

Contents

Preface xi

Chapter 1 Introduction 1

- 1.1 Hardness in materials science and engineering 1
- 1.2 Microhardness in polymer science 5
 - 1.2.1 *Microhardness and deformation modes in polymers* 5
 - 1.2.2 *Microhardness additivity law* 6
 - 1.2.3 *Tabor's relation* 6
 - 1.2.4 *Microhardness of polymers in contrast to metals* 8
- 1.3 References 9

Chapter 2 Microhardness determination in polymeric materials 11

- 2.1 Mechanics and geometry of indentation 13
- 2.2 Time dependence 15
- 2.3 Experimental details: sample preparation 16
 - 2.3.1 *Microhardness measurement on cylindrical surfaces* 18
- 2.4 Microhardness calculation of crystalline polymers 19
- 2.5 Crystal destruction boundary 20
- 2.6 Temperature dependence of microhardness in crystalline polymers 21
- 2.7 Microhardness of oriented materials 24
 - 2.7.1 *Effect of plastic deformation on the microhardness* 24
 - 2.7.2 *Anisotropy behaviour of oriented polymers* 26
- 2.8 Microindentation vs nanoindentation 31
 - 2.8.1 *Microindentation instruments* 33
 - 2.8.2 *Nanoindentation instruments* 35

2.9	Outlook	41
2.10	References	42
Chapter 3	Microhardness of glassy polymers	46
3.1	Introduction to glassy polymers	46
3.1.1	<i>The glass transition</i>	46
3.1.2	<i>Physical ageing</i>	49
3.2	Temperature dependence of microhardness in polymer glasses: determination of T_g	50
3.3	Physical ageing of polymer glasses as revealed by microhardness	56
3.3.1	<i>Homopolymers</i>	56
3.3.2	<i>Copolymers</i>	61
3.4	Correlation between microhardness and the glass transition temperature	62
3.5	Micromechanics of polymer glasses	65
3.5.1	<i>Crazing in glassy polymers</i>	65
3.5.2	<i>Micromechanics of crazes studied by ultramicrohardness</i>	67
3.5.3	<i>Microhardness and elastic moduli of glassy microfibrils</i>	70
3.6	References	77
Chapter 4	Microhardness of crystalline polymers	80
4.1	Introduction to crystalline polymers	80
4.1.1	<i>Polymer crystallization</i>	80
4.1.2	<i>Morphology</i>	82
4.1.3	<i>Polymorphism</i>	85
4.2	Microhardness of lamellar structures	87
4.2.1	<i>Deformation mechanism</i>	87
4.2.2	<i>Effect of crystallinity on microhardness</i>	90
4.2.3	<i>Models to predict hardness of lamellar crystals: role of lamellar thickness</i>	95
4.2.4	<i>Relationship between crystal hardness and melting temperature</i>	100
4.3	Microhardness and surface free energy	101
4.3.1	<i>The role of entanglements</i>	102
4.3.2	<i>Influence of chain ends</i>	103
4.4	Influence of molecular weight on microhardness through physical structure	106
4.5	Transitions in crystalline polymers as revealed by microhardness	109
4.5.1	<i>Polymorphic transitions</i>	109
4.5.2	<i>Curie transition</i>	109
4.6	Crystallization kinetics as revealed by microhardness	113
4.7	Correlation of microhardness to macroscopic mechanical properties	117
4.7.1	<i>Mechanical models</i>	118

- 4.7.2 *Correlation between hardness and yield stress* 118
 4.7.3 *Comparison with elastoplastic models* 119
 4.7.4 *Correlation between hardness and elastic modulus* 121
 4.8 References 123
- Chapter 5 Microhardness of polymer blends, copolymers and composites** 127
- 5.1 Blends of polyolefins 127
 5.1.1 *Model predictions in PE blends* 127
 5.1.2 *Deviations from the microhardness additivity law: PE/PP blends* 132
 5.1.3 *Blends of non-crystallizable components* 136
 5.2 Microhardness of coreactive blends: the influence of chemical interactions 137
 5.2.1 *Coreactive blends of PET and PC* 138
 5.2.2 *Blends of PET and PEN* 141
 5.2.3 *Blends with functionalized polyolefins* 144
 5.3 Mechanical studies of condensation copolymers 144
 5.4 Microhardness of multicomponent systems with T_g below room temperature 148
 5.4.1 *Systems which deviate from the hardness additivity law* 157
 5.4.2 *Some limits of the equation $H = kT_g + C$* 161
 5.5 Microhardness of polymer composites 161
 5.5.1 *Carbon fibre composites* 162
 5.5.2 *Sintered materials* 164
 5.5.3 *Fullerene-polymer matrix composites* 164
 5.6 Mechanical model of microfibrillar-reinforced composites 165
 5.7 References 172
- Chapter 6 Microhardness of polymers under strain** 176
- 6.1 Polymorphic transitions in crystalline polymers 176
 6.2 Stress-induced polymorphic transition in homopolymers, copolymers and blends 178
 6.2.1 *Effect of stress-induced polymorphic transition of PBT on microhardness* 178
 6.2.2 *Microhardness behaviour during stress-induced polymorphic transition in block copolymers of PBT* 185
 6.2.3 *Microhardness behaviour during stress-induced polymorphic transition in the blend of PBT with its block copolymers* 193
 6.3 Reversible microhardness in polyblock thermoplastic elastomers with PBT as the hard segments 198
 6.4 References 202

Chapter 7	Application of microhardness techniques to the characterization of polymer materials	205
7.1	Effect on microhardness of processing conditions of polymers	205
7.1.1	<i>Microindentation anisotropy in injection-moulded PE</i>	206
7.1.2	<i>The influence of processing parameters on injection-moulded PET</i>	211
7.2	Characterization of natural polymers	214
7.2.1	<i>Starch</i>	214
7.2.2	<i>Gelatin</i>	218
7.2.3	<i>Keratin</i>	221
7.3	Mechanical changes at polymer surfaces	222
7.3.1	<i>Wearing of polymer implants</i>	222
7.3.2	<i>Characterization of irradiated and ion-implanted polymer surfaces</i>	225
7.4	Weatherability characterization of polymer materials	227
7.4.1	<i>Very-near-surface microhardening of weathered window-grade PVC</i>	227
7.4.2	<i>Damage characterization of carbon-reinforced composites</i>	227
7.4.3	<i>Weathering of i-PP pipes</i>	228
7.5	Conclusions	230
7.6	References	230
	Author index	233
	Subject index	236