Book Reviews

Polymers: Properties and Applications Volume 2 – Polymer Fracture

H. H. Kausch

Springer-Verlag, Heidelberg, 1978 pp. x+332, 180 illust., DM128

Professor Kausch examines a wide range of fracture and failure phenomena in polymers, and relates them to the response of molecular chains under applied stress. This approach, which he calls the 'kinetic theory of fracture', is sometimes in danger of being overlooked in favour of treatments based purely on continuum mechanics. Many questions remain unanswered at present, but the molecular interpretation is of fundamental importance in understanding the basic differences in fracture between individual materials.

The book can conveniently be divided into four roughly equal sections. The first, comprising chapters 1–4, is introductory, covering the structure and deformation behaviour of amorphous and semicrystalline polymers and composites, rate process theories of fracture, and bond dissociation energies. The second section (chapters 5–7) concentrates on the stress–strain response of individual chains, detection of free radicals by e.s.r. methods, and the factors affecting chain scission in bulk material. The third section (chapter 8) deals with the occurrence of chain scission throughout a loaded body; and the final section (chapter 9) is concerned with more localized events in the initiation and propagation of crazes and cracks, with particular reference to the role of chain entanglements, molecular slip, and bond scission. Chapters 8 and 9 include discussion of impact testing, fracture mechanics, fatigue, and environmental stress cracking.

The book is well illustrated by numerous line diagrams and photographs, and by tables of data ranging from bond dissociation energies to g_{IC} and K_{IC} values for some 20 types of polymers. The author has drawn on an impressive total of 867 references from English-, German-, and Russian-language journals, although, as he states, only chapters 6 to 8 are intended to cover the literature comprehensively. The writing is in places a little condensed, perhaps inevitably in a work that treats such a broad subject area in depth. Fuller definitions of symbols, either in the text or in the glossary, would have been helpful, and some of the illustrations, notably figures 5.9 and 8.5, are insufficiently labelled. However, these are minor criticisms.

The approach throughout is quantitative, critical, incisive, and authoritative. The field is a developing and often controversial one, and, where problems exist, the author presents both sides of the case, carefully arguing their respective merits. This stimulating book is recommended to all who are concerned with the relationship between fracture properties and molecular structure of polymers.

C. B. Bucknall

Advances in Polymer Science, Volume 26, Conformation and Morphology

Springer–Verlag (Berlin, Heidelberg, New York), pp. 183, $38.

This volume of the well-established series contains four review papers. The first is by W. Holzmüller and entitled *Molecular mobility deformation and relaxation processes.* The author's stated aim is to explain viscous and viscoelastic flow as molecular 'dislocations' meaning by this term changes of possible conformations caused by thermal vibrations.

In contrast to the more usual spring–dashpot description or those invoking a statistical distribution of holes, Holzmüller proposes a quasi-cubic structure of molecular segments in which the heights of barriers to conformational changes (dislocations) are determined by using a Lennard-Jones 6–12 potential. By this means calculation can be made of the energy term in the Arrhenius formula and analysis made of creep, stress relaxation and dielectric behaviour. By assuming a spatial fluctuation of density in the amorphous state the glass transition is also treated in this way. T_g is calculated by considering the energy required to form a hole and assuming it derived from an internal shearing stress. A relation similar to the WLF equation is found.

The quasi-cubic model is clearly a valuable approximation to the conformational changes occurring in polymers and this paper gives a good introduction to it, with a comprehensive list of references (60 in all). The paper is somewhat marred by a poor translation from the German resulting in occasional grammatical errors and misspellings but these are minor faults.

The second paper on *The iso-free volume state and glass transitions in amorphous polymers* is by Yu. Lipatov and forms a very useful introduction to the subject for the serious student. The list of references (109) is up-to-date and includes the most recent Russian work. The author reviews free volume theories and carefully distinguishes between the numerous definitions both of free volume and of fractional free volume. He emphasises that the latter is not a universal physical parameter but merely one useful for liquids. The thermodynamics of free volume formation is discussed and the case for the iso-free-volume state at T_g is stated together with evidence against it. The theories relating to distributions of free volume (Cohen-Turnbull, Bueche, Litt) are then described as well as recent work on free volume in heterogeneous polymer systems — glass-filled, carbon black filled etc. This subject is not often discussed in the literature. The effects of polymer structure including Lipatov's own work on epoxy-filled epoxy systems conclude the paper.

The author concludes that the free volume concept, though useful qualitatively, cannot be used quantitatively, and that it does not take sufficient account of intra- and intermolecular interaction and the flexibility of polymer chains. The discussion of *Model Networks* by J. E. Herz, P. Rempp and W. Borchard introduces the relatively new subject of the synthesis of well-defined networks to be as close as possible to ideality. Ideality is defined as requiring homogeneity, elastically effective chains only (i.e. no defects such as pendant chains or loops), Gaussian chain statistics and known functionality at crosslinks.

The methods of making such model networks from linear precursor polymers fitted with reactive groups at each end are briefly described and their approach to ideality discussed.

The experimental methods used to study the networks are swelling by solvents, small angle X-ray diffraction and neutron scattering. The model proposed for their description is an ensemble of spring-supported beads in which the cross links are the beads and the chains the springs.

The experimental results are discussed in terms of the theories of rubber elasticity and in general these theories adequately explain the behaviour of the synthetic networks. The method of *Model Networks* clearly has great value in the study of polymer mechanics particularly if, as seems likely, controlled *defect* structures could be incorporated. In this way we may be able to understand the behaviour of more conventional polymers.

There are 67 references.

The final paper is *NMR approach to the phase structure of linear polyethylene* by R. Kitamaru and K. Horii.

This reviews the recent (up to 1977) literature on the study by n.m.r. of the structure of LPE and covers the liquid state, melt crystallized and solution crystallized solid material and drawn fibres. Considering the molten polymer the authors show that the evidence from line width n.m.r. studies does not support the argument for inhomogeneous structure. Deviations from the Lorentz line shape are explained by a distribution of correlation times.

In the analysis of broad line spectra the method of Bergmann and Nawotki is described, breaking down the absorption spectrum into broad, medium and narrow parts, assigning each to a feature of the structure. In this assignment a schematic model of the folded-chain crystallized polymer is used and the three parts of the spectrum above correlated with the crystalline regions, hindered rotational groups and micro Brownian mobile methylene groups respectively. Analysis of various molecular weight samples both melt crystallized and crystallized from solution is then made including the effects of temperature.

At low molecular weight the broad component predominates while the emergence of the medium and narrow components takes different forms in the bulk and solution-grown material. Indeed, in the latter the liquid-like narrow component is absent, a fact the authors account for by the

restricted conformations resulting from solution growth.

On drawing (to draw ratio 10) the change in the broad component is small but the narrow increases at the expense of the medium, indicating an increase in freely mobile chains. Only one molecular weight (8×10^4) was studied in the fibre drawing experiments; it would be interesting to know how the results depended on molecular weight. It would also be instructive to study higher draw ratios. The authors propose that their n.m.r. studies of solution-grown samples cast doubt on the adjacent re-entry theories of lamellar crystals and support the Flory (1962) model of loops with random lengths connecting the crystal sequences.

R. G. C. Arridge

Flow-Induced Crystallization in Polymer Systems

Edited by Robert L. Miller
Gordon and Breach Science Publishers, New York, London and Paris, 1979. pp. x+370, £23.60. (Midland Macromolecular Monographs Volume 6)

It is not often that a reviewer thumbs through a book, notices a full-page reproduction of one of his own published diagrams and discovers that it has been ascribed to someone else (page 70)! This only serves to illustrate the problems facing an editor when preparing for publication a collection of conference papers. This said, however, it is pleasing to report that this volume suffers less than many such collections from the patchiness and uneven coverage that we have learned to associate with multi-author books of this kind. The reason, perhaps, is that the first five chapters, at least, are good reviews which lead on naturally to the more specific research papers that follow. The review chapters cover general crystallization phenomena, the analysis of crystallization kinetics, crystallization from solutions and crystallization from the melt. The research contributions, which occupy a further eleven chapters, are concerned with these and other subjects such as solidification of polymer fractions, flow induced crystallization, solid state extrusion of crystalline polymers, fibre spinning, ultra-drawing, biaxial stretching, crystal orientation, stiff-chain aromatic polymers and optical studies of stress-induced crystallization. Several of these contributions, though concentrating on their authors' own studies, are written in review style, which further aids the coherence of the book. Overall, then, the subject of polymer crystallization under conditions of flow and deformation is comprehensively covered in a highly readable manner. The book therefore constitutes a valuable statement on the state of knowledge in this field and its relevance to industrial processes.

Each chapter is followed by reported discussion which sometimes, but not always, justifies the space devoted to it. There are some unfortunate choices of running page titles. Thus a chapter on solid-state extrusion has the running title 'solid state crystallization', and one on crystallization under extreme temperature and pressure *gradients* is page-titled 'crystallization under extreme temperature', which is a totally different matter. These however are minor defects and the book can be recommended as a coherent up-to-date source on the subject of polymer crystallization under conditions of flow and deformation, with contributions from many recognised authorities in the field.

E. H. Andrews

Physical Testing of Rubbers

R. P. Brown
Applied Science, London, 1979. pp. xi+327, £18.00

The aim of this book is to present an up-to-date account of rubber testing procedures. It purports to be comprehensive, in that it covers all the tests which are in common use and some which are not. It is essentially a successor to Scott's book of the same title which was published several years ago.

This book largely achieves its aims and objectives. It should therefore prove to be a most useful addition to the library of the practising rubber technologist and also of engineers and designers who are concerned with the use of rubbers as stress-bearing materials. As far as the present reviewer can see, all the major types of test are covered, including tests on unvulcanized rubbers, electrical tests, thermal properties, and tests for resistance to environmental influences. Important matters such as the preparation of test-pieces and their conditioning before test are also considered.

Although the book in its present form will undoubtedly be most useful, and fulfils its aims in a general way, it must be pointed out that it does have some serious deficiencies. It is to be hoped that the author will see fit to rectify these in a second edition. Perhaps the most serious criticism is that the first 50 pages (i.e., approximately one sixth of the book) are virtually wasted. In a book of this size on a subject as large as the physical testing of rubbers, a chapter of 23 pages on standards and standards organizations (which includes, for instance, *inter alia*, the address of the Ghana Standards Board) is a luxury which cannot be afforded. The other main chapter occupying the first 50 pages is entitled "Limitations of Test Results — Statistics". This chapter is so misleading and full of errors as to be best omitted altogether in a subsequent edition. At the beginning of this chapter, the author draws attention to the unpopularity of statistics and attributes it in part to the subject having been severely neglected in schools and universities. A more likely cause is the confusion and error which often accompanies the presentation of the subject in chapter such as the one which this author offers! Two examples of the serious shortcomings of this chapter are as follows: (1) the ordinates of Figures 3.2 and 3.3 should not be labelled "frequency of readings"; the ordinates are frequency densities and not frequencies. The difference between these terms is far from trivial; it is fundamental to the matter of the presentation of frequency distributions for data which refer to a continuous variate, and so to a whole area of the theory and practice of statistics; (2) the basis of the process of Analysis of Variance is the partitioning of sums of squares, and not (as is implied on pp. 42–43) of variances. In preparing a second edition, the author should consider omitting much of the material contained in the first 50 pages of this edition, and using the space thereby made available to deal in more detail with certain aspects of the main theme of the book which are at present largely ignored. Two related aspects which immediately come to mind are (a) the way in which the various test procedures have evolved to their present forms, and (b) the effects of important test variables upon the result obtained.

The second criticism of this book is that the more fundamental aspects of the subject are on the whole not well presented. Students, for instance, will not be encouraged to think sensibly about the fundamentals of the subject. Examples of this deficiency are as follows. (i) The relationship between the two equations given on page 165 is obscure. (ii) It is most misleading to state on page 171 that the expressions for S' and S'' are the solutions of the given differential equation (which is an equation in a variable x). (iii) It is not in the least clear why it is convenient to consider stress as a vector having two components (page 160–161). There are also some unfortunate errors. Thus, for instance, a spring and dashpot in parallel are said to constitute a Maxwell model (page 159).

The third criticism, is that, although the book is generally well written, the language does need tightening up in places. A particularly blatant example is on page 31, where the author states that "All test are not equal"! Assuming that the concept of equality means anything at all applied to a physical test, did anyone ever suppose that all tests are equal? Having recovered from the shock of this statement, the next words are "some are more meaningful than others..."!

The final comment concerns units. Inevitably and regrettably the book deals almost entirely in SI units. However, the present reviewer wishes that the author had not been quite so fulsome in his commendation of these units (page 16). The SI system is seriously defective in at least three important respects. One of these should become immediately apparent if an attempt is made to perform calculations in SI units using the corrected version of the equation given on page 269. (The equation as it stands is incorrect in at least three respects, one of which is probably the result of a printer's setting error.)

To sum up then, this is a very useful book for the practising rubber technologist, and for the engineer and designer who work with rubber, but there is much scope for improvement in a second edition.

D. C. Blackley