

# Contents

Preface .....	v
<b>Part I Elementary Rheology of Polymers .....</b>	<b>1</b>
<b>1 Characteristic Features of Polymers .....</b>	<b>3</b>
1.1 Introduction .....	3
1.2 Chemical structure .....	3
1.3 Properties .....	4
<b>2 Thermodynamics of Dilute Polymer Solutions .....</b>	<b>5</b>
2.1 Thermodynamics of ordinary molecules .....	5
2.2 Entropy and heat of solution of polymers .....	6
2.3 Osmotic pressure and vapor pressure of the polymer solution .....	8
2.4 Phase separation .....	10
2.5 Arrangement of segments in polymer chains .....	12
2.6 End-to-end distance of polymer chains .....	13
2.7 Viscosity of polymer solution .....	14
References .....	16
<b>3 Transition Temperatures .....</b>	<b>17</b>
3.1 Melting point .....	18
3.2 Thermodynamic and rheological transitions of amorphous polymers .....	18
3.3 Empirical rule for $T_m$ .....	18
3.4 $T_m$ of crystalline polymer .....	20
3.5 Glass transition and softening temperatures .....	21
3.6 New thermodynamics and kinetics for polymers .....	24
3.7 Relation between $T_g$ and $T_s$ .....	26

References .....	26
<b>4 Mechano- and Hydrodynamics .....</b>	<b>27</b>
4.1 Measurement of elasticity and viscosity .....	27
4.2 Viscoelasticity .....	29
4.3 Dynamic spectrum .....	31
4.4 Viscosity .....	32
References .....	33
<b>5 Rubber Elasticity .....</b>	<b>35</b>
5.1 Thermodynamics of rubber elasticity .....	35
5.2 Chain configuration .....	36
5.3 Elastic force of vulcanized rubber .....	38
5.4 Elasticity at large deformation .....	39
5.5 Mooney-Rivlin equation .....	40
5.6 Effect of cohesion heat .....	42
5.7 Induced crystallization and orientation .....	42
5.8 Rebound resilience and $T_g$ .....	43
5.9 Sound velocity in rubber .....	43
5.10 Other theories .....	43
References .....	44
<b>6 Molecular Dynamics of Viscoelasticity .....</b>	<b>45</b>
6.1 Dynamic stress-relaxation spectrum .....	45
6.2 Superposition principle of Boltzmann .....	46
6.3 Models and theories .....	47
6.3.1 Free volume model of Eyring .....	47
6.3.2 Spring-beads model of Rouse .....	49
6.3.3 Reptation model of de Gennes .....	49
6.3.4 Tube model of Doi-Edwards .....	50
6.4 Theories on plastic zone .....	50
References .....	52
<b>7 Accounts of Viscoelasticity with the Pseudo Crosslink Model .....</b>	<b>55</b>
7.1 Viscoelasticity .....	56
7.2 Plasticity .....	57
7.3 Melt viscosity .....	57
7.4 Stress relaxation spectrum .....	58
7.5 Diffusion constant of polymer .....	59
References .....	59

8 Rheology for Large Deformation .....	61
8.1 Elongational viscosity .....	61
8.2 Accounts of elongational elasticity and viscosity .....	63
8.3 Yield and failure point .....	64
8.4 Creep of polymer .....	66
8.5 Creep of vulcanized rubber .....	68
8.6 Die swell .....	69
8.7 Compliance .....	70
References .....	71
9 Gel and Suspension .....	73
9.1 Transition points for solution .....	73
9.2 Elasticity and viscosity of concentrated solution .....	75
9.3 Osmotic pressure in gel .....	76
9.4 Coil-globule transition .....	76
9.5 Other transitions or critical points of chain molecules .....	77
9.6 Emulsion and suspensions .....	78
9.7 Stability of emulsion .....	78
9.8 Application of the lattice model to suspension .....	79
9.9 Thixotropy of suspension .....	79
References .....	80
10 Strength of Rubber and Active Filler .....	83
10.1 Strength as a function of vulcanization .....	83
10.2 Rupture of natural and synthetic rubber .....	84
10.3 Effect of active filler on elasticity .....	87
10.4 Effect of active filler on strength .....	88
10.5 Carbon black .....	88
10.6 Payne effect .....	89
10.7 Mullins effect .....	91
10.8 Gросch equation .....	92
References .....	93
11 Strength of Plastics and Fibers .....	95
11.1 Strength of plastics .....	95
11.2 Improvement of impact strength by rubbery dispersion .....	96
11.3 Strength of fiber .....	99
11.4 Super-strong fibers .....	101
References .....	102

<b>12 Adhesives</b>	.....	103
12.1 Chemical adhesives	.....	103
12.2 Tack adhesion	.....	104
12.3 Theory using the pseudo crosslink model	.....	106
12.4 Formation of voids and fibrils on peeling	.....	109
12.5 Tensile and shear strength of adhesives	.....	110
References	.....	110
<b>13 Friction and Abrasion of Rubber</b>	.....	111
13.1 Mechanics of friction	.....	111
13.2 Chemical aspect of friction	.....	112
13.3 Abrasion and anti-abrasion	.....	113
References	.....	115
<b>14 Polymer Blends</b>	.....	117
14.1 Homogeneous blend	.....	117
14.2 Heterogeneous blend	.....	118
14.3 Blend of block polymers	.....	118
14.4 Interpenetrating network structure and reactive processing	.....	119
14.5 Blend rules	.....	119
14.6 Blend of plastics	.....	121
14.7 Blend of block copolymers	.....	121
14.8 Modes of blend	.....	121
14.9 Blend rules	.....	123
14.9.1 Conventional blend rule	.....	123
14.9.2 Deviation from the average	.....	123
14.9.3 Blend for dispersion	.....	124
14.10 Remarks	.....	125
References	.....	126
<b>15 New Block Copolymers</b>	.....	127
15.1 SBS-TPE	.....	127
15.2 Polyurethane-TPE	.....	129
15.3 Special blend of rubber-polypropylene by dynamic vulcanization	.....	129
15.4 Polymer hybrids	.....	130
References	.....	133

<b>Part II Theory of Pseudo Crosslinks of Multi-Size .....</b>	<b>135</b>
<b>16 Pseudo Crosslink Model—A New Thermodynamics and Kinetics of Chain Molecules .....</b>	<b>137</b>
16.1 Entanglement of chains .....	137
16.2 Pseudo crosslink .....	138
16.3 Size of links and length of chains .....	140
16.4 Transition temperatures .....	142
16.5 Time for translation or relaxation .....	143
16.6 Relaxation time of unit segment .....	145
16.7 History of the pseudo crosslink model .....	146
References .....	147
<b>17 Theory of Glass Transition .....</b>	<b>149</b>
17.1 $T_g$ and $T_s$ .....	149
17.2 Effect of molecular length on $T_g$ .....	150
17.3 Effect of vulcanization on $T_g$ of rubber .....	152
17.4 $T_g$ of polymer solution .....	153
17.5 $T_g$ of polymer blends .....	154
17.6 $T_g$ of copolymers .....	155
17.7 $T_g$ of inorganic glass .....	156
17.8 Comparison with other theories .....	157
17.9 Conclusion .....	160
References .....	160
<b>18 Theory of Melting and Softening .....</b>	<b>161</b>
18.1 Melting temperature .....	161
18.2 Theoretical considerations .....	162
18.3 Softening temperature .....	163
18.4 Comparison with data in the literature .....	164
References .....	166
<b>19 Theory of Effect of Glass Transition Temperature .....</b>	<b>167</b>
19.1 Effect of $T_g$ on viscoelasticity .....	167
19.2 Thermal expansion coefficient .....	168
19.3 $T_g$ of polymer blends .....	170
19.4 Cooling condition and glass .....	170
References .....	172

<b>20 Theory of Viscosity and Diffusion</b>	<b>173</b>
20.1 Viscosity of ordinary liquid	173
20.2 Viscosity of polymer melt	174
20.3 Viscosity of polymer solution	175
20.4 Effect of high shear or shear rate	176
20.5 Diffusion constant of polymer	177
20.6 Comparison with the literature	178
References	178
<b>21 Theory of Viscoelasticity</b>	<b>179</b>
21.1 Stress relaxation spectrum	179
21.2 Explanation using the pseudo link model	179
21.3 Static spectrum	180
21.4 Dynamic relaxation spectrum	182
21.5 Effect of high shear or shear rate	183
References	184
<b>22 Theory of Rheology of Bulk Polymers</b>	<b>185</b>
22.1 Various mechanisms of stress dissipation	185
22.2 Elongational viscosity	186
22.3 Comparison with data in the literature	188
22.4 Yield and failure point	191
22.5 Creep of raw rubber	192
22.6 Creep of vulcanized rubber	193
References	194
<b>23 Theory of Elasticity of Rubber and Cohesion</b>	<b>195</b>
23.1 Vulcanized rubber	195
23.2 Alternating copolymers	196
23.3 Effect of structure of the repeating unit	197
23.4 Elasticity and plasticity of raw rubbers	197
References	199
<b>24 Theory of Strength of Vulcanized Rubber</b>	<b>201</b>
24.1 Rupture of bond	202
24.2 Natural rubber	202
24.3 Synthetic rubber	202
24.4 Effect of temperature and vulcanization	204
24.5 Alternating copolymers	206
24.6 Comparison with data in the literature	207
24.7 Effect of geometrical and sequential regularities	208

24.8 Tear strength .....	209
References .....	209
<b>25 Theory of Active Filler .....</b>	<b>211</b>
25.1 Basic concept of reinforcement by filler .....	211
25.2 Slip of adsorbed chains by large deformation .....	213
25.3 Effect of filler on strength of vulcanized rubber .....	214
25.4 Mullins effect .....	215
25.5 Grosch equation .....	217
25.6 Structure of carbon black .....	217
25.7 Payne effect .....	218
25.8 Comparison with the literature .....	220
References .....	220
<b>26 Theory of Impact Strength of Plastics .....</b>	<b>221</b>
26.1 Theory for brittle fracture .....	221
26.2 Improvement of impact strength by rubbery dispersion .....	222
26.3 Theory of relaxation of impact energy .....	223
26.4 Mechanical model for craze propagation .....	224
References .....	226
<b>27 Theory of Strength of Fiber and Ultimate Strength .....</b>	<b>229</b>
27.1 Scission of chemical bond .....	229
27.2 Cohesion and orientation .....	230
27.3 Super-strong fiber .....	231
27.4 Ultimate properties .....	232
References .....	232
<b>28 Theory of Thermoplastic Elastomer .....</b>	<b>233</b>
28.1 Triblock copolymer .....	233
28.1.1 Length of blocks .....	233
28.1.2 Micelle as hard domain .....	234
28.1.3 Softening temperature of commercial TPE .....	234
28.1.4 Elasticity .....	235
28.1.5 Strength and elongation at break .....	235
28.2 Segmented polyurethane .....	236
28.2.1 Preparation .....	236
28.2.2 Softening temperature .....	237
28.2.3 Elastic properties .....	237
28.2.4 Commercial polyurethane .....	239
28.3 TPE prepared by dynamic vulcanization (DV TPE) .....	240
28.3.1 Dynamic vulcanization .....	240

28.3.2 Elastic property .....	240
28.3.3 Deformation of hard layer .....	241
28.3.4 Rupture at interface .....	242
References .....	243
<b>29 Theory of Polymer Micelles and Suspension .....</b>	<b>245</b>
29.1 Polymer solution .....	245
29.2 Homogeneous blend of polymers .....	246
29.3 Formation of micelles .....	246
29.4 Core-shell structure .....	247
29.5 Micelles of soap and ionomers .....	248
29.6 Suspensions and emulsions .....	250
29.6.1 Thermodynamics of colloids .....	250
29.6.2 Viscosity of colloids .....	251
29.6.3 Ordered structure of suspension .....	252
29.7 Rheology of polymer with filler .....	253
References .....	255
<b>30 Theory of Tack Adhesion .....</b>	<b>257</b>
30.1 Physico-chemical mechanism .....	257
30.2 Adhesion force and bonding force .....	258
30.3 Peeling without void formation .....	259
30.4 Peeling with formation of voids and fibrils .....	260
30.5 Effect of backing film .....	262
30.6 Tensile force in adhesion .....	262
30.7 Shear force between parallel plates .....	262
30.8 Peeling spectrum .....	262
30.9 Comparison with data in literature .....	263
30.9.1 Adhesion force .....	263
30.9.2 Effect of peeling angle of adhesives .....	263
30.9.3 Effect of peeling velocity .....	264
30.9.4 Effect of thickness .....	264
References .....	265
<b>31 Theory of Friction and Abrasion .....</b>	<b>267</b>
31.1 Mechanics of friction .....	267
31.2 Chemical aspects concerning friction .....	268
31.3 Vibration caused by friction .....	269
31.4 Abrasion .....	271
31.5 Role of carbon black and filler .....	272
31.6 Rolling resistance of tires .....	273
31.7 Comparison with literature .....	273
31.7.1 Friction and abrasion .....	273

31.7.2 Carbon black and active filler .....	274
References .....	275
List of Symbols .....	276
Index .....	277