

## The Physics of Deformation and Fracture of Polymers

Demonstrating through examples, this book presents a mechanism-based perspective on the broad range of deformation and fracture responses of solid polymers. It draws on the results of probing experiments and considers the similar mechanical responses of amorphous metals and inorganic compounds to develop advanced methodology for generating more precise forms of modeling. This, in turn, provides better fundamental understanding of deformation and fracture phenomena in solid polymers. Such mechanism-based constitutive response forms have far-reaching application potential in the prediction of structural responses and in tailoring special microstructures for tough behavior. Moreover, they can guide the development of computational codes for deformation processing of polymers at any level. Applications can range from large-strain industrial deformation texturing to production of precision micro-fluidic devices, making this book of interest both to advanced graduate students and to practicing professionals.

ALI S. ARGON is Quentin Berg Professor Emeritus in the Department of Mechanical Engineering at Massachusetts Institute of Technology (MIT). He is recognized world-wide as an authority on the mechanical behavior of engineering solids, has published over 300 papers and three books, and is one of the internationally most widely cited authors in materials science. He has received a number of honors and awards, including membership of the US National Academy of Engineering, Fellowship of the American Physical Society, Distinguished Life Membership of the Alpha Sigma Mu (International Professional Society of Materials and Engineering), the Nadai Medal of the American Society of Mechanical Engineers, the Heyn Medal of the German Society for Materials Science, and a US Senior Scientist Award of the Alexander von Humboldt Foundation for research in Germany.

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A. S. ARGON

Massachusetts Institute of Technology



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**This book is dedicated to  
Ian M. Ward of Leeds University for his long-term friendship  
and to  
my wife Xenia for her enduring support**

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**“An insightful exposition from one of the most influential material scientists of our time. A must read for anybody wishing to gain a mechanician’s (not a chemist’s!) perspective on the physics and mechanics of polymers.”**  
*Vasily Bulatov, Lawrence Livermore National Laboratory*

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## Preface

The chemistry and physics of polymers, and their molecular microstructure, morphology, and larger-scale organization have been extensively studied and described in many treatises.

In comparison the plastic deformation and fracture processes, both in the laboratory and in industrial practice, have largely been dealt with at a phenomenological level, and often separately for different polymers and blends, rather than from a unified and comprehensive mechanistic perspective. This has left the mechanisms governing the deformation and fracture resistance of polymers far less well understood.

On the other hand, fundamental developments in polymer physics and polymer materials science in the recent past are now making it possible to consider broad ranges of their deformation and fracture from a mechanistic point of view at an appropriate molecular and morphological level. Moreover, insight gained from studies of corresponding responses of amorphous metals and semiconductors, reinforced by computational simulations and mechanistic modeling, has also broadened the perspective.

The purpose of this book is to present a coherent picture of the inelastic deformation and fracture of polymers from a mechanistic point of view, addressed to graduate students of material science and mechanical engineering and to professional practitioners in the field.

The book concentrates heavily on research conducted at the Massachusetts Institute of Technology from the mid 1980s to the mid 2000s by the author and a group of collaborators. It reports on extensive experimental studies and related computational simulations. In the latter there is much emphasis on development of mechanistic models ranging from unit plastic relaxation events to the evolution of deformation textures in channel die compression flow to large plastic strains. At every level the experimental results are compared in detail with predictions from the models.

The core of the book is devoted to subjects starting with anelastic behavior of polymers and rubber elasticity, but proceeds with greater emphasis in following chapters to mechanisms of plastic relaxations in glassy polymers and semi-crystalline polymers with initial spherulitic morphology. Other chapters concentrate on craze plasticity in homo-polymers and block copolymers, culminating with a chapter on toughening mechanisms in brittle polymers. To make the

main chapters on plastic flow and toughening tractable to the reader, the book starts with a brief tutorial chapter devoted to the structure of polymers from the chain molecular levels to morphological aggregation of crystalline lamellae and their further aggregation into spherulites. Since unit plastic relaxations are complex phenomena in glassy polymers, which, however, exhibit parallel phenomena that can be followed more transparently in amorphous metals and amorphous silicon, a chapter is also included at the start on the atomic structure of such simpler elemental glasses. Finally, since fracture involves propagation of cracks emanating from notches, with crack tips being modified by plastic zones of various levels of pervasiveness, a relatively comprehensive chapter on fracture mechanisms and mechanics is included to precede the chapter on toughening mechanisms.

Each chapter starts with an overview laying out the topics to be presented to give an overall perspective. Copious references are provided at the ends of chapters, often supplemented with lists of additional references that develop some topics in greater depth.

It is assumed that the reader has had an introductory course on materials science and perhaps on polymers such as e.g. *An Introduction to the Mechanical Properties of Solid Polymers* by I. M. Ward and J. Sweeney, John Wiley & Sons, second edition 2004.

Clearly, the present book covers in depth only a narrow subject area on the mechanical response of polymers; thus, as such, it is not intended as a review. The informed reader will note that much work of other investigators falling outside the main scope has not been included. This omission is intentional, in order to preserve a coherent central perspective.

Many colleagues at various levels contributed significantly to the conduct of the research discussed in the book and the overall development of the subject of this book, either in experimentation or in computational modeling. These include, in order of depth of involvement, R. Cohen, U. Suter, A. Gałęski, Z. Bartzak, E. Piórkowska, H. Brown, D. Parks, O. Gebizlioglu, S. Ahzi, M. Hutnik, P. Mott, O. Muratoglu, B. Lee, J. Vancso, J. Qin, and G. Dagli. In private discussions on many aspects of polymer research, G. Rutledge contributed some important perspective. M. Weinberg of DuPont supplied specially pedigreed polymer samples and blends for the experimental studies. P. Geil, B. Wunderlich, E. Kramer, and E. Ma generously furnished electronic files of some key micrographs and computer-generated images. The text was prepared, and numerous modifications were implemented, always cheerfully, by Doris Elsemiller. The illustrations were ably produced by Andrew Standeven. All this would not have been possible without funds provided by Deans T. Magnanti and S. Suresh and Department Heads R. Abeyaratne and M. Boyce. Finally, the very thorough copy-editing by Dr. Steven Holt on behalf of Cambridge University Press that uncovered a number of inconsistencies in referencing between the text and the lists of references at the ends of chapters is also gratefully acknowledged.



The serious entry of the author into the field of deformation and fracture of polymers started in 1971 during a sabbatical leave at Leeds University in Britain with Professor Ian Ward. The friendly association with Ward has continued until the present. For this reason the book is dedicated first of all to him in appreciation of his long-term friendship. Secondly, however, the book is dedicated in equal measure to my wife Xenia for her enduring support.

## Symbols

All mathematical symbols are fully defined in the text where they are introduced. Some material parameters have been referred to by different symbols, preserving their usage in the literature.

$A$	area of bar
$A_0$	area of perfect bar
$B(v,\beta)$	energy factor in ST
$C$	proportionality factor
$D$	diameter of craze fibril; diameter of particle
$D_c$	critical particle diameter for craze initiation
$D_0$	mean spacing of craze fibrils
$E$	Young's modulus
$F$	Helmholtz free energy
$F_0$	self Helmholtz free energy of ST
$F_{\text{int}}$	interaction (Helmholtz) energy with $\sigma_m$ of ST
$\Delta F_0$	$= F_0 + F_{\text{int}}$
$\Delta F_v$	activation free energy for viscous flow
$\mathfrak{F}_e$	edge-dislocation line energy
$\mathfrak{F}_s$	screw-dislocation line energy
$G_I$	mode I energy-release rate
$G_{IC}$	critical mode I energy-release rate for crack advance
$\Delta G^*$	Gibbs free energy of activation
$\Delta H^*$	activation enthalpy
$I_n$	normalization factor for stresses in $J$ integral field
$J_I$	$J$ integral non-linear crack-tip energy-release rate
$J_{IC}$	critical $J$ integral crack driving force
$J_U$	unrelaxed creep compliance
$J_R$	relaxed creep compliance
$K_I$	mode I stress intensity factor
$K_{IC}$	critical mode I stress intensity factor for crack growth in plane strain
$K_S$	critical mode I stress intensity factor for crack growth for plane stress
$K_C$	mode I stress intensity factor for growth of cracks between plane stress and plane strain: $K_S > K_C > K_{IC}$
$L$	load on deforming bar
$\mathcal{L}$	Langevin function
$M_e$	entanglement molecular weight in rubbers
$\overline{M}_n$	number-average molecular weight
$\overline{M}_w$	weight-average molecular weight
$\overline{M}_w/\overline{M}_n$	polydispersity ratio

$N$	strain exponent
$Q$	Heat; $dQ$ , heat increment
$R$	rate; universal gas constant
$R_{SD}$	strength differential ratio
$S$	entropy; $dS$ , change in entropy
$T$	temperature
$T_0$	( $= \Delta G^*/k$ )
$T_{BD}$	brittle-to-ductile transition temperature
$T_g$	glass-transition temperature
$T_m$	melting temperature
$U$	internal energy; $dU$ , change in internal energy
$V$	volume
$W^P$	plastic work; $dW^P$ , increment of plastic work
$Y$	tensile uniaxial yield strength
$Y_c$	intrinsic craze yield stress
$Y_0$	athermal tensile yield strength
$Y_C$	yield strength in compression
$Y_T$	yield strength in tension
$a$	crack length; Cartesian coordinate axis
$a_0$	molecular diameter
$a_T$	viscoelastic shift factor
$b$	Burgers vector; Cartesian coordinate axis
$c$	Cartesian coordinate axis; volume fraction
$c_f$	fraction; free-volume fraction
$c_{ij}$	Voigt elastic constant element
$c_{ijkl}$	tensor elastic constant element
$e_{ij}$	Voigt deviatoric strain element
$f$	fraction
$f_a$	amorphous fraction
$f_c$	crystalline fraction
$g(\lambda)$	( $= \lambda^2 - 1/\lambda$ ) Gaussian orientation hardening function
$k$	Boltzmann's constant; yield strength in shear
$k_T$	rate constant
$l$	monomer link length; generic length
$\dot{l}$	elongation rate
$m$	( $= d \ln \gamma / d \ln \sigma$ ) phenomenological stress exponent
$m_T$	Taylor factor in polycrystalline aggregates
$p$	pressure
$q$	cooling rate
$r$	radial coordinate
$s$	applied simple shear stress, deviatoric shear stress
$s_0$	athermal shear resistance
$s_{ij}$	Voigt elastic compliance
$s_{ijkl}$	tensor compliance element
$t$	time
$t_f$	time to fracture
$u_r$	radial displacement
$u_\theta$	angular displacement
$u_z$	axial displacement
$v_f$	volume fraction
$z$	polar coordinate axis

$x, y, z$	Cartesian axes
$\Phi$	fluidity
$\Delta$	process-zone length
$\chi$	interface energy, crystallinity
$\Lambda$	matrix ligament thickness
$\Lambda_c$	critical matrix ligament thickness where a toughness jump occurs
$\Omega$	atomic volume
$\Omega_f$	volume of ST cluster
$\Omega_{\text{mon}}$	monomer volume
$a$	proportionality constant
$\alpha$	( $= \hat{\tau}/\mu(0)$ ) normalized threshold shear resistance
$\alpha_b$	( $= v_{cb}/v_c$ ) proportionality factor between craze-border velocity and craze-tip velocity
$\beta$	( $= \varepsilon^T/\gamma^T$ ) activation dilatancy
$\beta$	level of porosity, secondary relaxation
$\beta_c$	activation-energy attenuation factor
$\gamma$	tangential shear strain
$\gamma^P$	plastic shear strain (deviatoric)
$\gamma^T$	transformation shear strain
$\dot{\gamma}$	shear strain rate
$\dot{\gamma}^P$	plastic shear strain rate
$\dot{\gamma}^e$	elastic shear strain rate
$\dot{\gamma}_0$	frequency factor in thermal activation
$\delta$	crack-tip opening displacement
$\delta_{ij}$	Kronecker delta
$\varepsilon$	normal strain
$\varepsilon^T$	free-standing transformation strain tensor
$\varepsilon^C$	constrained transformation strain tensor
$\varepsilon^T$	activation dilatation ( $= \beta\gamma^T$ )
$\bar{\varepsilon}$	equivalent total normal strain
$d\varepsilon_{ij}^P$	plastic normal strain increment
$d\bar{\varepsilon}$	equivalent total strain increment
$\varepsilon_C^T$	craze strain as dilatational transformation strain
$\dot{\varepsilon}$	nominal strain rate
$\varepsilon_e$	equivalent strain (deviatoric)
$\varepsilon_f^P$	plastic strain at fracture
$\varepsilon_y$	normal strain at yield ( $= \sigma_y/E$ )
$\varphi$	fraction, liquid-like-material fraction
$\varphi_s$	liquid-like-material fraction at the flow state
$\lambda_1, \lambda_2, \lambda_3$	principal extension ratios in a rubber
$\lambda_c$	chain-extension ratio in Langevin rubbery response
$\lambda_L$	locking stretch
$\lambda_e$	stress-attenuation factor in activation energy
$\lambda_n$	natural draw ratio between onset of instability and regaining of stability in fiber drawing, also in craze matter fibril strain
$\mu$	shear modulus
$\mu'$	storage modulus in viscoelasticity
$\mu''$	loss modulus in viscoelasticity
$\mu_u$	unrelaxed modulus in viscoelasticity
$\mu_r$	relaxed modulus in viscoelasticity, friction factor
$\nu$	Poisson's ratio

$\nu_D$	Debye frequency
$\nu_G$	pre-exponential frequency factor, an eigenfrequency
$\rho$	material density
$\rho_m$	mobile dislocation density
$\sigma$	generally an applied shear stress, sometimes normal stress (deviatoric)
$\sigma_B$	brittle strength
$\sigma_1, \sigma_2, \sigma_3$	principal normal stresses
$\sigma_c$	craze-border traction
$\sigma_C$	flow stress in compression
$\sigma_e$	uniaxial Mises equivalent axial stress
$\sigma_S$	flow stress in shear
$\sigma_T$	flow stress in tension
$\sigma_m$	mean normal stress ( $= \sigma_n$ )
$\sigma_{TH}$	thermal misfit negative pressure in particle
$\sigma_y$	( $= Y$ ) uniaxial yield strength
$\bar{\sigma}$	von Mises equivalent stress ( $= \sigma_e$ )
$\hat{\sigma}$	ideal cavitation strength in UBER model
$\sigma_\infty$	applied tensile stress promoting craze growth
$\theta$	angular coordinate
$\theta$	( $= \sigma/\mu(T)$ ) reduced shear stress normalized with shear modulus
$\theta$	( $= T/T_g$ ) reduced temperature normalized with the glass transition temperature
$\boldsymbol{\tau}$	stress tensor
$\tau$	time period
$\tau_a$	shear resistance of amorphous component in HDPE
$\tau_c$	shear resistance of a crystalline component in HDPE
$\hat{\tau}$	threshold plastic shear resistance at $T = 0$ K
$\hat{\tau}_C$	threshold uniaxial plastic resistance in compression

## Frequently used abbreviations

CD	constraint direction
CN	center-notched
CR	compression ratio
DAM	dry as molded
DEN	double-edge-notched
DGEBA	diglycidyl ether of bisphenol-A, a common epoxy resin
FD	free direction
HDPE	high-density polyethylene
HRR	Hutchinson–Rice–Rosengren (model)
KRO-1	a diblock resin
LD	loading direction
PB	polybutadiene
PMMA	polymethyl methacrylate
PS	polystyrene
QSC	quasi-single-crystalline (deformation texture)
RH	relative humidity
RVE	representative volume element
SANS	small-angle neutron scattering
SAXS	small-angle X-ray scattering
SEN	single-edge-notched
ST	shear transformation
TEM	transmission electron microscopy
WAXS	wide-angle X-ray scattering