Impact of selected chemical substances on the degradation of the polyolefin materials

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Introduction

In contemporary civilization plastics play an important role in nearly all spheres of life. They are widely used in the development of industry, technology, medicine or construction. Thanks to their properties they became indispensable. Products made of such materials as: cast iron, concrete, glass or others became replaced with lighter materials produced with plastics [1, 2, 3].

Plastics are materials which have particular physiochemical properties and strength during use. Among the largest fields of application, the following main branches of industry shall be distinguished:

- construction
- machine-building industry
- chemical industry
- light industry (electrotechnology, textiles, packaging).

They are also used in products of every day use and other branches of economy.

Most of plastic wastes consist on construction wastes (25%), packaging (21%), electrical products (15%), paints (10%), automobile parts (7%) and others (Fig.1) [1, 2, 3].

In such a way, both in Poland and worldwide use of plastics significantly expanded. Their production increases, the consumption rises and the amount of wastes which are directed to waste dumps accumulates. According to the sources [1] manufacture of plastic products in the world long time ago exceeded 100 mln Mg and is still growing. It is estimated that there are average 500 thousand Mg of wastes more every year.

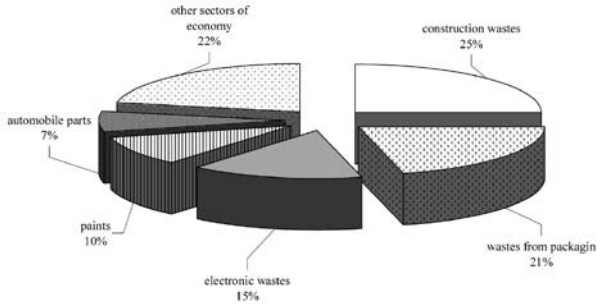


Fig. 1. Plastics in particular sectors of industry [2]

Therefore, rational management of plastic wastes is so important. In highly developed countries this branch of economy is the one of the most important activities of environment protection.

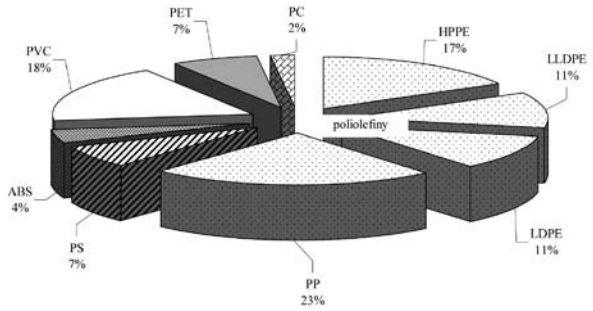


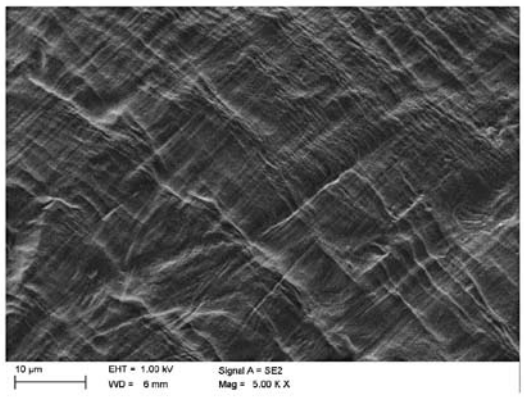
Fig. 2. World consumption of plastics in 2010 [2]

Plastics most widely used (Fig. 2) are: PP (polypropylene) as much as 23%, PVC (polyvinyl chloride) - 18%, and HDPE (high density polyethylene) - 17% of consumption. On the other hand, the least used are: PC (polycarbonate) 2%, ABS (Acrylonitrile butadiene styrene) - 4%, and PS (polystyrene) and PET (Polyethylene terephthalate) 7% each [2, 4, 5,6].

Testing characteristics of polyolefin plastics

Granulated plastic from polyolefin group was used for testing (Fig. 3). The mixture consisted of polyethylene wastes (such as foils, pipes) and polypropylene wastes (such as bottles, bags)[4].

a)



b)

Fig. 3. Granular polyolefin used for testing a) sample mechanically crushed, b) Picture showing surface of granulated material before testing

Granulated materials used for testing was sampled from the company EKOPARTNER – SILESIA SP. z o.o. The company deals with acquisition of plastic wastes and processing the wastes in such a way as to receive as a final product granulated material that forms feedstock for companies which manufacture plastic products [4].

The main sources that the company acquires plastic wastes from, are:

- wastes from sorting plant of municipal wastes
- wastes from selective collecting
- post-production wastes.

Chemical substances used in testing

For testing four types of substances were used. They are non organic chemical compounds [7]. Table 1 shows basic physical and chemical properties of the substances used.

Table 1

Physical and chemical properties of the substances used

	Hydrogen peroxide	Sodium hydroxide	Hydrochloric acid	Sulfuric acid(VI)
Molecular formula	H_2O_2	NaOH	HCl	H_2SO_4
Molar mass, g/mol	34.01	40.00	36.46	98.08
Density, g/ cm^3	1.47	2.13	1.18	1.8356
Water solubility	With any proportions	Highly hydro-scopic	Soluble	No limits
Melting temperature, °C	-0.9	318–323	-25	10.38
Boiling temperature, °C	150	1388–1390	51	279.6

Testing methodology

Testing consisted on total submersion of plastic waste in the below listed liquid substances, during long period of time and with moderate exposure to UV:

- Sodium hydroxide (NaOH 40% solution)
- Hydrogen peroxide (H_2O_2 3% solution)
- Hydrochloric acid (HCl 37% solution)
- Sulfuric(VI) acid (H_2SO_4 98% solution).

Tests were performed in ambient temperature (22°C). The experiment lasted 84 days with testing intervals of 7 days. Samples of granulated material first submerged in chemical substances according to valid standard were removed from the liquid, dried and weighted with an exactitude of 0.1 mg [8].

Variation of mass was calculated in percentage as compared to initial mass, according to the following formula [8]:

$$C_2 = \frac{(m_2 - m_1)}{m_1} \cdot 100[\%] \qquad (1)$$

where:

m_1 – initial mass, [g]

m_2 – mass of a sample after submerging in a chemical substances, tested every 7 days, [g]

Systematicity of the process made it possible to determine variations of the mass arising from the affect of chemical substances in given period of time.

Test results

Changes of the mass of polymers processed by chemical substances

Testing methodology applied to the experiment made it possible to determine the impact of chemical substances on the mass of tested plastics from the polyolefins group. Test results were presented on the diagram. Due to a large number of repetitions, presented values are an arithmetic mean of three measurements.

Sample of polyolefin plastics submerged in 3% hydrogen peroxide shows the largest mass gain in comparison to the initial mass. The extremum of the mass gain was observed in 21 day of experiment and it reached 12.51% with reference to the initial mass. In subsequent time intervals of the experiment a successive mass loss was observed with reference to the maximum reached in 21 of experiment (Fig. 4).

Granular polyolefins submerged in 40% sodium hydroxide in given period of time undergoes three stages – at the first stage the mass is growing when compared to the initial mass. The highest mass gain was noted in the 14 day of experiment. Mass gain reached 8.77%. At the second stage we observed a momentary mass loss with reference to the maximum reached in the 14 day of testing. On 28 day of experiment mass of the granular polyolefins dropped about 2.67%. In another testing interval (35 day of testing) mass of the granulated material raised about 1.40%. However, starting from the 42 day of testing, a successive mass loss of the polyolefin plastic submerged in 40% solution of sodium hydroxide was observed.

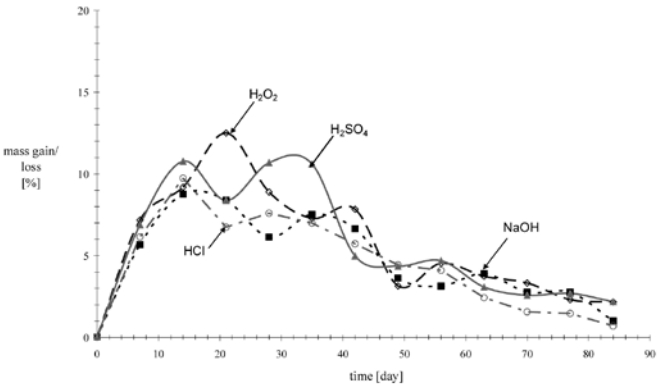


Fig. 4. Mass gain/loss of tested material submerged in selected chemical substances in given period of time

Change of the mass of granular polyolefins submerged in 37% hydrochloric acid was diversified: first, mass gain in comparison to the initial mass, than slight mass loss with reference to the maximum value. Starting from 35 day of testing a successive constant mass loss was observed until at the final stage it reached mass close to the initial mass of the analysed granulated material.

The highest mass gain of granular polyolefins submerged in 37% hydrochloric acid was noted in the 14 day of testing. The mass loss reached 9.74% with reference to the initial mass.

The highest mass gain of polyolefin submerged in 98% sulfuric(VI) acid was observed in the 14 day of testing. It reached 10.78% with reference to the initial mss. In 21 day of testing a short term mass loss was observed in relation to the maximum mass recorded. However, in the two following testing intervals, an increase and momentary stabilization of mass was noted. Starting from 42th day of testing the mass of tested granular polyolefins was constantly and successively dropping.

Structure of polyolefin materials processed by chemical substances

Long term impact of chemical substances on polymers may affect structural changes of tested material. In order to identify such changes tests with the use of SEM (Scanning Electron Microscope) were performed.

Results of scanning tests of the surface structure of granular polyolefin samples submerged in chemical substances are presented in Figures 5÷8.

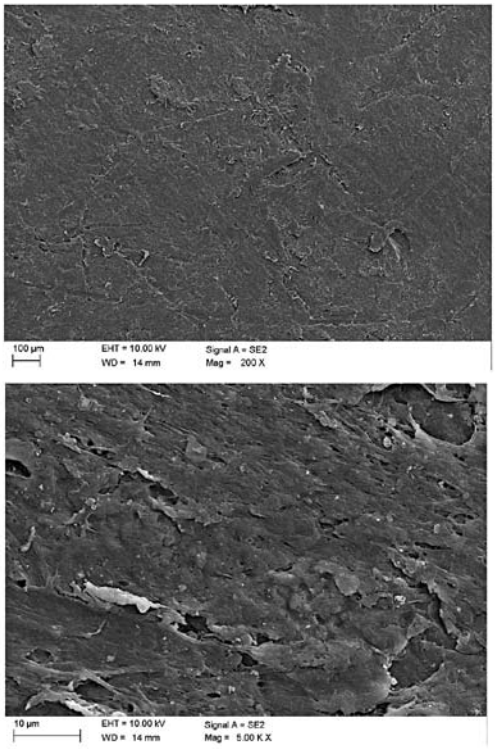


Fig. 5. Microphotography showing surface of the tested granular plastic from the group of polyolefin submerged in 40% solution of sodium hydroxide

Analysing scanning pictures of the granulated material submerged in 40% solution of sodium hydroxide, a distorted surface structure can be seen. (Fig. 5).

During visual analysis no particular changed were noted, which would occur under the effect of H_2O_2 (Fig. 6). No damages inside or outside, nor changes in the size of samples.

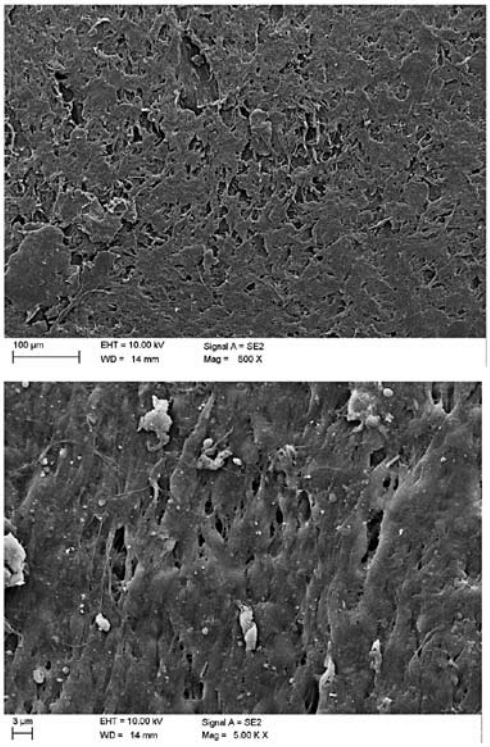


Fig. 6. Microphotography showing surfaces of the tested granular polyolefin submerged in 3% of hydrogen peroxide

Analysis of scanning microscopy shows impairment of the structure of tested granulated material. On the surface, numerous damages of 3 μm and pores of 100 μ were observed. On the basis of test results it can be concluded that hydrogen peroxide (H_2O_2) has highly oxidizing effect on granular polyolefins. In magnification, corrugations of the surface of tested sample are visible.

Visual analysis did not reveal any particular changes which would occur under the long term exposure to concentrated sulfurous(VI) acid (Fig. 8). No damages on the outside were noted, and the only "naked-eye" visible change was smoothing of the edges of the granulated material torn during mechanical processing.

Analysis of scanning microscopy shows slight impairment of the structure of tested material. On the surface numerous damages small pores are visible. Moreover, adsorption of sulfur by the analaysed granulated material was observed (Fig. 9).

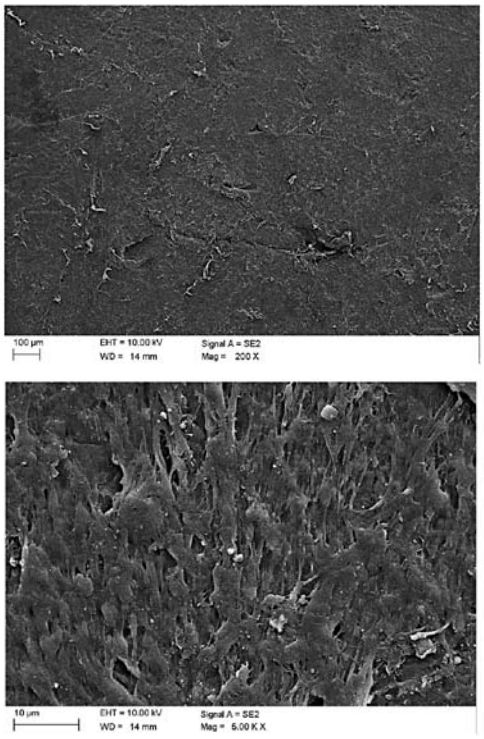


Fig. 7. Microphotography showing surface of the tested granulated plastic from polyolefin group submerged in 37% hydrochloric acid

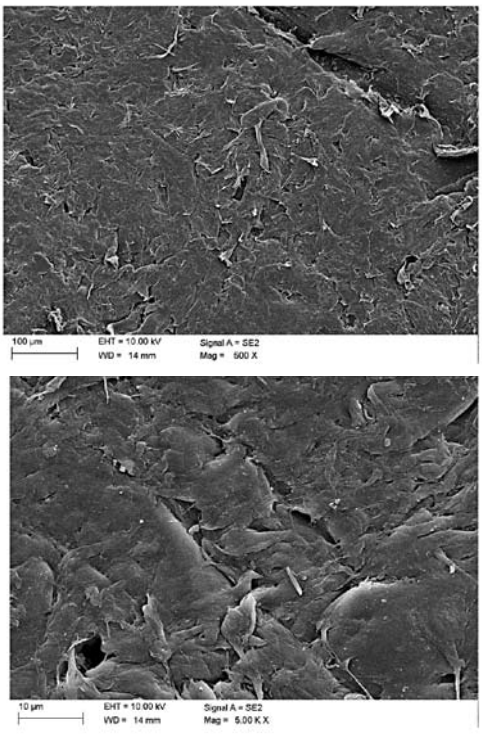


Fig. 8. Microphotography showing surface of the tested granulated plastic from polyolefin group submerged in 98% sulfurous(VI) acid

The content of sulfur was determined using Eschka method on sample submerged in concentrated sulfurous(VI) acid. Analysis showed that sulfur content in the sample submerged in concentrated sulfurous(VI) acid increased about 0.13% in comparison with the original elementary composition.

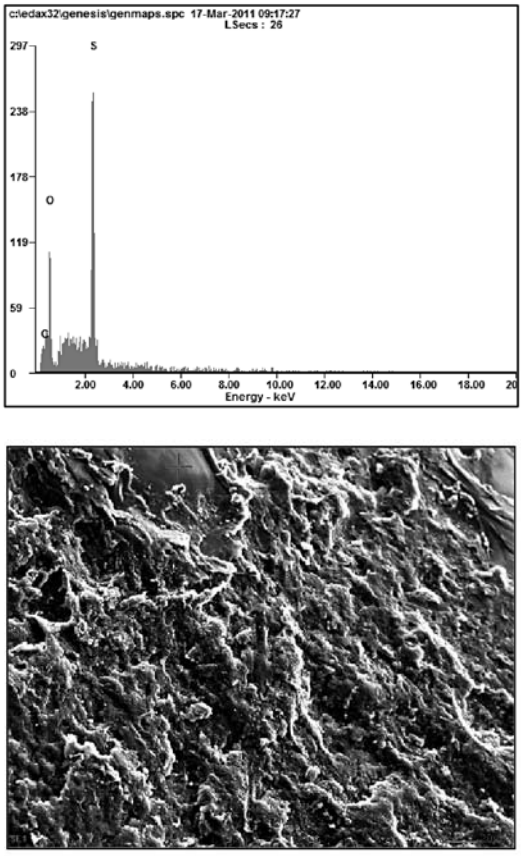


Fig. 9. Presence of sulfur in the granulated material after submerging in 98% sulfurous(VI) acid

Conclusions

Based on the performed tests of mass changes and structural verification of sampled granular polyolefin material, it was fund that:

- in case of chemical reagents, mass measurements show significant alterations
- in case of measurement of the mass of samples processed by chemical reagents the most mass loss is observed with 3% hydrogen peroxide. The least impact on the changes of the granulated material mass has 40% sodium hydroxide
- observed mass alternations of the tested granulated polyolefin may proof significant penetration of chemical substances into surface layer of samples
- scanning pictures of tested samples submerged in selected chemical substances show diversified character of destructive impact of these agents on surface layer of the plastic.

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Translation into English by the Author

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