

Mechanical and Thermal Properties of Poly(ethylene terephthalate) Fibers Crosslinked with Disulfonyl Azides

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ABSTRACT: A novel method for the crosslinking of poly(ethylene terephthalate) fibers is described using 1,6-hexanedisulfonyl azide, 1,3-benzenedisulfonyl azide, and 2,6-naphthalenedisulfonyl azide. The azides are diffused into poly(ethylene terephthalate) fibers (Dacron) from perchloroethylene solution, and the fibers are heat treated to bring about decomposition of the sulfonyl azide and give rise to crosslinking. A study is made of the mechanical and thermal properties of the resultant fibers, which are changed considerably in comparison to the untreated fiber. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1517–1527, 2002

Key words: mechanical and thermal properties; poly(ethylene terephthalate); crosslinking; disulfonyl azides

INTRODUCTION

Poly(ethylene terephthalate) (PET) fibers have become one of the most important textile fibers and account for over 50% of worldwide synthetic fiber production.¹ These fibers are characterized² by their high tenacity, extensibility, and modulus; they also have good resistance to the effects of humidity, acids, oils, and solvents. Many of these properties are due to the highly compact and crystalline nature of the polymer in the drawn fiber.

Because of the highly crystalline nature of PET fiber and its high glass-transition temperature (T_g), the diffusion of organic substances into the fibers can be difficult and modification of PET fibers has in the main been carried out during synthesis via the incorporation of comonomers, by the adjustment of molecular weight, and by vari-

ations in spinning conditions. These routes have been used to bring about significant changes in the dyeing properties,³ shrinkage,⁴ and pilling performance^{4,5} of commercial PET fibers. However, PET can be modified using finishing treatments, particularly to change the surface; for example, fluorocarbon residues⁶ are incorporated to give rise to enhanced oil repellency, polyether residues are added to increase wettability, and surface modification is made for use in composites⁷ where adhesion properties are of great importance. It is relevant that this latter effect was achieved making use of sulfonyl azide (SA) functional reagents.

The SA group was also used as an alternative method of functionalization for reactive dyes,^{8–15} which were applied to nylon,¹⁰ polypropylene,⁸ and cellulose acetate.⁹ The work of McDarmid et al.^{8–11} showed that fixation of these dyes was around 75% when applied via transfer printing to nylon and polypropylene, although it was realized that the sublimation properties of the dyes were substantially reduced as a result of their relatively high molecular weight and polarity. Their

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work and that of Holt and Milligan¹² showed that fixation was reduced if the dyes were applied from an aqueous dye bath, which was due to the hydrolysis of the SA to sulfonic acid. SA functionalized dyes were also applied to PET^{13,14} with high efficiency; an analysis of the substrate after fixation revealed that a reaction occurred only with the aromatic ring of the polymer, giving rise to aromatic sulfonamide and a small amount of an azipine ring structure, which formed from the ring expansion of the intermediate.

Following our earlier study of the crosslinking of an acrylic fiber with disulfonyl azides (DSAs),^{16,17} it was decided to attempt to crosslink PET by use of the thermal decomposition of DSAs. It seemed likely from the work done using SA functionalized dyes⁸⁻¹⁵ that a bifunctional analogue ought to be able to crosslink PET, especially if applied from an essentially anhydrous medium. Thus, a selection of DSAs that were synthesized earlier¹⁷ were applied under different conditions to investigate their potential for crosslinking PET. The physical and thermal properties of the resultant fibers were determined.

EXPERIMENTAL

Materials

1,6-Hexanedisulfonyl azide (1,6-HDSA), 1,3-benzenedisulfonyl azide (1,3-BDSA), and 2,6-naphthalenedisulfonyl azide (2,6-NDSA) were synthesized as described earlier.¹⁷ The PET was obtained as a partially oriented, continuous-filament yarn (167/34 dtex), which was supplied as grade 3 Dacron (Dupont). This yarn consisted of 34 filaments of round cross section giving a yarn count of 167 dtex. Analytical grade perchloroethylene (PER) and standard grade *o*-chlorophenol (OCP, Aldrich) were used as supplied. Undrawn PET yarns (~800/12 dtex) were available from the Department of Textiles (University of Leeds).

Preparation of Crosslinked Samples

A solvent dyeing procedure was used. Solutions were prepared in stainless steel tubes (100 mL) that contained 20 mL of PER, up to 20% on mass of fiber (omf) of the appropriate DSA, 2 g of PET yarn (prepared as hanks in such a way as to minimize entanglements during treatment), and

0.2 g (10% omf) of distilled water. The tubes were then sealed and fitted to a temperature calibrated rotary dyeing machine. A variety of treatment conditions were used: 100°C for 2 h, 110°C for 1 h, 120°C for 40 min, 130°C for 30 min, and 140°C for 20 min. The amount of azide (in 2.5% increments) used in the treatments was varied from 0 to 20% omf. Distilled water was added to the dye baths because this improves the equilibrium uptake of dyestuffs from PER dye baths by up to a factor of seven¹⁸⁻²⁰; this effect is thought to be due to the increased pressure within the system caused by the formation of a water-PER azeotrope, which thus increases the partitioning of the dye in favor of the fiber. Treatment times were selected so that they were twice the time required for equilibrium dyeings to be obtained when dyeing PET with typical disperse dyes from PER.^{2,18-22} The same procedure was used for the undrawn yarn samples but was limited to two concentrations of azide (10 and 20% omf).

After the PER treatment the tubes were quickly removed from the machine and the azide impregnated hanks were gently squeezed while hot and washed quickly with water, cold PER, and finally water; this was to prevent any azide from crystallizing on the fiber surface. Samples were then oven dried at 90°C for about 2 h to remove most of the PER from the fibers. (Later analysis showed that samples retained 3-4% PER, which was removed in the subsequent heat treatment at 200°C before generation of the nitrene species.) The hanks were then placed in a dry air stenter (Werner-Mathis) at 200°C for 20 min in order to decompose the DSA and hopefully crosslink the PET. The samples were then washed in warm water and dried in air.

Preliminary Investigations

A small sample (~0.1 g) of fiber was placed in a test tube with 10 mL of OCP at 90°C and shaken for 30 min. Observations of gelling and solubility were made. Any coloration of the samples was also recorded. Samples were also heated on a hot-stage microscope in order to record any discernible changes in the melting point and melt viscosity. Typically samples were heated to 300°C at 20°C/min. Elemental analyses for N and S were carried out on some samples after the pick-up of azide and before the treatment at 200°C.

Measurement of Mechanical Properties

The mechanical properties of the fibers such as the initial Young's modulus, tensile strength, and breaking extension were determined from their load–elongation curves. These curves were recorded on an Instron 1026 CRE tensile testing machine with computer control (series IX software) in accordance with the appropriate standards (British Standards 2545, EN 20139, and 3411). Individual fibers were very carefully extracted from yarns removed from the hank samples and taped onto cardboard squares with an inner dimension of 20 mm. The framed fibers were then clamped onto the Instron and their load–extension curves obtained. At least 20 fibers were tested from each sample and their averages and standard deviations were compared. The load cell used was 500 g (max); full-scale load was set to 50 g, and the crosshead speed was 50 mm/min. All fibers were conditioned for at least 24 h at $20 \pm 2^\circ\text{C}$ and $65 \pm 2\%$ relative humidity before testing.

Measurement of Thermal Properties

The thermal properties of the samples were measured using two consecutive DSC runs. The first DSC run gave information concerning the melt properties of the fibers and yielded an isotropic amorphous melt in the untreated sample that was then quenched so that a second run could be performed to yield information concerning the T_g and the crystallization and melting behavior of the quenched material. The fibers were finely chopped and placed in a DSC sample pan and the temperature was raised to 320°C and held for 2 min, giving the first DSC trace. The pan was then removed and quickly pressed against an ice cooled dry iron rod to quench the sample, and the quenched material DSC trace was obtained, the second run. The DSC traces were measured using a Dupont 910 DSC equipped with a TA 2000 control unit at a heating rate of $20^\circ\text{C}/\text{min}$ under an atmosphere of nitrogen (50 mL/min). The thermal stability was also assessed using a Dupont 951 TGA equipped with the same TA 2000 control unit at a heating rate of $20^\circ\text{C}/\text{min}$ with an atmosphere of nitrogen (50 mL/min).

RESULTS AND DISCUSSION

Preliminary Observations

A set of samples was obtained for each of the three DSAs under each of the five different treat-

ment conditions; each set contained samples treated with solutions containing between 2.5 and 20% omf of crosslinking agent. Blank standard treated samples were also produced via identical conditions but omitting the azides; these samples are henceforth referred to as the standard. It must be emphasized that the values of the azide concentrations used are much greater than the amounts taken up by the fibers, which we estimate (see later) to be not greater than 3% omf. This low level of azide uptake prevented the use of a spectroscopic means to evaluate the crosslinking process.

Visual inspection of the samples showed that, although no color was imparted to the fibers during the PER treatment, the subsequent heat treatment produced fibers of varying shades of brown. The coloration was related to the amount of azide applied so that for those samples treated with 1,6-HDSA and 1,3-BDSA there was a progression from slight yellowing (2.5%), through light brown (10%), to eggshell brown (20%), which was essentially independent of the conditions employed. Those samples treated with 2,6-NDSA at 130 and 140°C were browner, varying from yellow (2.5%), through eggshell (10%), to dark brown (20%). Samples treated with 2,6-NDSA at $100\text{--}120^\circ\text{C}$ were discounted from further study because of the very high discoloration, which was thought to be due to the lower solubility of 2,6-NDSA in the PER dye bath at these temperatures giving rise to high levels of surface deposition or near surface agglomeration (i.e., over dyeing). The coloration of the fibers was thought to be mainly attributable to polymerization of the azides within the fiber and as such was a function of the diffusional properties of the azide; similar variations in coloration were observed in our earlier studies on acrylic fiber treatments.¹⁶ The standard samples showed no coloration.

Solubility and Melting Behavior

The solubility studies of those samples treated with PER solutions of azide at 140°C and subsequently heat treated at 200°C showed that the samples were mainly largely soluble. The only samples that showed some insolubility after 30 min in OCP (90°C) were those of 1,6-HDSA and 1,3-BDSA, which had been treated with more than 10% omf of azide, and these were characterized by the formation of fibrous gel particles. The other samples displayed retarded dissolution of

up to 10 min, depending on the amount of agent applied, and no gel could be observed in the OCP. The standard samples dissolved in less than 1 min. Further studies of gel contents were not done because of the hazardous nature of OCP and because the preliminary studies gave rise to gel contents of less than 15%, making the insoluble material difficult to recover; however, we believe that in this case the measurement of the gel contents would be misleading due to the semicrystalline morphology of the PET. These results were in contrast to the earlier study using the same azides on Courtelle fiber.¹⁶ It was quite clear that crosslinking occurred in the latter system because the fiber form was maintained in DMF, although obviously considerable swelling occurred. In the PET we expected that the azides would only be taken up in the amorphous regions of the fiber so that any crosslinking would only occur in this part of the fiber. It could be that low levels of crosslinking in the amorphous regions might occur without the formation of much observable gel and certainly we could not expect to maintain the PET in fiber form because the crystalline regions would not be crosslinked and would therefore tend to cause fiber disruption as they swelled and dissolved. Such arguments prompted some experiments with undrawn PET fiber where much more crosslinking should be possible, given the essentially amorphous nature of the fiber. Samples treated with 20% solutions of any of the azides maintained their fiber form in OCP at 90°C while those treated with 10% were substantially insoluble. These experiments confirmed that the azides studied do in fact crosslink PET, although we believe crosslinking only occurs in the amorphous regions.

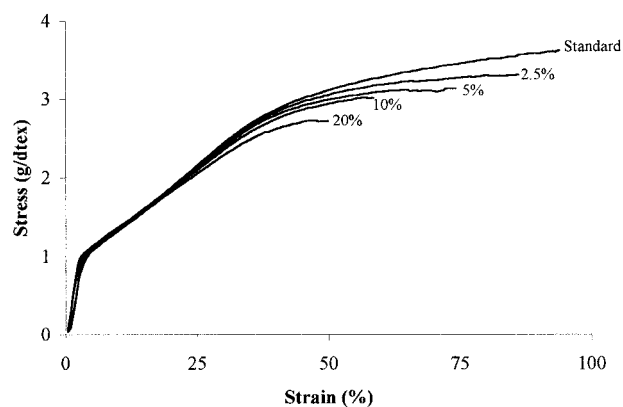


Figure 1 The stress-strain curves of PET fibers treated with 1,6-HDSA.

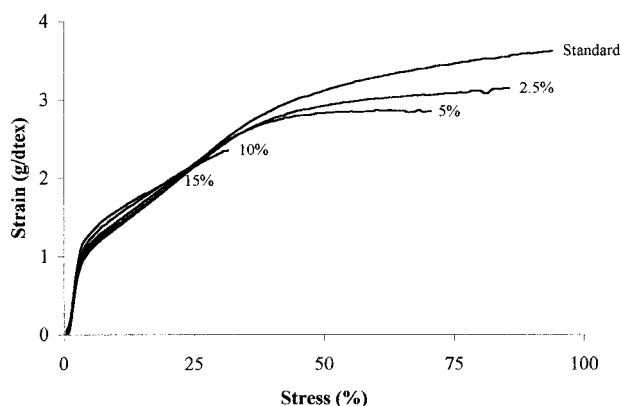


Figure 2 The stress-strain curves of PET fibers treated with 1,3-BDSA.

Samples were viewed on a hot-stage microscope while being heated to 300°C at 20°C/min and they showed melt behavior that varied with the degree of crosslinking. Those samples treated with relatively high amounts (20% omf) of DSA gave melts of notably higher viscosity than the standard sample and had a speckled appearance. The effect was most pronounced with the 1,3-BDSA and 2,6-NDSA samples, which were slow to lose their fiber form above 250°C. The samples prepared from the amorphous PET were found to only melt in the center, producing a hollow fiber that did not rupture on prolonged heating but darkened, presumably carbonizing at higher temperatures (~350°C). The implication was that the coarse amorphous PET filaments were crosslinked only in the outer 20–30 μm of the fiber diameter. Given the relatively large diameter of these fibers (80–90 μm), it is not surprising that limited diffusion of the azides had occurred.

Mechanical Properties

Effect of Azide Concentration on Tensile Properties

The stress-strain curves of selected samples treated with different concentrations of azide in PER at 140°C for 20 min followed by heating at 200°C for 20 min are shown in Figures 1 and 2. The most striking feature of these curves is the rapid decrease observed in the extensibility and tenacity of the samples on increasing the azide concentration and therefore increasing the degree of crosslinking. The modulus and the elastic yield point appear to be almost unchanged, except at higher concentrations of azide where the yield

Table I Mechanical Properties of Fibers Crosslinked with 1,6-HDSA

1,6-HDSA Concn (% omf)	Extensibility		Tenacity		Modulus	
	%	% of Std	g/dtex	% of Std	g/dtex	% of Std
Std (0.0)	93.9 (7.8)	100.0	3.66 (0.19)	100.0	36.3 (5.5)	100.0
2.5	84.0 (7.5)	89.5	3.37 (0.16)	92.1	34.2 (4.7)	94.0
5.0	71.2 (5.0)	75.8	3.16 (0.13)	86.4	33.9 (4.1)	93.2
7.5	73.2 (7.9)	77.9	3.11 (0.17)	84.9	37.4 (8.2)	102.9
10.0	66.5 (5.9)	70.8	3.04 (0.13)	83.1	38.7 (6.1)	106.4
12.5	62.3 (5.0)	66.3	2.97 (0.14)	81.1	37.7 (6.8)	103.9
15.0	58.5 (4.9)	62.3	2.73 (0.13)	74.6	42.5 (4.9)	117.1
17.5	57.1 (3.7)	60.8	2.77 (0.14)	75.7	39.7 (6.2)	109.4
20.0	51.2 (3.6)	54.6	2.76 (0.12)	75.4	39.3 (7.6)	108.1

point is increased. These features are most clearly observed in the curves obtained for 1,3-BDSA.

The extensibility, tenacity, and modulus values from the stress-strain curves are summarized in Tables I–III and Figures 3 and 4. The extensibility (Fig. 3) of the fibers is the property most affected by crosslinking and it reduces very quickly with an increasing concentration of azide applied from the dye bath; this is most pronounced in those samples crosslinked using 1,3-BDSA where the extensibility falls to a quarter of that of the standard sample at 12.5% azide; the tenacity (Fig. 4) of these samples is also reduced and follows the same pattern, eventually reaching a value of around half that of the standard. Fibers crosslinked with 1,6-HDSA showed a much lower reduction in extensibility and tenacity when increasing the degree of crosslinking, and the most crosslinked (20% azide) of the samples had about half of the extensibility of the standard sample

and three-quarters of the tenacity. Samples crosslinked with 2,6-NDSA gave values closer to those obtained with 1,3-BDSA. In contrast to the changes observed in extensibility and tenacity, the initial moduli of the fibers crosslinked with 1,3-BDSA and 2,6-NDSA were found to increase in magnitude with the extent of crosslinking, and this was again most marked for those samples crosslinked with 1,3-BDSA where the modulus increased by up to 50% of that of the standard sample. The moduli of those samples crosslinked with 1,6-HDSA were found to remain constant within experimental error, although perhaps a small increase could be claimed at 15–20% azide. The errors associated with the measurement of the moduli were somewhat larger than we had hoped. The changes in properties produced by higher levels of 1,6-HDSA (i.e., >5% omf) were always less than with the other two azides; for

Table II Mechanical Properties of Fibers Crosslinked with 1,3-BDSA

1,3-BDSA Concn (% omf)	Extensibility		Tenacity		Modulus	
	%	% of Std	g/dtex	% of Std	g/dtex	% of Std
Std (0.0)	93.9 (7.8)	100.0	3.66 (0.19)	100.0	36.3 (5.5)	100.0
2.5	84.6 (8.0)	90.1	3.15 (0.17)	85.9	39.6 (6.4)	109.1
5.0	68.5 (6.4)	72.9	2.89 (0.14)	78.9	41.6 (4.8)	114.4
7.5	38.2 (4.0)	40.7	2.41 (0.13)	65.7	41.2 (5.1)	113.5
10.0	32.0 (2.2)	34.0	2.34 (0.11)	64.0	49.1 (7.1)	135.2
12.5	24.8 (3.8)	26.4	2.13 (0.14)	58.2	48.7 (11.9)	134.1
15.0	21.7 (2.5)	23.1	1.97 (0.10)	53.7	55.0 (5.5)	151.3
17.5	22.4 (2.3)	23.8	1.98 (0.09)	54.0	52.4 (6.8)	144.3
20.0	24.7 (2.1)	26.3	2.05 (0.13)	56.0	49.3 (6.0)	135.7

Table III Mechanical Properties of Fibers Crosslinked with 2,6-NDSA

2,6-NDSA Concn (% omf)	Extensibility		Tenacity		Modulus	
	%	% of Std	g/dtex	% of Std	g/dtex	% of Std
Std (0.0)	93.9 (7.8)	100.0	3.66 (0.19)	100.0	36.3 (5.5)	100.0
2.5	78.2 (7.4)	83.3	3.34 (0.19)	91.2	38.9 (5.7)	107.1
5.0	62.8 (8.6)	66.9	2.96 (0.10)	80.9	41.8 (5.5)	115.0
7.5	47.1 (3.6)	50.2	2.64 (0.10)	72.1	46.6 (6.8)	128.3
10.0	38.8 (3.0)	41.3	2.45 (0.11)	66.9	46.4 (8.0)	127.8
12.5	41.4 (3.2)	44.2	2.53 (0.14)	69.2	43.3 (8.3)	119.3
15.0	37.5 (3.3)	40.0	2.40 (0.12)	65.5	47.2 (7.1)	129.9
17.5	35.8 (2.3)	38.1	2.41 (0.09)	65.7	47.1 (6.0)	129.7
20.0	28.1 (1.8)	30.0	2.11 (0.10)	57.6	47.3 (9.1)	130.2

example, 20% 1,6-HDSA produced effects similar to 6–7% of the other azides.

Thermal Properties

Melt Behavior of Crosslinked Fibers

The DSC traces of the standard sample and crosslinked samples (i.e., the first DSC runs) were obtained and found to contain only the endothermic peak relating to the melting of the polymer. The standard sample gave rise to a melting endotherm (ΔH_p) of 57.3 J/g (at 250.7°C), and the crosslinked samples were a little lower in the energy and melting temperature (T_m). The largest changes were observed in those samples crosslinked with 2,6-NDSA in which the endotherm fell progressively with an increasing degree of crosslinking to 49.8 J/g (at 246.6°C) at a

20% concentration of azide. For those samples crosslinked with 1,6-HDSA the endotherm fell to 52.8 J/g (at 246.7°C) at the same concentration whereas those samples crosslinked with 1,3-BDSA gave endotherms that changed little (to about 55 J/g) compared to that of the standard. The small changes associated with the melting process are perhaps unsurprising if the amorphous regions alone have been crosslinked; however, the differences are most likely due to crosslinking within regions of chain folding and on the surface of crystals, producing quite small changes in the melt properties as discussed in the crosslinking of polyethylene.^{23,24} It was thought that the quenching of the molten samples followed by controlled crystallization and remelting would yield more understanding.

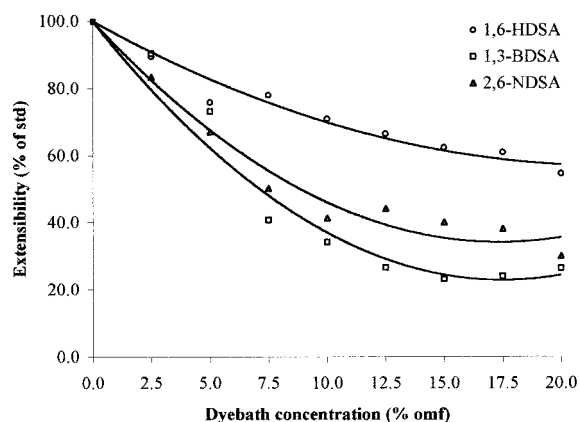


Figure 3 The variation of the extensibility with the azide concentration.

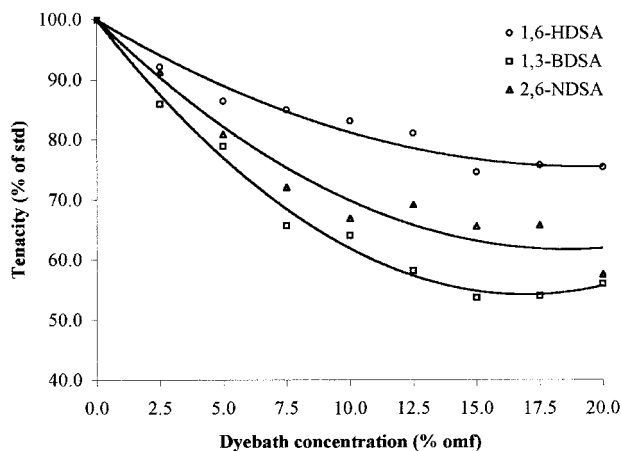


Figure 4 The variation of the tenacity with the azide concentration.

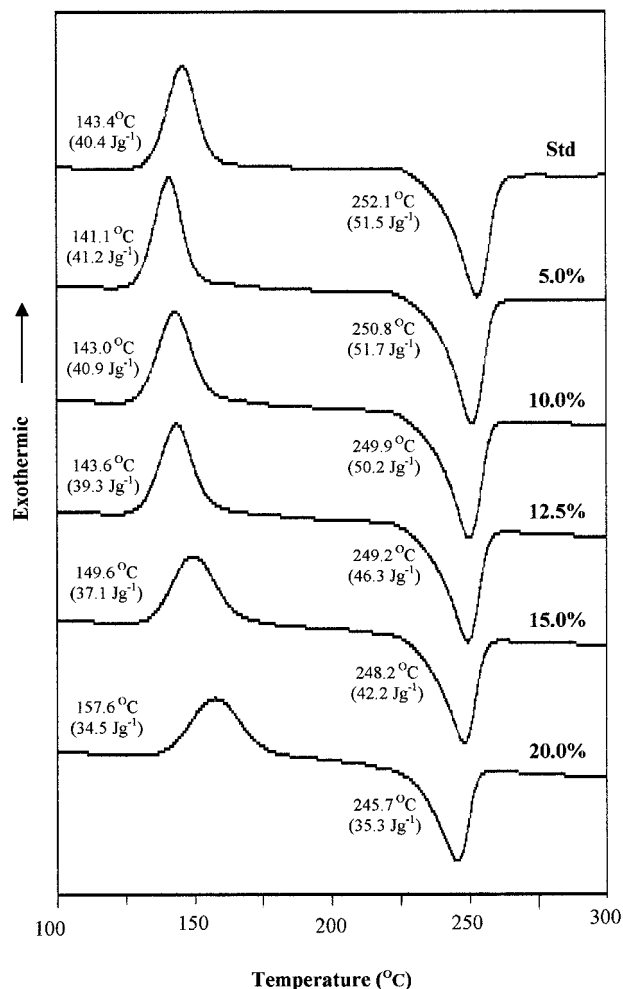


Figure 5 The DSC traces of PET fibers crosslinked with 1,6-HDSA.

Crystallization and Melt Properties of Quenched Material

The DSC traces of the quenched samples (second DSC runs) are shown in Figures 5 and 6 for 1,6-HDSA and 2,6-NDSA, and the variations of the thermal properties with the azide application concentration are shown in Figures 7–10. These figures do not show the glass transitions, which increased by only a maximum of 2°C; given the insensitivity of this procedure for measuring the T_g , the variation with the extent of crosslinking is not discussed. The samples crosslinked with 1,6-HDSA showed little change in thermal behavior up to the 10% treatment, apart from a small reduction in the T_m . As the concentration of azide was increased from 10 to 20%, the crystallization temperature (T_c) increased to 157.6°C, some 14°C

above the standard sample with an accompanying fall in the heat of crystallization (ΔH_c) of about 15%; the melting point and ΔH_f both decreased, the latter by about 30%. The increase in T_c is presumably associated with the need for the chains to have a higher mobility in order to crystallize. The extent of crystallization is clearly reduced as shown by the reductions in both the heats of crystallization and fusion. The similarity in these two values in the 20% 1,6-HDSA treatment implies that virtually no crystallization now occurs during quenching, compared to about 20% in the standard sample.

In contrast to the results obtained with 1,6-HDSA, those samples crosslinked with 1,3-BDSA and 2,6-NDSA exhibited quite different behavior. Samples treated with 5–7.5% of these two azides showed changes similar to those produced

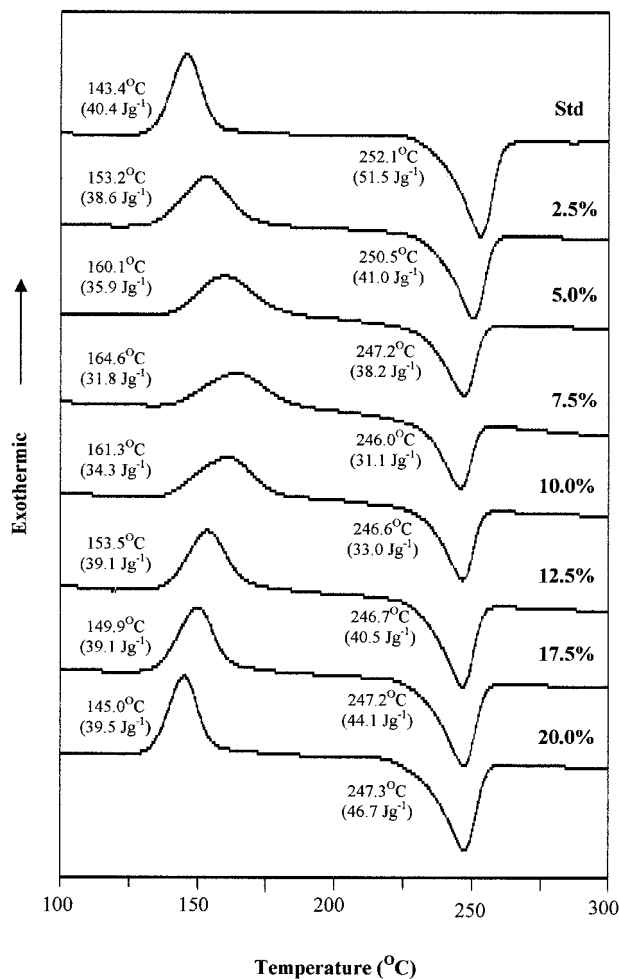


Figure 6 The DSC traces of PET fibers crosslinked with 2,6-NDSA.

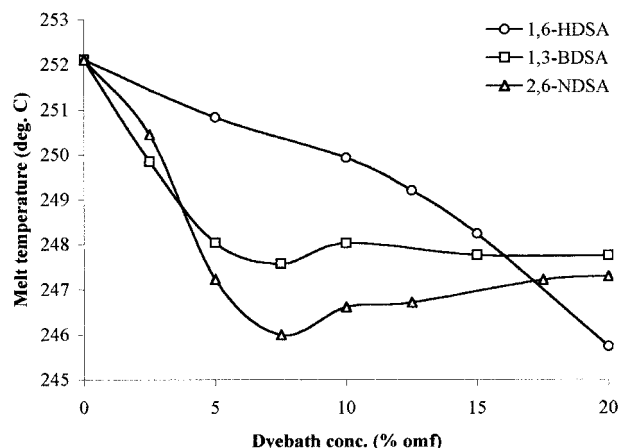


Figure 7 The variation of the melting point (after quenching) with the azide concentration.

by 20% of the 1,6-HDSA. What was most surprising was that at higher extents of crosslinking the trends reversed and the T_c , ΔH_c , and ΔH_f values became quite close to the standard values. Thus, as Figures 8–10 show, there are maxima in the variation of T_c with the azide concentration and minima in the variations of ΔH_f and ΔH_c at about 5–7.5% of both 1,3-BDSA and 2,6-NDSA. The greater efficiency of the latter two azides in changing the T_c , ΔH_f , and ΔH_c compared to 1,6-HDSA parallels the similar effects seen in the changes in the mechanical properties and could just represent less effective crosslinking by the 1,6-HDSA. What is more difficult to explain, and where the explanation must be tentative, is the apparent similarity between the standard un-

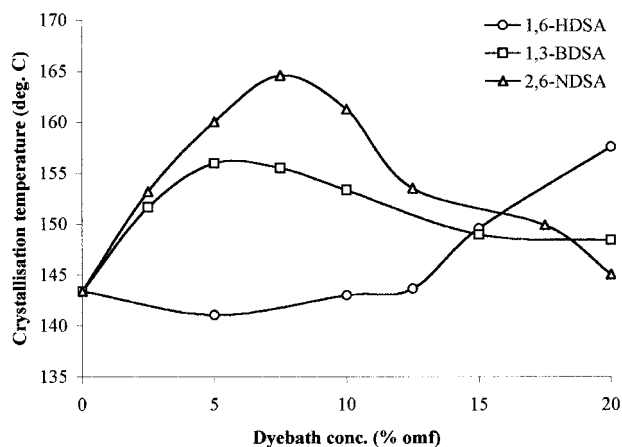


Figure 8 The variation of the crystallization temperature (T_c) with the azide concentration.

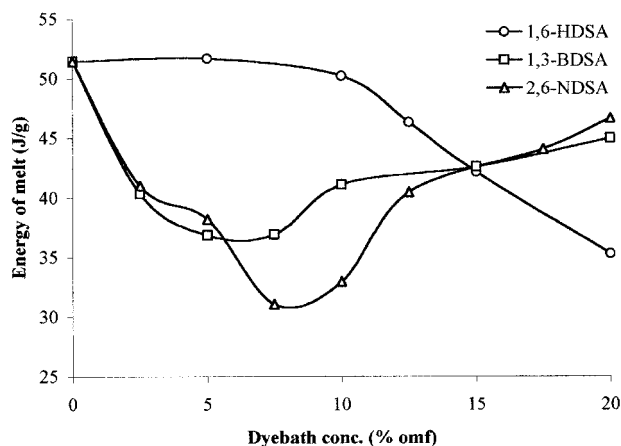


Figure 9 The variation of the energy of melting (ΔH_f) with the azide concentration.

crosslinked fiber and the samples considered to be the most crosslinked. A possible explanation envisages that with 1,3-BDSA and 2,6-NDSA, crosslinking only occurs in the outer region of the fiber due to limited diffusion. At low levels of crosslinking the major effect is a delayed crystallization as discussed above, as well as a reduced extent of crystallization. Hence, the T_c increases and ΔH_c and ΔH_f both decrease. However, above a certain level of crosslinking, the crosslinked outer region becomes a gel and is no longer able to mix with the inner, still linear polymer region during melting. On quenching and reheating the PET from the inner part of the fiber now behaves almost as a normal polymer. The value of ΔH_f at 20% treatment with 1,3-BDSA or 2,6-NDSA im-

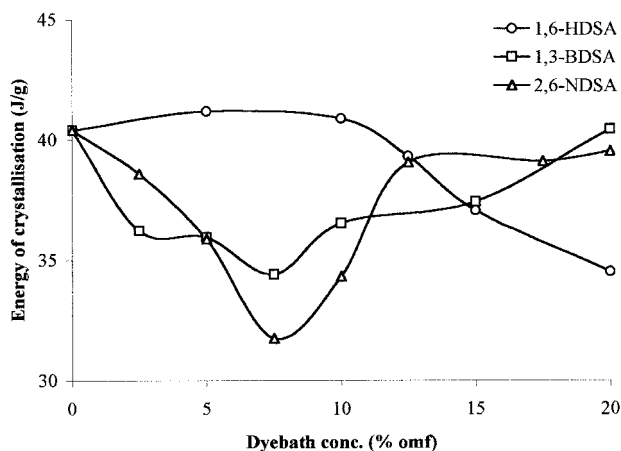


Figure 10 The variation of the energy of crystallization (ΔH_c) with the azide concentration.

plies that about 80% of the original polymer is able to crystallize, implying that crosslinking in these cases is limited to the outer 20% of the fiber.

Although this explains the observed maxima and minima in the variations of T_c , ΔH_c , and ΔH_f , it may also help to explain the differences observed between the three azides. Intuitively, based on the sizes and shapes of the three azides, we would expect the 1,6-HDSA to diffuse most readily, followed by the 2,6-NDSA, and the slowest diffusing azide being the 1,3-BDSA. The different behavior of the 1,6-HDSA in its effect on both the thermal properties and the mechanical properties may therefore be attributed to its ability to diffuse into a greater proportion of the accessible amorphous regions, giving a lower crosslinking density compared to the other two azides. However, the differences among the three azides may also be due in part to different levels of pick-up. Elemental analysis of the 20% treated samples (before heating at 200°C) gave amounts of azide of about 2% omf for 1,3-BDSA and 2,6-NDSA and about 3% for the 1,6-HDSA, although these values are only approximate.

Thermal Stability

The thermal decomposition of the crosslinked fibers was found to begin at an increasingly lower temperature but was extended over a greater range with increasing density of crosslinking. It was found that these trends were least within samples crosslinked with 1,6-HDSA while the trend was similar in form but of a greater magnitude for those samples treated with 1,3-BDSA and 2,6-NDSA; the differences are again thought to be mainly attributable to differing distributions of crosslinking. The residual mass at 550°C, also determined from the TGA traces, generally increased from 12.4% in the standard to 14.4% for 20% 1,6-HDSA, 17.9% for 20% 1,3-BDSA, and 15.4% for the same concentration of 2,6-NDSA; it can be said that crosslinking enhanced the thermal stability of the PET fibers to the extent of giving higher pyrolysis residues. Based on this, the crosslinking efficiency appeared to be in the order 1,3-BDSA > 2,6-NDSA > 1,6-HDSA. Accepting that the earlier arguments are correct, the results would lead to the conclusion that the pyrolysis yield is increased more by crosslinking the outer 20% of the fiber cross section than by the more homogeneous, less dense crosslinking produced by the 1,6-HDSA.

Distribution of Crosslinking

Given that the method of introduction of the DSAs to the fiber was by solvent dyeing, it is to be expected that this process will control the distribution of azide across the fiber cross section and hence affect the distribution of crosslinks across the fiber. If it is assumed that the reactivity of a typical sulfonyl nitrene formed during the heat treatment is structure independent and that the insertion of it along the polymer chain is nonselective and equally efficient, then the effectiveness of the crosslinking process will be largely dependent on the amount and distribution of the crosslinking agent within the fiber.

The mechanical properties of the samples crosslinked with 1,3-BDSA were most changed when increasing the crosslinking density, followed by those treated with 2,6-NDSA, and finally those samples treated with 1,6-HDSA; the relative azide content was found to be approximately 1:1:1.5, respectively. The differences observed among each of the three azides are taken to mainly indicate differences in distribution of the azide across the fiber diameter. With the 1,3-BDSA and the 2,6-NDSA there is a localized concentration of azide in the outer 20% of the fiber so that above 12.5% azide the increase in crosslinking brings about little further change in mechanical properties. Indeed, the much higher localized concentration of azide may bring about competing reactions, such as polymerization of the SA that causes brown coloration. By contrast, the 1,6-HDSA is considered to diffuse more deeply into the fibers and hence crosslink a larger proportion of the fiber, albeit with a lower crosslink density.

The unexpected reversal in trends of crystallization and melting observed in the quenched samples of the 1,3-BDSA and 2,6-NDSA crosslinked samples was explained as a consequence of the limited diffusion of the azides into the fiber. Judging by the values observed at the minima in their plots of ΔH_c and ΔH_f verses the azide concentration, the diffusion into the fibers was slightly greater for 2,6-NDSA. In the samples treated with 1,6-HDSA the less densely crosslinked amorphous regions were presumed to be able to form a homogeneous melt before quenching, thus giving rise to a continuous decrease in ΔH_c and ΔH_f . Presumably, at much higher pick-ups of 1,6-HDSA the behavior shown by the other

two azides will occur but, if the present thinking is correct, minima in ΔH_c and ΔH_f will be at much smaller values.

A further and perhaps the most important feature associated with the crosslinking of PET is that of the maintained solubility of the fibers in OCP. Our belief is that the major reason for the continued solubility of the treated fibers is the inability of the azide to penetrate the crystalline regions so that crosslinking can only occur in the amorphous regions. Additionally, the question arises as to the composition of the amorphous regions where there is expected to be a high concentration of cyclic and linear oligomers, as well as a possible high concentration of chain ends. If PET has a number-average molecular weight of around 20,000 and a repeat unit molecular weight of 192, then the number of repeat units in a chain is 100 and the linear atom count is 1000. The preliminary elemental analysis values suggest that at the most (20% application) we have around 3% by mass of azide (molecular mass of about 300) within the fiber and this equates to a crosslinking density of approximately two per chain. It is clear that this is unlikely to give rise to substantial insolubility, especially because the process may not be 100% efficient, in addition to the earlier arguments. In contrast, our work on an acrylic fiber at similar azide concentrations produced total insolubility, but then the crosslinking density, based on the number-average molecular weight of acrylic being 80,000, is of the order of eight per chain at 3% omf azide concentration. The insolubility observed in the amorphous PET was thought to be due to the much larger concentrations of azide within the fiber.

There are of course difficulties associated with the interpretation of the results, the most important feature of which being the complex nature of the fibrous structure. We assumed that the DSAs are of equal reactivity and give rise to crosslinking only. The results raise numerous questions about the distribution of the crosslinking agents within the whole fiber and locally within the microstructure; additionally, there may be some intramolecular reaction in the 1,6-HDSA. The crosslinking efficiency may be dependent on the length of the spacer between the SA groups or on the physical nature of the spacer. Clearly, further work is required to find answers to some of these questions.

CONCLUSIONS

Partially oriented PET yarn is crosslinked by making use of the thermal decomposition of three different SAs that were applied to the PET from a PER solution. It is believed that the reaction is restricted to the amorphous regions, so that extensive insolubility and infusibility are not observed, which is in contrast to amorphous PET samples that become essentially insoluble and infusible after analogous treatments. Crosslinking of the yarn causes progressive reductions in the extensibility and tenacity, most markedly in the treatments using 1,3-BDSA and 2,6-NDSA. These two azides also cause increases in the modulus. 1,6-HDSA causes smaller reductions in the tenacity and extensibility and has little effect on the modulus.

The DSC studies on 1,3-BDSA and 2,6-NDSA crosslinked samples after melting and quenching showed maxima in the T_c as the azide concentrations were increased and minima in the T_m , ΔH_c , and ΔH_f . By contrast, the equivalent 1,6-HDSA crosslinked samples showed little or no change at azide levels below 10% omf, but increases in T_c and decreases in T_m , ΔH_c , and ΔH_f at higher levels were observed. These differences in the behavior of the azides and the changes observed in the mechanical properties are believed to be caused by the different diffusional behavior of the each of the azides. Whereas the 1,6-HDSA diffuses more or less across the fiber diameter, it is likely that the 2,6-NDSA and 1,3-BDSA diffuse only into the outer periphery of the fiber. Hence, the latter two azides will produce crosslinking only in the outer layer of the fiber, while the 1,6-HDSA forms crosslinks in most, if not all, of the fiber. The TGA studies indicate higher pyrolysis yields as a result of crosslinking, although the effects are small.

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