INFLUENCE OF BETA RAYS ON POLYPROPYLENE

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The polypropylene samples for testing were injection moulded and subsequently irradiated by beta radiation at the dose of 15 and 33 kGy with the kind help of BGS Germany. Temperature stability, tensile test, bending test and Charpy-impact test were applied. The influence of beta irradiation low doses on thermal and mechanical properties was subsequently compared. Just dose of irradiation 15 kGy improves tensile and bending properties of polypropylene which expands usage of this material in new applications, especially in automotive.

KEYWORDS

mechanical properties, tensile test, radiation cross-linking, beta rays, polypropylene and temperature stability

1 INTRODUCTION

Polymers belong to constructive materials which find use in the most industry branches. The advantage is a low weight together with the excellent mechanical properties, very good chemical resistance and other properties, which assign them for various applications. Disadvantage is mainly low temperature stability which significantly reduces usage of these polymers. Every property improvement, especially temperature stability, helps to increase application possibilities. In addition, property modifications of standard polymers, which are relatively cheap products, give them the advantage for other usage [Clough 1996].

Cross-linking of rubbers and thermoplastic polymers is a well-proven improvement process of thermal properties. Chemical cross-linking or rubber vulcanization is normally induced by the effect of heating after processing with the presence of a curing agent. The cross-linking process for thermosets is very similar. In thermosets the polymer molecules are also chemically linked due to heat after processing. Cross-linked rubbers have a wide-meshed molecular network that keeps them soft and their properties change only slightly on a wide temperature scale. On the other hand, thermosets are characterized by a very narrow-meshed network. Due to this fact they hardly change their high level of stiffness on a wide temperature scale [Drobny 2010].

Radiation cross-linking with accelerated electrons offers several advantages in comparison with other radiation sources, particularly gamma rays and X-rays. The process is very fast, clean and can be controlled with a great deal of precision. In contrast to gamma rays and X-rays the electron beam can be steered relatively easy, thus allowing irradiation of variety of physical shapes. The large advantage includes flexibility and controllability in operation, beneficial economics, high throughput capability and the ability to switch off the source of radiation [Clegg 1991].

Polypropylene (PP) belongs to the family of polyolefins, it is a thermoplastic semicrystalline polymer, it has very good dielectric and mechanical properties and thereby is used in a various use in the plastics industry. Because of its good heat resistance and the low dielectric loss it is often used as a material for electrical insulation [Suljovrujic 2010]. In comparison with e.g. polyethylene, PP can offer much higher thermo-mechanical resistance and rigidity because of its higher melting point and crystallinity. Its disadvantage is that it is more sensitive to degradation and has lower aging resistance [Han 2004].

PP is sensitive polymer to oxidative degradation, which is mostly characterized by the increase of melt flow rate (MFR), which mostly increases with the radiation dose during irradiation. It is caused by lowering the molecular weight during this process. Despite the bad influence of radiation degradation of PP on physical properties, practical applications have been improved for disintegration by electron beam radiation to produce lower molecular weight material with better processability. In the plastics industry is this process commonly known as visbreaking of PP. In general, the lower molecular weight increases the melt flow of PP and thereby causes the improvement of the procesability for various processing methods such as injection moulding. PP treated by radiation visbroken is commonly used for fiber spinning aplications [Makuuchi 2012].

Radiation crosslinking of common PP leads to degradation and its mechanical properties worsen, unlike using crosslinking agent TAIC (triallylisocyanurate) leads to crosslinking of noncrystalline part of PP inside the PP structure. Typical X-ray diffraction spectra can show a gradual loss of beta phase with increasing beta radiation dose with the maximum loss at the radiation dose of 60 kGy. The crystal sizes decreases with radiation doses. During beta radiation crosslinking a loss of crystalline phase is caused, but crosslinking occurs in the noncrystalline phase and it has a big influence on the mechanical properties of the surface layer. Beta radiation crosslinking has also a big influence on microhardness and the indentation modulus of elasticity. The lowest value of microhardness and the indentation modulus of elasticity was found at non-irradiated PP, unlike the highest value of indentation hardess was obtained at PP irradiated by the dose of 45 kGy (75 % higher in comparison with non-irradiated PP) and the highest values of indentation modulus of elasticity were achieved at the dose of 45 kGy (95 % higher in comparison with non-irradiated PP) [Manas 2013].

Do Hung Han, Seung-Ho Shin and Serguei Petrov dealt with crosslinking and degradation of PP in the presence of trifunctional monomers. They used homo-polypropylene (HPP) and random terpolymer of propylene (RTPP), they found out that these two polymers can be successfully crosslinked at low doses of beta radiation after addition of crosslinking agents trimethylpropanetriacrylae (TMPTA) or triallylcyanurate (TAC). Much higher radiation stability shows HPP including TAC than TMPA [Han 2004].

This research paper deals with a possibility of using radiation cross-linked polypropylene as a suitable material in automotive industry, especially from the mechanical testing and temperature stability point of view.

Table 1. Setting of injection moulding machine parameters

Injection Parameters	Values
Injection Pressure [MPa]	80
Injection velocity [mm.s^{-1}]	50
Holding Pressure [MPa]	8
Cooling Time [s]	40
Mould Temperature [°C]	50
Melt Temperature [°C]	240

2 EXPERIMENTAL

Polypropylene (V-PTS-CREALEN-EP-2300L1*M800 natur) was used as the basic polymer. An ARBURG Allrounder 420C Advance Injection molding machine was used for sample preparation, with the processing conditional to comply with the polypropylene (PP) producer's recommendations as can be seen in Tab. 1.

Irradiation of tested polypropylene was performed with the kind help of BGS Germany, in the BGS Wiehl plant using accelerated electrons with irradiation dose of 15 and 33 kGy. These small doses were used because PP has strong tendency to degradation with increasing dose of irradiation. Real irradiation was measured 15.13 (required 15 kGy) and 33.21 kGy (required 33 kGy).

The cross-linking degree of irradiated polypropylene by gel measurements (gel content) was determined, according to the standard EN ISO 579. Gel content 75.6 % at 15 kGy and 72.4 % at 33 kGy was measured.

Mechanical properties of non-irradiated and irradiated polypropylene and temperature stability of irradiated polypropylene before and after irradiation were tested. The thermo-mechanical properties were measured. Perkin – Elmer Thermal Analyser DMA 7e was used for the thermo-mechanical analysis, heated from 50 °C to 400 °C at 20 °C/min, hold for 1 min at 50 °C. The tensile and bending behaviour of non-irradiated and irradiated samples of PP were measured at the ambient temperature. Tensile and bending tests were carried out on tensile test machine ZWICK 1456 for PP according to standard CSN EN ISO 527-1, 527-2 and ISO 178 with used rate 100 mm/min and 10 mm/min, respectively for tensile and bending test. Test data was processed by Test Expert Standard software and E-modulus [MPa], tensile strength [MPa], elongation at break [%], flexural modulus [MPa] and flexural strength [MPa] were determined. Charpy impact test was carried out on Zwick Roell HIT50P. For tests were used 50 J pendulum energy, according to standard ISO 179-1. Test data was processed by Test Expert Standard software and Charpy-Impact Strength [kJ/m^2] was determined.

3 RESULTS AND DISCUSSION

At first, the temperature stability with using of thermo-mechanical analysis and visual observation in temperature chamber was studied. Generally, radiation cross-linking has a huge influence to the temperature stability of plastics such as polyethylene, polyamide and polybutylene terephtahalate.

Then mechanical behaviour of non-modified and modified polypropylene by accelarated electrons were tested at ambient temperature (23 °C). As a widespread measurement of static tensile behaviour and bending test were carried out. After thermoplastics irradiation, there are cross-linked bonds which cause changes in behaviour of plastics.

At last, the charpy-impact test at ambient (23 °C) and reduced (-35 °C) temperature was carried out. Polypropylene is tough material which has impact resistance against dynamic load at ambient temperature and lower temperature too.

3.1 Temperature stability

First, the thermo-mechanical properties of polypropylene were measured. The thermo-mechanical behaviour was evaluated by thermomechanical analysis (TMA). In the Fig. 1 TMA results of non-irradiated and irradiated polypropylene with the irradiation doses of 15 and 33 kGy are depicted. Non-modified sample was melted at the temperature 170 °C. Irradiated polypropylene samples with the dose of irradiation 15 and 33 kGy were soften at the temperature 175 °C. At 200 °C measured probe penetrated into both of irradiated polypropylene samples, that value is slightly decreasing up to 350 °C, than with the increasing temperature stability of irradiated samples is falling down sharply.

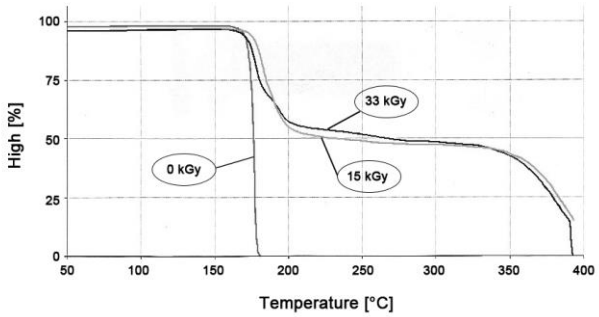

Figure 1. Polypropylene thermo-mechanical analysis

As can be seen in the Fig. 2 there is visual observation of polypropylene after one hour exposition at 170 °C (on the left) and 200 °C (on the right). Non-irradiated polypropylene specimen was melted after temperature exposition ; however, the irradiated (15 and 33 kGy) polypropylene specimens were almost without shape changes, just a sag occurred under own weight. Irradiated polypropylene specimens with increasing temperature change color from ivory (23 °C) through yellow (up to 170 °C) into yellow-brown (200 °C). The colour depends on amount of thermo-oxidative degradation.

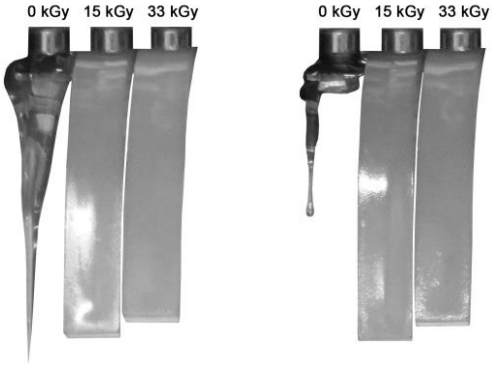

Figure 2. Polypropylene visual observation after 1 hour at 170 °C (left) and 200 °C (right)

3.2 Tensile test

The influence of radiation on tensile behaviour was measured at ambient (23 °C) temperature. After performing the tensile test three observed parameters (E-modulus, tensile strength, and elongation at break) were evaluated.

In Fig. 3 values of E-modulus are grafically displayed, at non-modified polypropylne E-modulus 749 MPa was measured. E-modulus with firstly used dose of irradiation 15 kGy increases to value 1040 MPa and with higher dose of irradiation 33 kGy E-modulus declines slightly to value 967 MPa. Decrease can be caused by beginning of degradation process during irradiation. Polypropylene without cross-linking agent is sensitive to degradation under irradiation by beta rays, however, in this research was used special type of polypropylene with cross-linking agent (TAIC) for precise modification by accelerated electrons.

In Fig. 4 trend at tensile strength in comparison with E-modulus can be seen. Non-irradiated polypropylene tensile strength 20.7 MPa was measured, at irradiated polypropylene with the dose of irradiation 15 kGy rise of tensile strength (value 25.6 MPa) was registred and then slow decrease at 33 kGy (value 25.0 MPa) was measured. From this point of view just small dose of irradiation 15 kGy should be chosen, because of worsens of tensile behaviour.

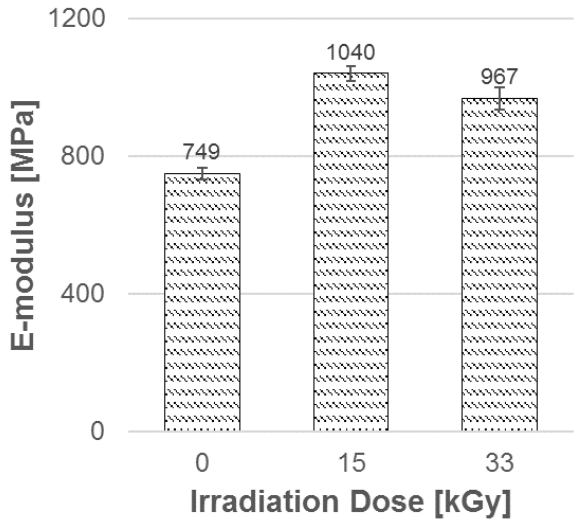

Figure 3. Polypropylene E-modulus

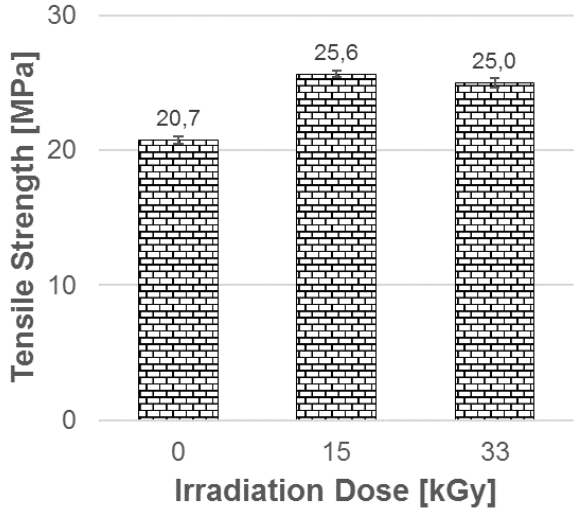

Figure 4. Polypropylene tensile strength

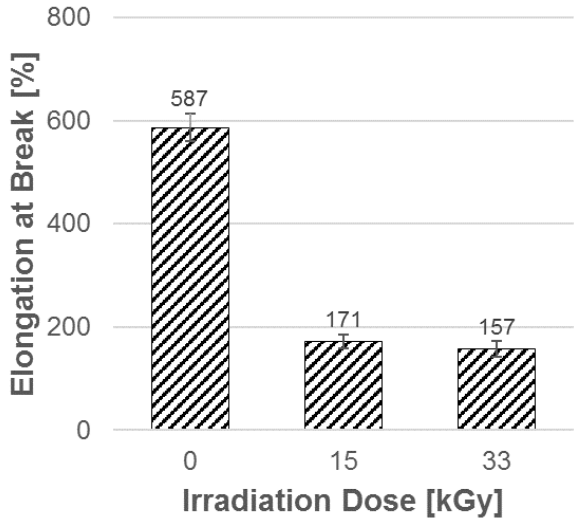

Figure 5. Polypropylene elongation at break

In Fig. 5 the dependence of polypropylene elongation at break on the radiation dose is displayed. At non-modified polypropylen elongation at break 587 % was measured, at both of irradiated polypropylene samples elongation at break decreases sharply to value 171 and 157 % at 15 and 33 kGy, respectively. It is caused by changing of the thermoplastic structure to cross-linked polypropylen which has worse elasticity because of rigid cross-linking bonds.

In Fig. 6 the percentage comparison of tensile parameters (E-modulus, tensile strength and elongation at break) is shown. Irradiated sample was compared with non-irradiated sample at each parameter separately. Improvement of E-modulus by 39 % at 15 kGy and tensile strength by 24 % at the same dose of irradiation was measured, on the other hand, deterioration of elongation by 71 % at 15 kGy was measured. From tensile test ensues that higher dose of irradiation than 15 kGy does not need to bring desirable improvement of tensile behaviour.

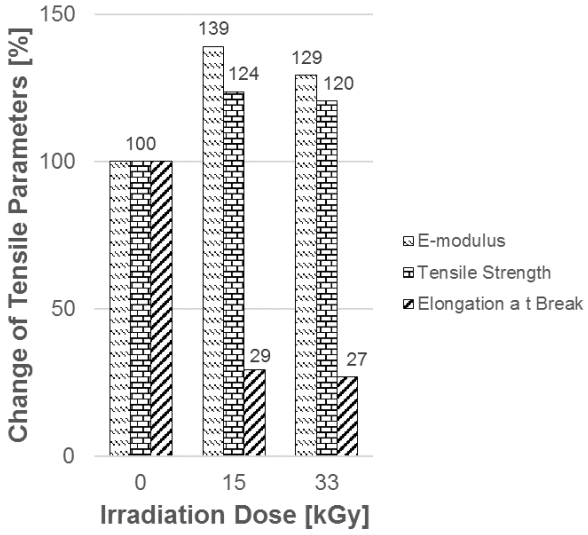

Figure 6. Polypropylene comparison of tensile parameters

3.3 *Bending test*

The influence of irradiation on flexural modulus and strength was measured at ambient (23 °C) temperature. Testing specimens were laid on two supports and the force of testing machine impact staticaly into center of tested specimens was evaluated.

In Fig. 7 the improvement of flexural modulus after irradiation can be seen. Non-irradiated polypropylene flexural modulus 753 MPa was measured; however, flexural modulus 1127 MPa at 15 kGy and 1083 MPa at 33 kGy was measured. In comparison with tensile test, the tendency of the flexural modulus is similar with trend of the E-modulus. Small dose of irradiation up to 15 kGy has better influence on flexural modulus, with increasing irradiation it is worsen for polypropylene.

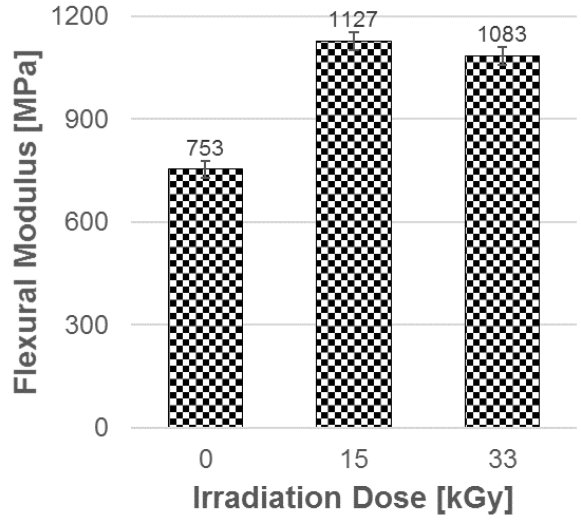

Figure 7. Polypropylene flexural modulus

In Fig. 8 the flexural strength of polypropylene at ambient temperature is recorded. Polypropylene without irradiation has the flexural strength 24.3 MPa. Flexural strength with irradiation 15 kGy rises sharply on value 32.8 MPa and then decreases slightly (32.0 MPa at 33 kGy) with incerasing dose of irradiation.

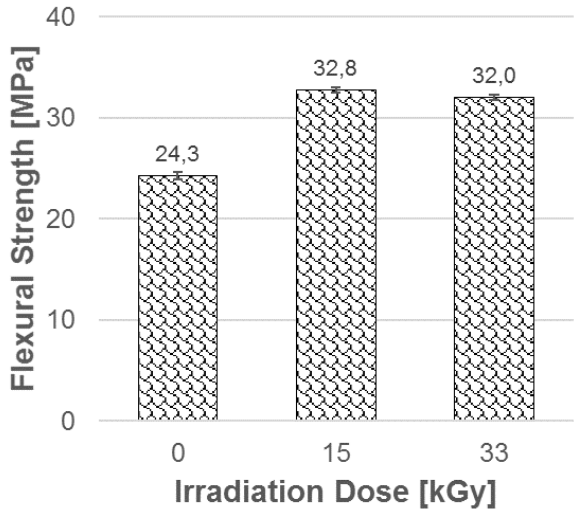

Figure 8. Polypropylene flexural strength

Comparison between flexural modulus and strength in percentage is displayed in Fig. 9. The dose of radiation 15 kGy is optimal in the tensile and bending test point of view. Flexural modulus grows by 50 % and flexural strength increases by 35 % at the dose of irradiation 15 kGy in comparison with non-modified polypropylene. Higher irradiation causes deterioration of mechanical properties (measured by tensile and bending test), it can be generated by begining degradation of the structure.

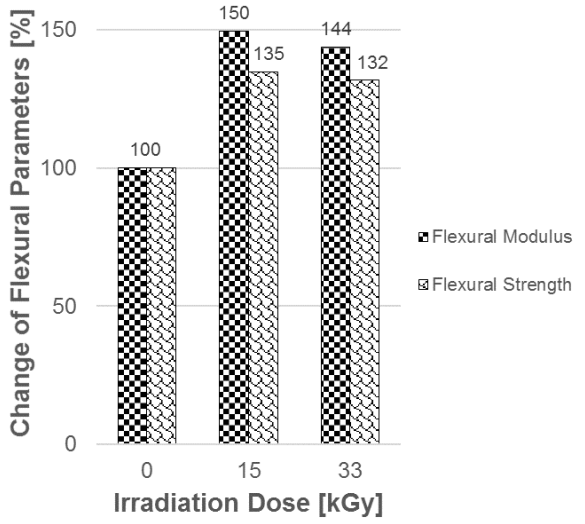

Figure 9. Polypropylene comparison of flexural parameters

3.4 Charpy-impact test

The last measurement charpy-impact test demonstrates difference of impact test against static tests, such as tensile and bending test. In Fig. 10 the influence of irradiation on charpy-impact strength which decreases with increasing dose of irradiation can be seen. Charpy-impact strength 51.2 kJ/m^2 for non-modified polypropylene was measured. Increasing dose of irradiation causes the decrease of charpy-impact strength by 22 % at 15 kGy and by 48 % at 33 kGy in comparison with non-irradiated polypropylene.

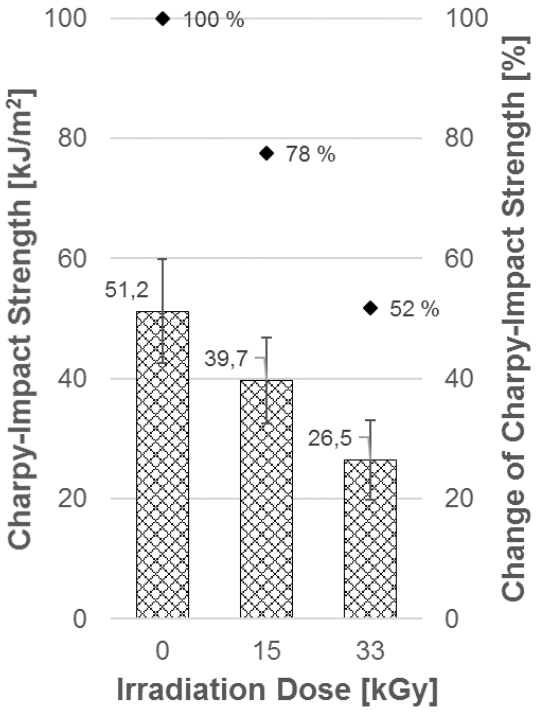

Figure 10. Polypropylene charpy-impact strength

4 CONCLUSIONS

In this study the influence of irradiation on polypropylene mechanical properties (static and impact) was evaluated. Measured experiments displayed significant changes in mechanical properties of polypropylene. In last studies degradation and deterioration of mechanical properties of polypropylene without cross-linking agent was found. Because of that, polypropylene with cross-linking agent was used here. Small dose of irradiation changes mechanical properties of polypropylene significantly. Nevertheless, increasing of irradiation does not lead to the improvement of polypropylene mechanical properties as was registered for polyethylenes and polyamides.

Radiation cross-linking improves temperature stability of polypropylene. After irradiation polypropylene cannot melt, because of the modified polypropylene can be applied in higher temperature (than melting point of pure polypropylene), usually for a short time. After longer time at higher temperature polypropylene becomes softer (creep) and change colour due to thermo-oxidation process.

In point of view tensile and bending test improvement of parameters of irradiated polypropylene with dose of irradiation 15 kGy was spotted out. At 33 kGy tensile and bending behaviour worsen which can cause the degradation of the structure under irradiation. However, charpy-impact strength of polypropylene decreases with dose of irradiation sharply down.

Irradiation has significant influence on polypropylene; however, polypropylene with cross-linking agent and small dose of irradiation (up to 15 kGy) should be used and also selection of application should by chosen precisely.

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