

Relaxation processes in polyethylene fibre-reinforced polyethylene composites

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Abstract

The dynamic mechanical properties of filament-wound composites comprising ultrahigh-molecular-weight polyethylene (UHMWPE) extended-chain fibres in matrices of linear low-density polyethylene (LDPE), high-density polyethylene (HDPE), and thermally treated HDPE have been studied in tensile mode over a wide frequency range. The study focused on the additional effects of the fibres, for three winding angles of 26°, 34° and 45°, on the dynamic properties of the polyethylene-fibre-reinforced polyethylene composites. These effects were expected to result from transcrystallinity, which is induced in the matrix and which may invade a significant proportion of the composites, and from the extra restraint imposed by the reinforcement. The effects of the fibres are expressed by the real and imaginary moduli and the loss tangent and are analysed in terms of frequency dependence and activation energies for the α , β and γ transition processes. The effects of the fibres and of the crystallinity are evident in significantly higher moduli and activation energies of the relaxation processes. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Relaxation processes in polyethylene (PE) have been studied extensively for two main reasons. The first pertains to the fact that PE is a broadly used polymer in a wide range of applications, for which a knowledge of the relaxation and phase transition temperatures is essential for establishing processing technologies and predicting performance and durability. The second reason is that PE can represent highly crystalline polymers and — because of its ready availability in different forms — is very useful in studies of the effects of the degree of crystallinity and molecular branching.

Because PE has been widely studied, the scientific literature contains extensive information on its relaxation transitions measured by different techniques such as dynamic mechanical or dielectric thermal analysis, by which transitions are detected through the temperature dependence of the loss tangent ($\tan \delta$) or the loss modulus (E''). Most of the information is included in a

number of primers such as [1,2], which summarize and discuss relaxation phenomena in polymers. A thorough discussion of the subject can be found in [3], where, from a comparison of high- and low-density PE (HDPE and LDPE, respectively) four main transitions are identified and related to molecular processes either in the amorphous or the crystalline phase. It is generally accepted that the γ relaxation at around -120°C occurs in the amorphous phase and is associated with the glass transition. The β relaxation below 0°C is attributed to motion of very loose folds and relatively non-extended tie chains and is, therefore, more marked in LDPE. The α relaxation in the temperature range from 50 to 120°C is associated with an interlamellar shear process and is often separated into two processes (α and α') with different activation energies, probably as a consequence of inhomogeneous crystallinity of the specimen.

A special aspect of relaxation transitions in polyethylene is presented in this study dealing with single-polymer composites, in which both the matrix and the fibres consist of polyethylene. All-polyethylene (PE/PE) composites were first prepared in 1975 by Capiati and Porter [4] who practically extended the definition of composite materials to include physical heterogeneity,

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namely, different morphologies of chemically identical constituents. That concept was then adopted by others who expanded the studies both with continuous [5,6] and short-fibre-reinforced composites [7]. This group's research on PE/PE composites, carried out in the last few years, consisted of a range of studies of particular properties and characteristics. The first study determined the manufacturing conditions for PE/PE composites in which fibre relaxation was avoided despite the high temperature required to melt the matrix [8]. That was followed by an investigation of transcrystallinity and its effects on the mechanical properties [9] and by X-ray diffraction investigations of the crystallography of bulk crystallinity and transcrystallinity [10], discovering epitaxial nucleation and lamellar twisting in transcrystalline PE. The processing of PE composites reinforced with chopped PE fibres was studied to examine the feasibility of an alternative route to molecular composites [11]. Finally, the fatigue behaviour of flat filament-wound PE composites was investigated as a function of the winding angle [12].

This work attempts to focus on the additional effects due to the fibres while using as background the literature information on relaxation transitions in polyethylene. The additional effects stem from transcrystallinity, which is induced in the matrix and which may invade a significant proportion of the composite [9,10,13–15], and from the extra restraint imposed by the reinforcement, expected to depend on composites structural parameters such as the volume fraction and reinforcement angle.

2. Experimental

2.1. Materials

The composites were made of Spectra 1000 UHMWPE fibres (Allied Signal) and of either one of the following two 30 μm thick polyethylene films, namely, LDPE from Ganigar Plastics (Israel) and HDPE from Plastnir (Israel). Filament winding was performed with a bench winder (Burlington Instruments Co., Vermont) [12]. A flat mandrel (5 mm wide, 1 mm thick and 150 mm long) was wrapped by a matrix film onto which the fibre was wound and then wrapped again by a matrix film. The resulting preform was removed from the mandrel and pressed (Carver Laboratory Press) at either 120 or 137°C with LDPE and HDPE, respectively, under 15 MPa for 1 h, followed by ice-water quenching. Thermal treatment of HDPE specimens (HDPE-tt) was carried out in the press by cooling at 2°C/min from 137 to 123°C, at which temperature the specimens were maintained for 1 h and thereafter cooled slowly to room temperature. Specimens of three winding angles (the angle between

the fibres direction and the mandrel axis) of 26°, 34° and 45° were produced at a fibre weight fraction of about 0.80. The final strips were on average 9 mm wide and 0.9 mm thick. For a schematic presentation of the composite strips see [12].

2.2. Testing

Tensile dynamic mechanical tests were conducted by a dynamic mechanical thermal analyzer (DMTA, model MKII, by Polymer Laboratories Ltd, Loughborough, UK). All samples were tested at various frequencies (0.3, 1, 3, 10, 30, 50 Hz), in a temperature range from –150 to 150°C, at a heating rate of 0.4°C/min, under a constant tensile load of 4 N and a peak-to-peak displacement of 32 μm . The specimen gauge length was about 15 mm. Specimen clamping followed exactly the recommended procedure in the Operators' Manual to ensure optimum clamping pressure. That procedure resulted in a clamping torque of 40 cNm.

The DMTA equipment used here is also designated for the testing of single fibres, and so its precision is sufficient for both matrix and composites specimens. The results presented here are an average of two or three runs. It was found that the error in the location and magnitude of the transition temperatures signal was of about $\pm 1^\circ\text{C}$ and about $\pm 5\%$, respectively.

3. Results and discussion

3.1. Effects of temperature and frequency on relaxation transitions

Because this work is concerned with the influence of the PE fibre its dynamic behaviour is discussed first. Fig. 1a presents plots of E' and E'' against temperature for a single PE fibre, showing significant α and γ peaks as well as a small β peak. Fig. 1b characterizes the behaviour of the fibre by plotting its loss tangent and displacement as a function of temperature. It is seen that the loss tangent is less distinctive than E'' with regard to the transition processes, and that the displacement exhibits a typical negative thermal expansivity up to room temperature [8]. Dynamic mechanical behaviour of LDPE, HDPE, and HDPE-tt matrices is reported in Fig. 2a–c. Despite its extended chain configuration and its significantly higher degree of crystallinity, the general picture for the fibre is very similar to that of the HDPE matrix, as seen in Fig. 2b, while in contrast, that of the LDPE matrix is distinguished by significant α and β peaks as well as a small γ one (see Fig. 2a). The effect of the thermal treatment on the pure HDPE matrix is illustrated in Fig. 2c, showing a similar trend as the original HDPE, however, with higher E' and E'' values, and perhaps a slightly higher β peak.

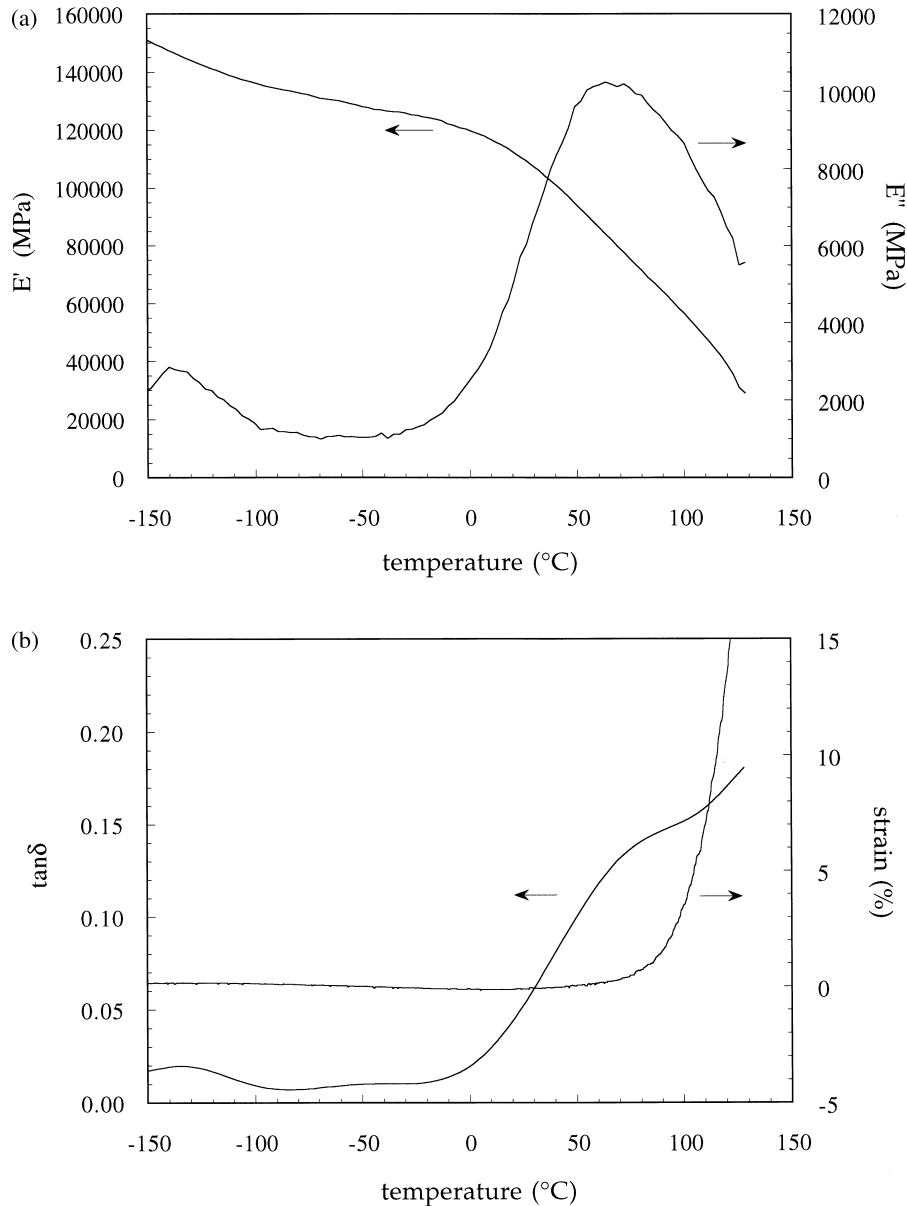


Fig. 1. Dynamic mechanical response at a frequency of 1 Hz for a single UHMWPE Spectra 1000 fibre as a function of temperature: (a) storage and loss moduli, (b) loss tangent and strain.

The behaviour of the composite materials is expected to reflect a superposition of those of the constituents, so that any deviation could be assigned to one of the anticipated effects of the fibres. Fig. 3a–c presents plots of E' and E'' against temperature for the composites obtained with LDPE, HDPE and HDPE-tt matrices, respectively. Data of Fig. 3a–c refer to composites with a winding angle of 26° , being the results representative of the other composites also, of 34° and 45° angles (the effect of the winding angle is discussed below). Comparing, for example, the plots in Fig. 1a and Fig. 2a with those in Fig. 3a shows that the results of the composites indeed reflect a superposition of those of the constituents. Yet, on the basis of the results in Fig. 3a–c

two specific observations can be made, namely, the thermal treatment increases the magnitude of the β peak significantly and the frequency dependence of E'' is inverted from the γ to α peak. It can also be generally stated that the effect of the fibre in the composite is similar to that of increasing the degree of crystallinity in the pure matrix.

Because of the time-temperature equivalence in viscoelastic materials, the dynamic mechanical behaviour may be tested against frequency as well as against temperature, when the effect of longer time (lower frequency) is equivalent to that of higher temperature. Thus, the γ peak, T_g , of the DMTA test will be shifted to a lower temperature as the frequency is decreased (see

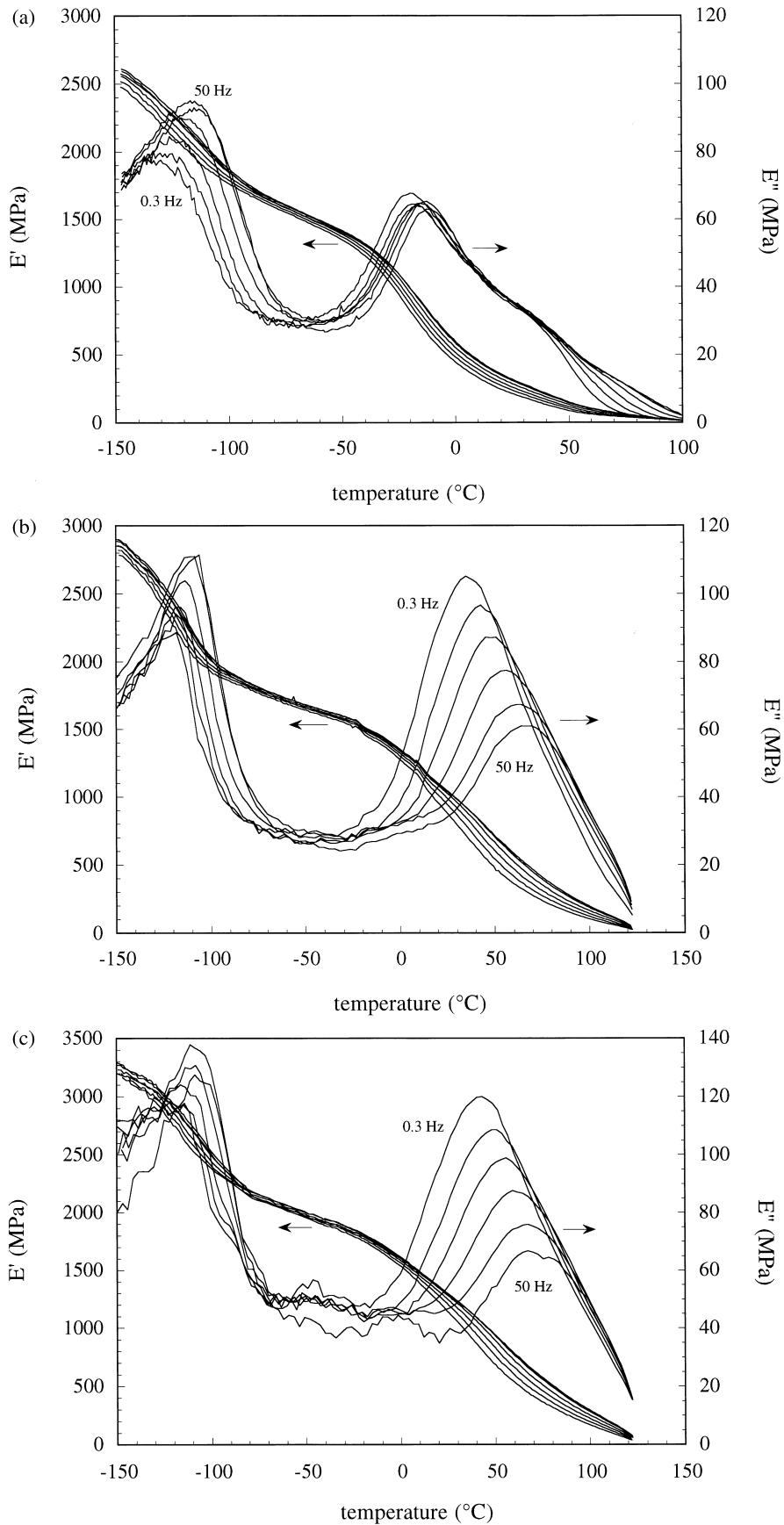


Fig. 2. Tensile storage and loss moduli as a function of temperature at various frequencies for (a) LDPE, (b) HDPE, and (c) thermally treated HDPE.

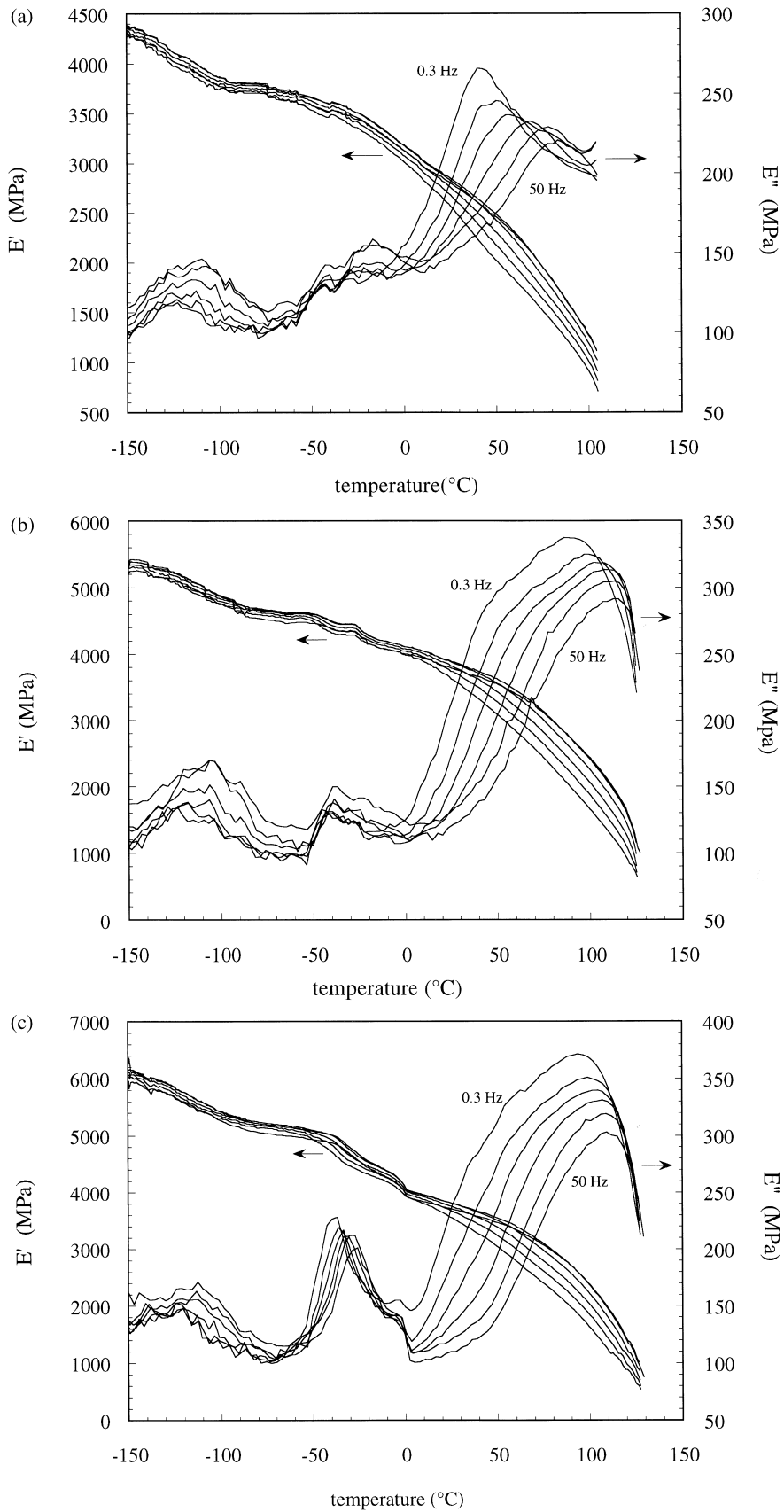


Fig. 3. Tensile storage and loss moduli as a function of temperature at various frequencies for composites with UHMWPE fibres wound at a winding angle of 26° in (a) LDPE, (b) HDPE, and (c) thermally treated HDPE matrices.

for example [1]). The frequency-temperature dependence is usually expressed by an Arrhenius type equation, as follows:

$$v = A \exp\left(\frac{-\Delta E}{RT}\right) \quad (1)$$

where ΔE is the activation energy for relaxation, corresponding to the energy barrier for polymer chain movement from one location to another.

Fig. 4 presents examples of Arrhenius plots for the α and γ transitions, from the slopes of which the activation energy values presented in Table 1 were obtained. It is seen that the activation energies of the γ transition are approximately half those of the α transition values, indicating different processes. In general the activation energies reported in Table 1 are comparable to the literature values for various polyethylenes as reviewed in [1]. Because the activation energies relate to specific molecular motion processes both their absolute values and their relative magnitude are typical of each polymer. For example, for Nylon-66 activation energies of 306, 80 and 88 kJ/mol for α , β and γ transitions,

respectively have been reported [16] (it is noted — for comparison with PE — that in Nylon-66 the glass transition is the α relaxation).

For both the α and γ transitions a significant decrease in the activation energy either with decreasing crystallinity of the matrix or with increasing winding angle is apparent in Table 1. Evidently, this observation is consistent with the restraint level, as both factors represent various forms of restraint of segmental chain mobility, either by the reinforcing fibres or by the crystalline phase.

3.2. The magnitude of E' and E''

So far E' and E'' have been discussed in the context of their temperature dependence, expressing the various relaxation processes, and reflecting frequency, angle of reinforcement and degree of crystallinity effects. Next, the magnitude of these properties is examined, first of E' and then of E'' . As expected, the results in Fig. 2a–c show that the storage modulus, E' , exhibits a steady increase with matrix crystallinity with room temperature values at a frequency of 1 Hz of 240, 940 and 1200 MPa, for LDPE, HDPE and HDPE-tt matrices,

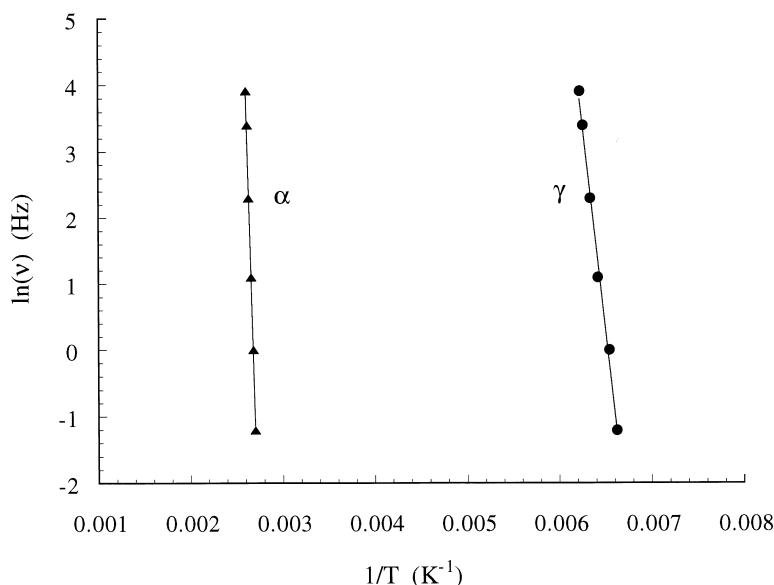


Fig. 4. Arrhenius plot for the activation energy evaluation for the (▲) α and (●) γ relaxation processes in a composite with UHMWPE fibres wound at a winding angle of 26° in a thermally treated HDPE matrix.

Table 1
Activation energies for the α , β , and γ transitions of pure matrices and composites at various winding angles (w.a.)

	α Transition ΔE (kJ/mol)			β Transition ΔE (kJ/mol)			γ Transition ΔE (kJ/mol)		
	LDPE	HDPE	HDPE-tt	LDPE	HDPE	HDPE-tt	LDPE	HDPE	HDPE-tt
Matrix	139.6	137.2	169.1	352.2	—	—	46.2	73.1	123.8
Composite w.a. = 26°	151.8	327.7	434.5	138.4	318.3	217.7	66.1	77.8	105.6
Composite w.a. = 34°	139.3	197.4	410.4	185.9	150.3	365.9	59.9	61.4	81.3
Composite w.a. = 45°	96.6	159.3	393.4	154.1	134.9	161.2	55.1	58.5	76.2

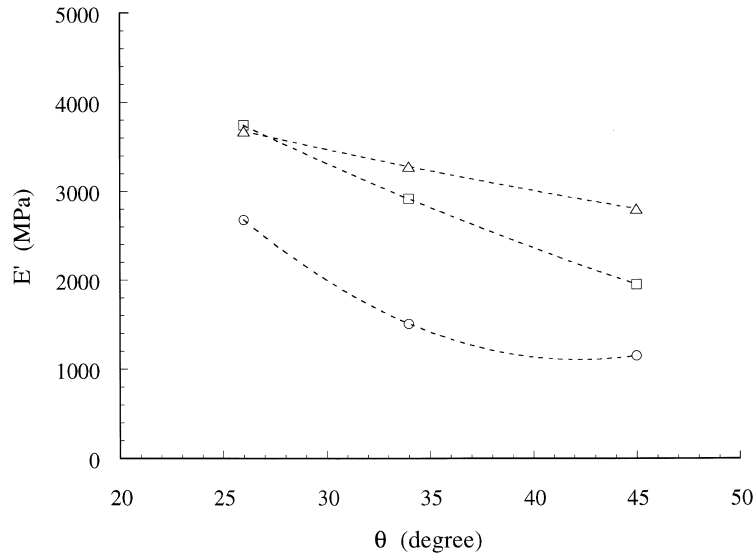


Fig. 5. Storage modulus (at 25°C and frequency of 1 Hz) as a function of the winding angle for composites with (○) LDPE, (□) HDPE, and (△) thermally treated HDPE matrices.

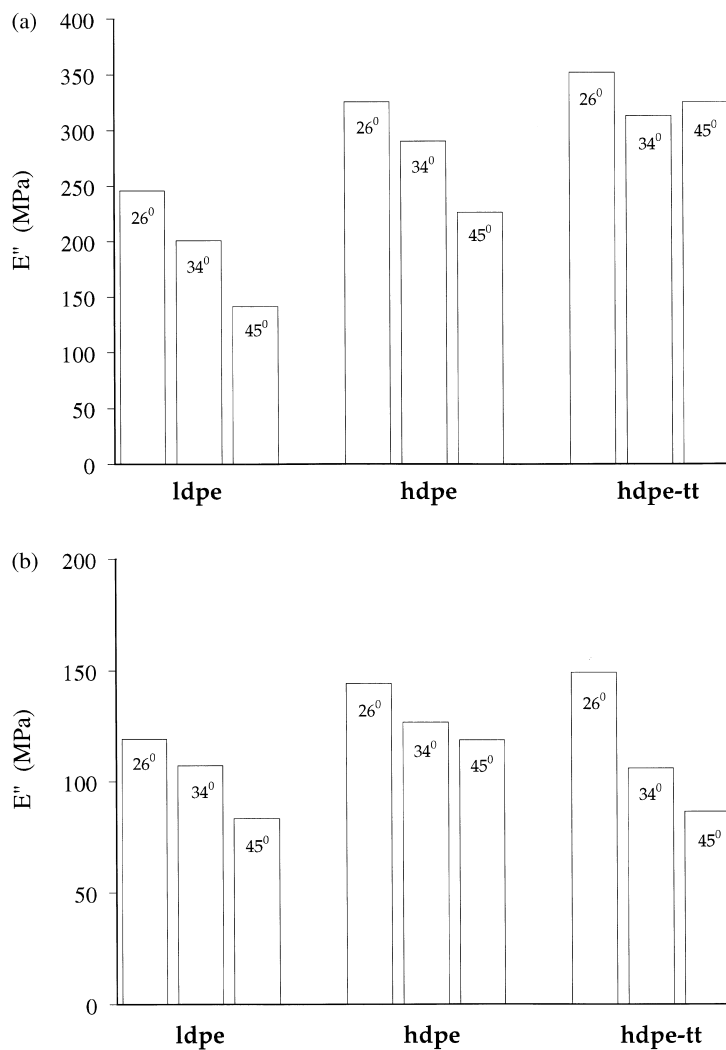


Fig. 6. Loss modulus peak values evaluated for the composites under investigation in correspondence of the (a) α , and (b) γ transitions.

respectively. Also, the trend of E' with winding angle qualitatively fits the laminate theory prediction of the variation of engineering constants of orthotropic lamina (see for example [17]), as exemplified in Fig. 5, showing a monotonic decrease with angle of reinforcement. E' values for HDPE composites are in quite good agreement with previously reported elastic-modulus data obtained by static tensile mechanical testing [12]. As illustrated in Fig. 5, the effect of the thermal treatment on the composite storage modulus is increasingly pronounced as the winding angle increases.

By contrast with E' , the imaginary component, E'' , expresses the viscoelastic nature of the transitions and, therefore, it depends on whether a relaxation transition occurs in the crystalline or amorphous phase.

Correspondingly, the effect of the degree of crystallinity of the polymer on E'' will depend on the transition type. Fig. 6a–b presents bar charts of E'' as a function of the polymer type and the winding angle for the α and γ transitions. It is seen that both for the α and γ transitions, the behaviour of E'' as a function of the winding angle follows the trend of E' . Evidently, for E'' at the α transition, which is associated with an interlamellar shear process in the crystalline phase, a clear increasing trend with the degree of crystallinity is apparent, while for the γ transition, which is associated with the glass transition in the amorphous phase, the trend with the degree of crystallinity is not consistent.

The difference between the α and γ transitions is also expressed by the frequency dependence of E'' . As

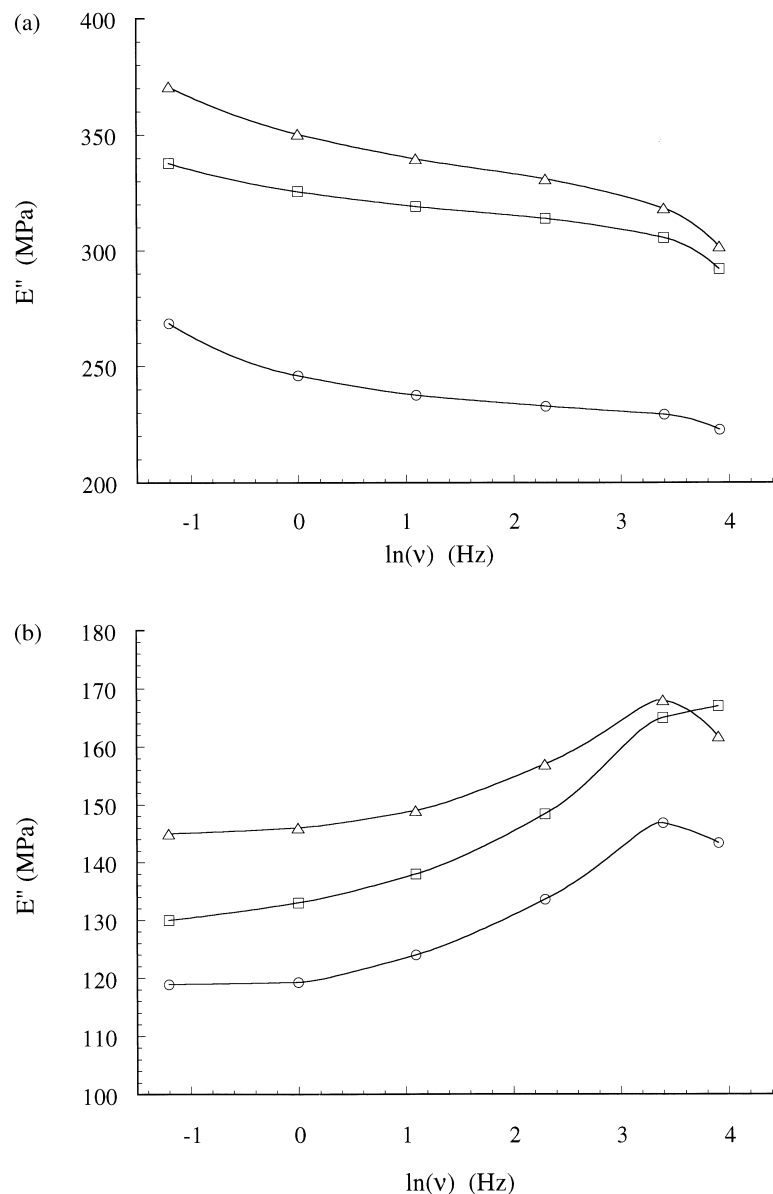


Fig. 7. Frequency dependence of the loss modulus peak values in correspondence of the (a) α , and (b) γ transitions evaluated for composites with UHMWPE fibres wound at a winding angle of 26° in (○) LDPE, (□) HDPE, and (△) thermally treated HDPE matrices.

demonstrated in Fig. 7a–b for composites with a winding angle of 26° , whereas at the γ transition the magnitude of the E'' peak increases with frequency, at the α transition that trend is reversed.

4. Conclusions

The activation energies for both the α and γ transitions show a significant decrease either with decreasing the crystallinity of the matrix or with increasing of the fibre winding angle, i.e. with increased molecular mobility.

Of the two potential effects of the fibre, namely, of reinforcement and of transcrystallinity, the first has a marked influence on the dynamic mechanical properties of the composites, manifested in their stiffening. The latter effect cannot be supported by significant evidence to satisfy the anticipation that a transcrystalline layer – formed during the crystallization process — contributes beyond the bulk crystalline matrix. Yet, the increase in the activation energy (both at the α and γ transitions — Table 1) from HDPE to thermally treated HDPE is higher than the difference between that of LDPE and HDPE, which may be attributed to a contribution from transcrystallinity.

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