

# Rigid-Rod Polymeric Fibers

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**ABSTRACT:** This paper traces the historical development of high temperature resistant rigid-rod polymers. Synthesis, fiber processing, structure, properties, and applications of poly(*p*-phenylene benzobisoxazole) (PBO) fibers have been discussed. After nearly 20 years of development in the United States and Japan, PBO fiber was commercialized with the trade name Zylon® in 1998. Properties of this fiber have been compared with the properties of poly(ethylene terephthalate) (PET), thermotropic polyester (Vectran®), extended chain polyethylene (Spectra®), *p*-aramid (Kevlar®), *m*-aramid (Nomex®), aramid copolymer (Technora®), polyimide (PBI), steel, and the experimental high compressive strength rigid-rod polymeric fiber (PIPD, M5). PBO is currently the highest tensile modulus, highest tensile strength,

and most thermally stable commercial polymeric fiber. However, PBO has low axial compressive strength and poor resistance to ultraviolet and visible radiation. The fiber also loses tensile strength in hot and humid environment. In the coming decades, further improvements in tensile strength (10–20 GPa range), compressive strength, and radiation resistance are expected in polymeric fibers. Incorporation of carbon nanotubes is expected to result in the development of next generation high performance polymeric fibers. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 791–802, 2006

**Key words:** fibers; high performance polymers; high temperature materials; mechanical properties; nanocomposites

## INTRODUCTION

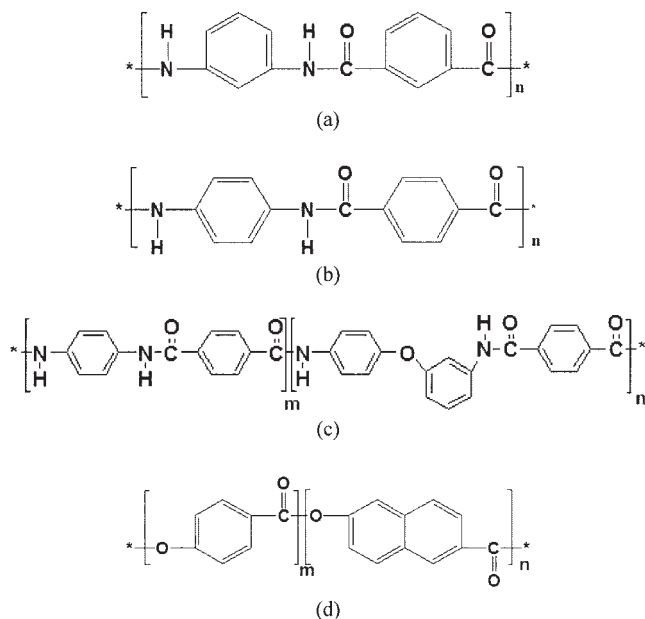
At the turn of nineteenth century, there were fibers (cotton, wool, silk, and rayon) with tensile strength and modulus of less than 0.5 and 10 GPa, respectively. During 1920s, Herman Staudinger proposed the concept of macromolecules.<sup>1</sup> In 1926, Charles Stine proposed to the DuPont company's board of directors that they should invest in this unproven concept of macromolecules. After more than 10 years of research effort by Carothers and his team, DuPont company announced to the world, at the 1939 world trade fair in New York city, the development of a textile fiber, nylon 66, made from petroleum. These revolutionary developments became the basis of synthetic polymer and fiber industry. Stine's vision, coupled with DuPont company's resources, and Carothers research efforts laid the foundation that made DuPont company the largest fiber manufacturer of the world for the twentieth century, and ultimately have led to the development and commercialization of fibers such as Nomex® and Kevlar® during 1960s and 1970s, respectively. Flexible polymeric fibers such as polyethylene (PE), polypropylene (PP), poly(ethylene terephthalate) (PET), nylon 6, polyacrylonitrile were also developed during 1940s and 1950s. High strength, high modulus,

and extended chain PE fibers were commercialized during 1980s. Tensile strength, tensile modulus, and service temperature of flexible polymeric fibers such as PE, PP, PET, nylon 6, nylon 66, etc. are typically limited to below 1 and 20 GPa, and 100°C, while these values for the commercial Kevlar® fibers approach 4 and 185 GPa, and 500°C. Commodity textile fibers are processed from polymers, typically with molecular weight in the range of 20,000–100,000 g/mol, while extended chain PE fibers<sup>2,3</sup> are processed from very high molecular weight PE (~3 × 10<sup>6</sup> g/mol). Though extended chain PE fibers possess high modulus and high tensile strength, their service temperature is limited to below 100°C.

Efforts were underway in the United States and Russia during 1960s to synthesize high temperature resistant polymers.<sup>4–10</sup> Initial results of the US Air Force research program on high temperature polymers were presented at the American Chemical Society in 1977 and a series of papers encompassing all aspects of the program, including synthesis, polymerization kinetics, rheology, fiber processing, structure, and properties were published in *Macromolecules* in 1981<sup>11–20</sup> and a *Materials Research Society Proceedings* on the subject appeared in 1989.<sup>21</sup> Further development on these materials occurred at Stanford Research Institute (Menlo Park, CA) and Dow Chemical Co. (Midland, MI), and the PBO fiber was ultimately commercialized by Toyobo Co. (Japan) in 1998.

In general, rigid-rod polymers are classified into lyotropic and thermotropic liquid crystalline poly-

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**Figure 1** Rigid-rod polymeric fibers: Aramid fibers (a) Nomex<sup>®</sup>, (b) Kevlar<sup>®</sup>, (c) Technora<sup>®</sup>, and copolyester fiber (d) Vectran<sup>®</sup>.

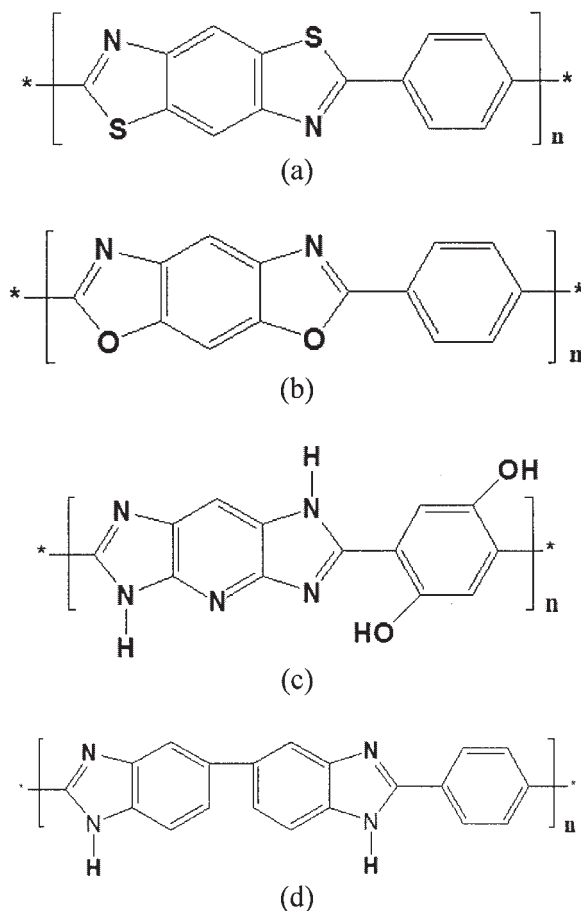
mers. Lyotropic polymers exhibit liquid crystallinity in solution as a function of polymer concentration, and thermotropic polymers exhibit liquid crystallinity in the melt state. Vectra<sup>®</sup>, a copolymer of hydroxy benzoic acid and hydroxy naphthoic acid (Fig. 1), is an example of successful thermotropic liquid crystalline polyester, and it was commercialized in 1985. The tensile strength, modulus, and decomposition temperature of this fiber are 2.85 and 65 GPa, and 400°C, respectively.<sup>22</sup> Both Kevlar and PBO exhibit lyotropic liquid crystalline behavior. Aramid polymers include *m*-aramid and *p*-aramid polymers that are linked to the *meta*- and *para*-positions of the phenylene ring, respectively. In the 1960s, poly(*m*-phenylene isophthalamide) was commercialized by DuPont with the trademark Nomex<sup>®</sup>,<sup>23</sup> followed by the commercialization of poly(*p*-phenylene terephthalamide) (PPTA) as Kevlar<sup>®</sup> (Fig. 1). PPTA was the first fiber exhibiting high degree of molecular order, long relaxation times,<sup>24,25</sup> high strength, and high modulus. Kevlar<sup>®</sup> properties deteriorate in strong acids and bases, as well as on exposure to ultraviolet radiation. Copolymer fiber of PPTA was developed and commercialized by Teijin (Japan) as Technora<sup>®</sup> in 1985,<sup>24,26</sup> exhibiting improved chemical resistance. The chemical structure of Technora<sup>®</sup> is also given in Figure 1.

Heterocyclic rigid-rod polymers can be classified into three categories: polybenzazole, polybenzimidazole, and polypyridobisimidazole. Polybenzimidazole (PBI) fiber was commercialized for its thermal stability<sup>27</sup> in 1983 by Celanese (Fig. 2). Polybenzazole polymers include poly[(benzo 1,2-d:5,4-d' bisoxazole-2,6-

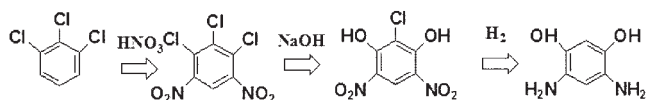
diyl)-1,4-phenylene] (PBO) and poly[(benzo 1,2-d:4,5-d' bisthiazole-2,6-diyl)-1,4-phenylene] (PBZT) (Fig. 2).<sup>28–33</sup> Because of its excellent properties,<sup>34</sup> this paper is primarily focused on synthesis, processing, properties, and applications of PBO. More recently, the poly(2,6-diimidazo(4,5-b:4'5'-e)pyridinylene-1,4(2,5-dihydroxy)phenylene) (PIPD), a member of polypyridobisimidazole class, was synthesized (Fig. 2).<sup>35</sup> This polymer forms intermolecular hydrogen bonds in two dimensions,<sup>36–40</sup> and has the highest compressive strength (1–1.7 GPa) of any polymeric fiber to date.

## SYNTHESIS

PBO is synthesized using 2,5-diamino-1,3-benzenediol (DABDO) and terephthalic acid (TA) or TA derivative (e.g. terephthaloyl chloride) in poly(phosphoric acid) (PPA). The DABDO was initially synthesized by Wolfe et al.<sup>41,42</sup> However, this scheme was expensive in preparation and purification.<sup>43</sup> Cost-effective meth-



**Figure 2** Heterocyclic rigid-rod polymers: (a) poly(*p*-phenylene-2,6-benzobisthiazole) (PBZT), (b) poly(*p*-phenylene-2,6-benzobisoxazole) (*cis*-PBO, Zylon<sup>®</sup>), (c) poly(2,6-diimidazo(4,5-b:4'5'-e)pyridinylene-1,4(2,5-dihydroxy)phenylene) (PIPD), and (d) poly(2,2'-(*m*-phenylene)-5,5'-bisbenzimidazole) (PBI).



**Figure 3** Synthetic route to obtain 2,5-diamino-1,3-benzenediol for *cis*-PBO (from ref. 43).

ods to synthesize DABDO have been developed by Lysenko (Fig. 3)<sup>33</sup> and Morgan et al.<sup>44</sup> Besides the DABDO, ultrahigh purity TA is available in particle sizes of 50–100  $\mu\text{m}$  and is easier to handle than terephthaloyl chloride. For efficient polymerization in PPA, the particle size should be reduced to less than 10  $\mu\text{m}$  to obtain complete dissolution. Recent work indicates that poly(terephthalic anhydride) as a latent monomer in PBO synthesis generated TA particle size of less than 2.4  $\mu\text{m}$  in PPA.<sup>45</sup>

In the synthetic procedure of PBO, PPA plays a role as solvent as well as catalyst and dehydrating agent. The three functionalities of PPA allow formation of polybenzobisazoles in situ without any separation process. The spinnable solutions are obtained directly from the polymerization mixtures. To obtain high molecular weight PBO, the final content of  $\text{P}_2\text{O}_5$  must be carefully adjusted in PPA. Extensive research has been carried out to understand PBO polymerization mechanism.<sup>46</sup> Unlike the conventional step-growth polymerization reactions, PBO oligomers are not statistically end-capped with the two monomers, and only DABDO is found at PBO oligomer chain ends. This is a result of poor solubility of TA in PPA. The polymerization mechanism shown in Figure 4 was proposed to account for this unusual oligomer structure and the remarkable fact that high molecular weight PBO was obtained even when 5% excess of TA was used. In addition, by being isolated the PBO oligomer, the molecular weight of PBO oligomer can increase again when it is redissolved in PPA, and TA is added. To control the molecular weight of PBO, the isolation of PBO oligomer can be used in plant scale. Less than stoichiometric amount of TA is loaded at the beginning of polymerization reaction to obtain oligomer mixture end-capped with DABDO. Then the TA and PPA are added to the reaction mixture. By controlling the amount of TA at this stage, the molecular weight of PBO can be adjusted.<sup>47</sup>

### SOLUTION PROPERTIES

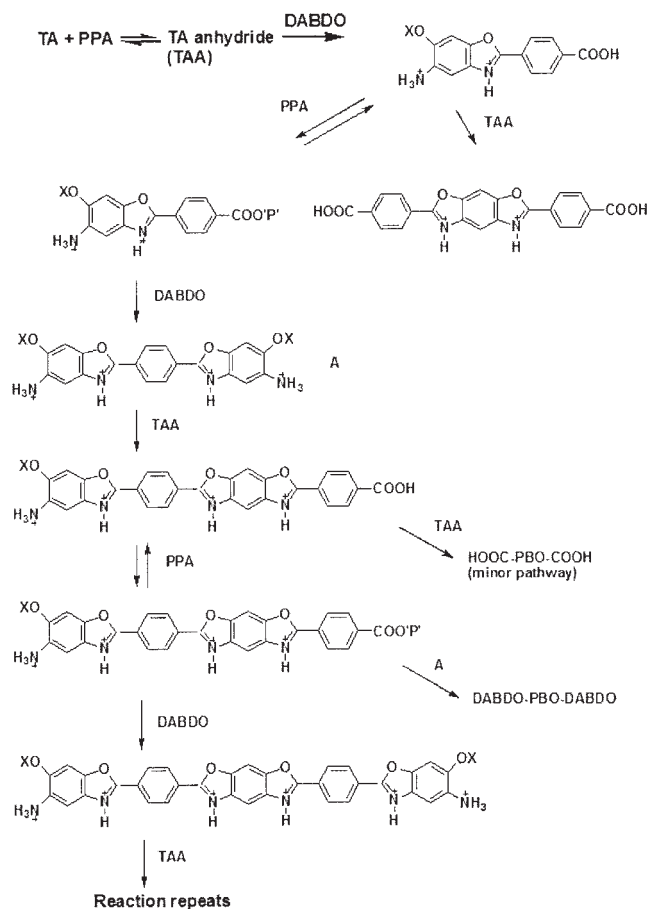
PBO is soluble in strong protic acids such as PPA, methanesulfonic acid (MSA), chlorosulfonic acid, and trifluoroacetic acid<sup>48</sup> via backbone protonation, which weakens intermolecular interaction and reduces chain stiffness.<sup>49, 50</sup> Chain conformation of polymers in solvents can be assessed by measuring intrinsic ( $[\eta]$ ) or inherent viscosity ( $\eta_{\text{inh}}$ ), which represents the hydro-

dynamic volume of molecule in a given solvent. Chain end-to-end distance increases with increasing chain rigidity and with increasing molecular weight. Rotational motion of the molecule is hindered by the presence of the neighboring extended chain molecules. Mark–Houwink exponent for ideal random coil polymers is 0.5 under the  $\theta$ -condition and that for the semirigid polymers, it is 1.0. Several research groups have studied the solution properties of *cis*-PBO<sup>13,15,31,51</sup> and the reported Mark–Houwink equation in MSA at 30°C is given by:

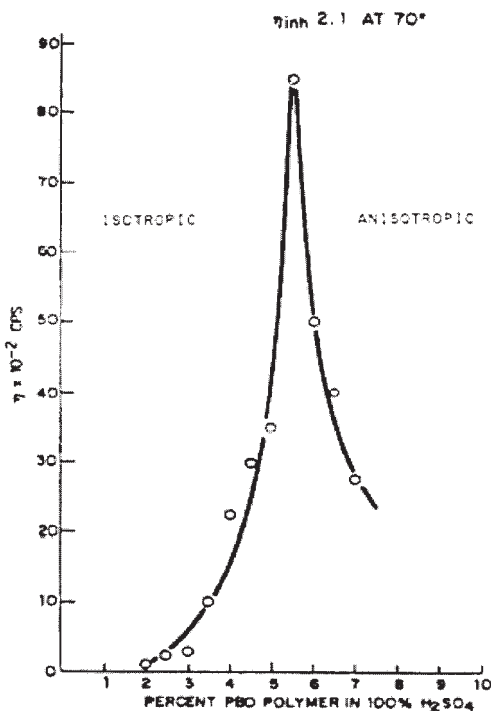
$$[\eta] = 2.77 \times 10^{-7} \overline{Mw}^{1.8}$$

Exponent value of 1.8 implies high chain rigidity.

Polymer persistence length is another measure of chain rigidity. Light scattering experiment in MSA showed that the persistence length of *cis*-PBO is about 20–30 nm<sup>52</sup> and 50 nm,<sup>30,51</sup> whereas the theoretically calculated values were in the range of 22–65 nm.<sup>53–55</sup> *Cis*-PBO persistence length values were longer than those of Kevlar® (PPTA),<sup>51</sup> *trans*-PBO,<sup>57,58</sup> and *cis*-PBZT.<sup>56,57</sup> By comparison, the persistence length of flexible polymers such as PE are much shorter (1 nm



**Figure 4** Polymerization mechanism of PBO (from ref. 46).



**Figure 5** Viscosity as a function of PBO concentration in 100% sulfuric acid (from ref. 13).

or less). Choe and Kim<sup>13</sup> showed anisotropic liquid crystal PBO phase in 100% sulfuric acid at 70°C at about 5.5 wt % PBO (Fig. 5).

PBO can also be dissolved in aprotic organic solvents such as nitroalkanes and nitrobenzene in the presence of Lewis acids because of electron donor-acceptor complex formation.<sup>58-62</sup> The dissolution process in aprotic organic solvents under Lewis acid such as  $\text{BCl}_3$ ,  $\text{AlCl}_3$ , and  $\text{GaCl}_3$  increases the average effective diameter of the polymer chains by complex formation, which results in the decrease in L/D ratio. From an industrial point of view, the higher critical concentration and the utilization of organic solvents are attractive as compared with the protonated PBO using protic strong acids. However, fibers could not be processed from these solutions.

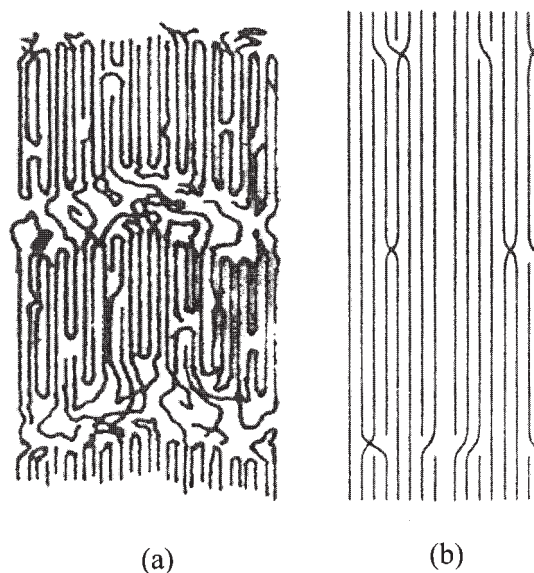
### FIBER SPINNING

Polymerized lyotropic liquid crystalline PBO/PPA solution is directly spun without polymer precipitation and redissolution. The processing method used is dry-jet wet spinning. In this method, as the polymer dope comes out of the spinneret, it exits into an air gap before entering the coagulation bath. Because of liquid crystalline behavior, polymer molecules attain significant orientation during flow in the spinneret with further major orientation development in the air gap. Use of the air gap was one of the key factors in the development of high modulus Kevlar<sup>®</sup> processing in

1960s. Polymer is spun from the liquid crystalline medium where the solution viscosity is very low. The typical PBO concentration in PPA for fiber spinning is in the 10–15 wt % range and the typical dope temperature can be in the range 100–170°C. Water at room temperature is the common coagulant. Coagulation speed can be varied by changing the bath temperature as well as by changing coagulation media. Acidic, basic, as well as organic coagulants have also been experimented with. Coagulation conditions significantly affect the ultimate fiber structure. In the post processing step, coagulated fiber is washed, dried, and heat-treated under tension. Heat treatment under tension is a key step for obtaining high molecular orientation and hence high modulus. For high tensile strength fibers, the PBO solution with the intrinsic viscosity of the order of 50 dL/g and molecular weight of the order of 40,000 g/mol (chain length of about 210 nm) is typically used.

### STRUCTURE AND MORPHOLOGY

The structure of commodity polymeric fibers (PP, nylon, polyester, etc.) is highly defective and contains chain folds and amorphous regions [Fig. 6(a)]. Crystallinity in these fibers is typically in the 30–65% range, while the crystalline orientation is in the 0.9–0.98 range. However, these commodity fibers typically exhibit low amorphous orientation. By comparison, extended chain PE (Spectra) and liquid crystalline polymeric fibers (Vectran, PPTA, PBO) exhibit high degree of order and orientation [Fig. 6(b)]. These fibers do contain defects such as chain ends, chain bends,



**Figure 6** Schematic descriptions of molecular chain arrangement: (a) commodity fibers and (b) extended chain fibers.

TABLE I  
Unit Cell Parameters of PBO

Crystal system	a (nm)	b (nm)	c (nm)	$\gamma$ (degrees)	References
Monoclinic	1.1201	0.3540	1.205	101.3	Fratini et al. <sup>[70]</sup>
Monoclinic	0.5651	0.3570	0.603	101.4	Takahashi and Sul <sup>[74]</sup>

and voids. Degree of crystallinity in these fibers can approach 100% and orientation factor is greater than 0.99.

The PBO fiber structure and morphology have been studied.<sup>63–69</sup> The crystal structure of PBO has been determined by several groups<sup>66,67,70–73</sup> (Table I).<sup>74</sup> Figure 7(a,b) are the crystal structures of PBO and PIPD, respectively. The dashed lines in Figure 7(b) represent the hydrogen bonding between molecules. Crystal size for as-spun and heat-treated PBO was determined by wide angle X-ray diffraction (WAXD).<sup>67,75</sup> The crystal size increase with heat-treatment along *c*-axis (also the fiber axis) was less than in the lateral direction. Dark field transmission electron microscopy (TEM),<sup>67,76</sup> and high resolution TEM<sup>76,77</sup> studies were in good agreement with the WAXD data, indicating greater crystal growth in transverse direction than in the axial direction. Lattice images confirm that the PBO crystal perfection improved on heat-treatment (Fig. 8).

Structure development in PBO fiber has been studied during fiber spinning using synchrotron X-ray source.<sup>78</sup> WAXD patterns suggested that the lyotropic liquid crystalline structure before coagulation is a

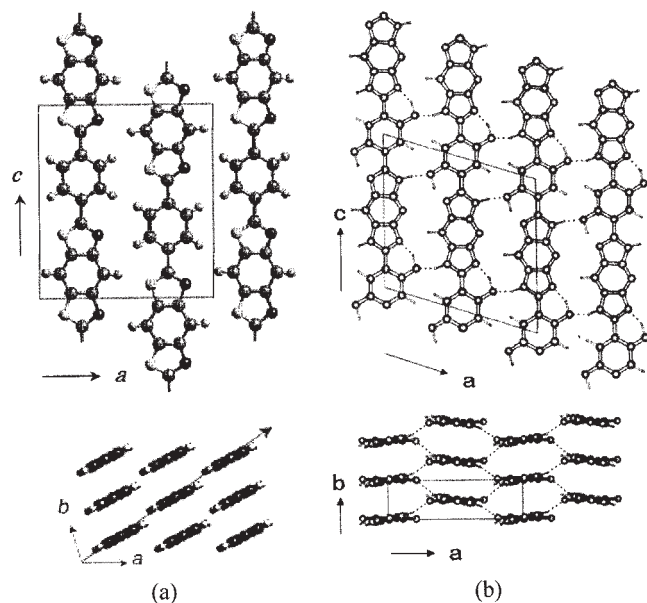


Figure 7 Crystal structures of (a) PBO and (b) PIPD (from ref. 39, 72, and 73).

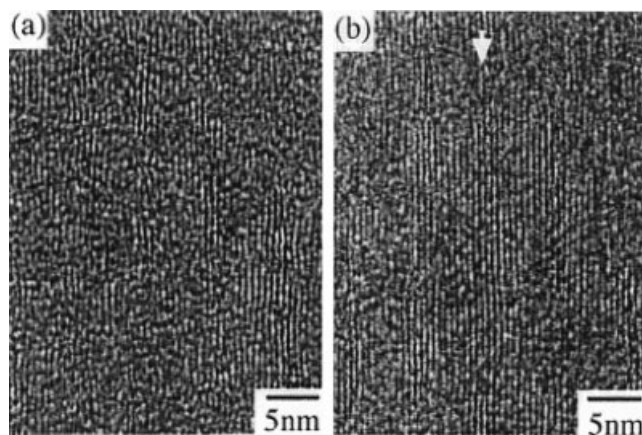


Figure 8 Lattice images of PBO fiber: (a) as spun fiber and (b) heat treated fiber (from ref.80).

PBO-PPA complex. When fiber from 750  $\mu\text{m}$  diameter spinneret was coagulated for  $\sim 2$  s in water at room temperature, the PBO-PPA complex structure was preserved. However, the long coagulation times ( $\sim 30$  min) lead to complete disappearance of the PBO-PPA complex, and to the formation of pure PBO crystals. Small angle X-ray scattering (SAXS) showed equatorial streaks due to the presence of voids elongated along the fiber axis originating from the large volume reduction during coagulation. The effect of chain orientation on mechanical properties was investigated in terms of postprocessing condition and morphologies by the SAXS study.<sup>79,80</sup> The so-called Northolt's plot is given in Figure 9. The SAXS patterns for the fiber with open circle show four-point pattern, suggesting inhomogeneity along the fiber axis within the fibrils.<sup>68,81</sup> However, the higher modulus PBO fiber represented by filled circle exhibited the absence of four point pattern, which implies the development of homogeneous structure along the fiber axis. Figure 10 represents the structural model of PBO fiber and TEM

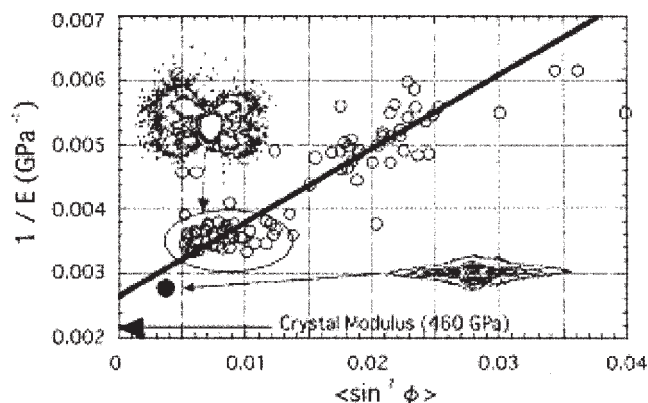
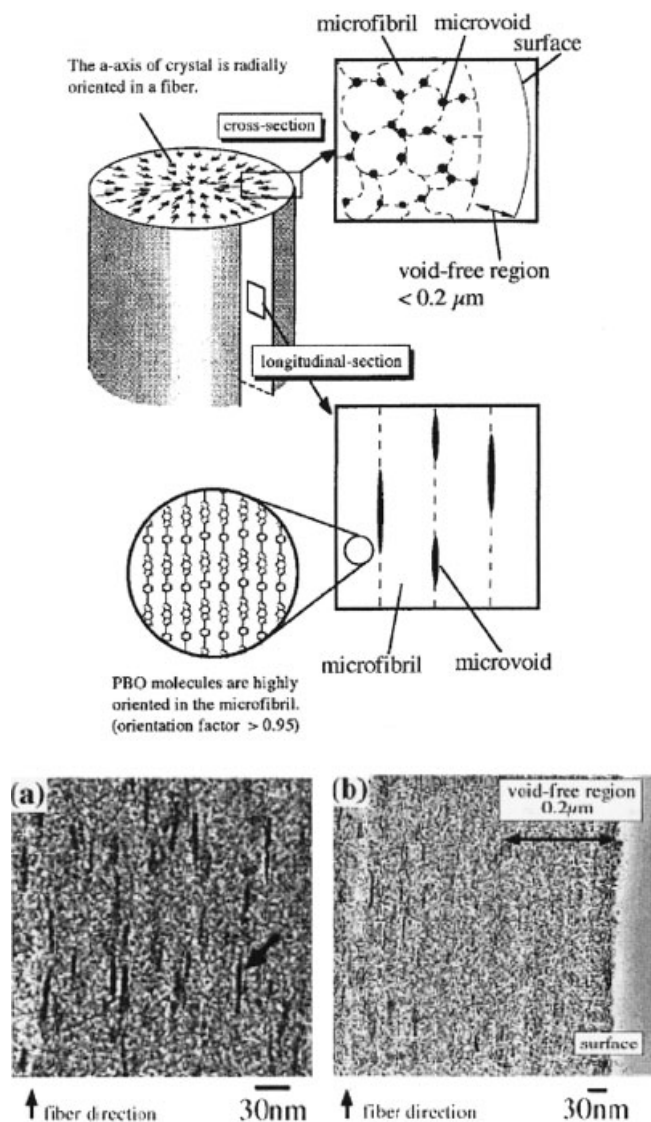


Figure 9 Northolt's plot for PBO fibers with SAXS patterns (from ref. 79).



**Figure 10** Structural model of PBO fiber and TEM images of (a) microvoids containing region and (b) void-free region (from ref. 80).

images showing elongated microvoid structure in the fiber. The morphological studies by SEM also showed fibrillar structure (Fig. 11).

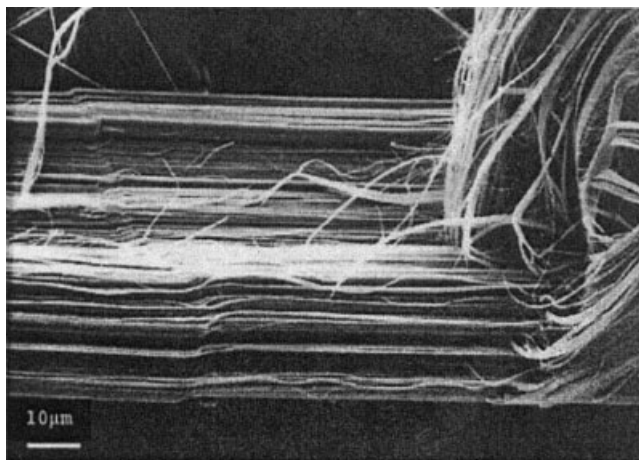
## PROPERTIES

### Mechanical properties

Table II summarizes properties of various fibers. The tensile strength and modulus of PBO fibers were reported to be as high as 5.8 and 352 GPa (experimental fiber), respectively.<sup>82,83</sup> The mechanical properties of PBO fiber depend on polymer molecular weight, as well as on processing and postprocessing conditions.<sup>43,84,85</sup> PBO fiber modulus from X-ray diffraction was measured to be in the range of 460–480 GPa.<sup>86–88</sup> Figure 12 exhibits crystal modulus versus fiber mod-

ulus of various high performance fibers. The figure indicates that there is room for improvement in the modulus of Zylon® fiber.

Tensile strength and modulus retention rates were also investigated under various environmental conditions such as temperature, humidity, and exposure to ultraviolet and visible light.<sup>34</sup> At 400°C, PBO fiber (Zylon® HM) retains 75% of the room temperature modulus (Fig. 13). However, high temperature with humidity has a drastic effect on strength (Fig. 14). At 250°C with saturated steam, the strength retention in PBO is below 20% of its room temperature value. Therefore, PBO fibers should be stored in humid-free environment. PBO tensile strength also drops sharply with UV exposure in the initial stage, which indicates that the products of PBO fiber for outdoor use have to be protected from the UV radiation (Fig. 15). Exposure to visible light also affects PBO strength. For example, one month exposure to two 35 W fluorescent lamps placed 150 cm away from the sample is reported to reduce the PBO fiber tensile strength to nearly 70% of its original value. The excellent chemical resistance to various organic solvents, acids, and bases leads to high strength retention; however, the PBO staple fiber showed low resistance under acid and base at high temperature. Besides tensile properties, fiber dimensional stability is also important for structural materials. The thermal shrinkage of PBO fiber after hot air treatment for 30 min without applying load was only about 0.2%, while under the same conditions, *p*-aramid and copoly-aramid exhibited about 0.5 and 0.7% shrinkage, respectively. Based on the creep testing, at 60% of the failure stress, failure time of 19 years is predicted for the Zylon® HM fiber. Abrasion resistance of PBO on metal is higher than that of aramid fibers under the same load, while both the PBO and aramid exhibit much lower abrasion resistance than that of nylon or ultra high molecular weight extended chain polyethylene (UHMW-PE, Fig. 16). Shear mod-



**Figure 11** SEM images of peeled experimental PBO fiber.

TABLE II  
Properties of Various Fibers

	Density (g/cm <sup>3</sup> )	Tensile strength (GPa)	Tensile modulus (GPa)	Elongation at break (%)	Moisture regain (%)	Decomposition temperature (°C)	LOI
Zylon AS	1.54	5.8	180	3.5	2	650	68
Zylon HM	1.56	5.8	270	2.5	0.6	650	68
Kevlar 49	1.44	3.6–4.1	130	2.8	4.5	550	28
Kevlar 149	1.47	3.4	185	2	3	550	30
Nomex 450	1.38	0.65	17	22	4.5	400	30–32
Technora	1.39	3.4	71	4.5	3.5–5.0	500	25
PIPD (M5)	1.7	3.5–4.5	330	2.5	4.5	500	>50
Steel	7.8	2.8	200	1.4	—	—	—
Spectra 900	0.97	2.4	70	4	—	150 <sup>a</sup>	16
Spectra 1000	0.97	3.1	105	2.5	—	150 <sup>a</sup>	16
Vectran	1.4	2.85	65	3.3	<0.1	400	>30
PBI	1.4	0.4	5.6	30	15	550	41
Polyester	1.38	1	15	20	0.4	260 <sup>a</sup>	17

Zylon AS and Zylon HM, PBO; Kevlar 49 and 149, *p*-aramid (PPTA); Nomex, *m*-aramid; Technora, copoly-aramid; Spectra 900 and 1000, extended chain ultra high molecular weight polyethylene; and Vectran, copolyester.

<sup>a</sup> Melting temperature.

ulus of PBO fiber at room temperature is 1 GPa and its temperature dependence has also been studied.<sup>89</sup> By comparison, the shear moduli of commodity textile fibers are generally in the 0.5–1 GPa range, whereas for carbon fibers it can range from 4 to 16 GPa. Sound velocity in a fiber depends on the modulus. In a PBO reinforced uniaxial composite, sound velocity of 9000 m/s was measured at low temperature (77 K) and decreased with increasing temperature.<sup>90</sup>

For many composite applications, fiber compressive strength is also important. However, the compressive strength of PBO fiber (200–300 MPa) is only a small fraction of its tensile strength. Extensive studies on

compression behavior of polymeric fibers have been carried out over last 25 years.<sup>83,91,92</sup> Unlike carbon and inorganic fibers, rigid-rod polymeric fibers do not show a catastrophic failure under compressive stress but exhibit failure via kinking (Fig. 17). The deformation mechanism involving kinking of individual molecules was confirmed by observing sharp, high angle tilt boundaries. Several theoretical models have been developed to explain compressive failure in high performance polymeric fibers. A model proposed the elastic instability of perfectly oriented rigid-rod chains.<sup>93,94</sup> From this model, the relationship between compressive strength and shear modulus, depending on buckling mode, is suggested that the compressive failure is dominated by fibrillar instability rather than molecular instability. The other theories concerned the misalignment between fibrils, crystals, or domains of well-oriented molecules and applied load direction.<sup>95,96</sup> The compressive strength of rigid-rod polymers such as PBO is in the 200–300 MPa range, for Kevlar® it is about 400 MPa, and for most flexible polymeric fibers as well as bulk polymers, the compressive strength values are below 200 MPa. The newly developed experimental fiber, PIPD, with a value of over 1 GPa, exhibits the highest compressive strength of any polymer (bulk or fiber) (Fig. 18). By comparison, compressive strength of carbon fibers is in the range of 1–3 GPa, and those of Boron, Al<sub>2</sub>O<sub>3</sub>, and SiC fibers these values can reach 7 GPa. Reviews on compressive strength of fibers<sup>92</sup> and bulk glassy polymers<sup>98</sup> have been published.

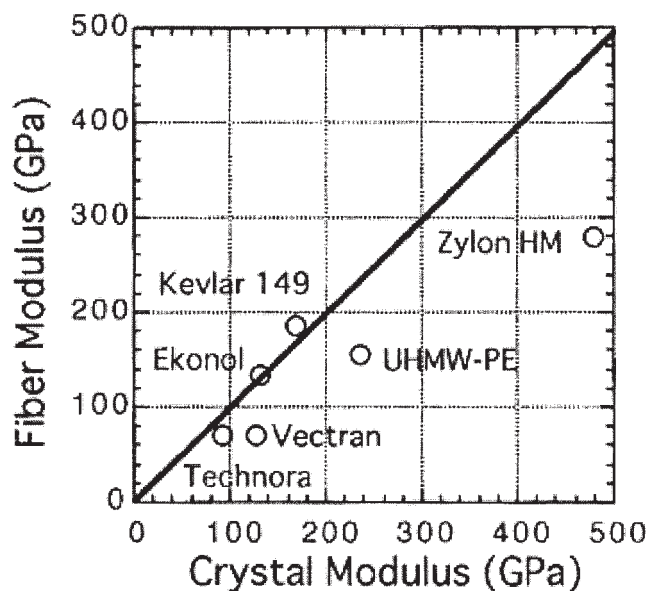


Figure 12 Microscopic fiber modulus as a function of crystal modulus for various fibers (from ref. 79).

### Ballistic properties

The combination of high strength, modulus, and toughness are some of the key factors for the candi-

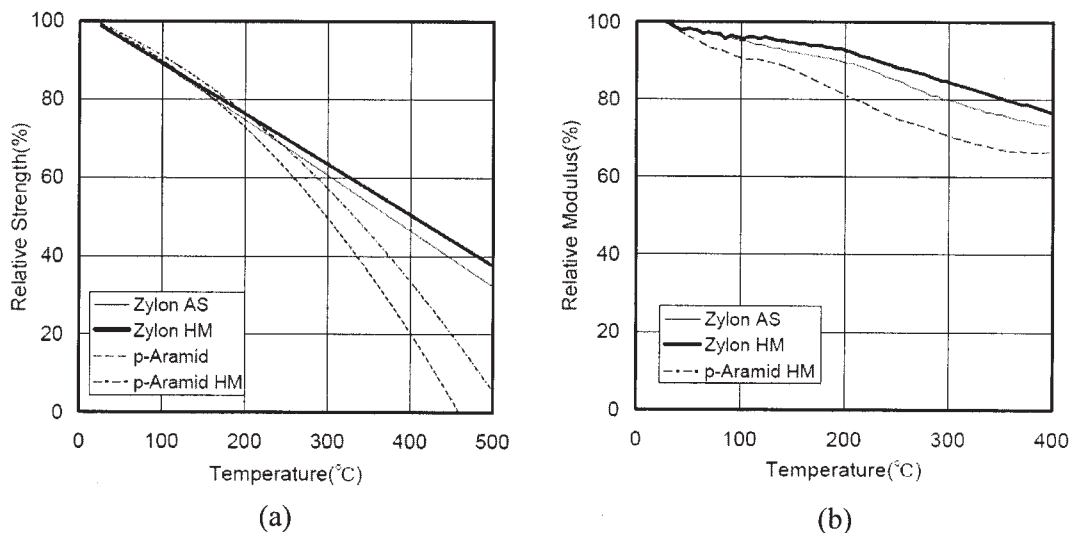


Figure 13 Tensile strength and modulus retention in PBO and aramid fibers with temperature (from ref. 34).

date materials for high-performance applications. The high toughness is especially important for ballistic application. An analytical model for the ballistic impact response of fibrous materials in body armor applications has been developed.<sup>99</sup> Recently, NASA Glenn Research center has conducted research on the ballistic properties of PBO fiber<sup>100</sup> for jet engine containment using braided Zylon® fabric. They prepared circular ring test specimen, whose inner diameter, axial length, and wall thickness were 40, 10, and 1.5 in., respectively. The specimens were mounted on a table at a slight incline from horizontal in front of gas gun. Small titanium disks were shot out of gas gun into the specimen at various speeds. The required energy for penetrating PBO fabric was approximately twice the energy required for Kevlar® fabric penetration.

### Thermal properties

Thermal decomposition temperature of PBO is about 650°C in air, which is about 100°C higher than that for the *p*-aramid fiber.<sup>34</sup> Under nitrogen or argon atmosphere, it increases to more than 700°C. Isothermal weight loss at 400°C indicates that PBO fiber retained more than 95% of original weight after 180 min in air. The elemental analysis during degradation was carried out by TG-mass spectral analysis and TG-Fourier transformed infrared spectroscopy.<sup>101-103</sup> Small molecules such as H<sub>2</sub>O, CO, CO<sub>2</sub>, and NH<sub>3</sub> were released during thermal degradation. Coefficient of thermal expansion (CTE) of PBO fiber is -6 ppm/°C.<sup>28</sup> PBO fiber also showed the highest limiting oxygen index (intrinsically noncombustible) among the polymeric

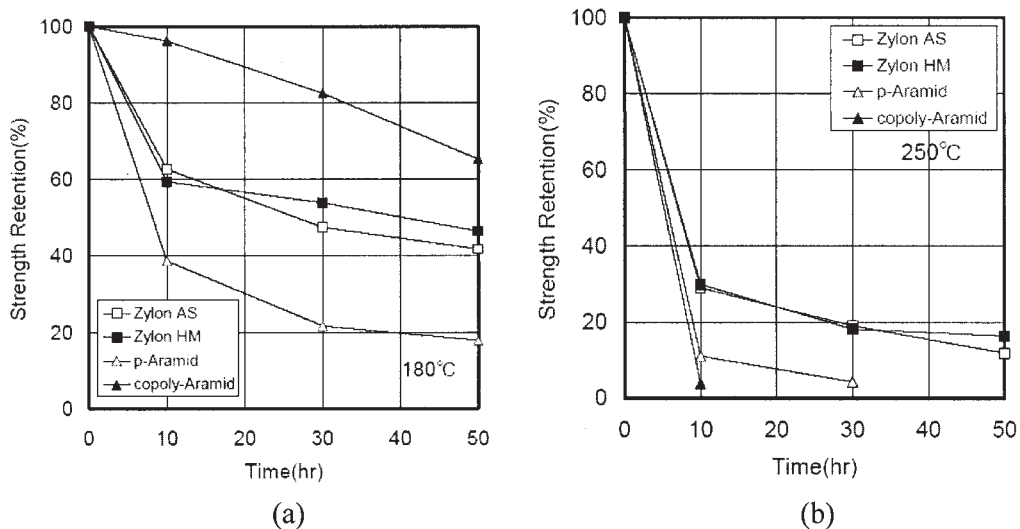


Figure 14 Tensile strength retention in PBO and aramid fibers with saturated steam at (a) 180°C and (b) 250°C (from ref. 34).



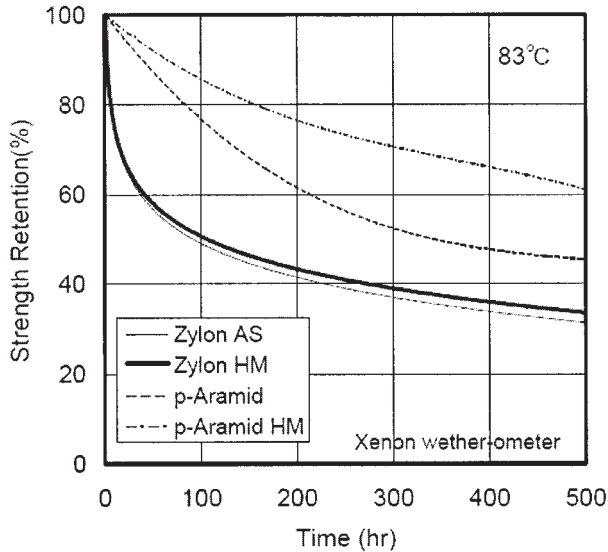


Figure 15 Tensile strength retention in PBO and aramid fibers as a function of UV exposure time (from ref. 34).



Figure 17 Kink band in experimental PBO fiber.

fibers.<sup>28,104,105</sup> In addition, exceptional fire resistance of PBO was also reported.<sup>106</sup>

APPLICATIONS

PBO fibers are used for fire fighters clothing, heat resistant clothing, and as felt in industry, high temperature cut resistant gloves,<sup>107</sup> gloves for high voltage electrical work, body armor, sail cloth, and aircraft engine fragment barrier.<sup>108</sup> PBO also finds applications in composites<sup>109-111</sup> where compressive strength is not a requirement. World's strongest ropes have been made from PBO. PBO is finding increasing applications in space exploration. Prototype of Mars exploration balloon tested in 2002 utilized PBO tendons.<sup>112,113</sup> The concept of ballute (with features of balloon and parachute) currently under investigation is also expected to utilize fibers such as PBO for high

strength, stiffness, and temperature resistance, coupled with low density.<sup>114</sup>

Achievable magnetic fields are determined by the strain limitation of the conductor, and the strength and stiffness of the reinforcement. Because of its high strength and stiffness, PBO fiber is used as reinforcement for producing high magnetic field at the National High Magnetic Field Laboratory in Tallahassee, FL, where efforts are currently underway to develop up to 100 Tesla pulse magnet.<sup>115</sup> PBO fiber has also been tested for high temperature gas chromatography in fused silica capillary, showing improved results over the conventional capillary.<sup>116</sup>

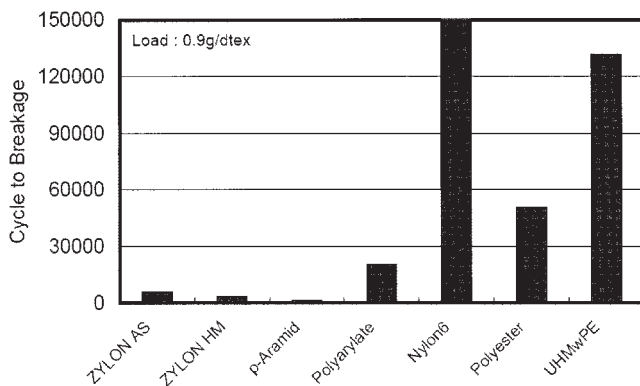


Figure 16 Comparison of abrasion resistance of various fibers (from ref. 34).

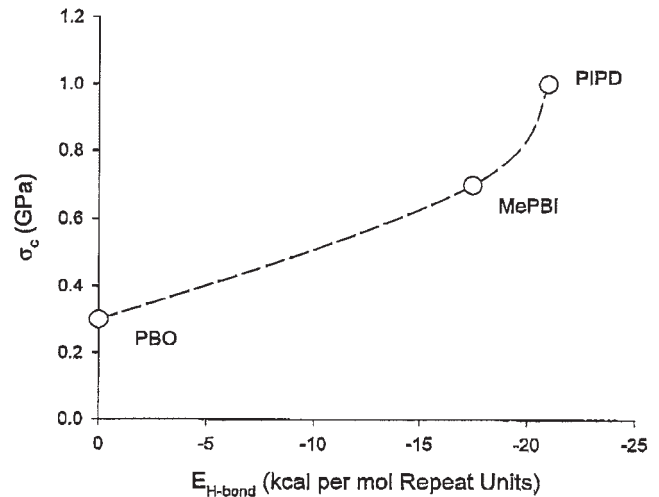
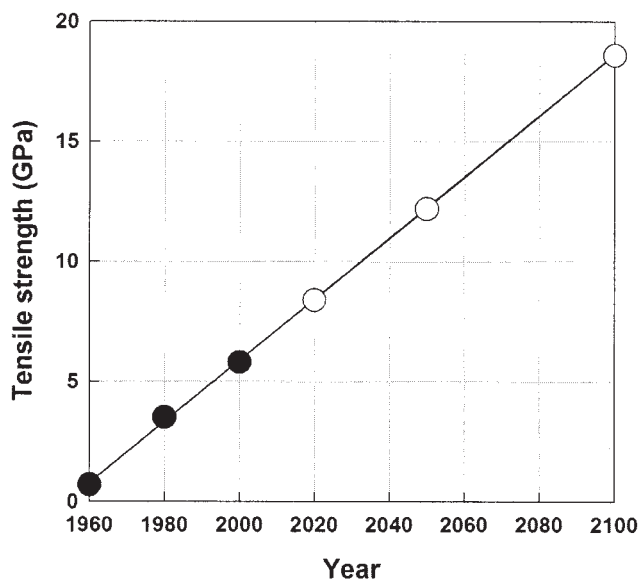


Figure 18 Compressive strength as a function of hydrogen bonding strength (from ref. 97).

### RESEARCH TRENDS

Development in the tensile strength of polymeric fibers as a function of time is shown in Figure 19. So far, only about 15% of the theoretical tensile strength has been achieved, while fibers with tensile modulus up to 50–80% of the theoretical value have been commercialized. Tensile modulus, a low strain property, is not very sensitive to defects, whereas tensile strength is highly dependent on defects including chain ends. Molecular weight and hence the chain length has been shown to be directly related to the tensile strength of high modulus polymeric fibers. Because of difficulties in polymerization and processing, using current technologies, molecular weight can not be increased without limit. As previously discussed, typical PBO molecule length for fiber spinning is about 200 nm, which is slightly longer than that for the commodity fibers such as PET (Table III). On the other hand, UHMW-PE and carbon nanotubes have much longer length. Tensile strength of ultrahigh molecular weight PE is supposed to be limited due to its low melting temperature. PBO, with only 200 nm length, exhibits highest tensile strength among polymeric fibers. Addition of high purity single wall carbon nanotubes without sonication has resulted in 60% increase in PBO tensile strength in the laboratory.<sup>117</sup> Similar increase in Zylon® would result in a fiber with a tensile strength of over 9 GPa. Carbon nanotubes can be produced with much longer length, which are expected to result in appropriately higher tensile strengths. As for the modulus, an experimental Zylon® HM+ fiber with a modulus of 350 GPa has been reported, while the experimentally measured modulus of the PBO crystal is



**Figure 19** Development in the tensile strength of polymeric fibers with time. Solid circles represent actual data. Open circles represent expected future development.

**TABLE III**  
Molecular Length of Various Molecules

	Molecular length
Poly(ethylene terephthalate)	~100 nm
PBO	~200 nm
High molecular weight PE	20–30 $\mu\text{m}$
Carbon nanotube (sonicated)	100–500 nm
Carbon nanotube (as produced)	1–100 $\mu\text{m}$

above 460 GPa. In the coming decades, we can hope to see a PBO or PBO/carbon nanotube fiber with tensile strength and modulus values approaching and ultimately exceeding 10 and 400 GPa, respectively.

Low compressive strength limits PBO applications. Efforts to improve compressive strength include incorporation of inorganic components to provide lateral support to fibrils,<sup>118–120</sup> inducing morphological changes for interfibrillar entanglement,<sup>121–123</sup> covalent crosslinking by radiation<sup>124</sup> or by heat, as well as the development of intermolecular hydrogen bondable structures. Of the various approaches used, crosslinking<sup>91,97</sup> and hydrogen bonding<sup>125</sup> appear to be most promising. However, the drawback of the crosslinking approach is that it tends to make the fiber more brittle and leads to a decrease in tensile strength. Hydrogen bonding approach appears to be the most successful to date. Because of hydrogen bonding, Kevlar® has higher compressive strength than PBO, and an experimental hydrogen bondable rigid-rod polymer methyl pendant PBI<sup>126</sup> has higher compressive strength than Kevlar®. Recently developed rigid polymer, poly(2,6-diimidazo-[4,5-b:4'5'-e]pyridinylene-1,4(2,5-dihydroxy)phenylene) (PIPD, M5®), with two-dimensional hydrogen bonding ability has the highest compressive strength of any polymer to date.<sup>37,40</sup> Use of carbon nanotube in polymers has also resulted in improved compressive strength.<sup>117</sup>

### CONCLUSIONS

The PBO fiber (Zylon®) commercialized in 1998 has tensile strength and modulus values of 5.8 and 270 GPa, respectively, with a density of 1.56 g/cm<sup>3</sup>. The fiber exhibits high thermal and chemical resistance as well as ballistic protection. PBO fiber has relatively low axial compressive strength (200–300 MPa), low shear modulus (1 GPa), negative CTE (–6 ppm/°C), poor resistance to ultraviolet and visible radiation, as well as to the hot-humid environment. In the coming decades, we can look forward to further improvements in tensile strength, modulus, compressive strength, and radiation resistance. Some of the property improvements in polymeric fibers will come via the use of carbon nanotubes.<sup>117,127–137</sup> Considering that the rate at which the technology is changing, is

increasing, would suggest that materials development in the 21st century will exceed the developments in the 20th century, and the field of high performance polymeric fibers will not be a laggard.

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