Environmental Engineering and Management Journal

October 2023, Vol. 22, No. 10, 1753-1758
http://www.eemj.icpm.tuiasi.ro/; http://www.eemj.eu
http://doi.org/10.30638/eemj.2023.150

"Gheorghe Asachi" Technical University of Iasi, Romania

SYNTHESIS OF BIO-BASED WOOD ADHESIVE

Salise Oktay[1,3]*, Nilgün Kızılcan[2], Başak Bengü[3]

[1]*Istanbul Technical University, Graduate School of Science Engineering and Technology Department of Polymer Science and Technology*
[2]*Istanbul Technical University, Faculty of Science and Letter, Department of Chemistry*
[3]*Kastamonu Entegre Ağaç San. Tic. A.Ş.*

Abstract

The wood-based panel industry plays a crucial role in facilitating the industrial production of everyday products like particleboard and fiberboard, which are commonly used in flooring, furniture, and more. Key inputs for board production include thermoset resins, which act as binders. Traditionally, resins based on urea-formaldehyde, melamine-formaldehyde, and melamine-urea-formaldehyde are widely used due to their reactivity and cost-effectiveness. However, the sustainability of these resins is a growing concern, and stricter regulations regarding formaldehyde emissions are impacting the industry.
In response to this challenge, this study introduces a bio-based resin formulation, utilizing corn starch and Mimosa tannin as alternatives to formaldehyde-based resins. The choice of corn starch and Mimosa tannin as raw materials is motivated by their chemical compatibility and ready availability. The study involved the determination of the solids and gel times of the synthesized resins. Additionally, laboratory-scale board production was undertaken to assess the performance of the newly developed resin formulations. The mechanical and physical properties of the resulting boards, along with formaldehyde content, were measured. Mechanical test results were evaluated in accordance with the EN 312 standard.
The findings suggest that the developed resin formulations show promise for particleboard production suitable for interior applications, as they generally meet the standard requirements for mechanical properties.

Key words: corn starch, furanic derivatives, Mimosa tannin, wood adhesive

Received: May, 2023; Revised final: October, 2023; Accepted: October, 2023; Published in final edited form: October, 2023

1. Introduction

Formaldehyde-based thermoset resins, including urea-formaldehyde, melamine-formaldehyde, and melamine-urea-formaldehyde, have found extensive utility in the wood-based panel industry due to their cost-effectiveness and high reactivity, as corroborated by numerous studies (Ji et al., 2017; Kim, 2009; Liu et al., 2018; Nuryawan et al., 2017; Perminova et al., 2019; Philbrook et al., 2005). These resins have been instrumental in manufacturing various products integral to our daily lives, such as particleboard and fiberboard, which serve as fundamental components in flooring, furniture, and more.

However, despite their practical advantages, formaldehyde-based resins present substantial drawbacks, particularly in terms of sustainability and their contribution to formaldehyde emissions. These concerns have curtailed their widespread adoption.

Formaldehyde-based resins, being derived from non-renewable sources, are entwined with the issue of formaldehyde emissions, a prominent environmental pollutant with adverse implications for human health and ecological well-being. As a result, there has been a growing emphasis on research and development aimed at formulating wood adhesives that are both sustainable and devoid of formaldehyde, echoing the industry's shift towards greener and more responsible practices (El Mansouri et al., 2007; Liu et

* Author to whom all correspondence should be addressed: e-mail: salise.oktay@keas.com.tr; Phone: +902165543587

al., 2018; Moubarik et al., 2010, 2013; Yang et al., 2013; Zhao et al., 2016).

Within the academic domain, attention has increasingly gravitated towards starch and tannin-based wood adhesive formulations as promising avenues to produce natural, formaldehyde-free wood adhesives. These materials have been favored for their compatible chemical composition and eco-friendly attributes. However, it is recognized that bio-based resins, despite their sustainable advantages, tend to exhibit comparatively lower reactivity when juxtaposed with traditional formaldehyde-based adhesives. Consequently, this study embarks on the task of synthesizing a starch-tannin-based resin endowed with heightened reactivity, thus striving to bridge this performance gap (Ahmad et al., 2020; Gu et al., 2019; Kuakpetoon and Wang, 2008; Pizzi, 1979; Sumathirathne and Karunanayake, 2017; Tondi, 2017).

The paramount objective of this research revolves around the creation of a renewable, eco-conscious resin formulation that stands as a compelling alternative to formaldehyde-based counterparts. In this context, starch and tannin were judiciously chosen as raw materials owing to their harmonious chemical makeup and environmentally sustainable attributes. The outcome of this effort revealed a resin formulation that not only exhibited excellent mechanical properties but also, importantly, showcased minimal formaldehyde emissions when utilized in the production of particleboards. As a collective testimony to these findings, it becomes evident that the newly developed starch and tannin-based wood adhesive formulations have the potential to be effectively harnessed within the wood-based panel industry as efficient binders. In doing so, they aptly address and mitigate the critical concerns associated with conventional formaldehyde-based adhesives, thereby propelling the industry towards a more sustainable and eco-friendly trajectory.

2. Experimental

2.1. Chemicals and reagents

Corn starch (CS) was obtained by Sunar Mısır (Adana, Turkey). Amylose and moisture content of the CS were 25.3% and 11.9% by weight on a dry basis, respectively. Wattle bark (Mimosa) tannin (MT) was purchased from Bondtite Pty. Ltd (Dorpspruit, South Africa). The moisture content of the MT was 7% by weight on a dry basis. Laboratory-scale particleboards were manufactured in Kastamonu Entegre Ağaç San. Tic. A.Ş. Besides, mechanical, physical, and formaldehyde content tests of the produced boards were also carried out in Kastamonu Entegre.

2.2. Synthesis of tannin-based wood adhesive

Primarily for resin synthesis with 46% solid content by weight, 1110 g of tannin was mixed into 1110 g of distilled water and dispersed at room temperature using a mechanical stirrer. Finally, hexamine (HMTA) was added to the resin system as a hardener. The hardener content used was 10% by weight of the resin solid content. Finally, the pH value of the resin was adjusted to the range 8-9 with a 40 wt.% NaOH aqueous solution.

2.3. Synthesis of starch-based wood adhesive

A quantity of 350 g of corn starch was added to 1000 g of distilled water and mixed at room temperature using a mechanical stirrer. Then, 75 g of sugar and 70 g of urea were added. Finally, 70 g of furfural was added to the system and the pH value of the resin was adjusted to the range of 8-9 with 40% NaOH.

2.4. Physical properties: Solid content and viscosity determination

Firstly, about 1.5 g of synthesized wood adhesives were poured into a piece of aluminum foil and then dried at 120°C in an oven for 2 hours. After drying, the dried sample was taken out of the oven. Following that, the dried sample was reweighed. The solid content by percentage (S) of the tannin-based adhesive was determined according to Eq. (1).

$$S = \frac{M_2 - M_0}{M_1 - M_0} x\ 100\% \qquad (1)$$

where: S was solid content, M_0 was the mass of aluminum foil, M_1 was the mass of aluminum foil and adhesive sample and M_2 was the mass of aluminum foil and dry adhesive sample+.

The calculated solid content value was an average of three replicates (Zhao et al., 2018a). The viscosity of the prepared adhesives at 20°C was measured using Brookfield CAP 2000+ instrument at 200 rpm. An average of three test results was presented.

2.5. Fourier transform infrared (FT-IR) spectroscopy

The chemical structure of the cured tannin-based wood adhesive sample was characterized by Fourier transform infrared spectroscopy (FT-IR). FT-IR analyses were carried out by using Bruker Tensor 37 spectrophotometer and the samples were scanned between 400 and 4000 cm^{-1}. To obtain a cured tannin adhesive sample, the synthesized tannin-based wood adhesive of 55 g and an HMTA of 2.5 g were added sequentially to a beaker, and the HMTA was dissolved completely in the resin. The pH value of the resin was adjusted to the range 8-9 with a 40 wt.% NaOH aqueous solution. 2 g of the prepared resin sample and stir bar was placed in the test tube. Then, as soon as the test tube was immersed in boiling water, the chronometer was started and the resin was mixed with the rod.

The chronometer was stopped when the resin took solid form. The recorded time was determined as the curing time. After the cured resin samples were completely dried, FT-IR analyses of the samples were carried out.

2.6. Particleboard preparation and testing

Particleboards are mainly composed of three layers which are 2 surface layers (SL) and 1 core layer (CL). Laboratory scale particleboards of dimensions 500 mm x 500 mm x 12 mm were prepared. The total resin solid by weight was 12% for the surface layers and 7% for the core layer. Particleboard samples bonded with the developed bio-based resin formulations were assembled and hot-pressed at 200°C, for 4 minutes press time. In general, it is known that the core layer of the particleboard determines the mechanical properties, and the formaldehyde content is determined by the surface layer.

Therefore, in the study, tannin-based resin with higher mechanical strength was used in the core layer, and corn starch-based resin was used in the surface layer. Particles were dried to approximately 4% moisture content before the application of resin. The aimed board density was 700 kg/m^3. All tests were conducted by appropriate European Standards. Internal bond (IB), bending strength (BS), modulus of elasticity (MOE), and surface soundness of the produced particleboards were performed according to EN 319, EN 310, and EN 311 test standards, respectively (Wager and Kleinert, 2011).

2.7. Formaldehyde content by perforator method

The formaldehyde content of the manufactured particleboards was measured according to the European Norm (EN 12460-5), also called the perforator method. It is used to determine the formaldehyde content of the uncoated and non-laminated wood-based board. In this method, the amount of formaldehyde (mg) within the 100 g sample was measured.

Firstly, formaldehyde was extracted from the test samples by boiling toluene and transferred into de-mineralized water. After that, the formaldehyde content of this aqueous solution was determined photometrically (Oktay et al., 2021).

3. Results and discussion

3.1. Physical properties: Solid content and viscosity determination

Resin solid content and viscosity significantly affect the processability of adhesives in a board production line. The solid content of the tannin and starch-based resin was 46%. The viscosity values for tannin and starch-based wood adhesives were 350 and 30 mPa-s, respectively. The resin solid content was at a level that prevented excessive moisture during board pressing, and the resin viscosity was such that it could spread evenly on the chips. Additionally, it was observed that the resin solid content and viscosity obtained were similar to those of commercial formaldehyde-based wood adhesives (Zhao et al., 2018a).

3.2. Fourier transform infrared (FT-IR) spectroscopy

The chemical structure of the cured tannin-based adhesive sample was illuminated with FT-IR and their spectra are shown in Fig. 1. As could be seen from Fig. 1, the detected bands at 1587 and 1458 cm^{-1} in the Mimosa tannin spectrum which were attributed to the aromatic -C=C- stretching, disappeared in the cured resin spectrum possibly due to the increment of the aromatic ring substitution of tannin. Likewise, compared with the Mimosa tannin spectrum, the band at 1148 cm $^{-1}$ related to the C–O and O–H groups of resorcinol molecule of mimosa tannin, disappear after the reaction. Besides, three new peaks at around 1010 cm^{-1}, 1230 cm$^{-1,}$ and 1605 cm^{-1} which were respectively ascribed to the antisymmetric deformation of -C–O–C- in ether groups, presence of –C-N- groups, and formation of the azomethine groups (–CH=N-) were detected in the FT-IR spectrum of the cured tannin-based resin (Peña et al., 2009).

Moreover, to elucidate the chemical structures of the cured corn starch-NaOH and corn starch-NaOH-sugar mixtures, FT-IR analyses were performed. Their spectra are shown in Fig. 2. As could be seen from Fig. 2, compared with the corn starch spectrum, the broadband at around 3300 cm^{-1} related to the hydroxyl groups of the starch gradually weakened in the cured corn starch-NaOH and corn starch-NaOH-sugar mixtures. This could be attributed to the reducing –OH content after oxidization. Likewise, the band at 1147 $^{-1}$ cm disappeared. Besides, two new peaks were detected in the FT-IR spectrum of the cured corn starch-NaOH and cornstarch-NaOH-sugar at around 1560 cm$^{−1}$ and 1410 cm^{-1}. These peaks were ascribed to the –$COO^{-}Na^{+}$ group on the starch molecule chains (Yaacob et al., 2011). On the other hand, compared to the corn starch and cured corn starch-NaOH spectra, a new peak at 778 cm$^{−1}$ was detected according to the FT-IR spectrum of the cured corn starch-NaOH-sugar mixture, which was related to the unsubstituted CH=CH group of 5-hydroxymethyl-2-furfural (5-HMF) ring (Zhao et al., 2018a).

It was known that sugar decomposes at high temperatures and produces furanic derivatives such as 5-HMF (Fig. 3) (Tondi et al., 2012; Zhao et al., 2016; Zhao et al., 2018b). It was known that the chemical interaction between corn starch and 5-HMF with dimethylene ether bridges was possible. These observations revealed that chemical interactions between corn starch and NaOH occurred in the cured corn starch-NaOH mixture. In the cured corn starch-NaOH-sugar mixture, in addition to the interaction of corn starch and NaOH, a possible interaction between corn starch and 5-HMF could be formed.

3.3. Particleboard preparation and testing

To examine the performance of the developed resin formulation, at least 3 laboratory-scale particleboards were produced. The physical (thickness and density) and the mechanical test results (internal bond, surface soundness, bending strength, and modulus of elasticity) of the particleboards were illustrated and compared with similar studies in the literature in Table 1.

Since the boards were intended to be used in a dry environment, water uptake and thickness swelling tests were not performed.

All of the obtained results showed that the produced board by using a developed bio-based resin formulation met the standard values and was comparable with similar studies' results. In addition, the formaldehyde content of the produced boards is significantly lower and originates from the wood itself (Oktay et al., 2022).

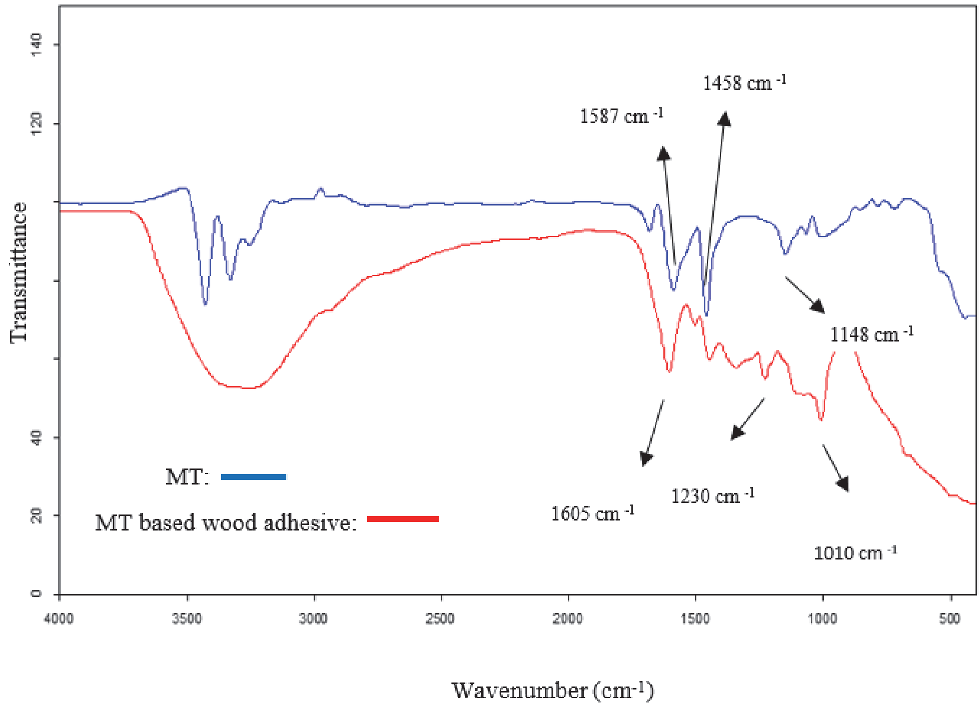

Fig. 1. FT-IR spectra of the Mimosa tannin and cured tannin-based resin

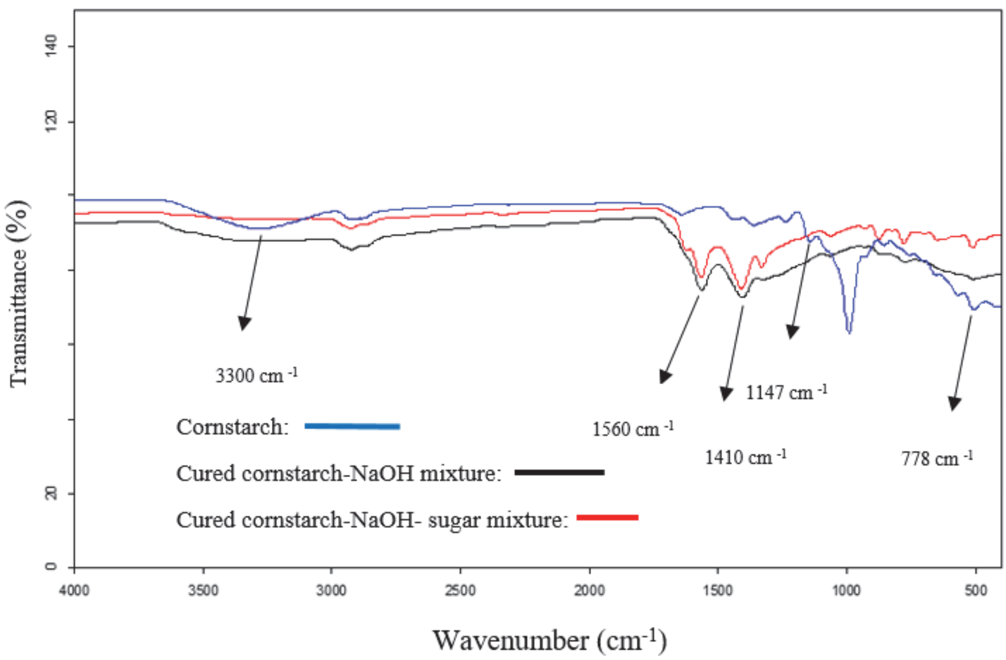

Fig. 2. FT-IR spectra of the corn starch, cured corn starch-NaOH mixture, and cured corn starch-NaOH- sugar mixture

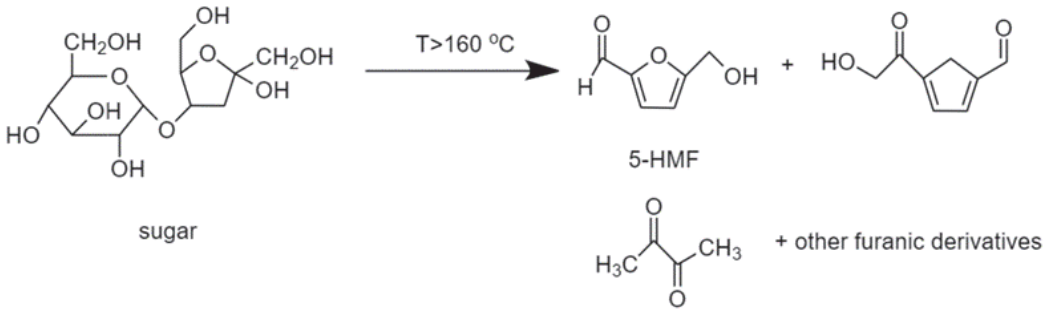

Fig. 3. Thermal decomposition of sugar at high temperatures

Table 1. Particleboards test results

Hybrid resin formulation (by weight%)		*Thickness mm Density kg/m³*	*IB N/mm²*	*MOE N/mm²*	*MOR N/mm²*	*Surface soundness N/mm²*	*FA content (mg/100g)*
Resin 1 35% CS 7% furfural 7.5% sucrose 7% urea	**Resin 2** 50% MT 10% HMTA	11.08 739	0.60	2843	15.07	1.14	1.36
Oktay et al., 2021		10.47 761	0.97	2220	10.36	1.34	0.94
Oktay et al., 2022		11.45 695	0.43	2472	11.14	0.72	0.92
P2 class std.		6<x≤13	> 0.40	> 1800	> 11	> 0.80	-

4. Conclusions

We have proposed sustainable, environmentally friendly, cost-effective, and formaldehyde-free corn starch and tannin-based wood adhesive formulations. The chemical structure of the cured adhesive samples confirmed that the desired crosslinked network was successfully achieved. Additionally, to determine the performance of the prepared resin formulations, we produced laboratory-scale particleboards. Their physical and mechanical properties were determined, and their formaldehyde content values were measured.

All of the obtained test results demonstrated that the boards made with the developed bio-based resin formulations generally satisfied the exigencies of panels for interior fittings used in dry medium (P2) according to European norms EN 312 (2010). Besides, good mechanical properties, the panels produced with the prepared formaldehyde-free resin formulations had significantly lower formaldehyde content. The low formaldehyde content of the boards produced with the prepared resins was not due to the resin but from the natural structure of the wood raw material.

All of the obtained results showed that the developed bio-based resin formulations have a high potential to be used for producing interior-grade particleboard.

Acknowledgements

The authors would like to thank the Scientific and Technical Research Council of Turkey (TUBITAK) - 2244 - Istanbul Technical University-Kastamonu Entegre Ağaç Sanayi - Project No: 118C107. The authors acknowledge funding from the Research Fund of the Istanbul Technical University, Turkey (ITU BAP; Project No.: TDK-2021-43282 and THD-2022-44082).

References

Ahmad A.N., Lim S.A., Navaranjan N., Hsu Y.I., Uyama H., (2020), Green sago starch nanoparticles as reinforcing material for green composites, *Polymer*, **202,** 122646, https://doi.org/10.1016/j.polymer.2020.122646.

El Mansouri N.E., Pizzi A., Salvadó J., (2007), Lignin-based wood panel adhesives without formaldehyde, *Holz als Roh - und Werkstoff*, **65**, 65-70.

Gu Y., Cheng L., Gu Z., Hong Y., Li Z., Li C., (2019), Preparation, characterization and properties of starch-based adhesive for wood-based panels, *International Journal of Biological Macromolecules*, **134,** 247-254.

Ji X., Li B., Yuan B., Guo M., (2017), Preparation and characterizations of a chitosan-based medium-density fiberboard adhesive with high bonding strength and water resistance, *Carbohydrate Polymers*, **176,** 273-280.

Kim S., (2009), Environment-friendly adhesives for surface bonding of wood-based flooring using natural tannin to reduce formaldehyde and TVOC emission, *Bioresource*

Technology, **100**, 744-748.

Kuakpetoon D., Wang Y.J., (2008), Locations of hypochlorite oxidation in corn starches varying in amylose content, *Carbohydrate Research*, **343**, 90-100.

Liu M., Wang Y., Wu Y., He Z., Wan H., (2018), "Greener" adhesives composed of urea-formaldehyde resin and cottonseed meal for wood-based composites, *Journal of Cleaner Production*, **187**, 361e371, https://doi.org/10.1016/j.jclepro.2018.03.239

Moubarik A., Allal A., Pizzi A., Charrier F., Charrier B., (2010), Preparation and mechanical characterization of particleboard made from maritime pine and glued with bio-adhesives based on corn starch and tannins, *Maderas: Ciencia y Tecnologia*, **12**, 189-197.

Moubarik A., Mansouri H.R., Pizzi A., Charrier F., Allal A., Charrier B., (2013), Corn flour-mimosa tannin-based adhesives without formaldehyde for interior particleboard production, *Wood Science and Technology*, **47**, 675-683.

Nuryawan A., Risnasari I., Sucipto T., Heri Iswanto A., Rosmala Dewi R., (2017), Urea-formaldehyde resins: Production, application, and testing, *IOP Conference Series: Materials Science and Engineering*, **223**, 012053, http://doi.org/10.1088/1757-899X/223/1/012053.

Oktay S., Kızılcan N., Bengü B., (2021), Development of bio-based corn starch - Mimosa tannin - sugar adhesive for interior particleboard production, *Industrial Crops and Products*, **170**, 113689, https://doi.org/10.1016/j.indcrop.2021.113689.

Oktay S., Kızılcan N., Bengü B., (2022), Environment-friendly corn starch and tannin-based wood adhesives for interior particleboard production as an alternative to formaldehyde-based wood adhesives, *Pigment and Resin Technology*, https://doi.org/10.1108/PRT-06-2022-0075.

Peña C., De La Caba K., Retegi A., Ocando C., Labidi J., Echeverria J.M., Mondragon I., (2009), Mimosa and chestnut tannin extracts reacted with hexamine in solution, *Journal of Thermal Analysis and Calorimetry*, **96**, 515-521.

Perminova D.A., Malkov V.S., Guschin V., Eisenreich N., (2019), Influence of glyoxal on curing of urea-formaldehyde resins, *International Journal of Adhesion and Adhesives*, **92**, 1-6.

Philbrook A., Blake C.J., Dunlop N., Easton C.J., Keniry M.A., Simpson J.S., (2005), Demonstration of co-polymerization in melamine-urea-formaldehyde reactions using 15N NMR correlation spectroscopy, *Polymer*, **46**, 2153-2156.

Pizzi A., (1979), The chemistry and development of tannin/urea–formaldehyde condensates for exterior wood adhesives, *Journal of Applied Polymer Science*, **23**, 2777-2792.

Sumathirathne L.D., Karunanayake L., (2017), Synthesis of novel porous tannin-phenol-formaldehyde cation exchange resin from Terminalia arjuna (Kumbuk), *Journal of the National Science Foundation of Sri Lanka*, **45**, 219-227.

Tondi G., (2017), Tannin-Based copolymer resins: Synthesis and characterization by solid state 13C NMR and FT-IR spectroscopy, *Polymers*, **9**, 223, http://doi.org/10.3390/polym9060223.

Tondi G., Wieland S., Wimmer T., Schnabel T., Petutschnigg A., (2012), Starch-sugar synergy in wood adhesion science: Basic studies and particleboard production, *European Journal of Wood and Wood Products*, **70**, 271-278.

Wager E., Kleinert S., (2011), Responsible research publication: international standards for authors, *Macedonian Journal of Chemistry and Chemical Engineering*, **35**, 29-33.

Yaacob B., Amin M.C.I.M., Hashim K., Bakar B.A., (2011), Optimization of reaction conditions for carboxymethylated sago starch, *Iranian Polymer Journal (English Edition)*, **20**, 195-204.

Yang L., Liu J., Du C., Qiang Y., (2013), Preparation and properties of cornstarch adhesives, *Advance Journal of Food Science and Technology*, **5**, 1068-1072.

Zhao X.F., Peng L.Q., Wang H.L., Wang Y.B., Zhang H., (2018a), Environment-friendly urea-oxidized starch adhesive with zero formaldehyde-emission, *Carbohydrate Polymers*, **181**, 1112-1118.

Zhao Z., Miao Y., Yang Z., Wang H., Sang R., Fu Y., Huang C., Wu Z., Zhang M., Sun S., Umemura K., Yong Q., (2018b), Effects of sulfuric acid on the curing behavior and bonding performance of tannin-sucrose adhesive, *Polymers*, **10**, 651, https://doi.org/10.3390/polym10060651.

Zhao Z., Umemura K., Kanayama K., (2016), Effects of the addition of citric acid on tannin-sucrose adhesive and physical properties of the particleboard, *BioResources*, **11**, 1319-1333.