Property opportunities with polyolefins: a review. Preparations and applications of high stiffness and strength by uniaxial draw*

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Major progress has been made in preparation of high-modulus and high-strength fibres and films by uniaxial drawing of semicrystalline polyolefins. Solid-state coextrusion followed by tensile drawing on ultra-high molecular weight polyethylene (UHMWPE) and polypropylene (UHMWPP), and poly(4-methyl-1-pentene) starting from single-crystal mats, prepared from dilute solutions, produces superdrawn films with tensile moduli approaching the theoretical values reported for the crystal for each of these three polyolefins. For PE, a modulus of 220 GPa and strength of 6 GPa have been achieved. For PP, the corresponding maximum values are 37 and 2.2 GPa. This two-stage drawing technique has also been successfully applied for ultradrawing PE reactor powders. Films of compacted powder, prepared below the melting point of the powder, have been solid-state coextruded at 110°C to a draw ratio of 6, followed by tensile drawing at 120–135°C. The drawability and the uniformity of the resultant fibres and films are sensitively affected by the drawing temperatures and rates, and also by the choice of reactor powder. The maximum draw ratio achieved directly for reactor powder is ~85, with a corresponding tensile modulus of $\leqslant$ 130 GPa. For special conditions, high uniaxial draw and high modulus for selected reactor powders have been achieved simply by direct compaction plus calendering. In none of these processes is the polyolefin melting point exceeded. Applications of the oriented polyolefins are cited in terms of use as tapes, yarn and fabrics.

(Keywords: polyolefins; physical properties; preparation)

INTRODUCTION

Researchers throughout the world strive to make the stiffest and strongest polymers. The potential is to compete with the mechanical properties of all other compositions, see *Table 1*. Three diverse routes have predominated for maximizing tensile properties[1,2]:

1. as carbon fibres made from pyrolysis of polyacrylonitrile (PAN) or by reaction of a liquid crystalline pitch derived from crude oil;
2. by polymers chemically constructed with rigid and linear backbones, exhibiting liquid crystal behaviour;
3. from conventional, flexible chain polymers, drawn to produce morphology transformations into fibres and films.

The first two topics are discussed briefly. This sets the stage for the main subject of interest: the preparations and applications of high stiffness and strength by uniaxial draw of polyolefins. Fibre and film characterization and some of their applications are also considered.

CARBON FIBRES

A range of properties for carbon fibre derived from PAN or pitch is achieved by altering the orientation of the graphite basal planes, their crystallinity and microstructure. The main morphology in carbon fibres is like a graphitic ribbon, rippled parallel to the fibre axis. There is major prowess in these technologies by the multiple competitors, mainly from Japan, and particularly by the Toray Company. PAN-based fibres in the USA either come from Japan or are made in the USA under Japanese patents. In the USA Amoco is a producer and Celion Carbon Fibers has commercialized a carbon fibre. The latter process can control fibre cross-section: rectangular cross-sections and three, four and six lobed structures are prepared for enhanced stiffness and surface area.

The use of carbon fibres has grown from about 1.4×10^6 kg in 1980 to $\sim 4.5 \times 10^6$ kg in 1988. Growth has been steady, but appears limited by several factors,

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including the cost of fibre, their vulnerability in compression, and the limited toughness of carbon fibre composites.

The quality and performance of carbon fibres has been steadily improved, resulting in fibres with tensile strengths up to 7 GPa and moduli $\leqslant 1000$ GPa, but with trade-offs in stiffness and strength in individual carbon fibre products.

POLYMER LIQUID CRYSTALS

The liquid crystalline state is a facile route for structure control in polymer systems[1-4]. The synthesis and processing of both lyotropic (in solvent) and thermotropic (heat generated) polymer liquid crystals have been widely pursued. The liquid crystal (nematic) phase in such polymer systems provides favourable characteristics for processing, in terms of low viscosity and normal force, and as an oriented precursor to a highly ordered crystalline state for achievement of enhanced tensile properties.

Chemical construction of the appropriate rigid, rod-like macromolecules has been attained by syntheses, leading to para-substituted aromatic rings in the polymer backbone. From a lyotropic solution, DuPont produces Kevlar poly(*p*-phenylene terephthalamide) fibres of high stiffness and strength; several grades are available[4].

Research sponsored by the US Air Force Wright-Patterson Materials Laboratory and the US Air Force Office of Scientific Research (Ordered Polymers Research Program) has investigated the performance potential of several rigid macromolecules. Three of the polymers synthesized are a polybenzimidazole (PDIAB), poly(*p*-phenylene benzobisoxazole) (PBO) and poly(*p*-phenylene benzobisthiazole) (PBZT). Of these structures the PBZT polymer offers the greatest thermal and oxidative stability. Since 1978 emphasis had centred on its development. The viscosity of such solutions of rod-like macromolecules passes through a maximum with increasing polymer concentration, indicating formation of a lyotropic liquid crystal phase. These PBZT solutions have been spun with formation of high-modulus/high-strength fibres. Heat-treated fibres with moduli of 300 GPa and strength of 3 GPa have been attained.

A range of thermotropic liquid crystal polymers have also been made. Commercial among these is Vectran fibre, marketed by Hoechst Celanese. It is based on copolymers of hydroxy benzoic acid and 2,6-naphthonic acid, as patented by Calundann[5]. Tensile properties of Vectran are comparable to Kevlar 49[4].

Table 1 Mechanical properties of some strong, stiff fibres

Material	Tensile modulus (GPa)	Breaking strength (GPa)
Steels	~210	~1
Glass fibres	<80	6
Whisker crystals	200–500	10–20
Kevlar fibres	60–120	~3
Carbon fibres	400–800	~4
Drawn melt-crystallized polyethylene (PE) fibres	<70	2
Drawn gel fibres of ultra-high molecular weight (UHMW)	~120	~4
Drawn single-crystal mats of UHMWPE	~220	~6

THE POLYOLEFINS

The flexible and random chains of the polyolefins can be drawn into highly oriented chain conformations, resulting in substantially increased tensile properties. This drawing may be done from several different starting states: from a dilute flowing solution, from a gel state[6], by extruding a supercooled melt, by solid-state extruding, or on tensile drawing below the polymer melting point[7,8]. After years of research in several countries on these states and their processing, fibres of polyethylene (PE) are now available. These fibres float on water; however, they melt, as expected for PE, at its maximum melting point of about 140°C.

From the inspiration of Pennings, fibres are produced by DSM in The Netherlands (Dynema) and by Allied Signal (Spectra) in the USA. DSM started plant production of several hundred tonnes per year in 1991[9] and at about the same time Allied Signal started producing about a million tonnes per year[10]. These processes all involve a solvent or second phase with PE to aid deformation by extrusion and tensile deformation from the gel state[11]. These gel-spun fibres, from ultra-high molecular weight (UHMW) PE, are stronger and lighter than Kevlar. UHMW is undefined, but has come to mean molecular weights $>10^6$ (ref. 6).

The two main paths to high-modulus PE fibres are shown in *Table 2*, as via the solution–gel states vs. the solid states via crystalline morphology draw. By both processes, the UHMWs perform best, owing to increased draw efficiency and minimum chain ends in the drawn product. Research on these methods continues to the present[12].

Research on PE fibre preparation has been conducted at the University of Massachusetts, being reported since 1968[13,14], and subsequently also at the Science University of Tokyo, in the early single-crystal draw studies by Maeda *et al.*[15] and Statton[16]. Our research has centred on the solid-state (co)extrusion and rolling as the initial deformation step for uniaxial draw[8]. The superdrawing of UHMWPE and of UHMW polypropylene (PP) was achieved initially by solid-state coextrusion and subsequent tensile drawing of solution-grown crystals precipitated

Table 2 Two routes to high modulus polyethylene fibres

Route 1	*Route 2*
Solution stirring, led to gel spinning with ideas of Pennings followed by many other workers	Solid state compaction draw of reactor powder with many improvements after ideas of Porter

Common characteristics

Higher molecular weights give the highest draw ratios
Draw is aided by the removal of entanglements
Properties approach those of continuous crystals

Table 3 Steps in the solid-state drawing process

POLYETHYLENE REACTOR POWDER
Powder compacted to sheet <120°C
Sheet pressure-drawn at ~110°C

BARS AND FIBRE PRECURSOR
Tensile-drawn to fibre 110–130°C

HIGH STRENGTH POLYETHYLENE FIBRE

from dilute solutions (0.05–0.2 wt%)[17,18]. These techniques produced ultraoriented films with the total draw ratio (DR_t) up to 350 for UHMWPE and 88 for UHMWPP. The DR_t is the product of the first stage solid-state extrusion draw and the second stage free-pulling *DR* at controlled temperatures and rates. The steps in this process are shown generally in *Table 3*, and as approached by others[19], specifically for PE reactor powder, in *Table 4*. For a production process, reactor powder may be used directly, rather than solution-grown crystals. An interesting feature is that polymerization conditions dictate the subsequent level of possible uniaxial extension[20]. Smith, while at DuPont, patented an aspect of this process[21], as has Sano with associates at Nippon Oil[22], with activities also in Russia[23].

The systematic improvements in tensile modulus over time by different workers and methods for PP are shown in *Table 5*[24–27]. Superdrawn films of PE exhibit tensile moduli and strengths $\leqslant 220$ GPa and $\leqslant 6.0$ GPa, respectively[8]. This may be the highest specific strength of any fibre. The moduli approach a somewhat uncertain theoretical maximum as reported for the crystal for each of the two polyolefins[28,29]. Researchers have long pursued this goal of creating ideal polyolefin structures with well-aligned, extended and closely packed polyolefin chains: thus ideal structure constitutes a perfect continuous crystal[30].

All the commercial polyolefins have been uniaxially drawn by our groups and others[17–43]; the linear PEs[17–25], PPs[17–27], poly-1-butenes[31] and poly(4-methyl-1-pentene)s (PMPs)[32–35]. Of these, most attention has been directed to the polyolefin with the highest potential tensile modulus and strength, PE. *Figure 1* shows a log scale in ascending order of PE properties, and is compared with the tensile moduli of other materials. Absolute PE tensile levels comparable to aluminium are now readily attained in a single step of $DR \approx 30$. The levels of moduli achieved for PE are shown in *Figure 1* and as attainable on full chain extension. This required extension, even for affine deformation, is far higher than the so-called natural *DR*s and increase as the half power of molecular weight[44].

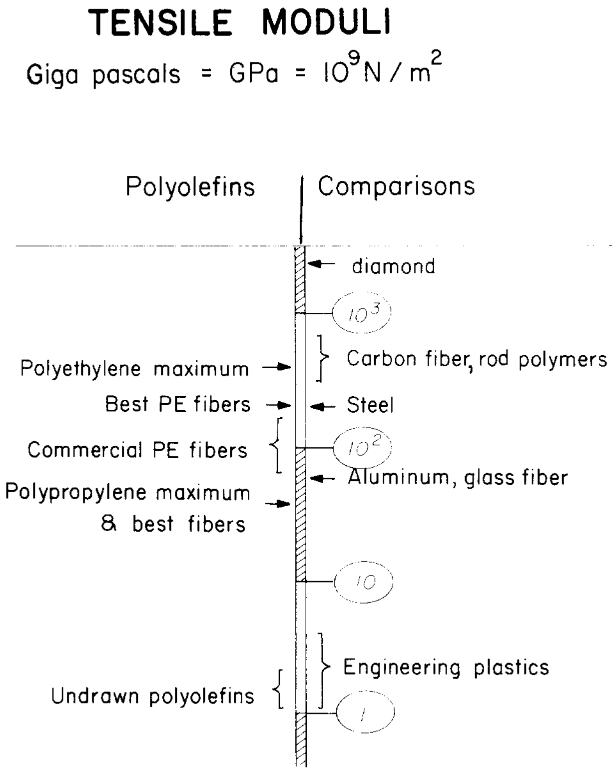

Figure 1 Comparative moduli values

Table 4 Fibres produced by cold forming the solid-state processing of polyolefins (direct forming from polymer powder, below the melting point, without solvent)

Steps:

1. Pressure compaction of powder
2. Drawn under pressure by
   (a) solid-state (co)extrusion or by
   (b) calendering, rolling
3. Free space extension to the draw limit

The result is a fibre of high modulus and strength

Table 5 Maximum tensile moduli reported for polypropylene

Investigator	Year	Draw method	Maximum modulus (GPa)
Sheehan and Cole	1964	Hot drawing	11
Noether and Singleton	1964	Multi-step drawing	14
Desper	1973	Hot-drawing	16
Williams	1973	Hydrostatic extrusion	17
Capaccio *et al.*	1976	Super drawing	19
Tayler and Clark	1978	Two-step drawing	22
Takayanagi *et al.*	1979	Zone-drawing	15
Kunugi *et al.*	1981	Zone-annealing	21
Kanamoto *et al.*	1984	Solid state and draw	37

The tensile properties of efficiently drawn polyolefins can increase regularly towards a limit with extent of draw. The total extension can exceed 300 times, i.e. over 10 times more than a stretched rubber band. Moreover, with proper conditions, all the bonds in the PE can survive the draw. We have been researching for over two decades to find the narrow windows of ideal initial compositions, morphologies and subsequent draw processes. Students at Tokyo Science University and at the University of Massachusetts have made crucial contributions to the research[8]. The goal is to make a perfect continuous crystal with random chain ends in the lattice[30].

Figure 2 shows the moduli attained on draw for PE. Greatest ductility has been attained by starting with compressed mats of solution-grown crystals. The advantage in this initial morphology appears to be a single-crystal-like lamellar structure with a minimum of trapped entanglements. The total draw is the product of the draw in each of the two stages. Using an initial extrusion draw ratio (*EDR*) of 6–25 by solid state coextrusion[45], see *Figure 2*, aids draw by contributing to structure coherence by the application of pressure. *Figure 2* shows that samples simply drawn at the same conditions, but without the solid-state extrusion step, do not result in such high draw and moduli. At higher values of solid-state extrusion, compressive buckling occurs[8,46], limiting the draw achievable by solid-state extrusion alone. Fibres are vulnerable in compression at low strains of ~1%. The effect causes buckling. This sensitivity is predictable from independent measurements of the shear modulus of fibres[46]. In some applications, buckling is an advantage, as for applications that involve knotting.

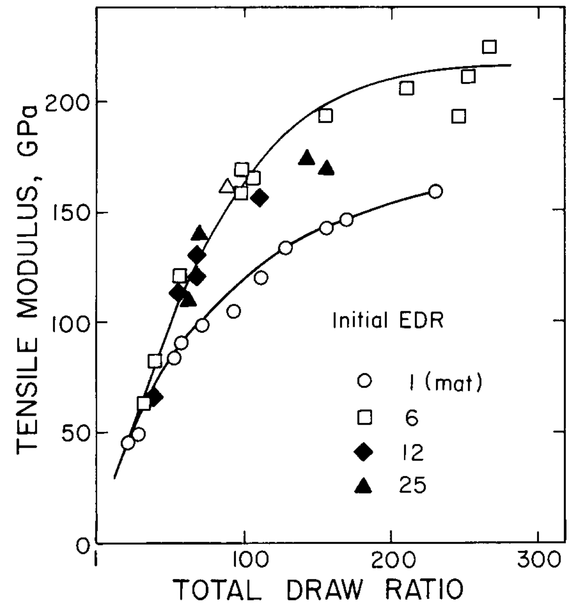

Figure 2 Tensile modulus *versus* total draw ratio for polyethylene

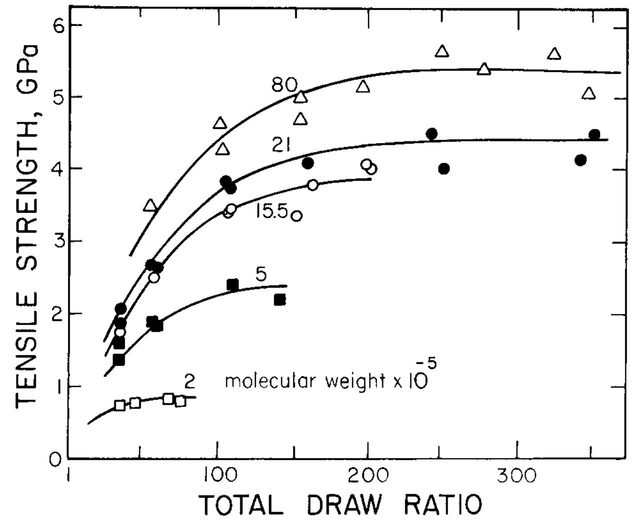

Figure 3 Polyethylene tensile strength at different molecular weights

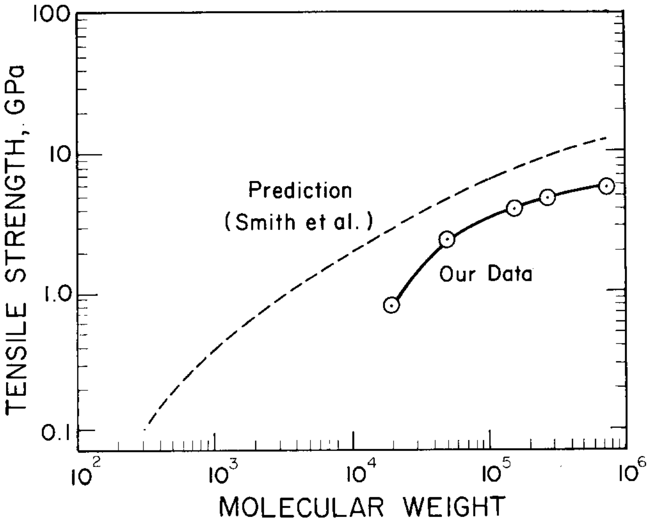

Figure 4 Maximum strength, measurement *versus* prediction

Figures 3 and *4* show the tensile strength properties for the PEs drawn and tested from data in *Figure 2*. *Figure 3* shows the importance of higher molecular weights for attaining high draw and strength[36]. *Figure 4* shows maximum strengths compared to the theoretical prediction, although even much higher strengths, up to 50 GPa, have been suggested[37,38]. Certainly, PE fibre strength can depend on the strain rate and gauge length of testing[38].

The corresponding and comparable two-stage draw process on PP has been performed at the Science University of Tokyo[17,24,25,31,36]. Gel drawing of high molecular weight PP has also been accomplished[39,40]. The progress in developing improved tensile moduli over time by different workers is shown in *Table 5*[26,27]. The samples used to obtain the highest values were isotactic PPs having viscosity-average molecular weights (M_v) of (3, 5, 25, 36) × 10^5. The solution-grown crystals of these PPs were isothermally precipitated from a dilute solution (0.1 wt%) in xylene kept at 55°C over 20 h. The solution-grown crystal mats were again drawn by the two-stage drawing, a combination of solid-state coextrusion followed by conventional tensile drawing. For solid-state coextrusion, a solution-grown crystal mat was placed between split billet halves of high density PE, and coextruded at constant temperatures and rates through conical dies of 20° occluded angle, which provided a nominal *EDR* of 3–25. These extrudates were tensile drawn in free space in an Instron at constant temperatures from 90 to 185°C and at the various constant extension rates. The DR_t for the two-step process is again defined by $DR_t = EDR \times DR$.

The effect of PP M_v on the drawability was not so significant as observed for PE. This may be due to differences in molecular weight distribution, with the higher molecular weight component probably controlling drawability and consequent modulus. Moreover, during these superdrawing processes, no chain scission was observed by the viscosity measurements made before and after drawing. The higher M_v PP samples resulted in higher tensile moduli and strengths. The highest modulus achieved closely approaches the theoretical lattice modulus (35–42 GPa) for the perfect crystal of isotactic PP[28,29]. The highest strength values of ~2.2 GPa correspond to 16–27% of the theoretical strength[33] estimated on the basis of a chain-breaking mechanism (9–16 GPa) and almost 50% higher than expected for breakage through chain slippage (1.6 GPa). The crystallinity of superdrawn PP samples estimated from the heat of fusion and the density is no more than 85%. The X-ray analyses also showed that PP samples had more structural disorder and crystal distortion, compared to the superdrawn PE.

The two additional polyolefins that have been uniaxially drawn via the same methods and range of morphologies and molecular weights are poly-1-butene[31] and PMP[17,32–35]. In general, this research has been directed towards optimizing the draw parameters, including the maximum (linear) molecular weight, minimum entanglements in the initial morphology, and achieving maximum molecular draw efficiency in each draw step[7].

For each of the polyolefins, two-stage drawing of solution-grown crystal mats, under controlled rates and temperatures, produced the high draw among the techniques examined. Both the drawability and tensile properties of drawn samples increased remarkably with increasing sample molecular weight. Superdrawn films of

UHMWs exhibited tensile moduli and strength of, respectively, $\leqslant 220$ GPa and $\leqslant 6.5$ GPa for PE; $\leqslant 37$ GPa and $\leqslant 2.2$ GPa for PP; and $\leqslant 8$ GPa and $\leqslant 0.81$ GPa for PMP. These moduli approach yet uncertain theoretical maximum moduli reported for the chain direction in the crystals for each of these polyolefins[28,29]. Furthermore, the tensile moduli (7.5–9.1 GPa) of superdrawn UHMW PMP, determined at higher strain, were remarkably higher than the crystal modulus (2.9–6.6 GPa) reported for the common tetragonal form (7_1 helix), as caused by conformational changes during extension even at room temperature[41].

FIBRE CHARACTERIZATION

Evaluations of polymer anisotropy have generally been approached through an assessment of chain segment orientation, using one or more of several complementary measures, such as sonic modulus, Raman, broadline n.m.r. and polarized fluorescence. In addition, there is birefringence for the orientation of both crystal plus amorphous phases, i.r. dichroism for possibly analysing orientation in each phase separately, and wide-angle X-ray scattering for crystal orientation. However, these measures of orientation give only averages of different moments. Unseen in these traditional orientation evaluations, and of major importance for polymer properties, are measures of polymer chain extension, as also induced by draw[42]. Moreover, the idealized fully aligned crystal structure shown in *Figure 5* differ by 100-fold in tensile properties, i.e. by the ratio of bond strengths for covalent and Van der Waal's interactions. The regularly folded structure gives the lowest (*Figure 5A*) and the non-folded gives the highest (*Figure 5C*) tensile properties. There are major analytical challenges to show the distinction between states in *Figure 5*. Ideally, the characterization of crystal continuity in polymers must include an estimation of the crystal lengths and their length distribution. Other evidence for crystal continuity in the microstructure has been inferred from (a) the observed superheating of melting by d.s.c.; (b) the lack of maxima in small-angle X-ray scattering; (c) through X-ray diffraction studies; (d) by electron microscopy; (e) by nitric acid etching plus gel permeation chromatography; and (f) by Raman spectroscopy[42,43].

Effective analyses for polymer chain extension are listed in *Table 6*. A dramatic feature is that the linear expansion coefficient goes through zero at the conditions where modulus increases steeply, both due to the development of a component of continuous crystals. The listed tensile mechanical test, also in *Table 6*, represents an analysis of chain extension as well as a measure of property achievement. The goal is to reduce imperfections and to distribute then (such as chain ends) as widely as possible. Except for increasing molecular weight, the further reduction of imperfections remains an elusive goal.

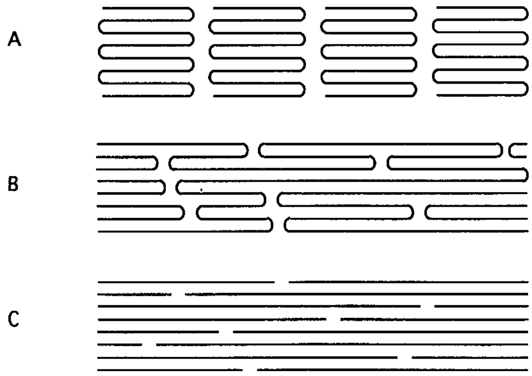

Figure 5 Idealized polyethylene structures for tensile modulus limits, ~ 1–240 GPa

Table 6 Chain extension analyses

Test method	Molecular analysis
Crystals	
Raman bands for longitudinal acoustical mode	Discrete crystal lengths are required
Oxidative etching of amorphous, followed by g.p.c. on unreacted	Chain continuity through crystals is measured
Small angle X-ray scattering	For changes in lamellae, limited at high values
Onset of crystal continuity	
Thermal conductivity	May be the most sensitive test for chain continuity
Linear expansion coefficient	For comparison with the perfect polymer crystal
Tensile modulus tests	Provides a scale for continuous crystal content
General	
Shrinkage on rapid heating above transitions	Shrink must be all elastic, not viscous dissipation
Neutron scattering with deuterated probes	Same and more information than elastic recovery
I.r. analysis of rotational states	Chain extension means more in desired *trans* states

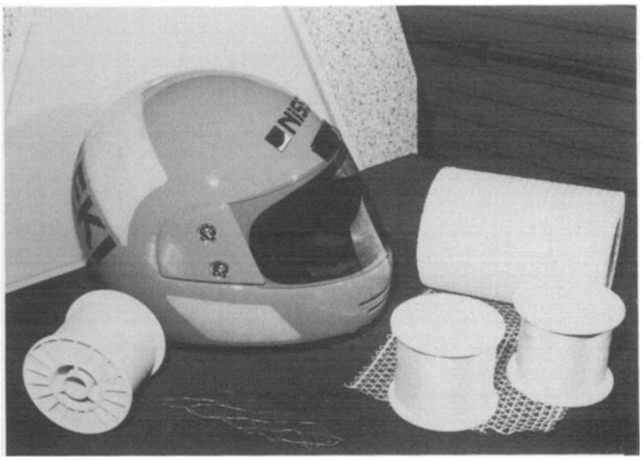

Figure 6 High-strength high-modulus polyethylene tape, yarn and fabric: helmet is yarn with epoxy

POLYOLEFIN FIBRE APPLICATIONS

All of the polyolefins can be prepared in fibre form. The higher polyolefins have progressively less potential for fibre tensile modulus and strength[28,29,41]. PP fibres have long been items of commerce. Even in 1989, fibre production had reached 0.7×10^6 tonnes per year. PP is over 20% of the fibre market. Its development has been detailed[11]. An advantageous feature is that uniaxially oriented PP is readily fibrillated into fibre as widely used, e.g. for indoor–outdoor carpet. Other available forms are PP filaments and stable fibres.

PE fibres are a more recent development. Initially available from DSM in The Netherlands and subsequently from Allied Signal in the USA, both are made by the gel drawing process. The brief history of PE fibre development has been delineated[8]. Likewise an extraordinary number of spectacular applications for PE fibres have been described[11]. The impetus has been by DSM and Allied Signal, and in particular by Prevorsek. Bulletproof vests[12,43], sails for America's Cup competition and cut-proof gloves are examples.

Pilot plant production of fibres by Nippon Oil has also been evaluated. These fibres have been made by the process described here of direct PE reactor powder draw[47,48]. No solvent nor PE melting is involved. Their potential applications, shown in *Figure 6*, are both diverse and unique. The properties are similar for the PE fibres made by the wet (gel) process and the dry (reactor powder) processes. The PE fibres are also readily surface-reacted for bonding, as for reinforcement in composites, such as for the helmet shown along with fibre forms in *Figure 6*.

REFERENCES

1 Yang, H. H. 'Aromatic High Strength Fibers', Wiley Interscience, New York, 1989

2 Tam, T. Y., Boone, M. B. and Weedon, G. C. *Polym. Eng. Sci.* 1988, **28**, 871

3 Adams, W. W., Eby, R. K. and McLemore, D. E. (Eds) 'Rigid Rod Polymers', Symposium Proceedings of the Materials Research Society, Vol. 34, 1989

4 Yang, H. H. 'Kevlar Aramid Fibers', Wiley Interscience, New York, 1993

5 Calundann, G. W. Hoechst Celanese patents and personal communications

6 Smith, P., Lemstra, P. J. and Booj, H. C. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 877

7 *Science* 1991, (Feb. 22), 845

8 Southern, J. H., Capiati, N. J., Kanamoto, T., Porter, R. S. and Zachariades, A. E. in 'Encyclopedia of Polymer Science and Engineering' (Eds H. Mark, N. Bikales, C. Overberger and G. Menges), Wiley, New York, 1989, Vol. 15, p. 346

9 *Chem. Eng. News* 1989, (Jan. 16), 14

10 *Business Week* 1989, (Aug. 30), 18

11 Seymour, R. B. and Porter, R. S. 'Manmade Fibers', Elsevier, London, 1992

12 *Sci. American* 1992, (March), 106

13 Mark, H. F. *Polym. Adv. Technol.* 1990, **1**, 5

14 *Chem. Eng. News* 1969, (Sept. 22), 43

15 Maeda, M., Miyasaka, K. and Mishikawa, K. *J. Polym. Sci. A-2* 1972, **8**, 355

16 Statton, W. O. *J. Appl. Polym. Sci.* 1967, **38**, 4149

17 Kanamoto, T. and Porter, R. S. in 'Proceedings of Rolduc Polymer Conference—3' (Eds L. A. Kleintjens and P. J. Lemstra), Elsevier Applied Science, 1988

18 Kanamoto, T., Sherman, E. S. and Porter, R. S. *Polym. J.* 1979, **11**, 5497

19 Furuhata, K., Yokohama, T. and Miyasaka, K. *J. Polym. Sci., Polym. Phys. Edn* 1984, **22**, 133

20 Wang, L. H., Ottani, S. and Porter, R. S. *Polymer* 1991, **32**, 1776

21 Smith, P. *et al.* US Patent 4,436,689, 1984

22 Sano, A. *et al.* US Patents 4,879,076, 1989; 4,996,011, 1991; 5,002,714, 1991; 5,106,558, 1991

23 Selikhova, V. I. *et al. Polym. Sci. USSR* 1992, **34**, 151

24 Kanamoto, T., Tsuruta, A., Tanaka, K. and Takeda, M. *Polym. J.* 1984, **16**, 75

25 Taraiya, A. K., Richardson, A. and Ward, I. M. *J. Appl. Polym. Sci.* 1987, **33**, 2559

26 Kunugi, T., Ito, T., Hashimoto, M. and Ooiska, M. *J. Appl. Polym. Sci.* 1983, **28**, 179

27 Kunugi, T. *J. Polym. Sci., Polym. Lett.* 1982, **20**, 329

28 Sakurada, I., Ito, I. and Nakamae, K. *J. Polym. Sci.* 1966, **615**, 75

29 Nakamae, K., Nishino, T. and Ohkubo, H. *J. Macromol. Sci., Phys.* 1991, **B30**, 1

30 Porter, R. S. *Am. Chem. Soc., Polym. Prepr. Suppl.* 1971, (Sept.), 2

31 Ball, R. and Porter, R. S. *J. Polym. Sci., Polym. Lett. Edn.* 1977, **15**, 519

32 He, T. and Porter, R. S. *Polymer* 1987, **28**, 946

33 He, T. and Porter, R. S. *Polymer* 1987, **28**, 1321

34 Kanamoto, T. and Ohtsu, O. *Polym. J.* 1987, **20**, 179

35 Richardson, A. and Ward, I. M. *Polym. Commun.* 1987, **28**, 274

36 Tsunoda, S., Kanamoto, T., Tanaka, K. and Takeda, M. *Rept. Prog. Polym. Phys. (Japan)* 1986, **29**, 269

37 Coleman, B. D. *et al. Textile Res. J.* 1957, **27**, 393

38 Schwartz, P., Netravali, A. and Sembach, S. *Textile Res. J.* 1986, **66**, 502

39 Cannon, C. G. *Polymer* 1982, **23**, 1123

40 Peguy, A. and St. John Manley, R. *Polym. Commun.* 1984, **25**, 39

41 Nakamae, K., Nishino, T. and Takagi, S. *J. Macromol. Sci., Phys.* 1991, **B30**, 47

42 Chuah, H. H., Kanamoto, T. and Porter, R. S. in 'High Modulus Polymers: Approaches To Design And Development' (Eds A. E. Zachariades and R. S. Porter), Marcel Dekker, New York, pp. 259–1988

43 Desper, C. R., Cohen, S. H. and King, A. O. *J. Appl. Polym. Sci.* 1993, **47**, 1129

44 Kanamoto, T. and Porter, R. S. *J. Polym. Sci., Polym. Lett. Edn.* 1983, **21**, 1005

45 Griswold, P. D., Zachariades, A. E. and Porter, R. S. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 859

46 DeTeresa, S. J., Porter, R. S. and Farris, R. J. *J. Mater. Sci.* 1988, **23**, 1886

47 Sano, A., Iwanami, Y., Matsuura, K., Yokoyama, S. and Kanamoto, T. International Symposium on Macromolecules, 8–13 July 1990, Montreal, Book of Abstracts, Session 2.2.6

48 Nippon Oil, High Tech. New Materials Exhibition, 1992, Japan