Oryginalny artykuł naukowy (Original research paper)

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Influence of accelerated ageing on microstructure and mechanical properties of grain husk reinforced polymer composite

Wpływ przyspieszonego starzenia na mikrostrukturę i wybrane właściwości mechaniczne profili z kompozytów polimerowych zbrojonych łuskami zbóż

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Abstract. The influence of atmospheric factors on the ageing of polymer composites reinforced with lignocellulose fibres has been analysed. Three natural fibres obtained from the husks of cultivated plants: rice, oat, and millet husk, were used as fillers. The microscopic analysis of the surfaces revealed melting of the top layer of the polymer matrix, leading to the exposure of the filler particles. The mechanical tests showed the best properties for profiles with oat hulls in the initial state and after ageing, whose properties were comparable to those of commercial profiles reinforced with rice hulls.

Keywords: ageing resistance; polymer composites with cellulose fibres; building profiles; microstructure; mechanical properties.

Streszczenie. Analizowano wpływ czynników atmosferycznych na przebieg starzenia kompozytów polimerowych zbrojonych włóknami lignocelulozowymi, które zostały pozyskane z łusek roślin uprawnych. Poddanie profili kompozytowych procesowi starzenia wyraźnie zmienia morfologię powierzchni. Analiza mikrostruktury powierzchni zewnętrznych uwidoczniła przetopienia wierzchniej warstwy osnowy polimerowej prowadzące do odsłonięcia powierzchni cząstek wypełniacza. Przeprowadzone badania wykazały najlepsze właściwości użytkowe profili z dodatkiem łusek owsa w stanie wyjściowym oraz po starzeniu, których właściwości były porównywalne z komercyjnymi profilami zbrojonymi łuskami ryżowymi.

Słowa kluczowe: odporność na starzenie; kompozyty polimerowe z włóknami celulozowymi; profile budowlane; mikrostruktura; właściwości mechaniczne.properties.

Increasing environmental protection requirements force plastics manufacturers to modify thermoplastic polymers with fillers of plant origin. Owing to their appearance, good dimensional stability, and high resistance to atmospheric factors, polymer composites reinforced with lignocellulose fibres (NFPC) obtained from different species of trees, grass and cultivated plants are used. NFPCs composites are used in such architectural elements as terrace covering, facade panels, fencing, railing, stairs and balustrades [1]. Products made of NFPC are characterised by low density, good mechanical properties, higher rigidity and lower absorbability compared with wood, OSB, and MDF [3].

Resistance to atmospheric conditions is a vital aspect determining the durability of building structures. Fulfilling the building structure's durability criterion depends, e.g. on the construction products" resistance to operating factors, including but not limited to environmental ones [3], which is of particular significance in the case of outdoor use products such as terrace planks and façade cladding. They are subject to direct and long-lasting exposure to solar radiation, water, temperature changes and microbiological factors [4].

Environmental ageing is a physical and chemical process leading to the slow destruction of materials, typically due to changes in the chemical structure initiated by simultaneous and interrelated photooxidation and thermal oxidation triggered by free radicals [5]. Thermal oxidative degradation occurs throughout the entire polymer mass. At the same time, photodegradation essentially takes place on the surface and in the sub-surface layer because of the limited capacity of UV light penetrating the material's deeper layers [5]. The type and intensity of changes in the material properties when using a product manufactured from them depend on the structure and its defects, morphology, type and share of auxiliary substances (e.g. fillers, modifiers, contaminants), and the shape, volume, type and intensity of the factors causing changes in the polymer as well as their impact duration [6]. The results of previous studies reveal that for NFPC facade profiles and terrace planks, cyclic exposure to light and water cause the most significant loads [7]. Resistance is typically verified with accelerated ageing methods in laboratory conditions using different sources of light and exposure sequences.

The degradation extent in the material subject to ageing is typically determined by the change in its physical properties,

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such as colour change; fogging; cracking of the surface layer and change in the functional properties, including but not limited to mechanical characteristics, e.g. tensile strength, flexural strength, impact strength and hardness. It is assumed that if the measured property deteriorates by more than 50%, the material is disqualified from further use [5]. At the same time, atmospheric ageing of NFPC composite products proceeds most intensively on its surface, and that is why by using the right set of supplementary analyses of the structure and morphology changes preceding the performance changes, the material's safe usage time can be accurately predicted. [8].

The paper analyses the impact of atmospheric factors on the course of ageing of polymer composites reinforced with lignocellulose fibres obtained from cultivated plant husks. Chamber profiles made of composites with polyvinyl chloride (PVC) reinforced with pulverised oat and millet husks were tested. For comparison, composites reinforced with rice husks, which is a commercial solution, were tested. The influence of the applied ageing procedure on the composites' microstructure correlated with selected mechanical properties was analysed.

Testing methods

Composite profiles. Chamber profiles (Photo 1) intended for outdoor floors were used for the tests. The profiles were made of polyvinyl chloride (PVC) matrix composites with pulverised rice, oat and millet husks with plasticising and modifying agents. Three series of samples were obtained, each containing a different filler (Table 1).

The profiles were extruded in a plastics processing plant. The profiles were 125 mm wideand 22 mm high, the face walls were 5 mm thick, and the chambers were 20 mm wide. The profiles used for the tests had brushed usable surfaces.

Photo 1. Chamber profiles with the addition of pulverized rice, oat and millet husks
Fot. 1. Profile komorowe z dodatkiem pulweryzowanych łusek ryżu, owsa i prosa

Table 1. The filler content in the tested profiles
Tabela 1. Zawartość wypełniaczy w badanych profilach

Composition designation	Plant filler type	Content of composition ingredients	
		mineral filler $CaCO_3$ [phr]	plant filler [phr]
Rice	rice husks	50	60
Oat	oat husks	50	30
Millet	millet husks	50	30

Ageing exposure. The ageing procedure was carried out in the UV Test apparatus produced in Germany, featured with 1A type of fluorescent lamps complying with EN 16474-3 [9], with the maximum emission at 343 nm (Table 2). The exposure pattern complied with EN 927-6 [10].

The exposed samples had been cut out from brushed flat usable surfaces of profiles. The samples were 300 mm long, and the profiles' full width was maintained (125 mm). The exposure pattern per cycle is summarised in Table 2.

Table 2. Ageing exposure
Tabela 2. Ekspozycja starzeniowa

Total exposure duration	Number of cycles	Exposure pattern per cycle
2016	12	– 24 h wetting by condensation, at T45±3°C – 168 h of alternative exposure to light and sprinkling in the following sequence: a) 2.5 h of exposure to UVA-340 light, radiation intensity: 0.89 W/m^2 (340 nm), BST 60±3°C, b) 0.5 h of sprinkling with water, no UV exposure, spraying intensity: 6 – 7 l/min

Microstructure analysis. The composite profiles' microstructure was analysed with Sigma 500 VP scanning electron microscope with a cold cathode field emission. The tests were carried out at a 5 KeV accelerating voltage of the excitation electron bundle, using the SE detector for gold-sprayed samples. The profiles' usable surface microstructure was observed in their original condition and after ageing. All observations were carried out at 200x magnification.

Mechanical properties testing. Mechanical properties were tested on samples obtained from files cut out from a brushed surface in the original condition and after ageing. Flexural strength and flexural modulus were tested using the Instron class 1 strength testing machine. Three-point bending was executed on samples sized 15 x 100 x 5 mm, cut out from the central part of the profile's face wall, parallel to vertical webs, according to EN ISO 178 [11]. Supports with a 5 mm radius were spaced every 80 mm, corresponding to 16 times the samples' thickness; a 5 mm radius pressing element placed in the middle of the span. The samples were freely supported. The load was applied to the face surface at the constant rate of 5 mm/min until destruction. Twelve samples were tested in each series.

Results

Morphology analysis involved a qualitative assessment of the surface and verifying the top layer's damage. The surface microstructure of NFPC composites with an addition of rice, oat and millet in their original condition revealed that the fibres were uniformly coated with polymer. The images did not show any visible filler clusters or exposed wood fibres. Directed streaks and scratches can be seen on the profiles' surfaces, being the signs of the composite's surface topography resulting from brushing (Fig. 2a, 3a, 4a).

Subjecting composite profiles to ageing changes their surface morphology significantly. The microscopic images revealed melting of the polymer's outermost layer, exposing the non-wetted filler surfaces in the form of large platelets and clusters of wood fibres, which can be observed in the composites with an addition of rice and oat (Fig. 2b and 3b). Changes were noticedin the morphology of pulverised rice and oat husks whose swelling is visible in the form of bundles (clusters). In the composites containing millet, surface cracks form fissures which become deeper and broader in some areas, creating a network of cracks leading to the formation of a separate structure fragment and, consequently, the top layer deformation (Fig. 4b).

The microstructure examination revealed that exposing the profiles to light emitted by fluorescent lamps alternately with their wetting caused significant surface degradation [12]. The surface morphology analysis revealed melting of the polymer matrix's top layer, exposing wood fibre surfaces. Under the influence of UV light, the surface layer between the polymer matrix and the wood fibres became more brittle.

Strength tests in the original condition revealed that the analysed material was characterised by the flexural strength of 45 MPa for composites reinforced with rice husks and 43 MPa for those reinforced with oat husks (Figure 1). Introducing pulverised millet husks in the same polymer matrix reduced the flexural strength to 31 MPa for millet in the original condition. The result can testify to a lack of proper dispersion of millet fibres in the polymer matrix [13]. The ageing of composite profiles contributed to a slight increase in the flexural strength to 49 MPa for composites reinforced with rice husks and 46 MPa for the composites reinforced with oat husks. The changes are so insi-

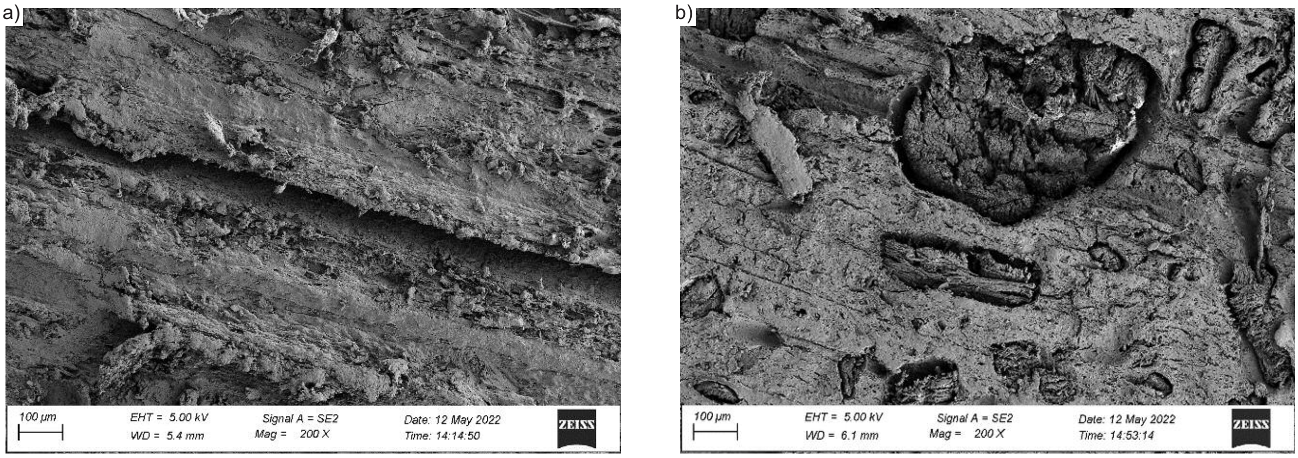


Photo 2. Surface microstructure of NFPC composites with PVC matrix reinforced with pulverised rice husks: a) before ageing; b) after ageing
Fot. 2. Mikrostruktura powierzchni kompozytów NFPC na osnowie PVC z pulweryzowanymi łuskami ryżu: a) przed starzeniem; b) po starzeniu

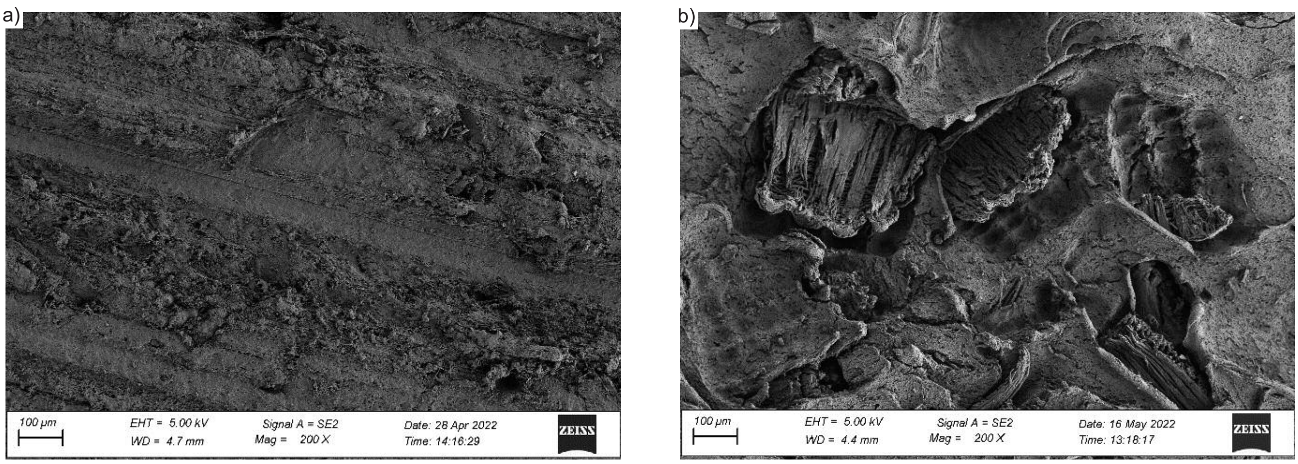


Photo 3. Surface microstructure of NFPC composites with PVC matrix reinforced with pulverised oat husks: a) before ageing; b) after ageing
Fot. 3. Mikrostruktura powierzchni kompozytów NFPC na osnowie PVC z pulweryzowanymi łuskami owsa: a) przed starzeniem; b) po starzeniu

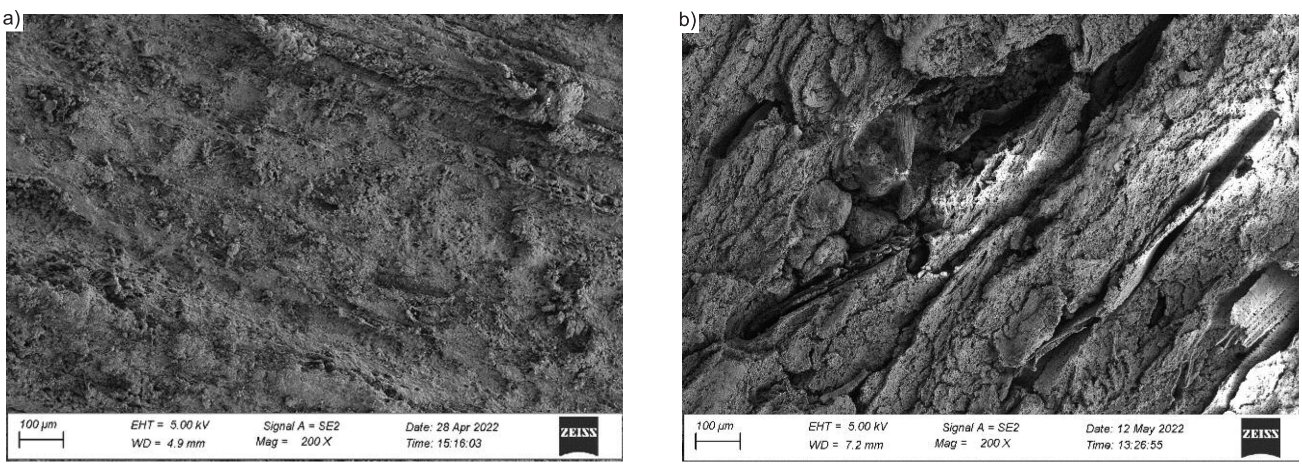


Fig. 4. Surface microstructure of NFPC composites with PVC matrix reinforced with pulverised millet husks: a) before ageing; b) after ageing
Fot. 4. Mikrostruktura powierzchni kompozytów NFPC na osnowie PVC z pulweryzowanymi łuskami prosa: a) przed starzeniem; b) po starzeniu

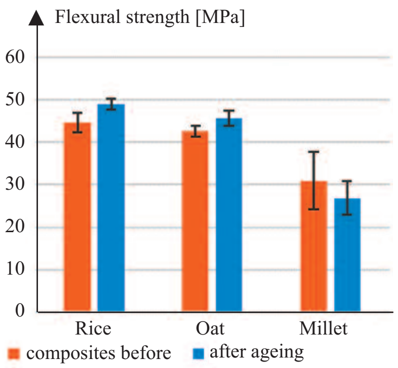
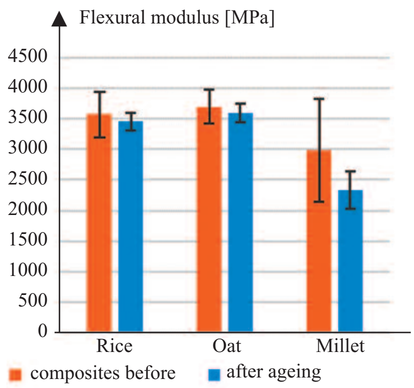


Fig. 1. Comparison of tensile properties of NFPC composites before and after ageing
Rys. 1. Porównanie wytrzymałości na zginanie kompozytów NFPC przed starzeniem oraz po starzeniu



Rys. 2. Porównanie modułu sprężystości kompozytów NFPC przed starzeniem oraz po starzeniu
Fig. 2. Comparison of elastic modulus properties of NFPC composites before and after ageing

gnificant that they fall within the error limits. No change in the flexural strength of the composites reinforced with pulverised rice and oat husks after ageing, despite changes in the surface microstructure, is evidence that ageing lasted too short for the changes to occur throughout the composite's volume. A minor decrease in flexural strength to 27 MPa is observed after ageing for the profiles reinforced with millet husks. Considering the drop in the composite's strength in the original condition compared to other composites and a minor drop in the strength after ageing, one can conclude that adhesion at the phase border is insufficient, leading to a reduction in the mechanical parameters. Moreover, due to the hydrophilic nature of the fibres, they swell in a water environment, causing cracks in the hydrophobic polymer matrix [5, 8].

The flexural modulus is another mechanical property analysed in the study. It illustrates the material's stiffness which is vital for products installed with a point support, e.g. on a grid, as is the case of terrace and façade profiles [14]. The flexural modulus value determines the profile's susceptibility to strain under operating loads. The values of the flexural modulus for the tested solutions in the original condition amounted to 3,570 MPa for the composites reinforced with rice husks, 3,700 MPa for profiles reinforced with oat husks and a minor decrease in the value after ageing (ca. 3%) for both composites (Figure 2). A significant decrease in the flexural modulus (to 2,990 MPa) compared to other profiles was reported for the profiles reinforced with millet husks in the original condition. Additionally, ageing reduced the flexural modulus by 22% compared to the non-aged material, which is a testimony to significant deterioration in its performance.

Conclusions

The analysis of the experimental data collected in the study suggests that alternating exposure of construction profiles made of PVC composite with pulverised rice, oat and millet husks to light and wetting leads – as expected – to their usable surface degradation. The microstructure analysis revealed melting of the polymer matrix's top layer and exposing the filler particle surfaces. The extent of the changes can be considered to deteriorate the profiles' appearance and decorative value significantly. No change in the flexural strength after the ageing of composites reinforced with pulverised rice and oat husks, despite microstructure changes on the surfaces, suggests that ageing lasted too short for changes to occur throughout the entire composite's volume. Introducing pulverised millet husks into the PVC matrix reduced the flexural strength in the original condition by 30% compared to the profiles reinforced with rice and oat husks. Additionally, the ageing of profiles with millet husks reduced the flexural modulus by 22% compared to the non-aged material, indicating significant deterioration in their performance. The studies revealed the best performance of the profiles reinforced with oat husks in the original condition. After ageing, their properties were similar to those of commercial profiles reinforced with rice husks.

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