

POLYMER MATERIALS

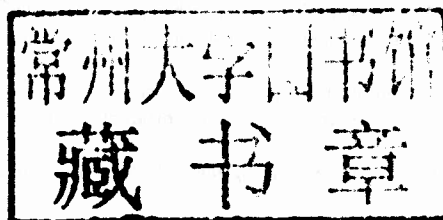
Macroscopic Properties and Molecular Interpretations

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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 ^1H 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 familiar. 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	e_g	thickness of the glassy layer at the filler surface
a_{cc}	critical length for crack propagation	E	Young modulus
a_{tube}	tube diameter	E'	storage modulus
a_{T/T_0}	shift factor	E''	loss modulus
a_0	radius of an initial cavity inside a particle	E^*	complex modulus
A	free energy	\tilde{E}	general Young modulus for plane stress and plane strain conditions
A_a	area of diffuse halo	E_a	activation energy
A_c	area of crystalline peak	E_{ab}	absorbed energy in an impact test
A_{cr}	area of crystallization peak	E_{coh}	cohesive energy
A_m	area of melting peak	$E_{d,f-el}$	dispersive energy of filler-elastomer interactions
A_{net}	free energy of a network	E_{ff}	energy of filler-filler interactions
A_0	cross section	E_m	Young modulus of a polymer matrix
b	length of a bond	E_R	Young modulus at the rubbery plateau
b_K	length of a Kuhn link	ΔE_{lh}	energy difference between low- and high-energy conformations
B_M	bulk modulus	f	loading frequency
B	sample thickness	f^*	reduced stress
$B_{M,c}$	bulk modulus of the core of a particle	f_{cc}	probability of a conformational change
$B_{M,el}$	elastomer bulk modulus	f_c	functionality of the network cross-links
C_{mn}	elastic constant	F	tensile force intensity
C_N	characteristic ratio	F_e	force required to maintain the ends of a Rouse subchain
C_p	heat capacity	$\mathcal{F}(t)$	creep compliance
C_{p0}	capacity of a capacitor filled with polymer	g	gravity
C_0	capacity of an empty capacitor	g	gauche
C_1^g, C_2^g	WLF coefficients at T_g	g_e	number of chain ends
C_1^{MR}, C_2^{MR}	Mooney-Rivlin coefficients	g_0	proportionality coefficient in the expression of the plateau shear modulus
C_1^0, C_2^0	WLF coefficients at T_0	G	shear modulus
$d_{h,k,l}$	distance between successive planes of the crystal lattice	G'	storage shear modulus
d_p	elastomer particle diameter	G''	loss shear modulus
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		

G^*	complex shear modulus	K_{Ics}	toughness in mode I with a very sharp crack
G_c	critical strain energy release rate or fracture energy per surface unit	l	bar length
G_{cr}	free enthalpy of crystal formation	ℓ_b	mean distance between two branches in PE
G_{el}	storage shear modulus of the elastomer matrix	ℓ_h	hammer displacement
G'_{el}	storage shear modulus of a filled elastomer	ℓ_r	length of the slow crack propagation zone in unstable semi-brittle fracture
G_{Ic}	critical strain energy release rate or fracture energy per surface unit in mode I	L_{ch}	length of a network chain
G_m^{ru}	free enthalpy of melting per repeat unit	$L_{h,k,l}$	crystal dimension along the normal to the (h,k,l) plane
G'_{red}	reduced modulus in Payne effect studies	L_{pp}	length of primitive path
G_0^N	shear modulus at the rubbery plateau	L_{S-S}	surface to surface interparticle distance
ΔG_a	activation free enthalpy	$L_{S-S,c}$	critical surface to surface interparticle distance
ΔG_m^0	enthalpy variation at melting	L_{tube}	tube length
$\Delta G'$	Payne effect amplitude	$\langle L_C \rangle$	average distance between cross-links
h	Planck constant	$\mathcal{L}(x)$	Langevin function
H_b	fracture hysteresis	$\mathcal{L}(\tau)$	retardation time spectrum
$H(\epsilon_m)$	hysteresis associated with a ϵ_m deformation	m_a	weight of the amorphous phase
H_0	magnetic field	m_c	weight of the crystalline phase
ΔH	quantity of heat	m_i	molar mass of an atom
ΔH_a	activation enthalpy	m_l	molecular weight of a link
ΔH_{cr}	crystallization enthalpy per unit mass	m''	dielectric loss modulus
ΔH_m	melting enthalpy per unit mass	$\overline{m_1}$	average molecular weight of a backbone bond
ΔH_m^0	variation of enthalpy at melting of a fully crystalline polymer	M	polymer molecular weight
$\mathcal{H}(\tau)$	relaxation time spectrum	M_e	molecular weight between entanglements
I_P	polydispersity index	M_K	molecular weight of a Kuhn segment
I_1, I_2, I_3	invariants of the strain tensor	M_{ru}	molecular weight of a repeat unit
I_θ	scattered intensity at angle θ	$\overline{M(t)}$	transverse magnetization
j_{ru}	number of bonds per repeat unit	$\overline{M_C}$	average molecular weight between cross-links
J_{co}	contour integral	$\overline{M_n}$	number average molecular weight
$J_{co,c}$	critical value of the contour integral	$\overline{M_w}$	weight average molecular weight
J_{del}	delayed compliance	\vec{n}	director in a liquid-crystalline phase
J_{inst}	instantaneous compliance	n_e	number of entanglements per chain
J_s	spring compliance	n_h	number of high energy conformations
J_{visc}	viscous compliance	n_l	number of low energy conformations
J'	storage compliance	n_r	number of real bonds per repeat unit
J''	loss compliance	n_v	number of virtual bonds per repeat unit
J^*	complex compliance	n_{ru}	number of repeat units
k	Boltzmann constant	$\langle n_{ru,e} \rangle$	average number of repeat units between entanglements
k_b	bond stiffness constant	N	number of bonds
k_θ	angle stiffness constant	N_A	Avogadro number
K_c	stress intensity factor, toughness	N_c	number of fatigue cycles
K_{Ic}	toughness in mode I	$N_{c,b}$	number of fatigue cycles at break
K_{Ica}	toughness in mode I at a crack propagation arrest in unstable semi-brittle fracture	N_{ch}	number of network chains per volume unit
K_{Icp}	toughness in mode I at a crack propagation in unstable semi-brittle fracture	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	t_b	loading duration until fracture
$N_{K,e}$	number of Kuhn segments between entanglements	t_s	simulation time
N_{ms}	number of adjacent sites in a mobile cluster	$t_{1/2}$	contact time to reach half of the maximum magnetization for a ^{13}C nucleus
N_R	number of Rouse subchains	T_{aging}	aging temperature
N_s	total number of sites	T_{cr}	crystallization temperature
$\langle N_C \rangle$	average number of chain backbone bonds between cross-links	T_g	glass transition temperature
P	hydrostatic pressure	$T_g(z)$	glass transition temperature at a distance z from the filler surface
P_a	applied load	T_g^u	upper glass transition temperature
$P_{a,c}$	critical applied load for crack propagation	T_m	melting temperature
P_{max}	maximum load at crack propagation	T_m^0	melting temperature of a crystal of an infinite size
P_2	order parameter	$T_{b/d}$	brittle-ductile transition temperature
P_∞	limit pressure at which the glass transition motions would occur at an infinitely low frequency	$T_{b/sb}$	transition temperature from brittle to semi-brittle
PSS	plastic strain softening	$T_{sb/d}$	transition temperature from semi-brittle to ductile
$\mathcal{P}(t)$	mechanical energy	$T_{susd/sd}$	transition temperature from stable-unstable ductile to stable ductile
q_f	number of filaments to break for fracture	T_1	spin-lattice relaxation time in the laboratory frame
q_R	number of monomer units in a Rouse sub-chain	$T_{1\rho}$	spin-lattice relaxation time in the rotating frame
Q	heat	T_{2m}	spin-spin relaxation time associated with the motional modulation of the dipolar coupling
Q_e	electric charge	$T_{2\sigma}$	spin-spin relaxation time associated with the motional modulation of the chemical shift anisotropy
$r_y^{p\sigma}$	radius of plastic zone under plane stress conditions	T_α	main (α) transition temperature as observed by dynamic mechanical analysis
$r_y^{p\epsilon}$	radius of plastic zone under plane strain conditions	T_β	temperature of the β relaxation
R	gas constant	T_∞	limit temperature at which the glass transition motions would take place at an infinitely slow cooling rate
R	end-to-end distance	u	free volume reduction per cross-link
R_{fel}	reinforcement characteristic of a filled elastomer	U	internal energy
R_p	radius of an elastomer particle	U_{bond}	bond energy
R_{CH}	impact strength in Charpy test	U_e	stored elastic energy
R_D	length of the Dugdale plastic zone	U_{init}	initiation crack propagation energy
R_{IZ}	impact strength in Izod test	U_{prop}	crack propagation energy
$\langle R^2 \rangle$	mean-square end-to-end distance	v	cell volume
$\langle R_0^2(t_s) \rangle$	mean-square displacement of polymer beads during a t_s simulation time	$v(T)$	volume at temperature T
$\mathcal{R}(t)$	relaxation modulus	v_a	volume of the amorphous phase
s_i	distance of a segment to the center of gravity	v_c	volume of the crystalline phase
S	entropy	v_{act}	activation volume
S_{ch}	entropy of a network chain	v_{ch}	volume occupied by a chain in a bulk polymer
S_{dam}	area of damage surface or fracture surface	v_{coil}	volume of a coil
S_l	entropy of a chain in the melt	v_f	total dynamic free volume
S_{mn}	compliance constant	v_{fg}	dynamic free volume at T_g
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		

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

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

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