Contents

face to the Second Edition

Preface to the First Edition

knowledgements xi

Chemistry and Basic Intermediates
Introduction
Basic Chemistry
Basic Structure of a Polyurethane Elastomer
Synthesis of Basic Urethane Building Blocks
Isocyanates
Storage Life and Reactions of Isocyanates with Themselves—Dimers (Uretidinediones) 15
Uretidiones 19
Polyols. 19
Polyesters 21
Polyethers 24
Chain Extenders and Crosslinking Agents 27
Catalysts 27

2. Polyurethane Elastomer Chemistry 29
Liquid Processing Routes 29
Millable Elastomer Synthesis 30
Thermoplastic Linear Urethane Elastomers 34
Concept of Equivalent Weights 36
Concept of the Complete Urethane Chemical System 38
Polyol Quantization by Chemical Analysis 40
Other Isocyanate Analytical Terms 42
Other Useful Terms 43
Example Calculation for a Typical Polyurethane Elastomer Synthesis 45
Blends 46
Calculation of Isocyanate Proportions for a Water Blow Foam System. 48
Effect of Flexible to Rigid Segment on Urethane Properties 50

3. Property–Structure Relationships in Polyurethanes . . .
Introduction . . . . . .
Flexible Segments . . . . . .
Polyethers . . . . . .
Polycaprolactones . . . . . .
Rigid Segments . . . . . .
Aliphatic *Versus* Aromatic Diisocyanates . . . . . .
Aliphatic Diisocyanates and Transparency . . . . . .
Effect of Diisocyanate Structure on the Relative Thermal Stability of Polyurethane Elastomers . . . . . .
Chain Extension of Unsymmetrical Diisocyanates . . . . . .
Glycols . . . . . .
Chain Extension of Symmetrical Diisocyanates with Diols . . .
Synthesis. . . . . .
Even Molar Ratio Effects . . . . . .
Influence of the Diol Structure on Thermal Stability of the PU Elastomer: Molar Ratios 1:2:1 . . . . . .
Loss Tangent Values and Chain Extender Composition. . . . .
Uneven Molar Ratio Effects with Respect to the Diisocyanate . .
Comparison of the Thermal Stability Effects of a Diamine with Diols (as Chain Extenders) in Polyurethane Elastomers (Molar Ratio 1:3:2)
Differential Scanning Calorimetry (DSC) as a Means of Predicting Thermal Stability (Molar Ratio 1:2:1) . . . . . .
DSC Studies and the Molar Ratio 1:2.6:1 . . . . . .
DSC as a Means of Predicting the Relative Thermal Stability of a Diamine (Polacure) with Diol Chain Extenders . . . . . .
Contribution of Crosslinks to Properties . . . . . .
Crosslinking and Thermal Stability in Polyurethane Elastomers .
Synthesis Technique . . . . . .
In-Situ Isocyanate and Isocyanurate Crosslinking . . . . . .
PU Elastomer Compositions . . . . . .
Influence of % Free NCO on the Properties of the PU Elastomer at Room Temperature . . . . . .
Strength Properties at Elevated Temperature . . . . . .
Dynamic Mechanical Thermal Analysis (DMTA) . . . . . .
Thermal Equilibrium Properties . . . . . .
Low Temperature Stiffening and Glass Transition Temperature (T_g) .
Hazards . . . . . .
Thermal Stability and Crosslink Structure in PUs . . . . . .
Structure in Polyurethane Elastomers . . . . . .
Continued Crystal Growth . . . . . .
Plasticization . . . . . .

4. Reaction Rates, Catalysis and Surfactant
Reaction Rates . . . . . .
Diisocyanates . . . . . .
Polyols. . . . . .
Temperature

Catalysis 113
Acid Catalysis and Prepolymer Stability (Shelf Life) 113
Shelf Life Stability of Prepolymers . . . 113
Base Catalysis 115
Additional Comments on RIM Catalysis . .
Tertiary Amines 117
Organometallic and Other Metal Compounds . 118
Catalyst Combinations 120
Surfactants (Surface Active Agents) . . . 120
Ionic Surfactants 120
Non-ionic Surfactants 120

5. Liquid Polyurethane Elastomer Systems. 122
Stable Prepolymer Systems 124
Simple Hand Casting Procedure 125
Chain Extenders 127
Processing of TDI Prepolymers 129
Processing Variables 131
Type of Curative. 132
Reaction Temperature 134
Other Representative Polymer Systems 135
Unstable Prepolymer System 152
Water Crosslinked Millable Vulkollan for Compression Moulding . 158
Cellular Polyurethane Elastomers 158
Vulkollan System 158
Cellular Urethanes from Stable Prepolymers 159
Solvents 160
Compression Moulding of Cast Elastomers 161
Spray Application of Urethane Elastomers 163
Note on Water Content of Polypols of Urethane Elastomers. . . 164
Alternative Chain Extenders to MOCA 165
3,3′-Dimethyl-4,4′-diaminodicyclohexylmethane 166
Diols as Chain Extenders 167
Synthesis and Properties of Polyurethane Elastomers Based on Aromatic *Versus* Aliphatic Diisocyanates 169
CHDI Prepolymer Synthesis and Chain Extension. 169
PPDI Prepolymer Synthesis and Chain Extension 171

6. Reaction Injection Moulding (Liquid Injection Moulding) 174
The Process 178
RIM Formulation 179
Water 181
Physical Properties of RIM Urethane Systems . . . 182
RIM Machine Design 182
Energy Requirements of RIM. 186
Mechanism of Impingement Mixing 187
Mould Design. 187
Transition Zone 189

Catalysis 113
Acid Catalysis and Prepolymer Stability (Shelf Life) 113
Shelf Life Stability of Prepolymers . . . 113
Base Catalysis 115
Additional Comments on RIM Catalysis . . 117
Tertiary Amines 117
Organometallic and Other Metal Compounds . 118
Catalyst Combinations 120
Surfactants (Surface Active Agents) . . . 120
Ionic Surfactants 120
Non-ionic Surfactants 120

Liquid Polyurethane Elastomer Systems. 122
Stable Prepolymer Systems 124
Simple Hand Casting Procedure 125
Chain Extenders 127
Processing of TDI Prepolymers 129
Processing Variables 131
Type of Curative. 132
Reaction Temperature 134
Other Representative Polymer Systems 135
Unstable Prepolymer System 152
Water Crosslinked Millable Vulkollan for Compression Moulding . 158
Cellular Polyurethane Elastomers 158
Vulkollan System 158
Cellular Urethanes from Stable Prepolymers 159
Solvents 160
Compression Moulding of Cast Elastomers 161
Spray Application of Urethane Elastomers 163
Note on Water Content of Polypols of Urethane Elastomers. . . 164
Alternative Chain Extenders to MOCA 165
3,3'-Dimethyl-4,4'-diaminodicyclohexylmethane 166
Diols as Chain Extenders 167
Synthesis and Properties of Polyurethane Elastomers Based on Aromatic *Versus* Aliphatic Diisocyanates 169
CHDI Prepolymer Synthesis and Chain Extension. 169
PPDI Prepolymer Synthesis and Chain Extension 171

6. Reaction Injection Moulding (Liquid Injection Moulding) 174
The Process 178
RIM Formulation 179
Water 181
Physical Properties of RIM Urethane Systems . . . 182
RIM Machine Design 182
Energy Requirements of RIM. 186
Mechanism of Impingement Mixing 187
Mould Design. 187
Transition Zone 189

Moulding
Ribs and Radius
Runners
Mould Sealing
Processing Economics
Reinforced Reaction Injection Moulding Machinery
Dispersion of Fibre Reinforcement

7. Millable Polyurethane Elastomers
Sulphur Vulcanized Grades
Millable Polyether Polyurethane Elastomers
Plasticization
Filler Reinforcement
Isocyanate-Cured Urethane Rubber
Peroxide-Cured Polyurethane Elastomers
Cure Temperature
Effect of Fillers
Combined Peroxide and Diisocvanate Cures

8. Polyurethane Adhesives
Reasons for Adhesive Properties of Polyurethane and Diisocyanate-Based Adhesives.
Isocyanate Reactivity
Self Polymerization
Surface Wetting Properties
Polarity
Graded Physical Properties
Reaction with Unreactive Surfaces
Reasons for the Apparent Universal Applications of Polyurethanes as Adhesives
Methods of Using Isocyanates as Adhesives
As an Isocyanate Primer
By In-Situ Polyurethane Polymerization
As Polyurethane Elastomer Without or With Added Polyisocyanates
Thermoplastic Polyurethane Elastomer Types
Elastomer Gum Types
Blocked Di- or Polyisocyanate Adhesives
Aqueous Dispersions of Polyurethanes
Film and Tape Polyurethane Adhesives
Powdered Polyurethane
Stabilization of Adhesives

9. Thermoplastic (Linear Polyurethane Elastomers)
Partially Crosslinked Thermoplastic Polyurethanes
Synthesis of Thermoplastic Polyurethane
Preparation
Notes on Large-Scale Production Synthesis Procedures
Processing of Thermoplastic Polyurethanes

Extrusion 250
Injection Moulding 251
Calendering 253
Hot-Melt Calendering 254
Film Lamination 255
Solution Applications 256
Reactive Coatings 256
100%-Solids Reactive Systems 257
Commercially Available TPUs 257
Comment About the Set Properties of TPUs 260
Microporous Thermoplastic Polyurethanes 260
Blends 263
Processing of Transparent Thermoplastic Polyurethane Elastomer by Injection Moulding 264
Thermoplastic Polyurethane Elastomers as Hydraulic Seal Materials . 264
CHDI-Based Polyurethanes 267
Polyester TPUs 268
Mixed Aliphatic Diols as Chain Extenders (CHDM and BDO) . . 277
Polyether TPUs 277
Thermal Stability 278
Polycaprolactone/CHDI Polyurethanes 278
Polycaprolactone/PPDI Polyurethanes 278
Polyether/PPDI Polyurethanes 278
Polyether/CHDI Polyurethanes 279
Energy Absorption (tan δ) 279
Post-Cure Prediction Responses 279
Conclusions 279

10. Water Dispersions of Polyurethane Elastomers 281
Self-Emulsifying Latex 281
Emulsified Latex 282
Polyurethane Ionomers 284
Special Features of Water-Dispersed Polyurethane Elastomers . . 286
Anionic Dispersions 287
Cationic Dispersions 289
Practical Example for the Preparation of a Polyurethane Dispersion (Melt-Dispersion Technique) 290

1. Analysis and Characterization of Polyurethane Elastomers 292
Diisocyanates 292
Measurement of NCO Content 293
Total Chlorine: Principle of the ASTM Method D1638 . . 295
Acidity 295
Hydrolyzable Chlorine 296
Isomer Ratio 297
Activity of Diisocyanate 297
Diisocyanates in the Atmosphere 298
Polyol Analysis 303

Hydroxyl Number
Primary and Secondary Hydroxyl Groups
Water Content
Acid Number
Measurement of pH (Apparent)
Hydrolytic Stability
Unsaturation
Peroxide Content
General Analytical Parameters for Polyols
Infrared Spectroscopy Techniques
Determination of Isomer Ratio of TDI by Infrared Spectroscopy
Determination of Unreacted NCO Groups in a Polyurethane Elastomer
An Additional Rapid Infrared Method for the Quantitative Analysis of NCO Present in a Polyurethane Elastomer
Chromatography Techniques
Gas–Liquid Chromatography
Thin Layer Liquid Chromatography
Thermal Analysis
Identification of the Components in a Polyurethane
Polyesters
Polyethers
Differentiation of Polymers Present in a Polyurethane
General Analysis of Miscellaneous Elements in a Polyurethane Elastomer
Colour Reactions for Polyurethane Identification
References

12. Special Types of Polyurethane Elastomers
Hydroxy-Terminated Polybutadienes
Process Oils and Plasticizers
Low-Temperature Resistance
Transparent Polyurethane Elastomers
Amine-Terminated Polyols
Fluorinated Polyolls
UV Light Curable PU Systems

13. Properties and Applications
Tensile Properties
In Tension
In Compression
Load Deflection Properties
Comparison of Physical Properties of Polyurethane Elastomers with Common Rubbers and Plastics
Energy Absorption Properties
Wear Resistance
Friction Properties
Environmental and Ageing Properties
Light Resistance
High Energy Radiation Effects
Electrical Properties

Applications 390
Current Types of PU Elastomer . . 391
Solid Tyres 392
Pneumatic Polyurethane Tyres . . 392
Microcellular Shoe Solings . . . 395
Blends of TPU with other Thermoplastics 397
Rollers 397
Automotive Body Panels and Bumpers
Rain-Erosion Protection of Surfaces . 398
Cold-Curing Elastomers . . . 398
Low-Speed Tyre-Filling Compositions 398
Water Vapour Permeable PU Elastomers 399
Polyurethane Elastomers in Medicine . 400
Millable Polyurethane Elastomers . . 403
Fillers for Cold-Cast Polyurethane . 404
Plasticizers for Polyurethane Elastomers 405
Manufacturing Factors 405
Moulding 405
Shrinkage 405
Mould Lubricant 405
Mould Cleaning 406
Machining 406

14. Health Hazards and Precautions 407
Toluene Diisocyanate (TDI) 409
Diphenylmethane Diisocyanate (MDI) 409
1,5-Naphthalene Diisocyanate (NDI) 411
Toxicity Data for the Analogues Aromatic and Aliphatic Diisocyanates 411
General Toxicity Problems 413
Handling Isocyanates and Manufacture of Polyurethane Products . 413
Skin Irritation 414
Protective Clothing 416
First Aid 416
Specific Hazards Associated with the Manufacturing Processes . . 417
Urethane Rubbers 417
Manufacture of Moulded Articles 417
Surface Coatings 418
Printing Inks 419
Adhesives 420
Isocyanate Monitoring and Detection 420
Analytical Monitoring Techniques 421
Alternative Method 423
Determination of TDI in Solvent Atmosphere 424
Diamines 425
Polyols and Glycols 425
Waste Disposal 426
References and Bibliography 427
Index 429