

Composites Science and Technology

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Eco-Friendly Adhesives for Wood and Natural Fiber Composites

Characterization, Fabrication
and Applications

 Springer

Composites Science and Technology

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Composites Science and Technology

ISBN 978-981-33-4748-9

ISBN 978-981-33-4749-6 (eBook)

<https://doi.org/10.1007/978-981-33-4749-6>

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Preface

Bioadhesives are the substitute of petroleum-based adhesives that have received great attention from environmental concerns, academic researchers and industries. They are available in both forms: thermosets and thermoplastics. Several researchers have explored the easy way to synthesize more bioadhesives having acceptable properties for industrial applications. Bioadhesives have some peculiar advantages such as biodegradability, biocompostibility, involvement of non-hazardous chemicals, good mechanical properties, handling, toughness, excellent flame retardance, good heat resistance and good interfacial bonding. Several bioadhesive-based products have been produced and are being used daily usage.

This book will explore the potentiality of the chemical structure, synthesis process and derivatives of thermoset and thermoplastic bioadhesives. Several synthesis processes of bioadhesives from biodegradable sources have been studied, and their mechanical and thermal properties, flammability and rheological properties are tested. The obtained data helped in comparative studies with synthetic polymers. Bioadhesives are very much equal to synthetic polymers in their properties but in some requirements, they performed better, e.g. Biodegradability. Due to the versatile properties, they can be used for both outdoor and indoor applications. With this approach, Bioadhesives can easily enter eco-friendly market segments and can be a promising material for the automotive, marine, aerospace, construction and building, wind energy and consumer goods, etc.

This book has clearly shown the syntheses, derivations and utilization of bioadhesive which helps to understand this polymer and its application in the real polymer world as per the need of markets. This book also covers challenges, advantages and future perspectives of bioadhesives as compared to the polymers/composites industries, waste material-based bioadhesives, thermoplastic and thermoset-based bioadhesives, physical, mechanical, thermal and fire-retardant properties of bioadhesives, natural fiber-based biocomposites, wood-based biocomposites and nanocellulose biocomposites. This versatile version of bioadhesives and their composites help to develop lightweight, durable and biodegradable components which can be used for heavy duty.

We are highly thankful to all the authors who contributed to and provided their valuable ideas and knowledge in this edited book. We attempted to gather all the scattered information of authors from diverse fields around the world (Malaysia, India, Libya, Canada, Thailand, Italy, China, Algeria, France, Iran, etc.) in the areas of polymers and biocomposites and finally completed this venture in a fruitful way. We greatly appreciate the contributor's commitment for their support to compile our ideas in reality. We are highly thankful to Springer Nature, Singapore team, for their generous cooperation at every stage of the book production.

Serdang, Malaysia
Pune, India
Banda, India
Serdang, Malaysia

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Mohammed Nasir
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About the Editors

Dr. Mohammad Jawaid is currently working as Senior Fellow (Professor) at Biocomposite Technology Laboratory, Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia (UPM), Serdang, Selangor, Malaysia, and also has been Visiting Professor at the Department of Chemical Engineering, College of Engineering, King Saud University, Riyadh, Saudi Arabia since June 2013. He has more than 16 years of experience in teaching, research, and industries. His area of research interests includes hybrid composites, lignocellulosic reinforced/filled polymer composites, advance materials: graphene/nanoclay/fire retardant, modification and treatment of lignocellulosic fibers and solid wood, biopolymers and biopolymers for packaging applications, nanocomposites and nanocellulose fibers, and polymer blends. So far, he has published 38 books, 65 book chapters, more than 350 peer-reviewed international journal papers, and several published review papers under top 25 hot articles in science direct during 2013–2018. He also obtained 2 Patents and 5 Copyrights. H-index and citation in Scopus are 53 and 12632 and in Google scholar, H-index and citation are 61 and 17568; H-index = 51 (Web of Science). He is founding Series Editor of Composite Science and Technology Book Series from Springer-Nature, and also Series Editor of Springer Proceedings in Materials, Springer-Nature. Beside that he is also a member of International Advisory Board of Springer Series on Polymer and Composite Materials. He worked as guest editor of special issues of SN Applied Science, Current Organic Synthesis and Current Analytical Chemistry, International Journal of Polymer Science, IOP Conference Proceeding. He is also an Editorial Board Member of Journal of Polymers and The Environment, Journal of Plastics Technology, Applied Science and Engineering Progress Journal, Journal of Asian Science, Technology and Innovation and the Recent Innovations in Chemical Engineering. Recently he get Fellow and Chartered Scientist from Institute of Materials, Minerals and Mining (IOM), UK. He is a life member of Asian Polymer Association, and Malaysian Society for Engineering and Technology. He is also a member of Society of Plastics Engineers, American Chemical Society, Athens Institute for Education and Research, and International Association of Advanced Materials. Besides that, he is also a reviewer of several high-impact international peer-reviewed journals of

Elsevier, Springer, Wiley, Saga, ACS, RSC, Frontiers, etc. Presently, he is supervising 12 Ph.D. students (4 Ph.D. as Chairman, and 8 Ph.D. as Member) and 7 Master's students (1 Master as Chairman, and 6 Master as Member) in the fields of hybrid composites, green composites, nanocomposites, natural fiber-reinforced composites, nanocellulose, etc. 24 Ph.D. and 12 Master's students graduated under his supervision in 2014–2020. He has several research grants at university, national, and international levels on polymer composites of around 3 million Malaysian ringgits (USD 700,000). He also delivered plenary and invited talks in international conferences related to composites in India, Turkey, Malaysia, Thailand, the United Kingdom, France, Saudi Arabia, Egypt, and China. Besides that, he is also a member of technical committees of several national and international conferences on composites and material science. Recently Dr. Mohammad Jawaid received Excellent Academic Award in Category of International Grant-Universiti Putra Malaysia-2018 and also Excellent Academic Staff Award in industry High Impact Network (ICAN 2019) Award. Beside that Gold Medal-Community and Industry Network (JINM Showcase) at Universiti Putra Malaysia. He also Received Publons Peer Review Awards 2017, and 2018 (Materials Science), Certified Sentinel of science Award Receipient-2016 (Materials Science) and 2019 (Materials Science and Cross field). He is also Winner of Newton-Ungku Omar Coordination Fund: UK-Malaysia Research and Innovation Bridges Competition 2015.

Tanveer Ahmed Khan is a Planner, implementer & achiever with multi-cultural experience of over 8 years in spearheading the Development functions across Biomass, Bio-Adhesive, and Bio-Composites. He is currently an Innovation Center Manager at Modern Mill Inc. & Gigantic Bag Co. llc. McComb, Mississippi, USA. Prior to this, He was working as a post-doctoral researcher in the Laboratory of Adhesion & Bio-Composites, Seoul National University. He has completed his Ph.D. in October' 2015 in the Faculty of Chemical and Natural Resources Engineering at University Malaysia Pahang. His project "Woody Biomass Advanced Materialization Technology" bagged Brilliant Korea (BK21) Fellowship for his postdoc. He secured many national and international awards at various international conferences and scientific exhibitions. He has over 8 years of experience in the areas of Research and Development, Teaching & Training, Project Management, Laboratory Operations, besides others across Synthesis of carbon Fibers, carbon nanomaterials, Bio-Adhesives, Wood Composites, Wood Plastic Composites, Natural Fiber composites, Biomass, Nano-Cellulose, Lignin Chemistry, Polymer Synthetic Chemistry, Polymer Nano-composites, Advance Materials, Superabsorbent composites, Polymer Materials, and Engineering. He has published 18 papers in high-end journals, 2 book chapters, 14 conference proceedings, and several other publications are currently under review. He has successfully formulated nano-based polymer composites for 3D printing. He has considerable experience in securing external funding and managing large-scale research projects. He has been a key researcher in various grants related to the

synthesis of nano/micro-structured carbon materials, Woody Biomass Advanced Materialization Technology, Development of Oil Palm Empty Fruit Bunch/ Sugarcane Bagasse Fiber-Based Hybrid Composites Insulation Board for Construction Applications, and Development of UV Curable Polymer Nano Composites Based on Inorganic Nano Fillers for 3D Printing. He received a Gold medal and Out Standing Achievement Award for his Ph.D. project at Seoul International Youth Invention Contest (IYIC), South Korea & at the International Innovation Festival (INNOFEST), Malaysia in 2014.

Dr. Mohammed Nasir is currently working as assistant professor at forest Products Utilization, College of Forestry, Banda University of Agriculture and technology, Banda (UP) India. He was born on 17th June 1982, in Mau Uttar Pradesh, India. He did his B.Sc. Degree in Forestry (Hons.) from Chandra Shekhar Azad University of Agriculture & Technology Kanpur, M.Sc. in Wood Science and Technology from Forest Research Institute Dehradun and Ph.D. in Chemical Engineering (wood composites) from Universiti Malaysia Pahang, Malaysia. During his Ph.D. he worked on “Bio-composite fabrication from enzyme treated fiber from lignin based bio adhesive”. He extended his research work further as postdoc fellow at School of Industrial Technology, Universiti Sains Malaysia for two years, where he focused on developing an “Eco-friendly method of nano-cellulose synthesis from oil palm trunk waste”. He has also worked as a National postdoc fellow at Forest Research Institute Dehradun for one year before joining the current service. His focused research interests are: 1) Lignin based Bio adhesive preparation, 2) Researching the scope of wood alternative, 3) Bamboo utilization in composite products manufacturing. He has published 39 research paper and 3 book chapters in various national and international journals. Furthermore, his two Malaysia patents for adopting a new method and preparing a composite from lignin based bio-adhesive are under consideration.

Dr. Mohammad Asim is currently a post-doctoral fellow in the Laboratory of Biocomposite Technology at the Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia. He was born on the 2nd August 1988 in Mau, Uttar Pradesh, India. He completed his bachelor's degree in forestry from C. S. Azad University of agriculture and technology, Kanpur, India in 2011. Afterward, he continued his study and obtained his MSc in wood science and technology from Forest Research institute, Dehradun, India in 2013 and finally Ph. D degree in the field of biocomposite technology from Universiti Putra Malaysia in 2017. His main research areas are: Treatment and modification of natural fibres, Hybrid Reinforced/Filled Polymer Composites, Advance Materials: Nanoclay/Fire Retardant, Lignocellulosic Reinforced/Filled Polymer Composites, Nano Composites and Nanocellulose fibres, thermosets and thermoplastics. Dr. Asim has published more than 35 international journal papers, 5 review papers, 6 conference proceedings, 7 book chapters and edited 2 book in springer Nature. Dr. Asim also have copyrights the design of Meat Tray Prototype by Using 3D Printing and Vacuum Bagging Process for Natural Fibre Based Composite, Dr. Asim is also a

regular reviewer of different international journals published by Elsevier, Wiley, Springer, etc. H-index and citation in Scopus: 13 and 650 respectively, in Google scholar: H-index and citation are 15 and 900 respectively.

Introduction of Eco-Friendly Adhesives: Source, Types, Chemistry and Characterization



Anisah Sajidah Saud, Gaanty Pragas Maniam,
and Mohd Hasbi Ab. Rahim 

Abstract Natural and wood-based fiber composites and adhesive industry have shown remarkable progress during the last decades. Adhesives play a central role in wood-based panel production. Knowledge about wood bonding is quite limited although it is one of the ancient techniques. Wood structure having so many variability including; cell structures, complex morphology at all spatial scales that make it hard to model the process. The main driving forces today are to develop cheaper but more complex structured adhesives. Despite these problems, many adhesives have been commercialized that are stronger, more durable than the wood and allowing the wood pieces to be glued together in economical manner. Adhesives play a central role in wood-based panel production. The quality of bonding, and hence the properties of the wood-based panels, are determined mainly by the type and quality of the adhesive. The development of the physical properties during the setting process and the interaction of the adhesive with the wood need to be further investigated to develop cost effective new adhesives. Development in wood-based panels, therefore, is always linked to development in adhesives and resins.

Keywords Eco-friendly adhesives · Bio-based adhesives · Synthetic adhesives · Natural adhesives · Wood composite adhesives

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1 Introduction

Manufactured wood composite panels commercially used to produce furniture such as particleboard, plywood, fibreboard and other composites (Li et al. 2018; Valarmathi et al. 2020). The process typically involved adhesives with the aim to create require bonding between the wooden elements or different materials. For centuries, they were bonded using various fossil-derived polymers such as formaldehyde, isocyanate, vinyl acetate-based adhesives in which, many wood-based materials are solely prepared from formaldehyde-based adhesives (DeVito 2016; Ling et al. 2018; Catto et al. 2017). These are likely to be cost-effective and a benign to bonding performance, mechanical properties, thermal stability and water resistance (Jin et al. 2010; Zhang et al. 2013; Jivkov et al. 2013a, b; Yang et al. 2015). Adhesives comprise formaldehyde have already been used industrially for many large-scale applications due to their very highly reactive compound, making it well suited for use as a binder.

However, the US Environmental Protection Agency (EPA) has identified formaldehyde as a “probable human carcinogen” (Marshall 1987) and in fact numerous committee’s review addressing all aspects of formaldehyde toxicity and potential for adverse health effects profile in the regulatory and other authoritative bodies, including the National Toxicology Program (NTP), US Department of Health and Human Services (Panel 2009) and the World Health Organization (WHO) (Chemicals and Organization 2010). There is sufficient evidence that long-term formaldehyde exposure can cause cancer of the nasopharynx, leukaemia and sinonasal cancer (Cancer 2006). Thus, to reduce the free formaldehyde emissions from wood composites, especially in indoor-related applications, along with the more environmentally conscious, focus on the sustainability of raw materials and final products, as well as more stringent environmental legislation, are the main driving factors for shifting the scientific and industrial interest from the traditional formaldehyde-based synthetic adhesives to the new bio-based adhesives for production of eco-friendly wood composites and related materials (Dunky 2004; Frihart 2005; Kües 2007; Pizzi 2006; Navarrete et al. 2013; Valyova et al. 2017).

Increasing environmental reports and legislation about emission of formaldehyde putting an adverse effect on production of these adhesives. Moreover, it is a move forward to reduce dependency on fossil-derived resources that has spurred the wood industry to develop the renewable eco-friendly adhesives. Nowadays there are only a few bio-based adhesives for production of wood composites and they are highly likely that these adhesives are not economically feasible through both niche and mainstream production of wood composites. For these adhesives and for the ones still in development, due to their low cost, a synthetic cross-linker are still more commonly required (Hemmilä et al. 2017). Thus, on-going research in eco-friendly and renewable based adhesives could partially-substitute and supplement synthetic adhesives subsequently that make the wood-based adhesives are more sustainable, green, and biodegradable (Pizzi 1991; Pang et al. 2020).

Tannin and lignin polymeric-based adhesives are found to be among eco-friendly types of adhesives (Pizzi 1980; Nimz 1983). Both adhesives are extensively studied

due to their applications as wood panel adhesives (Trosa and Pizzi 2001; Pizzi 2006; Ballerini et al. 2005; Pichelin et al. 2006; Pizzi and Salvadó 2007; Mansouri et al. 2011). In addition to polymeric-based adhesives, several types of adhesives such as plant protein adhesives (Khosravi et al. 2010; Xu et al. 2011; Jang et al. 2011), crop-based, carbohydrate adhesives (Tondi et al. 2012; Sulaiman et al. 2013), wheat gluten (Khosravi et al. 2011) and animal protein glue (Konnerth et al. 2009) have also been developed. The adhesive properties provided by these materials are comparable to conventional formaldehyde-based adhesive. As they are derived from renewable raw materials, they can have favourable sustainability characteristics, like reduced the rate of accumulation of CO₂ in the atmosphere and reduced or no toxicity. Table 1 shows the lignocellulosic materials and adhesives reported in prior-art.

1.1 Source, Types, Chemistry, and Characterization of Wood Composites Adhesives

The utilization of renewable raw materials for the production of wood adhesives have taken much attention since the world's oil crisis of the 1970s (Pizzi 2006). Bio-based adhesives are indeed derived from natural materials requiring or using novel technologies, formulations, and methods. Examples for adhesives include starch, tannin, lignin, proteins, carbohydrates, and oil (Ferdosian et al. 2017b; Pizzi 2006). They were found to be less petroleum dependent, sustainable sourcing and meet the requirements for indoor applications compared to formaldehyde adhesives (He and Wan 2017).

Economical and fast production of adhesives to fulfil industrial standards and requirement initiate the early development of wood composite industry. For example, early plywood were made by conventional hand method, with very slow adhesive setting speed (Muller 1992). To increase the rate of production, protein adhesives manufacture could be used. The curing time, final use of panel and the speed at which the panel can made has become a generic point for manufacturing of medium density fiberboard. As an example, in 1930s, for the development of wood-based panel (particle board and medium density fibreboard, MDF), urea–formaldehyde, was found to be a cheap commodity adhesive. However, following advanced performance criteria, melamine substituted the urea–formaldehyde due to its better moisture resistance for manufacturing of more moisture resistant boards.

Moreover, in nineteenth century, phenol formaldehyde (PF) adhesive was originally developed while their commercialization begins in 1930s for the manufacturing of plywood and engineered wood products. PF adhesives got more attention due to high moisture resistance in comparison to urea–formaldehyde adhesives. In recent years, due to be overwhelmed environmental concerns changed the driving force for adhesive development. For example, in the 1980s, the European Union started to strict the limits on formaldehyde emission in panel products. In 1985,

Table 1 Reported lignocellulosic materials and adhesives

Lignocellulosic materials	Adhesives	References
Pine, Spruce	Wheat gluten	(Khosravi et al. 2010)
Industrial wood	Crop-based starch and sugar	(Tondi et al. 2012)
Wood specimen	Polyvinyl acetate/ cellulose nanocrystals	(Mabrouk et al. 2020)
Poplar (<i>Populus deltoides</i>)	Oxidized demethylated corn lignin	(Chen et al. 2020)
Maple wood veneer	Cottonseed protein-based	(Cheng et al. 2019)
Poplar veneers, Pine wood pencil sandwich slats	Cottonseed meal-based	(He et al. 2019)
Sweet sorghum bagasse	Citric acid	(Kusumah et al. 2017)
Bagasse, wood	Urea–formaldehyde	(Hazrati-Behnagh et al. 2015)
Recycled softwood particles	Citric acid and sucrose	(Umamura et al. 2014)
Oil Palm trunk	Binderless	(Baskaran et al. 2015)
Rubberwood	Urea–formaldehyde	(Hua et al. 2015)
Apple tree pruning, sunflower stalk	Urea–formaldehyde	(Ghofrani et al. 2015)
<i>Rhizophora spp.</i>	Gum Arabic	(Abuarra et al. 2014)
Date Palm	Urea–formaldehyde and Phenol formaldehyde adhesive	(Amirou et al. 2013)
Macadamia nut shells	Castor oil derived adhesives	(Wechsler et al. 2013)
Bagasse	Binderless	(Nonaka et al. 2013)
Tobacco stalks, <i>Paraserianthes falcataria</i>	Urea–formaldehyde	(Acda and Cabangon 2013)
Willow, Pine	Urea–formaldehyde	(Warmbier et al. 2013)
Pine	Pine tannin	(Valenzuela et al. 2012)
Reed, wood	Urea–formaldehyde	(Ghalehno et al. 2011)
Sugar cane bagasse, Pine	Phenol–formaldehyde	(Hein et al. 2011)
Rice husk	Soybean protein concentrate-based adhesive	(Ciannamea et al. 2010)
White birch	Urea–formaldehyde adhesive	(Pedieu et al. 2009)
<i>Eucalyptus</i>	Urea–formaldehyde adhesive	(Colak et al. 2009)

Austria, Denmark, Germany and Sweden started to regulate formaldehyde emissions E1 (0.1 ppm boards) became obligatory. Likewise, in 2002, European standard for wood-based panels (EN 13,986) became obligatory across the Europe. The EN 13,986 was classified into two classes E1 and E2. The E1 referred to panels with no formaldehyde additions while E2 referred to rest of formaldehyde adhesives-based panels. The existing E1 standard was further modified in 2006, by the European panel federation (EPF7) and ‘Blue Angel’ (an additional environmental label) was

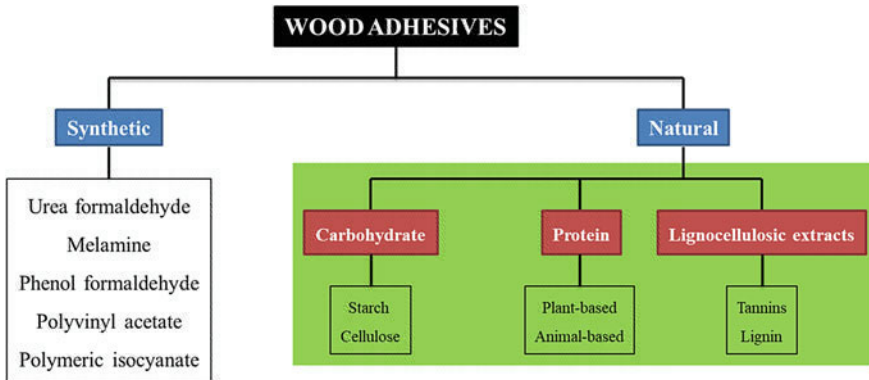


Fig. 1 Classification of wood adhesives

specified a steady-state concentration less than 0.05 ppm formaldehyde. Other testing method such as Japanese- F limits and the legislation of the state of California in the USA are among the important methods and limit around the globe.

However, the only possible move away from commodity adhesives is to manufacture and commercialization of a niche premium product. In contrast to above scenario, any product and process adaptation to new adhesive system is forbidden and insignificant in manufacturing of panel products.

Figure 1 shows the classification of wood adhesives.

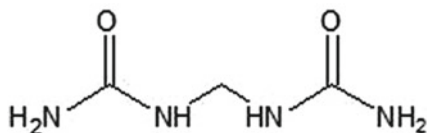
1.2 Synthetic Adhesives

The urea–formaldehyde (UF), melamine urea formaldehyde (MF), and phenolic (PF) adhesives are common synthetic adhesives that have been using for current composite technologies. The other currently used synthetic adhesives are including poly vinyl acetate and isocyanate adhesives. Meanwhile, the future natural adhesives for composites applications are carbohydrate, protein, and lignocellulosic extracts adhesives.

1.2.1 Urea–formaldehyde Adhesives

In early nineteenth century, urea–formaldehyde (UF) adhesive was developed (Dinwoodie 1979) and widely used in the composites industry (Fig. 2). Around 90% of the particleboard is produced using UF adhesive (Dinwoodie 1979; Pizzi 1994a; Pizzi 1994b; Xian-qing et al. 2020; Khan et al. 2020). The main features of UF adhesives were summarised as follows:

Fig. 2 Urea–formaldehyde chemical structure



- (a) Adhesive hardness.
- (b) Low flammability.
- (c) High thermal properties.
- (d) The colour absence in the crude polymer.
- (e) The curing conditions with variety adjustability.

Urea–formaldehyde adhesives are considered to be suitable for largeness and low-priced production due to the initial water solubility. However, the presence of moisture or acid opens up the hydrolytic degradation of adhesives. This is caused by the hydrolysis process towards amino plastic and the methylene bridges.

The Production of Urea–formaldehyde (UF) Adhesive

The most common method for UF adhesive formation involved the addition of urea to formaldehyde while keeping the ratio of both reactants in between 1:2 and 1:2.2 along with methylation at temperatures between 90 and 95 °C under reflux. The completion of adhesive formation is indicated when the exotherm has subsided followed by the addition of acid to maintain the lower level of 5.0–5.3 which let the polymer to build.

To avoid the increase in polymer size, pH of the mixture is increased soon after the correct viscosity is attained. Another urea is added to complete the repeating chain of free formaldehyde until a ratio range from 1:1.1 to 1:1.7.

Finally, different structured polymers such as linear, branched and 3D matrix can be found in cured adhesive due to different functionalities of urea and formaldehyde. Typically, formaldehyde has a functionality of two while urea has four due to two and four replaceable hydrogen respectively (Fig. 3).

The size and viscosity of the adhesive molecule has crucial importance towards the commercial production of UF adhesives. The size of the molecules increases during the change in viscosity, and the change of the properties of the adhesive can be observed (Goulding et al. 1994). The condensation process propagated the random splitting off the adhesive molecules due to water causing an increase in molecular weight. However, aqueous conditions are suitable for the condensation reaction. The quality of the adhesive based on the viscosity, pH, concentration and solubility of the adhesive while preparation.

Therefore, it can be summarized that there are three main factors that affect the properties of the finished urea–formaldehyde product;

- (a) The relative molarities of the reactants.
- (b) The reaction temperature.

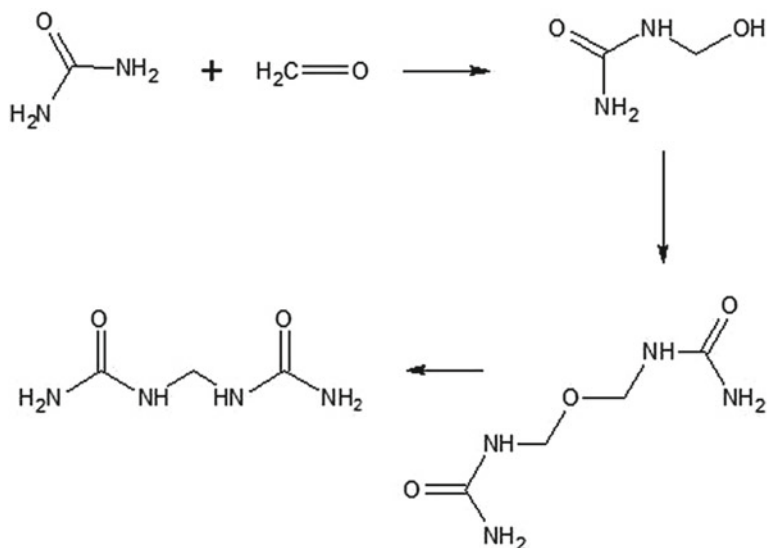


Fig. 3 Basic reactions of urea and formaldehyde

(c) The pH of the condensation reaction.

Urea–formaldehyde Curing Mechanism

Citric acid and formic acid that act as acid catalyst in the UF curing process is performed under ambient conditions. However, the process is a slow process. To boost up the speed or production rate at industrial level, heat is needed to the curing reaction. Another possible of two condensation reactions of hot UF curing that resulted the ridged three-dimensional structure, which are methylene and ether bridge. Methylene bridges are formed during first step of reaction through condensation between adjacent nitrogen from amide group and adjacent polymers. While ether bridges are formed through condensation reaction between methylol groups. As a result of UF curing process, it increases the viscosity of adhesives to form a gel until the process is complete.

1.2.2 Melamine Urea–formaldehyde (MF) Adhesives

Due to high water solubility and less resistance of water attack to UF adhesives, there is a need to find an alternatives material possessing high water resistance. Among them, melamine formaldehyde adhesives taken over the market for domestic use especially for outdoor project (exterior rated) and furniture panel. However,

the cost of melamine formaldehyde is 2.5 times more expensive than that of urea-formaldehyde and therefore a number of urea must be supplemented to adhesives offering the best cost and performance.

The Production of Melamine Formaldehyde (MF) Adhesive

The formation MF adhesives initiated by the condensation reaction between melamine and formaldehyde. In a typical reaction, formaldehyde attacks on the amino group of melamine resulting formation of methylol compounds. This reaction has similarity with UF adhesives synthesis. However, the MF adhesive formation occurs relatively more freely and completely than the UF adhesive formation.

Goulding and Pizzi with their own co-researchers reported that complete methylation take place in case of MF adhesives while it is practically not occurred during UF adhesive formation (Pizzi 1983; Goulding et al. 1994). The hydrophobic intermediaries appeared during early stage of MF adhesive formation reaction as compared to UF formation mainly due to rapid proceeding of the hydrophilic stage of the reaction. Goulding et al. (Goulding et al. 1994) investigated that the condensation and curing of MF adhesive continued not only in acid conditions but also in neutral and alkaline conditions.

The mechanism of reaction involved the similar steps involved in UF adhesive formation including the urea-formaldehyde, and the bridges (methylene and ether) formation along with a rapid increase in molecular weight of the adhesive. The final desired insoluble, infusible adhesives are formed through amino and methylol groups reaction during transformation step of final curing process. Several researchers have investigated the ether bridges besides un-reacted methylol groups and methylene bridges (Koehler 1943; Frey 1935). It was also found that no considerable amounts of formaldehyde are liberated for MF adhesive curing up to 100 °C temperature whereas urea-formaldehyde is considerable.

In term of commercial production, the current process is almost equally approach to the UF adhesive while the development of MF adhesive system relies mostly of the intended applications. In certain cases, the compounds such as acetoguanamine and E-caprolactam have been added at 3–5% (w/w) for desired application, which is for the impregnation of paper and fibres (Goulding et al. 1994). The function is to reduce the brittleness of MF adhesives when the degree of cross-linking is decrease in the cured adhesive by adding the such modifying compounds acetoguanamine and E-caprolactam.

Another important parameter in tuning the MF property is through viscosity control. In order to prevent the adhesive penetration into wood substrate higher viscosity of adhesives is use on the wood panel. The penetration may cause the cell wall swells or components of the cell wall may be chemically modified. High viscosity adhesives could produce by increase the level of condensation degree.

In case of low viscosity MF adhesives which theoretically having good penetration power, it can be produce through few approaches including by increase the content of methylol group and lowering the level of condensation. Another method is applied

by adjusting the ratio of (melamine:formaldehyde) to (1:1.8 to 1:2) along with lower level of condensation.

In term of economic perspectives with the aims to lessen the cost of the adhesive, sugars have been used as modifiers. However, at the same time, it adversely affects the life-time of adhesive typically indicated by colour change and cracking which degrade to the adhesive's properties for long periods of time.

Melamine Formaldehyde-Based Adhesives Curing Process

Typically, the curing methods for MF-derived adhesives are quite similar with UF-derived adhesives. The only difference is the process is carried out without presence of acid catalyst and perform curing under hot conditions (Marra 1992). The curing process completed via formation of the methylene bridges.

The pure MF-derived adhesives have advantage over UF (and MUF) adhesives due to that can be cured under 100 °C avoiding the release of formaldehyde. Moreover, a small amount of formaldehyde release between 100 and 150 °C while curing MF-derived adhesives-based panels which is lower than UF –derived adhesives under similar conditions.

1.2.3 Phenolic Adhesives

The development of synthetic polymer of Phenolic adhesive (PF) is started at the end of nineteenth century. However, these adhesives were not fully commercialised until 1930s. Typically, PF adhesives are used in the wafer board and the plywood.

The Production of Phenolic Adhesives

There are two main manufacturing routes for Phenolic adhesives which is Novolac and Resol process. The later process is commonly used throughout the panel industry. The Resol process involve the reaction of phenol with formaldehyde in excess form catalysed by an acid catalyst and produced the quinone methide molecule. The ratio of phenol and formaldehyde is crucial and it's kept within the range of 1.6:1 to 2.5:1. Linear structures could be produced by selecting the lower range while cross-linked structures produced following the higher ratio for both the reactants (Ormondroyd 2015).

The condensation of quinone methide is occurred under alkaline conditions intended to form the methylol bridges due to C–C bonds which ultimately strengthens the phenolic adhesives. Marra et al. reported that the bridges are having the bonds which are strong and durable (Marra 1992).

On heating, reactive methylol groups in Resol combine firstly to make larger molecules, afterwards gel formation and finally transformed to solid state adhesives.

During the whole manufacturing process an alkaline pH is maintained which ensures the stability and shelf life of the adhesives.

The Curing of Phenolic Adhesives

The curing of PF adhesives undergoes three phases which are phase A, B, and C. In initial phase (A) results in the formation of adhesives having low molecular weight (<200) (Sellers 1985; Bliem et al. 2020). In this stage, the viscosity of adhesives may be a low to high. The products would be soluble in sodium hydroxide solution and several polar solvents. The stage also makes the solid melts when being heated.

Phase B is the polymerization and methylol bridges are occurred in the presence of heat. This indicated the formation of second stage adhesive called as Resitol. Due to partial polymerization, Resitol adhesive is having the variance molecular weight of molecules. The Resitol adhesive is insoluble in most of the solvents; however, it become soft and rubbery on heating and can be in swollen state due to existing crosslinking.

In third curing stage, the Resitol become soft and again start polymerisation on heating where upon the process completed, Resitol is converted to Resite. After this stage no further re-melting or dissolution of adhesive into any solvent occurs.

1.2.4 Polyvinyl Acetate Adhesives

Poly vinyl acetate (PVA) is a thermoforming adhesive. The applications are based on wood DIY (Do it yourself) industries. The history of PVA begins from June 1920 when a German State patent office registered a patent for manufacturing of PVA (Pizzi 1983). While research on free radical vinyl polymerisation is in between 1915 to 1930 highlighted the practical applications of PVA and commercial production of PVA was begins since 1930 and onwards. The production of PVA has expanded enormously since the Second World War due to widely application in DIY wood work glue and also replacement of animal glue.

In comparison to conventional UF adhesives, PVA is much different in a sense, on curing PVA become flexible and converted to linear polymer with aliphatic backbone. PVA is characterized by its strong hydrogen bonding between acetates groups. This leads to an adhesive interaction within wood cell wall with OH^{-1} group. According to Rowell et al., a good adhesive should have the ability to maintain strength even after there is a wood expand. The internal and applied energies may be dissipated at the flexing in the bonded polymer (Rowell 2012). Their work further elaborated that creep and moisture resistance is almost negligible for adhesives. However, by adding cross linker can give them better improvement prior to the application of adhesive which essentially modified the thermoforming adhesive into a thermosetting system.

1.2.5 Isocyanate Adhesives

Isocyanate adhesives were discovered around 1884, but they were not fully developed as adhesives until Second World War (Pizzi 1983). Isocyanate adhesives found their early applications in tyre manufacturing industry followed by wide applications in wood industry (Ormondroyd 2015).

Wood panel industry utilised numerous types of Isocyanate adhesives, the most commonly form is MDI (4,4-diphenylmethane diisocyanate). MDI has certain advantages over other adhesive belonging to same category. Some of the feature of MDI resins are summarised as below;

- (a) Lower vapour pressure at ambient temperatures.
- (b) Lower viscosity in comparison to other isocyanates.
- (c) Lower cost in comparison to other isocyanates.
- (d) High moisture tolerance (i.e. required less energy for fiber drying).
- (e) High OH^{-1} bond making ability in wood comparative to other isocyanate adhesives.

However, MDIs have their disadvantages as listed;

- (a) Highly toxic when uncured especially in gas or droplet form.
- (b) High risk of lung infections (for unprotected operators at plant due bonding of gas with reactive sites in lungs).
- (c) MDI composites exhibit low tack and fragile.

Based on aforementioned disadvantages, the usage of MDI is limited in wood industry especially in Europe. However, MDI exhibit certain applications including MDI adhesive without formaldehyde and outdoor applications of MDI adhesive composites. Since MDI adhesives in oriented strand board (OSB) and strand board; though, another modified form of MDI known as MDF is also successfully manufactured.

The Manufacture of MDI Adhesives

The basic manufacturing of MDI adhesives consisted of a chemical reaction between 1° amines and phosgene. In 1884, Henschel, performed this reaction for the first time while further improvement to this synthesis method continued over the years.

In a typical reaction, a non-aqueous (xylene) solution of 1° amine is mixed with non-aqueous (xylene) solution of phosgene at a temperature $> 60\text{ }^{\circ}\text{C}$. The mixture is digested in multiple steps with an increment of $20\text{ }^{\circ}\text{C}$ along with addition of additional phosgene. Finally, to recover the excess phosgene and any impurities, distillation process is performed.

MDI Curing Process

MDI curing mechanism involved two main steps. The first step involves chemical reaction between MDI and OH^{-1} groups containing compounds. While second step involved direct reaction between MDI and water. A polyurethane formation take place through reaction between MDI and water molecules which then proceeded to setting of adhesives in a way similar to UF adhesive. The whole process of polyurethane formation involved several reactions such as the production of carbamic acid (unstable) in first step, which on decomposition produced an amine and CO_2 . A substituted urea compound formed via direct reaction between released amines and isocyanate molecules. Substituted urea molecule and carbon dioxide are the final products produced by decomposition of carbamic acid aldehyde. In addition, to aforementioned process, a very significant reaction takes place between MDI and wood. The reaction involved the covalent bond formation between wood and MDI whilst the MDI undergoing curing process (Ormondroyd 2015).

1.3 Natural Adhesives

1.3.1 Bio-Adhesives

Due to increasing industrialization and strict legislation for environment, protection around the globe triggers the research on wood adhesives and adhesives from natural and sustainable resources. However, after the world's first oil crisis in the 1970s the awareness and commercialization dramatically increased. It is worth mentioning that the key factor for extensive research work on various types of adhesives in late twenty first century was not only due to public perception, but also due to an rise in national and international regulations (Pizzi 2006).

Bio-based adhesives include the adhesives derived from natural, non-mineral and organic sources. A variety of renewable materials such as tannins, carbohydrates, oils and liquefied cellulosic can be utilized for production of adhesive products. A brief discussion about synthesis, curing and application of important bio-based adhesives is carried out in this book chapter.

Tannin-Based Adhesives

Hydrolysable tannins and condensed tannins are two main types of phenolic nature tannins (Kües 2007; Péguy et al. 2020). The bark, wood, leaves and fruits of different plant species are the main sources of tannins while a fewer number of plants can provide enough concentration of extractable tannins. The plants, which can be used to extract tannins, includes pine, oak, chestnut, wattle, eucalyptus, myrtle, maple, birch, willow, etc. The adhesive properties of tannins are closely related to their method of extraction such as powdered tannins are produced by plant extraction,

followed by purification and finally subjected to spray drying process (Pizzi 2003). Other components of the extraction include sugars, pectins and other polymeric carbohydrates, amino acids, as well as other substances (Antov et al. 2020).

Phenol–formaldehyde resins used upto 50% hydrolysable tannins as partial substitutes (Kulvik 1976, 1977). However, lower macromolecular structure, the lower degree of phenol substitution, limited the global production and being expensive hinders their commercialization in comparison to condensed tannins (Pizzi 2003, 2006). Condensed tannins with an annual production of 200 000 tons covers around 90% of the global production (Pizzi 2003, 2006).

The adhesives application of tannins for wood-based panels depends mainly on two factors: the content of reactive polyphenols, and the reactivity of these components towards formaldehyde. Tannins can be used as adhesives alone (with a formaldehyde component as cross linker) or in combination with aminoplastic or phenolic resins. MDF produced with tannins replacing parts of phenol in phenol-urea formaldehyde resins or even with 100% tannin resin can meet interior grade requirements but still unable to fulfil exterior grade specifications (Roffael et al. 2000; López-Suevos and Riedl 2003). Characteristics of resulting boards remarkably effected by the tannin source and tannin addition time during production of MDI chain (Müller et al. 2007). Adhesive formulations for wood applications, prepared using different hardeners and tannin powder from Turkish red pine bark, have been developed and tested by (Gonultas 2018; Ucar et al. 2013). A thermosetting tannin-based wood adhesive system from formaldehyde reaction with both condensed and hydrolysable tannin has been studied (Özacar et al. 2006).

On the other hand, there are studies focused on formaldehyde free resins by combination of bio-based materials e.g. protein and tannins (Li et al. 2004; Brossard et al. 2020). The development of tannins based particleboard adhesives have been studied by Santos et al. (Santos et al. 2017) following the complete removal of formaldehyde from adhesive formulations. They typically extracted from raw industrial lignocellulosic wastes, namely chestnut shell, chestnut bur and eucalyptus bark. Nath et al. have studied the properties and possibilities for production of particleboard with tannin-based adhesive from mangrove species (Nath et al. 2018). Cui et al. added cellulose nanofibers into tannin-based adhesives for particleboard production and reported significant increase of the mechanical properties of the produced panels (Cui et al. 2015).

Countries such as Australia, Argentina, Brazil, Chile, New Zealand, South Africa, and Zimbabwe used tannins as adhesives for production of wood-based panels (Li and Maplesden 1998; Dunky and Pizzi 2002). The application in Europe is rather limited, only for special products with specific properties.

Lignin-Based Adhesives

Lignin is the second most important component of plant biomass after cellulose. Lignin has an estimated production of 300 billion total tons in the biosphere and about 20 billion tons as an annual resynthesis (Mandel 1988). Lignocellulosic present in

plants including agricultural residues, wood, grass, and other plants (Fu et al. 2010; Yousuf et al. 2020). Annually more than 50 million tons of lignin produced as by-product of pulp production worldwide (Kües 2007). About 10% of the technical lignin is commercially utilised. While the remaining amount is either combusted or not utilized at all (Kharazipour et al. 1991; Gargulak and Lebo 2000; Chakar and Ragauskas 2004; Gosselink et al. 2004). The possibilities for use of lignin in adhesive applications have been extensively studied by many authors (Hemmilä et al. 2017; Ferdosian et al. 2017a; Ghaffar and Fan 2014; Pizzi 2016; Nasir et al. 2019). The main interest in lignin is due to its phenolic structure with several favourable properties for formulation of wood adhesives such as high hydrophobicity and low polydispersity. However, the reactivity of the resin lowered by chemical structure of the lignin, which acts as disadvantage towards its applications, needed fast curing time.

Adhesives based on lignin can be classified into two clusters - formaldehyde-free lignin-based adhesives and lignin-based phenol–formaldehyde adhesives. In different studies, lignin is often combined with synthetic resins such as phenol–formaldehyde (Cetin and Özmen 2002; Çetin and Özmen 2003; Ghaffar and Fan 2014; Olivares et al. 1995; Guo et al. 2015; Pizzi 2016) or urea–formaldehyde resins (Podschun et al. 2016) to decrease the cost (Shimatani et al. 1994) or free formaldehyde emissions (Yang et al. 2015). Certain interest in this field represent the laboratory studies for manufacturing MDF by adding lignin as a binder (Zhou et al. 2011; Nasir et al. 2014) which allow the production of ecological low-toxic panels. Another studies in the MDF field considered addition of lignin activated by laccase enzyme to the fibers or lignin activated by enzyme treatment to the fibers (Kharazipour et al. 1991, 1998; Nasir et al. 2015). This method required the addition of 1% isocyanate to the panel to press at acceptably short press times or significantly extending the pressing time (Felby et al. 1997). There are also a number of successful attempts to produce MDF in laboratory conditions on the basis of lignosulfonates (Yotov et al. 2017; SAVOV and MIHAILOVA 2017a, 2017b; Savov et al. 2019; Antov et al. 2019).

The use of lignosulfonate as a replacement of phenol for phenolformaldehyde resin synthesis (up to 50 wt. % replacement level) were studied by Akhtar et al. (Akhtar et al. 2011). Phenol–formaldehyde resin contains 50% of lignosulfonate showed improved strength than commercial adhesives. The highest values of shear strength in both wet and dry conditions were attained at 20% substitution of phenol by lignosulfonate.

Another study was focused on the application of Kraft lignin-based phenol–formaldehyde resin (50 wt. % Kraft lignin) as an adhesive for production of oriented strand board panels (Cavdar et al. 2008). Addition of 3 - 8% Kraft lignin in hardboards facilitates in reduction of swelling, (Westin et al. 2001). In another study, water stability, inner bond strength, and mechanical properties were stated to be enhanced in panels made from fibers of softwood residues defibrated in presence of extra lignin (Anglès et al. 2001).

Jin et al. studied the application of enzymatic hydrolysis lignin for phenol–formaldehyde resin synthesis (Jin et al. 2010; Qiao et al. 2015). The research data reported on the production of formaldehyde-free lignin-based adhesives is relatively

low. Geng and Li (2006) prepared a formaldehyde-free wood adhesive using Kraft lignin and polyethylenimine. While the physical and mechanical properties of a modified ammonium lignosulfonate/ polyethylenimine mixture as a green adhesive for MDF production was studied by Yuan et al. (2014). In addition, a novel process to substitute formaldehyde in wood adhesive for particleboard production developed in 2007 by El Mansouri et al. (Pizzi and Salvadó 2007). The as prepared formulation met the EN 312 standards 312 for exterior grade panels and proved equivalent reactivity to formaldehyde-based adhesives.

Furthermore, a novel synthetic resin free bio-based adhesive prepared by Navarrete et al. (Navarrete et al. 2010) mainly derived from a low molecular mass lignin and tannin. The as prepared adhesive proved to be zero formaldehyde emission based on the desiccator method. A novel bio-adhesive for wood using kenaf core lignin and glyoxal was developed and tested (Hussin et al. 2019).

Starch-Based Adhesives

Starch being a natural polymer found applications including food, papermaking, additives, and adhesives, mainly because of its renewability, abundance, good adhesion, and low price (Imam et al. 1999; Norström et al. 2018; Zhao et al. 2018; Gu et al. 2019a; Lamaming et al. 2020). Starch is the combination of amylose and amylopectin, two distinct polysaccharide composed of glucose with different sizes and shapes (Tester et al. 2004). The proportion of amylose to amylopectin varies in accordance with the botanical origin of the starch and affects the properties of the wood adhesive (Norström et al. 2018).

The strength of Starch-based adhesives depends on degree of hydrogen bonding. These adhesives can easily develop hydrogen bonds with water molecules, leading to poor water resistance. Therefore, it is essential to modify starch in order to increase its performance for adhesive applications. Higher bonding strength and better water resistance can be achieved by combining starch with another component, for example polyvinyl alcohol, formaldehyde, isocyanates, and tannins (Qiao et al. 2016). There are several studies about starch-based adhesives prepared by grafting vinyl acetate onto starch using ammonium persulfate as the initiator (Wang et al. 2011, 2012).

Wang et al. demonstrated graft efficiency as an important parameter, which directly related to bonding performance of the starch adhesive (Wang et al. 2015). Esterification is a typical method for chemical modification of starch by converting OH^{-1} groups into esters in order to improve the hydrophobic properties of starch is esterification. Qiao et al. obtained esterified corn starch by reacting with maleic anhydride and then crosslinking with a polyisocyanate pre-polymer (Qiao et al. 2016). The optimal amount of pre-polymer was determined to be 10 wt %, resulting in the dry and wet shear strengths of 12 and 4 MPa, respectively. In another study, Tan et al. modified the starch-based adhesive by addition of blocked isocyanate and auxiliary agent (Tan et al. 2011). Gu et al. synthesized an environment friendly starch-based adhesive for wood-based panels by grafting polymerization of vinyl acetate monomer onto corn starch and crosslinking polymerization with N-methylol acrylamide (Gu et al.

2019b). The water resistance of the obtained adhesive was significantly improved to more than one MPa. The enhancement in overall performance achieved mainly due to increase in degree of crosslinking density and complex network structure formation.

Epoxy resins are another class of bio-based adhesives used as cross linker of starch. They are tested in combination with polyvinyl acetate grafted starch adhesives for veneer gluing. Epoxy resin provides good shear strength in both dry and humid conditions due to three-dimensional networks (Nie et al. 2013).

Protein-starch composite (Anderson et al. 2015; Gadhave et al. 2017b) and tannin-starch composite (Moubarik et al. 2010) could be used for wood and wood composites adhesives being eco-friendly (zero formaldehyde emissions). A partial substitution of phenol-formaldehyde with corn starch-quebarcho tannin-based resin was reported for the production of plywood (Moubarik et al. 2010). The optimal replacement value was determined to be 20% (15% cornstarch and 5% quebracho tannin). The addition of this resin enhanced the water-resistant properties and lowered the formaldehyde emissions. The same authors developed a non-volatile and non-toxic corn starch-tannin adhesive for interior plywood (Moubarik et al. 2010). The mechanical properties of the produced plywood were greater in comparison with the conventional phenol-formaldehyde resin along with less toxicity, more environment-friendly, and having advantage of short reaction time.

The urea-formaldehyde resin was reactively blended with various concentration of starch (Osemeahon et al. 2013), esterified starch (Gadhave et al. 2017a; Zhu 2014), and oxidized starch (Ni 2014; Sun et al. 2018) as wood and wood composite adhesive. The modified system with urea starch blending has lower brittleness and formaldehyde emission. The as prepared adhesive has good chemical stability, insulating properties, temperature resistance, aging resistance, and oil resistance making it suitable for application towards wood adhesion (Dunky 1998; Bloembergen et al. 2005).

The performance of starch-based adhesives can be improved by incorporating the additives or fillers into the formulated adhesives (Wang et al. 2011). The addition of silica nanoparticles was reported to enhance the adhesive properties such as thermal stability, bonding strength, and water resistance. The shear strength improved by a factor of 5.12 MPa and 2.98 MPa respectively on addition of 10% silica both in dry and wet conditions.

Soy-Based Adhesives

A new type of adhesives using Soy as biomass raw materials commonly known as Soy-based adhesives. These adhesives are synthesized by partial hydrolysis of soy protein and their properties in accordance with panel standards (Xi et al. 2019; Xu et al. 2020).

Soy-derived adhesives based on soy protein which could be available in three different forms: At first, a non-effective adhesive based crude extract; at second a protein rich concentrate; and at third; an effective adhesive base protein isolate.