The Influence of Cross-linking Agent on Mechanical Properties of Polyamide Modified by Irradiation Cross-linking

ZDENEK HOLIK, MICHAL DANEK*, MIROSLAV MANAS, MICHAL DANEK, JAKUB CERNY
Department of Production Engineering
Tomas Bata University in Zlín
nám. T.G.Masaryka 5555, 760 01 Zlín
CZECH REPUBLIC
holik@ft.utb.cz http://www.holik.webnode.cz *danek@bgs.eu

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.

Key-Words: Irradiation cross-linking, beta radiation, cross-linking agent, polyamide

1 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 optimise properties of standard and engineering polymers and impart them the properties of high performance polymers. (Fig.1). 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. Behaviour 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.

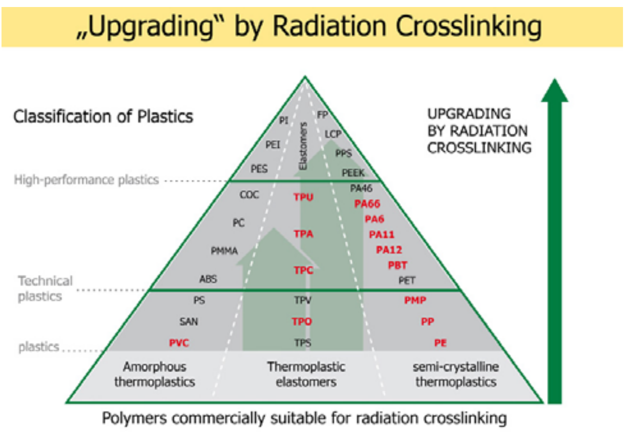

Fig.1 Pyramid of Polymers [5]

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. 2). [1]

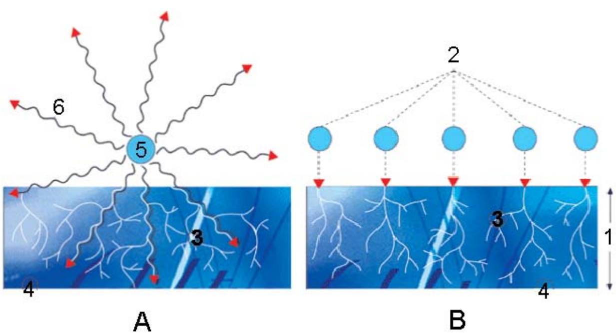

Fig.1 Design of Gamma rays (A) and Electron rays (B) [5]

1 – penetration depth of electron, 2 – primary electron, 3 – secondary electron, 4 – irradiated material,5 – encapsulated Co – 60 radiation source, 6 – Gamma rays

2 Problem Formulation

The samples were prepared by using the injection moulding machine (ENGEL e-max 310/100).

ISBN: 978-1-61804-004-6

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:

1. 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.
2. Impact hammer test carried out on tensile machine ZWICK 5113, according to standard CSN EN ISO 2818 - Energy 2,87J.
3. Determining the degree of cross-linking by gel measurements – (gel content), according to the standard EN ISO 579.

3 Problem Solution

Table 1 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 3 and Figure 4. 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.

Table 1 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

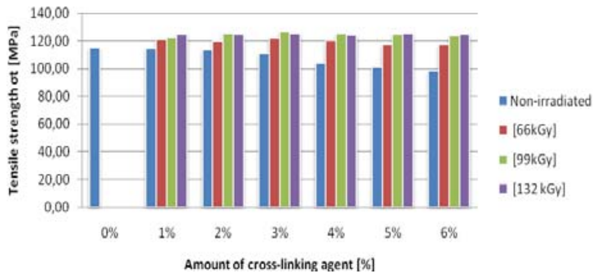

Fig.3 Influence of the amount of cross-linking agent on tensile strength at room temperature

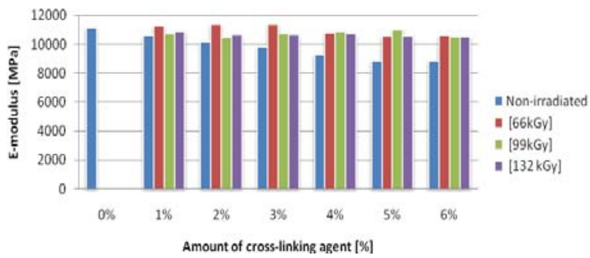

Fig.4 Influence of the amount of cross-linking agent on E-modulus at room temperature

Comparison of tensile strength and E - modulus (at 100°C) of polyamide 6 before and after irradiation is given in Figure 5 and Figure 6.

Irradiated polyamide shows significantly better values of tensile strength after the irradiation – increase of 8% in case of addition of 5% of cross-

ISBN: 978-1-61804-004-6

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.

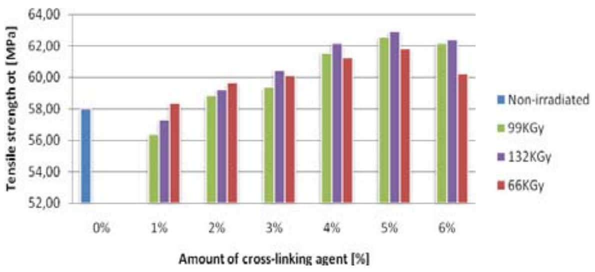

Fig.5 Influence of the amount of cross-linking agent on tensile strength at 100°C

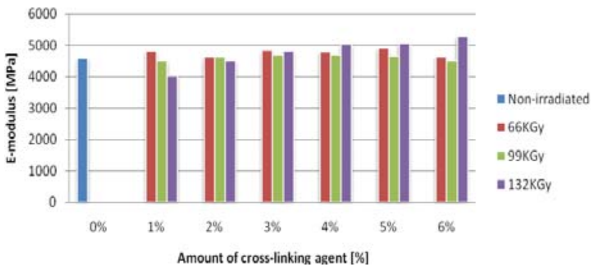

Fig.6 Influence of the amount of cross-linking agent on E-modulus at 100°C

Comparison of impact strength of polyamide 6 before and after irradiation is given in Figure 7 and Figure 8. 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.

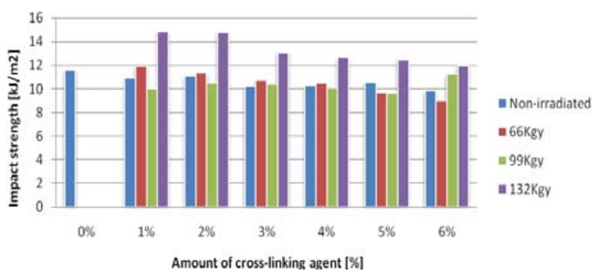

Fig.7 Influence of the amount of cross-linking agent on impact strength at room temperature

If you look at the Figure 8, 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.

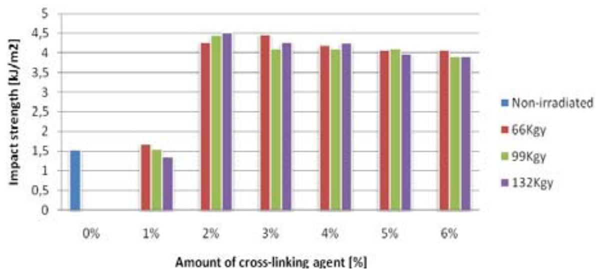

Fig.8 Influence of the amount of cross-linking agent on impact strength at -30°C

4 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.

5 Acknowledgement

"This article is financially supported by the Ministry of Education, Youth and Sports of the Czech Republic under the Research Plan No. MSM 7088352102 and by the European Regional Development Fund under the project CEBIA-Tech No. CZ.1.05/2.1.00/03.0089.“

References:

[1] Woods, R. J.: *Applied radiation chemistry: radiation processing*, 1994, ISBN 0-471-54452-3.

[2] Manas, D. – Manas, M. – Stanek, M.: *Properties of Irradiated Polypropylene*, Chapter 37 in DAAAM International Scientific Book 2008, p. 433-448, Published by DAAAM International, ISBN 978-3-901509-69-0, ISSN 1726-9687, Vienna, Austria DOI: 10.2507/daaam.scibook.2008.37.

[3] Maňas, D. – Maňas, M. – Staněk, M. – Drga, T.: *Irradiation of Polymers Materials*. In: Chemické listy. Volume 101, 2007, s.27-28, ISSN 0009-2770.

[4] Manas, D. – Stanek, M. – Manas, M. – Drga, T.: *Influence of Radiation on Polymer Properties* . In: International Science Conference of Materials Science and Manufacturing Technology, 26. - 27.6.2007, Czech University of Life Science Prague, p.200-205, ISBN 978-80-213-1650-8.

[5] [online] http://www.bgs.com/

[6] [online] http://www.pts-marketing.de/

[7] Zyball, A.: *Strahlungsenergie zur Modification von Kunststoffen – Industrielle Anwendungen der Bestrahlungstechnik, In: Strahlenvernetzte Kunstoffe* , Springer VDI verlag, Dusseldorf, 2006, ISBN 3-935065-30-2

[8] Drobný, J.G.: *Radiation Technology for Polymers*, Boca Raton: CRC Press, 2003, , ISBN 1-58716-108-7.