UTILIZING INSTRUMENTED HARDNESS TEST TO MEASURE PROPERTIES OF POLYAMIDE SURFACE LAYER

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The goal of this study was to determine the extent, to which beta radiation modified mechanical properties of surface layer on scale of nano meters. The current trend of replacing varying metal products by plastic products leads to lesser weight, but also a decrease of the tear resistance. This can be countered by exposing the material to electron radiation, which causes a creation of 3D network within the polymer structure. This process is an equivalent to heat treatments of metals. Properties of irradiated polyamide (hardness, modulus, deformation work, creep, etc.) were tested by contemporary indentation method (NHT3). This data was then evaluated by OLIVER & PHARR method. The results have shown that modifying the surface layer of polyamide led to a 50 % increase of mechanical properties.

KEYWORDS

Polyamide 6, radiation, cross-linking instrumented hardness, surface layer, gel content

1 INTRODUCTION

This study is focused on measuring nano hardness of the surface layer of a polyamide material influenced by varying levels of radiation. The material was enriched by cross-linking agent Triallyizokyanurat (TAIC) and then irradiated, thus initiating a creation of a 3D network. Mechanical properties consist of indentation hardness, indentation elastic modulus, indentation creep and plastic and elastic deformation work and were determined by instrumented hardness test.

Polyamide was used as a tested material. It is a linear polymer containing amide group and it is commonly used within the plastic industry. Polyamide is a semi-crystalline thermoplastic polymer which is used in many applications for its great material properties. In this case, the test subject was modified by ionizing radiation in order to increase the required properties.

Boo Young Shin and Jae Hong Kim studied rheological and mechanical properties of polyamide 6 modified by electron-beam initiated mediation process. Glycidyl methacrylate (GMA) was used as a mediator and it played a key role in the electron beam initiation. Mechanical properties were improved without scarifying of processability **[Shin, 2015]**.

Shifeng Zhu, Meiwu Shi and Meifang Zhu studied effects of electron-beam irradiation cross-linking on PA6 fibers. They found out that incorporating mediator in form of triallyl cyanurate (TAC) in PA6 reduces the amount of required radiation dosage required for gel formation **[Zhu, 2013]**.

There is another possibility how to improve further mechanical properties of PA GF, it is electron beam cross-linking. Cross-linking of PA is rather rare method of this type polymer modification, but there are significant changes which lead to the improvement of this polymer **[Porubska 2011].**

Mária Porubská dealt with PA 6 GF 30 % and its properties after electron beam radiation at the doses of 50, 100, 200, 300 and 500 kGy. She compared PA 6 GF 30 % and PA 6 after irradiation. The highest difference she found at Young´s modulus. Pure PA 6 had the highest value of this modulus at the dose of 500 kGy around 2 800 MPa while PA 6 GF 30 % at the same dose around 8 800 MPa and also Vicat softening temperature differed significantly, its highest values were found at the radiation dose of 50 kGy, for PA 6 was 190 °C and for PA 6 GF 30 % was slightly under 210 °C **[Porubska 2014].**

A lot of research papers have been concentrated on mechanical properties of cross-linked polyamides filled with glass fibres, but there is a gap in the area of nano-indentation properties measured using Nano-Combi Tester. This article deals with these measurement, which is very important to long-time life time of the final product.

2 EXPERIMENTAL

2.1 Material

The PA 6 FRIANYL B63 VN produced by Frisetta company was chosen as a test material. It was shipped in the shape of granules that were later enriched by 6 % of cross-linking agent labeled TAIC (triallyl isocyanurate). Exposure of the cross-linking agent to radiation causes a creation of 3D network within the polyamide structure, which is faster than the degradation of the polymer caused by the ionizing radiation.

2.2 Sample preparation

Test samples were manufactured by injection molding technology on injection machine Arburg Allrounder 470H (Loßburg, Germany). They were manufacture according to the ČSN EN ISO 179 standard. As can be seen in figure 1, the dimensions were (80 x 10 x 4) mm. The injection molding process parameters were set in agreement with the material sheet of the tested polyamide. Table 1 displays these parameters.

Parameters	Unit	PA6
Injection Pressure	MPa	70
Cooling Time	s	20
Mould Temperature	°C	65
Zone 1	°C	260
Zone 2	°C	265
Zone 3	°C	270
Zone 4	°C	275

Table 1: Process parameters

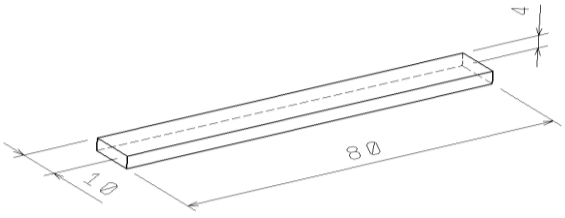

Figure 1: Dimension of sample

2.3 Irradiation

The cross-linking causes the connection of polymeric chains to each other, the most often using covalent bonds to form the spatial network. Given the ever increasing performance requirements of polymer properties the importance and need for its modification increase proportionally. Test bodies were irradiated under industrial conditions on commercially available irradiation device in a wider range of radiation doses (0, 66, 132 and 198 kGy) in comparison to doses corresponding to the experience in the practice. Irradiation of the tested polyamidu 6 was performed with the kind help of BGS Germany (Wiehl, Germany), in the BGS Wiehl plant, using accelerated electrons. A Rhodotron R E-beam accelerator (Tongeren, Belgium) with 10 MeV electron energy was used for this purpose. Each passage under the accelerator scanner is equal to 66 kGy.

2.4 Gel Content

A gel (content) test is performed in order to determine the non-dissolved gel content of the given material—according to the ASTM D 2765 standard—Test Method C. A portion of 0.5 g (of electron-beam irradiated PA 6 material) weighed with a precision of five decimal places on a "SWISS MADE EP 125 SM" weighing apparatus (Dietikon, Switzerland) was mixed with 100 mL of solvent. Xylene was used on the PA 6 because it dissolves the amorphous part of this material, and the cross-linking part does not dissolve. The mixture was extracted for 24 h. Then, the solutes were separated by distillation. After removing the residual xylene, the cross-linked extract was dried for 8 h, in a vacuum, at 100 °C. The dried and cooled residue was weighed again with a precision of five decimal places and compared to the original weight of the portion. The result is stated in percentage as the degree of cross-linking [Ovsik 2016]:

$$G_i = \frac{m_3 - m_1}{m_2 - m_1} \cdot 100 \quad (1)$$

where G_i is the degree of cross-linking of each specimen expressed in percentage, m_1 is the weight of the cage and lid in milligrams, m_2 is the total of the weights of the original specimen, cage and lid in milligrams, and m_3 is the total of the weights of the residue specimen, cage and lid in milligrams **[Manas 2018].**

2.5 nano-indentation test

The testing of the surface layer properties was done on nano-indentation tester (NHT³) made by Anton Paar company located in Graz, Austria. The tester uses principles of instrumented hardness test, which measures parameters in the specified place of indentation. The measured parameters are then evaluated by OLIVER and PHARR method. The measurements were done in consonance with ČSN EN ISO 14577 standard. Four sided diamond pyramid with 136° (VICKERS) was chosen as an indentation body. Measured parameters are displayed in table 2.

Parameters	Unit	Value
Maximum Load	mN	10
Load/Unload Speed	mN/min	20
Holding Time	s	90

Table 2: Measurement parameters.

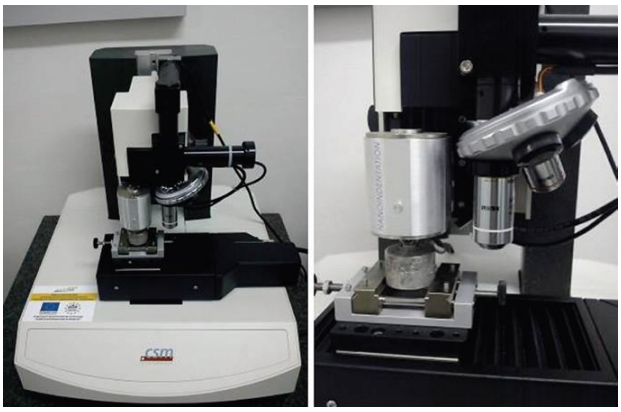

Figure 2: Nano-indentation tester

The indentation hardness (H_{IT}) was calculated as maximum load (F_{max}) to the projected area of the hardness impression (Ap) and the indentation modulus (E_{IT}) is calculated from the Plane Strain modulus (E*) using an estimated sample Poisson's ratio (ν) according to : **[Oliver 2004] [Pharr 1998]**

$$H_{IT} = \frac{F_{max}}{A_p} \quad (2)$$

$$E_{IT} = E^* \cdot (1 - \nu_s^2) \quad (3)$$

Determination of indentation creep C_{IT}, where h_1 is the indentation depth at time t_1 of reaching the test force (which is kept constant), h_2 is the indentation depth at time t_2 of holding the constant test force : **[Oliver 2004] [Pharr 1998]**

$$C_{IT} = \frac{h_2 - h_1}{h_1} \cdot 100 \quad (4)$$

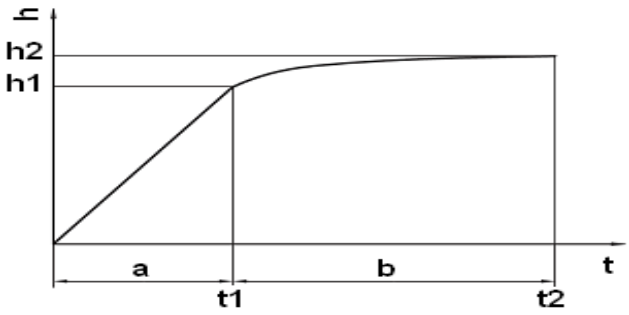

Figure 3: Expression of indentation creep, a - Application of the test force, b - Test force kept constant from t_1 to t_2.

Measurement of all above mentioned properties was performed 10 times to ensure statistical correctness.

3 RESULTS AND DISCUSSION

Radiation cross-linking includes a process of the chemical bonds formation between individual molecules or individual particles of one molecule. It is a process, during which the material is exposed to ionizing radiation to produce free radicals. During radiation cross-linking, the main assumption is the formation of cross-links, not scission of macromolecules – degradation, after ionizing radiation. Both processes, cross-linking and degradation run in parallel. The detection if predominant cross-linking or degradation was determined by the gel content test.

Parameters	Unit	0 kGy	66kGy	132kGy	198kGy
Gel Content	%	0,00	52,00	65,00	55,00
Ind. Hardness	MPa	101,87	141,70	146,40	89,17
Vickers Hardness	Vickers	9,43	13,56	13,12	8,26
Ind. Modulus	GPa	1,72	2,50	2,55	1,97
Ind. Creep	%	12,24	11,61	10,14	10,53

Table 3: Measured value.

The gel content test is carried out for the purpose of non-filterable phase content measurement of the given material according EN ISO 579. The determination of the gel content at polyamide 6 in the dependence of applied dose of radiation is evident from Figure 4. Non-crosslinked (basic) material has zero value of the gel. The higher dose of radiation, the higher gel content. The highest value of the gel content was measured at non-filled polyamide 6 at the dose of 132 kGy. At higher doses of radiation, the small decrease of gel content at both materials occurred. It is caused because of predomination of the degradation over cross-linking at materials. The results of the gel content copy exactly the nano-indentation properties results, when the most cross-linked material showed the best values of nano-indentation hardness. The decrease of the gel content shows the worsening of nano-indentation properties.

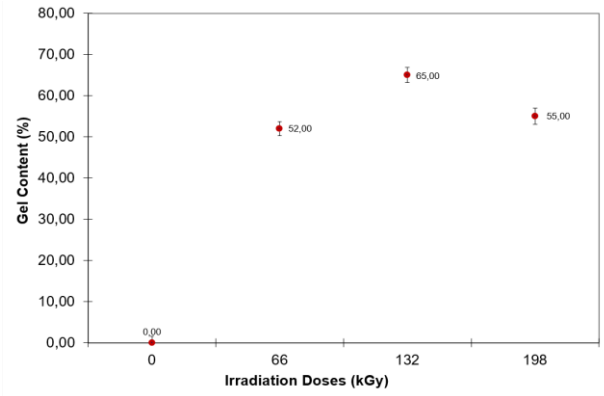

Figure 4: Gel content of tested PA 6

DSI method is a modern technology used to measure the properties of surface layers in scale of nano meters. The main principle of this test is to detect a depth change of the indentation in dependence on force and time. These parameters are then evaluated by OLIVER and PHARR method, thus obtaining values of complex surface layers' properties, such as achieved depth, indentation hardness, vickers hardness, elastic modulus, deformation work and creep behavior. Polyamide 6 is used in common applications that require an increased resistance of the surface layer. Improvements of said resistance and mechanical properties were achieved by applying electron radiation on the tested material.

Basic outputs of measurements done by DSI method are indentation curves (dependence of indentation time on depth of the indentation and dependence of depth of the indentation on indentation force). These curves display basic information about the behavior of the surface layer and can be used to extrapolate important mechanical properties such as hardness, modulus, creep, etc. As can be seen in figure 5, the application of 66 and 132 kGy of radiation allowed the indentation to reach lower depth (1900 nm) than the application of 0 and 198 kGy of radiation (2700 nm).

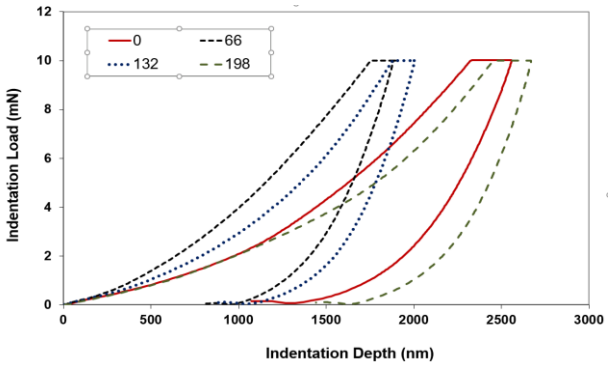

Figure 5: Indentation characteristic of tested PA 6

Figure 6 displays the dependence of indentation time on the depth of indentation. The time run of the indentation depth is the important run of measurement for the purpose of the determination of the creep behaviour of polyamides (indentation creep), which is determined from the difference of the loading after achieving of the indentation depth which is holding on the constant level and after time when the indentation depth was held on the constant level.

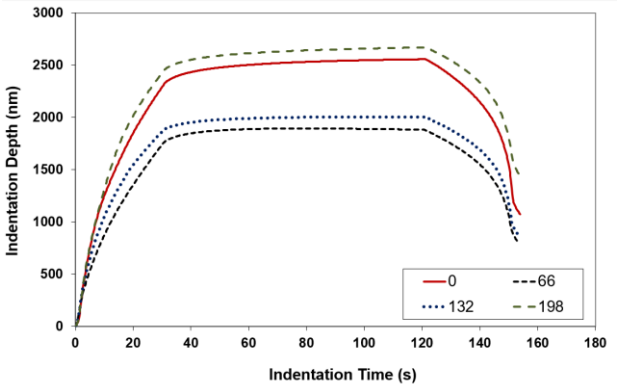

Figure 6: Indentation characteristic of tested PA 6

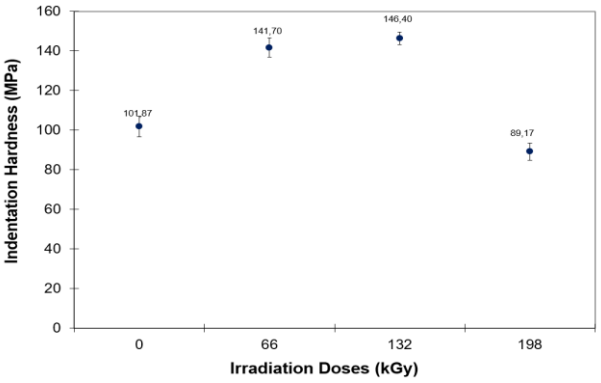

Figure 7: Indentation hardness of tested PA 6

The main parameter used for description of surface layer behavior is hardness (Figure 7). It defines the resistance of the surface layer against abrasion. The surface layer of the tested polyamide was modified by varying amounts of radiation (66, 132 and 198 kGy), which induced a change of properties by cross-linking. An unaltered material indentation hardness was 102 MPa. The difference between irradiated and unaltered PA6 was 44% (132 kGy). As additional measurements showed, not only did higher amounts of radiation effect the hardness of the surface layer in negative way, but it also decreased the hardness of the surface layer. This could be caused by degradation of the surface layer due to high intensity of the

radiation. Irradiating the tested material by 198 kGy resulted in decrease of the hardness value (89 MPa).

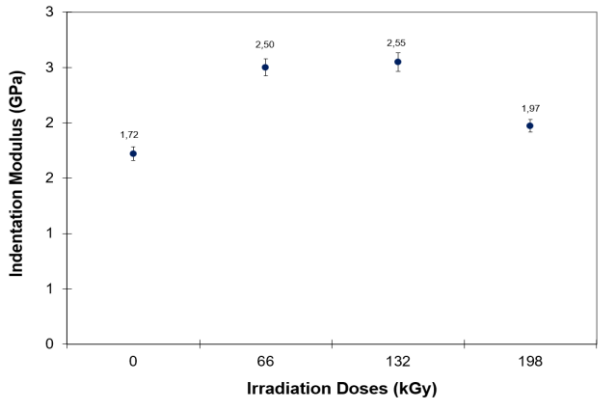

Figure 8: Indentation modulus of tested PA 6

Results of indentation modulus and hardness were similar. Indentation modulus characterizes rigidity of surface layer. The indentation modulus of the unaltered material was approximately 1.7 GPa and it was increased by application of radiation (66 and 132 kGy) up to 2.6 GPa (Figure 8). Due to the irradiation of the tested material, the elastic modulus was increased by 53%. Indentation modulus of the material irradiated by the highest dose of radiation (198 kGy) was decreased to 2 GPa.

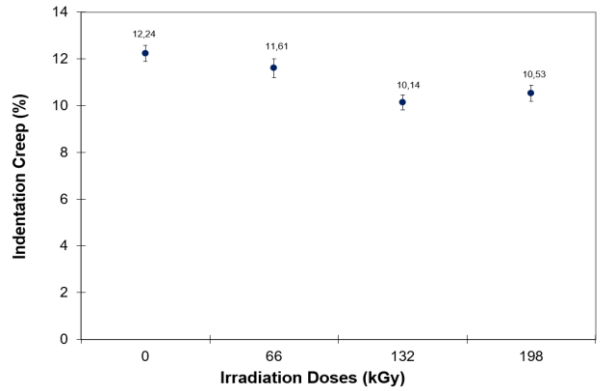

Figure 9: Nano-indentation creep of tested PA 6

The results show that radiation cross-linking influences positively the creep behaviour (indentation creep) of tested polyamide 6 how is evident from Figure 9. From the results obtained using Instrumental test of hardness was proved that the highest value of indentation creep was measured at non-irradiated polyamide 6 (12.2 %). The lowest value of indentation creep was at polyamide 6 irradiated at the dose of 132 kGy (10.1 %), which was 21 % lower in comparison with non-irradiated polyamide 6. At higher doses of radiation, the significant increase of the indentation creep was measured, which the degradation of tested polymer could cause, mainly in surface layers. After comparison of indentation creep with the gel content (Figure 4) is evident, that results correspond. The higher gel content, the highest drop of indentation creep.

Results of the instrumented hardness test (hardness, modulus, creep) of the polyamide show that the best properties and the highest amounts of gel were achieved in material irradiated by a dose of 132 kGy. Radiation dosages higher than 132 kGy resulted in decrease of both mechanical properties and the amounts of gel present in the material. These results were caused by degradation of the material within the surface layer due to high energy of used radiation (198 kGy).

4 CONCLUSIONS

The goal of this article is to describe the effect of varying dosages of ionizing beta radiation on surface layer's nano-mechanical properties and the content of gel of the tested polyamide.

The measurements were measured with the repeatability at least 10. Also a gross error check was performed including the norm it tests. All presented conclusions are determined on the basis of sample files of frequencies of given repeatability.

Results of the instrumented test show that the ionizing radiation is positively effecting mechanical properties, such as hardness, modulus and creep, of the surface layer of the tested polyamide. By exposing the tested material to a dose of 66 and 132 kGy of radiation, the indentation hardness rose by 44%, the elastic modulus increased by 53% and the creep properties improved by 21%. These positive changes were achieved due to a creation of the 3D network induced by the ionizing radiation. Using higher than 132 kGy of radiation results in a decrease of mechanical properties, which is caused by degradation of material. These findings were later confirmed by gel test. While dosages lower than 132 kGy of radiation support the creation of the 3D network, the dosages higher than 132 kGy of radiation inhibit the creation of the 3D network and degrade properties of the tested polyamide surface layer.

As can be seen from the results of this study, during ionizing radiation, structural material such as polyamide 6 can move from the field of structural materials to the area of high-tech polymers. Findings presented in this article can in expanding the range of a practical use of the tested polyamide in cases where good surface layer toughness is required.

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