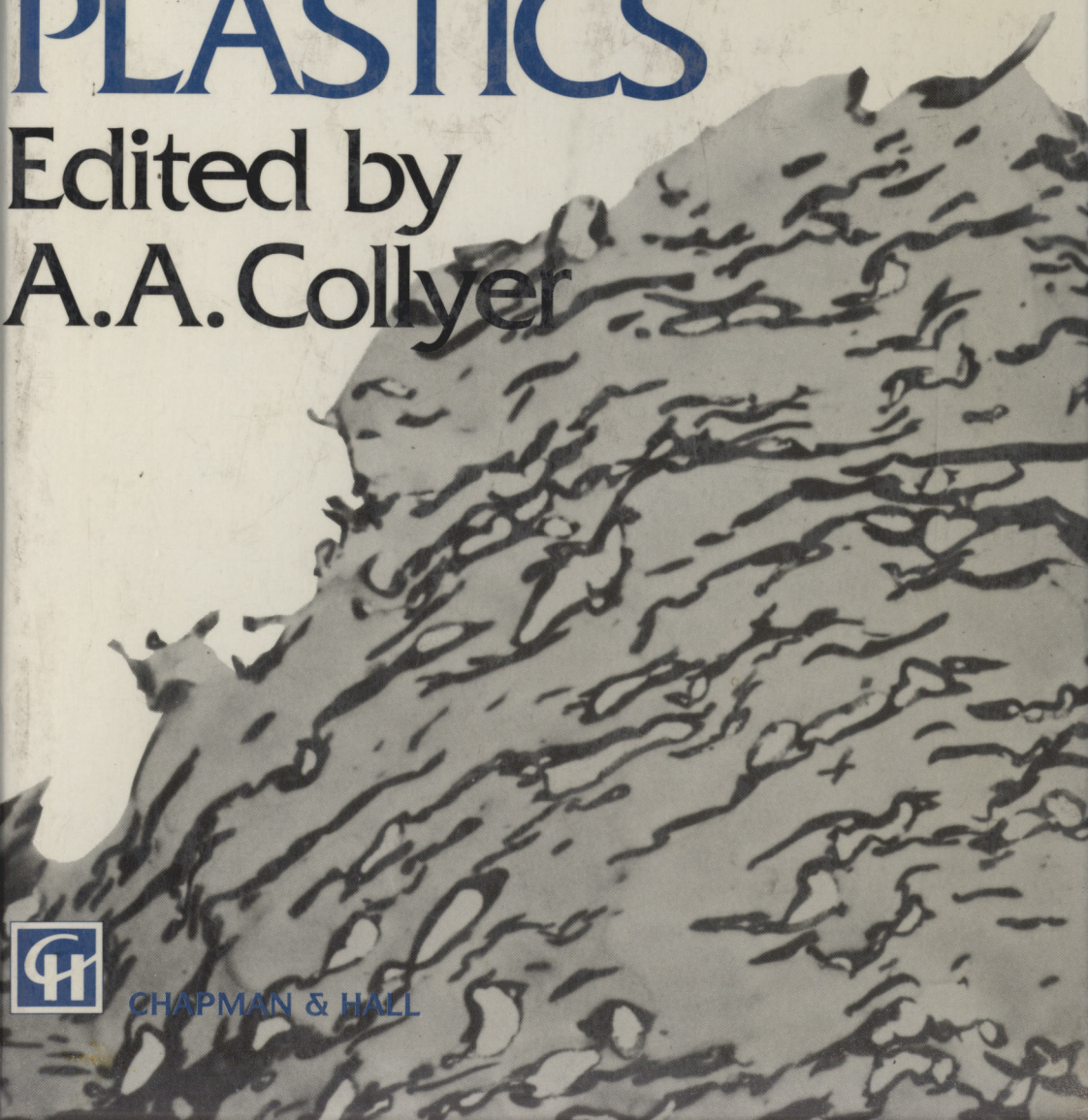


RUBBER TOUGHENED ENGINEERING PLASTICS

Edited by
A.A. Collyer



CHAPMAN & HALL

TQ322.3

W 1

Rubber Toughened Engineering Plastics

Edited by

A. A. Collyer

*Formerly at the Division of Applied Physics
School of Science
Sheffield Hallam University, UK*

江苏工业学院图书馆
藏书章



CHAPMAN & HALL

London · Glasgow · Weinheim · New York · Tokyo · Melbourne · Madras

Published by Chapman & Hall, 2-6 Boundary Row, London SE1 8HN, UK

Chapman & Hall, 2-6 Boundary Row, London SE1 8HN, UK

Blackie Academic & Professional, Wester Cleddens Road, Bishopbriggs,
Glasgow G64 2NZ, UK

Chapman & Hall GmbH, Pappelallee 3, 69469 Weinheim, Germany

Chapman & Hall Japan, Thomson Publishing Japan, Hirakawacho Nemoto
Building, 6F, 1-7-11 Hirakawa-cho, Chiyoda-ku, Tokyo 102, Japan

Chapman & Hall Australia, Thomas Nelson Australia, 102 Dodds Street, South
Melbourne, Victoria 3205, Australia

Chapman & Hall India, R. Seshadri, 32 Second Main Road, CIT East, Madras
600 035, India

First edition 1994

© 1994 Chapman & Hall

Typeset in Times 10/12pt by Thomson Press (India) Ltd, New Delhi
Printed in Great Britain at the University Press, Cambridge

ISBN 0 412 58380 1

Apart from any fair dealing for the purposes of research or private study, or criticism or review, as permitted under the UK Copyright Designs and Patents Act, 1988, this publication may not be reproduced, stored, or transmitted, in any form or by any means, without the prior permission in writing of the publishers, or in the case of reprographic reproduction only in accordance with the terms of the licences issued by the Copyright Licensing Agency in the UK, or in accordance with the terms of licences issued by the appropriate Reproduction Rights Organization outside the UK. Enquiries concerning reproduction outside the terms stated here should be sent to the publishers at the London address printed on this page.

The publisher makes no representation, express or implied, with regard to the accuracy of the information contained in this book and cannot accept any legal responsibility or liability for any errors or omissions that may be made.

A catalogue record for this book is available from the British Library

Library of Congress Catalog Card Number: 93-74886

Rubber Toughened Engineering Plastics

List of contributors

A. A. Collyer
Flat 2, 9 Elmhyrst Road
Weston Super Mare BS23 2SJ
UK

A. M. Donald
Department of Physics
University of Cambridge
Cavendish Laboratory
Madingley Road
Cambridge CB3 0HE
UK

R. J. Gaymans
University of Twente
PO Box 217
7500 AE Enschede
The Netherlands

D. J. Hourston
The Polymer Centre
Lancaster University
Lancaster LA1 4YA
UK

H. Keskkula
Department of Chemical Engineering
University of Texas
Austin
TX 78712
USA

S. Lane
The Polymer Centre
Lancaster University
Lancaster LA1 4YA
UK

G. C. McGrath
Engineering Department
TWI
Abington Hall
Abington
Cambridge CB1 6AL
UK

D. Parker
ICI Advanced Materials
PO Box 90
Wilton
Middlesbrough TS6 8JE
UK

D. R. Paul
Department of Chemical Engineering
University of Texas
Austin
TX 78712
USA

A. Savadori
EniChem
Casella Postale 12120
20120 Milano
Italy

S. J. Shaw
Materials and Structures Department, Defence Research Establishment,
Building R178, Farnborough, Hampshire GU14 6TD, UK

I. Walker
International Paints Ltd
18 Hanover Square
London W1A 1AD
UK

G. W. Wheatley
3 Hermes Close
Hull HU9 4DS
UK

Preface

The rubber toughening of polymers such as polystyrene has been successfully carried out for many years, and has led to many diverse engineering materials such as high impact polystyrene (HIPS), acrylonitrile-butadiene-styrene (ABS) and styrene-butadiene-styrene copolymers (SBS). The synthetic routes to manufacture are well understood and most adequately documented. For the high temperature engineering and speciality plastics this is certainly not the case; difficulties are encountered both in the choice of rubber for the dispersed phase and in the synthetic routes involved for obtaining the optimum particle size for toughening and in obtaining adequate interfacial adhesion. This book is intended to bring out the main physical principles involved in optimum toughening and to describe the synthetic strategies used to obtain satisfactorily toughened grades in these materials.

The book may be divided into two parts: in the first section Chapters 1, 2 and 3 deal with failure mechanisms and toughening mechanisms in pure polymer matrices and in fibre reinforced composites, with Chapter 4 discussing the numerous methods available for the evaluation of toughened plastics materials. Chapter 5 reviews the wide spectrum of toughening agents available for engineering polymers. The second section of the book is devoted to describing the synthetic routes and toughening strategies involved for various polymer matrices, namely epoxies, polyamides, polyesters and polycarbonates, polysulphones and polyaryletherketones, and polyimides.

This work is intended for research and development workers in universities and industry with an interest in polymeric materials and polymer chemistry, and it is hoped that the book acts as a satisfactory focus for the current thought on rubber toughening principles and the methods employed for the rubber toughening of major engineering and speciality plastics.

Contents

| | |
|---|-----------|
| List of contributors | ix |
| Preface | xi |
| 1 Failure mechanisms in polymeric materials | 1 |
| <i>A. M. Donald</i> | |
| 1.1 Introduction | 1 |
| 1.2 Mechanical properties – some definitions | 4 |
| 1.3 Shear deformation | 8 |
| 1.4 Crazeing | 12 |
| 1.5 Interactions of crazes and shear bands | 20 |
| 1.6 Molecular mechanisms involved in deformation | 20 |
| 1.7 Conclusions | 26 |
| References | 27 |
| 2 Rubber toughening mechanisms in polymeric materials | 29 |
| <i>I. Walker and A. A. Collyer</i> | |
| 2.1 Introduction | 29 |
| 2.2 Miscibility and dispersion of the rubber phase | 34 |
| 2.3 Effect of the dispersed rubber phase | 36 |
| 2.4 Toughening mechanisms | 47 |
| References | 53 |
| 3 Fracture and toughening in fibre reinforced polymer composites | 57 |
| <i>G. C. McGrath</i> | |
| 3.1 Introduction | 57 |
| 3.2 Matrices for composite systems | 57 |
| 3.3 Micromechanical analysis | 61 |
| 3.4 Damage in composite materials | 68 |
| 3.5 Failure of laminates | 73 |

| | |
|---|------------|
| 3.6 Fracture toughness | 78 |
| 3.7 Concluding remarks | 86 |
| References | 87 |
| 4 Methods of measurement and interpretation of results | 90 |
| <i>A. Savadori</i> | |
| 4.1 Introduction | 90 |
| 4.2 Basic mechanical parameters | 92 |
| 4.3 A traditional approach to strength evaluation | 98 |
| 4.4 Fracture mechanics approach | 105 |
| 4.5 Fractography | 123 |
| 4.6 Engineering design requirements | 126 |
| 4.7 Conclusions | 129 |
| Appendix 4.A Symbols and abbreviations | 130 |
| References | 132 |
| 5 Toughening agents for engineering polymers | 136 |
| <i>H. Keskkula and D. R. Paul</i> | |
| 5.1 Introduction | 136 |
| 5.2 Background | 137 |
| 5.3 Gum elastomers | 140 |
| 5.4 Emulsion made elastomers | 146 |
| 5.5 Block copolymers | 150 |
| 5.6 Maleic anhydride modified polymers | 154 |
| 5.7 Future trends | 160 |
| References | 161 |
| 6 Rubber modified epoxy resins | 165 |
| <i>S. J. Shaw</i> | |
| 6.1 Introduction | 165 |
| 6.2 Formulation and chemistry | 165 |
| 6.3 Toughening mechanisms | 173 |
| 6.4 Comparison of toughening methods | 177 |
| 6.5 Bulk fracture and mechanical properties | 180 |
| 6.6 Adhesive joint properties | 197 |
| 6.7 Composite fracture | 205 |
| References | 207 |
| 7 Toughened polyamides | 210 |
| <i>R. J. Gaymans</i> | |
| 7.1 Introduction | 210 |
| 7.2 Blend formation | 213 |
| 7.3 Parameters affecting impact toughness | 220 |
| 7.4 Fracture graphics | 229 |

| | |
|---|------------|
| 7.5 Toughening mechanisms | 230 |
| 7.6 Rubber toughened composites | 235 |
| References | 239 |
| 8 Toughened polyesters and polycarbonates | 243 |
| <i>D. J. Hourston and S. Lane</i> | |
| 8.1 Introduction | 243 |
| 8.2 Polybutylene terephthalate | 243 |
| 8.3 Polycarbonates | 254 |
| 8.4 Polyethylene terephthalate | 258 |
| References | 259 |
| 9 Toughened polysulphones and polyaryletherketones | 264 |
| <i>G. W. Wheatley and D. Parker</i> | |
| 9.1 Introduction | 264 |
| 9.2 Toughened Udel polysulphone blends | 271 |
| 9.3 Toughened polyethersulphone blends | 286 |
| 9.4 Toughened Victrex polyetheretherketone blends | 304 |
| 9.5 Conclusions | 306 |
| Acknowledgement | 308 |
| References | 308 |
| 10 Toughened polyimides | 310 |
| <i>S. J. Shaw</i> | |
| 10.1 Introduction | 310 |
| 10.2 High temperature processable polymers | 311 |
| 10.3 Rubber modification | 322 |
| 10.4 Comparisons with other toughening techniques | 352 |
| 10.5 Concluding remarks | 353 |
| References | 353 |
| Index | 357 |

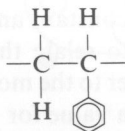
Failure mechanisms in polymeric materials

A. M. Donald

1.1 INTRODUCTION

Polymers differ from other molecules by virtue of their size. They are macromolecules, whose total molecular weight (or relative molar mass) may reach millions. As we shall see, this has important consequences for their response to mechanical stress or strain. In particular, whereas most materials (including polymers) which exhibit any degree of ductility may show a shear response, an alternative mode of deformation is also open to polymeric materials and to them alone, the mechanism known as crazing. In order to understand toughening and failure mechanisms in polymers, one therefore has first to look at the nature of the polymer chains. Only a brief overview of salient facts will be presented here to introduce the key factors and terminology. The interested reader is referred to other texts (e.g. Refs 1–3) for a broader picture.

Many of the recent fundamental studies of micromechanisms of deformation have been carried out on the vinyl polymer polystyrene (PS), which forms the basis of the rubber toughened material high impact polystyrene (HIPS), and this will be used as a model to introduce some basic concepts. A polymer consists of a series of monomer units joined together to form a long chain. For most of the materials to be discussed in this book the polymer will consist of only one type of unit, and for PS this monomer is



This unit is repeated n times, where n is known as the degree of polymerization.

One of the attractions of polystyrene as a model material is that it can be obtained in monodisperse form. This means that a polymerization route exists

(so-called anionic polymerization) enabling control over the molecular weight to be achieved, so that the chains are all essentially the same length (same n). This is in contrast to normal commercial materials which will be polydisperse. The degree of polydispersity is normally characterized by considering different moments of the molecular weight distribution, the most normal ratio chosen being that of \bar{M}_w/\bar{M}_n . In this expression \bar{M}_w , the weight-average molecular weight, and \bar{M}_n , the number average, are defined by

$$\bar{M}_w = \frac{\sum (N_i M_i) M_i}{\sum N_i M_i} \quad \text{and} \quad \bar{M}_n = \frac{\sum N_i M_i}{\sum N_i}$$

where N_i is the number of molecules of molecular weight M_i , and \sum implies summation over all i molecular weights. If all the chains are the same length, then the ratio \bar{M}_w/\bar{M}_n will be unity. For monodisperse PS the best achievable samples will have $\bar{M}_w/\bar{M}_n \approx 1.03$, whereas commercial samples of most polymers are likely to have $\bar{M}_w/\bar{M}_n \approx 2$. In practice, as will be seen below, the presence of a low molecular weight tail to the molecular weight distribution may have a significant effect on the deformation. Useful samples of PS are likely to have $\bar{M}_w > 200\,000$.

The conformation of a PS chain in both the melt and the glass has been shown to be that of a random or Gaussian coil [4]. This means that the chain follows a random walk, whose root mean square (r.m.s.) end-to-end distance is proportional to the square root of the number of monomers in the chain. Each chain can therefore be thought of as a loose coil which is penetrated by its neighbours, and this will be true both above and below the glass transition temperature T_g .

In the melt it has long been recognized that the presence of entanglements plays a key role in determining the viscoelastic response of the polymer (see, for example, Ref. 5). These entanglements were originally thought of as simple topological knots analogous to crosslinks in a rubber. This idea was based on the similarity of rheological data of linear (non-crystalline) polymers above T_g and crosslinked rubbers, as shown schematically in Fig. 1.1. For a rubber the shear modulus G in the so-called plateau region (Fig. 1.1) above T_g is related to the molecular weight between crosslinks M_c by

$$G = \frac{\rho RT}{M_c}$$

where ρ is the density, R the gas constant and T the absolute temperature. A similar expression is then used to relate the shear modulus in the plateau region of an uncrosslinked polymer to the molecular weight between entanglements, M_e . For PS this leads to a value for M_e of $\sim 19\,000$, this value being independent of total chain length for high molecular weight polymers. It will become clear that this quantity, which can only be established unequivocally above T_g , appears to play a crucial role in determining the response of the polymer to mechanical stresses below T_g .

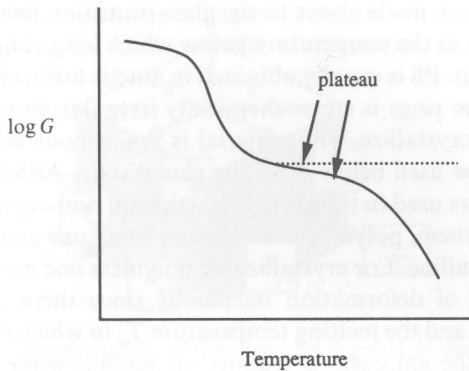


Fig. 1.1 Schematic representation of the variation of shear modulus with temperature for crosslinked (.....) and uncrosslinked (—) polymers.

Recent ideas no longer necessarily envisage the entanglements as being localized point constraints. The approaches of De Gennes [6] and Doi and Edwards [7] suggest instead that the constraints imposed on one chain by its neighbours can be represented by a tube, of diameter equal to the distance between entanglements, within which the particular chain is confined (Fig. 1.2). When the chain moves it can only do so along the tube, a process known as **reptation**; it cannot cross the boundaries of the tube. As the chain moves and its end comes out of one end of the tube, then the memory of that part of the tube is lost. Ultimately this means that the whole chain in a melt can diffuse across a sample, but the process is obviously far slower than it would be if the tube were not present.

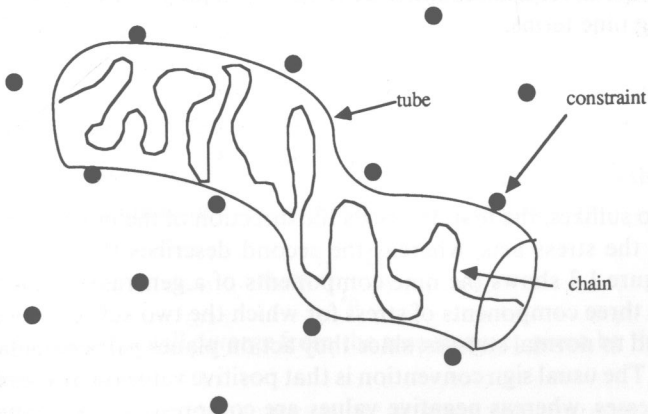


Fig. 1.2 Schematic representation of the tube model of De Gennes [6] and Doi and Edwards [7]. The chain is confined to a tube by entanglements arising from the presence of other chains.

Reference has been made above to the glass transition temperature T_g . This is frequently taken as the temperature below which long-range motions of the chain are frozen out. PS is usually obtained in atactic form, i.e. the distribution of pendent benzene rings is stereochemically irregular along the chains and thus they cannot crystallize. The material is amorphous and in engineering applications will be used below T_g in the glassy state. Although many of the important polymers used in toughened plastics are non-crystalline, this is not the case for all of them, polyetheretherketone being one example of a matrix that is highly crystalline. For crystallizable polymers one may expect an additional complexity of deformation behaviour since there is a temperature regime between T_g and the melting temperature T_m in which one population of chains – those in the amorphous regions – is mobile, while other chains (or indeed other parts of the same chains) are pinned in the crystals. At the fundamental level comparatively little is known about the behaviour in this regime (for a description of deformation in crystalline polymers the reader should consult the recent reviews by Friedrich [8] and by Narisawa and Ishikawa [9]). This chapter will confine itself to amorphous polymers for which the picture is becoming rather clearer.

1.2 MECHANICAL PROPERTIES – SOME DEFINITIONS

Whereas, to the layman, stress and strain are often used synonymously, in the context of mechanical properties they have very distinct meanings. **Stress** is a force per unit area. Since during deformation the cross-sectional area of a sample usually changes, it is important to distinguish between **true** stress – the force per instantaneous cross-sectional area – and **nominal** (or engineering) stress which is the force divided by the initial (undeformed) cross-sectional area. In general, for a solid, the stress can be represented by a stress tensor σ_{ij} containing nine terms:

$$\sigma_{ij} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix}.$$

Of the two suffixes, the first describes the direction of the normal to the plane on which the stress acts, whereas the second describes the direction of the stress. Figure 1.3 shows the nine components of a general stress acting on a cube. The three components of stress for which the two suffixes are equal, σ_{ii} , correspond to normal stresses, since they act on planes perpendicular to their direction. The usual sign convention is that positive values of σ_{ii} correspond to tensile stresses, whereas negative values are compressive. The remaining six stresses are shear stresses which tend to cause the body to rotate. In order for this motion not to occur, it is necessary for σ_{ij} to equal σ_{ji} so that there is no resultant torque. This means that in a static situation only six of the nine compo-

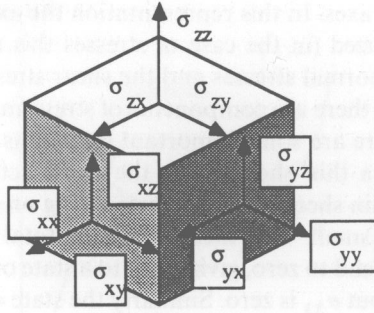


Fig. 1.3 Schematic representation of the nine components of stress acting on a cube.

nents of the stress tensor are independent. It is frequently useful to split the stress applied to a polymer into two components: a hydrostatic or dilational component, which gives rise to a volume change, and a deviatoric or pure shear component, which causes a change in shape. The hydrostatic component p can be written

$$p = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33}).$$

The deviatoric component σ'_{ij} can then be written by subtracting the hydrostatic component from the original tensor to yield

$$\sigma'_{ij} = \begin{bmatrix} \sigma_{11} - p & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} - p & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} - p \end{bmatrix}.$$

Strain ϵ_{ij} is likewise a tensor, and can be written using nine components in the most general case:

$$\epsilon_{ij} = \begin{bmatrix} \epsilon_{11} & \epsilon_{12} & \epsilon_{13} \\ \epsilon_{21} & \epsilon_{22} & \epsilon_{23} \\ \epsilon_{31} & \epsilon_{32} & \epsilon_{33} \end{bmatrix}.$$

In a simple uniaxial test, strain is particularly easily defined. If l_0 is the original length and l_1 is the final, then the **nominal** strain ϵ_n is given by

$$\epsilon_n = \frac{l_1 - l_0}{l_0}.$$

For larger strains this will diverge from the **true** strain ϵ_t , given by the integral of the above equation:

$$\epsilon_t = \int_{l_1}^{l_0} \frac{dl}{l} = \ln \left(\frac{l_1}{l_0} \right).$$

Both stress and strain can be described in terms of three **principal** components

acting along principal axes. In this representation the axes are so chosen that the tensor is diagonalized (in the case of stresses this means that the three principal stresses are normal stresses and the shear stresses are zero).

Although in general there are components of stress and strain acting across all faces of a cube, there are some important situations where this is not the case. One example is a thin sheet. Since the stress acting normal to a free surface is zero, for a thin sheet all the stresses acting on planes parallel to the sheet surface must be small. This means that the total stress normal to the plane of the sheet will tend to zero, giving rise to a state of **plane stress** in which σ_{11} and σ_{22} are finite but σ_{33} is zero. Similarly the state of strain in which one of the principal components vanishes is known as **plane strain**. This situation arises for instance in relatively thick samples in the vicinity of a crack tip where the material is constrained.

Stress and strain are related through a modulus. The familiar example is Young's modulus that relates stress and strain in a tensile test, but more generally, since stress and strain are both tensors, a fourth-order tensor c_{ijkl} is required:

$$\sigma_{ij} = c_{ijkl} \epsilon_{kl}$$

where summation is implied over both i and j . Although this stiffness tensor c_{ijkl} in principle contains 81 components, symmetry reduces this to only 2 for an elastically isotropic solid such as a glassy polymer [10]. Three parameters are commonly used to characterize the polymer: Young's modulus E , the shear modulus G , and Poisson's ratio ν . (When a stress σ_{11} is applied along the 1 axis there are resulting strains of $-\nu\sigma_{11}/E$ along the 2 and 3 directions.) These three are related by the equation $E = 2(1 + \nu)G$.

It is clearly important, when attempting to characterize the response of a material to a stress or strain field, that these fields are as well characterized as possible. To this end it is necessary to work with samples of well-defined geometry. The chapter by Bowden in Ref. 1 provides an excellent review of the subject. With this information it then becomes possible to map out the different stress states that give rise to a particular type of deformation. However, many studies restrict themselves to the simplest cases of uniaxial tension or plane strain compression.

Most materials show a linear elastic response at low strains, and polymers are no exception. As the stress and strain increase, for many polymers a **yield point** is passed, as shown in Fig. 1.4. Loosely speaking, the yield point corresponds to the point after which increasing strain occurs under a lower stress, so that (as in Fig. 1.4) it corresponds to the maximum in the curve. Beyond this point, deformation is certainly occurring plastically (i.e. the deformation cannot be recovered if the stress is removed), but for many polymers the onset of plastic deformation actually precedes the yield point defined as above.

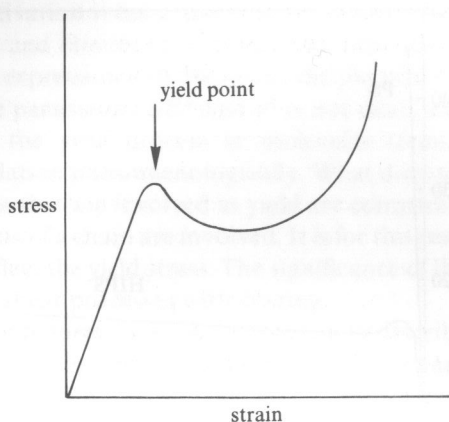


Fig. 1.4 Schematic stress–strain curve with yield point.

When identifying the yield point with the maximum in Fig.1.4 a couple of caveats are in order. Firstly, if nominal stress is plotted against strain a maximum may occur which actually reflects a geometrical instability of the sample rather than a true intrinsic yield point; to identify the intrinsic yield point requires that true stress is plotted. Secondly, not all polymers exhibit a maximum; for those that do not, an intrinsic yield point can usually be identified with a kink in the true stress–strain curve. In general, as strain continues to rise a point will be reached at which orientation hardening sets in. This means that whereas beyond the yield point strain increases under a decreasing stress, when orientation hardening sets in the stress required for further strain increases again, and often quite steeply. Although for most polymers stressed at temperatures close to T_g homogeneous plastic deformation may occur uniformly throughout a sample, in many instances of room temperature testing the deformation actually proceeds inhomogeneously, with localized regions of extensive deformation surrounded by material that has only deformed elastically. These regions may consist of either shear deformation or crazing, to be described fully below.

Since in this book we are interested in toughened polymers, we need to define what we mean by **toughness**. A tough material is one that absorbs a large amount of energy before failure, in contrast to a brittle one that does not. This means that there needs to be available to the polymer one or more deformation mechanisms which absorb energy before crack propagation occurs. Figure 1.5 shows the contrasting behaviour of PS and HIPS. PS is a brittle material which fractures before yield. Crazing does precede fracture, but only to a very limited extent. In contrast to this, in HIPS the rubber particles promote extensive craze formation throughout the sample, and since a large number are generated before any fail to give rise to crack propagation this is an