

Manmade Fibers One Hundred Years: Polymers and Polymer Design

DOETZE J. SIKKEMA

Akzo Nobel Central Research, P.O. Box 9300, 6800 SB Arnhem, The Netherlands

Received 8 November 2000; accepted 18 November 2000

ABSTRACT: A brief overview of a century of manmade fiber development (particularly technical, i.e., strong and high E-modulus, fibers), emphasizing the last quarter century where the work increasingly grew in the direction of rational design of new structures, as the understanding of what makes a fiber do its job well grew. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 484–488, 2002

INTRODUCTION

Progress takes hard work. Our beacons are (1) the examples furnished by Nature for solutions to problems. Sadly, it is often only *after* the fact of finding some solution that it is discovered that Nature had evolved a similar approach to the problem. (2) Trying to build on knowledge gained and combining knowledge from various areas, hoping for so-called synergies. But finally, Lady Luck has to smile on us, when we (3) find something else than what we were looking for.

Nature is the Mother of Invention: a century ago people knew strong fibrous saccharides—cotton—and knew that chemically similar material constituted wood pulp. Much experimentation finally produced viscose; other cellulose derivatives would follow. In a similar vein, much later, work ultimately based on the realization that strong proteins formed silk and wool, and the simplification that proteins might be simulated by simple polyamides led to the invention of nylon-66, followed by nylon-6 and inspiring much work on polyurethanes. Not only did this produce new fibers, it also vindicated the theories about macromolecules that had been struggling for acceptance. A new era began with the work of Carothers: yes,

high strength materials can in fact be manmade from coal tar or petrochemicals; they can be made from high molecular weight polymers, and fibers can be made from such newfangled materials by spinning the melt or the solution.

Polyethylene terephthalate (PET), polyacrylonitrile, polyvinyl chloride, polypropylene, polypropylene ether, polyvinyl alcohol . . . fiber experimenters would try to spin essentially any polymer that came along. This continues to this day: nylon-46; various polyimides; polyethylene naphthalate (PEN). New hope is placed on syndiotactic polystyrene and on the new narrow MWD polypropylene. The outcome of work in those areas is still difficult to predict. Such an opportunistic approach of creating new fibers as new polymers come along, as spin-offs of what goes on in the plastics industry, will be restricted to thermoplastic products that will show indifferent or poor performance at elevated temperatures.

Soon, it was discovered that not all polymers are created equal. Many, or in fact most, polymers cannot be spun into anything like decent fibers. Different polymers give different fibers.

START OF POLYMER DESIGN—THE 1960S; FROM THERE TO THE PRESENT

Some design work had gone into N66 (mostly: what polymer *can* you make by polyamidation)

and into PET (mostly: what polyester is *not* a waxy goo). At an early stage, it was already realized that crystallinity helps and that the availability of extended zigzag conformations helps crystallinity.

We now get to the point in which you see, for instance, differential dyeing nylon, basic dyeable PET, and better dyeable polyacrylonitrile; bicomponent spinning; the quest for higher T_g values to combat wrinkling by washing. PEN and early aramids belong in this category.

Manmade fibers also proved essential in technical applications such as parachute fabrics and tire reinforcement. Polymer design here strives for better tenacity and modulus. The first triumph was presented by ARAMIDS. Rigid polymers were understood to be better orientable. Having the polymer in a liquid crystalline (LC) phase seemed to help, which led to an absolute craze for designing LC polymers, preferably thermoplastic to allow meltspinning. It was overlooked that their very thermoplastic nature by itself would limit their usefulness at higher temperatures, and this whole effort has run its course without producing a commercially viable fiber. It did lead to some very high-end special plastics. These things have found their way into encyclopedias, textbooks, and several reviews.

The superdrawn polyethylene (PE) discovery, based originally on a chance discovery but which was brought to fruition very much by rational design and scientific reasoning, inspired much work to expand that type of fiber-making to other polymer systems. It led to the realization that PE is a very special case indeed, specifically designed for superdrawing, with the important additional fact that the PE chain is very slender in its extended conformation to arrive at a high chain modulus. The fine work on fiber spinning at Akzo Nobel and at DSM with the alternating ethylene-carbon monoxide polymer invented at the Royal Dutch/Shell lab in Amsterdam was motivated in large part by the reasoning that this was a polymer with a slender extended chain that was more polar than PE, but which could be drawn to unusually high drawing ratios by virtue of its borderline polarity. Interesting fiber properties were achieved by processes analogous to the gel spinning and superdrawing of PE; this polymer could make a fine tire yarn, provided meltspinning can be controlled to give similarly high properties. A report by Bert-Jan Lommerts detailing work aimed at such melt spinning is presented in conjunction with this review.

Rigid rod polymers (PBZ) also presents a triumph of polymer design. From a historical viewpoint, some serendipity was involved to get from the very stiff polymers investigated mainly for their expected thermal properties, to the high modulus fibers that now are coming to market in the form of Zylon. The breakthrough depended on getting those polymers in sufficiently high concentration and acceptably high molecular weight. The rigid rod polymers will be discussed below.

SOME OTHER RECENT DEVELOPMENTS

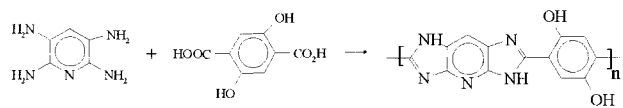
In recent decades, the old workhorse of manmade fibers, viscose rayon, has come under a lot of fire from environmental and economical viewpoints: for many years it has been uneconomical to build new rayon plants with acceptable environmental impact. Worldwide, a large effort has been directed over the years at finding a better dissolving system for cellulose, requiring both rational speculation and luck. Two independent major inventions in this field have occurred in laboratories belonging to what now is known as Akzo Nobel: the *N*-methyl morpholine *N*-oxide (NMMO) solvent system was developed into a direct cellulose spinning proposition at then-American Enka. After a number of years, this lab work was terminated, but later taken up again by Courtaulds, and developed into a commercial operation necessitating painstaking attention to recovery and reuse of the NMMO. Other firms have joined this bandwagon in recent years. The NMMO system yields mechanically relatively weak fibers, albeit with a high E modulus, useful for some textile applications only. High modulus, high tenacity cellulose yarns have been made by spinning cellulose esters, notably the formate, from liquid crystalline solution and regenerating the cellulose. Such processes are at an economic disadvantage. The second important invention, done only a couple of years ago at the Akzo Nobel lab in Arnhem, showed spinning cellulose from solution in phosphoric acid to yield high strength, high modulus fibers much better than the very best rayon tire yarns, in an environmentally friendly process with a low cost solvent.

Many people hoped that PEN would be the tyre yarn of the future: better than PET, hopefully not much more expensive and lower cost than rayon. Work at our lab has shown that this is going to be a problematic proposition because of the thermal behavior of PEN, showing a large loss factor at

tyre working temperatures. An article by Jurriaan van den Heuvel on the work leading to that realization is presented in conjunction with this review. He attributes the hysteresis to the crankshaft-like chain motion that accompanies ring flipping of naphthalene units (by contrast, phenylene units can ring flip without such difficulties).

The excellent work at Twente University in cooperation with DSM, all this in Holland, on making nylon-46 accessible has led to a commercial venture with the fiber spun from that polymer. That type of work goes on: when a new polymer becomes available, why not try spinning it and see whether your expectations as a fiber scientist are borne out by the results? In this case, the exceptionally fast crystallization in the spinline presented some problems (spherulites), but people succeeded in making attractive yarns that are proving hard to beat as automotive airbag construction material—based on the high melting point and the high melting enthalpy of N46.

Returning to rigid rod polymers: work has been directed at rigid rod-like materials in an effort originating with the U.S. Air Force culminating in the PBO fiber that is now becoming commercially available from Toyobo after much development at Wright-Patterson AFB, at SRI International, and at Dow Chemical.¹ Although PBO shows very impressive tensile properties, its composites showed compressive yielding at unsatisfactorily low stress and strain. Much work has been done in various ways to correct the problem, without making much headway, however. Various schemes have been tried to increase lateral strength in PBO after fiber formation,^{2–8} often by crosslinking. One attempt at introducing hydrogen bonds in such a polymer did not afford the improved compression performance hoped for; its lack of success in attaining improved compression properties was attributed to the hydrogen bonds being formed intra- rather than intermolecularly.⁹ Thus, reinforcement of stiff composites remains overwhelmingly dominated by the inorganic fibers like glass, (polymer-derived) carbon, boron, and so on. These fibers are characterized by covalent networks, resulting in intrinsically



Scheme 1

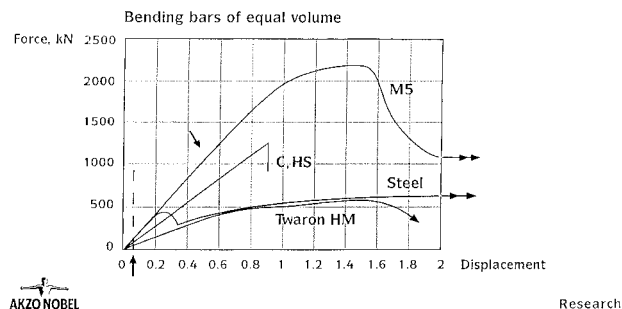


Figure 1 UD epoxy bars, 60 v/v fibers, compared with steel.

brittle behavior. It has been the ambition of this author to create polymers as rigid rod-like as PBO, with strong intermolecular hydrogen bonds.

After much experimentation, we found the novel polymer, formed from 2,3,5,6-tetraaminopyridine and 2,6-dihydroxyterephthalic acid, routinely called “M5” (an abbreviation from the IUPAC polymer name that is sometimes used is “PIPD”) to seem to fit the bill (see Scheme 1).

Conventional air gap wet spinning of the as-polymerized nematic solutions at about 180°C proceeded readily, usually yielding filaments with a diameter of about 10 microns, which are further washed to a low phosphorus content and drawn (by a few percent at most) at high temperature (>400°C) to produce the final, high modulus product.

Although much optimization remains to be done, we soon achieved promising mechanical properties and structure data in our new “M5” fibers in bench scale work. The crystal structure features hydrogen bonds in both the *x* and the *y* direction (*z* being the polymer main chain direction).¹⁰ Moduli over 300 GPa, tenacities over 2.5 N/tex, elongation at about 1.5%, and compressive strain in Elastica test of 0.4% (corresponding to a compressive strength of 1.4 GPa) were recorded—the highest compressive strength by far shown in this test by any polymer fiber. The first composite test bars that were tested in 3- and 4-point bending tests confirmed the high compressive properties of the new fiber in composite form.^{11,12} Creep under constant loading is controlled by shearing compliance, analogous to compressive yielding. Indeed, first creep test results of the new fiber are very favorable (Fig. 1; Table 1).

The mechanical properties of the new fiber make it competitive with carbon fiber in most applications with the added bonus of easy fabrication into composite form and high damage tolerance plus large energy absorption during a damage event (Fig. 1),

Table I Provisional Characterization of M5 Fiber Spun at Bench Scale

	Twaron HM	C HS ^a	PBO ^b	M5 Experiment
Tenacity (GPa)	3.2	3.5	5.5	4.6
Elongation (%)	2.0	1.5	2.5	1.4
<i>E</i> modulus (GPa)	115	230	280	330
Compression stress (GPa) ^c	0.58	2.1	0.4	1.6
Compression strain (%) ^c	0.5	0.9	0.15	0.5
Density	1.45	1.8	1.56	1.7
Water regain (%)	3.5	0	0.6	2
LOI (% O ₂)	29		68	>50
Onset of thermal degradation, air	450	800	550	530
Electrical conduction	—	++	—	—
Impact resistance	++	—	++	++
Damage tolerance	+	—		++
Weaving props	+	—	+	(+)
Knot strength	+	—	0	0

^a Mechanical properties of carbon are evaluated in resin impregnated strands to protect the material against premature brittle failure in the tensile testing machine. The *organic* fibers are tested as such, averages of 10 filament measurements are given for the tensile data.

^b Toyobo data.

^c Measured in UD composite test bars, three-point bending test, onset of deflection for the organic fiber reinforced composites; catastrophic failure for the carbon composites. M5 composites proved to be able to carry much higher loads than the load at onset of deflection, and to absorb much energy at high compressive strains in a mode analogous to the flow behavior in steel being damaged.

contrasting the new composites with existing (brittle) carbon fiber composites. First indications about impact resistance in composites are very favorable as well. The high electrical resistance of the new fiber would enable it to perform in areas where carbon fiber presents problems (corrosion in metal contacts) or is completely unsuitable, such as in photonic, electrical, and electronic enduses. The high polarity of M5 aids in easy adhesion to a variety of matrix materials, judging by bundle pull-out tests performed with various epoxy, unsaturated polyester, and vinyl ester resins. These gratifying results were obtained without any optimization, suggesting further possibilities of even higher or (if needed) specifically tailored adhesion levels, depending on the application.

WHAT OF THE FUTURE?

I find it hard to believe that substantially better and cheaper thermoplastic fibers than the presently known polyesters and polyamides will be found, but that should not stop anyone from striving to invent one. The work on ethylene/carbon monoxide alternating copolymer melt spinning is an example of work focused more at lower cost

than at higher performance. The wet spinning field, however, is extremely promising.

For textile fabrics, new vistas in wood pulp cellulose to supplant viscose rayon and cotton are desirable invention and development targets. The advantages are elimination of CS₂ and all its entails in the case of viscose, as well as avoiding the production of large amounts of worthless sodium sulfate, *plus* decreased cotton planting, a singularly agro-poison-intensive industry. This will, in time, set acreage free for food crops or forests. The recent successes with NMMO and phosphoric acid indicate that the older schemes to dissolve and spin pulp cellulose are not the last word. Indeed, (still) better schemes for cellulose manipulation may be found by hard work and a bit of luck.

For rubber reinforcement, in extreme cases aramid is the material of choice. In most cases by far, the new phosphoric acid solution spun cellulose yarn seems an eminent candidate by virtue of high mechanical properties and easy adhesion coupled with excellent thermo-mechanical response, compared with thermoplastic fibers. Thus, a recent invention is waiting to be commercialized. It should serve as an incitement to invent still better materials.

For reinforcing stiff composites, the new M5 polymeric fiber seems a very desirable material in the cases in which high mechanical performance, and especially damage and impact tolerance are desirable. It seems entirely possible that further refinement of the idea "rigid rod polymer + strong interchain (but not covalent!) interactions" is possible, leading to still better performance.

In conclusion, the first century of manmade fibers has brought a tremendous amount of knowledge and insight; a giant industry has grown up, but the work is far from complete and in fact whole new areas of endeavor are continuing to present themselves.

REFERENCES

1. Adams, W. W.; Eby, R. K.; McLemore, D. E.; Eds., *The Materials Science of Rigid-Rod Polymers*; Materials Research Society Symposium Proceedings, 1989, p 134.
2. Sweeny, W. *J Polym Sci* 1992, A30, 1111.
3. Rakas, M. A.; Farris, R. J. *J Appl Polym Sci* 1990, 40, 823.
4. Sahafeyan, M.; Kumar, S. *J Appl Polym Sci* 1995, 56, 517.
5. Dotrong, M.; Dotrong, M. H.; Evers, R. C. *ACS Polym Prepr* 1993, 34(2), 408.
6. Dang, T. D.; Arnold, F. E. *ACS Polym Prepr* 1995, 36(1), 455.
7. McGarry, F. J.; Moalli, J. E. *Polymer* 1991, 32, 1816.
8. Kozey, V. V.; Jiang, H.; Mehta, V. R.; Kumar, S. *J Mater Res* 1995, 10, 1044.
9. Tan, L. S.; Arnold, F. E.; Dang, T. D.; Chuah, H. H.; Wei, K. H. *Polymer* 1994, 35, 3091.
10. Klop, E. A.; Lammers, M.; Northolt, M. G. *Polymer*, to appear.
11. van der Jagt, O. *Polymer*, to appear.
12. van der Jagt, E. *SAMPE Proc*, Spring 1998.