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Dielectric relaxation spectroscopy of reactively blended amorphous poly(ethylene terephthalate)–poly(ethylene naphthalate) films

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Abstract

Reactively blended poly(ethylene terephthalate)–poly(ethylene naphthalate) films of different compositions and degrees of ester exchange reaction have been investigated by dielectric relaxation spectroscopy. The α-relaxation peaks associated with the glass transition have been fitted by the semi-empirical Havriliak–Negami relaxation function to frequency scans. The parameter relating to relaxation broadness, β, and the relaxation strength, $\Delta\varepsilon$, were quantified and were found to be a parameter sensitive to processing conditions. Both values were affected on a molecular level by concentration fluctuation and the molecular chain architecture (such as polymer chain blockiness). Molecular coupling of the blends was determined from the slope of log frequency maxima vs. reduced temperature T_g/T, as commonly done in coupling theory analysis. It was found that the initial materials, PET and PEN show very similar coupling behaviour. Molecular coupling of the blends was little affected by the blend composition or the degree of transesterification. Activation energies of molecular motions have also been determined and show a positive deviation from the rule-of-mixtures averages of the homopolymers which indicates greater chain hindrance to motion of both blocky or the random copolymers formed by the transesterification process. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Dielectric; Relaxation; Poly(ethylene terephthalate)

1. Introduction

The use of poly(ethylene terephthalate) (PET) in packaging [1] and electrical, electronic or other engineering [2] applications has found widespread acceptance. However, its thermal and barrier properties are not sufficient for a number of attractive applications [3]. An increase in UV and gas barrier properties as well as heat distortion temperature resistance are all desirable if the material is to be used in more speciality packaging such as bottling highly gaseous beverages such as beer or other foods which require hot filling.

A recent progress in this context is the development of PET/PEN blends. Poly(ethylene naphthalate) (PEN) offers significantly improved performance over conventional PET in critical areas such as thermal resistance, a higher glass transition, mechanical properties, dimensional properties and lower gas permeability [4]. One approach for combining the attractive economics of PET with better thermal and barrier properties is through blends with PEN. These blends are initially immiscible but quickly react and phase structure changes via transesterification in the melt. Whilst the dielectric properties of PET [5,6] have been investigated, PEN has been much less investigated [7]. Ezquerra et al. [8] undertook a detailed study into the primary and secondary relaxations of amorphous random copolymer films of PET and PEN. To our knowledge, there has been no detailed characterisation of the blends as a function of degree of transesterification. We limit ourselves in this work to consideration of the primary α-relaxation process only.

In this study, the amorphous region of the blends of differing composition and degrees of reaction are studied. This is achieved by studying quenched films, which have not yet crystallised. This is the same state from which the preforms are ultimately stretch-blow moulded. Dielectric spectroscopy can thus be used to investigate properties of the amorphous mixture in a fundamental sense without the complication of crystallinity, which subsequently occurs during the blow moulding stage. In this sense, the

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Table 1
Composition, absolute (T_A) and relative (T_R) degree of transesterification and glass transition (T_g) data from calorimetry and dielectric measurements for the PET/PEN blend series. In cases where two T_gs were determined due to phase separation, both values are shown in the table

PEN (mol%)	Screw speed (rpm)	T_A (%)	T_R (%)	T_g DSC (°C)	T_g DRS (°C)
0	20	0	–	74	95
20	4	29	2.8	83	105
20	7	20	2.0	81	104.5
20	12	18	1.7	80	104
20	18	16	1.5	81	101/131
20	30	15	1.3	81/112	100/131
40	3	27	2.0	92	113
40	8	20	1.4	82/103	121
40	12	17	1.3	80/105	102/132
40	16	15	1.3	78/106	100/134
40	20	15	1.1	79	97/130
60	3	30	1.5	100	124
60	8	23	1.2	80/104	128
60	12	22	1.1	80/108	107/135
60	16	21	1.1	77/110	103/137
60	20	23	1.0	78/111	106/143
80	3	48	1.3	110	134
80	8	40	1.0	111	101/139
80	12	36	1.0	112	100/139
80	16	29	1.0	114	97/136
92	20	87	–	118	143

amorphous film reflects the state of the melt and quenched non-crystalline preforms. Aspects such as chain conformation and distribution of reacted chain chemistry can be assessed. In a practical sense, an understanding of the amorphous region which of cause still exists in the final, semicrystalline polymer is important since it is through these lower density regions (compared to crystals) that gas permeates.

2. Experimental

2.1. Materials

The PET resin used was BK-2180 from Bakrie Kasai and contains isophtalic acid as a comonomer. A commercial PEN copolymer NC 900Z of Mitsubishi, containing 8 mol% PET to aid transesterification was used in this study. A PEN-rich copolymer was used in this work, rather than pure PEN, as this is common practice industrially. Such a copolymer matches more closely PET in melting temperature and processing viscosity.

A wide range of blend compositions with different degrees of transesterification as shown in Table 1 has been produced using a Brabender single screw extruder (type PL 2000) where temperatures were varied from 275 to 285°C along the length of the screw and die. It has been previously reported [9] that the amount of transesterification is primarily determined by the blending time and temperature, while the composition of the blend and the residual polyester catalysts have little effect on the degree of transesterification. In this study, the degree of transesterification was controlled by the extruder screw speed within a range of 3–30 rpm.

2.2. Nuclear magnetic resonance (NMR)

^{1}H-NMR analysis was performed using a Bruker DRX 500 MHz NMR spectrometer. The degree of transesterification (% trans) was calculated using a method outlined by Stewart et al. [9]. The parameter has been defined such that the degree of transesterification for a PET/PEN blend that has undergone no ester exchange is 0% and the statistical random copolymer 100%. It is important to recall that the commercial PEN used for the blend production contains 8 mol% PET. This initial material thus already has a degree of transesterification of 87.2% compared to the random copolymer. Therefore, a direct comparison of the transesterification of different sets of polymer blends is not straightforward since the % transesterification characterises the amount of NET (ethylene unit between terephthalate and naphthalate group) linkages compared to the amount of naphthalate and terephthalate only. This means that a particular percent of transesterification of a blend containing 20% PEN is not equivalent to a blend of the same transesterification containing 40% PEN. A parameter which is a relative value of transesterification was developed to compare the level of transesterification before (due to the presence of PEN copolymer) and after reactive melt blending in the extruder and will be introduced later in this paper.

2.3. Differential scanning calorimetry (DSC)

Glass transition temperatures were determined using a Perkin–Elmer DSC-7 Differential Scanning Calorimeter.

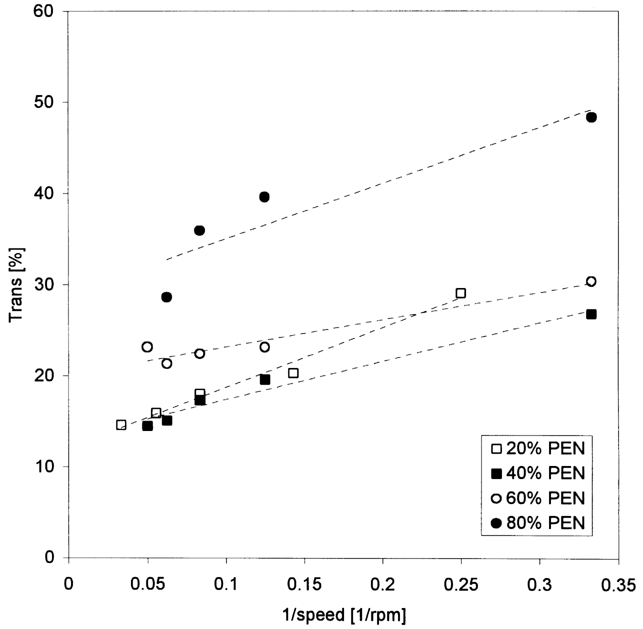

Fig. 1. Transesterification determined by ^{1}H-NMR as a function of the reciprocal extruder screw speed.

The temperature was calibrated using indium and zinc standards. Samples of 8–12 mg were sealed in aluminium pans and scanned at a rate of 10°C/min under a nitrogen atmosphere. The value of T_g was taken as the mid-point of the heat capacity step.

2.4. Dielectric relaxation spectroscopy (DRS)

Dielectric relaxation measurements were obtained on a Novocontrol dielectric spectrometer based on a HP 4284A frequency analyser using Win Deta software and capable of measurements between 20 and 10^6 Hz. Samples were obtained in the form of a quenched amorphous film which was covered with aluminium foil and fixed to the polymer with vacuum grease to optimise connectivity between electrode and polymer. Isothermal frequency scans were performed over the range of 20–10^6 Hz at temperatures between 60 and 180°C, using a temperature step size of 3°C. The imaginary component of the dielectric permittivity, ε'', which is the basic dielectric parameter, was calculated from the obtained data by the following equation:

$$\varepsilon'' = \frac{G}{C_0\omega} \tag{1}$$

where G is the conductance, ω the angular frequency and C_0 the empty capacitance of the sample. All measurements were preformed at temperatures some 30–50°C below the cold crystallisation region of the samples, as judged by DSC and did not crystallise [10].

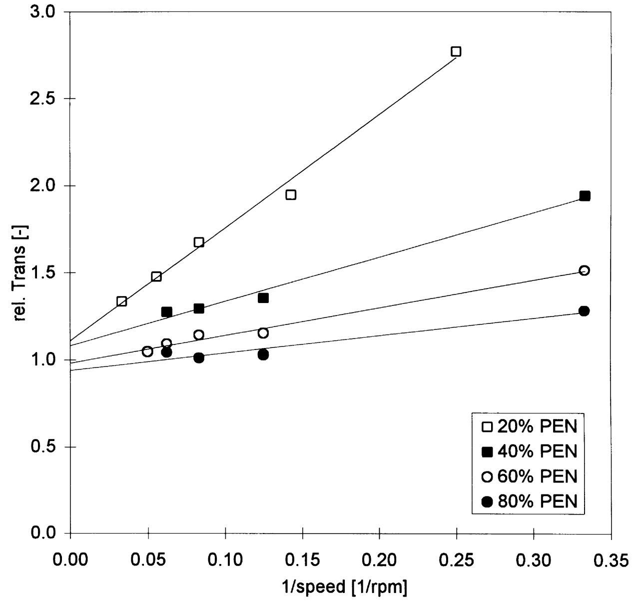

Fig. 2. Relative transesterification, T_R, as a function of the reciprocal extruder screw speed.

3. Results and discussions

Results of transesterification determined by ^{1}H-NMR analysis are summarised in Table 1. It can be seen that the transesterification decreases for each set of blends with increasing extruder screw speed. The value of relative transesterification was calculated from the equation

$$T_R = \frac{T_A}{T_I} \tag{2}$$

where T_R is the relative transesterification, T_A the absolute degree of transesterification after melt blending and T_I the initial transesterification due to the fact that one component is the PEN copolymer.

The comparison of transesterification and relative transesterification, T_R, in Figs. 1 and 2 indicates the usefulness of T_R. It can be seen that all sets of blends show a linear relationship between the degree of relative transesterification and the reciprocal extruder screw speed, with the gradient of the dependency decreasing with increasing PEN copolymer content. This dependency can be explained by the existing high level of transesterification in the PEN copolymer.

Glass transitions determined by DSC and DRS, respectively, are also shown in Table 1. Single and double T_gs were found depending on whether the sample was a single- or two-phase system. In two-phase systems, the lower temperature value is of a PET-rich phase and the higher T_g of a PEN-rich phase. It can be seen that the DRS method is more sensitive to the glass transition and double T_gs were identified in some instances where the DSC scans show only a single glass transition. In prior studies by Steward et al. [9] it has been reported that due to the limited resolution of the DSC method only a single T_g was found for PET/PEN blends even though there was evidence for a multiple

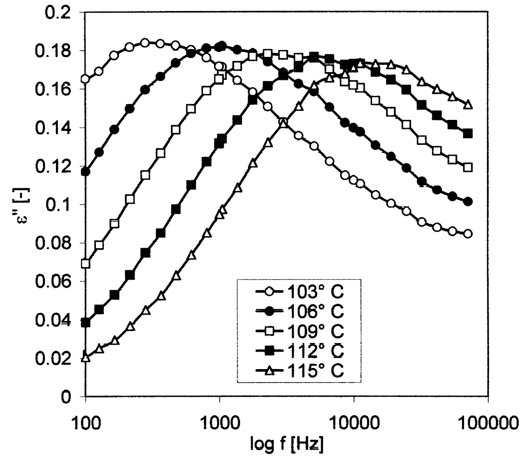

Fig. 3. The α-relaxation peak as a function of frequency of a PET high transesterified (3 rpm) blend containing 20% PEN.

phase system. The T_g by DRS was defined as the α-relaxation peak temperature at a frequency of 1 kHz. The α-relaxation is related to the Brownian motion of the main-chains associated with the glass transition and the relaxation of dipoles associated with it. It is generally found that the glass transition temperature related to the DRS maxima will be higher than the T_g measured by DSC due to the higher frequency of the DRS technique [11]. With increasing frequency, the relaxation peak shifts to higher temperatures, which is due to the increasing speed of motion of the molecules. Fig. 3, for example, illustrates the temperature dependence of the α-relaxation peak of a PET blend containing 20% PEN, produced at an extruder screw velocity of 4 rpm. This slow screw speed ensures the blends are well reacted, and certainly single phase. The α relaxation peak(s) of the other blends show a similar behaviour for increasing temperature. Results of the T_g determined by DRS are in good coincidence with the glass transitions determined by DSC, being consistently higher and reflecting the presence of either one or two phases.

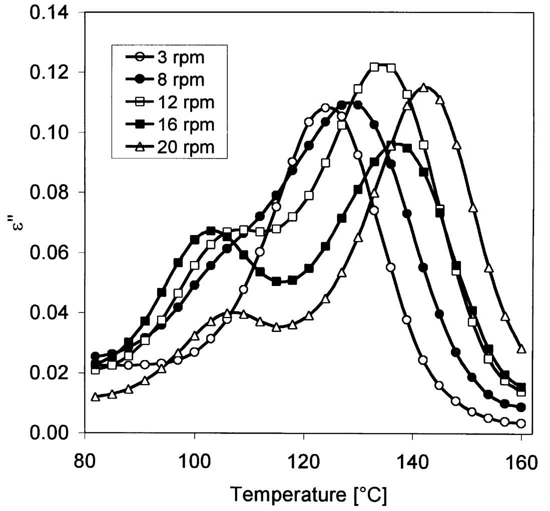

Fig. 4. ε'' as a function of temperature for blends containing 60% PEN produced at different extruder screw speeds.

However, in some cases the breadth of the α-relaxation peaks of the PEN and the PET rich phase means they are overlapped so that only a single peak can be observed even though the DSC analysis shows double T_gs. Fig. 4 illustrates single and double α relaxation peaks for the set of blends containing 60% PEN. It can be seen that, as expected, the lower temperature PET-rich phase increases as more PEN moieties become reacted with slower screw speed. At the same time, increased transesterification leads to a lower value of the PEN-rich phase. At 8 rpm one broad peak with a lower temperature shoulder exists whilst finally at the slowest screw speed of 3 rpm a single, relatively symmetric peak relating to a fully transesterified phase remains.

A method to parameterise dielectric data in the frequency domains is through curve fitting of model functions. The most commonly applied model function for the frequency domain is the Havriliak and Negami equation [12,13]

$$\varepsilon^*(\omega) = \frac{\Delta\varepsilon}{[1 + (\mathrm{i}\omega\tau)^{\beta}]^{\alpha}} \tag{3}$$

where $\Delta\varepsilon$ is the dielectric relaxation strength, τ the relaxation time, ω the angular frequency (rad/s), i the imaginary unit $\mathrm{i} = \sqrt{-1}$, and α and β are fractional shape parameters describing the skewing and broadening, respectively, of the dielectric loss function. Both α and β range between 0 and 1. The closer to zero are the α and β parameters, the more skewed (to high frequency) and broader, respectively, are the dielectric loss curves. Data was fitted to the curves using Jandel PeakFit™ software which uses the Marquardt–Levenberg fitting routine. Care must be taken with such a fitting (see our discussion Ref. [14]). Nonetheless, fits were found to be reliable, both in terms of the resultant observed fit and by the consistency of values of the parameters as successive temperatures of a given sample were undertaken (the "first guess" parameters of each fit were always reset to defaults and the program allowed to "find" the solution). In some cases where there were two components due to partial transesterification, only the strongest or major component peak could be fitted. Of the parameters in the HN equation, those of most interest are β and $\Delta\varepsilon$. The log of the relaxation time, τ, can be plotted against reciprocal temperature to obtain the activation energy of motion of the various phases. However, since there are difficulties in fitting the HN equation to minor phases, it was found to be easier to plot values of log f_m vs. $1/T$ where f_m is the frequency location of a given maximum of ε'' data plotted in the temperature domain for a given frequency. Even this method only allowed determination of activation energy values of the minor phase for 60 and 80% PEN samples (Table 2).

The parameter related to broadening, is shown in Fig. 5. Values are shown for a normalised temperature $T_g/T = 0.97$. The normalised temperature was chosen to allow a relevant comparison between measurements at the same

Table 2
Activation energy of motion of low and highly transesterified PET/PEN blends

Sample	Peak identification	E_a (kJ/mol)	Std deviation (kJ/mol)
PEN	Single	345	10
PET	Single	273	15
20% PEN 4 rpm	Single	371	13
20% PEN 18 rpm	PET-rich	370	12
20% PEN 18 rpm	PEN-rich	–[a]	–[a]
40% PEN 3 rpm	Single	328	7
40% PEN 20 rpm	PET-rich	402	17
40% PEN 20 rpm	PEN-rich	–[a]	–[a]
60% PEN 4 rpm	Single	342	11
60% PEN 20 rpm	PEN-rich	405	22
60% PEN 20 rpm	PET-rich	346	32
80% PEN 4 rpm	Single	379	14
80% PEN 16 rpm	PEN-rich	380	14
80% PEN 16 rpm	PET-rich	343	15

[a] The data determined from the minor phase in the blends of 20 and 40% PEN did not provide sufficient information for an accurate determination of E_a.

location temperature relative to T_g. This allows a better comparison than measurement at a common, absolute temperature. In addition T_g/T is also relevant in determining the intermolecular coupling between different polymer chains. The coupling of motion between chains would be expected to vary as the chemical structure of the chain becomes altered. It has been shown by Roland and Ngai [15] that the degree with which different polymers chains are intermeshed and hinder each others molecular motion in the region of the α-relaxation can be probed by relaxation techniques such as dielectric spectroscopy. It is found that the broader the relaxation (the lower the value of β) the more intermolecularly coupled the motions are. The slope of the plot of reduced temperature vs. log τ or $\log f_m$ at $T_g/T = 1$ is indicative of coupling (the so-called "cooperativity" or "fragility" plot based on work on a range of glass forming systems by Angel [16]). The greater the slope of the line, the more rapidly the molecular motion changes with temperature and the more intermolecularly coupled it is.

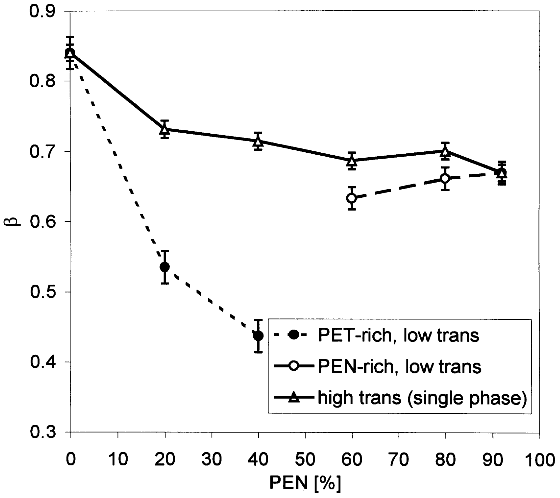

Fig. 5. The parameter from the Havriliak–Negami equation, β, which relates to broadening as a function of blend composition, for low and high transesterified blends.

The situation becomes more complex in miscible blend systems where the β parameter (and hence relaxation broadness) is also influenced by the degree of homogeneity of mixing at a molecular level (concentration fluctuations) and our interpretation of β in this work will include such consideration of fluctuations. Dielectric data was collected and analysed in this fashion only for the highest and lowest degree of transesterification for each system.

It can be seen from Fig. 5 that the PEN relaxation is broader than that of PET, likely due to its naphthalene moiety which would lead to a more hindered, coupled motion. Such a result was also found by Ezquerra et al. [8] for PET and PEN homopolymers. It is also clear from Fig. 5 that for blends with low levels of transesterification, the relaxation broadness of the PET-rich and PEN-rich phases are greater (β less) than that of the corresponding neat homopolymer. This is possibly due to changes in coupling as copolymers of the PET/PEN polymers form, but is also likely due to the distribution of chain types formed, both in terms of intramolecular chain sequence (i.e. blockiness), as well as microregions of differing degrees of transesterification, even in a nominally homogeneously reacted phase. The greater the content of the minority component, the even lower value of β and the broader the relaxation.

The highly transesterified, single-phase blends seen in Fig. 5 show much higher values of β (less broadness) than the less transesterified materials. This could be because further reaction has transformed the blocky, partially reacted, multi-phase material of low transesterification to a more homogeneous (due to greater reaction) random copolymer of PET and PEN sequences even on the microregion level. As before this homogeneity can be in terms of the sequence distribution or blockiness or microregion

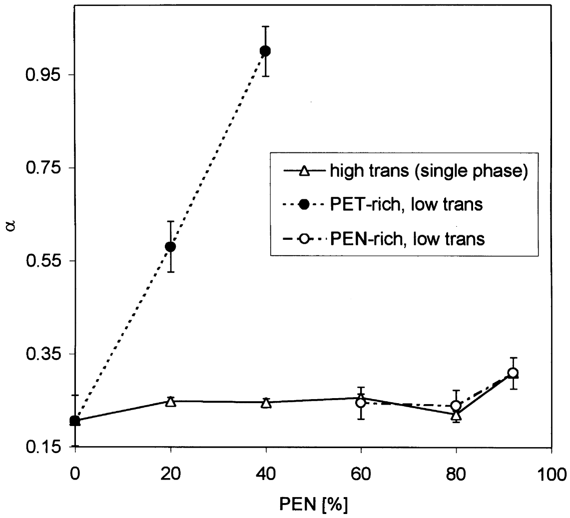

Fig. 6. The parameter from the Havriliak–Negami equation, α, which relates to high frequency skew as a function of blend composition, for low and high transesterified blends.

considerations. The blend components of the highly transesterified blends show a negative deviation from the rule-of-mixture between the β values for pure PET and pure PEN. This means that the reacted blend has a greater range of molecular environments than that expected from the rule-of-mixture average of the homopolymers. Alternatively, if it is due to coupling, the reacted materials are more coupled than expected from the rule-of-mixtures. This is likely due to the rather more complex sequence distributions and irregular chains that would result from reaction in the melt. The monontonic change in broadness with PEN composition of the highly transesterified materials seen in Fig. 5 is also observed in the work of Ezquerra et al. [8] where the copolymers are formed by copolymerisation during the synthesis stage, rather than the route of transesterification in the melt.

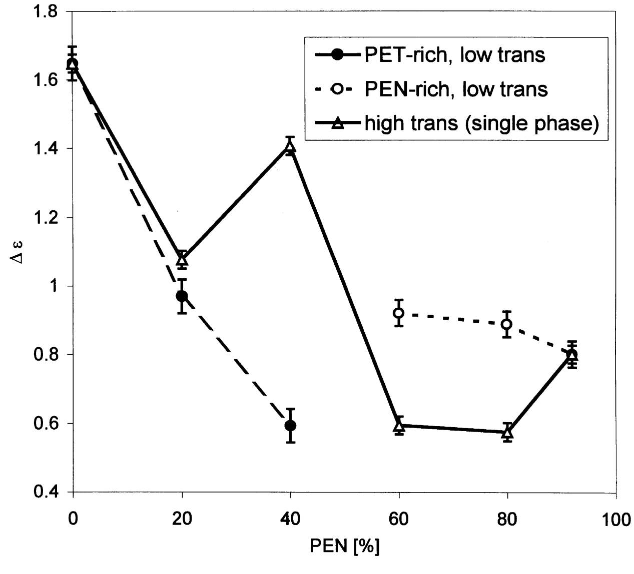

Fig. 7. Dielectric relaxation strength, $\Delta\varepsilon$, as a function of blend composition for low and high transesterified blends.

In order to shed further light on whether the β dependence as shown in Fig. 5 is due to concentration fluctuations in terms of copolymer nature or between phases, or alternatively due to coupling considerations, the data will be analysed in terms of the cooperativity or fragility plot. The precursor to this plot is the activation energy representation of data and will be presented shortly.

Another parameter which has been much less ascribed to a molecular origin is the HN parameter, α, from Eq. (3). This is related to the high frequency skew of the system (the lower value, the greater the skew). In the data shown in Fig. 6 the behaviour is complex. The values of single-phase materials (high transesterification) and PEN-rich low transesterification materials appear to be quite low, whereas the relaxation spectra for PET-rich materials showed some linearity with composition. The reason for the discontinuity between low and highly transesterified blends at approximately 50% composition is not clear. This parameter is often quite low in some thermoplastics, for example, values of 0.29 are reported for polycarbonate and 0.3 for poly(vinyl acetal) [17]. Likewise Ezquerra et al. [8] found a value of 0.3 for PET and 0.41 for amorphous PET. However, there is some variability in the literature. For example, Boyd and Liu [18] found that a symmetric, broad relaxation (Cole–Cole fit, Eq. (3) where $\alpha = 1$) fitted amorphous PET well. It should be noted that it has been observed in some miscible blend systems that the asymmetric homopolymer peaks do become broad and less skewed with addition of a miscible component. This has been reported [19] mainly in systems where one of the components is polar such as poly(vinyl methylether) (PVME) and polystyrene and ascribed to the different degrees of coupling in regions with different local concentrations. Such explanations are made more difficult to verify in systems such as that reported here where there are two polar components.

The dielectric strength, $\Delta\varepsilon$, as a function of composition for different levels of transesterification is shown in Fig. 7. The plot appears somewhat similar to that of the β parameter in Fig. 5 in that most of the blends show a negative deviation from the homopolymer values except for an unusual data point at 40% PEN for the highly transesterified material. In the case of the two phases of the low transesterified blends, the values are roughly intermediate to those of the homopolymers, except for the 40% PEN sample in the PET-rich phase, which is below that of pure PET. The relaxation strength of the highly transesterified material (except for the deviant 40% PEN point) appear to show strong negative deviation from the rule-of-mixtures. Since $\Delta\varepsilon$ is related to aspects such as dipolar density and chain conformation, both factors could be expected to contribute to the dependency. The greater complexity of the highly transesterified chains compared to the homopolymers could lead to poorer packaging and thus a lower density and dipolar strength. Indeed, we have evidence that

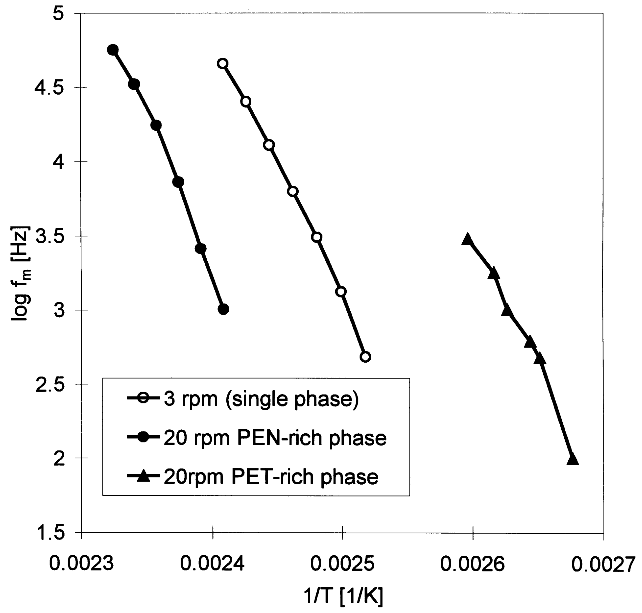

Fig. 8. Frequency maximum as a function of reciprocal temperature for blends containing 60% PEN.

indicates such a lower blend density [20]. It is also possible that the chain conformation and dipolar orientation could be such as to reduce the dipolar strength of the relaxation.

As mentioned above, an understanding of the interrelationship between temperature and frequency of the α-relaxation loss peak is important to understand molecular mobility in terms of activation energies and coupling. Isothermal frequency scans shift to higher peak frequency values (faster motions) with increasing temperature (Fig. 3). The temperature dependence of the α-relaxation loss peak may show an Arrhenius relationship (especially over a limited frequency range) [13]

$$f_m = A\exp\left(\frac{-E_a}{RT}\right) \tag{4}$$

where f_m is the peak frequency, A the pre-exponential factor, E_a the activation energy (energy barrier to motion), R the gas constant and T the thermodynamic temperature (K).

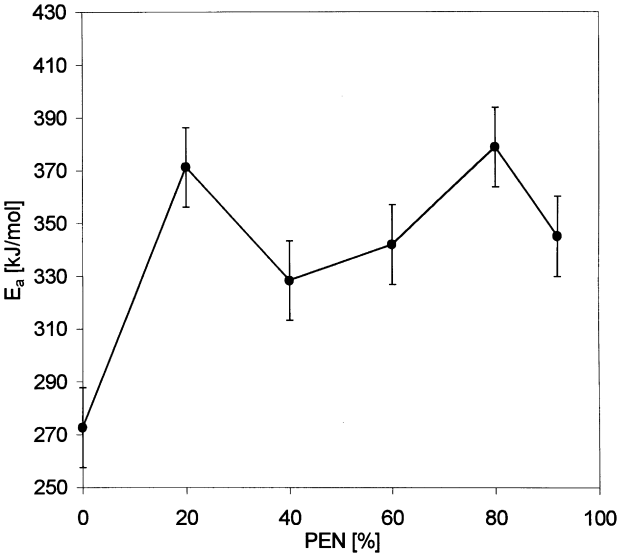

Fig. 9. Activation energy of motion as a function of blend composition for highly transesterified PET/PEN blends.

Alternately, the temperature dependence can be described by the Vogel–Fulcher dependence [21] which considers that the relaxation time of the α-relaxation increases rapidly at lower temperatures due to reduction in free volume

$$f_m = A\exp\frac{(-B)}{R(T - T_0)} \tag{5}$$

where A, B (J/mol) and T_0 (K) are fitted parameters and T_0 is the temperature at which essentially no α-relaxation occurs, which is usually at about 50°C below the value of T_g. Fig. 8 shows log f_m vs. $1/T$ traces for low and high transesterified blends containing 60% PEN. As a first approximation, log f_m vs. $1/T$ traces can be regarded as a straight line which allows the evaluation based on the Arrhenius relation as given in Eq. (4).

Activation energies were found to be 345 kJ/mol for PEN and 273 kJ/mol for PET. The value determined for PEN is in good correspondence with the activation energy $E_a = 350.3$ kJ/mol that has been determined previously from an Arrhenius plot by Bellomo and Lebey [7]. However, there is disagreement about the energy of activation for PEN in the literature. A different value of 198.8 kJ/mol has been reported recently by Canadas et al. [22]. The activation energy of PET was found in our study to be lower than the values reported in the literature, which are 384.1 kJ/mol [7] and 753.6 kJ/mol [6]. It has to be noted, that the activation energy determined by the Arrhenius relationship varies with the frequency range over which it is measured and could explain the discrepancies between the values determined in this study and those in the literature. This has been noted particularly in a recent paper by Struik [23]. However, since all activation energies in this study have been determined over the same frequency range, these values can be used in a comparable way as a function of composition and degree of transesterification. The low activation energy of PET compared to PEN can be explained by the lower bulkiness of the terephthalate ring compared to the more bulky naphthalate group in PEN. Results of the activation energies determined by the Arrhenius relationship are shown in Fig. 9 for highly transesterified blends and Fig. 10 for low transesterified blends.

It can be seen in Fig. 9 that the activation energies of the highly transesterified blends are greater than the rule-of-mixtures. That is, the energy barrier to motion, which the units must overcome, is greater where the dissimilar units form a copolymer. In particular, compositions with a low content of either material (20 and 80% PEN) show an enhanced barrier to motion, possibly due to the disruptive nature of the units. In Fig. 10 for the multiphase, low

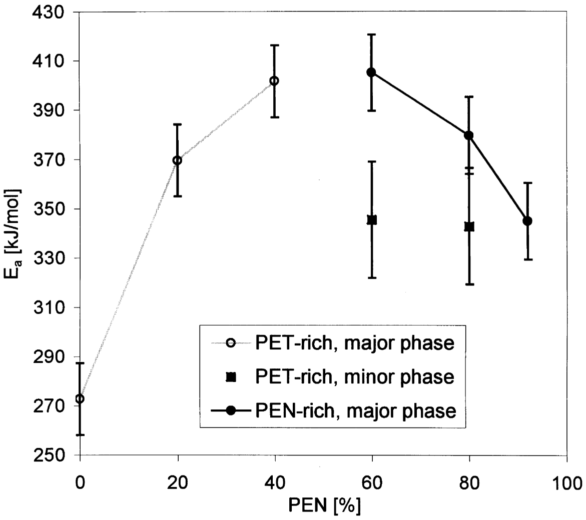

Fig. 10. Activation energy of motion as a function of blend composition for low transesterified PET/PEN blends. The data determined from the PEN-rich phase minor phase did not provide enough data to allow an accurate determination of E_a.

transesterified blends it can be seen that for a high PEN content, the PET-rich minor phase has been largely influenced by the incorporation of the PEN into it. Likewise, the corresponding PEN-rich major phase is increased in activation energy due to incorporation of PET, even though PET homopolymer itself has lower activation energy. In the case of the lower PEN-content blends, the relaxation of the PEN-rich minor phase could not be observed sufficiently for activation energy to be determined. Nonetheless, the PET-rich phase activation energy clearly increased with incorporation of PET. The data for low transesterified blends is thus such that it appears that incorporation of either component of the other material leads to higher activation energy. It can be seen that both initial polymers show a similar behaviour with increasing content of the other polymer. That is, both demonstrate a monotonic increase of the activation energy with increasing concentration of the other component. The PEN-rich blends are slightly shifted towards higher temperatures. The major phase of blends containing 20 or 80% PEN, respectively, show identical activation energies for low and highly reacted blends of 370–380 kJ/mol. By contrast, blends of 40 and 60% PEN show different activation energies for low and high transesterified blends. In both cases, the activation energy of the low transesterified blend is 65–70 kJ/mol higher than the higher transesterified polymer. The minor phases of the low-trans blends (60 and 80% PEN) show similar activation energies to the highly transesterified blends. This indicates that both blocky copolymers (low degree of transesterification) or random copolymers (high degree of transesterification) have greater energy barriers to rotate, i.e. greater chain hindrance, than expected from an average behaviour.

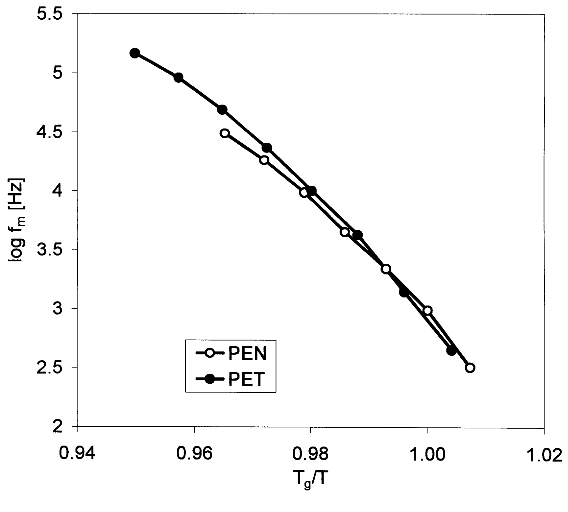

Fig. 11. Log f_m as a function of normalised temperature, T_g/T for PET and PEN (cooperativity or fragility plot).

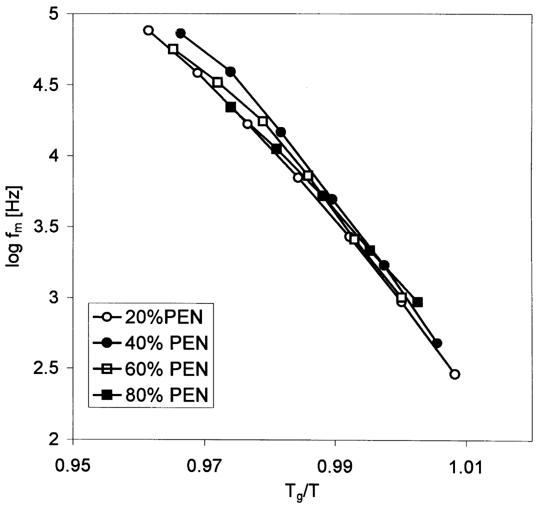

Fig. 12. Log f_m as a function of normalised temperature for high transesterified PET/PEN blends of different compositions (cooperativity plot).

The intermolecular coupling behaviour of the high transesterified blends has also been investigated. Log f_m has been plotted against T_g/T to investigate if changes in the intermolecular coupling occur between different blend compositions or different degrees of transesterification, respectively. The T_g was defined as the α-relaxation peak temperature at a frequency of 1 kHz. A cooperativity plot of the initial components, PET and PEN, is shown in Fig. 11. As explained by Ngai and Roland [24], the slope of these traces at $T_g/T = 1$ correlates with the intermolecular coupling of the polymer, a greater slope implying greater coupling. It can be seen that PET is only slightly more coupled, possibly due to higher flexibility and greater entanglement of the molecular chains. However, it should be noted that the difference is very small. In Fig. 12, log f_m the fragility plot of the highly transesterified blends of different blend composition is shown. It was found that neither the blend composition nor the degree of transesterification significantly influences the intermolecular coupling of the blends.

Therefore, the broadening behaviour as discussed before in terms of the low β parameter for the highly transesterified blends cannot simply be related to changes in intermolecular coupling. That is, the broadening and its variation with different levels of ester exchange reaction and blend composition must be explained by concentration fluctuation and the distribution range of chains with an inhomogeneous spread of blockiness formed by the melt reaction. It appears, therefore in that system, that the value of β is quite a sensitive indicator of the inhomogeneity of blends of these materials.

4. Conclusions

Dielectric relaxation spectroscopy is shown to be a powerful tool to investigate the number of phases and concentration fluctuation in these blends. Activation energies of motion, coupling and relaxation broadness all seem to be sensitive to the state of material. It was found that PET, PEN and its blends show very similar degrees of intermolecular coupling. Therefore, the broadness of α-relaxation observed in both low or highly reacted blends is likely due to concentration fluctuations and the range of blocky materials present. The β parameter from the Havriliak–Negami equation is thus a potentially sensitive indicator of the inhomogeneity of blends of this material that changes as a function of reaction. Although a monotonic relationship between E_a and blend composition could not be found, it appeared that the activation energies of motion of the blends had a synergistic positive deviation from the rule-of-mixture average of PET and PEN components, even if a component with lower activation energy (PET) is being incorporated. Molecular motion appears to be hindered formation of blocky and/or copolymeric materials.

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References

[1] Nentwig J. Neue Verpackungen 1991;12:44–49.
[2] Du Pont Bulletin, E-39467-1 09/83.
[3] Tacker M. ZFL 1997;48(1/2):48–51.
[4] Amoco Bulletin FA-13b, USA, 1996.
[5] Neagu E, Pissis P, Aspekis L, Gomez Ribelles JL. J Phys D Phys 1997;30:1551.
[6] McCrum NG, Read BE, Williams G. Anelastic and dielectric effects on polymeric solids. London: Wiley, 1967.
[7] Bellomo JP, Lebey T. J Phys D: Appl Phys 1996;29:2052.
[8] Ezquerra TA, Balta-Calleja FJ, Zachmann HG. Acta Polym 1993;44:18.
[9] Stewart ME, Cox AJ, Naylor DM. Polymer 1993;34:4060.
[10] Becker O, Simon GP, Rieckmann T, Forsythe J, Rosu R, Völker S, O'Shea M. Submitted for publication.
[11] Simon GP. Mater Forum 1994;18:235.
[12] Havriliak S, Negami S. J Polym Sci 1966;C14:99.
[13] Havriliak S, Negami S. Polymer 1967;8:261.
[14] Goodwin AA, Simon GP. Macromolecules 1995;28:7022.
[15] Ngai KL, Roland CM. Macromolecules 1993;26:6824.
[16] Angell CA. In: Ngai KL, Wright GB, editors. Relaxations in complex systems. Washington, DC: Government Prints Office, 1985.
[17] Havriliak S, Watts DG. Polymer 1986;27:1509.
[18] Boyd RH, Liu F. In: Runt JP, Fitzgerald JJ, editors. Relaxations in complex systems. Washington: ACS, 1997 (chap. 4).
[19] Roland CM, Ngai KL. Macromolecules 1992;25:363.
[20] Becker O, Simon GP, Rieckmann T, Forsythe J, Rosu R, Völker S. Unpublished data.
[21] Vogel H. Phys Z 1921;2:625.
[22] Canadas JC, Diego JA, Mudorra M, Belana J, Diaz-Calleja R, Sanchez MJ, James C. Polymer 1999;40:1181.
[23] Struik LCE. Polymer 1997;38:733.
[24] Roland CM, Ngai KL. Macromolecules 1991;24:5315.