

The Influence of Ionizing Radiation on Chemical Resistance of Polymers

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Abstract— The topic of this research paper is a comparison of influence of chemical and petrochemical products on the mechanical properties of the selected types of polymers modified by irradiation cross-linking. After irradiation by beta radiation the materials were load into the chemicals. For the evaluation of the mechanical properties of irradiated and non-irradiated test specimens the tensile test and impact hammer test were used.

Keywords— Radiation Cross-linking, Beta Radiation, Chemical Resistance, Polymers Modification.

I. INTRODUCTION

HAVING marked present according to the most characteristic material, which has served the mankind, it certainly would be called time of polymers. Due to specific features, processing and application polymeric materials have gradually replaced the most widely used materials such as wood and metal. However, demands on their properties increase with their increasing applications.

Resistance to the effects of environmental degradation is an important property of plastic materials. Resistance to the effects of chemical products is an important factor that has a particular impact on their applicability in various industries. They cannot be applied properly and thus their maximal lifespan cannot be guaranteed unless their resistance is known. If the materials resistance to the effects of the environment increases, the products lifespan and thus material and financial savings also increase.

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II. PROBLEM FORMULATION

THE aim of this work is to find out the impact of the chemical agents on the mechanical properties of the specified radiation cross-linked polymers.

One of the ways how to increase resistance of plastics is the method of radiation cross-linking by beta or gamma radiation ionization. It results into improvement of mechanical, chemical and other properties of materials at affordable price.

As the trend of plastic components development is determined by the automotive industry, these types of liquids used in the industry are chosen: Methanol testing fluid, bio diesel, engine oil, concentrated coolant, anti-freeze mixture and brake fluid. The tested materials are the following plastics: PBT and PA 66 filled with 30% of glass fibers.

In the next step the pieces will be sent BGS company to be radiated to the desired degree of cross-linking. Furthermore, Robert Bosh company will provide soaking of the specimens into chemicals under the given conditions. Subsequently, the specimens will be subjected to mechanical tests. Finally, comparison and results evaluation will be done.

A. Test specimens preparation

The materials of the test specimens were:
Polyamide 6.6 Frianyl A63 VNGV30
PBT PTS-CREATEC-B3HZC* M800/25 natur
PA 11 V-PTS-CREAMID-11T *M600/13 transparent
PA12 V-PTS-CREAMID 12- AMN 0 TLD *M800/13 natur

The test specimens were prepared on the injection moulding machine (ARBURG ALLROUNDER 420 C 1000-350).

Processing conditions during the injection moulding were set according to the recommendation of the producers.

B. Test specimens modification

All samples were irradiated with electron rays (electron energy 10MeV) in BGS Beta Gamma Service GmbH & Co, Saal am Donau – Germany.

Table I. The values of irradiated doses

Materials	Dosis [kGy]
PBT	165
PA 6.6 (30% GF)	99
PA 11	99
PA 12	99

C. Chemical soaking of tensile test specimens

Chemical soaking of the specimens was carried out by Robert Bosh, Ltd. company. Two chemicals used in automotive industry were chosen: methanol testing liquid labeled FAM B and blended diesel oil Biodiesel B30. Test conditions:

Time of soaking: 96 hours

Temperature of the chemicals: 70°C

Other chemicals were chosen:

- Engine oil Mogul®SAE 10 W 40
- Concentrated coolant based on ethylene glycol with organic corrosion inhibitors Sheron® Antifreeze G48
- Anti-freeze mixture Carlson®-30°C
- Brake fluid ABS® SAE J 1703 DOT4

Time of soaking: 168 hours

Temperature of the chemicals: room temperature

D. Methanol testing liquid FAM B

Methanol testing liquid FAM is applied for testing of polymeric materials and plastic components, which comes in intense contact with motor fuels, used in the automotive and petrochemical industries. This liquid is not currently any commercially available fuel and is suitable only for testing purposes. FAM testing liquid is divided into FAM A, FAM B and C types. The FAM B liquid composes mostly of FAM A liquid and methanol. The composition can be seen in Table II.

Table II. Content of testing chemical FAM B

FAM B			Content
➤ FAM A			84,5 %
•	pure toluene	50 %	
•	isooctane	30 %	
•	di-isobutylen	15 %	
•	ethanol reagent	5 %	
➤ methanol			15 %
➤ deionised water			0,5 %

E. Blended diesel oil Biodiesel B30

Biodiesel (its trade name is Naturdiesel) is an environmentally friendly fuel based on methyl esters FAME (unsaturated fatty acids of vegetable origin). It is produced by a refining process from any vegetable oil. Compared to conventional diesel fuel Biodiesel reduces emissions and is biodegradable. The main advantage is its production from renewable sources. Biodiesel is a stronger solvent than

conventional diesel, thus causing greater destruction and deposition in the fuel system.

The composition of blended diesel fuel can be seen in Table III.

F. Engine oil Mogul®SAE 10 W 40

It is an engine oil for lubrication of gasoline and diesel engines of passenger cars. Its use is possible at wide range of temperatures. Classification and specification: SAE 10W-40 • API SL/CF • VW 500.00/505.00 • MB 229.1

G. Concentrated coolant based on ethylene glycol with organic corrosion inhibitors Sheron® Antifreeze G48

This coolant based on ethylene glycol can be used all year round. A range of its application is wide as it can be used in passenger cars and trucks with aluminium alloys engines. It contains silicate-organic additives. The coolant meets the standard VW TL 774 C/G11.

H. Anti-freeze mixture Carlson®-30°C

This antifreeze is based on water-based ethanol and ethylene glycol. It contains surfactants to remove dirt.

I. Brake fluid ABS® SAE J 1703 DOT4

This is the classic brake fluid based on the basis of 2,2'-oxybisethanol and butylpolyglycol.

Table III. Content of testing chemical B30

B30	Content
➤ fossil diesel	69 %
➤ rapeseed oil methyl ester	31 %

J. Testing instruments

The following tests were carried out and equipment used:

Tensile test, according to standard CSN EN ISO 527-1, 527-2 was carried out on tensile machine ZWICK 1456. The test was carried out at the room and at the evaluated temperature (80°C). Test data was processed by Test Xpert Standard software and modulus (E [MPa]), tensile strength (σ [MPa]) were determined. (in case of PBT and PA 6.6)

Impact hammer test carried out on tensile machine ZWICK 5113, according to standard CSN EN ISO 2818 - Energy 2,87J. (in case of PBT, PA11, PA12)

III. PROBLEM SOLUTION

A. Result of polyamide 6.6 – tensile test

As you can see in the Figure 1, the value of E-modulus of PA6.6 which has not been soaked (at room temperature) is higher about 20% after irradiation. The value of E-modulus declines rapidly after chemical soaking in FAM B. In the case of irradiated test specimens the value of E-modulus is higher about 14% than non-irradiated samples. But this value is still lower than the results of E-modulus of specimens which has not been soaked.

E-modulus of test specimens soaked in B30 is about 15% lower than in case of non-soaked test specimens. In the case of irradiated test specimens the value of E-modulus is higher of about 8% than non-irradiated samples.

The similar results are in case of tensile strength (Figure 2). All results are higher after irradiation than non-irradiated, but in comparison with samples without soaking the value of tensile strength is still lower.

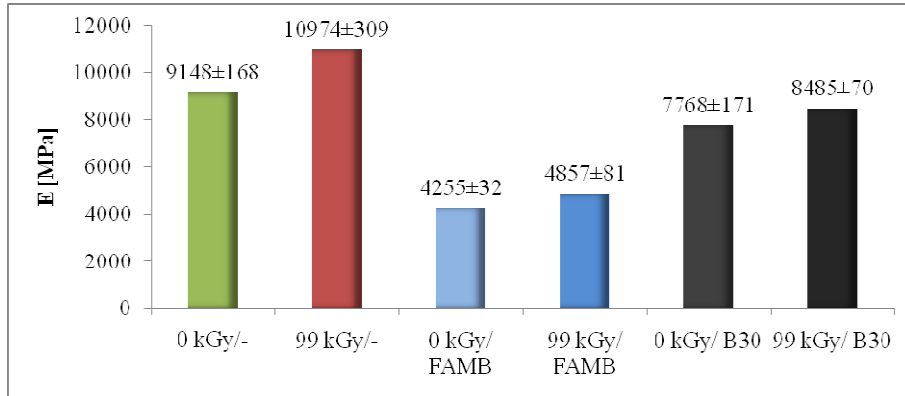


Fig. 1 Result of E-modulus of irradiated and non-irradiated PA6.6 GV30 at 23°C in dependence of chemical soaking

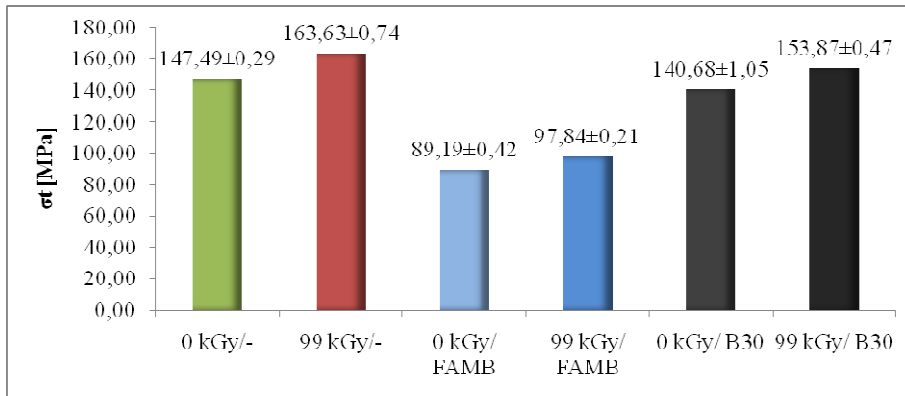


Fig. 2 Result of tensile strength of irradiated and non-irradiated PA6.6 GV30 at 23°C in dependence of chemical soaking

If we look at the evaluated temperature, the situation analogous is here. On the other hand, the results of test specimens soaked in B30 show higher value of E-modulus

than non-irradiated and non-soaked test specimens. The improvement is about 33% (Figure 3).

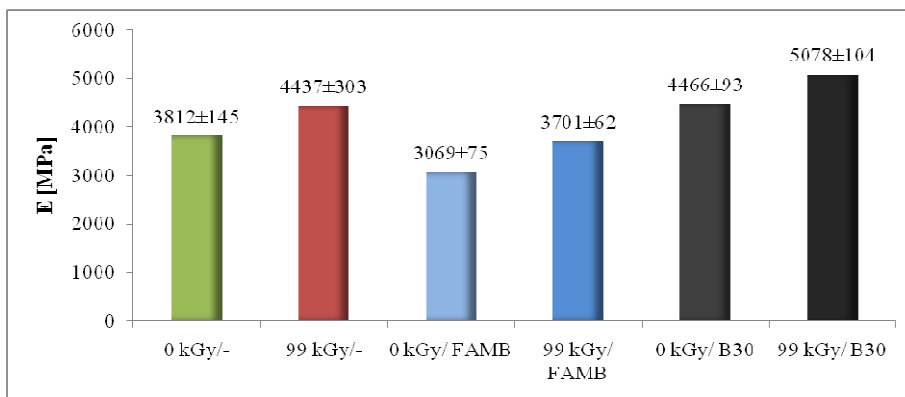


Fig. 3 Result of E-modulus of irradiated and non-irradiated PA6.6 GV30 at 80°C in dependence of chemical soaking

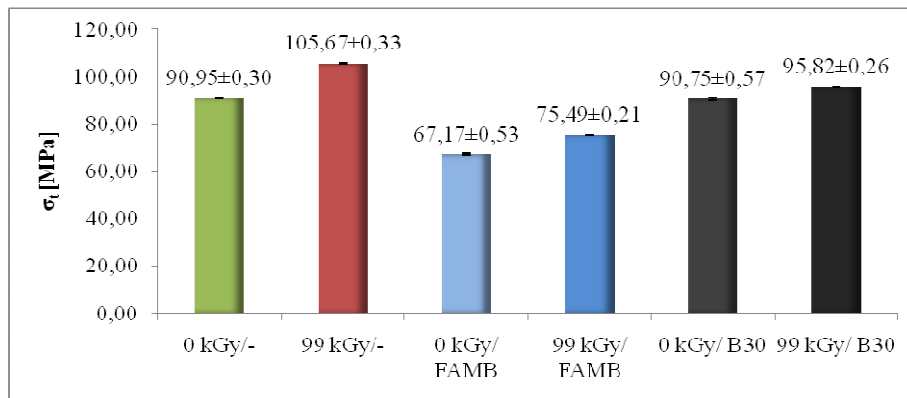


Fig. 4 Result of tensile strength of irradiated and non-irradiated PA6.6 GV30 at 80°C in dependence of chemical soaking

B. Result of PBT – tensile test

As you can see in the Figure 5, the value of E-modulus of non-soaked PBT (at room temperature) is higher about 55% after irradiation. After chemical soaking in FAM B the value of E-modulus declines rapidly. In the case of irradiated test specimens the value of E-modulus is higher of about 63% than non-irradiated samples. However, this value is still lower than

the results of E-modulus of specimens which has not been soaked.

E-modulus of irradiated test specimens soaked in B30 is higher of about 55% than in case of non soaked and non-irradiated test specimens.

Also the results of tensile strength of PBT show certain improvement (Figure 6).

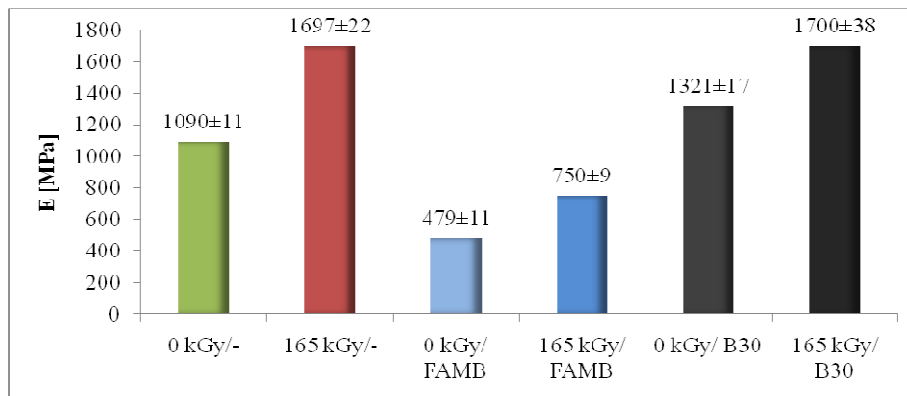


Fig. 5 Result of E-modulus of irradiated and non-irradiated PBT at 23°C in dependence of chemical soaking

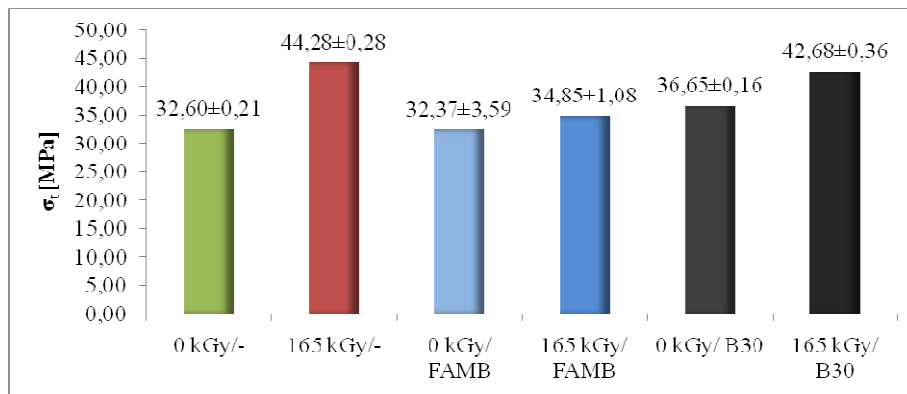


Fig. 6 Result of tensile strength of irradiated and non-irradiated PBT at 23°C in dependence of chemical soaking

If we look at the evaluated temperature, we got the best results here. E-modulus of irradiated test specimens soaked in B30 is higher of about 65% than in case of non-soaked and non-irradiated test specimens. (Figure 7).

Also the results of tensile strength of PBT show an improvement of about 33% - in case of test specimens irradiated and soaked in B30 in comparison with non-soaked and non-irradiated test specimens.(Figure 8).

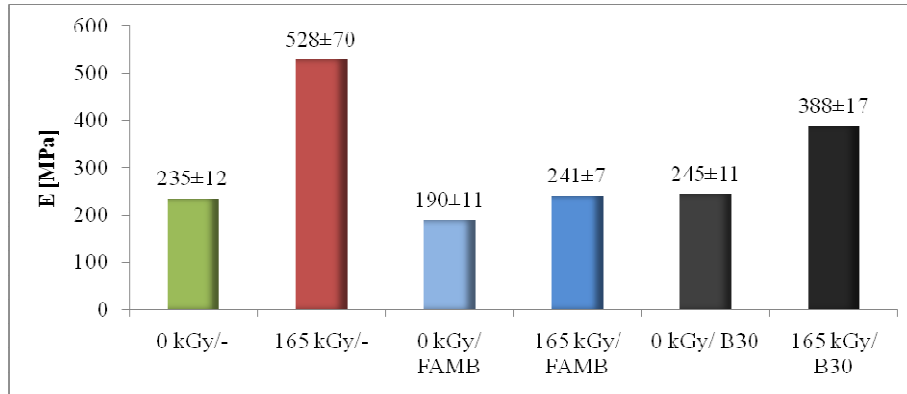


Fig. 7 Result of E-modulus of irradiated and non-irradiated PBT at 80°C in dependence of chemical soaking

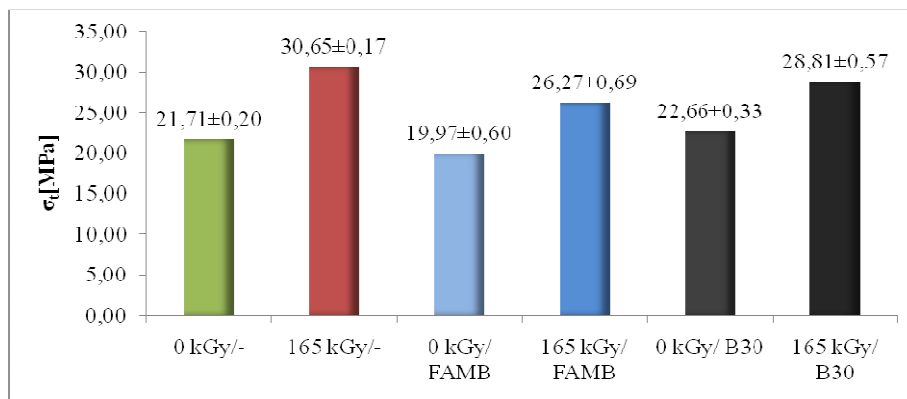


Fig. 8 Result of tensile strength of irradiated and non-irradiated PBT at 80°C in dependence of chemical soaking

If you look at the tables below, you can see the results of improvement of E-modulus and tensile strength (in the brackets) of each material after irradiation cross-linking in comparison with non-irradiated test specimens. If we look only at the materials which have been soaked in chemicals – the best improvement is in case of irradiated PBT in B30 at evaluated temperature (+58%).

T = 80°C	Unloaded	FAM B	Biodiesel B30
PA 6.6	+16 % (+16)	+20% (+12)	+14 % (+6)
PBT	+125 % (+41)	+27 % (+32)	+58 % (+27)

Table III. Results of improvement E-modulus and tensile strength (in bracket) after irradiation at room temperature

T = 23°C	Unloaded	FAM B	Biodiesel B30
PA 6.6	+20 % (+16)	+12 % (+10)	+9 % (+9)
PBT	56% (+36)	+57 % (+8)	+29 % (+16)

Table IV. Results of improvement E-modulus and tensile strength (in bracket) after irradiation at evaluated temperature

C. Result of PBT – impact hammer test

Impact hammer strength of PBT in dependence on chemical soaking did not change so much. Concentrated coolant based on ethylene glycol caused the swelling of the test specimens whereupon the impact hammer strength increased about 17% in case of non-irradiated test specimens. Test specimens soaked in biodiesel (B30) showed decreasing of impact hammer strength as you can see in the Fig. 9. Radiation cross-linking of PBT resulted in increase of impact hammer strength about 285% in comparison with non-irradiated non-soaked test

specimens. The results of impact hammer strength of test specimens soaked in engine fluid showed decrease. Lower value of swelling is in case of irradiated test specimens soaked in engine oil, where the decrease of impact hammer strength is about 12% in comparison non-soaked test specimens. The similar results are in case of test specimens

soaked in ethylene glycol, where the decrease is 16%. Because of swelling of test specimens in brake fluid the impact hammer strength increased about 8.5% in comparison with non-soaked irradiated test specimens.

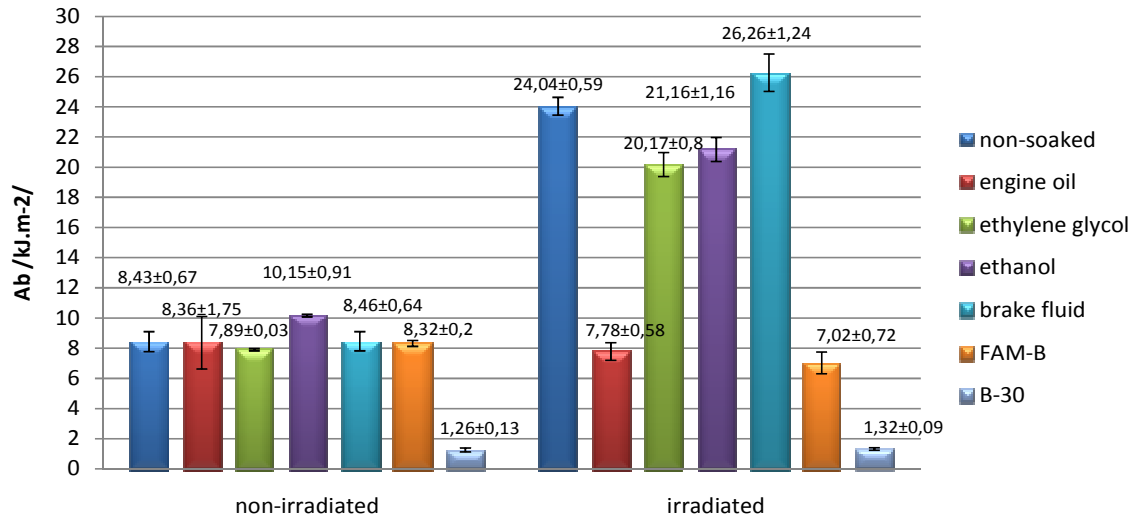


Fig. 9 Result of impact hammer strength of irradiated and non-irradiated PBT in dependence of chemical soaking

D.Result of PA11 – impact hammer test

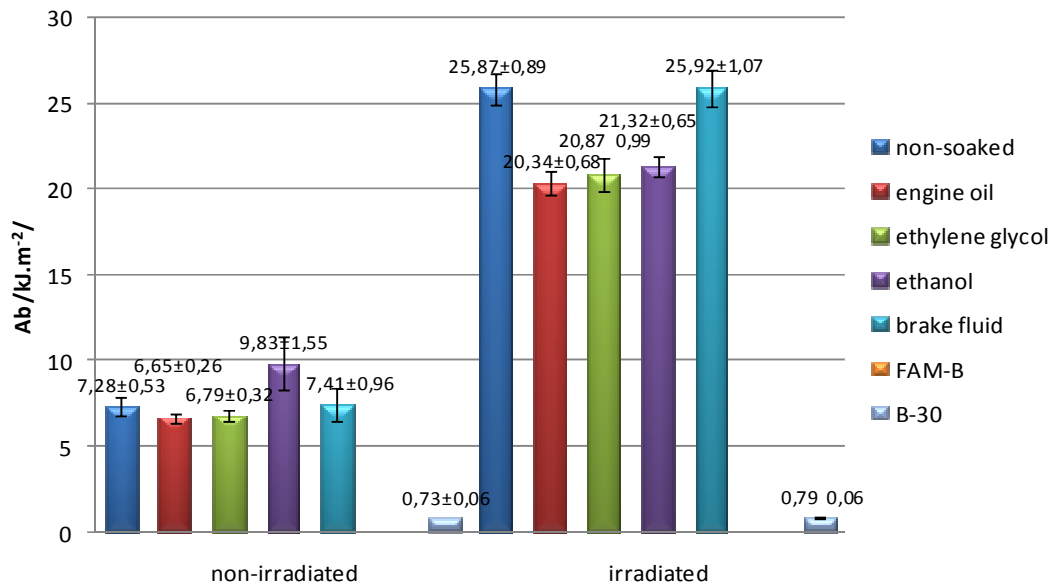


Fig. 10 Result of impact hammer strength of irradiated and non-irradiated PA11 in dependence of chemical soaking

In the Figure 10 we can see the improvement of impact hammer strength after irradiation. Test specimens soaked in anti-freeze mixture showed improvement in impact hammer strength about 35%. Opposite

to this it was unable to measure test specimens soaked in FAM B because of destruction of these test specimens. In case of test specimens irradiated and soaked in FAM B it was also unable to measure properties because of high impact

resistance. Test specimens soaked in B30 lost 90% of impact hammer strength in comparison with non-soaked test specimens.

With irradiation of test specimens we received the improvement of impact hammer strength about 355% in comparison with non-irradiated test specimens. But the

E. Result of PA12 – impact hammer test

The impact hammer strength of PA12 soaked in engine oil and ethylene glycol is on the same level in comparison with non-soaked test specimens. Opposite to this the test specimens soaked in ethanol fluid showed improvement of impact hammer strength (98%) because of swelling. The similar result we got in case of FAM B, where the improvement was 24%. The other testing fluids brought down the impact hammer strength – bare fluid about 20%, B30 about 84%.

Irradiation of PA12 caused improvement of impact hammer strength in comparison with non-irradiated test specimens.

influence of ethanol, ethylene glycol and engine oil cause deterioration of impact hammer strength about 20%. In case of brake fluid the properties did not change in comparison with non-soaked test specimens. Irradiated test specimens were also susceptible to B30 testing fluid.

Irradiation of test specimens improved stability against brake fluid as well. Deterioration in properties is in case of material soaked in engine oil (-11%), FAM B (-53%) and biodiesel B30 (-96%). Concerning the engine oil, its characteristic was lowered but still, in comparison to non-irradiated samples loaded in this liquid, its value was still higher of about 100%.

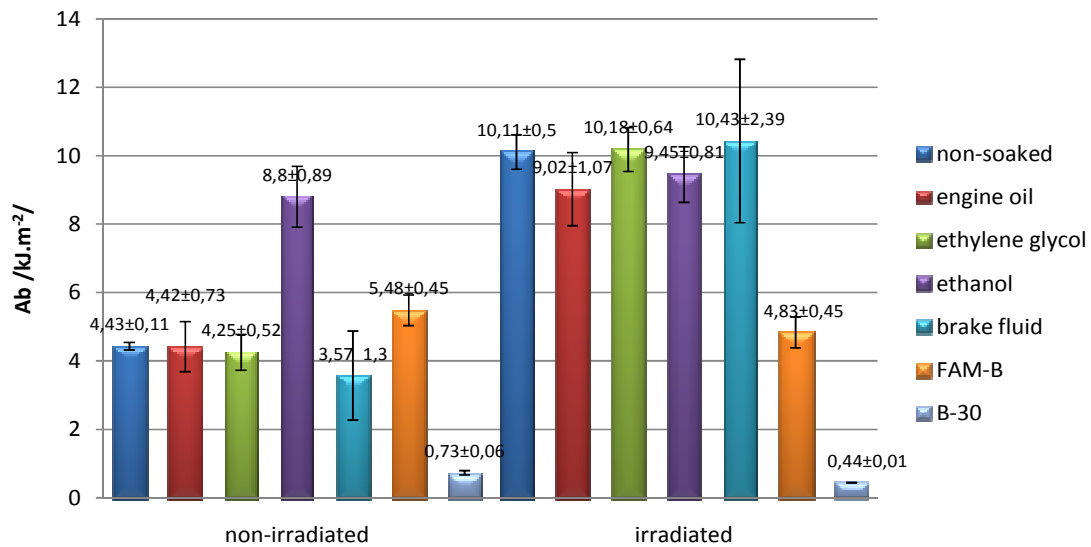


Fig. 11 Result of impact hammer strength of irradiated and non-irradiated PA12 in dependence of chemical soaking

IV. CONCLUSION

In all cases the exposure resulted in the highest increase of the mechanical properties of PBT, which resisted to the tested chemicals.

Concerning the increase of resistance to chemicals, the type of used chemicals, temperature and demands of the application in which the product is used play an important role.

Based on the results, radiation cross-linking can be recommended. However, it is necessary to always carry out specific tests in real conditions.

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REFERENCES

- [1] M. Stanek, M. Manas, D. Manas, "Mold Cavity Roughness vs. Flow of Polymer," *Novel Trends in Rheology III*, 2009, American Institute of Physics, New York, USA, p.75-85, ISBN 978-0-7354-0689-6
- [2] D. Manas, M. Stanek, M. Manas, V. Pata, J. Javorik, "Influence of Mechanical Properties on Wear of Heavily Stressed Rubber Parts," *KGK – Kautschuk Gummi Kunststoffe*, Hüthing GmbH, 62. Jahrgang, Mai 2009, p.240-245, ISSN 0948-3276
- [3] Vratislav Ducháček, *Polymery - výroba, vlastnosti, zpracování, použití*, Praha, VŠCHT, 2006
- [4] Vishu Shah, editor: *Plastics testing and failure analysis*, USA, Library of Congress Cataloging-in-Publication Data, 2007
- [5] Myer Kutz, editor: *Handbook of materials selection*, USA, Library of Congress Cataloging-in-Publication Data, 2001
- [6] Dr. Gi-Dae Choi, *Engineering plastics handbook*, Daejeon, Korea, 2006
- [7] Josef Mleziva, *Polymery – výroba, struktura, vlastnosti a použití*, Praha, Sobotáles, 1993
- [8] Holik, Z., Danek, M., Abraham, J. In Vliv množství síťovacího činidla na vlastnosti ozářeného polyamidu: *PLASTKO 2010*, 13-14. April 2010. Zlín, Czech Republic, 2010, ISBN 978-80-7318-909-9.
- [9] Holik, Z.; Kyas, K.; Krupal, M.; Cerny, J. & Danek, M. (2010). Improvement of Polypropylene Properties, *Annals of DAAAM for 2010 & Proceedings of the 21st International DAAAM Symposium*, 20-23rd October 2010, Zadar, Croatia, ISSN 1726-9679, ISBN 978-3-901509-73-5, Katalinic, B. (Ed.), pp. 1191-1192, Published by DAAAM International Vienna, Vienna
- [10] Sanda, S., Manas, M., Manas, D., Stanek, M., Knot, J.: Comparison of injection mold cooling systems, 2011, *Chemicke Listy 105 (15 SPEC. ISSUE)*, pp. s381-s383,
- [11] Manas, M., Stanek, M., Manas, D., Sanda, S., Holik, Z., Danek, M.: Temperature stability of irradiated polyme, 2011, *Chemicke Listy 105 (15 SPEC. ISSUE)*, pp. s254-s256
- [12] Manas, D., Manas, M., Stanek, M., Sanda, S., Cerny, J., Ovsik, M., Pata, V.: Wear of off - road tires evaluation, 2011, *Chemicke Listy 105 (15 SPEC. ISSUE)*, pp. S264-S266
- [13] Javorik, J., Dvorak, Z.: The testing of hyperelastic properties of the rubber materials, 2011, *Chemicke Listy 105 (15 SPEC. ISSUE)*, pp. s273-s274)
- [14] Sanda, S., Manas, M., Manas, D., Stanek, M., Senkerik, V.: Gate effect on quality of injected part, 2011, *Chemicke Listy 105 (15 SPEC. ISSUE)*, pp. s301-s303
- [15] Kyas, K., Staněk, M., Mañas, M., Mañas, D., Křůmal, M.: Simulation of rubber injection molding process, 2011, *Chemicke Listy 105 (15 SPEC. ISSUE)*, pp. s354-s356
- [16] Stanek, M., Manas, M., Manas, D., Pata, V., Sanda, S., Senkerik, V., Skrobak, A.: How the filler influence the fluidity of polymer, 2011, *Chemicke Listy 105 (15 SPEC. ISSUE)*, pp. s303-s305
- [17] Woods, R. J.: *Applied radiation chemistry: radiation processing*, 1994, ISBN 0-471-54452-3.
- [18] Drobny, J.G.: *Radiation Technology for Polymers*, Boca Raton: CRC Press, 2003, , ISBN 1-58716-108-7.
- [19] M. Stanek, D. Manas, M. Manas, J. Javorik, "Simulation of Injection Molding Process," 13 th WSEAS, 2011, WSEAS Press, p.231-234, ISBN 978-1-61804-004-6
- [20] M. Stanek, D. Manas, M. Manas, O. Suba, "Optimization of Injection Molding Process by MPX," 13 th WSEAS, 2011, WSEAS Press, p.212-216, ISBN 978-1-61804-004-6
- [21] M. Pastorek, R. Cermak, J. Navratilova, M. Obadal, The effect of crosslinking and thermal ageing on the morphology of ethylene-vinyltrimethoxysilne copolymer, 3rd WSEAS International Conference on ENGINEERING MECHANICS, STRUCTURES, ENGINEERING GEOLOGY (EMESEG '10), Corfu Island, Greece, 2010, WSEAS Press, p.271-274, ISBN 978-960-474-203-5
- [22] Vaskova, H., Raman spectroscopy as an innovative method for material identification. In: 13th WSEAS International Conference on AUTOMATIC CONTROL, MODELLING&SIMULATION (ACMOS'11), Lanzarote, Canary Island, Spain, 2011, p. 292 - 295. Published by WSEAS Press, ISBN: 978-1-61804-004-6.
- [23] Vaskova, H., Kresalek, V., Raman spectroscopy of epoxy resin crosslinking. In: 13th WSEAS International Conference on AUTOMATIC CONTROL, MODELLING&SIMULATION (ACMOS'11), Lanzarote, Canary Island, Spain, 2011, p.357 - 361. Published by WSEAS Press, ISBN: 978-1-61804-004-6.
- [24] Vaskova, H. Raman spectroscopy: a modern technique for material properties identification. In: Proceedings of the 21st International DAAAM Symposium 2010 Zadar, Croatia. Vienna: DAAAM International Vienna, 2010, p. 1321-1322. ISBN 978-3-901509-73-5.