1 Introduction, Background, and Research Objectives

This chapter outlines the initial context of the work and explains the questions and objectives that guide the subsequent investigations.

The aim of the projects RayPlast (ZIM, ZF4068923VS8, duration: 03/01/2019 – 11/30/2021) and RayPrint (INNO-KOM, 49MF210084, duration: 10/01/2021 – 03/31/2024), conducted at the Thuringian Institute for Textile and Plastics Research e.V., Rudolstadt, and funded by the BMWi and BMWK, was to identify and characterize new crosslinking enhancers for the radiation crosslinking of polyamide 6, PA6. For broad industrial applicability, the new crosslinking enhancers should be suitable for use in food contact applications and, if possible, based on bio-based raw materials.

New compounds were identified, among which some from the class of allylamides proved particularly suitable for thermally demanding applications. Their excellent thermal stability, their safety in relevant genotoxicity tests, and their low to moderate migration tendencies suggest that a positive evaluation by the EFSA and subsequent inclusion in Annex 1, Table 1 of EU Regulation 10/2011 by the European Commission (= approval) can be expected.

The current state of the art for the radiation crosslinking of PA6 using the toxic and volatile crosslinking enhancer triallyl isocyanurate (TAIC) and the approval process for food contact additives in the European Union are described. Compounds with double bonds, which are important for radiation crosslinking, are partially epoxidized during biotransformation in the body (toxification of C=C double bonds). No crosslinking could be achieved with the bio-based, potentially crosslinkable soybean oil and lycopene.

The introduction of hydrogen atoms to the TAIC molecule resulted in N, N´-Diallylurea, the first member of the homologous series of allylamides. Many experiments were conducted with N, N´-Diallylurea, including the study of the effects of further co-additives such as antioxidants and nucleating agents.

All polyamide samples modified with allylamides showed high gel content after irradiation, a reduction in elongation at break with increasing radiation dose, a higher glass transition range, and often improved heat deflection temperatures.

The results of genotoxicity tests were predicted using the artificial intelligence tool "VEGA-Hub." N, N’-Diallyldodecanediamide underwent an Ames test according to OECD TG 471 and an in vitro micronucleus test according to OECD TG 487 with human lymphocytes. The results confirmed the prediction: N, N’-Diallyldodecanediamide is not genotoxic.

The migration of N, N’-Diallyldodecanediamide from polyamide samples was determined using methods for assessing overall migration. Depending on the food simulant used, the migration was in the range of low to moderate.

Thus, N, N’-Diallyldodecanediamide fulfills most of the requirements for successful food contact approval: thermal stability, compliance with OECD TG 471 and TG 487, and migration stability.

Research Questions

In total, this work aims to investigate and answer the following three research questions:

- What structure must the compounds under investigation possess to effectively crosslink PA6 during electron beam irradiation?
- Does crosslinking lead to increased heat deflection temperature?
- How can the thermal stability of the additives be specifically controlled?

In summary, this chapter establishes the overall context of the work and defines the guiding research questions. These form the basis for the experimental and conceptual developments presented in the following chapters.

2 Radiation Crosslinking of Polymers: Fundamentals and Mechanisms in Polyamide 6

The following section summarizes the current state of knowledge on radiation crosslinking of polymers to facilitate the later interpretation of the present results.

2.1 State of the Art in Radiation Crosslinking of Polymers

Ionizing radiation causes chain scission and new crosslinking in polymers. Depending on the ratio of these two effects, the mechanical properties of irradiated plastic parts can change positively. When a radiated sample is dissolved in an appropriate solvent, a crosslinked plastic retains an insoluble gel fraction g (0% < g ≤ 100%). Charlesby and Pinner were the first to study the effects of electromagnetic radiation on polymers [3, p. 2] and described the soluble fraction "s" (s = 100% − g) of an irradiated sample as a function of the absorbed radiation dose.

In doing so, they discovered the linear relationship between $s + \sqrt{s}$ and the reciprocal of the absorbed radiation dose$\frac{1}{D}$ [4, p. 379].

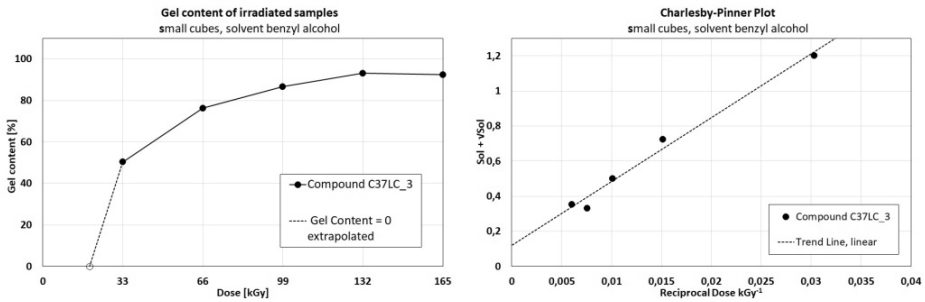

Fig. 4: Left: Dependence of the gel fraction of irradiated samples on the radiation dose Right: Derived Charlesby-Pinner plot

The probability with which a monomer in a polymer molecule becomes crosslinked is referred to as the network density q [%]. When it is related to the unit of radiation dose D [kGy], q corresponds to q_0 [%/kGy]. The number of chain scissions per unit dose is denoted as p_0 [%/kGy]. For a network to form and gel to develop, the number of chain scissions p_0 must be less than $2*q_0$, in other words, crosslinking points must form that are not caused by main chain scission.

When

$$s + \sqrt{s} = \frac{p_0}{q_0} + \frac{1}{D} \cdot \frac{1}{q_0 u_1} \qquad \textbf{Equation 1}$$

is plotted, the intersection with the ordinate represents the ratio of scission yield to crosslinking yield for a theoretically infinite dose, p_0/q_0 [5, p. 282]. In Fig. 4 (right), this value is 0.118. The slope of this line is $\frac{1}{q_0 u_1}$, where u_1 is the degree of polymerization or the number of monomers in the original, number-average molecule.

The considerations and experiments by Charlesby and Pinner are based on the assumption that at sufficiently high doses, numerous chain scissions lead to a random molar mass distribution with a polydispersity of 2. At high doses (e.g., for polyethylene > 100 kGy) or when using crosslinking enhancers, this assumption is no longer valid, and $\frac{1}{q_0 u_1}$ is not constant across the entire dose range. In this work, this is the case, for example, for Compound 12.

For the gel fraction as a function of the network density, the following relationship applies:

$$g = 1 - \frac{\sum nu \frac{1}{e^{qug}}}{\sum nu} \qquad \textbf{Equation 2}$$

From the slope of this curve, information about the original molecular weight distribution can be derived [6, p. 547].

The G-value [mol J^{-1}] quantifies chemical changes in polymers caused by radiation and is defined as the ratio between the amount of generated (crosslinked) molecules and the absorbed energy [3, p. 4].

When the amount of chain scissions G(S) per 100 eV of absorbed radiation is related to the amount of crosslinks G(X) per 100 eV of absorbed radiation, the following relationship applies:

$$\frac{G(S)}{G(X)} = 2 \cdot \frac{p_0}{q_0} \qquad \textbf{Equation 3}$$

The G-value can also be specified for the formation of chain scissions, the formation of double bonds, or the formation of other chemical substances [7, p. 17]. For PA6 without crosslinking enhancers, *G(X)* = 0,35 – 0,7; *G(S)* = 0,7; *G(S)/G(X)*= 1,0 [8, p. 17] and thus p_0/q_0 = 0.5 to 1.0

Ionizing radiation is essential for the radiation crosslinking of plastics. In the case of gamma radiation, it consists of photons with an energy of 1.17 MeV or

1.33 MeV, while in the case of electron radiation, it consists of accelerated particles.

Type of Radiation	Frequency [Hz]	Wavelength [µm]	Energy [eV]
Electron beam	$10^{21} – 10^{18}$	$10^{-7} – 10^{-5}$	124,000 – 12,400,000
Gamma radiation	10^{20} - 10^{18}	$10^{-6} – 10^{-5}$	124,000 – 1,240,000
X-rays	$10^{19} – 10^{16}$	$10^{-4} – 10^{-2}$	124 – 12,400
UV light	$10^{17} – 10^{15}$	$10^{-2} – 10^{0}$	1.24 – 124
Infrared	$10^{15} – 10^{12}$	$10^{0} – 10^{2}$	0.0124 – 1.24
Microwaves	$10^{12} – 10^{10}$	$10^{3} – 10^{5}$	0.0000124 – 0.00124

Tab. 1: Electromagnetic Radiation Types and Their Properties [7, p. 2] (own additions)

The term ionizing radiation indicates that this radiation is capable of splitting molecular bonds heterogeneously into ions. The recombination of these ions creates molecules in highly excited states, which may subsequently decay into radicals after energy transfer. Before radical formation, the absorbed energy can be transferred to positions with weak bonds. Such positions include, for example, β-positions relative to C=C double bonds or nitrogen atoms with a freely movable electron pair [3 p. 2, 6 ff.].

$AB + e^- \rightarrow AB^+ + 2\ e^-$	Ionization
$AB^+ + e^- \rightarrow A^1B^{1**}$	Recombination
$A^1B^{1**} \rightarrow A^2B^{2**}$	Transfer
$A^2B^{2**} \rightarrow A^\bullet + B^\bullet$	Radical Formation

Fig. 5: Radical Formation by Ionizing Radiation

During ionization, there are no reactive differences; all molecular bonds can be ionized equally. Before recombination, electrically charged particles are formed in the plastic object. However, increased electrical conductivity [7], [6, p. 24] cannot be experimentally detected in solid plastics. In addition to the recombination of radiation-induced ions, highly excited states AB∗∗ can also form directly through interaction with radiation [3, p. 8].

During the course of the reactions, the emission of hydrogen can be observed [3 p. 10]; [9, p. 3]. This hydrogen is formed by the recombination of hydrogen radicals, which were previously cleaved from polymer chains. In addition to hydrogen, carbon monoxide and carbon dioxide can also be released from polyamides. If irradiation is performed without excluding air and with non-degassed samples, a G-value can be specified for the amount of oxygen consumed during oxidation. This value depends on the reciprocal of the square root of the dose rate d, with the unit Gys^{-1}.

$$G = A + \frac{B}{\sqrt{d}}$$ **Equation 4**

Antioxidants delay oxidation. Since phenolic antioxidants transfer hydrogen atoms to radicals, they should compete with crosslinking. Phosphitic antioxidants, known as hydrogen peroxide decomposers, are expected to have a positive effect on processing stability without interfering with crosslinking—unless crosslinking occurs via peroxide bridges.[2] However, atmospheric oxygen reduces the crosslinking outcome [9, p. 12] which argues against peroxide bridge crosslinking. The tensile strength of irradiated PA66 can decrease by 50% if oxygen is present during irradiation [10, p. 129].

Units: The activity of a radioactive source is expressed in becquerels, where 1 Bq =1 decay per second. No direct correlation can be made between the activity of a source and its effects on a sample, as each source emits a different combination of radiation types. In practice, the specific energy (dose) is used, which refers to the energy absorbed per kilogram of sample: 1 Jkg^{-1} = 1 Gy. The dose rate, expressed as $kGyh^{-1}$ represents the dose absorbed per hour.

Radiation Types: Unstable $cobalt^{60}$ atoms emit gamma radiation with a constant energy of 1.17 and 1.33 MeV. Due to this high energy, gamma rays can penetrate deeply into the irradiated product. However, the emitted dose rate is low, ranging from 0.5 to 10 $kGyh^{-1}$, requiring the irradiated object to remain under the radiation source for a longer period. This is usually achieved by passing the object through the radiation source multiple times. Longer exposure times under the radiation source accelerate oxidation, as the process is typically carried out without excluding air and without degassed samples [3, pp. 13-14].

The dose rate of electron beams is significantly higher. It can be adjusted in a high vacuum using a heated cathode [7, p. 7]; [11, p. 1 ff.], and ranges between 3600 and 36000 $kGyh^{-1}$. However, their penetration depth is much lower due to increased interactions with the electrons of the target molecules (inelastic collisions).

Gamma rays and X-rays consist of photons, with gamma rays being generated in the atomic nucleus and X-rays in the electron shell. To produce X-rays with sufficiently high ionization energy for radiation crosslinking, tantalum targets are bombarded with electron beams. This process is costly due to the

[2] The effect of copper stabilizers suitable for polyamide on radiation crosslinking has not been researched and does not play a role in this work, as compounds with food contact approval are being studied, and copper stabilizers are subject to strict migration limits.

significant heat generated. However, since cobalt-60 is produced in nuclear power plants, X-ray radiation generated in this way is becoming more competitive as the number of nuclear power plants decreases and the demand for sterilization services increases.

The reviewed literature highlights both the strengths and the limitations of current radiation crosslinking approaches. This provides a clear reference point for evaluating the new concepts introduced later in the book.

2.2 Radiation-Induced Reactions and Crosslinking Mechanisms in Polyamide 6

This section describes the fundamental reactions that polyamide 6 undergoes during irradiation and that form the basis for understanding the subsequent material analyses.

The radiation crosslinking of semi-crystalline polyamides is achieved with doses ranging from 60 to 120 kGy [12, p. 2080]. Radicals can react with the surrounding molecular chains, with primary radicals being replaced by more stable ones [13, pp. 3044-3045]. A more stable radical, for example, is a $CH^{\bullet}$-radical in the α-position relative to the amide nitrogen. The processes inside the polyamide sample can be observed through a range of phenomena. For polyamides, the total amount of gas released is approximately 25 ml/g of polyamide [7, p. 23] and consists of hydrogen, carbon monoxide, carbon dioxide, and nitrogen-containing gases.

Another phenomenon is the increase in the amino end groups of the polyamide. The formation of radicals in the α-position relative to the amide nitrogen leads to an increase in amino end groups after bond cleavage [14, pp. 169-170]. The number of amino end groups formed is dose-dependent.

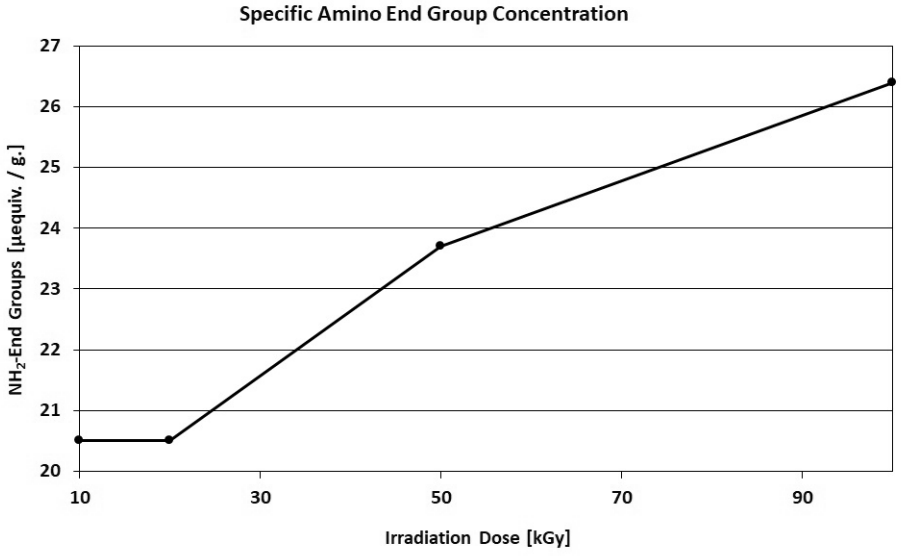

Fig. 6: Formation of Amino End Groups in PA6 as a Function of Radiation Dose [14, p. 170] (similar)

For PA66, similar trends have been reported, including increases in long-term service temperature, hardness, tensile strength, flexural modulus, and impact strength [15] [16, p. 46]. Furthermore, a reduced water absorption of irradiated samples has been reported.[3]

During the radiation crosslinking of **PA6**, the mentioned phenomena—gas evolution, an increase in the concentration of amino end groups, and improved mechanical properties—occur. Additionally, a change in the concentration of the monomer caprolactam is observed. This can be important for the approval of additives for use in plastics intended for food contact applications.[4]

Radiation Dose [kGy]	Residual Caprolactam in PA6 [ppm]
0	71
5	164
10	162
30	143
60	152
100	122
200	124

Tab. 2: Change in Residual Caprolactam Content in Irradiated Samples [8, p. 242]

During the production of a component made of PA6, for example, through injection molding, the material solidifies in a semi-crystalline state. The crystallites grow as long as they have sufficient energy or until their growth is hindered by neighboring crystallites. The combination of amorphous and crystalline phases makes PA6 a tough and rigid material with a high long-term service temperature.

When a solid is irradiated in the presence of atmospheric oxygen, $CH^{\bullet}$-radicals form in the α-position relative to the amide nitrogen [13, p. 3045]. Similar processes appear to take place as in the thermo-oxidation of PA6 [18, p. 3285]. The oxygen attack always occurs at the $CH^{\bullet}$-radical in the α-position relative to the amide nitrogen. The radical must have formed through processes similar to those in thermo-oxidative degradation and appears to be more stable than other radicals [19], [20, p. 442].

During crystallization (in an unirradiated sample), the molecular chains of PA6 align in the crystallites similarly to the folded sheet structure of peptides. Within a sheet, hydrogen bonds form between the amide nitrogen and the

[3] It is possible, that samples that were stored in PE bags have taken up moisture

[4] In [17] in Appendix I the specific migration limit for caprolactam is set to 4 mg/kg food simulant

carbonyl oxygen of neighboring molecular chains. This structure is characteristic of the α-modification of PA6 crystals cf. [21].

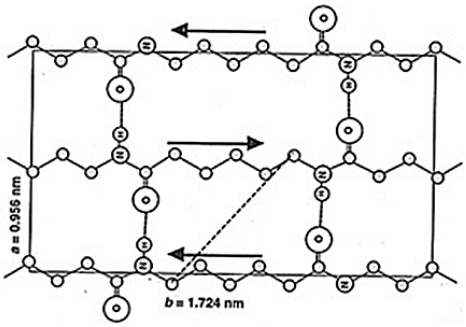

Fig. 7: α-Crystal Modification, PA6. Figure modified and adapted from Kohan, M. I.; Nylon Plastics Handbook; Hanser, 1995. With kind permission of Carl Hanser Verlag GmbH & Co. KG; [22, p. 115]

Since they are too far apart, the CH•-radicals in the α-positions of the amide nitrogens within the crystals cannot crosslink with each other. A hypothetical covalent bond between two radical centers of neighboring chains is indicated with a dashed line in Fig. 7. Similarly, in the alternative crystal modification γ, the radicals are also too far apart to form a covalent bond. When crosslinking enhancers are used, they are not present within the crystals, as they are pushed into the amorphous regions during crystal growth.[5]

The success of crosslinking in the amorphous regions of PA6 depends on the mobility of the chain segments in these regions and whether crosslinking enhancers are used. Good chain mobility can be achieved by crosslinking at higher temperatures, particularly above the glass transition temperature.

The mobility of the chains is increased by plasticizers. While phthalates reduce the crosslinkability of a material by capturing radicals through their aromatic ring system, esters of fatty acids, such as soybean oil, are expected to lead to improved crosslinking results [8, p. 81].

Zhang, Zhang, and Chen demonstrated for polyamide 1010 an increase in gel content with increasing thickness of the boundary layer between the crystalline and amorphous phases [23]. Brocka observed a higher gel content in PA66 samples that were nucleated [24, p. 61].

The mechanisms outlined in this chapter show how PA6 responds to ionizing radiation through radical formation, chain scission, and crosslinking.

[5] The basis of this concept is the purification of a solid through recrystallization, during which the impurity is not incorporated into the growing crystal