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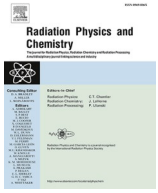

The impact of post-radiation high-temperature shear grinding on the thermal and mechanical properties of polypropylene☆

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ABSTRACT

The effect of input doses of ^{60}Co γ-radiation from 80 to 12,000 kGy on the thermophysical properties and thermal stability of samples of polypropylene granules and powder obtained by high temperature shear grinding of irradiated granules, as well as on the tensile strength properties of a plate made from irradiated granules and their corresponding powders, was studied. The thermophysical properties of the powder are determined by the changes introduced by radiation into the initial polymer granules. The effects of radiation in air (environments with oxygen) were studied. Grinding redistributes oxygen-containing functional groups from the surface layer of irradiated granules throughout the entire volume of the obtained powder leading to the destruction of polymer chains as there is a component due to thermal destruction of radiolyzed polymer chains. High-temperature shear grinding of irradiated granules has a significant effect on the product powder, reducing its thermal stability but increasing the tensile strength of plates pressed from it at low absorbed doses. The current work shows that radiation treatment coupled with high temperature shear grinding could be a method for modifying the properties of polymers so that polypropylene waste can be processed for other applications.

1. Introduction

Polypropylene (PP) is a versatile, chemically stable polymer with attractive mechanical, electrical, and thermal properties (Moore, 1996; Tripathi, 2002; Karger-Kocsis and Bárány, 2019; Harutun, 2003). Of the five most common plastics in terms of production, PP ranks second after polyethylene, (Khunová et al., 2012) and is one of the least expensive plastics. Important markets for PP homopolymer are threads and fibers, automobile components, household appliance components, packaging materials, furniture, high tenacity yarn, and tufted carpets (Moore, 1996; Tripathi, 2002; Karger-Kocsis and Bárány, 2019; Ulrich, 1993). Due to its low toxicity, PP has found wide application in food containers and medical products, (Sevil and Güven, 1995; Fintzou et al., 2006; Goulas et al., 2004a; Yagoubi et al., 1999; Oka et al., 2011) where sterilization is required before use. A preferred method for sterilizing such items is radiation treatment, in particular γ-radiation. The advantage of γ-irradiation for sterilization lies in its high penetrating power, and because it is a cold process, in contrast to other sterilization methods. Radiation treatment is often used to sterilize disposable PP medical devices such as syringes, surgical gloves, gowns, orthopedic implants, surgical kits, sutures, and trays. It is also used to sterilize laboratory equipment and cosmetics, for example (Sevil and Güven, 1995; Fintzou et al., 2006; Goulas et al., 2004a; Oka et al., 2011). The recommended input radiation dose for sterilization is usually 25 kGy in accordance with the IAEA Code of Practice (1974) and standards of the pharmaceutical industry (Darboir et al., 1985). In practice, sterilizing doses range from 25 to 40 kGy (Fintzou et al., 2006).

Irradiation of PP with ionizing radiation can affect its performance characteristics due to PPs known low radiation resistance (Rivaton et al., 2004; Gavrila and Gosse, 1994; Khoylou and Katbab, 1993). The degree of radiation-induced changes in PP depends on many factors, including material crystallinity, additives, (Soebianto et al., 1995) the type of ionizing radiation, input dose and rate of exposure, the environment in which irradiation occurs, and the temperature of irradiation (Goulas

☆ This article is dedicated to the memory of Yuri Andreevich Olkhov, a prominent scientist in the field of studying the molecular-topological structure of polymers, and the developer of the method of thermomechanical spectrometry.

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et al., 2004a). A range of physical and physicochemical methods can be used to determine the effects of such input radiation doses (Sevil and Güven, 1995; Yagoubi et al., 1999; Krupa and Luyt, 2001). Independent of the input radiation dose, ionizing radiation leads to excitation and ionization of atoms leading to chemical bond breaking and the subsequent formation of active free radicals (Ivanov, 1992; Milinchuk and Tupikov, 1986; Dole, 1972; Woods and Pikaev, 1994). The final radiative transformations leading to irreversible changes in the properties of irradiated PP depend on the conditions and input dose of irradiation. Prior work on the radiolysis of PP has shown chain destruction, (Yagoubi et al., 1999; Goulas et al., 2004b; Damir et al., 2014; Otaguro et al., 2010; Lugão et al., 2000; Wang et al., 2018) often in combination with chain crosslinking, (Otaguro et al., 2010; Czvikovszky, 1996; Zhang et al., 2010; Oliani et al., 2010) an increase in chain unsaturation, (Saha et al., 2000) and the loss of crystallinity (Krupa and Luyt, 2001; Maeda et al., 2016). Cross-linking of PP increases the molecular weight and improves the thermal stability and mechanical properties of the polymer. The destruction of PP chains, in contrast, leads to decreases in molecular weight, (Otaguro et al., 2010; Auhl et al., 2004) thermal stability, (Krupa and Luyt, 2001) melting temperature, (Damir et al., 2014) and strength (Goulas et al., 2004b; Tahtat and Mahlous, 2008). Chain destruction contributes to changes in the solubility of the polymer (Milinchuk and Tupikov, 1986; Singh et al., 2004) and increases the degree of branching (Otaguro et al., 2010; Lugão et al., 2000; Oliani et al., 2010; Auhl et al., 2004; Mousavi et al., 2010). Destruction of PP chains under irradiation is enhanced in the presence of oxygen due to radiation oxidation of the polymer through mechanisms such as the Bolland-Gee oxidation cycle with high level computational thermodynamics recently published (Rychlý et al., 2011; Gijsman et al., 1993; Philippart and Gardette, 2000; Allayarov et al., 2024). When exposed to oxy radicals generated by peroxides, it has been shown that PP undergoes chain degradation through a β-scission mechanism in comparison to polyethylene which undergoes crosslinking through radical recombination (Braun et al., 1998). The formation of oxidation products leads to degradation of the mechanical properties of the polymer such as surface cracking and reduces its molecular weight (Fintzou et al., 2006; Tahtat and Mahlous, 2008; Grecco Romano et al., 2018). A recent study investigated the chemical and thermophysical properties of thermooxidized, but not γ-irradiated, isotactic PP with varying concentrations of ethylene moieties (Nguyen et al., 2023). For thin films, oxygen can diffuse into the material leading to changes in the entire volume under irradiation, (Wilson, 1974) whereas for thick films, oxidation due to radiation takes place primarily on the surface of the film with oxidation deep within the film due to oxygen diffusion (Shen and Mc Kellop, 2002; Seguchi and Yamamoto, 1984). The degree of oxidation with respect to depth for thick films will vary based upon the extent of irradiation, formation of an oxidized layer on the outside of the film, and the crystallinity of the polymer based upon polyethylene reports (Seguchi and Yamamoto, 1984). In our prior work on irradiated PP, (Allayarov et al., 2024) we hypothesized that radiation induced oxidation is primarily found on the surface of the pellet due to the high concentration of available oxygen at the surface and that the interior of the pellet (the majority of the volume) is irradiated under a nominally inert environment. The ATR FTIR measurements (Allayarov et al., 2024) on which this hypothesis is based predominantly examine the surface oxidation of the pellets due to the low penetration depth of IR light in the experiment.

Most studies of the effect of irradiation on the properties of PP mainly consider relatively low input doses of radiation such as those used to sterilize PP products, approximately 25 kGy (Fintzou et al., 2006; Keene et al., 2014). However, polymers, including PP, are used as structural materials which can be exposed to various types of radiation, for example, in space applications, nuclear power plants, particle accelerators, and radiation and nuclear medicine. In these cases, the polymers can receive quite large input doses of ionizing radiation. Under such operating conditions, the durability of the polymer is an important property (Novikov and Voronina, 2008; Zhdanovic, 2014). Thus, it is important to study the behavior of thermoplastics under the influence of high input doses of ionizing radiation, for example, the types of radiation ultra-high molecular weight polyethylene would receive when serving as a shielding layer in a multilayer structure designed to protect against cosmic rays, or when using thermoplastic treated with γ-radiation for cable insulation (Chodak, 1998). A focus of the current work is to study the effect of a range of γ-irradiation input doses from 80 to 12, 000 kGy on the thermal and thermomechanical properties of PP. The degradation of PP with heat, ultraviolet, and sunlight light treatment and resulting mechanical and structural property changes have been studied but are outside the scope of the current work (Kotek et al., 2004; Raab et al., 1982; Nakatani et al., 2022).

The creation of environmentally friendly and economically viable methods (Holmes-Walker, 1975; La Mantia, 2002; Scheirs, 1998; Thakur, 2015) for the reuse/recycling of polymeric materials remains significant, (Burillo et al., 2002) especially for the types of applications of a polymer such as PP where there is production waste and waste from its use in disposable goods. The importance of the use of radiation in polymer recycling has been described by the International Atomic Energy Agency (IAEA). (See the IAEA Nuclear Technology; IAEA Coordinated Research Project) A recent review consistent with the IAEA initiative reviewed the use of radiation for plastic sorting, increasing plastic mix compatibility through oxidation and surface chemistry modification, polymer recycling preprocessing, and direct polymer degradation (Ponomarev et al., 2022). It is important to avoid processes that can further impact the environment in terms of the atmosphere, soil, or groundwater (Ragaert et al., 2017; Maris et al., 2018; Alsabri and Al-Ghamdi, 2020; Alsabri et al., 2022). According to the Federal Classification Catalog of Wastes of the Russian Federation, (Federal Classification Catalog of Waste) most PP waste is assigned to the fourth hazard class, since they are not dangerous to humans, but impact the environment. Since ionizing radiation can change the structure and properties of polymer materials, it might be an effective tool for processing polymer waste. The surface oxidation of polymers through irradiation in air increases mixed plastic compatibility and integration with binders that are used in material production (Ponomarev et al., 2022). In addition, PP may be recycled by production of small molecule precursors via γ-radiation driven oxidation (Ponomarev et al., 2022). Increasing compatibility in mixed plastic recycling is likely to be important in recycling or upcycling environmentally captured micro and nanoplastics where separation is likely challenging or infeasible. The influence of the preliminary input dose of γ-irradiation on the process of high-temperature shear grinding (HTSG) of PP was studied to develop a method for post-radiation processing of PP waste. HTSG of pre-irradiated PP was demonstrated to homogenize radiation induced surface oxidation (Allayarov et al., 2024) which is hypothesized to increase the structural quality of recycled PP plates. Our prior work (Allayarov et al., 2024) also demonstrated that HTSG of un-irradiated PP in air resulted in only minor variation in the relative intensities of IR absorption bands showing that HTSG does not have a meaningful effect on the chemical composition of un-irradiated PP. The HTSG method has been used on an industrial scale for processing rubber products, for example, automobile tires (Nikolskii et al., 2014; Berlin et al., 2018). It has been proposed that HTSG could be used for processing polytetrafluoroethylene (PTFE) waste which is difficult to recycle (Allayarov et al., 2007a, 2017). When processing PTFE waste using the HTSG method, a prerequisite is preliminary exposure to ionizing radiation due to the physical-chemical properties of PTFE (Allayarov et al., 2017; Panshin et al., 1978). Preliminary γ-irradiation of PTFE leads to molecular-topological changes in its structure by partially destroying the polymer macromolecule which increases the number of defects allowing a critical value to be reached so that a rheological explosion occurs during HTSG (Olkhov et al., 2006; Allayarov et al., 2007b). In this case, the low radiation resistance of PTFE significantly increases the efficiency of radiation exposure to its post-radiation grinding (Gavrila and Gosse, 1994; Holmes-Walker, 1975). The HTSG of radiolyzed PTFE yielded powders of average sizes of

about 100–300 μm (Kotek et al., 2004).

Our previous work (Allayarov et al., 2024) on the irradiation and subsequent HTSG of PP focused on understanding the fundamental changes in the polymer using infrared spectroscopy and electronic structure calculations. In the current work, a comprehensive study of the effect of HTSG on the thermal, mechanical, and strength properties of γ-irradiated polypropylene is reported.

2. Experimental methods

2.1. Materials

PP waste due to manufacturing defects of the PPH007EX trademark produced by POLYOM LLC of the Omsk PP plant was used in the work. The original PP granules had a cylindrical shape with a diameter and height of 5 ± 1 and 2.5 ± 0.5 mm, respectively. The manufacturer stated that they did not contain impurities. An infrared study of these granules also showed no evidence of impurities (Allayarov et al., 2024).

2.2. γ-irradiation

Radiolysis by ^{60}Co γ-rays of PP samples was carried out in air using a UNU Gammatok-100 unit of the Federal Research Center for Problems of Chemical Chemistry and Medicinal Chemistry of the Russian Academy of Sciences at an input dose rate of 3 Gy/s γ-irradiation of oxygen exposed PP granules was carried out in 1 L glass vessels with a constant supply of oxygen.

2.3. High temperature shear grinding (HTSG)

Grinding of initially γ-irradiated PP samples was performed using special rotary dispersers at 200 ± 10 °C. HTSG was carried out in the "continuous rheological explosion" mode (Nikolskii et al., 2014; Wolfson and Nikolskii, 1997; Balyberdin et al., 1998). The rotational speed of the screw was 0.6 s^{-1}. The screw had a diameter of 32 mm and a length of 350 mm. The time window between the end of irradiation and the beginning of HTSG ranged from 1 h to 24 h due to the inertia of the dispersant entering the mode.

2.4. Thermal analysis

Thermal analyses of the samples including determination of the temperature of their phase transitions and enthalpies of melting and crystallization processes were preformed using a DSC822e differential scanning calorimeter (Mettler Toledo, Switzerland). A sample weighing 5–8 mg was cooled in a stream of nitrogen to −100 °C, kept at this temperature for 5 min, and then scanned in the temperature range −100 to +200 to −100 °C, at a rate of 10 °C/min. The time interval between the preparation of polymer samples and their analysis by differential scanning calorimetry (DSC) and thermomechanical analysis (TMA) was no more than two days.

2.5. Thermomechanical analysis

Thermomechanical analysis (TMA) of the polymer was performed following the established procedures used for the thermomechanical spectrometry of polymers (Olkhov et al., 2008, 2012). One of the measurements from TMA is the change in the linear size of the sample between the substrate and the probe. This measurement was completed when the temperature of the steady molecular flow was reached. The accuracy of the TMS method was previously analyzed (Jurkowski and Olkhov, 2004). Temperature measurements are ± 0.05 °C. The error in determining the molecular-topological parameters of the polymer was no higher than 10%.

2.6. Pressing/heating granules and powder

For two series of samples of PP from granules and powders obtained by grinding granules, mechanical properties were studied to compare them as a function of the accumulated input doses of γ-irradiation, as well as the presence/absence of the effects of shear grinding on the samples. To elucidate the effect of radiolysis and HTSG on the physical and mechanical properties of the material, irradiated PP granules and powders obtained from dispersion in the HTSG mode were pressed into homogeneous plates on a hydraulic press under the same pressing conditions for each polymer. To carry out the pressing, eight Teflon® spacers were placed in a collapsible mold equipped with a hole for a thermocouple in such a way as to completely cover the bottom of the mold with half of each spacer. Teflon® gaskets were used to prevent contamination of the inside of the mold and leakage of the polymer melt. Then, a portion of the powder or polymer granules weighing 6 g was distributed evenly over the entire area, and the free halves of the gaskets were stacked on top of each other and pressed from above with a large mold punch. The assembled form with the sample was placed between two heating plates of the press with holes for thermocouples. Temperature control was carried out using temperature controller TRM500 manufactured by Oven, Russia. Two Chromel-Copel thermocouples were connected to the thermostat. At the first stage of heating of the press plates, thermocouples were placed in the holes of the upper and lower plates; then, when the mold was placed between the plates, the thermocouple from the upper plate was placed in the hole in the mold. The conditions for pressing PP are given in Table 1.

2.7. Tensile strength properties of plates

From the pressed PP plates, samples in the form of blades were obtained to study the physical and mechanical properties using a punching knife. The resulting blades correspond to the parameters recommended by GOST 11262-2017 (GOST 11262-2017, 2018). The mechanical properties were studied on a universal testing machine ZWICK TC-FR 010 TH Material Testing Machine-test Control. The machine is equipped with a temperature chamber with a temperature range of −80°C to +250°C. The thickness of the PP blades was measured with a micrometer in the working area at three points on both sides, after which the samples were fixed in a tensile testing machine for tensile testing. If the maximum and minimum measured blade thickness differed by 0.2 mm or more, then it was not used for testing. The speed of the test was 12 mm/min.

3. Results and discussion

3.1. Thermal properties of γ-irradiated PP granules

The shape of the calorimetric curves provides useful information about the structural characteristics and thermal history of irradiated polymer samples. Figs. 1 and 2 show DSC thermograms of primary and reheating and cooling of samples of initial and irradiated PP granules and powders obtained by grinding the corresponding granules by HTSG.

Table 1
Pressing parameters for samples of irradiated PP granules and powder obtained by the HTSG method.

Stage #	Stage	Duration (min)
1	Press heating up to 200 °C	45
2	Placement of the mold with the sample between the plates of the press, heating up to 200 °C.	30
3	Maintaining the mold with the sample at 200 °C	20
4	Pressing a sample at a constant pressure of 2000 kgf/cm^2 and a constant temperature of 200 °C.	10
5	Gentle airflow cooling of the mold to room temperature	40

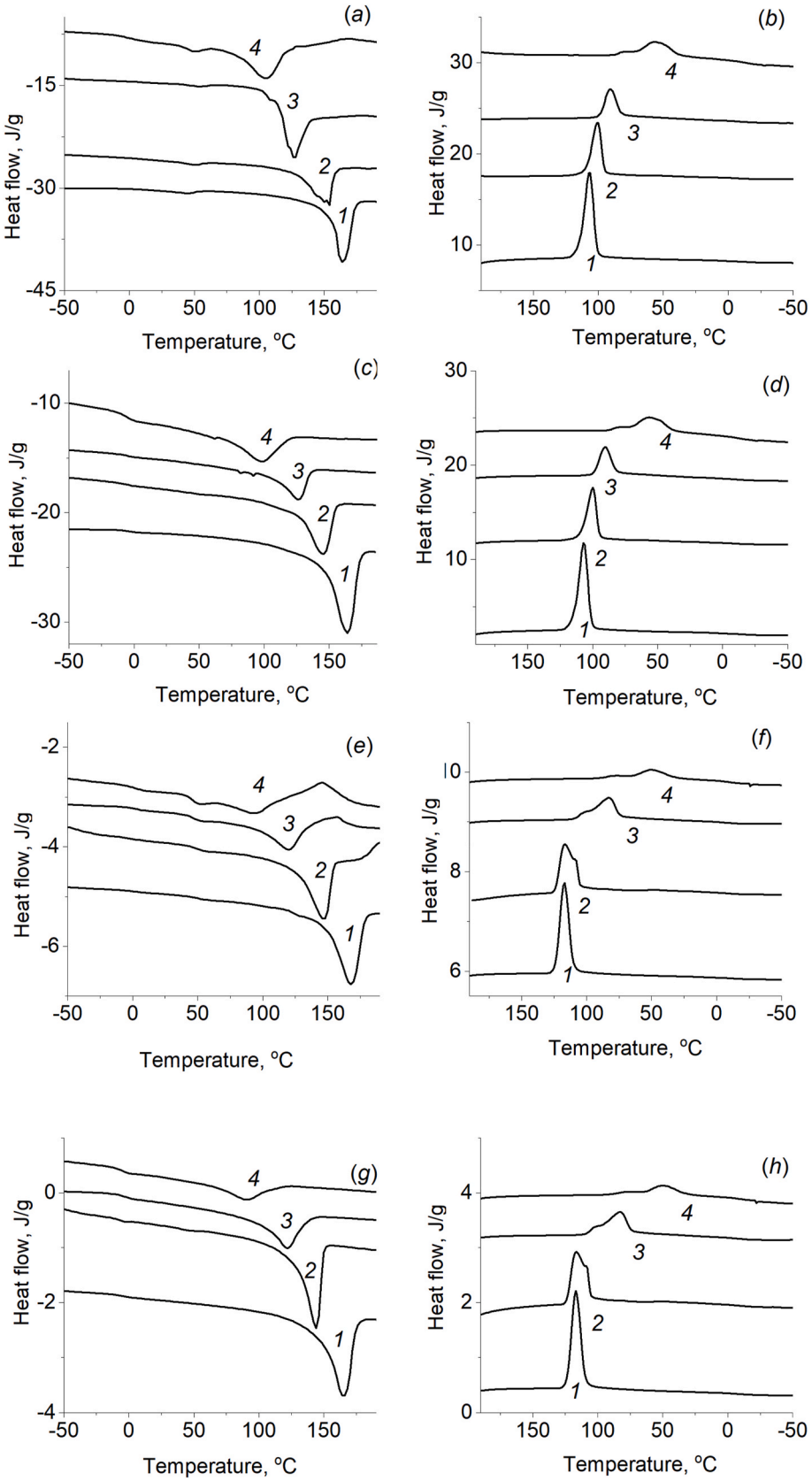

Fig. 1. DSC thermograms of the input dose dependence of γ-irradiation of PP granules (a, b, c, d) and powders (e, f, g, h) obtained after post-irradiation milling of the initial granules. Heating from −100 °C (a, c, e, g) and cooling from 200 °C (b, d, f, h) performed at a rate of 10 °C/min. Input doses of γ-irradiation (kGy) are: 0 (curve 1), 400 (curve 2), 2000 (curve 3), and 4000 (curve 4).

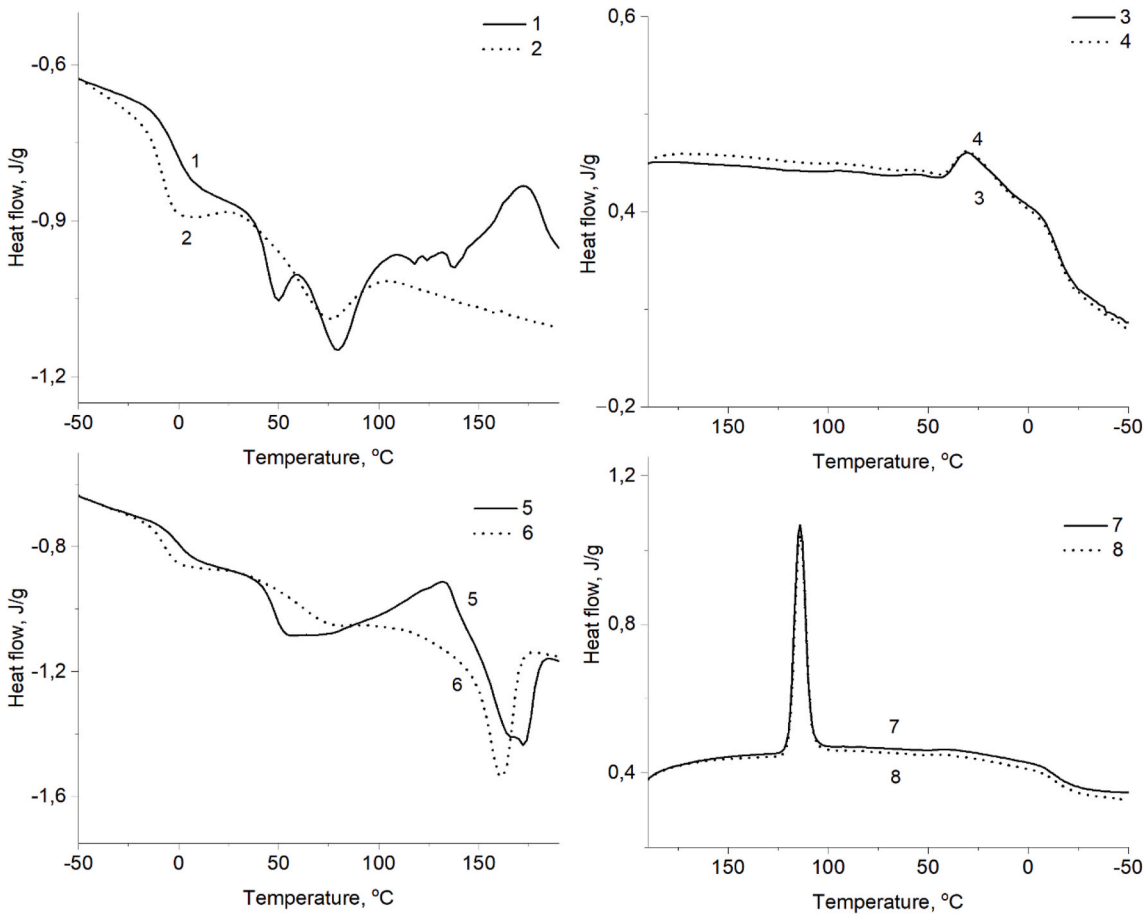

Fig. 2. DSC thermograms of PP granules (1, 2, 3, 4) irradiated with an input dose of 8000 kGy and powder (5, 6, 7, 8) obtained after post-radiation milling of these granules. Samples heated from −100 °C (1, 2, 5, 6) and cooled from 200 °C (3, 4, 7, 8) at a rate of 10 °C/min.

Thermal parameters determined from experimental DSC thermograms are shown in Table 2.

The DSC curve of the initial PP granules shows an endothermic melting peak with a maximum at 163 °C and a small glass transition step at −4 °C (Fig. 1a, curve 1). Such a melting temperature is characteristic of isotactic PP (Zhang et al., 2010) and indicates that the PP granules used in this work have an isotactic structure, like the samples of this polymer studied previously (Fintzou et al., 2007). Depending on the input dose of γ-irradiation, a change in the shape of the DSC thermograms is observed, both during heating (Fig. 1a) and during cooling after heating to 200 °C of irradiated PP samples (Fig. 1b). After irradiation, the melting and crystallization peaks of the polymer move towards

Table 2
Thermal parameters from DSC thermograms of irradiated PP granules and powder obtained after post-irradiation milling of irradiated granules.

Parameter[a]	Procedure[b]	Input Dose, kGy							
		0	80	200	400	1200	2000	4000	8000
granule									
Q_m, J/g	I	−79.5	–	−80.3	−76.3	−79.8	–	−24.2	−20.3
Q_m, J/g	II	−89.7	–	−93.9	−92.6	−58.4	−59.4	−28.2	−12.2
Q_{cr}, J/g	I	93.4	–	92.5	77.1	60.1	49.2	27.9	−23.7
Q_{cr}, J/g	II	93.1	–	86.2	76.3	59.2	58.7	25.6	−22.0
T_m, °C	I	163.0	157	148.8	146.2	134.0	126.6	104.6	
T_m, °C	II	163.7	158	151.6	143.3	134.3	126.0	97.3	
T_{cr}, °C	I	107.3	105	103.4	100.8	97.0	90.8	56.7	
T_{cr}, °C	II	107.3	105	103.5	100.1	95.9	90.5	56.5	
Powder									
Q_m, J/g	I	−67.0	−83.2	−76.2	−66.4	−73.7	−49.9	−25.2	−24.9
Q_m, J/g	II	−72.0	−96.9	−86.8	−78.8	−66.2	−51.3	−30.6	−22.1
Q_{cr}, J/g	I	91.9	97.7	87.0	79.9	66.5	55.3	32.0	25.8
Q_{cr}, J/g	II	88.5	97.0	86.1	76.9	66.3	53.4	30.5	25.8
T_m, °C	I	167.0	164.0	157.3	146.7	132.1	120.0	94.5	164.18
T_m, °C	II	164.4	156.8	152.2	143.7	133.4	121.2	90.4	160.8
T_{cr}, °C	I	117.9	124.9	124.5	117.0	101.4	83.0	50.1	114.5
T_{cr}, °C	II	117.6	123.8	124.0	116.8	101.4	83.0	49.9	114.3

[a] Temperatures of melting (T_m) and crystallization (T_{cr}) and heats of melting (Q_m) and crystallization (Q_{cr}).
[b] Data obtained at the primary scan (I) and re-scanning (II) of the DSC-thermogram.

lower temperatures. An analysis of the experimental curves made it possible to obtain a set of DSC parameters for the irradiated samples as illustrated in Figs. 3 and 4, and in Table 2, as a function of the input dose of irradiation of the granules.

Curve 1 in Fig. 3 of the dependence of the temperature of the maximum melting rate on the input dose of irradiation of PP granules shows that an increase in input dose to 500 kGy leads to a rapid decrease. This steep decrease is followed by a linear decrease with a less steep slope for input absorbed doses from 500 to 4000 kGy. The decrease in the melting temperature of irradiated granules is mainly associated with chain destruction and a decrease in the molecular weight of the polymer depending on the input absorbed dose (Yagoubi et al., 1999; Dole, 1972; Zhang et al., 2010). A decrease in the melting temperature with an increase in the input absorbed dose is associated with breaking bonds in the main chain in the amorphous regions of the polymer (Dahal and Kim, 2013). A decrease in the crystallization temperature of PP granules with an increase in the input absorbed dose (curve 3, Fig. 3) is most likely due to the polymer becoming amorphic because of a decrease in the number and size of crystalline domains as a result of chain destruction (Krupa and Luyt, 2001; Dahal and Kim, 2013).

Irradiation with high-energy radiation, in addition to radiation-chemical processes, can also cause structural damage in the crystalline matrix of the polymer introducing defects into the primary crystalline structure. As a result of the accumulation of point radiation defects with an increase in the input radiation dose, stable structures with their own melting peaks can arise. These additional species are hypothesized to be the source of the appearance of shoulders in the melting peaks of the polymer on DSC thermograms of irradiated PP granules (Fig. 1, curves 2–4). The results obtained by analysis of the IR spectra (La Mantia, 2002) provided further confirmation of the amorphization of PP with an increase in the input absorbed dose.

A decrease in PP crystallinity with input absorbed dose leads to a decrease in the enthalpy of melting (curve 1) and crystallization (curve 5) of irradiated PP granules (Fig. 4). At the same time, there is a noticeable decrease in the heat of fusion of granules during irradiation in the input dose range of 1000–4000 kGy. Note that smaller doses (<1000 kGy) do not lead to any noticeable changes in the heat of fusion of irradiated granules. The curve of the heat of crystallization released during cooling after heating to 200 °C of irradiated PP granules (Fig. 4, curve 5) shows the absence of the effect of low input doses of irradiation on the heat of crystallization of the polymer. A further increase in the input absorbed dose to 4000 kGy is accompanied by a rapid decrease in the heat of crystallization.

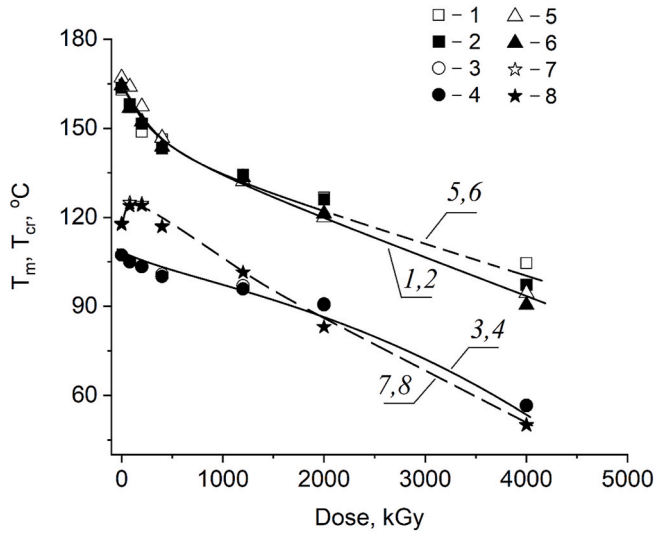

Fig. 3. Dependence on the dose of γ-irradiation of the melting temperature (1, 2, 5, 6) and crystallization (3, 4, 7, 8) in samples of irradiated granules (1, 2, 3, 4) and powders (5, 6, 7, 8) obtained for HTSG irradiated granules. DSC thermograms taken during the primary scan (1, 3, 5, 7) and re-scan (2, 4, 6, 8).

To study the changes in melting and enthalpy of irradiated PP granules during the primary heating and cooling procedures, an additional reheating and cooling procedure was carried out for the polymer samples. DSC thermograms of reheating and cooling of irradiated PP granules are shown in Fig. 1c and d, respectively. After reheating non-irradiated PP granules, there is a melting peak with a maximum at 163.7 °C (Fig. 1c, curve 1). During cooling to −100 °C of this sample, initially preheated to 200 °C, the crystallization peak is observed at 107.3 °C (Fig. 1d, curve 1). Melting (163.0 °C) and crystallization temperatures (107.3 °C) were observed on DSC thermograms during the initial scanning of non-irradiated granules. In the samples of granules, there is an overlap of the values of the heat of crystallization during rescanning with the heat of crystallization released during the primary cooling of polymer granules initially heated to 200 °C. A similar overlap of melting and crystallization temperatures, as well as the heat of crystallization during the initial and repeated scanning of DSC thermograms, is observed for heating and cooling of γ-irradiated PP granules. Thus, during the primary scanning, no post-radiation physical-chemical or chemical processes leading to a change in the molecular weight of the polymer or other properties, which would change the melting and crystallization temperature during the re-scanning, occur. In addition, the primary heating of the irradiated polymer to a melt does not affect its viscosity, which determines the rate of nucleation and growth of crystals, and ultimately, the heat of crystallization of irradiated granules.

During repeated scanning, the heat of fusion of granules irradiated with input doses up to 80 kGy (curve 3, Fig. 4) is approximately 10% higher than the heat of fusion of the same granules during their primary scanning (Fig. 4, curve 1). However, such a difference during the primary and rescanning in the heats of melting of irradiated granules disappears at absorbed doses of 400–8000 kGy. The increase in the heat of fusion during reheating is associated with the recrystallization of radiation damaged regions of the polymer matrix crystal structure during the primary heating to the melt of granules irradiated with an input dose of 80–400 kGy. Defects in the crystal structure introduced by radiation are eliminated during the primary heating of the irradiated sample, so the heat of crystallization of the polymer during rescanning coincides with the heat of crystallization of primary cooling.

It has previously been observed (Auhl et al., 2004; Vıctor et al., 2015) that there is a decrease in the melting temperature and enthalpy of melting during rescanning of irradiated PP samples, as compared to their initial scans. During primary heating, post-radiation destruction occurs due to radical centers inside the crystalline regions of the irradiated polymer, which leads to a decrease in the thermophysical properties of the polymer during rescanning. The differences in the effects of primary scanning on the thermophysical parameters of irradiated granules in the current work and prior work (Zhang et al., 2010; Berlin et al., 2018) are associated with the specifics of the irradiation conditions and the nature of the PP samples.

Significant changes in the crystallinity of PP granules depending on the input absorbed dose, (Figs. 3 and 4) may be associated with an increased temperature of the radiolysis of the granules. The radiolysis temperature of 65 °C can contribute to the occurrence of radiation-chemical processes in the solid matrix of granules γ-irradiation. To study possible relaxation processes associated with the movement of units of macromolecules initiated by heating to 65 °C, a thermomechanical analysis of PP granules was performed in the temperature range from −100 °C to 200 °C. The thermomechanical curve of PP granules (curve 1 Fig. 5) is characteristic of a di-block polymer with a pseudo-network structure. According to the theory of thermomechanical spectrometry, (GOST 11262-2017, 2018) such a polymer matrix consists of an amorphous block, and crystalline fragments of macromolecules serve as branching nodes of the polymer pseudo-network. In the process of heating the polymer from −100°C, the vitrified structure expands at a constant rate, characterized by a coefficient of linear thermal expansion

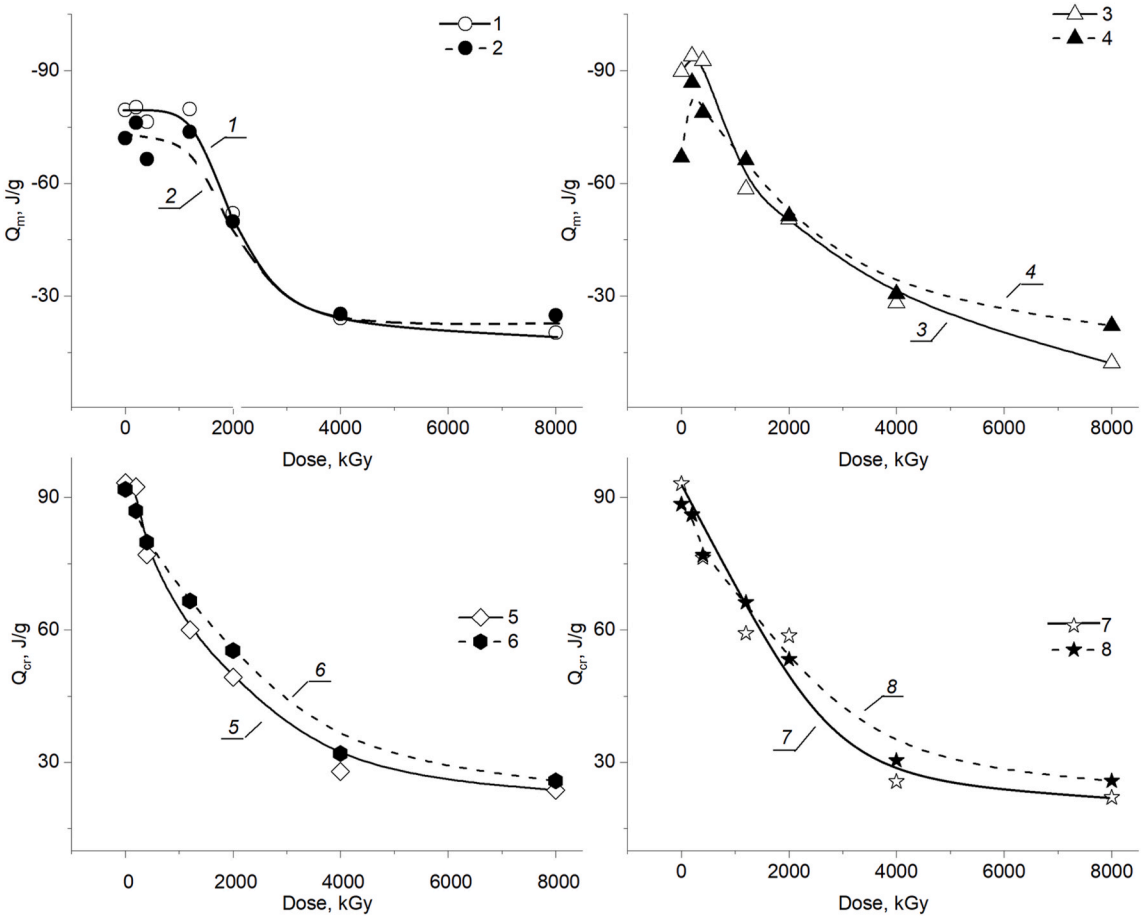

Fig. 4. Dependence on the dose of γ-radiation of PP granules of thermal effects of melting (1, 2, 3, 4) and crystallization (5, 6, 7, 8) in irradiated granules (1, 3, 5, 7) and PP powders (2, 4, 6, 8) obtained by HTSG of the respective irradiated beads. DSC thermograms taken during the primary scan (1, 2, 5, 6) and re-scan (3, 4, 7, 8).

$\alpha_1 = 4.35 \times 10^{-5}$ deg^{-1}. At a temperature of about −18 °C, the segmental mobilities of the internodal chains of the pseudo-network begin to unfreeze and the transition region of the thermomechanical curve (curve BC) is formed. This region contains the envelope of deformation jumps performed by polymer homologues of different molecular weights when they complete segmental relaxation.

The highest molecular weight internodal homolog of this block passes into the sol state at a temperature $T_\infty = 100$ °C (point C). After point C, the polymer passes into the region of a plateau of high elasticity (straight line CD). In this area, the polymer expands due to free volume at a rate of $\alpha_2 = 21.6 \times 10^{-5}$ deg^{-1}. Upon reaching a temperature of 151 °C, a sharp increase in the expansion rate to $\alpha_k = 45.7 \times 10^{-5}$ deg^{-1} is observed on the thermomechanical curve of PP granules. The amorphous state is characterized by a certain ratio between the coefficients in the glassy state (α_1) and the highly elastic state (α_2), namely, $\alpha_2/\alpha_1 \leq 6$. It has been shown, (Olkhov and Jurkowski, 2005) that in the thermomechanical analysis of crystalline polymers at the beginning of the melting of the crystalline fraction, the polymer expands at a rate (α_{cr}) exceeding the same rate in the amorphous state (α_1). The condition for assigning the type of polymer change is the inequality $\alpha_{cr}/\alpha_1 \geq 6$. According to this condition, the change observed at 151 °C (point D) with the expansion rate ratio $\alpha_{cr}/\alpha_1 = 10.5 > 6$ is the result of the onset of melting of the crystalline modification of PP. The molecular flow of a polymer, as in any linear polymer, begins after the completion of relaxation at the highest temperature phase transition. In the granules of the investigated PP, molecular flow occurs at $T_f = 177$ °C (curve OT) after the melting of the crystalline modification. The beginning of molecular flow of PP granules practically coincides with the end of their melting peak on the DSC thermogram (Fig. 5, curve 2).

Based on the thermomechanical analysis, at the moment of γ-irradiation of PP granules at 65 °C in the amorphous phase of the polymer, the process of relaxation of macromolecules and the transition of polymer homologues of this topological block to the sol state occurs. Consequently, this contributes to intramolecular and intermolecular radiation-chemical processes of destruction and cross-linking of polymer macromolecules under a beam of γ-rays. Thus, γ-irradiation at 65 °C damages the crystal structure of the polymer to a greater extent than radiolysis at room temperature.

The analysis of experimental heating data and melting and crystallization temperatures from DSC thermograms during the initial and repeated scanning of PP granules irradiated with an initial dose of up to 12,000 kGy revealed a decrease in the crystallinity of the polymer up to an input absorbed dose of 4000 kGy, and a sharp decrease in melting and crystallization of the irradiated polymer. At the same time, an increase in the input absorbed dose from 4000 to 8000 kGy does not lead to further noticeable changes in the parameters of the thermal effects of irradiated granules. The heat of fusion of PP granules after 8000 kGy of irradiation decreases to 26.2 J/g, compared with the heat of fusion of 84.6 J/g of non-irradiated PP.

3.2. *Thermal properties of the powder obtained by HTSG of γ-irradiated PP granules*

Fig. 1e shows the dependence of the shape of DSC thermograms of PP powders obtained after grinding the corresponding radiolyzed polymer granules on the input absorbed dose. A comparative analysis of DSC thermograms shows that the general form of the powder heating curves (Fig. 1e, curves 2, 3) coincides with the heating curves of the

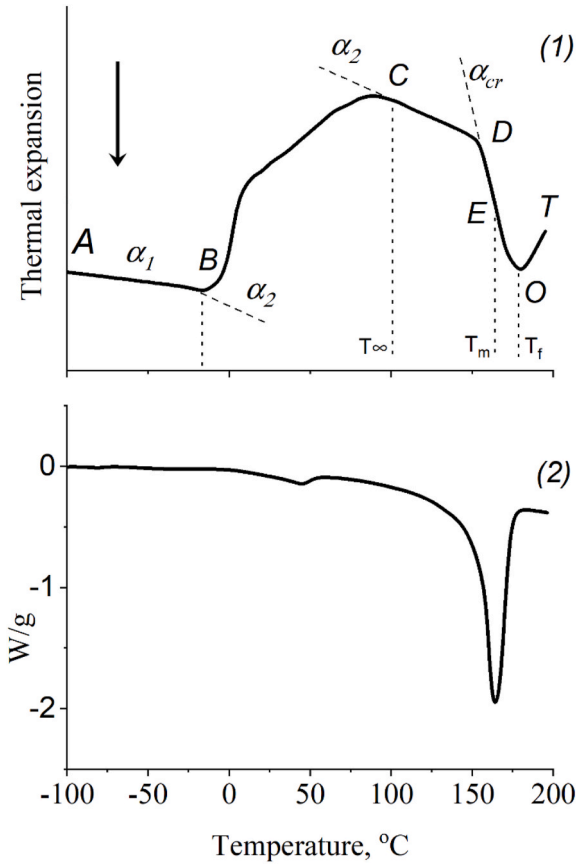

Fig. 5. Thermomechanical curve (1) and DSC thermogram (2) of granules of PP.

corresponding irradiated polymer granules (Fig. 1a, curves 2, 3) for granule input absorbed doses up to 2000 kGy. One endothermic melting peak of a crystalline polymer with close melting temperatures (Fig. 3, curves 1, 5) is observed. Input absorbed doses of 4000 kGy and above lead to noticeable differences in the heating curves of powders and corresponding granules. Analysis of the heating curves of these powders is complicated by their multicomponent nature (Fig. 1, curve 4; Fig. 2, curve 5). Subtle exothermic peaks are observed ($T_{m1} = 170.5°C$ ($Q_{m1} = 10.16$ J/g), $T_{m2} = 116.5°C$ ($Q_{m2} = 15.96$ J/g), $T_{m3} = 148.5°C$ ($Q_{m3} = 2.39$ J/g)) and kinks appear at temperatures of −5.05°C, 46.9°C, and 68.55°C, corresponding to a smooth change in the heat capacity in the polymer sample, on the heating curve of PP powder obtained by grinding granules irradiated with an input dose of 12,000 kGy. No such peaks are observed on the DSC heating curve of PP granules irradiated with an input dose of 12,000 kGy before grinding. Some components of the macromolecules in the powder obtained by grinding PP granules irradiated with input doses of 8000–12,000 kGy can be readily ordered and form structural regions during grinding. These regions are similar in their thermal characteristics to crystallites of non-irradiated PP. In contrast to the thermogram of the granules irradiated with an input dose of 8000 kGy (Fig. 2, curves 1–4), where there are practically no melting and crystallization peaks, the DSC thermograms of the powder obtained by grinding such granules (Fig. 2, curves 5–8) exhibit melting and crystallization, which have temperature maxima coinciding with the peak temperatures of melting and crystallization of non-irradiated PP granules. In the PP powder obtained by grinding granules irradiated with an input dose of 12,000 kGy, several fractures are noted, likely related to the glass transition, which does not allow one to unambiguously determine the glass transition temperature of such a powder. In other cases, the glass transition temperature of both granules and powders obtained during their grinding is within 7 ± 3 °C.

In contrast to the coincidence of the melting temperatures of the granules (curve 1, Fig. 3) and the corresponding powders (curve 5, Fig. 3) in the irradiation input dose range of 80–4000 kGy, overlap in the crystallization temperatures of the granules (curve 3, Fig. 3) and the corresponding powders (curves 7, Fig. 3) is observed only at input radiation doses above 1000 kGy. At input doses smaller than 1000 kGy, a strong dependence on the irradiation input dose of the initial granules is observed on the curves of the powder crystallization temperature with a maximum at 200 kGy (Fig. 3). The crystallization temperature of the powder is higher than the crystallization temperature of the corresponding granules. At such input absorbed doses, the heat of fusion of powders (curve 2, Fig. 4) is slightly less than the heat of fusion of the corresponding granules (curves 1, Fig. 4). The heat of fusion in the corresponding powders is also observed during repeated DSC scanning of irradiated granules and powders. In the process of grinding polymer granules irradiated with an input dose of up to 1000 kGy, powders with a lower crystallinity than the granules themselves are obtained.

The dependence of the heat of melting and crystallization of the powder coincides with those for the corresponding granules, both in the process of primary and re-scanning of the DSC thermogram (Fig. 3). An analysis of the data shows that the melting and crystallization temperatures of the powders practically coincide with those of the corresponding PP granules irradiated with input doses of 1000 kGy–4000 kGy (Fig. 3). It was experimentally established at all input absorbed doses except for 12,000 kGy, that the rate of decrease in the heat of fusion and crystallization of powders (curves 2, 6, Fig. 4) is comparable to the rate of change in these parameters of PP granules (curves 1, 5, Fig. 4). Further evidence of the similarity of the crystallinity of the powders to the crystallinity of the granules from which they were obtained was observed (La Mantia, 2002) in the IR spectra which is also sensitive to crystallinity. This conclusion is consistent with the DSC-thermograms of primary (Fig. 1a–e) and reheating (Fig. 1c–g), as well as primary (Fig. 1b–f) and repeated (Fig. 1d–h) cooling of the studied samples of both PP powders (Fig. 1e, f, g, h) and corresponding irradiated PP granules (Fig. 1a, b, c, d). On the basis of the data, we suggest that the nature of the change in the thermophysical parameters of powders and granules largely depends on the effect of radiation on the content and structure of the crystalline phase of PP granules from which the powders are obtained after grinding. Thus, the powders obtained by the HTSG method have a crystallinity close to that of the initial irradiated granules.

3.3. Thermal destruction of irradiated PP granules and powders obtained by HTSG

During the heating of PP granules, a single-step curve is observed on the TGA curve (Fig. 6, curve 1). From 341 °C to 460 °C, the rate of polymer mass loss gradually increases with increasing temperature. When heated from room temperature to 341 °C, the weight of PP decreases by less than 1.5 wt %. A further rise in temperature from 341 °C to 430 °C leads to additional degradation at a constantly increasing rate, and the polymer weight is reduced by 54%. As the temperature rises from 430 °C to 460 °C, the loss of mass has an approximately linear correlation with temperature at a rate of 1.67% per degree of temperature rise. After heating to 460 °C, about 4% of the primary mass remains in the polymer, which decreases to 1% upon heating to 465 °C. Then the mass of the charred residue slowly decreases to 0.08% of the primary mass of polymer granules after heating to 600 °C.

Fig. 6 shows the TGA curves of PP granules irradiated with different input doses of γ-radiation. A comparative analysis of the TGA curves of samples of the original and γ-irradiated PP granules showed that irradiation input doses of granules up to 1000 kGy does not lead to noticeable changes in the TGA curves. There is even a slight decrease in the effective decomposition rate, especially at low input absorbed doses of 80–400 kGy (Fig. 6, curve 2). However, input doses of γ-radiation above 1000 kGy lead to a shift to lower temperatures for the effective

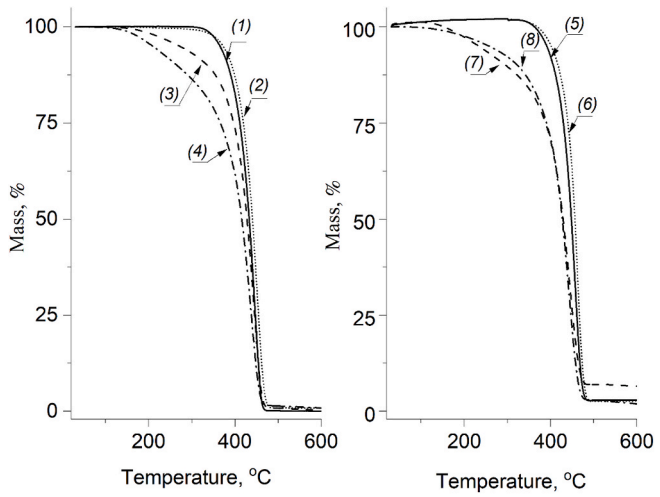

Fig. 6. Thermogravimetric curve of PP granules (1, 2, 3, 4) and powder obtained by grinding (5, 6, 7, 8) before (1, 5) and after γ-irradiation of granules with an input dose (kGy): 200 (2, 6), 8000 (3.7), and 12,000 (4, 8).

destruction of PP granules (Fig. 6, curves 3, 4).

The dependence of the temperature of the beginning of the destruction of PP granules on the input dose of γ-irradiation is shown in Fig. 7 (curve 1). There is a rather strong decrease in the temperature of the onset of thermal degradation of irradiated granules with an increase in the input absorbed dose above 4000 kGy, Destruction of granules irradiated with 4000 kGy begins at 344 °C, only 3 °C lower than the beginning of the destruction of non-irradiated granules. After irradiation of granules up to 8000 kGy, the onset of thermal degradation decreases to 303 °C, and the destruction of granules irradiated with an input dose of 12,000 kGy begins at a temperature that is 144 °C lower than the temperature of the onset of destruction of non-irradiated granules. The dependence of the temperature for a 16% loss (curve 2), 50% loss (curve 3), and 84% loss (curve 3) of the initial polymer mass on the dose of γ-irradiation is shown in Fig. 7. A loss of 16% of the mass of the polymer follows the pattern, the higher the input dose of irradiation of PP granules, the lower the temperature of loss of this mass by the polymer. The input dose of preliminary γ-irradiation has practically no effect on the temperature of 50% or more loss of its initial mass. This is clearly

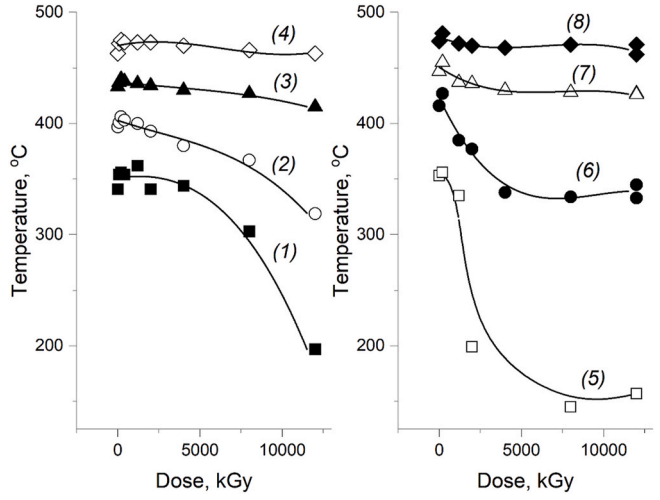

Fig. 7. Dependence of the temperature onset of effective thermal degradation (1, 5), loss of 16% (2. 6), 50% (3. 7) and 84% (4. 8) of the polymer mass during heating of granules (1, 2, 3, 4) and polymer powder (5, 6, 7, 8) obtained by grinding the corresponding granules on the input γ-absorbed dose of PP granules.

illustrated in Fig. 6, which shows that the higher the heating temperature, the greater the proportion of thermally degraded polymer, and the smaller the dependence of this proportion on the input dose of irradiation of the granules. As a result, in granules irradiated with an input dose of 8000 kGy, the loss of 50% of the initial mass of the polymer occurs at 451 °C, only 1 °C lower than the loss of the same mass in non-irradiated granules (Fig. 7, curve 4). The loss of 16% of the initial mass of granules irradiated with the same input dose occurs when the granules are heated to a temperature of 367 °C, which is 30 °C lower than the temperature required for loss of the same percent mass by non-irradiated polymer granules (Fig. 7, curve 2). The higher the heating temperature, the smaller the difference in the proportions of thermally decomposed parts of polymer granules irradiated with different input doses. Radiation oxidation products with low thermal stability accumulate in a narrow surface band of irradiated granules and these products decompose at relatively low temperatures. The thermal decomposition of such structures created by radiation leads to a decrease in the temperature of the onset of thermal destruction. For thermal destruction of 50% or more of the polymer mass, both polymer granules that are not subject to radiation oxidation, but irradiated and not subjected to radiolysis, decompose. As shown in Fig. 7 (curves 3, 4), such granules have similar thermal stabilities and control the kinetics of polymer decomposition in the high temperature region for loss of polymer mass >50%.

The TGA curves (Fig. 6, curves 5, 6, 7, 8) for heating of the PP powder obtained by grinding irradiated granules are similar to the TGA curves of the corresponding granules (Fig. 6, curves 1, 2, 3, 4). A distinctive feature of TGA of PP powders as compared to their granular analogs is the decrease in the temperature of the onset of thermal degradation of powders. For example, thermal degradation of PP granules irradiated with an input dose of 2000 kGy begins at a temperature of 303 °C, which is 158 °C higher than the temperature of the start of destruction of the powder obtained by grinding such granules. However, for polymer mass loss >50%, the difference in the mass loss rates of the powder (curves 7, 8) and the corresponding granules (curves 3, 4 for samples irradiated with any dose essentially disappears (Fig. 7). Powders obtained by grinding irradiated granules begin to thermally decompose at relatively lower temperatures than the corresponding granules.

Further evidence that the grinding of PP granules by the HTSG method to a powder leads to a decrease in the thermal stability of the polymer is a comparative analysis of the change in the color of the powder and the corresponding granules depending on the heating temperature. There is a noticeable decrease in thermal stability after HTSG when the powders obtained after grinding γ-irradiated granules are heated. A change in the color from light yellow to light brown of the granules irradiated with an input dose of 400–500 kGy is observed on heating to 120 °C. When the temperature rises to 145 °C and above, the powder becomes dark brown. On heating non-irradiated PP granules to 200 °C, no color change is observed, and they remain transparent. The change in the color of PP granules, observed when a polymer is irradiated with γ-rays, is due to the accumulation of various chromophore and auxochromic groups in the polymer structure due to radiation degradation of polymer chains (La Mantia, 2002). Heating the powder is accompanied by thermal degradation with the formation of similar molecular fragments, leading to a change in color. The powders obtained by HTSG of irradiated PP granules have low thermal stability as compared to the stability of the corresponding granules. The HTSG process reduces the thermal stability of PP during the transition from irradiated granules to powder.

3.4. Tensile strength properties of PP plates

Fig. 8 shows the dependence of the ultimate tensile strength of samples made from granules and PP powder obtained by grinding granules after preliminary radiolysis with various input doses of irradiation. The tensile strength values are almost the same for samples obtained by pressing the original granules and the powder obtained by

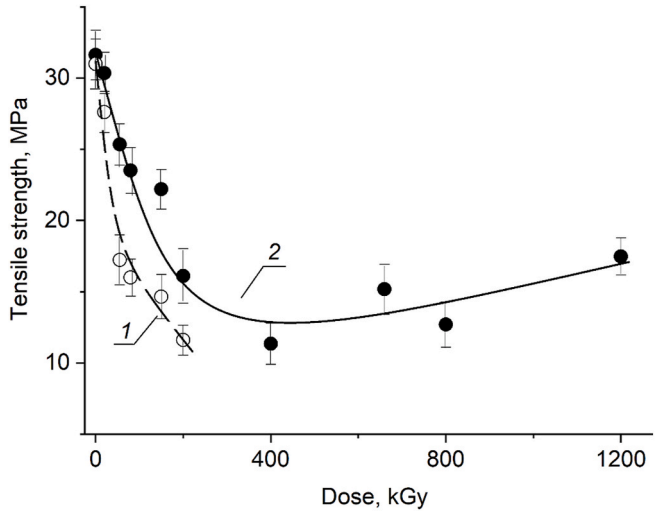

Fig. 8. Dependence of the tensile strength of plates from granules (1) and from their powder (2) on the input dose of preliminary γ-irradiation of PP granules.

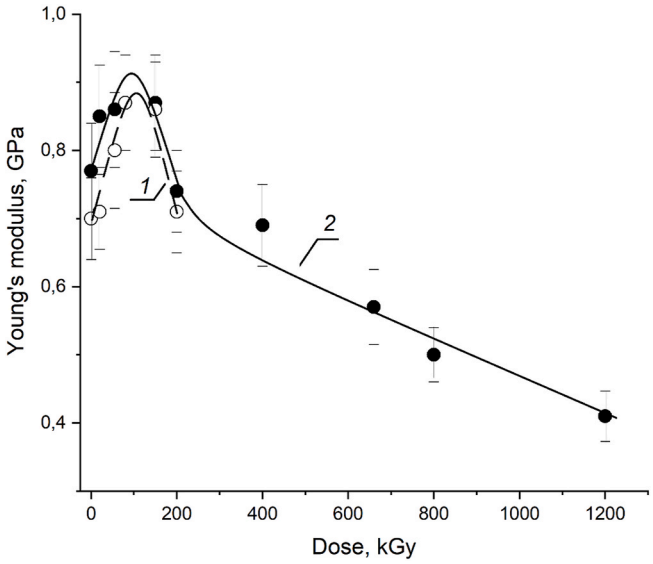

Fig. 9. Dependence of the Young's modulus of plates from granules (1) and the powder obtained by grinding the corresponding granules (2) on the dose of preliminary γ-irradiation of PP granules.

dispersing non-irradiated PP granules. With an increase in the input absorbed dose, a sharp drop in the value of the tensile strength at low absorbed doses is observed for both series of samples. In plates obtained by pressing a powder made by dispersing irradiated granules, a decrease in tensile strength occurs up to an input dose of 200 kGy; further increase in the input absorbed dose leads to an insignificant increase in tensile strength. The decrease in tensile strength is associated with the predominance of the processes of destruction of macromolecules over the processes of their crosslinking during γ-irradiation with input doses up to 200 kGy. A slight increase in the tensile strength at input doses above 400 kGy is associated with the predominance of crosslinking over the process of polymer degradation. Thus, in PP plates made from powders obtained by grinding pre-irradiated polymer granules, crosslinking processes begin to manifest with an increase in the input dose of radiation above 400 kGy. This is indirectly indicated by the fact that samples from granules irradiated with input doses of more than 200 kGy did not melt during pressing. Such plates were a mosaic of aggregated granules.

A comparative analysis of the tensile strength of plates obtained from granules and their powders shows that the degree of heterogeneity in the distribution of chemical structures created during the radiation oxidation of macromolecules in the volume of the irradiated polymer is important in determining the tensile strength of an air-irradiated polymer. As a result of HTSG, the powder obtained by grinding granules irradiated by a wide input dose range (80–8000 kGy) can be easily pressed into uniform plates on a hydraulic press. In addition, the tensile strength of such plates increases with an increase in the input absorbed dose of the initial polymer granules due to an increase in molecular weight as a result of radiation induced crosslinking. Shear grinding with mechanical heating destroys the most stressed areas of irradiated granules and creates conditions for the thermal decomposition of oxygen-containing functional groups introduced in large quantities on the surface of irradiated granules by radiation oxidation. Grinding also redistributes such groups from a thin surface layer of the granules into the volume of the powder, thereby significantly reducing the likelihood of mutual fusion of the radiation-oxidized surface, which reduces the strength properties of the plates.

The dose dependence of the Young's modulus of plates made from irradiated PP granules and their powders is shown in Fig. 9. From the analysis of these curves, for samples made from granules and powders obtained from granules, at low input doses (up to 150 kGy), there is a slight increase in the value of Young's modulus, and with a further increase in the absorbed dose, Young's modulus decreases. This indicates the initiation of stress relaxation processes. PP granules have areas of residual stresses in their structure due to the production processes. Small input doses of radiation promote processes that can relax residual stresses in the structure. Indeed, low input doses of irradiation have been shown to initiate relaxation processes in the region of residual stresses in polyolefins, which leads to an increase in the strength of macromolecule chains (Allayarov et al., 2005). Since the input absorbed doses are small, the destruction processes do not have a strong effect on the elasticity of the material, and the main contribution to the ability to elastically deform under tension is the relaxation of residual stresses in the structure of the granules. The decrease in the Young's modulus observed at input absorbed doses above 150 kGy is associated with amorphization of the crystalline zones under the action of irradiation. As irradiation causes significant changes in the structure of PP macromolecules, the geometries of the macromolecules change. This prevents the chains from forming a regular arrangement and, consequently, reduces the degree of crystallinity. With an increase in the input dose of irradiation of polymer granules, cross-linking bonds accumulate. These bonds are the sources of reduction of the plasticity of plates made of polymer powders, which increase tensile stresses, and reduce the rate of decrease of the Young's modulus with input absorbed dose. Thus, the decrease in the value of Young's modulus, observed at input absorbed doses above 150 kGy, may also be the result of amorphization of crystalline zones under the action of irradiation.

4. Conclusions

The effect of ^{60}Co gamma input absorbed doses from 80 to 12,000 kGy on the thermophysical properties and thermal stability of polypropylene (PP) granules, powders, and plates was studied. The current work shows that this range of input absorbed doses significantly changes the thermophysical, thermal, and other properties of both the irradiated granules and the powder obtained by grinding the irradiated granules. The DSC curve of non-irradiated granules and powders have a melting peak characteristic of isotactic PP. Due to chain destruction and a decrease in the molecular weight of the polymer with an increase in the input absorbed dose to 500 kGy, there is a rapid decrease in the temperature of the maximum melting rate. Input absorbed doses of 500–4000 kGy of granules and their corresponding powder from HTSG led to much smaller changes on the DSC thermograms. The decrease in the crystallization temperature with an increase in the input absorbed

dose is associated with amorphization of the structure of polymer granules, most likely due to a decrease in the number and size of crystalline domains due to chain destruction. The crystallization temperature and melting heat of granules and corresponding powders are the same only for samples of granules irradiated with an input dose of more than 1000 kGy. At input absorbed doses less than 1000 kGy, a strong dependence of the powder crystallization temperature on the input absorbed dose is observed with a maximum at 200 kGy; the crystallization temperature of the powder is higher than the crystallization temperature of the corresponding granules. In the process of grinding polymer granules irradiated with an input dose of up to 1000 kGy, the powders have a lower crystallinity than the initial granules. Thermomechanical analysis showed, at 65 °C in the amorphous phase of the polymer, that relaxation of macromolecules and the transition of polymer homologues of this topological block into the sol state occurs. Input absorbed doses of granules up to 1000 kGy shows a slight decrease in the rate of effective decomposition of γ-irradiated granules, especially at input absorbed doses of 80–400 kGy. A further increase in the dose of γ-radiation leads to a shift to lower temperature for the effective destruction of PP granules. There is a lower temperature for the onset of thermal degradation in powders. A noticeable decrease in the tensile strength of plates made from granules, as well as from the corresponding powders, is observed due to the predominance of degradation processes over cross-linking when irradiating granules to 200 kGy. An increase in the input absorbed dose above this level leads to an increase in the tensile strength of the plates made from the powder of irradiated granules. Shear grinding during heating leads to a relatively homogeneous plate in the process of pressing due to mechanical destruction of the most stressed areas of irradiated granules. During heating to 200 °C, thermal decomposition of oxygen-containing functional groups introduced on the surface of irradiated granules by radiation oxidation processes occurs. The grinding of granules to powder by the HTSG method redistributes similar functional groups from the thin surface of the granules into the volume of the powder sample, significantly reducing the probability of mutual fusion of only the radiation-oxidized surface of the granules.

Radiation treatment in combination with post-radiation high-temperature shear grinding could be used to modify polymers properties to improve the processing of polypropylene waste due to the following factors: (i) the radiolysis induces molecular topological changes in the structure of PP partially destroying the macromolecules and increasing the number of defects so that a critical value for a rheological explosion during HTSG can be reached, thereby it is reduced energy consumption for grinding; (ii) the radiation functionalization of the polymer macromolecules makes it possible to modify the surface properties of both the polymer waste itself and the powder obtained after grinding the irradiated polymer, which significantly expands the scope of polymer waste processing products; (iii) post-irradiation shear grinding of irradiated waste makes it possible to obtain relatively homogeneous powders and durable plates during the pressing process due to the redistribution of functional groups introduced into the thin surface of irradiated initial polymer waste during irradiation throughout the powder obtained by grinding. This significantly reduces the likelihood of having only a radiation-oxidized surface of the polymer waste, which is not conducive to forming plates. The study presented here, in conjunction with our prior IR and computational study, (Allayarov et al., 2024) helps to provide the basis for irradiation aided polymer recycling as highlighted by the IAEA. (See the IAEA Nuclear Technology).

CRediT authorship contribution statement

Sadulla R. Allayarov: Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Sergei V. Demidov:** Writing – review & editing, Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Data curation. **Artur T. Kapasharov:** Writing – review & editing, Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Data curation. **Oleg N. Golodkov:** Writing – review & editing, Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Data curation. **Georgii V. Malkov:** Writing – review & editing, Writing – original draft, Visualization, Validation, Investigation, Formal analysis, Data curation. **Matthew P. Confer:** Data curation, Formal analysis, Investigation, Visualization, Writing – review & editing. **David A. Dixon:** Writing – review & editing, Writing – original draft, Resources, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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