The use of gas chromatography for the determination of radiolytic molecular hydrogen, the detachment of which initiates secondary phenomena in the radiation modification of polymers

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Abstract: The paper summarizes long-term research into the radiolysis of polymers. The starting point in all cases was the preliminary determination of the radiolytic efficiency of hydrogen evolution. This value is approximately proportional to the number of radicals arising as a result of irradiation, which determines post-radiation phenomena. It was not about accurately describing the radiolysis of a specific polymer, but about paying attention to the benefits of starting the study of radiolysis from the analysis of hydrogen evolution. The Table 2 gives specific hydrogen yields for selected polymers. The results of these studies were used in the planning of the radioactive waste repository in Los Alamos National Laboratory.

Keywords: polymers, gas chromatography, polypropylene, polystyrene, hydrogenated nitrile-butadiene rubber, radiolysis, radiation degradation, radiation crosslinking.

Zastosowanie chromatografii gazowej do oznaczania radiolitycznego cząsteczkowego wodoru, którego oderwanie inicjuje wtórne zjawiska w radiacyjnej modyfikacji polimerów

Streszczenie: Artykuł podsumowuje wieloletnie badania autora nad radiolizą polimerów. Punktem wyjścia we wszystkich omawianych wypadkach było wstępne określenie radiolitycznej wydajności wydzielania wodoru. Wartość ta jest w przybliżeniu proporcjonalna do zawartości powstających w wyniku napromieniowania rodników, które inicjują zjawiska postradiacyjnej modyfikacji. Tabela 2 podaje wybrane, uzyskane przez autora, konkretne wydajności wodoru w odniesieniu do wybranych polimerów. Wyniki badań wykorzystano, przykładowo, przy planowaniu składowiska odpadów promieniotwórczych w Los Alamos National Laboratory.

Słowa kluczowe: polimery, chromatografia gazowa, polipropylen, polistyren, uwodorniony kauczuk nitrylowo-butadienowy, radioliza, degradacja radiacyjna, sieciowanie radiacyjne.

Detachment of gaseous hydrogen from any hydrogen bearing material, (from inorganics to polymers), at ambient temperature is the original contribution to polymer chemistry. Hydrogen can appear at room temperature when generated by biological metabolic processes, outside the topic of the present paper. At elevated temperature, gaseous hydrogen can appear over polymers heated to high temperatures, well above the melting or decomposition temperature. Free H_2 formation is incorporated in that case in the thermal degradation process, and that process is also outside the scope of the paper.

On the other hand, in the radiolytic decomposition at room temperatures and even under cryogenic conditions, hydrogen is the main constituent of the gas phase above any hydrogen bearing products. For instance, in the case of all polymers, hydrogen dominates over the concentration of low molecular weight products of the degraded polymer.

Release of hydrogen from all materials irradiated by ionizing radiation, from internal or external sources, has been observed first in aqueous systems by Skłodowska-Curie [1]. Radiolysis of water into explosive mixture of hydrogen with air became the topic of concern and initiated studies on diminishment of water decomposition. Later all other materials have been observed from that point of view for products of radiolysis, especially of organic matter under the action of ionizing radiation in connec-

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tion to immobilization of radioactive waste (α-emitters) in the asphalt [2, 3]. These papers show how complicated is the investigation of effects caused by α-ray emitters and how efficient can be the simulation of these effects by electron radiation, permitting to make wider investigation, incorporating long list of very different materials and very different doses, *i.e.* equivalent to very different concentrations of radionuclides.

The phenomenon of hydrogen detachment occurs in gases, liquids and solids, but the last ones dissolved, *e.g.* in water, can show completely different behavior, because radiolysis starts from the main constituent of the system, in that case in the solvent. The solvent is absorbing the most of ionizing energy and its reactive products are entering with the reaction with the solute, *e.g.* with macromolecules. For instance [4], gelatin in aqueous solution creates during irradiation many different products of reaction with water radiolysis intermediates. Also the crosslinking of gelatin into collagen-like supramolecular entities occurs, but without release of gaseous hydrogen. However, H_2 appears with the yield of 0.45 molecules/100 eV in radiolysis of aqueous solution of polymers as the product of multi-ionization spurs in water, not involved in reactions with dissolved polymer and not destroyed by radical products of H_2O, being used for reactions with the polymer.

The analytical method to be applied for hydrogen determination is obviously gas chromatography (GC) already applied successfully to the determination of radiation yield of multiionization spurs in alanine, from the yield of carbon dioxide [5]. However, the link between irradiation and the gas chromatography (GC) operation, developed for that purpose cannot be applied for the case of hydrogen.

EXPERIMENTAL

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 closed with a rubber stopper and consideration of different solubility of hydrogen in a variety of polymers, resulted in new procedures. Three milliliter glass vials, closed by a rubber stopper, 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 (energy 13 MeV, 9 kW power) [6], leaving the rubber stopper intact. This technique allows application of small doses of radiation energy, by triggering single pulses of electron beam. The Fig. 1 shows the arrangement of the cell in the beam, positioning is secured by a laser beam.

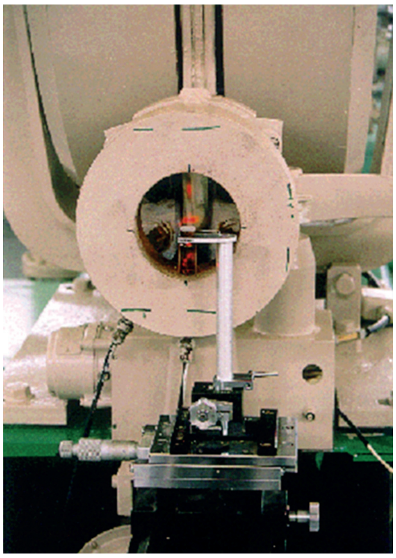

Fig. 1. The cell in the beam-positioning is secured by a laser beam (LAE 13/9 accelerator, 13 MeV energy, 9 kW power)

The use of 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 (diffuse reflectance spectroscopy) measuring method. The method is using the fact, that the free radical derived from alanine shows optical absorption spectrum [7–9]. The use of straight electron beam is similar to its use in first versions of our pulse radiolysis system [10].

Application of higher, radiation doses proved to be more convenient by conventional, technological irradiation on the conveyor, by the bent beam of electrons. The rubber stopper are covered with a thick hood made of lead in this case. Experiment with an empty vial did not show the presence of hydrogen, what has demonstrated no significant irradiation of stopper made of rubber. This technique was applied for high doses only; application of this mode for low doses of radiation yields erratic doses, because of the structure of the beam. That limitation has been recognized already before the construction of the machine and cannot be avoided due to the pulsing regime of the accelerator action and scanning frequency of 5 Hz. Lower doses were applied in the cobalt 60 γ source, with due analysis of differences of radiation quality in comparison to the EB, if any.

Technical details of hydrogen determination

The gas chromatograph Shimadzu-2014 has been installed in air conditioned and thermostated [23.5 °C] room. The column was 1 m long and packed with molecular sieves 5A, the detector was thermo-conductivity [TCD-2014] element by Shimadzu. The chromatograph was attached by interface to the computer where the data were acquired by program CHROMAX. The carrier gas was argon [99.99%], calibration gas hydrogen 99.99%. Operations were done with syringes vol. 10, 25 and 500 μL. The system was working at 220 °C, on the column kept at 70 °C and the detector at 100 °C. The rate of flow of carrier gas was 10 cm^3/min.

Separation parameters (Table 1) were calculated based on the average values found for samples in the H_2 range 0.023–250 μM: $R = (t_R[O_2] - t_R[H_2])/0.5 \cdot (W[H_2] - W[O_2])$, $A = a/b$, $N[H_2] \approx 5.545 \cdot (t_R[H_2]/W[H_2])^2$

Table 1. Parameters of separation

H_2	Retention time: $t_R[H_2]$ = 1.48 min Distribution coefficient H_2 from O_2: $R[H_2\text{-}O_2]$ = 2.7 Coefficient of peak symmetry: $A[H_2]$ = 1.14 Number of theoretical shelves: $N[H_2] \approx 86$
O_2	Retention time: $t_R[O_2]$ = 2.77 min Distribution coefficient O_2 from N_2: $R[O_2\text{-}N_2]$ = 3.7 Coefficient of peak symmetry: $A[O_2]$ = 1.2 Number of theoretical shelves: $N[O_2] \approx 488$
CH_4	Retention time: $t_R[CH_4]$ = 7.75 min Coefficient of peak symmetry: $A[CH_4]$ = 1.22 Number of theoretical shelves: $N[CH_4] \approx 375$
CO	Retention time: $t_R[CO]$ = 13.00 min Coefficient of peak symmetry: $A[CO]$ = 1.2 Number of theoretical shelves: $N[CO] \approx 488$

where: W – width of the chromatographic peak at the base, a, b – half widths of a given peak.

According to accepted criteria of chromatographic peaks symmetry and separation coefficients, the A should be in the range of 0.9–1.2, and R should be higher than 1.5, the method is suitable to quantitative determination of H_2 in gas mixtures like air.

The minimum detectable amount of H_2, which generates a signal in the detector twice as high as the noise amplitude is estimated to ~0.005 μL, *i.e.* at normal conditions relates to $\sim 2 \cdot 10^{-10}$ mole or $\sim 4 \cdot 10^{-10}$ g of H_2. Using the method of "head space" for the determination of hydrogen in solid samples of density close to 1 g/cm^3 irradiated to the dose of 10 kGy in cells of relation of volume of the gas phase to the solid phase *ca.* 3 and gas phase sampling by 20 μL the limit of hydrogen detection will be the radiation yield of 0.0003 μmol/J.

The application of the developed technique to the particular material was always proceeded by a study of kinetics of the release of hydrogen, as well as of its distribution between the sample and the gas phase. The behavior of different polymers, even of comparable surface area of the sample, is, in this respect, different.

Combination of different processes and operations demanded a careful analysis of accuracy and precision of the full procedure. Accuracy was fulfilled, because no gaseous product of radiolysis of any material can interfere with hydrogen peak in chosen conditions. Precision of the procedure has been checked on parallel, independent determinations starting with filling of irradiation cells to the final measurement supplied by the computer combined with the gas chromatograph. Precision depends on the radiation yield in particular cases.

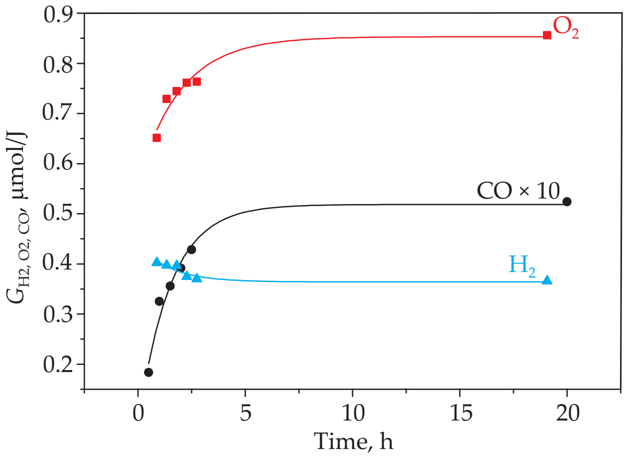

Fig. 2. The phenomenon postradiation degradation of polypropylene; ionizing radiation initiates the process of chain oxidation, the changes in hydrogen, carbon monoxide and oxygen efficiency have been shown as a function of time from irradiation to analysis over time, the yield of carbon monoxide and the efficiency of oxygen absorption by samples of primary polypropylene (without additions of antioxidants and light stabilizers) increases

Applications of gas chromatography to the radiation chemistry of polymers are not limited to the determination of hydrogen. In the same experimental arrangement the possibility exists to study oxydegradation of polymers in the postradiation stage.

The changes in hydrogen, carbon monoxide and oxygen efficiency have been shown as a function of time from irradiation to analysis. Over time, the yield of carbon monoxide and the efficiency of oxygen absorption by samples of primary polypropylene (without additions of antioxidants and light stabilizers) increases. Figure 2 shows an example of an interrelation efficiency of hydrogen evolution, the oxidation and degradation (carbon monoxide

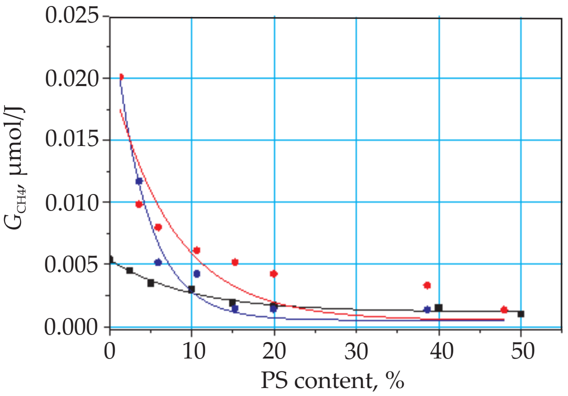

Fig. 3. The protective effect of the addition of polystyrene on the performance of methane emission; hydrogen evolution performance for various polypropylene/polystyrene compositions; the deviation from additivity dependence of G_{CH4} as a function of % PP is a measure of the protective effect within the area of multionization spurs

formation) of or in polypropylene. Results of extension of the approach, applied for the first time will be reported in the second part of the present paper. Irradiated polypropylene, after determination of hydrogen yield, is exposed to air, and disappearance of oxygen is followed, accompanied with the formation of CO. Methane can be formed in the zone of multiionization spurs as well as in the induction period of oxydegradation of the polymer [11], Fig 3.

DISCUSSION

Several types of most different materials have been investigated for radiation yield of hydrogen, from inorganics like concrete [12, 13] to organics [alanine], to commercial and laboratory polymers and biopolymers. Detailed data are published fully in publications dealing with particular systems and their radiation chemistry. Here are remarks important to all materials. Irradiation by the EB produced by the most reliable, versatile, oldest linear accelerator LAE 13/9 in the Centre for Radiation Research and Technology of the Institute of Nuclear Chemistry and Technology has been applied. All samples were of geometry and size securing the homogeneity *DUR* = 1.2 (Dose Uniformity Ratio – maximum to minimum absorbed dose within the irradiation container) of dose distribution. The split dose technique has been applied to avoid the warming of samples higher than by 35 K [14]. All goals of investigations were well defined, *e.g.* the simulation of radiolytic effects in elastomers, contaminated with α-emitters, investigated from the point of view of storage of radioactive waste. Dose applied was also adjusted to realize the primary task. Important were lowest doses, which represented radiolysis of waste in the initial stage, from the preparation to the transportation to the deposition site. Higher doses were also applied to exclude unforeseen phenomena. In the case of many polymers for moderate doses, the crosslinking process competes with degradation. For very large doses the degradation phenomenon is already dominant. The radiation yield at higher doses, when the additives are destroyed, was accepted as the maximum radiation yield.

Basic aspects of radiation chemistry of polymers became involved, when the H_2 radiation yields were confronted with the composition of commercial polymers and with the effects of polymer irradiation. As concerns the composition: the spectrum of additives present in commercial polymers is very wide; otherwise the processing of polymers for their application in industry and household would have been impossible. Comparatively pure polymers, *i.e.* obtained directly from the polymerization line, after basic purification from catalysts and unwanted isomers, are used in basic research only. That was the case with polypropylene used by W. Głuszewski in his Ph.D. [15]. For the completeness of research, hydrogen determination in irradiated polypropylene has been investigated. That kind of polymer yields important results concerning its radiation chemistry, in spite of the fact that it can be processed, *e.g.* into films, after addition of stabilizers only. Hydrogen determination in irradiated polypropylene was not discussed in Głuszewski Thesis.

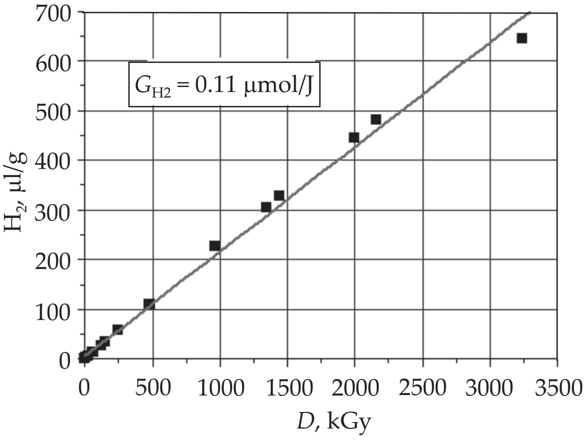

Fig. 4. For the HNBR elastomer, for example, a weld showing the radiolytic efficiency of hydrogen has been shown; in this case, it is an average value for a very large range of radiation doses (up to 3500 kGy)

Consideration of G_{H2} radiation yields as a part of complete radiation chemistry of polymers, had permitted to draw important conclusions. The majority of commercial polymers show a typical curve of hydrogen yield *vs.* the dose, with a visibly lower yield at the beginning of the curve (Fig. 4).

After that initial step, the growth of hydrogen production is linear with dose. Production of hydrogen from a neat polymer, polypropylene, is linear from the beginning. Evidently the mechanism of radiolysis of commercial polymer at the beginning of irradiation is different. Leaving the full discussion to the detailed publications, we can explain the phenomenon by the consumption of additives present in polymers, by intermediate species of radiolysis. The degree of crosslinking *vs.* the dose is usually parallel to the hydrogen-detachment curve, *i.e.* at the beginning the crosslinking cannot occur. The additive which is present next to the chain, is winning here the competition for the positive hole [h^+]. The loser is the energetically favorable site where two chains of the polymer are sufficiently close together. At subsequent higher doses, the meeting sites of two chains, the irradiated and unirradiated chain are only places where the transfer of h^+ stops, to release hydrogen and form the crosslinking bond. Comparison of hydrogen yields *vs.* dose is the vital part of the future work, because crosslinking of polymers shows also the effect of diminished yield at starting doses of irradiation [16].

If the polymer additive has aromatic groups, and that is usually the case, or the polymer is a mixture or copolymer aliphatic-aromatic, the energy transfer to aromatic moieties results in dissipation of absorbed energy in single ionization steps. The ionizing energy is changing into emission of visible light, and/or changing into molecular vibrations manifested as chemically ineffective heat. The main source of hydrogen in the zone of low dose irradiated, protected polymers are multiionization spurs which occur also in random sites, but cannot be transferred. The result is an immediately broken chain of the polymer and sometimes additional formation of low molecular weight debris of the polymer from sites around the scission point.

The initial, low degradation zone of radiolysis is welcomed, if radiolysis of polymers is considered from the point of view of safety of transportation of contaminated waste.

The behavior of biopolymers (cellulose, wool, *etc.*) present in the waste is in general different. The radiation yield of hydrogen is lower, and the starting part of the curve does not show the prestep like in C-H polymers with additives. As an example, Fig. 5 shows the radiolytic hydrogen generation curve of two kinds of keratin.

The radiation chemistry of biopolymers as a part of our hydrogen research was not developed as thoroughly as of C-H polymers, due to much lower yields of hydrogen. Hydrogen released from polymers containing, in addition to carbon and hydrogen, also O, N, S atoms does not appear as dangerous H_2, but as water, ammonia, or other compounds which can have unpleasant smell but do not present the danger of fire or explosion.

In conclusion, our investigations of radiation yields of hydrogen release from irradiated polymers have shown important regularities. In general, the detachment of H_2 is an irreversible reaction, a substantial element of definite degradation, positive from the point of view of desintegration of waste. An also positive, from the point of view of repository chemistry fact is the presence of additives in commercial polymers, present in the waste. All known additives, according to our investigations cause diminished production of hydrogen.

Every organic compound degrades under ionizing radiation, releasing hydrogen from its composition. Radiation induced dehydrogenation can have their variants, *e.g.* in chlorine containing compounds the hydrogen is released rather as hydrogen chloride (HCl) and in amines or compounds generally with nitrogen, hydrogen can appear in the gas phase as ammonia. Radiation yield of hydrogen can be modified in wide limits, especially at starting doses of radiation. At that stage results of radiolysis are influenced by additives present always in plastics.

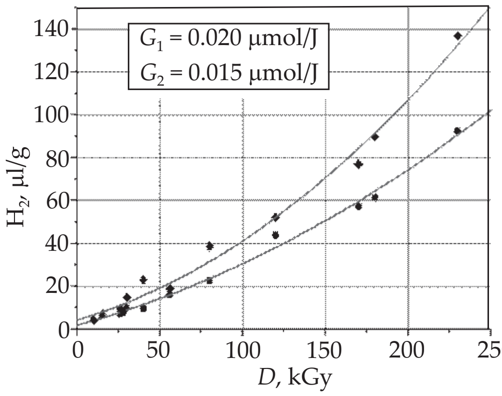

Fig. 5. Radiolytic hydrogen generation curve of two kinds of keratin; hydrogen evolution yields from an exemplary natural polymer, the published yields of G_{H2} are average in the form of doses up to 250 kGy

All experiments on the radiation yield of hydrogen are directed to answer the important question that is whether a chemical chain reaction is possible, *i.e.* if a *G* value of H_2 higher than 3 effects per 100 eV (~0.3 μmol/J) is possible. That could generate concern about safety, but in the decades of history of radiation chemistry of hydrogen generating systems, mainly polymers, nothing like this has been observed. Production of hydrogen in organic waste, in polymers in particular, although very important represents only a fragment of the total, always complex, radiolysis. Dehydrogenation is closely related to formation of double bonds, sometimes in cumulated form, which are responsible for specific characteristics of the material, including change of color. Our method of optical investigation, diffuse reflected light spectrophotometry [DRS] allows to estimate the quality and quantity of other, than hydrogen, products of radiolysis, enabling a formulation of the total balance of products. Unsaturations occurring in the consequence of dehydrogenation are related to chain reactions of oxidation, which can run to the point of exhaustion of oxygen in a closed system.

Here are examples: polyethylene of different sources: the *G* value in 7 different products, all as G_{H2} from 0.396 to 0.468 μmol/J. That is the highest observed level of hydrogen. There are no indications of chain decomposition of that polyolefin. The next group of lower yields of hydrogen is polypropylene. Its virgin form, without additives, as obtained from polymerization line, shows hydrogen with yield almost exactly like in cases of polyethylene, *i.e.* 0.39 μmol/J. In a typical composition with additives, which contain aromatic compounds, radiation yield is already down to 0.246 μmol/J. Mixtures with increasing amounts of aromatics, *e.g.* with polystyrene lower the hydrogen yield rapidly (to 0.196 μmol/J with 10% of polystyrene to 0.155 at 25%, 0.108 at 50% and to 0.061 at 75%, respectively). Polystyrene as an aromatic compound is most resistant to ionizing radiation (typically, the yield of hydrogen in polystyrene without polyolefins is 0.003 μmol/J).

Polyethylene occurring as so called parafilm, widely used in chemical laboratories and present in the waste, yields hydrogen with 0.324 μmol/J.

Elastomers have lower radiolytic efficiency of hydrogen evolution from polyolefins [17–20]. The high technology rubber, hydrogenated nitrile butadiene rubber has been carefully investigated. The typical yields were 0.117–0.133 μmol/J. That yield is worth mentioning, because almost fully hydrogenated rubber was suspected as the source of radiation generated hydrogen. Nothing like this was observed, probably due to specific crosslinking reactions by entangling which produce only half of hydrogen produced in the case of olefins. It is also possible to crosslink with the separation of one hydrogen atom through acrylonitrile groups. The low danger of increased hydrogen production resembles early fears,

Table 2. Selection radiation yield for hydrogen evolution for some polymers*)

Kind of polymer materials	*G* (radiolytic efficiency)	
	molecules/100 eV	μmol/J
Polypropylene		
PP neet	3.90	0.40
PP isotactic	2.51	0.26
PP syndiotactic	3.23	0.33
Parafilm	3.25	0.34
Polyethylene among 7 kinds 3.96–4.68		
Borealis FA 3220	3.96	0.41
Borealis FT 5230	4.68	0.49
Elastomers		
NBR N33	1.17	0.12
HNBR (depending on hydrogenation degree, acrylonitryle degree) among 5 kinds 1.18–1.33		
Therban A3407	1.33	0.14
Therban A4550	1.18	0.12
PP/PS		
% PP		
100	3.20	0.33
90	2.50	0.26
75	2.00	0.21
50	1.40	0.15
25	0.80	0.08
0	0.01	0.001
Alanine		
Alanine L	0.183	0.019
Alanine LD	0.231	0.024
Alanine β	1.835	0.190

*) This yield can be regarded as a measure of radiation resistance of polymers (natural and plastics).

60 years ago, in nuclear reactor technology, when polyethylene insulations of electric cables were suspected of generating explosive mixtures. At that time the radiation induced crosslinking was not known.

CONCLUSIONS

Polymers containing chlorine [poly(vinyl chloride)] are producing hydrogen in the form of hydrogen chloride. It is highly corrosive and speeds up the decay of copper wires, if used as insulation of electric cables.

Polymers containing nitrogen release hydrogen as ammonia, because the radiation induced deamination reaction is energetically most probable. It is again non-interesting from the point of view of safety. Pure hydrogen yields from such materials are low, *e.g.* from natural wool it is only 0.026 μmol/J.

More data are in Table 2. The research was carried out on the occasion of various projects concerning the modification of polymers.

REFERENCES

[1] Skłodowska-Curie M.: "Collection of Reprints of All Papers" PWN, Warsaw 1954.

[2] Kosiewicz S.T.: *Nuclear and Chemical Waste Management* **1980**, *1*, 139, ISSN 0191-815X.

[3] Kosiewicz S.T.: *Nuclear Technology* **1981**, *54*, 92.

[4] Kosiewicz S.T.: *Nuclear Technology* **1990**, *92*, 428.

[5] Zagórski Z.P.: *Radiation Physics and Chemistry* **1999**, *56*, 559. https://doi.org/10.1016/S0969-806X(99)00315-1

[6] Zagórski Z.P.: *Radiation Physics and Chemistry* **1983**, *22*, 409. https://doi.org/10.1016/0146-5724(83)90046-8

[7] Przybytniak G.K., Zagórski Z.P.: *Journal of Radioanalytical Chemistry and the Radiochemical and Radioanalytical Letters* **1996**, *212*, 373.

[8] Zagórski Z.P., Przybytniak G.K.: *Nukleonika* **1997**, *42*, 373, ISSN 0029-5922.

[9] Zagórski Z.P.: *International Journal of Polymeric Materials* **2003**, *52*, 323. https://doi.org/10.1080/00914030304917

[10] Głuszewski W., Zagórski Z.P., Rajkiewicz M.: *Kautschuk Gummi Kunststoffe* **2015**, *68* (*11/12*), 46.

[11] Głuszewski W., Zagórski Z.P.: *Nukleonika* **2008**, *53*, S21 ISSN 0029-5922.

[12] Głuszewski W., Boruc B., Kubera H., Abbasowa D.: *Nukleonika* **2015**, *60* (*3*), 665. http://dx.doi.org/10.1515/nuka-2015-0090

[13] Kubacki R., Głuszewski W., Laskowski D. *et al.*: *International Journal of Microwave and Wireless Technologies* **2018**, *10* (*7*), 754. https://doi.org/10.1017/S1759078718000223

[14] Zagórski Z.P.: "Radiation Processing of Polymers" (Eds. Singh A., Silverman J.), Hanser Publishers, Munich, Vienna, New York 1992, pp. 271—287.

[15] Głuszewski W.: "Protective phenomenes in polypropylene radiation chemistry" [*in Polish*], Ph.D. Thesis, Instytut Chemii i Techniki Jądrowej, Warszawa 2008.

[16] Zagórski, Z.P.: *Radiation Physics and Chemistry* **2002**, *63*, 9. https://doi.org/10.1016/S0969-806X(01)00475-3

[17] Głuszewski W., Zagórski Z.P., Rajkiewicz M.: *Radiation Physics and Chemistry* **2014**, *105*, 53. https://doi.org/10.1016/j.radphyschem.2014.06.024

[18] Głuszewski W., Zagórski Z.P., Rajkiewicz M.: *Radiation Physics and Chemistry* **2014**, *94*, 36. https://doi.org/10.1016/j.radphyschem.2013.07.019

[19] Bik J., Głuszewski W., Rzymski W.M., Zagórski Z.P.: *Radiation Physics and Chemistry* **2003**, *67*, 421. http://dx.doi.org/10.1016/S0969-806X(03)00078-1

[20] Głuszewski W., Stasiek A., Raszkowska-Kaczor A., Kaczor D.: *Nukleonika* **2018**, *63*, 81. http://dx.doi.org/10.2478/nuka-2018-0010

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