Book Reviews

Polymers: Properties and Applications Volume 2 – Polymer Fracture

H. H. Kausch

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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