Open Journal of Organic Polymer Materials, 2022, 12, 17-30
https://www.scirp.org/journal/ojopm
ISSN Online: 2164-5752
ISSN Print: 2164-5736

Starch Grafted Water Resistant Polyvinyl Acetate-Based Wood Adhesive: A Review

Ravindra Vilas Indubai Gadhave

Department of Polymer and Surface Engineering, Institute of Chemical Technology, Mumbai, India
Email: ravi.gadhave3@gmail.com

How to cite this paper: Gadhave, R.V.I. (2022) Starch Grafted Water Resistant Polyvinyl Acetate-Based Wood Adhesive: A Review. *Open Journal of Organic Polymer Materials*, **12**, 17-30.
https://doi.org/10.4236/ojopm.2022.122002

Received: February 16, 2022
Accepted: April 27, 2022
Published: April 30, 2022

Abstract

Global energy issues and the reliance on hydrocarbon resources have resulted in the reduction of petroleum sources, and the focus of the chemical industries has shifted to substitute raw material sources. The major raw materials used in wood adhesives, such as hydrocarbons like polyvinyl acetate, would be gradually replaced by renewable natural polymers. Currently, polyvinyl alcohol has the limitation of petroleum origin, which is non-economical and it will be replaced by biopolymers. Conventionally available wood adhesive emulsions are colloid-like polyvinyl alcohol stabilized. Starch, being a naturally available polymer, has gained interest from researchers for replacing polyvinyl alcohol as a stabilizer. New research on sustainable, economical, biodegradable, renewable, and environmentally friendly starch grafted polyvinyl acetate emulsion that was synthesized by the graft polymerization of vinyl acetate monomer onto starch. However, starch grafted polyvinyl acetate emulsion-based adhesive's properties, such as poor water resistance, weak adhesion, delayed drying rate and delayed setting speed, have resulted in limitations in its application as a wood adhesive. A detailed review of starch grafting on vinyl acetate and comonomers like acrylamides, and acrylic acid, and the addition of nano-fillers to enhance the water resistance and performance properties of sustainable adhesives has been explained.

Keywords

Starch, Water Resistance, Grafting, Polyvinyl Acetate, N-Methylol Acrylamide

1. Introduction

Recently, the emulsion polymerization technique has attracted adhesive industries and the adhesive market as the demand for eco-friendly and solvent-less adhesives increased, which has the advantage of the absence of volatile organic compounds (VOC). In the carpentry and furniture segment, Polyvinyl acetate (PVAc) emulsion adhesives, which are also called white adhesives, are thermoplastics softening when the temperature is increased to a glass transition temperature and hardening again when cooled. PVAc adhesive solidifies by evaporation, absorption or penetration of water by the gluing material [1] [2]. Polyvinyl alcohol (PVA) which acts as a protective colloid for PVAc has a different degree of hydrolysis (DH) and polymer chain length, good rheological properties with high wet tack, and due to hydroxyl group, its affinity to porous substrates made them applicable in carpentry applications. Emulsion polymerization of Vinyl acetate (VAc) to PVAc needs PVA for stability and to enhance the thermos-mechanical properties of the prepared adhesive as shown in **Figure 1**.

In partially hydrolyzed PVA (DH = 88% - 90%), reduction in crystallinity due to the presence of acetate side groups makes it soluble in cold water [4] [5]. Modifications in PVA are done to further improve the properties of PVAc emulsion-based adhesives [6]. The white adhesive is used for assembly applications in carpentry, high-pressure lamination, wood veneer, and edge bonding as a furniture adhesive [7].

2. Need of Starch in PVAc Emulsion-Based Adhesives

Due to the increasing global energy crisis and shortage of petroleum sources, chemical industry' focus has moved their approach to new raw material resources. The main focus of raw materials in wood adhesives, such as hydrocarbon and natural gas [8] [9], would be gradually substituted by sustainable natural polymers [10] that are inexpensive [11] [12] [13]. The key raw materials of PVAc adhesive depended on non-renewable resources such as hydrocarbon and

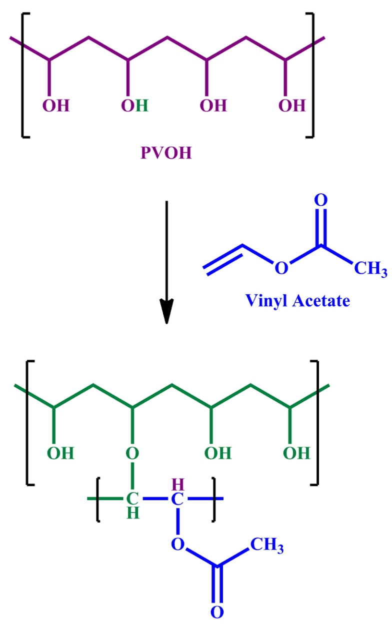

Figure 1. Vinyl acetate grafting on polyvinyl alcohol [3].

natural gas. With the aggravated global energy crisis, the key raw material used in wood adhesives is being replaced by sustainable biopolymers, such as cellulose, protein, tannin and starch [14]-[22].

Starch is a relatively inexpensive, sustainable, and renewable material from abundant plants. It is easy to be processed and has been used as adhesives, binders and pastes in various applications, but its bonding capacity is not strong enough to bond the woods [23] [24] [25]. Starch is a polysaccharide, basically polymers of the six-carbon D-glucose. Starch consists of D-glucose units, which are referred to as homoglycan or glucopyranose, and two major bio-macromolecules, amylose (strength chain) and amylopectin (branched chain) [26]-[48]. Extensive research has been carried out on improving the performance properties, especially water resistance of starch-based adhesives. In starch-based wood adhesive, many new research approaches have come forward for effective use of starch in wood adhesive and giving a comparable performance to synthetic adhesives [49]. Starch is one of the important materials in wood adhesive formulation influencing the polymerization mechanism with VAc and the performance of the end product [50]. This review paper aims to showcase the application of starch as stabilizing media for PVAc wood adhesive with improved water resistance. The starch-based adhesives are made with the focus on starch grafting on various comonomers for improving water resistance and performance properties.

3. Starch Grafted Polyvinyl Acetate Emulsions

Adhesives made of conventional materials when compared with natural polymer-based wood adhesives are usually too weak for practical use [51], so the structural strength and other performance properties of starch-based adhesive should be strengthened to achieve high-performance wood adhesive. Grafting was an important technique for modifying the physical, chemical and mechanical properties of polymers. The graft polymerization of synthetic polymers onto a natural polymer like starch backbone was one of the best ways of improving the mechanical properties of starch. There were many reports on the synthesis, characterization, and performance properties of starch graft copolymers [52]-[57]. Graft polymerization of VAc on starch was done to prepare wood adhesive which can be used and give excellent bonding performance [58] [59]. The improved properties were attributed to the modified structure of the graft-copolymerized starch-based adhesive [60] [61]. Renewable starch-based wood adhesive that could be used for wood bonding was prepared by the grafting VAc onto starch using ammonium persulfate as the initiator [62] [63]. Graft polymerization of VAc monomer on starch as shown in **Figure 2** and its usage in wood adhesives have gained interest among scientists and industries [64] [65].

Urea was often used in the starch system to bring about considerable rheology changes [67] [68] [69] [70]. Addition of urea changed the gelatinization and retrogradation characteristics of starch [71]. In aqueous suspensions, urea helps starch gelatinization and solubilization [72] [73] [74] [75]. Furthermore, urea

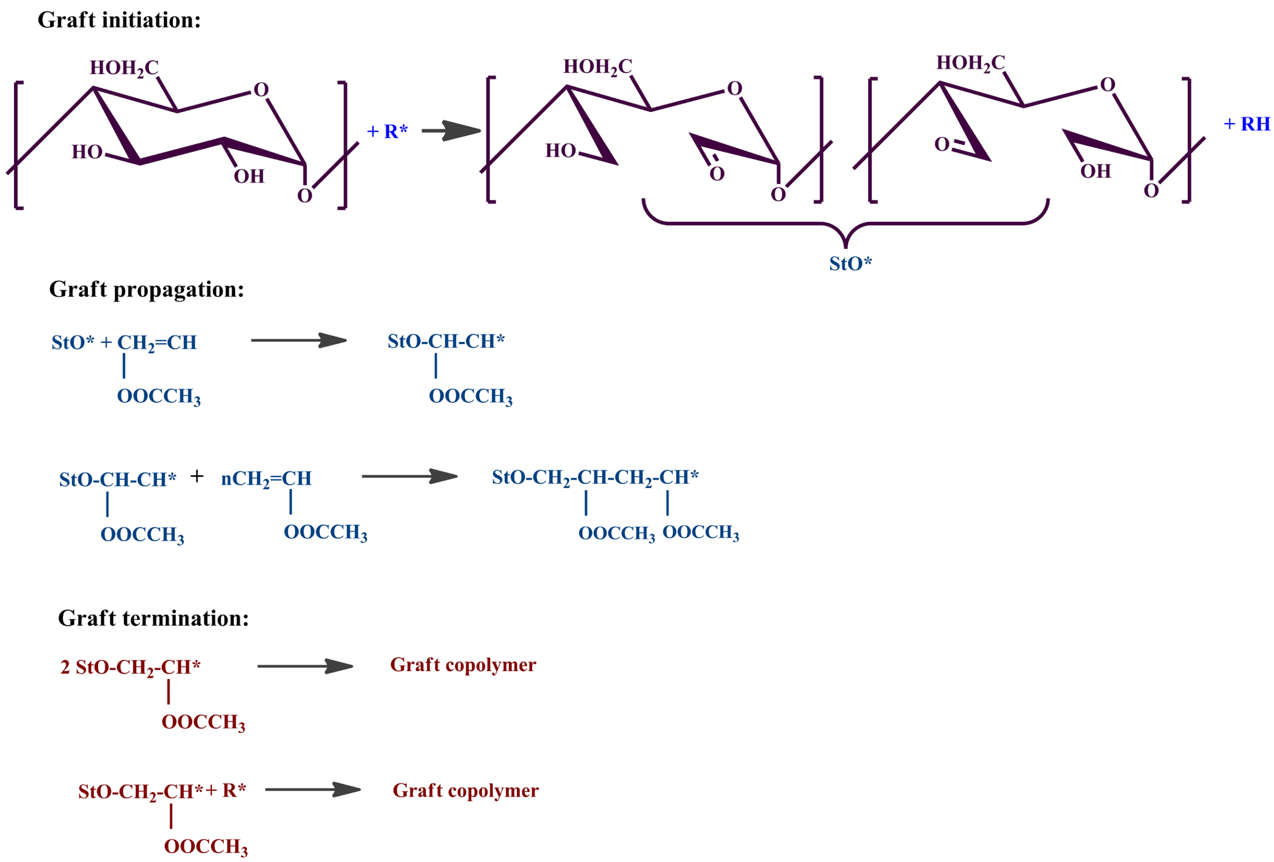

Figure 2. Vinyl acetate monomer grafting on starch [66].

could also effectively reduce the retrogradation process of starch [76] [77] [78]. Therefore, urea could likely be used to improve the freeze-thaw stability of starch grafted emulsion [79]. In some studies, before graft polymerization of VAc onto starch, sodium dodecyl sulfate (SDS) was added to improve the performance of the starch-stabilized wood adhesive. Compared with the starch-stabilized wood adhesive without SDS, both the mobility and storage stability of the adhesives were significantly enhanced by the presence of SDS [80] [81] [82]. The graft copolymerization of mixed grafting monomers VAc and butyl acrylate (BA) onto grafting skeleton of corn starch had been studied using ammonium persulfate as an initiator. Starch-stabilized adhesive prepared in emulsion synthesis have green material, superior property, and low cost [83]. According to some studies, designed and demonstrated the use of two co-monomers VAc and BA for promoting the graft copolymerization while improving the bonding performance of wood adhesive. The results showed that the properties of wood adhesive could improve dramatically by using two co-monomers [84]. For improving the performance of a cornstarch-based biobased adhesive, corn starch graft glycidyl methacrylate adhesive was prepared [85]. Graft copolymerization, which has improved the structural, physical, chemical and mechanical properties of adhesive, is considered to be one of the most effective methods employed to modify many different properties of starch-based polymers. Improvements in thermal properties along with bonding strength were shown by graft polymerization of VAc on starch [86].

4. Water Resistance Starch-Based Emulsion

Currently, starch has been gaining increasing attention in chemical industry, due to its being abundant, inexpensive, renewable, sustainable and fully biodegradable. Consequently, it is a trend to produce a wood adhesive using starch grafted emulsion as base materials. However, starch grafted adhesive properties, such as lacking water resistance, weak bonding and delayed drying rate, are resulted in restrictions in its various application [87]. To improve the water resistance and performance of adhesive, some agents were used to enhance the adhesive strength. Addition of nanoparticles in the wood adhesive is one of the most effective ways to enhance the performance of starch-stabilized wood adhesive. Inorganic nanoparticles have unique characteristics to improve the performance of adhesive, such as small size, high surface energy and unsaturated chemical bonds on the surface. In the past year, nano-silica (SiO_2) and montmorillonite (MMT) were used to enhance the properties of adhesives [88] [89].

The wood adhesive showed significant improvement in the water resistant and bonding performance to some degree. In previous research, it is reported that the polymers with low content of nano-titanium dioxide (TiO_2) can obtain barrier, thermal and mechanical properties, showing the promising application of nano-TiO_2 in nano-composite adhesives [90]. As a kind of inorganic material, nano-TiO_2 can be dispersed into the starch grafted emulsions at a nanometric level to improve the physical and mechanical properties of wood adhesives [91] [92].

A series of starch graft polymers were prepared from commercial starch and vinyl monomers and were evaluated as adhesives. Adhesive strength of starch graft polyacrylamide copolymers containing little amount of polyacrylamide was considerably superior water resistance to the commercial starches as paper coating adhesives [93]. N-methylol acrylamide (NMA) is a water-soluble functional monomer with a condensed hydroxymethyl group. A number of studies on the emulsion polymerization of NMA with vinyl acetate or acrylate monomers have been reported [94] [95] [96]. There are also reports of NMA being used to make hydrogels. The synthesis was conducted by grafting copolymerization of VAc monomer onto corn starch and crosslinking polymerization with NMA. Compared with the traditional starch-stabilized wood adhesive, the water resistance of starch-stabilized adhesive with NMA was greatly improved [97] [98] [99]. The preparation method for water resistant adhesive comprises oxidation of corn starch by the use of sodium hypochlorite followed by co-polymerizing the oxidized corn starch with N-hydroxymethyl acrylamide and acrylic acid (AA). According to the preparation method, the NMA was adopted to replace the conventional acrylamide to copolymerize with the starch; the AA was added to provide protons for being beneficial for the starch to form the copolymer; the reaction was stable; the starch grafting effect was efficient; the adhesive prepared by the preparation method was free from formaldehyde, was safer, and was good in bonding performance, and the problems such as poor water resistance of common starch adhesive were solved [100]. In one embodiment of the invention, the cross-linking monomer used NMA, N-methoxyl group Methacrylamide, N-isopropoxymethyl acrylamide, N-butoxymethyl acrylamide, N-hydroxyethyl acrylamide etc., which had copolymerized and condensed at acidic pH [101]. Synthesizing of described starch-VAc cross connect graft copolymer with starch was sustainable raw material, with N,N'-methylene- bisacrylamide was a comonomer, carried out polymerization reaction and synthetic starch-VAc cross-connect graft copolymer obtained [101] [102] [103] [104].

5. Conclusions

Conventionally, PVA's were used as a colloidal stabilizer for PVAc dispersion, but starch, which is a relatively cheaper and sustainable product obtained from large quantities of plants, is of easy processibility and can be used as a colloidal stabilizing media for PVAc emulsion. But starch adhesive exhibited poor bonding strength and water resistance preventing its use in practical applications. Urea and SDS were added to the starch so that starch could easily be grafted on VAc and other monomers to produce a graft-copolymerized emulsion. Also, nanoparticles like MMT, SiO_2 and TiO_2 were used to improve the mechanical and barrier properties of starch-stabilized wood adhesives. The properties of wood adhesive could be improved dramatically by using two co-monomers VAc and BA during the graft copolymerization reaction.

Therefore, in order to improve the water resistance and performance properties of starch-stabilized PVAc adhesive, starch grafts on vinyl acetate and comonomers like acrylamide derivatives; AA and the addition of nano-fillers improve the water resistance of sustainable adhesives. Taken together, the graft modification of starch with acrylamide derivatives, and AA and acrylic monomers can be an encouraging way to produce starch-stabilized wood adhesive with improving water resistance and good performance for wood adhesive.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

References

[1] Skeist, I., Ed. (1990) Handbook of Adhesives. Springer, New York. https://doi.org/10.1007/978-1-4613-0671-9

[2] Gadhave, R.V.I. and Dhawale, P.V. (2022) State of Research and Trends in the Development of Polyvinyl Acetate-Based Wood Adhesive. *Open Journal of Polymer Chemistry*, **12**, 13-42. https://doi.org/10.4236/ojpchem.2022.121002

[3] Gonzalez, G.S.M., Dimonie, V.L., Sudol, E.D., Yue, H.J., Klein, A. and El-Aasser, M. S. (1996) Characterization of Poly(Vinyl Alcohol) during the Emulsion Polymeriza-

tion of Vinyl Acetate Using Poly(Vinyl Alcohol) as Emulsifier. *Journal of Polymer Science Part A*: *Polymer Chemistry*, **34**, 849-862.
https://doi.org/10.1002/(SICI)1099-0518(19960415)34:5<849::AID-POLA14>3.0.CO;2-I

[4] Nakamae, M., Yuki, K., Sato, T. and Maruyama, H. (1999) Preparation of Polymer Emulsions Using a Poly(Vinyl Alcohol) as Protective Colloid. *Colloids and Surfaces A*: *Physicochemical and Engineering Aspects*, **153**, 367-372.
https://doi.org/10.1016/S0927-7757(98)00458-0

[5] Qiao, L., Coveny, P.K. and Easteal, A.J. (2002) Modifications of Poly(Vinyl Alcohol) for Use in Poly(Vinyl Acetate) Emulsion Wood Adhesives. *Pigment & Resin Technology*, **31**, 88-95. https://doi.org/10.1108/03699420210420378

[6] Mori, A., Kitayama, T., Takatani, M. and Okamoto, T. (2004) A Honeymoon-Type Adhesive for Wood Products Based on Acetoacetylated Poly(Vinyl Alcohol) and Diamines: Effect of Diamines and Degree of Acetoacetylation. *Journal of Applied Polymer Science*, **91**, 2966-2972. https://doi.org/10.1002/app.13491

[7] D'Amico, S., Hrabalova, M., Müller, U. and Berghofer, E. (2010) Bonding of Spruce Wood with Wheat Flour Adhesive—Effect of Press Temperature on the Adhesive Bond Strength. *Industrial Crops and Products*, **31**, 255-260.
https://doi.org/10.1016/j.indcrop.2009.11.001

[8] Imam, S.H., Gordon, S.H., Mao, L. and Chen, L. (2001) Environmentally Friendly Wood Adhesive from a Renewable Plant Polymer: Characteristics and Optimization. *Polymer Degradation and Stability*, **73**, 529-533.
https://doi.org/10.1016/S0141-3910(01)00114-8

[9] Zhu, W., Zheng, X., Shi, J. and Wang, Y. (2021) Grafted Starch Foam Stabilizer ESt-g-NAA for High-Temperature Resistant CGA Drilling Fluid via Inverse Emulsion Polymerization. *Starch-Stärke*, **73**, Article ID: 2000240.
https://doi.org/10.1002/star.202000240

[10] Gadhave, R.V., Mahanwar, R.A. and Gadekar, P.T. (2017) Starch-Based Adhesives for Wood/Wood Composite Bonding: Review. *Open Journal of Polymer Chemistry*, **7**, 19-32. https://doi.org/10.4236/ojpchem.2017.72002

[11] Ruka, D.R., Sangwan, P., Garvey, C.J., Simon, G.P. and Dean, K.M. (2015) Biodegradability of Poly-3-Hydroxybutyrate/Bacterial Cellulose Composites under Aerobic Conditions, Measured via Evolution of Carbon Dioxide and Spectroscopic and Diffraction Methods. *Environmental Science & Technology*, **49**, 9979-9986.
https://doi.org/10.1021/es5044485

[12] Duchemin, B., Le Corre, D., Leray, N., *et al.* (2016) All-Cellulose Composites Based on Microfibrillated Cellulose and Filter Paper via a NaOH-Urea Solvent System. *Cellulose*, **23**, 593-609. https://doi.org/10.1007/s10570-015-0835-4

[13] Arolkar, G.A., Salgo, M.J., Kelkar-Mane, V. and Deshmukh, R.R. (2015) The Study of Air-Plasma Treatment on Corn Starch/Poly(ε-Caprolactone) Films. *Polymer Degradation and Stability*, **120**, 262-272.
https://doi.org/10.1016/j.polymdegradstab.2015.07.016

[14] Marinich, J.A., Ferrero, C. and Jiménez-Castellanos, M.R. (2012) Graft Copolymers of ethyl Methacrylate on Waxy Maize Starch Derivatives as Novel Excipients for Matrix Tablets: Drug Release and Fronts Movement Kinetics. *European Journal of Pharmaceutics and Biopharmaceutics*, **80**, 674-681.
https://doi.org/10.1016/j.ejpb.2011.12.005

[15] Zhang, J., Kasuya, K., Takemura, A., Isogai, A. and Iwata, T. (2013) Properties and Enzymatic Degradation of Poly(Acrylic Acid) Grafted Polyhydroxyalkanoate Films

by Plasma-Initiated Polymerization. *Polymer Degradation and Stability*, **98**, 1458-1464. https://doi.org/10.1016/j.polymdegradstab.2013.04.010

[16] Lu, S., Duan, M. and Lin, S. (2003) Synthesis of Superabsorbent Starch-Graft-Poly(Potassium Acrylate-co-Acrylamide) and Its Properties. *Journal of Applied Polymer Science*, **88**, 1536-1542. https://doi.org/10.1002/app.12025

[17] Grøndahl, L., Chandler-Temple, A. and Trau, M. (2005) Polymeric Grafting of Acrylic Acid onto Poly(3-Hydroxybutyrate-co-3-Hydroxyvalerate): Surface Functionalization for Tissue Engineering Applications. *Biomacromolecules*, **6**, 2197-2203. https://doi.org/10.1021/bm050127m

[18] Li, K., Geng, X., Simonsen, J. and Karchesy, J. (2004) Novel Wood Adhesives from Condensed Tannins and Polyethylenimine. *International Journal of Adhesion and Adhesives*, **24**, 327-333. https://doi.org/10.1016/j.ijadhadh.2003.11.004

[19] Li, Z., Wang, J., Cheng, L., Gu, Z., Hong, Y. and Kowalczyk, A. (2014) Improving the Performance of Starch-Based Wood Adhesive by Using Sodium Dodecyl Sulfate. *Carbohydrate Polymers*, **99**, 579-583. https://doi.org/10.1016/j.carbpol.2013.08.062

[20] Parvathy, P.C. and Jyothi, A.N. (2011) Synthesis, Characterization and Swelling Behaviour of Superabsorbent Polymers from Cassava Starch-Graft-Poly(Acrylamide). *Starch-Stärke*, **64**, 207-218. https://doi.org/10.1002/star.201100077

[21] Xiao, C., Lu, D., Xu, S. and Huang, L. (2011) Tunable Synthesis of Starch-Poly-(Vinyl Acetate) Bioconjugate. *Starch-Stärke*, **63**, 209-216. https://doi.org/10.1002/star.201000128

[22] Gadhave, R.V., Mahanwar, P.A. and Gadekar, P.T. (2018) Starch Stabilized Polyvinyl Acetate Emulsion: Review. *Polymers from Renewable Resources*, **9**, 75-84. https://doi.org/10.1177/204124791800900203

[23] Kim, S. and Kim, H.-J. (2006) Study of Miscibility of Melamine-Formaldehyde Resin and Poly(Vinyl Acetate) Blends for Use as Adhesives in Engineered Flooring. *Journal of Adhesion Science and Technology*, **20**, 209-219. https://doi.org/10.1163/156856106775897739

[24] Athawale, V.D. and Rathi, S.C. (1997) Role and Relevance of Polarity and Solubility of Vinyl Monomers in Graft Polymerization onto Starch. *Reactive and Functional Polymers*, **34**, 11-17. https://doi.org/10.1016/S1381-5148(97)00016-3

[25] Zhang, Z., Chen, P., Du, X., Xue, Z., Chen, S. and Yang, B. (2014) Effects of Amylose Content on Property and Microstructure of Starch-Graft-Sodium Acrylate Copolymers. *Carbohydrate Polymers*, **102**, 453-459. https://doi.org/10.1016/j.carbpol.2013.11.027

[26] Buléon, A., Colonna, P., Planchot, V. and Ball, S. (1998) Starch Granules: Structure and Biosynthesis. *International Journal of Biological Macromolecules*, **23**, 85-112. https://doi.org/10.1016/S0141-8130(98)00040-3

[27] Biliaderis, C.G. (2010) ChemInform Abstract: Structures and Phase Transitions of Starch Polymers. *ChemInform*, **29**. https://doi.org/10.1002/chin.199847350

[28] Mua, J.P. and Jackson, D.S. (1997) Fine Structure of Corn Amylose and Amylopectin Fractions with Various Molecular Weights. *Journal of Agricultural and Food Chemistry*, **45**, 3840-3847. https://doi.org/10.1021/jf960877a

[29] Takeda, Y., Hizukuri, S., Takeda, C. and Suzuki, A. (1987) Structures of Branched Molecules of Amyloses of Various Origins, and Molar Fractions of Branched and Unbranched Molecules. *Carbohydrate Research*, **165**, 139-145. https://doi.org/10.1016/0008-6215(87)80089-7

[30] Li, A., Liu, R. and Wang, A. (2005) Preparation of Starch-Graft-Poly(Acrylamide)/

Attapulgite Superabsorbent Composite. *Journal of Applied Polymer Science*, **98**, 1351-1357. https://doi.org/10.1002/app.22302

[31] Yoshimoto, Y., Tashiro, J., Takenouchi, T. and Takeda, Y. (2000) Molecular Structure and Some Physicochemical Properties of High-Amylose Barley Starches. *Cereal Chemistry*, **77**, 279-285. https://doi.org/10.1094/CCHEM.2000.77.3.279

[32] Tanrattanakul, V. and Chumeka, W. (2010) Effect of Potassium Persulfate on Graft Copolymerization and Mechanical Properties of Cassava Starch/Natural Rubber Foams. *Journal of Applied Polymer Science*, **116**, 93-105. https://doi.org/10.1002/app.31514

[33] Yamak, H.B. and Yıldırım, H. (2013) Improvement of Film Properties of Vinyl Acetate Based Emulsion Polymers by Using Different Types of Maleic Acid Diesters. *Progress in Organic Coatings*, **76**, 1874-1878. https://doi.org/10.1016/j.porgcoat.2013.05.032

[34] Tester, R.F., Karkalas, J. and Qi, X. (2004) Starch—Composition, Fine Structure and Architecture. *Journal of Cereal Science*, **39**, 151-165. https://doi.org/10.1016/j.jcs.2003.12.001

[35] Tester, R.F. and Morrison, W.R. (1990) Swelling and Gelatinisation of Cereal Starches. I. Effects of Amylopectin, Amylose and Lipids. *Cereal Chemistry*, **67**, 551-557.

[36] Tester, R.F. and Morrison, W.R. (1990) Swelling and Gelatinisation of Cereal Starches. II. Waxy Rice Starches. *Cereal Chemistry*, **67**, 558-563.

[37] Tester, R.F. and Morrison, W.R. (1992) Swelling and Gelatinisation of Cereal Starches. III. Some Properties of Waxy and Normal Non-Waxy Barley Starches. *Cereal Chemistry*, **69**, 645-658.

[38] Takeda, Y., Shibahara, S. and Hanashiro, I. (2003) Examination of the Structure of Amylopectin Molecules by Fluorescent Labeling. *Carbohydrate Research*, **338**, 471-475. https://doi.org/10.1016/S0008-6215(02)00488-3

[39] Nuryawan, A., Ridwansyah, Alamsyah, E.M. and Widyorini, R. (2020) Starch Based Adhesives Made from Durian Seed through Dextrinization. *IOP Conference Series: Materials Science and Engineering*, **801**, Article ID: 012088. https://doi.org/10.1088/1757-899X/801/1/012088

[40] Gadhave, R.V., Mahanwar, P.A., Gadekar, P.T. and Kasbe, P.S. (2020) A Study on the Effect of Starch-Polyvinyl Alcohol Blends by Addition of Citric Acid and Boric Acid for Enhancement in Performance Properties of Polyvinyl Acetate-Based Wood Adhesive. *Journal of the Indian Academy of Wood Science*, **17**, 9-20. https://doi.org/10.1007/s13196-019-00249-6

[41] Zhang, N., Wang, S., Gibril, M.E. and Kong, F. (2020) The Copolymer of Polyvinyl Acetate Containing Lignin-Vinyl Acetate Monomer: Synthesis and Characterization. *European Polymer Journal*, **123**, Article ID: 109411. https://doi.org/10.1016/j.eurpolymj.2019.109411

[42] Dhawale, P.V., Vineeth, S.K., Gadhave, R.V. and Mahanwar, P.A. (2021) Cellulose Stabilized Polyvinyl Acetate Emulsion: Review. *Open Journal of Organic Polymer Materials*, **11**, 51-66. https://doi.org/10.4236/ojopm.2021.112002

[43] Lineback, D.L. (1986) Current Concepts of Starch Structure and Its Impact on Properties. *Journal of the Japanese Society of Starch Science*, **33**, 80-88. https://doi.org/10.5458/jag1972.33.80

[44] Yoshimoto, Y. (2002) Molecular Structure and Some Physicochemical Properties of Waxy and Low-Amylose Barley Starches. *Carbohydrate Polymers*, **47**, 159-167. https://doi.org/10.1016/S0144-8617(01)00184-9

[45] Rayas-Duarte, P., Robinson, S.F. and Freeman, T.P. (1995) *In Situ* Location of a Starch Granule Protein in Durum Wheat Endosperm by Immune-Cytochemistry. *Cereal Chemistry*, **72**, 269-274.

[46] Greenwell, P. and Schofield, J.D. (1986) A Starch Granule Protein Associated with Endosperm Softness in Wheat. *Cereal Chemistry*, **63**, 379-380.

[47] Cozzolino, D. and Degner, S. (2016) An Overview on the Role of Lipids and Fatty Acids in Barley Grain and Their Products during Beer Brewing. *Food Research International*, **81**, 114-121. https://doi.org/10.1016/j.foodres.2016.01.003

[48] Biliaderis, C.G., Page, C.M. and Maurice, T.J. (1986) On the Multiple Melting Transitions of Starch/Monoglyceride Systems. *Food Chemistry*, **22**, 279-295. https://doi.org/10.1016/0308-8146(86)90086-5

[49] Gadhave, R.V., Mahanwar, P.A. and Gadekar, P.T. (2019) Cross-Linking of Polyvinyl Alcohol/Starch Blends by Epoxy Silane for Improvement in Thermal and Mechanical Properties. *BioResources*, **14**, 3833-3843.

[50] Doane, S.W., *et al.* (2004), Starch Graft Copolymers and Method of Making and Using Starch Graft Copolymers for Agriculture. US20040068073.

[51] Bordes, P., Pollet, E. and Averous, L. (2009) Nano-Biocomposites: Biodegradable Polyester/Nanoclay Systems. *Progress in Polymer Science*, **34**, 125-155. https://doi.org/10.1016/j.progpolymsci.2008.10.002

[52] Athawale, V.D. and Lele, V. (2000) Thermal Studies on Granular Maize Starch and Its Graft Copolymers with Vinyl Monomers. *Starch-Stärke*, **52**, 205-213. https://doi.org/10.1002/1521-379X(200007)52:6/7<205::AID-STAR205>3.0.CO;2-3

[53] De Bruyn, H., Sprong, E., Gaborieau, M., Roper, J.A. and Gilbert, R.G. (2007) Starch-Graft-(Synthetic Copolymer) Latexes Initiated with Ce^{4+} and Stabilized by Amylopectin. *Journal of Polymer Science Part A*: *Polymer Chemistry*, **45**, 4185-4192. https://doi.org/10.1002/pola.22189

[54] Mani, R., Tang, J. and Bhattacharya, M. (1998) Synthesis and Characterization of Starch-Graft-Polycaprolactone as Compatibilizer for Starch/Polycaprolactone Blends. *Macromolecular Rapid Communications*, **19**, 283-286. https://doi.org/10.1002/(SICI)1521-3927(19980601)19:6<283::AID-MARC283>3.0.CO;2-C

[55] Ouchi, T., Kontani, T. and Ohya, Y. (2003) Modification of Polylactide upon Physical Properties by Solution-Cast Blends from Polylactide and Polylactide-Grafted Dextran. *Polymer*, **44**, 3927-3933. https://doi.org/10.1016/S0032-3861(03)00308-2

[56] Manzano, V.E., Kolender, A.A. and Varela, O. (2017) Synthesis and Applications of Carbohydrate-Based Polyurethanes. In: Goyanes, S. and D'Accorso, N., Eds., *Industrial Applications of Renewable Biomass Products*, Springer, Cham, 1-43. https://doi.org/10.1007/978-3-319-61288-1_1

[57] Sugahara, Y. and Ohta, T. (2001) Synthesis of Starch-Graft-Polyacrylonitrile Hydrolyzate and Its Characterization. *Journal of Applied Polymer Science*, **82**, 1437-1443. https://doi.org/10.1002/app.1981

[58] Wang, Z., Gu, Z., Li, Z., Hong, Y. and Cheng, L. (2013) Effects of Emulsifier on the Bonding Performance and Freeze-Thaw Stability of Starch-Based Wood Adhesive. *Cellulose*, **20**, 2583-2590. https://doi.org/10.1007/s10570-013-9984-5

[59] Meshram, M.W., Patil, V.V., Mhaske, S.T. and Thorat, B.N. (2009) Graft Copolymers of Starch and Its Application in Textiles. *Carbohydrate Polymers*, **75**, 71-78. https://doi.org/10.1016/j.carbpol.2008.06.012

[60] Zhang, Y., Ding, L., Gu, J., Tan, H. and Zhu, L. (2015) Preparation and Properties of

a Starch-Based Wood Adhesive with High Bonding Strength and Water Resistance. *Carbohydrate Polymers*, **115**, 32-37. https://doi.org/10.1016/j.carbpol.2014.08.063

[61] Hui, R., Chen, Q.-H., Fu, M.-L., Xu, Q. and He, G.-Q. (2009) Preparation and Properties of Octenyl Succinic Anhydride Modified Potato Starch. *Food Chemistry*, **114**, 81-86. https://doi.org/10.1016/j.foodchem.2008.09.019

[62] Kennedy, H.M. (1989) Starch- and Dextrin-Based Adhesives. In: Hemingway, R.W., Conner, A.H. and Branham, S.J., Eds., *Adhesives from Renewable Resources*, ACS Publications, Washington DC, 326-336. https://doi.org/10.1021/bk-1989-0385.ch023

[63] Kumar, R. and Khatkar, B.S. (2017) Thermal, Pasting and Morphological Properties of Starch Granules of Wheat (*Triticum aestivum* L.) Varieties. *Journal of Food Science and Technology*, **54**, 2403-2410. https://doi.org/10.1007/s13197-017-2681-x

[64] Lai, S.M., Don, T.M., Liu, Y.H. and Chiu, W.Y. (2006) Graft Polymerization of Vinyl Acetate onto Granular Starch: Comparison on the Potassium Persulfate and Ceric Ammonium Nitrate Initiated System. *Journal of Applied Polymer Science*, **102**, 3017-3027. https://doi.org/10.1002/app.24672

[65] Zhang, N., Wang, S., Gibril, M.E. and Kong, F. (2020) The Copolymer of Polyvinyl Acetate Containing Lignin-Vinyl Acetate Monomer: Synthesis and Characterization. *European Polymer Journal*, **123**, Article ID: 109411. https://doi.org/10.1016/j.eurpolymj.2019.109411

[66] Gong, Q., Wang, L.-Q. and Tu, K. (2006) *In Situ* Polymerization of Starch with Lactic Acid in Aqueous Solution and the Microstructure Characterization. *Carbohydrate Polymers*, **64**, 501-509. https://doi.org/10.1016/j.carbpol.2005.09.005

[67] Hebeish, A., El-Thalouth, I.A. and Kashouti, M.E. (1981) Gelatinization of Rice Starch in Aqueous Urea Solutions. *Starch-Stärke*, **33**, 84-90. https://doi.org/10.1002/star.19810330305

[68] Li, J., Vasanthan, T. and Bressler, D. C. (2012) Improved Cold Starch Hydrolysis with Urea Addition and Heat Treatment at Subgelatinization Temperature. *Carbohydrate Polymers*, **87**, 1649-1656. https://doi.org/10.1016/j.carbpol.2011.09.061

[69] Chiou, H., Fellows, C., Gilbert, R. and Fitzgerald, M. (2005) Study of Rice-Starch Structure by Dynamic Light Scattering in Aqueous Solution. *Carbohydrate Polymers*, **61**, 61-71. https://doi.org/10.1016/j.carbpol.2005.02.011

[70] Kuo, M.-I. and Wang, Y.-J. (2006) Effects of Urea Concentration on Thermal and Rheological Properties of Rice Starches. *Cereal Chemistry Journal*, **83**, 478-481. https://doi.org/10.1094/CC-83-0478

[71] Tamaki, Y., Konishi, T. and Tako, M. (2011) Gelation and Retrogradation Mechanism of Wheat Amylose. *Materials*, **4**, 1763-1775. https://doi.org/10.3390/ma4101763

[72] Karim, A. (2000) Methods for the Study of Starch Retrogradation. *Food Chemistry*, **71**, 9-36. https://doi.org/10.1016/S0308-8146(00)00130-8

[73] Choi, S.-G. and Kerr, W. L. (2003) ^{1}H NMR Studies of Molecular Mobility in Wheat Starch. *Food Research International*, **36**, 341-348. https://doi.org/10.1016/S0963-9969(02)00225-9

[74] Liu, D., Chen, H., Chang, P.R., Wu, Q., Li, K. and Guan, L. (2010) Biomimetic Soy Protein Nanocomposites with Calcium Carbonate Crystalline Arrays for Use as Wood Adhesive. *Bioresource Technology*, **101**, 6235-6241. https://doi.org/10.1016/j.biortech.2010.02.107

[75] Hoover, R. and Senanayake, S.P.J.N. (1996) Composition and Physicochemical Properties of Oat Starches. *Food Research International*, **29**, 15-26.

https://doi.org/10.1016/0963-9969(95)00060-7

[76] Ogawa, K., Aso, K., Ono, S., Yoshimura, T., Rengakuji, S., Nakamura, Y. and Shimasaki, C. (2000) Effects of the Noncyclic Cyanamides on the Retrogradation of Waxy Corn Starch. *Bulletin of the Chemical Society of Japan*, **73**, 1283-1284. https://doi.org/10.1246/bcsj.73.1283

[77] Tako, M., Tamaki, Y., Konishi, T., Shibanuma, K., Hanashiro, I. and Takeda, Y. (2008) Gelatinization and Retrogradation Characteristics of Wheat (Rosella) Starch. *Food Research International*, **41**, 797-802. https://doi.org/10.1016/j.foodres.2008.07.002

[78] McGrane, S.J., Mainwaring, D.E., Cornell, H.J. and Rix, C.J. (2004) The Role of Hydrogen Bonding in Amylose Gelation. *Starch-Stärke*, **56**, 122-131. https://doi.org/10.1002/star.200300242

[79] Russell, P.L. (1987) The Ageing of Gels from Starches of Different Amylose/Amylopectin Content Studied by Differential Scanning Calorimetry. *Journal of Cereal Science*, **6**, 147-158. https://doi.org/10.1016/S0733-5210(87)80051-6

[80] Gudmundsson, M. (1992) Effects of an Added Inclusion-Amylose Complex on the Retrogradation of Some Starches and Amylopectin. *Carbohydrate Polymers*, **17**, 299-304. https://doi.org/10.1016/0144-8617(92)90173-N

[81] Gurruchaga, M., Goñi, I., Valero, M. and Guzmán, G.M. (1984) Graft Polymerization of Acrylic Monomers onto Starch Fractions. II. Effect of Reaction Time on Grafting of Methyl Methacrylate onto Amylopectin. *Journal of Polymer Science: Polymer Letters Edition*, **22**, 21-24. https://doi.org/10.1002/pol.1984.130220104

[82] Witono, J.R., Noordergraaf, I.W., Heeres, H.J. and Janssen, L.P.B.M. (2012) Graft Copolymerization of Acrylic Acid to Cassava Starch—Evaluation of the Influences of Process Parameters by an Experimental Design Method. *Carbohydrate Polymers*, **90**, 1522-1529. https://doi.org/10.1016/j.carbpol.2012.07.024

[83] Wu, Y.B., Lv, C.F. and Han, M.N. (2009) Synthesis and Performance Study of Polybasic Starch Graft Copolymerization Function Materials. *Advanced Materials Research*, **79-82**, 43-46. https://doi.org/10.4028/www.scientific.net/AMR.79-82.43

[84] Zia-ud-Din, Chen, L., Ullah, I., Wang, P. K., Javaid, A. B., Hu, C. and Wang, Z. (2018) Synthesis and Characterization of Starch-g-Poly(Vinyl Acetate-*co*-Butyl Acrylate) Bio-Based Adhesive for Wood Application. *International Journal of Biological Macromolecules*, **114**, 1186-1193. https://doi.org/10.1016/j.ijbiomac.2018.03.178

[85] Zhang, S.F., Zhou, L.L., Gao, Q., Guo, X.X., Chen, L.O., Han, C.R. and Li, J.Z. (2011) Preparation and Performance of Bio-Adhesive Based on Acorn Starch Graft Glycidyl Methacrylate. *Applied Mechanics and Materials*, **121-126**, 293-296. https://doi.org/10.4028/www.scientific.net/AMM.121-126.293

[86] Gurruchaga, M., Goñi, I., Valero, M. and Guzmán, G.M. (1992) Graft Copolymerization of Hydroxylic Methacrylates and Ethyl Acrylate onto Amylopectin. *Polymer*, **33**, 2860-2862. https://doi.org/10.1016/0032-3861(92)90467-B

[87] Samaha, S.H., Nasr, H.E. and Hebeish, A. (2005) Synthesis and Characterization of Starch-Poly(Vinyl Acetate) Graft Copolymers and Their Saponified Form. *Journal of Polymer Research*, **12**, 343-353. https://doi.org/10.1007/s10965-004-7937-2

[88] Wang, Z., Gu, Z., Hong, Y., Cheng, L. and Li, Z. (2011) Bonding Strength and Water Resistance of Starch-Based Wood Adhesive Improved by Silica Nanoparticles. *Carbohydrate Polymers*, **86**, 72-76. https://doi.org/10.1016/j.carbpol.2011.04.003

[89] Wang, Z., Li, Z., Gu, Z., Hong, Y. and Cheng, L. (2012) Preparation, Characterization and Properties of Starch-Based Wood Adhesive. *Carbohydrate Polymers*, **88**,

699-706. https://doi.org/10.1016/j.carbpol.2012.01.023

[90] Cheng, H., Chen, L., McClements, D.J., Yang, T., Zhang, Z., Ren, F. and Jin, Z. (2021) Starch-Based Biodegradable Packaging Materials: A Review of Their Preparation, Characterization and Diverse Applications in the Food Industry. *Trends in Food Science & Technology*, **114**, 70-82. https://doi.org/10.1016/j.tifs.2021.05.017

[91] Wang, Z., Gu, Z., Li, Z., Hong, Y. and Cheng, L. (2013) Effects of Emulsifier on the Bonding Performance and Freeze-Thaw Stability of Starch-Based Wood Adhesive. *Cellulose*, **20**, 2583-2590. https://doi.org/10.1007/s10570-013-9984-5

[92] Gu, Z., Li, Z., Cheng, L., Hong, Y. and Wang, J. (2012) Starch Adhesive for Nano Material Modified Wood and Preparation Method of Starch Adhesive. CN102634306A.

[93] Carr, M.E. (1992) Preparation and Application of Starch Graft Poly(Vinyl) Copolymers as Paper Coating Adhesives. *Starch-Stärke*, **44**, 219-223. https://doi.org/10.1002/star.19920440605

[94] Wu, X.Q. and Schork, F.J. (2000) Batch and Semibatch Mini/Macroemulsion Copolymerization of Vinyl Acetate and Comonomers. *Industrial & Engineering Chemistry Research*, **39**, 2855-2865. https://doi.org/10.1021/ie990861k

[95] Krishnan, S., Klein, A., El-Aasser, M.S. and Sudol, E.D. (2003) Agitation Effects in Emulsion Copolymerization of n-Butyl Methacrylate and N-Methylol Acrylamide. *Polymer Reaction Engineering*, **11**, 335-357. https://doi.org/10.1081/PRE-120024418

[96] Krishnan, S., Klein, A., El-Aasser, M.S. and Sudol, E.D. (2003) Relative Importance of the Effects of Seed and Feed Stage Agitations on Latex Properties in Semibatch Emulsion Copolymerization of n-Butyl Methacrylate and N-Methylol Acrylamide. *Polymer Reaction Engineering*, **11**, 359-378. https://doi.org/10.1081/PRE-120024419

[97] Gu, Y., Cheng, L., Gu, Z., Hong, Y., Li, Z. and Li, C. (2019) Preparation, Characterization and Properties of Starch-Based Adhesive for Wood-Based Panels. International *Journal of Biological Macromolecules*, **134**, 247-254. https://doi.org/10.1016/j.ijbiomac.2019.04.088

[98] Zhou, Y., Zhang, Y., Xu, J. and Li, X. (2012) Hot-Pressed Veneer Adhesive and Preparation Method Thereof. CN102585736A.

[99] Gu, Z., Li, Z. and Hong, Y. (2005) Method for Preparing Starch Adhesive for Lumber. CN1293159C.

[100] Chen, H. (2016) Preparation Method for Corn Starch-Based Wood Adhesive. CN105754524A.

[101] Cheng, L., Gu, Z., Gu, Y., Li, Z., Hong, Y. and Li, C. (2018) A Kind of Thermosetting Property Wood-Based Plate Starch Adhesive and Preparation Method Thereof. CN109266265B.

[102] Gu, Z., Hong, Y., Li, Z. and Wang, Y. (2006) Preparation Process and Application of Water-Resistant Starch-Base Timber Adhesive. CN100415845C.

[103] Cheng, L., Kim, J., Gu Z., Li, Z., Hong, Y. and Li, C. (2021) Low-Viscosity Thermosetting Particle Board Starch Adhesive and Preparation Method Thereof. CN114106749A.

[104] Van, W., Wang, Z., Guo, Y., Ji, X. and Wang Y. (2017) Acrylic Acid Copolymer Graft Starch Environment-Friendly Adhesive. CN109385239A.

Abbreviations

VOC—Volatile Organic Compounds
PVAc—Polyvinyl Acetate
PVA—Polyvinyl Alcohol
DH—Degree of Hydrolysis
VAc—Vinyl Acetate
SDS—Sodium Dodecyl Sulfate
BA—Butyl Acrylate
MMT—Montmorillonite
NMA—N-Methylol Acrylamide
AA—Acrylic Acid