

The influence of accelerated aging on selected mechanical properties of polypropylene with organic fillers

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Abstract: The aging effect in water at the temperature of $100\pm 2^\circ\text{C}$ on selected mechanical properties of polypropylene with organic fillers (hemp chaff, a mixture of oak, birch and maple leaves) was investigated. A significant influence of the aging process on the impact strength and elongation at break was observed. The degradation processes were also visible on the surface of the samples.

Keywords: accelerated aging, polypropylene, mechanical properties, biocomposites, organic fillers.

Wpływ przyspieszonego starzenia na wybrane właściwości mechaniczne polipropylenu z napełniaczami organicznymi

Abstrakt: Zbadano wpływ starzenia w wodzie w temperaturze $100\pm 2^\circ\text{C}$ na wybrane właściwości mechaniczne polipropylenu z napełniaczami organicznymi (plewy konopne, mieszanina liści dębu, brzozy i klonu). Stwierdzono istotny wpływ procesu starzenia na udurowienie i wydłużenie względne przy zerwaniu. Procesy degradacji widoczne były również na powierzchni próbek.

Słowa kluczowe: przyspieszone starzenie, polipropylen, właściwości mechaniczne, biokompozyty, napełniacze organiczne.

Renewable materials are increasingly used as additives to polymers, ensuring their biodegradability or facilitating the recycling process while reducing carbon dioxide emissions [1]. Many researchers have attempted to produce materials with the use of various organic fillers in order to modify the currently commonly used plastics, e.g., polypropylene or polyethylene, and to develop better bio-composites. So far, natural fibers [2] have been used, for example: kenaf [3], pine sawdust [4], wood flour [5–7], walnut shells [8], ram [9], cotton, hemp [10] or coconut fibers [11], sunflower husk [12], jute, sisal, flax [13], wheat bran [14], bamboo, starch [15] and many others of natural origin, which to a varying degree change the properties of the obtained composites, and above all, their biodegradability. Fibers found in this type of fillers consist mainly of organic compounds (cellulose, hemicellulose, and lignin), which limit the maximum processing temperature to about 200°C . Moreover, the pectins, waxes and other water-soluble substances that they contain have an impact on biodegradation [16]. This results in the

choice of thermoplastic polymer composites such as polyethylene, polyvinyl chloride, polystyrene, and polypropylene, which also have low viscosity at high melt index values. A frequent unfavorable effect of introducing this natural filler type is the deterioration of mechanical properties and flammability [17].

The research carried out as part of the work concerns the selected organic fillers influence on the strength properties of products over a five-year product life. The changes were forced through accelerated aging [18, 19] in specific environmental conditions simulating the actual operating conditions of the material. This approach was chosen to assess whether the material is still fully capable of performing its intended function in a given time and whether its continuous use does not pose a threat. The research aims to determine the influence of two selected environmental factors, i.e., temperature and tap water, on the produced bio-composites. According to the Rawe correlation [20] and Arrhenius law [21], the degradation reactions (although not only) can be accelerated by the influence of increased temperature. The aging process of polypropylene [22–26], known and described in the literature, generally leads to a loss of plasticity, as evidenced by a reduction in elongation at break, a decrease in impact resistance, and the development of structural heterogeneities in the amorphous phase of the semi-crystalline material after aging. Using forecasting methods, it is possible to simulate the degree of further changes

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Table 1. Polypropylene properties (producer data)

Property	Unit	Value
Density	kg/m ³	900
Melting flow rate	g/10min	7.5
Young's modulus	MPa	1050
Yield point	MPa	21
Elongation at break	%	>50
Charpy impact strength	kJ/m ²	45

in the tested product properties occurring in a period longer than the assumed test time. Forecasting is a scientifically recognized method of analyzing issues related to determining future changes in the materials performance. The literature [27] reports that products made of polypropylene slowly degrade in landfills, and their complete decomposition takes about 20–30 years, which in the case of waste is a huge problem related to environmental pollution. Introducing natural raw material to a polymer material will not cause its complete biodegradation, but it is an ecological solution expected by the current market of new engineering plastics adapted to the sustainable development policy requirements [28, 29].

In the paper the aging effect in water at the temperature of 100±2°C on selected mechanical properties of polypropylene with organic fillers (hemp chaff, a mixture of oak, birch and maple leaves) was investigated.

EXPERIMENTAL PART

Materials

Polypropylene (PP), Moplen EP340M with increased impact strength produced by Basell Orlen Polyolefins (Poland) was used for the composites preparation (Table 1). The fillers were hemp chaff with a fraction of 1 mm and a leaves mixture: oak (*Quercus L.*), birch (*Betula*

Table 2. Materials' symbols

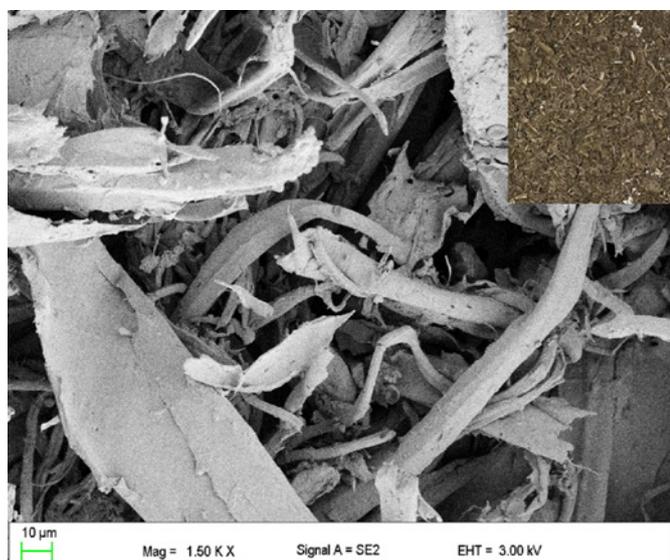
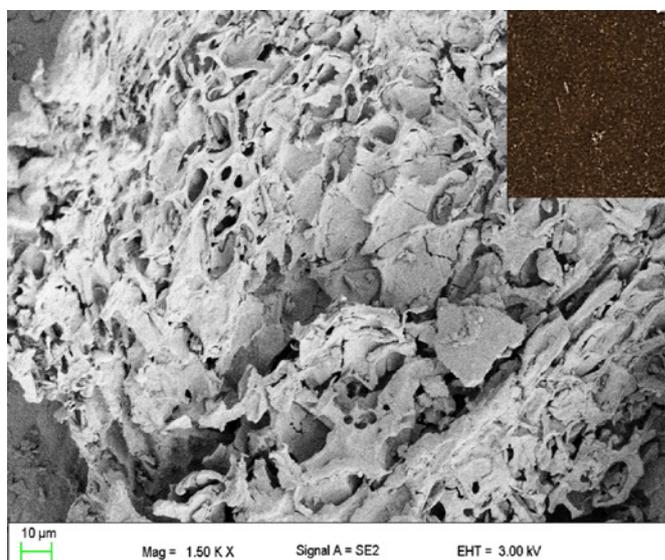
Material	Symbol
PP	RR_P
PP + 5% leaves	L5
PP + 10% leaves	L10
PP + 15% leaves	L15
PP + 20% leaves	L20
PP + 5% hemp chaff	P5
PP+ 10% hemp chaff	P10
PP + 15% hemp chaff	P15
PP + 20% hemp chaff	P20

L.), and maple (*Acer L.*). Depending on the tree, the leaves contain, respectively:

- oak: quercetin, pentosans, polysaccharides, tannins, acylated polyphenols, lignin, flavonoids [30, 31],
- birch: flavonoids, phenolic acids, catechin tannins, saponins, botulin and botulinic acid, starch [32],
- maple: fatty acid, carbohydrates, alkaloids, vitamins E and B, nitrogen-containing compounds, ascorbic acid, tannins, fiber, aldehydes, and organic acids [33].

The composition of leaves and their structure depend on the climatic conditions in which the trees grow [32]. The hemp chaff contains cellulose, hemicellulose, lignin, pectins, waxes, fats, and minerals [34]. The selected materials required proper preparation before further processing. First, the fillers were dried at 60 °C for two hours in thermal chambers. Then the leaf mixture was ground to a fine flour in a two-blade grinder to the smallest possible fraction. The fillers prepared in this way were mixed with the polymer matrix in the amount of 5, 10, 15 and 20 wt% (Table 2).

Figures 1 and 2 show microscopic images of the fillers. The morphology of the fillers was visualized using a Zeiss Supra 35 scanning electron microscope.

**Fig. 1. Microscopic image of hemp chaff****Fig. 2. Microscopic image of leaves mixture**

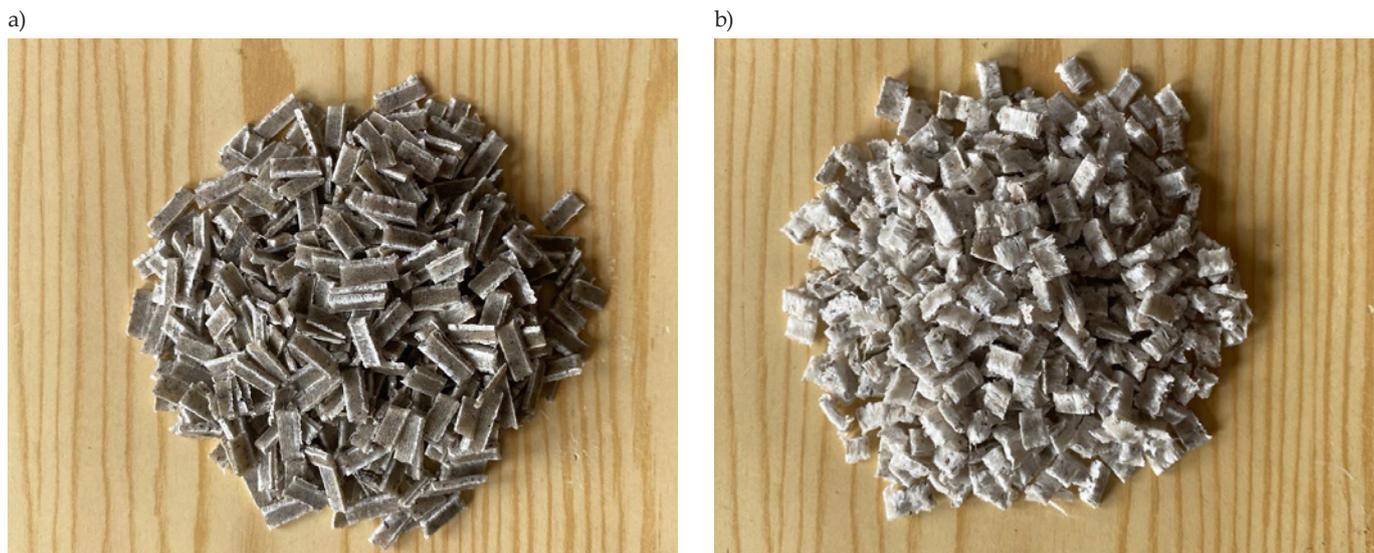


Fig. 3. Composites: a) 5 wt% leaves, b) 5 wt% hemp chaff

Composites preparation

All the composites were prepared by compounding in a twin counter-rotating extruder ($L/D = 10.1$, Göttfert Feinwerktechnik GmbH, Germany) with a rotational speed of 150 rpm. The barrel temperature was 180–195°C. After compounding, the material was pelletized (Fig. 3). The composites were injection molded at 195–220°C using a single screw injection machine (Victory 80/200, ENGEL, Austria) to obtain samples for mechanical tests. The mold temperature was 70°C.

Methods

The aging tests were carried out in a water bath at a temperature of 100 ± 2 °C for 40h. The samples were mounted in a glass chamber, ensuring free water flow. A 200×450 mm glass chamber was placed in a forced air dryer. The time was counted from the moment of obtaining a constant temperature – 100 ± 2 °C. The aging time was defined according to Raw's correlation, which says that two hours of aging at a temperature of 100 ± 2 °C correspond to 2 months of aging under actual conditions. The carried out aging process corresponds to five years of operation in real conditions, which is adequate to the most frequently provided warranty. However, the adopted test program eliminates the influence of UV radiation, a vital degradation factor for polyolefins. The chamber was secured with a metal cover to minimize the medium evaporation, and the water level was checked each time the samples were taken out. In the case of medium level reduction, the bath was completed with water at a temperature of approx. 100°C. Water with a hardness of 361 mg/l CaCO_3 was used as the medium.

Density was determined according to ISO 1183 using a laboratory balance equipped with a hydrostatic density measurement kit. First, the sample's mass was measured in air and later in distilled water. The measurements were repeated five times.

Mass melt flow rate (MFR) measurements were carried out at a temperature of 230°C under 2.16 kg load, using a Zwick/Roell Mflow load plastometer according to the standard ISO 1133.

The static tensile properties were performed according to ISO 527 using a Shimadzu kN10D testing machine cooperating with TrapeziumX V software. The crosshead speed was 50 mm/min.

Notched Charpy impact tests (ISO 179) were performed using a Zwick/Roell impact tester (Zwick Roell Group, Germany). A V-notch was made onto the samples using a mechanical notching device prior to the impact tests. All tests were carried out at room temperature. Five measurements were done for each data point in all mechanical property tests.

Hardness measurements were carried out according ISO 868 using a Sauter Shore D hardness tester. The test was repeated five times, keeping a distance of at least 10 mm from the edge.

RESULTS AND DISCUSSION

The density is shown in Fig. 4. The introduction of fillers decreases the density of the composites. However, the higher the filler content, the higher the density. These changes are minimal and within the error limits, and

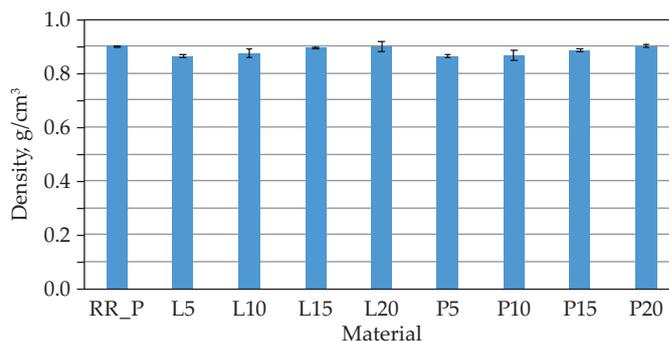


Fig. 4. Density of composites

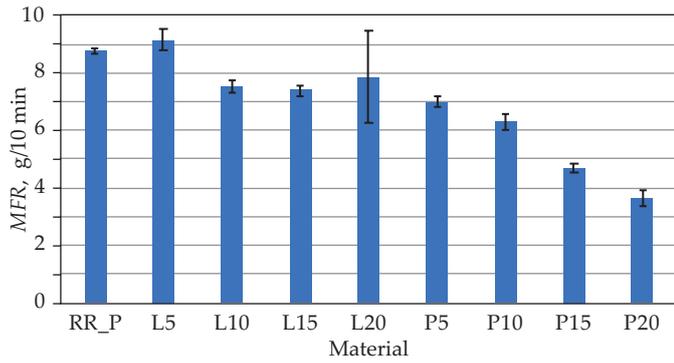


Fig. 5. Mold flow rate of composites

the results are repeatable because the highest standard deviation is approx. 0.02 equaling 2.2% of the density of composites with the highest filler content (L20 and P20). The higher the filler content, the higher the variation. It is related to the filler distribution in the sample and the sampling area.

Figure 5 shows the averaged melt flow index. It can be observed that the fillers reduce the melt flow rate compared to reference material, except for L5, which may be related to the filler content, properties, and distribution. However, this requires the chemical composition analyzing of individual leaves and their percentage share in the mixture. In L5 composite, with a mixture content of 5%, there are correspondingly fewer phenols and tannins, which affect the processing and operational properties, among others. It is observed that the color of the water after aging is related to the leaf mixture content. The higher the filler content, the darker the brown color. A decrease in MFR is observed for L10, L15, and L20, but there is no strict dependence on the leaf content. The melt flow rate for composites with hemp chaff depends on the filler content. The higher the hemp chaff content, the lower the flow rate. The filler size and the moisture content influence the MFR index. It should be noted that the fillers were not dried to a constant weight; therefore, they contained water.

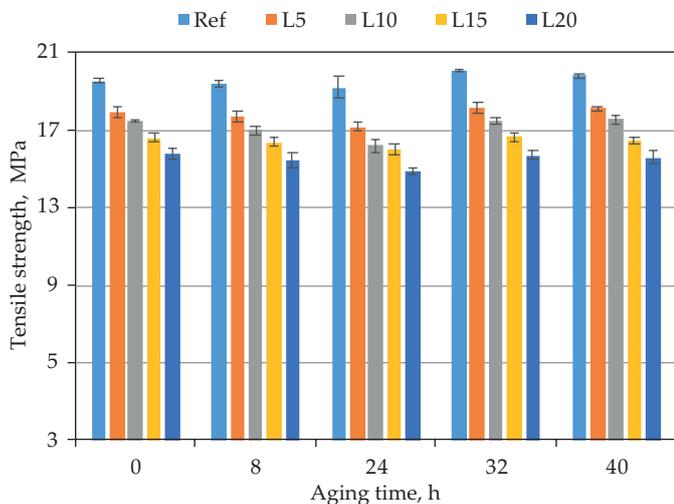


Fig. 6. Effect of aging time on tensile strength of composites with different leaf mixture content

Figure 6 shows the tensile strength for leaves composites after accelerated aging.

When analyzing the influence of the leaf mixture content on the tensile strength, the smallest decrease in properties for the L5 composite is observed. However, introducing 5% of the filler decreases the strength by 10%, and up to 3 years, it still decreases by 1.5%, then increases by 2.5%. For L10, the tensile strength decreases by 13%, and for L15 by 16%. In the case of L20, a 22% reduction in properties is observed. In each case, the tensile strength is reduced to 3 years (24h accelerated aging = 26286 h under real conditions without UV exposure): 1.5% for RR_P, 4% for L5, 7% for L10, 4% for L15, 5% for L20. The changes in strength in real-time (log h) for the tested materials is shown in Fig. 7.

The crystallization degree and the leaf mixture composition (the content of phenols, tannins, sugars) can explain the changes in the mechanical properties. After three years, an increase in strength to the initial value is observed, and the material strengthens periodically. During aging, a sediment is observed on the surface of samples L5, L10, and L15, which may be related to water hardness. In the case of L20, such sediment does not occur. An argument may be put forward that the substances contained in the leaves neutralize CaCO₃. After aging, the water is brown, indicating the release of flavonoids and other substances from the composites. The observed changes confirm the elongation under tension (Fig. 8). Up to three years, an increase in elongation is observed, followed by a decrease. Modifying the properties with the mixture of leaves significantly reduces the elongation.

Figure 9 shows the tensile strength for composites with hemp chaff as a function of aging time under accelerated conditions.

The tensile strength of composites filled with hemp chaff do not show changes similar to the materials with the mixture of leaves. The tensile strength values decrease with aging and depend on the filler content. For samples P5 and P10 without aging, the strength decreases by 7%, for P15 by 5%, and for P20 by 3%. During aging,

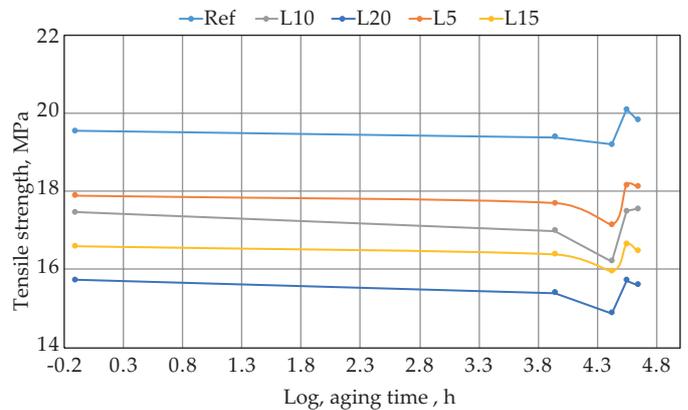


Fig. 7. Effect of aging time (converted to real-time) on tensile strength of composites with different leaf mixture content

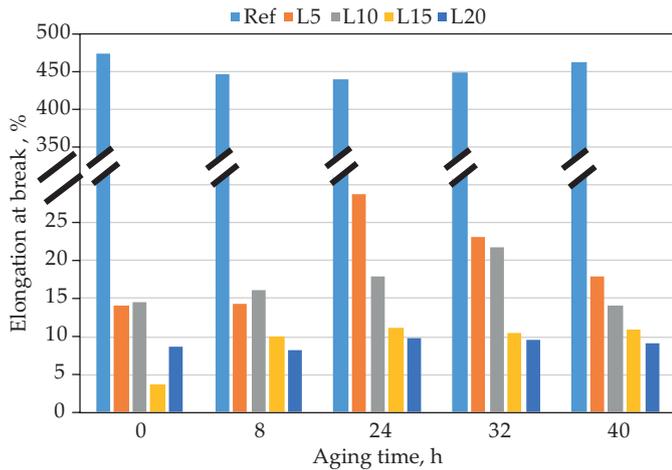


Fig. 8. Aging time effect on elongation at break of composites with different leaf mixture content

the tested characteristics decreases by approx. $5\pm 1\%$ in relation to the samples without aging. The observed differences result from the filler content. The higher the content, the higher the tensile strength but lower than the reference samples. As aging progresses, the difference between the reference samples and the filled hemp chaff increases.

Figure 10 shows the changes in real-time tensile strength (log h), *i.e.*, 1 year = 8 h accelerated aging. All composites with hemp chaff show a gradual decrease in tensile strength. No characteristic inflection point is observed after 3 years as in the case of reference material and leaf mixture composites. Therefore it can be assumed that the mixture of leaves does not change the matrix material structure but shows a greater decrease in properties. Hemp chaff, on the other hand, changes the nature of the tensile strength-aging curve. There is no characteristic point of inflection over the studied time. After 5 years, L5 and L10 show slightly higher values than P5 and P10, but the opposite is true for L15 and L20.

Figure 11 shows the change in elongation with aging time for hemp-filled polypropylene.

The elongation is reduced to 5% for P5 and even to 2% for P20 with respect to unmodified polypropylene. The elongation decreases with the filler con-

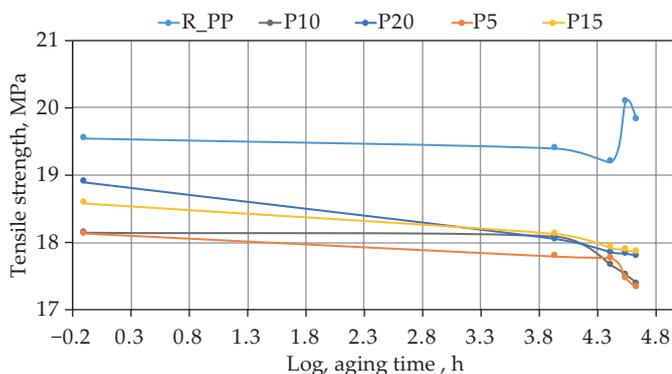


Fig. 10. Aging time effect (converted to real-time) on tensile strength of composites with different hemp chaff content

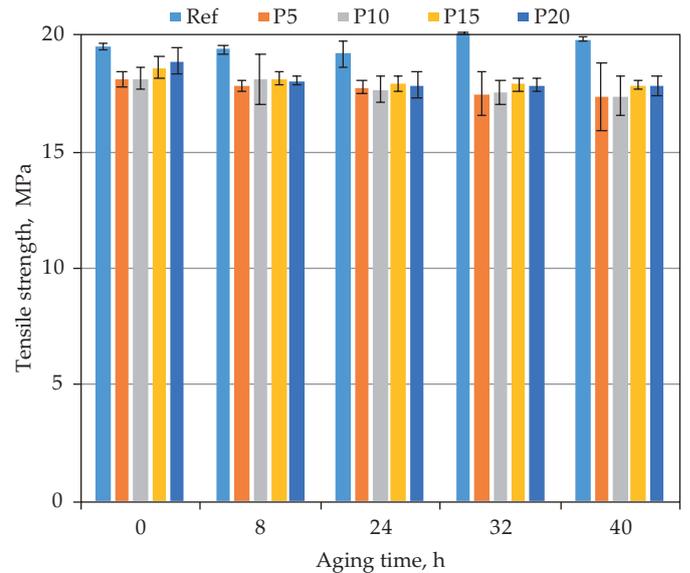


Fig. 9. Effect of aging time on tensile strength for composites with different hemp chaff content

tent, increases up to one year of aging for particular composites, and decreases afterwards. The shape and size of the filler are also important. The hemp chaff has an oblong, fibrous shape (Fig. 2.1) with a fraction size of less than 1mm, which affects the processing process, the distribution of the filler in the composite, and the performance characteristics. In an improperly homogenized material, agglomerates can act as notches and reduce elongation and tensile strength. Moreover, on the walls of the glass chamber, an oily milky precipitate, most likely CaCO_3 , is observed. The same occurred on the samples. The water retained its color.

The composites show significantly lower impact strength (Fig. 12) than the reference material. For composites with 5% filling, the impact strength is approx. 23% of the reference samples for L5 and approx. 40% for P5. For the remaining contents, the impact toughness is lower. In the case of P5, a significantly higher impact toughness than for L5 is observed. The differ-

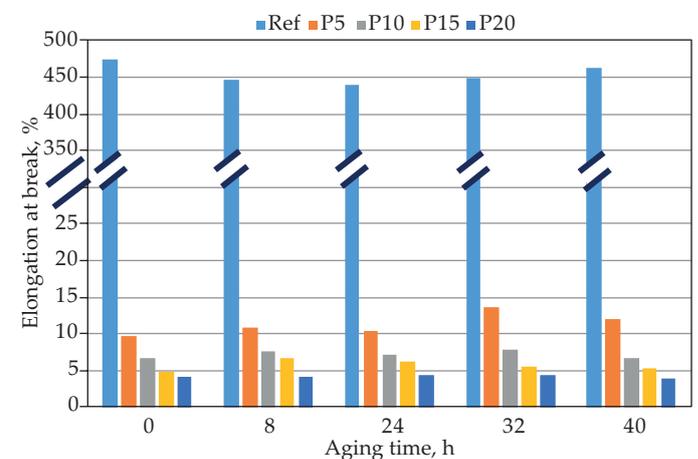


Fig. 11. Effect of aging time on elongation at break for composites with different hemp chaff content

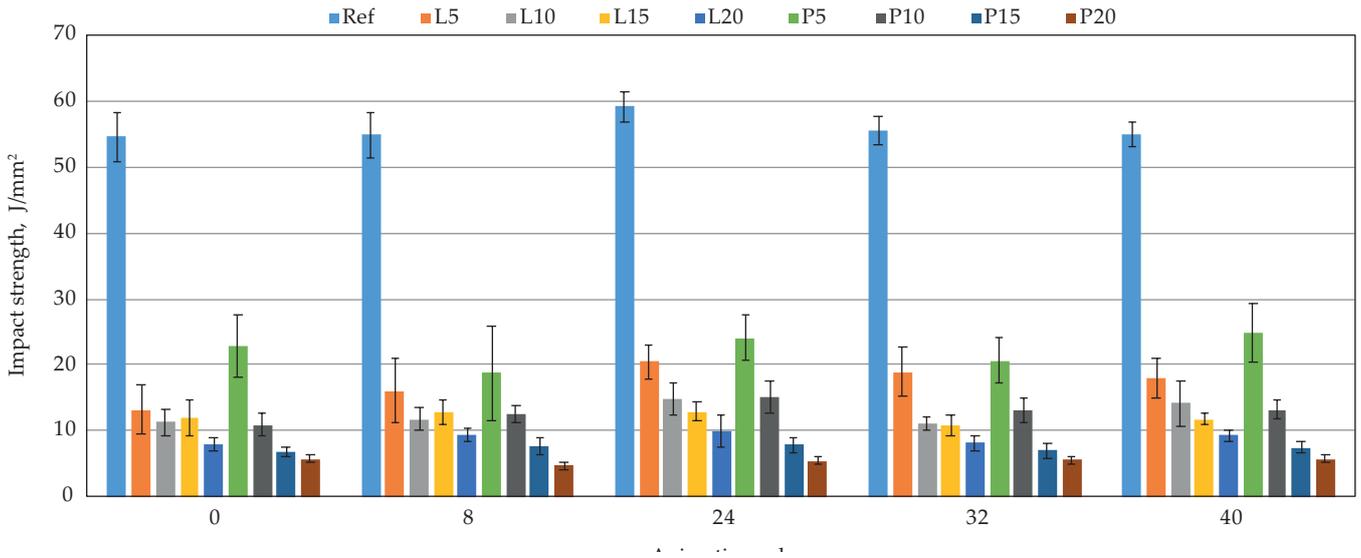


Fig. 12. Effect of aging time on impact strength for different composites

ence between the impact toughness for composites containing 10% is approx. 1 kJ/m², but with higher content, the impact toughness for composites with a mixture of leaves is higher than for composites with hemp chaff. It is related to the shape and size of the filler, which affects the homogenization degree and the homogeneity of the material structure. The observed effect is also the result of sample preparation. The higher hemp chaff content, the bigger the burrs when notching. In the case of leaves, just like the tensile strength in the first period, a decrease in impact toughness can be observed. There is an increase in impact toughness for 3 years and then a decrease again. Chaff composites also show an increase in impact toughness after 3 years, followed by a gradual decrease. This is different from the changes in tensile strength and may be related to the sample preparation method.

All composite samples show higher hardness than polypropylene (Fig. 13). Composites filled with hemp chaff are characterized by higher Shore D hardness; however, a higher standard deviation is also observed. For P10 – P20, after one year of aging, the deviation is from about 5 to 10%. The progressive aging process reduces the differences between individual composites for a given filler and content. The differences result from the decomposition of the filler in the matrix and the sample preparation method, but also from the effects of degradation. In the initial period of aging, a sediment appears on the samples, not present in the samples aged 5 years, which may affect the hardness. The water absorption by the samples, that is which causes the hardness reduction, is also essential.

Table 3 shows the superficial changes in the samples after aging. A white precipitate is observed in the case

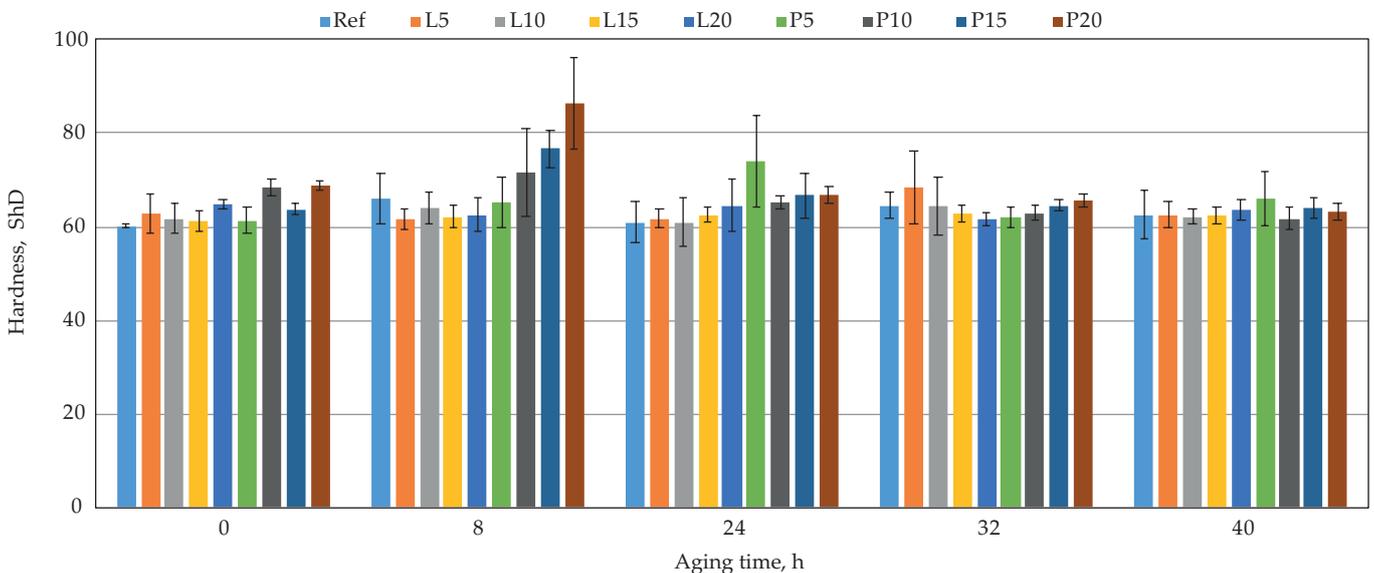


Fig. 13. Effect of aging time on hardness for different composites

Table 3. Samples' surfaces after aging

Sample	Aging time, h				
	0	8	24	32	40
RR_P					
L5					
L10					
L15					
L20					
P5					
P10					
P15					
P20					

of composites filled with the leaf mixture, which can be removed by rubbing with a spatula. It may be related to the content of waxes in leaves [31–33]. The biggest sediment is observed for the samples after 32 hours of aging (4 years), but after five years for the L15 and L20, a sediment reduction is noted. The samples also turned into a less intense color, and the water in which they were aged is brown. The higher the filler content, the darker brown it was. Such intense sediment is not observed in the case of hemp chaff composites, but the samples were stickier. Visually, it appears that the filler is more visible at the surface regardless of the content with aging time.

CONCLUSIONS

Any effect of the type, size and content of organic fillers on the density of PP was observed. As could be expected, the melt flow rate decreased with increasing filler content, with a more significant effect seen with the use of hemp chaff. Moreover, the type, size and content of organic fillers have been found to influence the tensile properties and impact strength. The higher the filler content, the lower the tensile strength and elongation at break, and the impact strength at each aging stage. All the composites after 24 hours of aging at a temperature of $100\pm 2^\circ\text{C}$ showed an increase in impact strength followed by a decrease after 32 hours. The composites showed higher hardness than PP. The changes observed during the aging process indicate the degradation of composites. However, a detailed description of the degradation mechanism requires further research, e.g., the composition of fillers and particle size.

REFERENCES

- [1] Edebali S: "15 - Methods of engineering of biopolymers and biocomposites" in "Advanced Green Materials: Fabrication, Characterization and Applications of Biopolymers and Biocomposites", (editor Shakeel A.), Woodhead Publishing, Sawston 2021, p. 351.
<https://doi.org/10.1016/B978-0-12-819988-6.00015-X>
- [2] Thakre R.A., Baxi R.N., Shelke R.S. *et al.*: *International Journal of Research in Engineering, IT and Social Sciences* **2018**, 8(12), 2018, 56.
- [3] La Mantia F.P., Morreale M., Mohd I.Z.A.: *Journal of Applied Polymer Science* **2005**, 96(83), 1906.
<https://doi.org/10.1002/app.21623>
- [4] Coutinho F.M.B., Costa T.H.S., Suarez J.C.M. *et al.*: *Polymer Testing* **2000**, 19(6), 625.
[https://doi.org/10.1016/S0142-9418\(99\)00034-3](https://doi.org/10.1016/S0142-9418(99)00034-3)
- [5] Ichazo M.N., Albano C., González J. *et al.*: *Composite Structures* **2001**, 54(2-3), 207.
[https://doi.org/10.1016/S0263-8223\(01\)00089-7](https://doi.org/10.1016/S0263-8223(01)00089-7)
- [6] Liber-Kneć A., Kuciel S., Dziadur W.: *Polimery* **2006**, 51(7-8), 571.
<https://doi.org/10.14314/polimery.2006.571>
- [7] Bazan P., Salasińska K., Kuciel S.: *Industrial Crops and Products* **2021**, 164, 113356.
<https://doi.org/10.1016/j.indcrop.2021.113356>
- [8] Dobrzyńska-Mizera M., Barczewski M.: *Przetwórstwo Tworzyw* **2014**, 5(161), 399.
- [9] Sathish T., Palani K., Natrayan L. *et al.*: *International Journal of Polymer Science* **2021**, 2021, 8.
<https://doi.org/10.1155/2021/2462873>
- [10] Kijeński J., Kijeńska M., Osazuwa O.: *Polimery* **2016**, 7–8(61), 465.
<https://doi.org/10.14314/polimery.2016.467>
- [11] Gelfuso M.V., da Silva P.V.G., Thomazini D.: *Materials Research* **2011**, 14(3), 360.
<https://doi.org/10.1590/S1516-14392011005000056>
- [12] Barczewski M., Andrzejewski J., Majchrowski R. *et al.*: *Journal of Renewable Materials* **2021**, 9(5), 841.
<https://doi.org/10.32604/jrm.2021.014490>
- [13] Kuciel S., Liber-Kneć A., Zajchowski S.: *Polimery* **2010**, 55, 718.
<https://doi.org/10.14314/polimery.2010.718>
- [14] Rahman A., Fehrenbach J., Ulven Ch. *et al.*: *Industrial Crops and Products* **2021**, 172, 114028.
<https://doi.org/10.1016/j.indcrop.2021.114028>
- [15] Umoren S.A., Solomon M.M.: "Polypropylene (PP)/ Starch-Based Biocomposites and Bionanocomposites" in "Polypropylene-Based Biocomposites and Bionanocomposites", (editor Visakh P.M., Solomon M.M.), John Wiley & Sons, Hoboken, 2017, p. 55.
<https://doi.org/10.1002/9781119283621.ch3>
- [16] Fuqua M.A., Huo S., Ulven C.: *Polymer Reviews* **2012**, 52(3), 259.
<https://doi.org/10.1080/15583724.2012.705409>
- [17] Samuńto B.A.: *Advances in Science and Technology Research Journal* **2020**, 14(4), 139.
<https://doi.org/10.12913/22998624/126971>
- [18] White J.R.: *Comptes Rendus Chimie* **2006**, 9(11-12), 1396.
<https://doi.org/10.1016/j.crci.2006.07.008>
- [19] Holliday L.: "Composites materials", Elsevier, 1966.
- [20] Rod M.: "Ageing of Composites", Woodhead Publishing, Cambridge, 2008.
- [21] Broughton W.R., Maxwell A.S.: "Accelerated Environmental Ageing of Polymeric Materials", National Physical Laboratory, Middlesex, 2007.
- [22] Brzozowska-Stanuch A., Rabiej S., Stanuch W.: *Czasopismo Techniczne. Mechanika* **2009**, R.106, 43.
- [23] Hedir A., Slimani F., Moudoud M., Lamrous O., Diahm S.: "Thermal ageing effects on polypropylene properties" Materials from 2019 IEEE Conference on Electrical Insulation and Dielectric Phenomena (CEIDP), Richland, WA, USA, October 20–23, 2019, p. 130.
- [24] Fiebig J., Gahleitner M., Paulik C. *et al.*: *Polymer Testing* **1999**, 18(4), 257.
[https://doi.org/10.1016/S0142-9418\(98\)00023-3](https://doi.org/10.1016/S0142-9418(98)00023-3)
- [25] Krzyżak A., Prażmo J., Kucharczyk W.: *Advanced Materials Research* **2014**, 1001, 141 Trans Tech Publications, Ltd.

- <https://doi.org/10.4028/www.scientific.net/amr.1001.141>
- [26] Samujło B.A.: *Advances in Science and Technology Research Journal* **2020**, 14(4), 139.
<https://doi.org/10.12913/22998624/126971>
- [27] Fotopoulou K.N., Karapanagioti H.K.: “Degradation of Various Plastics in the Environment” in “Hazardous Chemicals Associated with Plastics in the Marine Environment”, Volume 78, (editor Takada H., Karapanagioti H.), Springer, Cham, 2017, p. 71.
https://doi.org/10.1007/698_2017_11
- [28] Mannheim V., Simenfalvi Z.: *Polymers* **2020**, 12(9), 1901.
<https://doi.org/10.3390/polym12091901>
- [29] Moretti C., Junginger M., Shen L.: *Conservation and Recycling* **2020**, 157, 104750.
<https://doi.org/10.1016/j.resconrec.2020.104750>
- [30] Hofmann T., Visi-Rajczi E., Levente L.: *Current Bioactive Compounds* **2022**, 18(1), 14.
<https://dx.doi.org/10.2174/1573407217666210215090330>
- [31] Rocha-Guzmán N.E., González-Laredo R.F., Vázquez-Cabral B.D. *et al.*: “11- Oak Leaves as a New Potential Source for Functional Beverages: Their Antioxidant Capacity and Monomer Flavonoid Composition” in “Functional and Medicinal Beverages”, Volume 11, (editor Grumezescu A.M., Holban A.M.), Academic Press, Cambridge, 2019, p. 381.
<https://doi.org/10.1016/B978-0-12-816397-9.00011-X>
- [32] Oksanen E., Riikonen J., Kaakinen S. *et al.*: *Global Change Biology* **2005**, 11(5), 732.
<https://doi.org/10.1111/j.1365-2486.2005.00938.x>
- [33] Prasad R.B.N., Gülz P.G.: *Zeitschrift für Naturforschung C* **1990**, 45, 81.
<https://doi.org/10.1515/znc-1990-7-811>
- [34] Liu M., Thygesen A., Summerscales J. *et al.*: *Industrial Crops and Products* **2017**, 108, 660,
<https://doi.org/10.1016/j.indcrop.2017.07.027>

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