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Influence of surfactants used in the paper industry on polymer-wood composites under static test conditions

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ABSTRACT

This study analysed the influence of surfactants used in the paper industry for cleaning paper machines on polymer-wood composites which can be used in wastewater treatment technology. NALCO 8683 and NALBRITE 2623 surfactants as well as specially prepared composites – thermoplastic and crushed wood samples were used for the research. The mechanical properties of wood-polymer composites (WPC) treated with surfactants were tested under the conditions of static bending and stretching. During the research, it was found that the influence of surfactants on the wood-polymer composites is determined by the residence time of the samples in the solution and the amount of filler used. The test results confirm that wood-polymer composite-based fittings exhibit higher bending and tensile strength compared to those consisting of pure polypropylene. On the basis of the obtained results, it can be concluded that wood-polymer composites can be successfully used as materials for the production of elements used in the moving bed bioreactor technology.

Keywords: Surfactants; Wood-polymer composites (WPC); Moving bed bioreactor technology; Wastewater treatment; Paper industry

1. Introduction

The paper and pulp industry is among the industrial sectors that use the highest volumes of water worldwide. Typically, pulp and paper operations require an average of approx. 54–70 m^3 of water per metric ton of processed paper goods. Water is used at almost every step of the pulp and paper production process [1–5]. It is estimated that the paper industry uses approx. 905.8 million m^3 of water annually and the discharged sewage accounts to approx. 695.7 million m^3 [6].

The pulp and paper wastewater contains compounds characterized by high recalcitrance and low biodegradability; these mainly include high molecular weight lignin compounds (lignin) [7–9]. In addition, there are low molecular weight compounds which are toxic to aquatic organisms, including activated sludge microorganisms: resin acids and organochlorine compounds, mainly chlorophenols. Lignin and resin acids are currently viewed as two groups of compounds that are “challenging” to remove using the traditional wastewater treatment processes [10,11]. Organochlorine compounds, including dioxins and furans, currently do not pose a threat to the activated sludge used in wastewater treatment due to the introduced technological changes (elimination of bleaching of cellulose pulp with elemental chlorine). Dioxin concentrations in the effluent from the bleaching plant have decreased to an undetectable level. The concentrations of chlorophenol compounds also decreased significantly. Additionally, the formation and emission of organochlorine and chlorophenol compounds in Polish pulp plants have been minimized due to the specificity of the technologies used; the concentrations of these compounds in the wastewater are usually at the ppb (μg/L) level, and below 1 ppb in case of wastewater discharged to

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the receiver. Therefore, these compounds do not constitute a notable environmental problem. The wastewater treatment, commonly used in the pulp and paper industry, includes mechanical (sedimentation) and biological methods. The latter are most often based on aerobic processes (aerobic pond and activated sludge methods), possibly assisted by chemical precipitation, which is associated with the introduction of additional chemical compounds, often with unknown toxic effects [12–15]. The reduction of the chemical oxygen demand (COD) index is usually considered as the measure of the effectiveness of the wastewater treatment process in a biological treatment plant. Studies have shown that traditional biological treatment does not remove toxic compounds as effectively as the total content of organic compounds (as COD) and may even lead to the formation of metabolites with higher recalcitrance and toxicity. Examples of parameters of wastewater from paper production are presented in Table 1.

It was established that the high content of resin acids in the wastewater supplied to the biological treatment plant negatively influences the metabolism of the activated sludge, reducing the overall effectiveness of the treatment plant, also with regard to the reduction of COD [16]. The increasing requirements resulting from environmental protection are a driving force to search for new and improved methods of limiting the discharge of pollutants to water bodies. Multi-stage technology is a promising approach to the problem of treating wastewater which contains persistent and non-readily biodegradable compounds. In case of such processes, the first stage is the physicochemical treatment of the most polluted streams, and the biological treatment of wastewater combined with the use of methods based on mobile biological beds is final stage [12–14,17]. In this technology, the growth of microorganisms is possible in the entire volume of the biological reactor, thus solving the problem of bed clogging. The moving bed technology is based on the immobilization of biomass on elements that are immersed in the treated sewage and move freely in it. Fittings can consist of various materials, with various shapes and sizes, and therefore they may be characterized by different specific surface. The movement of the fittings in the reactor occurs due to mechanical agitators under anaerobic conditions or an aeration installation under aerobic conditions. Additionally, specially designed sieves mounted on the outflow prevent the flow of carriers from the reactor.

Table 1
The quantity and quality of wastewater from cardboard production

Parameter	Value
Wastewater quality, m^3/h	300
Organic load, t/d	52.5
Temperature, °C	45.0
pH	3.9
Total suspensions, mg/L	7,300
Easily falling suspensions, mg/L	7.0
COD, mg O_2/L	6,000
BOD, mg O_2/L	2,000

The active area of currently tested or commercially available carriers ranges from 200 to 2,000 m^2/m^3. Such carriers most often consist of "clean" plastics (e.g., polyethylene K1, K2, K3 and polypropylene), polyurethane foam, activated carbon (granular and powdered), natural materials (e.g., sand, zeolite, diatomaceous earth, lightweight aggregate, etc.), non-woven supports, ceramic supports, modified supports (e.g., BIOCONS support), polyvinyl alcohol supports or biodegradable polymeric polycaprolactam supports. Development in this field is mainly based on increasing the active surface and researching new materials in order to develop the bed that would be most susceptible to biofilm formation [17–19]. Wood-polymer composites (WPC) are an advantageous and modern solution in this treatment method [17,20–23]. They can be defined as thermoplastically processable composites. They consist of wood, polymer material and auxiliary compounds. Recently, there has been an increased interest in WPC materials. The promising properties of products obtained from combining wood and polymer certainly contribute to this phenomenon. But will such carriers be resistant to the aggressive agents used in the paper industry for cleaning paper machines?

The article presents the study of the effect of selected surfactants (NALCO 8683 and NALBRITE 2623), used in the paper industry for machine cleaning, on selected wood-polymer composites that can potentially be used as carriers in the moving bed technology. The influence of the surfactant on composites as a function of the residence time in the surfactant solution and the composition of the composite was determined.

2. Materials and methods

The research material consisted of a wood-polymer composite (WPC) and a comparative pure PP. Polypropylene (PP, Moplen HP648T) produced by Basell Orlen Polyolefines was used as the matrix of the composites. Moplen HP648T is a homopolymer intended for injection moulding. Wood flour from conifers was used as the filler: Lignocel C 120 with a particle size of 70–150 μm originating from the German company J. Rettenmaier and Söhne GmbH CoKG. The filler content was equal to 30%, 40% and 50% by weight. Homogenization of polymers with wood flour was carried out in the single-screw extrusion process; thus, the composite granulate was obtained. The temperature of the extruder heating zones ranged from 120°C to 160°C, the rotational speed of the extruder screw was equal to 50 rpm. The samples in the form of paddles (PN-EN ISO 527-2), fitting type 1A, were produced from the composite material prepared in this way by injection. The temperature of the cylinder heating zones, starting from the material hopper, was respectively equal to 150°C, 180°C and 185°C ± 5°C; screw rotational speed was at 100 min^{-1}; with an injection time of 3 s; pressing time of 7 s and cooling time of 30 s. The temperature of the two-cavity mold was 20°C. In the next stage, laboratory tests were carried out regarding the effect of 20% solutions of commercial surfactants NALBRITE 2623 and NALCO 8683 on the obtained materials in accordance with the PN-EN 317 standard. The analysed materials were placed in flasks filled with the solution. Before the test, the samples were weighed, and the procedure was repeated after removing them from the solution after one month and two months, which allowed to test their absorbency. Then, the samples were dried at 50°C for 2 h and in the next stage they were subjected to strength tests in a static tensile and bending test according to the standard [PN-EN ISO 527-1] (Zwick Z020 machine).

2.1. Surfactants used in the studies

NALBRITE 2623 is a cleaning agent, a highly foaming organic acid, used to remove contaminants such as urea formaldehyde, wet strength agents, alum and calcium carbonate. It is suitable for foam cleaning of the paper machine frame and its crates.

NALCO 8683 is a low viscosity formulation consisting of non-ionic and anionic surfactants and chelating agents. NALCO 8683 is highly effective for preventing the build-up of dirt and recycled fibre contamination. NALCO 8683 effectively removes inks and sticky stains, thereby inhibiting the formation of problem deposits in a system using recycled fibres. The basic information regarding the physical and chemical properties of NALBRITE 2623 and NALCO 8683 are presented in Table 2.

Table 2
Chemical and physical properties of NALBRITE 2623 and NALCO 8683

Parameter	Substance NALCO 8683	Substance NALBRITE 2623
Form	Liquid	Liquid
Color	Light yellow	Light amber
Smell	No distinct smell	Mild
Density at temperature 25°C	1.08 g/cm^3	1.09–1.13 g/cm^3
Water solubility	Completely soluble	Completely soluble
pH	10.9	<1.0
Flash-point	>93.3°C (>200 F)	Non-flammable

3. Results

The tested materials exhibited a high tendency to absorb surfactants. After one month, that is, 30 d from immersion, the mass of the samples increased by more than 2% on average. The absorption of liquid by WPC mainly depends on the hydrophilic nature of the wood, the presence of gaps and cracks at the matrix-filler interface as well as microcracks in the matrix formed during processing. Thus, the absorbency of the tested composites results from the properties of their matrix and the form of the filler. The polypropylene matrix shows the absorption capacity close to zero, while the water absorption of the wood may reach more than 12%. Despite the fact that a relatively small amount of the introduced flour is in contact with the external environment, since most of the filler particles are enclosed in the polymer matrix, the tested WPC materials exhibited absorbency even above 3% under the influence of surfactants. After being immersed in the solutions of both surfactants for a month, the composites with the highest amount of filler showed the highest absorbency, that is, the 50% HP 648T/50% C120 sample. However, after two months, the highest absorbency was observed in case of composites consisting of 40% C120 flour and 60% HP6458T polypropylene. The 30% C120/70% HP 648T composite was characterized by the lowest absorbency. The results of the absorbency of the samples after a month and two-month stay in the NALCO 8683 and NALBRITE 2623 solutions are presented in Fig. 1.

During the experiment, the strength properties of composite samples were also tested by performing a static tensile test (in accordance with the PN-EN ISO-527 standard) and a bending test (in accordance with the PN-EN ISO-178

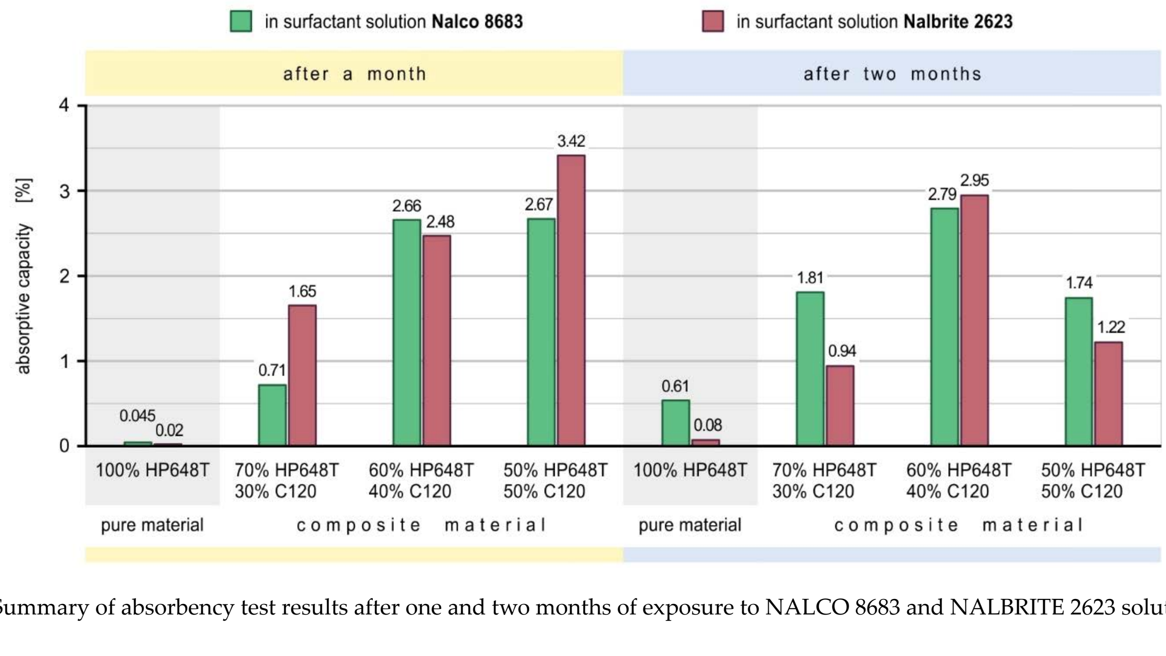

Fig. 1. Summary of absorbency test results after one and two months of exposure to NALCO 8683 and NALBRITE 2623 solutions.

standard). The static tensile test is one of the basic methods used to determine the quality of construction materials according to the stress criterion under static loads. It enables the observation of the behaviour of the material in the entire range of deformations (elastic, elastic-plastic up to fracture). On this basis, it is possible to determine not only the strength but also plastic properties of the material. During the static bending test, the bending force acting perpendicular to the sample is recorded as a function of the deflection arrow. The sample is slowly loaded in a uniform manner with a strictly defined speed until it is destroyed or the contractual value of the greatest deflection is reached (deflection arrow). On the basis of the values determined using the bending diagram, it is possible to determine the bending strength, the bending proportionality limit, the bending elasticity limit and the assumed bending yield strength. The performed tests confirmed the influence of the composition of the composite and the residence time in the surfactant solution on the strength parameters of the materials.

The obtained values of Young's modulus during the bending test for pure HP648T material and composites, taking into account the residence time in the NALCO 8683 and NALBRITE 2623 surfactant solutions, are presented in Fig. 2.

Initially, the 50% HP64/50% C120 (4.57 GPa) composite, which was not exposed to surfactant solutions, showed the highest value of Young's modulus. After the composite stayed in the solutions for a month, a decrease in the modulus value by approx. 1.8 GPa was observed. Similarly, a decrease in the modulus value was observed for the 70% HP648T/30% C120 composite, however in this case the decrease was lowest and amounted to approx. 0.35 GPa. In the composite with a 40% share of wood flour, a decrease in the modulus value by approx. 0.8 GPa was observed after a month of staying in a 20% solution of NALCO 8683 surfactant. After two months, the modulus stabilized in each of the tested composites, assuming an average value of approx. 2.5–2.8 GPa, regardless of the analysed composition. Taking into account the type of surfactant used and the residence time in the solution, pure polypropylene showed lower Young's modulus values (approx. 1.55–1.67 GPa) in the bend test compared to composite materials.

After the observed increase in the Young's modulus value from 1.15 to 1.24 GPa in the static tensile test performed using pure HP648T polypropylene, the material elasticity changed slightly in the following month, reaching the value of 1.22 GPa (Fig. 3). In the case of composites, the Young's modulus decreased to 1.57 (50% HP648T/50% C120) and 1.74 GPa (70% HP648T/30% C120). The initial modulus values before placing the samples in both surfactant solutions were the highest and were equal to 2.25 GPa in both cases. Unfortunately, after two months of submersion, the modulus of elasticity decreased. Only the 70% HP648T/30% C120 composite retained the highest elasticity. The value of Young's modulus oscillated at approx. 1.7 GPa. Compared to pure polypropylene, this value was higher by approx. 0.5 GPa.

During the static tensile test, the stress [MPa] was determined and expressed as the ratio of the force F to the initial cross-section of the sample S0 (Fig. 4). In the case of pure polypropylene, the σ values increase with the residence time in the surfactant solutions of both NALCO 8683 and NALBRITE 2623, their values fluctuate from 35 to 37 MPa. The opposite situation occurs in the case of composites, in case of which the stress values decrease with time. It can be observed that the stress values decrease with the increase of the amount of filler. In the case of the 50% C120/50% HP648T composite, it was observed that the stress value is practically two times lower than in the case of the stress values observed for the pure material at the same time (approx. 20 MPa after two months). Similar relationships were observed for composites with 30% and 40% wood flour content. In these cases the stress values ranged from 25 to 28 MPa.

The dependence of deformation (ε) on the time of staying in surfactant solutions is presented in Fig. 5.

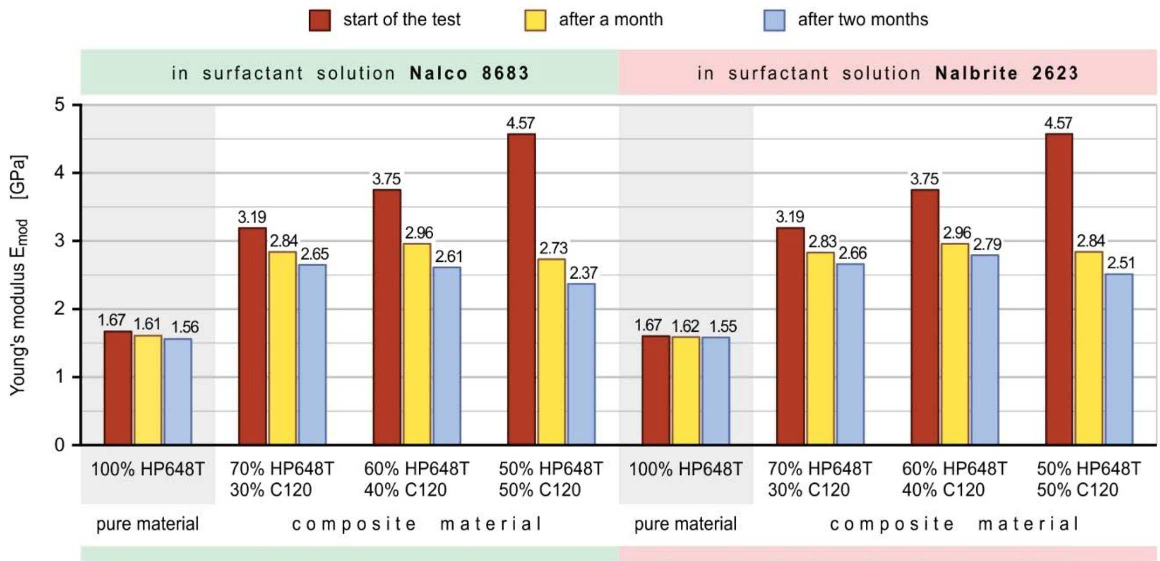

Fig. 2. Comparison of Young's modulus during the bending test for pure HP648T polypropylene and composites relative to the composition and residence time in NALCO 8683 and NALBRITE 2623 surfactant solutions.

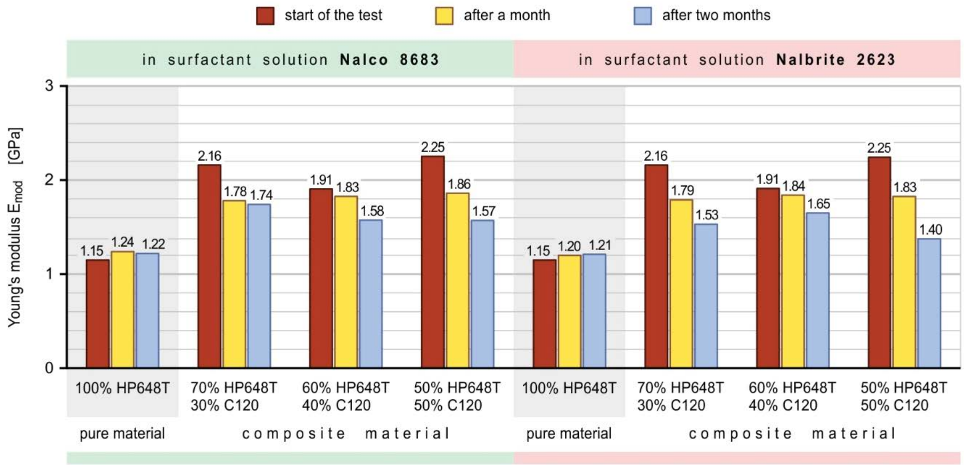

Fig. 3. Comparison of Young's modulus of elasticity during the tensile test – for pure HP648T polypropylene and for composites with different composition relative to the residence time in NALCO 8683 and NALBRITE 2623 surfactant solutions.

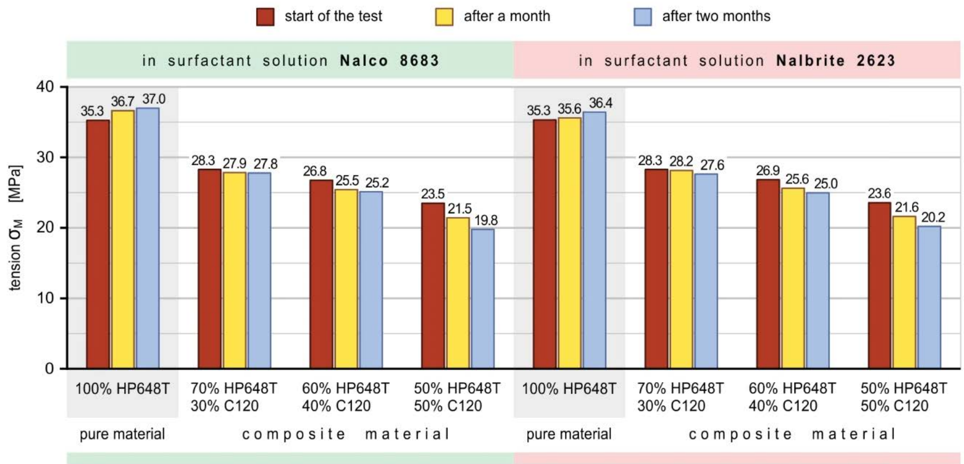

Fig. 4. Comparison of the tensile stress for pure HP648T polypropylene and composites relative to the residence time in NALCO 8683 and NALBRITE 2623 surfactant solutions.

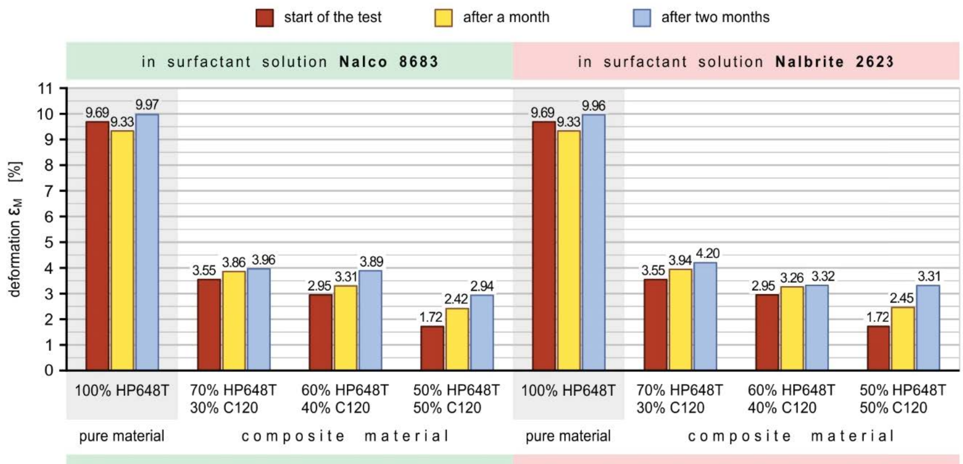

Fig. 5. Comparison of strains during tensile testing for pure HP648T material and HP648T/C120 composites relative to the residence time in NALCO 8683 and NALBRITE 2623 surfactant solutions.

The strain values for pure polypropylene are much higher than for composites. After two months of submerging PP in the solution, the deformations reached 10%. It was found that the value of (ε) gradually increased with the residence time of the samples in the solution. The lowest deformation values were observed in the case of the 50% HP648T/50% C120 composite, in case of which the deformation value after two months was lower than 3%, while for composites with wood flour content between 30% and 40%, the ε values were equal to approx. 4%.

4. Discussion

The influence of surfactants on the strength properties of wood-polymer composites was determined with respect to the residence time of the samples in the solution and the concentration of the filler used. After comparing the mechanical properties of pure PP and composites with a polypropylene matrix, it was found that the composites are characterized by much better strength parameters. In each analysed case, the value of Young's modulus was higher for WPC composites, regardless of the composition, compared to fittings consisting of pure HP648T polypropylene.

The stress was also determined during the static tensile test. In the case of pure PP material, the σ value increased as a function of the residence time in the solution. Wood-polymer composites showed the opposite tendency, that is, the stress value decreased. Additionally, the advantage of WPC composites can be noticed in the case of deformations (ε). The tests showed two-times lower deformation values in the case of WPC materials compared to pure PP. Unfortunately, the absorbency (i.e., the water absorption) of selected composite materials increased upon treatment with 20% solutions of NALCO 8683 and NALBRITE 2623 surfactants. This confirms the assumptions that the chemicals used in the paper industry, particularly surfactants which are used to clean the devices, have an impact on wood-polymer composites. The increasing ratio of wood in the composite reduces the interfacial adhesion between the hydrophobic polymer matrix and the hydrophilic wood filler. Improved compatibility could be obtained by appropriate modification of the filler, for example by esterification of hydroxyl groups, impregnation with monomers or coating with surfactants. All these methods are primarily focused on replacing the –OH groups of the cellulose with less polar groups. This high absorbency of composites exposed to surfactant solutions disqualifies the use of wood-polymer composites for the production of carriers.

5. Conclusions

The presented test results indicated a direct effect of the addition of the used fillers on the strength characteristics of the produced wood-polymer composites in relation to the used polymer matrix (PP). The modification of PP with the use of wood in the form of flour directly results in a change of the susceptibility of the composite to biofilm formation, which was confirmed in previous publications. Taking into account the changes in the considered strength parameters for composite samples in relation to the polypropylene polymer matrix, there is a real possibility of using WPC as a material for the production of moving bed elements which can also be applied during treatment of wastewater from the paper industry. However, due to the excessively high absorbency of composites treated with 20% solutions of NALCO 8683 and NALBRITE 2623 surfactants, it is necessary to carry out additional modifications to the composite materials, otherwise they will not be effective in this application during the treatment of wastewater from the paper industry.

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