

# Thermomechanical and Creep Properties of Poly(ethylene terephthalate) Fibers Crosslinked with Disulfonyl Azides

D. A. Baker,<sup>1</sup> G. C. East,<sup>2</sup> S. K. Mukhopadhyay<sup>2</sup>

<sup>1</sup> Centre for Advanced Engineering Fibers and Films, Clemson University, Clemson, South Carolina 29634

<sup>2</sup> School of Textile Industries, University of Leeds, Leeds, LS2 9JT, United Kingdom

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**ABSTRACT:** The thermomechanical and creep properties of poly(ethylene terephthalate) fibers crosslinked with 1,6-hexanedisulfonyl azide, 1,3-benzenedisulfonyl azide, and 2,6-naphthalenedisulfonyl azide were investigated. Significant improvements in these properties were observed between the standard fibers and those produced by crosslinking. Cyclic loading studies highlighted minor differences not

detectable by normal thermomechanical analysis. The creep at room temperature could be reduced to about one-third of the normal values observed in the untreated fiber. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1556–1562, 2003

**Key words:** creep; crosslinking; fibers; polyesters; thermal properties

## INTRODUCTION

We recently described studies of the crosslinking of acrylic fibers<sup>1</sup> and poly(ethylene terephthalate) (PET) fibers<sup>2</sup> with disulfonyl azides. Although the acrylic fibers could be crosslinked sufficiently to maintain their fiber form in dimethylformamide, the partially oriented Dacron yarn always disintegrated in *o*-chlorophenol. Although some gel could be observed, it did not seem possible to use the gel content to estimate the extent of crosslinking. This difference in behavior between the two fibers after crosslinking was principally attributed to the greater crystallinity of PET, which limited the uptake of the azide to the amorphous regions of the fiber, so that crosslinking only occurred in these regions. Additionally, the longer chain length of the acrylic polymer favored the production of a more effectively crosslinked structure. A further factor that might have limited the effectiveness of the crosslinking in PET was the high content of the oligomer (e.g., cyclic trimer), which was presumed to concentrate in the amorphous regions. A final difference between the fibers was related to the ease of diffusion of the azides into the fibers; differences in the behaviors of three different azides applied to PET were interpreted in terms of differences in the extent of diffusion across the fiber cross section, so that in some cases only the amorphous regions in the outer periphery of the fiber were thought to be crosslinked.

After this work,<sup>2</sup> we considered it worthwhile to determine how the mechanical properties of the fibers

varied under different conditions of temperature and loading because of crosslinking. It was thought that a thermomechanical examination of the crosslinked fibers in comparison with the blank-treated standard fibers would yield valuable information concerning how the crosslinking affected the thermal extensibility of the fibers under increasing temperatures and under oscillating loads; the latter was thought to be informative of changes in the elastic modulus with respect to temperature due to the crosslinking. Preliminary creep studies were also made as a qualitative evaluation of how the crosslinking had affected the creep behavior of the fibers; it must be stressed, however, that a thermomechanical analyzer is not the usual device employed to obtain creep data because creep is a complex phenomenon and its determination often requires the use of specific and complex machinery.<sup>3–5</sup>

## EXPERIMENTAL

### Instrumentation and materials

The instrument used for all the experiments discussed was a Mettler TA3000 system (Leicester, UK), which consisted of a TC10 TA control unit and data processor and a TMA 40 mechanical analyzer fitted with film and fiber support. The system was attached to a printer so that the data could be retrieved; however, there was no other method of data storage, and no computer interface was available. The data were retrieved as a stream of raw data or as a graph so that where no raw data were retrievable, graphs were produced to minimize the errors involved in the manual measurement of data for transfer to a computer.

The crosslinked samples used in the experiments were those prepared previously,<sup>2</sup> that is, samples that

Correspondence to: D. A. Baker (darrenbaker@clemson.edu).

were treated at 140°C for 20 min to impregnate the fibers with azide and then at 200°C for 20 min to bring about crosslinking. The standard sample mentioned throughout the article was subjected to exactly the same treatment as the crosslinked samples, except that no azide was used so that no crosslinking would occur. The PET used, as before,<sup>2</sup> was obtained as a high-end, partially oriented, continuous filament yarn in the form of grade 3 Dacron from DuPont (Pontypool, UK). This yarn consisted of 34 filaments with a circular cross section measuring a total of 167 dtex. The disulfonyl azides used, synthesized as described earlier,<sup>6</sup> were 1,6-hexanedisulfonyl azide (1,6-HDSA), 1,3-benzenedisulfonyl azide (1,3-BDSA), and 2,6-naphthalenedisulfonyl azide (2,6-NDSA). The application was from a perchloroethylene solution with concentrations of the azides between 5 and 20%. The levels of the azides in the fibers were not known precisely but were believed to lie between 2 and 3% at a 20% application.

#### Machine setup and sample preparation

The calibration of the machine was only required once in agreement with the manual, so the calibration was stored internally. The probe of the TMA 40 was first centered so that the display on the machine read zero for each of the experiments. For a specimen to be produced for testing, a sample of yarn was fixed between two specially made clamps that were fitted on a jig so that the fiber between the clamps was 10 mm long and just taut; the clamps were then tightened, and excess fiber removed. The sample was attached at the appropriate time to the TMA 40 support with care so that minimal handling took place. Much preliminary work was done to determine the optimum conditions for the sample measurements, as described next.

#### Thermal extension under constant loading

The yarn sample was prepared in the usual manner, and the machine was set up to record the changes in the sample length with respect to temperature at a heating rate of 20°C/min under a constant load. The program was set so that the temperature started at 50°C and finished at 230°C, with two total loads, 0.6 and 4.0 g. The lower clamp mass was 0.6 g, which was permitted in the total load applied. When the machine had reached the required starting temperature, the sample was attached to the support and the program was run so that the changes were recorded graphically and as a stream of data so that plots could be made. The samples that were tested were those treated in solutions containing 5, 10, 15, and 20% 1,6-HDSA, 1,3-BDSA, or 2,6-NDSA and the standard sample containing no azide.

#### Thermal extension with load cycling

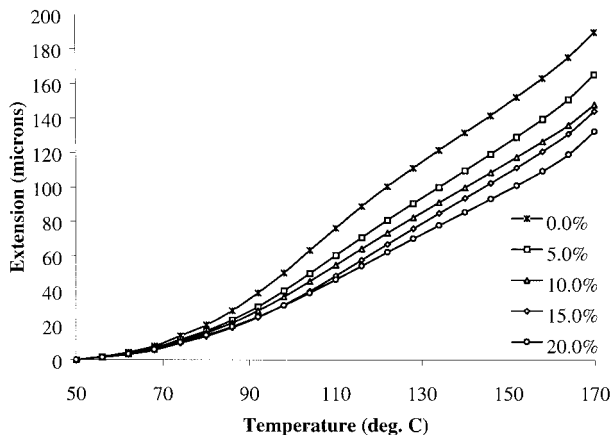
The yarn sample was prepared as before, and the machine was set up to record the changes in the sample length on heating from 50 to 230°C at a rate of 20°C/min. The total load was adjusted to 3.0 g with an additional oscillating mass of  $\pm 2.0$  g, (so that the mass switched between 1 and 5 g), the time of the oscillation being 6 s, the machine's preset value. When the machine had reached the starting temperature, the sample was mounted and the program was run so that the results were recorded graphically with an appropriate scale so that measurements on the graphs could be made with a ruler. The samples that were tested were those treated in solutions containing 10 and 20% 1,6-HDSA, 1,3-BDSA, or 2,6-NDSA and the standard sample containing no azide.

#### Isothermal load cycling measurements

The yarn sample was prepared as before, and the machine was set up for isothermal measurements at 50, 100, or 150°C with an oscillating mass so that the total mass applied to the sample was  $3.0 \pm 2.0$  g, as before. When the machine had reached the desired temperature, the sample was mounted, and the program was started and run for 30 min. The changes in length with respect to time were recorded on the chart so that manual measurements could be made later. The samples that were tested were those treated in solutions containing 10 and 20% 1,6-HDSA, 1,3-BDSA, or 2,6-NDSA and the standard sample containing no azide.

#### Creep studies

The yarn sample was again prepared as discussed earlier, and the machine was set up for isothermal creep measurements under a constant loading. Two temperatures were selected for the study, 25 and 100°C, the latter being close to the glass transition of the PET fibers (ca. 120°C). Two different levels of loading were also applied; in one case, the total mass was 75 g, that is, approximately 12% of the breaking load of the standard sample at 20°C, within the Hookean region of the stress-strain curve of the standard sample.<sup>1</sup> The higher level of loading used was 150 g (24.5% of the breaking load and just outside the Hookean region of the standard sample). The machine was allowed to reach the starting temperature at which the sample was mounted; the machine was then allowed to run with the load applied after the data recording had begun. For the tests performed at 100°C, the machine was subjected to a forced start so that the machine's default thermal equilibration time was aborted. The samples tested were those treated with solutions containing 20% 1,6-HDSA, 1,3-BDSA,



**Figure 1** TMA traces of samples crosslinked with 2,6-NDSA (4.0 g, 20°C/min).

or 2,6-NDSA, except at 100°C under a load of 150 g, under which conditions the latter two azide-treated samples were substituted with those treated with 10% azide.

Unfortunately, the maximum amount of data the machine could hold for manipulation was only enough for a creep test of 2-h duration, so complete studies were not possible. Further and extensive experimentation was not done because of the possibility of damage to the machine due to the high loads employed, given that extra loading had to be added to the counterbalance of the TMA 40 because the machine had a maximum internal capacity of 50 g. The TMA 40 manual states that there is provision for additional mass, but it does not say to what level it can be applied.

## RESULTS AND DISCUSSION

### Thermal extension under constant loading

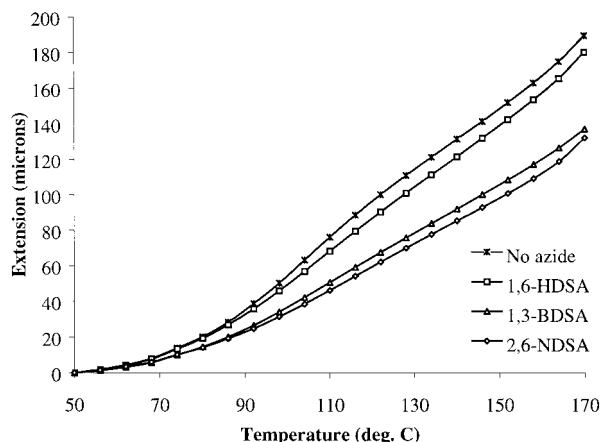
Figure 1 shows the thermal mechanical analysis (TMA) traces for the PET fiber samples treated with different concentrations of 2,6-NDSA under the 4.0-g load and at a heating rate of 20°C/min. Very similar data were obtained for the 1,3-BDSA-treated samples. The traces for the samples treated with 1,6-HDSA were, by contrast, only slightly different from those of the standard sample. This result is in line with the smaller changes noted in the mechanical properties of the 1,6-HDSA-treated samples, discussed in our previous publication.<sup>1</sup> Again, this was interpreted to be due to a more uniform distribution of crosslinks rather than less reaction. Similar trends were observed when the load was set to 0.6 g, although the differences were of a lower magnitude.

It is evident that the traces changed significantly and consistently with an increasing level of crosslinking, so that for the sample treated with a solution containing 20% 2,6-NDSA, the extension at 170°C was

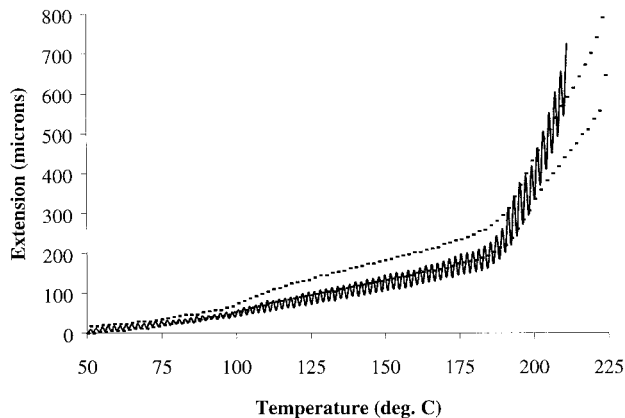
approximately three-quarters of that of the standard sample under a 0.6-g load and two-thirds of that of the standard under a 4-g load. It was concluded that the crosslinking brought about a significant improvement in the dimensional stability of the fibers. A further feature was the increased extension of the standard sample observed above 120°C at the 4-g loading, so that the curve obtained was different in form from that obtained from crosslinked samples; this feature was probably associated with the smaller specific volume change occurring at the glass transition due to the increasing levels of crosslinking that restricted molecular motion within those amorphous regions that were crosslinked.

Figure 2 shows the relative effects of using the different azides at the same concentration: 2,6-NDSA appeared to be slightly more effective than 1,3-BDSA, whereas the 1,6-HDSA-treated sample was barely distinguishable from the standard. We argued earlier<sup>1</sup> that the differences between the two aromatic azides might reflect the greater extent of diffusion of 2,6-NDSA into the fiber.

The full curves have not been given in the figures, so that the changes discussed previously could be observed more clearly. However, the region between 170°C and the temperature at which the samples failed revealed further differences; the crosslinked samples always failed at a lower temperature than that of the standard. The standard sample failed at approximately 223°C, under both levels of loading, whereas the crosslinked samples failed at lower temperatures, depending on the level of crosslinking, so that the samples treated in a solution containing 20% 1,3-BDSA or 2,6-NDSA failed around 212°C. This feature was thought to be related to the differences in the polymer microstructure, which caused the deformation of the crosslinked samples to be greater, at temperatures close to the melt, than that of the standard. At temperatures above approximately 200°C, some



**Figure 2** TMA traces of samples crosslinked with 20% of each azide (4.0 g, 20°C/min).

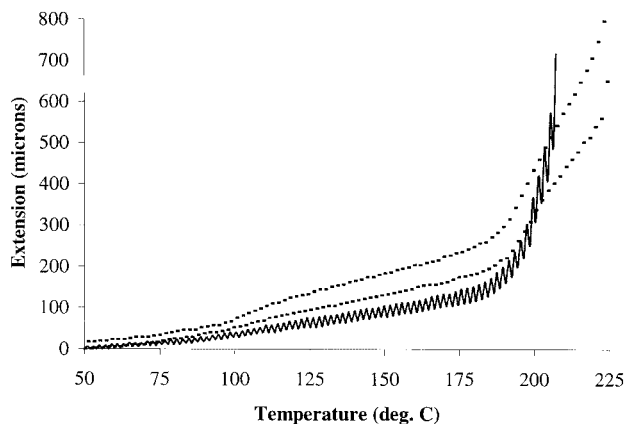


**Figure 3** TMA trace of a sample crosslinked with 20% 1,6-HDSA (cyclic load of  $3.0 \pm 2.0$  g,  $20^\circ\text{C}/\text{min}$ ).

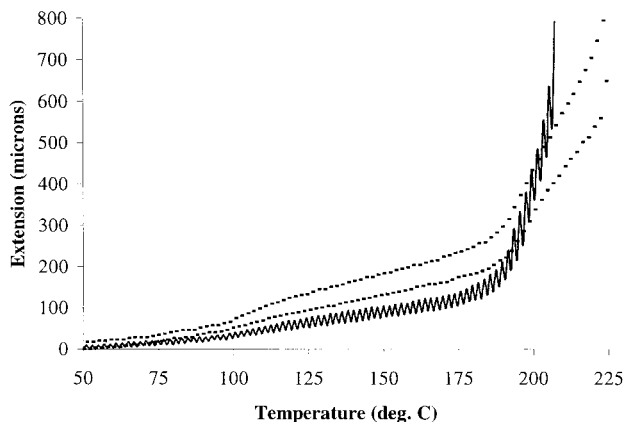
localized melting or annealing took place, so that under a load, the polymer would start to flow more freely and the polymer chains would rearrange in both the crystalline and amorphous regions, so that slippage occurred; recrystallization of the chains was favorable because interaction occurred as the chains were relatively free from restriction. However, when some of the amorphous regions were crosslinked, this recrystallization process was hindered; the crystalline regions still flowed, so the overall effect was catastrophic failure of the sample at a lower temperature.

#### Thermal extension with load cycling

The TMA traces from the cyclic loading experiments are given in Figures 3–5, in which the curve of the standard sample is shown as a dotted line in each case; these indicate the envelope of the oscillation curve of the standard sample. The traces obtained for each sample show that the cyclic loading caused the expected dimensional oscillation; this oscillation was of a much higher amplitude at temperatures above the glass transition and increased yet again at tempera-



**Figure 4** TMA trace of a sample crosslinked with 20% 1,3-BDSA (cyclic load of  $3.0 \pm 2.0$  g,  $20^\circ\text{C}/\text{min}$ ).



**Figure 5** TMA trace of a sample crosslinked with 20% 2,6-NDSA (cyclic load of  $3.0 \pm 2.0$  g,  $20^\circ\text{C}/\text{min}$ ).

tures at which localized melting (annealing) was considered to occur, so that the standard sample eventually failed around  $225^\circ\text{C}$ .

Samples treated in solutions containing 10 and 20% 1,6-HDSA gave traces that were similar but significantly different than that obtained for the standard sample in terms of a reduced amplitude of dimensional oscillation that decreased with an increasing density of crosslinking; the overall extension of the crosslinked samples was lower than that of the standard. However, as expected from the constant-load traces, these samples failed at a lower temperature than the standard for the reasons discussed earlier. The load cycling data contrasted with the standard TMA procedure, which failed to show significant differences for the 10% 1,6-HDSA treatments, and this suggested the former to be a more sensitive detector for low levels of crosslinking.

The reduction in the level of the amplitude of oscillation was most pronounced in those samples crosslinked with 1,3-BDSA and 2,6-NDSA in comparison with the standard; this was found to change significantly with an increasing level of treatment from a 10% solution to a 20% solution of the crosslinking agent. It was very obvious from the traces, as observed before in the constant-load experiments, that the glass transition was greatly affected, so that the overall curves did not exhibit the same shifts that were observed in the curve of the standard sample. Also above  $120^\circ\text{C}$ , the level of oscillation was much lower for the crosslinked samples than for the standard sample, as was the overall extension. The samples again failed at a lower temperature than that of the standard, as was the case with the 1,6-HDSA-treated samples.

#### Isothermal load cycling measurements

The isothermal load cycling results confirmed the observations made in the previous section, and the re-

**TABLE I**  
Amplitude of Mass Oscillation for Isothermal Load Cycling

Azide	% Azide	Amplitude due to mass ( $\mu\text{m}$ )		
		50 °C	100 °C	150 °C
None	0	9.3	16.8	36.4
1,6-HDSA	10	10.1	16.1	35.3
	20	8.9	12.8	33.3
1,3-BDSA	10	7.8	12.2	22.3
	20	6.6	10.9	22.3
2,6-NDSA	10	8.9	10.7	23.1
	20	6.6	9.5	22.3

sults are given in Table I. The standard sample in general exhibited a greater amplitude of extension oscillation in comparison with the crosslinked samples, apart from the samples crosslinked with 10% 1,6-HDSA. The samples treated with solutions containing 20% 1,6-HDSA were slightly lower, whereas those treated with 10 or 20% 1,3-BDSA or 2,6-NDSA were shown to be much lower. This indicated that the levels of crosslinking attained with 1,6-HDSA were probably lower than those obtained with the other azides, possibly because of some chemical inefficiency, but more likely, as argued before, because this azide gave a more homogeneous distribution of crosslinking than the other two agents. It was claimed earlier<sup>2</sup> that a distribution gradient of azide gave rise to a much higher concentration of crosslinks in the amorphous regions closer to the fiber surface in the case of 1,3-BDSA and 2,6-NDSA, so that this near surface layer would control the overall fiber properties.

The reduction in the amplitude of extension oscillation exhibited by the crosslinked samples in comparison with the standard sample suggested an increased initial modulus, so that a greater force was required to stretch the fiber. However, it is appropriate to comment that these experiments were essentially comparative. Notable again is the large increase in the amplitude of motion above the glass transition of the fibers.

### Creep studies

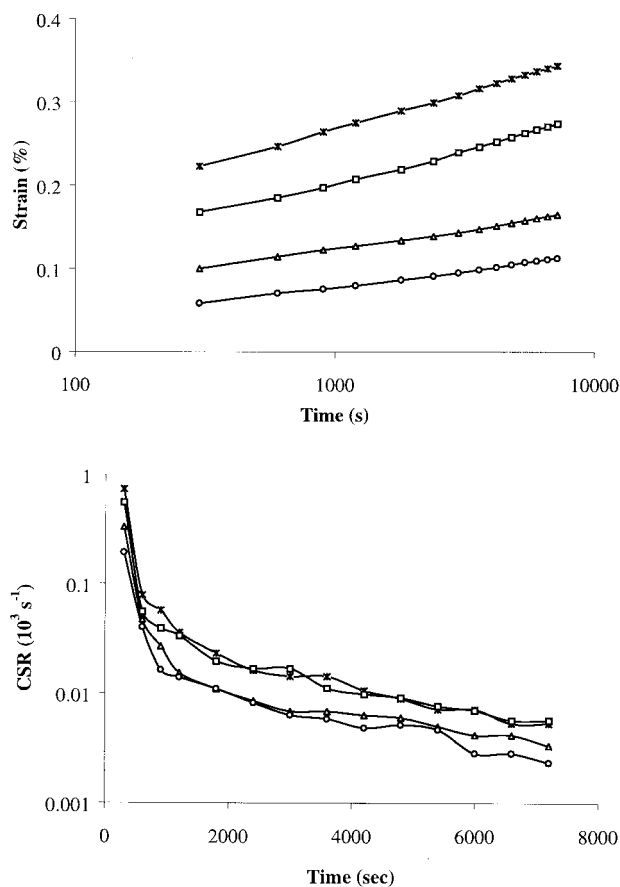
The creep measurements are shown in Figures 6 and 7, and the two plots within each figure represent two common methods of presenting the data. The first shows the strain of the sample against the logarithm of time, and the second shows the logarithm of the creep strain rate (CSR) against time; the CSR is the rate of change of the strain applied to the sample with respect to time.

The measurements at room temperature and under a load of 75 g (Fig. 6) clearly show the effect that crosslinking had on the creep properties of the fibers, so that the initial extension was much reduced in the primary creep region for all the crosslinked samples;

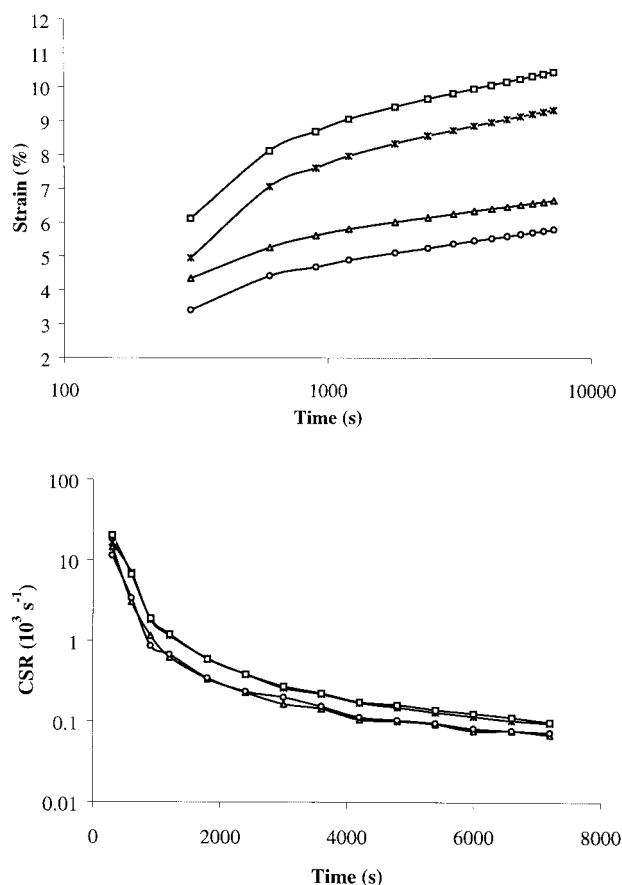
this was most marked for that sample treated in a solution containing 20% 2,6-NDSA and least for the sample treated in a solution containing 20% 1,6-HDSA. After this initial extension, the curves flattened so that the plots of the strain versus the logarithm of time were almost linear within the secondary creep region, as expected. It was obvious that the CSR was reduced for those samples treated with 1,3-BDSA and 2,6-NDSA to about one-third of that observed in the standard sample, whereas the CSR of the sample treated with 1,6-HDSA was largely unchanged, even though the initial extension was substantially reduced.

The picture remains the same under a load of 150 g at the same temperature (not shown), so that the samples had equivalent relative creep properties, even though the strain values increased in magnitude by a factor of 10. Under both sets of conditions, the creep properties of the fibers were improved by the crosslinking process so that the initial extension and the CSR were reduced substantially, and again in this latter case, the plots of strain against the logarithm of time were linear, as expected for creep studies.

When the temperature of testing was increased to 100°C, which was closer to the glass transition of the



**Figure 6** Creep measurements at 25°C and under a 75-g load for the standard sample (\*) and for samples treated in a solution containing 20% 1,6-HDSA (□), 1,3-BDSA (△), and 2,6-NDSA (○).



**Figure 7** Creep measurements at 100°C and under a 75-g load, for the standard sample (\*) and for samples treated in a solution containing 20% 1,6-HDSA (□), 1,3-BDSA (△), and 2,6-NDSA (○).

fibers, a different picture emerged, in that the creep properties of the crosslinked samples began to approach those of the standard samples under a 75-g load (Fig. 7) and actually became worse still under a load of 150 g (not shown). The initial curvature of the strain-time plot indicated the presence of primary creep, so that under these conditions the initial extension was much higher; the sample, therefore, required more time to extend before exhibiting secondary creep. An examination of the crosslinked samples showed that the creep properties under a 75-g load at 100°C had still in the main improved relative to the standard, except for the sample treated with 1,6-HDSA, which exhibited poorer properties. It was evident that at some level of loading the creep properties of all the crosslinked samples would exhibit poorer creep performance than that of the standard sample. When the load was increased to 150 g, the crosslinked samples exhibited a poorer creep performance at 100°C than the standard sample, so that those samples treated in a solution containing 20% 1,3-BDSA or 2,6-NDSA could not be measured because of mechanical failure and only the 10% samples could be compared.

The failure of the former samples was thought to be due to their lower tenacity (described earlier<sup>2</sup>), so that the 150-g load might have exceeded the maximum strength of the samples at 100°C; the tenacity of fibers is known to decrease with increasing temperature, and it is unfortunate that it could not be measured for the fibers used in this study at elevated temperatures within this laboratory.

The lower creep performance of the crosslinked fibers at higher temperatures and under greater loads was thought to be a function of the stress-strain properties of the fibers and, therefore, the mechanism of deformation that occurred in each of the regions described in such a curve. It seemed that if the creep measurements were made within the Hookean region, the crosslinked samples performed much better than standard untreated fibers; when the measurements were made outside the Hookean region, in which crystallite deformation occurred, the opposite might be true. This was thought to be due to the reduced compliance of the crosslinked amorphous regions, in comparison with the standard material, when crystallite deformation occurred. The generation of stress points, at which the crosslinks gave rise to chain scission in preference to slippage, led to earlier failure.

The severity of the conditions used in this study can be exemplified by a comparison of the relative magnitudes of strain experienced by the samples under each of the conditions. At 100°C, the strain experienced by the fibers was approximately 25 times that at 25°C under a 75-g load, after the initial extension, and 100 times that at 25°C, under a 75-g load, when the 150-g load was used. These conditions were used because PET had such a low creep rate that smaller changes in length would have been impractical to measure on the TMA 40 and impossible to measure with a hanging mass assembly because long yarn samples were not available on account of yarn entanglement that occurred during the perchloroethylene treatment.

## CONCLUSIONS

The crosslinking of PET fibers was shown to affect the mechanical properties under standard tensile testing conditions, as discussed in our previous publication,<sup>2</sup> and this was also found to be true here via measurements under increasing temperatures and cyclic loading. The crosslinked samples exhibited a lower extension under small loadings in comparison with the blank-treated sample, unless the temperature at which the measurement occurred was so high that chain slippage and crystallite deformation occurred so that the crosslinked samples failed more quickly. The use of cyclic loading confirmed the lower extension of the crosslinked samples under minimal loading and a

higher elastic modulus that was more easily identified at elevated temperatures.

Creep studies, although rather qualitative, indicated that the crosslinking brought about a very large reduction in creep at ambient temperatures, so that the initial extension under loading was much reduced and the creep rates were reduced by up to two-thirds. At higher temperatures, the trends reversed so that the creep performance of the standard sample was better than that of the crosslinked samples. These features were thought to be associated with the stress-strain properties of the polymer under each of the conditions, so that when the measurements were conducted within the Hookean region, the crosslinked samples

performed better, and outside this region, they performed worse.

### References

1. Baker, D. A.; East, G. C.; Mukhopadhyay, S. K. *J Appl Polym Sci* 2002, 84, 1309.
2. Baker, D. A.; East, G. C.; Mukhopadhyay, S. K. *J Appl Polym Sci* 2002, 83, 1517.
3. Nkiwane, L. Ph.D. Thesis, University of Leeds, 1999.
4. Vangeliume, L. *Text Res J* 1992, 62, 586.
5. Tewary, V. K. *Mechanics of Textile Composites*; Wiley Eastern: New Delhi, 1978.
6. Baker, D. A.; East, G. C.; Mukhopadhyay, S. K. *J Appl Polym Sci* 2001, 79, 1092.