

# The effect of functionalized ethylene-*n*-octene copolymer on mechanical properties of bioPET with organic waste fillers

Karina Rusin-Żurek<sup>1</sup>, Stanisław Kuciel<sup>1, \*</sup> (ORCID ID: 0000-0001-9244-7499), Maria Kurańska<sup>2</sup> (0000-0003-4611-3724)

DOI: <https://doi.org/10.14314/polimery.2023.6.4>

**Abstract:** The effect of compatibilizer – ethylene-*n*-octene copolymer grafted with maleic anhydride (EOC-g-MAH) used in the amount of 3 wt% on tensile and flexural properties and impact strength of bioPET with the addition of 10 wt% filler derived from organic waste (egg and mollusc shells, coffee grounds) was investigated. EOC-g-MAH slightly decreased tensile strength, flexural strength, and modulus of elasticity, while significantly increasing impact strength (up to 426%). Moreover, ability of bioPET-based composites to dissipate mechanical energy was improved.

**Keywords:** bioPET, composites, compatibilizer, organic waste, mechanical properties.

## Wpływ funkcjonalizowanego kopolimeru etylen-*n*-okten na właściwości mechaniczne bioPET z napełniaczami pochodzącymi z odpadów organicznych

**Streszczenie:** Zbadano wpływ kompatybilizatora – kopolimeru etylen-*n*-okten szczepionego bezwodnikiem maleinowym (EOC-g-MAH) użytego w ilości 3% mas. na właściwości mechaniczne przy rozciąganiu i zginaniu oraz udarność bioPET z dodatkiem 10% mas. napełniacza pochodzącego z odpadów organicznych (skorupki jaj i mięczaków, fusy z kawy). EOC-g-MAH nieznacznie obniżył wytrzymałość na rozciąganie, zginanie i moduł sprężystości, jednocześnie znacznie zwiększył udarność (aż do 426%). Ponadto zwiększyła się zdolność kompozytów na bazie bioPET do rozpraszania energii mechanicznej.

**Słowa kluczowe:** bioPET, kompozyty, kompatybilizator, odpady organiczne, właściwości mechaniczne.

In recent years, there has been a significant trend in the production of biobased materials from renewable sources as an alternative to traditional petrochemical polymers. Biomaterials allow to reduce the carbon footprint in nature and enable better protection of the planet's green areas [1-3]. This is due to public awareness of the environmental and energy crisis, as well as government regulations being introduced around the world [4, 5].

Two-thirds of the world's demand for plastic materials is provided by five types of polymers: polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(vinyl chloride) (PVC) and poly(ethylene terephthalate) (PET) [6]. Due to technological development, it is possible to obtain plastics from renewable raw materials [7, 8]. The production of biopolymers around the world is dynamically developing and has recorded a significant increase in recent years [9, 10]. The largest markets for biopolymers are Asia,

Europe and North America, and the leading countries in the production of biopolymers include the United States, Germany, Italy, and China [11]. However, the production of biopolymers still only accounts for a small part of the total world production. According to data published by European Bioplastics, biopolymers still account for less than 1% of the 390 million tons of plastic produced annually. Overall global polymer production stagnated in 2020 due to the Covid-19 pandemic, however, it has been increasing again since 2021. Nevertheless, the large growth expected after the pandemic is slowing down and the entire global economy suffers from global inflation [11, 12]. According to the latest market data compiled by European Bioplastics in cooperation with the nova-Institute, the production of biopolymers is expected to increase from 2.2 million tons in 2022 to approx. 6.3 million tons in 2027. Of all biobased plastics, we can distinguish biodegradable and non-biodegradable materials. Currently, biodegradable plastics such as PLA account for 51.5% of all bioplastics produced, while non-biodegradable plastics account for 48.5%, of which bioPET accounts for 4.2% [12].

BioPET is a type of thermoplastic polymer that has been made from biological raw materials such as lactic acid or ethylene from such plants as sugarcane, corn,

<sup>1</sup> Cracow University of Technology, Faculty of Materials Engineering and Physics, al. Jana Pawła II 37, 31-864 Kraków, Poland.

<sup>2</sup> Cracow University of Technology, Faculty of Chemical Engineering and Technology, Warszawska 24, 31-155 Kraków, Poland.

<sup>\*</sup> Author for correspondence: [stask@mech.pk.edu.pl](mailto:stask@mech.pk.edu.pl)

molasses, and not from traditional petroleum-derived raw materials [13]. The main advantage of bioPET is its environmental friendliness. The production of this polymer emits a significantly lower amount of carbon dioxide compared to conventional PET, which reduces the impact on climate change [14]. BioPET has similar physical properties to traditional PET, so it can be used in similar applications such as packaging, bottles, fabrics, etc. [15, 16]. However, despite its many benefits, bioPET is not without disadvantages. One is to ensure access to sufficient bio-based raw materials to remain price-competitive with traditional materials. That is why research on improving production processes and the search for innovative sources of biopolymers are still underway. The most popular producers of bioPET in the world are currently FKUR (Germany) under the Elaston brand, NaturePlast (France), SK Chemicals (South Korea), Ecozen and Trema (South Korea).

The production of biopolymers from plant raw materials has many advantages, such as reducing greenhouse gas emissions, increasing sustainable production, and reducing dependence on oil [17]. The addition of organic waste fillers reduces the impact strength of polymers by almost 10 times. Montava *et al.* [18] described bioPET-based composites with fibers from textile industry waste, the addition of which caused a color change from gray to brown and a slight increase in density. The composites showed increased flexibility and hardness. However, the textile fibers also reduced tensile strength and, to a greater extent, elongation at break and impact strength. Montava *et al.* [19] observed that the use of a small amount of multifunctional copolymer can improve the properties of biodegradable polyesters when melt-compounded with their recycled petrochemical counterparts and efficient mechanical recycling is achieved. Dissanayake *et al.* [20] used PET-degrading microbes and successfully identified the relevant PET hydrolase enzymes. The characterization and engineering of these enzymes to selectively depolymerize PET to original monomers such as terephthalic acid and ethylene glycol has been successful. Presented papers highlighted the strong metabolic pathways leading to the biodegradation of PET into biotransformed molecules of high value. New synthetic micro-organisms will help establish a circular material economy, mitigate the negative energy and environmental impacts of PET, and provide market incentives for recycling PET. However, the production of biopolymers still needs further research and technology development to become more competitive and cost-effective compared to traditional polymers. It can be assumed that the production of biopolymers is more expensive than conventional polymers. The reason for the higher price of biopolymers is, among others, the fact that the raw materials used for their production (e.g. cane sugar, vegetable oils) are more expensive than petrochemical raw materials, such as crude oil or natural gas. In addition, the biopolymer production process is more complicated

and requires specialized equipment and knowledge. On the other hand, the production costs of biopolymers can be more competitive for applications where lower efficiency is required, such as for single-use products such as packaging and garbage bags. In these cases, waste disposal costs can be much lower than with traditional polymers. It is a new field that is constantly developing and improving. Polymeric biomaterials such as bioPET represent a crucial step towards a more sustainable future, contributing to reducing the negative impact on the environment. Their development and implementation are of key importance in the fight against climate change and in building a more responsible economy based on renewable and environmentally friendly raw materials.

Therefore, this study aims to investigate the effect of compatibilizer - maleic anhydride grafted ethylene-*n*-octene copolymer (EOC-g-MAH) on the tensile, flexural and impact properties of bioPET filled with organic waste (egg and mollusk shells, coffee grounds). A constant amount of EOC-g-MAH and organic waste filler was used, which was 3 wt% and 10 wt%, respectively. The ability to dissipate mechanical energy was also determined by low-cycle dynamic tests.

## EXPERIMENTAL PART

### Materials

BioPET (ECOZEN T120) was provided by SK Chemicals (South Korea) and had a density of 1.27 g/cm<sup>3</sup>, yield point of 51 MPa, flexural strength of 76 MPa, flexural modulus of 1800 MPa, and Izod notched impact strength of 93 kJ/m<sup>2</sup>. It is a glycol-modified PET, which contains 15% carbon derived from plant-based biomass components. It does not contain bisphenol derivatives (BPA, etc.) and phthalate-based plasticizer components regulated by the EU RoHS regulations. Organic waste such as mollusc shells, eggshells, and coffee grounds were ground on a mill Retsch ZM 200 (Hann, Germany) with a sieve mesh size of 1 mm at a speed of 6000 rpm. No sieve analysis was performed because it was desired to use all the waste generated by grinding. To remove substances such as essential oils, waxes, egg white and yolk etc. particles were treated with 2.5 mol/dm<sup>3</sup> NaOH solution for one hour, then rinsed with water and dried. Maleic anhydride grafted ethylene octene copolymer (SCONA TSPOE 1002 GBLL) was purchased from BYK (Germany). It is a high impact strength modifier for polyamide as well as PET which improves notch impact strength.

### Samples and composites preparation

Samples for mechanical tests were obtained by injection molding (KM 40-125 Winner Krauss Maffei, Krauss Maffei, Munich, Germany) in accordance with PN-EN ISO 3167. The process was carried out at the temperature profile of 180-250-255-265-270°C, and the injection pres-

**Table 1. Samples designations, composition, and density**

Sample	Composition	Density, g/cm <sup>3</sup>
bioPET	bioPET	1.251
bioPET+3K	bioPET + 3 wt% compatibilizer	1.244
bioPET+10s	bioPET + 10 wt% mollusc shells	1.362
bioPET+10s+3K	bioPET + 10 wt% mollusc shells + 3 wt% comp.	1.226
bioPET+10es	bioPET + 10 wt% eggshells	1.342
bioPET+10es+3K	bioPET + 10 wt% eggshells + 3 wt% comp.	1.302
bioPET+10cg	bioPET + 10 wt% coffee grounds	1.255
bioPET+10cg+3K	bioPET + 10 wt% coffee grounds + 3 wt% comp.	1.212

sure of 800 bar. The used sample designations, composition and density are presented in Table 1.

### Test methods

#### Optical and scanning electron microscopy

The optical microscope Keyence VHX 5000 (Osaka, Japan) with digital image analysis was used to assess the size and surface of the organic waste particles. Tensile fractures of the composites were evaluated using a scanning electron microscope (JEOL JSM-IT200, Tokyo, Japan) in a vacuum at 20 kV. The samples were coated with gold particles using sputter coater (DII-29030SCTR, JEOL, Tokyo, Japan).

#### Mechanical properties

Static tensile properties and low-cycle dynamic tests were carried out on a Shimadzu AGS-X 10 kN testing machine (Kyoto, Japan). The tensile test was performed in accordance with the PN-EN ISO 527-1 standard at a crosshead speed of 5 mm/min. In the dynamic test, a cyclically loaded deformation from a minimum value of 100 N to a maximum of 1000 at a speed of 10 mm/min was used. Flexural properties were determined on a universal testing machine MTS Criterion 43 (Minnesota, United States) with MTS TestSuites 1.0 software in accordance with the PN-EN ISO 178 at a crosshead speed of 10 mm/min. Charpy impact strength was measured using a Zwick/

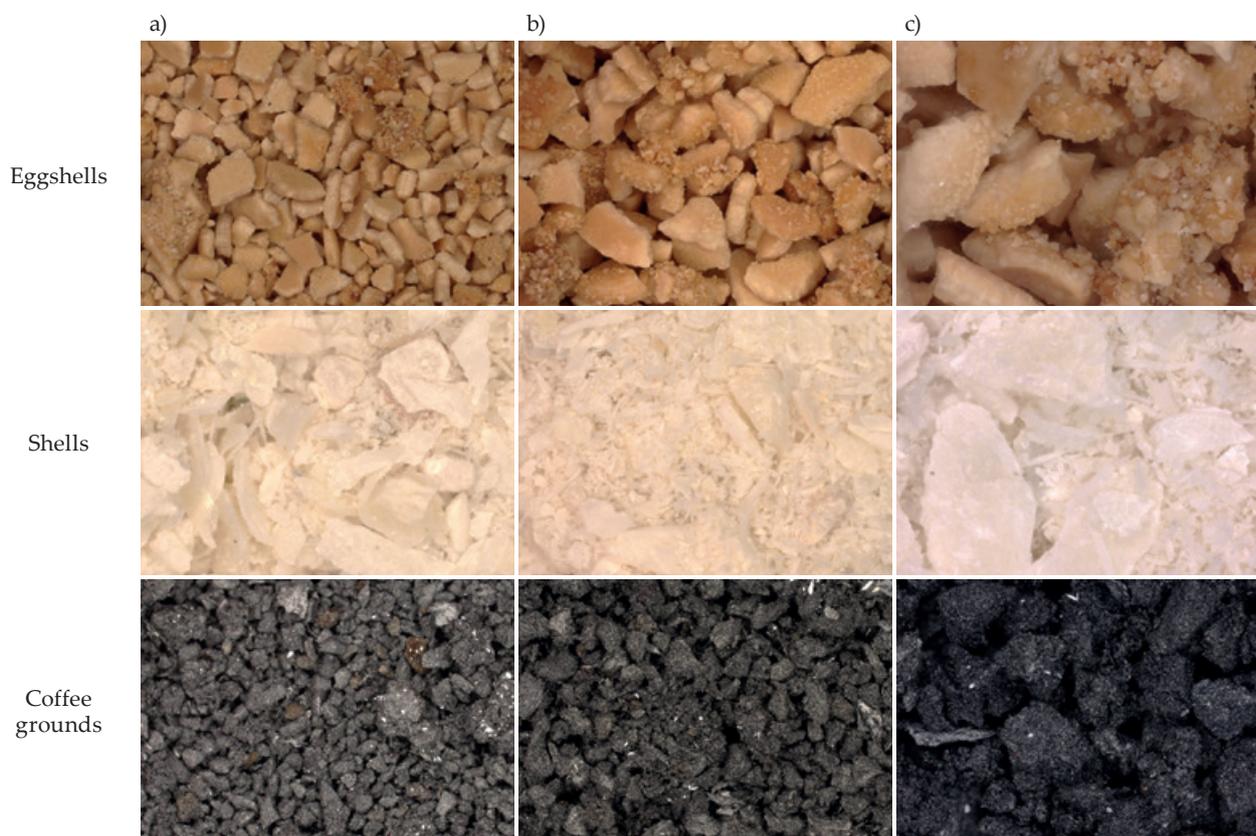


Fig. 1. Optical microscope images of organic waste fillers at different magnification: a) 30 $\times$ , b) 50 $\times$ , and c) 100 $\times$

Roell MTS-SP testing machine (Ulm, Germany). Impact energy of 2 and 5 J was used for unnotched samples in accordance with the PN-EN ISO 179-1.

## RESULTS AND DISCUSSION

### Organic fillers characteristic

Optical microscope images of organic waste fillers are presented in Figure 1.

The images present different grinding effects on the same mill, sieve, and speed. The particles of mollusc shells and eggshells have a lamellar structure, while mollusc shells are larger, their dimensions reach 1 mm, and some are fragmented to several micrometers. Eggshell plates are smaller and reach a maximum of 500–700  $\mu\text{m}$ , there are also fewer microparticles with a size of several microm-

eters. The thickness of the shell plates is smaller and amounts to about 20–30  $\mu\text{m}$ , while the thickness of the eggshells reaches 50  $\mu\text{m}$ . The effect of coffee grinding is the creation of more spatial grains with a rhomboid structure of varying sizes from 150  $\times$  200  $\mu\text{m}$  to 500  $\times$  300  $\mu\text{m}$ .

### Morphology

In SEM micrographs (Fig. 2) at increasing magnifications diversified morphology of organic fillers can be observed. There is a significant geometric similarity between egg and mollusc shells. White lines mark characteristic elements of the fillers. The composites with the addition of egg and mollusc shells particles are brittle, while those with the addition of coffee grounds are developed and more plastic. In the case of a composite with coffee grounds, we observe insufficient adhesion and single microparticles

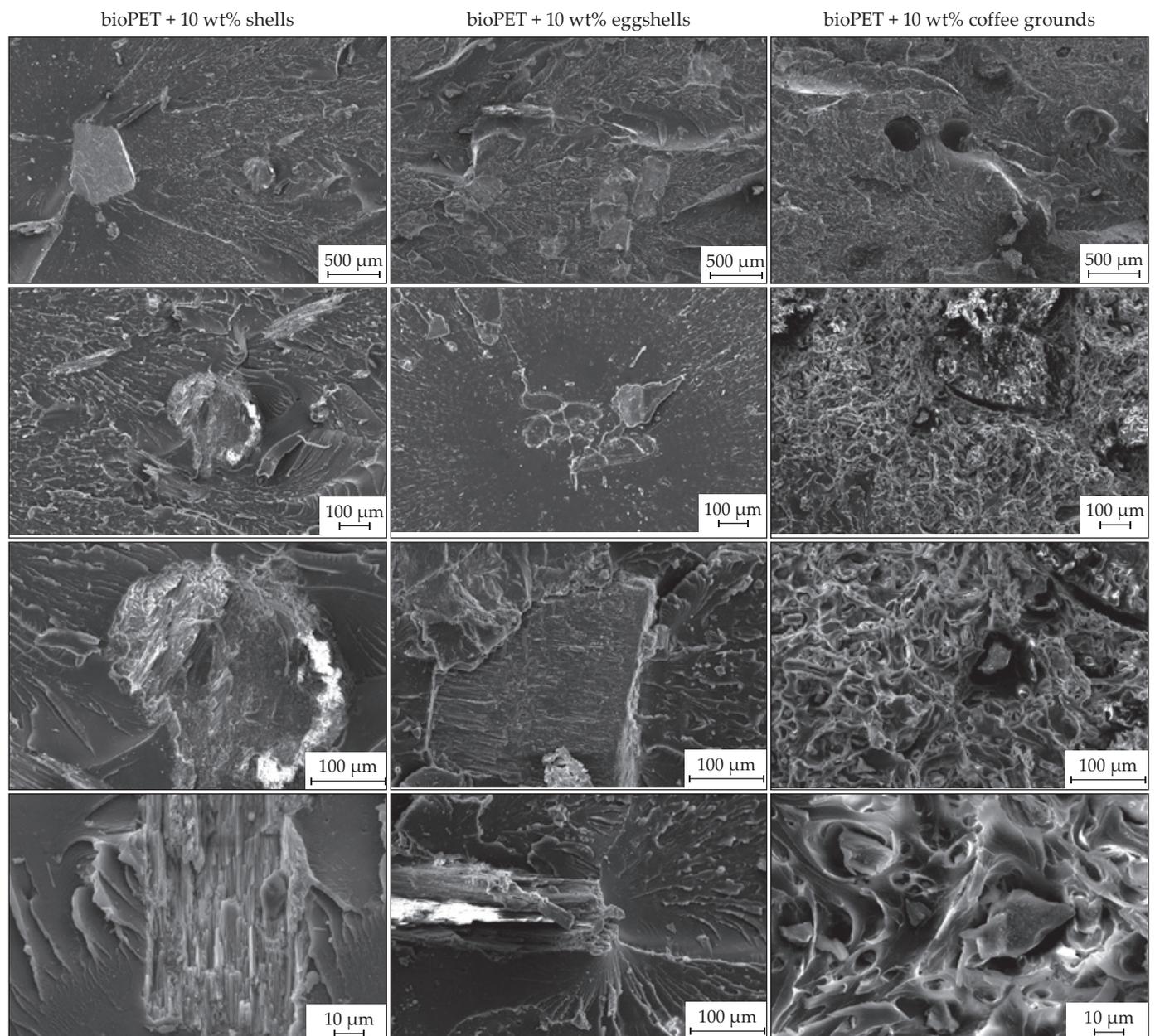
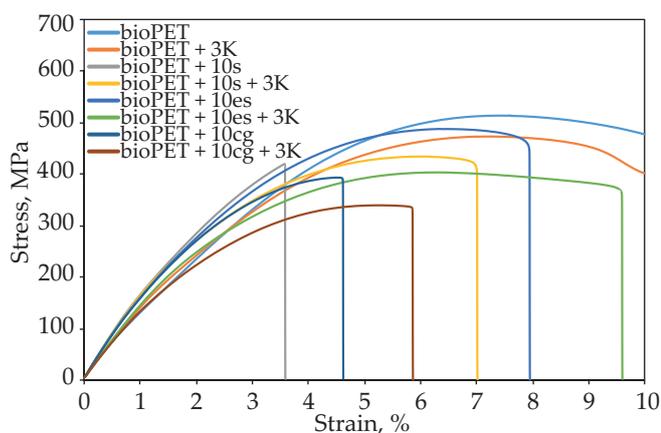


Fig. 2. SEM micrographs of compatibilized bioPET-based composites after tensile test

**Table 2. Tensile and flexural properties of bioPET-based composites**

Sample	Tensile strength MPa	Young's modulus MPa	Elongation at break %	Flexural strength MPa	Flexural modulus MPa
bioPET	47.1 ± 2.8	2455 ± 123	40.2 ± 2.2	72.1 ± 3.6	1874 ± 96
bioPET + 3K	46.3 ± 1.8	2122 ± 93	100.5 ± 9.3	60.4 ± 2.4	1648 ± 62
bioPET + 10s	44.1 ± 1.1	2808 ± 133	4.6 ± 0.3	75.5 ± 2.8	2110 ± 105
bioPET + 10s + 3K	43.0 ± 2.2	2649 ± 64	6.8 ± 0.2	61.7 ± 3.7	1868 ± 89
bioPET + 10es	45.9 ± 3.7	2839 ± 183	6.6 ± 0.2	72.9 ± 0.5	2071 ± 111
bioPET + 10es+3K	40.6 ± 1.2	2436 ± 111	8.5 ± 0.3	62.2 ± 4.2	1857 ± 91
bioPET + 10cg	40.4 ± 1.3	2631 ± 67	4.9 ± 0.1	69.9 ± 0.6	2031 ± 87
bioPET + 10cg+3K	33.9 ± 1.8	2098 ± 101	6.3 ± 0.2	55.1 ± 3	1474 ± 54

**Fig. 3. Stress-strain curves of bioPET and the composites**

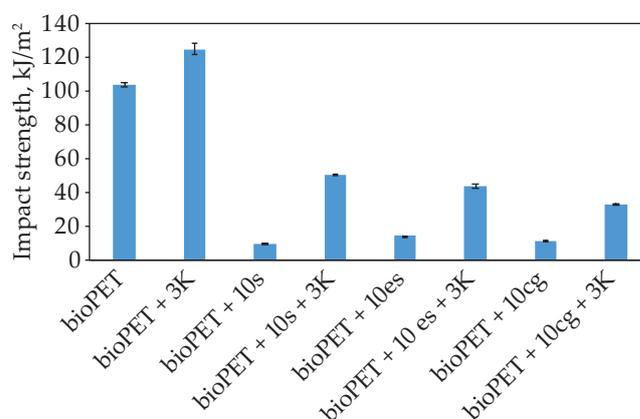
with a size of several tens of micrometers which detach from the matrix during tensile test. Particles of egg and mollusc shells are quite firmly embedded in the matrix and the phenomenon 'pull out' does not occur. However, it can be observed that such a single plate detaches the entire side surface from the matrix.

### Mechanical properties

Figure 3 shows the stress-strain curves of bioPET-based composites. Tensile and flexural properties are listed in Table 2.

In the case of composites without a compatibilizer, the addition of fillers slightly reduces the tensile strength (decrease by 2.5% to 14.2% compared to neat bioPET). However, Young's modulus increased by 7.2% to 15.6% depending on the filler used. The decrease in flexural strength did not exceed 5%. As with Young's modulus, the flexural modulus also increased.

For each composite, the addition of a compatibilizer slightly reduces both tensile and flexural strength and increases elongation at break. This phenomenon can be explained by the fact that functionalized EOC is a flexible rubber-type polyolefin. Its presence in the composites would remarkably soften the material and increase the mobility of the polymer chains, thus resulting in the

**Fig. 4. Impact strength of bioPET and the composites**

slight decrease in tensile and flexural strength but an increase in elongation at break. The lowest decrease in tensile strength was 1.7% for bioPET without the addition of organic fillers, and the largest 16% for bioPET with coffee grounds. In the case of flexural strength for each composite, the decreases were at a similar level of 14.7–21.2%, while Young's and flexural modulus decreased by 5.6–27.4%.

As expected, the addition of EOC-g-MAH caused a significant increase in the impact strength of the composites (Fig. 4) as often reported when functionalized elastomers were used [21, 22]. In the case of pure bioPET, the impact strength increased by 20%. The addition of 10 wt% of organic fillers reduced the impact strength of the composites almost 10 times. The highest increase in impact strength (increase by 426%) showed the composite with the addition of mollusc shells. The increase in impact strength of the composites with the addition of eggshells and coffee grounds was 209% and 191%, respectively, compared to the composites without the compatibilizer. Other authors reported similar observations [18, 19, 21].

### Mechanical energy dissipation

In Figures 5 to 7 we can observe the effects of energy dissipation in the first loops of mechanical hysteresis.

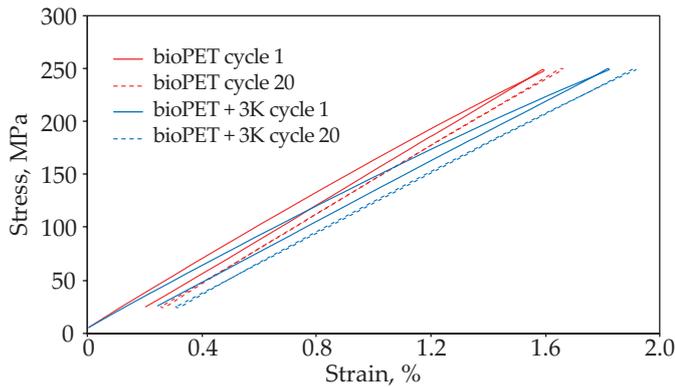


Fig. 5. Comparison of energy dissipation loops for 1st and 20th cycle of bioPET and the composites with 3 wt% EOC-g-MAH

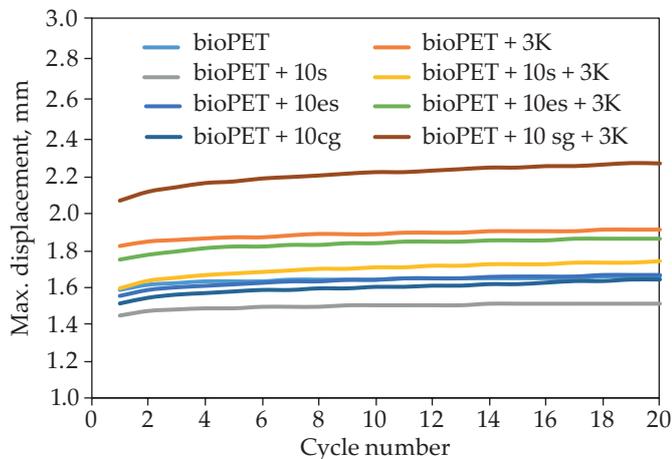


Fig. 6. Maximum displacement as a function of the cycles number

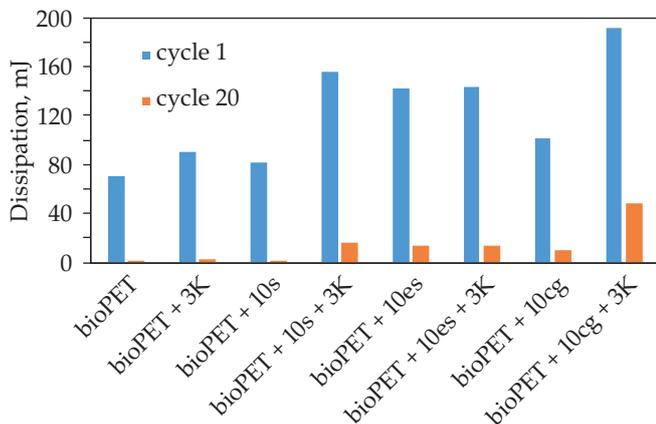


Fig. 7. Energy dissipation between 1st and 20th cycle of bioPET and the composites

The addition of the compatibilizer results in an increase in the ability to dissipate mechanical energy both in the first and in the 20th cycle, which results in an increase in the maximum displacements in subsequent cycles and an increased creep ability of the dynamic polymer and composites. This confirms the results of impact strength test and maximum deformation determined in a static tensile test. The addition of waste fillers increases the mechanical energy dissipation ability, of mollusk shells and egg-

shells to a lesser extent, and coffee grounds to a greater extent. This is due to the microparticles detachment and the friction force between them and the matrix during the dynamic process.

## CONCLUSIONS

The injection molding was used to obtain composites based on bioPET with the addition of organic fillers. To increase interactions at the interface, EOC-g-MAH was used as a compatibilizer. The addition of EOC-g-MAH significantly increased the impact strength of bioPET and the composites as well as ability to dissipate mechanical energy. However, the compatibilizer slightly decreased the tensile and flexural strength, and modulus of elasticity.

This phenomenon can be explained by the fact that functionalized EOC is a flexible rubber-type polyolefin that significantly softens the material and increases the mobility of the polymer chains, thus causing a slight decrease in tensile and flexural strength, but an increase in elongation at break and impact strength.

## ACKNOWLEDGEMENTS

This research was funded by NCBiR Project "Durable bio-based polymer composites reinforced with natural waste fillers with antibacterial properties" mERA.NET3/2021/79/EcoMat/2022.

## REFERENCES

- [1] Reddy M.M., Vivekanandhan S., Misra M. *et al.*: *Progress in Polymer Science* **2013**, 38(10–11), 1653. <https://doi.org/10.1016/j.progpolymsci.2013.05.006>
- [2] Correa J.P., Montalvo-Navarrete J.M., Hidalgo-Salazar M.A.: *Journal of Cleaner Production* **2019**, 208, 785. <https://doi.org/10.1016/j.jclepro.2018.10.099>
- [3] Spierling S., Knüpffer E., Behnsen H. *et al.*: *Journal of Cleaner Production* **2018**, 185, 476. <https://doi.org/10.1016/j.jclepro.2018.03.014>
- [4] Brodin M., Vallejos M., Opedal M.T. *et al.*: *Journal of Cleaner Production* **2017**, 162, 646. <https://doi.org/10.1016/j.jclepro.2017.05.209>
- [5] Wang S., Muiruri J.K., Soo X.Y.D. *et al.*: *Chemistry an Asian Journal* **2023**, 18, e202200972. <https://doi.org/10.1002/asia.202200972>
- [6] Schwarz A., Ligthart T., Boukris E., van Harmelen T.: *Marine Pollution Bulletin* **2019**, 143, 92. <https://doi.org/10.1016/j.marpolbul.2019.04.029>
- [7] Nakajima H., Dijkstra P., Loos K.: *Polymers* **2017**, 9, 523. <https://doi.org/10.3390/polym9100523>
- [8] Sousa A.F., Silvestre A.J.D.: *Current Opinion in Green and Sustainable Chemistry* **2022**, 33, 100557. <https://doi.org/10.1016/j.cogsc.2021.100557>
- [9] Nanda S., Patra B.R., Patel R. *et al.*: *Environmental Chemistry Letters* **2022**, 20, 379. <https://doi.org/10.1007/s10311-021-01334-4>

- [10] Notaro S., Lovera E., Paletto A.: *Journal of Cleaner Production* **2022**, 330, 129870.  
<https://doi.org/10.1016/j.jclepro.2021.129870>
- [11] <https://www.european-bioplastics.org/> (access date 14.08.2023)
- [12] <https://www.marketsandmarkets.com/> (access date 14.08.2023)
- [13] Siracusa V., Blanco I.: *Polymers* **2020**, 12, 1641.  
<https://doi.org/10.3390/polym12081641>
- [14] Sid S., Mor R.S., Kishore A., Sharanagat V.S.: *Trends in Food Science and Technology* **2021**, 115, 87.  
<https://doi.org/10.1016/j.tifs.2021.06.026>
- [15] Sharifian S., Asasian-Kolur N.: *Journal of Analytical and Applied Pyrolysis* **2022**, 163, 105496.  
<https://doi.org/10.1016/j.jaap.2022.105496>
- [16] Benyathiar P., Kumar P., Carpenter G. et al.: *Polymers* **2022**, 14, 2366.  
<https://doi.org/10.3390/polym14122366>
- [17] Jha M.K., Joshi S., Sharma R.K., et al.: *Nanomaterials* **2021**, 11, 3140.  
<https://doi.org/10.3390/nano11113140>
- [18] Montava-Jordà S., Torres-Giner S., Ferrandiz-Bou S. et al.: *International Journal of Molecular Sciences* **2019**, 20(6), 1378.  
<https://doi.org/10.3390/ijms20061378>
- [19] Montava-Jorda S., Lascano D., Quiles-Carrillo L. et al.: *Polymers* **2020**, 12(1), 174.  
<https://doi.org/10.3390/polym12010174>
- [20] Dissanayake L., Jayakody L.N.: *Frontiers in Bioengineering and Biotechnology* **2021**, 9, 656465.  
<https://doi.org/10.3389/fbioe.2021.656465>
- [21] Jeziorska R., Abramowicz A., Szadkowska A. et al.: *J. Renew. Mater.* **2018**, 6, 772.  
<http://dx.doi.org/10.7569/JRM.2018.634114>
- [22] Studzinski M., Jeziorska R. et al.: *Polimery* **2014**, 9, 623.  
 Received 12 IV 2023.

Instytut Robotów i Konstrukcji Maszyn Wydział Inżynierii Mechanicznej  
 oraz

Instytut Logistyki Wydział Bezpieczeństwa, Logistyki i Zarządzania  
 Wojskowej Akademii Technicznej  
 zapraszają do udziału w

**VI Konferencji Naukowej**  
**„Szybkie Prototypowanie, Druk 3D i 4D**  
**w zastosowaniach inżynierskich”**  
 14–15 września 2023 r., Warszawa

**Patronat Honorowy:**

JM Rektor Wojskowej Akademii Technicznej – gen. bryg. prof. dr hab. inż. Przemysław WACHULAK  
 Komitet Budowy Maszyn Polskiej Akademii Nauk

**Przewodniczący Komitetu Naukowego:** prof. dr hab. inż. Lucjan ŚNIEŻEK

**Przewodniczący Komitetu Organizacyjnego:** dr inż. Krzysztof GRZELAK

**Wiceprzewodniczący Komitetu Naukowego:** prof. dr hab. inż. Grzegorz BUDZIK  
 prof. dr hab. inż. Mariusz OLEKSY  
 dr hab. inż. Sławomir BŁASIAK

**Tematyka konferencji:**

- Technologie przyrostowe
- Prototypowanie
- Metody badawcze, symulacje, eksploatacja i niezawodność elementów wytwarzanych przyrostowo
- Przemysł 4.0 – wytwarzanie przyrostowe
- Polimery i kompozyty polimerowe w zastosowaniach technologii przyrostowych
- Materiały kompozytowe w druku 3D/4D
- Smart Manufacturing, Smart City i Smart Factory
- Systemy komputerowe CAx w kontekście zastosowań w druku 3D/4D
- Systemy CAD/CAM/CAE i ich aplikacje przemysłowe
- Systemy edukacyjne w obszarze technologii druku 3D/4D
- Przemysłowe systemy druku 3D, druk wielkogabarytowy
- Projektowanie zorientowane na procesy addytywne
- Inżynieria odwrotna
- Metody pomiarowe, systemy Rapid Inspection i skanowanie 3D
- Zastosowanie druku 3D/4D

**Ważne terminy:**

Zgłoszenie udziału – 30.06.2023 r.

Nadesłanie abstraktów – 31.07.2023 r.

Uiszczenie opłaty – 31.07.2023 r.

**Miejsce konferencji:** Wojskowa Akademia Techniczna, ul. gen. S. Kaliskiego 2B Warszawa, Wydział Bezpieczeństwa, Logistyki i Zarządzania (budynek 135)

**Kontakt:** +48 261 837 6463, [dprinting2023@wat.edu.pl](mailto:dprinting2023@wat.edu.pl)