



INFLUENCE OF AIR CONTENT ON THERMAL DEGRADATION OF POLY(ETHYLENE TEREPHTHALATE)

Wojciech Rejmer

ORCID: 0000-0002-1955-1553
Faculty of Technical Sciences
University of Warmia and Mazury in Olsztyn

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Abstract

The aim of these research is to investigate the air content on aging of poly(ethylene terephthalate) (PET) preforms. Three air pressures were selected and in each pressure 5 samples were aged during 21 days in 80°C. Three samples were selected to be cut for determination of density with the use of hydrostatic method. Sample mass, Young modulus and surface roughness were measured for each sample before and after aging and differences between those parameters were presented as results. The changes of parameters may lead to a conclusion that mechanism of polymeric chain oxidation is dominant during thermal aging of PET. However aging process is not the fastest in atmospheric pressure but in lower air contents. This effect may be caused by greater evaporation of small molecule degradation products and shifting of reaction equilibrium in the direction of further decomposition.

Correspondence: Wojciech Rejmer, Katedra Technologii Materiałów i Maszyn, Wydział Nauk Technicznych, Uniwersytet Warmińsko-Mazurski, ul. Oczapowskiego 11, 10-719 Olsztyn, e-mail: wojciech.rejmer@uwm.edu.pl

Introduction

The varied properties of polymers turned out to be extremely useful for industry, which resulted in large scale use. With time, however, irreversible and often negative changes in the properties of the material occur. Physical and chemical changes generated by usage are called aging. Natural aging proceeds under the influence of the surrounding natural environment during storage and use. Artificial aging of the material occurs under specially designed conditions and is used for research purposes. Several types of polymer aging can be observed based on physical conditions that cause structural change. This processes include: biological aging, electrical aging, mechanical aging, chemical aging and photochemical aging, thermal aging. Thermal degradation of polymers is called “molecular degradation resulting from overheating”. In high temperatures molecules of the polymer are defragmenting (molecular defragmentation) (SOBKÓW, CZAJA 2009). Products of this process can react with each other and with remaining polymer chains resulting in change of materials properties. During thermal degradation the molecular mass of polymer chains is impacted the most. Physical and optical properties that the process influences are: strain at break, maximum stress, rigidity, color change.

In this work poly(ethylene terephthalate) (PET) products are studied. PET is one of most common polymers used in industry. It is used for production of bottles, sprockets, and garments. The reason for PET popular use is that it retains its shape memory, i.e. after deformation it returns to the shape given before crystallization. The properties of PET depend on its degree of crystallinity. With the normal proportion of the crystalline phase (approx. 40%), it is characterized by high dimensional stability, good chemical resistance, and good sliding and dielectric properties. PET is not resistant to factors such as phenols, concentrated acids and solutions, alkalis and long-term exposure to hot water (hydrolysis). Sterilization of PET products is carried out in an atmosphere of ethylene oxide or by irradiation. It is mainly processed by injection molding at 260-290°C (injection shrinkage is 1.2-2%). With extrusion technique films, rods, plates and fibers are formed. Extrusion temperature is 260-280°C (LÓPEZ-FONSECA et al. 2011). Researchers have studied the degradation of recycled PET during processing and concluded that chain scission can occur and that formation of grafted copolymers and crystallization can be facilitated (ITIM, PHILIP 2015) and others concluded that during repetitive extrusion, chain scission is a dominant process and no chain branching or cross-linking were observed which decreased capabilities and crystallinity (BADÍA et al. 2009), whereas others concluded that cross-linking and chain branching occur during extrusion (NAIT-ALI et al. 2011). Researchers currently focus on the influence of physical ageing on the mechanical properties of semicrystalline PET, using several methods to characterize both the change in morphology and physical properties of PET:

Such as calorimetric analysis, FTIR, X-ray, NMR and other. These studies were carried out to enhance understanding of the structure–property relationships, which are important for materials that require stability and durability during their lifetime (ALJOUMAA, ABOUDI 2016). During the exposure to sunlight, many reactions in PET molecular chains may occur: chains scission reaction due to thermal degradation of vinylic and carboxylic chain ends, which may recombine by trans-esterification reaction (EL-TOUFAILI 2006), photo-degradation of methylene groups which will cause an irreversible rupture of the polymeric chain, and change in the color of the bottle to yellow due to many substances used in the process of synthesis and fabrication (YANG et al. 2010). Moreover, at outdoor ageing, the exposure to light and air will cause a photooxidation of PET (photochemical ageing). It is known that PET absorbs at the extreme limit of the UV band ($300 \text{ nm} < \lambda < 330 \text{ nm}$). This phenomenon is superficial, thin layer may degrade by this reaction and is limited by the O_2 diffusion and superficial light absorption. This material is also susceptible to physical aging below the glass transition temperature caused by the slow change of quenched material at a thermodynamically non-equilibrium state to equilibrium. This is related to the relaxation processes with characteristic, different time constants (SATO, SPRENGEL 2012). It results in a reduction in entropy, enthalpy and specific volume with an increase in yield stress and tensile and flexural module. Hay investigated the effect of the crystalline phase on the behavior and properties of PET (KONG, HAY 2003). It turned out that the crystalline phase limits mobility of the chain segments, influencing the macroscopic properties of the material (PANOWICZ et al. 2021). The aim of this paper is to investigate changes in PET surface structure and mechanical properties under thermally accelerated aging conditions and variable air content.

Materials and methods

Research material consisted of 26 preforms made from PET (Fig. 1). Samples undergone the same heating cycle with variable air pressures. Samples from 1-5 were heated to 80°C under atmospheric pressure and kept for 21 days. Samples 7-12 were kept in a 6.8 l vacuum chamber under 5.7 Pa of air pressure. Aging conditions for samples 13, 14, 15, 17, 18, 19 were the same in terms of temperature and aging time but the vacuum chamber was depressurized to 2.8 Pa. The air pressure for aging process of samples 19, 21, 22, 23, 24 was 0.3 Pa. Mass and dimensions of samples were measured and presented in Table 1. Mass was determined with analytical scale RADWAG AS60/220.R2.

The samples roughness, Young modulus and mass were measured before and after aging process for all samples. Roughness was measured using SJ-210 Mitutoyo profilometer with elementary distance 0.8 mm and measuring

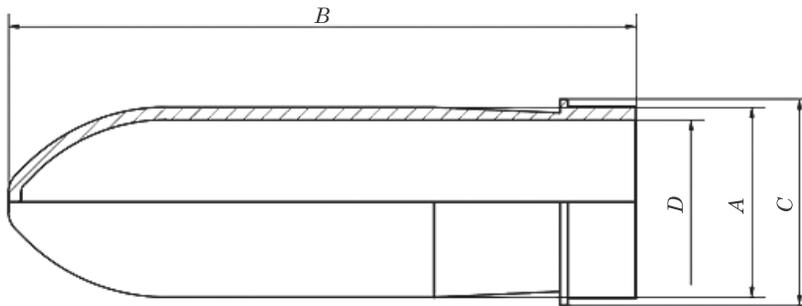


Fig. 1. Shape of investigated samples

Table 1

Dimensions and mass of samples

Sample no.	Dimension A [mm]	Dimension B [mm]	Dimension C [mm]	Dimension D [mm]	Mass [g]
1	47	159	51.54	41.1	98.1944
2	46.99	159.4	51.44	41.14	97.9173
3	46.97	159.6	51.55	41.11	98.2353
4	47.1	159	51.54	41.2	98.1148
5	47.4	159.4	51.5	41.19	98.0271
6	47.38	159.65	51.5	41.16	98.1842
7	47.37	159.6	51.45	41.13	98.0106
8	47.33	159.5	51.44	41.16	98.0271
9	47.43	159.6	51.51	41.19	97.9228
10	47.33	159.5	51.5	41.19	97.9176
11	47.36	159.4	51.48	41.13	97.8713
12	47.45	159.5	51.5	41.17	97.9062
13	47.36	159.6	51.57	41.2	98.2994
14	47.53	159.6	51.54	41.16	98.1164
15	47.54	159.6	51.45	41.14	98.0129
16	47.28	159.5	51.48	41.13	98.0319
17	47.43	159.5	51.5	41.18	98.1736
18	47.51	159.6	51.52	41.17	98.1608
19	47.6	159.5	51.55	41.19	98.2664
20	47.32	159.4	51.52	41.21	98.0329
21	47.36	159.5	51.49	41.1	97.9409
22	47.49	159.5	51.55	41.17	98.1704
23	47.4	159.5	51.59	41.19	98.1057
24	47.27	159.2	51.46	41.11	98.0223
25	47.48	159.5	51.58	41.19	98.3136
26	47.62	159.4	51.52	41.18	98.0894

distance 4 mm. Roughness was measured in 3 places inside of each sample (Tab. 2). Young modulus was determined using Impulse Excitation Technique (IET) with RFDA MF system by IMCE (Tab. 3).

Samples 6, 16 and 20 were chosen to measure non aged sample density by hydrostatic method with analytical scale RADWAG AS60/220.R2 equipped with density determination kit KIT-85 from Radwag. For density measurements distilled water was used as a submerging agent. With nondestructive tests (mass, roughness and Young modulus) difference between pre and post aging state were presented as results.

Table 2

Roughness of investigated samples

Sample no.	<i>Ra</i> 1 [μm]	<i>Ra</i> 2 [μm]	<i>Ra</i> 3 [μm]	Average [μm]
1	0.113	0.146	0.153	0.137
2	0.229	0.329	0.224	0.261
3	0.144	0.173	0.111	0.143
4	0.235	0.087	0.139	0.154
5	0.201	0.177	0.102	0.160
6	0.147	0.193	0.069	0.136
7	0.151	0.129	0.148	0.143
8	0.142	0.123	0.163	0.143
9	0.281	0.32	0.214	0.272
10	0.275	0.327	0.235	0.279
11	0.186	0.273	0.154	0.204
12	0.252	0.176	0.164	0.197
13	0.109	0.233	0.147	0.163
14	0.154	0.168	0.204	0.175
15	0.205	0.262	0.148	0.205
16	0.088	0.109	0.109	0.102
17	0.114	0.105	0.157	0.125
18	0.151	0.117	0.088	0.119
19	0.157	0.123	0.134	0.138
20	0.13	0.113	0.163	0.135
21	0.232	0.24	0.247	0.240
22	0.183	0.205	0.257	0.215
23	0.114	0.187	0.198	0.166
24	0.235	0.144	0.156	0.178
25	0.115	0.118	0.228	0.154
26	0.137	0.163	0.147	0.149

Table 3

Young modulus of pre aged material	
Sample no.	Young modulus [GPa]
1	2.92
2	2.97
3	2.96
4	2.92
5	2.81
6	2.81
7	2.8
8	2.84
9	2.81
10	2.85
11	2.81
12	2.78
13	2.85
14	2.76
15	2.75
16	2.84
17	2.8
18	2.76
19	2.75
20	2.84
21	2.82
22	2.78
23	2.83
24	2.83
25	2.8
26	2.69

Results and discussion

The mass of all aged samples decreased. Mass decrease of samples kept under atmospheric pressure was between 0.099 to 0.10 g. The samples kept under 5.7 Pa decreased their mass by 0.25-0.27 g. Preforms kept under 2.8 Pa of pressure decreased their mass by 0.27-0.28 g. The lowest pressure samples decreased their mass by 0.2-0.21 g. Results of mass decrease were presented on Figure 2.

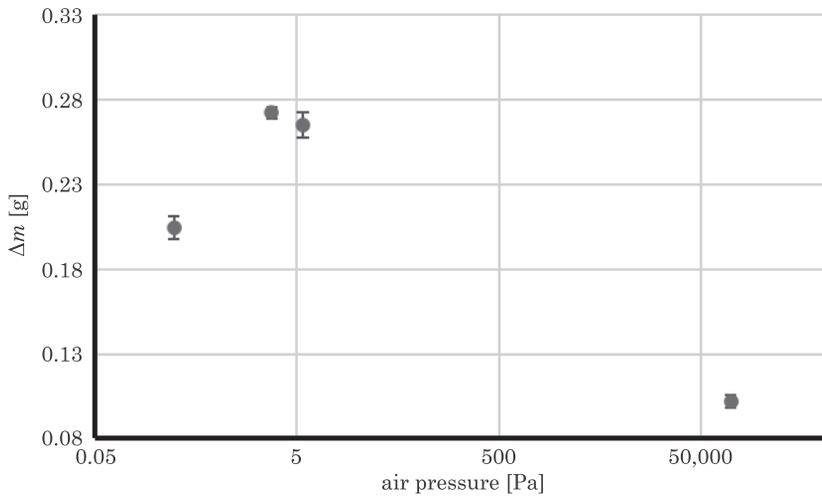


Fig. 2. Mass decrease versus air pressure during aging process

Samples aged with highest air content had lowest decrease of mass during the process this effect might be caused by oxidation of polymer chains which increases the molecular mass. The second processes that occurs during aging at increased temperatures is evaporation of small molecule additions to polymer such as plasticizers and thermostabilizers. In lower air pressures this effect is probably more predominant which causes higher mass decrease. In the lowest pressure the mass decrease is second lowest. Under such conditions both oxidation of polymer chains and conversion of addition compounds to vaporous oxides is least likely. This may give a value of mass loss caused only by terminal depolymerization of PET. The effect may also be caused by oxidation of polymeric chain it self predominantly to products such as carbon mono and di oxide, ethylene and ethyl aldehyde. Evaporation of these degradation products can also be the cause of mass decrease during aging time (VENKATACHALAM et al. 2012).

The decrease of mass is accompanied by change of mechanical properties. In this study this change was measured by calculation of Young modulus obtained with IET. The rigidity of the material decreased only in the samples aged under atmospheric pressure by 0.03-0.05 GPa. Samples aged under 5.7 Pa showed increased Young modulus by 0.4-0.6 GPa. Samples kept under 2.8 Pa of air showed the same effect in the magnitude of 0.4-0.5 GPa. Samples with least amount of air in their environment increased their rigidity by around 0.3 GPa. Results of Young modulus change were presented on Figure 3.

The Young modulus change of polymer material is largely dependant on degree of crystallinity (DONG et al. 2020). The decrease of rigidity in sample aged under atmospheric pressure may be caused by plastifying effect of some of decomposition products such as ethylene glycol (PIVSA-ART et al. 2016). In higher

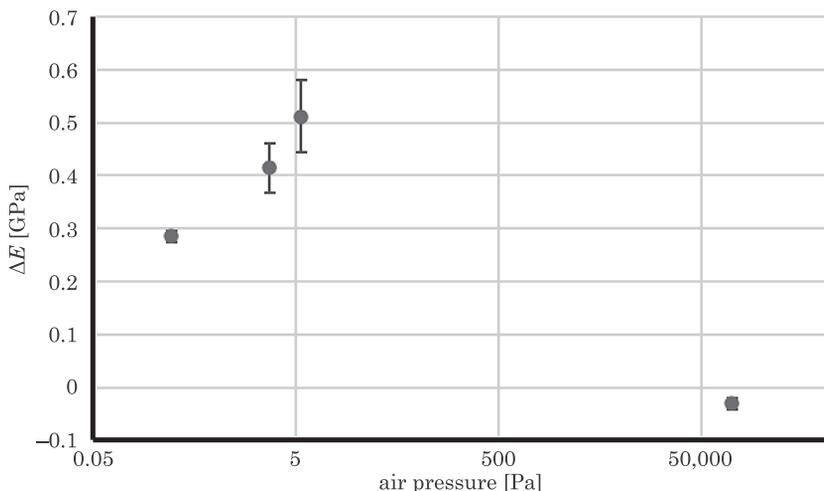


Fig. 3. Young modulus change versus air pressure

air pressures evaporation of those products is higher than in lower pressures under same temperatures. Higher oxygen contents provide also creation of more hydroxyl groups as well as cyclization reactions (KHEMANI 2000). Hydroxyl groups generally lead to increase of crystallization rates, and thus rigidity, due to formation of hydrogen bonds (SANG et al. 2020). In lowest pressure creation of hydrogen bonds can be assumed as minimal, but cyclization processes that cause the reduction of degrees of crystallinity still occur (CHANG et al. 2015). Therefore a lower rigidity of samples aged in 0.3 Pa in comparison to two kinds of samples kept under higher pressures can be observed.

Thermal aging caused increase of surface roughness. For samples aged under atmospheric pressure average roughness increased by 0.19-0.24 μm . Material aged under 5.7 Pa of air pressure had roughness increased by 0.06-0.11 μm . Polyester samples aged in presence of 2.8 Pa of air exhibited roughness increase of 0.15-0.21 μm . Samples heated with the least amount of air showed roughness increase of 0.15-0.22 μm . Figure 4 shows dependence of average roughness increase on air content.

The effect of greatest surface roughness increase in samples aged under atmospheric pressure may be caused by combined effect of oxidation and plastifying effect of decomposition products. The samples aged under 0.3 Pa and 2.8 Pa show similar increase of roughness which can imply similar sizes of crystal structures. Samples aged under 5.7 Pa of air pressure show lowest increase in surface roughness and highest increase of Young modulus, which implies creation of most new crystalline structures and their smaller sizes. Studies by ZABOROWSKA et al. (2021) have shown that significant changes of polymeric material roughness are present only with minimal changes

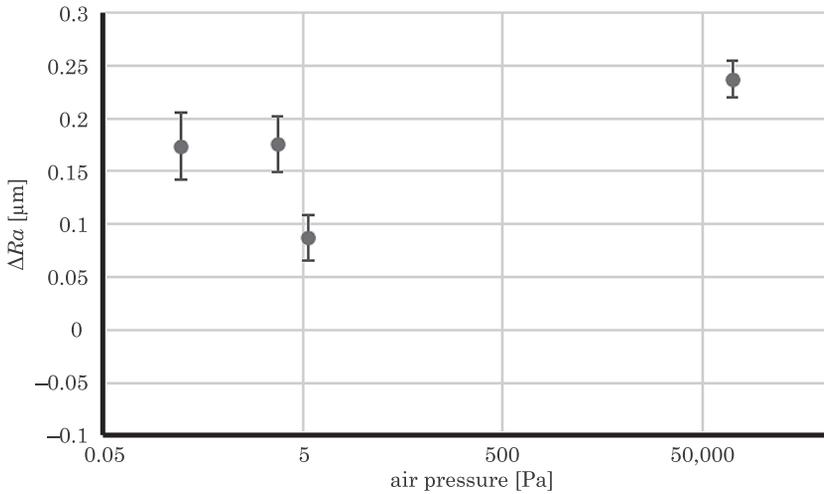


Fig. 4. Average roughness increase versus air pressure

to polymeric chains chemistry, with regard to methane production. However the significant changes in PET samples can be attributed mainly to changes occurring because of oxidation reactions.

Samples density was measured for every type of samples. The results of measured density for aged and non aged samples is presented on Figure 5. Nonaged samples had density of $1.35 \pm 0.02 \text{ g/cm}^3$. Samples aged at atmospheric pressure and at 0.3 Pa exhibited similar values of $1.35 \pm 0.02 \text{ g/cm}^3$ and $1.36 \pm 0.003 \text{ g/cm}^3$ respectively. PET preforms aged at 5.7 Pa and 2.8 Pa exhibited slight increase of density values being $1.37 \pm 0.005 \text{ g/cm}^3$ and $1.39 \pm 0.005 \text{ g/cm}^3$.

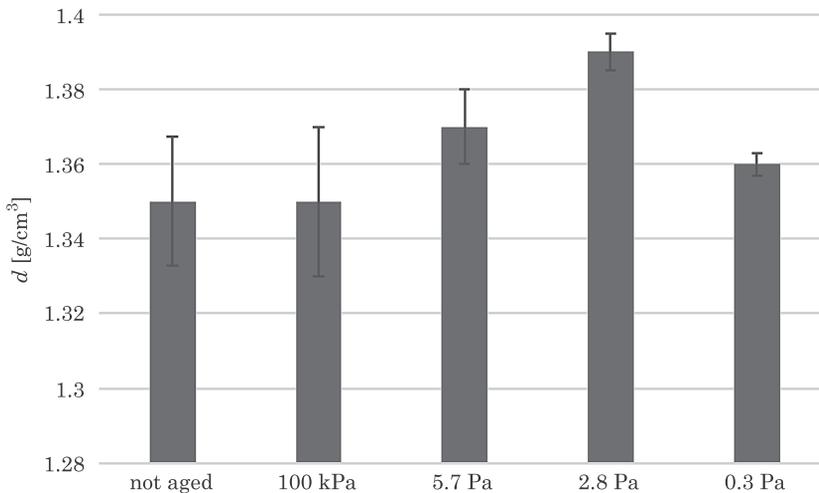


Fig. 5. Density of investigated samples

Density is usually correlated with rates of crystallinity. Higher crystallinity rate is associated with more polymer chains in a given space. Results of density change after aging are similar to mechanical properties results and show that greatest rates of crystallinity are to be expected in samples aged under 5.7 Pa and 2.8 Pa of air pressure (XU et al. 2016)

Conclusions

The air content influences structural and mechanical properties of poly(ethylene terephthalate). Lower air pressure can lead to higher degrees of degradation than atmospheric pressure due to faster vaporization of degradation products. This effect can be used for faster degradation on PET products after reprocessing effects its utility properties to the point of non recyclability. Degradation in high temperatures (80°C) also provides additional increase of small molecule degradation products evaporation, causing accelerated degradation rate. Aging time in conjunction with increased temperature helps to assess PET degradation degree at around 1 year period. Minimal or small values of mechanical properties, density and mass loss at normal air pressure prove almost no degradation during annual periods. Changes of roughness can be attributed strictly to temperature process as it is characteristic only to surface regions and is probably caused by small heat conductivity of polymer.

References

- ALJOURMAA K., ABOUDI M. 2016. *Physical ageing of polyethylene terephthalate under natural sunlight: correlation study between crystallinity and mechanical properties*. Applied Physics Letters A, 122(6): 1-10.
- BADÍA J.D., VILAPLANA F., KARLSSON S., RIBES-GREUS A. 2009. *Thermal analysis as a quality tool for assessing the influence of thermo-mechanical degradation on recycled polyethylene terephthalate*. Polymer Testing, 28(2): 169-175.
- DONG J., LIU J., LI X., LIANG Q., XU X. 2020. *Relationship between the Young's Modulus and the crystallinity of cross-linked poly(ϵ -caprolactone) as an immobilization membrane for cancer radiotherapy*. Global Challenges, 4: 2000008.
- EL-TOUFAILI F.A. 2006. *Catalytic and mechanistic studies of polyethylene terephthalate synthesis*. Ph.D. Dissertation, University of Berlin.
- ITIM B., PHILIP M. 2015. *Effect of multiple extrusions and influence of PP contamination on the thermal characteristics of bottle grade recycled PET*. Polymer Degradation and Stability, 117: 84-89.
- KHEMANI K.C. 2000. *A novel approach for studying the thermal degradation, and for estimating the rate of acetaldehyde generation by the chain scission mechanism in ethylene glycol based polyesters and copolyesters*. Polymer Degradation and Stability, 67: 91-99.
- KONG Y., HAY J.N. 2003 *Multiple melting behaviour of poly(ethylene terephthalate)*. Polymer, 44: 623-633.

- LIU CH., HU L., LU Y., ZHAO W. 2015. *Evolution of the crystalline structure and cyclization with changing tension during the stabilization of polyacrylonitrile fibers*. Journal of Applied Polymer Science, 132: 42182.
- LÓPEZ-FONSECA R., DUQUE-INGUNZA I., DE RIVAS B., FLORES-GIRALDO L., GUTIÉRREZ-ORTIZ J.I. 2011. *Kinetics of catalytic glycolysis of PET wastes with sodium carbonate*. Chemical Engineering Journal, 168: 312-320.
- NAIT-ALI L.K., COLIN X., BERGERET A. 2011. *Kinetic analysis and modelling of PET macromolecular changes during its mechanical recycling by extrusion*. Polymer Degradation and Stability, 96: 236-246.
- PANOWICZ R., KONARZEWSKI M., DUREJKO T., SZALA M., ŁAZIŃSKA M., CZERWIŃSKA M., PRASUŁA P. 2021. *Properties of polyethylene terephthalate (PET) after thermo-oxidative aging*, Materials, 14: 833.
- PIVSA-ART W., FUJII K., NOMURA K., ASO Y., OHARA H., YAMANE H. 2016. *The effect of poly(ethylene glycol) as plasticizer in blends of poly(lactic acid) and poly(butylene succinate)*. Journal of Applied Polymer Science, 133: 43044.
- SANG T., WALLIS C.J., HILL G., BRITOVSEK G.J.P. 2020. *Polyethylene terephthalate degradation under natural and accelerated weathering conditions*. European Polymer Journal, 136: 109873.
- SATO K., SPRENGEL W. 2012. *Element-specific study of local segmental dynamics of polyethylene terephthalate upon physical aging*. Journal of Chemical Physics, 137: 104906.
- SOBKÓW D., CZAJA K. 2009. *Badanie odporności materiałów na starzenie atmosferyczne*. Czasopismo Techniczne. Mechanika, 106: 429-430.
- VENKATACHALAM S., NAYAK S.G., LABDE J.V., GHARAL P.R., RAO K., KELKAR A.K. 2012. *Degradation and recyclability of poly (ethylene terephthalate)*. In: Polyester. Ed. H. Salach. InTech Open, London.
- XU M., HUANG G., FENG S., MCSHANE G.J., STRONGE W.J. 2016. *Static and dynamic properties of semi-crystalline polyethylene*. Polymers, 8: 77.
- YANG J., XIA Z., KONG F., MA X. 2010. *The effect of metal catalyst on the discoloration of poly(ethylene terephthalate) in thermo-oxidative degradation*. Polymer Degradation and Stability, 95: 53-58.
- ZABOROWSKA M., BERNAT K., PSZCZÓLKOWSKI B., WOJNOWSKA-BARYŁA I., KULIKOWSKA D. 2021. *Challenges in sustainable degradability of bio-based and oxo-degradable packaging materials during anaerobic thermophilic treatment*. Energies, 14: 4775.

