POLYMER MATERIALS

Macroscopic Properties and Molecular Interpretations

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PREFACE

In the middle of the 1970, the first oil crisis led to a new development of polymer materials. To lighten vehicles and to save energy, polymers replaced metals. However, such a replacement necessitated an improvement of the properties of existing polymers and the development of new chemical structures. An important research activity was generated in order to get a deeper understanding of polymer properties—and, especially, mechanical properties—and of their relations with the chemical structure of the polymer chains.

Such a research benefited from very recent experimental techniques such as ^{1}H and ^{13}C solid-state nuclear magnetic resonance (NMR), molecular modeling, transmission and scanning electronic microscopy, and atomic force microscopy.

Since the 1980, our research group has been intensively involved in this field. Our interest was mostly focused on polymer dynamics and on local motions in solid polymers, as well as on their consequences on the plastic properties and fracture behavior in thermoplastics and in elastomers. This research was performed in close relation with the major European companies involved in polymer materials. Over the years, our academic lectures and industrial trainings have dealt with all these different aspects.

Several textbooks have already been published on polymer properties. However, they are mainly oriented toward specific behaviors such as viscoelasticity, fracture, and toughening or toward materials like thermoplastics, thermosets, and elastomers.

The purpose of this textbook is to cover and emphasize the relationships that can be established between the chemical structure and the mechanical properties of the various types of rigid polymers and elastomer materials. These relations are extended to materials that are either toughened by rubber particles or reinforced by inorganic fillers. The optical and electrical properties, the surface properties, the permeability, and the fire-resistance are not considered.

For each topic under study, the experimental results are described first; in a second step, they are analyzed by taking advantage of the information obtained at the nanomolecular or molecular scales by microscopies, NMR, and molecular modeling, in order to achieve a molecular approach of the properties.

The book is divided into five parts.

Part I (Chapters 1 to 6) is devoted to the necessary polymer background, with a special emphasis on polymer dynamics.

Part II (Chapters 7 to 10) deals with the concepts of mechanical properties.

Part III (Chapters 11 to 15) describes the behaviors of typical rigid polymers.

Part IV (Chapters 16 to 20) is centered on the toughening of rigid polymers.

Part V (Chapters 21 to 23) focuses on pure and filled elastomers and thermoplastic elastomers.

After these five parts we present some comprehensive problems that have been the matter of course final examinations.

This book is designed for graduate and post-graduate students in Polymer Science. An increasing number of graduates in Physics, Mechanics, and Materials Science and Engineering have an interest in polymer materials: In spite of their limited background in Polymer Science, the book is intended to make them aware, without too many difficulties, of the chemical dimension of the macroscopic behaviors with which they are familar. The book should also be of use to the academic teachers who are looking for a unified and interdisciplinary course on polymer mechanics and are interested in selected case studies. We hope that the engineers and scientists in industry and research, who are often searching for predictive recipes on mechanical behavior, will also find useful guidelines to rationalize their application needs.

Finally, we would like to thank all our former students who have enriched the different chapters of this textbook and helped us to upgrade, year after year, our original presentations by their questions, comments, and suggestions. We also would like to express our sincere gratitude to our respective spouses, namely Monique, Jean-Michel, and Monique, for the understanding and support that they never failed to show during the preparation of this new book.

Jean Louis Halary
Françoise Lauprêtre
Lucien Monnerie

Paris, France
October 2010

LIST OF SYMBOLS

a	length of half a crack
a_{cc}	critical length for crack propagation
a_{tube}	tube diameter
a_{T/T_0}	shift factor
a_0	radius of an initial cavity inside a particle
A	free energy
A_a	area of diffuse halo
A_c	area of crystalline peak
A_{cr}	area of crystallization peak
A_m	area of melting peak
A_{net}	free energy of a network
A_0	cross section
b	length of a bond
b_K	length of a Kuhn link
B_M	bulk modulus
B	sample thickness
$B_{M,c}$	bulk modulus of the core of a particle
$B_{M,el}$	elastomer bulk modulus
C_{mn}	elastic constant
C_N	characteristic ratio
C_p	heat capacity
C_{p0}	capacity of a capacitor filled with polymer
C_0	capacity of an empty capacitor
C_1^g, C_2^g	WLF coefficients at T_g
C_1^{MR}, C_2^{MR}	Mooney–Rivlin coefficients
C_1^0, C_2^0	WLF coefficients at T_0
$d_{h,k,l}$	distance between successive planes of the crystal lattice
d_p	elastomer particle diameter
d_t	density of occupied sites
D_{tube}	diffusion coefficient of a chain along its tube
$\overline{DP_n}$	number average degree of polymerization
$\mathcal{D}(t \text{ or } \omega)$	viscoelastic descriptor
e_g	thickness of the glassy layer at the filler surface
E	Young modulus
E'	storage modulus
E''	loss modulus
E^*	complex modulus
$\widetilde{E}$	general Young modulus for plane stress and plane strain conditions
E_a	activation energy
E_{ab}	absorbed energy in an impact test
E_{coh}	cohesive energy
$E_{d,f-el}$	dispersive energy of filler–elastomer interactions
E_{ff}	energy of filler–filler interactions
E_m	Young modulus of a polymer matrix
E_R	Young modulus at the rubbery plateau
ΔE_{lh}	energy difference between low- and high-energy conformations
f	loading frequency
f^*	reduced stress
f_{cc}	probabibility of a conformational change
f_C	functionality of the network cross-links
F	tensile force intensity
F_e	force required to maintain the ends of a Rouse subchain
$\mathcal{F}(t)$	creep compliance
g	gravity
g	gauche
g_e	number of chain ends
g_0	proportionality coefficient in the expression of the plateau shear modulus
G	shear modulus
G'	storage shear modulus
G''	loss shear modulus

G^* complex shear modulus
G_c critical strain energy release rate or fracture energy per surface unit
G_{cr} free enthalpy of crystal formation
G'_{el} storage shear modulus of the elastomer matrix
G'_{fel} storage shear modulus of a filled elastomer
G_{Ic} critical strain energy release rate or fracture energy per surface unit in mode I
G_m^{ru} free enthalpy of melting per repeat unit
G'_{red} reduced modulus in Payne effect studies
G_0^N shear modulus at the rubbery plateau
ΔG_a activation free enthalpy
ΔG_m^0 enthalpy variation at melting
$\Delta G'$ Payne effect amplitude
h Planck constant
H_b fracture hysteresis
$H(\varepsilon_m)$ hysteresis associated with a ε_m deformation
H_0 magnetic field
ΔH quantity of heat
ΔH_a activation enthalpy
ΔH_{cr} crystallization enthalpy per unit mass
ΔH_m melting enthalpy per unit mass
ΔH_m^0 variation of enthalpy at melting of a fully crystalline polymer
$\mathcal{H}(\tau)$ relaxation time spectrum
I_P polydispersity index
I_1, I_2, I_3 invariants of the strain tensor
I_θ scaterred intensity at angle θ
j_{ru} number of bonds per repeat unit
J_{co} contour integral
$J_{co,c}$ critical value of the contour integral
J_{del} delayed compliance
J_{inst} instanteneous compliance
J_s spring compliance
J_{visc} viscous compliance
J' storage compliance
J'' loss compliance
J^* complex compliance
k Boltzmann constant
k_b bond stiffness constant
k_θ angle stiffness constant
K_c stress intensity factor, toughness
K_{Ic} toughness in mode I
K_{Ica} toughness in mode I at a crack propagation arrest in unstable semi-brittle fracture
K_{Icp} toughness in mode I at a crack propagation in unstable semi-brittle fracture
K_{Ics} toughness in mode I with a very sharp crack
l bar length
ℓ_b mean distance between two branches in PE
ℓ_h hammer displacement
ℓ_r length of the slow crack propagation zone in unstable semi-brittle fracture
L_{ch} length of a network chain
$L_{h,k,l}$ crystal dimension along the normal to the (h,k,l) plane
L_{pp} length of primitive path
L_{S-S} surface to surface interparticle distance
$L_{S-S,c}$ critical surface to surface interparticle distance
L_{tube} tube length
$\langle L_C \rangle$ average distance between cross-links
$\mathcal{L}(x)$ Langevin function
$\mathcal{L}(\tau)$ retardation time spectrum
m_a weight of the amorphous phase
m_c weight of the crystalline phase
m_i molar mass of an atom
m_l molecular weight of a link
m'' dielectric loss modulus
$\overline{m_1}$ average molecular weight of a backbone bond
M polymer molecular weight
M_e molecular weight between entanglements
M_K molecular weight of a Kuhn segment
M_{ru} molecular weight of a repeat unit
$M(t)$ transverse magnetization
$\overline{M_C}$ average molecular weight between cross-links
$\overline{M_n}$ number average molecular weight
$\overline{M_w}$ weight average molecular weight
$\vec{n}$ director in a liquid-crystalline phase
n_e number of entanglements per chain
n_h number of high energy conformations
n_l number of low energy conformations
n_r number of real bonds per repeat unit
n_v number of virtual bonds per repeat unit
n_{ru} number of repeat units
$\langle n_{ru,e} \rangle$ average number of repeat units between entanglements
N number of bonds
N_A Avogadro number
N_c number of fatigue cycles
$N_{c,b}$ number of fatigue cycles at break
N_{ch} number of network chains per volume unit
N_e number of bonds between entanglements
N_{eq} number of equivalent bonds between entanglements
N_K number of Kuhn segments

$N_{K,C}$ number of Kuhn segments between cross-links
$N_{K,e}$ number of Kuhn segments between entanglements
N_{ms} number of adjacent sites in a mobile cluster
N_R number of Rouse subchains
N_s total number of sites
$\langle N_C \rangle$ average number of chain backbone bonds between cross-links
P hydrostatic pressure
P_a applied load
$P_{a,c}$ critical applied load for crack propagation
P_{max} maximum load at crack propagation
P_2 order parameter
P_∞ limit pressure at which the glass transition motions would occur at an infinitely low frequency
PSS plastic strain softening
$\mathcal{P}(t)$ mechanical energy
q_f number of filaments to break for fracture
q_R number of monomer units in a Rouse sub-chain
Q heat
Q_e electric charge
$r_y^{p\sigma}$ radius of plastic zone under plane stress conditions
$r_y^{p\varepsilon}$ radius of plastic zone under plane strain conditions
R gas constant
R end-to-end distance
R_{fel} reinforcement characteristic of a filled elastomer
R_p radius of an elastomer particle
R_{CH} impact strength in Charpy test
R_D length of the Dugdale plastic zone
R_{IZ} impact strength in Izod test
$\langle R^2 \rangle$ mean-square end-to-end distance
$\langle R_0^2(t_s) \rangle$ mean-square displacement of polymer beads during a t_s simulation time
$\mathcal{R}(t)$ relaxation modulus
s_i distance of a segment to the center of gravity
S entropy
S_{ch} entropy of a network chain
S_{dam} area of damage surface or fracture surface
S_l entropy of a chain in the melt
S_{mn} compliance constant
S_{net} entropy of the network
$\langle S^2 \rangle$ mean-square radius of gyration
ΔS_a activation entropy
ΔS_m^0 variation of entropy at melting
t *trans*
t_b loading duration until fracture
t_s simulation time
$t_{1/2}$ contact time to reach half of the maximum magnetization for a ^{13}C nucleus
T_{aging} aging temperature
T_{cr} crystallization temperature
T_g glass transition temperature
$T_g(z)$ glass transition temperature at a distance z from the filler surface
T_g^u upper glass transition temperature
T_m melting temperature
T_m^0 melting temperature of a crystal of an infinite size
$T_{b/d}$ brittle–ductile transition temperature
$T_{b/sb}$ transition temperature from brittle to semi-brittle
$T_{sb/d}$ transition temperature from semi-brittle to ductile
$T_{susd/sd}$ transition temperature from stable–unstable ductile to stable ductile
T_1 spin–lattice relaxation time in the laboratory frame
$T_{1\rho}$ spin–lattice relaxation time in the rotating frame
T_{2m} spin–spin relaxation time associated with the motional modulation of the dipolar coupling
$T_{2\sigma}$ spin–spin relaxation time associated with the motional modulation of the chemical shift anisotropy
T_α main (α) transition temperature as observed by dynamic mechanical analysis
T_β temperature of the β relaxation
T_∞ limit temperature at which the glass transition motions would take place at an infinitely slow cooling rate
u free volume reduction per cross-link
U internal energy
U_{bond} bond energy
U_e stored elastic energy
U_{init} initiation crack propagation energy
U_{prop} crack propagation energy
v cell volume
$v(T)$ volume at temperature T
v_a volume of the amorphous phase
v_c volume of the crystalline phase
v_{act} activation volume
v_{ch} volume occupied by a chain in a bulk polymer
v_{coil} volume of a coil
v_f total dynamic free volume
v_{fg} dynamic free volume at T_g

v_{fs}	dynamic free volume per main-chain segment
v_s	sample volume
v^*	free volume associated with a conformational change
v_∞	equilibrium volume at T_g
v_h	hammer speed
$\mathrm{v}_{b/sb}$	transition speed from brittle to semi-brittle
$\mathrm{v}_{sb/d}$	transition speed from semi-brittle to ductile
$\mathrm{v}_{susd/sd}$	transition speed from stable–unstable ductile to stable ductile
V	potential energy
w	sample width
w_i	weight fraction of component i
W	work
W_c	critical elastic energy density
$W_{stab}(\varepsilon)$	elastic energy of a filled elastomer associated with a stabilized stretching curve until ε deformation
$W_1(\varepsilon)$	elastic energy of a filled elastomer associated with a first stretching to ε deformation
$x_h(T)$	fraction of high energy conformations at temperature T
Z	number of other chains located within a coil
α	oscillation amplitude
α_g	volumetric thermal expansion coefficient in the glassy state
α_{fv}	thermal expansion coefficient of the free volume fraction
α_l	volumetric thermal expansion coefficient in the liquid state
β_g	isothermal compressibility in the glassy state
β_{fv}	isothermal compressibility of the free volume fraction
β_l	isothermal compressibility in the liquid state
γ	shear strain
$\dot{\gamma}$	shear rate
γ_i	accelaration of atom i
γ_{max}	maximum strain amplitude
γ_s	van der Waals surface energy
Γ	torque
Γ_{CDC}	surface energy between the fibril and micro-void in a chain disentanglement craze
Γ_{CSC}	surface energy between the fibril and micro-void in a chain scission craze
$\Gamma_{f,el}$	surface energy between a filler and an elastomer
Γ_t	tearing surface energy of an elastomer particle
δ	Hildebrand solubility parameter
$\tan\delta$	loss tangent
δ_c	crack aperture
δ_{cc}	critical crack aperture
δ_v	excess volume
Δ	displacement
ε	strain
ε_c	critical strain for craze formation
$\varepsilon_{c,e}$	critical strain for craze formation in chemical environment
ε_N	engineering strain
ε_T	true strain
ε_y	yield strain
$\dot{\varepsilon}$	strain rate
ε_e	dielectric constant
$\bar{\bar{\varepsilon}}_{ij}$	strain tensor
ε^*	complex dielectric permittivity
ε'	dielectric permittivity
ε''	dielectric loss
$\zeta(x)$	craze growth rate
η_0	Newtonian viscosity
η^*	complex viscosity
η'	dynamic viscosity
$\eta_{0,d}$	dashpot viscosity
θ	angle
Θ	Θ conditions
κ	intensity of the effect of constraints on the amplitude of the junction fluctuations
λ	wavelength
λ_a	extension ratio of a cavity
λ_b	extension ratio at break
λ_i	extension ratio along the i direction
Λ	number of available conformations
Λ_{ch}	number of conformations per network chain
Λ_{net}	number of conformations of the network
μ	chemical potential
μ_c^{ru}	chemical potential of the repeat unit in the crystalline state
μ_{Ch}	Coulomb internal friction coefficient
μ_f	internal friction coefficient
μ_l^{ru}	chemical potential of the repeat unit in the liquid state
μ_{vM}	von Mises internal friction coefficient
μ_1	chemical potential of the solvent in the solution
μ_1^0	chemical potential of the pure solvent
$\overrightarrow{\mu_i}$	electric dipole moment
ν	frequency of conformational changes
ν_c	frequency of cooperative motions
ν_C	cross-link density
ν_{eqC}	equivalent cross-link density

ν_e	entanglement density
ν_P	Poisson coefficient
ν_{Pm}	Poisson coefficient of a polymer matrix
ν_{st}	density of stable links
ν_{unst}	density of unstable links
ξ	friction coefficient of a bead
ξ_a	friction coefficient of a "blob"
ξ_i	friction coefficient of atom i
ξ_0	friction coefficient of a monomer
ρ	polymer density
ρ_{cav}	radius of curvature of a cavity
σ	stress
σ_c	critical stress for craze growth
σ_{cc}	critical stress for craze propagation
$\sigma_{c,e}$	critical stress for craze growth in chemical environment
σ_{cs}	stress at the surface of a craze
σ_{eq}	von Mises equivalent stress
σ_{fold}	surface energy of folded chains
σ_h	hydrostatic stress
σ_{hp}	hydrostatic stress applied to a particle
σ_{h0}	hydrostatic component of the applied stress, σ_0
σ_{ii}	principal component of the chemical shift tensor
σ_{or}	surface energy of oriented chains
σ_N	engineering stress
σ_p	plastic flow stress
σ_{sb}	stress of shear band formation
σ_T	true stress
σ_y	yield stress
σ_{zp}	Dugdale internal stress
σ_{CDC}	critical stress for chain disentanglement craze growth
σ_{CSC}	critical stress for chain scission craze growth
σ_0	stress applied to a sample
$\bar{\bar{\sigma}}_{ij}$	stress tensor
τ	shear stress
τ_c	correlation time of WLF cooperative motions
τ_{max}	maximum shear stress
τ_p	relaxation time corresponding to the pth Rouse mode
τ_{rep}	reptation time
τ_{sm}	correlation time of segmental motions
τ_A	Doi–Edwards transverse relaxation time
τ_B	Doi–Edwards longitudinal relaxation time
τ_C	Doi–Edwards relaxation time for reptation
τ_1	correlation time of overall chain motions
ϕ_i	internal rotation angle
φ_1	molar fraction of solvent
φ_2	molar fraction of solute
φ_i	molar fraction of impurity
Φ_{cp}	volume fraction of cavitated particles
Φ_d	crystalline weight fraction derived from density
Φ_{DSC}	crystalline weight fraction derived from DSC
Φ_{el}^m	volume fraction of elastomer within an epoxy matrix
Φ_{el}^p	volume fraction of elastomer
Φ_{el}^0	initial volume fraction of elastomer
Φ_f	volume fraction of filler
Φ_{fv}	dynamic free volume fraction
Φ_i	volume fraction of component i
Φ_m^p	polystyrene volume fraction inside a particle
Φ_p	volume fraction of elastomer particles
Φ_w	crystalline weight fraction
Φ_{XR}	volume fraction of the crystalline phase derived from X-ray diffraction
χ_{12}	interaction coefficient between components 1 and 2
ψ	phase angle
ω	angular frequency

CONTENTS