Influence of the Amount of Cross-linking Agent on Properties of Irradiated Polyamide 6

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***Abstract*—** The main objective of the study is investigation of mechanical properties of polyamide 6. These properties were examined in dependence on the dosage of the ionizing electron beam (beta) radiation and in dependence on the amount of cross-linking agent. Non-irradiated samples and those irradiated by dosage 66, 99 and 132 kGy were compared.

***Keywords*—** Irradiation cross-linking, beta radiation, cross-linking agent, polyamide.

I. Introduction

IRRADIATION cross-linking of thermoplastic materials deals with creation of a cross-link among the macromolecular strings. Intermolecular forces are replaced by a covalent bond. As a result, we can optimize properties of standard and engineering polymers and impart them the properties of high performance polymers. (Fig.3). Irradiation of polymers turned out to be interesting because of economic reasons, production costs and a life time of products. However, these benefits depend on the type of irradiated polymer and the radiation dosage. Behavior of each material is different after irradiation. We cannot expect the improvement in all areas, such as mechanical, thermal and chemical. Most of polymers are not suitable for irradiation because of degradation and deterioration of their properties.

The most common forms of employed radiation are electromagnetic (gamma) radiation from the radioisotopes cobalt-60 and celsium-137, and electron beams (beta) generated by electron accelerators. The main difference between the beta and gamma rays lies in their abilities of penetrating the irradiated material. Gamma rays have high penetration capacity. Penetration capacity of electron rays depends on energy of the accelerated electrons (Fig. 1). [1]

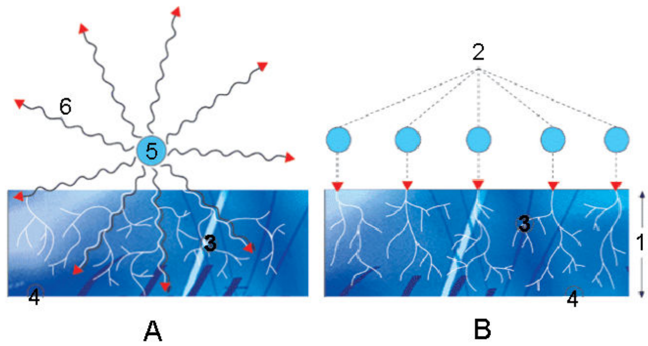

Fig. 1 Design of Gamma rays (A) and Electron rays (B) [5]
1 – penetration depth of electron, 2 – primary electron, 3 – secondary electron, 4 – irradiated material,5 – encapsulated Co – 60 radiation source, 6 – Gamma rays

The nonuniform dose distribution generated by electrons has led t concept of the useful range of electrons. This is the depth of material at which the entrance and exit doses are the same (i.e., the depth at which the absorbed dose is the same as the absorbed dose at the surface of the sample).

The useful range can be increased by irradiating the material from two opposite sides, either by successive irradiations from one side and then the other or by using two accelerators. Irradiation from two sides gives a useful range about 2.2-2.4 times greater than single-sided irradiation. This is illustrated in Fig. 2, which depicts depth-dose curves for 5-MeV electron irradiation of a unit-density material from two opposite faces.

The limited penetrating power of electron beams means that they are best employed for irradiating relatively thin objects. At the present time electron beams are used mainly for cross-linking polyethylene and poly(vinyl chloride) wire and cable insulation, curing coatings, the manufacture of heat-shrinkable films and tubing and foamed polyolefins, and the treatment of tire components. [1]

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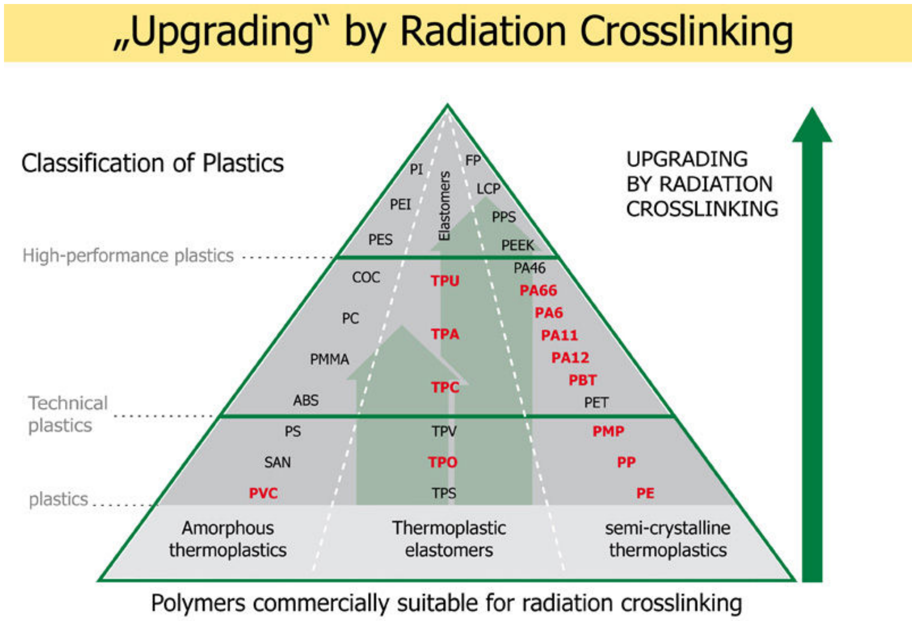

Fig. 2 Pyramid of Polymers [5]

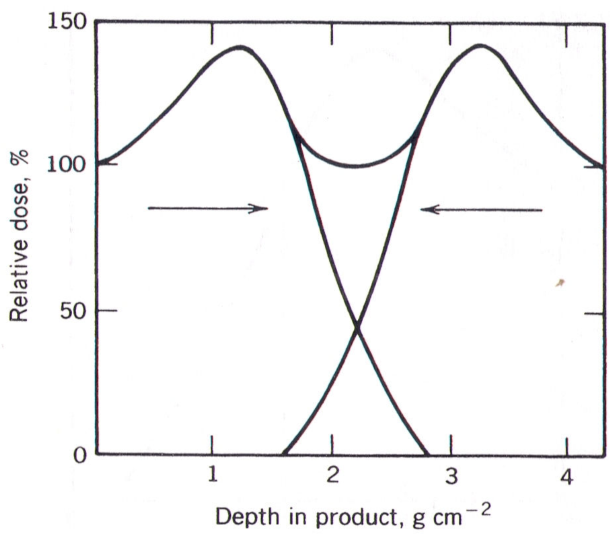

Fig. 3 Depth-dose curves for irradiation of a unit-density material with 5-MeV electrons [1]

Radiation modification of materials refers to the production of beneficial changes by exposure to radiation. High-energy (ionizing) radiation is used most often to modify polymers. The main group presents standard polymers and it is the most considerable one and it is share in the production of all polymers is as high as 90%. The engineering polymers offers much better properties in comparison with standard polymers. The production of these types of polymers takes less than 10 %. High performance polymers have the best mechanical and thermal properties but the share in production and use of all polymers is less than 1%.

Radiation processing covers use those beta or gamma radiations to break up bonds between atoms. Consequently, free radicals (H2) rise in materials that react with one another during chemical reactions (Fig. 4).

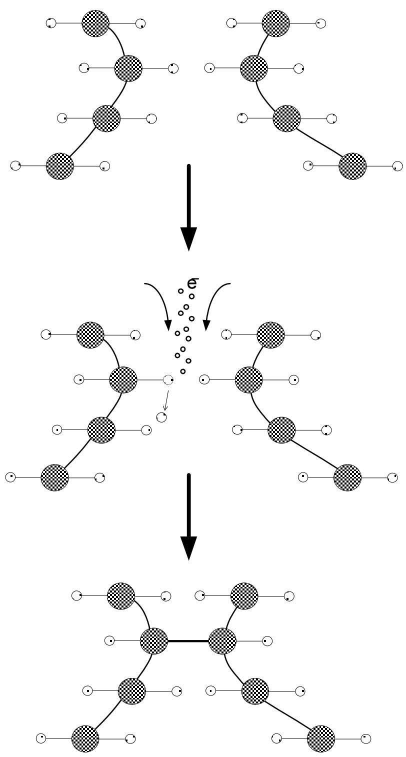

Fig. 4 Principe of radiation cross-linking

II. PROBLEM FORMULATION

The samples were prepared by using the injection moulding machine (ENGEL e-max 310/100). Materials of all test specimens was polyamide 6 (EPLAMID 6 GFR30 FRV0 NATURAL) provided by the EPSAN PLASTIK SAN. VE TIC. LTD. STI. company.

Basic material was mixed with 1 to 6% of the cross-linking agent Masterbach BETALINK®-Master IC/W65PA6 provided by the PTS Marketing- & Vertriebs-GmbH company. Processing conditions during the injection moulding were set according to the producer's recommendation.

All test specimens were exposed to radiation of electron rays (electron energy 10MeV, dosage: 66, 99 and 132 kGy) in the German company BGS Beta-Gamma-Service GmbH & Co. KG, Saal am Donau.Three tests were done by using the following:

Tensile test was carried out on tensile machine ZWICK 1456, according to standard CSN EN ISO 527-1, 527-2. Used rate: 50mm/min. Test data was processed by Test Xpert Standard software and modulus (E [MPa]) and tensile stress (σt [MPa]) were determined.

Impact hammer test carried out on tensile machine ZWICK 5113, according to standard CSN EN ISO 2818 - Energy 2,87J.

Determining the degree of cross-linking by gel measurements – (gel content), according to the standard EN ISO 579.

III. PROBLEM SOLUTION

Table I The degree of cross-linking by gel measurements

Amount of cross-linking agent (%)	Dosage (kGy)	Cross-linking degree (%)
1	66	22.5
1	99	25.7
1	132	61.2
2	66	79.4
2	99	78.2
2	132	77.4
3	66	79.7
3	99	78
3	132	77.5
4	66	81.3
4	99	85.1
4	132	84.3
5	66	84.3
5	99	84.9
5	132	84.8
6	66	80.9
6	99	80.2
6	132	79.6

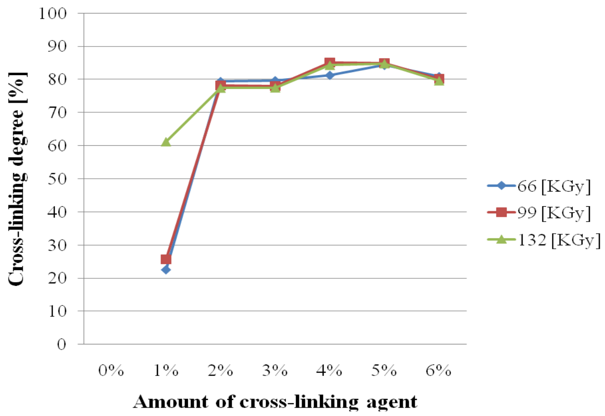

Fig. 5 Influence of the amount of cross-linking agent and radiation dose on cross-linking degree

Table I illustrates the determination of degree of cross-linking by solvent extraction. The measured data shows that the highest value is reached when 4% of cross-linking agent and dosage of 99 kGy are applied.

Comparison of tensile strength and E - modulus (at room temperature) of polyamide 6 before and after irradiation is given in Figure 6 and Figure 7. A comparison of the measured data indicate minor changes of the tensile strength (σt) and E – modulus of PA6 in dependence on different amount of added cross-linking agent. According to the expectations the influence of low molecular character of cross-linking agent was maximum decrease of mechanical properties (tensile strength at about 15% and E – modulus at about 20%) at non-irradiated test specimens with allowance of 6% of cross-linking agent.

Comparison of tensile strength and E - modulus (at 100°C) of polyamide 6 before and after irradiation is given in Figure 8 and Figure 9.

Irradiated polyamide shows significantly better values of tensile strength after the irradiation – increase of 8% in case of addition of 5% of cross-linking agent and dosage of 132 kGy. Measured E-modulus at 100°C indicates minor changes with the different amount of added cross-linking agent.

Comparison of impact strength of polyamide 6 before and after irradiation is given in Figure 10 and Figure 11. The measured data shows a decrease of impact strength. The highest drop (about 22%) recorded test specimens filled with 6% of cross-linking agent and irradiated by dosage of 66 kGy. Opposite to this, test specimens irradiated by dosage of 132 kGy recorded increase of impact strength. The highest increase (about 28%) was in case of 1 and 2 % of cross-linking agent.

If you look at the Figure 11, you can see the improvement of impact strength after irradiation at -30°C, but only in case of test specimens filled with 2 to 6% of cross-linking agent. The highest increase (about 193%) was recorded at specimens with content of 2 % of cross-linking agent.

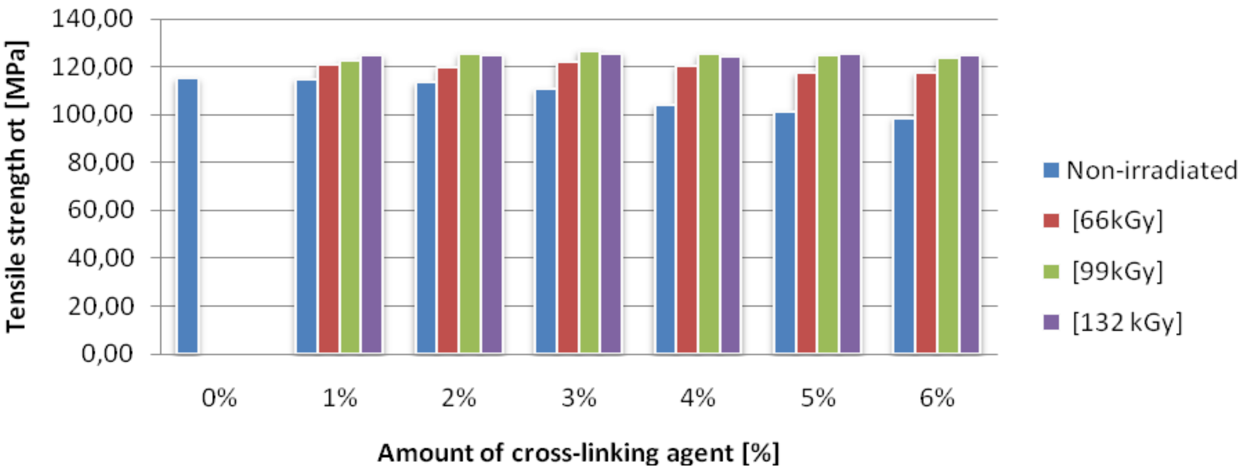

Fig. 6 Influence of the amount of cross-linking agent on tensile strength at room temperature

Table II Influence of the amount of cross-linking agent on tensile strength at room temperature

Amount of cross-linking agent	Non-irradiated [MPa]	66kGy [MPa]	99kGy [MPa]	132kGy [MPa]
0%	115,12±4,04	-	-	-
1%	114,91±1,42	120,78±4,56	122,7±3,84	124,6±1,8
2%	113,44±1,04	119,91±5,3	125,31±3,23	124,94±2,68
3%	110,5±1,53	121,77±4,79	126,71±1,88	125,57±3,33
4%	104,08±4,7	120,46±2,7	125,22±2,45	124,31±2,91
5%	101,07±3,65	117,32±3,66	124,75±2,21	125,29±2,08
6%	98,58±3,15	117,58±5,05	123,64±4,16	124,63±2,76

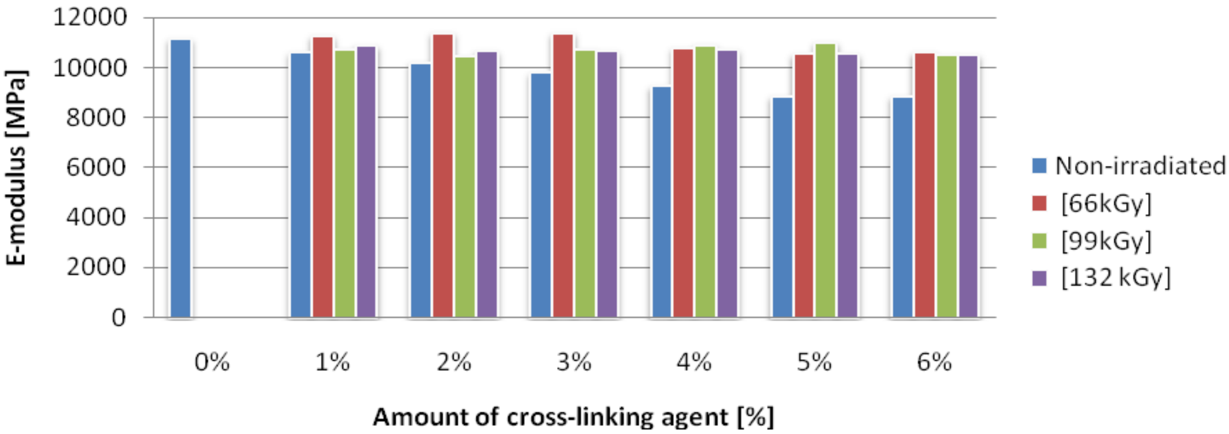

Fig. 7 Influence of the amount of cross-linking agent on E-modulus at room temperature

Table III Influence of the amount of cross-linking agent on tensile E-modulus at room temperature

Amount of cross-linking agent	Non-irradiated [MPa]	66kGy [MPa]	99kGy [MPa]	132kGy [MPa]
0%	11143±812	-	-	-
1%	10594±674	11258±976	10722±599	10864±350
2%	10197±578	11380±733	10419±833	10647±1810
3%	9779±427	11370±455	10703±503	10642±776
4%	9247±619	10774±470	10897±581	10699±461
5%	8845±438	10537±748	11003±558	10536±659
6%	8842±512	10604±385	10494±638	10513±340

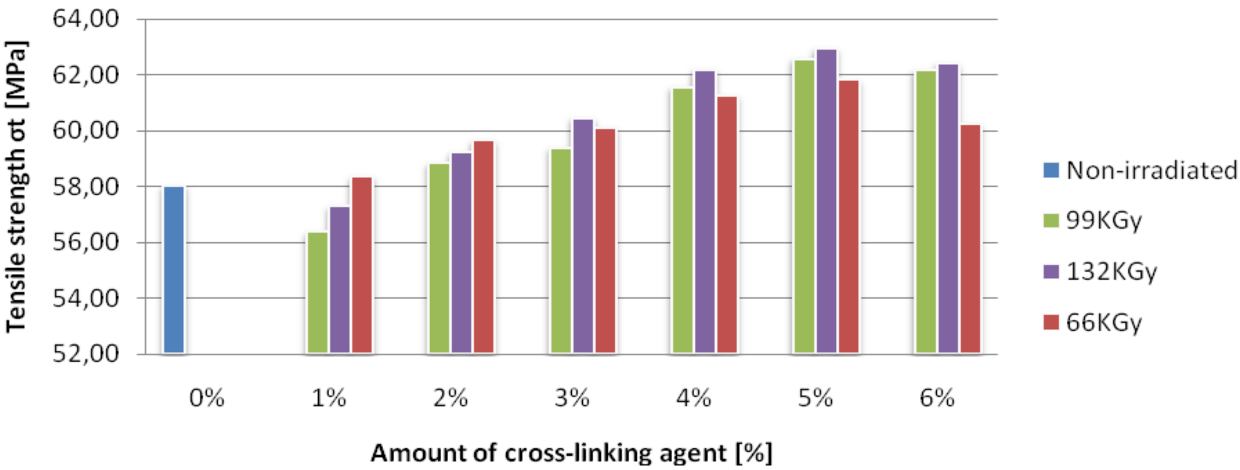

Fig. 8 Influence of the amount of cross-linking agent on tensile strength at 100°C

Table IV Influence of the amount of cross-linking agent on tensile strength at 100°C

Amount of cross-linking agent	**Non-irradiated [MPa]**	**66kGy [MPa]**	**99kGy [MPa]**	**132kGy [MPa]**
0%	58,01±0,68	-	-	-
1%	-	58,35±0,61	56,36±1,64	57,28±1,07
2%	-	59,65±0,73	58,83±1,06	59,23±0,73
3%	-	60,09±0,87	59,38±2,24	60,45±0,75
4%	-	61,25±0,84	61,56±0,88	62,19±0,91
5%	-	61,82±1	62,57±0,37	62,93±0,81
6%	-	60,24±1,24	62,17±1,44	62,41±0,66

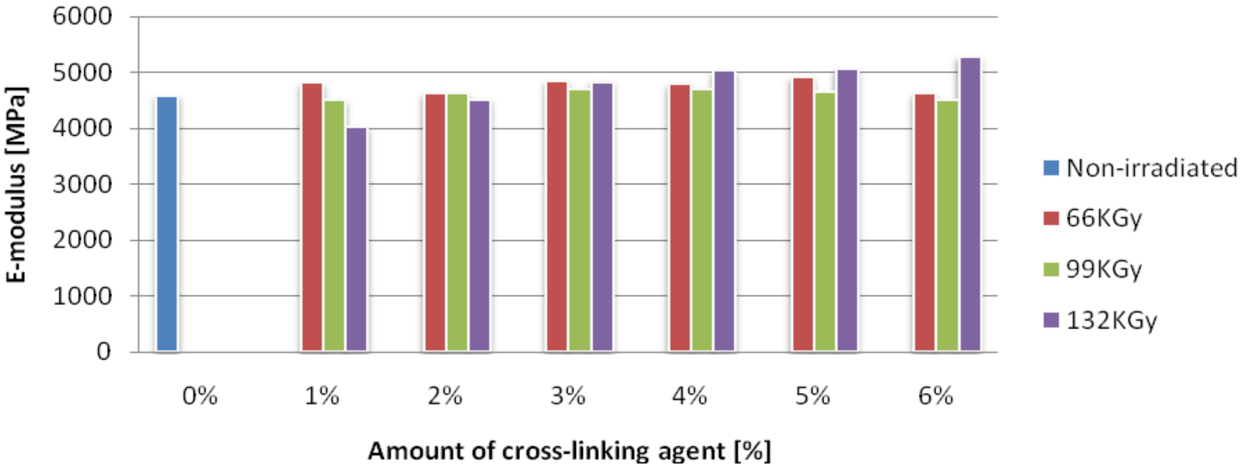

Fig. 9 Influence of the amount of cross-linking agent on E-modulus at 100°C

Table IV Influence of the amount of cross-linking agent on E-modulus strength at 100°C

Amount of cross-linking agent	**Non-irradiated [MPa]**	**66kGy [MPa]**	**99kGy [MPa]**	**132kGy [MPa]**
0%	4578±476	-	-	-
1%	-	4808±360	4498±225	4017±471
2%	-	4620±308	4622±217	4517±683
3%	-	4841±641	4693±274	4820±205
4%	-	4787±321	4699±211	5024±92
5%	-	4907±356	4653±231	5051±294
6%	-	4623±250	4508±267	5278±237

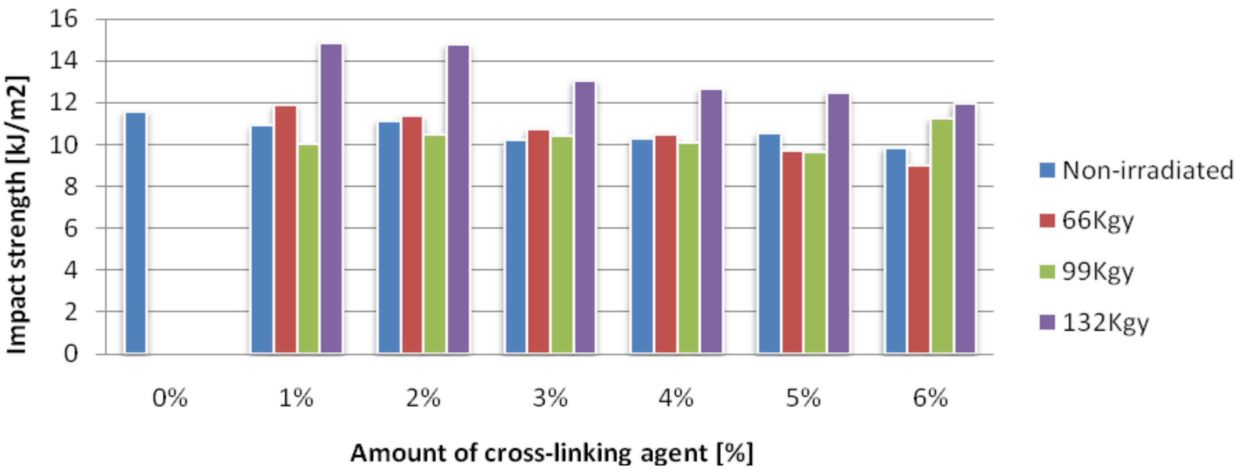

Fig. 10 Influence of the amount of cross-linking agent on impact strength at room temperature

Table V Influence of the amount of cross-linking agent on impact strength at room temperature

Amount of cross-linking agent	**Non-irradiated [kJ/m^2]**	**66kGy [kJ/m^2]**	**99kGy [kJ/m^2]**	**132kGy [kJ/m^2]**
0%	11,58±1,5	-	-	-
1%	10,89±1,03	11,9±0,95	10,03±2,71	14,87±0,6
2%	11,13±0,54	11,34±0,59	10,47±0,74	14,79±0,55
3%	10,21±2,13	10,72±0,78	10,41±0,99	13,06±0,9
4%	10,27±0,72	10,44±0,7	10,1±0,9	12,63±0,64
5%	10,53±1,05	9,68±0,57	9,64±0,62	12,49±0,92
6%	9,84±1	9,01±0,29	11,27±1,55	11,98±0,61

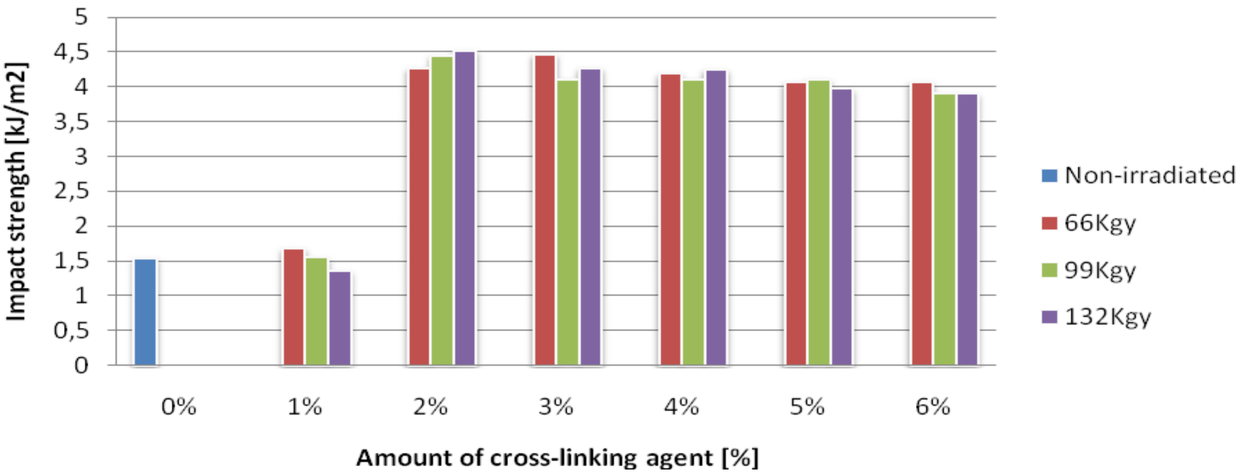

Fig. 11 Influence of the amount of cross-linking agent on impact strength at -30°C

Table V Influence of the amount of cross-linking agent on impact strength at -30°C

Amount of cross-linking agent	**Non-irradiated [kJ/m^2]**	**66kGy [kJ/m^2]**	**99kGy [kJ/m^2]**	**132kGy [kJ/m^2]**
0%	1,54±0,2	-	-	-
1%	-	1,68±0,05	1,55±0,09	1,36±0,06
2%	-	4,27±0,52	4,45±0,41	4,52±0,4
3%	-	4,47±0,36	4,11±1,16	4,27±0,28
4%	-	4,19±0,28	4,11±0,26	4,25±0,42
5%	-	4,06±0,35	4,11±0,37	3,97±0,2
6%	-	4,07±0,38	3,9±0,28	3,9±0,28

IV. Conclusion

Influence of different amount of added cross-linking agent and different absorbed doses of radiation on measured mechanical properties (E-modulus and tensile strength) at room temperature is not substantial.

The improvement is more considerable in case of higher temperature (100°C) at which tensile strength increases. The consequence of irradiation is the creation of the covalent bonds among the macromolecular strings which are more flexible during thermal load than intermolecular forces.

Optimal amount of added cross-linking agent and absorbed doses of radiation was determined to be 5% of cross-linking agent and dosage of 132 kGy.

The radiation cross-linking can be good way for improvement of properties of the products operating at negative temperatures. As a result, impact strength at -30°C shows dramatic increase.

Table VI Improvement of properties after irradiation

	Temperature [°C]	Amount of cross-linking agent [%]	Dosis [kGy]	Improvement [%]
Tensile strength	23 100	3 5	99 132	10 8
E-modulus	23 100	2 6	66 132	2 15
Impact hammer strength	21 -30	1 2	132 132	22 290

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