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1 **Development of High Shrinkage Polyethylene Terephthalate (PET) Shape**  
2 **Memory Polymer Tendons for Concrete Crack Closure**

3 Oliver Teall<sup>1</sup>; Martins Pilegis<sup>2</sup>; John Sweeney<sup>3</sup>; Tim Gough<sup>4</sup>; Glen Thompson<sup>5</sup>; Anthony  
4 Jefferson<sup>6</sup>; Robert Lark<sup>7</sup>; Diane Gardner<sup>8</sup>

5 <sup>1</sup>*Cardiff University School of Engineering, Queen's Buildings, The Parade, Cardiff CF24 3AA*

6 <sup>2</sup>*Cardiff University School of Engineering, Queen's Buildings, The Parade, Cardiff CF24 3AA*

7 <sup>3</sup>*Bradford University School of Engineering, Bradford, West Yorkshire, BD7 1DP*

8 <sup>4</sup>*Bradford University School of Engineering, Bradford, West Yorkshire, BD7 1DP*

9 <sup>5</sup>*Bradford University School of Engineering, Bradford, West Yorkshire, BD7 1DP*

10 <sup>6</sup>*Cardiff University School of Engineering, Queen's Buildings, The Parade, Cardiff CF24 3AA*

11 <sup>7</sup>*Cardiff University School of Engineering, Queen's Buildings, The Parade, Cardiff CF24 3AA*

12 <sup>8</sup>*Cardiff University School of Engineering, Queen's Buildings, The Parade, Cardiff CF24 3AA*

13

14 Correspondence to: Tony Jefferson (Email: JeffersonAD@cardiff.ac.uk)

15

16 **ABSTRACT**

17 The shrinkage force exerted by restrained shape memory polymers can potentially be used  
18 to close cracks in structural concrete. This paper describes the physical processing and  
19 experimental work undertaken to develop high shrinkage die-drawn Polyethylene  
20 Terephthalate (PET) shape memory polymer tendons for use within a crack closure system.  
21 The extrusion and die-drawing procedure used to manufacture a series of PET tendon samples  
22 is described. The results from a set of restrained shrinkage tests, undertaken at differing  
23 activation temperatures, are also presented along with the mechanical properties of the most  
24 promising samples.

25 The stress developed within the tendons is found to be related to the activation temperature,  
26 the cross-sectional area and to the draw rate used during manufacture. Comparisons with  
27 commercially-available PET strip samples used in previous research are made, demonstrating  
28 an increase in restrained shrinkage stress by a factor of two for manufactured PET filament  
29 samples.

30

31 **1 INTRODUCTION**

32 Shape Memory Polymers (SMPs) alter their physical shape in response to various stimuli, such  
33 as a change in heat, light (UV and infrared) or chemical concentration (e.g. moisture, pH).<sup>1-3</sup>

34 The simplest type of SMP is formed from amorphous polymer. In this case the SMP is created

35 by heating the material to a temperature above the glass transition temperature ( $T_g$ ), inducing  
36 molecular chain orientation by stretching it, and then freezing in the orientation by cooling.  
37 The orientation can be released at a later time by increasing the temperature to a trigger  
38 temperature, which is at or above  $T_g$ , at which point the material reverts wholly or partially  
39 to its pre-oriented shape. Other types of SMP can be formed from semi-crystalline polymer,  
40 in which case the stretching and trigger temperatures will be governed by the temperature  
41 dependence of the mechanical properties of the crystals. Similar macroscopic physical  
42 behaviour can be accomplished for both amorphous and semicrystalline polymer, and in  
43 either case this shape change ability can be categorised as a shape memory effect (SME).<sup>1,2,4</sup>

44 If an amorphous SMP, having been stretched into its oriented state (“programmed”), is then  
45 heated above  $T_g$  while restrained, a restrained shrinkage stress will be generated. Restrained  
46 shrinkage stresses observed in unmodified SMPs generally range from a few tenths of a  
47 megapascal (MPa) to a few tens of MPa, depending on the material and programming regime  
48 used.<sup>2,5,6</sup> A key parameter which determines the final stress achieved is the temperature at  
49 which the SMP has been programmed, and the maximum value for the stress upon reheating  
50 generally occurs at or near the programming temperature initially used.<sup>3,7</sup> The restrained  
51 shrinkage stress also depends upon the programming strain and strain rate.<sup>3,7</sup>

52 The magnitude of the restrained shrinkage stress is positively correlated with the energy  
53 stored by the SMP during deformation, and is limited by the relatively low elastic modulus of  
54 the material in the rubbery state (above  $T_g$ ). Efforts to improve the rubbery state elastic  
55 modulus have included increasing the cross-linking density and the incorporation of fillers  
56 into the polymer matrix. Common fillers include carbon nanotubes (CNTs) and carbon  
57 nanofibres (CNFs), as well as glass or Kevlar fibres, carbon powders and SiC particles.<sup>5,6</sup> Such

58 inclusions have been shown to increase the recovery stress;<sup>2</sup> however, the associated  
59 increase in cost and  $T_g$  of the SMP would likely be a prohibiting factor within a concrete crack  
60 closure system. The focus of the experiments within this paper, therefore, is on comparing  
61 the restrained shrinkage stresses of unmodified drawn PET (in essentially amorphous form)  
62 with differing cross sections and processing methods.

63 In terms of thermal activation, the triggering temperature must be chosen to suit the  
64 application. Polymers may be specially formulated to produce the required activation  
65 temperatures. In this case, the upper limit to the trigger temperature is governed by the  
66 presence of setting concrete which can be damaged at temperatures above 100°C.

67 In amorphous polymers, the temperature for both inducing orientation and triggering shape  
68 recovery are closely related to  $T_g$ . PET has a glass transition temperature in the range 60 – 80  
69 °C.<sup>9</sup> Previous work undertaken at Cardiff University suggested that the peak uniaxial shrinkage  
70 stress for drawn PET tape is achieved at 120 °C;<sup>10</sup> however, to ensure the system can be  
71 activated within concrete, an activation temperature of 90°C was chosen for the experiments  
72 described in this paper.

73 The purpose of this paper is to expand on the previous work on the use of shape memory  
74 polymer tendons as a crack closure system within concrete structural elements.<sup>10,11</sup> A number  
75 of other investigators have explored the use of shape memory materials for closing, or  
76 preventing, cracks in a range of other materials.<sup>12-17</sup> The particular interest of the current work  
77 is large structural concrete applications, for which higher shrinkage stresses than those  
78 previously observed are required for the crack closure system to be viable. The shrinkage  
79 stress value sought is of the order of 100MPa but lower values, in the range 30-50MPa, would  
80 allow the system to close early age cracks and enhance autogenous healing mechanisms.<sup>18,19</sup>

81 This paper describes some new restrained shrinkage stress experiments on a set of  
82 manufactured drawn PET samples of varying cross-section, which were undertaken with the  
83 aim of finding a higher shrinkage stress solution for use within the concrete crack closure  
84 system.

85 The polymer samples tested in the present investigation, with the exclusion of the  
86 commercially available PET shrink tite strips, are bespoke and have been produced at  
87 Bradford University for the purpose of assessing their potential for use within the concrete  
88 crack closure system. SMPs have never before been manufactured specifically for this  
89 purpose and maximising the polymer restrained shrinkage stress, for use within a  
90 cementitious system, is the long-term objective of the present work.

91

92 The geometry of the tendons tested, including their lengths of the elements and cross-  
93 sectional areas, were chosen to provide data relevant to the type of tendon required for  
94 typical structural elements.<sup>19</sup>

95

96

## 97 **2 EXPERIMENTAL STUDY**

98 An experimental study into the restrained shrinkage stress generated by both commercially  
99 available PET strips and PET filament samples produced at Bradford University of varying  
100 cross-section is now described. Details of the specimens tested are given in in TABLE 1 and an  
101 image of the cross-sections of all manufactured samples shown in Figure 2.

102

103 **TABLE 1 Details of shape memory polymer samples tested**

Designation	Material	Dimensions (unit)	Draw ratio	Draw rate (mm min <sup>-1</sup> )	Tests and repetitions	
Strips	Oriented PET <sup>a</sup>	0.046mm thickness 32mm width	unknown	unknown	TS1	3
					TS2	1
					TS3	10
					TS4	3
					TS5	3
Solid filament	Drawn PET	0.95mm dia.	4.0	1000	TS1	3
					TS2	1
					TS3	10
					TS4	3
					TS5	3
Filament tube	Drawn PET	0.95mm dia.	4.0	1000	TS1	1
					TS2	1
					TS3	10
					TS4	3
Tube	Drawn PET	6.61mm external dia. 2.56mm internal dia.	3.9	40 (initial)	TS1	1
					TS2	1
					TS3	1
Tube with filaments	Drawn PET	6.54mm dia.	4.0 (tube)	40 (initial)	TS1	1
			4.4		TS2	1
			(filament)		TS3	1

104 <sup>a</sup>Manufacturing details commercially sensitive

105

106 **2.1 Material manufacturing details**

107 ***PET solid and tube filament***

108 For the PET solid filaments and tube filaments, a commercial grade of PET (Dow Lighter C93)  
 109 was obtained in granular form. This polymer has a T<sub>g</sub> of 78 °C according to manufacturer's  
 110 figures and is recommended for injection moulding, stretch blow moulding and  
 111 thermoforming. It was first made into fibres by melt extrusion. This was done using a single-  
 112 screw Killion S1748 25 mm extruder operating at a screw speed of 15 rpm and a screw  
 113 pressure of 30 bar. The maximum melt temperature in the extruder was 280 °C and the die  
 114 head was at 270 °C. The material was extruded through a circular die of 4mm internal

115 diameter and hauled off at  $5\text{ m min}^{-1}$ . On exit from the die it was cooled in a glycerol bath at  
116 room temperature. The final diameter of the cooled product was 1.8 mm.

117 The second stage of the process was to introduce molecular orientation into the fibres. The  
118 technique of die-drawing was used, as described for polymers by Coates and Ward<sup>20</sup>. Fibre at  
119 room temperature was pulled through a 1.5 m length fan-assisted oven with a controlled air  
120 temperature. On exit from the oven, it entered a converging conical die with cone angle  $30^\circ$   
121 and final diameter 1 mm, held at a constant temperature. After the die, the fibre was gripped  
122 by a caterpillar-type haul-off device operating at a constant linear speed. Since the highest  
123 levels of orientation are associated with the highest haul-off speeds and lowest temperatures,  
124 the caterpillar speed was set at its maximum  $1\text{ m min}^{-1}$  (corresponding to an average axial  
125 strain rate in the die of  $17\text{ s}^{-1}$ ) and both the oven and die temperatures were lowered in  $1^\circ\text{C}$   
126 increments from  $80^\circ\text{C}$  until stress whitening and failure of the fibre were observed at  $75^\circ\text{C}$ .  
127 The die temperature was then raised incrementally until satisfactory fibre was produced; the  
128 final settings were thus  $75^\circ\text{C}$  in the oven and  $80^\circ\text{C}$  in the die. After exiting the die, further  
129 drawing took place during cooling between the die and the caterpillar, resulting in a final  
130 diameter of 0.9 mm, corresponding to a draw ratio of 4.0. At the start of the process the haul-  
131 off force was measured as 80 N, and this reduced to a steady load of 50 N as the process  
132 stabilised; these loads correspond to stresses of 99 and 62 MPa respectively, to be compared  
133 with the yield strength of 55 MPa according to the manufacturer's data sheet.

134

### 135 ***PET tube***

136 The outer cylinder was made from the same grade of PET as with the monofilaments  
137 described above. Tubes were extruded using the same Killion extruder operating at a screw

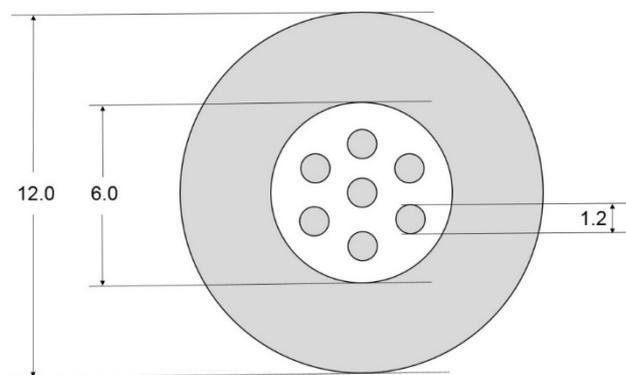
138 speed of 70 rpm and a pressure of 200 bar. The maximum temperature in the extruder was  
139 280 °C and the die head was at 260 °C. Extrusion was through a circular section die of diameter  
140 14mm, with a central internal pin of diameter 4 mm to create the central hole. The haul-off  
141 speed was 500 mm min<sup>-1</sup> and final dimensions were outer diameter 13 mm and inner  
142 diameter 6mm.

143 The tubes were then die-drawn from 1 m lengths through a 30° conical die with an exit  
144 diameter of 7 mm. Otherwise, the die-drawing equipment was as used for the drawing of the  
145 monofilaments described above. Both the die and oven air temperatures were set at 75 °C.  
146 The initial haul-off speed was 40 mm min<sup>-1</sup> (corresponding to an average strain rate in the die  
147 of 0.1 s<sup>-1</sup>), and was increased during the die-drawing process to reach the maximum draw  
148 ratio. The tube's final outer diameter was on average 6.61 mm, corresponding to a draw ratio  
149 of 3.9.

150

### 151 ***PET tube with filaments***

152 An alternative system was studied that consisted of PET monofilaments inside the hollow PET  
153 tube samples. This was assembled in its initial isotropic state (see configuration in Figure 1)  
154 and then the complete assembly was die-drawn.



155

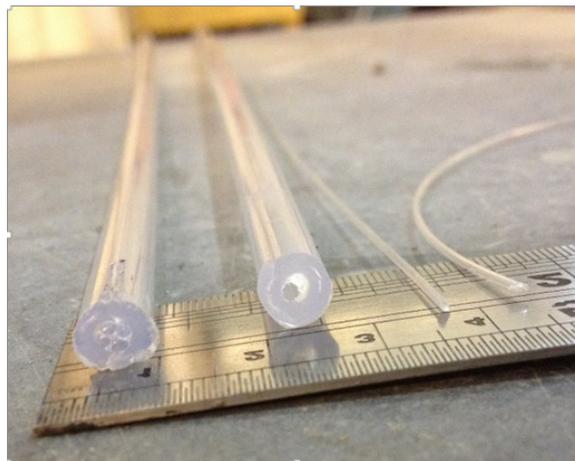
156 **FIGURE 1 Indicative cross-section of multifilament system before drawing. Dimensions in mm**

157

158 The internal fibres were extruded from Tergal grade T74F9 PET. Extruder and die  
159 temperatures were both 280 °C, with extrusion through a 2.5 mm spinneret at a screw speed  
160 of 5.4 rpm to achieve a final fibre diameter of 1.2 mm. The outer cylinder was manufactured  
161 following the same process described for the PET tube samples.

162 1 m lengths of tube and filaments were assembled and then die-drawn through a 30° conical  
163 die with an exit diameter of 7 mm, following the same procedure as for the PET tube samples.

164 This resulted in a final external diameter of 6.54 mm for the samples, with internal fibres of  
165 average diameter 0.57 mm. This corresponds to a draw ratio of 4.0 for the tubes and 4.4 for  
166 the internal fibres.



167

168 **FIGURE 2** Manufactured PET samples, left to right: tube with filaments, tube, solid filament, filament tube

169

170 ***PET strips (commercially available)***

171 The PET strip specimens are commercially available under the name ‘shrink tite tape’ and  
172 were obtained from Cytec.<sup>21</sup> The shrink tite strips used in a previous study were purchased  
173 from Aerovac, part of the Umeco Composites group, which was acquired by Cytec in 2012.<sup>21</sup>  
174 These strips are made from oriented PET but the manufacturing details are not available.

175

## 176 **2.2 Thermal characterisation**

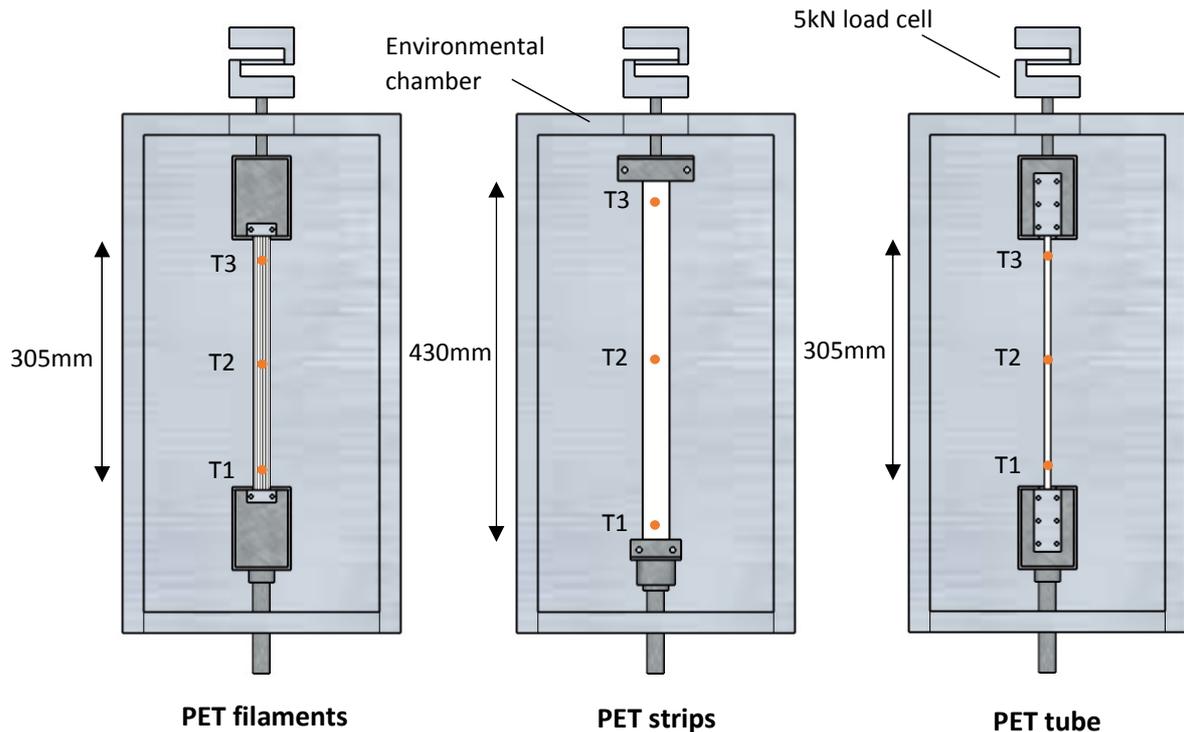
177 For the Dow Lighter C93 material, Modulated Differential Scanning Calorimetry (MDSC) was  
178 performed on 5 mg samples of both the unoriented and oriented fibres, corresponding to the  
179 two stages of fibre production outlined in the previous section. A TA Instruments Discovery  
180 DSC was used, programmed with a mean temperature ramp of 3 °C min<sup>-1</sup> from 0 °C to 300 °C.  
181 In order to decouple the reversible heat flow measurements from non-reversible thermal  
182 events a modulation of ±1.0 °C on a period of 1 min was continuously applied to the samples  
183 during heating. The glass transition determined from the reversible signal of the MDSC,  
184 occurred in the range 70.10 - 77.95 °C for the unoriented sample, with the upper end of the  
185 range in good agreement with the manufacturer's value of 78.0 °C. Further unmodulated  
186 testing at a ramp of 2°C min<sup>-1</sup> established that crystallinity was in the range 9 – 12%. The  
187 results of the measurements on the oriented fibre will be discussed in section 3.1.

188

## 189 **2.3 Equipment and test specimen preparation**

190 Thermal triggering was achieved by direct heating in an Instron environmental chamber. Each  
191 sample was clamped within steel friction grips, which were subjected to preliminary testing  
192 to ensure there was no significant slippage of the samples during activation.

193 A diagram of the rig used to test each sample is shown in Figure 3. The rigs were connected  
194 to a 5kN load cell and three thermocouples were placed on the samples, denoted T1, T2 and  
195 T3. The load cell and thermocouples were attached to a data logger set to record at a rate of  
196 1 Hz. Each sample was pre-loaded manually to a stress of 2 MPa to ensure that there was no  
197 slack which would affect the shrinkage results.



198

199 **FIGURE 3 Environmental chamber rig setup for each sample type**

200

201

202 **2.4 Test procedure**

203 The samples used within each test are detailed in TABLE 1. The testing procedures used were  
 204 as follows:

205

206 **Shrinkage stress at 90°C (Test Series 1, TS1):** The samples were heated to 90 °C in the  
 207 environmental chamber and left for a soak time of 1 hr. The environmental chamber was then  
 208 turned off and the sample allowed to cool back to room temperature. Load and temperature  
 209 were measured continuously at a sample rate of 1 Hz. The *strip* and *filament* samples were  
 210 tested in bundles of 10, whilst the *tube* and *tube with filaments* were tested as single samples.

211

212 **Temperature-shrinkage profile (Test Series 2, TS2):** The samples were heated to 60 °C within

213 an Instron environmental chamber and held at a constant temperature for 30 mins (soak  
214 time). The temperature was then increased in 10 °C increments, keeping the soak time  
215 constant at each increment, up to 140 °C. The environmental chamber was then turned off  
216 and the sample allowed to cool back to room temperature. Load and temperature were  
217 measured continuously at a sample rate of 1 Hz. The *strip* and *filament* samples were tested  
218 in bundles of 10, while the *tube* and *tube with filaments* were tested as single samples.

219

220 **Free shrinkage (Test Series 3, TS3):** Samples of original length 305 mm were placed within  
221 the environmental chamber and heated to 90 °C for 18 hrs. They were then allowed to cool  
222 to room temperature and their final lengths recorded.

223

224 The above test series were used to select a form of PET for further investigation. *Solid filament*  
225 and *filament tube* samples, having exhibited greater shrinkage stresses than the PET *strips*,  
226 were then subjected to additional testing along with the strips to compare their mechanical  
227 properties.

228

229 **Tensile strength tests (Test Series 4. TS4):** Individual PET *solid filament*, *filament tube* and  
230 *strip* samples were subjected to tensile loading in a Zwick Z100 tensile testing machine.  
231 Loading was displacement-controlled. For the PET *strips*, loading rates of 0.05 mm s<sup>-1</sup>, 0.1 mm  
232 s<sup>-1</sup> and 0.2 mm s<sup>-1</sup> were used to check the effect of loading rate. For the *solid filament and*  
233 *filament tube* samples, a 0.1 mm s<sup>-1</sup> rate was used. Loading was continued until the samples  
234 failed. PET *strip* samples, which had been activated (heated to 90 °C for 1 hr), were also tested  
235 for comparison. Load and displacement were measured continuously at a sample rate of 1  
236 Hz.

237

238 **Effect of temperature on Young's modulus (Test Series 5, TS5):** Using a Dartec tensile testing  
239 machine and an Instron environmental chamber, individual PET *solid filament* samples and  
240 PET *strips* in stacks of four were held at a constant load, equivalent to a stress of 10 MPa,  
241 while the temperature was increased in increments of 10 °C from 30 °C to 130 °C with a soak  
242 time of 5 mins. At each temperature increment, a cyclic stress with amplitude 10 MPa was  
243 applied to the sample. Three rates of stress were used: 3.4 MPa s<sup>-1</sup>, 0.34 MPa s<sup>-1</sup> and 0.034  
244 MPa s<sup>-1</sup>. Load and displacement was measured continuously at a sample rate of 10 Hz and  
245 used to calculate Young's modulus at each temperature.

246

247

### 248 **3 RESULTS AND DISCUSSION**

#### 249 **3.1 Peak shrinkage stress in TS1 samples**

250 In all of the TS1 samples, the peak restrained shrinkage stress, during the heating phase,  
251 occurred when the environmental chamber temperature was 90 °C. In some cases, higher  
252 stresses were observed upon cooling, which is thought to be due to the thermal contraction  
253 of the steel rig. This issue is discussed below. The peak stress results are shown in TABLE 2.

254

255 **TABLE 2 Peak restrained shrinkage stress results**

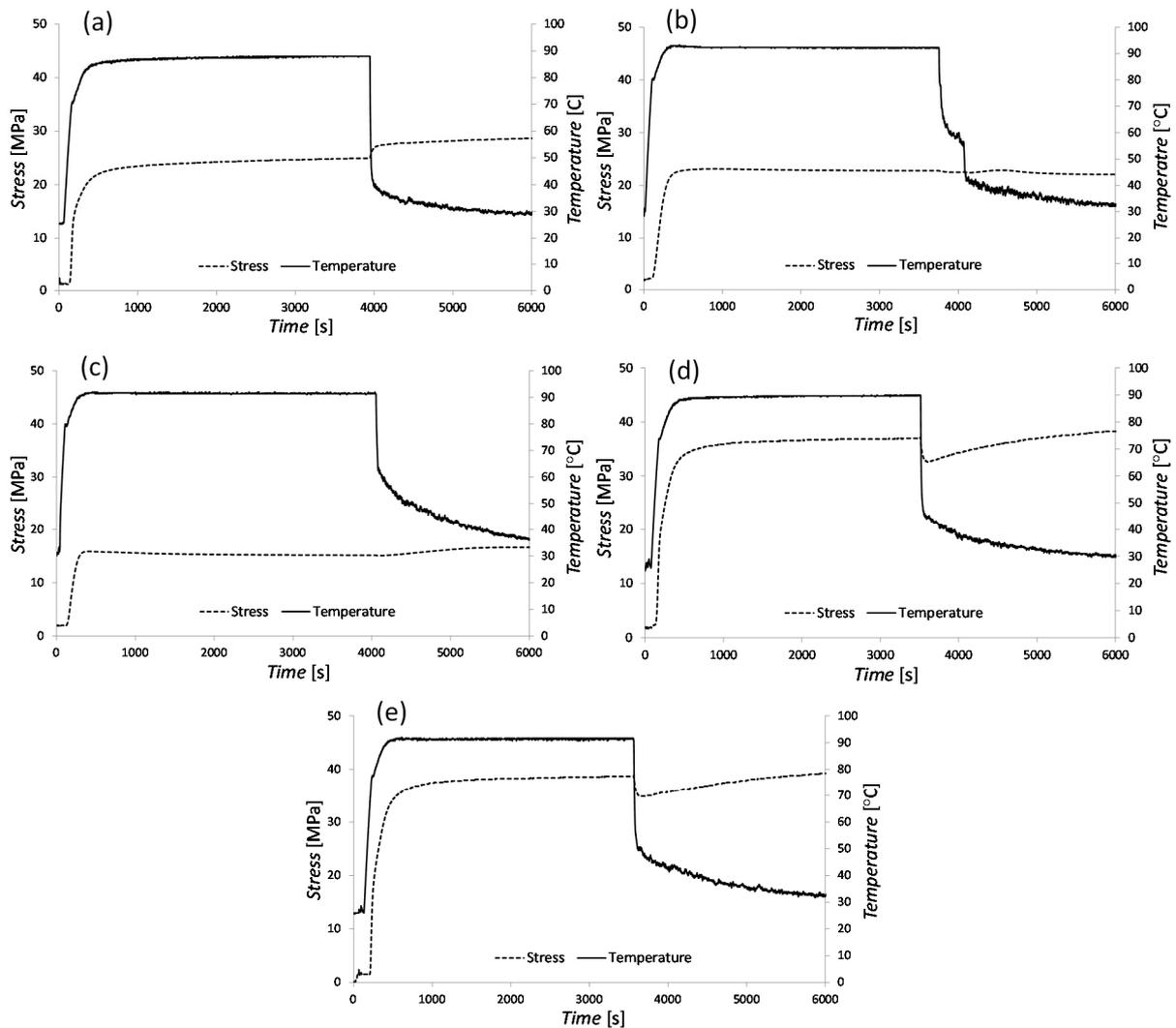
Polymer	Restrained shrinkage stress for TS1 specimens at 90 °C (MPa)			
	Highest	Lowest	Average	CoV (%)
Strips	24.93	23.03	24.02	3.97
Solid filament	41.50	36.98	38.58	6.56
Filament tube	43.33	38.67	40.93	5.7
Tube	23.10	-	23.10	-
Tube with filaments	17.01	-	17.01	-

256

257 As can be seen from the stress results, the highest average shrinkage stress was observed in  
258 the PET *filament tube* samples, with the lowest stress exhibited by the *tube with filaments*  
259 specimens. Both of the *filament* samples produced significantly higher stresses than either  
260 the *strips* or the larger PET *tubes*. The trend in these results is supported by the fact that the  
261 degree of crystallisation reduces with the cross-sectional area of a sample and that  
262 crystallisation of the polymer matrix reduces the shape recovery potential of shape memory  
263 polymers by increasing the material's resistance to shrinkage.<sup>22</sup>

264 In addition, since the shrinkage stress is correlated to the stored energy within the polymer,  
265 maximising the force used to draw the filaments - through the use of a high drawing rate (1m  
266 min<sup>-1</sup>) - further contributed to the increased shrinkage stresses in the *filament* samples  
267 relative to those of the *tube* samples (40 mm min<sup>-1</sup> initial). The *tube with filament* samples  
268 exhibited similar shrinkage behaviour to the *tube* samples, indicating that the maximum  
269 stress seems to be limited by the external tube.

270 The graphical results of the restrained shrinkage stress at 90°C for all samples can be seen in  
271 Figure 4. In all cases, heating to 90 °C produces a rapid increase in stress followed by a plateau.  
272 Upon cooling, there was a subsequent increase of 2-3 MPa in all but one test set (i.e. 4b).



273

274 **FIGURE 4** Restrained shrinkage stress at 90°C for (a) Strips; (b) Tube; (c) Tube with filaments; (d) Solid  
 275 filaments & (e) Filament tube. Typical results graphs shown for samples with repetitions.

276

277 This increase in stress can be attributed to the contraction of the steel rig used to transfer the  
 278 shrinkage stress of the PET to the load cell. This was later confirmed in some separate tests in  
 279 which samples were heated using a system of embedded wires. This system caused no  
 280 appreciable change in temperature in the steel rig. In this case, there was no increase in the  
 281 polymer stress during the cooling phase.

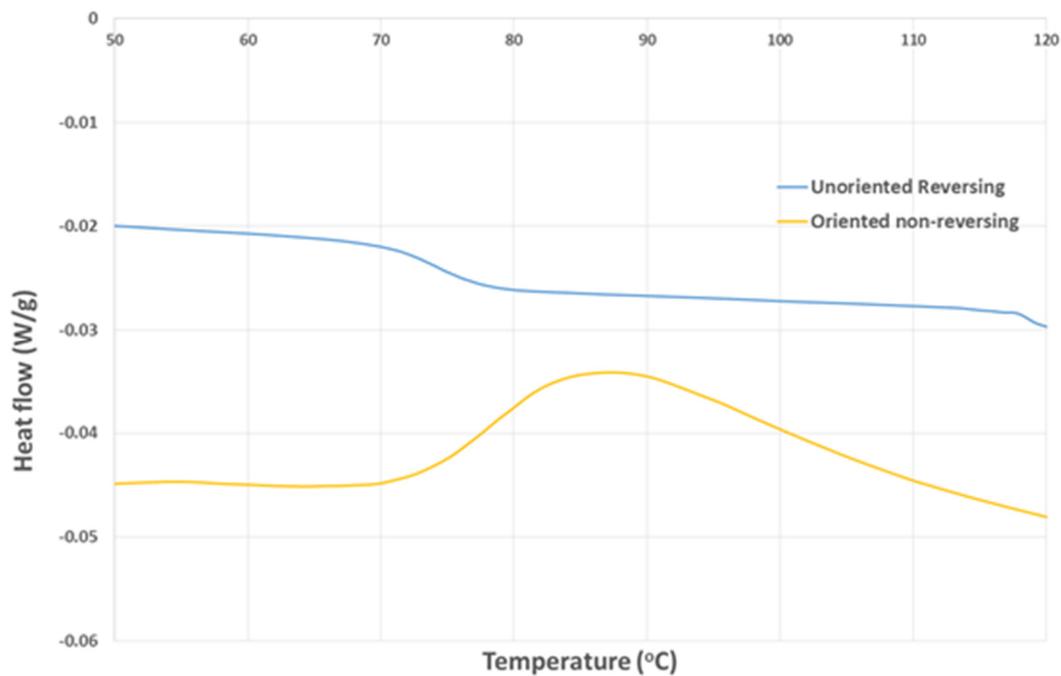
282 It is noted that the peak stress observed at 90 °C in the PET *strip* samples is lower than the  
 283 30-35 MPa found in previous study.<sup>10</sup> This variation may be due to manufacturing process

284 changes since the original tests were undertaken and is discussed in more detail in section  
285 3.5.

286 The *filament* samples produced an initial drop in stress upon cooling, which was not observed  
287 in the other samples or in previous shrinkage experiments on PET *strip* samples. The testing  
288 temperature of 90 °C is well above  $T_g$  (78 °C), so we may assume that the shrinkage stress is  
289 entropic and is proportional to  $NkT$ , where  $N$  is the number of molecular chains per unit  
290 volume,  $k$  is Boltzmann's constant, and  $T$  is the absolute temperature.<sup>23</sup> Thus, the stress drop  
291 is expected to be directly related to the drop in  $T$ . However, during the course of the stress  
292 drop the temperature falls below  $T_g$ , whereupon the stress will cease to be proportional to  
293  $NkT$  and will attain a constant value as the molecules become confined within the structure.  
294 On this basis we would expect the ratio of stresses before and after the stress drop to be  
295  $T_{\text{test}}/T_g$ , where  $T_{\text{test}}$  is the testing temperature and both temperatures are expressed in  
296 degrees Kelvin.

297 To assess quantitatively the validity of this argument, we must decide upon the appropriate  
298 value of  $T_g$  in the context of a cooling oriented polymer. Values for PET both in isotropic form  
299 and oriented to a draw ratio of 4, using differential scanning calorimetry (DSC) and dynamic  
300 mechanical thermal analysis (DMTA), have been found to exhibit significant differences.<sup>24</sup> The  
301  $T_g$  was measured as around 80 °C for isotropic material, with the glass transition process  
302 starting at 70 °C; however, in oriented form the onset of glass transition was lower by 15 °C,  
303 with the  $T_g$  correspondingly lower. We have investigated the effects of molecular orientation  
304 on the Dow Lighter material by TDSC, as described above. The measurements apply most  
305 specifically to the results of Figure 4(d).

306 For oriented fibre, it was possible to detect in the non-reversible signal an exothermic peak  
307 commencing at a temperature of 72.906 °C with a peak value occurring at 86.637 °C (see  
308 Figure 5). This we interpret as related to relaxation of the residual stresses, which would  
309 correspond to the onset of shrinkage stresses for a restrained specimen. This is consistent  
310 with the effectiveness of the test temperature of 90 °C.



311

312 **FIGURE 5 Results from TDSC testing on oriented fibre material.**

313

314 The glass transition was not found to significantly differ from that of the unoriented material,  
315 occurring in the range 70 - 78 °C. This gives a range of values of the ratio  $T_{\text{test}}/T_g$  of  $1.03 <$   
316  $T_{\text{test}}/T_g < 1.05$ , to give a maximum stress drop of 1.6 MPa from the observed maximum 35 MPa  
317 in Figure 4(d). This compares with an observed drop of 4.3 MPa. This is a significant  
318 discrepancy, for which two factors may be relevant. First, in the shrinkage experiments, the  
319 polymer is restrained while cooling, whereas it is free to contract in the TDSC tests, possibly  
320 leading to different  $T_g$  values. Secondly, the temperatures in the restrained shrinkage tests

321 recorded are air temperatures, which during cooling will in general be higher than those  
322 obtaining at the core of the fibre bundle, leading to a longer time above  $T_g$ .

323

### 324 **3.2 Temperature-shrinkage profiles in TS2 specimens**

325 The restrained shrinkage stress recorded at each temperature interval has been plotted as  
326 temperature-shrinkage profiles in Figure 6.

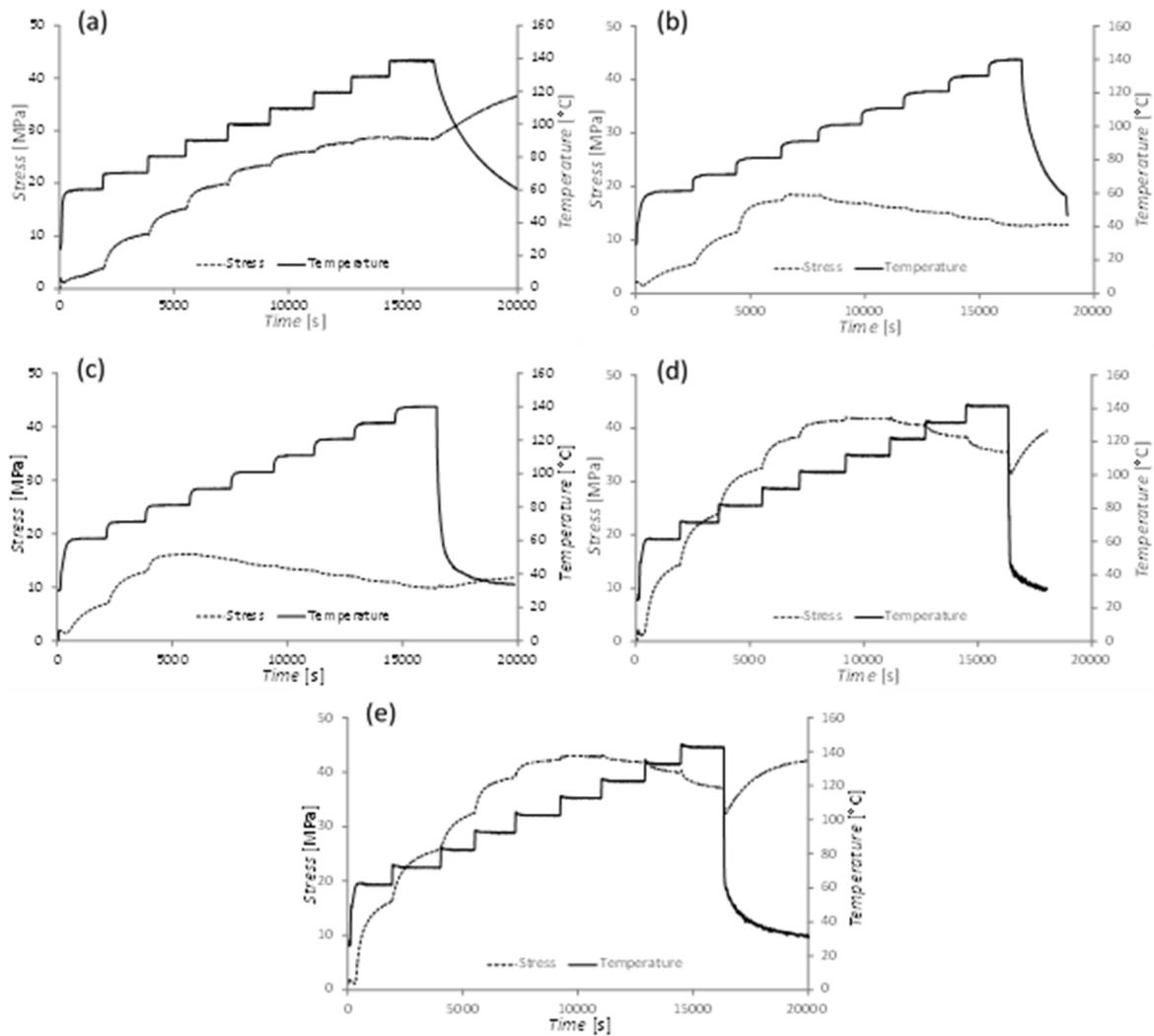
327 It is observed for the PET *strip* samples that the shrinkage stress starts to increase significantly  
328 when the temperature exceeds 70 °C, reaching a peak of 28.7 MPa at 130 °C. Thereafter, the  
329 stress starts to fall as the temperature increases further, which is consistent with the findings  
330 from previous tests on similar materials.<sup>10,11</sup>

331 The *solid filament* and *filament tube* samples exhibited stress peaks of 41.8 MPa and 42.9  
332 MPa respectively, both at 110 °C.

333 The PET *tube* and *tube with filaments* samples showed peak stresses of 18.3 MPa and 16.2  
334 MPa respectively at the lower temperature of 90 °C. It is not clear why the peak activation  
335 temperature of the *tubes* are lower than the *filament* samples, although this could be related  
336 to the lower drawing temperature of 75 °C in comparison to the 80 °C of the *filament* samples  
337 and the different crystalline phase relative volumes.

338

339



341

342 **FIGURE 6** Temperature-shrinkage profiles for (a) Strips; (b) Tube; (c) Tube with filaments; (d) Solid filaments  
 343 and (e) Filament tube.

344

345 The low peak shrinkage stress measured in the *tube with filament* samples may be associated  
 346 with a degree of relative slip between the external tube and the inner filaments, both along  
 347 the length of the specimens and at the grips. Such slip behaviour would cause a reduction in  
 348 the contribution of the filaments to the overall composite shrinkage force and therefore to  
 349 the mean shrinkage stress.

350 All samples show a drop in shrinkage stress beyond the peak activation temperature. This is  
 351 believed to be caused by the reduction in yield stress that accompanies an increase in

352 temperature, as predicted by Eyring’s model,<sup>23</sup> which becomes very significant beyond 140  
 353 °C. In addition to this effect is the fact that at these temperatures the polymer has released  
 354 most of the energy stored during the drawing process.

355

356 **3.3 Free shrinkage tests in TS3 specimens.**

357 Results of the free shrinkage experiments, presented in TABLE 3, show that the shrinkage at  
 358 90 °C observed for all manufactured samples exceeds that of the PET *strips*. This trend is  
 359 attributed to the relatively high draw ratio used in the manufacture of the former specimens.  
 360 The difference in draw rate between the *filament* samples and the *tube* samples does not  
 361 seem to have altered the free shrinkage properties.

362 **TABLE 3 Free shrinkage at 90°C results**

Sample type	Number of samples	Draw ratio	Draw rate (mm s <sup>-1</sup> )	Average shrinkage (% length)
Strips	10	unknown	unknown	1.6
Solid filament	10	4.0	1000	5.0
Filament tube	10	4.0	1000	4.7
Tube	1	3.9	40 (initial)	5.2
Tube with filaments	1	4.0 (tube) 4.4 (int. filaments)	40 (initial)	7.2

363

364 The *solid filament*, *filament tube* and *tube* samples all produced similar free shrinkage results,  
 365 whilst the shrinkage of the *tube with filaments* sample was 2 % greater than any of the other  
 366 specimens. This contrasts with the peak shrinkage results in which the *tube with filaments*  
 367 sample produced the lowest restrained shrinkage stress. Free shrinkage in this case seems to  
 368 have no correlation to the restrained shrinkage stress or to the draw rate.

369 It is noted that the free shrinkage strain is opposite in sign to conventional thermal expansion.  
 370 The coefficient of thermal expansion of these PET materials at 20°C varies from 60 to 80×10<sup>-6</sup>  
 371 °/°C , which –in the absence of any shape memory or softening effects- would equate to an  
 372 total expansion strain of approximately 0.5% over the temperature range 25 to 90 °C.

373

### 374 3.4 Tensile strength tests in TS4 specimens

375 The results of the tensile strength tests are given in TABLE 4. The rate of loading has little  
 376 effect on the tensile stress of the samples at failure. Furthermore, the tensile strengths of the  
 377 activated PET *strip* samples are similar to those of the non-activated *strips*. This indicates that  
 378 activating the polymers does not weaken the material in tension, which is beneficial in the  
 379 context of their use within the concrete tension zone.

380 TABLE 4 Tensile strength test results

Sample	Type	Rate (mm s <sup>-1</sup> )	Stress at failure (MPa)	Strain at failure (%)	Avg. tensile strength (MPa)	CoV (strength) (%)	Average strain at failure (%)
1	PET strip	0.1	186.5	14.6	189.2	1.9	20.1
2	PET strip	0.1	187.0	18.3			
3	PET strip	0.1	194.2	27.5			
4	PET strip	0.2	188.7	15.0	187.3	0.5	13.2
5	PET strip	0.2	186.8	12.4			
6	PET strip	0.2	186.4	12.3			
7	PET strip	0.05	177.6	9.7	179.7	1.2	10.8
8	PET strip	0.05	181.9	11.9			
9	PET strip - heated	0.1	188.9	11.4	185.0	2.4	10.5
10	PET strip - heated	0.1	178.8	7.7			
11	PET strip - heated	0.1	187.3	12.5			
12	PET filament solid	0.1	305.2	6.7	304.9	1.4	6.6
13	PET filament solid	0.1	309.9	7.2			
14	PET filament solid	0.1	300.0	6.0			
15	PET filament tube	0.1	317.8	7.8	308.5	2.2	7.4
16	PET filament tube	0.1	305.7	6.9			
17	PET filament tube	0.1	302.1	8.0			

381

382 These results show that the solid and tube filament samples exhibit significantly higher tensile  
383 strengths than the strips. Lower 'strain at failure' results indicate an increased stiffness in the  
384 *filament* samples. These results, along with the restrained shrinkage stress values, suggest  
385 that the *strip* samples are probably drawn to a lower draw ratio than the filaments. This  
386 deduction is supported by the well-established trend that stiffness in drawn polymers  
387 increases with the draw ratio.<sup>23</sup> This also agrees with the free shrinkage results, since a lower  
388 draw ratio for the strip samples would result in a reduced degree of orientation and therefore  
389 a smaller free shrinkage strain than measured in the other samples.

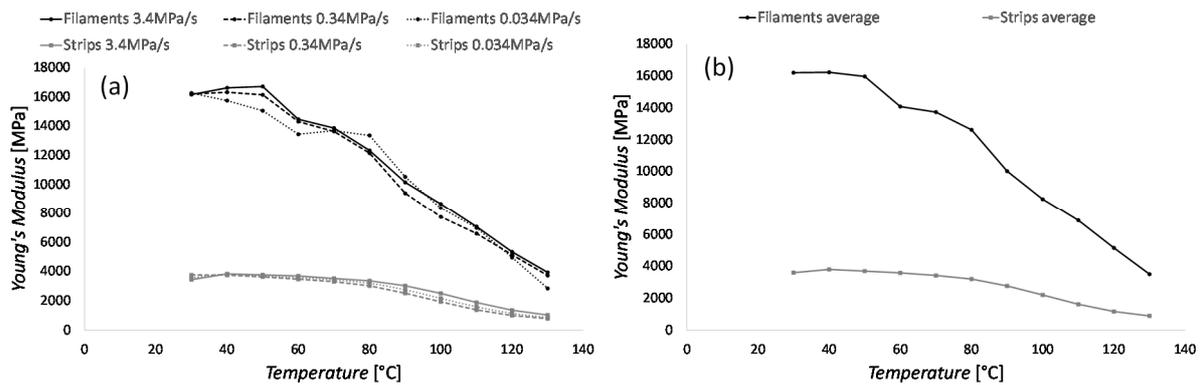
390 The tensile tests results indicate that the two *filament* types, solid and tube, have very similar  
391 tensile strength properties.

392

### 393 **3.5 Effect of temperature on Young's modulus in TS5 specimens**

394 The results of the Young's Modulus (YM) tests on the PET *solid filaments* and the PET *strips*  
395 are shown in Figure 7. As the PET *solid filament* and *tube filament* samples had exhibited  
396 almost identical shrinkage and tensile properties, having been subjected to identical methods  
397 of manufacture, YM experiments were carried out only on the *solid filament* samples.

398 At each temperature, Young's modulus ( $E_{ap}$ ) was calculated from the loading and unloading  
399 portions of three 10 MPa stress cycles and averaged. Both the stress and strain were assumed  
400 to be uniaxial, with strain being computed from the change in displacement over the initial  
401 gauge length, and stress from the applied load divided by the undeformed area.



402

403 **FIGURE 7** Young's Modulus with temperature for drawn PET solid filaments and PET strips (a) using 3.4 MPa  
 404  $s^{-1}$ , 0.34 MPa  $s^{-1}$  and 0.034 MPa  $s^{-1}$  load cycles, and (b) as an average over all load cycles

405

406 The data presented in Figure 7 show that the  $E_{ap}$  value is relatively insensitive to the stress  
 407 rate for both sets of specimens. A previous study by the authors<sup>10</sup>, conducted on a similar PET  
 408 material, showed a slightly stronger (although still modest) stress-rate dependency. These  
 409 earlier data were interpreted in the light of an SLS-based (Standard Linear Solid) rheological  
 410 model in such a way that viscosity values and strain-rate independent low and high  
 411 temperature Young's moduli were extracted from the data. However, in the present case, the  
 412 stress-rate dependency was considered too weak to warrant such an analysis and therefore  
 413 only the average  $E_{ap}$  values are presented. It is also noted that other authors have suggested  
 414 that the best way to compute Young's moduli is to use the slope of stress vs. strain response  
 415 in the early unloading stages of each cycle.<sup>25</sup>

416 The stress excursion of 10MPa (3 to 5% of the unheated tensile strengths) is greater than the  
 417 values used in some previous studies<sup>10</sup> but the consistency of the results and linearity of the  
 418 unloading-reloading cycle suggest that this stress change value was reasonable.

419

420 For both polymer forms, there is a clear reduction in  $E_{app}$  with increasing temperature. This is  
421 expected because the slower the testing rate the greater will be the contribution to strain  
422 changes from viscous effects. Furthermore, as the melting point of the polymer is approached  
423 the polymer softens. The results show a clear drop in  $E_{app}$  once the glass transition  
424 temperature of around 70 °C has been reached, with continuing loss of stiffness to 130 °C.

425 The *filament* samples produced significantly higher  $E_{app}$  values than the *strips*, which is  
426 consistent with the findings from the tensile strength tests. We note that the strip results  
427 presented here are significantly different from those obtained in the previous study,<sup>10</sup> where  
428 higher  $E_{app}$  results were observed for the commercially available *strips*, around 6000 MPa at  
429 30 °C compared to below 4000 MPa measured for the current samples. This difference may  
430 be due to a change in the processing of the *strip* samples during manufacture, which would  
431 also explain the differences in shrinkage stress results. These findings suggest that the  
432 commercially available strips were previously drawn to a higher draw ratio, leading to higher  
433 orientation and stiffness in the samples tested in previous studies.<sup>10,11</sup>

434

### 435 **3.6 General Discussion**

436 Neither long-term relaxation, nor its creep counterpart, were considered in the present work.  
437 The Cardiff team<sup>26</sup> has previously investigated the relaxation of shrinkage stresses over a 6  
438 month period for Shrink tite PET samples.<sup>26</sup> The main conclusions from this study were that  
439 the long-term relaxation of the restrained shrinkage stress in drawn PET is relatively small, i.e.  
440 2 to 3 % of the peak stress, and the majority of stress loss occurs over the first 12 days after  
441 activation. The same conclusions cannot be transferred to other polymers.<sup>25</sup>

442 The work reported in this paper concentrated on peak shrinkage stresses but, as with all  
443 prestress systems, there will be some losses due to concrete creep and shrinkage, as well as  
444 relaxation of the tendons, although the latter losses are likely to be small for reasons  
445 explained above. The present system is targeted at closing early-age cracks and promoting  
446 the conditions for early-age autogenous healing; therefore, long-term losses are of secondary  
447 importance.

448

#### 449 **4 CONCLUSIONS**

450 Experiments undertaken to test the shrinkage stress of PET samples of varying cross-section  
451 and processing histories has resulted in the development of a high shrinkage PET filament for  
452 use within a concrete crack closure system.

453 It is concluded from our tests that the restrained shrinkage stress potential in drawn PET  
454 samples increases with increasing draw ratio, increasing draw rate and decreasing specimen  
455 cross-section. The restrained shrinkage stresses achieved in a series of drawn PET *filament*  
456 specimens, manufactured at Bradford University, were significantly larger than those  
457 obtained from the commercially available PET *strips* used in previous experiments.<sup>10,11,18</sup> The  
458 shrinkage stress measured was also higher than that produced by PET *tube* and *tube with*  
459 *filament* samples subjected to similar die-draw processing. This is attributed to a higher draw  
460 rate resulting in a greater amount of stored energy within the filament samples.

461 The PET *filaments* exhibited a stress drop upon cooling not previously observed for drawn  
462 polymer samples. This is believed to be due to the drop in stress caused by a reduction in the  
463 entropic elasticity with falling temperature (for  $T$  below  $T_g$ ) being greater than the increase in

464 stress from restrained thermal contraction. It is concluded that the balance between these  
465 mechanisms is different in the PET *filaments* from that in the other materials tested.

466 This programme of work has succeeded in developing a PET form which produces  
467 approximately double the restrained shrinkage stress potential, and 1.7 times the tensile  
468 strength, of commercially available *strip* samples. The PET *filament*, having exhibited the  
469 largest shrinkage stress potential, has been subsequently used in a series of crack closure  
470 experiments in concrete structural elements.

471

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475

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