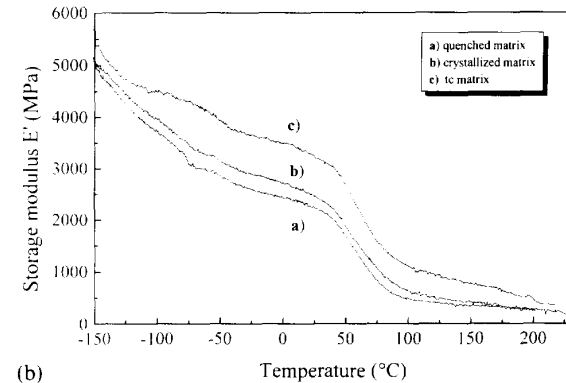
Because of the time-temperature equivalence in viscoelastic materials, the dynamic mechanical behaviour may be tested against frequency as well as against temperature, whereby the effect of longer time (lower frequency) is equivalent to that of higher temperature. Thus, the main tan δ peak, T_g , of the d.m.t.a. test will be shifted to a lower temperature as the frequency is increased^{23,24,33,34}. The frequency-temperature dependence is usually expressed by an Arrhenius-type equation, as follows:

$$\omega = A \exp(-\Delta E/RT) \tag{4}$$

where ΔE is the activation energy for relaxation, corre-



(a)



(b)

Figure 5 Storage modulus versus temperature for: (a) quenched and crystallized nylon 66 and microcomposite specimens; (b) strip specimens of quenched, crystallized and tc matrices

sponding to the energy barrier for polymer chain movement from one lattice site to another.

Figure 6 presents the Arrhenius plots whose slopes produced the activation energy results that are presented in Table 1. The activation energies reported in Table 1 are in agreement with the literature, where Woodward *et al.*²¹ reported values of 73, 21 and 21 kcal mol⁻¹ for α-, β- and γ-transitions, respectively, and Quistwater and Dunell³⁵ reported activation energies from 60 to 80 kcal mol⁻¹ for the α-transition. For comparison, the activation energies reported for other polymers are 191 kcal mol⁻¹ for polycarbonate³⁴, 80–250 kcal mol⁻¹ for poly(methyl methacrylate)^{34,36} and 180 kcal mol⁻¹ for poly(vinyl chloride)³⁴.

The trend of the activation energy values in Table 1 corroborates the conclusions stated above on the role of crystallinity and reinforcement. It is apparent that ΔE is increased by the same order as E' in Figure 5a, implying that stiffness and restriction of movement are linked to higher activation energies. The activation energy value of the crystallized microcomposite is significantly higher than that of the others, which might be attributed to the presence of a tc layer in the crystallized microcomposites.

SUMMARY

The transcrystalline layer which forms on the fibre surface in aramid fibre-reinforced nylon 66 is an additional source for stiffness and restriction of polymer

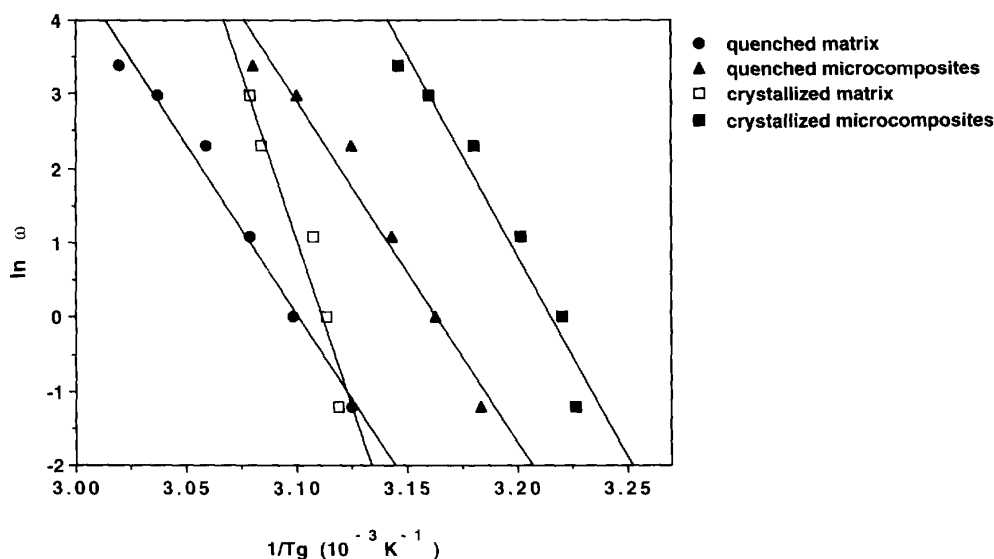


Figure 6 Arrhenius plots for quenched and crystallized nylon 66 and microcomposite specimens. The slopes represent the values of activation energy for relaxation

chain mobility, to the common factors of crystallinity and reinforcement. This is reflected in the very low viscoelastic energy damping in the reinforcement direction. The total energy damping of the composite is given by a rule of mixtures which sums the proportional contributions of the crystalline matrix and the tc layer. The reduced energy damping and increased dynamic modulus induced by the tc layer reflect calculated values of $\tan \delta_{tc} = 0.064$ and $E'_{tc} = 4.6$ GPa for 100% transcrystallinity, which are half and double the respective properties of the crystallized matrix.

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