

Study on Manufacturing and Applicability of Natural Adhesive for Paper Craft Using Corn Starch

Koang Chul Wi¹†

Received November 15, 2022; Received in revised form December 13, 2022; Accepted December 14, 2022

ABSTRACT

A natural adhesive of starch (corn) that can be used to make and repair paper crafts was manufactured. The purpose of this study was to explore a composition of an adhesive having maximum adhesive strength while controlling a catalyst, a reaction initiator, and an oxidizing agent added to an aqueous starch solution at room temperature. The best composition was when a 35% starch aqueous solution was used. The 2.0% NaOH aqueous solution was added to the 35% starch aqueous solution to adjust pH from 10.0 to 11.0, and 0.20 g NiSO₄, 20.0 g NaOCl, 30.0 g of 30.0% NaOH solution, and 3.0 g of 1.0% sodium thiosulfate were sequentially added. In the last step, the 3.0% HCl aqueous solution was added to adjust the pH of the adhesive to 7.5, and the adhesive strength of the prepared adhesive was 213 kgf/cm². It was stable at room temperature for more than 60 days without physical changes such as viscosity, phase separation, precipitation, etc. In addition, TVOC, HCHO, and heavy metals were not detected, and the excellent result was found in antibacterial and reversible tests. This adhesive is an excellent natural adhesive that can be easily used by the user and does not contain harmful substances. It was an adhesive that could maintain the reputation of traditional materials in addition to their production and preservation.

Keywords: *Starch adhesive, traditional adhesive, corn starch, adhesive for paper craft and natural adhesive*

1. Introduction

Natural adhesives are made using animal and vegetable components, and generally used as adhesives are soybean proteins,[1,2] tannins,[3-5]

and starch.[6] It is renewable, biodegradable, and inexpensive, so many studies have been conducted on it.[7-14]

Among them, starch is an inexpensive, renewable biodegradable polymer, and is the second most

¹ Department of Cultural Heritage Conservation, Hanseo University, Professor

† Corresponding Author: E-mail: kcwi@hanseo.ac.kr (Address: Department of Cultural Heritage Conservation, Hanseo University, Chungcheongnam-do, 31962, Republic of Korea)

widely used adhesive material after cellulose.

Starch has been added as a composite material of synthetic adhesive and UF resin is a representative example. UF resin is added to starch as cross-linking material mainly due to its ability to drastically reduce formaldehyde released. Adhesive for which diversified concentrations of starch,[15] esterized starch[16,17] and oxidized starch[18] have been added as composite cross-linking material has outstanding advantages including not only a low level of formaldehyde release but also water-resistant characteristic, chemical stability, insulation, heat-resistance, anti-aging, oil-resistance, and anti-mold characteristics.[19,20]

Among them, corn starch-based adhesives, in particular, are used as starch graft glycidyl methacrylate (AS-g-GMA) adhesives, and are known to be less harmful, more environmentally friendly, and inexpensive.[21] Starch ether and starch ester can also be used as hot melt adhesives and exhibit lower melting points and higher adhesion.[22-24]

Starch ether and starch ester can also be used as hot melt adhesives and exhibit lower melting points and higher adhesion, but they still have influence on synthetic resin parts, and it is difficult to approach the proposition of eco-friendly.

However, starch may result in reducing moisture adsorption, molecular migration, and expansion even at high humidity when an oxidizing agent is appropriately used.[25,26]

In particular, corn starch adhesives have good fluidity, milky white, fine, and glossy appearance. After drying, the strength and wetting strength are large, and the processability and water resistance are excellent.[27]

When the adhesive was oxidized under alkali conditions using nickel sulfate and sodium hypochlorite at room temperature, the results showed the best initial adhesion and the best bonding strength (initial adhesion was 98.7% and adhesion strength was 11.4 N/25 mm).[28-30]

The purpose of this study is to manufacture starch-based natural adhesives that can be used as manufacturing and repair adhesives in the field of paper crafting. Adhesive strengths and physical properties were measured according to the change in the composition of the starch adhesive, and a natural starch adhesive was prepared using the best composition.

2. Materials and Methods

2.1 Reagents and devices

The reagents including corn starch, resorcinol, HCl, NaOH, Borax, Na_2CO_3 , NaOCl, NaOH, sodium thiosulfate (STS), and H_2O_2 were purchased from Samchun Chemicals (Korea). Tributylphosphate (TBP), thio-urea and ammonium persulfate (APS) were purchased from Aldrich (US). Simple primary distilled water was used and all other reagents were manufactured by using ordinary class reagents.

For the reactor, the temperature controller, agitator, and cooler were included in the 3-section top portion and heating bottom portion segregation-type 500 mL reaction chamber. The heating mantle was used as the source of heat and the required internal temperature was adjusted within the range of $\pm 0.5^\circ\text{C}$ by using a temperature controller and sensor.

2.2 Manufacturing of starch adhesive

2.2.1 Gelatinization of starch without a catalyst

After having induced oxidation for each temperature and time by adding NaOCl oxidant to corn starch aqueous solution, the prescribed quantity of NaOH aqueous solution was added to cause a gelatinization reaction for each temperature and time to measure viscosity change and adhesion strength (total of 67 types).

2.2.2 Starch adhesive using resorcinol as denaturant

After having induced oxidation at each temperature and time by adding NaOCl and H₂O₂ to corn starch aqueous solution, each concentration of resorcinol aqueous solution was added along with catalysts such as TBP, Borax, Na₂CO₃, and AFS, etc. to induce reaction for each temperature and time before measuring viscosity change and adhesion strength (total of 34 types).

2.2.3 Starch adhesive using epichlorohydrin without an oxidant

After having produced a suspended starch solution by adding corn starch to the alkaline solution at low temperature, starch was degraded by adding epichlorohydrin and NaOH aqueous solution while slowly stirring the mixture at a stable and appropriate rate. Boric acid was added to this solution and the reaction was induced by heating. It was then neutralized with acetic acid to manufacture adhesive using epichlorohydrin without oxidant.

2.2.4 Gelatinized starch adhesive containing an oxidant and a catalyst

The aqueous starch solution produced with each of the required concentrations by using a catalyst and a stabilizer was pretreated with an alkaline solution for each pH, before inducing an oxidation reaction by using NaOCl for each time while a catalyst has been added.

Then, 30.0% NaOH solution was added by adjusting the quantity of addition to induce a reaction each time to achieve gelatinization. Sodium thiosulfate solution was added to complete the reaction. After the final solution was neutralized, viscosity change, adhesion strength and retention of adhesiveness were measured (a total of 41 types).

2.3 Measurement of material properties

2.3.1 Tensile and shearing adhesion strength

As such, tensile and shearing adhesion strengths were measured in accordance with KS M 3720. After having coated the overlapping section of the timber specimen with 0.3 g of adhesive produced, they were fixed with a clamp at room temperature and allowed to dry for 24 hours. Measurements were then taken with universal materials testing device at the tensile speed of 2 mm/min. For changes in viscosity and layer separation stability with the passage of time, the daily extent of flow at consistent temperature was checked visually and the extent of change was checked by remeasuring adhesion strength after a prescribed period of time.

2.3.2 Reversibility

For reversibility, the change in the weight was checked by applying 1 g of the product on a slide glass and allowing it to dry naturally for 24 hours before immersing it in 100 mL of distilled water for 24 hours.

2.3.3 Harmfulness

It was attempted to determine harmfulness by measuring TVOC, HCHO, and heavy metal contents. For this purpose, TVOC was analyzed with head surface GC-MSD with detection limits for benzene (0.00002%), toluene (0.00002%), ethylbenzene (0.00025%), and xylene (0.0006%). For HCHO, solution extracted with purified water over 1 hour at 40°C was reacted with DNPH before taking measurements using high pace liquid chromatography (HPLC) with a quantification limit of 40 µg/g. For heavy metals, lead (Pb), cadmium (Cd), and chromium (Cr) were analyzed by using ICP-OES after having degraded the specimen with acid. Quantification limits for lead, cadmium, and chromium were 2.0 µg/g, 1.0 µg/g, and 2.5 µg/g, respectively.

2.3.4 Total aerobic viable bacteria

A total aerobic viable bacterial cell count test was conducted to confirm the antibacterial property of the product. Modified letheen agar was used for the viable bacterial cell count test and the fungal count test was proceeded by using potato dextrose agar containing the antibiotic substance. For the viable bacterial cell count test, 1 mL of the test solution was put into a petri dish with a diameter of 9–10 cm. Then 15 mL of sterilized culture medium cooled to 45°C was added and mixed thoroughly before incubating at least 2 for each specimen for 48 hours at the temperature range of 30–35°C. At this time, the total viable bacterial cell count was measured by means of the maximum number of colonies. The fungal cell count test was conducted in the same method by using a culture medium for the fungal cell count test. Total fungal cell count was measured by means of the No. of fungal colonies after having been incubated for 5 days at the temperature range of 20–25°C.

3. Results and Discussions

3.1 Starch gelatinization without a catalyst

The viscosity of the adhesive prepared by varying the temperature, reaction time, and amount of alkali using NaOCl as an oxidizing agent increased over time. The reaction was not completely finished completed even under sufficient oxidation time, oxidation conditions, and Prezelatinized Starch conditions, and thus the viscosity continued to increase for 14 days.

Their maximum adhesive strength also did not exceed 50.0 kgf/cm², so it seemed difficult to manufacture a starch adhesive by proceeding with only oxidation and pregelatinized.

3.2 Starch adhesive using resorcinol as a denaturant

When resorsinol was used as a modifier and TBP, Borax, and Na₂CO₃ AFS were used as catalysts, the adhesive showed relatively high adhesive strength (maximum adhesive strength 241.0 kgf/cm²), but its viscosity increased and color change occurred over time.

In the case of the TBP catalyst, the adhesive maintained an adhesive strength of about 104.0 kgf/cm², but layer separation and color change were severe, and in the case of borax, the maximum adhesive strength was 163.0 kgf/cm², but the viscosity was severely increased. In the case of using Na₂CO₃ and AFS, the color change, layer separation, viscosity change, and low adhesion strength of the adhesive were followed.

These adhesives did not increase the adhesion strength and stability even when they changed the concentration of starch, the type of oxidizing agent, the oxidation time and the oxidation temperature, the reaction time, and the reaction temperature. Rather, when a 10% starch solution and 10% resinsinol were used without using a catalyst, the adhesion strength of 200.0 kgf/cm² was shown, but this also occurred within 14 days.

3.3 Starch adhesive using epichlorohydrin without an oxidant

In the case of an adhesive that reacted with urea and epichlorohydrin under alkali conditions, the adhesion strength was 100 kgf/cm², but the change of viscosity and phase separation were observed after 2 weeks. From this result, it seems that a reaction terminator should be required in the manufacture of this adhesives.

3.4 Gelatinized starch adhesive with an oxidant and a catalyst

As a result of using a 25% to 50% aqueous starch solution, the result of the 35% aqueous solution

was the best, indicating a maximum adhesion strength of 257.0 kgf/cm². Although there was no change in viscosity after manufacturing, the manufacturing method was adjusted for convenience of use. STS, thiourea, and NiSO₄ were used as catalysts and stabilizers.

The adhesive strength of the adhesive prepared by adding 3.0 g of a 1% sodium thiosulfate solution to this and stirring for 15 minutes was 257.0 kgf/cm². Even when the pH was changed to 5.0, the maximum adhesive strength of 198.0 kgf/cm² was maintained and the adhesive state was stable for 60 days or more. The maximum adhesive force was 265.0 kgf/cm² if 50% of the aqueous starch solution was used, but the viscosity was very high and the usability was degraded. From these results, it was found that the optimal concentration of the starch aqueous solution was a 35% starch aqueous solution with an adhesive strength of 257.0 kgf/cm² (Fig. 1).

When the starch aqueous solution was adjusted to a pH of 10.0 to 11.0 using a 2.0% NaOH aqueous solution, the stability of the final product was shown. At a pH of 9.0 or lower, the oxidation progression was late, so oxidation proceeded only after 40 minutes or more. It could be seen that main-

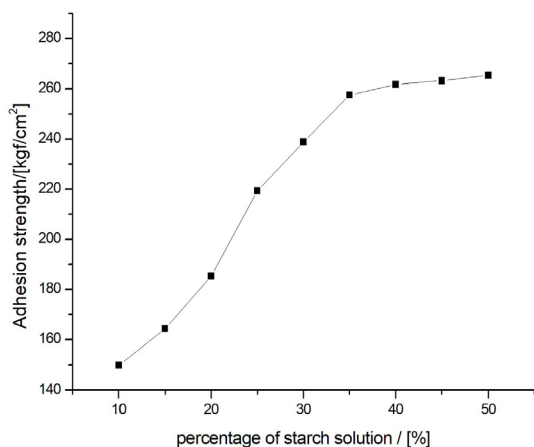


Fig. 1. Change in adhesion strength for timber according to the concentration of starch aqueous solution.

taining the pH of 10.0 to 11.0 during the oxidation process was essential because the color change of the aqueous starch solution may not occur at low temperatures.

When the pH was 12.5 or higher, Pregelatinized proceeded in advance, resulting in a continuous increase in the viscosity of the adhesive or a result that the solution was not uniform.

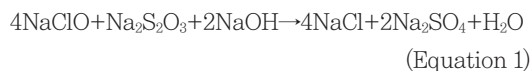
The adhesives using catalysts of TBP, borax, Na₂CO₃, and AFS showed low adhesive strength overall. It was assumed that the catalyst could not contribute to the polymerization of starch because it did not reduce adsorption, molecular movement and expansion of starch by moisture. In the case of catalysts, the use of TBP, Borax, and Na₂CO₃ AFS was not appropriate, and the use of NiSO₄ showed the best results. When 0.1 g or less of NiSO₄ was added, it was difficult to proceed with the reaction, and when 1.5 g or more was added, the color was changed. From the viewpoint of the eco-friendly adhesive, the most appropriate amount of NiSO₄ used was 0.20 g and the reaction time was 15 minutes.

The use of 20.0 g of NaOCl as an oxidizing agent seemed most appropriate than H₂O₂. When 25.0 g or more of NaOCl was added, oxidation proceeded excessively and the viscosity and adhesion strength of the final product decreased. For oxidation time, excellent results were shown at 45 minutes or more. In this reaction, when NaOCl, an oxidizing agent, reacts simultaneously with NiSO₄, a reaction initiator, polymerization of starch as the most appropriate adhesive proceeds. For this, the alkali conditions must be maintained. Under this alkaline condition, expansion of starch by moisture in the aqueous solution was suppressed and polymerization proceeds simultaneously. Under alkali conditions, the NiSO₄ catalyst lowered the active energy barrier to prevent the gelatinization of starch at low temperatures and proceeded with the reaction.

When 3.0 g or more of 1.0% STS aqueous solution was added, the reaction was terminated. When

2.50 g or less was added, the viscosity of the adhesive was changed in the final product. The viscosity of the produced adhesive decreases due to an increase in the amount of solution added during neutralization, and thus the concentration of the adhesive was diluted and the adhesive strength was only shown to decrease.

The produced final adhesive exhibited an adhesive strength of 213 kgf/cm² at a pH of 7.5 which could be seen as the adhesive strength of the final adhesive (refer to Fig. 2). The color change problem pointed out as the problem of NiSO₄ was solved by exhibiting a bleaching effect in the process of terminating the polymer reaction with the addition of thiosulfate. The reaction of starch and sodium thiosulfate under the NiSO₄ catalyst was similar to the iodine reaction of starch. In the process of terminating the reaction, thiosulfate reduces hypochlorite and bleaches the starch adhesive (see Equation 1).



Since the reaction was performed at a low tem-

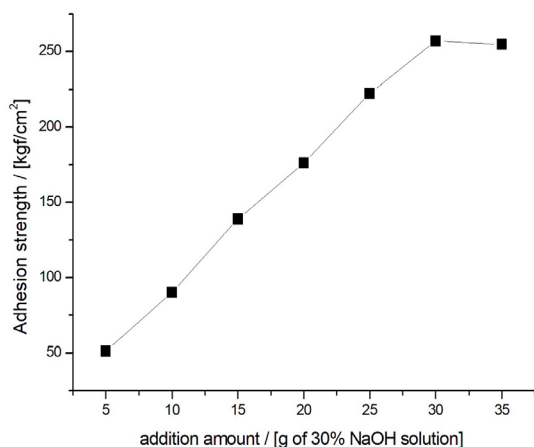


Fig. 2. Change in adhesion strength for timber according to addition of gelatinization agent.

perature without gelatinization of starch due to pyrolysis, very high concentration of starch participates in the reaction, and thus it might be seen that a relatively long chain polymer was generated. That is, the high adhesion strength of this adhesive can be seen as the reason for the polymerization of many starch at low temperature.

3.5 Reversibility, harmfulness, antibacterial property

As the results of the reversibility test, a gelatinized starch adhesive containing an oxidant and a catalyst can be 100% removed, thereby confirming its excellent reversibility. As the results of the harmful material property experiment, it was confirmed that TVOC and HCHO were not detected in the gelatinized starch adhesive containing the oxidant and the catalyst.

Moreover, the results of measurement of heavy metals, lead (Pb), cadmium (Cd), and chromium (Cr) were not detected. Based on these results, it was deemed that human harmlessness of adhesive has been secured and an optimized foundation as a bio-adhesive has been established. As the results of the measurement of total aerobic viable bacterial cell count of synthesized adhesive, the fungus was not cultured, and there was no mold development after more than 30 days.

4. Conclusions

In this study, the applicability and substitutability of corn starch adhesives manufactured to replace other starch adhesives and various synthetic adhesives used in manufacturing traditional and modern paper crafts in Korea were evaluated, and the following conclusions were obtained.

The final adhesion strength of this adhesive was found to be 213 kgf/cm². This adhesive was stable for more than 60 days at room temperature with

no physical changes including viscosity change, separation of physical phase and sedimentation, etc. Moreover, consistent adhesion strength was maintained. As such, it is deemed that there is no problem with its use as an adhesive.

Harmful substances such as TVOC, HCHO, and heavy metals were not detected, thereby equipping itself with a foundation as a bio-adhesive. Moreover, the preservative nature and antibacterial property of the adhesive were confirmed through a total aerobic viable bacterial cell count test. Accordingly, it is determined that applicability and preservation properties, which were the weaknesses of natural adhesives, could be improved.

This implies that the problem of supply and demand of the materials can be resolved to a certain extent and improvements can be made for the consistency in material properties of the natural adhesive, which generally differs whenever they are manufactured, for continuous use for the prescribed period of time.

Therefore, it is deemed that starch-based adhesive manufactured with improved performances and compositions can be used easily by users and applied to the production and preservation of traditional paper crafts by maintaining the aspects of traditional materials by providing the possibility as a substitute material for natural adhesive through the improvement of its functionality along with an endowment of the advantage of not containing harmful substances.

Acknowledgement

This paper was researched by the intramural research support project 2022 of Hanseo University.

Literature Cited

1. Vnučec, D., Goršek, A., Kutnar, A. and Mikuljan, M., Thermal modification of soy proteins in the vacuum chamber and wood adhesion, *Wood Science and Technology* 49:225–239 (2015).
2. Ciannamea, E. M., Stefani, P. M. and Ruseckaitė, R. A., Medium-density particleboards from modified rice husks and soybean protein concentrate-based adhesives, *Bioresource Technology* 101:818–825 (2010).
3. Kim, S., Environment-friendly adhesives for surface bonding of wood based flooring using natural tannin to reduce formaldehyde and TVOC emission, *Bioresource Technology* 100: 744–748 (2009).
4. Pizzi, A., Recent developments in eco-efficient bio-based adhesives for wood bonding: opportunities and issues, *Journal of Adhesion Science and Technology* 20:829–846 (2006).
5. Navarrete, P., Pizzi, A., Bertaud, F. and Rigolet, S., Condensed tannin reactivity inhibition by internal rearrangements: detection by CP-MAS ¹³C NMR, *Maderas* 13:59–68 (2011).
6. Conner, A. H., Lorenz, L. F. and River, B. H., Carbohydrate modified phenol formaldehyde resins formulated at neutral conditions, *ACS Symposium Series* 385:355–369 (1989).
7. Kennedy, H. M. and Fischer, A. C., Chap. XX—starch use in foods, In *Starch: Chemistry and Technology*, 2nd Edition, Whistler, R. L., Be Miller, J. N., and Paschall, E. F., (ed.), Academic Press, Inc., New York (1983).
8. Wang, Z. J., Li, Z. F., Gu, Z. B., Hong, Y. and Cheng, L., Preparation, characterization and properties of starch-based wood adhesive, *Carbohydrate Polymers* 88:699–706 (2012).
9. Athawale, V. D. and Lele, V., Thermal studies on granular maize starch and its graft copolymers with vinyl monomers, *Starch (Starke)*

- 52:205–213 (2000).
10. Goni, I., Gurruchaga, M., Valero, M. and Guzman, G. M., Graft polymerization of acrylic monomers onto starch fractions. i, effect of reaction time on grafting methyl methacrylate onto amylose, *Journal of Polymer Science Part A: Polymer Chemistry* 21:2573–2580 (1983).
 11. Gurruchaga, M., Goni, I., Valero, M. and Guzman, G. M., Graft copolymerization of hydroxylic methacrylates and ethyl acrylate onto amylopectin, *Polymer* 33:2860–2862 (1992).
 12. Kaewtatip, K. and Tanrattanakul, V., Preparation of cassava starch grafted with polystyrene by suspension polymerization, *Carbohydrate Polymers* 73:647–655 (2008).
 13. Kim, S. and Kim, H. J., Thermal stability and viscoelastic properties of MF/PVAc hybrid resins on the adhesion for engineered flooring in under heating system; *ONDOL, Thermochimica Acta* 444:134–140 (2006).
 14. Meshram, M. W., Patil, V. V., Mhaske, S. T. and Thorat, B. N., Graft copolymers of starch and its application in textiles, *Carbohydrate Polymers* 75:71–78 (2009).
 15. Dimas, B. J., Osemeahon, S. A., Maitera, O. N. and Hotton, A. J., Influence of starch addition on properties of urea formaldehyde/starch copolymer blends for application as a binder in the coating industry, *Journal of Environmental Chemistry and Ecotoxicology* 5:181–189 (2013).
 16. Xu, Z., -Z., Shuang, H. and Tu, Y., -Q., Esterified-starch modified urea formaldehyde adhesive, *CN 102898987 A* 12, 30 January (2013).
 17. Zhu, L., Preparation method for high-strength water-resistant starch adhesive for corrugated paperboards, *CN 104119816 A* 14, 29 October (2014).
 18. Ni, K., Oxidized starch modified urea-formaldehyde resin adhesive, *CN 103911103 A* 15, 9 July (2014).
 19. Dunkey, M., Urea-formaldehyde (UF) adhesive resins for Wood, *International Journal of Adhesion and Adhesives* 18:95–107 (1997).
 20. Bloembergen, S., Kappen, F. and Beelen, B., Environmentally friendly biopolymer adhesives and applications based thereon, *US 6921430 B2*, 26 July (2005).
 21. Kaboorani, A. and Riedl, B., Effects of adding nano-clay on performance of polyvinyl acetate (PVA) as a wood adhesive, *Composites, A: Applied Science and Manufacturing* 42:1031–1039 (2011).
 22. Petrie, E. M., Biobased components in hot melt adhesive formulation, *SpecialChem*, 11 July (2012).
 23. Zhang, Z., Macquarrie, D. J., Clark, J. H. and Matharu, A. S., Chemical modification of starch and the application of expanded starch and its esters in hot melt adhesive, *RSC Advances* 4: 41947–41955 (2014).
 24. Billmers, R. J., Paul, C. W., Hatfield, S. F. and Kauffman, T. F., Starch ester based hot melt adhesive, *US Patent*, 5360845, 1 November (1994).
 25. Olsson, E., Effects of citric acid on starch-based barrier coatings, *Karlstad University, Sweden* (2013).
 26. Sarwono, A., Man, Z. B. and Bustam, M. A., Effect of urea and borate on water uptake of urea modified tapioca starch film, *Journal of Applied Science and Agriculture* 9:95–101 (2014).
 27. Luo, P., Liu, Y., Zhao, X., Song, P., Tan, N. and Sun, M., Development of a starch adhesive for corrugated board under room temperature, *Advanced Materials Research* 179–180:812–817 (2011).
 28. Onusseit, H., Starch in industrial adhesives: new developments, *Industrial Crops and*

- Products 1:141–146 (1992).
29. Conner, A. H., Carbohydrates in adhesives: introduction and historical perspective, ACS Symposium Series 385:271–288 (1998).
30. Li, Z., Wang, J., Chong, L., Gu, Z., Hong, Y. and Kowalczyk, A., Improving the performance of starch-based wood adhesive by using sodium dodecyl sulphate, Carbohydrate Polymers 99:579–583 (2014).