Journal of Food Engineering and Technology 2024;13(2):41-46
https://doi.org/10.32732/jfet.2024.13.2.41

Evaluation of Rice-based Alternatives to Titanium Dioxide for Colour-masking in Iron-Fortified Salts

Diana L. Teichman, Naayaab Nagree, Ariel Chan, Levente L. Diosady

Dept. of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College St., Toronto, M5S 3E4, Canada
E-mail: diana.teichman@mail.utoronto.ca (Corresponding author); naayaab.nagree@mail.utoronto.ca; ariel.chan@utoronto.ca; l.diosady@utoronto.ca

Received: 22 May 2024; Accepted: 26 June 2024; Available online: 10 August 2024

Abstract: Titanium dioxide (TiO_2) is a common whitening agent used in the food industry, used in candies, baked goods and confectionaries. Several food regulatory agencies have banned or severely restricted TiO_2 use due to potential carcinogenic/ genotoxicity. Rice starch and rice flour were investigated as alternatives to TiO_2, since they are cheap, opaque, white and are widely used in industry. Due to its amorphous granules and resulting low electrostatic forces, the adhesion of rice starch to extruded materials was much weaker than that of TiO_2. Adhesives were synthesized from crosslinking citric acid with rice starch and rice flour through esterification reaction pathways. The results were tested on extruded ferrous fumarate cylinders used in salt fortification and compared with TiO_2 was as control. The results show that rice starch as a whitening agent with a modified rice starch adhesive was a promising option for replacing TiO_2 as a colour masking/whitening agent. It was observed that higher mass fractions of citric acid in the adhesive produced better results. Rice flour performed comparably to the rice starch in adhesives however, the ease of use was poorer due to higher viscosity and clumping. The cost for using rice starch was a cost-effective alternative to TiO_2 as rice starch is a cheaper, widely available food additive.
Keywords: Adhesives; Food processing; Food fortification; Food engineering.

1. Introduction

Titanium dioxide is used widely in the food industry in products such as candies, gum, chocolate, coffee creamers, mints and in cosmetics and sunscreens as a whitening ingredient [1]. In 2018, the annual consumption of titanium dioxide was four million tons globally [2]. Titanium dioxide is unscented and increases the white colour and opacity of products. It is ideal for light reflection due to its light scattering properties [1]. Opaque materials reflect some light and absorb the remaining light, whereas transparent objects such as a glass transmit light which allows seeing through it. Smooth polished surfaces reflect more light [3]. Food-grade titanium dioxide is typically 200-300 nanometers in diameter [2] and this small size facilitates coverage of material for high light scattering [1]. Nano-sized particles have high surface-to-mass ratio which increases light scattering [2].

Food-grade titanium dioxide is 99% pure [1] and may contain low levels of contaminants including lead, arsenic, mercury [2]. During the manufacturing process, the by-product of food grade titanium dioxide is a nano-sized fraction [2]. Nanoparticles have a tendency to cross cell membranes such as the intestinal mucosa [3]. The European Food Safety Authority (EFSA) banned titanium dioxide E171 in food due to concerns of potential genotoxicity, from a series of toxicity studies of titanium dioxide nanoparticles [4-6]. Genotoxicity is the capacity for the chemical to injure DNA in cells, possibly resulting in cancer over time [6].

After a detailed review by the U.S. Food and Drug Administration (FDA), titanium dioxide is still permitted in Canada [6] and the United States of America. The FDA permits 1% by weight of titanium dioxide in food [7]. The California Food Safety Act bill 418 originally banned titanium dioxide as well as brominated vegetable oil, potassium bromate, propylparaben from foods [5]. However, as of October 2023, the bill was amended to eliminate the ban on titanium dioxide, stating further studies of the adverse impacts on human health are required [5]. Although the debate is ongoing in the scientific community, finding safe alternatives for titanium dioxide is prudent.

Rice flour and rice starch are attractive alternatives for titanium dioxide, as they are white, opaque, bland in taste, chemically stable, and they will not chemically react with other nutrients. Rice is a major staple, and its derivatives have been used in the food industry for decades. Rice flour is milled, dehulled white rice containing amylose, amylopectin, and crystalline protein bodies of glutelin and prolamin [8]. Rice flour is used in cereals, snack foods, baby foods, pancakes, coatings for fried products [9,10]. Rice flour particle sizes range from 63 to 200 μm [11].

Rice starch, derived from the flour, is a white powder composed of amylose and amylopectin, and is gluten free [8,12]. Rice starch comprises small granules packed tightly together, with size range 2-4 μm [8]. The smaller the particle size, the larger the contact area between particles. Rice starch is usable for edible films and coatings due to its mechanical properties [13]. Das et al. used rice starch with glycerol and a lipid to form an edible coating on tomatoes, to protect tomatoes during storage [14]. There are also health benefits to starch since amylose facilitates slower digestion, similar to a prebiotic and amylopectin has promising baking properties [14].

Starch is semi-crystalline, meaning it is composed of amorphous and crystalline regions [15]. Due to the disordered nature of amorphous regions, rice starch has weaker electrostatic forces than titanium dioxide which is a crystalline material, consisting of brookite, anatase and rutile [16,17]. For food applications such as adherence to the extruded materials, an additional adhesive is required.

Adhesives made by cross-linking glucose (as in rice flour) with citric acid have been applied on wood as a bio-based glue, due to its high strength and low cost [18]. Li et. al produced a biomass-based adhesive from the esterification reaction of glucose and citric acid with high strength and eco-friendly properties [18]. Citric acid to glucose ratios above 0.6 were optimal, with more ester links between citric acid and wood [19].

Another alternative for the adhesive is cross-linking rice starch with citric acid. Heat facilitates the cross-linking of starch molecules with citric acid, through a process called starch esterification, or starch modification. It is used in the food industry to alter the properties of starch for various applications. During heating, citric acid reacts with the hydroxyl groups on the starch molecules, forming ester bonds. These ester bonds cross-link starch molecules, resulting in modified starch with altered properties including increased adhesion [20,21]. The concentration of citric acid is an important factor for the strength of the resulting starch films.

Reddy et.al. found that cross-linking starch with citric acid in concentrations of up to 5% (w/w) raised the molecular weight of the starch and enhanced interactions between molecules, resulting in higher tensile strength than non-cross-linked starch films [21]. They found that above 5% (w/w), excess cross-linking decreased the mobility of the starch molecules, decreasing their tensile strength.

This study investigated rice flour-citric acid and rice starch-citric acid adhesives for adherence of rice starch to extruded ferrous fumarate particles as colour masking agent in salt double fortification with iron and iodine. The fortified salt consists of an extrusion-based premix mixed with iodized salt. The ferrous fumarate core of the premix is reddish brown. For consumer acceptability, the organoleptic properties of the salt should not be altered by the addition of the premix. Therefore, the premix must be colour-masked prior to blending into salt. Current premix formulations use TiO_2 for colour-masking. In replacing of titanium dioxide with rice flour or rice starch the maintenance of organoleptic properties including colour and flavour is critical.

2. Materials and Methods

2.1 Materials

Ferrous fumarate and rice flour were obtained from Wella Nutralogicals, and rice starch and citric acid were obtained from Sigma Aldrich.

2.2 Preparation of the Ferrous Fumarate Core

Extruded ferrous fumarate was produced based on the methods described by Li YO et. al. (2011) [22]. The extruded ferrous fumarate was ground to 500-700 μm cylindrical particles using a burr grinder.

2.3 Synthesis of Adhesives

The synthesis of the rice starch and citric acid-based adhesive was adapted from the methods outlined by Uliniuc, A. et al. (2013) [23]. Briefly, rice starch was dispersed in gently warmed water and citric acid was added at a predetermined mass ratio with continuous stirring for 30 minutes., Rice flour dispersions were prepared similarly, and the rice flour-citric acid mixture was stirred for an hour with no heating. Three mass ratios of citric acid to rice starch were studied – 0.05, 0.1 and 0.2. Three mass ratios of citric acid to rice flour were studied – 0.05, 0.07 and 0.08.

2.4 Coating of Iron Core with Whitening Agent and Preparation of Fortified Salt

Rice starch was used as the coating material. As is convention for layer-by-layer methods, the amount of coating material added was calculated and reported as a Baker's percentages of 25-100% of the extruded core's weight. A rotating aluminum pan was used to hold the extruded ferrous fumarate while the adhesive was sprayed on, followed by addition of the whitening agent i.e. rice starch in 25% increments. Between increments, the layer was allowed to air dry. An overcoat of 15% soy stearin was applied onto the dried particles, to create a moisture barrier. This premix was mixed into iodized salt (50 ppm iodine), in order to achieve salt fortified with 1000 ppm iron. A control premix sample was prepared with 25% titanium dioxide and 15% soy stearin.

2.5 Colourimetric Analysis of the Coated Particles

A 3nh Colourimeter was used to evaluate the effectiveness of rice starch as a whitening agent. The colour difference relative to iodized Indian salt was quantified using the L*, a* and b* values. The colour difference between TiO_2 and the Indian salt was used as the baseline for the comparison. The equation used to determine the DE value, used in industry, was as follows:

$$\Delta E^{*}_{ab} = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \tag{1}$$

where, L is the measure of whiteness, a is the measure of the red/green and b is the measure of blue/yellow.

2.6 Imaging of the Coated Particles

A Fisher light microscope was used to examine the particles at 10x and 60x zoom. The microscope images were used to determine the quality of the coating. Additionally, a lightbox and digital camera were used to take macroscopic images of the produced samples.

3. Results and Discussion

Rice starch and rice flour were evaluated as alternatives to TiO_2. Citric acid was used as a cross-linking agent to synthesize an adhesive for the whitening agent coating. The results were compared to TiO_2 as the control in terms of colour, cost and ease of use.

3.1 Rice Starch – Citric Acid Adhesive with Rice Starch as Coating Material

Three mass ratios of citric acid to rice starch were studied – 0.05, 0.1 and 0.2. Each of the samples were run triplicate. The average ΔE values are reported in Figure 1. As the citric acid content increased, the ΔE of the coated particles decreased. This is likely due to the formation of a higher amount of starch-citrate in the adhesive. The increase of starch-citrates i.e. higher esterification acts as a better adhesive [24]. For the 0.05 and 0.1 mass ratio the higher ΔE value for the 100% rice starch is likely due to the adhesive loading capacity reaching a maximum. The 100% rice starch sample produced with 0.2 mass ratio adhesive formulation performed marginally better than the TiO_2 control.

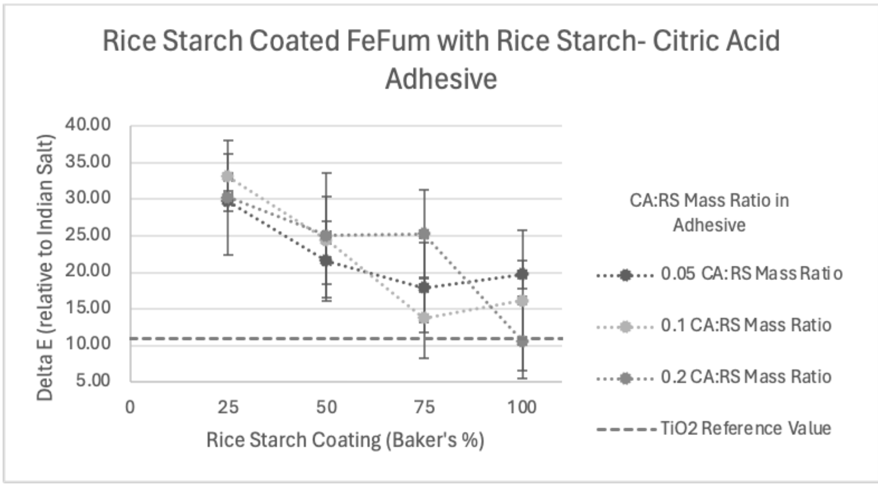

Figure 1. Rice Starch – Citric acid Adhesive with Rice Starch Coating Material

3.2 Rice Flour – Citric Acid Adhesive with Rice Starch as Coating Material

Three mass ratios of citric acid to rice flour were studied – 0.05, 0.07 and 0.08. Each of the samples were run triplicate. The average ΔE values are reported in Figure 2. Similarly to the rice starch- citric acid trend (Figure 1), as the citric acid content increased, the ΔE value decreased (Figure 2). This shows that the adhesive is able to bond to more of the rice starch to form a coat. Generally, the trends for rice flour are more erratic than the rice starch adhesive trends. The ΔE values were low due to the rice starch appearing white, but under the microscope, large clumps of rice starch with exposed iron particles were observed (Figure 3). It was noted that while performing the experiment, the rice flour suspensions were more difficult to work with and required constant stirring and/ or vortexing to maintain the suspension. Therefore, the rice starch-citric acid adhesive performed better than that utilizing rice flour-citric acid as an adhesive.

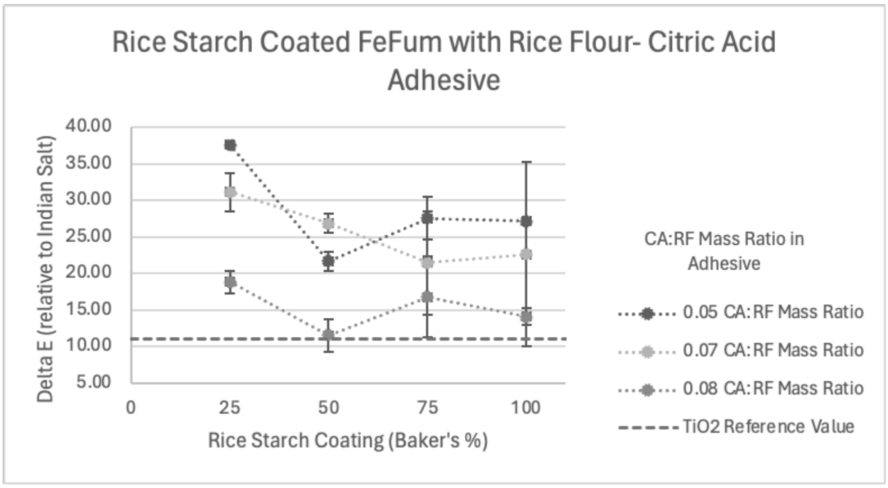

Figure 2. Rice Flour – Citric Acid Adhesive with Rice Starch Coating Material

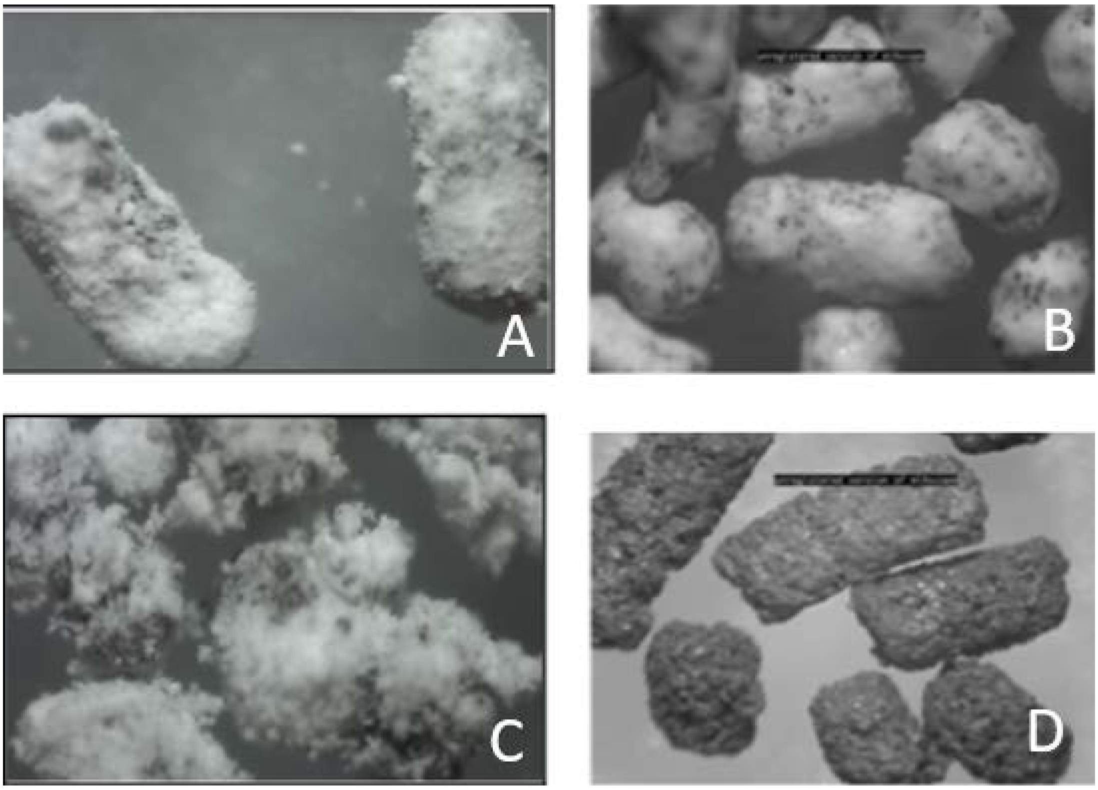

Figure 3. Microscope Images of Premixes Colour-masked with A) Rice Starch with CA:RS adhesive, B) Titanium Dioxide (control) C) Rice Starch with CA:RF adhesive, D) extrudate no coating.

As seen in figure 3, the premixes are colour-masked with rice starch with rice starch: citric acid adhesive appear similar to the control (TiO_2 coated premix), with minimal exposed surfaces. They are slightly larger than TiO_2 premixes (25% bakers' percentage) due to more coating material required (75-100% bakers' percentage) to achieve the same level of whiteness. Larger amounts of coating material decrease the overall iron content per premix from 18% iron in TiO2 premixes to 10%-14% iron in rice starch premixes. To compensate for lower iron concentration in the premix, more of the rice starch premix is needed per kilogram of salt for fortification attain 1000 ppm iron compared with salt fortified with TiO2 premixes. Based on the results shown in Figures 1-3, rice starch-coated samples with adhesives made from rice starch with citric acid is a viable alternative to replace titanium dioxide as a colour masking system. While rice flour based adhesive formulations are slightly less expensive than those based on, rice flour is a less effective adhesive for attaching rice starch to the extruded core of the premix.

While more rice starch premix is needed per kilogram of salt for fortification, the cost of the formulation is not significantly higher than salt fortified with TiO_2 based premix. Based on 2023 market prices of ingredients in India, the total costs for the rice starch formulations were calculated as 4-5 US cents/kg salt, or 14-19 US ¢/year per capita. This is a slightly lower than the cost of salt made with premix colour masked with 25% TiO_2: 7 US¢/kg salt, and 24 US ¢/year per capita. Even though more premix is required for the rice formulation than titanium dioxide, rice is less expensive resulting in the lower overall cost.

4. Conclusion

Rice starch is a viable alternative to replace titanium dioxide as a whitening or colour masking agent in food formulations. The high stability of rice, limited interaction with micronutrients and its low cost makes it an attractive alternative to TiO_2. As rice flour or starch do not adhere well to extruded ferrous fumarate, an adhesive is required. An adhesive produced by the cross-linking of rice starch with citric acid resulted in the effective coating of ferrous fumarate, resulting in premixes that can be blended into iodized salt without significantly altering its colour or taste. Although appropriate colour requires more rice-based colour masking coating, resulting lower iron loading in the premixes when compared to those based on TiO_2. The low cost of rice flour and starch results in a reduction in the per capita cost of salt fortification with iron and iodine to only 14-19 US¢/year. Long-term stability testing of these premixes in iodized salt are ongoing, results will be reported when available. In the current and anticipated regulatory environment, the rice-based whitening systems developed here ensure that technology is available to address the widespread iron deficiency in developing countries, especially India and Sub-Saharan Africa through salt double and multiple fortification.

Acknowledgments

We would like to thank Manpreet Chada and Daniel De Lopez from Nutrition International, Dr. Amy Bilton, and The Food Engineering Research Group at the University of Toronto for their support.

Statement of authors' contributions

Diana L. Teichman and Naayaab Nagree conducted the research, wrote the manuscript and designed the research plan. Dr. Ariel Chan edited the manuscript. Dr. Levente L. Diosady designed research (project conception), supervised the research, edited the manuscript. All authors have read and approved the final manuscript.

Financial support

This work was undertaken with support from the Government of Canada, through Nutrition International.

5. References

[1] Weir A, Westerhoff P, Fabricius L, Hristovski K, von Goetz N. Titanium Dioxide Nanoparticles in Food and Personal Care Products. Environ Sci Technol. 2012;46(4):2242–2250.

[2] Winkler HC, Notter T, Meyer U, Naegeli H. Critical review of the safety assessment of titanium dioxide additives in food. Journal of Nanobiotechnology. 2018;16(1):51.

[3] Ghebretatios M, Schaly S, Prakash S. Nanoparticles in the Food Industry and Their Impact on Human Gut Microbiome and Diseases. Int J Mol Sci. 2021;22(4):1942.

[4] Shammas MA, Ahmad D, Nguyen MD, Rajput S, Unmack J, Ahmad G. Suggested Safe Harbor Limit for Titanium Dioxide: An Exposure Level Which Protects Consumers from Cancer Incidence. Front Oncol [Internet]. 2015 [cited 2024 Jul 1];5. Available from: https://www.frontiersin.org/journals/oncology/articles/10.3389/fonc.2015.00076/full

[5] Von Der Lyen U. Regulation - 2022/63 - EN - EUR-Lex [Internet]. 32022R0063, 2022/63 Jan 14, 2022. Available from: https://eur-lex.europa.eu/eli/reg/2022/63/oj

[6] Health Canada. Titanium dioxide (TiO_2) as a food additive: Current science report [Internet]. 2022 [cited 2024 Jul 1]. Available from: https://www.canada.ca/en/health-canada/services/food-nutrition/reports-publications/titanium-dioxide-food-additive-science-report.html

[7] Nutrition C for FS and A. Titanium Dioxide as a Color Additive in Foods. FDA. 2024 Apr 3 [cited 2024 Jul 1]; Available from: https://www.fda.gov/industry/color-additives/titanium-dioxide-color-additive-foods

[8] Li H, Fitzgerald MA, Prakash S, Nicholson TM, Gilbert RG. The molecular structural features controlling stickiness in cooked rice, a major palatability determinant. Sci Rep. 2017;7:43713.

[9] Kim MH. Review on Rice Flour Manufacturing and Utilization. Journal of Biosystems Engineering. 2013;38(2):103–112.

[10] Qian H, Zhang H. Chapter 25 - Rice flour and related products. In: Bhandari B, Bansal N, Zhang M, Schuck P, editors. Handbook of Food Powders (Second Edition) [Internet]. Woodhead Publishing; 2024 [cited 2024 Jul 1]. p. 437–452. (Woodhead Publishing Series in Food Science, Technology and Nutrition). Available from: https://www.sciencedirect.com/science/article/pii/B9780323988209000740

[11] Chaiwanichsiri S, Thumrongchote D, Suzuki T, Laohasongkram K. Properties of Non-glutinous Thai Rice Flour: Effect of rice variety. Research Journal of Pharmaceutical, Biological and Chemical Sciences. 2012;3.

[12] Li H, Prakash S, Nicholson TM, Fitzgerald MA, Gilbert RG. The importance of amylose and amylopectin fine structure for textural properties of cooked rice grains. Food Chemistry. 2016;196:702–711.

[13] Das DK, Dutta H, Mahanta CL. Development of a rice starch-based coating with antioxidant and microbe-barrier properties and study of its effect on tomatoes stored at room temperature. LWT - Food Science and Technology. 2013;50(1):272–278.

[14] Zhuang X, Yin T, Han W, Zhang X. Chapter 10 - Nutritional Ingredients and Active Compositions of Defatted Rice Bran. In: Cheong LZ, Xu X, editors. Rice Bran and Rice Bran Oil [Internet]. AOCS Press; 2019 [cited 2024 Jul 1]. p. 247–270. Available from: https://www.sciencedirect.com/science/article /pii/B978012812828200010X

[15] Song MR, Choi SH, Oh SM, Kim Hyun, Bae JE, Park CS, et al. Characterization of amorphous granular starches prepared by high hydrostatic pressure (HHP). Food Sci Biotechnol. 2017;26(3):671–678.

[16] Review: understanding the properties of amorphous materials with high-performance computing methods. PubMed Central (PMC). Accessed: Mar. 15, 2024. [Online].Available: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC10200347/#:~:text=Owing%20to%20their%20structural%20disorder,are%20usually%20insulators%20or%20semiconductors

[17] Inagaki, M. & Kang, F. Engineering and Applications of Carbon Materials in Materials Science and Engineering of Carbon: Fundamentals. 219–525 (Butterworth-Heinemann, 2014).

[18] Li C, Lei H, Wu Z, Xi X, Du G, Pizzi A. Fully Biobased Adhesive from Glucose and Citric Acid for Plywood with High Performance. ACS Appl Mater Interfaces. 2022;14(20):23859–23867.

[19] American Chemical Society [Internet]. [cited 2024 Jul 1]. A nontoxic glue for plywood – from glucose, citric acid. Available from: https://www.acs.org/pressroom/newsreleases/2022/may/nontoxic-glue-for-plywood-from-glucose-citric-acid.html

[20] Reddy N, Yang Y. Citric acid cross-linking of starch films. Food Chemistry. 2010;118(3):702–711.

[21] Garg S, Jana AK. Studies on the properties and characteristics of starch–LDPE blend films using cross-linked, glycerol modified, cross-linked and glycerol modified starch. European Polymer Journal. 2007;43(9):3976–3987.

[22] Li YO, Yadava D, Lo KL, Diosady LL, Wesley AS. Feasibility and optimization study of using cold-forming extrusion process for agglomerating and microencapsulating ferrous fumarate for salt double fortification with iodine and iron. J Microencapsul. 2011;28(7):639–649.

[23] Uliniuc A, Hamaide T, Popa M, Băcăiă S. Modified Starch-Based Hydrogels Cross-Linked with Citric Acid and their use as Drug Delivery Systems for Levofloxacin. Soft Materials. 2013;11.

[24] Watcharakitti J, Win EE, Nimnuan J, Smith SM. Modified Starch-Based Adhesives: A Review. Polymers. 2022;14 (10):2023.