Fabrication of Novel Biocomposite Made of Chemically Treated Sludge Fibers and Various Molecular Weight Polypropylene

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The effect of the chemical treatment of paper mill sludge fibers and polypropylene molecular weight were studied relative to the physical, mechanical, and morphological properties of a novel cellulosic biocomposite. Paper mill sludge fibers were treated with acetic anhydride, and succinic anhydride was mixed with maleic anhydride polypropylene (MAPP) and coupling agent (0 and 3%). The ratio of fibers and polymer materials was considered 30 to 70, which was manufactured by the hotpressing method at 180 °C. Water absorption, volume swelling, and contact angle were examined on each specimen according to ASTM standards, while Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) explored the efficiency of chemical modification of fibers and the morphology of biocomposites, respectively. The results showed that chemical treatment of fibers reduced the water absorption and volumetric swelling. Both tensile and flexural strength were increased with chemical treatment using the coupling agent. Comparison of fibers treated with succinic acid and acetic acid showed that the succinic acid enhanced the mechanical properties better than the acetic acid treatment. Finally, FTIR analysis showed that the hydroxyl groups decreased, and SEM images indicated the interface between fibers and polypropylene improved via chemical treatment of sludge fibers.

DOI: 10.15376/biores.18.2.3479-3495

Keywords: Paper mill sludge; Cellulose; Biocomposite; Acetic anhydride; Succinic anhydride; Polypropylene

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INTRODUCTION

In recent years, using natural fibers to make a wood-plastic composite (WPC) has increased because of their high strength-to-weight ratio, low density, low price, and easy degradability (Malakani *et al.* 2015). The most obvious problem of using lignocellulosic fibers as reinforcement in the synthetic matrix is the incompatibility of lignocellulosic material with the matrix (Ayfer and Cavdar 2014). Lignocellulosic materials are hydrophilic due to their high content of hydroxyl groups, while most synthetic polymers used in plastics are hydrophobic. As a result of this divergent behavior, the adhesion between natural fibers and polymers can be crucial. The bonding between the reinforcing material and the matrix plays a key role in determining the mechanical properties of a composite material (Nilgül *et al.* 2013). Water absorption in WPC is an essential factor affecting properties in end applications. Increasing humidity in plastic wood simply leads to the destruction of mechanical and physical properties. Water absorption causes the swelling of lignocellulosic fibers and destroys the bonding between the fibers and the polymer matrix, which may cause poor mechanical properties (Adhikary *et al.* 2008). Most WPC applications are associated with exterior surfaces of buildings in direct contact with weather conditions and humid climates, so consideration of water absorption becomes essential for these materials (Espert *et al.* 2004).

Many studies have been conducted on the chemical treatment of wood fibers with the aim to reduce water absorption and thickness swelling and increase the dimensional stability of wood-plastic composites (Bledzki and Faruk 2003; Tajvidi et al. 2003; Kazemi et al. 2007; Adhikary et al. 2008). It is necessary to enhance the interface phase between the hydrophilic parts of fiber and hydrophobic regions of the polymer and improve the mechanical properties. Chemical modification of wood flour with different reagents (maleic, succinic, and propionic anhydrides, etc.) is applied to increase the physical and mechanical properties of thermoplastic composites. In this regard, wood flour modified with anhydrides can be successfully used as a filler in polymer matrices (Ayfer and Cavdar 2014). It was also observed that the acetylation of wood flour caused a significant increase in the mechanical properties and thermal stability of WPCs. It was concluded that acetylation of cellulose fibers improves thermal stability, dispersion in the polymer field, and compatibility with the polymer matrix (Cavdar et al. 2014). Acetylation of wood and lignocellulosic materials, as a modification method, has been found to be effective in changing their hydrophilic nature. Many researchers have reported that moisture absorption inhibition, dimensional stability, and biological durability increase due to acetylation (Rowell et al. 1993, 1999; Mohebby and Hajhasani 2008). Most of the research on esterified natural fibers has focused on improving the mechanical properties of polymer composites. The inclusion of cellulose materials in thermoplastics improves the mechanical and physical properties of thermoplastic composites using acetic anhydride. Madhu et al. (2020) studied the effect of various chemical treatments on Agave americana fiber. They found that the chemical treatments on the fibers brought a significant reduction in the amorphous contents, such as hemicellulose, lignin, and other impurities, and made them less resistant to water molecules. In addition, the thermal properties of the fibers were enhanced after surface modification.

Sludge from recycled paper mills is a promising source of cellulosic wastes resulting from various papermaking processes that are mainly composed of cellulosic materials and minerals (Salmah *et al.* 2006). Sludge from paper mills is usually disposed of in the environment or possibly burned. Burning paper mill sludge has a critical impact on the environment through emitted greenhouse gases (GHGs) and potentially generates toxic matter in soil. Using the paper mill sludge not only provides a lignocellulosic source for making value-added products but also enables reduction of environmental concerns. Few types of research have been conducted on the use of paper mill sludge fibers for use in making lignocellulosic composites. The potential of recycled paper mill sludge was evaluated on the physical and mechanical properties of wood-plastic composite (Hamzeh *et al.* 2011). Zhou *et al.* (2019) determined that recycled sludge fibers have a circular economy in wood-plastic composite products. The highlight of these studies is to introduce sludge fiber as a bioresource into the development of wood polymer composite manufacture.

This research aims to find out the factors, such as chemical modification of fibers and molecular weight of polypropylene, that influence the physical and morphological properties of the WPC. Moreover, the critical point of this research is to find out whether the chemical modification of lignocellulosic fibers can be introduced as an alternative method instead of using coupling agents in cellulosic composites.

EXPERIMENTAL

Polypropylene (Polymer Matrix)

In this research, high molecular weight polypropylene (C30S), with a melt flow index (MFI) of 6 g per 10 min at a temperature of 230 °C, and low molecular weight polypropylene (Z30S), with a melt flow index (MFI) of 25 g in 10 min at a temperature of 230 °C, produced by Iran's Shazand Arak Company, was used as a base polymer.

Paper Sludge Fibers

Papermaking sludge was obtained from Latif Paper Co. in Karaj-Iran. Latif Paper Co., which is the producer of tissue paper from waste paper equipped with deinking plant. The tissue is produced by 80% deinked pulp and 20% long fiber virgin pulp. The following table shows the characteristics of the sludge.

Table 1.	Characterization	of Paper	Mill Sludge

Factor	Amount (wt %)	
Moisture content	49.20	
Minerals content	56 [*]	
Organic matters	44	

*: TAPPI T2110m-02

Coupling Agent

Maleic anhydride grafted polypropylene (MAPP) with a density of 0.9 g/cm³ (MFI 64 g/10 min, grafted maleic anhydride 1% by weight) was prepared by Javid Kimia Sepahan Co. and used as a coupling agent.

Chemical Modification of Fibers

For the treatment, the prepared sludge fibers were dried in the oven at a temperature of 103 ± 2 °C for 24 h; then they were stored in a desiccator to balance the temperature until ambient temperature was reached, and the chemical treatment was performed afterward.

Acetic Anhydride

To treat fibers with acetic anhydride, 75 g of the fiber content based on dry weight was poured into a glass flask with 225 cc acetic anhydride, 15 cc sulfuric acid, and 225 cc acetic acid and treated at 60 °C for 120 min. After finishing the modification process, the fibers were washed with distilled water and acetone to remove excess substances, and then dried in an oven at a temperature of 80 ± 2 °C for 24 h and stored in special plastics to prevent moisture exchange.

Succinic Anhydride

Fibers were treated with succinic anhydride. In this regard, 75 g of the fiber content based on dry weight was poured into a glass flask with 225 cc succinic anhydride, 15 cc sulfuric acid, and 225 cc acetic anhydride and then treated at 60 °C for 60 min. After finishing the modification process, the fibers were washed with distilled water and acetone to remove excess substances and then dried in an oven at a temperature of 80 ± 2 °C for 24 h and stored in special plastics to prevent moisture exchange.



Fig. 1. The reaction of wood with (a) succinic anhydride and (b) acetic anhydride

Fourier Transform Infrared (FTIR) Analysis

Infrared spectroscopy (2017 model Cary 630 spectrometer made by Agilent Technologies, Santa Clara, CA, USA) was used to assess and confirm the changes in chemical treatments on sludge fibers. For this purpose first, the control fibers and the modified fibers were dried in the oven at 103 ± 2 °C for 24 h. Then, the specimens were mixed with potassium bromide and pressed by hand. Then, the produced disc was exposed to infrared radiation in the device cell in the range of 4000 to 500 cm⁻¹ and was separated from each specimen of the corresponding spectrum by scanning. Finally, spectroscopic analysis was performed through spectrum intensity and absorption in different areas.

Biocomposite Preparation

The process of mixing the materials was performed according to Table 2 as follows: a) the materials were mixed using a Haake internal mixer (HBI System Haake Buchler, Karlsruhe, Germany); b) temperature of 180 °C and speed of 60 rpm were used; c) in all modification treatments, the mixing percentage of fibers and polymer materials was 30 to 70. After mixing the polymer and sludge, the resulting amorphous material was cooled. The compounded materials were ground using a pilot-scale grinder (WIESER, WGLS 200/200 model, Dortmund, Germany). The resulting granules were dried at 105 °C for 24 h and finally transferred to the semi-industrial injection molding machine model EM80 manufactured by the Aslanian company (Tehran, Iran). In this device, the granules were first melted and injected into the mold with high pressure. The temperature of the injection cylinder was 180 °C, the injection pressure was 100 bar, and the injection time was 20 s. Finally, the biocomposite was taken out of the mold. To ensure uniform temperature and humidity conditions, all the standard test specimens made were placed at a temperature of 23 °C and a relative humidity of 50% for one week to reach equilibrium with the moisture and temperature of the environment. The polypropylene, oven-dried paper mill sludge fibers, and MAPP were then weighed and bagged according to the formulations given in Table 1.

No	Treatment Code	Chemical Modification	Polypropylene	MAPP		
1	AAH0		High Molecular	0%		
2	AAH3	Acetic	Weight	3%		
3	AAL0	Annyunue	Low Molecular	0%		
4	AAL3		Weight	3%		
5	SAH0		High Molecular	0%		
6	SAH3	Succinic	Weight	3%		
7	SAL0	Annyunue	Low Molecular Weight	0%		
8	SAL3			3%		
9	UNH0		High Molecular	0%		
10	UNH3	Untropted	Weight	3%		
11	UNLO	Uniteated	Low Molecular	0%		
12	UNL3		Weight	3%		
13	Z30S					
14	C30S					

Table 2. Com	position of t	the Studied	Formulations
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AA: Acetic Anhydride, SA: Succinic Anhydride, UN: Untreated Fiber

Z30S: Low Molecular Weight polypropylene, C30S: High Molecular Weight polypropylene

H0: High Molecular Weight Polypropylene without MAPP.

H3: High Molecular Weight Polypropylene with 3% MAPP.

L0: Low Molecular Weight Polypropylene without MAPP.

L3: Low Molecular Weight Polypropylene with 3% MAPP

Water Absorption and Volume Swelling

From the manufactured specimens, a small test specimen with dimensions of $80 \times 50 \times 10 \text{ mm}^3$ was prepared to investigate the water absorption and volumetric swelling of a biocomposite based on ASTM D7031-04 (2004) regulations. Five repetitions were considered for each treatment and they were dried in the oven for 24 h at a temperature of 103 ± 2 °C. The weight and dimensions of the dried samples were measured and then samples immersed in distilled water (at room temperature). The weight and dimensions of the specimens were measured after 2, 24, and 48 h. Based on the obtained data, the percentage of water absorption and volumetric swelling at different times were calculated based on Eqs. 1 and 2,

$$WA_{(t)} = [(W_t - W_0) / W_0] \times 100$$
⁽¹⁾

where $WA_{(t)}$ is the water absorption (%) at time *t*, W_0 is the oven-dried weight (g), and $W_{(t)}$ is the weight (g) of the specimen at a given immersion time *t*.

$$V_{\rm (t)} = \left[\left(V_{\rm s} - V_0 \right) / V_0 \right] \times 100 \tag{2}$$

where $V_{(t)}$ is the volumetric swelling (%) at time *t*, V_0 is the oven-dried volume (mm), and $V_{(t)}$ is the volume (mm) of the specimen at a given immersion time *t*.

Contact Angle

To measure the contact angle, the sticky drop method was used as a standard method to determine the wettability characteristics of solid surfaces. For this purpose, 10 μ L of distilled water were placed as one drop using a micropipette on the surface of the specimen measuring 5 x 5 cm². After the water drop was placed on the surface of the specimen, the spreading of the water drop until it turned into a thin film was imaged by an

optical microscope. Then, a photo was taken of the gradual change of the drop using the Movie Maker software (Microsoft, version 1.5.36, Redmond, Washington, USA), in the time sequence of 1, 5, 10, 15, and 20 min.

Scanning Electron Microscopy (SEM)

The Philips dynamic electron microscope (30 XL, Eindhoven, Netherlands) installed at the Amir Kabir University of Technology in Tehran was used to investigate the morphology of the biocomposites.

Flexural and Tensile Test

Flexural and tensile tests were performed on the specimens according to ASTM D790 (2007) and ASTM D638 (2007) standards and at a loading speed of 5 mm/min. For this purpose, the Santam model DBBP-2T device full was used.

RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy Analysis (FTIR)

Fourier transform infrared spectroscopy for untreated sludge fibers and modified sludge fibers with succinic anhydride, and acetic anhydride is shown in Fig. 2.





Fig. 2. FTIR spectra of untreated (a), acetic anhydride-modified (b), and succinic anhydride-modified (c) paper sludge

Based on these spectra, the absorption of hydroxyl groups in the absorption band of 3463 cm⁻¹ decreased due to the chemical modification of sludge fibers. This change indicates the chemical modification of sludge fibers and the replacement of their chemical groups instead of hydroxyl groups. The introduction of acetic anhydride and succinic anhydride into composites leads to the appearance of new absorption peaks at 1620 and 1680 cm⁻¹.

Water Absorption

The effect of the type of chemical treatment of sludge fibers and the molecular weight of polypropylene and the coupling agent content on water absorption of biocomposites is shown in Figs. 3 and 4. The results of the statistical analysis show that

the type of chemical treatment, the molecular weight of polypropylene, and the coupling agent content had a noticeable effect on the water absorption of the constructed biocomposites.

Water absorption in biocomposites is completed through different mechanisms, which include water absorption through the cell wall of lignocellulosic material, caused by their hygroscopic nature leading to thickness swelling of the composite. The absorption of water is completed *via* the capillary process through the gaps between the polymer and the sludge fibers due to the weak connection between the fibers and the polymer, as well as the voids created in the cellulosic material and the polymer during the production process. On the one hand, it is expected that because of the chemical treatment of sludge fibers, the hydrophilic nature of lignocellulosic fibers will be significantly reduced. On the other hand, the gaps and cracks between fibers and sludge were reduced due to chemical treatment. As the adhesion between the polymer matrix and fibers in biocomposite improves due to chemical treatment, the processes of moisture diffusion into the composite take place much more slowly, because then there are fewer cracks at the bonding of fibers. Mishra *et al.* 2001; Liu *et al.* 2004; Kord and Haratbar 2014).



Fig. 3. The effect of fiber treatment with acetic anhydride and MAPP content on water absorption

In biocomposites with high molecular weight polymer, the water absorption of samples treated with acetic anhydride and without coupling agent was more than the samples treated with 3% coupling agent. In other words, the coupling agent was more effective in reducing water absorption than chemical treatment, while the reverse results were obtained by polymers with low molecular weight. In the acetic anhydride treatment, biocomposites made from polymers with low molecular weight and without MAPP had less water absorption. However, for succinic anhydride treatment, this result was the opposite. It was anticipated that the chemical treatment of fibers with succinic anhydride has no effect on reducing water absorption in the biocomposite. In fact, biocomposites containing fibers treated with succinic anhydride had higher water absorption than untreated biocomposites. Generally, regarding the water absorption in biocomposites, it can be concluded that the chemical treatment of fibers increased the water absorption of the biocomposites.



Fig. 4. The effect of fiber treatment with succinic anhydride and MAPP content on water absorption

The water absorption rate in biocomposites made with polypropylene grade C30S was higher than grade Z30S. This issue can be related to the lower melt flow index of this grade of polypropylene. Because with the increase of the melt flow index, the minimal distances between the polymer chains are reduced, and for this reason, the penetration of water molecules between the polymer chains is diminished. In contrast, through increasing the melt flow index, the polymeric matrix, like a sheath, covers the hydrophilic fibers well and facilitates the water access to them (Espert *et al.* 2004).

Volumetric Swelling

Figures 5 and 6 show the process of volume swelling of biocomposite made with treated fibers in immersion at 2, 24, and 48 h (at room temperature). It is indicated that acetic anhydride and succinic anhydride treatments reduced the swelling of biocomposites in both low and high molecular weights. The reason is that the hydrophobic groups in the acetic anhydride and succinic anhydride are gradually being replaced with the hydroxyl groups of the fibers. The higher the replacement of hydrophilic hydroxyl groups (OH) by hydrophobic groups, the fewer hydroxyl groups will be available to bond with water molecules, resulting in reduced water absorption, where less water is placed in the interfacial surfaces of fibers and polymer, and thus the biocomposite is less swollen (Rowell 1993).



Fig. 5. The effect of fiber treatment with acetic anhydride and MAPP content on volumetric swelling



Fig. 6. The effect of fiber treatment with succinic anhydride and MAPP content on volumetric swelling

The coupling agent increases the bonding strength between fiber and polymer resulting in more dimensional stability in the biocomposite. In addition, the coupling agent reduces the surface tension of cellulose fibers, resulting in a value closer to the surface tension of molten polymer. With the formation of cross-linkage by coupling agents, the fiber-fiber hydrogen bonds are weakened and the dispersion of fibers in the thermoplastic matrix becomes more accessible and the bonding is improved (Tjong *et al.* 1999; Lu *et al.* 2005). In this research, it was found that the use of MAPP in biocomposite causes a decrease in biocomposite volume swelling.

The volumetric elongation of biocomposites that were made by acetic anhydridetreated sludge with low molecular weight polymer (no coupling agent) was lower than biocomposite made by a coupling agent. This behavior repeated by biocomposites was caused by higher molecular weight polymers (Fig. 6). It revealed that although the coupling agents had a significant effect on dimensional stability, the volumetric elongation of WPC was more influenced by chemical treatments rather than coupling agents.

Contact Angle

The effect of the chemical treatment of cellulosic material and coupling agent on the contact angle of sludge-polypropylene biocomposite is illustrated in Figs. 7 and 8. It is indicated that chemical modification (acetic anhydride and succinic anhydride) treatments reduced the swelling of biocomposite in both low and high molecular weights.

Thus, the highest change in contact angle was observed in the case of untreated fibers, while the treated fibers showed the lowest change. In this regard, the raw polymers did not demonstrate any significant changes. These results proved that the chemical treatment of the cellulose material leads to reducing the speed of spreading and decay of the droplet in the sludge-polypropylene biocomposite, consequently, the time required to reduce the contact angle of the water droplet on the surface of the specimen increased. The reason is attributed to the reducing of the number of hydroxyl groups on hemicellulose chains and ester reaction.



Fig. 7. The effect of fiber treatment with acetic anhydride and MAPP content on water contact angle



Fig. 8. The effect of fiber treatment with acetic anhydride and MAPP content on water contact angle

SEM Analysis

The images of the modified fiber surface and the fracture surface of untreated specimens treated with acetic acid and succinic anhydride were utilized to explore the effect of chemical modification on sludge fibers and joint fracture surfaces of polymer and natural fibers. Figure 9 shows a specific change in cellulose fiber micro-structure after treatment. Most of the holes in the fibers were removed by chemical treatments. The chemical treatment leads to the overlapping of the fibers by the polymer matrix material in the absence of the coupling agent (Fig. 9 a through d). Thus, it makes a proper interaction between the fibers and the polymer. In these figures (a to d), the rupture zone occurred only in the polymer-fiber matrix because of chemical treatment. In contrast, Fig. 9 (f) shows the polymer failed individually, and no fiber breakage is seen. It is worth noting the positive effect of chemical treatment in creating strong connections in the interphase region. With the addition of the maleic coupling agent, the complete inclusion of the fiber was performed by polypropylene (Fig. 9 e). In this region, the fibrillated fiber or polymer was not separated, which indicated the completion of the interlocking. It is anticipated that there will be a significant synergistic effect between the coupling agent and chemical modification. Exploring the surface acetylated in biocomposite specimens without using a coupling agent, there is an increasing intensity in acetylation treatment that causes a decrease in porosity in MAPP of plastic wood specimens.



Fig. 9. Scanning electron micrographs of the composites filled with modified paper sludge: (a) AAH0, (b) AAL0, (c) SAH0, (d) SAL0, (e) UNH3, and (f) UNL3

Tensile and Flexural test

The effect of chemical treatment and molecular weight of polypropylene on flexural and tensile strength is shown in Figs. 10 and 11. The results of the statistical analysis showed that the type of chemical treatment, the molecular weight of polypropylene, and the coupling agent had significant effects on the tensile and flexural strengths of the manufactured biocomposite. In polymers with high molecular weight, acetic anhydride treatment did not change the tensile strength significantly. In contrast, the polymers with low molecular weight, acetic anhydride treatment noticeably increased the biocomposite tensile properties. It seems that the molecular weight of the polymer had a significant correlation with the tensile strength of biocomposites. With 3% addition of coupling agent in biocomposite production, the tensile strength of biocomposite treated with acetic anhydride was much higher than untreated samples under the same conditions. These results were obtained from bio-composite made with low molecular weight polymer. It was revealed that the coupling effects of acetic anhydride treatment and using the coupling agent simultaneously played an essential role in increasing the tensile strength of biocomposites. In addition, there were composites made from the low molecular weight polymer without a coupling agent. The tensile strength was higher than the untreated samples. Therefore, the molecular weight of the polymer has a role in changing the tensile strength of the biocomposite. The chemical treatment of sludge fibers with succinic anhydride increased the biocomposite tensile strength. The effect of treatment with succinic anhydride in increasing the tensile strength of the biocomposite was more noticeable than the effect of the coupling agent. These results were obtained from biocomposites made with different molecular weight. However, the tensile strength was higher in biocomposites made with low molecular weight polymers. Finally, it can be concluded that in general, the succinic anhydride treatment in sludge fibers, compared to acetic anhydride treatment, had a higher effect in increasing the tensile strength of biocomposites.

In polymers with high molecular weight, acetic anhydride treatment alone did not change the flexural strength remarkably. By contrast, in polymers with low molecular weight, acetic anhydride treatment increased the biocomposite flexural strength noticeable. It seems that the molecular weight of the polymer has a relationship with the tensile strength of biocomposites. If 3% coupling agent was used in biocomposite production, the flexural strength of biocomposite in samples treated with acetic anhydride was much higher than in untreated samples under the same conditions. These results were obtained from biocomposites made with low molecular weight polymer. It seems that the coupling effect of acetic anhydride treatment and the use of a coupling agent simultaneously play a vital role in increasing the flexural strength of biocomposite. When the low molecular weight polymer without a coupling agent was used in the biocomposite, the flexural strength was higher than the untreated sample. Therefore, the molecular weight of the polymer had a role in changing the flexural strength of the biocomposite (Fig. 11). In succinic anhydride treatment, the effect of chemical treatment of sludge fibers increased the biocomposite tensile strength. The impact of treatment with succinic anhydride in increasing the flexural strength of biocomposite was more remarkable than the effect of the coupling agent. The same conditions were obtained from biocomposite made by polymers with different molecular weights. However, the flexural strength was higher in biocomposites made with low molecular weight polymers. Finally, it can be concluded that the succinic anhydride treatment in sludge fibers had a higher effect on the flexural strength of biocomposites than the acetic anhydride treatment.



Fig. 10. The effect of fiber treatment with acetic anhydride and succinic anhydride, polypropylene and MAPP content on Tensile strength values of biocomposite

It is expected that the chemical treatment of wood flour decreased the distance (in the nano-scale) between sludge and polypropylene, leading to improved interface bonding between these two phases (Dominkovics *et al.* 2007). In contrast, during the acetylation process, the nature of the wood material changes from polar to non-polar and becomes closer to the polymer matrix in terms of hydrophobicity. In this case, the connection of two phases of wood and polymer was improved and, accordingly, the mechanical strength was enhanced. Therefore, strength is recognized as a significant parameter associated with acid treatment, which is related to the density of fibers by substituting the hydroxyl groups with heavier acetyl groups. In other words, the rigidity of each fiber was increased due to acetylation; therefore, it can be expected that the strength of the composite will increase because the decrease in porosity and consequently the increase in the density of the composite (Ismaeilimoghadam *et al.* 2016).



Fig. 11. The effect of fiber treatment with succinic anhydride and acetic anhydride polypropylene and MAPP content on flexural strength values of biocomposite

CONCLUSIONS

- 1. By chemical treatment of sludge fibers with acetic anhydride and succinic anhydride, volumetric swelling, and the contact angle of water drops on the biocomposite surface were reduced.
- 2. Water absorption in the biocomposites with chemically treated fibers increased.
- 3. Fourier transform infrared spectroscopy confirmed the chemical modification of sludge fibers. The results of the SEM analysis also showed that the interface between the sludge fibers and the background material was improved due to chemical modification.
- 4. Chemical treatment improved the binding between sludge and polymer resulting in increased flexural and tensile strength without use of coupling agent.
- 5. The comparison of fibers treated with succinic anhydride *vs*. acetic anhydride showed that the succinic anhydride enhanced the mechanical properties higher than the acetic anhydride treatment.

REFERENCES CITED

- Adhikary, K. B, Pang, sh., Staiger, M. P. (2008). "Long-term moisture absorption and thickness swelling behavior of recycled thermoplastics reinforced with *Pinus radiata* sawdust," *Chemical Engineering Journal* 142(2), 190-198. DOI: 10.1016/j.cej.2007.11.024
- ASTM D638 (2007). "Standard test method for tensile properties of plastics," ASTM International, West Conshohocken, PA, USA.
- ASTM D790 (2007). "Standard test method for flexural properties of unreinforced and reinforced plastics and electrical insulating materials," ASTM International, West Conshohocken, PA, USA.

- ASTM D7031-04 (2004). "Standard test method for mechanical and physical properties of wood plastic composite," ASTM International, West Conshohocken, PA, USA.
- Ayfer, D., and Cavdar, A. F. (2014). "Effect of chemical modification with maleic, propionic, and succinic anhydrides on some properties of wood flour filled HDPE composites," *BioResources* 9(4), 6490-6503.
- Bledzki, A. A., and Faruk, O. (2003). "Wood fiber reinforced polypropylene composites: Effect of fiber geometry and coupling agent on physico-mechanical properties," *Applied Composite Materials* 10, 365-379. DOI: 10.1023/A:1025741100628
- Dominkovics, Z. D., Dányádi, L., and Pukánszky, B. (2007). "Surface modification of wood flour and its effect on the properties of PP/wood composites," *Composites Part A: Applied Science and Manufacturing* 38(8), 1893-1901. DOI: 10.1016/j.compositesa.2007.04.001
- Espert, A. V., Vilaplana, F., and Karlsson, S. (2004). "Comparison of water absorption in natural cellulosic fiber from wood and one-year crops in polypropylene composites and its influence on their mechanical properties," *Composites Part A: Applied Science and Manufacturing* 35(11), 1276-1276. DOI: 10.1016/j.compositesa.2004.04.004
- Hamzeh, Y., Ashori, A., and Mirzaei, B. (2011). "Effects of waste paper sludge on the physico-mechanical properties of high density polyethylene/wood flour composites," *Journal of Polymers and the Environment* 19, 120-124. DOI: 10.1007/s10924-010-0255-3
- Ismaeilimoghadam, S., Masoudifar, M., Shamsian, M., and Nosrati, B. (2016). "The effects off chemical treatment of wood flour on some properties of wood--plastic," *Iranian Journal of Wood and Paper Industries*, 449-462. DOI: 20.1001.1.20089066.1395.7.3.12.2
- Kazemi, N. S., Kiaefar, A., and Tajvidi, M. (2007). "Water absorption behavior and thickness swelling rate of composites from sawdust and recycled plastics," *Journal of Reinforced Plastic and Composites* 26(3), 341-348. DOI: 10.1177/0731684407072519
- Kord, B. A., and Haratbar, D. T. (2014). "Influence of fiber surface treatment on the physical and mechanical properties of wood flour-reinforced polypropylene bionanocomposites," *Journal of Thermoplastic Composite Materials* 29(7), 979-992. DOI: 10.1177/0892705714551592
- Liu, W. M., Mohanty, A. K., Ashkeland, P., Drazel, L. T., and Misra, M. (2004).
 "Influence of fiber surface treatment on properties of Indian grass fiber reinforced soy protein-based bio composites," *Journal of Polymer Science* 45(22), 7589-7596. DOI: 10.1016/j.polymer.2004.09.009
- Lu, J. W., Wu, Q., and Negulescu, I. (2005). "Wood-fiber/high-density-polyethylene composites: Coupling agent performance," *Journal of Applied Polymer Science* 96(1), 93-102. DOI: 10.1002/app.21410
- Madhu, P., Sanjay, M. R., Jawaid, M., Siengchin, S., Khan, A., and Pruncu, C. I. (2020).
 "A new study on the effect of various chemical treatments on *Agave americana* fiber for composite reinforcement: Physico-chemical, thermal, mechanical and morphological properties," *Polymer Testing* 85, article 106437. DOI: 10.1016/j.polymertesting.2020.106437
- Malakani, M., Bazyar, B., Talaiepour, M., Hemmasi, A. H., and Ghasemi, I. (2015)."Effect of acetylation of wood flour and MAPP content during compounding on physical properties, decay resistance, contact angle, and morphology of

polypropylene/wood flour composites," *BioResources* 10(2), 2113-2129. DOI: 10.15376/biores.10.2.2113-2129

- Mishra, S., Misra, S., Tripathy, S., Nayak, S. K., and Mohanty, A. K. (2011). "Graft copolymerization of acrylonitrile on chemically modified sisal fibers," *Macromolecular Material and Engineering* 286(2), 107-113. DOI: 10.1002/1439-2054
- Mohebby, B., and Hadjihassani, R. (2008). "Moisture repellent effect of acetylation on poplar fibers," *Journal of Agricultural Science and Technology* 10(2), 157-163.
- Özmen, N., Çetin, S. N., Mengeloğlu, F., Birinci, E., and Karakuş, K. (2013). "Effect of wood acetylation with vinyl acetate and acetic anhydride on the properties of wood-plastic composites," *BioResources*, 8(1), 753-767.
- Rowell, R. C. (1993). "Results of chemical modification of lignocellulosic fibers for use in composites," in: Wood-fiber/polymer composites: Fundamental concepts, processes, and material options: Proceedings of 1st wood fiber-plastic composite conference, Madison, WI and 45th an. New Orleans, LA Madison, WI: Forest Products Society, 121-127.
- Rowell, R. S. (1999). "Properties of kenaf/polypropylene composites," in: *Kenaf Properties, Processing and Products*, Mississippi State University, Ag & Bio Engineering, pp. 381-392.
- Salmah, H. I., and Abu Bakar, A. (2006). "Effects of chemical modification of paper sludge filled polypropylene (PP)/ethylene propylene diene terpolymer (EPDM) composites," *Journal of Reinforced Plastics and Composites* 25(1), 44-58. DOI: 10.1177/0731684406055454
- Tajvidi, M., and Ebrahimi, G. H. (2003). "Water uptake and mechanical characteristics of natural filler-polypropylene composites," *Journal of Applied Polymer Science* 941-946. DOI: 10.1002/app.12029
- Tjong, S. C., Xu, Y., and Meng, Y.Y. (1999). "Composites based on maleated polypropylene and methyl cellulosic fiber: Mechanical and thermal properties," *Journal of Applied Polymer Science* 72, 1647-1653.
- Zhou, Y., Stanchev, P., Katsou, E., Awad, S., and Fan, M. (2019). "A circular economy use of recovered sludge cellulose in wood plastic composite production: Recycling and eco-efficiency assessment," *Waste Management* 99, 42-48. DOI: 10.1016/j.wasman.2019.08.037

Article submitted: December 31, 2022; Peer review completed: February 25, 2023; Revised version received: March 5, 2023; Accepted: March 11, 2023; Published: March 28, 2023.

DOI: 10.15376/biores.18.2.3479-3495