

Dielectric and mechanical characterization of aryl ester dendrimer/PET blends

Paul L. Carr*, Geoffrey R. Davies*, W. James Feast††, Neil M. Stainton† and Ian M. Ward*

IRC in Polymer Science and Technology, *University of Leeds, Leeds LS2 9JT, UK and

†University of Durham, Durham DH1 3LE, UK

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The structure–property relationships of miscible blends of two aryl ester dendrimers with poly(ethylene terephthalate) (PET) have been investigated. Although dielectric studies show relatively small effects on the glass transition process, the addition of dendrimers to PET produces a significant modification of the tensile drawing behaviour which may be interpreted in terms of the stretching of a molecular network. The smaller of the two dendrimers investigated acts as a plasticizer and reduces the chain entanglement density of the blend, whereas the larger dendrimer acts as an antiplasticizing agent and increases the entanglement density. Copyright ©1996 Elsevier Science Ltd.

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INTRODUCTION

The synthesis of macromolecular, three-dimensional species with hyperbranched architectures was pioneered by Tomalia *et al.*¹ and Newkome *et al.*² in the early 1980s. Since then, there have been many reports of the stepwise synthesis of families of such structurally well defined, regularly branched and monodisperse polymeric species. A universally accepted nomenclature has not yet been agreed and these molecules have been termed ‘starburst’ polymers, cascade molecules and dendrimers.

In general, only relatively small quantities of dendrimers can be prepared by the iterative synthetic processes involved, so it is clear that if such materials are to be of any practical value, applications must be sought in two key areas. One is the field of ‘smart technology’, for example nanoengineering and pharmaceutical applications, in which appropriately functionalized dendrimers might be used to carry out specific tasks. Alternatively, dendrimers may find application as additives in conventional materials if enhancement of physical properties and/or advantageous modification of processing behaviour results.

We have previously reported the synthesis and characterization of aryl ester dendrimers³. Here, we describe the blending of two of these materials with poly(ethylene terephthalate) (PET). Our initial interest was to examine the effect of dendrimer incorporation on the relaxation processes of the linear polymer in these blends and hence to determine structure–property relationships. More importantly, we have now studied the effect of the addition of dendrimers on the tensile drawing behaviour and on the development of molecular orientation and modulus with draw ratio. Connolly and

co-workers recently prepared aryl ester dendrimers similar to those described by us, and investigated the effect of blending them with bisphenol-A polycarbonate⁴. Dielectric characterization of the blends showed that with increasing dendrimer content, the polycarbonate glass transition temperature was progressively reduced whilst the magnitude and width of the subambient transition was greatly enhanced. Both of these observations were attributed to an increase in free volume of the system brought about by the introduction of the dendrimer molecules.

EXPERIMENTAL AND RESULTS

Preparation of the dendrimer/PET blends

Solutions of dendrimers [7], [16] (*Figure 1*) and of PET in dichloroacetic acid ($\text{CHCl}_2\text{CO}_2\text{H}$) were prepared and mixed in the appropriate ratios to form 5%, 10% and 20% w/w dendrimer/PET solutions. After stirring to ensure complete mixing, solutions were poured into excess distilled water, and white leathery solids precipitated. The solids were recovered by filtration, washed with water and extracted, using a Soxhlet apparatus, with distilled water for 24 h to remove any residual traces of dichloroacetic acid. The products were dried under vacuum (50°C, 0.1 torr) to constant mass to yield white fibrous materials. A sample of pure PET ($M_w \approx 20\,000$ supplied by ICI p.l.c.) was subjected to the same cycle of treatments to provide a reference material.

Dielectric analysis of dendrimer/PET blends

The polar nature of PET makes thermally stimulated current (t.s.c.) analysis and dielectric analysis appropriate techniques for investigation of structural motion. Both of these techniques have been used to assess changes in dielectric relaxation behaviour of dendrimer

† To whom correspondence should be addressed

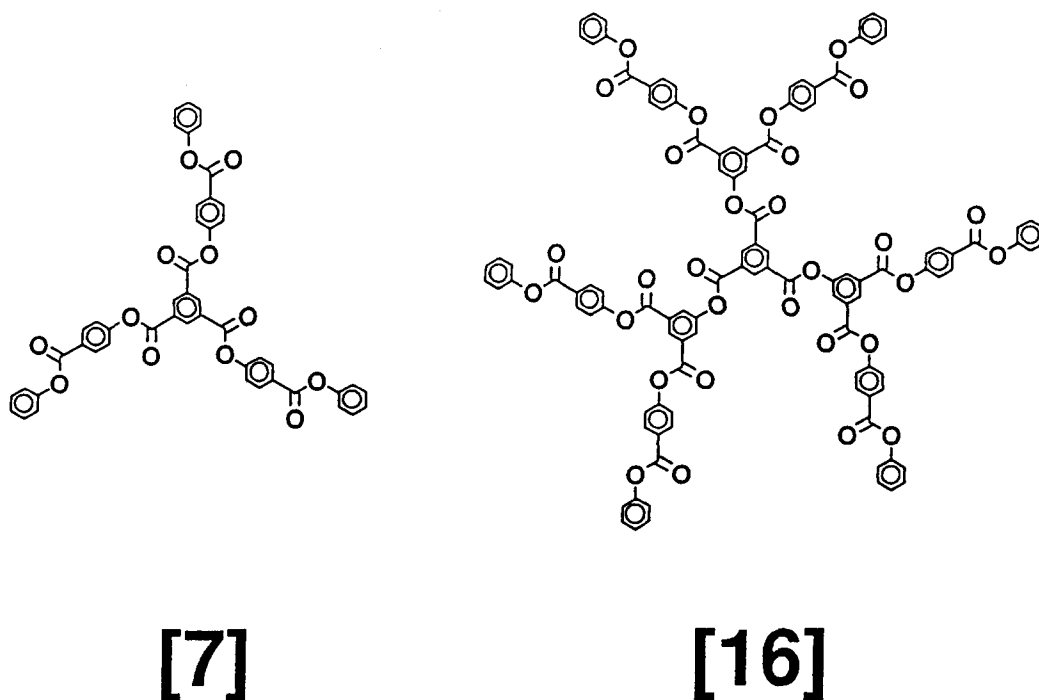


Figure 1 The [7] and [16] aryl ester dendrimers

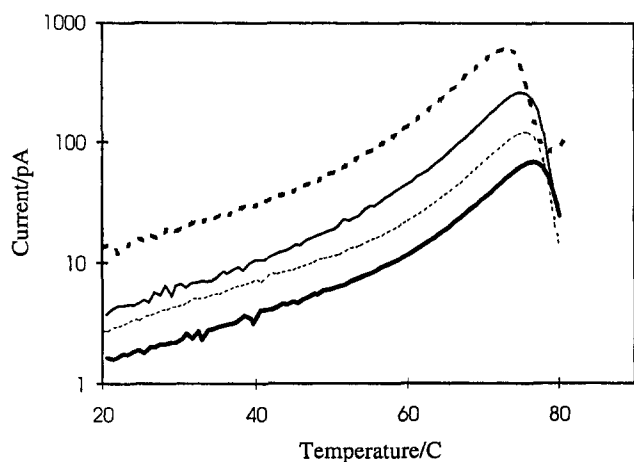


Figure 2 Thermally stimulated current data for dendrimer [7]/PET blends. The traces are vertically shifted by a scaling factor of 2 between each trace in order to show the α peak positions more clearly. —, PET; - - - - - , 5% w/w [7]/PET; —, 10% w/w [7]/PET; - - - - - , 20% w/w [7]/PET

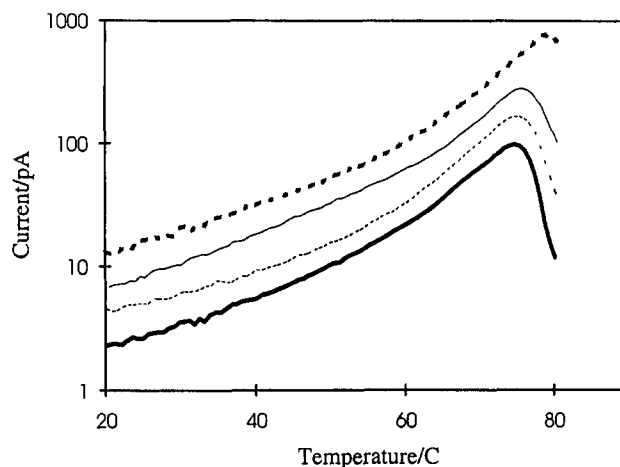


Figure 3 Thermally stimulated current data for dendrimer [16]/PET blends. The traces are vertically shifted by a scaling factor of 2 between each trace in order to show the α peak positions more clearly. —, PET; - - - - - , 5% w/w [16]/PET; —, 10% w/w [16]/PET; - - - - - , 20% w/w [16]/PET

[7] and dendrimer [16]/PET blends with respect to pure PET.

Sample preparation for t.s.c. and dielectric analysis

Thin uniform films of dendrimer/PET blends were cast from dichloroacetic acid solutions (10% w/w) onto glass cover slips coated with 30 nm thick aluminium electrodes. The films were dried on a hotplate for 3 h at 60°C followed by further drying in a vacuum oven at 10^{-3} torr and 140°C overnight. The opaque samples were melted on a hotplate at 280°C for 5 s and then quenched in a stream of compressed air to produce amorphous films. A 30 nm thick aluminium electrode was evaporated onto the polymer films and the film thicknesses measured using a micrometer gauge. Typical film thicknesses were in the range 10–15 μm .

Experimental t.s.c. analysis

The polymer films were heated rapidly to 80°C, slightly above the glass transition temperature of PET⁵, and a potential difference in the range 40–60 V was applied across the electrodes to induce dipolar alignment. The same electric field, $4.6 \text{ V } \mu\text{m}^{-1}$, was applied to all the samples. After holding at 80°C for 5 min, the samples were cooled at $10^\circ\text{C min}^{-1}$ to -80°C , the field was removed and the sample was short-circuited via a recording pico-ammeter to measure the depolarization current. After 5 min at -80°C , the samples were heated at $10^\circ\text{C min}^{-1}$ to 90°C to observe the depolarization current as a function of temperature. The results for the dendrimer [7]/PET blends and dendrimer [16]/PET blends are shown in Figures 2 and 3 respectively. In

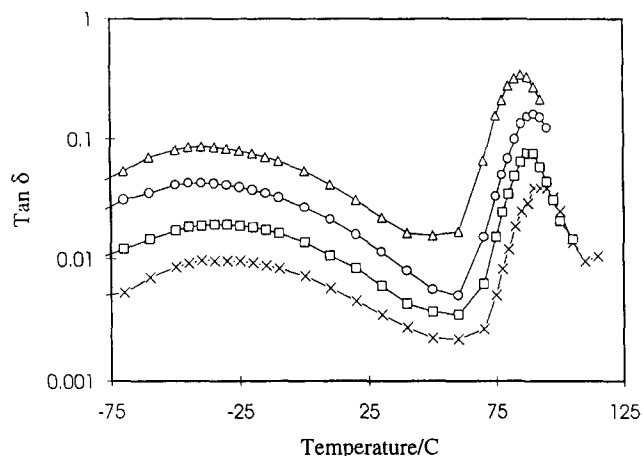


Figure 4 Dielectric loss at 1 kHz versus temperature for dendrimer [7]/PET blends. The traces are vertically shifted by a scaling factor of 2 between each trace in order to show the α peak positions more clearly. x, PET; □, 5% [7]/PET; ○, 10% [7]/PET; △, 20% [7]/PET

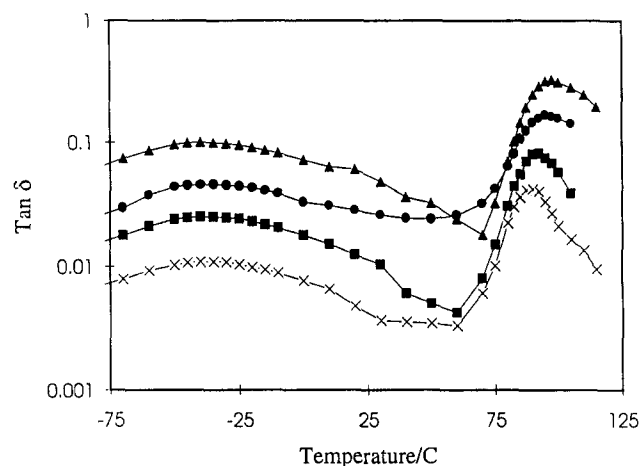


Figure 5 Dielectric loss at 1 kHz versus temperature for dendrimer [16]/PET blends. The traces are vertically shifted by a scaling factor of 2 between each trace in order to show the α peak positions more clearly. x, PET; ■, 5% [16]/PET; ●, 10% [16]/PET; ▲, 20% [16]/PET

each figure the raw data have been vertically shifted so that the shifts in the peaks can be seen clearly.

Experimental dielectric analysis

The capacitance and the dielectric loss tangent, $\tan \delta$, were measured at 1 kHz using a three-terminal cell and a General Radio capacitance bridge with an applied voltage of 3 V r.m.s. Measurements were made from -80°C to above the glass transition temperature. The variation of $\tan \delta$ as a function of temperature for the dendrimer [7]/PET and dendrimer [16]/PET blends are shown in Figures 4 and 5 respectively. Again, the raw data have been vertically shifted to allow easier comparison of the curves.

Discussion and interpretation of t.s.c. and dielectric measurements

The dielectric and t.s.c. analyses of the dendrimer/PET blends yield relaxation spectra of broadly similar appearance consisting of a relatively sharp peak at

elevated temperature and a broader subambient peak of much lower intensity.

Detailed examination of the raw t.s.c. data for dendrimer [7] and [16]/PET blends shows that increasing dendrimer incorporation appears to have little influence on the intensities of observed peaks, indicating little or no suppression of molecular relaxation processes. It is probable that the very small differences in the recorded α peak intensities are attributable to errors associated with measurement of film thicknesses, resulting in small differences in the applied poling field. However, in the dendrimer [7]/PET blends, there is a slight reduction in the temperature at which the α peak occurs with increasing dendrimer incorporation, whereas in the case of the dendrimer [16]/PET blend series increasing the proportion of dendrimer within the blend appears to have the opposite effect (Figures 2 and 3). As in the dielectric relaxation spectra, broad peaks in the low temperature β transition region could be detected but the data were very noisy in this region making the accessible information of doubtful value, and consequently the low temperature data have not been reproduced here.

Similar trends are seen in the dielectric relaxation spectra. Again, dendrimer [7] blends show a depressed α peak temperature with increasing dendrimer incorporation but in the case of dendrimer [16] blends the situation is less well defined (Figures 4 and 5), although a small increase in glass transition temperature (T_g) is suggested.

Lowering of the α peak temperature, as observed for dendrimer [7] blends, is equivalent to T_g depression. Such an effect is commonly associated with plasticization, and is explained on the basis that small molecules separate the polymer chains and increase the free volume of the system, disrupting interchain interaction and making reptation easier. This aids chain slippage which at a macroscopic level leads to increased flexibility and mechanical toughness at the expense of lowering the mechanical strength. Conversely, an increase in the α transition temperature is associated with increased intermolecular interaction such as an increase in cross-link density, entanglement or sample crystallinity; however, in the case of the latter, this is accompanied by a decrease in the peak intensity⁶.

On the basis of these experimental data, dendrimer [7] appears to behave as a plasticizer whereas dendrimer [16] shows some evidence of antiplasticizer behaviour. This was a surprising observation, bearing in mind the similarity of the dendrimer structures, and in order to investigate it, an investigation of the deformation behaviour of the blends has been undertaken by studying the effect of tensile drawing on molecular orientation and mechanical properties.

Sample preparation for tensile testing

Solutions of dendrimer/PET blends in dichloroacetic acid (10% w/w) were cast onto glass slides to form thin uniform films. Following the same drying procedure used for samples prepared for t.s.c. and dielectric analysis, the films were melted on a hotplate at 300°C for, at most, 15 s then removed and quenched in a stream of cool compressed air to minimize crystallization. The films were removed from the glass substrate by soaking in water for 24 h followed by prising them from the glass with a sharp blade.

Samples, typically $50\text{ mm} \times 2\text{ mm} \times 40\text{ }\mu\text{m}$ thick, were

cut from the amorphous films and drawn at 80°C in an Instron environmental chamber at a draw speed of 50 mm min⁻¹ to draw ratios between 3 and 6. The draw ratios were determined from the displacement of ink spots on the drawn film from their initial spacing of 2 mm on the unoriented material. Thickness measurements of the oriented samples, typically 10–15 μm, were derived from sample mass, length and width measurements, assuming a typical sample density of 1.35 g cm⁻³ (ref. 5). Birefringence measurements were made using a Zeiss 'Polmi A' polarizing microscope with an Ehringhaus tilting plate compensator attachment. It was not possible to remove the 20% w/w dendrimer/PET blends from the glass substrate because of their brittle nature. Consequently, no mechanical properties have been determined for these materials.

Transesterification

Polyester blends are known to undergo ester exchange in the melt. If the dendrimer/polyester blends were to undergo transesterification during formulation or processing, changes in molecular structure and molecular weight distribution would result, leading first to branched structures and eventually to extensively cross-linked networks. We carefully minimized melting and times spent at elevated temperature in order to avoid transesterification. To investigate the possibility that, despite this care to avoid it, transesterification had occurred in our samples, several attempts were made to extract unchanged dendrimer from free-standing films of the blended material cast from dichloroacetic acid solution. Prolonged Soxhlet extraction with chloroform followed by evaporation of solvent resulted in recovery of slightly more material than required for complete extraction of both dendrimers [7] and [16] from the blended materials; analysis of the extract by ¹H nuclear magnetic resonance (n.m.r.) spectroscopy indicated that it consisted of dendrimer plus traces of low molecular weight PET. These observations indicate that, within the limits of the experimental technique, essentially complete extraction of both dendrimers [7] and [16] occurred, and the observations are consistent with the absence of detectable transesterification during the preparation or subsequent processing of the blends to form the thin films used in this study.

Results and interpretation of tensile testing

In *Figure 6* the initial modulus of drawn samples is plotted as a function of birefringence, a measure of overall molecular orientation, for both dendrimer/PET blends and for the PET control samples. The solid line indicates the values obtained for PET film formed by melt extrusion followed by drawing at 80°C (ref. 7). It is clear that the incorporation of the dendrimers does not produce a significant change in the well-known correlation between modulus and overall molecular orientation. The close correlation of the PET values with those previously determined, particularly at lower birefringence, indicates that the film casting procedure from dichloroacetic acid is a valid preparative method giving results comparable with those from other techniques. The deviation from the reference data at high draw ratios is probably caused by variability in the solvent-cast films.

In *Figure 7* the initial modulus is plotted against draw ratio, λ . In contrast to *Figure 6*, this plot suggests that the

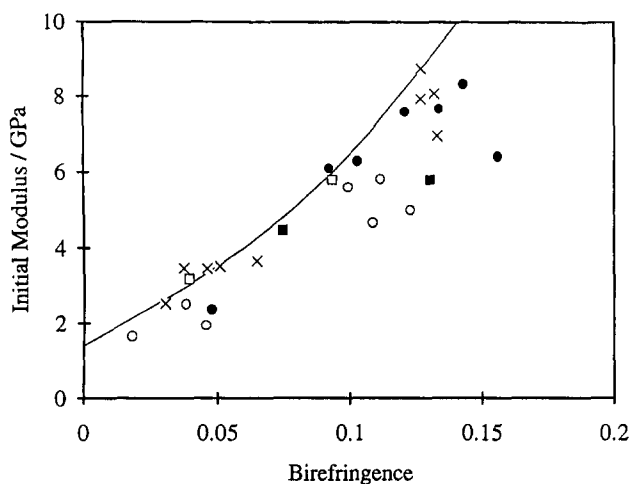


Figure 6 Initial modulus versus birefringence of drawn films. —, PET (reference); ×, PET (measured); □, 5% [7]/PET; ○, 10% [7]/PET; ■, 5% [16]/PET; ●, 10% [16]/PET

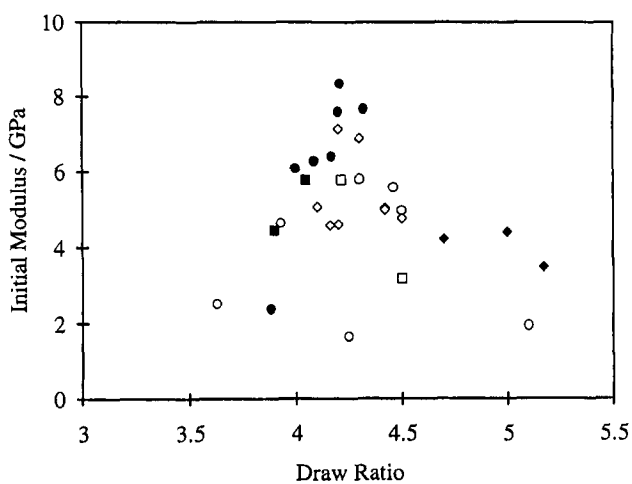


Figure 7 Initial modulus versus draw ratio. ◇, 2.5% [7]/PET; □, 5% [7]/PET; ○, 10% [7]/PET; ◆, 2.5% [16]/PET; ■, 5% [16]/PET; ●, 10% [16]/PET

dendrimer [7] blend and the dendrimer [16] blend may process differently. The scatter is again probably due to variability in the solvent-cast films, but this evidence was sufficient to initiate a more thorough investigation of the situation, concentrating on the 10% blends. These results are shown in *Figure 8* where the birefringence of the PET and the 10% blends of dendrimer [7] and dendrimer [16] are plotted as a function of $\lambda^2 - 1/\lambda$. Plotting the molecular orientation as a function of a processing parameter clearly differentiates between the two blends and the PET, confirming and reinforcing the tentative initial modulus results shown in *Figure 7*.

Stress optical behaviour⁸⁻¹⁶

In the Kuhn and Gr \ddot{u} n stress optical theory for rubbers⁸, a polymer network may be regarded as a series of chain segments attached to one another by crosslinks or entanglement points. Each chain segment can be considered to comprise a number of freely jointed rigid rods. These random rigid rod links correspond to a number of monomer units. Entanglement points are not

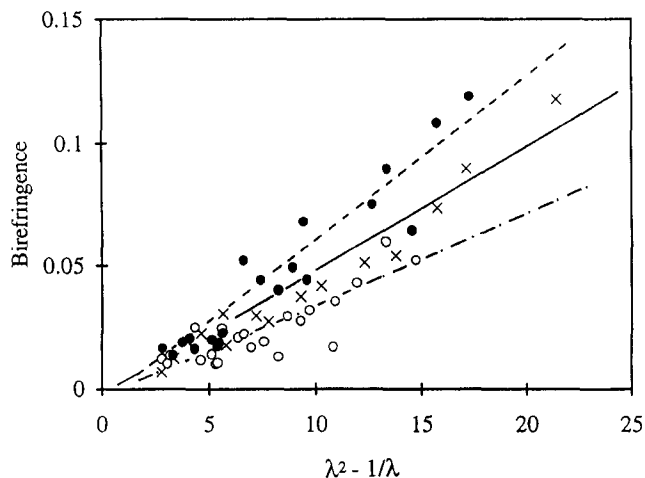


Figure 8 Birefringence versus $\lambda^2 - 1/\lambda$. —, PET (reference); ×, PET (measured); ○, 10% [7]/PET; ●, 10% [16]/PET

necessarily conventional covalent crosslinks; even in linear polymers, physical crosslinks arise as a consequence of trapped chains, loops and knots. This concept of a molecular network has been used by a number of authors to compare the drawing behaviour of polymers^{9,10}.

Molecular orientation and thus stress may be frozen into film samples during the drawing process if they are cooled below the glass transition temperature with the stress still in place. This may be recovered as a shrinkage stress on reheating above T_g whilst holding at constant strain. Measurement of the peak shrinkage stress relates to the frozen-in stress produced by stretching the network, as these measurements do not include the viscous term involved in measurements of the drawing stress. According to the molecular theory of rubber elasticity, the tensile stress, σ , on the strained cross-section is given by

$$\sigma = NkT(\lambda^2 - 1/\lambda) \quad (1)$$

where N is the number of chain segments per unit volume, k is the Boltzmann constant, T is the drawing temperature and λ is the draw ratio.

The optical anisotropy, Δn , is given by

$$\Delta n = \frac{2\pi(\bar{n}^2 + 2)^2}{45\bar{n}} N(\alpha_1 - \alpha_2)(\lambda^2 - 1/\lambda) \quad (2)$$

where \bar{n} is the mean refractive index and $(\alpha_1 - \alpha_2)$ is the optical anisotropy of the random link.

Hence the stress optical coefficient, $\Delta n/\sigma$, is given by

$$\frac{\Delta n}{\sigma} = \frac{2\pi(\bar{n}^2 + 2)^2}{45\bar{n}kT} (\alpha_1 - \alpha_2) \quad (3)$$

If the rubber elasticity theory applies and uniaxially oriented film can be considered as a strained network, heating an optically anisotropic film above the T_g should release frozen-in strain that is proportional to the initial optical anisotropy, Δn .

Sample preparation for shrinkage force measurements

Films with draw ratios ranging between 1.6 and 5 were prepared using solvent casting and Instron drawing techniques under the same conditions as those used for tensile testing samples. Only pure PET and 10% w/w dendrimer/PET blends were used in the course of this study.

Results of shrinkage force experiments

As discussed previously, Figure 8 shows clearly that the PET and the PET/dendrimer blends process differently. Figure 8 also suggests that the birefringence of the PET and the blends are separate linear function of $\lambda^2 - 1/\lambda$ over a wide range of draw ratios, as suggested by equation (2). However, the relation between the shrinkage stress and the birefringence of the drawn films, shown in Figure 9, does not distinguish between the PET and the blends. Furthermore, in agreement with previous work¹⁰, Figure 9 shows that the simple model of rubber elasticity is only valid for birefringences, Δn , less than 0.02, which in these experiments corresponds to draw ratios less than 2. Therefore it is this linear region that must be used to calculate the optical anisotropy of the random link ($\alpha_1 - \alpha_2$).

Figure 10 shows shrinkage stress as a function of draw ratio and illustrates differences between pure PET and the two dendrimer blends in a similar way to Figure 8. Dendrimer [7] blends exhibit lower shrinkage stress for a given draw ratio than PET, whereas for dendrimer [16] blends the opposite is true. Figure 10 also shows that the solvent-cast PET samples exhibit strain softening in the

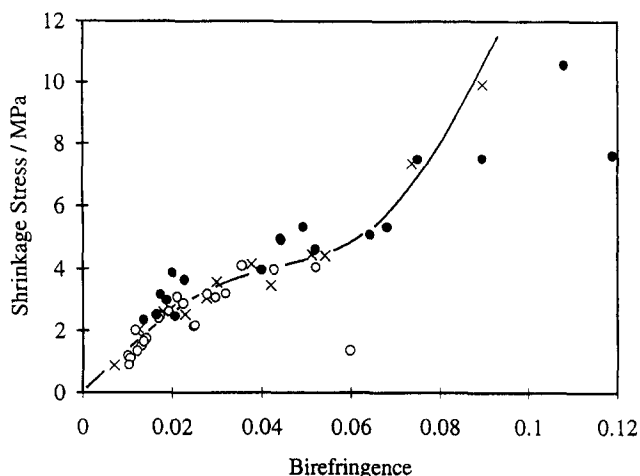


Figure 9 Shrinkage stress versus birefringence. —, PET (reference); ×, PET (measured); ○, 10% [7]/PET; ●, 10% [16]/PET

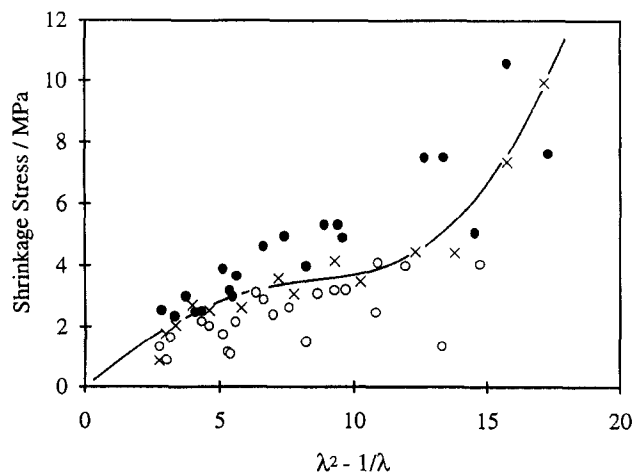


Figure 10 Shrinkage stress versus $\lambda^2 - 1/\lambda$. —, PET (reference); ×, PET (measured); ○, 10% [7]/PET; ●, 10% [16]/PET

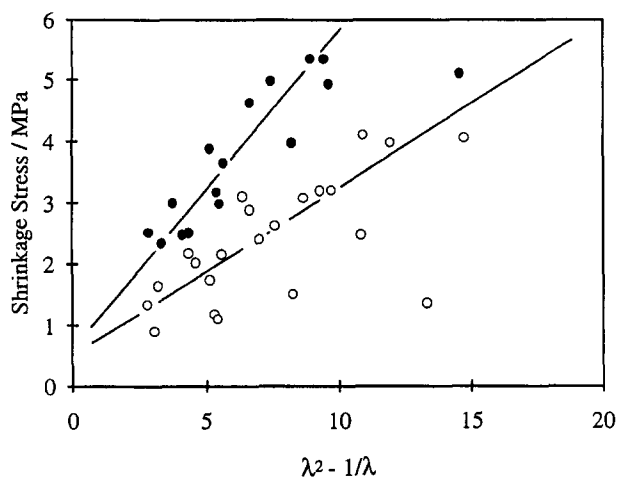


Figure 11 Shrinkage stress versus $\lambda^2 - 1/\lambda$. O, 10% [7]/PET; ●, 10% [16]/PET

draw ratio range 2–3.5 and strain hardening above this draw ratio, in agreement with previous work¹⁰. However, the dendrimer [7]/PET blend shows no evidence of strain hardening, while in the dendrimer [16]/PET blend there is less evidence of strain softening. Figure 11 is an expansion of the dendrimer [7] and [16] blend plots in Figure 10 for low shrinkage stress and emphasizes the difference between the two materials.

DISCUSSION

A significant difference in the tensile drawing behaviour of PET and the PET/dendrimer blends is illustrated by Figures 8, 10 and 11. Dendrimer [7] appears to plasticize the PET in the conventional manner by increasing the free volume of the system and reducing chain interactions, which leads to increased chain slippage and reduced chain orientation for a given draw ratio. In contrast, incorporation of dendrimer [16] leads to enhanced orientation for a given draw ratio, thus exhibiting an antiplasticization effect. This can be explained in terms of an interaction between the dendrimer and the PET chains that is sufficiently large to more than compensate for the reduced interaction between the PET chains themselves. If this is the real explanation, it is remarkable that such a relatively small molecule can become so effectively entangled.

Since it is known that the drawing temperature has a significant effect on the birefringence/draw ratio relationship of drawn films⁷, this requires consideration in any analysis of these experimental observations. As increasing proportions of dendrimers in the blends have an appreciable effect on T_g , it is necessary to understand the effect that different drawing temperatures with respect to T_g have on the orientation of PET. Padibjo and Ward⁷ have shown that although an increase in drawing temperature with respect to T_g leads to lower orientation for a given draw ratio and *vice versa*, this effect is small with respect to the birefringence effects recorded by ourselves and would at most be expected to provide approximately a 20% contribution to the observed effects.

The complete extraction of dendrimers from the blended films demonstrates that the observed effect is

not due to any significant level of chemical crosslinking brought about by transesterification, although we cannot absolutely eliminate the possibility of very low levels of reaction, leading to some branching. Since every precaution has been taken to minimize the crystallinity of the cast films, it is also thought unlikely that the effect is due to variable sample crystallinity. A further consideration is the contribution to the birefringence made by the dendrimer molecules themselves when they are oriented during the drawing process. We believe that at a concentration of around 10% w/w, any effect would be too small to explain the large changes in birefringence we have measured, particularly since the observed differences are in opposite senses depending on the type of dendrimer incorporated.

Consideration of the experimental data in terms of the molecular theory of the stress optical behaviour of rubber-like networks allows a quantitative interpretation in terms of entanglement at a molecular level. Thus from Figure 9, as was noted above, the simple elasticity theory is valid for $\Delta n < 0.02$, where the curve gradient and hence the stress optical coefficient, $\Delta n/\sigma$, is constant. From an expansion of this region it was deduced that the gradient and thus the polarizability of the random link ($\alpha_1 - \alpha_2$) is substantially the same for PET and the blended materials. A least-squares fit of all the data points within this region passing through the origin yields a mean stress optical coefficient of $6.90 \times 10^{-9} \text{ N}^{-1} \text{ m}^2$ which, from equation (3), gives the polarizability anisotropy of the random link ($\alpha_1 - \alpha_2$) as $1.85 \times 10^{-29} \text{ m}^3$, taking the mean refractive index of the polymer film as 1.6 (ref. 5) and the drawing temperature as 80°C. This compares favourably with published data^{9,10} which indicate that ($\alpha_1 - \alpha_2$) lies between 0.7×10^{-29} and $1.9 \times 10^{-29} \text{ m}^3$. Although it is recognized that the polarizability of each dendrimer is likely to be different from that of the PET random link, it is thought that the degree of dendrimer incorporation is sufficiently small that this is unlikely to affect the results significantly.

The value of N obtained for the dendrimer [7] blend is significantly lower than that for PET and shows the plasticization effect, while N for the dendrimer [16] blend shows evidence of a more entangled network than PET. These differences are of the order of those obtained when comparing the tensile drawing of other polymers such as PPS and PEMT¹³. In this respect it is interesting to note that the increase in entanglement density obtained by the addition of 10% w/w dendrimer [16] is, remarkably, very nearly equivalent to an increase of one entanglement per added dendrimer molecule.

From the experimentally determined value of N for PET, the mass of each chain segment between entanglement points can be determined. This is calculated to be 5140 assuming a sample density of 1.35 g cm^{-3} (ref. 5). As each monomer unit has a mass of 192, this corresponds to approximately 27 monomer units per chain segment. The value of ($\alpha_1 - \alpha_2$) can be compared to the value computed for a fully extended monomer¹² of $0.52 \times 10^{-29} \text{ m}^3$ to yield a value of 3.6 monomers per

Table 1 Number of chain segments per unit volume for film specimens

Sample	PET (ref.)	PET (measured)	10% [7]/PET	10% [16]/PET
$N/10^{26} \text{ m}^{-3}$	1.72	1.58	1.02	2.07

random link, thus implying a mean chain composition of 7.5 random links.

CONCLUSION

Both dielectric measurements and tensile testing of dendrimer/PET blend films indicated that incorporation of dendrimers has a noticeable effect on the material processing characteristics. Furthermore, the observed effect is dependent on the size or shape of the added dendrimer. Dendrimer [7] acts as a plasticizer and reduces the extent of chain interaction whereas dendrimer [16] acts as an antiplasticizing agent and enhances the overall intermolecular interactions. These effects have been quantified by stress optical measurements. It has been shown that dendrimer [7] has the effect of reducing the number of effective physical crosslinks or chain entanglements per unit volume with respect to a pure PET sample, whereas dendrimer [16] incorporation leads to a substantial increase in chain entanglement density (see *Table 1*). This may be accounted for in a simplistic manner by envisaging the PET chains as becoming interwoven with dendrimer [16], the larger and more highly branched dendrimer, thus increasing the extent of physical entanglement and overall interchain interaction. In contrast, dendrimer [7], the smaller and structurally simpler dendrimer, is less able to bind the PET chains together and disrupts the intrinsic interchain interaction.

On a macroscopic scale, although the tensile modulus for given molecular alignment as measured by optical anisotropy is not noticeably influenced by dendrimer incorporation, the extent by which a film must be drawn to achieve that orientation shows a marked dependence on the type of dendrimer added. Dendrimer [7]/PET films must be drawn to a greater extent than pure PET

films to obtain the same degree of orientation, whereas for dendrimer [16]/PET films the reverse is true. Although the behaviour of dendrimer [7] is typical of common plasticizers, the enhanced molecular orientation for a given draw ratio exhibited by blends containing dendrimer [16] is a desirable phenomenon believed to be of potential value in the production of oriented PET fibres and films.

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