

# Contents

<b>The Authors .....</b>	<b>V</b>
<b>Preface .....</b>	<b>VII</b>
<b>1 Overview of Rubber Rheology and Dynamic Property Tests .....</b>	<b>1</b>
1.1 Introduction to the Uniqueness of Rubber Rheology .....	1
1.2 Basic Tensile Testing .....	3
1.3 Hardness Testing .....	5
1.4 Density .....	6
1.5 Mooney Viscosity .....	7
1.6 ODR Curemeter .....	10
1.7 Capillary Rheometer .....	12
1.8 Moving Die Rheometer (MDR) .....	13
1.9 Rubber Process Analyzer (RPA) .....	15
1.10 Dynamic Mechanical Analyzer (DMA) .....	16
1.11 Flex Fatigue Testers .....	18
1.12 Flexometer Delta T .....	19
1.13 Measuring Dispersion .....	20
1.14 Other Relevant Rubber Tests .....	22
1.14.1 Compression Plastimeters .....	22
1.14.2 Tear Properties .....	23
1.14.3 Electrical Conductivity Properties .....	24
1.14.4 Differential Scanning Calorimetry (DSC) .....	24
1.14.5 Thermogravimetric Analysis (TGA) .....	25
1.14.6 Fourier Transform Infrared Spectroscopy (FTIR) .....	26

1.14.7 Attenuated Total Reflectance (ATR) .....	28
1.14.8 Gel Permeation Chromatography (GPC) .....	28
1.14.9 Nuclear Magnetic Resonance Spectroscopy (NMR) .....	28
1.14.10 BET (Brunauer, Emmett, and Teller) Nitrogen Adsorption Surface Area Apparatus .....	29
1.14.11 Thermal Conductivity Meters .....	29
<b>2 Mooney Viscometer .....</b>	<b>35</b>
2.1 Description of the Mooney Viscometer .....	35
2.2 Mooney Tests .....	37
2.3 Mooney Viscosity .....	37
2.4 Measuring Mooney Scorch .....	42
2.5 Measuring Mooney Stress Relaxation .....	46
2.6 Delta Mooney Test for Oil Extended Emulsion SBR .....	48
2.7 Variable Speed Mooney .....	49
2.8 Limitations of the Mooney Viscometer .....	51
<b>3 Capillary Rheometer .....</b>	<b>55</b>
3.1 Introduction .....	55
3.2 Basic Types of Capillary Rheometers .....	57
3.3 Measurement of Viscosity with a Capillary Rheometer .....	58
3.4 Types of Capillary Rheometer Tests .....	59
3.4.1 Stability Test .....	60
3.4.2 Shear Rate Sweep .....	61
3.4.3 Measure of True Viscosity with Capillary Rheometers by Using Corrections .....	63
3.4.3.1 Bagley Correction .....	63
3.4.3.2 Rabinowitsch Correction .....	64
3.4.4 Capillary Rheometer Wall Slippage .....	64
3.5 Behavior of Non-Newtonian Materials .....	65
3.6 Appearance of Capillary Rheometer Extrudate .....	69
3.7 Capillary Rheometry in Factory Problem Solving .....	71
3.8 Prediction of Factory Processability with Capillary Rheometers .....	72
3.9 Limitations of Capillary Rheometers in Rubber Testing .....	74

<b>4 Curemeters .....</b>	<b>77</b>
4.1 Oscillating Disc Rheometer .....	77
4.2 Moving Die Rheometer .....	79
4.3 ASTM D2084 and D5289 Data Points for Curemeters .....	84
4.4 Dynamic Properties Measured with an MDR .....	87
4.5 ASTM and ISO Standards for Curemeters and the Selection of Test Conditions .....	92
4.6 The RPA as a Curemeter .....	94
4.6.1 Description of the RPA as a Curemeter .....	94
4.6.2 Using RPA Dynamic Data for Analyzing Cure Curves .....	94
4.6.2.1 $t_{MAX S''}$ during Cure (Time to $S''$ Peak) .....	94
4.6.2.2 $S'$ and $S''$ due to Crosslink Density .....	96
4.6.2.3 $S'$ and $S''$ due to Filler Loading .....	97
4.6.3 Effect of Oil .....	99
<b>5 Viscoelastic Characterization of Rubber .....</b>	<b>101</b>
5.1 Introduction to the Viscoelastic Property .....	101
5.2 Pure Elasticity .....	101
5.3 Pure Viscosity .....	103
5.4 Modeling Viscosity .....	106
5.5 Viscoelastic Properties .....	107
5.6 Measurement of Viscoelastic Properties with Sinusoidal Deformation ..	110
5.7 Applications for Viscoelastic Properties .....	114
5.8 Instruments with Multiple Test Capabilities .....	114
5.9 RPA Test Conditions .....	123
5.10 The Advantages of the RPA over Scientific DMAs .....	125
5.11 The Basics of Measuring and Calculating Dynamic Moduli .....	128
5.12 The Basics of Measuring and Calculating Dynamic Viscosity .....	132
5.13 Compliance .....	136
5.14 Extension/Compression Modulus and Compliance .....	137
5.15 Spring Rate Constants and Damping Coefficients .....	140
5.16 Time Temperature Superpositioning (TTS) .....	142
5.17 Statistical Evaluation of Rheometers .....	145

<b>6</b>	<b>Types of Rubber RPA Rheological Tests .....</b>	<b>151</b>
6.1	Summary of RPA Rheological Data .....	151
6.2	Types of RPA Rheological Subtests .....	152
6.2.1	Timed .....	152
6.2.2	Temperature Sweep .....	154
6.2.3	VTA (Thermal Ramp) .....	157
6.2.4	Frequency Sweep .....	159
6.2.5	Strain Sweep: Low .....	161
6.2.6	Strain Sweep: High .....	163
6.2.7	Matrix .....	165
6.2.8	LAOS Sweep .....	165
6.2.9	Stress Relaxation .....	169
6.3	ASTM, ISO, and DIN Standard Methods for RPA Testing of Elastomers and Compounds .....	170
6.3.1	ASTM D6204 Part A .....	170
6.3.2	ASTM D6204 Part B .....	172
6.3.3	ASTM D6204 Part C .....	172
6.3.4	ASTM D6204AB for R&D .....	174
6.3.5	ASTM D6601 .....	175
6.3.6	ASTM D8059 .....	177
6.3.7	ASTM D6048 .....	179
6.3.8	ASTM D7050 .....	181
6.3.9	ASTM D7605 .....	182
6.3.10	ASTM D5289 .....	184
6.3.11	DIN 53529 .....	184
6.3.12	ISO 13145 .....	185
6.4	Nonstandard Methods for RPA Testing of Elastomers and Compounds ..	186
6.4.1	Dispersion Using Dynamic Mechanical Methods .....	186
6.4.2	Multiple Frequency Sweeps with Increasing Strains .....	187
6.4.3	Multiple Identical Strain Sweeps .....	188
6.4.4	Anaerobic Heat Aging .....	189
6.4.5	Aerobic Heat Aging .....	189
6.4.6	Viscous Heating of Uncured Rubber Compounds .....	190
6.4.7	Heat Buildup $\Delta T$ for Cured Rubber Compound .....	191

<b>7</b>	<b>Raw Rubber Effects on Processability</b>	<b>195</b>
7.1	Natural Rubber	195
7.2	Synthetic Raw Rubber	201
7.2.1	Average Molecular Weight	203
7.2.2	Molecular Weight Distribution	205
7.2.3	Long Chain Branching	207
7.2.4	Gel	209
7.2.5	Changes in the Chemical Composition	210
7.2.6	Statistical Confounding	212
7.3	High Strain Testing of Synthetic Elastomers	213
7.4	Measuring Imparted Differences in Shear Thinning Properties	214
7.5	Stress Relaxation of Elastomers and Processability	215
7.6	Master Curve and Glass Transition Temperature	217
7.7	WLF Shifts for Raw Elastomers	220
7.8	Testing Liquid Elastomers	221
7.9	Testing Thermoplastic Elastomers (TPE)	223
7.10	Processability Data Analysis	224
<b>8</b>	<b>Filler Effects on Rubber Compound Processability</b>	<b>229</b>
8.1	Filler Effects on Rubber Compound Properties	229
8.2	Carbon Black Effects	232
8.2.1	Carbon Black Surface Area	234
8.2.2	Correlation with Carbon Black Structure	240
8.2.3	Correlation with Carbon Black Surface Activity	245
8.2.4	Effects of Variation in Loading on Uncured vs. Cured Dynamic Properties	246
8.3	Oil Effects	249
8.4	Silica Effects	254
8.4.1	Effects of Silanization	254
8.4.2	Effects of Silica Surface Area	256
8.4.3	Effects of Silica Loading	257
8.4.4	Recovery of the Silica Network after Destruction	258
8.4.5	Special Role of Structure for Silica	259
8.5	Effects of Fully Reinforcing Fillers on the Cox-Merz Correlation	261

8.6	Effects of Filler Type and Concentration on Shear Thinning Profiles . . . . .	262
8.7	Effects of Filler Room Temperature Storage on Formation of Bound Rubber and Rheology of Filled Rubber Compounds . . . . .	263
<b>9</b>	<b>Measuring Quality of Mix and Processability . . . . .</b>	<b>267</b>
9.1	Dispersion of Fillers during Mixing . . . . .	267
9.2	Mastication of Elastomers during Mixing . . . . .	268
9.3	Rheological Changes during Mixing . . . . .	268
9.4	Optimal Rheological Conditions for Mix Quality Measurement . . . . .	269
9.5	State of Mix and Percent Dispersion . . . . .	271
9.6	Effect of Oil on Rubber Mixing . . . . .	272
9.7	Effect of Phase Mixing . . . . .	275
9.8	Special Test Conditions for Measuring State of Mix . . . . .	277
9.8.1	Mooney Viscosity . . . . .	277
9.8.2	RPA at $\pm 100\%$ Strain (ASTM D6204 Part B) . . . . .	277
9.8.3	RPA Payne Effect Plateau (ASTM D8059) . . . . .	280
9.8.4	RPA Stress Relaxation (ASTM D6048) . . . . .	281
9.8.5	Special Reflective Microscope with Computer Analysis (ASTM D7723) . . . . .	283
9.9	Scorch Safety Measurements . . . . .	283
9.9.1	Traditional Mooney Scorch . . . . .	284
9.9.2	Traditional Curemeter Scorch Measurements . . . . .	285
9.9.3	Dynamic Property Measurements of Scorch . . . . .	285
9.9.4	Lower Cure Temperature Effects . . . . .	286
9.9.5	Variable Temperature Measurements of Scorch . . . . .	286
9.9.6	Optimizing Strain and Frequency Effects for Scorch Measurements . . . . .	286
9.9.7	Effects of Controlled Stress Measurements on Scorch . . . . .	287
9.10	Cure Rate Measurements . . . . .	287
9.11	Work History vs. Heat History . . . . .	289
9.12	State of Cure . . . . .	291
9.13	Capillary Rheometer Viscosity vs. Dynamic Viscosity . . . . .	293
9.14	Selecting Best Test Conditions for Factory Control . . . . .	294
9.15	Using SPC Charts of Key Parameters . . . . .	295

9.16	Downstream Processability Stages .....	296
9.16.1	Calendering .....	297
9.16.2	Extrusion .....	297
9.16.3	Curing .....	298
<b>10</b>	<b>After-Cure Dynamic Properties .....</b>	<b>303</b>
10.1	Comparison of After-Cure Dynamic Properties and Product Performance .....	304
10.1.1	Tires .....	305
10.1.2	Automotive Isolators and Dampers .....	310
10.1.3	Sports Applications .....	312
10.1.4	Rubber Seals and Gaskets .....	313
10.1.5	Blowout Preventer .....	313
10.1.6	Conveyor Belts, Timing Belts, and Power Belts .....	313
10.2	Payne Effect for Cured Rubber Compounds .....	314
10.3	Mullins Effect for Cured Rubber Compounds .....	321
10.4	Low Strain vs. High Strain Measurements of Cured Vulcanizates .....	324
10.5	ASTM Standard Test Method Using RPA .....	325
10.6	Relation of Compression and Extension Dynamic Properties to Shear Measurements .....	330
<b>11</b>	<b>Methods for Analyzing the Cure Reaction .....</b>	<b>337</b>
11.1	Reaction Kinetics .....	340
11.1.1	The Reaction Rate Constant .....	340
11.1.2	Arrhenius Model .....	344
11.1.3	Order of Reaction ( $n$ ) in Cure Kinetics .....	349
11.2	Applications of the Maximum Cure Rate (MCR) .....	349
11.3	Applications for the RPA Thermal Ramp .....	351
11.4	Concept of Cure Equivalents .....	354
11.5	Direct Measurement of Complex Non-Isothermal Cures .....	357
<b>Index</b>	.....	<b>363</b>