Nanohardness of Electron Beam Irradiated Polyamide 6.6

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Abstract. Nanomechanical changes in the surface layer of polyamide 6.6 modified by beta radiation were measured by instrumented test of nanohardness. The specimens were prepared by injection technology and subjected to radiation doses of 0, 33, 66, 99, 132, 165, 198 kGy. Measurements of nanohardness showed considerable changes of behavior of surface layer in middle as well as high radiation doses with higher values of indentation hardness and stiffness.

Introduction

Nylon 6/6, or polyamide 6/6 (PA66), is a semicrystalline, thermoplastic commodity polymer that finds widespread use in applications that require considerable strength but low toughness.

PA 6.6 was crosslinked with high-energy radiation (consisting of neutrons and g-rays in vacuum) from an atomic pile. It was also reported that pile irradiation of PA 6.6 in air resulted in a rapid loss of strength and a considerable increase in –COOH (carboxyl) end-groups. Subsequent studies on PA 6.6 using high-energy pile radiation from atomic pile showed that the primary effect was crosslinking accompanied by considerable degradation and loss of crystallinity. Efficient crosslinking of PA 6.6 in the absence of degradation or where degradation was of little or no significance was impossible to attain upon straight radiation. Polyamide 6.6 irradiated to a dosage of 60 kGy by electron beam exhibited a gel content of 80% and at double the radiation dose, the gel content was only slightly decreased [1-2].

Experimental

For this experiment polyamide PA6.6 V-PTS – Creamid-B3H2, PTS-Plastics Technologie Service, Germany (unfilled, PA6.6+TAIC) was used. The material already contained the special cross-linking agent TAIC - triallyl isocyanurate (5 volume %), which should enable subsequent cross-linking by ionizing β – radiation. The prepared specimens were irradiated with doses of 0, 33, 66, 99, 132, 165 and 198 kGy at BGS Beta-Gamma Service GmbH & Co. KG, Germany.

The samples were made using the injection molding technology on the injection molding machine Arburg Allrounder 420C. Processing temperature 220–280 °C, mold temperature 70 °C, injection pressure 65 MPa, injection rate 45 mm/s.

Instrumented nanohardness tests were done using a Nanoindentation Tester (NHT2) – Opx/Cpx , CSM Instruments (Switzerland) according to the CSN EN ISO 14577-1. Load and unload speed was 100 mN/min. After a holding time of 90 s at maximum load 50 mN the specimens were unloaded. The specimens were glued on metallic sample holders. Fifteen specimens were tested and average values are reported.

The indentation hardness $H_{IT}$ was calculated as maximum load to the projected area of the hardness impression according to [3-4]:

$$H_{IT} = \frac{F_{\text{max}}}{A_p}$$

(1)
The indentation modulus is calculated from the Plane Strain modulus using an estimated sample Poisson’s ratio:
\[ E_{IT} = E \times (1 - \nu^2) \] (2)

Determination of indentation creep \( C_{IT} \) (as can be seen at Fig. 1):
\[ C_{IT} = \frac{h_2 - h_1}{h_1} \times 100 \] (3)

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 [5-6].

Elastic part of the indentation work \( \eta_{IT} \) (as can be seen at Fig. 2):
\[ \eta_{IT} = \frac{W_{elast}}{W_{total}} \times 100 \]

with \( W_{total} = W_{elast} + W_{plast} \) (4)

Results and discussion

Radiation crosslinking creates changes in the PA6.6 structure by creating 3D net. Beta radiation gradually penetrates more deeply into the polyamide structure through the surface layer. The surface layer undergoes changes which have a considerable influence on the nanomechanical properties of polyamide 6.6.

Measurements of nanohardness of PA6.6 modified by beta radiation showed that the highest values of indentation hardness were found for PA6.6 modified by the radiation dose of 99 kGy. At this radiation dose the measurements also showed the highest degree of crosslinking (gel content). The smallest value of indentation hardness was found for non-irradiated PA6.6 (zero degree of crosslinking degree). The increase of indentation hardness value for PA6.6 irradiated by the dose of 99 kGy was by 63% (Fig. 3) in comparison with the non-irradiated PA6.6. (0% of crosslinking degree).

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 behavior.

In the case of elastic modulus the highest value was found for PA6.6 irradiated by the radiation dose of 198 kGy. At this radiation dose the measurements also showed the second highest degree of crosslinking (gel content). Polyamide 6.6 irradiated by the dose of 99 kGy obtained the second highest value of elastic modulus. The smallest value of elastic modulus was found for non-irradiated PA6.6. The increase of the value of PA6.6 irradiated by the radiation dose of 198 kGy was by 78% in comparison to the non-irradiated PA6.6. In the case of the second highest value of elastic modulus the increase at the dose of 99 kGy was by 70% (Fig. 4).
Interesting results were found for elastic and deformation work. The highest value of elastic work was measured for non-irradiated PA6.6 while the highest value of plastic deformation work was found at the radiation dose of 132 kGy. The lowest value at both deformation work was found when the highest value of radiation dose of 198 kGy was applied (Fig. 5). Also, the value of elastic part of indentation work $\eta_{IT}$ which provides information about the relaxation of the indent created in PA6.6 was the smallest at radiation dose of 198 kGy.

Very important values were found for indentation creep. The lowest value of creep was measured at radiation dose of 33 kGy. The highest creep value measured for non-irradiated PA6.6. Decrease in creep values was 14% for irradiated PA6.6 compared to the non-irradiated one as is seen at Fig. 6.
Figure 7 demonstrated the influence of radiation on the change of nanomechanical properties in the surface layer of specimens. The non-irradiated material showed low hardness as well as increasing impression of the indentor in the surface layer. The irradiated PA6.6 showed considerably smaller indentation depth of the impression of the indentor (high hardness) which can signify greater resistance of this layer to wear.

Conclusion

The experimental study deals with the effect of modification of the surface layer by irradiation cross-linking on the properties of the surface layer of PA6.6. Polyamid 6.6 was modified by beta irradiation at doses of 33, 66, 99, 132, 165, 199 kGy. The greatest changes of nanomechanical properties were found at the radiation dose of 99 kGy, for indentation hardness, which increased by 63% compared to the non-irradiated PA6.6. Measurements of nano-stiffness of the surface layer represented by the indentation elastic modulus showed increase by almost 78%.

Results also show that elastic part of deformation work, which dropped by 35% at the highest radiation dose decreases with a higher degree of crosslinking.

Improvement of mechanical properties in micro and macro scale of radiated PA6.6 has a great significance also for industry. The modified PA6.6 shifts to the group of materials which have considerably better properties. Its micromechanical properties make PP ideal for a wide application in the areas where higher resistance to wear, creep are required. Commonly manufactured PA6.6 can hardly fulfill these criteria.

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