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ANALYSIS OF CROSS-LINKING IN PROCESSING OF PLASTICS

The cross-linking is the most important reaction of polymers that significantly changes product properties. In the cross-linking, the molecules join together and create a functional net. By radiation in cross-linking thermoplastic changes into thermoset. Increasing density of cross-linking increases rigidity and hardness and decreases the degree of bulking. Investigation of properties change of thermoplastics as a consequence of cross-linking was carried on the PP and PA66 materials.

Keywords: cross-linking, thermoplastics, radiation

Introduction

The cross-linking is the most important reaction of polymers that significantly changes product properties [1, 2]. In the cross-linking, the molecules join together and create a functional net. By radiation in cross-linking thermoplastic changes into thermoset. Increasing density of cross-linking increases rigidity and hardness, electric resistance and resistance to solvents, and decreases the degree of bulking [3, 4]. The cross-linking is carried out by peroxides, silanes, ionizing radiation (for example the radiation dose in PE is within the range 1÷30 Mrad) and vulcanization of sulphur (in caoutchouc).

In cross-linking by peroxides (dibenzoylperoxide, butylperoxide) higher temperatures are usually used (polymer is melted). In the first step, peroxide (ROOR) is decomposed by heat into free radicals RO which further react by polymer string. In the recombination of polymer radicals, there occurs joining of string through the C-C bond. The disadvantages of cross-linking are its low efficiency (side reactions of peroxides and free radicals) and necessity of using big amount of relatively expensive peroxides, and mixing the compound of polymers with peroxides and stabilizers in special equipment (in PE – Engel process).

Peroxide is used to create a primary radical. Molecules of silane are then inoculated with primary radicals. Si-O-Si bridges are created. For the optimal speed of reaction, elevated temperature is used (in PE from 80 to 90ºC) with the presence of catalyst. The advantage of cross-linking by silanes lies in using conventional machines, and in addition, wider temperature range is available in comparison with cross-linking by peroxides [5]. The problem is the occurrence of by-products (methanol and water) during reaction.

There is the basic assumption in this cross-linking, that materials during ionising radiation mainly cross-link and do not degrade. It is a physical method and chemical ingredients are not needed (for example in PP a cross-linking reagent TAIC is used). The main condition is the presence of three or more functional monomers. The interaction of radiation and polymers causes the creation of polymer radicals (decomposition of bonds C-H), which create nets by recombination in strings. A net is created by bonding of two free radicals between neighbouring strings with creation of a C-C

The properties of a composite filled with element filler depend on the physical properties of components (matrix, filler). The coherence of the matrix with the filler has a significant influence on the resultant transmission of stresses on reinforcement and the resultant mechanical properties. The radiation technology of beta or gamma rays is used to achieve joining of the matrix structure with the reinforcement, which increases the strength, as can be seen in the figure. Evaluation of composite structure is usually done in fracture area in tensile test. It is realized by REM RE-Detector with given magnification. Presented structure (Fig. 1) is for material filled with glass short fibres PA6GF30. Structure is irradiated by dose of 100 kGy.

One of the main demands of BMW Company was to increase the lifetime of interstage cooler in high temperatures of the charge air. A unique idea was to make the component of PPA – semi-crystalline polyamide. This material had the melting temperature of 325ºC and for a short term it resisted the temperature above 200ºC. Although PPA was common in previous application, its acoustic insulation qualities were unconvincing. Polyamide material was suggested for the purpose. Glass-fibre enforced PA66 is known for its good acoustic insulation properties. Unfortunately, this material with the maximum allowed working temperature of 150ºC did not meet the requirements on temperature resistance. To solve this problem, simple cross-linking was used. The plastic component is now made of PA66-GV in a conventional way and then is radiation cross-linked by beta rays. Due to radiation cross-linking, PA66-GV will resist the temperatures from 180 to 200ºC. Melting temperature is about by 30÷40ºC lower than that of PPA, and there are considerable energy savings due to lower temperature of mould processing. The decisive factor is the lower price of injection of PA66 compound per kilogram in comparison with other production methods. The radiation does not change the appearance of the components. The cross-linking is regularly controlled, so a customer can be sure, that the components have functional properties, which are exactly defined and guaranteed.

a) b)

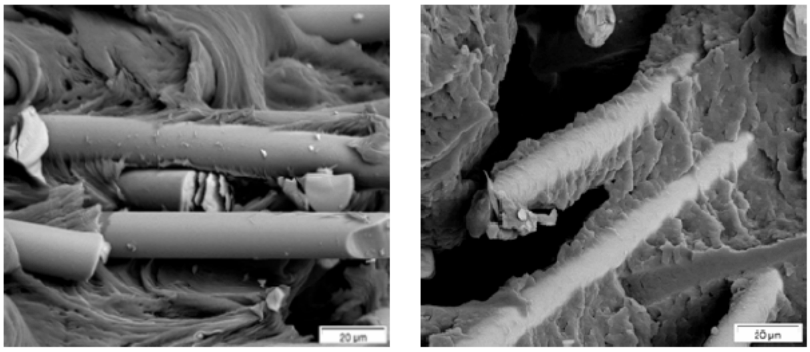


Fig. 1. Structure of unirradiated (a) and irradiated (b) PA66GF30 material

Rys. 1. Struktura nienapromieniowanego (a) oraz napromieniowanego (b) tworzywa wzmacnianego włóknem szklanym PA66GF30

Experimental procedure

Two type of polymer materials were used in the experiment: PTS-Crealen EP-2300L1-M800 – unfilled PP and PTS-Crealen EP8G5HS*M0083 – PP filled by 25% of glass fibres. Irradiation was carried out (in BGS Beta Gamma Service GmbH & Co. KG, Saal am Donau, Germany) by β electron radiation, with the energy 10 MeV, minimal dose 15 and 33 kGy. Properties of unirradiated and irradiated PP were compared (filled with 25% of glass fibres/unfilled). The dose size of ionizing electron radiation was 15 and 33 kGy. Testing samples were prepared in an injection moulding machine DEMAG-ERGOETECH 50-200 in laboratories of ÚIP FT in Zlín.

Tensile test was realized according to STN EN ISO 527-1, 527-2 standard in surrounding temperature of 23ºC on testing machine ZWICK 1456. Measurement of impact strength was carried out on Charpy hammer ZWICK 5113 Pendulum Impact Tester in surrounding temperature of 23ºC and temperature of –35ºC using the 5 J hammer.

Results and discussion

Radiation influences on mechanical and thermomechanical properties of the test samples were observed (Fig. 2). Irradiation of test samples causes changes in the ultimate strength and Young's modulus of filled and unfilled PP (Fig. 3 and 4), the changes reached relatively considerable values (15÷30%). Radiation of 15 a 33 kGy at ambient temperature improves the ultimate strength and Young's modulus in filled and unfilled PP. Failure of material in unfilled samples does not occur. The amount of radiation in this temperature has a minor influence on the ultimate strength, in favour of 15 kGy dose of unfilled PP compared to 33 kGy doses. Comparison of filled and unfilled PP shows considerable improvement of properties by filling the PP.

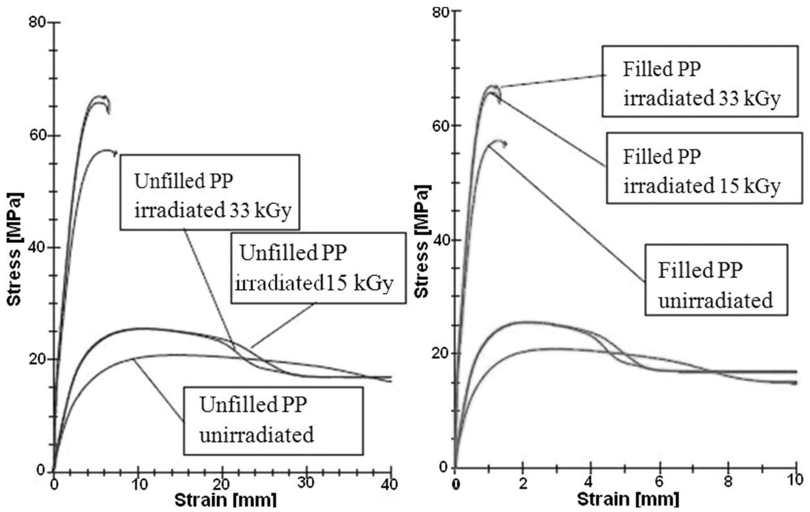


Fig. 2. Graphs of tensile curve in 23ºC

Rys. 2. Wykresy krzywych rozciągania w temperaturze 23ºC

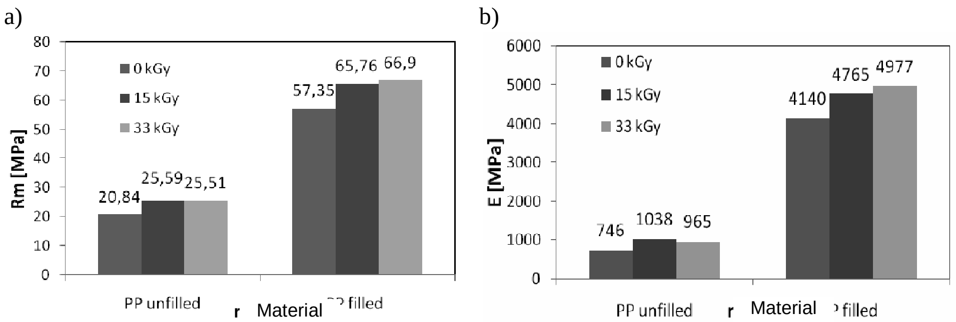


Fig. 3. Comparison of ultimate strength (a) and Young's modulus (b) determined under tensile test for unfilled and filled PP in 23ºC

Rys. 3. Porównanie wartości granicy wytrzymałości (a) oraz modułu Younga (b) wyznaczonych w próbie rozciągania w temperaturze 23ºC, wypełnionego oraz niewypełnionego PP

When the impact strength is concerned (Fig. 5 and 6), in the ambient temperature in all the unfilled PP no puncture occurs. Irradiation of filled PP decreases the impact strength in comparison with unirradiated filled PP. The

dose rate of irradiation does not matter. In testing the samples at the temperature of
–35ºC, punctures occur in all unfilled and filled materials. The impact strength is decreased. When comparing unfilled and filled samples, decreasing of toughness occurs in unirradiated filled material.

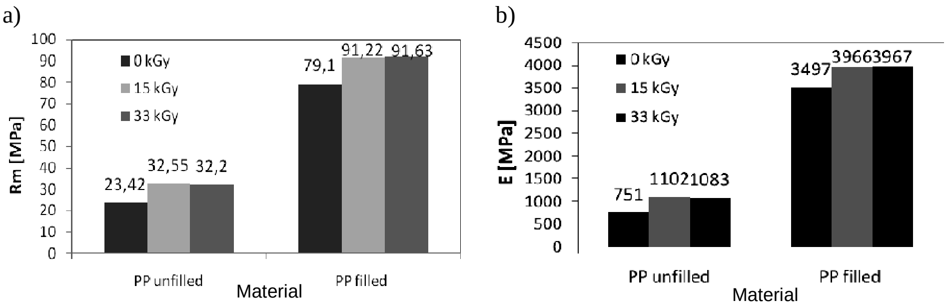


Fig. 4. Comparison of ultimate strength (a) and Young's modulus (b) determined under bending test for unfilled and filled PP in 23ºC

Rys. 4. Porównanie wartości granicy wytrzymałości (a) oraz modułu Younga (b) wyznaczonych z gięcia w temperaturze 23ºC, wypełnionego oraz niewypełnionego PP

In irradiation of 15 and 33 kGy toughness increases in filled materials. The result of toughness comparison of filled PP material is that in unirradiated PP material measured in –35ºC was observed decreased toughness compared to measurement in the ambient temperature. The radiation of 15 kGy in –35ºC increases the toughness compared to the measurement in the ambient temperature. In the radiation of 33 kGy, the toughness does not change in relation to temperature.

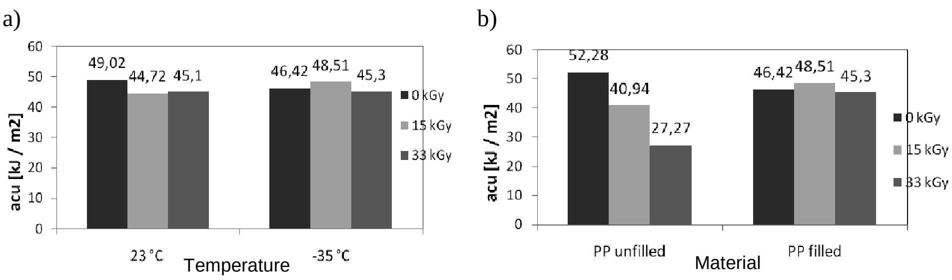
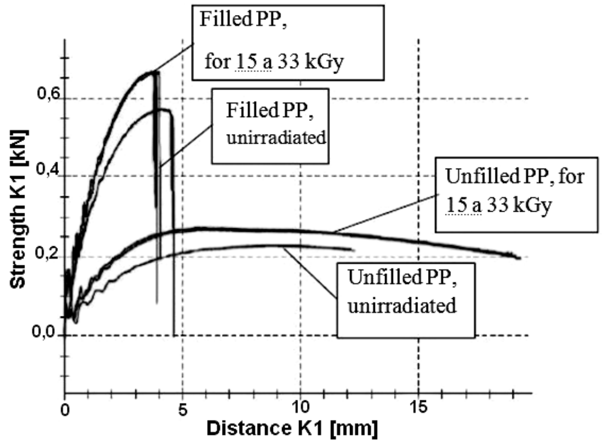


Fig. 5. Comparison of impact strength of filled PP in various temperatures (a) and of modified PP for the temperature of –35ºC (b)

Rys. 5. Porównanie wytrzymałości udarowej wypełnionego PP w różnych temperaturach (a) oraz modyfikowanego PP w temperaturze –35ºC (b) a)



b)

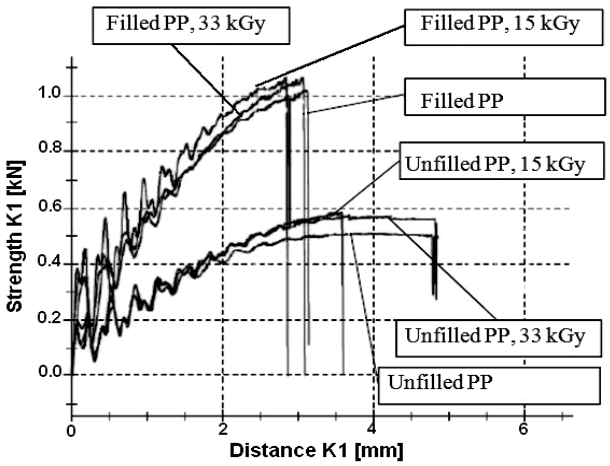


Fig. 6. Impact strength characteristics determined by Charpy test of PP in 23ºC (a) and in –35ºC (b)

Rys. 6. Charakterystyki wytrzymałości udarowej z próby Charpy'ego w temperaturze 23ºC (a) oraz –35ºC (b) dla różnych wariantów materiałowych PP

Conclusions

The tensile test showed that irradiation by 15 and 33 kGy at the ambient temperature of 23ºC increase the ultimate strength in both filled and unfilled PP by 15-20%. The highest values of both ultimate strength and module of elasticity were reached after irradiation by 33 kGy. The bending test showed that irradiations by 15 and 33 kGy at the ambient temperature of 23ºC improve the ultimate strength of both filled and unfilled PP by approximately 25 to 30%. The comparison of filled and unfilled materials showed that the filling increases the material resistance by approximately 400%. The influence of irradiation is less significant – it increases the resistance by approximately 12%. In the impact strength test of unfilled PP there occurred no failure in samples, in contrast to filled PP. The plasticity of unfilled PP was higher, that is why there was no failure in samples. Such samples cannot be evaluated according to the standard. Irradiation cross-linking typically aims from the surface of the product inwards and occurs exclusively in amorphous areas of the plastic. The influence of irradiation has only a little influence on the melting temperature. It ranges within 1÷2ºC, i.e. the influence is unimportant.

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ANALIZA EFEKTU SIECIOWANIA PODCZAS OBRÓBKI TWORZYW POLIMEROWYCH

Sieciowanie występujące w tworzywach polimerowych istotnie wpływa na zmianę właściwości wyrobów. Podczas sieciowania cząstki tworzywa łączą się, tworząc siatkę. Pod wpływem napromieniowania usieciowane termoplasty utwardzają się. Wzrost gęstości usieciowania skutkuje wzrostem sztywności i twardości oraz zmniejszeniem stopnia spęczenia. Badania zmian właściwości termoplastów na skutek sieciowania przeprowadzono dla dwóch tworzyw – polipropylenu PP oraz poliamidu PA66.

Słowa kluczowe: sieciowanie, termoplasty, napromieniowanie

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