

The Physics of Deformation and Fracture of Polymers

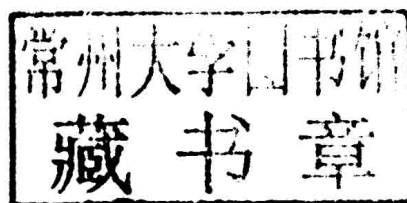
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The Physics of Deformation and Fracture of Polymers

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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.

**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**

“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

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 semicrystalline 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 Elsemillier. 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_{int}	interaction (Helmholtz) energy with σ_m of ST
ΔF_0	$= F_0 + F_{\text{int}}$
ΔF_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
ΔG^*	Gibbs free energy of activation
ΔH^*	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: $K_S > K_C > K_{\text{IC}}$
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_r	rate constant
l	monomer link length; generic length
\dot{l}	elongation rate
m	($= d \ln \dot{\gamma} / d \ln \sigma$) 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_θ	angular displacement
u_z	axial displacement
v_f	volume fraction
z	polar coordinate axis

x, y, z	Cartesian axes
Φ	fluidity
Δ	process-zone length
χ	interface energy, crystallinity
Λ	matrix ligament thickness
Λ_c	critical matrix ligament thickness where a toughness jump occurs
Ω	atomic volume
Ω_f	volume of ST cluster
Ω_{mon}	monomer volume
α	proportionality constant
α	($= \hat{\tau}/\mu(0)$) normalized threshold shear resistance
α_b	($= v_{cb}/v_c$) proportionality factor between craze-border velocity and craze-tip velocity
β	($= \varepsilon^T/\gamma^T$) activation dilatancy
β	level of porosity, secondary relaxation
β_e	activation-energy attenuation factor
γ	tangential shear strain
γ^p	plastic shear strain (deviatoric)
γ^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
δ	crack-tip opening displacement
δ_{ij}	Kronecker delta
ε	normal strain
ε^T	free-standing transformation strain tensor
ε^C	constrained transformation strain tensor
ε^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
ε_C^T	craze strain as dilatational transformation strain
$\dot{\varepsilon}$	nominal strain rate
ε_e	equivalent strain (deviatoric)
ε_f^p	plastic strain at fracture
ε_y	normal strain at yield ($= \sigma_y/E$)
φ	fraction, liquid-like-material fraction
φ_s	liquid-like-material fraction at the flow state
$\lambda_1, \lambda_2, \lambda_3$	principal extension ratios in a rubber
λ_c	chain-extension ratio in Langevin rubbery response
λ_L	locking stretch
λ_e	stress-attenuation factor in activation energy
λ_n	natural draw ratio between onset of instability and regaining of stability in fiber drawing, also in craze matter fibril strain
μ	shear modulus
μ'	storage modulus in viscoelasticity
μ''	loss modulus in viscoelasticity
μ_u	unrelaxed modulus in viscoelasticity
μ_r	relaxed modulus in viscoelasticity, friction factor
ν	Poisson's ratio

ν_D	Debye frequency
ν_G	pre-exponential frequency factor, an eigenfrequency
ρ	material density
ρ_m	mobile dislocation density
σ	generally an applied shear stress, sometimes normal stress (deviatoric)
σ_B	brittle strength
$\sigma_1, \sigma_2, \sigma_3$	principal normal stresses
σ_c	craze-border traction
σ_C	flow stress in compression
σ_e	uniaxial Mises equivalent axial stress
σ_S	flow stress in shear
σ_T	flow stress in tension
σ_m	mean normal stress ($=\sigma_n$)
σ_{TH}	thermal misfit negative pressure in particle
σ_y	($=Y$) uniaxial yield strength
$\bar{\sigma}$	von Mises equivalent stress ($=\sigma_e$)
$\hat{\sigma}$	ideal cavitation strength in UBER model
σ_∞	applied tensile stress promoting craze growth
θ	angular coordinate
θ	($=\sigma/\mu(T)$) reduced shear stress normalized with shear modulus
θ	($=T/T_g$) reduced temperature normalized with the glass transition temperature
τ	stress tensor
τ	time period
τ_a	shear resistance of amorphous component in HDPE
τ_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

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