book reviews

Degradation of Filled Polymers

M. T. Bryk

Ellis Horwood, New York and London, 1991, 185pp, £55.00

ISBN 0-13-202490-X

This volume, subtitled *High Temperature and Thermal-oxidative Processes*, is one of an expanding series on *Polymer Science and Technology* edited by T. J. Kemp and J. F. Kennedy. Professor Mikhail Bryk is the Head of the Department of Physical Chemistry of Membranes at the Institute of Colloid Chemistry, Ukranian Academy of Sciences, Kiev, and is known for his work in the field of polymer composites and filled polymers. The book was originally published in Russian (*Destrucktsiia napolnenykh polimerov*) in 1989 by Khimiya, Moscow, and has been translated by K. A. Babutkina, with translation editing by T. J. Kemp.

In relation to this background, two important comments can be made at the outset. First, the quality of the translation is as near perfect as could ever be expected. There are none of those angularities in the English which are so often present in translated scientific works, and no ambiguities in the science arising from the conversion of the Russian style. Indeed, the book is clear and readable from start to finish. Secondly, the book is a veritable mine of information and references about the compendious work on this subject in the (former) Soviet Union. There are 344 references in total, and it is extremely useful to have a conducted tour through these as one reads the text.

The book is structured quite logically in four sections. The first section considers the thermal and thermal-oxidative stability of a range of polymers of the type which are often used in composites. A wide variety of carbochain, heterochain, and corresponding cyclochain polymers are considered and their breakdown behaviour is discussed in terms of their structure. However, for those not so familiar with the problems of studying thermal and oxidative degradation, a cautionary note may be desirable. Many specific statements are made in the book about the values for rates, activation energies and other degradation parameters (e.g. 'the polymer begins to degrade at 423 K'). These statements do not have the absolute significance that the reader may be tempted to assume, because the values depend very much on how the experiment was performed, on sample size, and on the criteria used to make the judgement. The general significance of this comment is that comparative measurements of the types used may yield useful information about relative stabilities, but calculations based on (for example) the quoted activation energies could result in misleading conclusions about other degradation conditions.

The second section of the book considers the types of inorganic polymer fillers generally used, and examines their thermal properties in isolation. The materials include metals and their oxides and salts; silicas, silicates and glass; and carbon and graphite. The surface chemistry, and physical and chemical properties of these fillers are discussed in relation to their usefulness in providing thermal or thermal-oxidative stability of polymers. In most cases the introduction of a filler increases the stability of the host polymer, and this is generally attributed either to their effect in decreasing the kinetic mobility of the macromolecules, or the contributions of their surfaces to chain termination processes. However, some fillers, especially metals or metal oxides, can promote oxidative degradation of the host polymer.

The third section is concerned with methods of studying the thermal and oxidative degradation of the filled polymers. The methods themselves are not different from those used to study the degradation of conventional polymers (e.g. thermal analysis, spectroscopic, mass spectroscopic and chromatographic methods) but the special problems of studying filled polymers (not least of which are the methods of production and introduction of the filler into the polymer, and the form of the sample to be used for analysis) are given appropriate consideration. The use and limitations of dynamic t.g.a. (i.e. temperature-ramped t.g.a.) are discussed as a method for obtaining the total kinetic parameters for the degradation process. The usual mathematical treatment of this is given, involving the attribution of an 'effective reaction order'. The reviewer has little confidence in kinetic parameters obtained in this way, and would be rather more cautious than the author in recommending it.

The final section reviews a host of published work on the thermal and oxidative degradation of filled polymers, and a lot of ground is covered in the 44 pages devoted to this. Many contradictory results have been published in the literature, and the author sets out in a systematic way to assess the extent to which the structure and properties of the polymer and those of the filler (especially its surface chemistry) contribute to the thermal and oxidative degradation. It is, of course, inevitable that the selection of systems and examples will be coloured by the author's interests and experience, but the reviewer found it a little surprising that there appears to be no mention whatever of the effects of carbon on the thermal and oxidative degradation of rubber, whereas the effects of many metals and metal oxides are included.

This book is a valuable source book, not only for those who have to deal with and utilize commercial filled polymers, but also for those who are faced with the problem of selecting an appropriate filler for a host polymer. If, as a result of this book, an enlightened selection is made on the basis of the overall thermal stability, then the author and the translators should receive the credit they deserve.

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Frontiers of Organosilicon Chemistry

Edited by A. R. Bassindale and P. P. Gaspar

Royal Society of Chemistry, Cambridge, 1991, £52.50

ISBN 0-85186-097-4

This book reports the proceedings of the IXth International Symposium on Organosilicon Chemistry held in Edinburgh in July 1990, a very successful conference attended by over 500 participants who presented and discussed their work in a hundred or so papers and twice as many posters. Invited contributions from a mixture of established experts and younger scientists are reproduced here as short surveys (10–12 pp.) of their respective areas.

Inevitably, the treatment they give is varied. The use of camera-ready copy makes the occasional diagram difficult to decipher, and the subject matter is necessarily selective; styles range from highly personal to objective, and the coverage of relevant literature from full

to scant, though most articles exude authority. As a record of the highlights of the conference, and a series of snapshots of what is going on in this very lively area of chemistry, straddling the borderlines of organic and inorganic chemistry and their interface with polymer and materials science, this book will prove invaluable to all interested parties, including many who do not realize they have an interest until they dip into its pages.

The section of most interest to readers of this journal is the first (pp. 3–85), dealing with silicon-based polymeric materials. Later sections deal with mechanistic aspects (gas-phase and photochemical reactions, pp. 89–181; hypervalent silicon, nucleophilic substitution and biotransformations, pp. 185–228), with structural aspects and new organosilicon compounds (pp. 231–318) and with organic syntheses using silicon (pp. 321–398). The book concludes with a helpful (12 pp.) subject index, two pages of which provide rapid access to discussions of individual polymers.

The editors see polymeric materials as occupying a dominant position in organosilicon chemistry these days, and illustrate activity in the area by seven contributions. The book starts with a chapter by T. J. Barton surveying (with frustratingly few references) the 'wonderful world of silicon on unsaturated carbon', touching on the effects of silyl substituents on unsaturated compounds, syntheses of polymers incorporating silicon atoms and alkene or alkyne functions in the chain, silicon carbide generation therefrom, and organosilicon substituted polyacetylenes. Routes to silicon ceramics incorporating boron (Si_3N_4/BN blends) via silazane/borazine polymeric precursors are surveyed by D. Seyferth *et al.*, who have generated novel Si_2B_{10} icosahedral species in the course of work on decaborane-silylamine precursors. Dow Corning activity on organosilicon preceramic polymer technology is surveyed by W. H. Atwell, G. T. Burns and G. A. Zank who focus particularly on silicon carbide work. Routes to silicon carbide via polymers incorporating $SiCH_2$ units also feature in papers by J. Dunoguès *et al.* and by L. E. Gusel'nikov and Yu. P. Polyakov, while H. Schmidbaur *et al.* focus on routes to silicon/silicon carbide materials via silylmethane (as opposed to organosilylmethane) precursors. Polymers incorporating silicon–silicon as well as silicon–oxygen bonds in the chain are described by J. Chojnowski *et al.*, and A. Stroh concludes the section on polymers by drawing attention to an issue that is acquiring increasing importance in polymer work, i.e. the extent to which polymers – in this case silicones – can be recycled or made more efficiently.

Polymer interests, or features of interest to polymer chemists, abound elsewhere in this book, whether in discussions of reactions by which polymers may be made or degraded, or in studies of model monomers or oligomers, among which one notes the work of I. M. T. Davidson, T. Simpson and R. G. Taylor on the mechanism of pyrolysis of polysilanes, that of Y. Ito on Pd-catalysed insertion reactions of polysilanes, and M. F. Lappert's survey of systems with low coordination numbers stabilized by bulky bis(trimethylsilyl) methyl ligands, a model of how to lead the reader to the relevant literature.

To conclude, the wide range of topics covered in this book, including synthetic, mechanistic and structural aspects of molecular and macromolecular organosilicon chemistry, the authoritative manner in which these topics are discussed, and the short chapter format makes this, as the editors had hoped, a well-balanced introduction to the area for the industrialist as well as the academic.

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Oxidation of Stressed Polymers

A. Popov, N. Rapoport and G. Zaikov
Gordon and Breach, 1991, 335 pp, £50.00
ISBN 2-88124-735-0

This book is a translation from a Russian original, first published in 1987. The authors are all members of the Institute of Chemical Physics in Moscow.

The oxidative degradation of polymers in service use has been a significant problem for many years and has received a great deal of study. Surprisingly, the effects of mechanical stress on degradation have had very little attention, especially outside Russia, and this book is largely a summary of Russian work.

Over many years there has been a marked difference in approach between Russian and Western scientists to the problems of polymer oxidation. Russian workers have seen degradation as basically a collection of chemical reactions subject to kinetic analysis, albeit with rate constants which may depend upon the nature of the solid state in which the reaction occurs. This approach has produced huge volumes of highly mathematical papers. Western scientists have tended to dismiss kinetic analyses as irrelevant to the complex processes of heterogeneous oxidation in a solid polymer.

This book has a very Russian feel. It is full of kinetic arguments and detailed interpretations of the effects of stress or orientation on the rate constants of individual reaction steps. It would be easy to dismiss a lot of the arguments but this would be to throw away a very substantial amount of useful data and discussion. The book contains a very large amount of data on the effects of morphology, orientation and stress on the oxidation (mainly thermal) of polymers (mainly polyolefins). There is much of interest, much that is thought provoking, and much to disagree with!

This is an interesting book for its specialist audience. It is well produced though there are a fair number of minor proofing errors. It can be recommended but the reader is advised to engage his or her critical faculties fully before beginning reading. The index is dreadful, occupying about a half page.

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Polymer Processing Principles and Modeling

J.-F. Agassant, P. Avenas, J.-Ph. Sergent and P. J. Carreau
Hanser Publishers, Munich, 1991, 500 pp, £46.00
ISBN 3-446-14584-2

The authors have set themselves two targets: (i) to produce a student textbook; (ii) to assist engineers and technologists in the polymer processing industries to bridge the gap between theory and practical applications. The first aim appears to have been achieved with more success than the second. The student reader is taken through phenomena from first principles, with derivations of basic equations which are then modified to account for deviations from the basic theory and usefully applied to polymer processes. Each chapter is illustrated with examples of applications and with problems (and detailed solutions). Where necessary students can refer to appendices for the more detailed mathematical derivations of heat transfer, molecular interpretation of viscosity models for rheological behaviour and the effect of processing conditions on viscosity.

Much of this approach is equally relevant to the practising engineer but, as might be expected, the examples of applications are not comprehensive. Calendering, conventional single-screw extruders, selected extrusion dies, fibre forming and film forming (cast and blown) all receive detailed treatment but scant mention is made of twin screw extrusion, dispersive and distributive mixing and analysis of more complex dies (e.g. co-extrusion). Although stretching of a melt in uniaxial and biaxial modes under cooling conditions is well covered