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ELECTRON RADIATION EFFECT ON INDENTATION CREEP OF CONSTRUCTION POLYMERS

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Abstract. Cross-linking is a process in which polymer chains are associated through chemical bonds. Radiation, which penetrated through specimens and reacted with the cross-linking agent, gradually formed cross-linking (3D net), first in the surface layer and then in the total volume, which resulted in considerable changes in specimen behaviour. Creep value is an important parameter that describes the behaviour of a material for the duration of its exposure to long term stress. Most of the technical parts used in industry are subjected to the long term stress for their whole life cycle. This can lead to material creep, which directly results in the transformation of dimensions. To eliminate this problem, a number of construction materials was chosen and subsequently irradiated by a source of electrons. This created a 3D network within the polymer structure, which led to an increase of the micro-mechanical and micro-creep properties. Evaluation of these modifications was done by state of the art device Micro-combi tester manufactured by Anton Paar. This device lowers the time required to measure the creep by standard technology and it fluently records the changes of indentation depth in relation to applied force. This dependence is then used to calculate the creep values. Due to the electron irradiation, a 40 % increase was reached in creep resistance; therefore the useful properties of selected construction materials were improved.

Keywords: Construction polymers, creep, crosslinking, electron radiation, micro-indentation.

1. Introduction

In the last years, crosslinking of polymers using electron beam radiation has become increasingly used modification method to obtain better mechanical properties. It is an environmentally safe and managed method. During crosslinking, the polymer structure changes, a 3D network is formed from crosslinked bonds and the polymers become more mechanically resistant [1–4].

In the year of 2005, a team of researchers situated in Iran investigated the crosslinking of PA6, enriched by 1 to 3 % of crosslinking accelerator triallyl isocyanurate (TAC), exposed to accelerated electrons. In this experiment, an electron accelerator with 5 MeV was used to expose the samples to radiation doses in range of 40 to 150 kGy. The results showed, that the molecular weight of the polymer samples rose with increasing radiation doses, which was confirmed by the viscosity measurements. Furthermore, the gel test indicated, that the PA6 enriched by TAC started the crosslinking process even after being exposed to relatively low amounts of radiation. The contents of absorbed water declined with increasing amounts of TAC and the absorbed levels of radiation doses [5–9].

Maria Porubska investigated the radiation effect on PA6 filled with 30% glass fibres and its virgin version. The samples were injection moulded and later irradiated by accelerated electrons with 10 MeV energy in doses of 50, 100, 200, 300 and 500 kGy, where 50% of the dosage was applied to each side. The results showed, that regarding the material properties the radiation is more advantageous for unfilled PA6 [10, 11].

The goal of the paper was the study of PA6 irradiated by the electron beams in doses of 0, 66, 99 and 132 of kGy and the radiation effect on micro-creep.

2. Methods

2.1. Material

Two types of polyamides were chosen for this experiment, polyamide 6 PA6 V-PTSCreamid-11-AMN 0 TLD and polyamide 66 V-PTS-Creamid-12-AMN 0 TLD. These polyamides are used in technical practice. Polymer was delivered in granular form, from company PTS Plastics Technology Service, Germany. To ensure correct meshing, the supplier added 6% of meshing agent (special crosslinking agent TAIC - triallyl isocyanurate) that secures the meshing reaction and creation of 3D network.

2.2. Sample preparation

Process conditions were set according to the manufacturer. These samples were moulded by the injection moulding machine ARBURG Allrounder 470H according to the same process conditions. Process conditions (Table 1.) all injected materials were dried by dry and transport unit Arburg Thermolift 100-2. Test samples were manufactured with norm ČSN EN ISO 527 in mind.

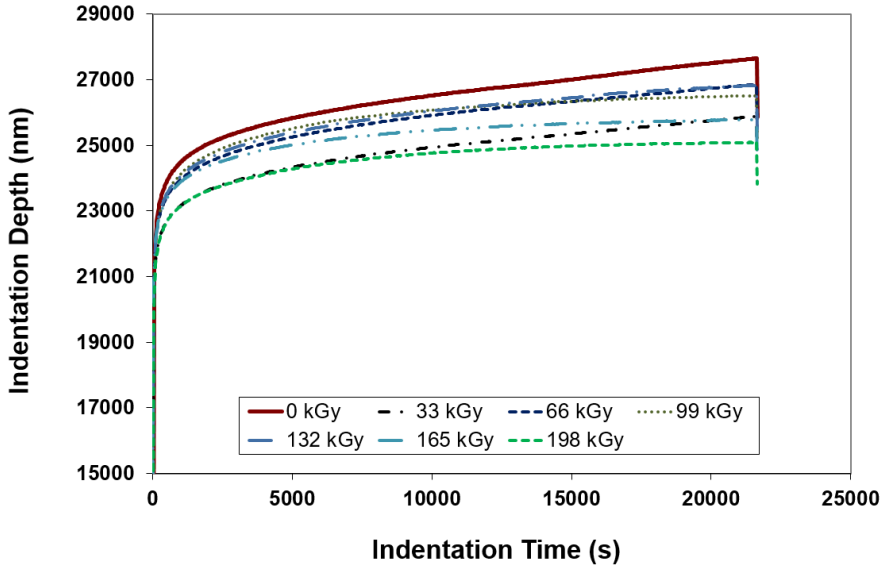

FIGURE 1. Dependence of indentation depth vs. indentation time of tested PA 6.

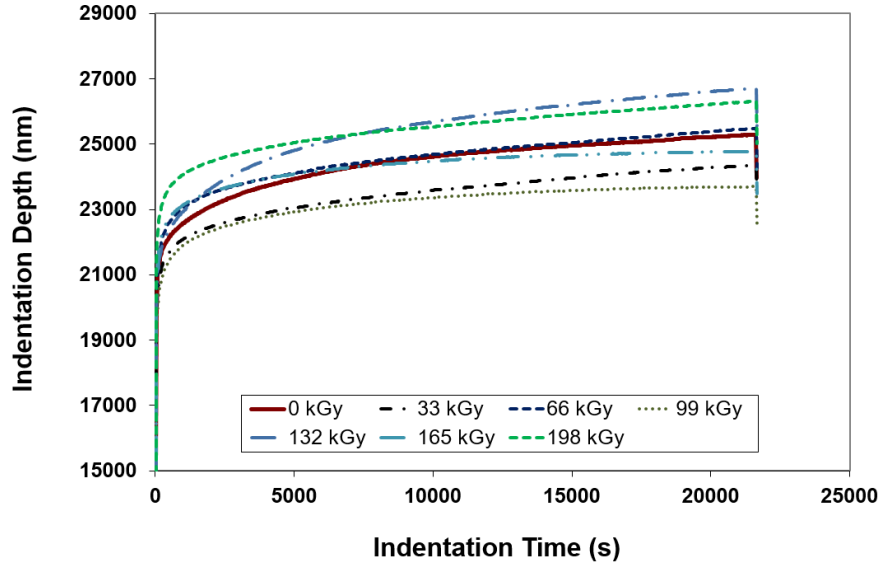

FIGURE 2. Dependence of indentation depth vs. indentation time of tested PA 66.

Parameters	Unit	PA6	PA66
Injection Pressure	MPa	65	80
Cooling Time	s	17	17
Mould Temperature	°C	70	70
Zone 1	°C	220	220
Zone 2	°C	250	250
Zone 3	°C	270	270
Zone 4	°C	310	310

TABLE 1. Injection conditions.

All these samples were sent to the company B. G. S. to Germany, where the samples were irradiated. The range of the dosages was set in compliance with experience gained from industrial practice to 33, 66, 99, 132, 165 and 198 kGy. Each cycle in the accelerator exposed the test sample to the radiation dose of 33 kGy (3 cycle of 33 kGy = 99 kGy). Beta rays are characterized by their ability to irradiate individual packages within a few seconds. All samples were irradiated with electron (beta) rays (electron energy 10 MeV).

2.3. Micro-indentation creep

Indentation creep was measured by means of Micro-Hardness Tester (MHT^3) by ANTON PAAR, Switzerland, using Vickers indenter tip, according to the CSN EN ISO 14577. On each material at least ten indents were made and the results were statistically treated. Standard simple loading-unloading mode was used. The indentation parameters were set according to the standard; see Table 2.

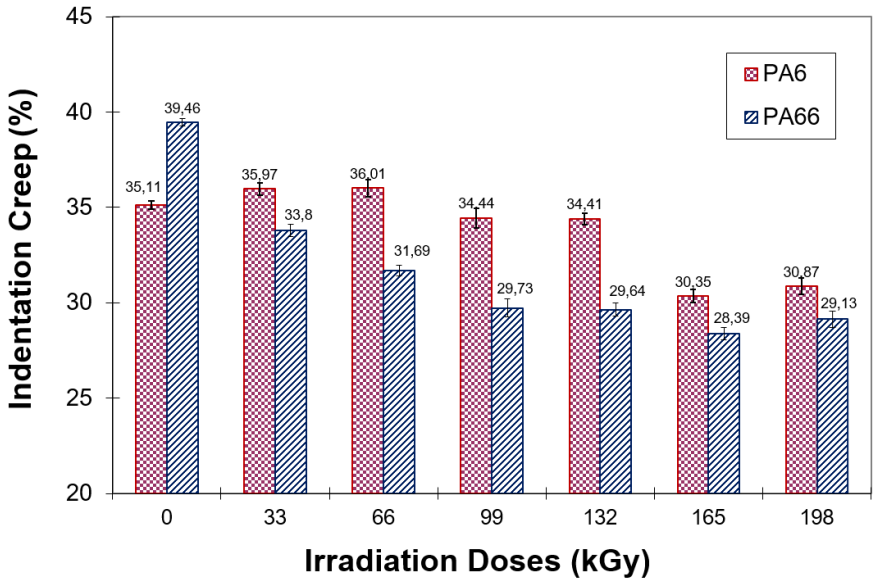

FIGURE 3. Indentation creep.

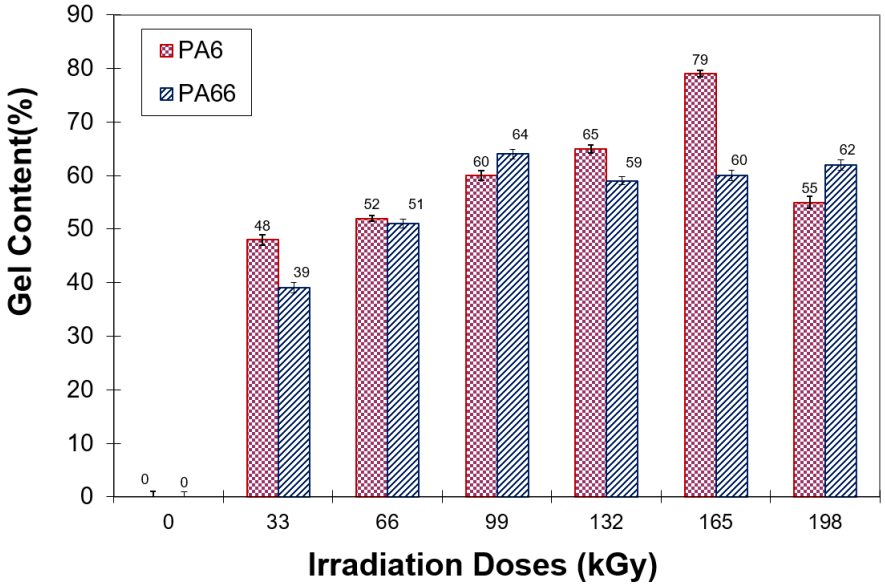

FIGURE 4. Gel content.

Parameters	Unit	Value
Maximum Load	N	1
Load/Unload Speed	N/min	2
Holding Time	s	21600

TABLE 2. Indentation parameters.

3. CONCLUSIONS

$$C_{IT} = \frac{h_2 - h_1}{h_1} \cdot 100, \qquad (1)$$

The identification creep was calculated according to the equation 1,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 [12, 13].

3.1. GEL CONTENT

A gel content (Eq. 2) 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 and PA 6.6 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 6.6 because it dissolves the amorphous part of this material, and the crosslinking part does not dissolve. The mixture was extracted for 24

h. Then, the solutes were separated by distillation. After removing the residual xylene, the crosslinking 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 crosslinking [14]:

$$G_i = \frac{m_3 - m_1}{m_2 - m_1} \cdot 100 \qquad (2)$$

where G_i is the degree of crosslinking 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.

4. Results and discussion

The contemporary indentation method allows the measurements of creep behaviour of different types of materials, including the polymers. This method is based on the principle of immediate detection of indentation depth in dependence on time. The differences in the depth, reached by the indentor during pre-set loading force (1N) with holding time 21 600s, can then be used to calculate the indentation creep.

Figures 1 and 2 display the indentation curves for individual radiation doses for two tested materials (PA6 and PA66). The variance in curves indicates the different behaviour of the tested materials as well as the change of creep behaviour.

The results of the indentation creep measurements show (Figure 3), that the radiation crosslinking improves the properties of the tested material. The virgin PA6 displayed higher value of indentation creep, while the material exposed to lower amounts of radiation showed a deterioration in properties (66 kGy). On the other hand, the samples exposed to higher amounts of radiation indicated an improvement in said properties, with the test sample irradiated by 165 kGy. The difference between the virgin PA6 and the irradiated PA6 was 16%. Finally, the test sample exposed to the highest doses of radiation demonstrated a slight decrease in the creep behavior.

For PA66, similar tendencies were found. The worst values of indentation creep were found in virgin PA66. With increasing radiation dosage, the indentation creep was measured to incrementally improve up to the maximum, which was found in test samples irradiated by 165 kGy. The difference between this sample and the virgin material was 39%. Samples irradiated by 198 kGy displayed a minor decline in the indentation creep.

The results of the indentation test were confirmed by the gel content test (Figure 4). The value of gel represents the percentage volume of 3D network created in the structure of tested polymers. The virgin versions of both tested materials contained 0% of gel. On the other hand, for PA6, the maximum value of the gel (79%) was measured in samples irradiated by 165 kGy, which directly corresponds with the results of the indentation test. Radiation higher than 165 kGy proved to decrease the content of gel, which was probably caused by the degradation of the material due to the high intensity of the radiation.

For PA66, the highest content of gel was measured in test samples irradiated by 99 kGy, which also confirms the results of the indentation creep measurements.

The goal of this study is to examine the effect of beta radiation on the indentation creep of the tested polymers (PA6 and PA66). The research that was done proved, that the irradiation of the samples has a positive effect on the creep behaviour of construction polymers which were chosen. The best improvement was measured in test samples irradiated by 165 kGy dosage for both materials. In comparison to virgin material, the indentation creep rose by 16% for the PA6 and by 39% for the PA66. The results of the indentation creep were confirmed by the gel content test, where the highest increase in crosslinking parts was found in test samples irradiated by higher amounts of radiation. The biggest radiation dosage that was used (165 kGy), proved to worsen the indentation creep as well as the gel content, which was probably caused by the degradation of the material due to the high intensity of the radiation.

Acknowledgements

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