Polymers for new materials*

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The relative roles of polymer chemistry, materials science and materials engineering have changed over the years. New applications require that the polymer fulfil multiple functions and so require a much closer link between molecular design and engineering design. There follows a discussion of a number of areas of materials where new polymers are needed.

(Keywords: new polymer materials; synthesis; applications)

INTRODUCTION

This paper is a response to a request to discuss how polymer chemistry can help to fulfil the need for new materials. I recognize that it is impossible to do this in an authoritative way. I will mention some examples of how polymer science has led to new materials in the past and will discuss a number of areas of current research where there is a need for new polymers or better polymers.

A very short history of polymer materials

The story of research on the commodity polymers might be summarized as chemistry followed by physics followed by engineering. In the 1940s and 1950s, the family of commercial plastics was developed and the industry became very large. During that time, new polymers such as nylon and polypropylene found their way rapidly into production. There was a great deal of research into new polymers, into mechanisms of polymerization and into characterization.

From 1960, the need for new polymers had apparently saturated and the emphasis of research switched to polymer physics. It was believed that, if we understood the relationship between structure, morphology and properties, we could tune existing materials to give better properties. By the mid-1970s, this too had saturated and there was a brief period of emphasis on processing methods to get better performance. It may be that the commodity polymers have now gone the way of sulfuric acid and fertilizer, to become important and mature products that need little attention from basic research.

Since that time the research emphasis has moved back to polymer chemistry, with the intention of making speciality polymers with exotic properties. Thus there has been much interest in piezoelectric polymers, electrically conducting polymers, non-linear optical polymers and liquid-crystalline polymers. In judging the importance of these efforts, it should be remembered that the first application of polyethylene was as a low-dielectric-constant insulation for use in radar. The expansion of polyethylene from a specialty material to a commodity with huge tonnage was not foreseen at the outset.

Examples of developments of speciality materials

Poly(vinylidene fluoride) has applications has a chemically resistant and photoresistant architectural coating. In 1969 Fukada was studying piezoelectricity in bone and looked for synthetic materials with similar properties. This led him to the high piezoelectric coefficient of this polymer[1] at about the same time as it was also discovered by Kawai[2]. Building on expertise in electrets, Murayama and coworkers at Kureha Chemical Co. studied this material for applications[3]. The result was a great burst of research activity from 1972 to 1980. Subsequent to that, a few military applications developed in hydrophones and then in microphones and small speakers. Surprisingly, despite many synthetic efforts, the first material found has also turned out to be the best, although other piezoelectric polymers have since been discovered and copolymers of poly(vinylidene fluoride) have slightly better properties than the homopolymer.

This relatively demanding application for a commercial plastic has proved a difficult product for the polymer industry, since the quantities needed are tiny and the market is unfamiliar.

Aromatic polyamides were known since Morgan's work in 1977[4]. The discovery of their lyotropic liquid crystallinity by Kwolek[5] led to the realization that very highly oriented and high-strength fibres were feasible. Kevlar thus seemed very suited to be used as tyre-cord, where the stiffness/weight ratio is important. In fact the material did not get accepted for this application, but slowly made its way into a range of composites and high-performance fabrics, chain-saw-resistant trousers being a notable example.

It seems to be generally true that a specialty polymer does not get used in the application for which it was originally intended, but other uses develop once the polymer is available. High-modulus polyethylene fibres, liquid-crystal polyesters and polyhydroxybutyrate are similar examples. It often takes a long time before it is clear whether a material does have a stable market or will go out of production. As a corollary, a new polymer

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should probably have some quite outstanding property before it is reasonable to develop it for production.

The recent wave of interest in conducting polymers arose from the discovery by Shirakawa, MacDiarmid and coworkers that thin films of polyacetylene could be formed on the surface of catalyst solutions and that these films could be doped to high conductivity[6,7]. This observation precipitated a rapidly expanding research effort on polyacetylene and then on polypyrrole, polyphenylene and other conjugated polymers. Various applications were proposed including batteries, electronic devices, solar cells and electromagnetic shielding. Many of these have foundered on the problems of instability of the doped polymers and low ionic and electronic mobility. This research wave has now receded but there is a steady flow of papers on applications, which may one day become a reality. Non-linear optical polymers and ceramic precursor polymers were similar research efforts that sprang from a good idea, quickly spawned a family of new polymers and are slowly plodding their way towards a possible application.

These newer examples of materials development differ from the previous development of commercial plastics in that the interface is between polymer chemistry and a parallel research effort in materials engineering. The requirements for the application can be clarified only as test devices are built. The interface is also one between universities and industrial laboratories rather than between an industrial (usually) laboratory and a manufacturing group.

CURRENT CHALLENGES

Composites

Composites fall roughly into two groups. Continuous-fibre composites, such as carbon-fibre-reinforced epoxy resin, have excellent properties parallel to the fibres but are expensive to process and very anisotropic (*Table 1*). Filled polymer composites can have greater stiffness than polymers, coupled with some improvement in strength, but usually show a great reduction in toughness. Filled polymers are generally limited to filler volume fractions of about 30% and a modulus increase of two or three times the base polymer. There is a need for mouldable composite materials of high stiffness and strength, which could then be applied to consumer goods rather than just to high-cost aerospace parts.

The components of the solution would seem to be better packing of long fibres, improved interfacial adhesion, a better understanding of how the mechanical properties of the matrix influence strength and finer fibres.

Structural biological materials are usually composites and can be seen as models for improved synthetic composites. Bone is essentially collagen reinforced with 40 to 50 vol% of thin (4 nm) hydroxyapatite plates. It shows an impressive combination of strength, modulus and toughness. These good properties may arise from the size, shape and packing of the plates, from the interfacial adhesion, or from the stress–strain properties of collagen. Collagenous tissues frequently show a J-shaped stress–strain curve, which, in tendon[8], arises from the kinked fibrils that straighten before stretching. This initial 'give' could be a method for avoiding the high stress concentrations that are normally associated with filler particles. It would be of considerable interest to develop a synthetic polymer with a similar stress–strain curve.

Macadamia shell appears to be a tightly packed array of cellulose fibres[9]. Isotropic properties are obtained by bundling the fibres to be locally parallel but changing direction between bundles. This results in great toughness since a crack is deflected by the changing fibre orientations. It is possible that this structure could be generated from short glass fibres by some combination of vibration and compression. Otherwise it may require that the fibres be grown in place in a matrix resin. We have been exploring methods of growing fibrous reinforcements in a polymeric matrix, but do not yet see how to achieve this structure[10].

Organic inorganic hybrids

Hybrid materials can be formed from various combinations of metal alkoxides and polymers to create a very fine admixture of inorganic oxide and organic polymer. Wilkes and coworkers have called these materials *ceramers*[11], Schmidt and colleagues refer to *ormosils* or *ormocers*[12] and Uhlmann and coworkers refer to *polycerams*[13,14]. Most of this work has been with silicon alkoxides in combination with short-chain hydroxylated polymers that become linked to the oxide during hydrolysis. Titanium and zirconium oxides have been studied to a lesser extent. Efforts to characterize these structures show that any separation of the organic and inorganic phases occurs on a scale of a few nanometres or less. Recent work by Schaefer has related this scale to the molecular weight of the polymer[15].

Table 1 Natural and synthetic composites

Composite[a]	Elastic modulus (GPa)	Strength (MPa)	Work of fracture (kJ m^{-2})	Fracture toughness, K_{Ic} (MPa m$^{-1/2}$)	Strain to break (%)
Bone (bovine femur)	20	220	1.7	5	10
Insect cuticle (35 vol% chitin fibres)	6–10	80			
PEEK–carbon fibre (61 vol%) longitudinal	140	2200	1.6		1
Transverse	8.3	73			1
PET +18 vol% glass fibre	9	144			6.6
PET +35 vol% glass fibre	20	165	3.2	9.5	1
SMC (35% glass fibre)	16	158			1.7
E glass	70	3000			
Hydroxyapatite	130	100			
PET	3.3	60	7.3	4.9	275
Collagen (tendon)	2	100			

[a] PEEK, poly(ether ether ketone); PET, poly(ethylene terephthalate); SMC, sheet moulding compound

Novak[16] has explored several interesting combinations of polymerization chemistry with alkoxide hydrolysis, and has shown that the scale of phase separation can be controlled kinetically.

The obvious goal of this work is to produce a family of materials with mechanical properties intermediate between those of polymers and glasses. This would place the moduli in the range of 10–100 GPa and extensions to break in the range of 1–100%. So far, significant modulus increases seem only to come at the expense of extreme brittleness[17], and it is not very clear why this should be. The solution may be microstructural, in that the preferred structure should be closer to that of bone. While these materials do not show good mechanical properties, they do allow thick, hard coatings to be produced, which may find applications as waveguides, for example[18].

The range of hybrid chemistry that has been explored is still very small. While there is every reason to believe that a unique and useful group of properties should be achieved, there are few guidelines to define what structures should be made or how the chemical composition and physical microstructure interact to control strength and toughness.

Aqueous processing of ceramics

Ceramics are densified by sintering a densely packed body of powder, which shrinks and becomes fully dense by solid-state diffusion. To achieve high strength, it is also desirable to limit the final grain size, which favours a fine starting powder. A poorly packed green body leads to a lower final sintered density[19].

These considerations have pushed ceramics processing towards trying to achieve very uniform close-random packing of submicrometre particles, which in turn requires reduction of interparticle attractions that otherwise lead to formation of loose aggregates. Good dispersions of fine particles in organic solvents, and good green-body strength, can be realized by adding polymer dispersants that provide steric stabilization[20]. However, environmental concerns are making it desirable to convert solvent-based processes to water. There are no very good dispersion systems for aqueous media. Ionic polymers or small molecules are effective dispersants, but the green-body strength tends to be low and counterions can interfere with the purity of the ceramic when very fine particles are used.

A good strategy for the synthesis of dispersants that act by steric stabilization, rather than by ionic repulsion, is to prepare a block copolymer where one block binds strongly to the particle surface and the other block is very soluble in the solvent[21]. For oxide ceramics in water, no dispersant has yet been produced that does a really satisfactory job of providing the required contrast between the bonding block and the soluble block. The problem is not trivial because oxide surfaces are hydroxylated and so are similar to water in structure[22]. Most dispersants exploit the contrast between the non-polar solvent and the polar surface. Although silica is much used as a model system for dispersion studies, it cannot be regarded as a model, both because of the very high acidity of the surface and because it is usually amorphous and densifies by viscous flow rather than by sintering.

From an industrial viewpoint, the problem is partly one of communication, in that the ceramics industry is not enthusiastic about paying higher prices for specialty polymers as opposed to using cheaper materials developed for other purposes. Likewise, the polymer industry does not see the market as being large enough to be interesting when compared to commodity polymers.

Polymer–ceramic chip carriers

One remarkable aspect of the growth of the electronics industry is that most of the materials innovation has taken place within the industry rather than being driven by materials companies. As a result, most photoresists and electronic packaging materials are adaptions of existing polymers rather than materials synthesized expressly for the purpose. Likewise, this large area of polymer technology has fostered little parallel effort in academic polymer science.

A current development area is in hybrid packages for semiconductors. High-performance packages comprise up to 40 stacked layers of ceramic sheet with metal lines and vias between the sheets to carry electrical power and signals[23]. The ceramic serves as a good thermal conductor and electrical insulator. The whole stack is sintered to form an enclosure into which the chip is hermetically sealed. Newer packages are being developed with ceramic lower layers and polymer upper layers[24]. The polymer is a poor thermal conductor but the layers can be made thinner and the low dielectric constant allows the conducting lines to be placed closer together. Polyimides are being used because of the high temperatures involved in making soldered connections. There is no reason to believe that existing materials offer the best solution, but any synthetic effort would need to be driven by the multiple goals of temperature resistance, moisture impermeability, low dielectric constant and high thermal conductivity. Each of these properties should be quite tractable with current modelling methods.

Devices from aqueous processing

Biomineralization processes show a high degree of control of precipitation of inorganic minerals, such as calcium phosphates and carbonates, by polymeric substrates and matrices[25]. Examples are seen in bone and shell formation. The detailed mechanisms are not understood, but it is widely believed that specific arrangements of anionic sites on protein surfaces are responsible for forming clusters of cations that then nucleate the mineral. Crystal size, position, shape, orientation and phase can apparently be controlled.

Given a similar degree of control over synthetic mineral deposition processes, it is possible to envisage a technology for depositing multiple layers of patterned structures on surfaces to form devices similar to those formed in silicon by VLSI (very-large-scale integration) methods. The difference would be that processing from aqueous media at low temperatures would allow a wider range of materials to be deposited with greater sensitivity to chemical signals. The work of Rieke and coworkers illustrates how modification of surface groups can control mineralization[26].

Intelligent materials

There has recently been a development of interest in 'intelligent' and 'smart' materials, although there is no very clear definition of what these terms mean. One area of interest is the inclusion of sensors in composite materials to monitor curing or detect damage[27]. A wide range of efficient sensors is available, and work to incorporate them into materials is proceeding. A further goal is to include actuators so that the material can cancel vibrations or respond to local stress concentrations by internal deformation. This raises the need for new actuator materials.

Current actuators include piezoelectric ceramics and polymers, shape-memory alloys, magnetostrictive materials and ionic polymer gels[28]. The archetypal actuator is muscle. The ceramics suffer from the drawback of being capable of very small strains, while the gels develop large strains but respond slowly and develop little force. Nothing yet approaches muscle in terms of speed of response and power density. Muscle response times are 10–100 ms compared to 1–10 s for gels[29]. Muscle power density is about 1 W cm^{-3} compared to 1 mW cm^{-3} for gels. If efficient robot arms are to be developed that do not depend on motors, new actuator materials will be needed.

A further characteristic of many biological composites is that they are capable of self-repair. It is possible to conceive of incorporating excess uncured resin into composites so that damage sites can be repaired. It is not clear if this can be done without seriously degrading the initial properties of the material.

Stereolithography

In recent years a number of commercial prototyping systems have been developed where a three-dimensional computer drawing is converted directly to a solid part. One system, called *stereolithography*, involves sequential photopolymerization of layers of monomer spread over the surface of the part. Each layer corresponds to one 2D slice of the 3D drawing. Highly crosslinking acrylic monomers are generally used. Alternative systems use laser fusion of powders, reactive consolidation of powders, deposition of a molten wax or curing of a composite slurry[30].

These free-body forming methods open up the possibility of controlling the structure and properties of a material point by point within a part. It also makes it possible to produce the kind of complex composites that would be needed for fully intelligent materials as outlined above. These systems do impose stringent requirements on the associated polymer chemistry. Sequential layerwise deposition requires that solidification in each layer occurs within about 1 min in order that a part can be built up in a reasonable time.

This need for rapid polymerization has driven current systems to rely on crosslinking materials or crystallizing waxes. This prevents high-molecular-weight linear polymers from being used and so limits the toughness and strength of the parts. As a result, most current parts are useful as prototypes but are not functional. Methods for rapid melt polymerization to tough polymers would allow a significant extension in the range of materials that can be used in free-body forming.

Batteries

The lead–acid secondary (rechargeable) battery has had a career of about 100 years, during which it has outperformed many potential replacement systems. The push towards battery-powered cars has renewed research on lightweight secondary batteries based on a lithium anode with a polymeric electrolyte[31]. The most promising polymer electrolyte is poly(ethylene oxide) with dissolved lithium salts, but this and rival systems all suffer from a low ionic conductivity at room temperature[32]. Many inorganic materials are good, fast, ion conductors owing to the transport of lithium ions through channels in the material. Attempts to design more efficient polymer electrolytes by increasing chain flexibility have not been successful so far. It seems that it should be possible to design a polymer that would provide channels for rapid lithium ion transport. There is also a need for improved polymeric electrodes.

Biomimetic polymers

A major challenge to polymer science that will occupy many years is the programmed synthesis of molecules with a predetermined sequence, like the synthesis of proteins and nucleic acids from templates. One area where there is clear application for such non-repeating structures is in artificial fibres that have properties similar to silk.

Natural silk is spun from a fluid aqueous suspension of protein stored in the silk gland of the silkworm[33,34]. As it is sheared through the spinneret at the entrance to the gland, the silk precipitates to a solid fibre. The silk is insoluble in water and silk can be spun under water, so drying is not part of the process. The amino acid sequence of silk contains regular crystalline regions and regions of amorphous, acidic residues. In the silk gland, the protein apparently folds into a metastable conformation that is converted to a stable extended structure on shearing. The ability to control polymer sequence at this level would allow much closer control of fibre crystallinity and would allow novel spinning processes. Genetic engineering is being used to form silks in bacterial hosts[35,36].

Another area where it is clear that specific sequences give unique mechanical properties is in cellular adhesion, where protein sequences are used to allow two surfaces to recognize and bond specifically to one another. This obviously could have interesting implications for synthetic adhesives.

CONCLUSIONS

Recent years have seen materials science become much more concerned with the synthesis of new materials. Previously much of the emphasis was on understanding the microstructures of commercial materials and their influence on properties. Polymer science has seen a revival of polymer synthesis, but with an emphasis on developing special structures and properties, rather than being driven by chemical curiosity. These developments are also moving us towards more complex combinations of materials.

Synthesis, processing and assembly have been separate activities. While a refrigerator can be disassembled into a collection of pure component materials, the same is not true of an animal, where synthesis, processing and assembly occur simultaneously to form what is essentially a single complex composite. Drexler's discussions of atomic assembly in nanotechnology portray a similar future for machines[37].

One consideration motivates against this trend, that of recycling. Composites are hard to recycle without complete chemical destruction and re-formation. In the case of animals, proteins are not recycled but are broken down at least as far as amino acids.

REFERENCES

1 Fukada, E. and Takashita, S. *Japan. J. Appl. Phys.* 1969, **8**, 960

2 Kawai, H. *Japan. J. Appl. Phys.* 1969, **8**, 975

3 Murayama, N., Oikawa, T., Katto, T. and Nakamura, K. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 929; Murayama, N. and Hashizuma, H. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 989; Murayama, N. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 1033

4 Morgan, P. W. *Macromolecules* 1977, **10**, 181

5 Kwolek, S. L., Morgan, P. W., Schaefgen, J. R. and Gulrich, L. W. *Macromolecules* 1977, **10**, 1390

6 Shirakawa, H. and Ikeda, S. *Polym. J.* 1971, **2**, 231

7 Shirakawa, H., Louis, E. J., MacDiarmid, A. G., Chiang, C. K. and Heeger, A. J. *J. Chem. Soc., Chem. Commun.* 1977, 578

8 Calvert, P. D. Biological systems: materials, in 'Encyclopedia of Materials Science and Engineering' (Ed. M. B. Bever), Pergamon, Oxford, 1986

9 Jennings, J. S. and Macmillan, N. H. *J. Mater. Sci.* 1986, **21**, 517

10 Burdon, J. and Calvert, P. Orientation in biomimetic polymer–mineral composites, in 'Hierarchically Structured Materials' (Eds. I. Aksay, E. Baer, M. Sarikaya and D. A. Tirrell), *Mater. Res. Soc. Symp. Proc.* 1992, **255**, 375

11 Wilkes, G. L., Huang, H.-H. and Glaser, R. H. in 'Silicon-Based Polymer Science' (Eds. J. M. Ziegler and F. W. G. Fearon), *Adv. Chem. Ser.* 1990, **224**, 207, American Chemical Society, Washington, DC

12 Schmidt, H. in 'Inorganic and Organometallic Polymers' (Eds. M. Zeldin, K. J. Wynne and H. R. Allcock), *ACS Symp. Ser.* 1988, **360**, 333, American Chemical Society, Washington, DC

13 Boulton, J. M., Thompson, J., Fox, H. H., Gorodisher, I., Teowee, G., Calvert, P. D. and Uhlmann, D. R. 'Non-Linear Organic Dyes in Polyceram Hosts' *Mater. Res. Soc. Symp. Proc.* 1990, **180**, 987

14 Boulton, J. M., Fox, H. H., Neilson, G. F. and Uhlmann, D. R. *Mater. Res. Soc. Symp. Proc.* 1990, **180**, 773

15 Ulibarri, T. A., Beaucage, G., Schaefer, D. W., Oliver, B. J. and Assink, R. A. *Mater. Res. Soc. Symp. Proc.* 1992, **274**, 85

16 Ellsworth, M. W. and Novak, B. M. *Chem. Mater.* 1993, **7**, 839; Novak, B. M. *Mater. Sci. Eng. (A)* 1993, **162**, 257

17 Coltrain, B. K., Landry, C. J. T., O'Reilly, J. M., Chamberlain, A. M., Rakes, G. A., Sedita, J. S., Kelts, L. W., Landry, M. R. and Long, V. K. *Chem. Mater.* 1993, **5**, 1445

18 Schmidt, H., Krug, H., Kasemann, R. and Tiefensee, F. *SPIE Proc.* 1991, **1590**, 36

19 McColm, I. J. and Clark, N. J. 'Forming, Shaping and Working of High Performance Ceramics', Blackie, Glasgow, 1988

20 Tormey, E. S., Pober, R. L., Bowen, H. K. and Calvert, P. D. *Adv. Ceram.* 1984, **9**, 140

21 Al-Lami, H. S., Billingham, N. C. and Calvert, P. D. *Chem. Mater.* 1992, **4**, 1200

22 Green, M. L., Rhine, W. E., Calvert, P. D. and Bowen, H. K. *J. Mater. Sci. Lett.* 1993, **12**, 1425

23 Tummala, R. R. and Rymaszewski, E. J. 'Microelectronics Packaging Handbook', Van Nostrand Reinhold, New York, 1989

24 Garrou, P. *Proc. IEEE* 1992, **80**, 1942

25 Calvert, P. and Mann, S. *J. Mater. Sci.* 1988, **23**, 3801

26 Rieke, P. C. and Bentjen, S. B. *Chem. Mater.* 1993, **5**, 43

27 Udd, E. (Ed.) 'Fiber Optic Smart Structures and Skins II' *SPIE Proc.* 1989, **1170**

28 Trolier-McKinstry, S. and Newnham, R. E. *Mater. Res. Soc. Bull.* 1993, April, p. 27

29 Shiga, T. and Kurauchi, T. *J. Appl. Polym. Sci.* 1990, **39**, 2305; Shiga, T., Hirose, Y., Okada, A. and Kurauchi, T. *J. Appl. Polym. Sci.* 1993, **47**, 113

30 Marcus, H. L., Beaman, J. J., Barlow, J. W., Bourel, D. L. and Crawford, R. H. (Eds.) 'Solid Freeform Fabrication Symposium 1993', University of Texas at Austin, 1993

31 Santhanam, K. S. V. and Gupta, N. *Trends Polym. Sci.* 1993, **1**, 284

32 Hooper, A., Gauthier, M. and Belanger, A. in 'Electrochem. Science and Technology' (Ed. R. G. Linford), Vol. 2, Elsevier, London, 1992

33 Shimura, K. *Experientia* 1983, **39**, 441

34 Kerkam, K., Viney, C., Kaplan, D. and Lombardi, S. *Nature* 1991, **349**, 596

35 Lombardi, S. J. and Kaplan, D. L. *Polym. Prepr.* 1990, **31**(1), 195

36 Kaplan, D. L., Fossey, S., Mello, C. M., Arcidiacone, S., Senecal, K., Muller, W., Stockwell, S., Beckwitt, R., Viney, C. and Kerkam, K. *Mater. Res. Soc. Bull.* 1992, **17**, 41

37 Drexler, K. E. 'Engines of Creation', Anchor Books, New York, 1986; Drexler, K. E. 'Nanosystems', Wiley, New York, 1992