ORIENTAL JOURNAL OF CHEMISTRY
An International Open Access, Peer Reviewed Research Journal
www.orientjchem.org
Est. 1984
ISSN: 0970-020 X
CODEN: OJCHEG
2023, Vol. 39, No.(4):
Pg. 867-880

Development in the Modification of Phenolic Resin by Renewable Resources: (A-Review)

MEET PATEL*, MITALIYADAV and MAHENDRASINH RAJ

Department of Polymer Chemistry, Institute of Science & Technology for Advanced Studies & Research (ISTAR), CVM University VallabhVidyanagar–388120, Gujarat, India.
*Corresponding author E-mail: meepatel83@gmail.com

http://dx.doi.org/10.13005/ojc/390407

(Received: June 30, 2023; Accepted: August 15, 2023)

ABSTRACT

Furfural and cashew nut shell liquid are both renewable resources that can be used for the manufacture of a multitude of useful products. Herein this review is studied to be made concerning the replacement of phenol and aldehyde compounds in the phenolic resin. Cardanol is a phenol-based by-product having an unsaturated alkyl chain and is thus a promising renewable substitute for the development of phenolic resin. This review focuses on the synthesis process of modified phenolic resin by renewable resources, which is further modified by epoxidation, esterification, urea-melamine modification etc. which improved thermal and adhesive and anti-corrosive properties. Mainly phenolic resin is used with natural and synthetic fiber reinforcement and hybrid fiber-reinforced composite, which promote improvements in mechanical properties.

Keywords: Phenolic resin, Thermosetting resin, Renewable Resources, Cashew Nutshell Liquid, Furfural, Composite.

INTRODUCTION

In recent years, researchers have explored every possibility in a major effort to find novel and sustainable polymers. Nowadays, work is focused on the modification of thermoset polymers. Thermoset polymers are extremely important in our daily lives because of their unique properties. These flexible materials and their properties depend on the functionality and molecular weight of the polymer.[1]

During polymerization, the thermosetting resin converted into an infusible and insoluble mass due to heat and catalyst. That process is an irreversible chemical reaction known as cross-linking. Thermosetting resins contain a functional group that has reactive sites for the curing process.[2] The number of reactive groups in it increases as functionality improves, enhancing the possibility of cross-linking. This process creates a three-dimensional network, which is possible through polymer modification.[3] Thermosetting resins and their properties are determined by their different chain length and molecular weight, based on which there is a change in the viscosity of the resin. Nowadays, thermoset resins such as phenolic resin, epoxy resin, polyester resin, and polyamides, have the ability to be developed hyperbranched functionalized polymers and modified by agricultural renewable resources-based chemicals as well as commercial chemicals for various applications such as defense, aerospace, and electronic industries because of their extraordinary chemical resistance, weather resistance, and versatility of product design.[4,5,6,7] Phenolic resins continue to be critical materials in numerous industries, as technological advancements and sustainability concerns grow; unmodified phenolic resin has certain drawbacks, including hazardous raw materials for humans and the environment due to toxicity and thermal decomposition occurring at high temperatures. The need for development in phenolic resin arises from the growing demand for sustainable and eco-friendly materials, and the desire to improve performance characteristics.[8,9] Thermoset polymers have the potential to develop chemical and physical modifications. The chemical modification provides precise control over the chemical structure of the resin, enabling the incorporation of functional groups and cross-linking agents to tailor properties with unparalleled precision. This results in improved mechanical strength, thermal stability, and adhesion to fulfill specific application requirements. Physical modification processes, including blending and reinforcement, represent a simple and potentially cost-effective alternative, giving enhanced properties through the addition of compatible materials.[10,11]

Phenolic resin, despite the fact that they were developed at the outset of the polymer era, they have continued to be developed for a variety of applications.[12] Polymer composites have unique properties and potential applications. It can be used as a composite material made up of combining fiber-reinforced hybrid materials to achieve superior properties. There has been an increasing demand to develop new polymeric applications with improved properties has increased the past few decades. In composites, various fiber-reinforced materials are used such as natural and synthetic fiber with thermoset resin. Glass fiber and carbon fiber thermoset resin systems are used in spacecraft, military aircraft, and sailboats. And also gives thermal stability and good mechanical properties in UV- assisted three-dimensional printing.[13,14]

Phenolic Resin

Phenolic resins are the oldest commercially manufactured synthetic polymer. Leo Hendrik Baekl and developed an economical method to convert these resins into moldable formulations which were transformed by heat and pressure into hard and thermal-resistant molded parts. As the first synthetic resin to be utilized, the phenolic resin can be considered the first commercially produced polymeric commodities derived from simple low molecular weight chemicals.[15] Right now, industries are focused on developing insulating materials, coating, adhesives, and so on. Phenolic resin is well known for its ability to bind a variety of substrates, including paper, rubber, fiber, wood, glass, and metallic components. Being the oldest thermosetting polymers, the influence of many synthesis parameters has already been studied. Many variables, including the kind and quantity of the catalyst, the potential of hydrogen (pH), temperature, and the aldehyde/phenol ratio, which affect the pre-polymerization and curing reactions, affect the resin's molecular structure and properties. Since phenolic resins have a wide range of applications, and while having some drawbacks including brittleness and shrinkage, it is one of the most widely used resins.[16] However, researchers have intensively studied phenolic resins for chemical use. There is still no alternative to phenolic resins in terms of stability and heat-resistant properties. Many researchers pay attention to how affects resin with the appropriate properties.[17]

Chemistry of Phenolic Resin

Phenolic resin is also known as phenol formaldehyde resin (PF). This is produced by the polymerization of phenol and formaldehyde.[18] Generally in phenolic resin used raw materials are phenols and their derivatives which contain hydroxyl groups. It behaves like weak acidic groups and has a different nature from alcoholic groups. Phenol is more readily soluble in polar organic solvents than it is in aliphatic hydrocarbons. Phenols are aromatic substances that have an aromatic ring linked to one hydroxyl group. Mono-hydroxy benzenes, especially phenol, are generally of the greatest importance for the manufacturing of phenolic resin. Bisphenol-A and Resorcinol, in addition to alkylphenols (cresol and xylenols), are only occasionally used in the production of phenolic resins.[19]

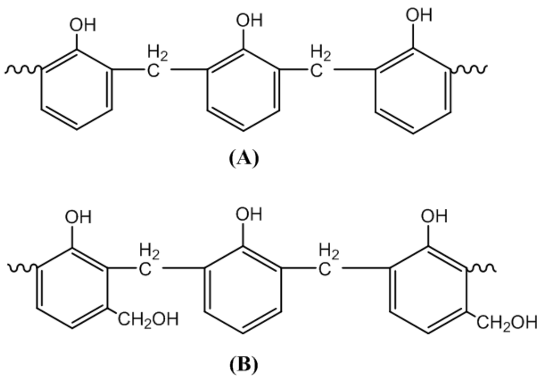

Fig. 1 (A). Novolac Phenolic resin, (B) Resol Phenolic resin. Renda, C.G *et al.,* (2018)[20]

Phenolic resins are formed by the reaction of phenol with formaldehyde under both basic and acidic conditions. The molar ratio of formaldehyde to phenol has different contributions to the reaction with acids and bases. Phenolic resins are of two types namely resol and novolac resin. For a highly cross-linked thermosetting material initial pH, temperature, time, and catalyst concentration are all factors that determine the behavior of this resin, Methylol phenols are formed during the resol production process as a result of a highly exothermic methylation reaction between phenol and formaldehyde. Ortho- and para-phenol are primarily joined by a methylene bridge in the molecules of resol resin.[21] Resol resin can be either a high-viscosity liquid or a solid form and is produced in a basic state with high formaldehyde content in phenol.

The characteristics of the resin have been improved by attempting to replace the phenol and aldehyde components in the typical phenol-formaldehyde condensate. Resorcinol and alkyl-substituted phenols including cresols, xylenol, p-tert-butyl-phenol, and p-phenyl-phenol were the most commonly used. Also, some aromatic and aliphatic aldehydes were studied, but acetaldehyde, butyraldehyde, chloral aldehyde, and furfural were among the more notable aldehyde used for modification.[22,23] These phenolic resin modifications improved the flow and electrical properties of the solubility and sped up the curing process. Therefore, the idea of utilizing the condensation byproduct of furfural was taken into consideration in order to enhance the thermal, electrical, mechanical, and chemical properties of the phenolic resin. Another important class of thermosetting resins of furfural is based on their condensation with phenol. Further improvements in mechanical and electrical properties can be obtained by modification of phenol-furfural resin with the addition of other resin-forming components like formaldehyde, urea, melamine, furfural alcohols, etc. These resins also find special importance in the coating. These resins have many advantages over phenol-formaldehyde. Because of high fluidity than that of the phenol-formaldehyde resins, these resins can be molded in various complex forms.[24,25]

Synthesis and Modification Phenolic Resin

The hydroxylation reaction and polycondensation reaction are the two steps of thermosetting phenolic resin production process (Fig. 2). In hydroxymethylation, when heated in an alkaline environment, phenol combines with the catalyst sodium hydroxide to produce the phenoxy anion. Because of its resonance form, phenoxy anion may act as a nucleophilic regent to attack the formaldehyde carbonyl group and produce phenol-hydroxymethyl. The phenolic hydroxyl group activates the ortho and para locations on the phenol nucleus, resulting in ortho- or para-phenol-hydroxymethyl when it reacts with formaldehyde.

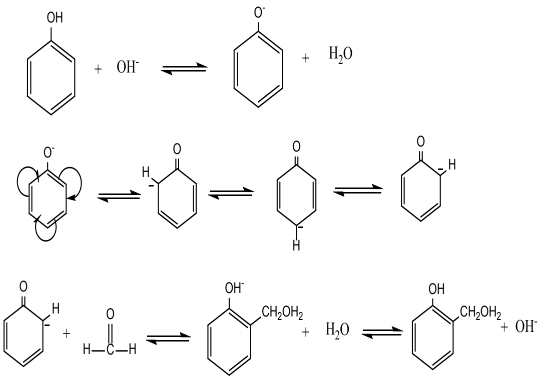

Fig. 2. Formation process of phenol-hydroxymethyl, Yanru Xu *et al.,* (2019)[26]

Developed dimethylol phenol and trimethylol phenol, the methylol phenol can continue to react with formaldehyde. (Shown in Fig. 3) In addition reaction, the phenolic hydroxyl group activates the ortho and para location on the phenol nucleus, resulting in ortho- or para- phenol-hydroxymethyl when it reacts with formaldehyde. To create dimethylol and trimethylol phenol, the methylol phenol can continue to react with formaldehyde. (Shown in Figure 3).[26]

Phenol-hydroxymethyl can be produced by the above addition reaction. It can react with phenol during the polycondensation reaction. Generally, resol-type resins have higher aldehyde content, and catalysts are used. Two ortho and one para positions on phenol are then replaced by hydroxymethyl groups. when the temperature is given, the viscosity increases as well as the molecular weight. An ether chain is formed between the methyl groups during the condensation reaction. And when a hydroxymethyl group attaches to an ortho- or para- active hydrogen atom on a phenol molecule, a methane chain is formed. As shown in Figure 4.[26]

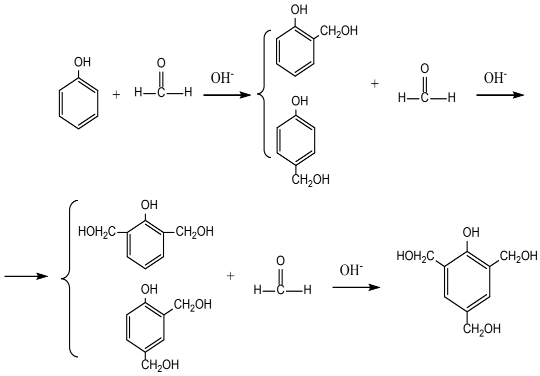

Fig. 3. Addition reaction process, YanruXu *et al.,*(2019)[26]

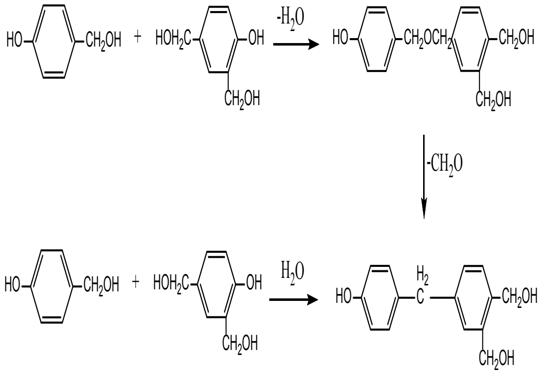

Fig. 4. Polycondensation reaction process, Yanru Xu *et al.,* (2019)[26]

Uyigue. L. *et al.,*[27] they took phenol and formaldehyde in different proportions and prepared novolac and resol-type resins. They also studied the effect of different proportions of phenol and formaldehyde on the reaction and properties of the prepared resin. The resins prepared had higher yield or resol resin than novolac resin. They had achieved higher yield in resol type resin than novolac resin. Furthermore, phenolic resins are modified by hardeners and a cross-linking agent. This is cured by a cross-linking network. And it has good chemical and water resistance as well as good thermal stability. Some phenolic resin can resist at 250^oC to 300^oC temperatures. Commonly used formaldehyde and other aldehydes and ketones are harmful, so phenolic resin requires modification. Current research on phenolic resin is based on the reduction of formaldehyde consumption, cost reduction, and environmental protection. These reports have shown that lignin, resorcinol, cardanol, and other materials can be used as substitutes for improved phenolic resins or further develop the synthesis cycle.[28,29]

A novel phenolic resin was also synthesized by Zhongshun Yuan *et al.,* in which 5-hydroxymethyl furfural was used instead of formaldehyde. They used different amounts of phenol and furfural in different proportions. In which the effect of mole ratios taken in different proportions was studied.[30] Wenzheng Zhang *et al.,*[31] these researchers have likewise investigated the utilization of these resins in structural adhesives, coatings, and advanced composite matrices utilizing sustainable materials. similar to phenolics. The resin was prepared using cardanol, a renewable resource, with formaldehyde. They studied the thermal degradation of cardanol-based phenol formaldehyde resin with comparison of phenol formaldehyde resin. Many research papers have detailed the replacement of bio-based heterocyclic aldehydes from agricultural wastes by furfural with cardanol-furfural resins. And using furfural instead of formaldehyde improves the thermal stability of the phenolic resin. The Thermo gravimetric analyzer (TGA) results showed that cardanol-furfural resin showed higher thermal stability than cardanol-formaldehyde resin. The furfural moiety of cardanol-furfural resins was shown to be thermally more stable than the methylene bridge of cardanol-formaldehyde resins.[32]

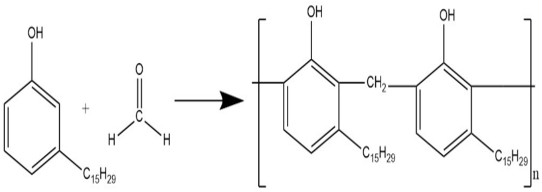

Fig. 5. Synthesis of cardanol-based phenolic resin, PutriRahmawati *et al.,* (2019)[33]

Renewable resources based phenolic resin

The conventional phenolic resin was prepared from formaldehyde and phenol. Formaldehyde used as a raw material in phenolic resins having high toxic nature. Which damages human eyes, and skin, and causes harm by inhalation. This is also to be an atmospheric pollutant.[34] a lot of substitutes for that have been investigated during the previous many years, for example, para-formaldehyde, acetaldehyde, glyoxal, and furfural. In comparison with the others referenced above, furfural is a sort of sustainable heterocyclic aldehyde with a brilliant industrialization prospect. It is primarily yielded from biomass wastes, for example, corncobs and sugarcane bagasse as of now, which is likely use to replace formaldehyde in the synthesis of phenolic resins. In a furfural structure, a furan ring with an aldehyde functional group is attached to in the second position. The replacement of formaldehyde by furfural promotes the thermal stability of the phenolic resin.[35]

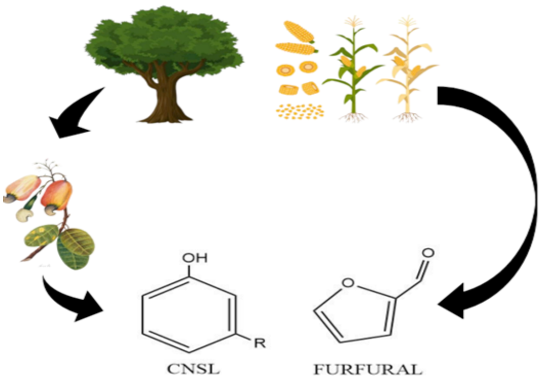

Fig. 6. Renewable resources CNSL, Furfural From bio-mass

Among the agricultural byproduct, Cashew nutshell liquid (CNSL) is the byproduct of the cashew industry and one of the renewable resources is special because it contains cardanol, anacardic acid, which is a phenolic lipid, and cardol, and other chemical compounds are also found in cashew nuts.[36] RiyaSrivastava *et al.,* was a renewable-based resin synthesized by using materials such as cardanol and furfural. They came to the conclusion that the produced cardanol resin can be used as a substitute for phenol resin based on petrochemical derivatives.[37] The tensile and flexural strength of the resin reduced as the amount of cardanol increased when phenol was substituted for it in different molar ratios with formaldehyde. After that, both novolac and resol resins were synthesized with partial substitution of phenol with cardanol. The cardanol-formaldehyde resin was replaced with furfural to enhance its properties. After that substitution of furfural, an increase in mechanical, chemical, and curing properties of cardanol-furfural resin was observed.[38,39]

Kelly Marie and Hambleton *et al.,*[40] collaborated with the Us Environmental protection agency (EPA) in 2012 to develop formaldehyde-free thermosetting polymers from phenolic liquids produced from various biomass sources. Although they succeeded in developing formaldehyde-free phenolic resins, the mechanical properties of phenolic resins were decreased. Yongsheng Zhang *et al.,*[41] developed a bio-based phenolic resin. In which hydrolysis lignin and glucose were used. After that thermal and curing behavior was studied using a hexamethylenetetramine (HMTA) curing agent along with the resin.

Functionalization by Epoxidation

Epoxy phenolic resin is formed by the potential reaction of the epoxide functional group with the hydroxyl group in phenolic resin. Therefore, increasing the functionality of the resin increases its ability to cross-link, creating a more ground polymer with stronger resistance properties. Phenolic resins by themselves produce a high degree of crosslinking through thermosetting, which has high resistance properties to chemicals and water. In these phenolic resins, the polymer repeating unit generated from polymerization may still contain unreacted hydroxyl group (-OH) (C_6H_5OH). Epoxy phenolic resins change this condition by adding an organic group, such as epichlorohydrin ($CL-CH_2-(C_2H_3O)$), that has an epoxy-functional group.[42] K. Shukla S. K. *et al.,*[43] Modified cardanol-based phenolic resins were used with different proportions of epichlorohydrin and functionalized resins were prepared. They studied that, an eco-friendly high-performance thermosetting bio-based epoxy resin is an environmentally friendly alternative compared to commercial epoxy resin.

Mohammad Ansari *et al.,*[44] they synthesized an epoxidized phenolic resin and blend it with shellac for better coating application. In which the abrasion and impact resistance properties are increased with increasing concentration of epoxidized phenolic resin. A unique multifunctional resin was developed by Paulina Bendnarczyk *et al.,*[45] based on the low-viscosity aliphatic trioxide triglycerides of trimethylolethane and acrylic acid. This carboxyl-epoxide addition esterification synthesis was carried out at 90°C. The structure of synthesized copolymers was confirmed by spectroscopic analysis and studied regarding its nonvolatile matter content (NV), and acid value (PAVs), as well as its epoxy equivalent weight (EEW). Natarajan M. *et al.,*[46] synthesized modified phenolic resin prepared by the epoxidation process of cardanol-based novolac resin with epichlorohydrin. It was prepared using a 40% Sodium Hydroxide at 120°C for 5 hours.

Resol type modified phenolic resin was synthesized and studied effect of different concentrations of formaldehyde in synthesis by Shravan Kumar Shukla *et al.,*[47] In which cardanol and formaldehyde were used at 80°C in the presence of a catalyst. The phenolic resin was then modified by an epoxidation process of cardanol/ formaldehyde resin (ERCF) with epichlorohydrin at 120°C. High-resolution gel permeation chromatography was used to measure the viscosity of resol phenolic resin. A two-step mass loss in the thermal degradation process was evident in the Thermo gravimetric Analysis (TGA) results. Also, the result finds that the viscosity increases the molecular weight of the resin also increases.

Cross-linking of Modified Phenolic Resin

Modified epoxidized phenolic resins are used by cross-linking with various curing agents Such as anhydride, amine base hardeners, etc. In which the resin is converted from a low molecular weight to a highly cross-linked network. During this process, there is an increase in the viscosity of the resin at a certain temperature which is the gel point.[48] At the same time, there is a significant increase in the glass transition temperature (Tg) and its physical properties. The gel point is the temperature at which a liquid has a sudden and irreversible change from a viscous liquid to an elastic gel.[49] This high molecular weight is due to the cross-linking of chains of molecules in a network. The amount and type of curing agent determine the curing time (also known as pot life). Thus, pot life at ambient temperature is less than one hour when an amine-based curing agent such as diethylenetriamine (DETA) or triethylenetetramine (TETA) is used with the resin. as shown in Fig. 8 when it is 6 h with m-phenylenediamine. Dicyandiamide (DICY) is considered a latent epoxy resin curing agent and has a pot life of six months when used with liquid or solid epoxy resins. This is because, at ambient temperature, it is not soluble in the resin. The most common curing agents are amines, and the curing process is regulated by an addition reaction between epoxy groups and the active hydrogen of polyamides.[50]

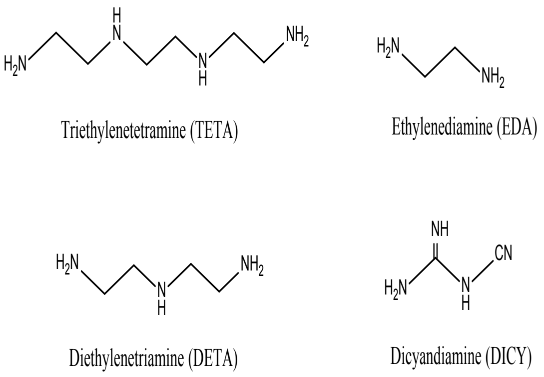

Fig. 7. Amine curing agent for crosslinking, (DETA, TETA, EDA) Wang Zhenyu *et al.,* (2021)[51], (DICY) Feng Wu *et al.,* (2018)[52]

WeikaiPeng *et al.,*[53] prepared composites by taking phenolic and epoxy resin with a Curing accelerator was used. They studied the mechanical and thermal properties and found that when a certain amount of curing accelerator was used, the curing temperature was 118°C which was lower than that of phenolic resin and phenolic/epoxy resin. In addition, they studied the glass transition temperature (Tg), mechanical characterization, and thermal decomposition. The curing ofdiglycidyl ether of bisphenol-A (DGEBA) and novolac epoxy resin blends with modified polyamide was done by Vijay Parasharet. al.,they observed variation in viscosity as the concentration of novolac epoxy resin increased. Also, water permeability increased.[54]

Phenolic Resin Composite

Generally, phenolic composites are cured by a condensation route resulting in a water-resistant matrix characterized by chemical and thermal stability toughness and low smoke and toxic smoke degradation products.[55]

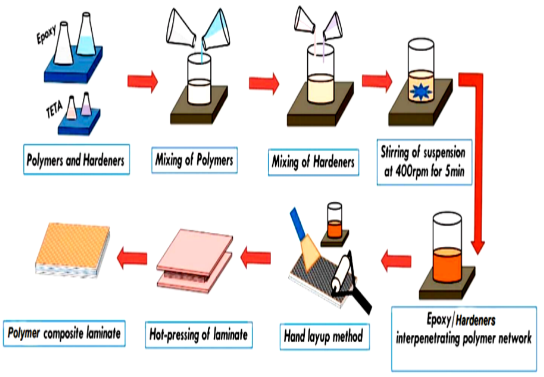

Fig. 8. Composite preparation from a thermosetting resin, B.N.V.S. Ganesh Gupta K *et al.,* (2021)[56]

Synthetic and natural fibers are also considered to be excellent reinforcements as they improve the properties of thermoset composite when incorporated into polymer matrices, where they are used for good adhesion with a matrix. And that composite is found to have good properties such as flexibility, low processing energy consumption, non-toxicity, and low health risk.[57,58] Asad M. Z. *et al.,* prepared Composites using montmorillonite clay and were then subjected to phenol/furfural resol-based resin thermal analysis done by using thermogravimetric analysis (TGA), mechanical and hardness tests showed that the resin and montmorillonite clay are very effectively banded to each other and enhanced properties of the composite compared to commercial plywood materials.[59] P Deepak *et al.,*[60] achieved excellent mechanical properties by using natural fiber and resins with amine-based hardeners such as containing phenalkamine, polyamides, and mixtures of both hardeners with jute fiber-reinforced epoxy resin at room temperature. The curing rate was studied to optimize the best curing agent in selected hardeners and prepared mixes. It achieved better mechanical performance. L. Asaro *et al.,*[61] Focused on studying the development of carbon fiber-reinforced phenolic composite prepregs and how the addition of nano clays to see how they would affect the overall performance of the materials. The resulting prepregs, composite materials, were fabricated by compression molding, and the mechanical properties were characterized. The incorporation of nano clay did not show any change in the behavior of the material in terms of heat dissipation. On the other hand, the modified composite had low fiber content, which reduced its strength and flexural modulus. N. Azalina Ramlee *et al.,*[62] used palm oil empty fruit bunch (OPEFB) and sugarcane bagasse (SCB) fiber-reinforced bio-phenolic hybrid composite. This study's findings suggest that silane treatment enhances the performance of agricultural residue and that bio-composite can be hybridized to create new classes of eco-friendly thermal insulation and environmentally friendly wall-building materials. An eco-sustainable hybridized nano bio-composite was made to reduce the amount of epoxy resin and increase the amount of phenolic resin. These successful trials were performed by fabrication using the hand layup method and analysis of the bonding behavior of the prepared bio-composite samples using a Scanning electron microscope (SEM). The morphology of the material indicates that the fabric layers within the polymer matrix have high bonding properties. S. Akash *et al.,*[63] In addition, the mixed hybrid composite of two fibers, with glass fiber mounted on the fringe because it is hydrophilic, and banana fibers in the center of the composite showed a much higher tensile strength of about 70% than the bi-layer composite of the two fibers.[64]

Properties
Toughness

External or internal toughening substances are typically added to materials to increase toughness. Natural rubber, nitrile rubber, and thermoplastic resin are frequently used as external toughening materials, whereas glass fiber, asbestos, and other materials are frequently used to increase the brittleness of phenolic resin internally. Internal toughening techniques also include etherification of the phenolic hydroxyl group and the introduction of long methylene chains and other exibility groups between phenolic cores.[65] Francisco Cardona *et al.,*[66] reported the co-modification of phenol formaldehyde resin with cardanol-based modified PF resin (CPF) used as a plasticizer and toughening agent. The thermal and mechanical properties of both resins (CPF/PF) were then determined by the resin was increased, the flexural strength and impact toughness of the cured CPF/PF resins also increased proportionally, while the flexural modulus decreased.

The hybrid polymer compositesare fabricated by using abaca-banana-glass reinforced materials and phenolic resins prepared by H. Venkatasubramanian *et al.,*they observed banana fibers has good mechanical and adhesion properties. Phenolic resins have good compatibility and miscibility with the fibers, which significantly increases the toughness and impact resistance.[67]

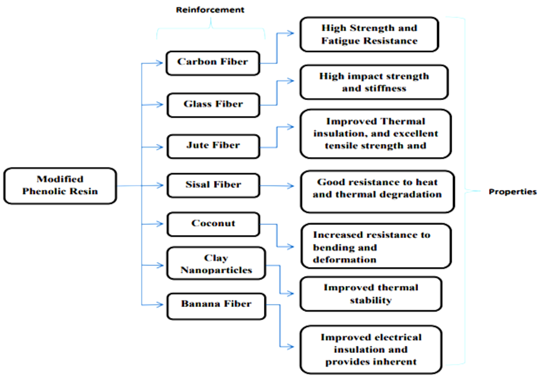

Fig. 9. Modified phenolic resin with different reinforcement, carbon fiber, and nano clay Asaro, Lucia *et al.,*[68], nano clay Jiang, Wei *et al.,*[69], banana, jute, glass, and sisal fibers Frollini, Elisabete *et al.,*[70] N. Saba *et al.,*[71] Raheem, Zainab *et al.,*[72]

Flame Retardant

Better thermal insulating qualities and low flammability are both properties of phenolic resin. The different factors account for the phenolic resin's superior flammability resistance or fire-retardant property: high degree of cross-linking, in which the carbonyl linkages in the polymeric chains occur as a result of the condensation between phenol, and the release of volatile constituents like CO and CO_2, and their capacity to form char that serves as thermal stability.[73] Because phenolic resin has such great qualities as heat resistance, thermal stability, and flame retardancy, it is also used in the automotive, aerospace, and composite materials industries, among other fields. Improvements in phenolic resins long-term-high-temperature oxidation resistance as ablative materials are urgently needed given the aerospace industry's growth.[74] In different ratio, phenolic resin and unsaturated polyester (UP) resin have been combined to create a homogenous blend with increased flame resistance compared to its parent polymers. Limiting oxygen index (LOI) and UL-94 vertical fire tests (ASTM D 3801 testing procedure) were the composites show greater flame retardancy as shown by the UL-94 vertical test (ASTM D 3801 testing procedure), the LOI (ASTM D 2863 Oxygen Index Method) rose with the phenolic resin content. M. M. Marliana *et al.,*[75]

Others properties

Rosin is an unsaturated acid and renewable resource chemical and it is widely used in the modification of phenolic resin, rosin-modified phenolic resin has enhanced properties such as chemical resistance and abrasion resistance and gives high hardness and good gloss.[76] Tammanna Thakur *et al.,*[77] synthesized rosin-modified novolac resin, and they did further modification by epoxidation for bio-based epoxy coating. Commercial-based curing agent like imidoamine is used for crosslinking, and their characteristics are better in mechanical, thermal stabilities and chemical resistance than commercial-based resins.

Table 1: Modification of phenolic resin and properties

Modified Phenolic Resin	Properties	References
Epoxy Modified Phenolic Resin	Excellent mechanical properties, improved oxidation resistance	[44], [47]
Urea, Melamine Modification	Improvement of flame retardant property	[82], [83]
Rosin acid–Modified Phenolic Resin	Improve the drying and gloss, and anti-corrosive properties	[76], [77]
Unsaturated polyester with Phenolic Resin	unsaturated Polyester in order to improve flame resistance property	[75]
Boron- modified Phenolic Resin	Enhancing flame retardant of phenolic resin	[78], [79]
Phosphorus modified Resin	Excellent heat resistance in oxidizing media and flame resistance	[80], [81]
Silicon modified Resin	Improved thermal resistance	[78], [79]

To get high-performance resin with better mechanical properties without using additives, it can be used boron, silicon, and phosphorus can be used in the modification of phenolic resin.[78] Li Zhang *et al.,*[79] prepared boron and silicon-modified phenolic resin, and this resin has a long shelf life and excellent heat resistance, phosphorus-containing phenolic resin can be used for epoxy resin curing, and it provides excellent flame-retardant properties, In order to further increase impact strength and flexibility, the addition of silicon to phosphorus-containing phenolic resin.[80,81]

There is currently a demand for materials that provide properties such as toughness, adhesiveness, and lightweight, which can be increased by the modification of urea and melamine in phenolic resin. Cao Wu *et al.,*[82] synthesized graphene oxide-based urea melamine phenolic resin with glass fiber for composite application. They achieved better mechanical properties and thermal conductivity. And also, melamine phenolic resin provides self-healing properties in microcapsules. These modifications possess the remarkable ability to autonomously repair damage and restore or increase their mechanical properties. these microcapsules, or networks rapture when a crack or fracture appears, releasing the healing agents into the damaged area. Zun-xiang Hu *et al.,*[83] Phenolic resins provide anticorrosive properties that can be used in self-healing microcapsules for coating application. Rajendra S Jadhav *et al.,*[84] synthesized phenolic resin microcapsules and observed that phenolic resin microcapsules repaired cracks and fractures in coatings and had anticorrosive properties. Shown in Figure 10.

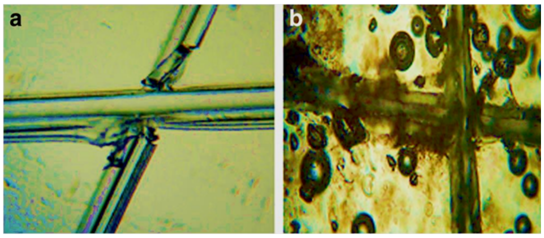

Fig. 10. Phenolic microcapsule coating (a) without microcapsule (b) with microcapsule, Jadhav, Rajendra *et al.,*(2019)[84]

CONCLUSION

A biomassbased modified phenolic thermosets polymer provides high mechanical performance to maintain industrial and commercial interest and outperforms most other polymeric resin systems. In comparison to phenolic resin, the structure of modified phenolic resin and its curing process is very good and fast. Because of their low cost and characteristics, phenolic resins are used in a variety of materials such as fiber, wood, glass, metal, paper, rubber, and so on. Functionalized phenolic resin is important to improve its brittleness, toughness, and capability with natural fibers as well as to expand its commercial application in many fields compared to other thermoset resins. Furthermore, it appears that high-performance engineering materials with noncombustible capability, as well as better properties, are possible with the modification of phenolic resin and fiber-reinforced modified composites. So, its study is attracting the attention of scientists and research students. In engineering applications, most epoxy matrices are used with synthetic as well as natural fibers because of their low cost, low weight, and good adhesion. The use of chemicals based on renewable resources as well as natural fibers results in improved renewability and biodegradability. Also, synthetic fiber and hybrid composite can be used in automotive and aerospace products due to their superior physical, mechanical, and thermal characteristics. Future work would include the development of novel phenolic and bio-phenolic resins, as well as their curing properties. Green composite materials with biodegradable modifying phenolic resin will improve the attention span for both structural and non-structural applications.

ACKNOWLEDGMENT

The author would like to thanks:-

Institute of Science and Technology for advance studies and Research (ISTAR), CVM University, VallabhVidyanagar, voluntarily contributed to this study.

Conflicts of interest

The author declared no potential conflict of interest with respect to the research, authorship, and/or publication of this article, and the authors also declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

REFERENCE

1. Jingkai, Liu.; Shuaipeng, Wang.; Yunyan, Peng.; Jin, Zhu.; Weiwei, Zhao.; Xiaoqing, Liu.; Advances in sustainable thermosetting resins: From renewable feedstock to high performance and recyclability, *Progress in Polymer Science.*, **2021**, *113* https://doi.org/10.1016/j.progpolymsci.2020.101353
2. Jaworski C.; Capricho.; Bronwyn, Fox.; Nishar, Hameed.; *Multifunctionality in Epoxy Resins, Polymer Reviews.*, **2020**, *60*(1), 1-41 https://doi.org/10.1080/15583724.2019.1650063
3. Raj, Mahendrasinh.; Raj Lata.; Maheta, Jaykumar.; Patel, Smit.; Comparative studies on carbon fiber reinforced composites based on trifunctional epoxy resin and commercial epoxy resin. *Polymers and Polymer Composites.*, **2020**, *29*(8), 1282-1290http://dx.doi.org/10.1177/0967391120967513
4. Khalid, Mahmood Zia.; Aqdas, Noreen.; Mohammad, Zuber.; Shazia, Tabasum.; Mohammad, Mujahid.; Recent developments and future prospects on bio-based polyesters derived from renewable resources: A review, *International Journal of Biological Macromolecules.*, **2016**, *82*, 1028-1040, https://doi.org/10.1016/j.ijbiomac.2015.10.040
5. Songqi, Ma.; Tingting, Li.; Xiaoqing, Liu.; Research Progress on Bio-based Thermosetting Resins. *Polymer International.*, **2015**, *65*, 164-170. http://dx.doi.org/10.1002/pi.5027
6. Dodiuk, Hanna.; Handbook of thermoset plastics. William Andrew., **2021**.
7. Ling, Chao.; Guo, Lamei.; Recent Developments and Applications of Hyperbranched Polymers as Flame Retardants. *Journal of Analytical and Applied Pyrolysis.*, **2022**, *169*, 105842. http://

dx.doi.org/10.1016/j.jaap.2022.105842

8. Boneka, Arfah.; Uyup, Mohd Khairun Anwar.; Lee, Seng Hua.; Nordahlia, As.; Salim, Sabiha.; Ashaari, Zaidon.; Sorption isotherm and physico-mechanical properties of kedondong *(Canarium spp.)* wood treated with phenolic resin, *Construction and Building Materials.*, **2021**, *288*, 123060. https://doi.org/10.1016/j.conbuildmat.2021.123060
9. Weijun, Yang.; Marco, Rallini.; Maurizio, Natali.; Jose, Kenny.; Piming, Ma,Weifu, Dong.; Luigi, Torre.; Debora, Puglia.; Preparation and properties of adhesives based on phenolic resin containing lignin micro and nanoparticles: *A comparative study, Materials & Design.*, **2019**, *161*, 55-63, https://doi.org/10.1016/j.matdes.2018.11.032
10. Gérardin, P.; New alternatives for wood preservation based on thermal and chemical modification of wood-a review. *Annals of Forest Science*., **2016**, *73*, 559–570. https://doi.org/10.1007/s13595-015-0531-4
11. Zixuan, Lei.; Jingru, Ji.; Qianqiu, Wu.; Junjie Zhang.; Yixun Wang.; Xinli Jing.; Yuhong Liu.; Curing behavior and microstructure of epoxy-POSS modified novolac phenolic resin with different substitution degree, *Polymer.*, **2019**, *178*, 121587.https://doi.org/10.1016/j.polymer.2019.121587
12. Feng, Ailing.; Wu, Guanglei.; Pan, Chen.; Wang, Yiqun.; The Behavior of Acid Treating Carbon Fiber and the Mechanical Properties and Thermal Conductivity of Phenolic Resin Matrix Composites, *Journal of Nanoscience and Nanotechnology.*, **2017**, *17*, 3786-3791. https://doi.org/10.1166/jnn.2017.13997
13. Joseph, P. Greene.; 12-Polymer Composites, *Automotive Plastics and Composites.*, **2021**, 191-222. https://doi.org/10.1016/B978-0-12-818008-2.00007-6
14. Invernizzi, M.; Natale, G.; Levi, M.; Turri, S.; Griffini, G. UV-Assisted 3D Printing of Glass and Carbon Fiber-Reinforced Dual-Cure Polymer Composites., *Materials.,* **2016**, *9*, 583. https://doi.org/10.3390/ma9070583
15. Hirano, Kazuhisa.; Asami, Masakatsu.; Phenolic resins-100 years of progress and their future, *Reactive and Functional Polymers.*, **2013**, *73*, 256-269. https://doi.org/10.1016/j.reactfunctpolym.2012.07.003
16. Daria I. Poliakova.; Oleg S. Morozov.; Sergey S. Nechausov.; Ekaterina A. Afanaseva.; Boris A. Bulgakov.; Alexander V. Babkin.; Alexey V. Kepman.; Viktor V. Avdeev.; Fast curing phthalonitrile modified novolac resin: Synthesis, curing study and preparation of carbon and glass fibric composites, *Reactive and Functional Polymers.*, **2022**, *181*, 1381-5148 https://doi.org/10.1016/j.reactfunctpolym.2022.105450
17. Mohd, Asima.; Naheed, Saba.; Mohammad, Jawaid.; A Review on Phenolic Resin and its Composites, *Current Analytical Chemistry.*, **2018**, *14*(3), 185-197 http://dx.doi.org/10.2174/1573411013666171003154410
18. Jie, Liu.; Dipan, Xuan.; Jing, Chai.; Diandian, Guo.; Synthesis and Thermal Properties of Resorcinol–Furfural Thermosetting Resin, *ACS Omega.*, **2020**, *5*, 10011–10020 https://doi.org/10.1021/acsomega.0c00365
19. Mohd, Asima.; Naheed, Saba.; Mohammad, Jawaid.; A Review on Phenolic Resin and its Composites*, Current Analytical Chemistry,* **2018**, *14*(3), 185-197 http://dx.doi.org/10.2174/1573411013666171003154410
20. Renda, C. G.; Bertholdo, R.; Study of phenolic resin and their tendency for carbon graphitization. *J Polym Res.*, **2018**, *25*(241). https://doi.org/10.1007/s10965-018-1635-y
21. Shuklaa, Shrawan Kumar.; Maithani, Arun.; Studies on the effect of concentration of formaldehyde on the synthesis of resole-type epoxidized phenolic resin from renewable resource material, *Designed Monomers and Polymers.*, **2014**, *17*, 69-77 http://dx.doi.org/10.1080/15685551.2013.840469
22. Johannes Karl Fink.; Chapter 4-Phenol/Formaldehyde Resins, In Plastics Design Library, Reactive Polymers Fundamentals and Applications (Second Edition), *William Andrew Publishing.*, **2013**, 155-177 https://doi.org/10.1016/B978-1-4557-3149-7.00004-8
23. Caillol, Sylvain.; Virieux, David.; David, Ghislain.; Foyer, Gabriel.; Chanfi, Bibi-Hadidja. Aromatic dialdehyde precursors from lignin derivatives for the synthesis of formaldehyde-free and high char yield phenolic resins. *European Polymer Journal.*, **2016**, *77*, 65-74. http://dx.doi.org/10.1016/j.eurpolymj.2016.02.018
24. Foyer, G.; Chanfi, B.-H.; Boutevin, B.; Caillol,S.; David, G.; New method for the synthesis of formaldehyde-free phenolic resins from lignin-based aldehyde precursors, *European Polymer Journal.*, **2016**, *74*, 296-309 https://doi.org/10.1016/j.eurpolymj.2015.11.036

25. Masli, M.; Zakaria, Sarani.; Chia, Chin-hua.; Roslan, Rasidi.; Polymeric reaction between aldehyde group in furfural and phenolic derivatives from liquefaction of oil palm empty fruit bunch fiber as phenol-furfural resin. *AIP Conf. Proc.*, **2016**, *1784*, 040030 http://dx.doi.org/10.1063/1.4966816
26. Xu, Yanru.; Guo, Lifang.; Zhang, Haonan.; Zhai, Huamin.; Ren, Hao. Research status, industrial application demand and prospects of phenolic resin, *RSC Adv.*, **2019**, *9*, 28924–28935, DOI: 10.1039/c9ra06487g
27. L. Kubiangha, Uyigue.; Estimation of Product Yield and Kinetic Parameters of Phenolic-Resin Pre-Polymer Synthesis using Acid and Base Catalyst, *IOSR Journal of Engineering (IOSRJEN).*, **2018**, *8*(9), ISSN (e): 2250-3021, ISSN (p): 2278-8719
28. Shuirong Li, and Zhifeng Zheng, Synthesis and Thermal Properties of Resorcinol–Furfural Thermosetting Resin, *ACS Omega.,* **2020**, *5*, 10011–10020. https://dx.doi.org/10.1021/acsomega.0c00365
29. Yanru Xu.; Lifang Guo. The Royal Society of Chemistry, Research status, industrial application demand and prospects of phenolic resin, *RSC Adv.*, **2019**, *9*, 28924–28935. http://dx.doi.org/10.1039/C9RA06487G
30. Yuan, Zhongshun.; Zhang, Yongsheng.; Xu, Chunbao. Synthesis and thermomechanical property study of Novolac phenol-hydroxymethyl furfural (PHMF) resin. *RSC Advances*. **2014**, *4*, 31829. http://dx.doi.org/10.1039/C4RA04458D
31. Zhang, Wenzheng.; Jiang, Ning.; Zhang, Tingting.; Li, Tiansheng.; Thermal stability and thermal degradation study of phenolic resin modified by cardanol, *Emerging Materials Research*., **2020**, *9*(1), 180-185. https://doi.org/10.1680/jemmr.18.00133
32. Laura Puchot, Cardanol: a bio-based building block for new sustainable and functional materials, PhD THESIS, Laboratoire de Physico-chimie des Polymers et des Interfaces, EA 2528, De l'Université de Cergy-Pontoise., **2016**.
33. Putri, Rahmawati.; Ari, HandonoRamelan.; Marliyana, SoeryaDewi.; Neng, Sri Suharty.; Sayekti, Wahyuningsih, Synthesis of Cardanol-Based Novolac Resin from Cashew Nut Shell Liquid, *Journal of Engineering Science*., **2019**, *15*, 23–33 https://doi.org/10.21315/jes2019.15.3
34. Pontel, Lucas.; Formaldehyde metabolism and its impact on human health. *Current Opinion in Toxicology*., **2018**, *9*, 28-34. https://doi.org/10.1016/j.cotox.2018.07.001
35. Jie Liu.; DipanXuan.; Jing Chai.; Diandian Guo.; Yuanbo Huang.; Synthesis and Thermal Properties of Resorcinol–Furfural Thermosetting Resin, *ACS Omega*., **2020**, *5*, 10011–10020 https://dx.doi.org/10.1021/acsomega.0c00365
36. Laura Puchot.; Cardanol: a bio-based building block for new sustainable and functional materials, PhD THESIS, Laboratoire de Physico-chimie des Polymères et des Interfaces, EA 2528, De l'Université de Cergy-Pontoise., **2016**.
37. Srivastava R.; Srivastava D.; Mechanical, chemical, and curing characteristics of cardanol-furfural-based novolac resin for application in green coatings. *J Coat Technol Res*., **2015**, *12*, 303–31. https://doi.org/10.1007/s11998-014-9630-7
38. Sarika, P.R.; Nancarrow, P.; Khansaheb, A.; Ibrahim, T. Bio-Based Alternatives to Phenol and Formaldehyde for the Production of Resins. *Polymers*., **2020**, *12*, 2237. https://doi.org/10.3390/polym12102237
39. Parameswaran, P.; Abraham, B.; Thachil, E.T. Cardanol-based ResolPhenolics–A Comparative Study. *Prog. Rubber Plast. Recycl. Technol*., **2010**, *26*, 31–50. (Cross reference)
40. Hambleton, Kelli Marie; "Synthesis and characterization of thermosetting epoxy resins from lignin-inspired phenolics". Theses and Dissertations., **2020**, 2841 https://rdw.rowan.edu/etd/2841
41. Zhang, Y.; Yuan, Z; Xu, C.; Engineering biomass into formaldehyde-free phenolic resin for composite materials, *AIChE Journal*., **2014**, *61*(4), 1275-1283.https://doi.org/10.1002/aic.14716
42. Bogdana Bashta and OlenaAstakhova, Epoxy Resins Chemical Modification By Dibasic Acids, *Chemistry & Chemical Technology*., **2014**, *8*, 52-58. http://dx.doi.org/10.23939/chcht08.03.309
43. Shukla, Shrawan.; Srivastava, Kavita.; Srivastava, Dr. Deepak. Synthesis, Spectral and Thermal Degradation Kinetics of the Epoxidized Resole Resin Derived from Cardanol. *Advances in Polymer Technology*., **2015**, *34*, 21469. http://dx.doi.org/10.1002/adv.21469

44. Ansari, Mohammad.; Sarkhel, Gautam.; Goswami, Dipendra.; Baboo, Bangali.; Coating properties of shellac modified with synthesisedepoxidised-novolac resin. *Pigment & Resin Technology.*, **2014**, *43*, 314-322 http://dx.doi.org/10.1108/PRT-06-2013-0111

45. Bednarczyk, P.; Irska, I.; Gziut, K.; Ossowicz-Rupniewska, P. Novel Multifunctional Epoxy (Meth)Acrylate Resins and Coatings Preparation via Cationic and Free-Radical Photopolymerization. *Polymers.,* **2021**, *13*, 1718 https://doi.org/10.3390/polym13111718

46. M, Natarajan.; Sevi, Murugavel.; Cure kinetics of bio-based epoxy resin developed from epoxidizedcardanol–formaldehyde and diglycidyl ether of bisphenol–A networks. *Journal of Thermal Analysis and Calorimetry.*, **2016**, *125*, 387-396. http://dx.doi.org/10.1007/s10973-016-5417-7

47. Shuklaa, Shrawan Kumar.; Maithani, Arun.; Studies on the effect of concentration of formaldehyde on the synthesis of resole-type epoxidized phenolic resin from renewable resource material, *Designed Monomers and Polymers.*, **2014**, *17*, 69–77 http://dx.doi.org /10.1080/15685551.2013.840469

48. Raj M.; Maheta J.; Raj L.; Synthesis characterization and application of hexafunctional epoxy resin and comparison against commercial epoxy resin, *Polymers and Polymer Composites.*, **2022**, *30* https://doi.org/10.1177/09673911221076721

49. Odagiri, N.; Shirasu, K.; Kawagoe, Y.; Amine/epoxy stoichiometric ratio dependence of crosslinked structure and ductility in amine-cured epoxy thermosetting resins. *J Appl Polym Sci.*, **2021**, *138*(23), 50542 https://doi.org/10.1002/app.50542

50. Varma, IK.; Gupta, VB.; thermosetting resin-properties, Comprehensive Composite *Materials II.*, **2018**, *2*, 401-468 https://doi.org/10.1016/B978-0-12-803581-8.03829-7

51. Wang, Z.; Gnanasekar, P.; Nair, S.S.; Yi, S.; Yan, N. Curing Behavior and Thermomechanical Performance of Bioepoxy Resin Synthesized from Vanillyl Alcohol: Effects of the Curing Agent. *Polymers.*, **2021**, *13*(17), 2891.https://doi.org/10.3390/polym13172891

52. Feng Wu.; Xingping Zhou and Xinhai Yu, Reaction mechanism, cure behavior and properties of a multifunctional epoxy resin, TGDDM, with latent curing agent dicyandiamide, *RSC Adv.*, **2018**, *8*, 8248-8258, https://doi.org/10.1039/C7RA13233F

53. Peng, Weikai.; Chen, Xi.; Wang, Jun; Study on the curing behavior of polythiol/phenolic/epoxy resin and the mechanical and thermal properties of the composites. *Mater. Res.*, **2021**, *8*, 055302. https://doi.org/10.1088/2053-1591/abeb4a

54. Parashar, Vijay.; Synthesis and Characterization of DGEBA Epoxy and Novolac Epoxy Blends and Studies on their Curing and Mechanical Behavior. *Knowledge of research.*, **2015**, *2*, 30 http://dx.doi.org/10.7598/kor2015.123

55. Naveen, J.; Muthukumar, C.; Jawaid, M. Thermal Properties of Phenolic Composites. In: Jawaid, M., Asim, M. (eds) Phenolic Polymers Based Composite Materials. Composites Science and Technology. *Springer.*, **2021**, 191-205 https://doi.org/10.1007/978-981-15-8932-4_12

56. Gupta K, B N V S Ganesh.; Hiremath, Mritunjay.; Ray, Bankim.; Prusty, Rajesh. Improved mechanical responses of GFRP composites with epoxy-vinyl ester interpenetrating polymer network, *Polymer Testing.*, **2021**, *93*, 107008 https://doi.org/10.1016/j.polymertesting.2020.107008

57. Ouarhim, Wafa.; Nadia, Zari.; Bouhfid, Rachid.; Qaiss, Abou. Mechanical performance of natural fibers–based thermosetting composites. In: Mechanical and physical testing of biocomposites, fibre-reinforced composites and hybrid composites. *Wood head Publishing, Elsevier.*, **2019**, 43–60.https://doi.org/10.1016/B978-0-08-102292-4.00003-5

58. Rashid, Bushra.; Leman, Z.; Jawaid, Mohammad.; Ghazali, Mariyam.; Ishak, Mohamad.Influence of treatments on the mechanical and thermal properties of sugar palm fibre reinforced phenolic composites. *BioResources.*, **2017**, *12*, 1447–1462. http://dx.doi.org/10.15376/biores.12.1.1447-1462

59. Asad, M.Z.; Mahmood, A.; Hussain Shah, S.T. Phenol-Furfural Resin/Montmorillonite Based High-Pressure Green Composite from Renewable Feedstock *(Saccharummunja)* with Improved Thermo-Mechanical Properties. *Polymers.*, **2020**, *12*, 1562 https://doi.org/10.3390/polym12071562

60. P. Deepak.; R. Vignesh Kumar.; Effects of Polyamide and/or Phenalkamine Curing Agents on the Jute Fibre Reinforcement with Epoxy Resin Matrix, *Materials Today: Proceedings.*, **2017**, *4*(2), 2841–2850. https://doi.org/10.1016/j.matpr.2017.02.164
61. Asaro, Lucia.; Rivero, Guadalupe.; Manfredi, Liliana.; Alvarez, Vera.; Rodriguez, Exequiel. Development of carbon fiber/phenolic resin prepregs modified with nanoclays. *Journal of Composite Materials.,* **2015**, *50*(10), 1287-2300. http://dx.doi.org/10.1177/0021998315590866
62. Ramlee,NorAzlina.;Jawaid, Mohammad.; Zakaria, Shaikh.; Zainudin, E. S.; Alamery, Salman. Effect of surface treatment on mechanical, physical and morphological properties of oil palm/bagasse fiber reinforced phenolic hybrid composites for wall thermal insulation application, *Construction and Building Materials.*, **2021**, *276*, 122239. https://doi.org/10.1016/j.conbuildmat.2020.122239
63. S Akash.; M. Ramachandra.; Fabrication and Bonding Behavior of Phenalkamine Resin Based Hybridized Silver Nano Bio-Composite Laminates with Less Epoxy Content, *AIP Conference Proceedings.*, **2020**, *2274*(1), 030027. https://doi.org/10.1063/5.0022649
64. Prashanth, B.; Manjunatha, T.; Gouda, P.; Edacherian, Abhilash. Improved Mechanical Properties of Jute-Banana Fiber Phenol Formaldehyde Composites through Low-Cost Portable Hot Pressing Machine. *Materials Performance and Characterization.*, **2021**, *10*, 20200025 http://dx.doi.org/10.1520/MPC20200025
65. Yanru Xu.; Lifang Guo. The Royal Society of Chemistry, Research status, industrial application demand and prospects of phenolic resin, *RSC Adv.*, **2019**, *9*, 28924–28935. http://dx.doi.org/10.1039/C9RA06487G
66. Cardona, Francisco.; Lau, Kin tak.; Fedrigo, Jessica. Novel Phenolic Resins with Improved Mechanical and Toughness Properties, *Journal of Applied Polymer Science.*, **2012**, *123*, 2131–2139. http://dx.doi.org/10.1002/app. 34719
67. Venkatasubramanian, H.; Srinivasan, Raghuraman. Mechanical behaviour of abaca-glass-banana fibre reinforced hybrid composites. *Journal of Engineering Science and Technology.*, **2015**, *10*(8), 958-971.
68. Asaro, Lucia.; Rivero, Guadalupe.; Manfredi, Liliana.; Alvarez, Vera.; Rodriguez, Exequiel. Development of carbon fiber/phenolic resin prepregs modified with nanoclays. *Journal of Composite Materials.*, **2015**, *50*(10), 1287-2300 http://dx.doi.org/10.1177/0021998315590866
69. Shukla, S R.; Sharma, S.; Improving physico-mechanical properties, thermal stability and decay resistance of fast grown Meliadubia wood by nanoclay fortified phenolic resin impregnation. *Journal of the Indian Academy of Wood Science.*, **2022**, *19*, 1-15 http://dx.doi.org/10.1007/s13196-022-00291-x
70. Nicolais, L.; Frollini, E.; Castellan, A. Phenolic Resins and Composites. *In Wiley Encyclopedia of Composites.*, **2012** https://doi.org/10.1002/9781118097298.weoc167
71. N. Saba.; M. Jawaid.; Othman Y. Alothman.; M. T. Paridah, A review on dynamic mechanical properties of natural fibre reinforced polymer composites, *Construction and Building Materials.*, **2016**, *106*, 149-159, https://doi.org/10.1016/j.conbuildmat.2015.12.075
72. Raheem, Zainab. Composite materials handbook, *Polymer Matrix Composites.*, **2019**. *2*.
73. Jawaid, Mohammad.; Asim, Mohammad. Phenolic Polymers Based Composite Materials, Composites Science and Technology. **2018** https://doi.org/10.1007/978-981-15-8932-4
74. Yanru Xu.; Lifang Guo. The Royal Society of Chemistry, Research status, industrial application demand and prospects of phenolic resin, *RSC Adv.*, **2019**, *9*, 28924–28935. http://dx.doi.org/10.1039/C9RA06487G
75. Marliana, M.; Hassan, Azman.; Mohd Yunus.; Nor Yuziah.; H. P. S, Abdul Khalil.; Inuwa, Ibrahim.; Syakir, M. I.; Haafiz, M. K. Flame Retardancy, Thermal and Mechanical Properties of Kenaf Fiber Reinforced Unsaturated Polyester/Phenolic Composite, *Fibers and Polymers.,* **2016**, *17*(6), 902-909. http://dx.doi.org/10.1007/s12221-016-5888-y
76. Zhang, Qing.; Huang, Li.; Wu, Mei.; Yu, Xiao. Primary Study on the Improvement and Application of Formulation Optimization of 2116# Rosin Modified Phenolic Resin. *Key Engineering Materials.*, **2020**, *837*, 168-173. http://dx.doi.org/10.4028/www.scientific.net/KEM.837.168

77. Thakur, T.; Jaswal, S.; Gaur, B.; Singha, AS. Thermo-mechanical properties of rosin-modified o-cresol novolac epoxy thermosets comprising rosin-based imidoamine curing agents. *Polym Eng Sci.*, **2020**, *61*, 115-135.
78. Li, Shan.; Chen, Fenghua.; Zhang, Bo-xing.; Luo, Zhenhua.; Li, Hao.; Zhao, Tong. Structure and improved thermal stability of phenolic resin containing silicon and boron elements. *Polymer Degradation and Stability.*, **2016**, *133*, 321-329. http://dx.doi.org/10.1016/j.polymdegradstab.2016.07.020
79. Zhang, Li.; Zhang, Yihe.; Wang, Lei.; Yao, Yalin.; Wu, Juntao.; Sun, Yi.; Tian, Moufeng.; Liu, Jing. Phenolic resin modified by boron-silicon with high char yield. *Polymer Testing.*, **2018**, *73*, 208-213 http://dx.doi.org/10.1016/j.polymertesting. 2018.11.033
80. Bao, Q.; Li, W.; Liu, Y; Wang, Q.; Preparation and Properties of Phosphorus and Silicon modified Phenolic Resin with High Ablation Resistance. *Polymer International.*, **2019**, *68*, 1322-1331. http://dx.doi.org/10.1002/pi.5819
81. Deng, P.; Liu, Y.; Liu, Y.; Xu, C.; Wang, Q.; Preparation of phosphorus-containing phenolic resin and its application in epoxy resin as a curing agent and flame retardant. *Polymers for Advanced Technologies.*, **2018**, *29*, 1294-1302 https://doi.org/10.1002/pat.4241
82. Wu, Cao.; Chen, Zhaofeng.; Wang, Fei.; Enhanced Anti-ablation and Alkali Corrosion Resistance of Graphene Oxide Modified Urea-Melamine-Phenol Formaldehyde Composites Reinforced by R-Glass Fiber. *Journal of Inorganic and Organometallic Polymers and Materials.*, **2019**, *29*, 1818-1826 https://link.springer.com/article/10.1007/s10904-019-01144-w
83. Hu, Xiangming.; Influence of synthetic conditions on the performance of melamine-phenol-formaldehyde resin microcapsules. *High Performance Polymers.,* **2019**, *31*(2), 197-210 http://dx.doi.org/10.1177/ 0954008318758489
84. Jadhav, Rajendra.; Mane, Vishal.; Bagle, Avinash.; Hundiwale, Dilip.; Mahulikar, Pramod.; Waghoo, Gulzar.; Synthesis of multicore phenol formaldehyde microcapsules and their application in polyurethane paint formulation for self-healing anticorrosive coating. *International Journal of Industrial Chemistry.*, **2013**, *4*(31) http://dx.doi.org/10.1186/2228-5547-4-31