

Contents

1	Characterisation of Elastomers Using (Multi) Hyphenated Thermogravimetric Analysis Techniques	1
1.1	Introduction	1
1.2	Instrumental Part	3
1.2.1	Experimental	12
1.3	Applications of Hyphenated Thermogravimetric Analysis Techniques	14
1.3.1	Thermogravimetry - Fourier Transform Infrared Spectroscopy	19
1.3.2	Thermogravimetry-Mass Spectrometry	25
1.3.3	Thermogravimetry - Differential Scanning Calorimetry	29
1.3.4	Thermogravimetry - Differential Scanning Calorimetry - Mass Spectrometry	30
1.3.5	Thermogravimetry - Differential Thermal Analysis	30
1.3.6	Thermogravimetry - Differential Thermal Analysis - Mass Spectrometry	33
1.3.7	Thermogravimetry - Gas Chromatography - Mass Spectrometry	34
1.3.8	Thermal Desorption - Gas Chromatography - Fourier Transform Infrared Spectroscopy/Mass Spectrometry	34
1.4	Future Prospects of Hyphenated Thermogravimetric Techniques in Elastomer Characterisation	35
1.5	Summary	36
2	Photoacoustic Fourier Transform Infrared Spectroscopy of Rubbers and Related Materials	49
2.1	Introduction	49
2.2	History of Photoacoustic Spectroscopy	49

Spectroscopy of Rubbers and Rubbery Materials

2.3	Theory of Photoacoustic Spectroscopy	50
2.4	Instrumentation for PA-FTIR Analyses	52
2.5	Analysis of Carbon-Filled Rubbers	57
2.6	Quantitative Analysis of Polymers	60
2.7	Surface Analysis and Depth Profiling	66
2.8	Determination of Orientation Function of Polymeric Materials	71
2.9	Conclusion	71
3	Infrared Spectroscopy of Rubbers	77
3.1	Introduction	77
3.2	Sample Preparation	80
3.3	Different Types of IR Spectroscopy	81
3.4	Quantitative Analysis	81
3.5	Applications of IR Spectroscopy	82
3.5.1	Rubber Blends	92
3.5.2	Self-crosslinking Blends	96
3.5.3	Polyurethanes	98
3.5.4	Rubber-filler Interaction	102
3.5.5	Milling	108
3.5.6	Adhesion	111
3.5.7	Degradation	113
3.6	Reverse Engineering	113
3.7	Conclusion	114
4	Application of Infrared Spectroscopy to Characterise Chemically Modified Rubbers and Rubbery Materials	125
4.1	Introduction	125
4.2	The Infrared Spectra of Commonly Used Diene Rubbers	125

4.3	Hydrogenation	126
4.4	Halogenation	135
4.5	Isomerisation	139
4.6	Cyclisation	139
4.7	Hydrosilylation	142
4.8	Hydroboration	144
4.9	Hydroformylation	144
4.10	Oxidation	146
4.11	Phosphonylation	146
4.12	Sulfonation	147
4.13	Ionomer Formation	147
4.14	Ionomeric Blends	151
4.15	Weathering and Degradation of Polymers	153
4.16	Modification by Radiation	156
4.17	Conclusion	157
5	Infrared Spectroscopy of Rubbery Materials	167
5.1	Introduction	167
5.2	Polyethylenes	168
5.3	Polyvinyl Chloride	180
5.4	Thermoplastic Elastomers	188
5.5	Conclusion	200
6	Crosslinking of EPDM and Polydiene Rubbers Studied by Optical Spectroscopy	207
6.1	Introduction	207
6.1.1	General Introduction to EPDM	207

Spectroscopy of Rubbers and Rubbery Materials

6.1.2	EPDM Crosslinking	208
6.1.3	Studies into the Chemistry of Rubber Crosslinking	209
6.1.4	Scope	210
6.2	Sulfur Vulcanisation	211
6.2.1	Sulfur Vulcanisation of Polydiene Rubbers	211
6.3	Peroxide-curing	225
6.3.1	General	225
6.3.2	Polydiene Elastomers	226
6.3.3	EPDM	227
6.4	Concluding Remarks and Future Outlook	237
7	NMR Imaging of Elastomers	247
7.1	NMR Imaging and Contrast	248
7.1.1	Principle of Fourier NMR	248
7.1.2	Spatial Resolution	251
7.1.3	Contrast	253
7.2	Applications	264
7.2.1	Defects and Heterogeneities in Technical Elastomer Products	265
7.2.2	Covulcanisation	269
7.2.3	Blending	271
7.2.4	Crosslink Density	271
7.2.5	Vulcanisation Process	273
7.2.6	Ageing	274
7.2.7	Sample Deformation	275
7.3	Spatially Resolved NMR	276
7.3.1	The NMR-MOUSE	277
7.3.2	Applications	279
7.3.3	Imaging with the NMR-MOUSE	282
7.4	Summary	282

8	NMR in Soft Polymeric Matter: Nanometer Scale Probe	291
8.1	Introduction	291
8.2	Polymeric Networks	292
8.2.1	Molten High Polymers	292
8.2.2	Crosslinked Chains	292
8.2.3	Semi-crystalline Polymers	292
8.2.4	Block Copolymers	293
8.2.5	Loaded Polymers	293
8.2.6	Aggregated Polymers	294
8.2.7	Network Distribution Function	294
8.3	Basis of the NMR Approach	295
8.3.1	Chain Elongation	296
8.3.2	NMR Evidence for Networks: Pseudo-solid Spin-echoes	298
8.4	Crosslinked Chains	299
8.4.1	End-linked Calibrated Chains	299
8.4.2	Characteristic NMR Rates	299
8.4.3	Strand Length Dependence	301
8.4.4	Randomly Crosslinked Chains	302
8.4.5	Latex Suspensions	306
8.4.6	Kinetics of Gelation	307
8.5	Polymeric Crystallisation	307
8.5.1	Crystallisation-NMR Relationship	307
8.5.2	Kinetics of Crystallisation	308
8.6	Entangled High Polymers	309
8.6.1	Temporary Networks	310
8.6.2	Short Chain Dynamics	312
8.6.3	Long Chain Dynamics	313
8.7	Adsorption on Mineral Aggregates	315
8.8	Conclusion	317

9	Chemical Characterisation of Vulcanisates by High-Resolution Solid State NMR	321
9.1	Introduction	321
9.2	Sulfur Vulcanisation Mechanism	322
9.3	The NMR Methods for Assigning Resonances to Chemical Structure	324
9.4	Unaccelerated Sulfur-vulcanisation of NR	327
9.5	Accelerated Sulfur-vulcanisation of NR and IR	327
9.6	Sulfur-vulcanisation of BR	333
9.7	Sulfur-vulcanisation of SBR	338
9.8	Peroxide, Radiation, and High Pressure Vulcanisation	338
9.9	Vulcanisation of Other Elastomer Systems	340
9.10	Effect of Carbon Black on Vulcanisation of Elastomers	341
➤ 9.11	Effect of Silica Filler on Vulcanisation Chemistry	347
9.12	Thermal-Oxidation of Network Structures	347
9.13	Summary	348
10	Characterisation of Chemical and Physical Networks in Rubbery Materials Using Proton NMR Magnetisation Relaxation	353
10.1	Introduction	353
10.2	Network Structure Analysis by Means of NMR Transverse Magnetisation Relaxation	355
10.3	Characterisation of Network Heterogeneity and Network Defects	360
10.4	Network Structure in Oil-Extended Rubbers - Effect of Chain Entanglements	366
10.5	Network Structure in Filled Rubbers - Rubber-Filler Interface and the Structure of the Physical Network	368

10.5.1	NMR Relaxation of Filled Rubbers	368
10.5.2	Carbon-Black-Filled Rubbers	369
10.5.3	Silica-Filled Silicon Rubbers	374
10.5.4	Silica-Filled Conventional Rubbers	378
10.6	Chains Grafted onto a Filler Surface	379
10.7	Semi-Crystalline Elastomers	381
10.8	Ionic Viscoelastic Materials	383
10.9	Rubbery Phases in Blends and Emulsions	384
10.10	Real-Time NMR Experiments	385
10.11	Low-Field NMR Magnetisation Relaxation Experiments for Quality Control Purposes	387
10.12	Conclusions	388
11	High Resolution NMR of Elastomers	401
11.1	Introduction	401
11.2	Structural Feature of Elastomers	402
11.3	Analysis of Chemical Composition and Sequence Distribution	404
11.3.1	Accuracy of NMR Measurements of Chemical Composition	404
11.3.2	Analysis of Chemical Composition Distribution using SEC-NMR	410
11.3.3	Analysis of Sequence Distribution	413
11.3.4	Analysis of Chemically Modified Structure and Graft Polymers	419
11.4	Analysis of End-groups and Branching	422
11.4.1	Assignment of Small Signals	422
11.4.2	Functionality of Telechelic Diene Polymers	423
11.4.3	Structure of Terminal Groups	424
11.4.4	Structure of Branch-points and Coupling Points	426

Spectroscopy of Rubbers and Rubbery Materials

11.5	Structural of Naturally Occurring Polyisoprenes	429
11.5.1	Structure of Natural <i>cis</i> - and <i>trans</i> -Polyisoprenes	429
11.5.2	Structure of Natural Rubber	433
11.6	Application of High-Resolution NMR	436
11.6.1	Multinuclear High-resolution NMR	436
11.6.2	NMR of Swollen State and Latex	443
11.7	Conclusion	448
12	¹²⁹Xe NMR of Elastomers in Blends and Composites.....	457
12.1	Introduction to ¹²⁹ Xe NMR Spectroscopy of Materials	457
12.1.1	¹²⁹ Xe NMR Spectroscopy	457
12.1.2	NMR of ¹²⁹ Xe in the Gas Phase	458
12.1.3	¹²⁹ Xe NMR of Polymers	459
12.1.4	¹²⁹ Xe Pulsed Field Gradient Echo (PFGE) Spectroscopy	462
12.2	Experimental	463
12.3	¹²⁹ Xe NMR of Ethylene/Propylene Copolymers in Blends and Block-copolymers with Polypropylene	465
12.4	¹²⁹ Xe NMR of an Ethylene/Propylene/Diene Terpolymer in Carbon Black Composites	474
12.5	The Self-diffusion Coefficient of Xe in Elastomers	480
12.5.1	General	480
12.5.2	Xe Diffusion in a iPP/EPDM Blend	482
12.5.3	Xe Diffusion as a Function of the Diffusion Time	485
12.6	Conclusions	487
13	Swollen Rubbery Materials: Chemistry and Physical Properties Studied by NMR Techniques	491
13.1	Introduction - The Swelling of Crosslinked Rubbers	491
13.1.1	The Theory of Rubber Swelling	491
13.1.2	Relationship with NMR Parameters	492

13.1.3	Reviews of NMR of Crosslinked Rubbers and Polymers	493
13.2	Motion of Polymer Chains in Polymer Solutions and Swollen Networks	494
13.2.1	Background	494
13.2.2	Solutions and Bulk Rubbers	494
13.3	Motion of Small Molecules in Swollen Rubbers	496
13.3.1	Self-Diffusion of Small Molecules in Rubbers	496
13.3.2	Self-Diffusion of Rubbers	498
13.4	NMR Imaging of Swollen Rubbers	499
13.4.1	Macroscopic Diffusion of Small Molecules in Swollen Rubbers	499
13.4.2	NMR Imaging of Swollen BR and Polyisoprene Rubbers	500
13.5	Studies of Network Density in Swollen Rubbers and Blends	502
13.5.1	Measurements of Transverse Relaxation Times	502
13.5.2	Estimation of Crosslink Density from NMR Linewidths	506
13.5.3	High-Resolution ^{13}C MAS NMR of Rubbers	510
13.6	Summary	511
14	Multidimensional NMR Techniques for the Characterisation of Viscoelastic Materials	519
14.1	Introduction	519
14.2	Basics of NMR in Viscoelastic Polymers	520
14.2.1	Anisotropic Spin Interactions	520
14.2.2	Manipulation of Spin Interactions	522
14.2.3	Residual Couplings and Dynamic Order Parameters	524
14.2.4	One-dimensional NMR Studies of Molecular Motions and Dynamic Order	526
14.3	Multidimensional NMR Spectroscopy of Viscoelastic Materials	529
14.3.1	Principle of Multidimensional NMR	529

Spectroscopy of Rubbers and Rubbery Materials

14.3.2 Two-dimensional NMR Techniques and Applications to Viscoelastic Polymers	530
14.5 Conclusion	550
15 Deuterium NMR in Rubbery Materials	557
15.1 Introduction	557
15.2 ² H NMR Background	559
15.3 Model, Labelled Rubber Systems	561
15.3.1 General Presentation: End-linked versus Randomly Crosslinked Networks	561
15.3.2 Pseudosolid Behaviour	561
15.3.3 Dangling Chains	563
15.3.4 Time Scale of Motions	563
15.3.5 Uniaxially Deformed Model Networks	566
15.3.6 Physical Origin of the Induced Orientation.....	573
15.3.7 Correlation to Elastic Properties	575
15.4 Using Deuterated Probes	579
15.5 Filled, Composite and Thermoplastic Elastomers	582
15.5.1 Filled Elastomers.....	582
15.5.2 Semi-crystalline Polymers.....	584
15.5.3 Thermoplastic Elastomers.....	585
15.6 Conclusion	588
Abbreviations	597
Contributors	607
Index	611