

Secondary relaxation processes in polyethylene terephthalate–additive blends: 2. Dynamic mechanical and dielectric investigations

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Dynamic mechanical and dielectric analysis have been used to examine the effects that low molecular weight additives have upon the secondary relaxation processes in polyethylene terephthalate. In each of the polymer/additives blends examined one main secondary relaxation peak, known as the β peak has been observed below the glass transition temperature. It would, however, appear from the dielectric and mechanical results that the β peak consists of two different relaxation processes, one on the high temperature side and one on the low temperature side of the peak. A closer examination of these relaxation processes suggests that the high temperature side of the peak is due to phenyl ring flips, whereas the low temperature side is due to the motion of the carbonyl groups. In addition, it would appear that the activation energy and the enthalpy of the phenyl ring flips are both considerably higher than that of the carbonyls. Finally, when low molecular weight additives were blended into the polymer it was observed that only the high temperature side of the peak was suppressed and that the low temperature side remained virtually unaltered. This would indicate that although the additives suppress the motion of the phenyl rings, they have little effect upon the motion of the neighbouring carbonyl groups. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The first detailed studies of relaxation processes in polyethylene terephthalate (PET) were the dielectric measurements of Reddish¹. This pioneering research was soon followed by dynamic mechanical measurements from the ICI group, including studies of the effects of crystallinity and orientation by Thompson and Woods² and a combination of dynamic mechanical and n.m.r. measurements on a wide range of polyesters by Ward and co-workers^{3,4}.

Reddish observed two relaxations at a frequency of 100 Hz, a peak in $\tan \delta$ at about 100°C (the α -peak) and a second peak at about -50°C (the β -peak). He attributed the α peak to micro-Brownian motions of the chains and associated it with the glass transition, an explanation which has been well confirmed by subsequent research. The β peak was attributed to the motion of the terminal -OH groups, but as early as 1956, Thompson and Woods remarked on the alternative possibility that it was associated with the motion of the aliphatic part of the chain. This latter explanation appeared to receive support from dynamic mechanical measurements³ on a series of poly *n*-methylene terephthalates where the methylene sequence was varied from $n = 2$ (as in PET) to $n = 10$. With increasing numbers of methylene groups the two main loss peaks moved by equal amounts to lower temperatures. For $n = 10$, the β peak at 100 Hz was at -125°C, very close to the γ transition in polyethylene. Broadline proton n.m.r. measurements on these polymers and several deuterated derivatives, however, showed that only very small molecular motions occur over the temperature range of the transition. Farrow *et al.*³

speculated that these motions involved some very restricted rotation of the glycol residue. They also pointed out that the β relaxation contained at least two superimposed loss processes, because of the asymmetry of the loss peak which reversed as the methylene sequence length increased, even showing a distinct shoulder when $n = 9$.

In 1963 Illers and Breuer⁵ published a detailed examination of the relaxation and gave an explanation of its asymmetry in terms of three peaks. In spite of the n.m.r. evidence of Ward and co-workers they proposed that a peak at -165°C should be attributed to hindered rotations of the CH₂ groups. They attributed a peak at -105°C to motions of carbonyl groups associated with the gauche conformation (which is in the aliphatic glycol residue⁶) and a peak at -70°C to motions of the carbonyl groups associated with the trans conformation.

Research in this area up to 1964 was very well reviewed by McCrum *et al.*⁷. It has, however, since been shown by English⁸ that molecular motions in the polymer chain below the α relaxation should be attributed to motion of the phenyl rings rather than that of the glycol residue. It is clear from the earlier n.m.r. studies of Ward and co-workers that there are no substantial molecular motions of the chains in terms of either the methylene group protons (e.g. trans-gauche conformational changes) or the benzene ring protons until the glass transition, i.e. the α -relaxation, and this has been confirmed recently by deuterium n.m.r. studies^{9,10}.

It would appear that there are significant differences between the relaxation behaviour determined from dielectric and dynamic mechanical data. Although multiple relaxation peaks⁵ are observed in the mechanical data, the dielectric measurements of Reddish and of Coburn and

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Boyd¹¹ show that the dielectric β peak can be modelled using a single relaxation process. The reason for these differences between the dielectric and mechanical results could result from the fact that the two techniques relate to different structural features within the polymer. For although the mechanical results display all the relaxation processes in the polymer, the dielectric results relate to the dipole moments that are associated with the carbonyl groups in the polymer chain. By comparing the dielectric and mechanical relaxation peaks it is therefore possible to determine whether the carbonyl groups are associated with any particular relaxation peak. Furthermore, by blending antiplasticisers into the polymer, it has been possible to suppress certain relaxation processes, thereby allowing the overlapping mechanical relaxation processes to be separated. Using mechanical, dielectric and n.m.r.¹⁰ results it has been possible to determine the local molecular

motions that are responsible for the relaxation peaks in PET and to identify the mechanisms that are responsible for suppressing the relaxation processes.

SAMPLE PREPARATION

To examine antiplasticisation in PET several low molecular weight additives were blended into the polymer. The PET used (grade E47) was supplied by ICI plc and had an intrinsic viscosity of 0.6. The additives that have been used are listed in *Table 1* and their chemical formulae shown in *Figure 1*. To blend the additives into the polymer, a table-top APV twin screw extruder has been used. To ensure the additives were sufficiently blended into the polymer, both the additive and the polymer were ground into a powder. The polymer was then dried and mixed with between 2 and 20% by weight of additive. This mixture was then fed through the twin screw extruder to produce a homogenous polymer/additive blend. The blends were then re-dried and pressed in a hot press into films with thicknesses of between 50 and 150 μm , their thickness being controlled to within 10% using spacers. Once pressed the films were quenched from above their crystallisation temperature to room temperature to ensure that they were amorphous.

Table 1 Low molecular weight additives used as antiplasticisers in PET

	Chemical name	Source
DMT	Dimethyl terephthalate	Aldrich Chemicals
DMN	Dimethyl naphthalate	ICI
TPDE	Tetrachlorophthalic dimethyl ester	ICI ^a
BDM	Benzene dimethanol	Aldrich Chemicals
CDM	Cyclohexane dimethanol	Aldrich Chemicals

^a Made by Zeneca from ICI Patent EP 0 395 237 A1¹²

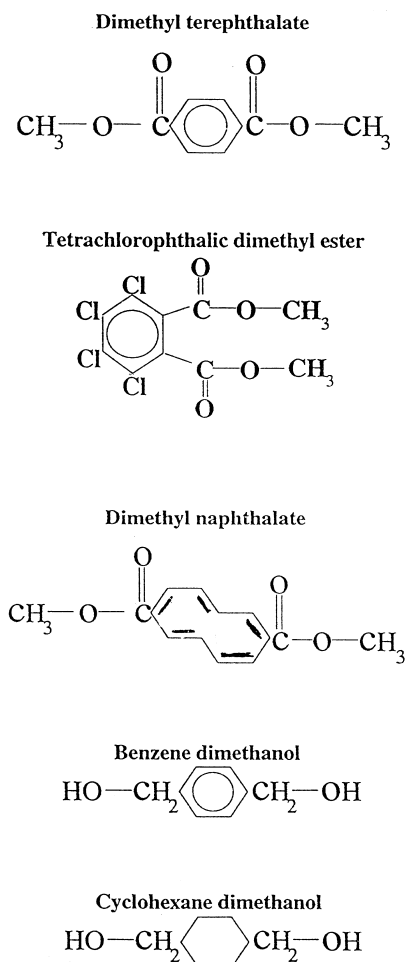


Figure 1 Chemical formulae of the low molecular weight additives that have been used as 'antiplasticisers'.

EXPERIMENTAL

Dynamic mechanical measurements have been made using specially designed equipment which has been described in detail in a previous publication¹³. The principle is to apply a sinusoidal extensional strain to the polymer, while simultaneously measuring the stress in the sample, using a computer-controlled frequency response analyser (FRA). The amplitude of the sinusoidal strain was fixed at 0.05%, with an additional static strain of 0.1% being applied to the sample to ensure that it never became slack. The relative amplitudes of the stress and strain and the phase shift between the two signals were then used to determine the storage and loss moduli and $\tan \delta$. This procedure was repeated on each sample at five different frequencies, over a range of temperatures from -150°C up to the glass transition temperature.

Dielectric measurements were made using a Kistler charge amplifier in conjunction with a Schlumberger Solartron 1260 impedance/gain-phase frequency response analyser¹⁴. Readings were made using a frequency sweep, taking measurements at decade intervals between 1 Hz and 100 kHz. Frequency sweeps were made at 5°C intervals over a range of temperatures from -120 to 150°C . The Solartron impedance/gain-phase analyser supplies an alternating voltage to the sample and measures the current flow and voltages V_1 and V_2 that occur across the polymer. The complex capacitance of the sample C_s can then be calculated from

$$C_s = -C_x \left(\frac{V_2}{V_1} \right)$$

where C_x is the reference capacitance.

The temperature was controlled in both the mechanical and dielectric experiments by enclosing the samples in an insulated polyurethane-lined chamber. Nitrogen gas was then boiled off from a nitrogen dewar, passed over a heating coil and fed into the chamber. Temperature control was achieved by heating the gas to the required temperature with the heating coil, before it was fed into the specimen chamber. Using thermocouples positioned around the

sample, it was estimated that the temperature was correct to within $\pm 1^\circ\text{C}$ of the required temperature.

Activation energies for both the mechanical and dielectric relaxation peaks were obtained from graphs of $\log f$ against $1/T$ using the Arrhenius equation:

$$\log f = A + \left(\frac{-E}{2.303RT} \right)$$

where f is the frequency used in the experiment, T is the temperature at which the $\tan \delta$ relaxation peak occurs, E is the activation energy, R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and A is a constant.

As can be seen from this Arrhenius equation, the activation energies can be determined from the gradient of the $\log f$ versus $1/T$ graphs.

RESULTS AND DISCUSSION

Dynamic mechanical analysis

The mechanical relaxation processes that occur in PET have been examined (Figure 2), at four different frequencies, over a range of temperatures between -150 and 75°C . The experimental error in these results for $\tan \delta$

has been estimated to be approximately ± 0.002 . At 1 Hz, the main secondary relaxation peak that occurs in PET is the β relaxation peak that appears at approximately -70°C . To examine the effect that the additives have on the β peak, PET has been blended with different amounts of dimethyl terephthalate (DMT) additive. By comparing the different relaxation peaks that have been obtained from these polymer/additive blends (Figure 3), it can be seen that the DMT additive reduces the height and the activation energy (Table 2) of the β peak. From repeated measurements an estimate was made of the errors in the activation energies and these are quoted in Table 2. Furthermore, it can be seen that the additive suppresses the high temperature side of the β peak considerably more than the low temperature side, confirming, as suggested by Illers and Breuer⁵, that the mechanical relaxation peak consists of more than one relaxation process.

To examine the effects that different additives have on the relaxation processes, a range of different additives was blended into the polymer. As can be seen from Figure 4, both the DMN and TPDE additives appear to have a similar effect to that of the DMT additive. As the only difference between the DMT and DMN additives is that the phenyl rings have been replaced by naphthalene groups, it would

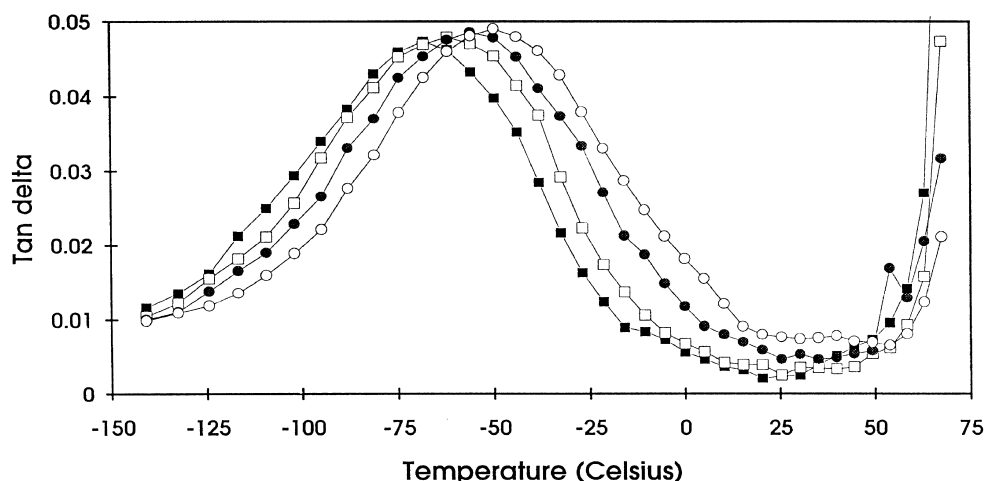


Figure 2 Dynamic mechanical relaxation processes in PET observed over a range of temperatures at: ■, 1 Hz; □, 3 Hz; ●, 10 Hz; ○, 30 Hz.

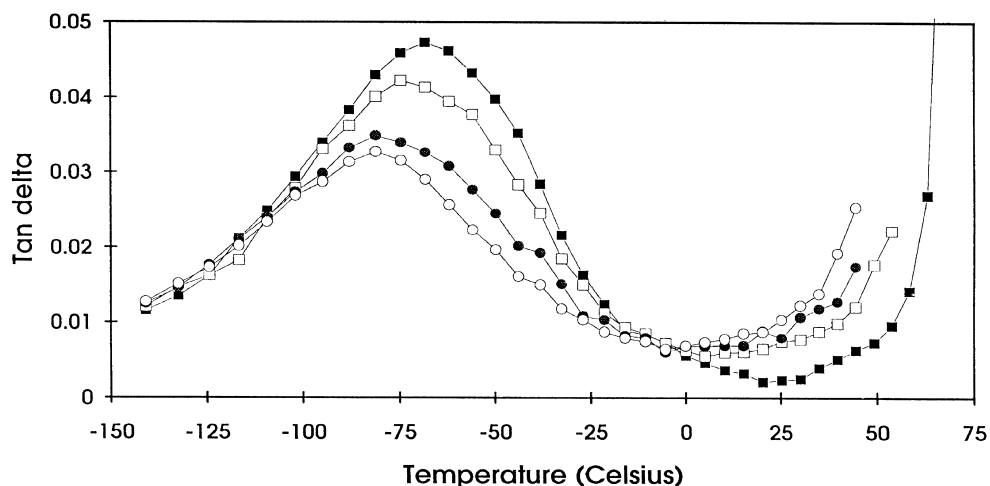


Figure 3 The effect that different amounts of DMT additive have on the mechanical relaxation processes in PET at 1 Hz: ■, original PET; □, 2% DMT; ●, 10% DMT; ○, 20% DMT.

Table 2 Activation energies for the β relaxation peak in PET/additive blends

Polymer/additive blend	Activation energy mechanical (kJ)
PET	70 \pm 8
PET/DMT	57 \pm 9
PET/TPDE	54 \pm 9
PET/DMN	57 \pm 9
PET/BDM	53 \pm 9
PET/CDM	48 \pm 9

appear that these two aromatic groups have a similar effect upon the relaxation peaks. Likewise, it would appear from the TPDE results, that the polarity of the aromatic groups also has little effect upon the relaxation peaks. It can, however, be seen in *Figure 5* that the relaxation peaks in the BDM and CDM blends are slightly higher than in DMT. The reason for this would appear to be that the ester groups in the DMT additive have been replaced with the methyl alcohol groups in the BDM and CDM additives. It is, however, important to note that although the low temperature side of the peaks are higher in the BDM and CDM samples, the high temperature side of the peaks and the activation

energies (*Table 2*) are similar to those in the PET/DMT blend.

Detailed analysis of mechanical relaxation processes

The relaxation peaks that have been obtained from the polymer/additive blends have been superimposed onto those obtained from the original polymer (*Figures 4 and 5*). As can be seen from these results, each of the additives appears to suppress the high temperature side of the β peak rather than the low temperature side. This would appear to support the theory that the β peak consists of more than one relaxation process⁵ and that the additives have suppressed the relaxation processes that occur on the high temperature side of the β peak.

To examine in more detail the possibility that the additives have suppressed a relaxation process on the high temperature side of the β peak, the relaxation peaks that were obtained from the PET/DMT blends have been subtracted from those obtained from the original PET (*Figure 6*). The result of subtracting these relaxation peaks was that a large bell-shaped peak appeared at approximately -45°C , which as would be expected moved to higher temperatures as the frequency increased. To determine the

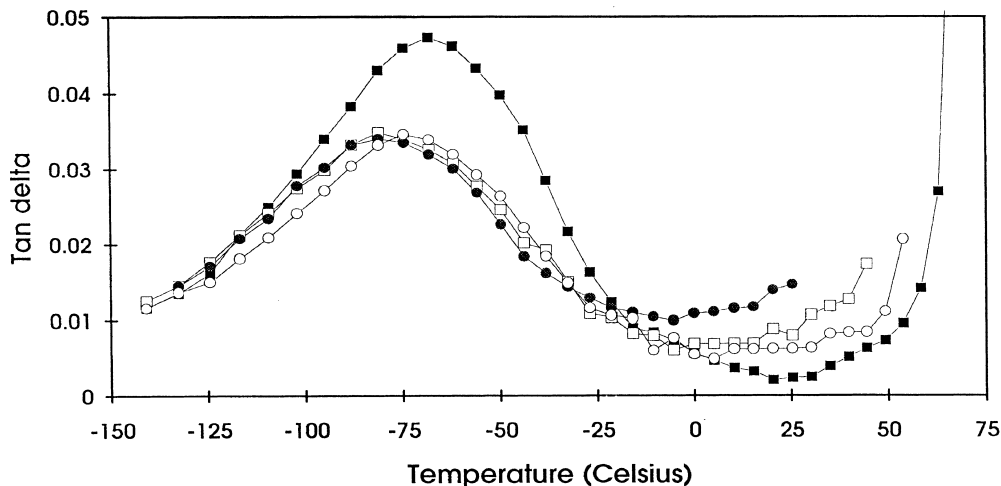


Figure 4 The effect that different additives have on the mechanical relaxation peaks of PET at 1 Hz: ■, original PET; □, 10% DMT; ●, 10% DMN; ○, 10% TPDE.

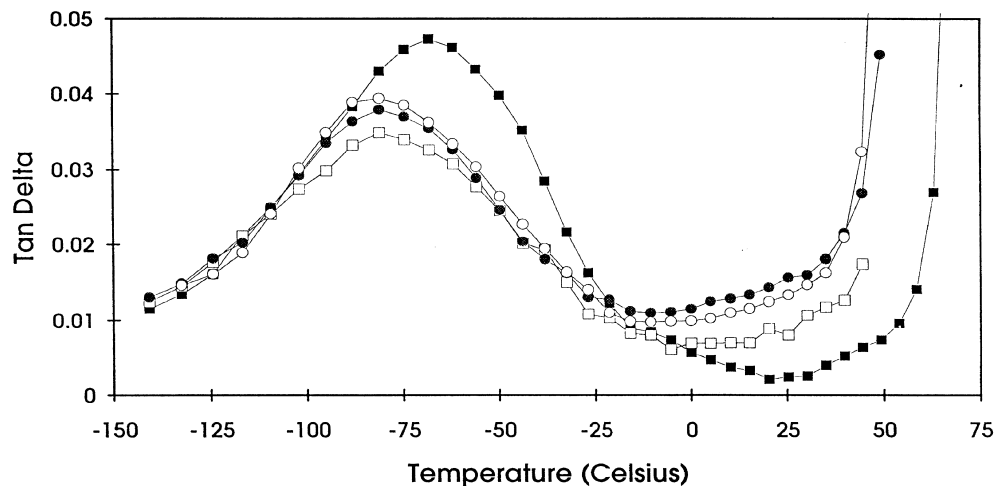


Figure 5 Mechanical relaxation peaks in samples of PET blended with different additives at 1 Hz: ■, original PET; □, 10% DMT; ●, 10% BDM; ○, 10% CDM.

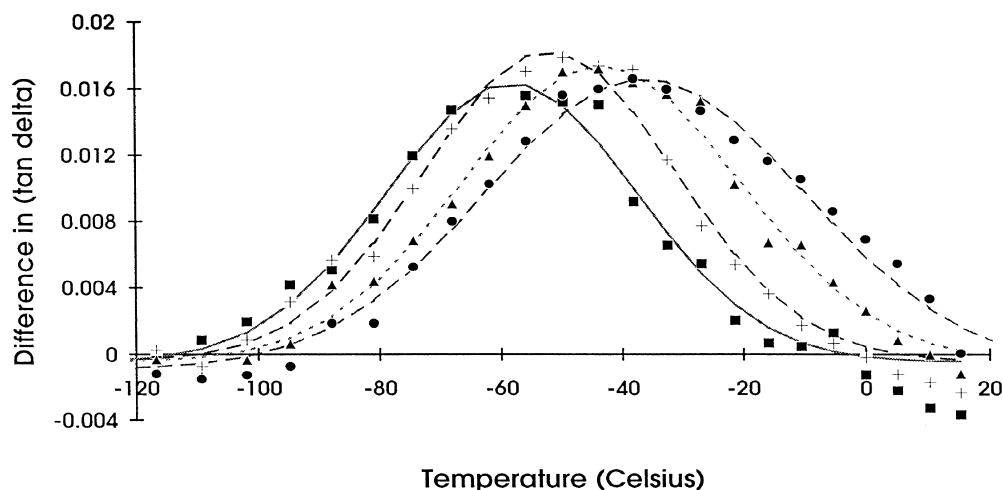


Figure 6 Gaussian peaks that have been fitted to the suppressed relaxation peak in PET at: ■, 1 Hz; +, 3 Hz; ▲, 10 Hz; ●, 30 Hz.

Table 3 Values used to fit Gaussian curves to the subtracted peaks in PET

	1 Hz	3 Hz	10 Hz	30 Hz
Height	0.017	0.019	0.018	0.018
Width	0.034	0.034	0.031	0.027
Centre	-58.47	-51.89	-43.38	-36.32

activation energy of this relaxation process, the data has been fitted to Gaussian peaks (Figure 6) using the parameters shown in Table 3. Using the results from the fitted relaxation peaks, it has been found that the activation energy of the suppressed relaxation processes was approximately 70 kJ mol^{-1} .

By comparing the activation energy of this suppressed peak with those obtained from the PET and polymer/additive blends (Table 2), it can be seen that the additives suppress a relatively high activation energy process (70 kJ mol^{-1}) that occurs on the high temperature side of the β peak. The result of this is that in the polymer/additives blends it appears that the activation energy of the β peak has been reduced as only the lower activation energy process of 57 kJ mol^{-1} remains.

In addition to examining the activation energies of the relaxation processes the degree of co-operative motion involved with each of these relaxation processes has also been estimated from the activation entropy ΔS . For simple relaxations, in which relatively little co-operative motion is required, the activation entropy is close to zero. If, however, complex relaxation processes take place, in which significant co-operative motion is required, then large positive activation entropies are obtained. To determine the activation entropy ΔS of a relaxation process Starkweather¹⁵⁻¹⁷ has derived the following expression:

$$E_A = RT \left[1 + \ln \left(\frac{k}{2\pi h} \right) + \ln \left(\frac{T}{f} \right) \right] + T\Delta S$$

where E_A is the activation energy of the relaxation process, f is the relaxation frequency, T is the relaxation temperature, R is the universal gas constant, k is Boltzmann's constant and h is Planck's constant.

Using this expression it has been possible to determine the activation entropy of the secondary relaxation peaks in each of the samples (Table 4). The errors for the entropies are directly due to the errors in determining the activation

Table 4 Activation entropies ΔS obtained from the β relaxation processes in the different polymer/additive blends

Polymer/additive blend	Activation entropy ΔS ($\text{J K}^{-1} \text{ mol}^{-1}$)
PET	106 ± 12
PET/DMT	57 ± 9
PET/TPDE	37 ± 9

Table 5 Activation entropies ΔS observed on the high and low temperature sides of the β relaxation peak in PET

Position in the β peak	Activation entropy ΔS ($\text{J K}^{-1} \text{ mol}^{-1}$)
Low temperature side	46 ± 7
Centre of relaxation peak	106 ± 12
High temperature side	129 ± 14

energy, as the errors due to temperature and frequency are negligibly small. As can be seen, the activation entropy of the original PET is considerably higher than that in the polymer/additive blends. This would indicate that the high temperature relaxation process that is suppressed in the polymer/additive blends involves considerably more co-operative motion than the relaxation processes found on the low temperature side of the peak. To confirm this observation the activation entropies at different positions in the β peak have been obtained (Table 5). These results show that the activation entropy of the relaxation process on the high temperature side of the peak is significantly higher than that on the low temperature side of the peak.

To determine the chemical features of the additive that are responsible for suppressing the secondary relaxation processes, a wide range of different additives has been examined (Figures 4 and 5). It can, however, be seen that all of the additives, apart from the BMD and CMD, appear to have a similar effect upon the relaxation peaks. This would appear to indicate that the chemical structure of the additives is less important than that of the polymer. The only exception to this is that the low temperature side of the β peak in the BMD and CMD blends is significantly higher than those in the other blends (Figure 5).

The most likely explanation for this increase on the low temperature side of the β peak is that the alcohol groups in the BDM and CDM additives have absorbed moisture from the atmosphere and that this moisture is responsible for

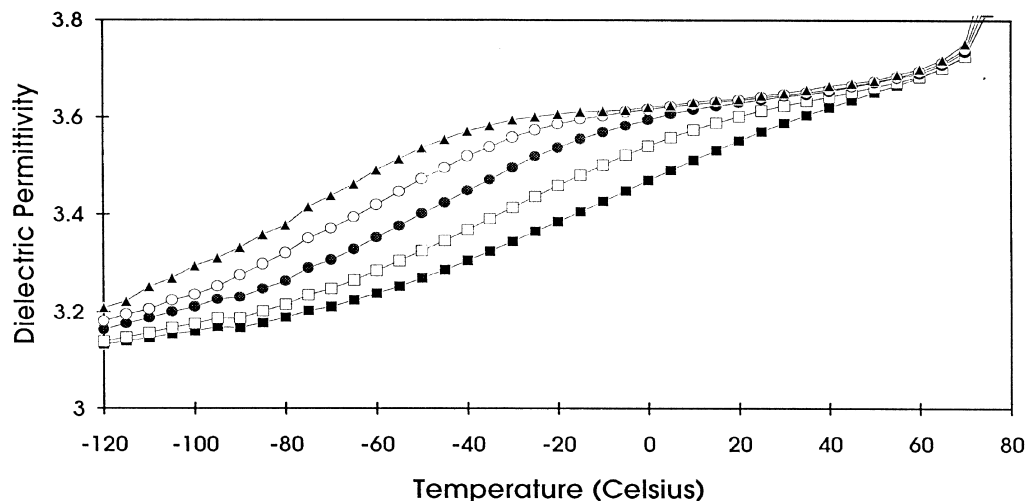


Figure 7 The increase in the dielectric permittivity of PET that is observed during the relaxation process: ■, 10 kHz; □, 1 kHz; ●, 100 Hz; ○, 10 Hz; ▲, 1 Hz.

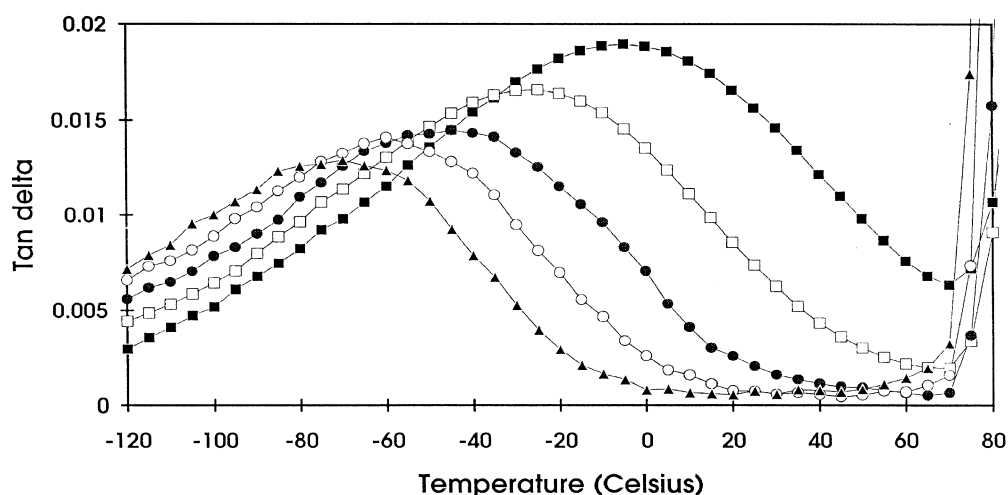


Figure 8 The dielectric $\tan \delta$ peaks in PET associated with the β relaxation process observed at: ■, 10 kHz; □, 1 kHz; ●, 100 Hz; ○, 10 Hz; ▲, 1 Hz.

plasticising the carbonyl groups. Detailed studies into the effects that water has on the relaxation peaks in PET have been reported by various authors^{1,5}. One of the earliest studies was conducted by Reddish¹, in which it was found that the intensity of the dielectric peak increased when water was present. Likewise, Illers and Breuer⁵ observed that, in dynamic mechanical experiments, absorbed water increases the low temperature side of the β peak, which is consistent with the BDM and CDM results. It would therefore appear reasonable to assume that although the BDM and CDM additives suppress the high temperature relaxation processes, the water that is absorbed by the additive increases the low temperature side of the β peak.

Dielectric analysis

Dielectric measurements have been obtained from samples of PET, over a range of five different frequencies between 1 Hz and 100 kHz, at temperatures between -120 and 150°C . Graphs showing the dielectric constant ϵ' and loss tangent ($\tan \delta$) are shown in *Figures 7 and 8* respectively. The experimental error in these dielectric measurements has been estimated to be approximately 2% for $\tan \delta$ and 10% for the dielectric constant. Two main

Table 6 Activation energies for the β relaxation peak in PET/additive blends

Polymer/additive blends	Activation energy (kJ)
PET	56 ± 10
PET/DMT	53 ± 14
PET/TPDE	55 ± 10

relaxation peaks have been observed in these dielectric results: at -80 and 120°C . The largest of these relaxation peaks is the α peak at 120°C due to the glass transition; the second peak, at -80°C , is the β peak and is due to local molecular motions.

To examine the effect that the additives have on the dielectric relaxation peaks, the relaxation peaks that were obtained for the original polymer have been plotted against the relaxation peaks that were obtained in the polymer/additive blends (*Figure 9*). From these results, it would appear that the additives have relatively little effect upon either the β peak itself or the activation energy (*Table 6*), although the additive does appear to reduce the glass transition temperature of the polymer by approximately 30°C .

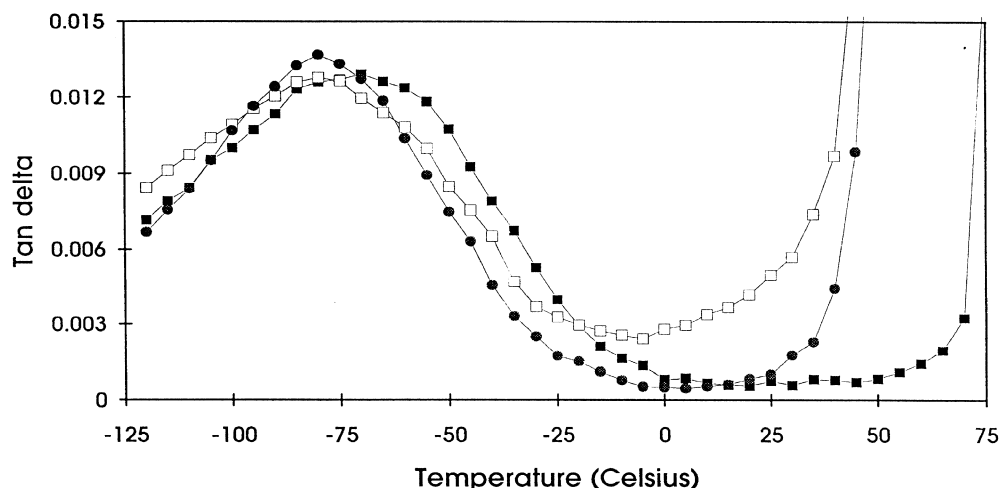


Figure 9 The effect that different additives have on the dielectric relaxation peaks in PET at 1 Hz: ■, original PET; □, PET with 10% DMT; ●, PET with 10% TPDE.

Comparison of dielectric, mechanical and n.m.r. results

By comparing the dielectric and mechanical results that have been obtained, it can be seen that there are significant differences between the two sets of results. The reason for this is that the two techniques examine different features within the polymer. The main difference is that whereas mechanical analysis is capable of detecting a wide range of different mechanical relaxation processes, dielectric analysis can only detect those relaxation processes in which a dipole is mobile. The dielectric results are, however, particularly useful in examining PET, as the only significant dipoles in PET that are mobile are the carbonyl groups. Dielectric analysis can therefore be used to examine the relaxation processes that result from the motion of the carbonyl groups.

In an attempt to model the carbonyl relaxation processes quantitatively using the dielectric results the Onsager equation¹⁴ has been used. This equation relates the increase in the permittivity $\Delta\epsilon'$ to the density N and magnitude μ of the dipoles:

$$\frac{\Delta\epsilon(2\epsilon_R + \epsilon_U)}{\epsilon_R(\epsilon_U + 2)^2} = \frac{N\mu^2}{9\epsilon_0 kT}$$

where ϵ_U is the permittivity of the unrelaxed polymer, ϵ_R is the permittivity of the relaxed polymer, ϵ_0 is the permittivity constant, k is Boltzmann's constant and T is the relaxation temperature.

Using a value of $1.4D$ for the dipole moment of the carbonyls¹⁴ and assuming that these groups undergo free rotation, the dielectric increment $\Delta\epsilon'$ of the β relaxation process can be estimated. Using this technique the dielectric increment has been estimated to be approximately 4.52, a value that is considerably larger than the 0.52 obtained from the dielectric experiments. There are at least three possible explanations a priori why the observed dielectric increment is smaller than expected. Firstly, the PET samples are crystalline, so that only the carbonyl groups in the amorphous regions, or perhaps only part of the amorphous regions are mobile. It is, however, unlikely that this is the total explanation, as the samples were known to be almost completely amorphous. Secondly, if the two carbonyl groups associated with each benzene ring are in the trans conformation and the terephthalate residue rotates as a

whole, the motion will not produce a change in the dipole moment. However, again this is not a likely explanation. Finally, even if there were 180° rotations of the carbonyl groups, the magnitude of the relaxation on a site model depends¹⁸ on the free energy difference ΔG between the two states and $\Delta\epsilon\alpha\{N\mu^2/[kT(\cosh^2 \Delta G/kT)]\}$. For $\Delta G \sim 3 \text{ kcal mol}^{-1}$, $\Delta\epsilon$ falls to 10% of its maximum value. Recent research at Leeds by Nicholson and Davies¹⁹ shows that it is plausible to assume that 180° flips of the carbonyl group occur with activation energies comparable with those determined here. There is no doubt, however, that such ring flips would be detected by our n.m.r. chemical shift anisotropy measurements, reported in the companion paper¹⁰. The most likely explanation of the present dielectric relaxation results is therefore that approximately 10% of the carbonyl groups are flipping, because this proportion would not be detectable in the chemical shift anisotropy measurements. Additional experiments performed on PEN confirm the low sensitivity of the chemical shift anisotropy experiments in detecting carbonyl flips.

In interpreting the dielectric relaxation behaviour it is also necessary to take into account the findings of the mechanical and n.m.r. results obtained for these materials. By comparing dielectric and mechanical results it can be seen that the β peak in the dielectric experiments occurs at a slightly lower temperature and has a lower activation energy than the β peak in the mechanical experiments. This is consistent with the work conducted by Illers⁵, who also observed that the activation energy of the β peak is lower in the dielectric experiments than in the mechanical experiments. Furthermore, when additives were blended into the polymer, it was observed that although the dielectric peaks are not significantly affected by the additive, the high temperature side of the mechanical peak is considerably suppressed and its activation energy reduced to a value close to that observed in the dielectric experiments. It has therefore been assumed that whereas the dielectric peak results from a single relaxation process, the mechanical peak consists of two different relaxation processes, one on the high temperature side of the β peak and one on the low temperature side of the peak.

By comparing the dielectric and mechanical relaxation peaks it can be seen that the dielectric peak occurs at approximately the same position and has the same

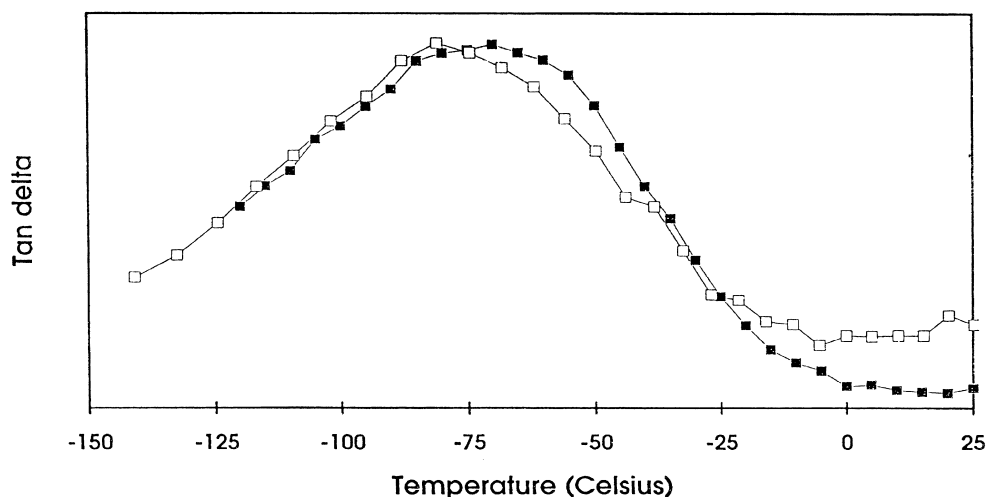


Figure 10 Graph illustrating the similarity between the dielectric relaxation peak in PET, ■, and the mechanical peak in a polymer/additive blend containing 10% DMT additive, □, at 1 Hz.

Table 7 The activation entropy ΔS for the β peak in different polymer/additive blends

Polymer/additive blend	Mechanical peak entropy ($\text{J K}^{-1} \text{mol}^{-1}$)	Dielectric peak entropy ($\text{J K}^{-1} \text{mol}^{-1}$)
PET	106	53 ± 10
PET/DMT	57	40 ± 11
PET/TPDE	37	51 ± 10

activation energy as the low temperature side of the mechanical peak. The similarity between these two relaxation processes can be seen most clearly in *Figure 10*, in which the dielectric β peak has been superimposed on the mechanical peak of a PET/DMT blend, in which the high temperature side of the β peak has been suppressed by the additive. It therefore appears that the low temperature side of the mechanical peak is closely related to the carbonyl relaxation processes that are responsible for the dielectric peak. Likewise, it appears reasonable to assume that the high temperature side of the β peak, which does not appear to be present in the dielectric results, must be due to a non-polar relaxation process. Moreover, it can be seen from the deuterium n.m.r. results¹⁰ that it is the phenyl rings and not the glycol units that are mobile during the β relaxation process. It therefore appears reasonable to conclude that the high temperature side of the β peak must be due to the motion of the phenyl rings. The additives therefore appear to suppress the phenyl ring motions on the high temperature side of the β peak rather than the carbonyl relaxation processes. The fact that the motion of the phenyl rings is suppressed by the additives is confirmed by both the cross-polarisation and static chemical shift anisotropy n.m.r. results¹⁰ which show that the mobility of the phenyl rings is greatly reduced when an additive is blended into the polymer.

One further feature of these relaxation processes which should be noted is that the motion of the phenyl rings appears to involve a considerably more co-operative motion than that in the carbonyl groups. This can clearly be seen from *Table 7*, where the activation entropy ΔS of the dielectric peak has been compared with that obtained from the mechanical peak using Starkweather's equation¹⁵⁻¹⁷. As can be seen, the entropy of the mechanical peak in PET appears to be considerably higher than that for the dielectric peak. Moreover, it can be seen from *Table 8* that the reason

Table 8 The activation entropy ΔS at different positions in the β peak of PET

Position in the β peak	Mechanical peak entropy ($\text{J K}^{-1} \text{mol}^{-1}$)	Dielectric peak entropy ($\text{J K}^{-1} \text{mol}^{-1}$)
Low temperature side	46	52 ± 10
Centre of relaxation peak	106	53 ± 10
High temperature side	129	49 ± 10

the entropy of the mechanical peak appears to be so much higher than that of the dielectric peak is that the entropy on the high temperature side of the mechanical peak is twice that on the low temperature side of the peak. This would indicate that the phenyl ring relaxation processes that occur on the high temperature side of the peak involve considerably more co-operative motions than the carbonyl relaxation processes on the low temperature side of the peak.

SUMMARY

By comparing the dielectric, mechanical and n.m.r. results, it can be seen that the β relaxation peak consists of two different relaxation processes: one on the high temperature side of the mechanical β peak and one on the low temperature side of the peak. A detailed examination of the β peak suggests that the high temperature side of the peak is probably due to the motion of the phenyl rings, whereas the low temperature side of the peak appears to be due to carbonyl relaxations. Moreover, it appears that the activation energy and the enthalpy of the phenyl ring relaxation processes are both significantly higher than those observed in the carbonyl relaxation processes. Finally, when additives are blended into the polymer it appears that the phenyl ring motions appearing on the high temperature side of the relaxation peak are suppressed considerably more than the motion of the carbonyl groups.

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