



GC investigation of post-irradiation oxidation phenomena on polypropylene

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Abstract. The paper summarizes the results of research on gas products of polypropylene (PP) radiolysis. Particular attention was paid to the phenomena of post-radiation degradation of PP. The protective effect of selected aromatic compounds was investigated. The research was carried out both from the point of view of obtaining radiation-resistant PP varieties and the possibility of accelerating biodegradation phenomena, e.g., PP/cellulose composition. The phenomena of post-radiation chain oxidation of PP were investigated by gas chromatography (GC). The GC in the system used (packed column, thermal conductivity detector, argon – carrier gas) enables the determination of H₂, O₂, CO, and CH₄ in one measurement. The samples were irradiated with electron beams (EBs) accelerated in accelerators: Elektronika 10/10 with a power of 10 kW and energy of 10 MeV and LAE 13/9 with a power of 9 kW and energy up to 13 MeV. In the tests, PP without stabilizing additives (obtained directly from the production line) and non-stabilized styrene were used. Radiolytic efficiency of hydrogen evolution allowed us to estimate the number of originally formed free radicals. The maintenance of the secondary oxidation processes was the loss of oxygen and the formation of oxidation products (CO, CH₄). Attention is paid to the protective effect of aromatic compounds (polystyrene (PS), polyethylene terephthalate (PET), anthracene, fluoranthene, acenaphthene, pyrene, naphthalene) both at the stage of hydrogen atom separation and the secondary oxidation process. The examples of post-radiation oxidation of PP irradiated in cryogenic conditions (–196°C) are presented. All used aromatic compounds showed a protective effect in PP radiolysis. We suppose that this phenomenon is responsible for the charge transfer along the polymer chain from the ionization spurs to the aromatic compound. The protective ranges of PS in PP radiolysis were estimated for the variously prepared PP/PS type compositions from 6 mers to 28 mers.

Keywords: Gas chromatography • Polypropylene • Post-radiation oxidation • Protective effect • Radiolysis

Introduction

Oxidation of polymers in the atmospheric environment is responsible for the degradation of properties. These processes are initiated by increased temperature and/or by UV light. The conventional prevention of these undesired phenomena in the application of industrial polymers is done through the addition of photostabilizers and antioxidants. The free radicals formed during the radiation modification of polymers are attacked by oxygen. In the case of polypropylene (PP), the process of post-radiation chain oxidation is also initiated [1–3]. The last-mentioned reaction prevents the application of common PP for the production of medical devices to be sterilized by ionizing radiation [4, 5]. Conventional additives mentioned above do not help to its full extent, and therefore additional components are looked for, in particular among specific aromatic compounds [6].

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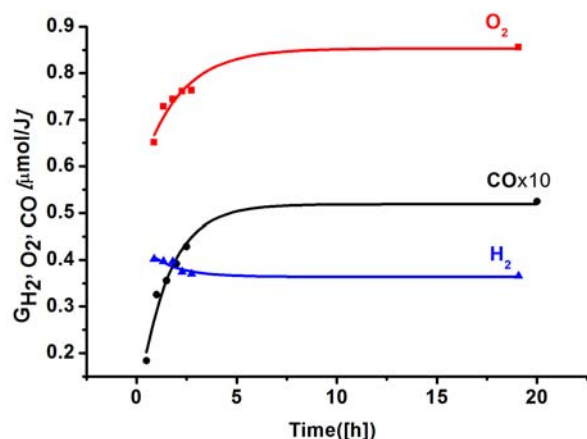


Fig. 1. Radiation yields of H_2 , O_2 , and CO in the function post-irradiation time (PP) [7].

Observation of dynamics of oxidation processes in polymers is made convenient by the gas chromatographic method. One record secures the determination of abstracted H_2 , O_2 , CO, and CH_4 . The present work also shows advantages of oxygen determination, in particular the loss of oxygen, consumed in the oxidation of polymer. Therefore the determination of the rate of oxidation is easily measured, as well as the formation of one of the oxidation products (Fig. 1).

Irradiation

The integration of irradiation and the GC determination, for the case of solids, involved a special approach to the specific technique of electron beam (EB) irradiation of cells closed with septa and consideration of different solubility of hydrogen in a variety of polymers. A special analytical procedure has been developed to test gaseous products resulting from polymer radiolysis. Three-milliliter glass vials, closed by septa, are filled only in one-third with the sample, and only this part is irradiated with a straight beam of electrons from the linear electron accelerator LAE 13/9, leaving the rubber septa intact. This technique allows the application of small doses of radiation energy, by triggering single pulses. The use of a straight beam of electrons has created some problems of dosimetry. The increased inhomogeneity (in comparison to scanned beam) of the radiation field is neutralized by the special alanine – powder dosimetry, with DRS measuring method [8]. The dose rate was 4 Gy per pulse. To position the sample in the center of the EB, a polyvinyl chloride foil was used, which changes colour under the influence of ionizing radiation. The center of the trace was then marked with a laser beam (Fig. 2).

The research also used the Elektronika 10/10 accelerator with an electron sweep beam. In this case, the dose was determined using graphite calorimetry dosimeters. The dose size was changed using the transporter speed at which the samples were transferred under an electron scanner. The dose rate is in the order of 14 000 kGy/h.



Fig. 2. LAE 13/9 electron accelerator in the setting for direct beam irradiation. Bottle with a PP sample on the background of the accelerator window.

Materials and methods

In the study of the post-radiation oxidation of PP, particular attention was paid to the possibility of using GC to study the protective effects of aromatic compounds. The influence of aromatic compounds on the radiolysis of compositions obtained in various ways has been described. In the case of using primary PP (without stabilizers), no high-temperature mixing was used. The designed gas chromatography (GC) system enables simultaneous determination of hydrogen released as a result of polymers radiolysis and post-radiation absorbed oxygen. Carbon monoxide and methane released with much lower efficiency can also be determined.

Gas chromatography

The gas chromatograph Shimadzu GC 2014 has been installed in air-conditioned and thermostated (23.5°C) room. The column was 1 m long packed

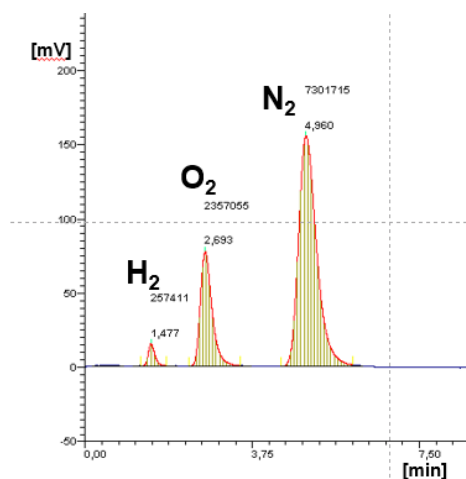


Fig. 3. Sample chromatogram of PP radiolysis products. The figure shows the retention times and the area under the peaks in relative units next to the peaks.

with molecular sieves 5 A, the detector was thermo-conductivity (TCD – 2014) element by Shimadzu. A 25 μl syringe was used (Fig. 3).

Materials

Sample A was prepared by mixing commercial polymers: PP Malen P J-400Z*1632/01 from Basell-Orlen and polystyrene (PS) from Owispol Dwory. Extrusion with a screw plasticizing system was used as a method of mixing polymers. The technological line included an extruder, a head, a calibration and cooling device, and a receiving device. By injection molding, a molded part was formed with a specific shape and a specific structure, resulting from the flow of the plasticized material in the mold and the course of its solidification. Following are the injection parameters that are taken into consideration: inlet temperature 160°C, zones: I – 170°C, II – 180°C, III – 190°C, nozzle – 195°C, injection volume 18.7 cm^3 , accumulation pressure 40 bar, injection speed 15 cm/s, pressure injection 1110 bar, cooling time 20 s. The processing of polymeric materials took place in the air atmosphere, which was the reason for the initial oxidation of PP. Polymer materials were obtained with PS content, respectively: 0% (PP), 10, 25, 50, 75, 100% (PS). Commercial polymers are also used to make PP blends with polyethylene terephthalate (PET content: 0.5%, 1.0%, 1.5%). In spite of the most thorough blending injection and pressing in a mechanical way, the surface area of contact between both polymers has not been expected to be most favourable for energy transfer and therefore two other procedures of sample preparation have been developed. Primary PP was impregnated with aromatic additives. This also avoids oxidation of the polymer by the heat treatment. Sample B was prepared from a virgin PP (F 401) powder, collected from the Orlen-Olefins production line, without additives. It was impregnated with PS dissolved in styrene monomer (freshly distilled, without stabilizers). Samples with PS content were obtained, respectively: 0, 10, 20, 25, 33, 44, 47, and 100%. Afterward, the styrene was removed by evaporation during gentle heating. Sample C was prepared by impregnating PP (F 401) powder with styrene without stabilizer and initiating polymerization/grafting of PS by gamma irradiation. All added styrene was polymerized totally, and its percentage was checked gravimetrically. The samples contained the following amounts of PS: 0, 10, 20, 30, 40, 50, 75, 100%. The influence of 5% additives (anthracene, fluoranthene, acenaphthene, pyrene, naphthalene) on the PP radiolysis process was also compared. PP powder was soaked with a solution of aromatics in benzene. The benzene was then evaporated.

Polypropylene radiolysis

The described method has proved its efficiency in the description of protective action of PS towards the degradation of PP, (Fig. 4).

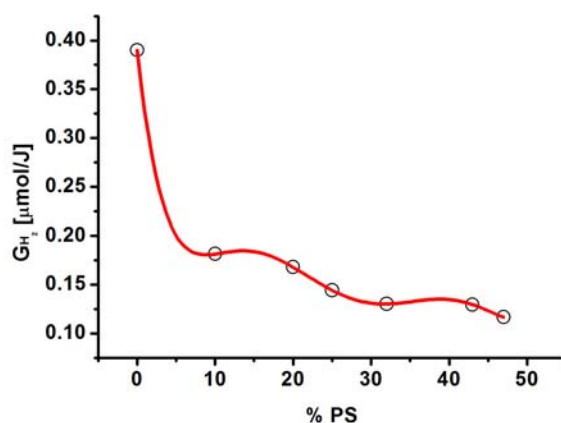


Fig. 4. Dependence of the radiation efficiency of hydrogen evolution on the PS content in the PP/PS blend "B".

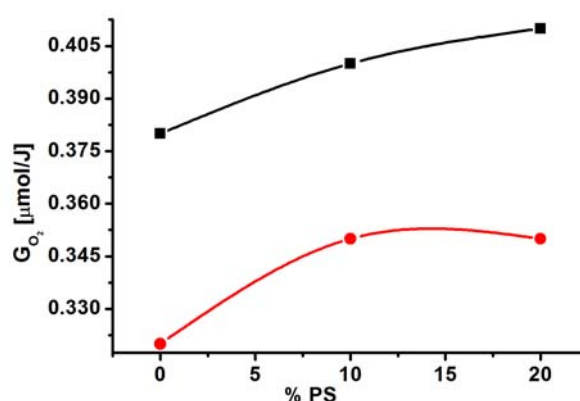


Fig. 5. Dependence of the radiation efficiency of oxygen absorption on the content of PS in the PP/PS blend "B." Irradiation was carried out at room temperature [●] and liquid nitrogen [■].

That method also helped to show that the rate of radiation-induced oxidation of PP at low temperature (under liquid nitrogen) is higher than at ambient temperature (Fig. 5).

That is the first exception of the rule of rather lowered radiation yields of radiation-induced reactions at cryogenic temperatures. Further investigations in this fragment of radiation chemistry will show to what extent physical conditions in the system are responsible for that exceptional behaviour.

The gas chromatographic method has also been applied in the study of post-irradiation oxidation processes of the aging of polymers. Particularly interesting is the case of PP, in which ionizing radiation initiates the chain oxidation process. The oxygen connection is accompanied by regeneration of the macroradical at a different point in the chain. In the case of studies of post-radiation oxidation phenomena, the original radiolysis products were first removed, and then the bottle was closed again and the changes in the gas phase composition over time were analysed. Oxygen was absorbed until its complete depletion in bottles (after about 250 h at 22°C and 400 h for –192°C) with average yields of 0.0784 $\mu\text{l}/\text{kGy}$ per h and 0.0321 $\mu\text{l}/\text{kGy}$ per h, Fig. 6.

In post-radiation phenomena, oxidation of polymers competes with cross-linking processes.

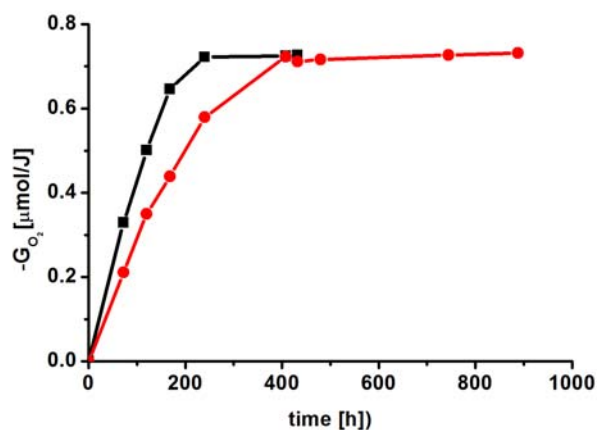


Fig. 6. Yields of post-radiation oxidation of PP, irradiated at room temperature and liquid nitrogen temperature (■ -196°C , ● $+22^\circ\text{C}$). Dose 28 kGy.

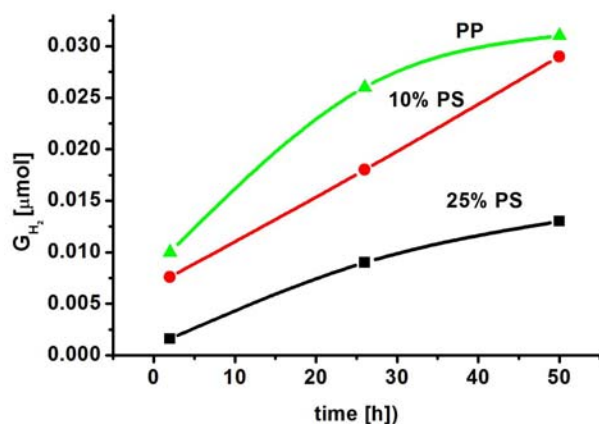


Fig. 7. Time dependence of the post-radiation efficiency of hydrogen evolution.

In the case of PP in the air atmosphere, the process of attaching oxygen to free radicals is much faster. In a situation where the O_2 pressure is reduced, the process of double bond formation is triggered, which is manifested by the evolution of post-radiation hydrogen Fig. 7.

Experimentally, the phenomena of post-radiation oxidation of PP and PP/PS composition during irradiation and up to 108 h after irradiation were compared, Fig. 8. In another experiment, the bottles were opened releasing gaseous radiolysis products. Then the bottles were closed and the efficiency of post-radiation absorbed oxygen was measured. The oxygen absorption efficiency was determined as a function of PS content after different times from the moment of opening the vial after irradiation, heating the samples for 2 h at the temperature of 50°C and then closing it again. The addition of several percent of aromatic PS reduces the oxidation of PP almost twice. The shape of the curves indicates the protective effect of PS addition in PP radiolysis, Fig. 9.

The loss of oxygen helped to trace the oxidation process, and the parallel production of hydrogen has helped to estimate the participation of aromatic compounds in the process of blocking peroxide groups and cross-linking with the PP chain. These processes interrupt the cycle of polymer degradation and can

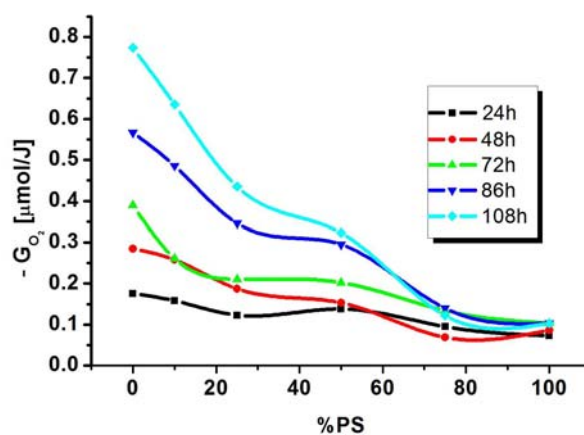


Fig. 8. Radiation performance of oxygen absorption by PP and PP/PS ("A") compositions during irradiation and after irradiation. The bottle was not opened after irradiation. Dose 10 kGy.

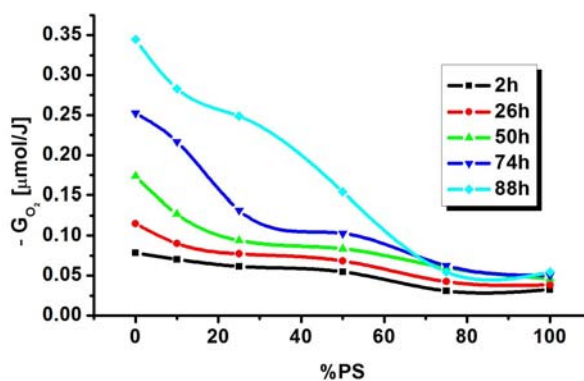


Fig. 9. Oxygen absorption efficiency in post-radiation processes ("A"). The irradiated bottles were opened and closed again after heating. Dose 10 kGy.

help in the branching of chains, thus improving the properties of the material. Analysis of the influence of PS content on the oxidation process shows that the protective effect is higher in the case of samples undergoing a longer aging process. One can explain that by the improved contact of aromatics with the PP matrix.

For example, the effect of 5% flavour addition on PP radiolysis was compared. Analyses were performed immediately after irradiation and after 24 h. The results are summarized in Table 1. The collected data shows that all aromatic compounds show a very pronounced protective effect. The addition of a 5% stabilizer reduces the hydrogen yield by an average of 21% to 36%. A smaller protective effect is observed in the oxidation process. This is because the oxidation rate is so high that after 2 h to 4 h most of the oxygen in the vial is consumed regardless of the original number of macroradicals. The protective phenomenon is very well visible at the post-radiation oxidation stage, which requires a longer induction time, which results in polymer degradation and the formation of carbon monoxide. Together, the stabilizing effect at the stage of ionization and post-radiation oxidation products allows to limit the degradation process, assessed by reducing

Table 1. Yields (G) of gaseous products in radiolysis of PP powder soaked with solutions of aromatic compounds. Analyses were made after irradiation (0.5 h) and after 24 hours (24 h)

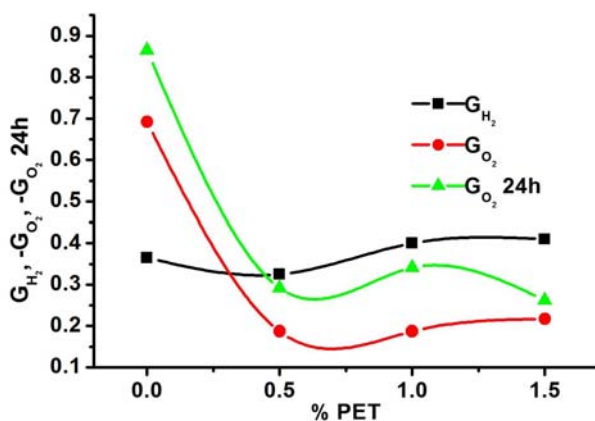
Addition	Yields (G) (μmol/J)				
	0.5 h		24 h		
	GH ₂	GO ₂	GCO	GO ₂	GCO
PP	0.377	-0.558	0.033	-0.609	0.100
Anthracene	0.299	-0.521	0.030	-0.608	0.063
Fluoranthene	0.274	-0.492	0.026	-0.584	0.059
Acenaphthene	0.263	-0.529	0.005	-0.610	0.017
Pyrene	0.215	-0.525	0.015	-0.603	0.051
Naphthalene	0.270	-0.431	0.012	-0.565	0.023

carbon monoxide from six times for anthracene, naphthalene and acenaphthene to two times for pyrene and fluoranthene. Analysing the obtained results, it should be concluded that at the stage of macroradical formation, pyrene and acenaphthene show the best protective properties. However, at the stage of post-radiation oxidation, the most effective stabilizers are acenaphthene and naphthalene. Acenaphthene effectively reduces the degradation of PP manifested by the release of carbon monoxide despite the high oxygen absorption capacity. This may mean that its stabilizing effect applies to post-radiation oxidation processes, not macroradicals, but rather peroxide radicals and their further oxidation products. Similarly to naphthalene, the antioxidant efficacy of acenaphthene concerns not only the irradiation process but also the post-radiation phenomena occurring after radiation treatment.

In other studies, it was shown on the example of a PP/PET composite that using GC methods we can pre-predict the direction and value of changes in radiation resistance of polymer materials (Fig. 10).

The obtained results should then be confirmed by much more labour-intensive tests of mechanical properties.

From the experimentally obtained, characteristic for the protective effect, relationships of hydrogen efficiency as a function of PS concentration in PP/PS compositions, it is possible to estimate the average ratios of the number of PS mers to the number of PP mers at which the formation of macroradicals

**Fig. 10.** Relationships of radiation efficiency of gas products as a function of PET content (analyses carried out after irradiation and after 24 h).**Table 2.** Estimation of the protective range of PS in the radiolysis of PP for samples: A, B, C

Polymer	% PS				Protective range (mers)			
	GH ₂	GCO	GCH ₄	GO ₂	H ₂	CO	CH ₄	O ₂
A	25	20	25	30	7	10	7	6
B	15	8	8	-	14	28	28	-
C	10	11	15	15	22	20	14	14

practically no longer occurs. In this way, the protective effect of PS was compared at the stage of ionic radiolysis products in various PP/PS compositions. Limiting ourselves only to single-ionization spurs, we can calculate the maximum distance a positive hole in the PP chain can travel as a result of primary damage to the polymer. To some extent, the range of protective aroma impact in PP chains was assessed immediately after the electron being struck from it. Oxygen absorption efficiency gives a general view of the final effect consist of protective phenomena at the stage of ionic processes and secondary processes of post-radiation polymer oxidation.

In the first part of Table 2, the percentage of PS is given at which the radiolytic yields (evolution of hydrogen, carbon monoxide, methane, and absorbed oxygen) practically do not change with the increase in % PS. In the second part of the table, the protective range of PS is calculated.

For example, for sample "A", the protective effect at the ionization stage was estimated at 25% PS. This means that on average for every 180 mers of PP there are 24 mers of PS. The ratio of these quantities, called the protective range, is about 7 mers.

Summary

The use of modern GC techniques has shown how important the determination of the radiation efficiency of hydrogen detachment is for the radiation chemistry of polymers. In the case of the study of protective effects in radiation chemistry of PP, the sensitive GC method allowed to describe the role of aromatic additives at the ionic radiolysis stage and post-radiation grafting and cross-linking stage [9]. Studies on the efficiency of post-radiation hydrogen released from polymers have not yet been described in the literature. Post-radiation chemistry of polymer oxidation initiated by the formation of macroradicals is basically similar to the typical phenomena observed in polymer processing chemistry. Radiation chemistry turns out to be a convenient method that allows you to produce free radicals in controlled ways. A relatively simple GC method turns out to be a good tool for describing these phenomena extremely important from the point of view of utility polymers.


The influence of several aromatic compounds on the yield of gaseous PP radiolysis products was described.

It was shown on the example of PP/PET composition that using the GC method we can initially predict the direction and value of changes in the radiation resistance of polymeric materials.

The comparison of the protective effects at the stage of macroradical formation as a result of hydrogen atom detachment with the effects of reducing post-radiation oxidation suggests that the first stage is equally important.

These few examples have shown, that the simple and sensitive at the same time analytical method helps to investigate not only radiation oxidation phenomena but also photo- and thermooxidation [10].

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