

UDK 67.017:669.058:544.543.1
Original scientific article/Izvorni znanstveni članek

ISSN 1580-2949
MTAEC9, 54(3)345(2020)

INFLUENCE OF APPLIED ELECTRON RADIATION ON THE PROPERTIES OF A POLYAMIDE 11 SURFACE LAYER

VPLIV OBSEVANJA Z ELEKTRONI NA LASTNOSTI POVRŠINSKE PLASTI POLIAMIDA 11

Martin Ovsik*, Petr Fluxa, Michal Stanek, Adam Dockal, Martin Reznicek

Tomas Bata University in Zlín, Vavrečkova 275, 760 01 Zlín, Czech Republic

Prejem rokopisa – received: 2019-07-15; sprejem za objavo – accepted for publication: 2019-12-23

doi:10.17222/mit.2019.155

This article deals with the influence of the radiation cross-linking of polyamide 11 (PA 11) on the mechanical properties. The aim of this study is to provide more detailed knowledge of the relation between the radiation dosage and the properties of cross-linked PA 11 and its mechanical behaviour. Electron-beam-unmodified and modified PA 11 test samples were exposed to electron radiation with dosages from 0 kGy to 198 kGy, which were graded at 33 kGy. The surface-layer properties of the modified PA 11 were tested using a state-of-the-art indentation technique, which detects the immediate change in the indentation depth, depending on the applied force. The evaluation of the measured mechanical properties (indentation hardness, modulus and creep) was done by the Oliver and Pharr method. A significant influence of the radiation cross-linking on the PA 11's mechanical properties improvement was confirmed by the measurements. This enhancement grows with the increasing radiation dosage. Due to the electron-radiation modification of PA 11, the mechanical properties of the surface layer were increased by up to 59 % compared with the unaltered material. Radiation crosslinking is an important thermoplastic modification method by which the desired properties can be achieved in a relatively short period of time. The main advantage is that the process is executed on the final product.

Keywords: polyamide, radiation, mechanical properties, indentation hardness

V članku avtorji opisujejo vpliv obsevanja prečno zamreženega poliamida 11 (PA11) na mehanske lastnosti. Študija naj bi zagotovila bolj natančen vpogled v poznavanje povezav med dozo obsevanja in lastnostmi prečno zamreženega PA 11 ter njihovim vplivom na mehanske lastnosti. Analizirali so originalne neobsevane vzorce in vzorce PA 11, obsevane s snopom elektronov z dozami med 0 in 198 kGy v stopnjah po 33 kGy. Lastnosti površinske plasti obsevanih vzorcev PA 11 so testirali z najmodernejšo indentacijsko tehniko, ki takoj zazna spremembe indentacijske (vdorne) globine v odvisnosti od uporabljene sile vtiskovanja trna (indenterja) v preiskovani material. Avtorji članka so ovrednotili rezultate izmerjenih mehanskih lastnosti (nanotrdoto, modul in lezenje) z Oliver in Pharr metodo. Rezultati meritev so pokazali pomemben vpliv obsevanja prečno zamreženega PA 11 na mehanske lastnosti. S povečano stopnjo obsevanja so se izboljševale mehanske lastnosti. Zaradi obsevanja PA 11 z elektroni so se mehanske lastnosti površinske plasti izboljšale za do 59 % v primerjavi z vzorci, ki niso bili obsevani. Prečno zamreženje zaradi obsevanja z elektroni je pomembna metoda termoplastične modifikacije, ki lahko hitro izboljša oz. modificira lastnosti površine izbranega materiala. Pomembna prednost je v tem, da lahko proces izvedemo na končnih izdelkih.

Ključne besede: poliamid, obsevanje, mehanske lastnosti, nanotrdota

1 INTRODUCTION

In general, polyamides have medium durability to ionizing radiation. This durability, for the polyamide types $-\text{CONH}-(\text{CH}_2)_n-$, decreases with the increasing number of the methyl groups in between the peptide links. As a result of sample irradiation, a process of cross-linking as well as fission commences. For most of the polyamides, the cross-linking process is prevalent, although, the process of network construction is not very strong. According to K. Kaindl and E. H. Graul,¹ free radicals begin to form within the structure during irradiation. Simultaneously, radicals are created around the C=N and C=C double bonds. According to K. Kaindl and E. H. Graul¹ a radiation dosage of 350 kGy with oxygen present incites the creation of gel. When the irradiation occurs in a vacuum, the cross-linking process

is prevalent, which leads to changes that improve the mechanical properties.

Adding a poly-functional monomer, e.g., triallyl isocyanurate (TAIC), enables the polyamides to begin the cross-linking process after being exposed to relatively low dosages of radiation, when the oxygen is present. Finding out the correct dosages for the improvement of the selected mechanical properties is the goal of this research paper. First, hydrogen bound to the carbon neighbouring with the nitrogen of the amide group is split, leading to the creation of water, carbon monoxide, carbon dioxide and methane. Three allyl groups of TAIC can, due to the irradiation, react and create additional bridges (network) in the polyamide structure.²

2 EXPERIMENTAL PART

For this experiment, PA11 called V-PTS-CREAMID-11T*M600/13 manufactured by PTS was used. To

*Corresponding author's e-mail:
ovsik@utb.cz (Martin Ovsik)

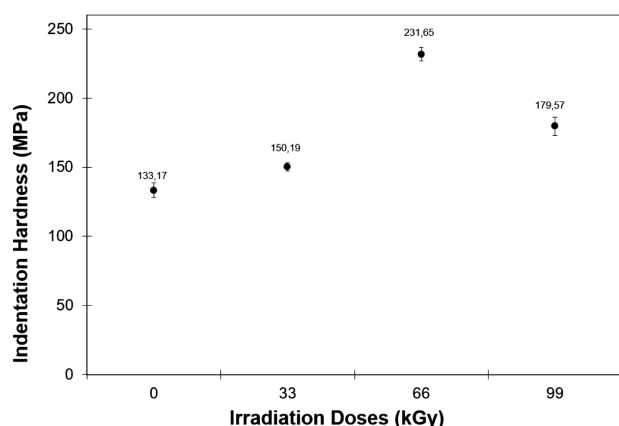


Figure 1: Indentation hardness

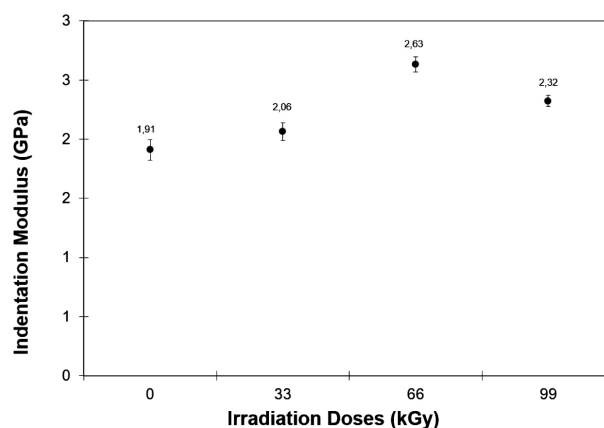


Figure 2: Indentation modulus

ensure the radiation induced cross-linking a cross-linking agent triallyl isocyanurate (TAIC) in 5 % volume was added. The samples were prepared by injection moulding on an Allrounder 470E-type ARBURG injection-moulding machine. The parameters of the machine were set according to the recommendation of the manufacturer. The material that was used was pre-dried in accordance with the instructions on an ARBURG THERMOLIFT 100-2 device. The test samples were prepared in a single-cavity mould in the shape of the beam, in agreement with the ČSN EN ISO 179 standard.

The test samples were exposed to the radiation in cooperation with company BGS Beta-Gamma-Service GmbH & Co. KG in a high-voltage accelerator-type Rhodotron. The radiation dosages were set to 33 kGy, 66 kGy and 99 kGy.

The mechanical properties of the surface layer were measured by the depth sensing indentation (DSI) on an ultra nano-indentation system (UNHT).³ The parameters were set to the following values: applied load 50 mN, loading and de-loading speed 100 mN/min and load duration 90 s. The measurements were made according to the ČSN EN ISO 14577 standard and then evaluated using the Oliver and Pharr method.³

3 RESULTS

The indentation hardness and modulus of the PA11 modified by various dosages of radiation were measured by the DSI. Each sample was measured 10 times and the results were afterwards statistically evaluated.

4 DISCUSSION

As can be seen in **Figure 1**, the indentation hardness was gradually increased due to the radiation cross-linking, even at the lower dosages. The highest values were measured in the material irradiated by a dose of 66 kGy, in which the indentation hardness rose by 73 % in comparison to the unaltered material. It is noteworthy that even the relatively low amounts of radiation (33 kGy)

increased the indentation modulus by 13 %. Additional levels of radiation displayed only a minor increase in the indentation hardness and modulus. In contrast, the use of radiation dosages of 99 and higher kGy caused the indentation modulus to decline. Considering the cost of the irradiation, it is non-profitable to consider higher dosages than 66 kGy for the indentation modulus.

As is evident from the measurements of the PA11 indentation elastic modulus at room temperature, the modulus rose with the increasing radiation dosage (**Figure 2**). The highest values of the indentation modulus were measured in the test samples irradiated by a dosage of 66 kGy. This modulus was 37% higher in comparison to the virgin material. Indeed, it can be said that the radiation cross-linking had a positive influence on the indentation modulus of the PA11. Radiation dosages higher than 66 kGy displayed a decreasing trend in the mechanical properties of the surface layer, which could have been caused the material degradation induced by the large amounts of radiation.

5 CONCLUSIONS

The measured data indicate that the most suitable dosage of radiation for the chosen materials appears to be 66 kGy. This value induced positive changes in the mechanical properties for each observed test sample. The improvements to the indentation hardness and indentation modulus directly caused by the radiation cross-linking are a desired result for some of the technical applications. The best enhancements of the indentation hardness were found in the test samples that were irradiated with dosages of 33 kGy or 66 kGy. Radiation dosages higher than these proved to significantly decrease the indentation modulus and indentation hardness in the observed test samples. This decline could be caused by the material degradation induced by the high dosages of electron radiation.

Acknowledgment

This work was supported by the European Regional Development Fund under the project CEBIA-Tech Instrumentation No. CZ.1.05/2.1.00/19.0376 and by the Ministry of Education, Youth and Sports of the Czech Republic within the National Sustainability Program project no. LO1303 (MSMT-7778/2014). Moreover, it was supported by the Internal Grant Agency of TBU in Zlin: no. IGA/2020/003.

6 REFERENCES

- ¹ K. Kaindl, E. H. Graul, Strahlenchemie, Dr. Alfred Hüttig Verlag, Heidelberg, 1967
- ² M. Ghidelli, M. Sebastiani, K. E. Johanns, Journal of the American ceramic society, 100 (2017), 5731–5738
- ³ W. C. Oliver, G. M. Pharr, Measurement of hardness and elastic modulus by instrumented indentation, Journal of Materials Research, 19 (2004), 1564–1583