N. G. McCRUM, C. P. BUCKLEY
and C. B. BUCKNALL

Principles of Polymer Engineering

SECOND EDITION

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Principles of Polymer Engineering

A note on the cover photograph

The cover photograph shows a footbridge over the River Tay at Aberfeldy in the Scottish Highlands. The bridge, made from polymer-based composites, was commissioned by a golf club, in order to extend its course from 9 to 18 holes. The design brief specified that: (a) capital and future maintenance costs should be kept to a minimum; (b) construction should not involve heavy machinery that might damage the course; and (c) the appearance of the bridge should be compatible with its location in an area of outstanding natural beauty.

The club consulted staff of the Engineering Department at nearby Dundee University, who after consultation with the Maunsell Group recommended the use of composites, and collaborated in the design and construction. The bridge deck is made from glass-reinforced polyester (GRP), and was installed manually by final-year engineering students from the University, without the use of cranes. The A-shaped pylons are also made from GRP, and the supporting cables are of Kevlar fibre, which is sheathed in a protective coating of low-density polyethylene.

The structure was designed and specified by Maunsell Structural Plastics, of Beckenham, Kent, who kindly supplied the photograph. The company has won many awards for its composites-based designs, which provide good illustrations of the principles of polymer engineering.

Preface to the second edition

Some eight years have passed since the first edition appeared. During this time we have used the first edition extensively in our own teaching at Oxford, UMIST, and Cranfield, and it has been widely used elsewhere. We have been delighted with the reception it has received. In particular, the distinctive style of the book—developing the principles of polymer engineering from a base of the underlying materials science, and aiming to treat topics at a self-contained quantitative level or not at all—seems to have worked well. In our experience it has engaged the interest and enthusiasm of student engineers. The large number of end-of-chapter problems has proved a particularly useful feature to instructors and students, as a means of exercising and testing an understanding of the text, expecially since the separate *Solutions Manual* was published (OUP, 1989).

Over the intervening years polymers have become even more firmly embedded in the university engineering curriculum, alongside traditional engineering materials. No engineering course can now afford to neglect the engineering properties of polymers or their important role in manufacturing. It is to serve this continuing teaching need that we have revised *Principles of Polymer Engineering*.

The original format is retained, but we believe we have strengthened the treatment in key areas. We find today's students much better attuned to the wider aspects of engineering decision-making, especially with respect to the environment, than used to be the case. We want to encourage this and have revised Chapter 0 substantially, to include a discussion of the environmental impact of polymers. Whether in providing lighter automobile components for fuel-saving, or in the ability of thermoplastics to be remelted and recycled, or in the recovery of heat by clean incineration, polymers seem set to play a vital role in the more environmentally aware engineering of the future. We have tried to give a taste of the important issues involved. A continuing trend has been the growth in the variety of grades of polymer available, tailored for different applications: many of them are toughened grades. There is now increased understanding of the mechanisms by which toughening is achieved in polymers, and of how to accommodate it in fracture test methods, and we have extended Chapter 5 on yield and fracture to reflect the improved state of knowledge. Another significant revision is an enlargement of Chapter 7 on processing, especially to include a treatment of heat transfer. Although the underlying theory will be familiar already to many students, it is so central a topic in

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polymer forming processes that we believe readers will prefer having it presented together with other aspects of processing in the same book. We have also added to the end-of-chapter problems, particularly on manufacturing and design, Chapters 7 and 8. The book now contains some 195 problems, and a revised edition of the *Solutions Manual* will be published shortly. Finally we have taken the opportunity to clarify some points and to make other minor improvements.

There are several areas of polymer science and technology that have seen recent dramatic advances but are not included. We continue to aim to provide a treatment that is self-contained and quantitative within a book of reasonable length, and this means that hard choices must be made. Examples of topics not discussed are liquid crystal polymers and electrical properties of polymers. Some excellent monographs are available on these topics and are included in our extensive list of Further Reading for students who are interested.

We trust our readers will find the revised book a stimulating introduction to a fascinating subject.

Oxford N.C.M.
Cranfield C.P.B.
June 1997 C.B.B.

Preface to the first edition

Our purpose in writing this book has been to prepare a text which is

- an integrated, complete, and stimulating introduction to polymer engineering,
- suitable for the core course in mechanical or production engineering, and
- directed at undergraduates in their third or fourth year.

The integrated course includes elements of polymer chemistry and physics which today are classed as materials science. The level of treatment assumes a preliminary standard in this subject which would be reached after an introductory course based on, for example, Van Vlack's *Elements of Materials Science and Engineering*. Other prerequisite courses include introductory elasticity, strength of materials, thermodynamics, and fluid mechanics.

A materials science framework is essential because of the need to master a new vocabulary and to acquire a conceptual underpinning for the later chapters in polymer processing and design. This is the modern educational route in engineering metallurgy, in which physical metallurgy is taught in parallel with the macroscopic, phenomenological theories of metal plasticity and fracture. This is a far more attractive route than that in favour until forty years ago, in which the teaching was entirely practical and was based on tables of properties and selection rules for materials. In our view, undergraduates, having been taught engineering metallurgy by the modern route, will anticipate and respond to the same method in the teaching of polymer engineering.

The eight main chapters present a logical development from materials science to polymer technology. The purpose of this treatment, in a book of 400 pages, is not to train specialists but to present a short, integrated course which will stimulate and be attractive to all mechanical and production engineers, including, of course, the small number who will later go on to specialize as polymer engineers and who will require specialist courses such as will be found in the books by Middleman or by Tadmor and Gogos. Our overriding purpose is to implant an understanding of the scope and promise of the polymer revolution by describing polymer science and technology as it exists today together with insights into what is to come.

In writing the book we have laid emphasis on describing phenomena in depth, or not at all. For example, linear viscoelasticity is described in some depth because

- it brings into one framework the fundamental polymer phenomena of creep, stress relaxation, and mechanical damping and shows clearly the relationship between them;
- it is rapidly accepted by engineers, being intimately related to electrical network theory; and
- it yields valuable insights into non-linear viscoelasticity.

The theory of rubber elasticity is described in depth because

- the nature of the force between cross-links in rubber is of fundamental interest and gives to rubbers and polymer melts their unique and extraordinary properties;
- it leads to a 3-D closed-form relationship between principal stresses and strains; and
- it is a condensed-phase analogue of the kinetic theory of gases, which is normally part of introductory engineering courses in thermodynamics.

In this way we hope the book will be entirely satisfying in that the treatment is everywhere complete up to an appropriate level. This has meant that some topics—for example heat transfer in polymer forming—are not discussed at all. The problem is one of selection and we hope that our choice, particularly in the balance between polymer science and polymer technology, will be found to be correct.

A note system is used to bring the real commercial world into the book in an incisive way which does not break up the flow of each chapter. For example, when the polymerization of polypropylene, and its molecular structure, are described in Chapter 1 the relevant note—placed at the end of the chapter—details the strengths and deficiencies of the plastic, its relative position in the hierarchy, and examples of its application. The note system is occasionally used to insert theory or an extended footnote which—for one reason or another—would break up the flow of the chapter. The text can be read without using the notes, but preliminary trials have shown that undergraduates will find it a most useful system, particularly at a second reading. We have made use of worked examples and each chapter has over twenty study problems.

1986

N.G.M.
C.P.B.
C.B.B.

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The frontispiece was kindly supplied by Maunsell Structural Plastics; a full description is given on p. ii.

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0 *Introduction*

Despite the central role that plastics play in life today, there remains a trace of the old view that plastic products are cheap and nasty. This is reflected in a poll held recently in Italy. Of those interviewed, 15% were neutral, neither for nor against plastics, 25% had no view, 35% thought they were essential and approved, but a surprising 25% of those surveyed were quite opposed to them.

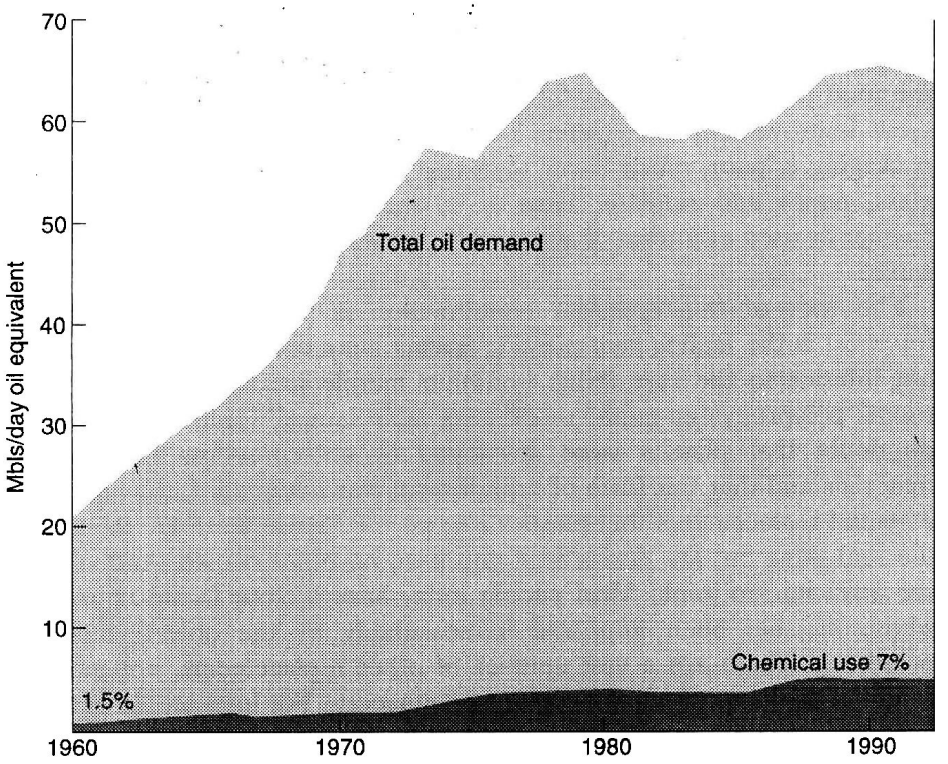
Polymers, in the form of plastics, rubbers and fibres, have for many years played essential but varied roles in everyday life: as electrical insulation, as tyres, and as packaging for food, to mention but three. There is no other class of material that could substitute for them. It might be thought that the public's view of plastics in food packaging would be favourable: after all, plastics packaging in the developed world leads to low wastage (less than 2%) whereas in the undeveloped world about 50% of the food produced becomes rotten. Plastic packaging brings with it also a great improvement in hygiene. Yet the public image of plastics as food packaging is poor, much lower than that of traditional materials such as glass, paper and tinplate. How is it, then, that the word 'plastic' is frequently used as a term of abuse in the sense of plastic bread or a plastic smile?

The root of this apparent contradiction is psychological. First and foremost is the feeling that plastics, having been conceived as substitutes, are inferior to the real thing: imitation marble laminates for the bathroom? polypropylene grass? mock onyx table lamps? Historically, there is no doubt that plastics were developed by entrepreneurs as imitation materials and that this form of replacement was intended. But what of the essential replacements that plastics also permit? False teeth are inferior to the real thing but are desirable if you have no other choice. And what of the artificial hip joint? Most people today have a close friend or relative whose life has been improved immeasurably by the polyethylene hip prosthesis. There are a vast number of other replacements, not quite so essential as these, which are highly advantageous. For instance, in automobile engineering, great improvements in safety, noise reduction, comfort and fuel economy are being derived from the increasing replacement of metal alloys with plastics.

The basic argument in favour of plastics is that they provide a choice,

functionally, aesthetically or monetarily. If you need an artificial hip joint or false teeth, the choice is straightforward: to be specific, there isn't one. If you prefer leather suitcases to vinyl, or silk stockings to nylon, you are at liberty to buy them and preserve the quality of your life.

The second major cause of public antagonism towards plastics stems from a perceived threat to the environment: hedgerows decorated with carrier bags, pavements littered with burger boxes and grass verges strewn with plastic bottles have cast the plastics industry in the role of environmental villain. In the past, in the days of glass and paper, the environment had to look after itself. Today, pressure groups react to environmental abuse, and rightly so. Later in this chapter, and elsewhere in more detail, we examine the environmental issues. But we note at once that the part the plastics industry plays in reducing the world's reserves of oil is very low, Figure 0.1. The favoured environmental route for many in the plastics industry is to recycle plastics back to energy through incineration with energy recovery. This makes a lot of sense: the energy of the oil is recovered after the oil-derived plastic has been used as a bottle or a car



0.1 The chemical share of the total world oil demand. Somewhat more than half of the chemical share is turned into plastics. It will be seen therefore that the greater part of the world's recovered oil is burnt to produce electrical power or for automotive propulsion etc.

bumper. There are other possibilities such as materials recycling or chemical recycling which we describe later.

The third major cause of public antagonism to plastics is the undoubted incidence of abysmal design. This failure was, and to some extent still is, caused by ignorance: a lack of awareness on the part of designers as to which plastic to use for a specific application and how to use it. For instance, polystyrene, a low-cost but brittle plastic, should not be used in its untoughened state in stressed applications. Plastics differ significantly one from another. A design failure brings criticism, not of the designer, but of plastics as a group. This irrational treatment of plastics does not extend to metals. The failure of a metal part through gross design negligence (for instance the use of mild steel in a corrosive environment which requires stainless steel) is seen by all to be a failure in design and not in the use of metal alloys. At root, there is a lack of awareness by engineers and the public that the name 'plastics' is used to cover a large group of similarly based but significantly different materials.

It is interesting to note that the image of being inferior substitutes is not associated with rubbers, simply because natural rubber when it was introduced commercially to the industrial world in the mid-nineteenth century was the very first material of its kind. Its first uses were in waterproof clothing, balls, erasers, and belting for machinery. It then helped to transform the bicycle from being a dangerous and uncomfortable contraption into the first personal mechanical vehicle. Finally, the application of pneumatic tyres to the motor car by Michelin towards the end of the nineteenth century made possible the phenomenal growth of motor transport which has dominated the use of rubber every since.

The contrast between the practical uniqueness and utility of rubber and the tarnished image of plastics in their early years effectively disguised from the ordinary person the fact that **plastics and rubbers are sub-groups of the same class of materials—organic high polymers—differing only in detail in their molecular structures.**

0.1 The past

A century ago, the polymer industry was in its infancy. The first man-made plastic, a form of cellulose nitrate, was exhibited at the Great International Exhibition in London in 1862. The exhibits were arranged into 36 classes. Amongst the 14 000 exhibits of Section C of Class 4 (animal and vegetable substances used in manufacture) was a set of small mouldings made by Alexander Parkes from a material he named Parkesine. It was described in the exhibition leaflet as a replacement for natural materials such as ivory and tortoiseshell which were becoming rare and expensive.

Parkes was born in 1813 and was apprenticed as a brass-founder. He became active in the youthful rubber industry and in 1843 patented a waterproof fabric, a patent he sold later to Charles Macintosh. The waterproofing of fabrics was naturally a major early use of natural rubber, which was obtained at the time from trees in the South American jungle. The unpleasant tackiness of the early products was eliminated with the discovery by Goodyear and Hancock in the 1840s of the vulcanizing effect of sulfur. At first the sulfur was merely dusted on the surface, but this was soon to be followed by mechanical mixing of rubber and sulfur. The interest of Parkes in the infant rubber and plastics industry is symbolic of the scientific and industrial relationship which has always existed between them.

However, Parkesine was not commercially viable, because of its high cost. Parkes employed a large quantity of expensive solvent which was not recovered. The first truly commercial process for the production of plastic material from cellulose nitrate (Celluloid) was due to John Hyatt of Albany, New York State. In 1863, Hyatt, who was then a twenty-six-year-old printer, sought to win a $10 000 prize offered by the Phelan and Collander Company for a new synthetic material to make billiard balls. He studied the literature on cellulose nitrate and knew of the discovery of Parkes that the combination of pyroxylin and camphor produced a plastic resembling ivory. Hyatt conceived the idea of using a small quantity of solvent and supplementing it with heat and pressure. After early experiments conducted in the kitchen of his boarding house, he was expelled to a shed. Celluloid is one of the lower nitrates of cellulose—one of the higher ones is gun cotton! Hyatt was completely successful with his process, and the patent was issued in 1870. The importance of Celluloid is not only that it was the first plastic but that it was for forty years, until the development of Bakelite, the only one. Celluloid is still used today to make billiard balls and table tennis balls.

Parkes, Hancock, Goodyear and Hyatt were typical of the gifted and energetic practical men at whose hands the plastic and rubber industries developed in the middle of the nineteenth century. Their method of working was quite different from the methods which became widespread after 1920. Before that time there was no understanding of the molecular structure of polymers. For natural rubber, Faraday in 1826 had deduced the empirical formula C_5H_8. But there was no appreciation of the fact that natural rubber comprises enormously long molecules. The prevailing confusion was finally dispelled by Staudinger in 1920. His revolutionary idea met heated resistance but by the 1930s it was commonly accepted that all plastics and rubbers are polymers, or macromolecules as Staudinger termed them. In the case of rubber, for instance, identical C_5H_8 units are strung one after another in an immensely long chain. Everything started to fall

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