Thermal characteristics and recycling of bolus – a polyurethane-based material used in radiotherapy

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Abstract: The thermal resistance was investigated and the potential for recycling of a polyurethane-based polymer material (bolus) in the form of a gel constituting medical waste after irradiation with ionizing energy was indicated. The same gel, which was not subjected to radiotherapy, was used as a reference material. Thermal stability, the course of oxidative decomposition and the type of volatile substances released during heating in an oxidizing atmosphere were examined using the TG/FT-IR method. The glass transition temperature (T_g) of the tested materials before and after irradiation was determined using the DSC method. It was found that irradiation caused a slight change in T_g and increased thermal stability. However, the irradiation time had no effect on the type of gaseous decomposition products released during heating in an oxidizing atmosphere. The used polyurethane material (bolus) was recycled to obtain new composite materials with different physicochemical properties.

Keywords: polyurethane, DSC, thermogravimetric analysis, radiotherapy, bolus, recycling.

Charakterystyka termiczna i recykling bolusa – materiału na bazie poliuretanu stosowanego w radioterapii

Streszczenie: Zbadano odporność termiczną i wskazano możliwości recyklingu materiału polimerowego na bazie poliuretanu (bolus) w postaci żelu stanowiącego odpad medyczny po ekspozycji na promieniowanie jonizujące. Jako materiał odniesienia zastosowano ten sam żel, który nie był poddany działaniu promieniowania. Zbadano stabilność termiczną, przebieg rozkładu w warunkach utleniających oraz rodzaj wydzielanych substancji lotnych podczas ogrzewania w atmosferze utleniającej, stosując metodę TG/FT-IR. Metodą DSC wyznaczono temperaturę zeszklenia (T_g) badanych materiałów przed i po napromienianiu. Stwierdzono, że napromienianie spowodowało nieznaczną zmianę T_g i zwiększyło stabilność termiczną. Czas napromieniania nie miał jednak wpływu na rodzaj gazowych produktów rozkładu wydzielających się podczas ogrzewania w atmosferze utleniającej. Zużyty materiał poliuretanowy (bolus) został poddany recyklingowi - stanowił jeden ze składników w syntezie nowych materiałów kompozytowych o odmiennych właściwościach fizyko-chemicznych.

Słowa kluczowe: poliuretany, DSC, analiza termograwimetryczna, radioterapia, bolus, recykling

Polymers have an extremely important role in modern life. They can be found both in commonly used everyday products and in high-tech materials. Among the numerous areas of life in which polymers have a crucial and sometimes fundamental role, medicine occupies a special place. The use of polymers in medicine is so wide and varied that it is difficult to imagine its existence without this group of materials.

One of the groups of polymers of particular interest for biomedical applications is polyurethanes (PU). These compounds were first synthesized in 1937 by Otto Bayer's group [1]. Over the years, polyurethanes have become one of the most diverse groups of polymers, both in terms of structure and properties.

Polyurethanes are obtained by the polyaddition reaction of multifunctional organic isocyanates with at least bifunctional compounds containing active hydrogen atoms – including, among others, in the hydroxyl groups of oligomerodiols. A characteristic feature of polyurethanes is the presence of a urethane group (-O-CO-NH-). A schematic of the formation of a linear polyurethane

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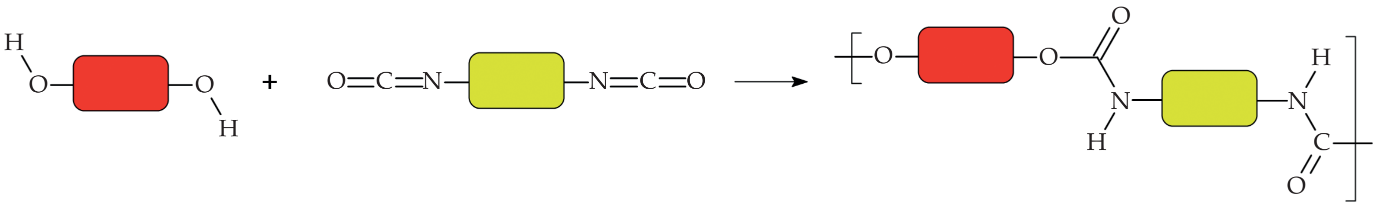

Fig. 1. Scheme of polyurethane synthesis by reacting a diol with a diisocyanate

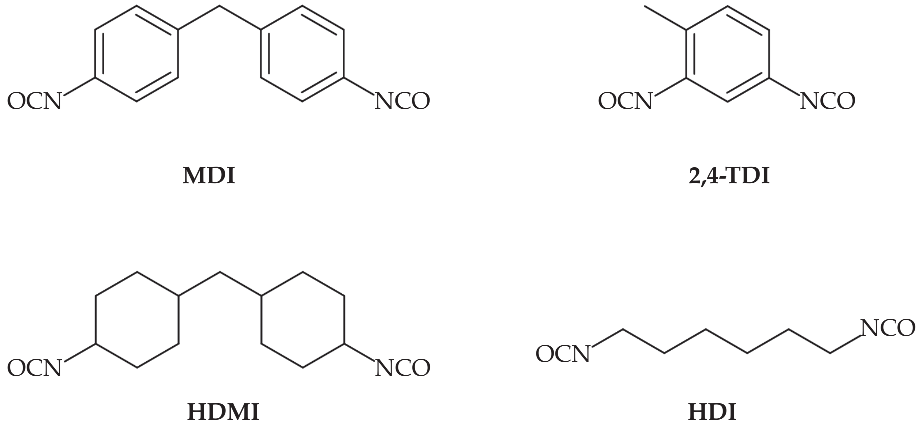

Fig. 2. Chemical formulas and abbreviations of selected aromatic (MDI; 2,4-TDI); cycloaliphatic (HDMI) and aliphatic (HDI) diisocyanates

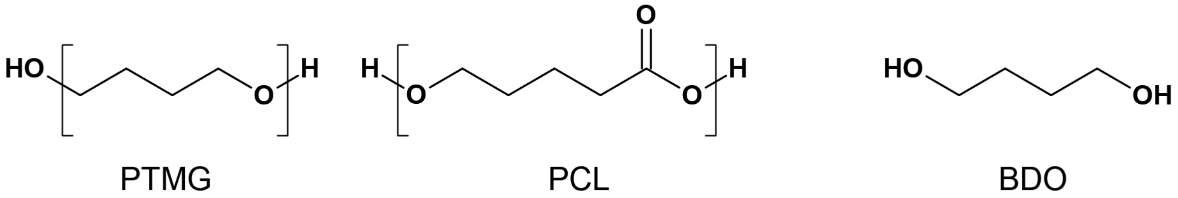

Fig. 3. Chemical formulas and abbreviations of selected polyetherols (PTMG), polyesterols (PCL), and chain extenders (BDO)

in the reaction of a diol with a diisocyanate is shown in Figure 1 [2].

Compared to polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS) or poly(tetrafluoroethylene) (PTFE), the structure of polyurethanes is more complex. Their chemical composition depends on the chemical structure of the two reactants, i.e., diisocyanate and oligomerodiol, and the presence of other substances (including chain extenders). Diisocyanate can be an aromatic, cycloaliphatic or aliphatic compound (Fig. 2), while polyetherols and polyesterols are most used as the oligomerodiol component. Low molecular weight glycols can act as chain extenders (Fig. 3) [1, 3].

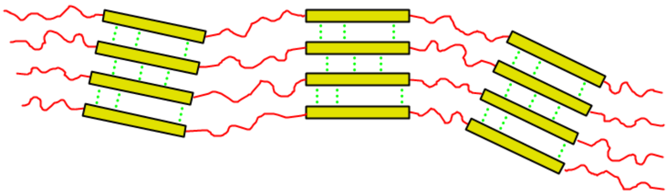

Fig. 4. Scheme of the segmented structure of linear polyurethane: rigid segment (yellow rectangle), flexible segment (red line)

Linear thermoplastic polyurethanes have a segmented structure. In the structure of the macromolecules, one can distinguish between a rigid segment formed by a diisocyanate and a chain extender and a flexible segment constructed from an oligomerodiol (Fig. 4) [4]. If the isocyanate or oligomerodiol molecules contain 3 or more functional groups (cyanate or hydroxyl, respectively), the product of polymerization is cross-linked structures.

The high demand for polyurethanes in medicine is a result of their extremely diverse and growing applications. Their versatility due to their biocompatibility, mechanical strength, and ability to tailor properties to specific applications make them a valuable tool in modern medical therapies and technologies [5–7]. Polyurethanes are widely used for catheters, wound dressings, implants, stents, joint and cardiovascular prostheses, dialysis, tissue engineering scaffolds, and drug delivery systems [5, 8–10].

One of the applications of polyurethanes in medicine is bolus [11]. In radiotherapy, a bolus is a special material used as a tissue shield to equalize the radiation dose, especially at the surface of the patient's body. With a bolus, the dose that reaches the tissues can be better controlled, especially in the treatment of cancers close to the skin surface. These materials have properties equiva-

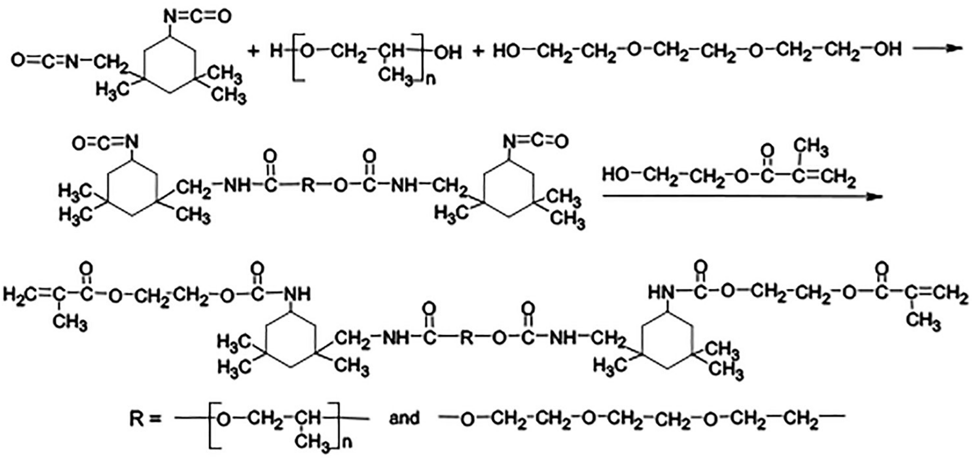

Fig. 5. Resin oligo(urethane-methacrylate) [OUM]

lent to tissue when irradiated. They are widely used in practice to reduce or alter dosing for targeted high-energy photon and electron radiation treatments. However, after use in radiation oncological therapy, such gel-based bolus materials are medical waste that are most often utilized during combustion. Therefore, studies determining the influence of the irradiation time of the medical waste gel-based bolus material for radiation therapy on the glass transition temperature (T_g), thermal stability under oxidative conditions, and the type of emitted volatile during its combustion were undertaken. In addition, a new recycling method for polyurethane-based polymer material used as patient protection in radiation oncology therapy has been proposed.

EXPERIMENTAL PART

Materials

The commercially available gel-based bolus, polyurethane used as a protective material for oncological radiation therapy (KSR-3005) was delivered by Klarity (Guangzhou, China). In this study, three bolus samples were used. The sample 1 was a reference sample (a sample not irradiated). Sample 2 was a sample exposed for 50 h and sample 3 was a sample exposed for 100 h to (ionizing radiation, photons, energy 6 MeV, standard doses for functional radiotherapy 2–3 Gy at a time). Isophoronediisocyanate (5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane), poly(oxypropylene)diol (M_w=2000 g/mol), triethylene glycol, butyl acrylate, 2-hydroxyethyl methacrylate, *N*-vinyl-2-pyrrolidone, 2,2-dimethoxy-2-phenylacetophenone (photoinitiator), and 1,4-diazabicyclo[2.2.2]octane were purchased from Sigma-Aldrich (Darmstadt, Germany).

Polyurethane recycling methodology

In the first step, the oligomer urethane-methacrylate (OUM) was synthesized by the reaction of 13.3 g (0.06 mol) isophoronediisocyanate, 30.0 g (0.015 mol) poly(propylene)diol and 2.3 g (0.015 mol) triethylene glycol. The reaction was performed at 85°C for 8 h. The urethane prepolymer obtained was cooled to 50° and then 7.8 g (0.06 mol) 2-hydroxyethyl methacrylate and 9.5 g butyl acrylate as an active diluent was added into the mixture of the prepolymer. The reaction was carried out at 60°C for 2 h and the reaction mixture was cooled down to 50°C and 0.25 g of 1,4-diazabicyclo[2.2.2]octane as a catalyst was added and stirred for 2 h to accelerate and complete the formation of urethane-methacrylate oligomer. In the final stages, the reaction was monitored until the signal for -N=C=O groups (at 2270 cm^{-1}) in the FT-IR spectrum disappeared [12].

Oligo(urethane-methacrylate) with M_w= 825 g/mol is a viscous liquid with a dynamic viscosity of 16500 mPa · s at 25°C, a C=C double bond content of 2.15 mmol/g. Figure 5 shows the formulas of the obtained resin oligo(urethane-methacrylate).

Synthesis of a new composite based on waste bolus

In the second step, the oligomeric composite was obtained by mixing the components: resin oligo(urethane-methacrylate) (OUM), *N*-vinyl-2-pyrrolidone (VP)

Fig. 6. Schematic diagram of the mold for preparing the PUM-bolus composite

(10 wt%), polymerization photoinitiator 2,2-dimethoxy-2-phenylacetophenone (3 wt%). Figure 6 shows a diagram of the mold for preparing the cured poly(urethane-methacrylate)-bolus (PUM-bolus) composite. The oligomeric composition (OUM) was cured by UV lamp irradiation for 10 min. The soft polyurethane (waste bolus) and the oligomeric composition (OUM) were sandwiched between two glass plates and then exposed to UV light for 20 min after compression. The cured PUM-bolus (poly(urethane-methacrylate)-bolus) composite was obtained and its physicochemical properties were examined.

Methods

ATR-FT-IR measurements

The ATR-FT-IR spectra in the range of 600–4000 cm^{-1} with 4 cm^{-1} resolution and 62 scans were collected (FT-IR Tensor 27 instrument with a diamond crystal, Bruker, Germany).

DSC measurements in inert atmosphere

The tested samples (10 mg) were heated in an aluminum crucible with a pierced lid in an inert atmosphere (argon, a flow rate of 30 mL/min) with the use of a DSC 204 Phoenix produced by Netzsch (Germany). The heating rate was 10°C/min. Two DSC scans, one from -130°C to 150°C and the second from -130°C to 500°C were done. The values of the glass transition temperature (T_g) from the first and second DSC scans were read. Also, the characteristic decomposition temperatures were evaluated.

Hardness

The materials hardness was measured by the Shore A method using a Zwick 7206/H04 analogy hardness testing apparatus (Germany) at 23°C. Readings were taken after 15 s.

TG/DTG/DSC/FT-IR measurements in oxidative atmosphere

The TG/DTG/DSC method to evaluate the thermal properties of the tested samples in the oxidative atmosphere such as the initial decomposition temperature marked as a 1% ($T_{1\%}$) and 5% ($T_{5\%}$) of mass loss, peak maximum decomposition temperatures (T_{max}), mass losses in each decomposition stage (Δm) was used. The analyses were made with the use of a STA 449 Jupiter F1 instrument produced by Netzsch (Germany). The tested samples (10 mg) were heated in an open corundum crucible from 40°C to 650°C in an oxidizing atmosphere (synthetic air, a flow rate of 100 mL/min) and with a heating rate 10°C/min.

The simultaneous TG/FTIR method to define and analyze the type of emitted gaseous products during the oxidative thermal decomposition of the tested samples was applied. The gaseous FT-IR spectra of the emitted volatiles were collected in the wavenumber range of 600–4000 cm^{-1} and with a resolution of 4 cm^{-1} and 32 scans per spectrum (a FT-IR TGA 585, Bruker, Germany).

RESULTS AND DISCUSSION

ATR-FT-IR analysis

ATR-FT-IR spectra for the samples are presented in Fig. 7. The wide absorption signal between 3100–31500 cm^{-1} is attributed to -N-H stretching vibrations, and the appearance of the sub near absorption signal at 3269–3280 cm^{-1} indicates hydrogen bonded –N-H stretching vibrations. The absorption signals in the range 2864– 2968 cm^{-1} confirm the stretching vibrations characteristic for C-H groups. The absorption signal near 1730 cm^{-1} proves the presence of C=O groups in the tested samples (the stretching vibrations) [13]. The absorption signal at 1535–1536 is due to the stretching vibrations of C-N and the bending vibration of -N-H. The presence of the urethane groups by the absorption signal at 1221–1223 cm^{-1} (C-N stretching) is confirmed. The high-intensity absorption signals attributed to the C-O stretching of the ether group at the range 1015–1097 cm^{-1} appeared. Other FT-IR signals at 1345–1373 cm^{-1} and 1412–1455 cm^{-1} relate to the C-H bending vibrations of the methylene group. Moreover, the obtained spectra indicate that no changes in the characteristic absorption signals for functional groups present in the structure of the tested bolus materials before and after exposure to irradiation are observed.

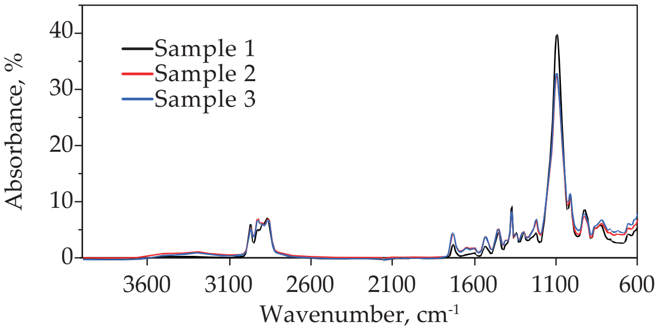

Fig. 7. ATR-FT-IR spectra of the samples

DSC in inert atmosphere

DSC analysis for the samples is presented in Fig. 8. DSC studies confirm that all the samples contain solvents bound by hydrogen bonds with a polymer matrix in their composition. Most often, water is used as a solvent in this type of commercially available gel-based bolus material for radiation therapy. The heating of all samples to a temperature of 160°C causes the evaporation of hydrogen-bonded water because of the breaking of hydrogen bonds. The maximum water evaporation rate of 85–101°C is visible. The second DSC scan indicates that after heat-

Table 1. DSC data of the samples

Sample	T_g, °C	T_{max0}, °C	T_{max1}, °C	T_{max2}, °C	T_{max3}, °C	T_{max4}, °C
1	-65.0	90	202	280	322	397
2	-63.7	101	210	295	342	402
3	-63.6	85	211	295	342	402

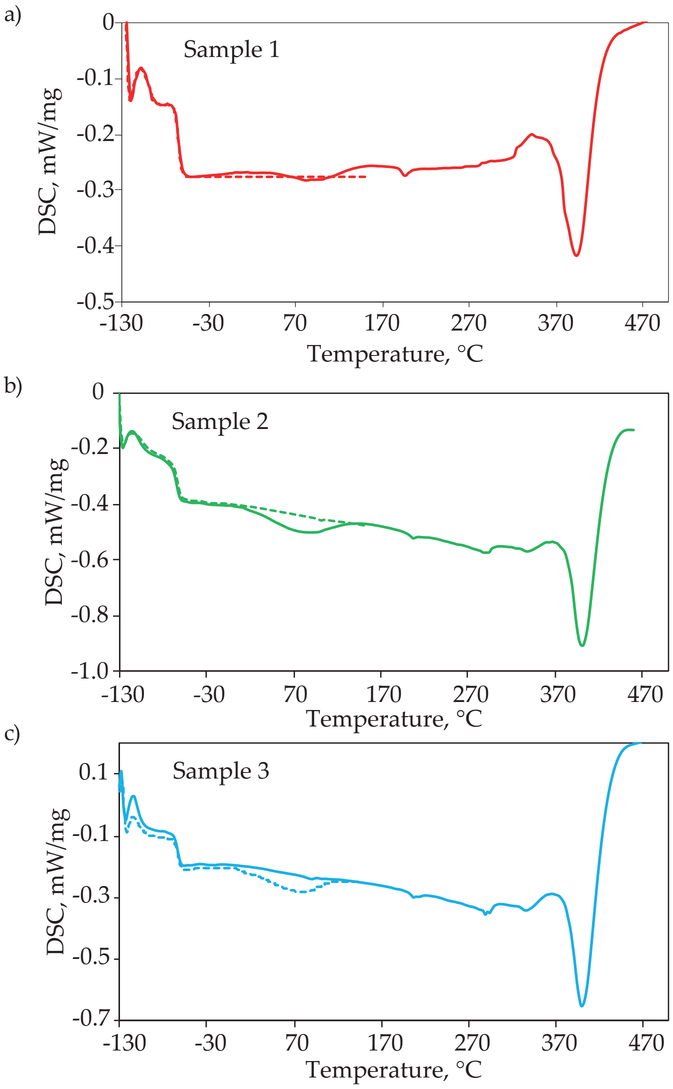

Fig. 8. DSC curves of the samples (dotted line: -130–150°C, continous line: -130–500°C)

ing the samples to 160°C, there is no longer water bound to the polymer matrix. Moreover, this analysis also confirms that both the presence and absence of water bound by hydrogen bonds to the polymer matrix do not affect the glass transition temperature (T_g) of the tested samples. In addition, irradiation of this material used as a protective material for healthy cells in irradiation oncology does not significantly affect the values of glass transition temperature (T_g) of the samples. The T_g for sample 1 (sample not exposed) is -65.0°C. In turn, the T_g values for irradiated samples are a little higher. The T_g for sample 2 is -63.7°C and for sample 3 is -63.6°C, respectively.

In addition, the heating of all the samples above 160°C leads to their thermal decomposition in an inert atmosphere. This decomposition includes several stages, visible as endothermic DSC signals. The first decomposition stage at T_{max1} between 201°C and 211°C described as a low-intensity endothermic DSC signal is observed. The second one endothermic with a low intensity DSC signal at T_{max2} between 280°C and 295°C is spread. The third decomposition stage also with a low intensity, endothermic DSC signal with T_{max3} at 322–342°C is visible. Finally, in the last decomposition stage with T_{max4} at 397–402°C and with high intensity, an endothermic DSC signal is observed, Table 1.

In addition, based on the obtained experimental DSC curves, one can notice a shift in the maximum decomposition temperatures (T_{max}) towards higher values for the irradiated samples compared to the unirradiated test sample (sample 1). While the exposure time of the samples does not cause any further change in the T_{max} values.

TG/DTG/DSC analysis in oxidative atmosphere

TG/DTG/DSC curves for the tested commercially available gel-based bolus material for radiation therapy before and after irradiation in an oxidizing atmosphere is presented in Fig. 9. Also, the results read from TG and DTG curves are placed in Table 2. As it is well visible, all the samples decomposed completely up to a temperature of 600°C during their heating in an oxidizing atmosphere. After heating them to 600°C, no residue is observed. Moreover, differences in the heat resistance of the tested materials were noticed depending on the exposure time.

The thermal resistance defined as 1% and 5% mass loss ($T_{1\%}$ and $T_{5\%}$) in oxidizing conditions for the reference sample (non-exposed sample) is 178°C and 219°C, respectively. However, for irradiated samples, an increase in $T_{1\%}$ and $T_{5\%}$ values are observed, which means an increase in their thermal resistance, Table 2. In addition, as the sample exposure time increases, the thermal resistance increases slightly. The characteristic thermal stability temperatures $T_{1\%}$ and $T_{5\%}$ increase by 11–15°C and by 21–29°C compared to the reference sample 1. The oxidative decomposition takes place in at least three main stages composed of several steps, as it is seen based on TG/DTG curves. The first decomposition stage starts at $T_{1\%}$ and ends at 280–285°C. This stage is described by an asymmetric DTG signal with at least two, poorly marked maxima. The DSC analysis performed simultaneously with the TG/DTG analysis indicates that at this stage of decomposition, the bonds in the structure of the samples are broken (endothermic signal at approx. 176°C), and the subsequent oxidation/combustion reactions of gaseous decomposition products may happen (exothermic signal with max. at 210°C and 260°C. The mass loss in this stage (Δm_1) is from 16.5% (sample 1) to 7.5%

Table 2. TG/DTG data

Sample	$T_{1\%}$, °C	$T_{5\%}$, °C	T_{max1}, °C	Δ_{m1}, %	T_{max2}/T_{max2a}/T_{max2b}, °C	Δ_{m2}, %	T_{max3}, °C	Δ_{m3}, %
1	178	219	213/263	16.5	313/332/371	73.3	499	10.2
2	189	240	219/257	8.9	314/330/365	79.4	501	11.7
3	194	248	225/261	7.5	314/348/385	82.5	488	10.0

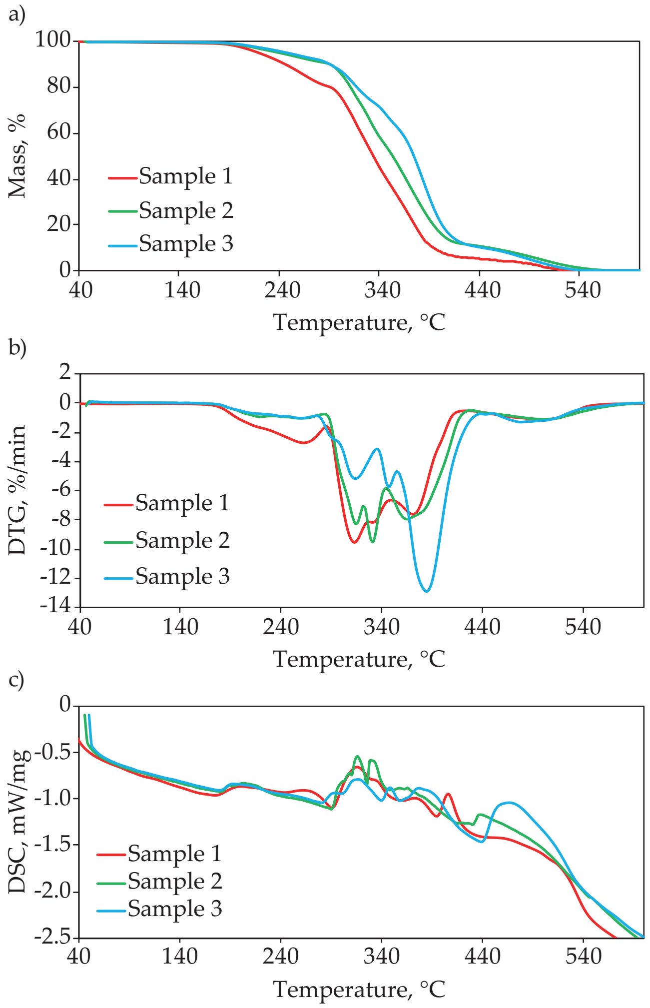

Fig. 9. Thermal analysis curves: a) TG, b) DTG, c) DSC

(sample 3). This stage may be due to the decomposition of end lower molecular mass macromolecules. Moreover, Δm_1 values decrease as a sample exposure time increases. The second oxidative decomposition stage is more complicated and is related to the main oxidative decomposition process of the sample related to the breakdown of the main macromolecule chains. The obtained results indicate that it is related to the decomposition and combustion/oxidation reactions taking place in the gas phase because exothermic DSC signals are observed in the DSC curves. This stage is observed between 280–285°C and 426–440°C. The mass loss (Δm_2) in this stage is from 73.3% (control sample 1) to 82.5% (sample 3) and it grows with increasing exposure time of the sample. Finally, the last, third decomposition stage with similar mass loss for all tested samples (10–11.7%) above the temperature of 426–440°C appeared. This stage is described by one broad DTG signal and exothermic DSC signal with one maximum for all the samples. This decomposition stage is directly connected with the combustion process of the residues formed during the main decomposition stage visible at $T_{max2.}$

TG/FT-IR analysis

Together with TG analysis, FT-IR analysis of gaseous decomposition products released during the heating of the gel-based bolus materials before and after irradiation, in an oxidizing atmosphere was performed to assess the influence of the exposure time on the type of gaseous products produced during combustion. The FT-IR spectra collected at specific characteristic temperatures are shown in Fig. 10. The collected gaseous FT-IR spectra clearly show that starting with $T_{1\%}$, the beginning of the emission of volatile is observed. This emission at $T_{1\%}$ is extremely low, however as the heating temperature increases, the gas emission intensity increases, reaching a maximum at T_{max2}. Moreover, it is well visible the emission of the same type of volatile over the whole heating range. Under the presence of oxidizing conditions, the FT-IR spectra for all the tested samples show absorption bands typical for water vapor formation (3500–4000 cm^{-1} and 1300–1800 cm^{-1} as "jagged" signals, associated with stretching and bending vibrations, correspondingly). In addition, the formation of CO_2 by the presence of the absorption bands at 2310–2359 cm^{-1} and 669 cm^{-1} characteristics for stretching and degenerate bending vibrations are confirmed. Among inorganic gases, the emission of CO as double characteristic bands with two maxima at 2092 cm^{-1} and 2163 cm^{-1} is visible. Moreover, during the oxidative decomposition of the tested materials, the creation of organic gases is detected. The FT-IR spectra display the absorption bands characteristic for organic carbonyl compounds, including aldehydes (the stretching vibrations of C=O at 1745–1749 cm^{-1}, the stretching vibrations of C-H at -CHO group at 2724–2800 cm^{-1} and the bending vibrations of C-H at 962-980 cm^{-1}). Also, other structure carbonyl compounds are emitted. This is confirmed by the appearance of the C=O absorption signals at 1794 cm^{-1} and 1680–1720 cm^{-1}. The location of these C=O bands and the presence of the additional bands, partially overlapping with the water vapor bands, at 3720 cm^{-1} (the stretching vibrations of OH), at 1520–1560 cm^{-1} (the bending vibrations of -N-H) and at 1105–1214 cm^{-1} (the stretching vibrations of C-O) may indicate the formation of organic acid, amide, and ether-based compounds. The presence of the bands at 1054 cm^{-1} (the stretching vibrations of O-H) combined with the presence of the absorption bands due to the vibrations of the -OH group proves the emission of

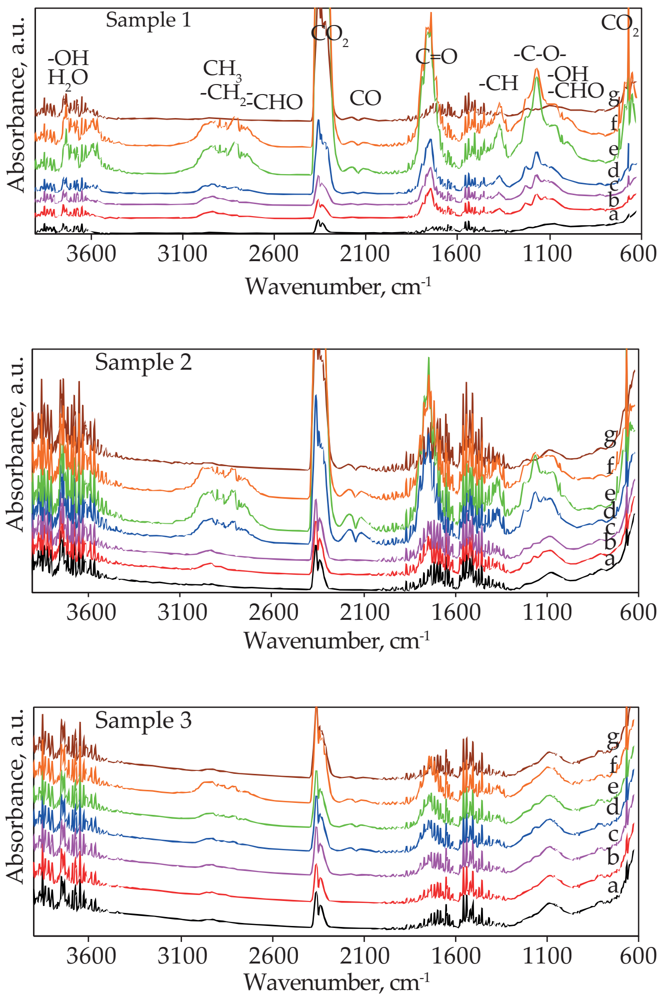

Fig. 10. The gaseous FT-IR spectra collected under combustion of the samples at specific temperatures: a) $T_{1\%}$, b) $T_{5\%}$, c) T_{max1}, d) T_{max2}, e) T_{max2a}, f) T_{max2b}, g) T_{max3}

alcohol. The type of gaseous decomposition products released during heating of the samples in the air atmosphere indicates the processes of bond cleavage connected with the oxidation and combustion/partial combustion of the gaseous decomposition products. As a result, a gas mixture containing H_2O, CO_2, CO, aldehydes, alcohols, acids, amid, and ether-based compounds and alcohols are created. Finally, in the temperature above 426–440°C, the emission of H_2O, CO_2 and CO is observed. It indicates the combustion process of the previously formed residues.

Properties of new composite

Figure 11 presents the ATR-FT-IR spectra, and DSC curves obtained for a crosslinked poly(urethane-methacrylate) (PUM) and composite with waste polyurethane-based bolus material (PUM-bolus). As it is well visible, all the characteristic absorption signals describing the structure of the prepared crosslinked materials, as marked in Fig. 11, are present. In addition, these spectra also confirm that the composite matrix is a crosslinked material. In the FT-IR spectra, no absorption bands originate from methacrylic groups at a wavenumber equal to 1635 cm^{-1} which indicates a high conversion of double bonds during the polymerization conditions used. Due to the high degree of crosslinking of PUM material, its transition from the glass to the rubbery state occurs with a small change in heat capacity, as is seen in Fig. 12. However, the glass transition temperature for PUM can be read from the DSC curve, which is 85°C. This PUM crosslinked polymer is characterized by one T_g value. In turn, the prepared composite with waste bolus (PUM-bolus) shows two glass transition temperature regions, one at a midpoint temperature of -63.6°C (characteristic for bolus) and the other at a midpoint temperature of 92.3°C. The second T_g value for a PUM-bolus composite is a little higher as compared to PUM polymer. It can be due to some interactions between the polymer matrix and bolus filler. The decomposition of the PUM-bolus composite runs through three main stages (T_{max}) in an inert atmosphere. These stages are related to the pyrolysis of the bonds present in the structure of the prepared material.

Table 3. Properties crosslinked poly(urethane-methacrylate) (PUM) and PUM-bolus

Materials	DSC				Hardness A
	T_g, °C	T_{max1}, °C	T_{max2}, °C	T_{max3}, °C	
PUM	–/85.0	–	329/344	432	41
PUM-bolus	-63.6/92.3	230	346	407/439	20

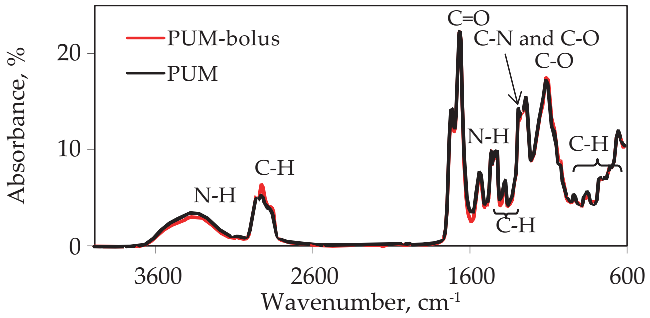

Fig. 11. ATR-FT-IR spectra of PUM and PUM-bolus

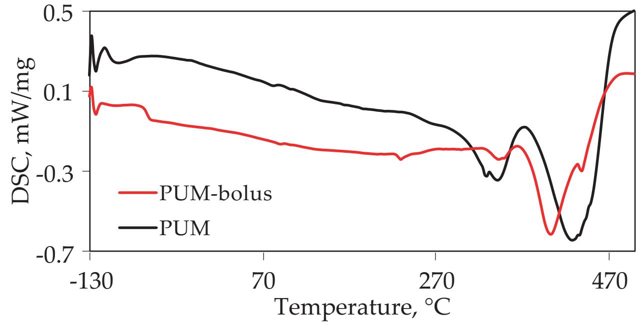

Fig. 12. DSC curves for PUM and PUM-bolus

CONCLUSIONS

In this work, the effect of irradiation time on the thermal properties and the type of gaseous products evolved during heating in an oxidizing atmosphere in medical waste after radiotherapy was investigated. As a medical waste, a gel-based bolus material irradiated by 50 or 100 h was used. All the obtained, experimental results were compared with an unirradiated gel-based bolus material (reference material). The performed analysis confirmed that irradiated material had a little higher glass transition temperature (about -63.6°C) as compared to reference material (-65°C). The TG analysis proved to increase the thermal stability of the tested irradiated material by approx. 11–15°C in oxidizing atmosphere depending on the irradiation time. The TG/FT-IR method certified that the oxidative decomposition process was complex. It involved several decomposition stages linked to bond breakdown, oxidation, and combustion processes (first and second oxidative decomposition stages). Regardless of the irradiation time of the tested material, the same type of volatile from $T_{1\%}$ to 426–440°C was emitted. As volatiles, a formation of a mixture of H_2O, CO_2, CO, aldehydes, alcohols, acids, amid, and ether-based compounds were created. However, in the third decomposition stage (above 426–440°C), the formation of inorganic volatiles (H_2O, CO_2, CO) because of combustion processes was observed. The proposed recycling method allowed effective use of the tested medical waste bolus-polyurethane based material to prepare novel composites. The use of waste as a component of the composite is important, among others, for environmental protection reasons. It allows limiting the accumulation of waste in landfills and reduces the emission of toxic organic gases released during combustion, including aldehydes, to the environment.

Authors contribution

M.W. – conceptualization, methodology, data curation, writing-original draft, visualization, resources, formal analysis, supervision, writing-reviewing and editing; Ł.Sz. – writing-original draft, visualization, formal analysis, writing-reviewing and editing; B.T. – conceptualization, methodology, writing-original draft, visualization, formal analysis; A.K. – supervision, writing-reviewing and editing; B.P. – conceptualization, methodology, writing-original draft, visualization, formal analysis, supervision, and reviewing and editing.

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Conflict of interest

The authors declare no conflict of interest.

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