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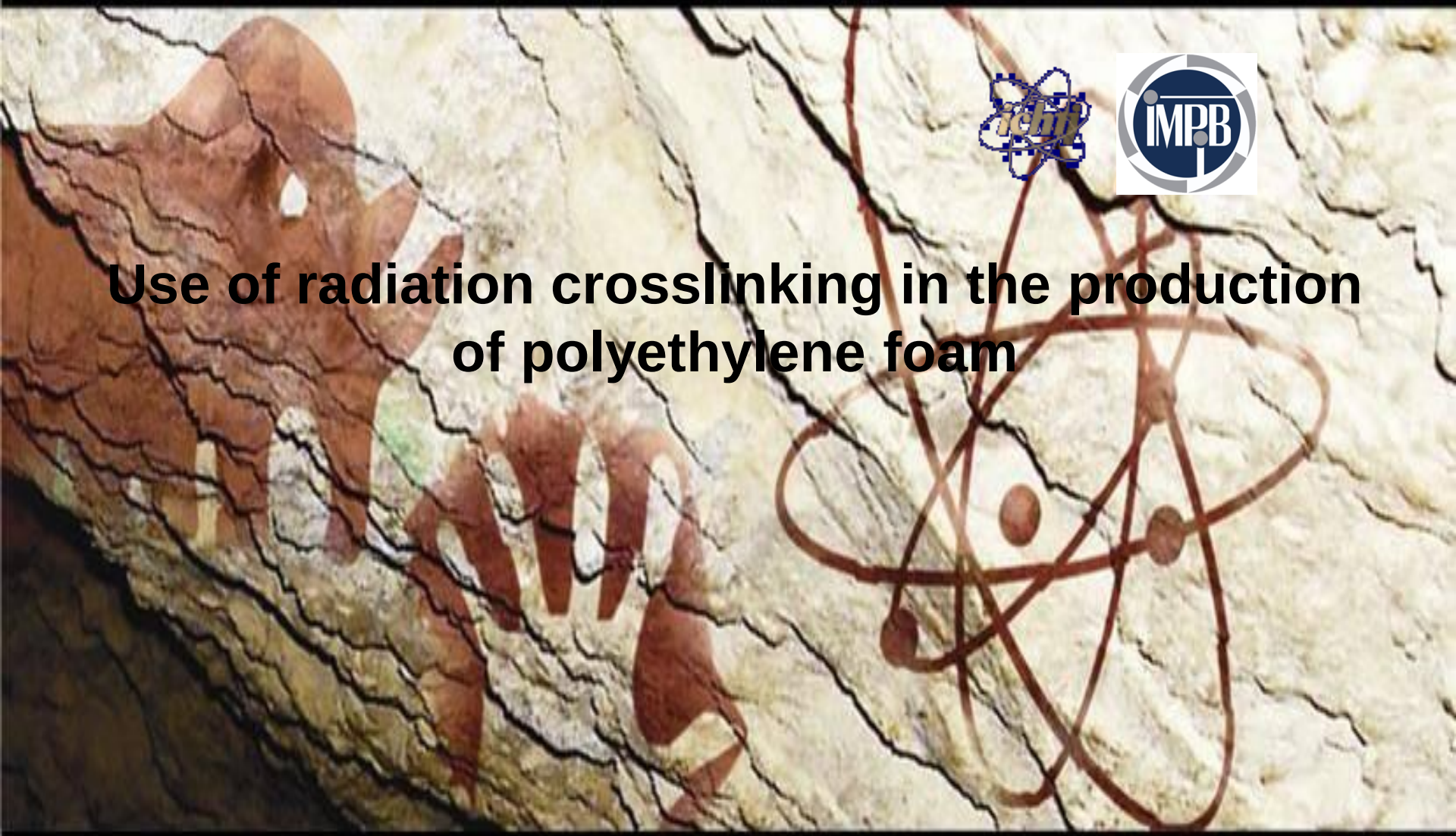

Use of radiation crosslinking in the production of polyethylene foam

Institute for Engineering of Polymer Materials and Dyes, Toruń
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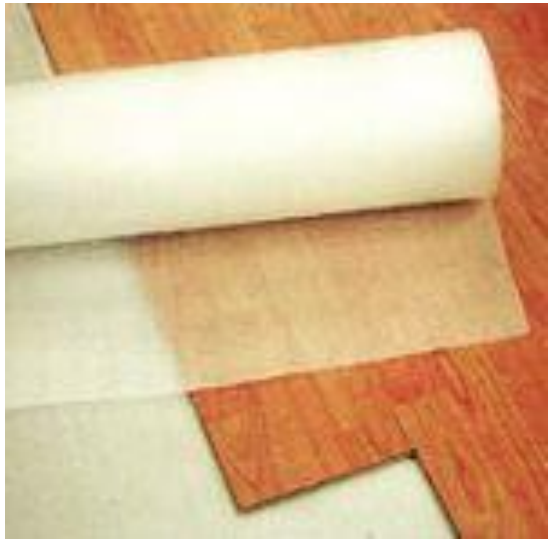
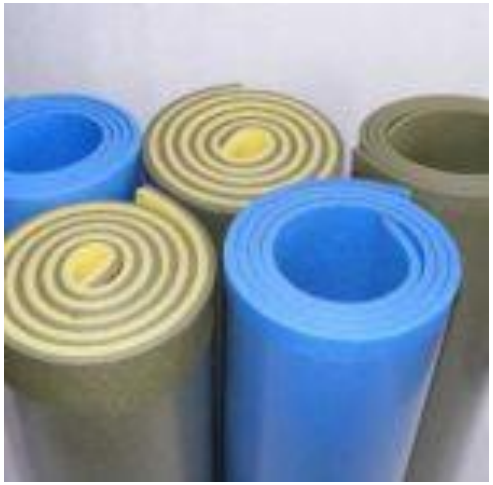
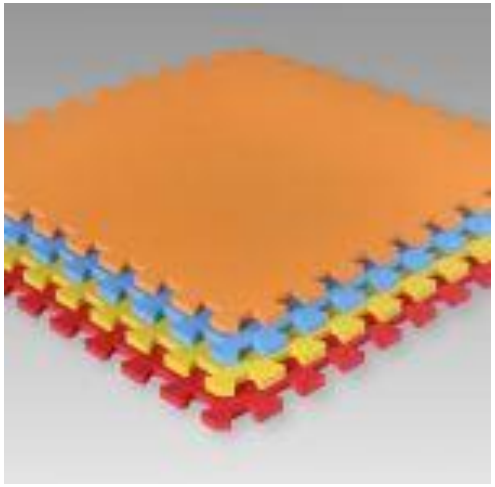
- Chemically crosslinked polyethylene foams are characterized by good thermal insulation properties. low density, low thermal conductivity. high sound absorption and chemical resistance. These properties cause their wide use in construction, automotive, packaging industry and the sport

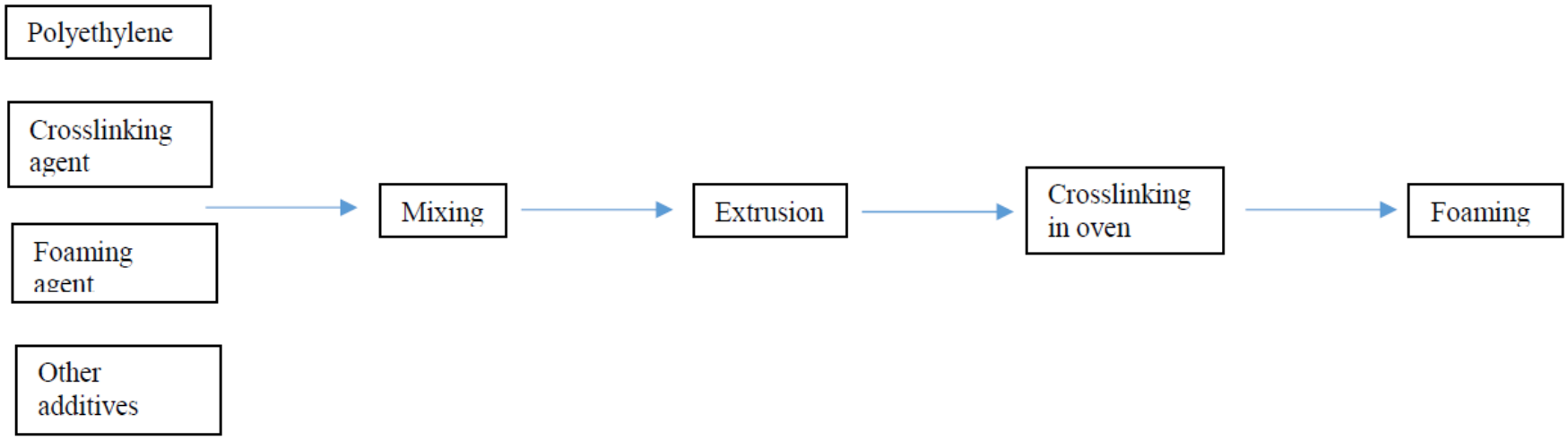




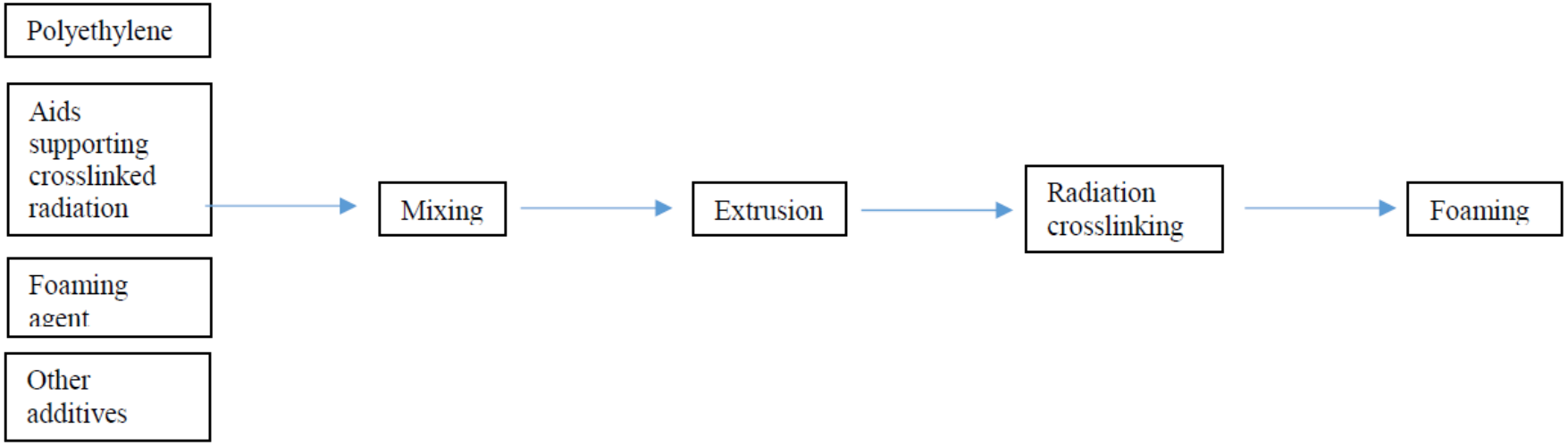


- Chemically or radiation crosslinked foams are produced in five stages.
- The first stage involves obtaining a mixture of polymer with a crosslinking agent (e.g. dicumyl peroxide) or aids supporting radiation crosslinked. a chemical foaming agent or and the others additives (for example: flame retardants, etc.). This step is carried out in a mixer.
- In the second step. the pellets are prepared in an extruder. When. the film is extruded to form the pellets it is subjected then to the process of crosslinking and foaming.

Chemically crosslinked foams



Radiation crosslinked foams




UWAGA!
UWAGA!

Materials

- The polyethylene used was low density polyethylene (LDPE) type Malen FGAN 23-D003 (density 0.922 g/cm^3 and MFR (190^{o}C/2.16 kg) 0.31 g/10 min) from Lyonellbasell.
- Azodicarbonamide type Unicell D1500TSK from Tramaco was used as a foaming agent.
- Zinc oxide.
- Zinc stearate.
- Tracryl PO 3501
- Irganox PS 802 FL (Ciba Speciality Chemicals) was used as antioxidant

samples	the addition of adjuvant radiation crosslinking name	Composition%			
		the addition of adjuvant radiation crosslinking	porophor content	antioxidant	PE
1	Zinc oxide	1	15	0.2	83.8
2		3	15	0.2	81.8
3		5	15	0.2	79.8
4	Tracryl	1	15	0.2	83.8
5		3	15	0.2	81.8
6		5	15	0.2	79.8
7	Zinc oxide and tracryl	0.5/0.5	15	0.2	83.8
8		0.7/0.3	15	0.2	83.8
9		0.3/0.7	15	0.2	83.8
10		1.5/1.5	15	0.2	81.8
11		2/1	15	0.2	81.8
12		1/2	15	0.2	81.8

Unicell D1500TSK Irganox PS 802 FL PE - LDPE FGAN 23 D003

The process for preparing a chemically/radiation crosslinked foams consisted of the following steps:

a) preparation of powder mixtures
b) extruding the pellets.
c) extruding the film.
d) crosslinking
e) foaming.

In the initial stage. the mixture consisting of polyethylene. crosslinking agent (e. g. dicumyl peroxide) or aids supporting crosslinking radiation. a chemical foaming agent and the others additives (for example: flame retardants. etc.). was prepared using a Brabender planetary mixer.

Extrusion process of pellets was realized using co-rotating twin-screw extruder.

Co-rotating twin-screw extruder

Film extrusion

- The polymer film was obtained by the lab equipment consisting of the single screw extruder type Plasti – Corder PLV 151 (Brabender) with the flat die and polishing rolls.
- The temperature profile along the barrel was: 100, 110, 125 and 125˚C
- The screw parameters were: working length 25D and compression ratio 3:1.
- The experimental stand was equipped with a device for measuring temperature of heating zone of the plasticizing system and the head.
- Screw rotation speed was 75 rpm.

Single screw extruder type Plasti – Corder PLV 151 (Brabender)

Chemical crosslinking

The crosslinking process was carried out in the oven type SLW 53 (POL-EKO company) at temperature 160°C for 5 min.

Electron and gamma radiation

- Radiation crosslinked – gamma radiation 60 and 100 kGy
- Radiation crosslinked – electron radiation 20. 60 and 100 kGy

Foaming

- Foaming process was conducted in silicone oil bath at 225°C for 1.5 min.

Total density

Total apparent density (ρ_a) was determined from crosslinked and foamed samples (dimension of samples approximately 50 mm x 50 mm - three samples for each film). Overall dimensions the samples were measured in accordance with PN-EN ISO 845. ISO 1923.

SEM Analysis

The determination was performed on a test stand equipped with: scanning electron microscopy **HITACHI SU8010** (Japonia, 2011) and **Cressington Sputter Coater** module measuring thickness of the sputtered gold layer (Germany, 2011). The microscope is equipped with a cold cathode field emission. two detectors SE. BSE and EDX detectorfor X-ray microanalysis.

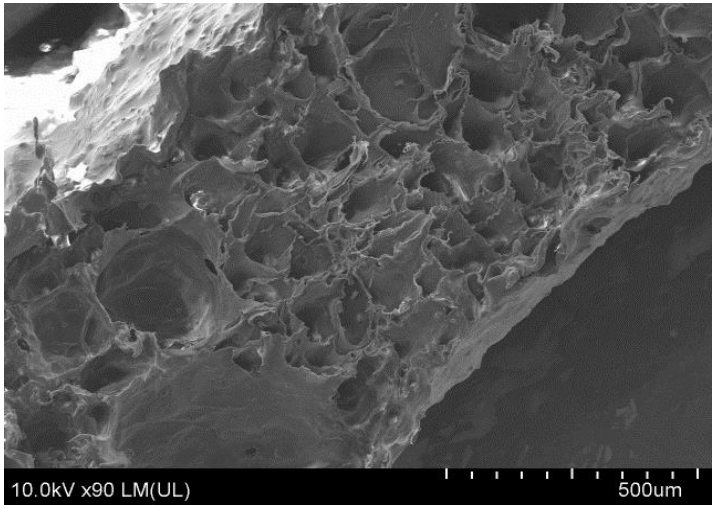
Density - Electron radiation 100 kGy

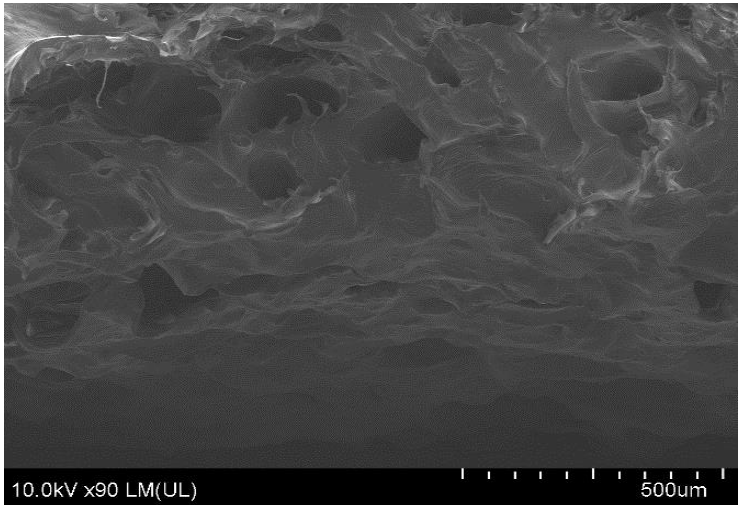
Sample name	Aids supporting radiation crosslinked -name	Aids supporting radiation crosslinked	Density. g/cm^3	Standard deviation
1	Zinc oxide	1	0.13	0.01
2		3	0.17	0.08
3		5	0.10	0.09
4	Tracryl	1	0.08	0.01
5		3	0.45	0.07
6		5	0.41	0.06
7	Zinc oxide/ tracryl	0.5/0.5	0.22	0.07
8		0.7/0.3	0.08	0.01
9		0.3/0.7	0.10	0.01
10		1.5/1.5	0.06	0.01
11		2/1	0.04	0.03
12		1/2	0.08	0.01

Density - Gamma radiation 100 kGy

Sample name	Aids supporting radiation crosslinked -name	Aids supporting radiation crosslinked	Density. g/cm^3	Standard deviation
1	Zinc oxide	1	0.47	0.01
2		3	0.23	0.08
3		5	0.22	0.06
4	Tracryl	1	0.36	0.06
5		3	0.28	0.06
6		5	0.33	0.08
7	Zinc oxide/ tracryl	0.5/0.5	0.24	0.09
8		0.7/0.3	0.18	0.01
9		0.3/0.7	0.26	0.01
10		1.5/1.5	0.27	0.01
11		2/1	0.60	0.01
12		1/2	0.68	0.01

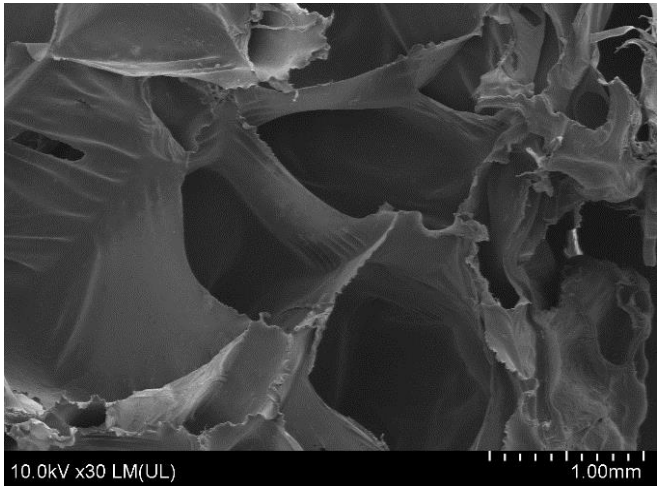
SEM





Electron radiation sample 4. dose 100 kGy

Gamma radiation sample 4. dose 100 kGy



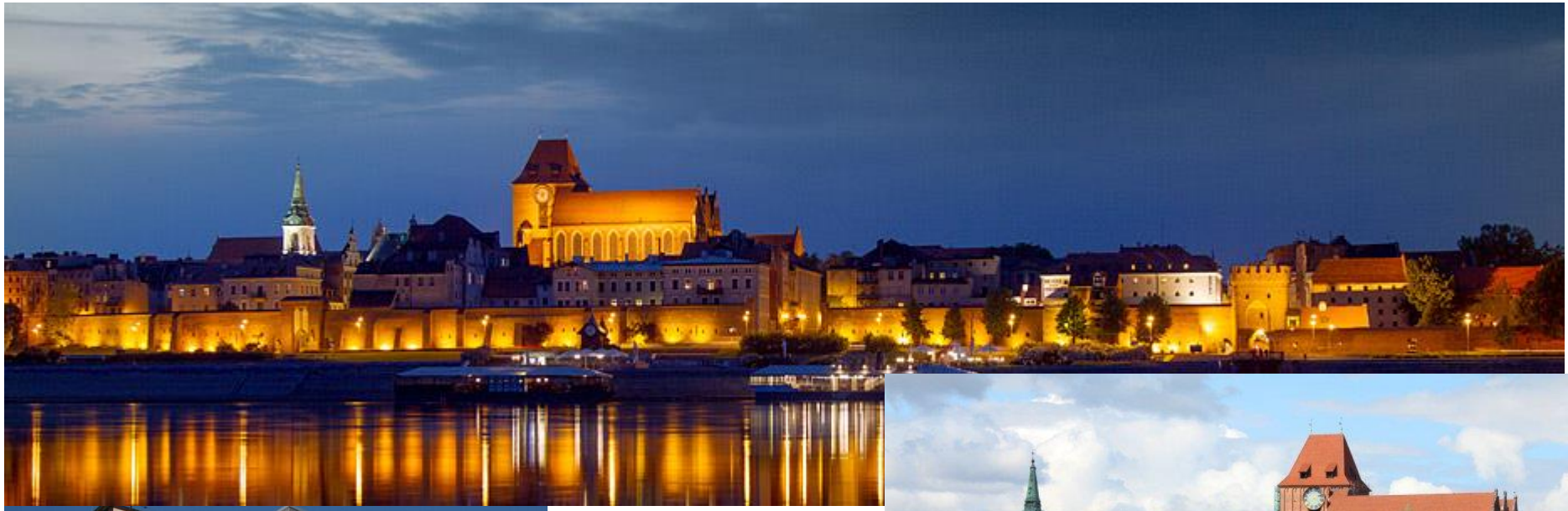
Chemically crosslinked foams

Comparison of chemical and radiation crosslinking

Parameters	Crosslinking radiation	Chemical radiation
Process control	easy	complcated
Production rate	fast	slow
Device (production line)	Rather simple	simple
Costs	Decrease with the volume of production	Relatively constant
Choice of foaming	simple	More complicated
Thickness. mm	3-6	5-16
Cell size. mm	0.2-0.4	0.5-0.8
Degree of crosslinking	30-40	60-70

Literature:

1. A.Stasiek, A. Raszkowska-Kaczor, K. Bajer, Wpływ obecności środka wspomagającego sieciowanie oraz zawartości środka porującego na właściwości polietylenowych pianek chemicznie sieciowanie, Przemysł chemiczny 2013, 92, 6, 1038.
2. A. Raszkowska-Kaczor, A., A. Stasiek, K. Janczak, E. Olewnik-Kruszkowska, Chemically crosslinked polyethylene foams of limited flammability, Polimery 2015, 60 (4), 283-285
3. A. Raszkowska-Kaczor, W. Głuszewski, A. Stasiek, Zastosowanie radiacyjnego sieciowania w produkcji polimetylenowych pianek, Tworzywa sztuczne w przemyśle, 5/2016, 47-48



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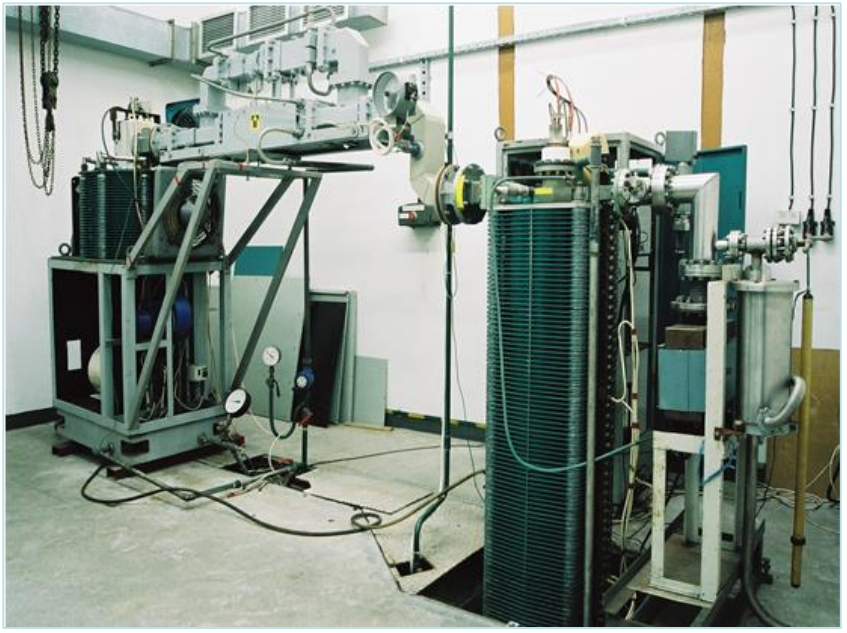
THE RESULTS OF THE RESEARCH RADIOLYSIS DIFFERENT VARIETIES OF PE

We appreciated the effect of ionizing radiation on linking processes and properties of foams.



Electron beam accelerator
Electronics 10/10

The study used the electron accelerator with an energy of 10 MeV and with a beam power of 10 kW

Gamma Chamber 5000
259 TBq (7000 Ci)
Dose rate: 3.95 kGy/h

For comparison. we also conducted a radiation treatment by gamma irradiation with an average energy of 1.25 MeV

Gas chromatography (GC)

Gas chromatograph Shimadzu (thermal conductivity detector. molecular sieves 5A) was used for the determination of radiation yield of hydrogen evolution (G_{H_2}) and absorption of oxygen ($-G_{O_2}$) from the dose of radiation in the range of 5 to 20kGy. Samples were irradiated in air. in closed vessels with gas phase subjected to gas chromatographic analysis at room temperature.

The gas chromatograph was attached by interface to the PC computer where the data were acquired by program CHROMAX. The carrier gas was argon (99.99 %). calibration gases were hydrogen 99.99 % and oxygen 99.99 %. Operations were done with syringes of volume 10. 25 and 500 ml. The chromatographic system was working at 220 °C. the column was kept at 40 °C and the detector at 100 °C. The rate of flow of carrier gas was 10 ml/min.

Diffuse reflection spectroscopy (DRS)

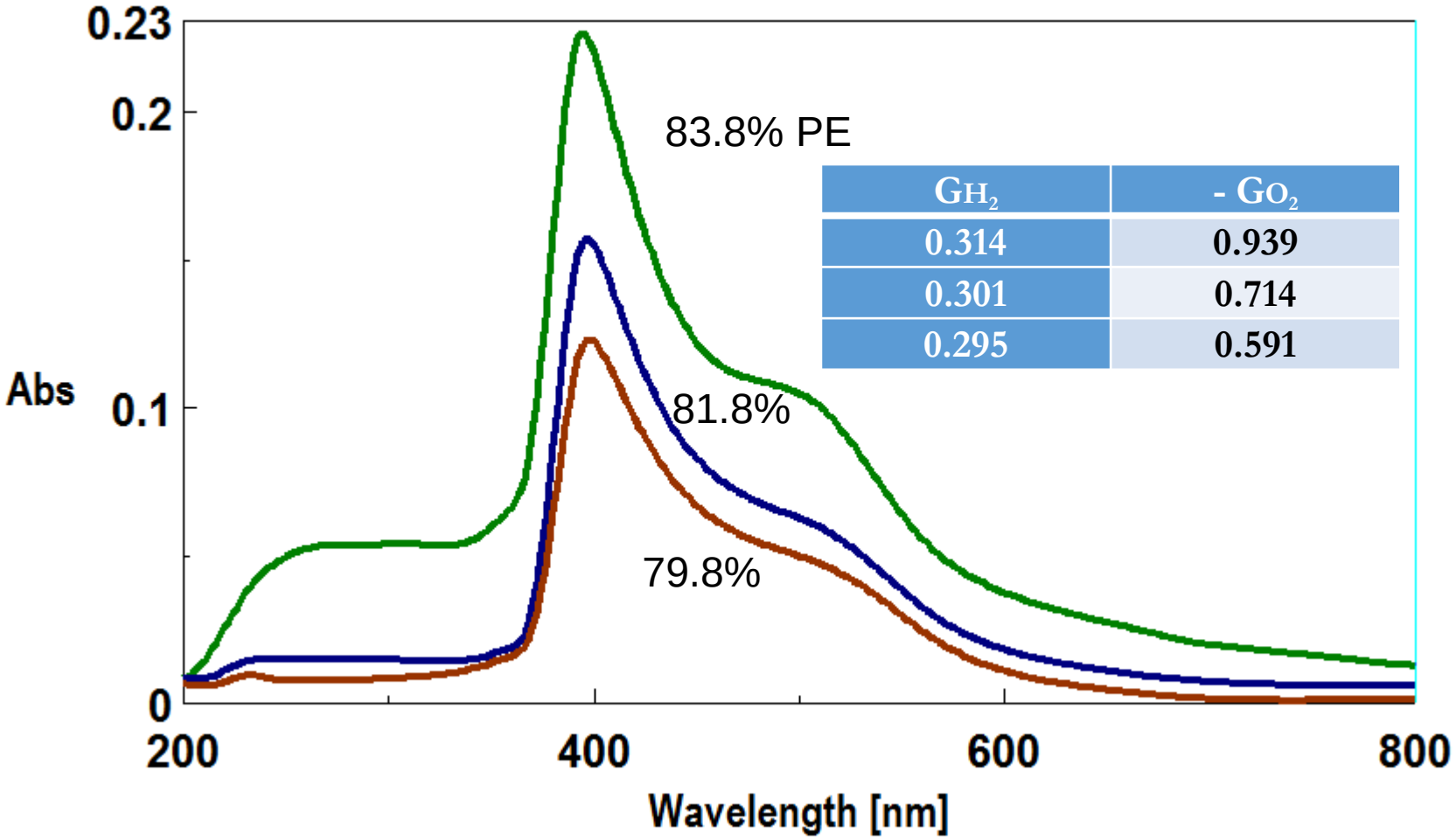
Due to the poor transparency of polymers occurring mostly as powders from the polymerization line. and the opacity or poor transparency of most processed polymers. the best mode of measurement is diffuse reflected light spectrophotometry (DRS) in UV-VIS.

The principle of measurement consists in directing the beam of analyzing light on the surface of the sample. Part of light is reflected back unchanged. but another is bent into the sample and after inside reflections is leaving the sample with spectral information about compounds formed in the result of irradiation and/or compounds present before and destroyed.
In our investigations the spectrophotometer JASCO V-670 equipped with reflection device was used.

sample irradiated in air
gamma radiation. dose rate of 4.2 kGy/h
measurement was made with respect to nonirradiated samples

sample No.	Electron beam (EB)		Gamma radiation (ɣ)	
	G_{H_2} [µmol/J]	- G_{O_2} [µmol/J]	G_{H_2}	- G_{O_2}
1	0.355	0.511	0.314	0.939
2	0.295	0.377	0.301	0.714
3	0.275	0.187	0.295	0.591
4	0.397	0.351	0.293	0.812
5	0.302	0.274	0.274	0.904
6	0.376	0.343	0.262	1.265
7	0.315	0.209	0.309	0.856
8	0.261	0.245	0.283	0.857
9	0.395	0.153	0.298	0.876
10	0.359	0.251	0.257	0.923
11	0.365	0.352	0.326	0.653
12	0.288	0.269	0.282	0.834

Wydajność pochłaniania tlenu w przypadku EB jest znacznie mniejsza niż przy promieniowaniu gamma
W większości przypadków im większa wydajność wodoru tym większa wydajność pochłaniania tlenu


0.23
0.2
0.1
0
Abs
200
400
600
800
Wavelength [nm]
83.8% PE
81.8%
79.8%
GH2
- GO2
0.314
0.939
0.301
0.714
0.295
0.591

1.2.3

	G_{H_2}	G_{O_2}	DRS	G_{O_2}/DRS
1	0.314	0.939	0.23	4.1
2	0.301	0.714	0.17	4.2
3	0.295	0.591	0.13	4.5
4	0.293	0.812	0.22	3.7
5	0.274	0.904	0.20	4.5
6	0.262	1.265	0.26	4.9
7	0.309	0.856	0.15	5.7
8	0.283	0.857	0.24	3.6
9	0.298	0.876	0.23	3.8
10	0.257	2.572	0.17	5.4
11	0.326	1.695	0.16	4.1
12	0.282	2.516	0.17	4.9

The results obtained using the DRS correspond well with the measurements of oxygen uptake.

Significant deviation recorded for the last sample.

ɣ g/cm3	EB g/cm3	ɣ/EB	ɣ -GO2	EB -GO2	ɣ/EB
0.58	0.22	2.6	0.939	0.511	1.8
0.3	0.23	1.3	0.714	0.377	1.9
0.34	0.22	1.5	0.591	0.187	3.2
0.15	0.09	1.7	0.812	0.351	2.3
0.49	0.37	1.3	0.904	0.274	3.3
0.58	0.41	1.4	1.265	0.343	3.7
0.11	0.17	0.6	0.856	0.209	4.1
0.19	0.24	0.8	0.857	0.245	3.5
0.28	0.09	3.1	0.876	0.153	5.7
0.56	0.11	5.1	2.572	0.251	10.2
0.38	0.09	4.2	1.695	0.352	4.8
0.54	0.08	6.8	2.516	0.269	9.4

60 kGy

Comparison processes radiation (ɣ, EB)

dose rate
ɣ 4 kGh/h
EB 14 000 kGy/h

An approximation can be assumed that irradiation of electron beam is carried out in vacuum.

ɣ g/cm^3	EB g/cm^3	ɣ/EB	ɣ -GO_2	EB -GO_2	ɣ/EB
0.47	0.13	3.6	0.939	0.511	1.8
0.23	0.17	1.4	0.714	0.377	1.9
0.22	0.1	2.2	0.591	0.187	3.2
0.36	0.08	4.5	0.812	0.351	2.3
0.28	0.45	0.6	0.904	0.274	3.3
0.33	0.41	0.8	1.265	0.343	3.7
0.24	0.22	1.1	0.856	0.209	4.1
0.18	0.08	2.3	0.857	0.245	3.5
0.26	0.1	2.6	0.876	0.153	5.7
0.27	0.06	4.5	2.572	0.251	10.2
0.6	0.04	15.0	1.695	0.352	4.8
0.68	0.08	8.5	2.516	0.269	9.4

100 kGy
Comparison processes radiation (ɣ, EB)

dose rate
ɣ 4 kGh/h
EB 14 000 kGy/h

An approximation can be assumed that irradiation of electron beam is carried out in vacuum.

Conclusions

- **Gas chromatography and DRS proved to be good analytical methods to observe the processes of postradiation oxidation of polymers**
- **The method of radiation is important for the density of crosslinked foams**
- **It can be assumed that competing with the cross-linking reaction of oxidation is important for the final effect**
- **It is not clear protective effect of aromatic antioxidants in the process of radiolysis of different types of mixtures used**
- **This will be the subject of further research.**

Publikacje:

Głuszewski W. Zagórski Z.P. Rajkiewicz M; Protective Effects in Radiation Modification of Elastomers. Radiation Physics and Chemistry. 2014. 105. 53

Głuszewski W. Zagórski Z.P. Rajkiewicz M; Synergistic effects in the processes of crosslinking of elastomers. Radiation Physics and Chemistry. 2014. 94. 36

50th IAEA General Conference meeting in Vienna.

I would like to recall that next year we will celebrate the 150 per year birthday of Maria Sklodowska - Curie.