

Table of Contents

Zusammenfassung	5
Table of Contents	11
List of Abbreviations	15
1 Introduction, Background, and Research Objectives	21
2 Radiation Crosslinking of Polymers: Fundamentals and Mechanisms in Polyamide 6	23
2.1 State of the Art in Radiation Crosslinking of Polymers	23
2.2 Radiation-Induced Reactions and Crosslinking Mechanisms in Polyamide 6	28
3 Conventional Crosslinking Enhancers and their Limitation	31
3.1 Triallyl isocyanurate	31
3.2 Potential	34
3.3 Environmentally Friendly Process	35
4 Regulatory Framework for Additives in Food-Contact Materials	37
4.1 Legal Basis: EU Regulation No. 10/2011	37
4.2 EFSA Requirements for Tests in Approval Procedures	39
4.3 Toxic Compounds with Food Contact Approval	45
5 Biotransformation and Toxicological Principles of Unsaturated Compounds	47
6 Requirements for Safe and Effective Radiation Crosslinking Enhancers	53
7 Molecular Design, Dosage Principles, and Reaction Mechanisms of Crosslinking Enhancers	57
7.1 Structures of Radiation Crosslinking Enhancers	57
7.2 Dosage	59
7.2.1 Elucidation of the Reaction Mechanism of Radiation Crosslinking of Polyamide 6 with Allylamides	63
7.2.2 Dosage and Reaction Probability	64
7.2.3 Length and Mobility of the Crosslinking enhancer	66
7.2.4 Calculation of Dosage Using Specific Iodine Value	66
7.2.5 Dosages of Potential Radiation Crosslinking Enhancers, Summary	68

7.2.6	Dosage of Other Additives	69
8	Synthesis Pathways, Semi-Biobased Routes, and Analytical Characterization of Allylamides	73
8.1	Crosslinking Enhancers Based on Soybean Oil	73
8.2	Crosslinking Enhancers Based on Lycopene	74
8.3	Synthesis of Allylamides and other Crosslinking Enhancers	75
8.4	NMR and DSC Results	96
8.5	Overview of the Synthesis Methods	105
9	Suitability of the Newly Developed Additives for Food-Contact Approval	107
9.1	Prediction of Genotoxicity and QSAR Models	110
9.2	VEGA Application	115
9.3	Raw Material Costs of the Crosslinking Enhancers	122
10	Thermal Stability of the Additives and Processing-Relevant Material Behaviour	131
11	Compounding, Irradiation Conditions, and Formation of Crosslinked Networks	138
11.1	Compounding	140
11.2	Injection Molding of Plates and ISO Standard Bars	141
11.3	Production of the Demonstrator "Frying Pan Handle"	142
11.4	Irradiation	144
11.5	Content and Crosslinking Degree	146
11.6	Gel Content of the Direct Compounds	149
11.7	Influence of the Molecular Weight of the Polyamide on the Crosslinking Result	156
11.8	Gel Content of Compounds with Masterbatches	160
11.9	Statistical Consideration of Gel Content Determinations	171
11.10	Network Density Determination According to Flory-Rehner	176
11.11	Statistical Analysis of Flory-Rehner Determinations	179
12	Mechanical and Thermomechanical Properties of Crosslinked Polyamide 6	183
12.1	Tensile Tests with Direct Compounds	184

12.2	Tensile Tests on Compounds with Masterbatches	192
12.3	Fused Deposition Modeling, 3D-printing	195
12.4	Dynamic-Mechanical Properties	198
12.4.1	DMTA Direct Compounds	202
12.4.2	DMTA Masterbatch Compounds	221
12.4.3	Summary Interpretation of the DMTA Studies	227
13	Heat Deflection Temperature and Thermal Service Performance of Crosslinked Polyamide 6	229
13.1	Heat Deflection Temperature of Direct Compounds	230
13.2	Heat Deflection Temperature of Masterbatch Compounds	235
14	Genotoxicity, Migration Behaviour, Safety Assessment, Summary and Conclusion	237
14.1	Suitable Solvents	237
14.2	OECD TG 471 Ames Tests	239
14.2.1	N, N'-Diallylurea	239
14.2.2	N, N'-Diallyldodecanediamide	243
14.3	OECD TG 487 In Vitro Micronucleus Tests	247
14.3.1	N, N'-Diallylurea	248
14.4	OECD TG 487 Cytotoxicity	260
14.4.1	N, N'-Diallylurea	261
14.4.2	N, N'-Diallyldodecanediamide	263
14.5	Migration Test	264
14.6	Summary of Key Findings	267
14.6.1	Objectives	267
14.6.2	Experiments	267
14.6.3	Findings	268
14.7	Unmet Objectives	271
14.8	Research Questions from Chapter 1	272
14.9	Costs, Sustainability and Outlook	273
14.10	Conclusion	275

References	277
Appendix I: Solution Attempts with Formic Acid	289
Appendix II: Statistical Information	291
Appendix III: Determinations According to Flory-Rehner	307
Appendix IV: VEGA HUB, Substances in the Training Set	313
OECD TG 471 Ames-Test	313
OECD TG 487 In-Vitro-Micronucleus-Test	335
Appendix V: Data from the Testing Service Provider LAUS GmbH	351