

RAPORTY IChTJ. SERIA B nr 3/2020

**RECENT DEVELOPMENTS
IN RADIATION PROCESSING
OF POLYMERS**

Marta Walo, Magdalena Rzepna

Warszawa 2020

AUTHORS

Marta Walo, Magdalena Rzepna
Institute of Nuclear Chemistry and Technology



This project has received funding from the European Union's research and innovation programme Horizon 2020 under grant agreement No 730871.

This work was supported by the Polish Ministry of Science and Higher Education – project 3697/H2020/2017/2 “Accelerator Research and Innovation for European Science and Society” (ARIES).

© Copyright by the Institute of Nuclear Chemistry and Technology, Warszawa 2020

EDITORIAL OFFICE

Institute of Nuclear Chemistry and Technology
Dorodna 16, 03-195 Warszawa, Poland
phone: 22 811 06 56, fax: 22 811 15 32, e-mail: sekdyrn@ichtj.waw.pl
www.ichtj.waw.pl

Paper is published in the form as received from the Authors

Recent developments in radiation processing of polymers

Radiation technologies used on industrial scale has been continuously developing for over 60 years. Ionizing radiation (gamma, X-ray and electron beam – EB) is used for modifying the properties of materials (crosslinking, degradation, radiation-induced grafting), sterilization of medical devices and tissue grafts and for environmental protection. By applying radiation technologies new specific properties of materials can be introduced by radiation-induced grafting of different types of monomers or modification of polymer physicochemical properties.

This report presents two examples of polymer modification by EB irradiation. The first part of the work involves surface modification of selected polymers by radiation-induced grafting whereas the second part includes radiation-induced modification of degradable copolymers based on aliphatic polyester.

Najnowsze osiągnięcia w radiacyjnej obróbce polimerów

Technologie radiacyjne stosowane na skalę przemysłową są rozwijane od ponad 60 lat. Promieniowanie jonizujące (gamma, rentgenowskie i elektronowe) wykorzystywane jest do modyfikowania właściwości materiałów (sieciowanie, degradacja, szczepienie indukowane radiacyjnie), sterylizacji sprzętu medycznego i przeszczepów tkankowych oraz w ochronie środowiska. Stosując technologie radiacyjne można zmieniać lub nadawać nowe, specyficzne właściwości materiałom poprzez szczepienie radiacyjne różnych typów monomerów lub modyfikację fizykochemicznych właściwości polimeru.

W raporcie przedstawiono dwa przykłady modyfikacji polimerów za pomocą wiązki wysokoenergetycznych elektronów. Pierwszy przykład dotyczy modyfikacji powierzchni wybranych polimerów metodą szczepienia radiacyjnego, natomiast drugi – radiacyjnej modyfikacji degradowanych kopolimerów na bazie poliestru alifatycznego.

CONTENTS

| | |
|--|-----------|
| 1. INTRODUCTION | 7 |
| 2. OBJECTIVES | 8 |
| 3. RESULTS | 8 |
| 3.1. Radiation-induced grafting onto polymers used in biomedical applications | 8 |
| 3.2. Radiation-induced modification of degradable copolymers based on aliphatic polyester | 13 |
| 4. CONCLUSIONS | 17 |
| 5. LITERATURE | 18 |

1. INTRODUCTION

Nowadays radiation is widely used in the polymer processing to improve properties of products manufactured on an industrial scale [1, 2]. High-current electron beam (EB) accelerators provide added value to many products made of polymer such as heat shrinkable tubes and types, electrical wires and cables, packaging films, foams, radial tire components, positive temperature coefficient heaters, coating and adhesives, hydrogels [1]. Additionally, the EB units are used for sterilization of medical devices and graft tissues, food irradiation, polytetrafluoroethylene and cellulose degradation, radiation grafting of membranes, water treatment, paper preservation, purification of exhaust gases from SO₂ and NO_x, seed and soil disinfection, *etc.* [3-5].

Ionizing radiation initiates the formation of very reactive species in polymers (free neutral radicals, cationic and anionic ions, excited molecules) leading the modification of physico-chemical changes of the irradiated materials.

Typically, the following processes are observed [1]:

- crosslinking, when the polymer macroradicals react with each other to form a three-dimensional network,
- chain scission leading to a reduction in the molecular weight of macromolecules,
- oxidation, when radiation-induced active centers react with oxygen molecules to form peroxy radicals (oxidation and chain scission often occurs simultaneously),
- long-chain branching – polymer chains are joined but a three-dimensional network is not yet formed,
- grafting – a new monomer is added onto the basic polymer chain.

Radiation processing of polymers is inherently related to the conditions of exposure to ionizing radiation (atmosphere, temperature, dose rate, type of radiation) [1]. One of the important factors is the availability of oxygen in radiation-induced radical processes. The use of an anaerobic atmosphere prevents reactions of alkyl radicals with oxygen and the formation of peroxy radicals, which in consecutive reactions convert to the stable oxidation products. Low oxygen permeability contributes to the resistance of the material to ionizing radiation degradation. Sterilization or modification of polymers in an inert gas atmosphere prevents oxidation processes, which mainly lead to breakage of macromolecular chains and deterioration of the functional properties of these materials. Rapid, one-time irradiation with a high dose gives an effect similar to exposure to an inert gas atmosphere, as the diffusion of oxygen into the interior of the product is not possible in a short time. In this case, in the outer layers the oxygen penetration favors oxidative degradation while crosslinking occurs in the bulk. Therefore, the use of the high electron beam generated by the accelerator in this case is more advantageous than using gamma sources.

Temperatures of irradiation may promote crosslinking reactions when polymers are irradiated in elevated temperatures. However, for some polymers decreasing the temperature of the product exposed to ionizing radiation reduces undesired processes resulting from radical reactions. Therefore, in some justified cases, *e.g.* radiation sterilization, irradiation can be carried out in dry ice.

In these studies a high energy electron accelerator was used for modification of selected materials dedicated to biomedical applications. The use of electron accelerator Elektronika 10/10 installed in the Institute of Nuclear Chemistry and Technology (INCT) relies on the transport of samples in a conveyor under a scanned electron beam. In such a system, the radiation treatment can refer to polymer materials placed in conveyor of certain sizes taking into account the surface density related to the electron beam energy. The width of the scanned electron beam creates an irradiation zone in the direction perpendicular to the direction of transport. In this arrangement, the dose distribution in the irradiated product is one of the most important parameters. Loading of irradiated films or other objects is determined by the depth of penetration of accelerated electrons. Therefore, the dose homogeneity for the selected electron beam energy and product geometry require careful evaluation. Usually such a solution is applied in R&D studies.

Radiation-induced modification of polymers requires exposure to specific, predetermined absorbed doses of ionizing radiation, usually to initiate homogeneous crosslinking between macromolecules. On the other hand, irradiation should not reduce functionality of the product due to degradation. Therefore, dosimetry is necessary to verify the values of the delivered energy and keep it in the established limit. This procedure allows for attaining desired radiation-induced macroscopic effects in irradiated materials [2]. To achieve this purpose process control and validation procedures are implemented in radiation processing.

2. OBJECTIVES

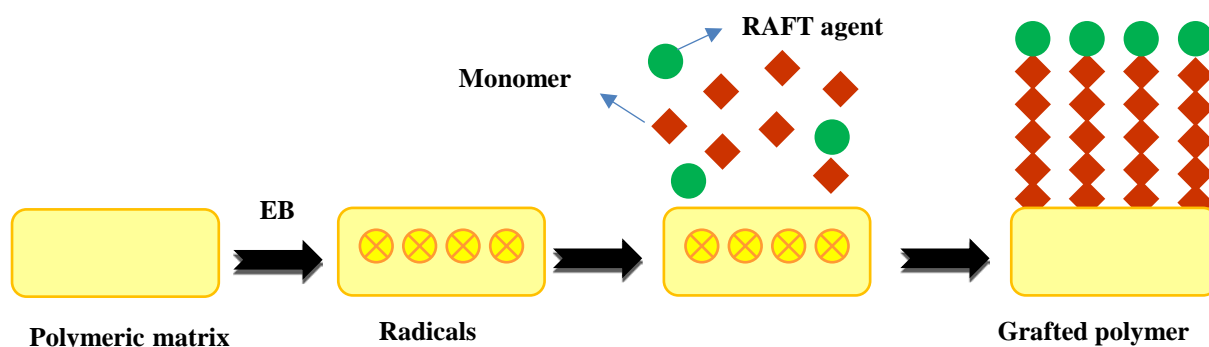
This report presents two examples of polymer modification by EB irradiation. The first part of the work involves surface modification of polymers by radiation-induced grafting whereas the second part includes radiation-induced modification of degradable copolymers based on aliphatic polyester.

3. RESULTS

3.1. RADIATION-INDUCED GRAFTING ONTO POLYMERS USED IN BIOMEDICAL APPLICATIONS

Radiation grafting is a well-known method used for surface modification of the wide range of materials dedicated to health-care applications including production of scaffolds in tissue engineering and to improve the surface properties of biomaterials. The presence of appropriate functional groups, surface hydrophobicity/hydrophilicity and the polymer surface topography are introduced into biomaterials increasing the possibilities of their use [6, 7].

In conventional grafting, the polydispersity (PDI) of grafted chains is out of control and in some cases, the surface homogeneity is insufficient for selected applications. As an alternative, the RAFT technique can be used which enables to introduce grafted layer of the assumed length of chains and changed in a very narrow range [8, 9]. Thanks to that, this method provides the synthesis of new materials with good surface hydrophilicity and homogeneity.



Scheme 1. Pre-irradiation grafting using RAFT-mediated polymerization initiated by EB radiation.

Surface modification onto three selected polymers, widely used in biomedical applications (as catheters, implants, bags, tubes), was carried out using conventional grafting and RAFT-mediated grafting (reversible addition – fragmentation chain transfer polymerization). The modified matrices were low-density polyethylene (LDPE), polypropylene (PP) and polystyrene (PS).

The modification of polymer surfaces was achieved by EB irradiation of polymers as shown in Scheme 1.

This technique initiated by ionizing radiation allows easy control the parameters of grafting (by the changes in the radiation exposure and reaction conditions, *e.g.* dose, dose rate, atmosphere, temperature), modify any type of synthetic and natural polymers in the various forms, carry out the reaction in non-demanding condition in a wide range of temperatures and obtain product with high degree of purity, free from initiating agent or catalyst [10, 11].

The monomer grafted on LPDE, PP and PS surfaces was acrylic acid (AAc) and RAFT agent was 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT) – Fig. 1.

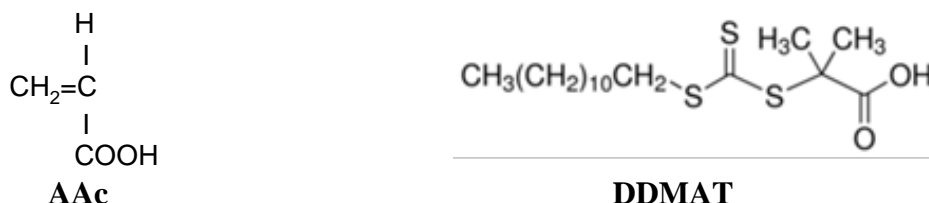


Fig. 1. Chemical formula of acrylic acid (AAc) and 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT).

In this study, reference matrices and matrices after grafting were characterized by attenuated total reflectance – Fourier-transform infrared spectroscopy (ATR-FTIR), scanning electron microscopy (SEM) and contact angle (CA) measurement. The molecular weight distribution of the graft polymer was performed using gel permeation chromatography (GPC). The radical products in PE, PP and PS as well as in grafted matrices were examined by means of electron paramagnetic resonance (EPR) spectroscopy.

The process of radiation-induced grafting

The samples were purged with an inert gas (nitrogen) for 15 min and irradiated at dry ice temperature in the Elektronika 10/10 accelerator to a dose of 112 kGy. Then, the samples were immersed in the monomer solution (25% (v/v) AAc in acetone/water) and kept at 40°C for 24 h.

The RAFT agent concentration was adjusted to provide grafted PAAc chains with assumed molecular weight of about 50 000 g/mol, at complete conversion of the monomer, *i.e.* [AAc]:[DDMAT] = 669:1, respectively, for 25% (v/v) AAc containing solution.

The theoretical number – average molecular weight, M_n , was calculated according to the following equation [12]:

$$M_n = M_{\text{RAFT}} + [(n \times M) / n_{\text{RAFT}}] \times k \quad (1)$$

where: M_{RAFT} – molecular weight of the RAFT agent, n – number of moles of the monomer initially present in the system, n_{RAFT} – number of moles of RAFT agent, M – molecular weight of the monomer, k – conversion.

After grafting, the samples were washed in an ultrasonic bath in a mixture of acetone/de-ionized water. The samples were dried at 40°C to constant weight. The degree of grafting (DG, wt%) was calculated using the following equation:

$$\text{DG} = (W - W_0) / W_0 \times 100\% \quad (2)$$

where W and W_0 are the weights of the grafted and pristine polymers, respectively.

Methods

ATR-FTIR spectroscopy

An Equinox 55 Fourier spectrometer (Bruker) was used to record the infrared spectra. The tests were performed using ATR reflection technique on ZnSe crystal. Measurements were carried out in the wavenumber range of 650-4000 cm^{-1} .

Electron paramagnetic resonance spectroscopy

Radiation-generated paramagnetic products were examined by EPR spectroscopy using EMXplus EPR Bruker cw X-band spectrometer. After irradiation in GC5000 to a dose of 4 kGy, tubes were placed without annealing in a resonant cavity and spectra were measured starting from 100 K with step of 50 K to room temperature.

Gel permeation chromatography

GPC measurements of PAAc precipitated from the grafting solution were performed at 45°C in DMF with 5 mmol/L lithium bromide (LiBr) using a nominal flow rate of 1 mL/min. A multiangle light scattering detector ($\lambda = 658$ nm, DAWN HELEOS, Wyatt Technology), refractive index detector (Dn-2010 RI, WGE Dr. Bures), column system (PL gel guard, PL gel MIXED-C x 2, PSS GRAM 100 Å) were used. An isocratic pump as the solvent delivery system was applied. The results were evaluated using ASTRA 5.3.4.10 software from Wyatt Technology and WinGPC Unity software.

Contact angle measurements

Measurements were carried out at 25°C with the use of the Krüss K100C apparatus. The reported results of the contact angle measurements are the arithmetic mean of 5 measurements.

Scanning electron microscopy

SEM images of the samples were characterized by scanning electron microscopy (Zeiss Ultra Plus). The samples in the form of a disk with a diameter of 5.0 mm and thickness of 0.5 mm were fixed with conductive glue and coated with a thin layer of carbon. The measurements were performed at an acceleration voltage of 2 kV at a magnification of $\times 500$.

Results

The first stage of research was focused on optimizing the radiation-induced grafting process using the conventional method, then an experiment with the RAFT was carried out under the same conditions. Results of the degree of grafting are collected in Table 1.

Table 1. The results of the degree of grafting by the conventional and RAFT method.

| Grafting method | Sample | DG [%] |
|------------------------|-------------------|--------|
| Conventional | PE- <i>g</i> -AAc | 16.8 |
| | PP- <i>g</i> -AAc | 12.7 |
| | PS- <i>g</i> -AAc | 4.1 |
| RAFT-mediated grafting | PE- <i>g</i> -AAc | 11.3 |
| | PP- <i>g</i> -AAc | 8.1 |
| | PS- <i>g</i> -AAc | 3 |

The obtained data clearly shows that DG depends on the type of polymer matrix and the ability to form radicals under the influence of ionizing radiation. The changes are in the following order PE > PP > PS.

For such selected process parameters, radiation grafting experiments with the RAFT agent were performed for average number molecular weights of the grafted chains: $M_n = 50\,000$ g/mol calculated according to the equation (1).

The efficiency of the grafting process by RAFT technique is lower than for conventional method. For PS-*g*-AAc, DG was comparable for both methods.

In the next stage of experiments, the molecular weight and polydispersity of grafted polymers were carried out using GPC. Estimation of the length of the grafted chains was carried out by GPC analysis of the polymer separated from the post-reaction solution, since in RAFT polymerization it is assumed that the polymer chains in the solution are in dynamic equilibrium with the chains grafted on the polymer surface [12].

GPC analysis showed that the EB-initiated RAFT polymerization process was controlled, but only for acrylic acid grafting onto PE matrix. The polydispersity (PDI) of the grafted chains was 1.27, while for the PP-*g*-AAc – 1.74 (Table 2).

The three polymer matrices selected for testing have different physicochemical properties and radiation stability. On the basis of our previous EPR spectroscopy studies, it was confirmed that the relative concentration of radicals after irradiation increased in the following order PE > PP > PS [13]. The previously discussed results of the efficiency of the radiation

Table 2. GPC results of RAFT-mediated grafting.

| Sample | DG [%] | M_n | M_w | PDI |
|-------------------|--------|--------|--------|------|
| PE- <i>g</i> -AAc | 11.3 | 48 650 | 61 786 | 1.27 |
| PP- <i>g</i> -AAc | 8.1 | 46 822 | 81 470 | 1.74 |

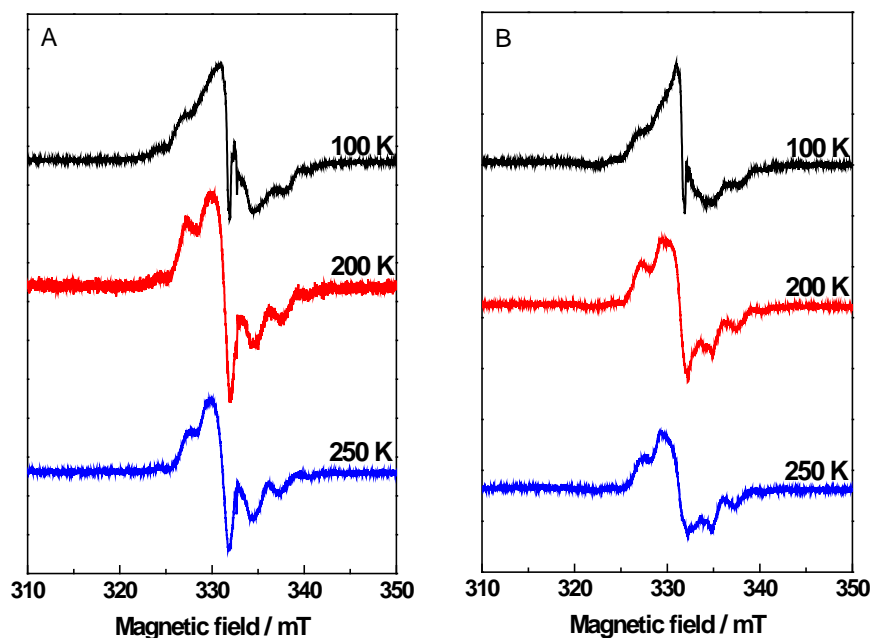


Fig. 2. EPR spectra recorded after irradiation with a dose of 4 kGy in a GC5000 source: (A) PE and (B) PE-*g*-PAAc (DG = 11.3%).

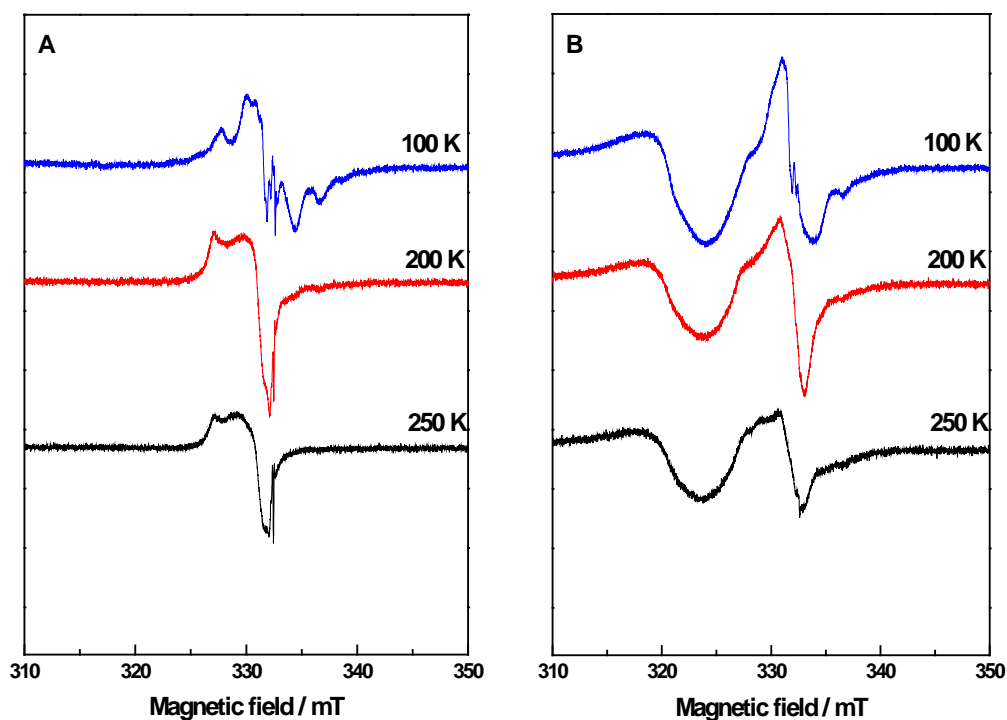


Fig. 3. EPR spectra recorded after irradiation with a dose of 4 kGy in a GC5000: (A) PP and (B) PP-*g*-PAAc (DG = 8.1%).

grafting process collected in Table 1 indicate that there is a close relationship between the concentration of radicals in the polymer and the efficiency of the grafting process.

From the analysis of the EPR spectra presented in Fig. 2A, it can be seen that the signals of alkyl radicals are visible before grafting in PE. Similar signals occur for the sample after grafting PE-*g*-AAc (DG = 11.3%) – Fig. 2B, however, the line multiplet is clearly broadened compared to the previous sample, and the entire signal is slightly distorted. This may indicate the overlapping of the spectrum of the grafted layer on the signal of the substrate.

In the case of the polypropylene matrix before grafting (Fig. 3A), the signal recorded at 100 K has the character of a multiplet which is likely derived from a radical center located on the carbon chain. At higher temperatures (> 200 K), a characteristic signal of the peroxy radical appears. After grafting, the multiplet is almost invisible already at 100 K; the central signal in the shape of an irregular singlet remains. At higher temperatures, the peroxy radical signal is strongly distorted, possibly due to an interaction with the grafted surface layer of PP-*g*-AAc (Fig. 3B).

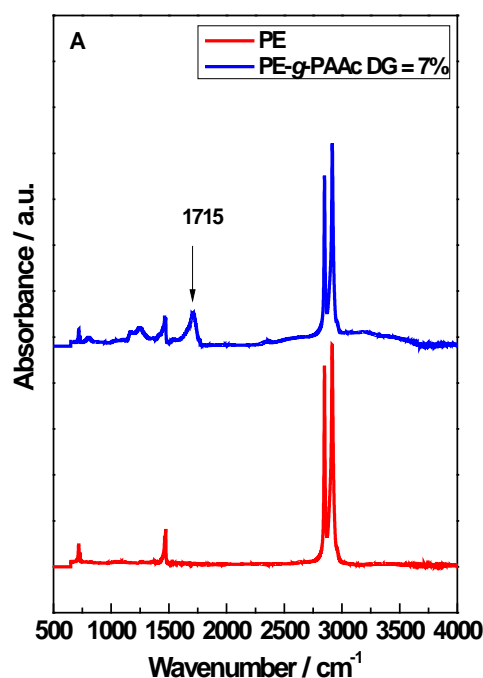


Fig. 4. ATR-FTIR spectra: (A) PE-*g*-PPAc (DG = 11.3%).

The analysis of the ATR-FTIR spectra allowed to confirm the radiation grafting by RAFT method. Based on the comparative analysis of ATR-FTIR spectra, it has been shown that as a result of radiation grafting, changes occur on the grafted surfaces, which is manifested by the presence of a band at 1715 cm^{-1} , characteristic for stretching vibrations of the C=O groups in PAA (Fig. 4).

Table 3. Contact angle measurements before and after modification by RAFT-mediated grafting.

| Sample | DG [%] | CA [deg] |
|-------------------|--------|----------|
| PE | - | 96 |
| PP | - | 102 |
| PS | - | 90 |
| PE- <i>g</i> -AAc | 11.3 | 86 |
| PP- <i>g</i> -AAc | 8.1 | 96 |
| PS- <i>g</i> -AAc | 3 | 90 |

Contact angle is important macroscopic parameter characterizing surface wettability. PE, PP and PS are hydrophobic polymers and therefore high values of average dynamic contact angles *vs* water were found for all samples (Table 3). CA for the modified samples decreased by a few degrees (5-10 deg) compared to the reference samples. More hydrophilic surfaces were obtained after radiation-induced grafting.

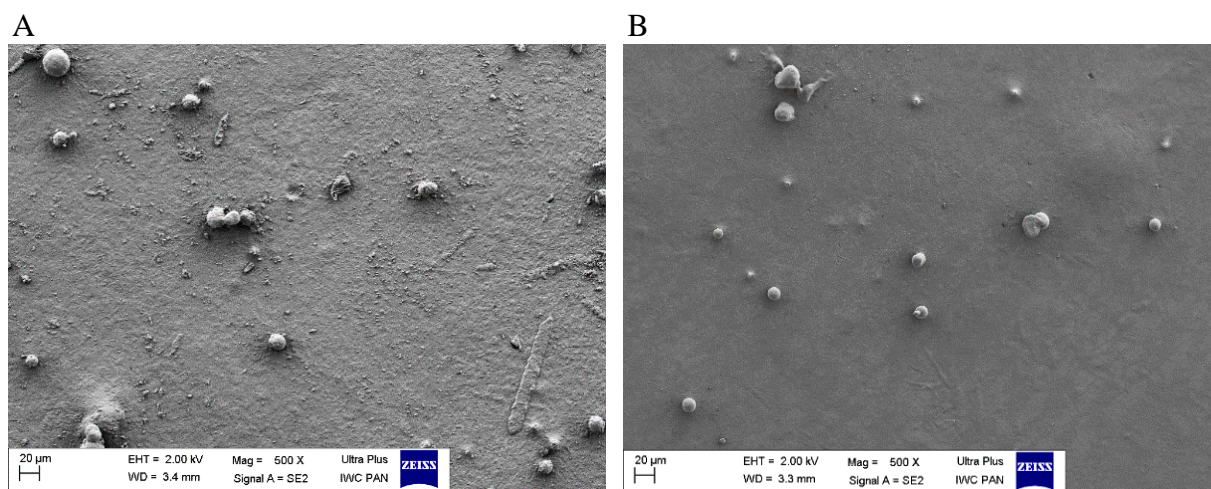


Fig. 5. SEM images of (A) PE and (B) PE-g-AAc (DG = 11.3%).

Figure 5 presents SEM images for PE and PE-g-AAc (DG = 11.3%) modified by RAFT method. A smooth surface (Fig. 5B) after modification was obtained confirming the presence of the PAAc grafted layer.

3.2. RADIATION-INDUCED MODIFICATION OF DEGRADABLE COPOLYMERS BASED ON ALIPHATIC POLYESTER

The market for degradable polymers has expanded significantly in recent years. Such materials, made from synthetic or natural raw materials, can solve problems related to waste disposal. They are widely used in medicine and biomedical engineering, packaging industry, as disposable products, *etc.*

An important group of biodegradable polymers is made on the basis of aliphatic polyesters. Their properties can be improved by incorporation of other compatible segments or dispersed additives, such as fillers, fibres or nanoparticles. The other promising method is radiation-induced modification, which additionally might ensure sterility of final products.

We selected aliphatic polycarbonate as a segment modifying polylactide (PLA), one of the most commonly used biodegradable polyesters.

The subject of the research were polylactide and poly(trimethylene carbonate) (PTMC) homopolymers and their statistical copolymers with a weight ratio of 30:70 and 70:30. Both copolymers and PTMC were synthesized at the Center for Polymer and Carbon Materials in Zabrze, Poland.

Methods

Several methods were used to follow radiation-induced changes, namely electron paramagnetic resonance spectroscopy, gel permeation chromatography and mechanical testing.

Electron paramagnetic resonance

The irradiated samples were placed in suprasil EPR tubes. The EMXplus EPR Bruker cw X-band spectrometer operating at 100 kHz field modulation and an ER 4131VT cryostat were used to measure spectra at various microwave power (0.1 mW and 10 mW) from 100 K every 30 deg to complete radicals decay. The following parameters were used: modulation amplitude – 0.1 mT, time constant – 1.28 ms and conversion time – 10 ms. For the analysis and simulation of spectra, WinEPR and Simfonia Bruker software were used, respectively.

Gel permeation chromatography

The molecular weight and the distribution were determined by gel permeation chromatography on a Viscotek system comprising GPCmax and TDA 305 (triple detection array (TDA): RI, IV, LS) equipped with DVB Jordi gel column(s) (10^2 - 10^7 , linear, mixed bed) in DCM as an eluent at 30°C at a flow rate of 1.0 mL/min.

Mechanical testing

Mechanical tests (determination of tensile strength, elongation at break and Young modulus) were carried out using the Instron testing machine, type 5565, at ambient temperature. The ramp velocity was 50 mm/min. The appropriate parameters were calculated on the basis of 5 measurements.

Results

The EPR spectra of PLA irradiated with gamma rays measured at 100 K and 280 K at different microwave power values are presented in Fig. 6A. Signal deconvolution results in the separation of four components with characteristic parameters:

(I) $-\dot{\text{C}}\text{H}-$ the product of methyl group release with an average hyperfine splitting (hfs) of about $A(H_\alpha) = 2.5$ mT and $g = 2.0034$.

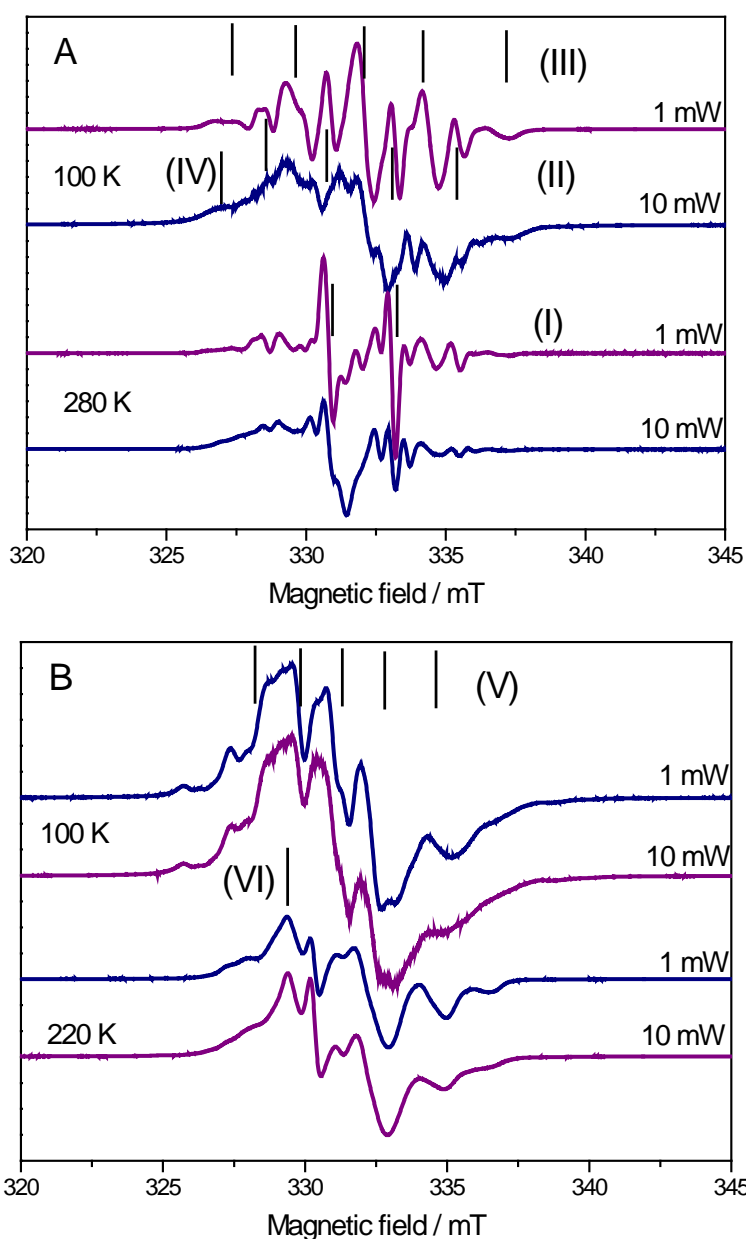


Fig. 6. EPR spectra of gamma-irradiated (A) PLA and (B) PTMC to a dose of 10 kGy at 77 K.

(II) $\cdot\text{C}(\text{CH}_3)\text{-}$ formed by the abstraction of a hydrogen atom from the backbone, showing a hfs of about $A(3\text{H}_\beta) = 2.22$ mT and $g = 2.0037$.

(III) $\cdot\text{CH}(\text{CH}_3)\text{-C}(\text{O})\text{-O}\cdot$ radical formed by chain cleavage showing $A(\text{H}_{\alpha x}) = 1.7$ mT, $A(\text{H}_{\alpha y}) = 1.2$ mT, $A(\text{H}_{\alpha z}) = 1.5$ mT and isotropic $3A(\text{H}_\beta) = 2.3$ mT.

(IV) $\text{-COO}\cdot$ peroxy radical being a product of carbon centered radical oxidation of characteristic $g = 2.031$.

During thermal annealing, radicals decay irreversible. (I) and (IV) radicals are stable even above 280 K.

The dominant spectrum for irradiated PTMC is a quintet demonstrating the following parameters: $A(4\text{H}) = 2.40$ mT and $g = 2.0034$ (Fig. 6B). The signal was assigned to the radical $\text{-CH}_2\cdot\text{CH}_2$ (V) resulting from cleavage of the bond between carbon and oxygen atoms. The second component with a characteristic g -factor of 2.012 can be attributed to the alkoxy radical (VI), which is formed as a result of the release of carbon dioxide from $\cdot\text{O-C}(\text{O})\text{-O-CH}_2\cdot$ intermediate. With high microwave power, the peroxy radical appears.

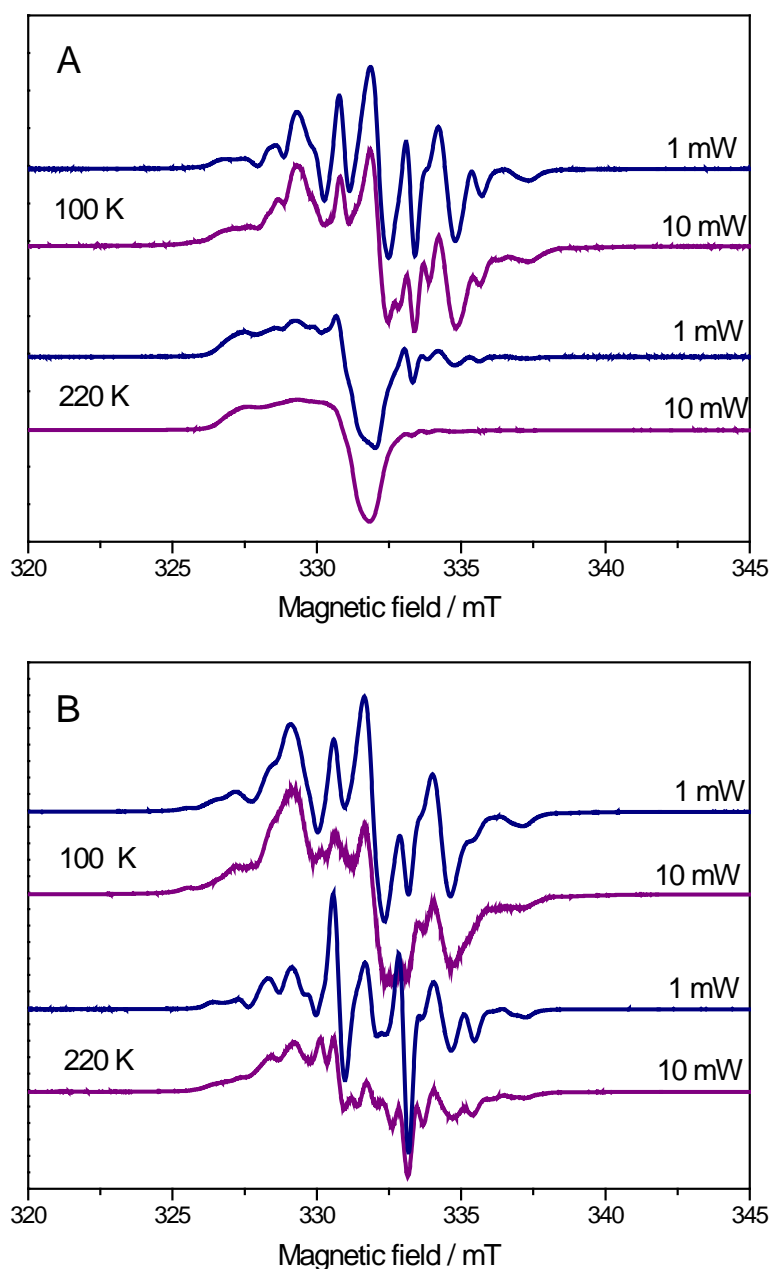


Fig. 7. EPR spectra of gamma-irradiated (A) 70% PLA+30% PTMC and (B) 30% PLA+70% PTMC to a dose of 10 kGy at 77 K.

On the basis of the obtained results for the homopolymers, the spectra of PLA and PTMC copolymers were interpreted. Two materials of different compositions were studied: 30% PLA+70% PTMC and 70% PLA+30% PTMC (Fig. 7). Interestingly, in both cases the main components of the experimental spectra are the signals of polyester radicals found in previously studied homopolymer. On the other hand, the content of PTMC paramagnetic intermediates is negligible. Thus, the radical centers were transferred to the PLA domains along the macromolecules. The intermolecular processes can be related to recombination of radicals leading to crosslinking.

In order to verify this hypothesis, gel permeation chromatography studies were carried out. The determined number-average molecular weight (M_n) and weight average molecular weight (M_w) make it possible to follow the evolution of scission and crosslinking in the irradiated materials.

Figure 8 shows the relative changes in the reduction of M_n and M_w with increasing dose. The PLA homopolymer and the PLA-rich copolymer are degraded upon irradiation, significantly decreasing the chain lengths. On the other hand, M_w of PTMC increases in the dose range of 0-100 kGy (negative reduction) and only for 200 kGy the tendency is the opposite. The effect is related to a longer linkages between the functional groups (three methylene groups) facilitating crosslinking. The trend increases with the lower content of functional groups which appear to be particularly sensitive to radiation. The yield of the degradation and crosslinking processes is comparable in the PTMC-rich copolymer.

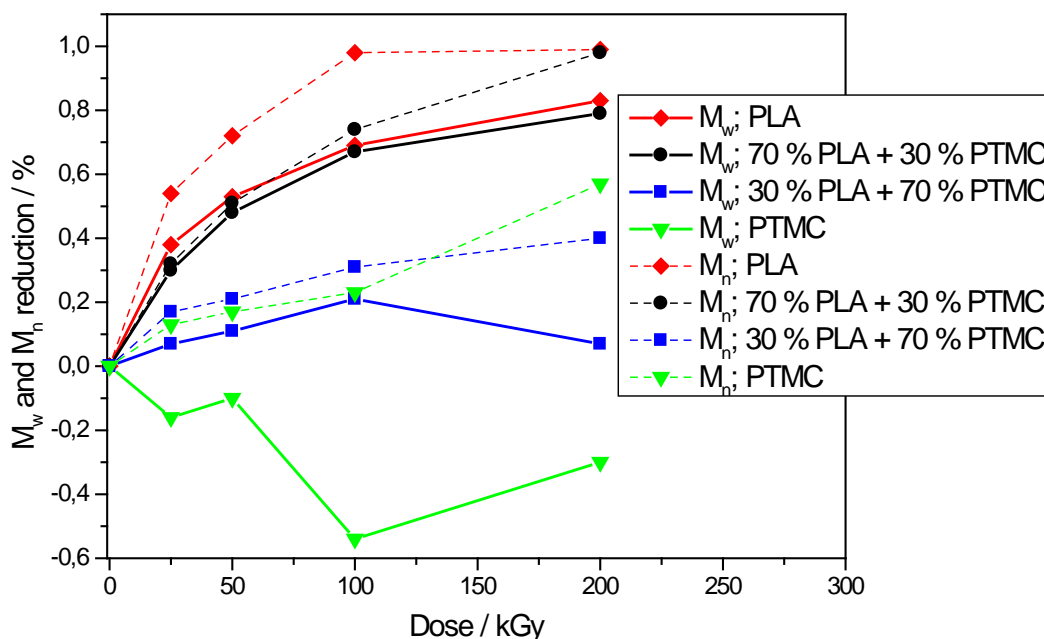


Fig. 8. Changes in M_n and M_w for PLA, 70% PLA+30% PTMC, 30% PLA+70% PTMC and PTMC irradiated to the selected doses.

Degradation with increasing dose leads to a reduction in elongation at break for PLA homopolymer and 70% PLA+30% PTMC copolymer. The relatively low elasticity of both materials results from the content of the crystalline phase, which, according to DSC measurements, ranges from 27% to 35%. Since PTMC and 30% PLA+70% PTMC have no crystalline phase, their initial flexibility is much higher. The results presented in Fig. 9 prove the negative influence of radiation on the flexibility of the PTMC-rich material, indicating that the scission efficiency in this case prevails over the crosslinking. The amorphous PTMC homopolymer does not change the elongation up to 50 kGy, while for higher doses the parameter increases. Thus, crosslinking does not deteriorate flexibility, forming a rubber-like product.

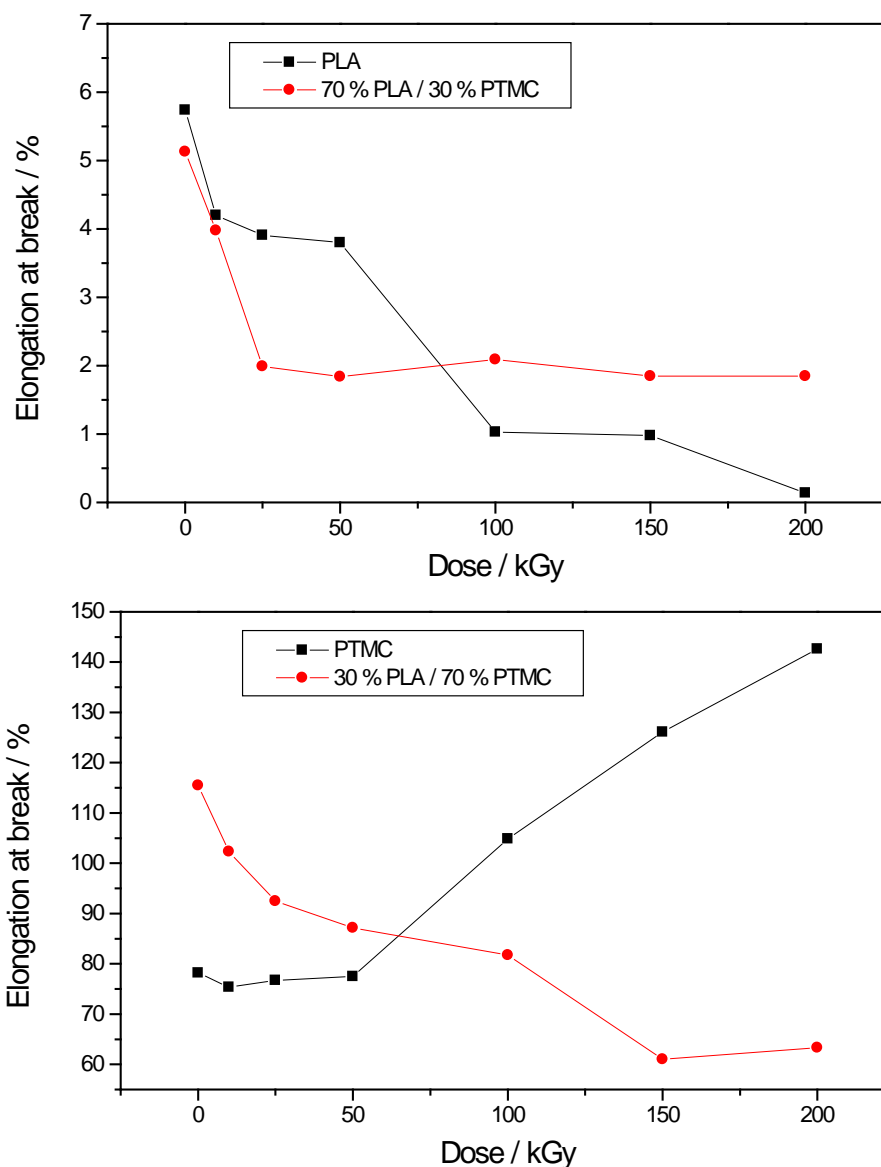


Fig. 9. Relationship between absorbed dose and elongation at break for PLA, 70% PLA+30% PTMC, 30% PLA+70% PTMC and PTMC.

4. CONCLUSIONS

Ionizing radiation is used to modify polymers in medicine and other applications, mainly to crosslink these materials. It is a well-established technology, however the treatment of materials by radiation is unlimited and can be successfully applied to a wide variety of polymer products. This work presented two examples of EB modification of the physicochemical properties of polymers which included: the improvement of surface wettability and the increase of resistance of biodegradable polymers to ionizing radiation.

At the first part of this work the results demonstrated that the radiation-induced grafting is useful method which allows the attachment of hydrophilic monomers to the hydrophobic surface of the polymer. On the basis of this results it was confirmed that the type of polymer matrix has a significant impact on the effectiveness of the radiation grafting process. The research results show that there is a close relationship between the concentration of radicals in the polymer and the efficiency of the grafting process.

The optimization of radiation grafting parameters for the PE/AAC system with the use of RAFT technique was performed by selecting the appropriate solvent mixture, monomer concentration, reaction time, and the type of RAFT agent.

At the second part it was found that the dominant role of PLA in its statistic copolymers with PTMC in radiation-induced processes results from the intensive transfer of radical centers to the aliphatic polyester regions. This phenomenon is associated with intramolecular processes due to weak interactions between chains having only low-polarity functional groups. Crosslinking requiring conformational chains movements is more efficient in fully amorphous PTMC and PTMC-rich materials. It appears that scission occurs in PLA regions mainly by β -fragmentation. The contribution of oxidation processes confirmed by EPR measurements can also lead to degradation. Thus, despite the tendency of PTMC to crosslinking, the final effect of irradiation in its copolymers does not counterbalance the effect of chain cleavage.

From a practical point of view, the addition of polycarbonate segments to PLA makes the final product flexible and more resistant to radiation degradation. The selection of appropriate ratios between the components allows for the production of a tailor-made copolymer, which after radiation modification, gains additional elasticity and can meet specific medical or packaging requirements.

5. LITERATURE

- [1]. Makuuchi, K., & Cheng, S. (2012). Application of radiation crosslinking. In *Radiation processing of polymer materials and its industrial applications* (pp. 134-163). New Jersey: Wiley.
- [2]. Drobny, J. G. (2010). *Radiation technology for polymers*. Boca Raton, London, New York: CRC Press Taylor and Francis Group.
- [3]. Przybytniak, G. (2016). Crosslinking of polymers in radiation processing. In Y. Sun & A.G. Chmielewski (Eds.), *Applications of ionizing radiation in materials processing* (vol. 2, pp. 249-267). Warszawa: Institute of Nuclear Chemistry and Technology.
- [4]. Walo, M., Gryczka, U., Chmielewska-Śmietanko, D., Chmielewski, A. G., Licki, J., Sun, Y., Pawelec, A., Zhao, L., Bułka, S., Zimek, Z., & Sudlitz, M. (2019). New developments based on the INCT facilities. In A. G. Chmielewski & Z. Zimek (Eds.), *Electron accelerators for research, industry and environment – the INCT perspective* (pp. 89-98). Warsaw: Institute of Electronic Systems, Warsaw University of Technology.
- [5]. Chmielewski, A. G. (2016). Future developments in radiation processing. In Y. Sun & A.G. Chmielewski (Eds.), *Applications of ionizing radiation in materials processing* (vol. 2, pp. 501-516). Warszawa: Institute of Nuclear Chemistry and Technology.
- [6]. Moad, G., Chong, Y. K., Postma, A., Rizzardo, E., & Thang, S. H. (2005). Advances in RAFT polymerization: The synthesis of polymers with defined end-groups. *Polymer*, 46(19), 8458-8468.
- [7]. Moad, G., & Thang, S. H. (2008). Radical addition–fragmentation chemistry in polymer synthesis. *Polymer*, 49(5), 1079-1131.
- [8]. Güven, O., & Sen, M. (1991). Preparation and characterization of poly(N-vinyl 2-pyrrolidone) hydrogels. *Polymer*, 32(13), 2491-2495. DOI: 10.1016/0032-3861(91)90093-X.
- [9]. Ratner, B. D., & Hoffman, A. S. (2004). Physicochemical surface modification of materials used in medicine. In B. D. Ratner, A. S. Hoffman, F. J. Schoen & J. E. Lemons (Eds.), *Biomaterials science: An introduction to materials in medicine* (2nd ed., pp. 201-218). USA: Elsevier Academic Press.
- [10]. Choi, J. H., Jung, C. H., Kim, D. K., & Ganesan, R. (2008). Radiation-induced grafting of inorganic particles onto polymer backbone: A new method to design polymer-based nanocomposite. *Nucl. Instrum. Meth. B*, 266(1), 203-206. DOI: 10.1016/j.nimb.2007.11.012.
- [11]. Hoffman, A. S. (1995). Surface modification of polymers. *Chinese J. Polym. Sci.*, 13(3), 195-203.
- [12]. Barsbay M., & Guven, O. (2013). RAFT mediated grafting of poly(acrylic acid) (PAA) from polyethylene/polypropylene (PE/PP) nonwoven fabric via preirradiation. *Polymer*, 54(18), 4838-4848.
- [13]. Przybytniak, G., Kornacka, E. M., Mirkowski, K., Walo, M., & Zimek, Z. (2008). Functionalization of polymer surfaces by radiation-induced grafting. *Nukleonika*, 53, 3, 89-95.