

# Mechanical and Thermal Properties of Acrylic Fibers Crosslinked with Disulfonyl Azides

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**ABSTRACT:** A novel method for the crosslinking of acrylic fibers was devised, which uses disulfonyl azides as crosslinking agents. This is a fiber-finishing process in which 1,6-hexanedisulfonyl azide, 1,3-benzenedisulfonyl azide, 4,4-biphenyldisulfonyl azide, 1,5-naphthalenedisulfonyl azide, and 2,6-naphthalenedisulfonyl azide were applied to an acrylic fiber (Courtelle) and thermally treated to bring about crosslinking. A study was made of the mechanical and thermal properties of the crosslinked fibers and of the abrasion and pilling performance of the associated fabrics. Crosslinking brought about significant improvements in the initial modulus, resistance to abrasion, pilling performance, and thermal stability of the fibers. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1309–1319, 2002; DOI 10.1002/app.2349

**Key words:** crosslinking agent; Courtelle; acrylic fiber; pilling performance; disulfonyl azide; dimensional stability

## INTRODUCTION

Much patent literature is to be found on the crosslinking of acrylic fibers and polymers. Primarily, crosslinking is discussed as a process to bring about improved dimensional stability,<sup>1–4</sup> although there are processes that require acrylic fibers to be crosslinked prior to conversion to fibers with specific properties.<sup>5–9</sup> Crosslinking can be achieved by irradiation,<sup>10,11</sup> by copolymerization with monomers containing additional functionality,<sup>1,12,13</sup> or by the use of hydrazine.<sup>5,14</sup> Apart from one recent study,<sup>15</sup> however, there is little literature on the physical properties of the crosslinked fibers formed by these processes.

The use of disulfonyl azides as crosslinking agents has been widely reported,<sup>16–19</sup> though their use has been limited to the production of

molded and blown articles, and they are not commonly associated with the crosslinking of fibers. However, they have been reported to crosslink wool<sup>20</sup> and polypropylene,<sup>17,21,22</sup> the latter process being achieved during the melt spinning of the fiber.

The reactions of sulfonyl azides with hydrocarbons were previously investigated<sup>23–29</sup> and are thought to involve the formation of sulfonyl nitrenes. The formation of sulfonyl nitrenes arises at or above the decomposition temperature (Scheme 1), that is about 160°C, or alternatively by the use of UV irradiation.

There are two ways in which a sulfonyl nitrene can react with a hydrocarbon substrate. The preferred reaction involves that of the singlet sulfonyl nitrene, which inserts into a C—H bond in one fully concerted step (Scheme 2), thus giving rise to a sulfonamide link. However, triplet nitrenes can also form and these react by hydrogen abstraction (Scheme 3a) and thereafter progress in one of two ways: the first is to abstract a second hydrogen (Scheme 3c) and the second is to com-

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**Scheme 1** Nitrene formation.

bine with the radical hydrocarbon formed in the initial abstraction (Scheme 3b), the latter being preferred because it gives rise to the same product as that formed by the singlet sulfonyl nitrene. The rate-determining step of the overall reaction is always the step involving the formation of the nitrene, given that the reactions involving the nitrene are almost instantaneous. Obviously for crosslinking, the insertion of a bifunctional sulfonyl nitrene between two polymer chains is required.

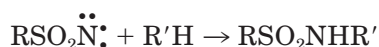
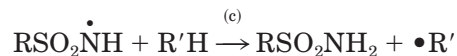
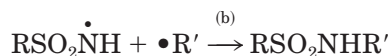
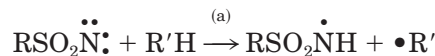
The efficiency of the insertion of sulfonyl nitrenes was previously investigated<sup>28,29</sup> and was shown to be much higher where movement of the molecule is restricted. Thus the efficiency of the insertion reaction of sulfonyl nitrenes with solid hydrocarbons and with hydrocarbon polymers is much higher than that in liquid hydrocarbons or solutions. It has been found that the efficiency of insertion can be typically as high as 95%.<sup>23</sup> Other possible reactions involving sulfonyl nitrenes include polymerization, intramolecular cyclization, and dimerization through radical combination, although it is thought that these are minor for azides dispersed in liquid hydrocarbon or polymer substrates.<sup>23</sup>

Following the earlier work detailing the synthesis of a range of disulfonyl azides,<sup>30</sup> the aims of this study were to find procedures to crosslink acrylic fiber, in the form of Courtelle, using a range of disulfonyl azides. The physical properties of the resultant fibers and fabrics were then to be examined together with a study of their thermal properties.

## EXPERIMENTAL

### Materials

1,6-Hexanedisulfonyl azide (1,6-HDSA), 1,3-benzenedisulfonyl azide (1,3-BDSA), 4,4'-biphenyldisulfonyl azide (4,4'-BDSA), 1,5-naphthalenedis-

**Scheme 2** Reaction of singlet nitrenes.**Scheme 3** Reactions of triplet nitrenes.

ulfonyl azide (1,5-NDSA), and 2,6-naphthalenedisulfonyl azide (2,6-NDSA) were synthesized as described earlier.<sup>30</sup> Solidokoll N (antimigratory agent) and Arkopal N-060X (wetting agent) were obtained from Hoechst (Bradford, UK). Dimethyl formamide was used as supplied by Lancaster Chemicals (Morecambe, UK). The acrylic fiber used throughout was Courtelle fiber [3.2 decitex (dtex)], obtained in the form of yarn as unwaxed Luxury Courtelle (2 × 62.5 tex, 2/32 m/c, Lot LC175; produced by Acordis). This was knitted as a 1 × 1-rib structure on a Shima-Seiki SEC-102KI 8-gauge V-bed machine, using a single yarn and a cam setting of 25.

### Stock Dispersions

Dispersions were made consisting of 10, 30, and 50 g/L of each of 1,6-HDSA, 1,3-BDSA, 4,4'-BDSA, 1,5-NDSA, and 2,6-NDSA to treat Courtelle fabric in a thermosetting process. A stock solution containing 20 g/L Solidokoll N and 2 g/L Arkopal N-060X in deionized water was made. Watertight jars (500 mL) containing 2, 6, or 10 g of each of the azides, together with ceramic beads (150 mL, 5 mm diameter) and 50 mL of the stock solution, were sealed and placed on a milling machine for 4 days. Each jar was then made up to 200 mL with an extra 150 mL of stock solution. A total of 16 dispersions were made, including a standard dispersion containing no azide, to act as a blank.

### Crosslinking Procedure

A rectangular sample (~ 8 g) was cut from the Courtelle fabric, shaken to remove loose selvage, and weighed. This was then placed in a clean jar with the appropriate dispersion and shaken for a

few minutes. The fabric was then padded to about 80 to 120% uptake and weighed again. Each of the dispersions was used to obtain two fabric samples containing different amounts of azide by varying the percentage uptake; the amount was expressed in millimoles of azide per gram of fiber. This gave a total of 31 samples, five azides each with six samples of differing concentrations and one standard fabric, that is, a blank treated sample.

Each of the fabrics was then mounted on a pin frame and heat-treated in a stentor at 170°C for 30 min, washed for a few minutes in water, and dried. The fabrics were mounted so that any shrinkage would not cause excessive force on the fibers, that is, they were slack enough so that they were still slack when they were removed from the stentor. An Ernst Benz (LFV 500/2R) laboratory pad mangle and pin-frame stentor, with adjustable roller pressure, normally used for thermosetting fabrics, was used.

#### Investigation of Solubility and Swelling Ratio

A small sample of fabric (2 cm<sup>2</sup>) was placed in a test tube with 10 mL of DMF at 90°C and observed over a period of 1 h with agitation. Those fabrics that did not dissolve were then assessed for swelling.<sup>15</sup> Approximately 0.3 g (weighed accurately) of fabric was immersed in DMF (20 mL, 90°C) for 30 min. The sample was removed and dabbed between two sheets of absorbent filter paper. The swelling ratio ( $q$ ) was then calculated, shown in the following equation, as an average of three determinations. The density of DMF was taken as 0.948 g/cm<sup>3</sup> and that of Courtele as 1.18 g/cm<sup>3</sup>.

$$q = 1 + \left[ \frac{\text{Polymer density}}{\text{Solvent density}} \right] \times \left[ \frac{(\text{Swollen weight} - \text{dry weight})}{\text{Dry weight}} \right]$$

#### 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 determined on an Instron 1122 CRE tensile-testing machine in accordance with the appropriate standard.<sup>31–33</sup>

Individual fibers were very carefully extracted from yarns removed from the fabric samples and

taped onto cardboard squares with an inner dimension of 20 mm. The framed fibers were then clamped on the Instron, and their load–extension curve obtained. At least 20 fibers were tested from each sample and their averages and standard deviations were compared. The load cell used was 200 g (max), the full-scale load was set to 10 g, and the crosshead speed was 10 mm/min. All fibers were conditioned for at least 24 h at 20 ± 2°C and 65 ± 2% relative humidity before testing.

Fabric abrasion and pilling were investigated on a Martindale (WIRA) abrasion tester under a 9-kPa load, in accordance with the published standard.<sup>31,32,34</sup> Four samples from each fabric were mounted on the Martindale; the number of pills was counted after every 500 rubbing cycles up to 5000 cycles. The mass of each of the samples, initially recorded, was then measured and recorded every 5000 cycles, to a maximum of 30,000 cycles. The fabrics were conditioned as before and the standard deviations calculated for each sample.

#### Thermal Analysis

Thermogravimetric measurements were made using a Dupont 951 TGA equipped with a Dupont TA 2000 control unit (Dupont, Rockville, MD). The heating rate was 20°C/min under nitrogen atmosphere (50 mL/min). DSC traces were also obtained using a Dupont 910 DSC, under identical conditions.

#### Thermomechanical Measurements

A preliminary study was made to assess the thermomechanical properties of the crosslinked fibers using a Mettler TA 3000 system equipped with a TMA 40 cell and TC 10 TA processor. It was found that a bundle of eight yarns taken from each of the fabrics gave the best results for testing. This bundle was then mounted between two clamps, 10 mm apart, and excess fibers were removed. The assembly was then mounted on the TMA under a constant load of 0.7 g (the clamp mass). The changes in length of the sample as a function of temperature were measured at a rate of 20°C/min.

## RESULTS AND DISCUSSION

#### Preliminary Observations

Six treated fabrics from each of the five azides were obtained plus one standard fabric, which

**Table I** Azide Concentrations Used for Crosslinking

Azide Concentration (mmol/g)				
1,6-HDSA	1,3-BDSA	4,4'-NDSA	1,5-NDSA	2,6-NDSA
0.021	0.024	0.018	0.021	0.021
0.035	0.034	0.028	0.029	0.033
0.081	0.086	0.058	0.061	0.068
0.133	0.141	0.087	0.088	0.091
0.166	0.148	0.100	0.108	0.107
0.226	0.227	0.158	0.150	0.150

had been treated in the same way but without the use of an azide. The amount of azide applied was recorded (Table I).

All of the samples had become yellow or brown after treatment. This was most apparent with those azides of higher molecular weight (4,4-BDSA, 2,6-NDSA, and to a lesser extent 1,5-NDSA) and in those samples treated with higher concentrations of azide (above 0.1 mmol/g). However, the heat treatment itself imparted some yellowing to the fibers as exemplified by the standard sample, and it was found that those samples treated with less than 0.1 mmol/g of the lower molecular weight azides (1,6-HDSA and 1,3-BDSA) were less yellow than the standard heat-treated sample.

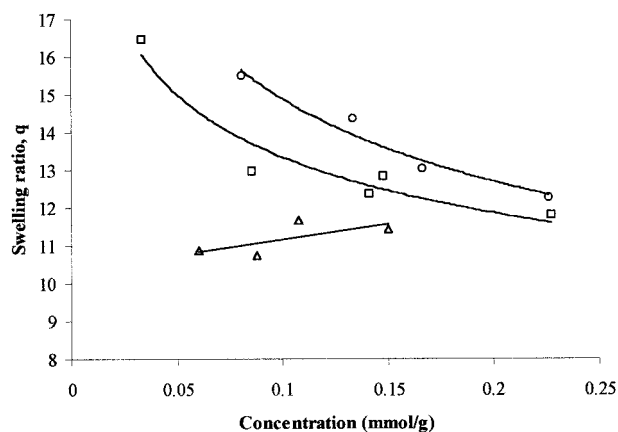
It is thought that an important factor in the coloration of the fabrics was the extent of diffusion of the azide into the fiber. Whereas the 1,6-HDSA and 1,3-BDSA diffused more readily into the fiber, the larger azides, especially at higher concentrations, were more likely to decompose to nitrenes before substantial diffusion had occurred. This was believed to have led to a more or less surface deposit of polymerized azide, accounting for the greater brown appearance.

The solubility of the crosslinked fibers in DMF was found to be inversely related to the concentration of azide used. The samples treated with less than 0.05 mmol/g were partially soluble with some gel formation, those treated with around 0.1 mmol/g were insoluble but formed a swollen gel, and those treated with a higher concentration were totally insoluble. By contrast, the standard sample dissolved in about 30 s. On the basis of the least discoloration, the crosslinked fabrics obtained by using 1,6-HDSA, 1,3-BDSA, and 1,5-NDSA were selected for further study.

### Swelling Behavior

The swelling ratios were measured and found to decrease with increasing azide concentration for 1,6-HDSA and 1,3-BDSA, as might be expected for increasing extents of crosslinking (Fig. 1). For 1,5-NDSA, by contrast, fairly constant values of 11 to 12 were obtained, implying essentially constant levels of crosslinking. Assuming that the swelling ratio measures the same extent of crosslinking for each azide, then the efficiency of the azides in crosslinking the fiber appears to be in the order 1,5-NDSA > 1,3-BDSA > 1,6-HDSA at concentrations below 0.15 mmol/g; above this, the differences are small.

These levels of swelling ratios indicate levels of crosslinking, which compare with those obtained by Shoshtari and East<sup>14</sup> using 2–4% v/v aqueous hydrazine at 100°C for 3 h,<sup>15</sup> and are never as high as can be obtained with higher concentrations of hydrazine (>4% v/v). However, they give



**Figure 1** Effect of azide concentration on swelling ratio for (○) 1,6-HDSA, (□) 1,3-BDSA, and (△) 1,5-NDSA.

**Table II Mechanical Properties of Crosslinked Courtelle Fibers**

Azide	Concentration (mmol/g)	Tenacity <sup>a</sup> (g/tex)	Extension <sup>a</sup> (%)	Modulus <sup>a</sup> (g/tex)
None	0.000	20.7 (1.9)	30.3 (4.8)	268 (40)
1,6-HDSA	0.035	22.2 (2.4)	30.8 (4.7)	338 (76)
	0.133	20.6 (1.4)	28.3 (2.4)	359 (38)
	0.226	21.0 (1.8)	28.5 (3.8)	310 (47)
1,3-BDSA	0.034	20.4 (1.4)	26.8 (3.3)	341 (44)
	0.141	20.6 (1.9)	25.5 (3.9)	383 (59)
	0.227	19.9 (1.8)	25.4 (2.6)	293 (57)
1,5-NDSA	0.029	21.7 (1.5)	32.0 (3.5)	342 (46)
	0.088	20.2 (1.5)	27.7 (3.8)	285 (42)
	0.150	19.5 (1.3)	25.6 (2.1)	312 (46)

<sup>a</sup> Standard deviation shown in parentheses.

extents of crosslinking above those obtained using 1,6-hexanediol and *p*-toluene sulfonic acid.<sup>14,15</sup> The failure to observe any increase in crosslinking on increasing the concentration of 1,5-NDSA suggests some competing reaction, as indeed do the relatively small decreases in swelling ratio values on increasing azide concentration for the other azides. We suspect that, at higher azide concentrations, reactions between nitrenes on or near to the fiber surface lead to polymer formation, as referred to earlier. It is possible that this surface polymer also affects the swelling behavior of the fibers. Samples crosslinked with the lowest two concentrations of each of the three azides were not tested for swelling because they were partially soluble in DMF.

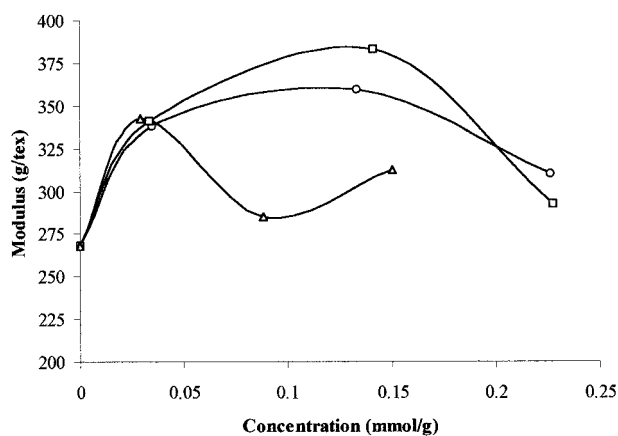
### Fiber Properties

The tenacity, extensibility, and initial modulus values of some of the crosslinked fibers were measured and are shown in Table II (figures in parentheses indicate the standard deviation). Although it was found that there was very little change in tenacity, the extensibility of the fiber was slightly reduced, more so for the fibers crosslinked by 1,3-BDSA and 1,5-NDSA; however, there were large increases in the initial modulus, up to 40% for 1,3-BDSA, for low levels of crosslinking for all three azides; above certain concentrations (see Fig. 2), the moduli of the fibers decreased, in which the pattern of behavior differed between 1,6-HDSA and 1,3-BDSA on the one hand and 1,5-NDSA on the other. In all cases, though, the modulus had increased relative to the standard and there was an optimum level of application for increasing the modulus. These re-

sults are very similar to those obtained by Shosh-tari and East<sup>14</sup> in the very small changes observed in tenacity and extensibility at low levels of crosslinking, although they observed much smaller changes in modulus.

### Fabric Properties

The abrasion performance was improved by all the crosslinking treatments compared with that of the standard fabric sample (Table III; standard deviations are shown in parentheses). The residual mass at 30,000 cycles shows a maximum as the azide concentration increases, following the same trend as that of the initial modulus (Fig. 3). This is perhaps unsurprising, given that other workers<sup>35-38</sup> previously showed that an increase in initial modulus can give rise to less fiber breakage in the abrasion process and ultimately a



**Figure 2** Effect of azide concentration on initial modulus. (Symbols as in Fig. 1.)



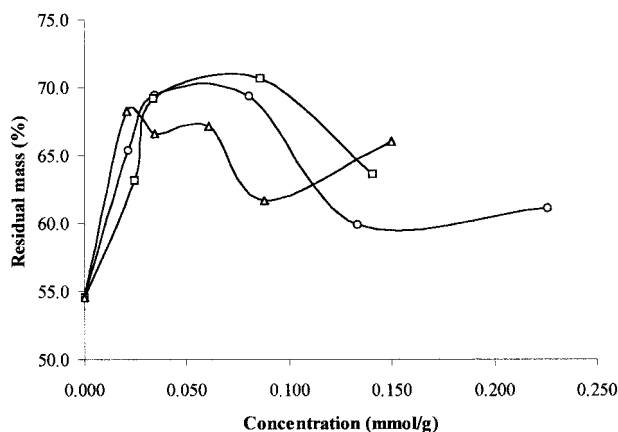
**Table III** Abrasion Performance of Crosslinked Courtelle Fabrics

Azide	Concentration (mmol/g)	Residual Mass After $x$ Cycles (%) <sup>a</sup>				
		10,000	15,000	20,000	25,000	30,000
None	0.000	88.3 (1.5)	82.0 (1.6)	73.1 (1.5)	64.1 (3.5)	54.5 (0.8)
1,6-HDSA	0.021	93.3 (2.1)	87.2 (2.4)	81.7 (3.1)	74.0 (3.6)	65.4 (4.6)
	0.035	93.3 (2.1)	86.9 (2.4)	79.7 (5.0)	73.6 (5.0)	69.4 (2.4)
	0.081	95.4 (0.8)	88.9 (1.3)	82.6 (2.2)	75.2 (4.6)	69.3 (5.1)
	0.133	89.9 (2.6)	83.5 (2.6)	75.6 (3.1)	65.4 (4.4)	59.9 (4.8)
	0.226	91.1 (1.9)	85.6 (1.9)	76.3 (3.6)	65.7 (4.1)	61.1 (3.9)
1,3-BDSA	0.024	95.1 (1.7)	89.9 (1.9)	82.9 (2.8)	74.1 (3.6)	63.1 (2.9)
	0.034	96.7 (1.4)	91.1 (2.0)	84.6 (2.5)	76.9 (3.1)	69.2 (2.6)
	0.086	95.0 (2.0)	89.2 (3.7)	83.5 (5.0)	76.0 (6.9)	70.6 (7.4)
	0.141	91.3 (2.4)	84.4 (3.8)	77.4 (5.6)	68.7 (8.9)	63.6 (7.6)
	0.227	91.8 (1.9)	83.2 (3.3)	74.6 (5.6)	69.5 (2.7)	Failed
1,5-NDSA	0.021	93.1 (1.2)	88.0 (1.4)	82.1 (2.0)	76.0 (2.2)	68.2 (3.3)
	0.035	94.1 (1.8)	86.4 (2.0)	79.7 (4.2)	72.9 (5.0)	66.6 (1.9)
	0.061	94.5 (1.4)	89.6 (2.5)	83.2 (3.5)	75.7 (4.4)	67.2 (5.5)
	0.088	94.4 (1.4)	86.4 (2.6)	78.2 (2.6)	71.2 (3.0)	61.7 (5.3)
	0.150	93.2 (2.5)	87.2 (2.9)	79.0 (3.4)	69.9 (5.8)	66.0 (6.0)

<sup>a</sup> Standard deviation shown in parentheses.

higher residue. Again, there is fair agreement with the work of Shoshtari and East,<sup>14</sup> where the abrasion resistance of the fabric went through a maximum with increasing extent of crosslinking and fell to a value below the standard only when very high levels of crosslinking were attained. The increase seen in the plot at higher azide concentrations may be attributed to the formation of polymer at the surface of the fiber, as discussed earlier.

The pilling performance (Table IV) again showed improvement in all the crosslinked sam-



**Figure 3** Abrasion performance; variation of residual mass with concentration of azide after 30,000 cycles. (Symbols as in Fig. 1.)

ples relative to that of the standard. The number of pills observed on the sample decreased rapidly with increasing concentration of crosslinking agent initially (Figs. 4 and 5), although the rate of decrease subsequently fell. A similar trend was observed for each of the three azides employed (Fig. 5). Unlike the trends found in the changes in modulus and residual mass, the pilling performance improved continuously with increasing azide concentration. This trend can perhaps be explained in the following way.

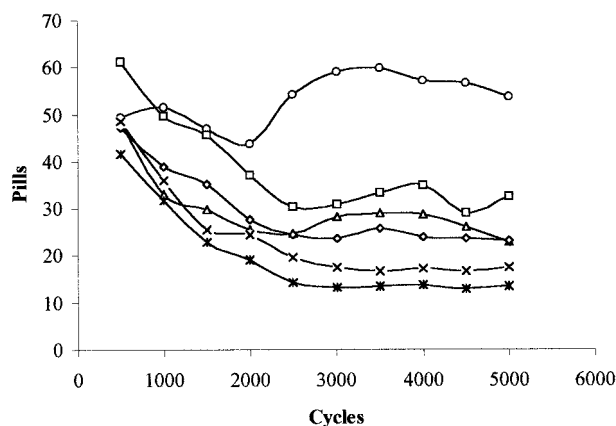
Pilling has been described to be a three-stage process.<sup>39</sup> The first process is fuzz formation, involving the initial formation of loose fibers on the surface of the fabric as a result of mechanical action; the next is pill formation, where the entanglement of the loose fibers form spherical bundles that are anchored to the fabric by fibers that are partially still part of the fabric structure; and the final stage is pill wear-off, where the spherical bundles are worn or pulled away by further mechanical action. Generally, the first process is thought to be highly dependent on the modulus of the fiber; if the modulus is increased, the fuzz formation is reduced. The second is attributed to the mechanical action and is thus inevitable. The final stage is largely dependent on the energy (which is dependent on the extensibility) required to break off the pill attached to the fabric surface. Given how the process of pilling occurs, it is pos-

**Table IV** Pilling Performance of Courtelle Fabric Crosslinked with Disulfonyl Azides

Azide	Concentration (mmol/g)	Pills Observed After $x$ Cycles <sup>a</sup>				
		1000	2000	3000	4000	5000
None	0	52 (7)	44 (3)	59 (7)	57 (3)	54 (4)
1,6-HDSA	0.021	50 (1)	37 (6)	31 (5)	35 (4)	33 (5)
	0.035	33 (4)	26 (3)	28 (2)	29 (5)	23 (3)
	0.081	39 (4)	28 (3)	24 (2)	24 (4)	23 (2)
	0.133	36 (4)	25 (3)	18 (1)	17 (3)	18 (2)
	0.226	32 (7)	19 (3)	13 (2)	14 (5)	14 (3)
1,3-BDSA	0.024	57 (6)	39 (4)	34 (4)	39 (3)	43 (3)
	0.034	53 (10)	33 (5)	30 (3)	33 (4)	27 (3)
	0.086	36 (2)	24 (3)	25 (3)	23 (3)	22 (5)
	0.141	36 (5)	17 (2)	14 (2)	14 (5)	10 (1)
	0.227	20 (3)	8 (1)	6 (1)	7 (1)	6 (1)
1,5-NDSA	0.021	53 (2)	39 (4)	43 (5)	40 (5)	46 (4)
	0.029	41 (7)	29 (5)	31 (4)	27 (5)	29 (5)
	0.061	44 (6)	24 (2)	24 (2)	25 (3)	23 (2)
	0.088	40 (4)	19 (2)	18 (3)	17 (1)	18 (2)
	0.150	33 (4)	17 (1)	14 (2)	13 (1)	15 (2)

<sup>a</sup> Standard deviation shown in parentheses.

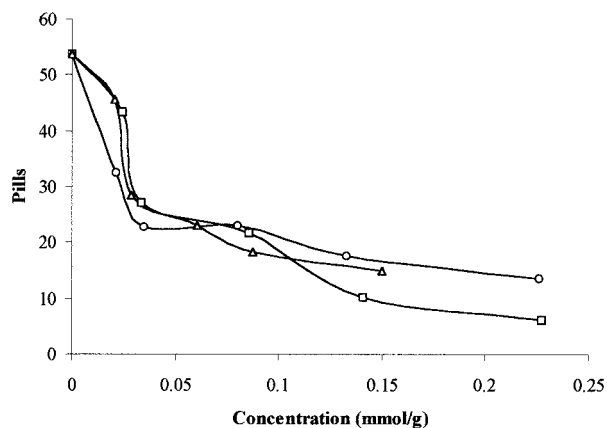
sible to see how the pilling of the fabric showed a continuous improvement. At low concentrations of azide, the modulus of the fiber increased, thus giving lower pill formation; however, the wear-off may have been little affected because the extensibility was not significantly affected. However, at higher concentrations the modulus began to fall, as did the extensibility, which may have given rise to a relative increase in pill formation, but also to an increase in wear-off and also, as observed, a decrease in the abrasion resistance.



**Figure 4** Variation of pilling performance with concentration of 1,6-HDSA: (○) standard, (□) 0.021, (△) 0.035, (◇) 0.081, (×) 0.133, and (✱) 0.226 mmol/g.

### Thermal Analysis

The differential scanning calorimetry curves for some of the samples were determined, a summary of which data is given in Table V. The DSC traces clearly show the characteristic initial exotherm attributed to the intramolecular cyclization and intermolecular polymerization of the nitrile groups.<sup>40,41</sup> Comparison shows that, at relatively lower levels of crosslinking, the onset and peak maximum temperatures of decomposition were



**Figure 5** Variation of the pilling performance after 5000 cycles with azide concentration. (Symbols as in Fig. 1.)

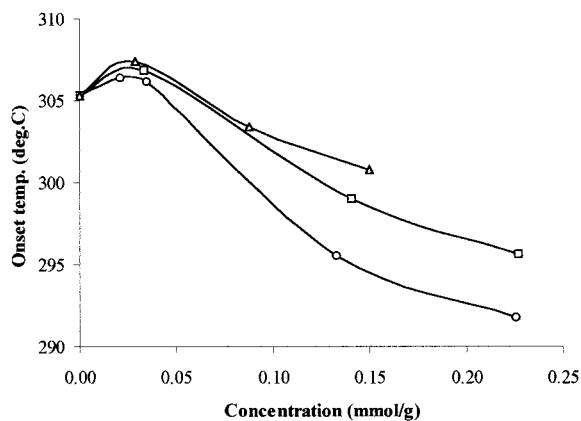
**Table V** DSC Data for Courttelle Fibers Crosslinked with Disulfonyl Azides

Azide	Concentration (mmol/g)	Onset (°C)	Peak Maximum (°C)	Energy (J/g)	Energy (%)
None	0.000	305.3	319.5	728.6	100.0
1,6-HDSA	0.021	306.4	320.6	688.5	94.5
	0.035	306.1	319.9	667.0	91.5
	0.133	295.5	313.9	647.4	88.9
	0.226	291.8	310.4	606.1	83.2
1,3-BDSA	0.034	306.9	321.2	704.8	96.7
	0.141	299.0	316.8	640.9	88.0
	0.227	295.6	314.0	645.1	88.5
1,5-NDSA	0.029	307.4	322.4	683.5	93.8
	0.088	303.4	319.7	665.3	91.3
	0.150	300.7	317.6	646.2	88.7

slightly increased; at higher levels they decreased progressively (Fig. 6); however, the changes in values were small.

The energy associated with decomposition was found to fall significantly; the exotherm widened and was less intense, varying in intensity from about  $15 \text{ J s}^{-1} \text{ g}^{-1}$  for the standard to about  $8 \text{ J s}^{-1} \text{ g}^{-1}$  for the most crosslinked. Part of this reduction in the exotherm may be caused by cyclization of the nitrile groups initiated during the heat treatment ( $170^\circ\text{C}$ , 30 min) used to produce the nitrene; some sulfonamide units produced in Scheme 3c would be expected to act as initiators for nitrile group cyclization.

The TGA traces for all of the samples are summarized in Table VI. It was observed that the temperature of the onset of weight loss decreased with increasing concentration of crosslinker; the derivative peak was also reduced but by a greater



**Figure 6** Variation in the DSC onset of degradation with azide concentration. (Symbols as in Fig. 1.)

magnitude (Fig. 7). The values imply that the observed decrease in the initial exotherm had given rise to less chain scission and is thus in agreement with the DSC data.

The pyrolysis residue was found to be higher in all cases compared to that of the standard sample, and increased with increasing concentration of azide for 1,6-HDSA and 1,3-BDSA (Fig. 8). The residues for 1,5-NDSA crosslinked Courttelle were only slightly higher and showed more scattered behavior with increasing azide concentration, as observed in the swelling behavior. This again is thought to be because of more polymerization of this azide at or near to the surface of the fiber. The pyrolysis residue for Courttelle crosslinked with 2,6-NDSA (not selected for detailed study on the basis of excessive fiber coloration) also remained more or less the same at all the concentrations studied. This perhaps underscores the relationship between fiber coloration and the relative effectiveness of the disulfonyl azide as a crosslinker on the basis of different rates of diffusion. Crosslinking with 4,4'-BDSA gave samples with pyrolysis residues between those obtained for 2,6-NDSA and 1,5-NDSA, and the sample coloration was likewise in the same order.

A comparison of the thermal properties of Courttelle fibers crosslinked with hydrazine and those of this study reveals some differences. The exotherms observed in the DSC traces of hydrazine-treated samples are similar in form, but of a reduced energy compared to that of the standard ( $\sim 30$  to  $50\%$ ); the thermogravimetric behavior mimics this in the reduction in mass loss during cyclization, implying that cyclization has again been initiated at the treatment temperature.



**Table VI** TGA Data for Courtelle Fibers Crosslinked with Disulfonyl Azides

Azide	Concentration (mmol/g)	Onset Temperature		Residual Mass at $T$ (%)	
		Temperature (°C)	Derivative (%/°C)	500°C	700°C
None	0.000	328.4	0.941	52.0	47.6
1,6-HDSA	0.021	328.5	0.954	53.3	48.6
	0.035	328.0	0.972	55.1	50.8
	0.081	319.9	0.638	56.3	52.0
	0.133	317.7	0.508	59.1	54.0
	0.166	316.7	0.450	60.4	55.6
	0.226	315.4	0.629	60.1	55.0
1,3-BDSA	0.024	328.2	0.956	53.4	48.5
	0.034	327.6	0.930	53.8	49.1
	0.086	321.4	0.728	57.1	51.9
	0.141	322.8	0.662	59.7	54.4
	0.148	321.4	0.623	59.6	53.1
	0.227	319.7	0.440	61.9	56.3
1,5-NDSA	0.021	328.5	0.976	52.4	48.0
	0.029	327.8	0.991	55.2	50.1
	0.061	326.8	0.881	56.5	51.3
	0.088	326.1	0.802	55.4	50.3
	0.108	322.9	0.733	57.4	52.9
	0.150	321.8	0.704	55.8	51.4

However, the pyrolysis residues of the structures formed in this study are a little higher than those formed with hydrazine, which may indicate that the sulfonamide crosslink is more stable than that formed by the reaction with hydrazine, although the differences in fiber decitex make direct comparison difficult.

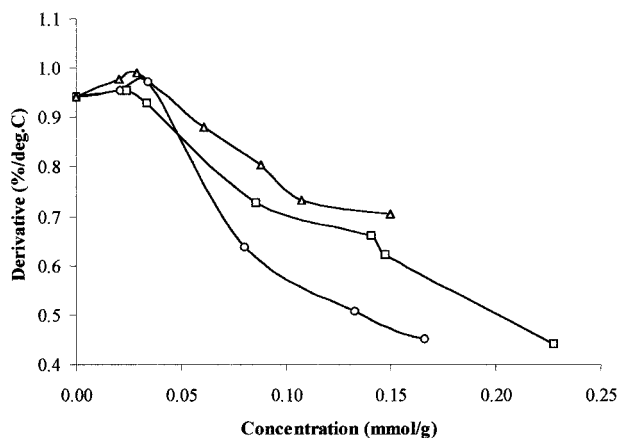
Further examination of the curves obtained from the DSC and TGA work revealed that no

exotherm or mass loss was found at or around the temperature associated with the thermal decomposition of sulfonyl azides (150–180°C). This implied that there was no detectable unreacted azide within the fibers and perhaps that milder conditions could be employed to bring about crosslinking.

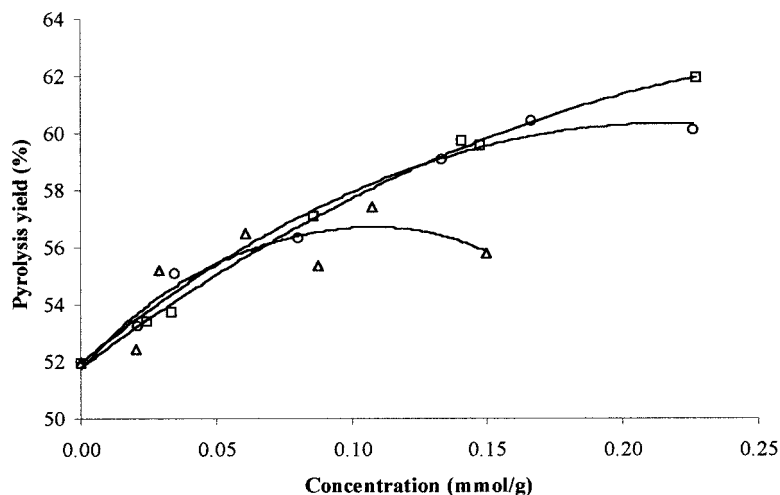
### Thermomechanical Properties

Preliminary investigations of the thermomechanical properties of the crosslinked acrylic specimens were performed because of the importance of these fibers in the manufacture of carbon fibers. One of the problems associated with the conversion of acrylic fibers to carbon fibers is the shrinkage and deformation of the fiber on heating. Previous work<sup>42,43</sup> showed that the shrinkage occurs in two stages: (1) shrinkage below 200°C, known as “entropic shrinkage,” caused in the main by the relaxation of the orientation and a little chemical shrinkage, and (2) shrinkage above 200°C, known as the “chemical reaction shrinkage.” It was thought that crosslinking would bring about a change in these properties.

The TMA traces of some of the samples crosslinked with differing amounts of 1,6-HDSA



**Figure 7** Variation of the maximum rate of mass loss with azide concentration. (Symbols as in Fig. 1.)



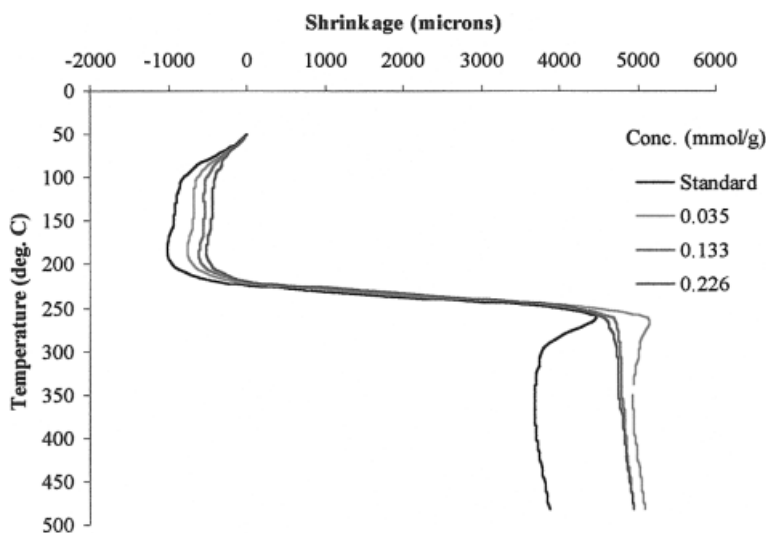
**Figure 8** Variation of pyrolysis yield at 500°C with concentration of azide. (Symbols as in Fig. 1.)

are shown in Figure 9; similar traces were obtained for samples crosslinked with 1,3-BDSA. No entropic shrinkage was observed in any of the samples below 200°C, which could be accounted for by the initial heat treatment imparted during the crosslinking process. However, the samples showed a progressive decrease in extension on increasing the degree of crosslinking, the extension being attributed to the mass of the clamp (0.7 g). The chemical reaction shrinkage, observed between 200 and 250°C, was approximately the same as that of the standard except at the highest levels of crosslinking, where it was reduced. The extension observed in the samples above 250°C

was found to drop rapidly with increasing extent of crosslinking; this extension again is thought to be attributed to the mass of the clamp. Crosslinking slightly reduced the chemical reaction shrinkage of the fibers and decreased the extension as a result of loading at higher temperature by a greater magnitude. It is thus concluded that the mechanical stability of the fibers was enhanced by crosslinking.

## CONCLUSIONS

Acrylic fibers, in the form of Courtele, were crosslinked with varying degrees of success with a



**Figure 9** TMA trace of Courtele fibers crosslinked with 1,6-HDSA. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

selection of disulfonyl azides. It is believed that crosslinking is brought about by the formation of bifunctional nitrene intermediates that insert into C—H bonds on separate polymer chains. Depending on the degree of crosslinking, the crosslinked fibers may show increased initial modulus, enhanced pilling performance, and improved resistance to abrasion, whereas the tenacity and extensibility are largely maintained. Their thermal properties are also enhanced with an overall improvement in dimensional stability on heating and a higher pyrolysis residue.

The results suggest that the degree of crosslinking is largely dependent on the diffusional behavior of the azide, and further examination is required to confirm this; it may also be advantageous to examine other application procedures. 1,6-HDSA and 1,3-BDSA appeared to be the most effective of the compounds selected for study, and this is thought to be because of their lower molecular mass and thus relatively increased mobility, giving rise to a more even distribution of crosslinking within the fiber. Both compounds also had the advantage of crosslinking with a minimum level of yellowing.

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