Structure, Morphology, and Properties of PBZT and Methyl Pendant PBZT Fibers

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ABSTRACT: The structure, morphology, and properties of the methyl pendant PBZT fiber have been studied with variations in thermomechanical treatment. For comparison, selected studies on PBZT fibers have also been carried out. Crosslinking in the methyl pendant PBZT fiber occurs in the 450–550°C range under free annealing, leading to a nonfibrillar structure. Recoil compressive strength, loop strength, torsional modulus, and the transverse compressive strength of the tension heat-treated MePBZT fiber are 50 to 100% higher compared to the comparably heat-treated PBZT fiber. Compressive strength and other mechanical properties could not be measured on highly crosslinked free annealed samples, as such samples showed significant transverse cracks. Reasons for the development of transverse cracks have been discussed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 305–314, 1999

Key words: PBZT; methyl pendant PBZT; structure; morphology; properties

INTRODUCTION

The axial compressive strength of high performance polymeric fibers is much lower than their tensile strength values. Intermolecular crosslinking has been considered an effective approach to improve the axial compressive strength of polymeric fibers.^{1–7} A number of crosslinkable systems have been made from this point of view. Results of these studies have previously been reviewed.⁷ Recently, it has been reported that a new fiber, poly(2,6-diimidazo (4,5-b : 4'5'-e)pyridi-nylene1,4(2,5-dihydroxy)phenylene) termed "M5," has good tensile and compressive properties (tensile modulus 330 GPa, tensile strength 4.0 GPa, compressive strength 1.6 GPa).⁸ To date, reported axial compressive strength of M5 fiber is highest among all polymeric materials (bulk or fiber). For comparison, the compressive strength of Kevlar and PBZT fibers is 400 MPa and 200 MPa, respectively. It is also reported that the crystal structure in M5 fiber features bidirectional hydrogen bonding transverse to the polymer chain direction.⁸ The bidirectional hydrogen bonding is considered responsible for the high compressive strength in the M5 fiber.

Fibers with three-dimensional ionic or covalent bonding (e.g., Boron, SiC, Al_2O_3) have high axial compressive strength values.⁷ The reported compressive strength of both boron and alumina fibers is approximately 7 GPa, and is much higher than their tensile strength values. Improved compressive strength in rigid rod polymers resulting from hydrogen bonding (e.g., M5 fiber) and high compressive strength in fibers such as alumina, silicon carbide, and boron fibers provide rationale that high compressive strength in polymeric fibers is possible in suitably three-dimensionally bonded structures. Improved compressive strength

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Crosslinking via an ethylene bridge.

Figure 1 Possible crosslinks in methyl pendant PBZT.

has also been reported in the tetra methyl biphenyl PBZT.⁹

Methyl pendant PBZT, a crosslinkable rigidrod polymer, was made at the U.S. Air Force Materials Laboratory.⁶ Repeat unit of the methyl pendant PBZT and the possible crosslinked structures are given in Figure 1. Evidence of crosslinking in this system has previously been reported with the conclusion that the heat treatment protocol of time, temperature, and tension will be critical, and that the highest temperatures of exposure for crosslinking will probably lie in the 450 to 550°c range.¹⁰ This article reports the changes in the structure, morphology, and properties of the methyl pendant PBZT fiber with variations in thermomechanical treatment. For comparison, studies on PBZT fiber have also been carried out and reported.

EXPERIMENTAL

The methyl pendant PBZT (intrinsic viscosity = 24 dL/g) fiber was spun from 10 wt % solution in polyphosphoric acid at $90-110^{\circ}$ C using the dryjet-wet spinning technique with an air gap of 10 cm. The as-spun fiber was washed in running distilled water for 3 to 5 days and subsequently dried in air. This fiber is referred to as "as-spun MePBZT" or "AS MePBZT." Fibers were annealed with no tension (free annealing) in a glass Petri dish in a small ceramic furnace. Tension annealing was carried out in the tubular Lindbergh furnace, and a tension of 100, 50, 25, or 7 MPa was maintained on the fibers. Sample designation scheme for various fibers is given in the appendix.

Equatorial and azimuthal wide-angle X-ray scattering scans were obtained using a pin-hole collimation on a Rigaku-Rotaflex diffractometer with a rotating anode generator operated at 45 kV and 150 mA. The wavelength of the K_{α} radiation used was 0.154 nm and the K_{β} component in the incident beam was attenuated by a standard nickel filter.

The apparent crystallite size was calculated from the full width at half maximum (FWHM) (B_0) of the equatorial radial scan using the Scherrer equation:

$$L(hkl) = \frac{K\lambda}{B_0 \cos \theta} \tag{1}$$

where *L* is the crystallite size perpendicular to the {*hkl*} plane; λ is the wavelength of the X-rays; *B*₀ is the full width at half maximum of the (*hkl*) reflection in radians; and θ is the diffraction angle for the{*hkl*} plane.

Value for the constant K was taken to be 1. No corrections were applied for the instrumental and microstrain broadening, paracrystallinity, or other lattice distortions. Thus, the reported values represent lower bound values of the crystal sizes.

Scanning electron microscopy was carried out on various as-spun and heat-treated fibers using a Hitachi S-800 microscope operated at 15 kV. Scanning electron microscopy was also carried out on samples treated with chlorosulfonic acid (CSA). For this treatment, fiber samples were kept overnight in CSA, removed from the acid, washed in water, and dried. All samples were coated using a gold sputter coater.



Figure 2 (a) Schematic of elastica loop, (b) representative plot of L/D versus L for a PBZT-530-N-30-100 fiber.

The tensile properties were measured on an Instron tensile tester at a gage length of 2.54 cm at a crosshead speed of 1.27 mm/min. For tensile testing, fibers were mounted on cardboard tabs. The torsional modulus measurements were carried out as previously described¹¹ using a free torsional pendulum apparatus placed in a vacuum oven. The fiber compressive strength was determined using recoil¹² and loop tests.¹³ Recoil test was conducted at 2.54-cm gage length, and an electric spark¹⁴ was used for cutting the fiber. Approximately 15 fibers (30 fiber halves) at each stress level were examined in the SEM for the development of a kink as the manifestation of fiber compression failure. From these observations, recoil compression failure probability (p)was determined as follows:

$$p = \frac{K}{K+N} \tag{2}$$

where K is the number of kinked halves, and N is the number of halves without kink.

The recoil failure probability was plotted against the recoil stress to determine the stress level at which the recoil failure probability was 0.5. This stress level is reported as the recoil compressive strength of the fiber. Compressive strength was also measured using the elastica loop test.¹³ In theory, the ratio of the major to the minor axis of the loop (L/D) [Fig. 2(a)] should be constant and equal to 1.34, as long as the fiber behaves elastically.¹⁵ As the loop is made smaller, the L/D ratio begins to increase [Fig. 2(b)], and the kinks develop on the compression side of the loop. The compressive yield stress (σ) and strain (ε) , when the L/D ratio deviates from 1.34, is given by⁷

$$\sigma = E\varepsilon = 1.43E\left(\frac{d}{L^*}\right) \tag{3}$$

where σ is the loop compressive strength; *d* is the fiber diameter; L^* is the critical value of the major axis of the loop at which the *L/D* ratio deviates from 1.34; and *E* is the fiber modulus.

 L^* was estimated from a plot of L versus L/D(Figure 2b). An average of 10 specimens was used to calculate the loop compressive strength. It should be noted that the modulus was obtained from the tensile test and was assumed to be the same in compression. Although this assumption may be reasonable for rigid-rod polymers, compression modulus of flexible polymers is generally lower than their tensile modulus. In the loop test, only a small volume of material is subjected to compressive stresses. Therefore, this test is practically equivalent to a zero gage length test. Because in the loop test the compressive stresses are highest at the fiber surface, this test represents compressive strength at or near the fiber surface. Compressive strength values measured from the loop test are generally higher than those measured from the recoil test.⁷

The transverse compression tests were conducted in Professor Kawabata's laboratory at the University of Shiga Prefecture (Japan) by Dr. Mari Inoue. The instrument and the method has been described elsewhere.¹⁶

RESULTS AND DISCUSSION

Evidence of Crosslinking

As-spun PBZT and as-spun MePBZT fibers readily dissolve in chlorosulfonic acid (CSA) as well as in methane sulfonic acid (MSA) at room temperature. On the other hand, PBZT fiber, tension heat treated for 30 to 60 s at 550°C (HT PBZT) required much longer time and elevated temperature (60°C) for dissolution in CSA. PBZT

Fiber	Major Equatorial Reflections, 2θ Values (°)	FWHM (0 1 0)	L (2 0 0) (Å)	L (0 1 0) (Å)
AS PBZT	15.75, 25.45	15.0°	15	19
HT PBZT	14.9, 25.0, 28.0, 29.9	9.5°	85	59
PBZT-530-N-30-100	14.9, 25.2, 28.2, 30.2	10.0°	80	59
PBZT-530-N-F	13.85, 15.3, 23.1, 25.5, 28.3, 30.5	11.0°	100	59
AS MePBZT	14.5, 25.3	20.0°	12	23
MePBZT-530-N-30-100	12.8, 14.1, 23.65, 26.0	10.5°	93	59
MePBZT-475-N-F	12.8 (w), 14.0, 23.4, 25.85	14.5	77	47

Table I Misorientation and Crystallite Size Data for the Various Fibers

fiber free annealed in nitrogen at 530°C for 10 min was partially insoluble, however, ¹³C solidstate NMR of this fiber is identical to the NMR of the HT PBZT fiber and does not indicate any changes attributable to crosslinking. As reported previously,¹⁰ MePBZT fiber, free annealed at 400°C, is also insoluble in chlorosulfonic acid; however, NMR studies show no evidence of crosslinking in this sample either. These observations suggest that the lack of dissolution cannot be taken as the sufficient evidence of crosslinking in these rigid-rod polymers.

A brief summary of the previously reported¹⁰ evidence of crosslinking, in the methyl pendant PBZT, from solid-state NMR is given here. ¹³C solid-state NMR of the MePBZT heat treated at 450°C for 10 min, showed a resonance at 38 ppm, albeit exceedingly weak (2% of the intensity of the methyl resonance), while the 550°C sample showed near absence of the methyl peak (only about 3% of the original methyl groups survive as methyl group), and shows a relatively low intensity peak at 38 ppm. The peak at 38 ppm was attributed to the presence of the --CH₂-- groups, while the CH_3 peak was observed at 27 ppm. It was concluded that at 550°C, methylene carbons dominate the aliphatic region but their intensity only represents about 18% of the original methyl intensity. This suggests that if -CH₂-CH₂linkages are formed (refer to Fig. 1), then 18% of the original methyl groups must be participating in this type of crosslinking reaction. However, if CH₂ linkages are formed by combining two methyl groups and evolving methane, then this would suggest the involvement of 36% of the original methyl groups in this type of crosslinking. In either case, significant probability remains for the occurrence of direct phenyl-phenyl crosslinking (Fig. 1). Due to the possibility of sample degradation at the crosslinking temperatures, no evidence of phenyl-phenyl crosslinking has yet been obtained.

Spectroscopic evidence of crosslinking in methyl pendant PBZT, to date, is limited to samples heat treated without tension. For sample quantity limitations, no solid-state NMR studies have yet been carried out on the tension-annealed samples.

WAXD Studies

Table I gives the misorientation as measured by full width at half maximum (FWHM) of azimuthal scan for (0 1 0) reflection and crystallite size data for (2 0 0) and (0 1 0) reflections in both PBZT and MePBZT samples. The slight misorientation increase from 9.5° in HT PBZT to 11° in the 530-N-F sample is attributed to greater bundle splay in the latter, which was quite brittle and, therefore, a very well-aligned fiber bundle could not be prepared. AS MePBZT fiber had higher misorientation (FWHM = 20°) than AS PBZT $(FWHM = 15^{\circ})$. Misorientation in MePBZT is reduced to about 10° on tension annealing and to about 14° upon free annealing. In the small scale spinning of MePBZT, high draw ratio could not be achieved, limiting the orientation in the as-spun MePBZT.

Crystallite size perpendicular to $(2\ 0\ 0)$ and $(0\ 1\ 0)$, both in PBZT and MePBZT, increased upon tension as well as free annealing. In the heat-treated fibers, the value of $L_{(2\ 0\ 0)}$ is about 1.5 times the value for $L_{(0\ 1\ 0)}$. This is similar to the observation of Allen¹⁷ for heat-treated PBZT fiber. In the as-spun PBZT and MePBZT fibers, $L_{(2\ 0\ 0)}$ is somewhat smaller than $L_{(0\ 1\ 0)}$. The crystallite size, $L_{(2\ 0\ 0)}$ in the case of heat-treated and the tension-annealed PBZT is between 80–85 Å. On free annealing, the crystallite size $L_{(2\ 0\ 0)}$ increases to 100 Å, indicating dormant potential of



Figure 4 Wide-angle X-ray diffraction equatorial scans for MePBZT fibers. (a) AS MePBZT, (b) MePBZT-530-N-30-100, and (c) MePBZT-475-N-F.

improving lateral order along the *a*-axis upon free annealing. $L_{(010)}$ of both the free and tension annealed PBZT is 59 Å. As-spun MePBZT shows significant increase in $L_{(2\ 0\ 0)}$ from 12 to 93 Å upon tension annealing (530-N-30-100), and from 12 to 77 Å upon free annealing (475-N-F). In the case of MePBZT, the orientation is significantly higher in the tension-annealed samples than that in the free-annealed samples. The orientational difference between free and tension annealed PBZT is not significant.



Figure 3 Wide-angle X-ray diffraction equatorial scans for PBZT fibers. (a) HT PBZT, (b) PBZT-530-N-30-100, and (c) PBZT-530-N-F.



Figure 5 Scanning electron micrographs of free annealed MePBZT fibers. (a) MePBZT-475-N-F, (b) MeP-BZT-475-N-F treated overnight in chlorosulfonic acid, (c) MePBZT-525-N-F, and (d) MePBZT-525-N-F treated overnight in chlorosulfonic acid.

Equatorial radial scans of various PBZT and MePBZT fibers are given in Figures 3 and 4. Figure 3 shows two equatorial reflections at 2θ = 13.8 and at 23.1° in free-annealed PBZT. Both these reflections are absent in the HT PBZT and tension-annealed PBZT. As seen from Figure 4, two reflections at $2\theta = 12.8$ and at 23.6° are observed in tension- and free-annealed MePBZT, but these reflections are not resolved in AS MeP-BZT. These two reflections, in PBZT or in MeP-BZT, to the best of our knowledge, have not been reported before. Monoclinic unit cell reported for $PBZT^{18}$ with a = 11.79 Å, b = 3.539 Å, c = 12.514 Å and $\gamma = 94.2^{\circ}$, does not predict these two reflections. These reflections may represent the development of a new crystal structure coexisting with the known crystal structure. Further work is needed to verify the presence of the second crystal structure in these systems.

Effect of Crosslinking on Morphology

Scanning electron microscopy shows that AS PBZT, HT PBZT, and AS MePBZT fibers have smooth surfaces and fibrillar morphology. Free annealing of AS MePBZT in nitrogen at 475°C (475-N-F) results in a skin-core morphology with



Figure 6 Scanning electron micrographs of tensionannealed MePBZT fibers. (a) and (b) MePBZT-530-N-30-100, (c) MePBZT-530-N-30-50, (d) MePBZT-530-N-30-50 treated overnight in chlorosulfonic acid, (e) MeP-BZT-530-N-30-25, and (f) MePBZT-530-N-30-7.

transverse cracks [Fig. 5(a)] on the fiber surface, while no surface cracks were observed on free annealing at 450°C (photograph not shown). When the MePBZT 475-N-F-10 fiber is soaked in CSA, the fibrillar nature of the core is clearly evident [Fig. 5(b)], and unlike the fiber free annealed at 450°C, the skin of which dissolves completely, the skin of the fiber heat treated at 475°C is only partially soluble. As the free annealing temperature is increased from 475 to 550°C, the fibrillar nature of the core is gradually reduced. MePBZT fibers free annealed at 525°C [Fig. 5(c)] does not exhibit fibrillar structure, even after overnight treatment in chlorosulfonic acid [Fig. 5(d)]. This appears to provide strong evidence for interfibrillar crosslinking.

To overcome the problem of transverse cracks in the free-annealed MePBZT, tension annealing, initially at 100 MPa, was carried out at 400 and 530°C for 30 min (400-N-30-100 and 530-N-30-100). No surface cracks were observed in these tension annealed fibers [Fig. 6(a)]. The sample annealed at 530°C with a tension of 100 MPa showed the development of a skin and a fibrillar core structure, with the skin thickness of $<1 \,\mu$ m [Fig. 6(b)]. Thus, annealing under a stress of 100 MPa, prevented the development of transverse surface cracks. However, because tension annealed fibers show fibrillar morphology, this suggests little or no interfibrillar crosslinking. Therefore, crosslinking, if any, in the tension-annealed samples, is only intrafibrillar.

To achieve crosslinking, while preventing surface cracks, further heat treatment was carried out at lower stress levels (50, 25, and 7 MPa) at 530°C [Figs. 6(c) to (f)]. None of these tension heat-treated fiber samples developed transverse cracks. However, these fibers also show skin and fibrillar core morphology. When heat treatment tension is reduced from 100 to 50 MPa, skin thickness increased from less than 1 μ m to 7 mm [Fig. 6(c)]. A further decrease in tension had little effect on the skin thickness. The skin of the tension annealed fibers dissolves completely and the fibrillar core is partially insoluble in CSA [Fig. 6(d)]. The dissolution of the skin clearly suggests absence of crosslinking in the fiber skin, and is in direct contrast to the behavior of the fibers free annealed at temperatures above 475°C, the skin of which is insoluble in strong protic acids. The sequential heat treatment, in which tension annealing both at 400 and at 530°C was followed by free annealing at 475°C, also yields well-defined surface cracks (Fig. 7).

The absence of crosslinking in the skin of tension annealed samples and the surface cracks in



Figure 7 Scanning electron micrographs of MePBZT fibers tension annealed followed by free annealing. (a) and (b) MePBZT-530-N-30-100 followed by 475-N-F. (c) MePBZT-400-N-30-100 followed by 475-N-F.



Figure 8 Schematic of fibrillar orientation in skin and core.²¹

the free annealed samples can be explained on the basis of orientational differences¹⁹⁻²¹ between the fiber skin and the core. Panar et al.²¹ have proposed a structure for Kevlar® 49 as shown schematically in Figure 8. It is suggested that the surface fibrils are highly oriented, whereas the fibrils in the core are imperfectly packed and have relatively low orientation and order. Based on this and other studies reported in the literature^{19,20} on the fibers spun from the lyotropic liquid crystalline solutions (viz. PBO, PPTA, etc.). it is reasonable to assume that in the MePBZT fiber also, the molecular orientation in the skin is higher than that in the core. Free annealing at high temperature provides sufficient molecular mobility. This facilitates crosslinking (above 450°C) by permitting necessary axial shifts of the molecules bringing pendent methyl groups (or the radicals) of the neighboring chains within suitable proximity of each other. Such axial shifts may be responsible for the transverse cracks generated in the relatively more oriented skin. On the other hand, in the case of tension-annealed samples, the chains may not be able to shift and align (as required for crosslinking) due to the restricted mobility under the applied external stress. Because the core has the lower orientation than the skin, some intrafibrillar crosslinking may have occurred in the core of the tensionannealed samples, as the mechanism for crosslinking in MePBZT is indeed available via methyl pendent groups, unlike the case of PBZT, as explained earlier.

To study the effects of intermolecular crosslinking, molecular mechanics and dynamics simulations have been performed on methyl pendant PBZT.²² All three types of crosslinks shown in Figure 1 were studied. Compared to methylene or ethylene crosslinks, the phenyl-phenyl crosslink was found to bring about the greatest disruption in chain packing relative to the uncrosslinked state. This results in much higher energy for the phenyl-phenyl crosslinked state compared to the uncrosslinked methyl pendant PBZT. It was also predicted that at low crosslinking densities chain packing parameters are disturbed, while at high crosslink densities, bond lengths, angles, and torsions are distorted from their equilibrium values. A significant axial stress (as high as 5 GPa at high degree of crosslinking) is predicted to build up on the formation of phenyl-phenyl crosslinks. This provides a reasonable explanation for the observation of transverse cracks on the fiber surface. Molecular modeling also suggests that the crosslinking in the MePBZT fibers via methylene or ethylene bridge are more likely to be accommodated in the crystal cell than the phenyl-phenyl crosslinking.

Mechanical Properties

Tensile stress-strain curves for PBZT and MePBZT fibers are given in Figure 9, and mechanical properties (including compressive and torsional properties) are listed in Table II. As-spun PBZT and asspun MePBZT fibers exhibit yield behavior in tension. High strain to failure in the as-spun MePBZT is a result of low spin draw ratio compared to the as-spun PBZT. Recoil compressive strength (RCS) versus torsional modulus for various PBZT and MePBZT fibers is given in Figure 10. With the exception of AS MePBZT, recoil compressive strength increases with increasing torsional modulus. A cor-



Figure 9 Stress-strain curves for various PBZT and MePBZT fibers. (1) AS PBZT, (2) HT PBZT, (3) PBZT-530-N-30-100, (4) PBZT-530-N-F, (5) AS MePBZT, (6) MePBZT-530-N-30-100, (7) MePBZT-475-N-F.

Fiber Type	Tensile Modulus E (GPa)	Tensile Strength (GPa)	Elongation at Break (%)	Torsional Modulus G (GPa)	E/G	RCS ^a (GPa)	Loop Strength (GPa)	Transverse Yield Strength (MPa)
PBZT								
AS PBZT	168 ± 22	2.00 ± 0.30	1.7 ± 0.3	1.30 ± 0.14	129	_	$0.3 \pm 0.08 $	
HT PBZT	224 ± 21	2.85 ± 0.35	1.3 ± 0.1	1.40 ± 0.10	160	0.17	0.25 ± 0.08	37.6 ± 7.4
530-N-30-100	248 ± 13	2.90 ± 0.30	1.2 ± 0.1	1.55 ± 0.15	160	0.22	0.31 ± 0.03	37.7 ± 2.9
530-N-F	200 ± 15	1.00 ± 0.30	0.5 ± 0.16	1.73 ± 0.06	115	0.29	0.26 ± 0.06	34.6 ± 3.1
MePBZT								
AS MePBZT	102 ± 18	2.20 ± 0.60	5.0 ± 1.0	1.70 ± 0.11	60	0.78	0.52 ± 0.08	_
530-N-30-100	198 ± 23	1.75 ± 0.20	1.0 ± 0.2	2.00 ± 0.20	98	0.44	0.89 ± 0.12	55.4 ± 7.4
475-N-F	76 ± 7	0.40 ± 0.15	0.5 ± 0.2	2.32 ± 0.16	33	_	_	58.2 ± 7.2

Table II Mechanical Properties of PBZT and Methyl Pendant (MePBZT) Fibers

^a Recoil compressive strength.

relation between torsional modulus and compressive strength, for a number of fibers, has also been reported previously.²³

A comparison of properties, in Table II, between PBZT (530-N-30-100) and MePBZT (530-N-30-100) is meaningful; recoil compressive strength, loop strength, torsional modulus, and transverse compressive strength all show that the MePBZT (530-N-30-100) fiber has 50 to 100% higher values compared to the corresponding values for the PBZT (530-N-30-100) fiber. It should be emphasized that the MePBZT (530-N-30-100), at best, has very limited intrafibrillar crosslinking in the core region while the skin is uncrosslinked, yet, moderate improvement in compressive strength is possible. Compressive strength measurements on fibers exhibiting high degree of inter- and intrafibrillar crosslinking, for example free annealed fiber MeP-



Figure 10 Recoil compressive strength versus torsional modulus of various fibers. (1) HT PBZT, (2) PBZT-530-N-30-100, (3) PBZT-530-N-F, (4) AS MeP-BZT, (5) MePBZT-530-N-30-100.

BZT-525-N-F [Fig. 5(c)], will be very meaningful, provided the crosslinking can be achieved without creating significant defects such as transverse cracks in the fiber.

Compressive strength is reported to increase with decreasing E/G in pitch- and PAN-based carbon fibers.²⁴ Similar dependence between recoil compressive strength and E/G is observed for PBZT and MePBZT fibers (Fig. 11).

Observed high recoil compressive strength value of 0.78 GPa, for the as-spun MePBZT fiber, needs further consideration. The tensile stress-strain behavior of this fiber is nonlinear, and exhibits a yield point (Fig. 9). Nonlinearity in aniso-tropic fibers has also been observed in longitudinal compression.²⁵ Energy loss will also occur due to viscoelasticity. The AS MePBZT did not exhibit any hysteresis in the cyclic tensile test, when the applied tensile stress was comparable to which



Figure 11 Recoil compressive strength versus E/G for various fibers. (1) HT PBZT, (2) PBZT-530-N-30-100, (3) PBZT-530-N-F, (4) AS MePBZT, (5) MePBZT-530-N-30-100.

the fiber is subjected to during recoil test; however, due to the above factors, we are reluctant to ascribe the observed 0.78 GPa as the true compressive strength of the AS MePBZT fiber. However, this merits further investigation, particularly from the view point that if 0.78 GPa represents the true compressive strength of the MePBZT fiber, then this might suggest a significant influence of the presence and the position of the methyl pendant group on the axial compressive strength.

CONCLUSIONS

Crosslinking in the methyl pendent PBZT fiber occurs in the 450-550°C range under free annealing. Surface cracks are developed in the fiber free annealed in this temperature range. Crosslinking in the free-annealed fibers appears to be both inter- and intrafibrillar, and annealing at or above 530°C leads to completely nonfibrillar structure. In the tension-annealed samples, crosslinking, if any, is intrafibrillar. However, no evidence of crosslinking in the tension-annealed samples has yet been obtained. Recoil compressive strength, loop strength, torsional modulus, and the transverse compressive strength of the tension heat-treated MePBZT fiber are 50 to 100% higher compared to the comparably heattreated PBZT fiber. Compressive strength and other mechanical properties could not be measured in highly crosslinked free annealed samples, as such samples show significant transverse cracks.

It is not only important to have a crosslinkable system and appropriate conditions for crosslinking but also that (a) the crosslinking should be both inter- and intrafibrillar, and (b) significant stresses should not be generated in the fiber as a result of crosslinking. Of these two conditions, only the first one has been achieved in the methyl pendant PBZT. Development of stresses on crosslinking in this fiber leads to cracks, which result in poor tensile strength. If internal stresses are not developed on crosslinking, then crosslinking will not be associated with a decrease in tensile strength. This calls for a judicious design of a chemical architecture that will meet such a criterion for facile crosslinking in the polymeric fiber.

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APPENDIX: SAMPLE DESIGNATION SCHEME

Fiber Designation	Heat Treatment Condi- tions
AS PBZT	As spun PBZT (no heat
	treatment)
HT PBZT	PBZT heat treated un-
	der tension in nitro-
	gen at 550°C for <60 s
PBZT-530-N-30-100	HT PBZT, at 530°C, in
	nitrogen, for 30 min,
	tension—100 MPa
PBZT-530-N-F	HT PBZT, at 530°C, in
	nitrogen, for 10 min,
	free annealed
AS MePBZT	As spun MePBZT (no
	heat treatment)
MePBZT-530-N-30-100	MePBZT, at 530°C, in
	nitrogen, for 30 min,
	tension—100 MPa
MePBZT-530-N-30-50	MePBZT, at 530°C, in
	nitrogen, for 30 min,
	tension—50 MPa
MePBZT-530-N-30-25	MePBZT, at 530°C, in
	nitrogen, for 30 min,
	tension—25 MPa
MePBZT-530-N-30-7	MePBZT, at 530°C, in
	nitrogen, for 30 min,
	tension—7 MPa
MePBZT-475-N-F	MePBZT, at 475°C, in
	nitrogen, for 10 min,
	free annealed
MePBZT-525-N-F	MePBZT, at 525°C, in
	nitrogen, for 10 min,
	free annealed

REFERENCES

- 1. Kumar, S.; Helminiak, T. E. Mater Res Soc Symp Proc 1989, 134, 363.
- 2. Kumar, S. Indian J Fiber Text Res 1991, 16, 52.
- Rigney, J.; Little, M. D.; Martin, D. C. J Polym Sci Polym Phys Ed 1994, 32, 1017.
- Sweeny, W. J Polym Sci Polym Chem Ed 1992, 30, 1011.
- Suter, U. W.; Rickert, C.; Neuenschwander, P. Macromol Chem Phys 1994, 195, 511.
- Tsai, T. T.; Arnold, F. E. Polym Preprints (ACS) 1988, 29(2), 324.
- Kozey, V. V.; Jiang, H.; Mehta, V. R.; Kumar, S. J Mater Res 1995, 10, 1044.

- 8. Sikkema, D. J. Polymer 1998, 39, 5981.
- Hu, H. Ph.D. Thesis, Georgia Institute of Technology (1997).
- Mehta, V. R.; Kumar, S.; Polk, M. B.; VanderHart, D. L.; Arnold, F. E.; Dang, T. D. J Polym Sci Polym Phys Ed 1996, 34, 1881.
- Mehta, V. R.; Kumar, S. J Mater Sci 1994, 29, 3658.
- 12. Allen, S. R. J Mater Sci 1987, 22, 853.
- 13. Sinclair, D. J Appl Phys 1950, 21, 380.
- Wang, C. S.; Bai, S. J.; Rice, B. P. Polym Mater Sci Eng (ACS Preprints) 1989, 60, 767.
- 15. Jones, W. R.; Johnson, J. W. Carbon 1971, 9, 645.
- 16. Kawabata, S. J Text Inst 1990, 81, 432.
- 17. Allen, S. R.; Farris, R. J.; Thomas, E. L. J Mater Sci 1985, 20, 4583.

- Fratini, A. V.; Lenhert, P. G.; Resch, T. J.; Adams, W. W. Mater Res Symp Proc 1989, 134, 431.
- Young, R. J.; Day, R. J.; Zakikhani, M. Mater Res Symp. Proc 1989, 134, 351.
- Dobb, M. G.; Johnson, D. J.; Saville, B. P. J Polym Sci Polym Phys Ed. 1977, 15, 2201.
- Panar, M.; Avakian, P.; Blume, R. C.; Gardner, K. H.; Gierke, T. D.; Yang, H. H. J Polym Sci Polym Phys Ed 1983, 21, 1955.
- Jenkins, S.; Jacob, K. I.; Kumar, S. J Polym Sci Polym Phys Ed 1998, 36, 3057.
- DeTeresa, S. J.; Porter, R. S.; Farris, R. J. J Mater Sci 1985, 20, 1645.
- Kumar, S.; Mehta, V. R.; Anderson, D. P.; Crasto, A. S. 37th Int SAMPE Sym 1992, 967.
- 25. Kawabata, S. J Text Inst 1995, 86, 347.