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Phenolic Polymers Based Composite Materials

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Composites Science and Technology
ISBN 978-981-15-8931-7 ISBN 978-981-15-8932-4 (eBook)
https://doi.org/10.1007/978-981-15-8932-4

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Preface

Phenolic resins are the one of the oldest resins and have received great attention from academic researchers, industrial works and one of good and acceptable resin for industrial applications among all thermoset resins. Several effective attempts have been made to explore different synthesis processes of producing phenolic in a more useful and advanced way. Phenolic resin has some peculiar properties such as easy handling, toughness, excellent flame retardance, good heat resistance, low smoke/toxic gas evolution and highly thermal stability. Since the date of innovation of phenolic resin, wood/fibre reinforced biocomposites and composites products have been produced for various applications.

This book will explore potentiality of the chemical structure of phenolic resins and its derivatives. Nowadays, synthesis of phenolic resin from natural resources or biomass attracting researchers and academician to conduct in depth characterization such as mechanical, thermal, and rheological properties to look suitability of bio-phenolic resin in market as compared to synthetic phenolic resin. Phenolic will also be used with biodegradable materials to provide lightweight materials for outdoor applications. With this approach, phenolic resin can easily enter in 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 beginning and transformation of phenolic which helps to understand this polymer and its utilization in the real world as per the need of markets. This book covered history of phenolic and its transformation (derivative), biobased phenolic natural fibre-based phenolic composites, wood-based phenolic composites, nanocellulose phenolic composites, thermal and fire retardant properties of phenolic and its composites. This versatile version of phenolic resin and its composites helps to develop lightweight and durable components which can be used for heavy duty.

We are highly thankful to all authors who contributed book chapters and provide their valuable ideas and knowledge in this edited book. We attempt to gather all the scattered information of authors from diverse fields around the world (Brazil, China, Australia, Bangladesh, USA, Thailand, India and Malaysia) in the areas of phenolic composites and biocomposites and finally complete this venture in a fruitful way. We greatly appreciate 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

Mohammad Jawaid
Mohammad Asim

Contents

About the Editors

Dr. Mohammad Jawaid is currently working as High Flyer Fellow (Professor) at Biocomposite Technology Laboratory, Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia, Serdang, Selangor, Malaysia, and also Visiting Professor at the Department of Chemical Engineering, College of Engineering, King Saud University, Riyadh, Saudi Arabia, since June 2013. Dr. Mohammad Jawaid received his Ph.D. from Universiti Sains Malaysia, Malaysia. He has more than ten years of experience in teaching, research and industries. His area of research interests includes hybrid reinforced/filled polymer composites and advance materials. So far, he has published 37 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 two patents and five copyrights. H-index and citation in Scopus are 51 and 11838, and in Google scholar, H-index and citation are 60 and 16232. He is founding Series Editor of Composite Science and Technology Book, and Springer Proceedings in Materials from Springer Nature. He is also International Advisory Board member of Springer Series on Polymer and Composite Materials. His five published review papers under hot cited articles in science direct during 2016–2019. He is reviewer of several high impact ISI journals (90 journals).

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Phenolic Resin and Its Derivatives

Caroliny Santos, Thiago Santos, Rubens Fonseca, Kátia Melo, and Marcos Aquino

Abstract Phenolic substances were the first thermosetting resins to be manufactured and marketed worldwide. These are produced from synthetic components that can be made from the chemical reaction process called polycondensation. In addition, this resin can be further cured by forming covalent crosslinking bonds in the process of forming composites based on fibrous materials. It is undeniable that phenolic resin and its derivatives when combined with fibrous materials enable the development of a wide variety of products. In this chapter 1 we will briefly discuss the use and types of Phenolic resin and its derivatives, the classification of thermoset matrices as well as the importance of phenolic matrix and its applications in composites. Phenolic resins can be divided into novolac and resol (polybenzoxazine, bisphenol A, bisphenol F are the major ones). Since phenolic resins are incorporated by fibers, they favor the high performance (stress, Flexural, heat resistance, MOE, strain and tenacity) and longitudinal mechanical behavior of phenolic composites.

Keywords Thermosetting resins · Novolac · Resole · Crosslinking bonds

1 Introduction

As phenolic resins are polymers resistant to high temperatures, chemicals and also presence of water. These were one of the first resins of industrial production. They are typically opaque and selected in their color (from tons of dark yellow to medium tons), and have a low cost coupled with high performance (Pilato 2013). They have good water and chemical resistance, but the fracture, elongation is low and therefore brittle (Biron 2004). They can solidify using acids or alkalis and cure without the presence of catalysts using only high temperatures. In the curing process, it is necessary to use

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M. Jawaid and M. Asim (eds.), *Phenolic Polymers Based Composite Materials*, Composites Science and Technology,
https://doi.org/10.1007/978-981-15-8932-4_1

Table 1 Applications for phenolic resins

Use area	Type of phenolic resin	Market
Ablation	Novolac and resole	Aerospace ablative
Abrasives	Novolac and/or resole	Variety of abrasive products (bonded, coated, and non-woven)
Composites (knitted, woven, non-woven and etc.)	Novolac, resole and its derivations	Multi-applications depend only on processing method (resin transfer molding, pultrusion, profile extrusion, filament winding and hand lay-up), mainly used aircraft and other aerospace.
Thermal and electrical insulation	Novolac, resole and its derivations	Electrical
Friction	Novolac and resole	Automotive, industrial, oil field and marine friction.
Dimensional stability; chemical resistance (closures)	Novolac and resole	Packaging
Adhesives	Novolac and resole	Wood bonding (wood, wood fibers, particleboard or wafer-board)

high pressure due to the presence of small molecules that can separate at this stage; curing resin has good compression performance (Nemoto et al. 2009; Konishi et al. 2010).

Phenolic resins are used in molding powder and short fiber molding compound, and can be used for fiberglass composite materials, tough materials. It is rarely used in carbon fiber and organic fiber composite material (Wang et al. 2011a; Carr 2017). The use of phenolic resins may be in addition to fillers or other reinforcements such as wood dust, cellulose, silica, carbon, glass, mica, paper and synthetic fibers, and the largest market segments using this resin are those related to wood products (plywood and chipboard) as bonding agents, thermal insulation and molding compounds, and are used in a range of applications, from lab benches, circuit boards, to billiard balls, to base contact adhesives rubber as adhesion promoter and adhesive (Allen and Ishida 2001). In foundry resins, they serve as sand binders in the manufacture of shell molds and cores. Phenolic resins are sometimes used instead of epoxies in fiberglass and carbon reinforced composites when some strength can be sacrificed in favor of superior fire resistance and lower smoke toxicity. In coatings, phenolic resins may be used alone or as a modifier resin, which serves as an adhesion promoter, crosslinker or hardener (Allen and Ishida 2001; Kopf 2002).

Composites derived from phenolic molding are well known for their thermal and dimensional stability and, in particular, for their unfriendliness (M et al. 2019). They also have low water absorption characteristics and are good electrical insulators. These thermosetting materials are chemically resistant to attack from common solvents, weak acids, weak bases and short-term ultraviolet exposure (Allen and Ishida 2001; Hirano and Asami 2013).

2 Polimerization

In the polymerization process, phenolics are produced by the polycondensation reaction between phenols and formalin (40% aqueous formaldehyde solution). Trifunctional phenol reacts with difunctional formaldehyde, resulting in a three-dimensional matrix when the reaction is performed beyond the gel point. After gel point, additional cure results in a thermoset (Pizzi and Ibeh 2013). Curing Process of a Phenolic Resin Composite: Phenolic resin is used in the dry process and has three stages in its curing process as shown in Fig. 1.

Stage 1: Phenolic resin is thermoset in its initial state, soluble and fusible. At this time, the resin is in “stage A”. It has low or medium molecular weight, with many polar groups and is soluble in alcohol.

Stage 2: Known as “stage B”, at this time the resin ceases to be soluble and becomes insoluble and infusible. This is due to warming conditions that cause intermediate stages of change. After impregnating the fibers into the resin, it is important not only to remove the solvent, but also to pre-cure the resin at the same time to control the degree of crosslinking, ensuring that the resin turns from A to B.

Stage 3: In stage C, the phenolic resin that was in stage B undergoes additional heating and will be completely solid, i.e. the phenolic will be cured (Wang et al. 2011b).

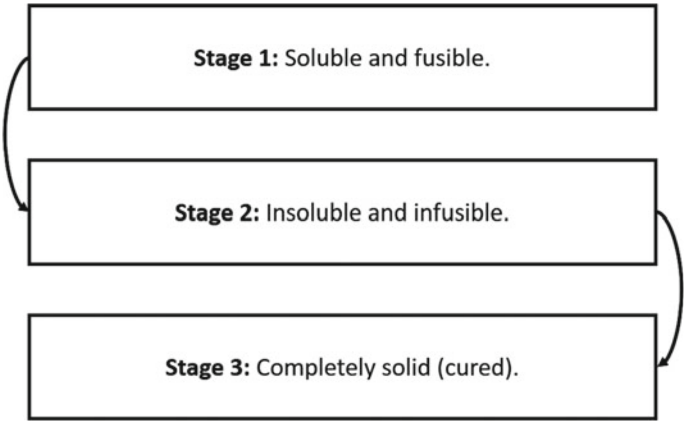

Fig. 1 Curing process of a phenolic resin composite

3 Classification of Phenolic Resins

There are two more traditional varieties of phenolic resins. They have high resistance to high temperatures, chemical loads and high-water loads. Phenolic resins are widely used condensation polymers because of their high chemical resistance, electrical insulation, and dimensional stability (De Medeiros et al. 2003). They are typically opaque and vary in color (from dark yellow to reddish tones), have an excellent market price coupled with excellent performance (Ibeh 1998). Phenolic resins are subdivided into two groups, which must be processed before the gel point. Based on this, there are two main types of phenolic resins:

Resoles or single stage resins.

Novolacs or two stage resins.

3.1 Novolac

Novolac is known as "two-stage phenolics". These resins are thermoplastic in nature because they melt with the application of heat, but without reticular as shown in Fig. 2. Unlike resolutions, novolacs resins require the addition of a hardener to cure this insoluble and infusible product (Fig. 3). Its attainment may occur through the reaction of phenol with formaldehyde in a highly acidic environment which may be oxalic, sulfuric, hydrochloric and toluene sulfonic. The reaction mixture is usually diluted in formaldehyde with 0.75 ± 0.85 mol of formaldehyde for each mole of phenol (Amrit Puzari 2010).

Polymerization reaction occurs by electrophilic substitution, producing a condensation reaction generating products with straight or slightly branched chains, linked by methylene bridges. The crosslinked compound is almost always hexamethylenetetramine (HMTA), although paraformaldehyde or trioxane can sometimes be used. After heating, the added HMTA decomposes to release the formaldehyde needed to complete the crosslinking reaction as well as an ammonia byproduct. Intermediate Novolacs are generally solid and brittle/brittle at room temperature and have a molecular weight below 5000. They have an almost infinite shelf life and are usually flaked, mixed with 8 ± 15% HMTA and then ground to powder. before processing (Wang et al. 2015).

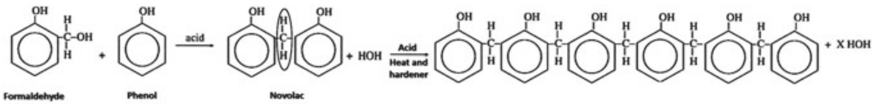

Fig. 2 Synthesis of novolac resins

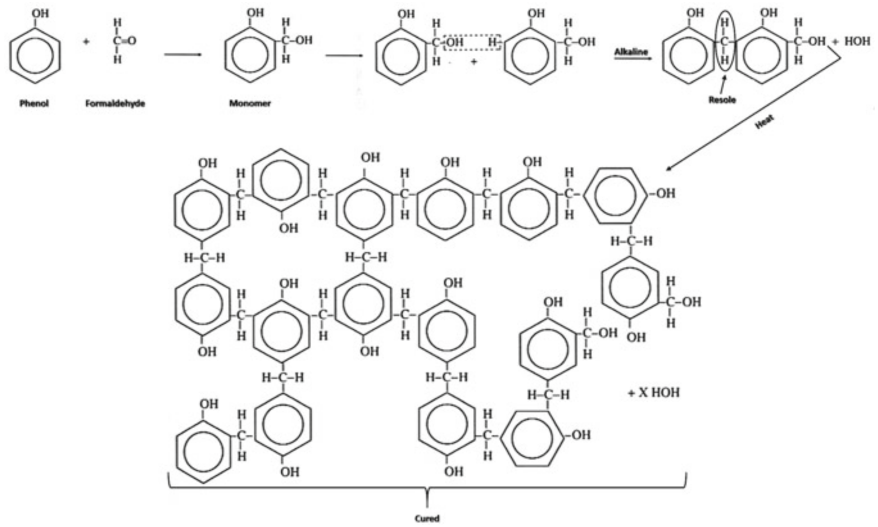

Fig. 3 Synthesis of resole resins

3.2 *Resoles*

Resoles are also known as single stage phenolics. Its production may occur by reaction of phenol with excess formaldehyde with the presence of an alkaline catalyst, such as ammonia, sodium carbide, or sodium hydroxide as shown in Fig. 3. The molar ratio of phenol to formaldehyde for this type of resin may range from 1: 1 to 1: 1.3. The reaction is carefully controlled and has an interruption before gelation occurs so that low molecular weight uncrossed resins can be produced, which are water soluble resins. The resolves are moderately branched due to the competition between the formaldehyde addition reaction and the methylol condensation reaction (may occur at ortho, meta, or para position) as shown in Fig. 3. Resolutions are usually liquid, but the reaction products may be vacuum dried or temperature controlled if a solid intermediate is desired. High aromatic content of phenolic resins is responsible for good strength retention at high temperatures and high char yield as shown in Fig. 3. Using alkyl phenols, the resin reduces reactivity and also reduces hardness, cross-link density, color formation, and increases solubility in non-polar solvents, flexibility, and compatibility with natural oils as shown in Fig. 3 (Bindu et al. 2000; Vijayakumar et al. 2013).

The synthesis of the resole may vary in various compositions and in molecular weight, this variation will depend on the type of catalyst used, the molar ratio and the reaction conditions. They have a relatively short shelf life within a few months. Thermal polymerization requires temperatures in the range of 130 ± 200 °C, and is a polycondensation reaction that releases water as a byproduct (shown in Fig. 3). Heat application transforms the resole into an insoluble, infusible thermoset and crosslinked polymer as shown in Fig. 3. Occasionally, acid catalysts may be used to cure these resoles, having as end products phenolic foams, injection molding, coatings and laminates (Hepworth et al. 2000; Allen and Ishida 2001). The essential characteristics of both cured resole and novolac-type phenolic resins are almost identical (e.g., mechanical properties, chemical resistance, etc.).

3.3 Others

3.3.1 Bisphenol-A

Bisphenol-A (4-hydroxyphenyl) propane (BPA) resin is an organic resin that belongs to the group of diphenylmethane and bisphenol derivatives. Production of colorless resins. These properties allow the use of BPA in various applications such as bearings (Roczniak et al. 1983). This is usually made up of glass or carbon fiber reinforcements as well as inorganic or ceramic mineral oxides (Brydson 1999; Arno Gardziella 2000). And because of its origin this offers and its properties make BPA an excellent matrix material. Use of fiber phase in polymer composites assists in improving tensile and compression properties, tribological characteristics, toughness (including abrasion) (Izumi et al. 2019). The bisphenol-A production process uses acetone and phenol (in excess), where they react in the presence of a resin catalyst which may be sulfuric acid as catalyst (Roczniak et al. 1983; Raghavendran et al. 1997).

3.3.2 Bisphenol-F

Bisphenol F is the simplest novolac resin. This is synthesized by a reaction of phenol and formaldehyde with a large excess of phenol under acidic conditions (pH). Protonation of methylol glycol, which reacts with phenol in the ortho and para positions, is involved during formation (Takeichi and Furukawa 2012). This is bisphenol of simple molecular structure, however, the most difficult to obtain (compared to bisphenol A, others) due to its propensity to undergo oligomerization for higher molecular weight materials (Gardziella et al. 2000).

3.3.3 Polybenzoxazine

This new thermosetting class has been produced to make it an attractive alternative to the more traditional phenolic resins of the novolac type (Ishida 2011). After the development of the fundamental chemistry of benzoxazine monomers and several initial attempts to produce their polymers, it was only in the last decade that the mechanical, physical, chemical and chemical properties of polybenzoxazine were discussed (Ishida 2011).

The production of benzoxazine monomer is can be carried out in solution or by fusion reaction using a combination of a phenolic derivative, formaldehyde and a primary amine (Jubsilp et al. 2011). Thereafter, the synthesized compound is subjected to thermal polymerization with or without an initiator in the reaction chemistry. Ring opening polymerization is easily achieved by heating the monomer to temperatures typically in the range of 140 to 220 °C, although polymerization may occur at much lower temperatures if a primer is used. Multifunctional phenolic molecules or amines can be used to synthesize benzoxazine resins that polymerize at high molecular weight crosslinked structures, however monofunctional substituents lead to essentially low molecular weight linear polymers (Hamerton et al. 2011; Jubsilp et al. 2011).

4 Use of Phenolic Resin in Composite Matrices

Among the matrices the polymeric matrices are two large groups of resins that are termed thermoset and thermoplastic as shown in Fig. 4. Phenolic resin retains its position in various industries a century after its introduction because of its good mechanical strength, heat and flame resistance, and also exhibits good chemical resistance against various solvents, acids and water. To improve the properties of the phenolic resin, many researchers tried out various reinforcement (binders, nanofillers, thermoplastic resin, fillers, fibre, woven, knitted uni, bi and tridirectional, etc. (Balaji et al. 2014). Processing of phenolic based thermosetting matrix composites materials

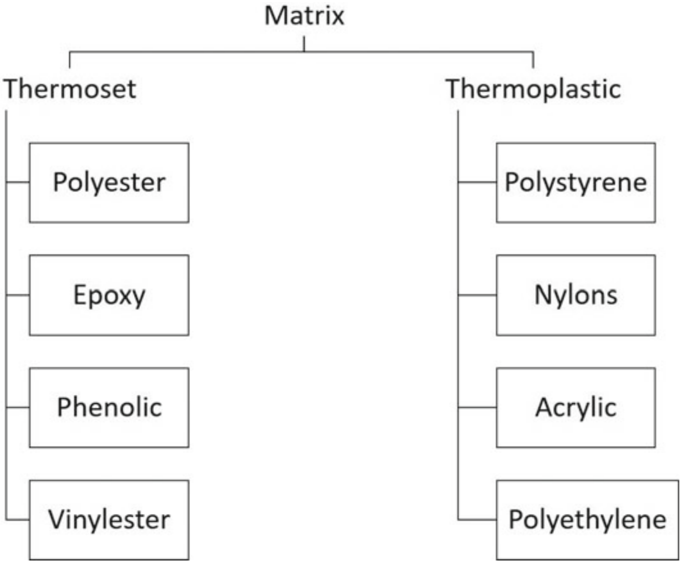

Fig. 4 Classification of polymeric matrices

requires processing conditions in order to control the development of the viscosity which is dependent on temperature and on polymer structure.

Continuous changes in resin due to low-viscosity liquid monomer (at starting point) to a solid polymer (at end of the process), affect the fiber wettability, formation and growth of bubbles (voids), and high presence of voids, which reduces performance, improvement and behavior of properties after composite consolidation. Thus, control of processing of these materials requires an accurate knowledge of polymerization kinetics of the matrix using modeling, mathematical simulation and advanced statistical analysis of the fundamental transport phenomena (associated processing technology) and curing kinetics as a function of the processing conditions applied such as temperatures and pressures (Kenny et al. 1995; Park et al. 1999; De Medeiros et al. 2003; Ramires and Frollini 2012). Therefore, thermosetting resins are currently widely used to make most composites. These materials during the polymerization or crosslinking process (crosslinking as shown in Fig. 5d) are converted from a liquid (Fig. 5a) into a solid (Fig. 5d), whereby the composites are cured by the aid of a catalyst, heat or a combination of both. Once cured or solid they cannot be converted back to their initial liquid form.

Phenolic resins are very attractive for application to composite materials which in turn consist of reinforcing material and matrix. During composites formation phenolic resins (matrix) go through many complex processes of physical, chemical and physicochemical changes to form a whole body (Frollini et al. 2013; Eslami et al. 2015). Therefore, the properties of the matrix directly affect the properties of composite materials, and the mechanical behavior of composites, especially the

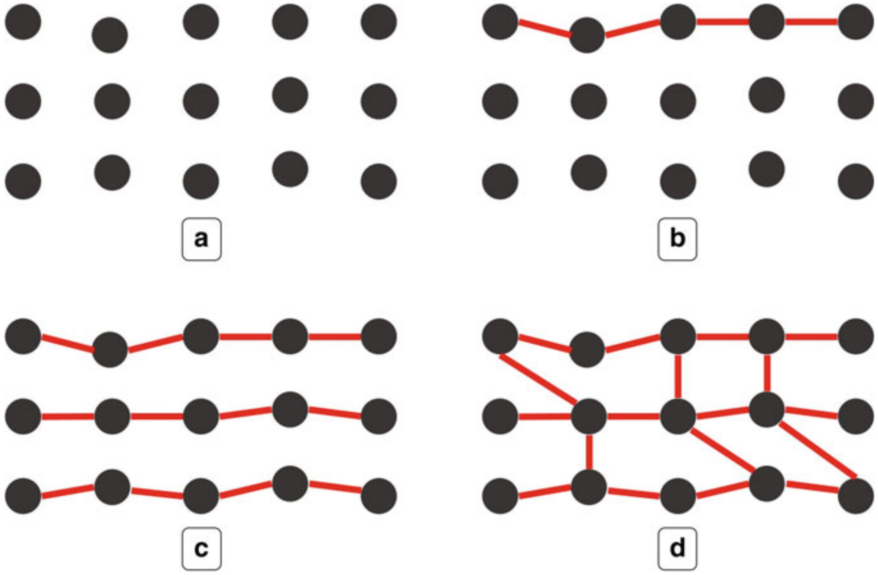

Fig. 5 Thermosets crosslink during the curing process

longitudinal tensile properties, undoubtedly depend mainly on the reinforcement material, but the role of the matrix cannot be ignored (Hou et al. 2006). For, polymeric phenolic resin matrix unites the reinforcement material (textile fibers) and promotes the improvement and enhancement of charge transfer between the fibers evenly. As well as the compressive, shear, heat resistance and weather resistance properties are closely related to phenolic resin matrices (Allen and Ishida 2001; Wang et al. 2011c).

5 Conclusion and Future Perspective

The fact that phenolic resins were the first industrially synthesized resins for use in human daily life and that they still represent a good portion of the industrial production of resins and their compounds is undeniable. This resin has as its chief position products that use them as a bonding agent, such as wood composites, plywood and agglomerates, which for a long time represent much of what is produced worldwide using of this, much of the world's production is made by China, Germany and the United States. The market trend of phenolic resins is growing year after year, as observed in data provided by Royal Society of Chemistry (Xu et al. 2019).

Acknowledgements The authors are grateful to our alive Lord who has blessed the "Textile Technology Study Group—GETTEX" located in from the Federal University of Rio Grande do Norte (Table 1).

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Synthesis of Bio Phenolic Polymer and Its Properties

Banchamlak Bemerw, Magdi Gibril, Shoujuan Wang, and Fangong Kong

Abstract Nowadays environmental friendlily and sustainable polymeric materials with the required specific properties is the focus of academic and business world research area. There is a large number of interests on using biophenolic polymers for development of new bio based polymeric materials. This chapter aims to give a compressive information on bio phenolic synthesis, properties and applications. Classification of bio phenols, synthesis of lignin based biophenolic polymer, tannins based bio phenolic polymers, cash nut shell liquid based biophenolic polymers and bio oil based bio phenolic polymers were discussed. We also addressed the properties of bio phenolic polymers required for various applications.

Keywords Phenolics · Bio phenolics · Lignin · Tannins and bio oils · **List of abbreviations** · BPA bis phenol A · BPP Bio-phenolic polymers · BPU Bio-based poly urethane · BE Bio-based epoxy · TBPP Tannin-Based Bio-phenolic polymers · LBPP Lignin-Based Bio-phenolic polymers · C-NMR Carbon-13 (C13) nuclear magnetic resonance · CSNL cash nut shell liquid · CST coconut shell tar · FTIR Fourier-transform infrared spectroscopy

List of abbreviations

BPA	Bis Phenol A
BPP	Bio-Phenolic Polymers
BPU	Bio-based Poly Urethane
BE	Bio-based epoxy

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M. Jawaid and M. Asim (eds.), *Phenolic Polymers Based Composite Materials*, Composites Science and Technology,
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TBPP	Tannin-Based Bio-phenolic Polymers
LBPP	Lignin-Based Bio-phenolic Polymers
C-NMR	Carbon-13 (C13) Nuclear Magnetic Resonance
CSNL	Cash Nut Shell Liquid
CST	Coconut Shell Tar
FTIR	Fourier-transform infrared spectroscopy

1 Introduction

Polymers is a Greek originated word meaning many parts, many identical or alike building blocks within long molecule, connected by covalent bonds. reiterating units that attend as the building block of polymers are called monomers which are unsaturated compounds (Alkenes, Alkadienes and their derivatives). Polymers are formed in the process called polymerization; method of combining such monomers and producing massive macromolecules of various sizes and shapes (Perry and Volpert 2004).

There exist two different main types of polymerization namely addition (chain reaction) polymerization and condensation (step-growth) polymerization. Addition polymerization happened by addition reaction that couple monomers using their multiple bonds (Ouellette and Rawn 2015) while in condensation polymerization, small molecules respond to each other to form larger structural units while discharging smaller molecules as a spin-off mostly water (Ramakrishnan 2017). Polymers can be thermoset or thermoplastic, the basic difference between the two types of polymers is while thermoset is irreversibly hardness after curing whereas thermoplastics are reversible (Bîrcă et al. 2019). Chain-growth reactions offer thermoplastics, whereas step-growth reactions could give thermoplastics or thermo-sets (Mikeš et al. 2002). Thermoplastics comprise several types of polymer, including acrylic best known as Plexiglas, nylon (polyamide) used primarily used as synthetic fiber replacements, polypropylene, polyethylene, polyvinyl chloride, polystyrene, polyether ether ketone, Teflon and polycarbonate (Yilmaz and Yagci 2020). Thermosets encompoass a wide variety of polymers, namely amino, phenolic, alkyd and silicones, polyimides, polyurethanes and epoxy (Fulcrand et al. 2019).

1.1 Phenolic Polymers

Phenolic polymers are the first commercialized synthetic polymers after discovered by Leo Baekeland in 1907 by phenol and aldehyde polymerization (Lattanzio 2013). Bakelite is a thermoset polymer that has low electrical conductivity, as a result, its widely used electrical switches and machine parts of electrical systems (Pereira et al. 2009) chemical structure of phenolic polymer is described in Fig. 1.

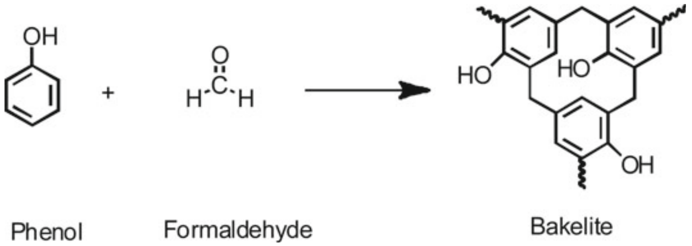


Fig. 1 Chemical structure of Bakelite (Pereira et al. 2009)

Phenol are an aromatic compound which has a benzene ring with an OH group, have molecular formula C_6H_5OH which is primarily gotten via coal tar or crude petroleum distillation contains phenyl group bonded to hydroxy Group as illustrated in Fig. 2, which has a mildly acidic nature and a strong hydrogen bond, result in higher melting points than for hydrocarbons with similar molecular weights and better stability in water (Shi et al. 2014). There are three ways to synthesis phenol namely oxidation isopropyl benzene, Chlorobenzene hydrolysis, and isopropyl benzene oxidation.

An aldehyde is an organic molecule that comprises CHO group, formed through alcohols oxidation or other organic compound, for that a carbon atom establishes a dual bond to an oxygen atom (Katritzky et al. 2010). Common bond with a hydrogen atom and a one bond with some other atom or atom unit can be considered as an aldehyde (Knop and Pilato 2013) as illustrated in Fig. 3. Formaldehyde is by far the most widely utilized aldehyde in the manufacture of phenolic resins, at room temperature, that is a pappery, colorless, combustible gas at room temperature. Formaldehyde is extremely reactive and is widely sold in methanol-stabilized aqueous solution, in which it primarily develops conjugates with the solvent, i.e. mixture of ethylene glycol, polyoxymethylene glycols and the formals for certain methanol glycols.

Higher aldehydes react likewise but significantly slower than formaldehyde with phenol. Whenever the reaction is carried out under highly acidic conditions to reduce the formation of aldol formation and by continuous aldehyde in a water-free environment is called novolac. when the reaction takes place in basic medium with an

Fig. 2 Synthesis of phenol (Knop and Pilato 2013)

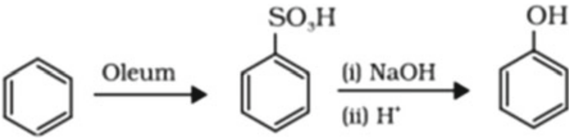
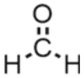


Fig. 3 Chemical structure of formaldehyde (Knop and Pilato 2013)



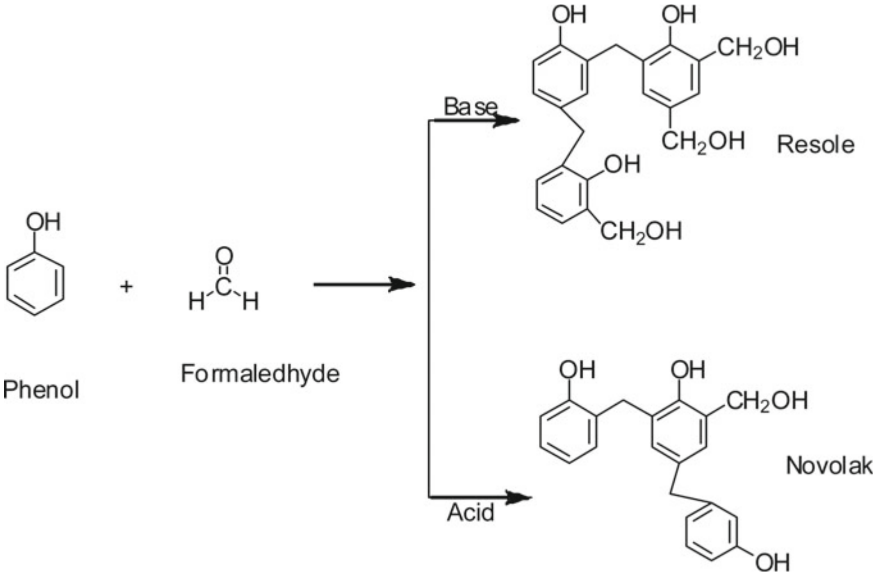


Fig. 4 Chemical structure of novolac and resole(Espinosa et al. 2004)

excess of formaldehyde called resole. The two types of phenolics resole and novolac illustrated in Fig. 4.

1.2 Biphenolic Polymers

After the first commercialized phenolic polymers by Baekeland, phenolic compounds have been used in several applications due to their dynamic properties. especially as wood adhesives and in polymerization of several materials such as polyester, epoxies, and polyurethanes. Owning to their thermal and dimensional stability, non-flammability, low water absorption, good electrical insulator and chemical resistance (Espinosa et al. 2004). however, the source of phenol petroleum and formaldehyde are considered highly contagious accordingly, several countries and organizations have banned the usage of bisphenols A (BPA) in different applications such as baby bottles and other packaging purposes (Fulcrand et al. 2019). Because the production of bio-based products becomes modern environmentally sustainable and also healthier for human use/intake than petroleum-based materials, the field of bio-based materials grows. Throughout this modern age, economic factors such as our price and availability are driving forces for the transition from crude oil-based materials to both natural and synthetic bio-based materials. furthermore, the source of phenol which is nonrenewable and the toxic nature of formaldehyde brings the modern world of scientists to focus on finding other sources of phenolic compounds, which result in obtaining them in plant secondary metabolism (Murawski et al. 2019). Phenolic compounds of plant source vary according to the compounds of the same class based on genetics (tissues, organs and plant types), pedoclimatic environment, physiological stages of plant development and health status, as certain polyphenols are metabolized in reply to pathogenic attacks (Fulcrand et al. 2019). The plant synthesizes phenolic compounds as a secondary metabolic which is chemically and structurally more complex than the main metabolism and usually known as polyphenols (Minatel et al. 2017). Secondary metabolism is not that important for plant photosynthesis rather required for plant defense mechanisms from environmental biotic and abiotic factors (Lochab et al. 2012). Biosynthetically, phenolic complexes are synthesized either through the shikimic acid pathway or the malonate/acetate pathway. On the basis of their structure, multiple types of phenolics were classified: C6—C1 (phenolic acid), C6 (simple phenol, benzoquinones), C6—C3 (hydroxycinnamic acid, coumarin C6—C2 (acetophenone, phenylacetic acid),, phenylpropanes, chromones), C6—C1—C6 (xanthones), C6—C2—C6 (stilbenes, anthraquinones), (C6—C3—C6) 2,3 (bi-, triflavonoids), (C6—C3)2 (lignans, neolignanes), C6—C3—C6 (flavonoids, iso flavonoids, neoflavonoids) (C6—C3)n (lignins), (C6)n (catechol melanins), and (C6—C3—C6)n (condensed tannins) C6—C4 (naphthoquinones). Naturally occurring polyphenolic compounds on the basis of the three repeated building blocks are:- Leucoan thocyanidins, Flavone glycosides, esters and amides of hydroxycinnamic acids (Handique and Baruah 2002) (Fig. 5).

Plants are the only natural source of phenolic compounds and they are classified as Proanthocyanidian derivatives, Galloyl and Hydroxycinnamic acid derivatives, hexahydroxydiphenyl ester derivatives, and phloroglucinol derivatives as illustrated in Fig. 6.

A most common class of biphenolic polymers include phenolic acids, coumaric acid, tannins, lignin, cash nut shell liquid, and others are discussed in this chapter on the following titles.

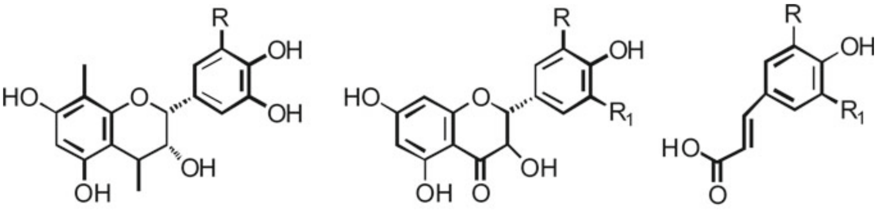


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Fig. 5 Esters, Leucoan thocyanidins, Flavone glycosides, amides of hydroxycinnamic acids (Handique and Baruah 2002)

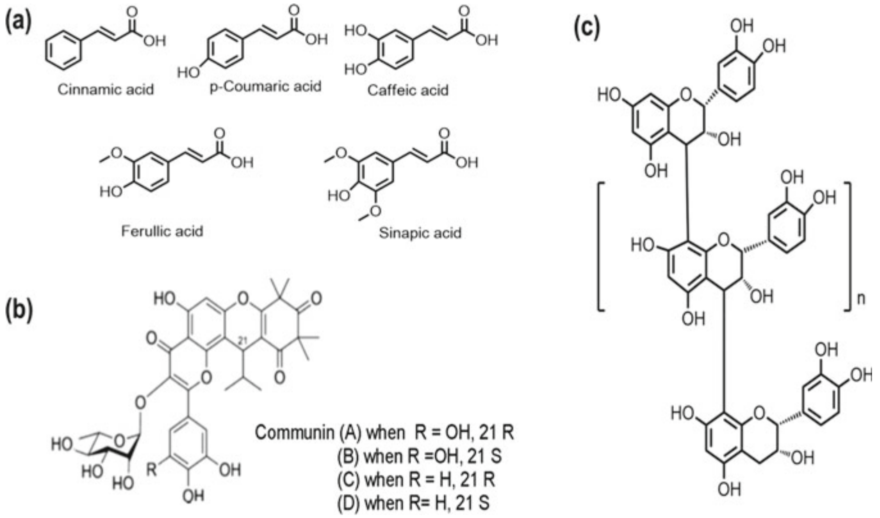


Fig. 6 Hydroxycinnamic acid derivatives (**a**), phloroglucinol derivative (**b**) and Proanthocyanidian derivatives (**c**) (Handique and Baruah 2002)

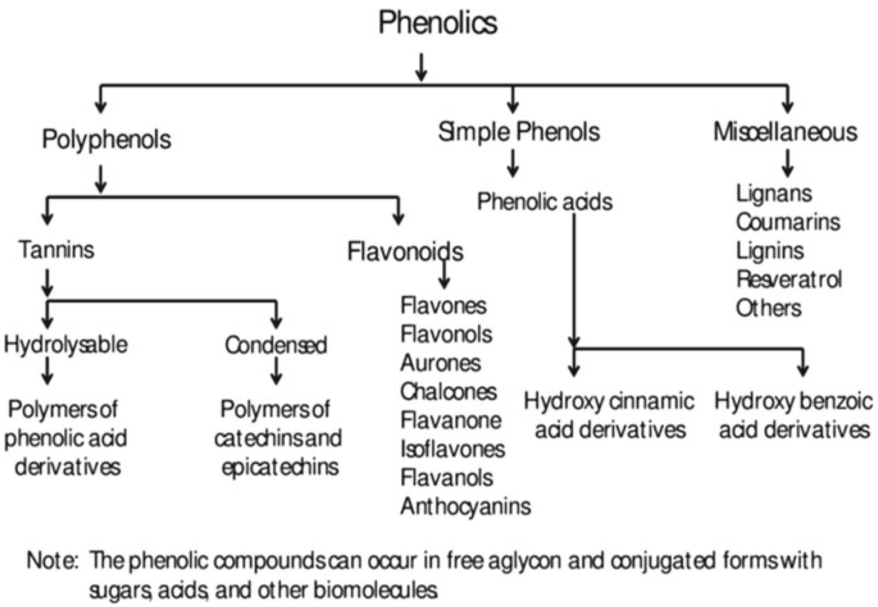
2 Classification of Biophenols

BiopPhenols are basically sorced from plants, mostily found in plant cellwall, can be easily distingshed by their hydroxyl group in the aromatic ring, they can be classified as polyphenonls (tannins and flavonides) and simple phenolics (phenolic acids and comarins), the broad classification of biophenols discussed in Fig. 7.

2.1 Phenolic Acids

Many plant species contain phenolic acids as secondary metabolic and distinguished by a carbon group attached to a benzene ring (C6—C1) are normally identified by gallic, syringic acids, p-hydroxybenzoic, protocatechuic, vanillic, and (Lattanzio 2013) as illustrated in Fig. 8. Phenolic acids get a carboxyl group linked to or associated with the benzene ring. It is possible to distinguish two groups of phenolic acids according to their structure: cinnamic acid derivatives (i.e. hydroxycinnamic acids, C6-C3) and benzoic acid derivatives (i.e. hydroxybenzoic acids, C6-C1) (Khadem and Marles 2010).

Phenolic acids are essential in the human nutrition because of their antioxidant properties and also have the potential to work against cancer (Rigoussen et al. 2018; Gomathi et al. 2015). Hydroxybenzoic acid is present in many plants, including grapefruit, olive and medlar fruits and extracted among plants like oil palm and many other organisms, including east African satinwood which shows antifungal,



Note: The phenolic compounds can occur in free aglycon and conjugated forms with sugars, acids, and other biomolecules

Fig. 7 General classification of plant phenolics

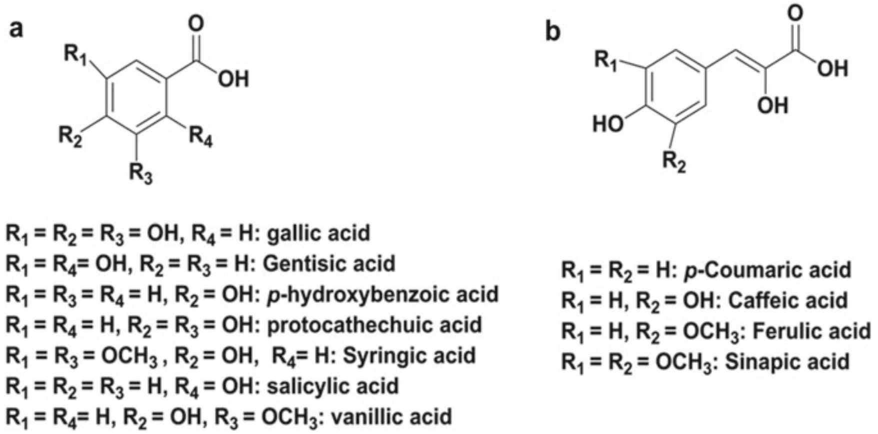


Fig. 8 Structures of phenolic acids: syringic, p-hydroxybenzoic,, vanillic, protocatechuic and gallic acids (Khadem and Marles 2010)

antimutagenic and antimicrobial activities (Bi et al. 2012). Phenolic acid antioxidant activity is determined by the number and role of the hydroxyl groups in the molecule, the antioxidant efficiency of mono-phenols is greatly improved by the addition of a second hydroxyl group in ortho- or para- positions, and enhanced by one or two

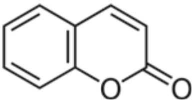


Fig. 9 Chemical structure of coumarins (Pereira et al. 2009)

ortho- position methoxy substitutions in relation to hydroxyl group (Pereira et al. 2009). Antioxidant application of phenolics will be discussed in the following titles.

2.2 *Coumarins*

Coumaric compounds are a category of lactones architecturally built by a benzene ring used in the α- pyrone ring, and basically obtain-conjugated with a rich electron system and strong charge—transport properties. Due to the fact that Coumarins have a range of biological properties, including antimicrobial, anti-inflammatory, antiviral, antioxidant, antidiabetic, and enzyme inhibitory activity: they are widely used for pharmaceutical applications (Lattanzio 2013). There are 1300 coumarins discovered as a derivative of 5,6-benzo-2-pirone, derivatives of coumarins such as furanocoumarin including furanic ring, liner pranocoumarins, dimeric coumarins, angular pyranocoumarins of dicoumarol is an example, useful for anticoagulant drug warfarin, photosensitizers to vasodilation (Fig. 9).

There has Recently been development in synthetic coumarins derivatives, such as 1azo and fluorinated coumarins which disrupted mild analgesic properties and an outstanding antimicrobial and anti-inflammatory activity (Pereira et al. 2009).

2.3 *Tannins*

Tannins are polyphenols by nature yellows or brownish bitter-tasting organic substances exist in many wood species especially in the southern hemisphere useful for plants to fight fungi and insect and found in tree barks (Khanbabaee and van Ree 2001). They are most widely found in the following plants: black mimosa, quebracho, oak bark, and chestnut pines and helps plants to fight insect and fungi attack (Pizzi 2008). They have a high binding nature with other materials such as protein as a result extensively used for leather tanning, pigments, macromolecular architectures and metallic ions including anti-oxidant activities (Hümmer and Schreier 2008). Tannins are produced in soft tissue, and can thus be used yearly without damaging the plant (Bisanda et al. 2003). Tannins are classified as hydrolyzable (flavenoellagitannins, ellagitannins,gallotannins, complex tannins) and condensed tannins (Tahir et al. 2019) as illustrated in Fig. 10. Hydrolyzable tannins obtained from myabolans, divi-divi, algarrobilla, tara, chestnut (Frollini et al. 2013). Basically, contains gallotannins or ellagitannins resulted in glucose, gallic or ellagic acids while hydrolyzes in acidic, basic or enzymatic conditions.

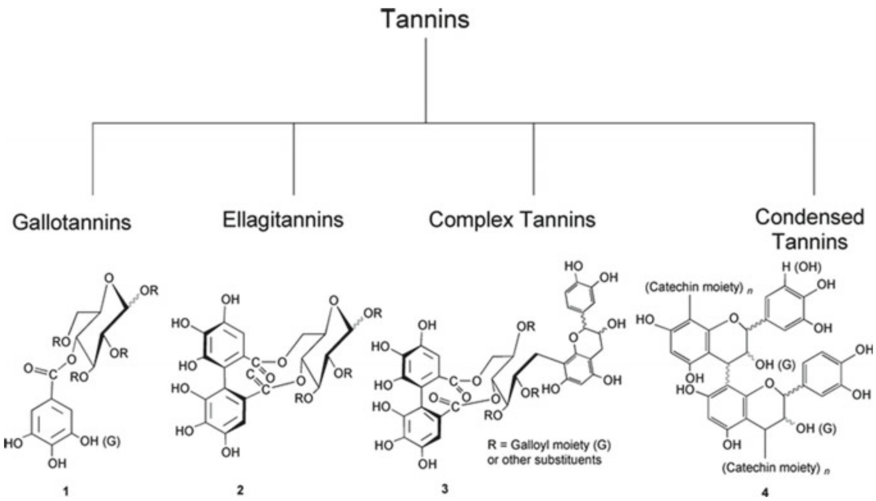
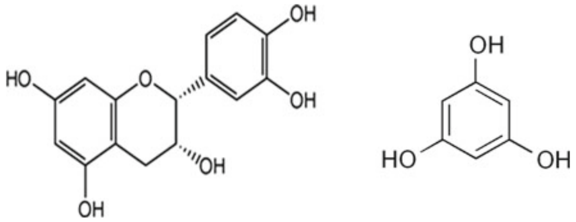


Fig. 10 Chemical structure of condensed, ellagitannins, complex tannins, flavenoellagitannins and gallotannins (Frollini et al. 2013)

Condensed tannins on their other name proanthocyanidins are the most versatile and reactive polyphenol, have freer hydroxyl group and molecular weight smaller than lignin. Condensed tannin reactivity lis related to the reactivity of each monomer ring and high PH dependency (Fulcrand et al. 2019). Many reactive condensed tannins are proanthocyanins with an A-ring form of phloroglucinol, with molecular weight ranging from 500 to 3000 Da illustrated in the Fig. 11 below.

Due to the greater number of position-free phenolic, condensed tannins are more suitable than hydrolysable tannins for the production of phenolic based polymeric matrix, groups present in the chemical structure enables them to participate in chemical reaction representing phenols (Pizzi 2019). Hydrolyzable is not commercially viable as CTs as a result of their lack of macromolecular structure not only that but also a high phenol replacement levels result higher nuleophilicity (Lochab et al. 2014). Condensed tannins have the potential to substitute phenolic resins by up to 90%, after increasing the reactivity of hydrolyzable modification such as hydrolysis, acetylation, polymerization, and condensation reactions (Amarowicz et al. 2000). Condensed tannins are most widely intended for copolymerization with isocyanates,

Fig. 11 Chemical structure of proanthocyanins with a phloroglucinol type A-ring9 (Fulcrand et al. 2019)



amyloplast, formaldehyde and phenolic resins (Zhou and Du 2019). Tannins are further classified further as type A and type B rely on differences in the chemical structure with weather patterns, type A are the ellagitannins and are hydrolysis tannins Type B tannins examples (Pizzi 2019). There are several extractions reported such as sub-critical solvents, ultrasonic waves and microwaves, polar and nonpolar solvents were used for the extraction of phenolics from tannins, the maximum yield of extracts was found in polar solvent extraction such as water, industrial tannin extraction employed in hot water (Lochab et al. 2014). Microwave assisted extraction shows improvement over conventional extraction methods with a short time, less use of solven, greater productivity and high yield. Precipitation of tannins with metals or protein is used to understand the nature and amount of hydrolyzable or condensed tannins (García et al. 2016). FTIR, NMR, MALDI-ToF are useful method to test, classify and assess the purity of the tannin content in extracts (Nouailhas et al. 2011). Relationship of phenolic acids and flavonoids Tannins have an antioxidant property not only because they also have a potential for treating of non-insulin dependent diabetes mellitus along with their ability to increase adiopgenesis inhibit glucose absorption (García et al. 2016). Tannins are the focus of many researches as a green source of phenolics, which will be discussed in the following sub chapters

2.4 Lignin

An aromatic polymer that is found primarily found in the cell wall of secondary thickened cells making them firm and tight. lignin is a cross-linked phenolic polymer with cellulose and hemicellulose. Eventhough Composition differs from species to species basically, Lignin is formed by combinatorial enzyme catalyzed oxidative 4-Hydroxphenyl propanol units (Mu et al. 2013). Lignin is a composition of Coniferyl alcohol, P-coumaric alcohol and sinapyl alcohol, (illustrated below in the Fig. 12)

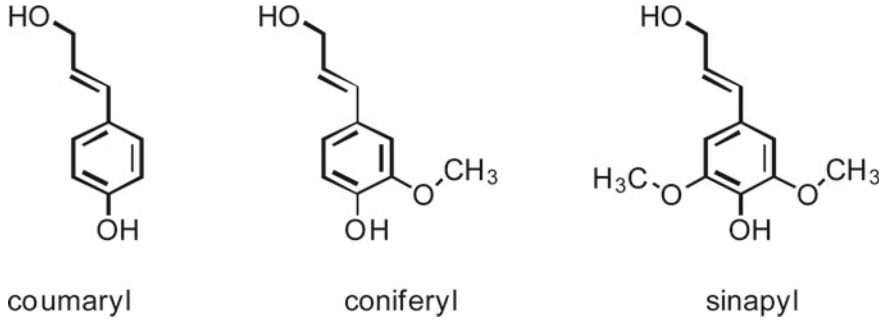


Fig. 12 Chemical composition of Coniferyl alcohol, P-coumaric alcohol and sinapyl alcohol (Solt et al. 2018)

Those are the sequences of aliphatic and aromatic patterns bound by C–C and C–O bonds, a most popular of which are β-β, β-5,5-5 and β-O-4, β-O5 bonds, and dibenzodioxin bonds, distinguished by the presence and location of methoxy groups respectively (Solt et al. 2018).

Lignin macromolecules have several functional groups affecting their reactivity such as benzyl alcohol, methoxy, aliphatic hydroxyl and phenolic, noncyclic benzyl ether and carbonyl groups. paper and pulp industry highly generate lignin as a waste, the waste has been used on the production of biogas but nowadays using lignin in different polymerization areas is taking the lead. Lignin coexists in the cell wall with cellulose and hemicellulose of accounting for 40% dry weight plants (Schutyser et al. 2018). Hydroxy, Methoxy, Carbonyl and Carboxyl are the major chemical constituent of lignin but the amount differs based on the extraction and nature of the plant not only that structure of lignin is also different from species to species. The primary existence of highly functionalized biomacromolecules possessing low polydispersity very advantageous for their high valueadded, applications in green polymeric materials. Lignin can give phenolic chemicals by chemical disassembly process, but the lignin framework is chemically very stable due to the existence of oxygen that inhibits its conversion into too simple green monomer, for that matter pretreatment, catalytic treatment and dissolution is an important area for production of replaced phenols and other significant chemicals (Schutyser et al. 2018). There are several processes for lignin extraction among those pyrolysis, thermochemical methods, phase separation, ultrasonic irradiation solid-state separation, and enzymatic modification can be mentioned (Lochab et al. 2014). In any case, pretreatment is needed to remove polysaccharides results from high molecular weight lignophenols performed in a depolymerization process (Wang et al. 2010). Phase separation is the next process in which cellulose and hemicellulose are hydrolyzed and transformed to sugar while lignin is converted to light-colored phenolic active ingredients. The resulting lignophenols has strong phenolic material, very light colors and excellent stability. **Pyrolysis is a method of chemical decomposition of organic materials at high temperatures, without oxygen. Usually, the cycle happens at temperatures above** 430 °C (800 °F) and under pressure. **it involves the differences in body phase and chemical composition at the same time**. Even though lignin extraction in pyrolysis condition will result high quantity of char generation and poor yield of low molecular weight chemicals used as renewable resin from biomass pyrolysis due to the high pyrolytic lignin yield of and easy assimilation into phenol-formaldehyde formulations. Thermal treatment in a hydrogen environment results in the production of chemicals such as phenols, whereas an oxidizing environment creates phenolic aldehydes and acids. Catalytic diagnosis of lignin mainly by the process of hydrodeoxygenation (HDO) process led to the establishment of higher percentage of phenolic compounds under relatively milder conditions. Depolymerization of lignin using a catalyst system such as silica-alumina, and additional catalytic cracking lead to the formation of alkoxy, coke and aromatic hydrocarbons (Rabemanolontsoa and Saka 2013). The scaling consists of a large temperature process for the recovery of lignin chemicals from lignin may not commercially viable due to the high energy requirements. Low-temperature processes are therefore preferable for extracting desired chemicals from lignin degradation. Greener approaches such as use of supercritical and ionic liquid solvents in organic solvents, use of enzymatic hydrolysis over acid/metal/alkaline catalysts and the use of microwave reactors in conventional reactors are explored either for of lignin extraction from lignocellulosic biomass or for recovery of lignin chemicals (Areskogh et al. 2010). Lignophenols Enzymatic modification is a possible way to convert lignin into chemical substances for industrial applications (Xia et al. 2003). Characterization of lignin can be done by either invasive or noninvasive methods or both. Noninvasive methods involve infrared matrix (IR), nuclear magnetic resonance (NMR) and UV visible spectroscopy all help to know the feasibility of the extractions. Invasive methods use chemical methods such as thi1.oacidolysis, oxidation of copper oxide, oxidation and derivatisation of nitrobenzene followed by reduction of cleavage. Thermal characterisation such as TGA and DSC and thermo-rheological analysis can also provide insight into the woods nature. As mentioned earlier, lignin is used for the fabrication of bio phenolic polymers more than any materials which will be discussed extensively on the following titles.

2.5 Cash Nut Shell Liquid (CNSL)

A dark brown viscous liquid found inside a soft honeycomb structure of the cashew nutshell is the called CNSL *(Anacardium occidental,* mainly harvested in Asia, Africa and South America (Akinhanmi et al. 2008). It is used as a raw material in industry as a waterproofing agent compounds in the manufacturing of paints and plastics, a preservative and for brake lining (Lubi and Thachil 2000). CNSL structure contains phenolic compounds which replace a benzene ring is with long unsaturated alkyl side-chains. This is a mixture of anacardic acid (71.7%), traces of cardol (18.7%), 2-methyl- cardol (2.7%), cardanol (4.7%)13 and the other 2.2% is an unidentified polymeric material.

The largest content of CNSL anacardic acid is highly poisonous as a result used for antimicrobial activities (Lomonaco et al. 2017). Cardanol and cardol are the most useful material for polymeric material such as plasticizers, adhesives and resin additives (Asogwa et al. 2008) chemical structures are illustrated above in Fig. 13. Isolation of CNSL pieces from cashew nutshell pyrolysis, by extraction of solvents, heat and carbon dioxide. Solvent extraction process engages organic solvents with harsh mechanical pretreatments which is useful for research on a small scale rather than for production on a large scale (Viswalingam and Emerson Solomon 2013). The heat extraction method uses a high temperature in the range 80–200 °C, after distillation heat extraction (Mwangi et al. 2014). Extraction of vacuum pyrolysis at 500 °C/720 mmHg and green extraction procedures such as supercritical carbon dioxide where cardanol was obtained at 70–90% (Patel et al. 2011), separation of cardanol from cardol is done most often by vacuum distillation. Characterization of the CNSL component is performed by mass analysis, IR, H-NMR, and C-NMR spectroscopies. CNSL in general or cardanol as a monomer used for bio oil or as a chemical modification for the generation of amphiphiles and phenol substitution.

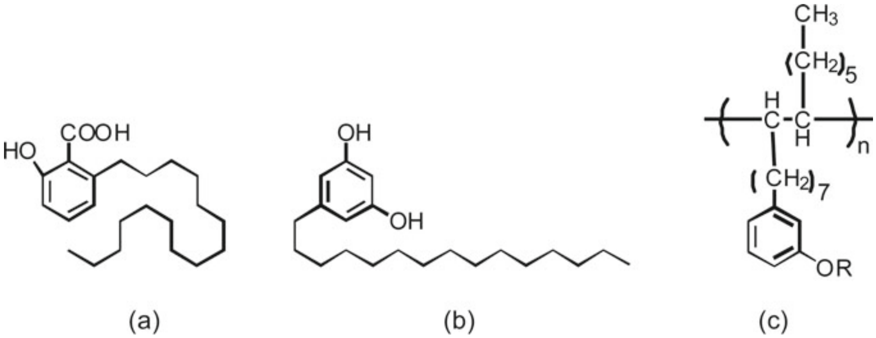


Fig. 13 Chemical structure of anacardic acid, cardanol and cardol (Lochab et al. 2014)

2.6 *Other Phenolic Sources*

Besides the previously mentioned phenolic sources, even if content and type of phenolic compounds might be different but most plants have phenolic compounds. Among those stilbenes, flavonoids, quinones and curcuminoids (Cai et al. 2004). Palm oil agricultural industry waste is rich in lignocellulosic materials and used as a green chemical source (Cherubini 2010). Pyrolyzed palm shell oil contains a high proportion of phenol and its derivatives, such as replaced guaiacol, cresol, eugenol, syringol and pyrocatechol (Abnisa et al. 2011). Coconut shell tar (CST) is a coconut byproduct during the distillation process and has been deemed as a waste, which is found to be Potential vanillin is produced through microbial fermentation and also 4-hydroxybenzoic acid (Fagbemi et al. 2001). Flavonoids occur in nearly all plants which has four forms as flavonoids, isoflavonoids, neoflavanoids and minor flavonoids, the general structure comprises a skeleton C_{15} (C_6–C_3–C_6) joined to a chroman ring. Flavonoids are increasingly becoming the medical research, owning to their useful properties; oestrogenic, anti-inflammatory, enzyme inhibition, antimicrobial, antiallergic, vascular and cytotoxic antitumor function (Harborne et al. 2013). Anthocyanins or also another source phenolics they are insoluble plant pigments the compounds are glycosylated polymethoxy-derivatives of 2-phenylbenzopyrylium (flavylium) salt, they basically used for antioxidant and food coloring purposes (Moyer et al. 2002) chemical structures are illustrated below in Fig. 14.

3 Synthesis of Polyphenols Based Polymers and the Resulting Properties

Synthetic phenolic compounds have been participating with several polymerizations for different purposes as a major source's materials regardless of their excellent physical and chemical properties, and mechanical properties. Nevertheless, the usage of

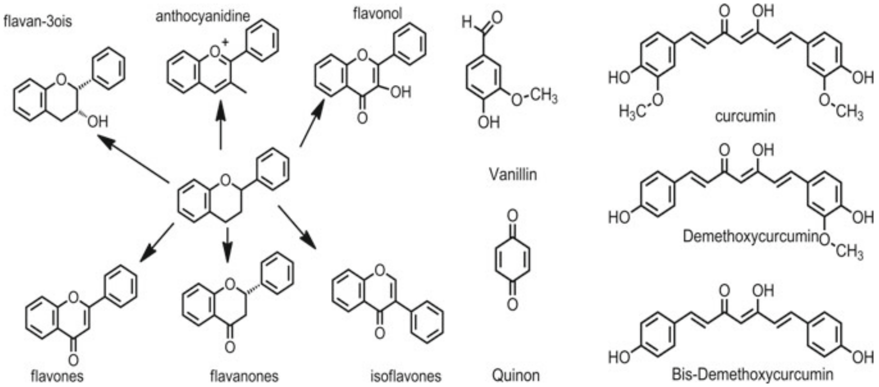


Fig. 14 Chemical structure of flavonoids, anthocyanins, vanillin, quinones, stilbenes and curcuminoids (Harborne et al. 2013)

petroleum-based phenolic compounds is in question because of renewability, sustainability, availability, cost and also environmental issues. Since polyphenols catch the eyes of the world as a substitution of phenol and aldehyde especially lignin, tannins, and cashew nut shell take the large portion in the development of thermosets to phenolic resins, polyurethanes, epoxy and unsaturated polyester.

3.1 Synthesis of Lignin-Based Biophenolic Polymers (LBPP)

Partial Substitution of phenol or formaldehyde in phenolic resin with polyphenols for the purpose of phenolic adhesive is widely addressed by several authors. Lignin takes the front seat in phenol substitution, 40 wt% lignin of different origin was used for substitution of phenol in PF adhesive production found to give the same properties as the unsubstituted phenol-formaldehyde adhesive. Although lignin beyond 50 wt% in phenol-formaldehyde resin shown a less thermal resistance (Xu and Ferdosian 2017; Moubarik et al. 2013). After activation on lignin by methylation, demethylation and Phenolation improvements in thermal properties and good strengths were observed even the usage of lignin beyond 50wt% (Faulstich de Paiva and Frollini 2006). Not only that but also, better adhesion strength than the untreated as a result of a higher percentage of hydroxy and methyl group ration.

The substitution of lignin in the place of phenol up to 75 wt% was achieved by catalytical degradation of lignin (Cheng et al. 2013). Organo lignin from pine sawdust was extracted via organo-solvent lignification method through hydrothermal degradation. Degraded lignin was used for substitute phenol for the development of bio phenol-formaldehyde resin with a rise standards ration of 50 and 75wt% each. All the degraded lignin phenol-formaldehyde (DLPF), Organo solvent lignin phenol-formaldehyde (DLPF) and pure phenol resins were prepared. The physical properties show that DLPFs and OLPFs have comparable physical properties as the unadulterated PF resin in relations of viscosity, non-volatile contents, loading time at 4 °C, but have slightly advanced allowed formaldehyde content. The OLPFs and DLPFs can be cured at a lower temperature than the unadulterated PF resin. OLPFs and DLPFs show faster curing time when used for plywood adhesiveness rather than pure phenol.

Literature also show the substitution of lignin in the place of formaldehyde for resole phenolic resin. From paper and pulp industry waste lignin was depolymerized, 4-Hydroxybenzaldhyde, Vanillin, and Syringaldehyde. Initially, such compounds are not reactive but their reactivity was activated by masking their hydroxy group. Resulting polymer shows higher thermal stability and char yield efficiency (Foyer et al. 2016). To increase the chemical reactivity of the degradation of lignin base catalytic depolymerization performed on kraft lignin from a liquor of a pulp mill using carbon dioxide (Solt et al. 2018). Lignin was placed in a NaOH solution for a specified time, pressure and temperature, as a result, the development of phenolic mono di and oligomers substance. Furthermore, the degraded lignin was used in the phenol substitution reaction to produce lignin-based phenolic resin by that up to 70% of phenol substitution was achieved.

3.2 Synthesis of Tannins—Based Biophenolic Polymers (TBPP)

Tannin has also been in use for the replacement of phenol in phenolic resin or adhesives. Especially chestnut and mimosa extracts are widely used. 40% of chestnut tannins replacement in the place of phenols shows the same properties as phenol-formaldehyde resin (Li et al. 2013). The resulting tanninfuranic thermosetting resin demonstrated significantly greater hardness than marketing acrylic and polyvinyl chloride and excellent carbon precursor was found in 52% char yield. Literature contains several reviews about the use of polyphenols as wood adhesives are extensively available (Khan et al. 2004; Navarrete et al. 2012). Tannins from pine bark have been extensively employed in preparing tannin adhesives, at least at lab scale(García et al. 2016). Tannin-based resins differentiate from other bioadhesives by strong adhesion and require no reinforcement of synthetic petroleum adhesives.

3.3 Synthesis of CSNL—Based Biphenolic Polymers (CSNL-BPP)

Cardanol from cash nutshell for the substitution of phenol alone or with other phenols were also been reported in several papers. When cardanol used for the substitution of phenol in a phenolic resin, it shows better flexibility but tensile strength and thermal stability are lower than phenol-formaldehyde resin (Rwahwire et al. 2019). But if the cardanol is 15wt% which shows improved chemical resistance and tensile strength as well as flexural resistance (Paysepar et al. 2020; Vithanage et al. 2017). Cardanol was also tested for the manufacture of phenolic froth as a substitution of phenol in a combination of 9,10-hydro-9-o-oxa-10 phosphaphenathrene -10-oxide (DOPO). Alteration of poly-(vinyl formal) insulating enamel varnish with cardanol phenol-formaldehyde resins was originate to recover physical and mechanical properties, heat resistance and electrical properties of the insulating enamel lacquer for copper ropes (Lochab et al. 2012).

Not only substitution of phenol or aldehyde but several properties such as antiaging, antioxidation and antimicrobial improvement on the final polymer are registered by different works.

3.4 *Synthesis of Bio-oils—Based Bio Phenolic Polymers (Bio Oil-BPP)*

Bio oils as the name indicate obtained from plant biomass by fast pyrolysis, which is rich in phenols, aldehydes, and other organic matter. Organic oil has been used to alter the aging properties of phenol-formaldehyde resin (Yu et al. 2018) phenol were partially substituted by bio-oil, the resin obtained showed better storage stability, thermal stability, Good shear strength, better toughness and water resistance. Bio-oil from the hydrothermal liquefication of eastern white pine sawdust was methylated with formaldehyde in the presence of sodium hydroxide. Phenol substitution by 75% for the wood adhesive purpose was obtained with acceptable quality whereas 60% phenol substitution were comparable to phenol-formaldehyde phenol-formaldehyde resin (Cheng et al. 2013). Cornstalk bio-oils, soluble resins were easily synthesized under the sodium hydroxide catalysis (Wang et al. 2009). The resins derived from biomass-were brown viscous liquids, with large distributions molecular weight, the result shows that bio-oil resol resin had typical thermosetting properties of phenol-formaldehyde resin. bio-oil from the rapid pyrolysis of renewable biomass has been used as the raw material for the synthesise bio-oil phenol-formaldehyde (BPF) resin desired resin for manufacture of phenolic material. Paraformaldehyde was used during the synthesis process to meet the requirement of high solid content and low viscosity. Results indicated that BPF resin with a 20% the bio-oil addition had good oxygen index and bending power, suggesting that adding bio-oil could alter the fire resistance and fragility of PF resin. From all the reports it can be concluded that, the addition of bio-oil affected the healing characteristics and thermal degradation of PF resin, but the effect was negligible when the addition was relatively small (Wang et al. 2009; Kim et al. 2016; Kar 2018).

3.5 Synthesis of Bio-based Polyurethane (BPU)

Polyurethane is one of the most extensively used polymeric materials for surface protection, good adhesion, and surface coating. Polyurethane is basically a result of isocyanate and polyol through addition polymerization process. Due to the toxic and irritating nature of isocyanate and polyol to respiratory, digestive and urogenital tracts replacement of the raw materials with biobased sources such as plant polyphenols also the low cost, availability and nontoxic nature. Polyphenols such as lignin, tannins and cash nutshell extract cardanols are used for the substitution of polyol or isocyanate in polyurethane. Lignin for the substitution of polyol needed to be a liquid polyol and the reactivity of hydroxy groups of lignin needs to be modified by alkoxylation, which consists of grafting polyalkoxylated chains of different lengths by lignin reacting with ethylene or propylene oxide. This incorporates highly accessible end-chain primary alcohols and generates liquefied lignin derivatives which are simpler for using. Polymer based on Lignin can be developed as adhesive, emulsion or coating. General patterns suggest that lignins will make up 40–50% of PU materials though maintaing or enhancing standard properties such as, compression power, moisture/flame resistance, or biodegradability. The technique of alkoxylation also led to a robust PU foam with a polyol derived from 100% lignin, with better mechanical properties than normal non-romatic PU.

Tannins are also used on bio-based polyurethane by increasing the reactivity of hydroxy groups by oxy- propylation Through an anionic ring-opening polymerization reaction of propylene oxide, polypropylene oxide strings are inserted across gambier tannins and obtained liquid polyols. The modified tannin reaction with 4,4′ methylene bis(phenyl-isocyanate) in the existance of isopentane as the blasting agent led directly to PU with relativily homogenous closed cells and increased flame resistance.

A polyol from Cash nutshell extract cardanol is used for the formulation of polyurethane rigid foam. Formulation of Mannich polyol Mannich bases and methanolic ethylene oxide 3 in the mole ratio 1:2 at 100 °C under self-generated pressure (50 Psi) for 3 h in a closed system. The process is initiated by the tertiary nitrogen present in a Mannich base structure (self- catalysis). Cardanol biobased PU foam via the stepwise oxazolidine route. Mannich cardanol polyols are highly reactive attributed to the prevalence of the tertiary nitrogen in their structure, exerting a significant catalytic effect in the reaction of hydroxyl and isocyanate groups. Bio-based cashew Mannich polyol was prepared successfully and finally used among fillers such as fly-ash, Teflon, ceramic, $Sb_2\ O_3$ and PVC, for the preparation of rigid polyurethane foam and its significant effect on the respective foam. The resulting bio-based PU have good physical, chemical properties and thermal properties.

3.6 *Synthesis Bio-based Epoxy (BE)*

Most specific epoxy resins are derived from a reaction among bisphenol-A (BPA) and epichlorohydrin (ECH), although the latter may be substituted by other raw materials (such as o-cresol novolacs, phenol, and aliphatic glycols) for the production of specialty resins. Epoxies are used widely for their execellent chemical, mechanical, and electrical properties in adhesives coatings, and composites. Lignin, Bio oils, cash nutshell extracts (cardanol and eugenol) and condensed tannins are reported for the substitution of epoxy raw materials.

After the modification of lignin reactivity (through methylation, Phenolation or demethylation), both kraft and oregano lignin were used for the synthesis of epoxy as a substitution in the place of bisphenol A owning to the free hydroxy groups within the lignin structure (Sun et al. 2007; Zhang et al. 2017). Lignin from wheat straw was epoxidized in alkaline aqueous media with polyethylene glycol diglycidyl ether (PEGDGE) and not epichlorohydrin. Mechanical and thermal properties evaluation showed that the resin obtained was a similar property to the epoxy by bisphenol A. Several attempts were made to develop bio-based epoxy from bio-oil (Celikbag et al. 2015; Liu et al. 2017; Celikbag et al. 2017). The bio-oil was found to be well compatible with epoxy resin and was capaible to processing thermoset materials with a high glass transition temperature and cross-linking density. Fast bio-oil pyrolysis has been used to replace up to 50 wt% for bio novolac synthesis. A glycidylation reaction was used to epoxidized the bio novolac and α-resorcylic acid. The result obtained showed that bio-oils can be epoxidized directly or synthesizing by prepolymer of the novolac form resulting in high glass transition temperatures and high moduli. a promising result as the can replace in composite, resin for coating and adhesives. The other polyphenol used for biobased epoxy is cardanol which is used for the synthesis of low temperature curable liquid epoxy (Rao and Palanisamy 2013), from cardanol both benzoxazine and epoxy has resulted a novel thermosetting resin, bio-based fluid monomers are good candidate for enhancing the processability and durability of traditional thermoset polymer epoxy and benzoxazine matrices for electronic packaging materials. Eugenol and cardanols were used to synthesized epoxy thermoset, four different monomers were obtained from the polyphenols by that four different thermosets were prepared (Ecochard et al. 2019). These new thermosets based on eugenol exhibit strong thermo-mechanical properties with high char yields. Condensed tannins were also used for the biosynthesis of epoxies (Nouailhas et al. 2011),

4 Properties and Application of Bio Phenolic Polymers

As discussed in the previous content of the chapter, bio phenolic polymers are used in different areas of the polymers industry and they resemble similar, sometimes better mechanical, thermal, physical and chemical properties than the traditional phenolic polymers. Most importantly bio phenolic polymers show biodegradability unlike petroleum-based polymers, which is the main concern of our scientific era. One evidence degradation of lignin-based polymers, i.e. lignocresol and lignocatechol in the presence of peroxidase and enzymes, CNSL also demonstrates biodegradable when tested using OECD system, tannin is also biodegradable polyphenol due to the presence of a core of glucose connected with phenolic moieties (Lochab et al. 2014). Due to those favorable properties, bio phenolic polymers are used for several applications, among those their use for food antioxidant purpose and nano modification contribution is discussed below.

4.1 Polyphenols for Antioxidant

t-butylhydroquinone (TBHQ), Butylatedhydroxyanisole (BHA), 3,5-di-t-butyl-4-hydroxytoluene (BHT) and propyl gallate, is used in polymer formulations food packaging. Problems regarding their possible toxicity due to carcinogenic activities, endocrine and mutagenic disruption have been posed as these small phenolic antioxidants can be released from the polymer matrices when in contact with aqueous multimedia. In order to substitute these harmful additives in an advantageous manner, non-toxic natural small phenolics (e.g., flavonoids, α-toco-pherol, ascorbic acid, natural rosemary extracts, curcumin, and caffeic acid) where introduced into packaging materials (Vilela et al. 2018).

There is also a increasing popularity of a greener approach centered on the use of lignin's derivatives as sustainable and biocompatible antioxidants for polymer stability, especially in packaging, is also becoming progressively popular. Without a doubt the most researched antioxidant activity was attributed to flavonoids (Alzand 2012). The well-established antioxidant function of flavonoids is also liable for certain biological processes in which it is useful to prevent oxidative stress. For example, some compounds anticancer activity is due to their ability to scavenge free radicals, thereby avoiding the early stages of cancer promotion. In addition to this function, flavonoids were also documented to act as an anticancer agents by controlling signal transduction pathways of cell growth and proliferation, suppressing oncogenes and tumor formation, inducing apoptosis, modulating enzyme activity related to detoxification, oxidation and reduction, stimulating the immune system and repairing DNA, and controlling hormone metabolism.

4.2 Polyphenols for Nano Modification

Polyphenols are also getting the attention of nanoparticle production sector called biocompatible nanoparticles especially in the production of biobased silver nanoparticle because of the fact that antimicrobial and antioxidant activities. Chemical synthesis of silver nanoparticles has a toxic effect, especially for medical applications. Bio-based nanoparticles register to have biocompatible, inexpensive and eco-friendly size-controlled nanoparticle also needs less purification compared to chemically synthesized. Pongamia pinnata leaf were used to biosynthesize silver nanoparticle. Pinnata leaf were selected as a result of flavonoids, glycosides, alkaloids, saponins, tannins, phenolic compounds, carbohydrates and fats. During the process pinnata, leaf did reduce the Ag^+ to Ag^o with will distinctly dimensions. Other than environmental protection and reducing toxicity Pinnata leaf bless the silver nanoparticle with very good possibility use for the defence of health against oxidizing stress-related degenerative diseases, such as cancer (Priya et al. 2016). Similarly, Cannabis sativa were used as a bio base for silver and gold nanoparticle formation for the purpose of their biofilm inhabitation. Cannabis sativa is composed of many biological compounds among those phenolics are the major ones that includes the properties of antibacterial, anti-inflammatory, antifungal and anticancer (Singh et al. 2018).

Furthermore, Holarrhena antidysenterica (L) were used to synthesis green silver nanoparticle, for the purpose to evaluate the larvicidal potential of bio-based silver nanoparticles. Traditionally chemical insecticides are used for killing and disrupting mosquitos to eliminate the lethal human diseases called dengue which is a viral infection transmitted by Aedes aegypti that is on the rise due to insecticide defense and sustainable development. Due to the harm of chemical insecticides to the non-target organisms, emerging mosquitos avoidance and insecticide-resistance actions. Holarrhena antidysenterica L was used for the stated purpose and the result obtained showed that are non-toxic clean, environmentally acceptable, stable, and have an excellent larvicidal activity against the larvae of A (Singh et al. 2018).

Bio- manufacturing of ZnO nanoparticles were performed by using Moringa Oleifera extract as an efficient chelating agent (Matinise et al. 2017), the synthesis involves sol-gel combustion, deposition of chemical vapor, hydrothermal l, wet polymerization sonochemica, ZnO nanoparticle 12.27 and 30.51 nm have been successfully synthesized natural by Moringa oleivera extract and considered using different techniques. Lignin nanotubes were successfully synthesized by peroxidase catalyzed reaction After isolated lignin from woody species of angiosperm and gymnosperm, herbaceous dicots of angiosperm and monocotus grasses covalently linked to the alumina membranes and dehydrogenated polymer (Caicedo et al. 2012), Phenolic monomers played the vital role by displaying different reactivity to adjust the polymer layers thickness inside pores, the subsequent nanotube thickness were 15 nm or 200 nm nominal diameter nanowires.

Andrographis paniculate were also used in nanoparticle reduction for ZnO nanoparticle, were the results show good anti-diabetic, anti-oxidant, and anti-inflammatory biological activity that could be used the food, cosmetic and biomedical industries (Rajakumar et al. 2018). ZnO was also used with gallic to produce biocompatible textile with enduring antibacterial properties resulting in fabric with the ZnO NPs-GA coated fabrics retained an antibacterial efficacy of over 60% even after 60 washing cycles at 75 °C hospital laundry (Salat et al. 2018). Phenolics and flavonoid were extracted from Ipomoea batatas plant for silver nanoparticles (Salat et al. 2018).

Phytofabricated selenium nanoparticles were prepared by Emblica officinali extract which is found to have several phenolic compounds such as flavonoids and tannins (Gunti et al. 2019). Emblica Nanoparticle (EpNPs) were synthesized by simple reduction and characterized, synthesized EpNPs were found to be bio-compatible and to have relatively fewer adverse effects on human.

5 Conclusion

The break through of bio phenolic polymers create one way of relief for the modern day of science as it can provide the expected similar and sometimes better physical, chemical, mechanical, thermal properties of phenolic polymers. It also provides one of the most desired properties which is bio degradability. They are most commonly used for substitution of phenols and formaldhyde but also for bio based epoxy and polyurethane polymers productions. There is a 75% substitution of lignin in the place of phenol which is found to be an outstanding achievement for the sector. The antioxidant properties were discussed in several papers but the nano modification of lignins can be taken as an eye opening research area for new researchers. We expect that more bio phenolic polymers increasingly and extensively will be discovered and fabricated for the next- generation polymer chemistry.

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Wood-Based Phenolic Composites

Ing Kong

Abstract Wood-based composites, also known as engineered wood products, wood-based products or reconstituted woods, are wood components that have been widely accepted as structural and non-structural components in product lines ranging from panels for interior and exterior purposes to furniture and support structures in building construction. Wood adhesives have played a major role in the woodworking industry with the aim to bond the wooden materials with each other or with other materials. Phenolic-based resins have more than a hundred-year history. They have been broadly used as the adhesives in woodworking industry. This chapter aims to review and discuss the development and performance of wood-based phenolic composites used in a variety of applications. It covers current knowledge and provides significant insight based on the recent research on wood-based phenolic composites.

Keywords Wood-based composites · Phenolic resins · Adhesives · Medium density fibreboard (MDF) · Oriented strand board (OSB) · Laminated veneer lumber (LVL) · Plywood

1 Introduction

Wood-based composites are the products consist of wood in refined form, often 94% or more by mass, with a thermosetting adhesive as binder (Stark et al. 2010). The common elements that have been widely used in the production of wood-based composites include veneers (thin slices), laminates, flakes, strands, particles and fibres. The commercial products such as plywood, laminated veneer lumber (LVL), oriented strand board (OSB) and medium density fibreboard (MDF) can be classified based on the particles size, process and density as shown in Fig. 1. According to Forestry Statistics in 2019 (Stagg and Ward 2019), Asia produced around three-fifth (60%) of all wood-based composites. Europe (mainly EU countries) produced around one fifth (22%) and 12% of the global production by North and Central America.

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M. Jawaid and M. Asim (eds.), *Phenolic Polymers Based Composite Materials*, Composites Science and Technology,
https://doi.org/10.1007/978-981-15-8932-4_3

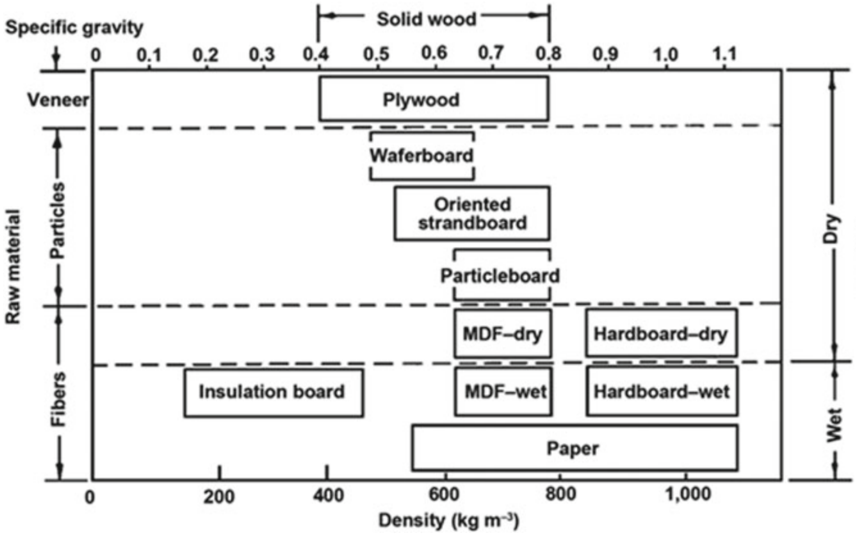


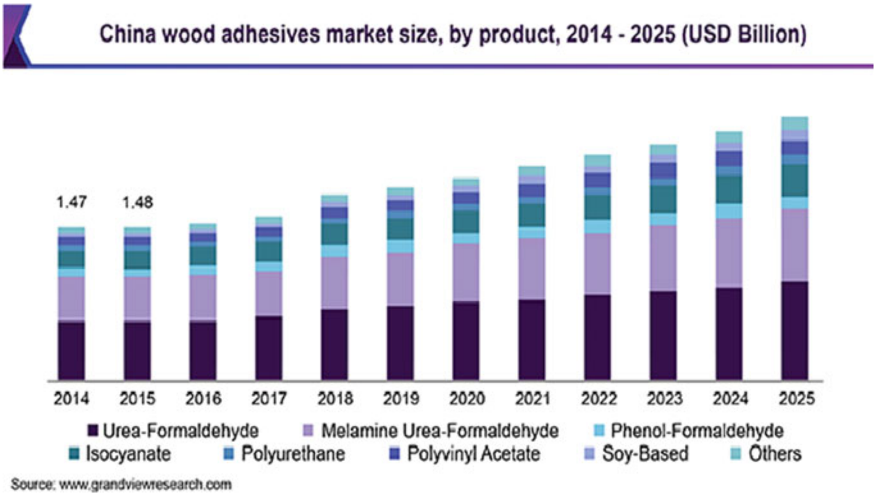
Fig. 1 Classification of wood composite panels by particle size, density and process (Suchsland and Woodson 1987)

Overall, wood-based composites production increased by 4% between 2015 (387 million m^3) and 2017 (404 million m^3) at a global level.

In the early 1960s, the most commonly used adhesives in the production of conventional wood-based composites were those derived from natural carbohydrates and protein polymers in blood, starch, soybean, casein, dextrin and other biomass (Yang et al. 2006; Frihart and Hunt 2010). These polymers are still in use today, although they have been largely replaced by petroleum-based synthetic resin due to economics, water resistance and ease of use (Frihart 2015). Synthetic resins can be thermoplastic or thermosetting; thermoplastics resins usually have less resistance to heat, moisture and long-term static loading than thermosetting polymers. Thermosetting resins undergo irreversible chemical change when cured, and on reheating, they cannot be reprocessed. They form cross-linked polymers that have high strength, high moisture and chemical resistance, and are rigid enough to support high, long-term static loads without deforming. Phenolic-based adhesives such as phenol–formaldehyde (PF), urea-based adhesive such as urea–formaldehyde (UF), melamine-based adhesive including melamine–formaldehyde (MF), isocyanate-based adhesive including polymeric methylene diphenyl diisocyanate (pMDI) are some examples of thermosetting resins.

UF resins are primarily made up of urea and formaldehyde via a two-stage synthesis. The resins are mainly used in the wood products for interior applications as the exposure to moisture as well as heat leads to a chemical breakdown of the bond-forming reactions. There are several advantages of using UF as the wood adhesives include lower cost, lower curing temperatures, good thermal properties, low flammability, absence of colour in the cure polymer and the adaptability in a variety of curing conditions (Ormondroyd 2015). MF resins are made from the interaction of melamine and formaldehyde by condensation of two monomers. Despite their high cost, this kind of resins provide good fire and heat resistance due to the release of nitrogen gas when burned or charred. It is quite common to blend MF with UF resins to produce melamine-urea–formaldehyde (MUF) for cost efficiency. They have been used in the production of exterior and semi exterior wood panels (Pizzi 2017). pMDI resins are relatively new synthetic formulation and unconventional adhesives for panel products compared to UF, PF and MF. Advantages of pMDI include high binding quality particularly for exterior products, high reactivity, high stability compared to other adhesives and they are free of formaldehyde (Pan et al. 2006). However, they cause irritation to eyes and skin. PF resins can be prepared by reacting phenol with formaldehyde under basic ('resole') or acidic ('novolak) conditions (Fabris and Knauss 1989). PF resins, which are the first class of fully synthetic polymers to be commercialized since 1911 (Allen and Ishida 2001; Hirano and Asami 2013), have been used widely for wood composites. They are typically used in the production of exterior wood composites such as construction plywood, particleboard and OSB panels attributable to their high strength and extremely resistant to moisture, low initial viscosity and good thermal stability (Zhang et al. 2018; Hoareau et al. 2006). Figure 2 shows the market size of wood adhesives in China from 2014 to 2025 (forecast).

As a contribution to updating the state of knowledge, this chapter aims to provide the readers an overview of the general types and compositions of wood-based phenolic composites and the materials and processing techniques used to manufacture them based on the recent literature review. The chapter is organized as follows.


China wood adhesives market size, by product, 2014 - 2025 (USD Billion)

Source: www.grandviewresearch.com

Fig. 2 China wood adhesives market size, by product from 2014 to 2025 (forecast) (Grand View Research 2019)

The first section covers the materials and adhesives common to conventional wood-based phenolic composites. A brief discussion on the adhesion mechanisms is presented in the second section. The third section reviews the research works done on the development of wood-based phenolic composites with an emphasis on MDF, plywood, OSB and LVL. The potential research directions and the development of adhesive technology based on renewable resources are highlighted in the future perspectives section. The conclusion drawn at the last section closed this chapter.

2 Components of Wood-Based Phenolic Composites

A wood-based phenolic composite can be defined as a composites material mainly composed of wood elements and phenolic resins as adhesives. More recently wood has also been combined with thermoplastic polymers to make wood-polymer composites (WPC) by using compression, extrusion and injection moulding methods. However, WPC will not be discussed in this chapter.

2.1 Wood Component

Wood is a composite material composed of two groups of chemical constituents: structural substances include cellulose, lignin, hemicellulose as major cell wall constituent polymers and non-structural substances such as extractives, water soluble organics and inorganics (Smailagić et al. 2019). Wood can be categorized into two kinds, softwood and hardwood. These names always lead to a common misconception that hardwoods are harder than softwoods. In fact, the names have nothing to do with how hard the wood is, but they have to do with the reproductive biology of the species. Hardwoods are woody-fleshed plant obtained from angiosperms where they produce flowers and the seeds are enclosed in the ovary of the flower while softwoods are gymnosperms, where they produce uncovered seeds. In term of their physical structure, hardwoods have broad leaves and they lose their leaves in the autumn while softwoods have more-needle like evergreen leaves and retain them through the winter. Some of the examples of hardwoods include birch, ash, beech and oak while spruce, pine and fir are the examples of softwoods. Hardwoods are most commonly used in construction for decking, flooring and panelling, and sometimes their lumber and dimension stock are remanufactured into high-quality furniture. Softwoods have a wide range of applications, they can be found in construction for the forms, framing, sheathing, scaffolding etc.

Industrially, once harvested roundwood is transported from the forest to a sawmill to be converted manufactured into chips, flakes, veneers or fibre pulps and then reconstituted into a variety of products. From the end application point of view, wood-based composites can be further classified into panel applications and beam

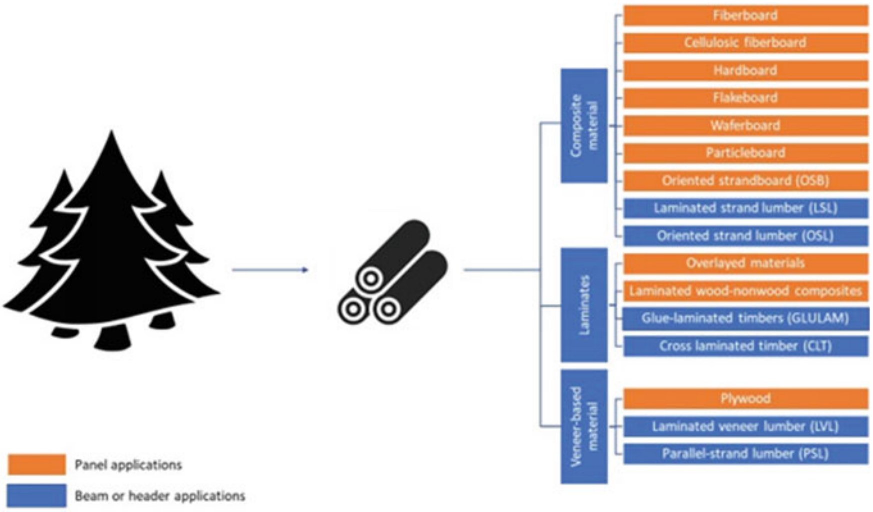


Fig. 3 Classification of wood-based composites, adapted from (Stark et al. 2010; Ramage et al. 2017)

or header applications (Shi and Walker 2006). The classification of wood-based composite products and their applications are illustrated in Fig. 3.

2.2 *Phenolic Resins*

Wood adhesives play an important role in the production of wood-based products. Today, wood adhesives are used in about 80% of the all wood and wood-based composite products worldwide (Lei et al. 2010). Phenolic resins are known as the oldest thermosetting polymers. In general, they can be divided into resole and novolak resins. Resole resins can be further classified into solid and liquid resins. The synthesis of resole and novolak resins is shown in Fig. 4. Novolak resins are thermoplastics that usually consist of formaldehyde, at molar excess of phenol and an acid catalyst such as sulfuric acid, phosphoric acid or hydrochloric acid. They often require a curing agent or hardener to form a thermoset, hence, sometimes they are also termed as "two-step" resins. They are mainly used to produce novolac resin-coated proppants or to prepare phenolic molding materials. Resole resins can be converted to 3-dimensional, cross-linked, insoluble and infusible materials simply by heating to 120 °C or above without any additional curing agents. Therefore, they are referred to as "one-step" resins (Fink 2013). Resole resins have been widely used as the adhesives for wood-based composites.

Phenol-resorcinol–formaldehyde (PRF) is a newer version of phenolic resin, developed from resorcinol–formaldehyde (RF) to lower the cost of the resorcinol.

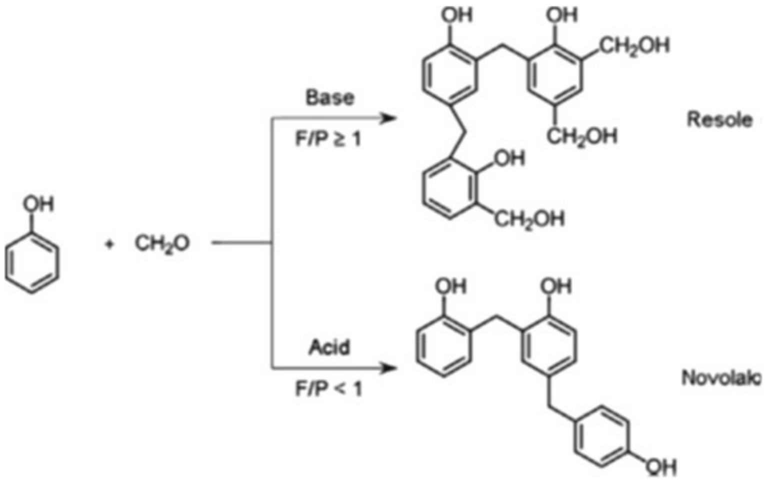


Fig. 4 Synthesis of resole and novolak resins (Pilato 2013)

The advantage of RF and PRF over PF resin is the low curing temperature and curing time, where RF and PRF are curable at room temperature due to the resorcinol being 10 times faster in reaction than phenol. They are very durable bonds and show good resistance to bond failure and degradation.

3 Wood Adhesion

The study of the science of wood adhesion becomes increasingly important as an excellent adhesive system improves the efficiency and effectiveness of processing methods and the use of wood. Wood materials characteristics, adhesive characteristics, the chemical bonds and interlocking of the polymer chains in adhesive, wood and adhesive-wood surfaces are the factors that affect the adhesive bonding performance.

3.1 Mechanism of Adhesion

A chain-link analogy is commonly used to describe an adhesive bond as proposed by (Marra 1992), shown in Fig. 5. Link 1 is the pure adhesive phase which shows the properties that are normally measured for an adhesive and links 8 and 9 represent unadulterated wood with the bulk properties of the wood substrate. Links 2 and 3 are the adhesive boundary layers where the adhesive has cured under the influence of the wood substrate next to it. The lack of mobility near the surface limits the collisions among molecules for a normal curing process. Links 4 and 5 are adhesive-wood

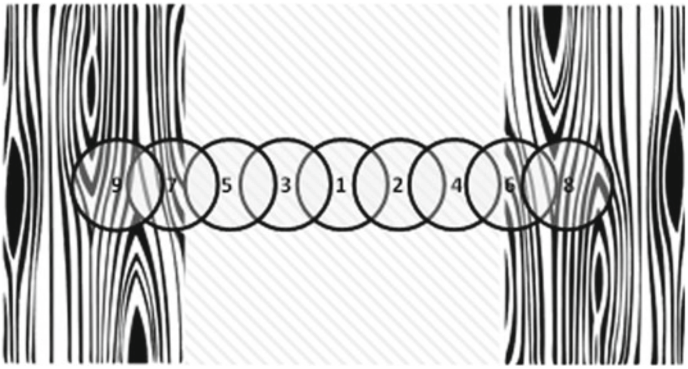


Fig. 5 Chain-link analogy for an adhesive bond in wood (Marra 1992)

interphase regions, where the adhesion occurs through the possible mechanisms such as mechanical interlocking, covalent bonding or secondary chemical bonds duet to electrostatic forces. Links 6 and 7 are interface links where the adhesive contacts the wood surface. The wood cells may be modified during the surface preparation or bonding process. The cells in this region could be weak and hence increase the risk of bond failure.

3.2 Bond Formation

To form a proper bond, it is very important to have a good adhesive wetting, proper curing of the adhesive and the sufficient deformability of cured adhesive. It is desirable for the adhesive to be able to wet and penetrate the wood, and to transfer when the wood surfaces are brought into contact, as illustrated in Fig. 6. Wetting can be defined as the ability of an adhesive drop to form a low contact angle with the surface upon contact. Penetration refers to the ability of the adhesive to move into the voids on the substrate surface or into the substrate itself while flow or spreading refers to the condition when a liquid move across a surface to cover more of the surface to allow a stronger bond. The contact angle and the viscosity of the adhesive are the factors that determining the ability of an adhesive to flow. Like flow, the ability for an adhesive to penetrate relies on the adhesive viscosity as well, but also on the surface energies and the size of capillary or void that it is penetrating (Frihart 2012; Ülker 2016).

As a natural porous and anisotropic material, wood has many different spatial levels of structure. The lumens of the cells are sufficient to provide a good pathway for liquid-phase resin flow. However, due to the polar surface of wood, only waterborne adhesives are suitable for bond formation. The criteria to be considered when choosing an adhesive to create a satisfactory adhesive wood bonding are the solubility of the adhesive in the adherends, the wetting tension of the adhesive has to be less

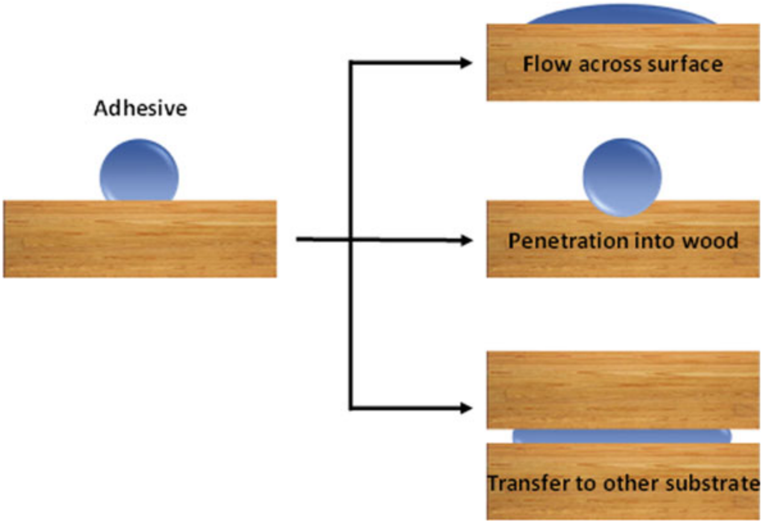


Fig. 6 Adhesive wetting of wood surfaces, showing the difference between flow, penetration and transfer (Frihart 2012)

than the surface energy of the adherend, the viscosity of the adhesive where low viscosity adhesives is preferred so that the equilibrium contact angle can be attained during the assembly time and also an adhesive that is compatible with the weak boundary layer (Gardner 2006).

4 Wood-Based Phenolic Composites

PF resins are widely used in many fields including in the manufacturing of wood-based composites because of the formation of bonds between the adhesives and the phenol-like lignin from the wood. The most common wood-based phenolic composite products are MDF, plywood, OSB and LVL. In this section, each of these composites will be discussed in term of their production, general manufacturing issues, properties as well as some recent research and development work.

4.1 Medium Density Fibreboard (MDF)

Fibreboard is a kind of engineered wood products that is manufactured by reconstituting refined wood fibres as raw materials into a panel with fibres bound together by synthetic adhesives through compression to its final thickness via hot-pressing. Fibreboard can be classified according to its density into three categories, hardboard (also called high density fibreboard) with a density of 900 kg m^{-3} and above, medium density fibreboard (MDF) between 500 and 900 kg m^{-3} and insulation board (also known as cellulosic fibreboard), between 150–500 kg m^{-3} (Kamke 2001; Park et al. 2001a).

The market of MDF is expected to increase from USD 22 billion in 2017 to USD 56.27 billion by 2026 due to the rising demand from the new domestic housing construction and commercial constructions (Ingle 2018). MDF panels have several advantages which include good mechanical and physical properties, good machinability comparable to solid wood, the relative insensitivity with the quality of raw material, molding ability for wide variety of surface decorations, smooth surface suitable for various finishing, and tightness of edge (Park et al. 1998, 2001a). UF resins have been traditionally used for the manufacturing of MDF. However, some of the disadvantages of MDF panels bonded with UF resins are the formaldehyde emissions and lower durability in humid environmental conditions. Due to this reason, most of the MDF panels bonded with UF resins are only suitable for interior applications. In comparison, PF resins have been widely used as an exterior adhesive, particularly for oriented strand board (OSB) and plywood due to their features such as ease in processing, low level of formaldehyde emissions, good glueline properties, high durability when exposed to water, weather and high temperature etc. They are rarely used for the manufacturing of MDF panels because they cost more than twice than that of UF resin. Another drawback of PF adhesives is that they have slower cure rate than UF resins, hence lower production speed and higher production cost.

Resin formulations, wood fibres characteristics and hot-pressing conditions influence the properties of the manufactured MDF panels. Several studies of PF resins bonded MDF panels have been conducted. (Park et al. 1999b) manufactured MDF panels by using mixed hardwoods fibres and three different PF resins as the adhesives. The modulus of rupture (MOR) and modulus of elasticity (MOE) obtained were satisfactory, however, the internal bond (IB) was found to be barely satisfied the standard requirement or didn't meet the minimum level. In addition, the use of PF resins in MDF manufacturing required high resin content (10 wt%) and long hot-press time (7 min). In as separate study, the effect of weight average molecular mass ($\bar{M}_W$) of the resin on the mechanical performance of MDF panels was investigated (Park et al. 1998). The viscosity of adhesives was found to increase by increasing the portion of high $\bar{M}_W$ resin in the prepared resin. MDF panels prepared with the blending ratio of 40:60 (low $\bar{M}_W$:high $\bar{M}_W$) gave the highest IB strength and 80:20 showed the highest MOR and MOE. Both the maximum values of MOR and MOE for mixed resins were above the required level of the MDF standard, which are 34.5 MPa for MOR and 3.45 GPa for MOE. Wood fibre characteristics such as fibre length, bulk density and acidity was found to affect the properties of MDF panels in a wide variety of ways too (Park et al. 2001a). Short hardwood species showed greater bulk density than that of long softwood fibres. Mixed species showed the highest bulk density, which could be attributed to the proper compaction between short and long fibres. The same trend can be observed in the mechanical properties such as IB and MOE where mixed species showed the highest values regardless of the adhesive types used. Compared to the UF bonded MDF panels, PF-bonded MDF panels showed better MOE and MOR and better dimensional stability in general.

As mentioned earlier, slower cure rate is one of the reasons that PF resins have not been widely used for MDF manufacturing. Several attempts have been made to accelerate the curing rate of PF resins by using different catalysts and additives such as amines, amides and ammonia (Pizzi 2003). Park et al. (1999a) modified PF resol resin with three carbonates (propylene carbonate (PC), sodium carbonate (NC) and potassium carbonate(KC) to speed up the cure of the resins. The thermal behaviour of the resins was characterized by using differential scanning calorimetry (DSC). By using a multi-heating rates method, they found that the rate of resin cure increased with an increase in the additive level and temperature selected. The analysis showed that all three carbonates added can speed up the cure rate of PF resin, with PC modified PF resins showed the fastest curing, followed by NC and KC. In addition, the results indicated that the pressing time for MDF could be reduced by incorporating the additives into PF resins. To further confirm this, the same group of researchers further applied these three carbonates for the manufacturing of MDF panels (Park et al. 2001b). Mixed species wood fibres and laboratory-synthesized PF resin with different carbonate types and contents were used to prepare the MDF panels by a conventional hot-press. The results obtained showed that PC modified resins performed the best in term of the mechanical properties of MDF panels produced. Hence, PC modified resins was chosen to further identify the optimum PC level (1.5–6.0 wt%), PF resin content (5–8 wt%) and pressing time (4–5 min). The results revealed that the optimum PC level was 3 wt% with 6 wt% of overall PF resin content for both face and core layers and the minimum pressing time required to produce the 19.1 mm thick MDF panels was 5 min. A more recent study (Feng et al. 2010) investigated the effects of ethylene carbonate (EC), PC, glyceryl triacetate (GT) and resorcinol on PF and UF resins as adhesives. The group argued that as much as esters were very effective in accelerating the cure rate of PF, they cause substantial loss of bonding IB strength. On the contrary, resorcinol showed similar effects on the reduction of PF gel time while preserves the IB strength. Compared to UF, which showed 0.11–0.18 ppmv formaldehyde emissions, PF bonded MDF panels did not emit any formaldehyde.

In order to widen the applications of fibreboard, which previously was limited to the applications that required low mechanical properties, Tang et al. (2017) fabricated an ultra-high-density fibreboard with high pressure and high resin content (>20% in total weight loss). The optimal conditions for good mechanical properties were achieved by using 40% of resol-type phenolic resin which was probably due to the strong interfacial adhesion occurred between the wood fibres and resin that allowed better fibre-resin interactions. Furthermore, the fibreboard produced showed an increase in the thermal stability and fire properties with the increasing of resin content which makes them competitive with other products.

Recently, Antov et al. (2020) developed the MDF by replacing calcium lignosulfonate (5–15%) into the glue composition to reduce the gluing content of conventional

PF resin content (3–5%). The results showed that the panel with at least 3.5% PF resin content complied with the EN standard requirements.

4.2 Plywood

An assemblage of wood veneers or thin layers (either softwoods or hardwoods) bonded together under pressure by an adhesive between plies to form a flat panel is termed as plywood. Each of these adjacent layers oriented perpendicular to one another to give greater strength to the panel. A panel usually contains an odd number of layers, with the outer layers (odd-numbered layers) have their grain direction oriented parallel to the long dimension of the panel. The middle plies are termed as "cores" and plies on either side of the cores but beneath the outer plies are called "crossbands" (Fig. 7).

In 2018, the annual production of plywood was 160 million m^3 worldwide, with China being the world's larger producer (113 million m^3), as shown in Fig. 8. Plywood is an ideal product for a various of applications, ranging from cabinet panels, construction sheathing, industrial components to highly-engineered structural designs and systems such as box beams, prefabricated I-joists and panelised roofs. The characteristics of plywood panels largely depend on the quality of the wood veneers, the number and order of layer placement, types of adhesives used and the bonding conditions. The commonly used adhesives are PF, UF and MF resins.

In Malaysia, the attempt to utilize oil palm stem (OPS), generated during the replanting of oil palm trees, as the raw materials for the manufacturing of plywood has been made. The stem of oil palm is surrounded by loose parenchymatous tissue (density of 180 kg/m^3), embedded in the higher density (630 kg/m^3) vascular bundles.

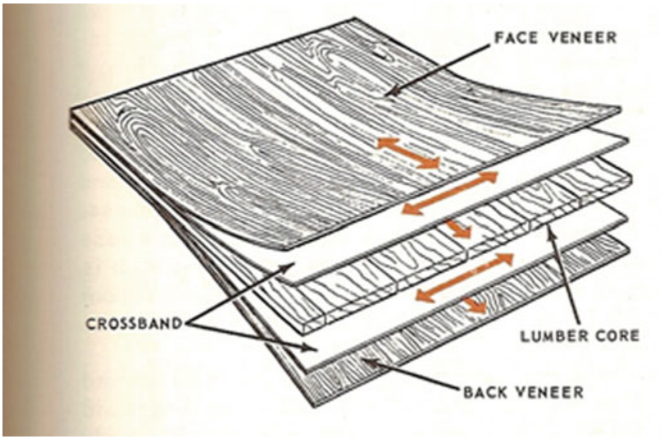


Fig. 7 The orientation of plywood

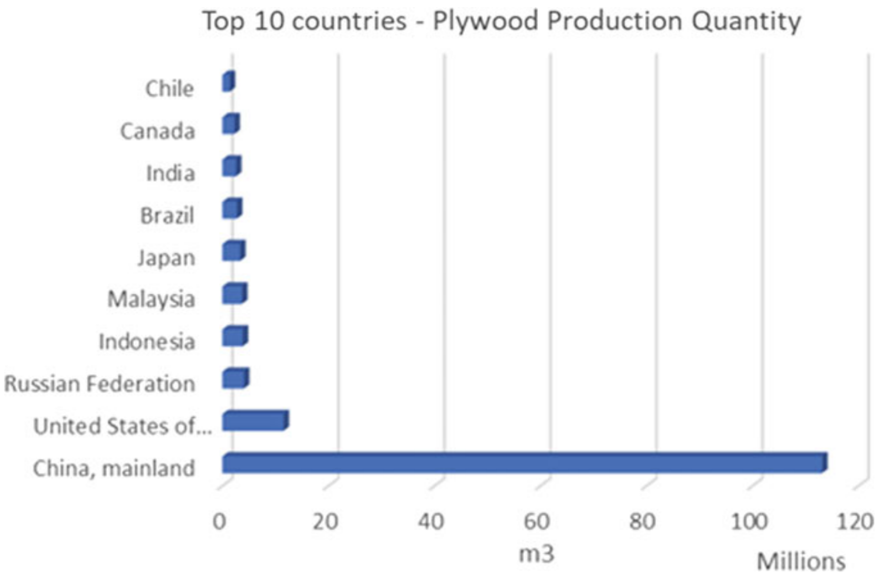


Fig. 8 Plywood production quantity by top ten countries in 2018 (Food and Agriculture Organization of the United Nations (FAO) 2019)

The difference in density between the two substances can become the main factor of various problems that affect the bonding and strength of the final products, if they are not properly controlled. A few methods have been proposed to enhance the performance of oil palm plywood, including treating the veneers with resin polymer via soaking or vacuum pressure. Low molecular weight PF (LMWPF) can penetrate into the cell wall of the woody materials easily and rapidly and upon curing it increases the density of parenchyma tissues and improves the strength and dimensional stability. (Loh et al. 2011) studied the surface characteristics of OPS treated by LMWPF and contact angle measurement revealed that the wettability of LMWPF treated veneers was much lower compared to the untreated veneers due to the attachment of partial cured LMWPF resin on the surface, hence, slows down the penetration of the water into the cells. Plywood was then manufactured by using LMWPF treated OPS with commercially-available UF resin as the adhesive. By controlling the concentrations, solid contents and molecular weight distribution of the resins, the plywood can be manufactured at the optimum condition to ensure the full penetration of adhesive into the veneers and a much smoother surface for better penetration of adhesive (Fig. 9). The mechanical properties of the plywood made from LMWPF treated veneers have been significantly improved, i.e. MOR by 104% and MOE by 56% for outer veneers and 47% and 39% for inner veneers, respectively.

(Wahab et al. 2012) investigated the adhesion properties of PF resin prepreg OPS veneers with three different molecular weights, low $\bar{M}_W$(LMWPF)—600 g/mol, medium $\bar{M}_W$ (MMWPF)—2000 g/mol and commercial—5000 g/mol. The three

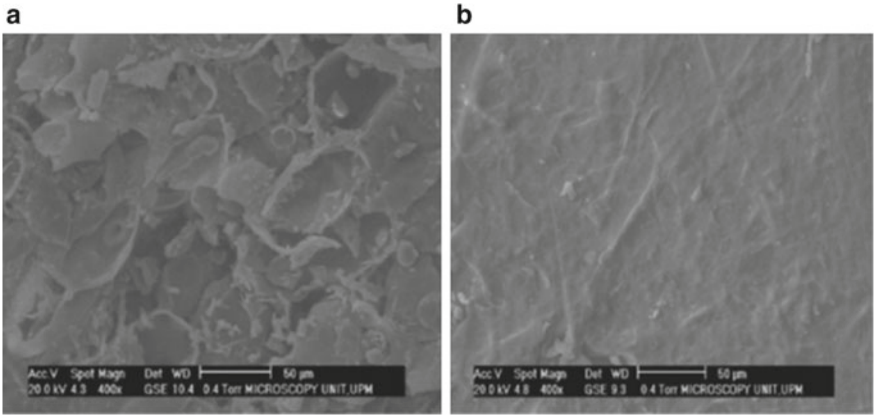


Fig. 9 Scanning electron microscopy (SEM) image of POS veneer surface **a** before and **b** after LMWPF treatment (Loh et al. 2011)

types of PF treated veneers were then used to produce plywoods by using hot-pressing method and their shear bonding properties were studied. Both of the volume percent gain (VPG) and weight percent gain (WPG) increased with decreasing molecular weight of PF resin. This was attributed to the shorter chain and lower viscosity of LMWPF and MMWPF that enhanced the adhesive penetration into the parenchyma tissues. In term of the mechanical properties, higher shear strength and wood failure always indicate good bonding between the veneers. The LMWPF treated OPS plywood exhibited high shear strength but a low wood failure percentage. This could be explained by the improvement of wood strength due to the deep penetration of LMWPF into the veneer. The same group (Wahab et al. 2014) further investigated the curing and thermal degradation of the plywood with different resin molecular weight. MMWPF was found to exhibit the highest thermal stability, MOR and specific strength and it was the most suitable resin for prepreg process for the manufacturing of OPS plywood.

The consolidation of plywood is achieved by hot-pressing process, hence, hot-pressing pressure and hot-pressing time are the important variables affecting the performance of the plywood. An increase of the pressing pressure leads to an improvement in the plywood density as the spongy OPS will be compacted into closer contact. The values of MOE and MOR for the plywood hot-pressed at the pressure of 20 and 30 bar, respectively, didn't show significant difference, however, when the hot-pressing was carried out in two-step, at 20 bar for the first 5 min and increased to 30 or 50 bar for the next 9 min, the MOR and MOE of the OPS plywood showed 200 and 259% as compared to commercial 5-ply OPS plywood panel (Hoong and Paridah 2013). This could be attributed to the increase of density which directly improved the strength of the plywood. Furthermore, the adhesion between wood substrate by the LMWPF provided mechanical interlocking and chemical bonding that further enhanced the strength of the plywood panel. By increasing the pressing time, it can be expected that the mechanical properties and bonding properties of plywood panel will improve accordingly. In the study carried out by (Hoong et al. 2012), it was found that when the pressing time was increased from 14 min (5813 MPa) to 18 min (5914 MPa), the MOE didn't change much but the value increased significantly when the pressing time was 20 min (7797 MPa) while the value of MOR increased when the pressing time increased from 14 min (53.4 MPa) to 16 min (55.4 MPa), and the value dropped at 18 min (44.9 MPa) and bounced back when the pressing time was 20 min (601 MPa). The mechanical shear strength properties of the OPS plywood increased with the increasing of pressing time from 14 to 20 min. In other words, sufficient pressing time is required in order to produce high quality plywood panel with excellent mechanical properties. The resin content may affect the mechanical properties, bonding quality and formaldehyde emission too if it is not properly controlled. Study (Hoong et al. 2013) showed that resin content of 32% showed the maximum MOE value, while MOR value increased gradually with the resin content up to 40%. However, the higher amount of formaldehyde was emitted when the amount of solid content in the resin increased.

Another group of researchers (Arif Nuryawan et al. 2020) have reported the improvement of physical, mechanical and thermal properties of the hybrid plywood which was produced by using hand lay-up techniques of oil palm trunk (OPT) veneer and empty fruit bunch (EFB) fibre mats and enhanced with PF resin filled with oil palm ash (OPA) nanoparticles as a binder. The PF resin filled with OPA was found to be able to stick to the surface of the layers, which led to a better capability to support stress transfer during shear test compared to the plywood with only PF resin as the binder. In addition, the higher the OPA nanoparticles loading in PF resin, the greater improvements can be noticed in dimension from water absorption and thickness swelling experiments.

4.3 Oriented Strand Board (OSB)

Oriented strand board (OSB) is an engineered wood product manufactured by layering wood strands in specific orientations bonded with water-resistant adhesives such as PF or pMDI. In general, the outer faces are made of larger strands that usually aligned in the long-direction of the panel. Core layers have smaller or finer strands and the strands are either counter-aligned or randomly laid, as illustrated in Fig. 9. The OSB wood panels are used in sheathing in walls, flooring and roofing as well as for furniture manufacturing. They are manufactured successfully in America (67.7%) and Europe (29.8%) but less popular in Asia. The OSB production quantity shared by region is shown in Fig. 11. The common raw materials used to produce OSB aspen and southern pine (*Pinus taeda* L.) (SP) and some other low-density hardwoods such as birch, sweetgum, beech etc. (Fig. 10).

During the manufacturing of OSB, the consolidation of the panel is achieved by a hot-pressing process, which involves simultaneous heat and mass transfer, curing of adhesives and forming panel strength. There are many factors affecting the properties

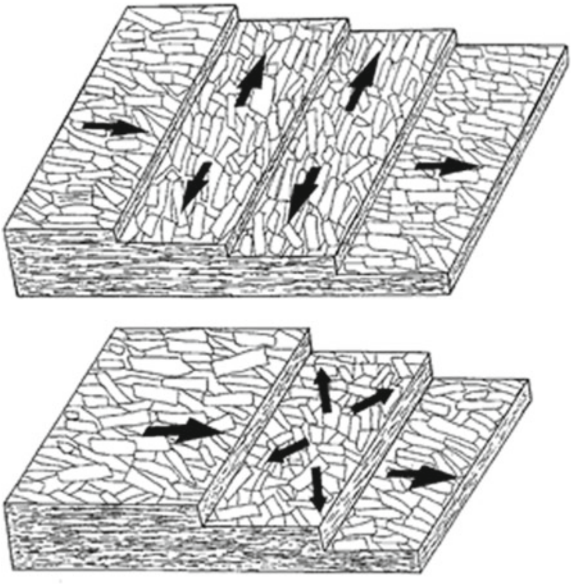


Fig. 10 A schematic illustrating strand orientation of a typical OSB (Hiziroglu 2006)

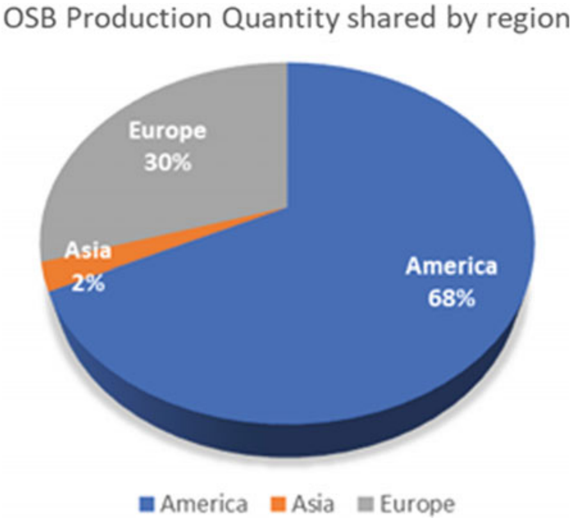


Fig. 11 OSB production quantity shared by region in 2018 (Food and Agriculture Organization of the United Nations (FAO) 2019)

of OSB, which include adhesive types, wood species, flake dimensions, adhesive loading levels, adhesive ratios, hot-pressing time, pressure and temperature etc.

Dimensional instability is one of the weaknesses of OSB that is largely affected by hygroscopic properties of wood strands used (Derkowski et al. 2015). It can be measured by moisture induced deformation, caused by humid air or liquid water. This can be improved by impregnating the wood strands with LMWPF, the similar method reported by (Loh et al. 2011) on the production of plywood. Wan and Kim (Wan and Kim 2006) impregnated SP wood with LMWPF using a vacuum/pressure method and performed the anti-swelling efficiency (ASE) measurements on the specimens based on three consecutive water-soak test. The specimens showed significant decreased in volumetric swelling in the first test cycle, however, the ASE values dropped in the second and third cycles, which indicating the impregnating resin was ineffective under exhaustive water exposure conditions. Generally, the ASE values of OSB increased with increased resin solids loading levels, longer hot-pressing time and higher temperature.

A comprehensive understanding of the curing behaviour of adhesives used in the production of OSB can be achieved through simulation using mathematical models or by differential scanning calorimetry (DSC). DSC has been widely used to analyse the cure process of thermosetting polymers, in particular PF, epoxy resins and isocyanate resins. The data that can be obtained from DSC include activation energy of the curing reaction, the heat of the reaction and the order of the reaction. (Lei et al. 2006) studied the cure kinetics of commercial PF resins (both face and core) for OSB manufacturing by using isothermal and dynamic DSC. The results showed that the data obtained from isothermal DSC method fitted the experimental data better than the dynamic DSC method and isothermal DSC method is more useful in determining the cure kinetic parameters. Face and core resins showed different curing mechanisms, where the cure of face resins completely followed an nth-order reaction mechanism with an activation energy of 79.29 kJ mol^{-1} while the cure of core resins was more complicated with an nth-order and an autocatalytic reaction. The addition of complexing agents and additives into PF resins may influence the cure of the resins. (Lei and Wu 2006) reported the effect of wood flour on the cure kinetics of PF resins used for OSB manufacturing. Two kinds of wood flours, namely maple (*Acer sp.*) and pine (*Pinus sp.*) were mechanical mixed with face and core resins, respectively and the cure reaction rates were studied by using DSC. The results indicated that the onset cure temperatures and activation energy of PFs were significantly reduced by the wood flour. A change of the cure mechanism has been observed for core resin, where the core resin and wood flour mixture only showed one cure kinetic mechanism, which was nth-order reaction mechanism compared to two cure mechanisms, nth-order reaction and an autocatalytic mechanism for core resin without wood flour.

Lee and Kim (2007) investigated the effects of urea and curing catalysts such as potassium carbonate, sodium carbonate and triacetin on the properties of OSB panels. 10% of urea was added in the early, middle and later part of resin synthesis procedure and it was found that adding urea in the different stages of the resin synthesis didn't lead to any significant performance improvement. However, it was suggested that adding urea in the later part was more convenient and provided consistency for the synthesis. Most importantly, it reduced the production cost by replacing the higher cost of PF resin.

Gunduz et al. (2011) studied the effects of production factors such as pressing time and adhesive content on the physical and mechanical properties of OSB panels made of mature Scots pine wood (*Pinus sylvestris* L.). It was reported that the IB, MOR, MOE and tensile strength (TS) increased with increasing of pressing time from 3 to 7 min and adhesive content from 3 to 6%. The same group of researchers also observed the effects of pressing pressure (35, 40 and 45 kg cm^{-2}) on the thermal conductivity of OBS panels (Yapici et al. 2010). The results indicated that the thermal conductivity of OSB panels improved with the increased of pressing time, adhesive content and pressing pressure, which the specimen with 6% adhesive content, 7 min press time and 45 kg cm^{-2} pressing pressure achieved the highest thermal conductivity achieved (0.169 W mK^{-1}).

Increasing PF resin content in OSB results in better moisture resistance and durability, but it also leads to higher production costs and higher brittleness of the products, hence lower in toughness. The toughness PF can be modified by adding a small amount of rubbery modifiers into the PF resins. (Chowdhury et al. 2011) investigated the effect of maleic anhydride polyolefins (MAPO) on the dynamic thermomechanical properties of PF resins. Maleic anhydride polyethylene (MAPE) and maleic anhydride polypropylene (MAPP) were mixed with PF resins, respectively. Basswood (*Tilia america* L.) was used to prepare the specimens for dynamic mechanical analysis while yellow poplar (L*iriodendron tulipifera*) was used to prepare the specimens for fracture testing. Overall, MAPP had a better performance compared to MAPE in improving dynamic stiffness and fracture toughness, which could be explained by the fact that MAPP had higher solid content, higher maleic anhydride content and lower viscosity. MAPP and PF resin blend was chosen for the manufacturing of unidirectional OSB with the commercially available wood strands (aspen and mixed hardwoods) (Chowdhury and Yadama 2011). The results indicated that the mechanical properties such as MOR and MOE of OSB increased with increasing PF resin content. The addition of MAPP didn't change the MOR and MOE significantly, however, it reduced IB in particular at higher PF levels.

OSB panels have been widely used as structural panels in residential construction, however, one of the potential weaknesses of OSB panels is they can easily deteriorate because of termites, decay fungi, and other wood destroying organisms. Work has been done to study the effect of zinc borate and calcium borate treatment on the *Formosan subterranean* termite (FST) resistance of OSB (Lee et al. 2004). It was found that both borate-treated OSB panels were resistant to FST attack, with the higher level of borates led to higher termite mortality. Decay and mold resistance tests with brown-rot, *Gloeophyllum trabeum*, and white-rot, *Trametes versicolar*, fungi for 8 and 12 weeks were carried out by (Wu et al. 2003). The results suggested that the incorporation of both borates gave a suitable protection against brown-rot and white-rot. Wood species and fungal species as well as the level of borate play important role in influencing the decay and mold growth.

4.4 Laminated Veneer Lumber (LVL)

Laminated veneer lumber (LVL) is an engineered wood product manufactured by gluing veneers together with structural adhesives such as PF, UF, MUF and PRF and pressing under heat rotary peeled veneers. (Kurt et al. 2012). Unlike plywood, all the veneers in LVLs are laid parallel to each other. The production of LVLs began in the 1940s where they were used for manufacturing of high strength aircraft structural parts because of their light weight and resistance (de Souza et al. 2011). Today, LVL boards are preferred for many applications such as permanent structural products including beams, columns, joists, headers, truss chords etc. They can safely be used as substitute for solid wood as they retain the structural properties of wood. There are several important factors in the manufacturing of LVLs including the wood species, quality, dimensions, mechanical, physical and other properties as well as the suitability for treatment and durability.

A study on the edgewise bending properties of five types of LVLs, fabricated with southern pine veneers of B, C and D grades (as shown in Table 1) and liquid PF, was conducted by Tang and Pu (Tang and Pu 1997). Results obtained indicated that the veneer grade has a noticeable effect on the edgewise static bending strength and stiffness properties of LVLs. LVL made of high-grade veneer (grade B) had the highest density, MOR and MOE compared to the specimens fabricated by low-grade veneers (grade C or D). In addition, the engineering performance of LVL can be improved by substituting two surface layers on both sides of the LVL with high-grade veneers.

Research has been carried out to evaluate the raw material for the manufacturing of LVLs, including off-grade, low density and fast-growing wood species. In India, rubber wood (*Heavea brasiliensis*) veneer and PF adhesive has been used to manufacture LVL and the physical and mechanical properties were reported (Kamala et al. 1999). The study indicated that LVL panels made of rubber wood showed better design strength over wood and another advantage was the raw materials were available in larger dimensions. The mechanical strength of LVL produced were comparable with solid wood such as *Artocarpus lakoocha* (lakooch), *Calophyllum elatum* (poon), *Cedrus deodar* (deodar) etc.

In Malaysia, there was an attempt to find balance utilization between high- and low-density wood species, where low density wood species pulai (*Alstonia sp.*) 210–500 kg m^{-3}, sesendok (*Endospermum* sp.) 305–655 kg m^{-3} and kekabu hutan (*Bombax* sp.) 415–545 kg m^{-3} were used in core layer and keruing (*Dipterocarpus* sp.) 690–945 kg m^{-3} was used as surface layers (H'ng et al. 2010). Increasing the number of keruing veneers as surface layers was found to increase the MOR and MOE. The finding has further emphasized that the quality, density and mechanical properties of materials used for face layers frequently affected the overall performance of LVLs. Other than keruing, oil palm trunk, one of the oil palm biomasses has been used as the raw material to produce LVL. Sulaiman et al. (2009) investigated the physical and mechanical properties of LVL made from oil palm trunk and different adhesives. The physical tests and shear tests were carried out before and after three pre-treatment which include cold water, hot water and cyclic boil-dry (CBD) pre-treatment. The density of LVL made from oil palm trunk was found to be higher than solid oil palm trunk. This could be explained by the cold and hot pressing during the production that resulted in a reduction of the total volume, hence an increase in density. Addition of adhesive is another reason for the increase of

Table 1 Veneer grades for plywood panels (APA 1995)

A	Smooth, painable Not more than 18 neatly made repairs, boat slad, of router type, and parallel to grain, permitted, Wood or synthetic repairs permitted. May be used for natural finish in less demanding application	
B	Solid surface. Shiira, sled or router repair, and light knots to 1 in. across groin permitted, Wood or synthetic repairs permitted. Some minor splits permitted	
C **Plugged**	Improved C veneer with splits limited to 1/8-in. width ond knotholes or other open defects limited to 1/4 × 1/2 in.—Wood at synlhetic repairs permitted. Admits some broken groin	
C	Tight knots to 1 − 1 /2 in. Knotholes across grain and some to 1 − 1/2 in. if total width of knots and knotholes is within specified limits. Synthetic or wood repairs-discoloration and sanding defects that do not impair strength permitted. Limited splits allowed. Switching permitted	
D	Knots and knotholes to 2 − 1/2 in. width across grain and 1/2 in. larger within specified limits. Limned splits are permitted. Switching permitted, Limited to Exposure 1 or Interior panels	

density especially for panels used higher adhesive spread level (500 g m^{-2}) as the average of the adhesive density used was 1.2 g cm^{-3}, compared to 0.31 g cm^{-3} of solid oil palm's density. Among the four types of adhesive used, LVL made using PRF resins exhibited the best shear strength and water resistance properties that made the panels very suitable for use in exterior, humid and interior climates. Another study employed CBD pre-treatment on the LVL fabricated from the tropical hardwood, bintangor (*Callophyllum sp.*) with PF resin as binder (Paridah et al. 2012). The results indicated that the number of CBD cycles can significantly influence the mechanical properties of LVL. The properties of LVL decreased with the increasing of CBD cycle and duration of outdoor ageing.

Other species of timber that have been investigated for LVL production include fast-growing melina (*Gmelina arborea*) trees in Costa Rica (Tenorio et al. 2011), *eucalyptus* (*Eucalyptus grandis* W. Hill ex Maiden) and *poplar clones* (*Populus x euramericana* I-214) (Bal 2016), *Populus deltoides* I-77/51 and *Populus deltoides* S.307–26 (Kurt et al. 2012) in Turkey, pinus (*Pinus oocarpa* Schiede ex Schltdl and *Pinus kesiya* Royle ex Gordon) in Brazil (de Souza et al. 2011). PF resin was the common adhesive used in the manufacturing of LVL panels. Other than the above-mentioned fast-growing species, mountain pine beetle (MPB)-affected lodgepole pine (*Pinus contorta*) timber in British Columbia has also been utilized for the manufacturing of LVL. A specially formulated PF resin consisting of components with a wide range of molecular weight was applied to treat the MPB-affected veneers using dipping and vacuum-pressure methods, and it was found that resin impregnation can improve the physical and mechanical properties of LVL made with MPB-affected veneers (Wang and Hei 2012).

The effects of adhesive types on the properties of LVL have been studied by a few research groups. It was reported that the elm wood bonded with MF showed higher bending strength compared to PF (Özçifçi 2007). As discussed earlier, the density of LVL is dependent on the type of adhesive. In this study, LVL with MF adhesive achieved the highest density. On the other hand, Bal and Bektas (2012) stated that the effect of adhesive type on the impact bending strength was insignificant while the load (flatwise and edgewise) directions of the play an important role in determining the IB and specific IB. Recently, Mirzaei et al. (2016) explored the role of adhesives in the durability of LVL. Four adhesives were used in the study which include EL-35 emulsion polymer isocyanate (EPI), PF, PRF and polyvinyl acetate (PVA). For crack propagation experiments, critical energy changes as the crack propagates, which can be measured by crack resistance curve, *R* curve. Based on the *R* curves obtained, it can be seen that the curves approached steady-state toughness (G_{ss}) at high crack growth. The most durable resin was found to be PF while the least durable one was PVA, where PVA bonded LVL lost the most toughness especially at high vacuum pressure soaking drying cycle.

Boron compounds are frequently used as wood preservatives to enhance the decay and termite resistance of wood by disrupting the enzyme system of the insect and fungi and destroying the microflora in the stomach of the insect, and hence stopping food digestion to take place. The advantages of boron compounds include their high durability and they do not breakdown into ineffective products nor do they evaporate or migrate far in soil (Currie 1997). Colakoglu et al. (2003) reported that the boric acid treatment resulted in the reduction of splitting strength of beech LVL. This was due to the swelling of intrapolymeric spaces by boric acid solution that led to the reduction of cross-linking and hence the reduction in strength. The treatment was found to reduce the compression strength in tangential direction too but increase the Brinell hardness and pull-out strength of screw. The same outcome was observed by Özçifçi et al. (2007) in their work to determine mechanical properties of LVL impregnated with boric acid and PF and MF as the adhesives.

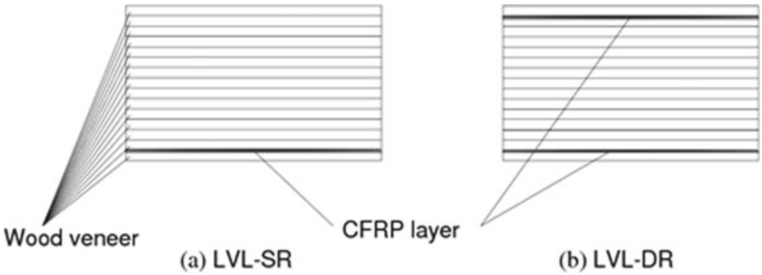


Fig. 12 Two configurations of LVL reinforcement: **a** single layer of CFRP between surface later and sub-layer on one side and **b** on each side (Wei et al. 2013)

In the past decade, several studies focusing on the development of new LVL reinforcement methods with synthetic fibres have been carried out. Wei et al. (2013) developed a theoretical model to predict the bending MOE of LVL reinforced by carbon fibre reinforced polymer (CFRP) and the model was validated experimentally by using two configurations as shown in Fig. 12. The model accurately predicted the experimental results. The MOE values of the reinforced LVL were improved by 40% for the one side reinforcement and 67% for reinforcement on each side, compared to the control LVL. Bal (2014a, b) investigated the physical and mechanical properties of reinforced polar LVL with woven glass fibres using PF. Test results obtained from this study showed the improvement in the density, shear strength, splitting strength, IB, MOR and MOE of the reinforced LVL. On the contrary, the tangential swelling, volumetric swelling, moisture content, specific IB, specific MOR and specific MOE decreased.

5 Future Perspectives

Although significant progresses have been made in the field of wood-based phenolic composites, there is still a great deal of research and development going on. For instance, phenol and formaldehyde are both derived from petrol. Despite the cost of the PF resins would vary with the oil price, formaldehyde is classified as toxic and carcinogenic. The use of PF resins in the production of wood-based phenolic composites has become a major concern with the scarcity of fossil feedstock and the increasingly restrictive regulations on health and safety. In addition, there are still some limitations which prevent the wider commercialization of these composites such as good flame resistance for fire-resistant building material, excellent decay and fungi resistance for residential construction use etc. Future work will be directed toward the development of wood-based phenolic composites that could overcome the above-mentioned issues by utilizing the bio-based, non-toxic and non-volatile resins as the adhesives and by incorporating functional nanoparticles into the composites to achieve the desired properties.

6 Conclusion

As one of the oldest class of synthetic polymers, PF resins have been widely used in the production of wood-based composites due to their outstanding durability. The aim of this chapter has been to present a selective review of the literature of wood composites with a focus on wood-based phenolic composites. Four conventional wood composite products, namely plywood, MDF, OSB and LVL, bonded with PF resins were discussed. In general, these wood-based products are able to meet the bonding needs for most of the wood applications. However, the recent concerns about the formaldehyde emissions and the depletion of fossil fuels have driven the trend to move away from using formaldehyde-based synthetic resins and to replace phenol using bio-based alternatives for wood-based panel manufacturing. The real challenge for the scientists is to develop adhesives with low-cost, good adjustable properties, fast reacting, easily distributable and have a long pot life by using biomass resources to solve the environmental issues arise from the use of carcinogenic and toxic materials.

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Natural Fibres Based Phenolic Composites

Thiago Santos, Caroliny Santos, Rubens Fonseca, Kátia Melo, and Marcos Aquino

Abstract Phenolic resins today have caught the attention of researchers and academics making it highly acclaimed among resins. Mainly its use with fibrous reinforcements (bast fibers, core fibers, leaf fibers, seed fibers and fruit fibers), thus, reinforced phenolic composite can be manufactured by a variety of phenolic resins classes. Which promote improvement of mechanical properties such as tensile, flexural and impact. Natural fiber reinforced phenolic resins are widely used to replace denser, environmentally polluting materials that have mainly lower mechanical properties. However, the importance of natural fibers (vegetable, animal and mineral fibers) incorporated into a matrix of phenolic resins (thermosetting) was emphasized, since long or short natural fibers when incorporated into phenolic resins. This book chapter promotes the enlargement of the frontier of knowledge about phenolic matrix composites (thermosetting composite) and thus presents a perspective of natural fibers based phenolic composites (use of natural fibers as reinforcement and their different classifications will be discussed).

Keywords Vegetable fibers · Thermosetting matrix · Phenolic resin and physical–mechanical properties

1 Introduction

According to the International Organization for Standardization - ISO, phenolic resins are obtained by reacting phenols with aldehydes (Standardization 1991). And originally developed in the early twentieth century, the nature and potential of phenolic resins were thoroughly explored to produce an extensive body of technical literature (Eslami et al. 2015). Both parent compounds, phenol and formaldehyde,

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M. Jawaid and M. Asim (eds.), *Phenolic Polymers Based Composite Materials*, Composites Science and Technology,
https://doi.org/10.1007/978-981-15-8932-4_4

are by far the most important components in commercial phenolic resin production for primarily application in composite materials (Asima et al. 2018). Composite materials in turn are defined as materials formed by the set of 2 or more materials (reinforcement and matrix). The synthesis of composite materials occurs by mixing compounds of different natures, however, in order to obtain a higher quality final product and with new properties to the materials (Kumar et al. 2009). So, as we can see the composite materials consist of a reinforcement material and the matrix, in which, during the composite molding process, the material used as matrix undergoes several complex processes of physical, chemical and physicochemical alterations, composites. with the reinforced material to form a well-defined whole body (Heimbs et al. 2007; Wang et al. 2011a). The main families of thermosetting matrices are epoxies, unsaturated polyesters, phenolics, amino resins (urea and melamine formaldehyde) and alkyds in order of importance. Phenolic resin is the 3rd largest family of thermosetting matrices, as it has excellent properties such as high temperature stability up to 300 and 350 °C, high chemical stability, excellent fire retardancy, good frictional properties as well as price/performance ratio (Fan and Njuguna 2016; Ouarhim et al. 2019). Thermosetting materials (phenolic resins) are preferred for structural applications because their strength is greater than that of thermoplastics. Due to their crosslinked or network structures with covalent bonds with all molecules. This way, they do not soften, but decompose with heating. So once solidified by a crosslinking process, it is not possible to remodel (Wang et al. 2011b, c; Milanese et al. 2012). This chapter is devoted to the presentation of different types and applications of natural fiber reinforced thermosetting dies. One section is dedicated to phenolic resin (matrix of thermoset composites). Then use of natural fibers as reinforcement and their different classifications will be discussed. Finally, the thermosetting composite physical and mechanical properties based on natural fibers will be presented.

2 Phenolic Resins

These are the 3rd largest family of polymers and oligomers, composed of a wide variety of structures having as synthesis the reaction of phenols with formaldehydes. The condensation reaction of formation of phenolic resins of origin to formaldehyde and phenol catalyzed by acid or base, these being the first synthetic plastic materials available on the market (Bouajila et al. 2002, 2003b). And yet, during the early twentieth century, almost every home was stocked with a variety of everyday household items, from combs to bowls and radios made from Bakelite, a mixture of phenolic resin and wood flour (Tyberg et al. 1999). Phenolic resins are further assigned to a wide range of applications, from commodity building materials to high-tech electronics and aerospace applications (Hepworth et al. 2000; Kopf 2002). Phenols are a group of aromatic compounds that are colorless solids (mostly) with the hydroxyl group (-OH) attached directly to the aromatic nucleus. But these phenols differ from other alcohols in that they behave as acids considered to be weak and dissolve rapidly

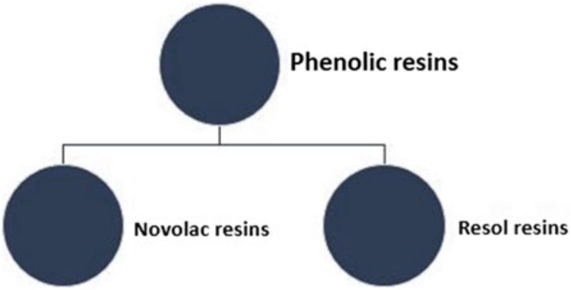

Fig. 1 Classification of phenolic resins

in aqueous sodium hydroxide (NaOH aq.), but are insoluble in aqueous sodium carbonate (Na_2CO_3 aq.) (Kopf 2002; Bouajila et al. 2003a).

2.1 Classification of Phenolic Resins

Thermosetting resins are used in molded and laminated plastics. The thermosetting resins are catalyzed and/or heated to end the polymerization reaction (see Fig. 1), thereby providing crosslinking and at the end of the curing process an almost infinite molecular weight is obtained (Singh et al. 2000). By achieving fully or nearly fully saturated cross-linking of phenol groups resulting in a material of exceptional hardness, good thermal stability and superior fire, smoke and smoke toxicity properties, and the physical properties of phenolic-based composites are superior ideas for industrial and architectural applications requiring corrosion and/or heat resistance (Hshieh and Beeson 1997; Tyberg et al. 1999; Martin et al. 2006; Mahendran et al. 2013). Once cured, phenolic resins cannot be reprocessed or reshaped, and the high crosslink density of thermosetting resins results in very high densities and very low ductility, but high rigidity and good chemical resistance.

Regarding the classification of phenolic resins there are 2 majores groups (Novolac and Resol) as shown in Fig. 1.

2.2 Novolac Resins

This class of resin is also called two-stage phenolic. It is manufactured by the reaction of phenol with formaldehyde in a strongly acidic environment in which an acid catalyst (such as oxalic, sulfuric, hydrochloric and toluene sulfonic acids) and phenol in a higher molar ratio compared to the molar ratio of formaldehyde (0.75–0.85 for one mole of phenol) are conditions used to produce novolac resins as set forth in Fig. 2 (Allen and Ishida 2001). In novolac resins it is necessary to add a

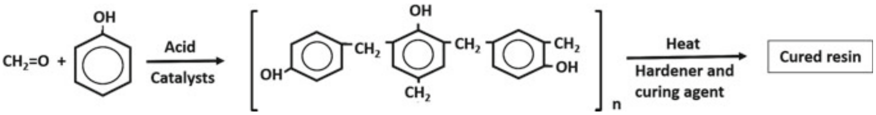

Fig. 2 Reaction of phenol with formaldehyde—Novolac resins

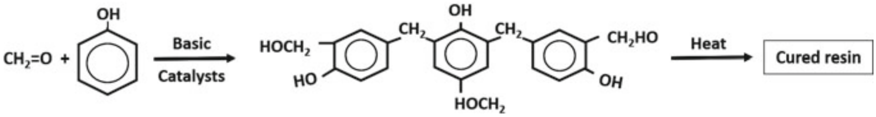

Fig. 3 Reaction of phenol with formaldehyde—Resol resins

hardener compound and cure the resin, and at the end of the curing process an insoluble and infusible material is obtained. The main compounds used to assist in the resin crosslinking mechanism are hexamethylenetetramine (HMTA), paraformaldehyde or trioxane ordered from most to least used. The crosslinking components are used at a concentration of 8–15% relative to resin concentration and are added after heating (Pizzi and Ibeh 2013). Then the previously added crosslinking compound decomposes to release the formaldehyde needed to finally complete the crosslinking reaction process (Allen and Ishida 2001; Patterson et al. 2013).

2.3 *Resol Resins*

Resol resins or single or single stage phenolic resins are currently produced from the reaction of phenol with excess formaldehyde in the presence of an alkaline or basic catalyst as shown in Fig. 3, are examples of commonly used catalysts for ammonia, carbonate sodium or sodium hydroxide. In the case of these resins the curing reaction can be completed in a heated environment (mold) without the use of any additional curing agents or catalyst as shown in Fig. 3. Further, the curing process must be carefully controlled and stopped only prior to gelling to allow the production of non-crosslinked resins, ie resins that are water soluble as opposed to novolac resins (Ibeh 1998; Allen and Ishida 2001).

2.4 *Differences Between the Classes of Phenolic Resins*

Phenolic resins have some similarities because they are produced materials by condensation of a phenol, or mixture of phenols, with an aldehyde, but, exhibit differences in the process of preparation and production (Ibeh 1998). So due mainly to the nature of the constituents of the resin (phenol and aldehyde) as well as the process

Table 1 Differences between Novolac and Resol resins

Factors	Novolac	Resol
Phenol and aldehyde ratio	Molar excess of phenol	Molar excess of formaldehyde
External curing agent	Require	Do not require
Cure stage	Two	Single
Hardener	Usually hexamethylenetetramine	–
Shelf life	Two year	Six months

of preparation and production of the phenolic resin, it has intrinsic characteristics and properties. Novolac resins are prepared by reacting phenol with formaldehyde at a molar ratio of approximately (1: 0.8 under acidic conditions) respectively (see Table 1) (Pizzi and Ibeh 2013). In which resin formation is slow, with rapid condensation and absence of active methylol. And the resins resins are prepared by reacting an excess aldehyde phenol in a molar ratio of approximately 1.5–2: 1 respectively, however, under basic conditions. Showing rapid resin formation, slow condensation and presence of methylol group (see Table 1) (Pizzi and Ibeh 2013).

3 Natural Fibers

3.1 Definition of Natural Fibres

Natural fibers are materials, primarily made up from natural sources composed of constituents with many different structures that enable in a wide range of chemical, physical–mechanical and biological properties. These fibers can be transforming into yarn and textile fabrics like woven, knitted and non-woven. This versatility allows natural fibers to be found in a wide variety of applications, especially in materials science and technology (Houck 2009; Shioya and Kikutani 2014; Desai and Kant 2016).

3.2 Classification of Natural Fibers

Textile fibers have been used since the past. There are currently many types of textile fibers that have been developed for use in textile production, technical and advanced textiles as well as composite materials. The textile segment divides the fibers into different groups based on the origin of the fibrous material. So, from this, fibers can be classified into two broad groups, called natural fibers and synthetic fibers known as man-made fibers (see Fig. 4) (Ibrahim 2011; Kicińska-Jakubowska et al. 2012; Qin 2016). Human developed and man-made fibers are obtained by

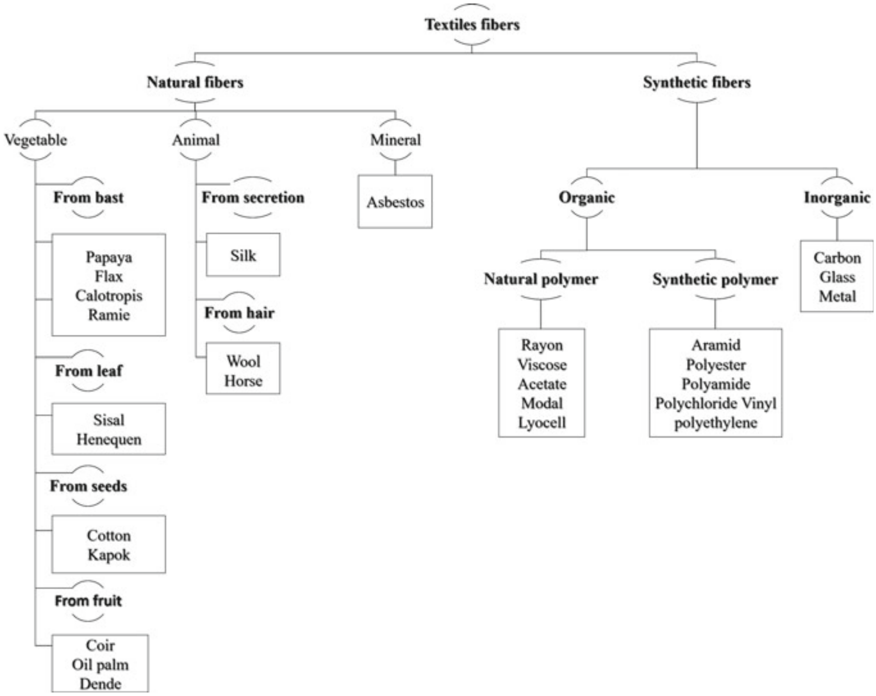

Fig. 4 Classification of textiles fibers

chemical and mechanical industrial processes, either those fibers that are manufactured from natural polymers and transformed by the action of chemical reagents or through chemically synthesized polymers (called synthetic fibers) (Tomar 2010; Da Silva Santos 2019). And the fibers said as natural are fibrous materials that grow or develop (exhibit maturity, are influenced by weather or food and nutrition of the animal), that is, they come from natural resources such as plants and animals (Kicińska-Jakubowska et al. 2012; Da Silva Santos 2019; Melo et al. 2019). Textile fibers in general are attractive for many applications as they have properties such as flexibility, fineness and high ratio (L/D) between longitudinal length and diameter (cross section). Among the most important natural fibers are those of cellulosic origin, such as flax, jute, cotton, sisal and papaya, next we have the group of protein fibers or animal origin and lastly those of mineral origin (see Fig. 4) (Houck 2009; Carr 2017).

3.3 *Importance of Natural Fibers in the Composites*

Today, with the global market looking for materials that reduce environmental pollution, which are recyclable or reusable. This has favored discussions in scientific conferences and congresses, as well as in industry and academia on the topic of sustainability. That is, forcing the transformation and use of fully synthetic petroleum products into fully or partially natural products in various application segments (Mohammed et al. 2015). This is what has further favored the importance of raw materials from renewable resources, as well as the production of products made from composites with recyclability and biodegradability (biobased) (Pereira et al. 2015; Summerscales 2019). So, with the excessive amount of materials sourced from natural resources makes the natural fibers with low availability difficulty. Natural fibers have characteristics such as low density, fineness, resilience and high strength properties such as stress, strain, elastic modulus and toughness (Al-Sulaiman 2002). They are advantageous for composite applications as they exhibit flexibility and low energy consumption for processing, are non-toxic and do not irritate the skin, low health risk (Ouarhim et al. 2019). And when incorporated into phenolic matrices, these fibers allow a good marriage to the matrix and are considered an excellent reinforcement as they enhance the properties of thermoset composites (Rashid et al. 2016). And yet, natural fibers are degraded by organisms other than synthetic fibers that just break up into microplastics that are one of today’s big problems (Peças et al. 2018; Ouarhim et al. 2019; Siakeng et al. 2019).

4 Physical and Mechanical Properties of Natural Fibers Based Phenolic Composites

Natural fiber phenolic composites exhibit properties comparable to those of synthetic fiber composites with respect to stress, strain, modulus of elasticity, impact resistance, density and Flexural strength (Al-Maadeed and Labidi 2013; BalaMurali Krishna and Krishna Bese 2017). Phenolic resin exhibits fragile mechanical behavior as well as low tensile, flexural and impact strength, still exhibits low elongation and is very poor in elastic modulus and impact strength (Sanjay et al. 2018; Binda et al. 2020; Wang et al. 2020b). However, with a low fraction of natural and group independent fibers (vegetable or natural), it is possible to significantly increase these main mechanical properties and reduce physical properties such as density and water absorption of natural fiber reinforced phenolic matrix composites (Sanjay et al. 2018; Zhen-Yu et al. 2019). These physical–mechanical properties are essential as they result in a great impact to provide understanding and understanding of material capacity and behavior during a practical or engineering application (Singh et al. 2000; Milanese et al. 2012). Efficiently characterizing and analyzing (following standards and using specific equipment) these properties (tensile strength, bending and impact, deformation, modulus of elasticity, density and water absorption) will reveal important reflections on phenolic composites reinforced with natural fibers such as, the nature of the ideal fiber, the efficiency and effectiveness of the phenolic resin interaction or interfacial union and the natural fiber (Ramlee et al. 2019). And thus, directing material richness or poverty during its advanced and engineering applications (Saba et al. 2019; Asim et al. 2019). As well, much has been studied to obtain effective means to explore different synthesis processes of phenolic resin production (Wang et al. 2020a). Among the various applications related to phenolic resin, molding composites is the most used method to make products of greater utility due to the obtained properties and mainly the cost–benefit ratio (Asim et al. 2020). Variables such as molecular weight, monomer and moisture content, viscosity, pH, particle size and reactivity during curing are just some properties that determine the application of phenolic resins (Agrebi et al. 2020; Xu et al. 2020). Thus, it is possible to achieve wide varieties of composite products.

5 Conclusion and Applications

In this chapter the importance of natural fibers incorporated into a matrix of phenolic resins (thermosetting) was emphasized, since long or short natural fibers when incorporated into phenolic resins favor high performance since the processing of composites and their characterization are performed properly. Throughout the chapter we find that the phenolic matrices stand out from the other thermoset matrices because they provide highly favorable characteristics in terms of strength, heat resistance, reliability and long-term cost, ie physical–mechanical performance. In addition, it can be concluded that the nature of the fibers is important for enhancing the properties of the matrix in order to obtain good interfacial adhesion between them. And this set of natural fibers and phenolic resins has attracted global attention and marketing as a lightweight alternative and solution for replacing metals and ceramics in a variety of applications such as automotive, buildings (false ceiling, walls) and electronics components.

Acknowledgements The authors are grateful to our alive Lord who has blessed the “Textile Technology Study Group—GETTEX” located in from the Federal University of Rio Grande do Norte.

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Natural Fibers Based Phenolic Hybrid Composites

G. Rajeshkumar, D. Elangovan, and V. Rajkumar

Abstract In recent decades, the usage of natural cellulosic fiber based polymeric composites in industrial and domestic applications has been increased because of its eco friendliness nature. It also has several benefits like high strength-to-weight, low cost, available in ample, sustainable etc. The advancements in the field of composite materials results in the development of hybrid composites by reinforcing two different fibers into a matrix. Because of the synergistic effect of reinforcements these hybrid composites offer better overall properties. The selection of appropriate combination of fibers, fiber contents and fiber surface treatments are the key for enhancing the properties of hybrid composite materials. This chapter presents the comprehensive review of performance of different phenolic hybrid composites in a view of selection of appropriate phenolic hybrid composite for industrial and domestic use.

Keywords Natural fibers · Phenolic · Hybrid composites · Mechanical properties · Sustainable reinforcements

1 Introduction

In recent days, composite industries are focusing on the usage of cellulosic fibers as reinforcement material for developing polymer matrix composites for different industrial applications (Asim et al. 2017). These composites offer various benefits such as low cost, light weight, favorable mechanical properties and abundant availability of reinforcement materials (Vigneshwaran and Rajeshkumar 2018; Rajeshkumar et al. 2020). Especially, it offers a solution to the reuse of bulk wastes from agricultural crops (Dong 2018). Based on the above benefits, the natural cellulosic fiber based composites finding its usage in automotive, construction, furniture, textiles, healthcare and pharmaceuticals, medical, personal and home care, packaging, food

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M. Jawaid and M. Asim (eds.), *Phenolic Polymers Based Composite Materials*, Composites Science and Technology,
https://doi.org/10.1007/978-981-15-8932-4_5

and feed additives, bioenergy and biofuel and paper and pulp fields (Peças et al. 2018; Ramakrishnan et al. 2019).

The increased use of natural fiber based polymer composites in several field leads to the development of novel hybrid composites by reinforcing two or more natural fibers in a common matrix. Any desired properties can be achieved in the hybrid composite because of synergistic effect whereas it is impossible in the single fiber reinforced composites (Jawaid et al. 2010; Rajeshkumar and Hariharan 2012). Some literatures have reported on selecting best or optimized combination of reinforcements to obtain the good results and to reduce the deleterious aspects (Jawaid and Khalil 2011; Jawaid et al. 2013). The hybrid composites are fabricated by using various manufacturing techniques such as hand layup, injection molding, compression molding, extrusion, hot pressing, resin transfer molding and automated fiber placement (Lotfi et al. 2019). In general suitable manufacturing process has to be used to fabricate the defect free composites. The factors to be considered in selecting suitable manufacturing process are: (i) size and shape of composites, (ii) production rate, (iii) processing characteristics of composite raw materials, (iv) manufacturing cost and (v) desired properties (Ho et al. 2012).

Literature studies revealed that the hybrid composites were developed by reinforcing two or more natural fibers into the thermoset and thermoplastic polymers. In particular the composites developed by using phenolic resin offer various advantages like good adhesive properties, excellent dimensional stability even at high temperatures, high mechanical strength and durability, excellent thermal properties, chemical stability, efficiency in glue-bond formation, better heat insulation properties and high rigidity (Asim et al. 2017). In this context, this chapter addresses the performance of different phenolic hybrid composites in a view of selection of appropriate phenolic hybrid composite for industrial and domestic use.

2 Natural Fibers (Reinforcements)

An increasing environmental awareness and government policies pulled the attention of industries, scientists, researcher and academicians to use renewable materials for the development of products. In this context, the usage of natural cellulosic fibers as reinforcement material for developing polymeric composites has gained the keen interest in various industrial sectors due to its favorable properties such as abundant availability, renewability, biodegradability, economic viability, non-toxicity and considerable mechanical properties (Rajeshkumar 2018; Kumar et al. 2019). The productivity of natural cellulosic fibers by different country across the globe was shown in Fig. 1 (Cesarino et al. 2020). These natural fibers are categorized into six groups namely: bast fibers (calotropis gigantea, kenaf, orka, jute and nettle), core fibers (kenaf, hemp and jute), leaf fibers (curaua, pineapple, istle, sisal, phoenix sp. henequen and caroa), seed fibers (kapok, cotton and coir), grass and reed fibers (elephant grass, bamboo, rice, sanseviera ehrenbergii, corn and wheat) and all other types (soft and hard woods and root) (Faruk et al. 2012). Though

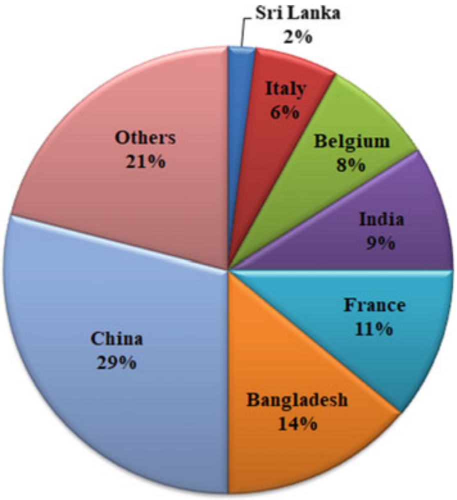

Fig. 1 Productivity of natural fibers by different countries across the globe

these fibers have various advantages it also has shortcomings like poor bonding with hydrophobic polymers and higher moisture uptake because of hydrophilic nature. One of the best solution to this problem is modifying the surface of the fibers using several chemical methods like sodium hydroxide, sodium chlorite, silane, acetylation, benzoyl peroxide, benzoylation, acrylic acid, maleated coupling agents, potassium permanganate, benzoyl chloride, isocyanate, and stearic acid etc. (Li et al. 2007).

3 Phenolic Resin (Matrix)

Phenolic resin is one of the synthetic polymers and is obtained by the reaction between phenol and formaldehyde and has several notable properties, such as good mechanical strength, resistance to heat, dimensional stability and good resistance against solvent, water and acids. These resins are naturally fire resistant and evolve less smoke upon burning. Based on these aspects, the composites developed using phenolic resins still find a major market from commodities to construction and aerospace industries etc., with an annual consumption of 6 million tons worldwide. Moreover, it is one of the widely used binders for substrates like metal, glass, wood, rubber and paper etc., with favorable performance/cost characteristics that surpass most of the existing polymers (Nair 2004; Pilato 2013).

4 Natural Fibers Reinforced Phenolic Hybrid Composites

4.1 Static Mechanical Properties (SMP)

The SMP (tensile, flexural and impact) of phenolic composites incorporated with jute/cotton fibers were determined by de Medeiros et al. (2005). The outcomes revealed that the fiber content, orientation, fabric characteristics and adhesion strongly influenced the investigated SMP of the fabricated hybrid composites. Based on the obtained experimental results, the jute/cotton fiber incorporated phenolic hybrid composites was suggested for light weight structural applications. The influence of stacking order of Coconut leaf sheath (C)/Jute (J) on SMP of phenolic based hybrid composites was explored by Bharath et al. (2018). The stacking sequence was in the order of: JJCJCJCJCJCJCJCJJ and CJCJJCJJCJJCJJCJC. The results disclosed that the first sequence has higher mechanical properties than the second one. The phenolic hybrid composites were made by reinforcing untreated and silane treated pineapple leaf fiber (PALF) and kenaf fibers using hand layup method (Asim et al. 2017). The results disclosed that the samples incorporated with treated fibers have better SMP than the untreated fiber composites because of improved interfacial bonding among the reinforcements and phenolic matrix. In another work, Athijayamani et al. (2017) developed the phenolic hybrid composites using areca, sisal and roselle fibers and investigated its mechanical properties. Moreover, single fiber composites were also fabricated and tested for comparison purpose. The experimental outcomes revealed that, the hybrid samples offered better results than the single fiber based composites. Especially, the hybrid composites made by using areca and sisal fiber showed optimal mechanical properties. Ramlee et al. (2019) determined the tensile properties of the single fiber composites and hybrid composites. The composites were prepared by varying the wt% of Oil Palm (OP) and Sugarcane Bagasse (SB) fibers and by maintaining the constant wt% of phenolic matrix as 50%. The results indicated that the hybrid composites have higher tensile strength and tensile modulus than the single fiber composites (Fig. 2). Especially, the hybrid composites made by using 35 wt% of OP and 15 wt% of SB fibers showed higher tensile property values among the composites investigated. This improvement is due to the better distribution of both the fibers in the phenolic matrix and enhanced interfacial bonding.

4.2 Dynamic Mechanical Properties (DMP)

The dynamic mechanical analysis is done on the composites to evaluate its dynamic mechanical properties such as storage modulus (E′), loss modulus (E″) and damping factor (tan δ) (Rajeshkumar et al. 2017). The E’ refers to the maximum energy stored in composite materials during one complete cycle of oscillation (Shinoj et al. 2011). The E’ vs. temperature curve affords the details about stiffness of materials, degree

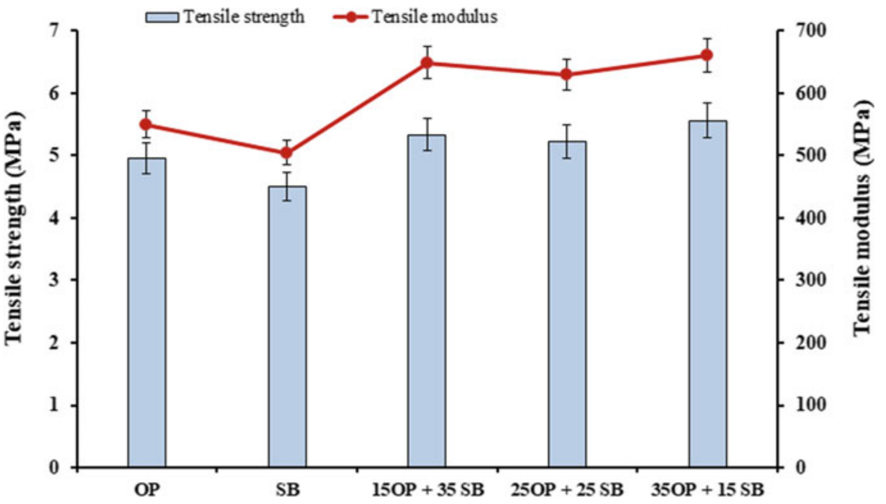

Fig. 2 Tensile properties of OP and SB fibers reinforced phenolic hybrid composites

of cross linking and interfacial adhesion between reinforcement and matrix (Jawaid et al. 2012). Loss modulus corresponds to the quantity of energy dissipated as heat per cycle under deformation experienced in a material. The damping factor is the ratio between E" and E', it give the balance between viscous and elastic phase in a polymer materials (Shinoj et al. 2011; Jawaid et al. 2012). A typical dynamic mechanical properties curve was shown in Fig. 3. The curves indicate that the material is hard (in glassy region) at lower temperature and transformed to soft state (in rubbery region) after crossing the glass transition temperature (Tg). The change of state is

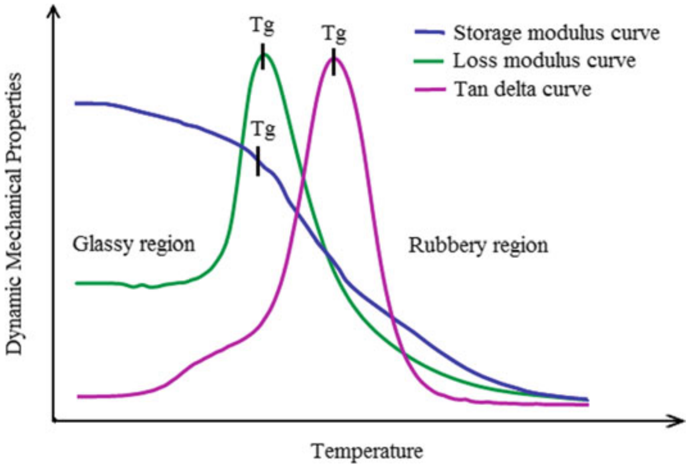

Fig. 3 A typical dynamic mechanical properties curve

Table 1 DMA results of PALF/Phenolic, Kenaf/Phenolic and hybrid composites (Asim et al. 2019)

Material	Storage modulus Tg value (°C)	Loss modulus Tg value (°C)	Tan δ peak (°C)
Phenolic resin	68.89	93.01	–
50% PALF + 50% Phenolic	51.74	106.1	–
50% Kenaf + 50% Phenolic	56.67	96.36	124.82
25% PALF + 25% Kenaf + 50% Phenolic	51.44	102.51	128
35% PALF + 15% Kenaf + 50% Phenolic	51.8	97.79	137
15% PALF + 35% Kenaf + 50% Phenolic	55.13	101.68	131

mainly due to the motion of polymeric chains (Rajeshkumar et al. 2017). The DMP of PALF/Phenolic, Kenaf/Phenolic and hybrid composites were determined by Asim et al. (2019). From Table 1, it was perceived that the hybrid composites have higher Tg values and this may be attributed to the restricted movement of polymeric molecules due to the presence of reinforcements. Moreover, the percentage of PALF and Kenaf fiber affects the DMP of hybrid phenolic composites. The composites reinforced with 15% PALF and 35% Kenaf offer better storage modulus while the composites reinforced with 25% PALF and 25% Kenaf offer better loss modulus and the composites incorporated with 35% PALF and 15% Kenaf offer good damping property. In another work, the storage modulus and damping factor of jute/cotton/phenolic hybrid composites was determine by de Medeiros et al. (2005). The outcomes revealed that the test direction significantly affect the above properties. Moreover, it was indicated that the jute fiber provides good reinforcing effect and cotton fiber evades catastrophic failure, hence a better hybrid composites could be fabricated by using this combination of natural fibers.

4.3 Thermal Properties

The evaluation of thermal degradation properties of composites is necessary to utilize it for high temperature applications (Rajeshkumar 2020). The thermal degradation properties of the phenolic based hybrid composites were inspected by Asim et al. (2019) and the outcomes were presented in Table 2. It was observed that the composites have more weight loss during the initial degradation stage because of the dehydration of moisture content existing in the cellulosic fibers (Kavitha et al. 2017). Moreover, no initial thermal degradation was found for pure phenolic sample, which confirmed the absence of moisture content in the phenolic matrix. Furthermore, the weight loss of single fiber composites (PALF/Phenolic and Kenaf/Phenolic) was

Table 2 TGA results of PALF/Phenolic, Kenaf/Phenolic and hybrid composites (Asim et al. 2019)

Material	Initial degradation temperature (°C)	Weight loss (%)	Final degradation temperature (°C)	Weight loss (%)	Residual mass (%)
Phenolic resin	-	-	420.73	32.16	55.97
50% PALF + 50% Phenolic	283.64	38.97	391.38	23.92	29.22
50% Kenaf + 50% Phenolic	293.14	39.16	447.99	24.91	24.23
25% PALF + 25% Kenaf + 50% Phenolic	278.57	34.23	397.66	23.82	30.60
35% PALF + 15% Kenaf + 50% Phenolic	279.50	36.72	394.58	20.84	32.91
15% PALF + 35% Kenaf + 50% Phenolic	280.70	35.59	401.36	22.95	29.42

found to be higher than the hybrid composites. This shows that the hybrid composites have higher thermal stability. This initial thermal degradation took place in the temperature range between 278.57 and 293.14 °C. The decomposition of glycosidic linkages of cellulose in fibers, hemicellulose, pectin and lignin at this temperature was responsible for weight loss ranges from 34.23 to 39.16% (Kumar et al. 2014). The final decomposition of composites occurs in between the temperature range of 391.38–447.99 °C. The weight loss occur at this stage was less when compared to the initial degrading stage and the weight loss at this stage was primarily due to the decomposition of cellulose present in the natural fibers and depolymerization of matrix material (Shukor et al. 2014). The weight loss of hybrid composites at final thermal degradation stage was also lower ensuring the good thermal stability of hybrid composites.

4.4 Water Absorption Properties

It is well known that the hydrophilicity of the cellulosic fibers is the main factor which influences the water uptake behavior and mechanical failure of the composites during an application (Fatra et al. 2016). Many researchers and industries working towards the minimization of water absorption of the cellulosic fiber based composites worldwide. Moreover, it is necessary to assess the composites water absorption rate before it is employed for various moist environmental condition applications. To this aim, the water absorption rate of PALF/kenaf fiber incorporated phenolic hybrid composites was studied at different fiber loadings maintaining a constant wt% (50) of phenolic matrix (Asim et al. 2018). Moreover, the single fiber composites were also tested for the comparison purpose. The water absorbed by the samples as a function of soaking time was presented in the Fig. 4. The graph showed that the composites incorporated with kenaf fiber showed very low moisture absorption rate and followed by PALF incorporated and hybrid composites. The lower moisture absorption of kenaf fiber composites attributed to the presence of lower cellulose content than the PALF. The amount of cellulose present in the kenaf fiber was 31–39% while the PALF has 70–82% of cellulose (Sahu and Gupta 2019). In addition to cellulose content the other factors like void content, porosity, lumen size, environmental temperature, viscosity of matrix and interface adhesion between composite constituents also affect the water uptake behavior of the composites (Mariatti et al. 2008; Rajeshkumar 2018). The water uptake behavior of OP and SB reinforced hybrid phenolic composites were investigated by Ramlee et al. (2019). The results revealed that the hybrid composites prepared using 70% of SB show lower water absorption rate. This could be due to the fact that the addition of SB reduced the porosity and void of the surface area visible on composites.

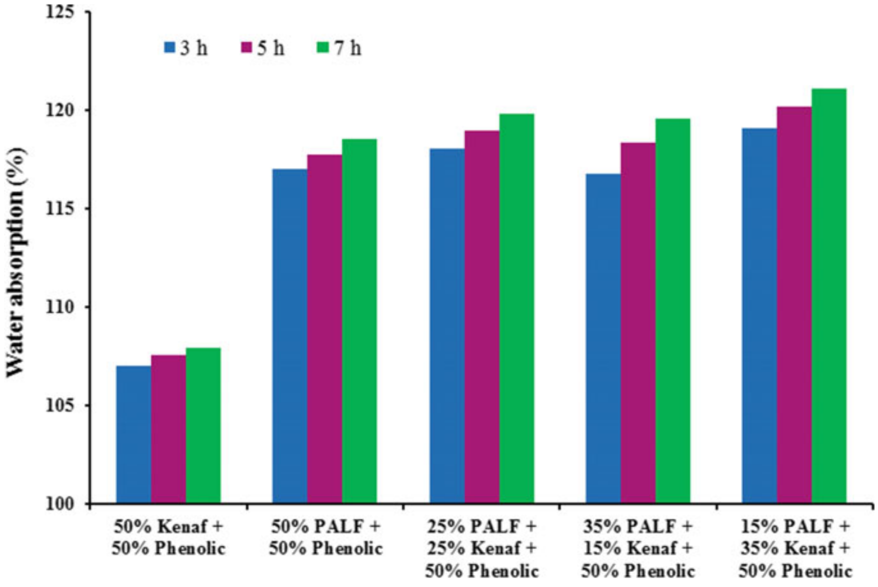

Fig. 4 Water absorption of phenolic composites at different immersion time

5 Conclusions and Future Perspective

Increasing environmental awareness and government policies push the scientists, researchers, academicians and various industries to focus on development of eco-friendly materials. The usage of natural fibers as reinforcement for developing composites was found to be the viable solution based on its advantages like biodegradable, less weight, high strength-to-weight ratio, non-toxic etc. Rapid growth of composites industry opens up the new path for developing hybrid composites by reinforcing two or more different natural fibers in to the thermoplastic or thermosetting plastics. This chapter addressed the performance of natural fibers based phenolic hybrid composites. The phenolic hybrid composites offer better tensile, flexural and impact properties due to synergistic effect of reinforcement. Moreover, a positive shift in Tg was observed in the hybrid composites. This reveals that after hybridization the stiffness and interfacial bonding between the constituents has improved. Furthermore, the phenolic hybrid composites have good thermal stability. The phenolic hybrid composites fabricated using chemically treated natural fibers show enhancement in static and dynamic mechanical properties. The studies on characterization of natural fiber based phenolic composites are relatively scarce. Therefore, this is a right time to develop new phenolic hybrid composites using different combinations of natural fibers and to characterize it. This will satisfy wide variety of requirements in the industrial sectors and lead to country's socioeconomic improvement.

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Properties and Applications of Phenolic-Nanocomposites

Maliha Marzana, Md Imran Howlader, and Md Milon Hossain

Abstract Phenolic nanocomposites are widely used in various applications due to their excellent flame retardant characteristics, low density, and thermal conductivity. Phenolic resin can be used with both natural and synthetic polymers. While the phenolic resin demonstrates some unique characteristics, the mechanical properties of the phenolic resin have always been a big concern. The low mechanical properties of phenolic resin can be improved by the uses of nanofillers. The interaction between nanofillers and the phenolic matrix dominates the performance of the composite structures. Therefore, the modification of nanofiller plays a crucial role in improving the mechanical performance of the phenolic nanocomposites. This chapter discusses the properties of various nanofiller reinforced phenolic composites. Three different nanofillers such as clay, carbon nanotube, and graphene reinforced in the phenolic matrix and their different properties are discussed. The chapter concludes by elucidating different applications and recycling process of phenolic nanocomposites.

Keywords Nanocomposites · Phenolic resin · Nanofillers · Mechanical properties · Recycling

1 Introduction

Nowadays composites materials are widely used in different applications due to their excellent mechanical, chemical, thermal, and lightweight characteristics. A material composed of two or more constituent components is usually acquainted as a composite material. When individual components with significantly different

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M. Jawaid and M. Asim (eds.), *Phenolic Polymers Based Composite Materials*, Composites Science and Technology,
https://doi.org/10.1007/978-981-15-8932-4_6

characteristics are combined, a synergistic effect is observed in the produced material showing superior performance from the individual ones (Fazeli et al. 2019). The most common matrix system of composites is metal, ceramic, and polymers and the reinforcements could range from zero to three-dimensional materials. The surface interaction between the matrix and reinforcement is greatly influenced by the size scale. Therefore, manipulating the composite materials at the nanometer scale has a profound impact on the properties of composites and facilitates the fabrication of composite materials with unprecedented performance. Composite materials containing at least one component with dimension in the nanoscale (i.e., one nanometer is one-billionth of a meter) is called nanocomposite. Nanocomposites vary from conventional composites because of the exceptionally high aspect ratio and high surface to volume ratio of the reinforcing components (Tjong 2006). Though nano-sized fillers based elastomeric composites dated back to 1959, extensive research on polymer nanocomposites started in 1990 inspired by automobile tires developed by Toyota. Toyota exfoliated clay nanofillers in nylon-6 and observed significant improvement in mechanical properties and heat deflection temperature. Currently, nanocomposites are used in various applications such as automotive, energy storage, aerospace, building and construction, marine, electronic, packaging, etc. (Akpan et al. 2019).

A phenolic-resin nanocomposite is a multiphase solid component which is attached to synthetic polymers obtained by the reaction of phenol or substituted phenol. Additionally, one of the phases has at least a dimension of less than 100 nm, or formation having nano-scale repeat distance between the different phases which make up the component. Phenolic resin is the first synthetic thermoset polymer that has a high resistance to flammability, high char yield, excellent thermal insulation and superior thermal stability (Eslami et al. 2015a). Synthetic and natural fiber reinforced nanocomposites are fabricated predominantly with modified phenolic resins (Zheng and Liang 2019). Phenolic-Nanocomposites can ameliorate the following properties.

- Mechanical characteristics like strength, modulus, and dimensional flexibility
- Surface appearance
- Optical clarity
- The reduced permeability of gas, water, and hydrocarbon
- Thermal stability like flame retardant properties
- Chemical resistance.

Phenolic resins have been using as a matrix material for various composites such as phenolic resin/silicone hybrid aerogel composites (Yin et al. 2017), phenolic resin/clay nanocomposites (Wang et al. 2008), composites from glyoxal–phenolic resins and sisal fiber (Ramires et al. 2010), graphene/phenolic resin composites (Yang et al. 2018, Sekhar and Varghese 2019), poly(p-phenylene benzobisoxazole) fiber-reinforced phenolic resin composite (Bian et al. 2014), carbon nanofiber/phenolic nanocomposites (Bafekrpour et al. 2013b), calcium aluminate–phenol resin composite (Pushpalal et al. 1999), etc. Phenolic resin is known for its unique flame retardant behavior exceeding 2000 °C and widely used in aerospace applications such as surfaces of the rocket, space vehicles, combustion chambers of rocket engines, and aircraft interiors. In the automobile industry, it is mainly used as a fuel line in most modern vehicles in addition to various components of a car. The electronics industry uses phenolic nanocomposites for producing chemical sensors, electroluminescent devices, batteries, smart windows, and memory devices. Unreinforced phenolic polymer nanocomposites are used for non-load-bearing applications. Phenolic nanocomposites are also used in the marine industry, environmental protection, food packaging, radar absorbing materials, solar cells, etc. This chapter focuses on different properties of phenolic nanocomposites produced from epoxy-clay, graphene, and carbon nanotubes (CNTs). Additionally, different applications and recycling process of phenolic nanocomposites are briefly explained.

2 Phenolic Resin

The phenolic resin was introduced by Bayer in early 1870 as a product of the reaction between phenols and aldehydes. Novolac and resole are the two major phenolic resin used in manufacturing nanocomposites. Characteristics features of novolac and resole are shown in Fig. 1.

Different structures and properties of phenolic resin can be obtained from various phenols, aldehyde, and catalysts. Additionally, resin properties can be tuned by varying the phenol/formaldehyde ratio, reaction temperature, and time. Novolac phenolic resins are obtained in different acidic medium and the reaction mechanism of novolac resin synthesis with a curing agent (hexamethylenetetramine) is shown in Fig. 2 (Pilato 2013).

The resole phenolic resins are produced in basic media with an excess of formaldehyde to phenol (see Fig. 3) (Pilato 2013). A significant number of hydroxymethyl groups are present in resole resin which is stable at room temperature. However, heating the resole resin may produce an insoluble and infusible three-dimensional cross-linked polymer. Resole resin is known as a single-step resin since it is produced by simple heating (Frollini et al. 2013).

2.1 Epoxy-Phenolic Clay Nanocomposites

Phenolic resin is brittle at room temperature which limits its applications where very good mechanical properties are desired. Therefore, applications requiring excellent mechanical properties phenolic resin is combined with reinforcements to enhance

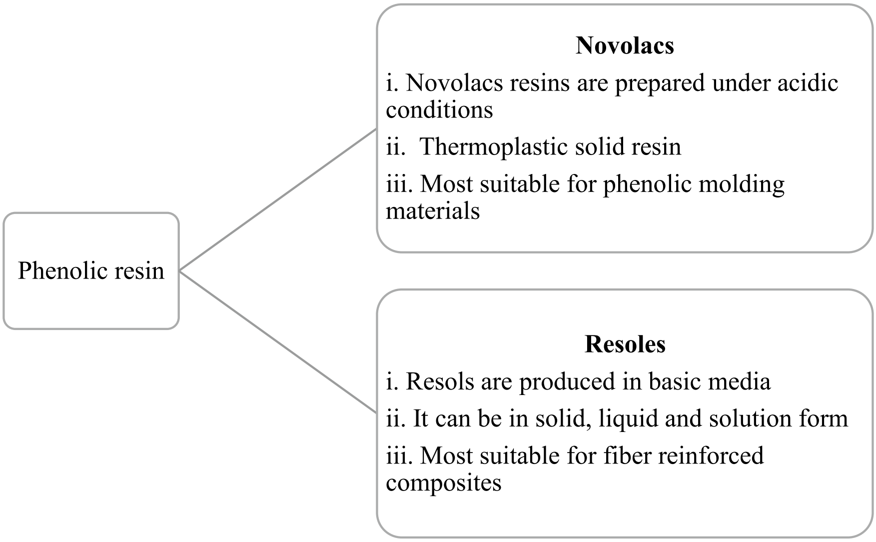

Fig. 1 Major two classes of phenolic resin and their characteristics

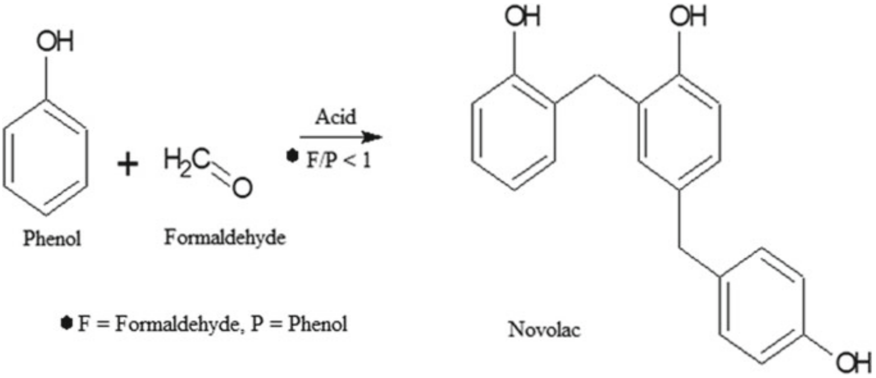

Fig. 2 Reaction of novolac resin (Pilato 2013)

mechanical performance (Frollini et al. 2013). The polar group of phenolic resin shows reactivity to different reinforcing materials resulting in improved adhesion between matrix and reinforcement. Clay is a layered silicate (clay minerals) contains traces of metal oxides and organic matter which is widely used as reinforcement with phenolic resin. However, the intralayer covalent bonds within the individual clay sheets cause difficulty in dispersion in a polymer matrix. Therefore, clay requires modification before using in polymer nanocomposites. Different researchers showed that phenolic nanocomposite can be intercalated (Yang et al. 2010) or exfoliated (Pappas et al. 2005) and demonstrated enhanced properties of the nanocomposite.

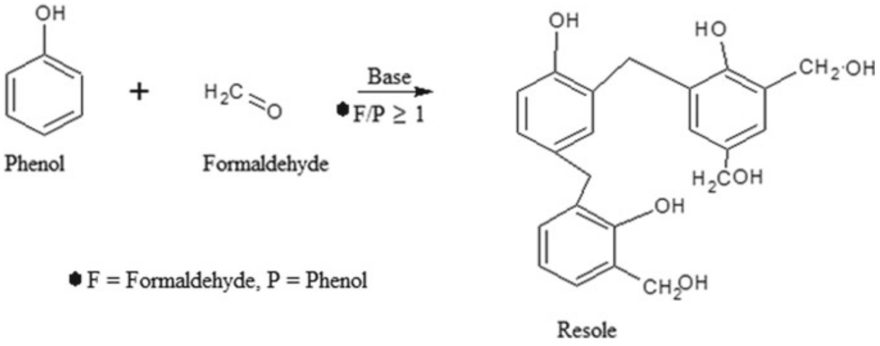

Fig. 3 Reaction of resole resin (Pilato 2013)

Intercalating long chains or grafting of functional groups are used to modify the interlayer spacing of clay, which generates new characteristics by converting hydrophilic character to hydrophobic (Kotal and Bhowmick 2015). The modification process of clay is shown in Fig. 4. A wide variety of clays are used to produce composites such as montmorilonite, sepiolite, hectorite, saponite, rectorite, laponite, vermiculite, bentonite, kaolinite, beidellite, and chlorite, as well as synthetic clays including various layered double hydroxides, synthetic montmorilonite, hectorite, etc. (Kotal and Bhowmick 2015).

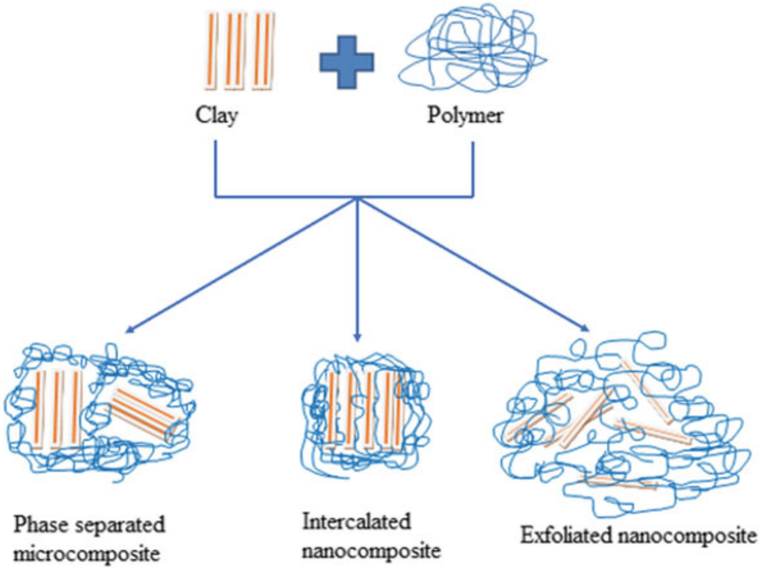

Fig. 4 Schematic of clay modification

There is a great influence of epoxy-phenolic clay on tensile strength, modulus, fracture behavior, and impact toughness of nanocomposites. The highest enhancement in stiffness and toughness can be achieved with filler content. The activation of multiple energy-dissipating damage mechanisms in the nanocomposites results in increased toughness characteristics. Hence, epoxy-phenolic clay nanocomposites are likely to be used in a wide range of modern applications in lightweight structural components, battery cathodes, non-linear optics, nanowires, sensors and many other systems (Auad et al. 2007).

2.1.1 Mechanical Properties

Montmorillonite (MMT) is abundantly available and widely used in nanocomposites due to their well-established intercalation/exfoliation chemistry, high reactivity, and surface area (Kotal and Bhowmick 2015). The layer structure of MMT facilitates the formation of various hybrids and composites. However, only well dispersed, and exfoliated MMT can produce nanocomposites with superior properties. A small exfoliation of clay dramatically enhanced the mechanical property of the nanocomposite as found by Pappas et al. 2005. When the MMT is exfoliated, the tensile modulus increased by 21% than the neat resin and fracture strength improved by 87%. In contrast, aggregated and unexfoliated MMT can act as a stress concentrator and the fracture strain may be lost. Therefore, it is essential to maintain a uniform dispersion of MMT to prevent agglomeration.

Resole type phenolic resin is generally produced from liquid resins which creates exfoliation (Tasan and Kaynak 2004). Compared to fiber reinforced polymer composites, low concentrations polymer/layered silicate nanocomposites have shown to exhibit higher mechanical performance (Barkoula et al. 2008). The mechanical properties of this type of phenolic nanocomposites are largely dependent on some factors such as the amount of clay loading, type of resin used, curing method, and effect of the modifier.

The best mechanical performances are found at very low clay loadings under acid curing. Agglomerates are formed over 1% clay layers, which causes a drop in mechanical properties. Moreover, phenolic-nanocomposites with modified clays gives better results than unmodified clays, which is probably due to the larger gallery space in between the clay layers of modified clays (Tasan and Kaynak 2004). It was found that both flexural and impact strength increased up to 10% when the amount of clay loading was 0.5%. Then the amount of strength dropped by around 50% as the amount of clay loading increased two folds. This is due to the tactoids structure formed at 1% clay loading which decreased the mechanical properties significantly (Tasan and Kaynak 2004). Resole type resin containing mono ethylene glycol and diethylene glycol showed improved mechanical properties. The superiority of resole type phenolic resins over other thermosetting polymers is the capacity to be cured absolutely by the application of heat as well as by the presence of acid. It is recognized that when the clay and resin type and all the other parameters are kept constant, acid cure provides better performance characteristics (Tasan and Kaynak 2004).

Flexural and Compressive Properties

Flexural modulus of the phenolic-nanocomposites can be increased to a great extent by the addition of nano clays in comparison with the neat polymer (Auad et al. 2007). For example, flexural modulus increased by 20% when 10 wt.% of organoclay was added. The mechanical characteristics of epoxy-phenolic clay nanocomposites are determined by multiple parameters including the filler's aspect ratio, level of dispersion in the matrix, and filler-matrix interface adhesion. Additionally, the modulus of epoxy-phenolic clay nanocomposite is influenced by the degree of exfoliation of the layered silicate in the polymer (Auad et al. 2007). Novolac phenolic resin nanocomposites with organoclay were fabricated by melt processing and the effects of the amine compatibilizer structure on the morphology and physical properties of the composites were observed. Composites with a long alkyl tail compatibilizer exhibited a larger extent of intercalation and higher flexural and impact strengths compared to two long alkyl tails (Kang et al. 2010).

Fracture Properties

Fracture toughness of composite material is an important property to sustain high load-bearing applications. A very small applied stress can cause failure to the composite structures if crack-like defects are present. Ductile materials deform locally at higher stress and reduce the intensity of the stress. However, crack present in brittle materials propagate through the stressed region with little deformation. It was found that phenolic-nanocomposite samples with epoxy-phenol ratio (35/65) and (50/50) exhibited absolute brittle fracture whereas a semi-brittle characteristic is displayed by the phenolic samples with an epoxy-phenol ratio of 67/33. Thus, limited plasticity is formed in the composite structure ahead of the crack tip. With the increasing ratios of phenol to epoxy up to a threshold in epoxy-phenol (50/50), the pure matrix toughness increased (Auad et al. 2007). As the epoxy-phenolic equivalent ratios of 1:1 changed to 1:4, the network densities decreased, but hydrogen bond formation increased due to the dangling chains from unreacted phenols resulting in higher intermolecular forces. Both factors contributed to a higher toughness of the composites. The fracture toughness of the epoxy-phenol nanocomposites increased up to 70% over the unmodified resin. Therefore, with higher epoxy content the cross-link density increased, and thus toughness decreased. However, compared to the matrix, phenolic-nanocomposites exhibited an increment in fracture toughness of 70% and Young's modulus of 20% (Auad et al. 2007).

2.1.2 Thermal Properties

The addition of MMT into polymer significantly improves the thermal stability of the nanocomposites by acting as an insulator, heat barrier, and a mass barrier to the gaseous products generated during thermal decomposition of the polymer (Zhu et al. 2019). The MMT barrier obstructs oxygen penetration and form char which increases the thermal stability of the nanocomposites. However, thermal stability is not always directly related to the amount of MMT loading in the nanocomposites. Modified MMT/polyamide 12 nanocomposites showed an inverse relationship with the MT content. Similarly, the dispersion media of MMT also influenced the thermal stability of MMT nanocomposites. MMT dispersed in toluene showed better thermal stability than water (Zhu et al. 2019). On the other hand, exfoliated and modified MMT has a higher aspect ratio which caused cross-linking with polymers and the movement of the cross-linked polymer chain is constrained resulted in a reduction in the thermal coefficient. The addition of 1 wt.% of modified MMT into thermoplastic elastomer showed about a decrease of 87% in thermal expansion compared to the pure thermoplastic elastomer. A similar polymer chain constraint was found for strong molecular interaction between MMT and polymers. The primary and secondary bonding between MMT and polymer increased the glass transition temperature (Tg) of the nanocomposites (Zhu et al. 2019). The addition of epoxy is expected to form higher crosslink density for equimolar epoxy-phenol (1:1). However, unexpectedly, maximum Tg was found for the 50/50 epoxy-phenol sample where the phenol-epoxy ratio was 2:1. This is due to the additional dangling chains from unreacted phenol groups. Cross-linking density and intermolecular forces greatly influenced the Tg of nanocomposites (Auad et al. 2007).

2.1.3 Shrinkage Properties

The shrinkage in epoxy-phenolic clay nanocomposites depends on the chemistry of the organic matrix. The polymerization shrinkage in nanocomposite resin was reported to be 1.4–1.6%. The low shrinkage property of epoxy-phenolic clay nanocomposites is mainly caused by the low shrinkage of epoxy resin. Moreover, strong interfacial interactions between resin and nanoparticles are also responsible for the lower shrinkage of nanocomposites (Lyapina et al. 2016).

2.2 Phenolic Resin-CNT Nanocomposites

Carbon nanotubes (CNTs) are extensively used in different nanocomposites applications due to their excellent electrical, mechanical, chemical, thermal, and piezoresistive properties. CNTs are tubular form rolled up from the planar graphene sheet. There are mainly two different types of CNTs structures such as single-walled CNT (SWCNT) and multi-walled CNT (MWCNT). Using CNTs as a filler in nanocomposites with both thermoplastic and thermoset resins, enhanced mechanical and new functional properties can be obtained. Solution mixing, melt mixing and in situ polymerization are commonly used for the fabrication of phenolic/CNTs nanocomposites. To obtain desired nanocomposites properties, it is essential to achieve homogenous dispersion of CNTs in the resin and degree of interaction between the CNTs with the matrix (Saeed et al. 2013). However, the homogenous dispersion of CNTs into the polymer matrix is challenging due to the strong van der Waals interactions in CNT bundles. Poor CNT dispersion results in poor performance of the composites. MWCNTs is one of the most popular reinforcements and has been used with various resins like starch (Famá et al. 2011), natural rubber (Medupin et al. 2019), poly(methyl methacrylate) (Stéphan et al. 2002), polyaniline (Dong et al. 2007), chitosan-silver nanoparticles/graphene (Lian et al. 2013), polyethylene (Lisunova et al. 2007), polyarylene ether nitrites (Liu et al. 2008), polypyrrole (Wu et al. 2009), phenolic-based, etc. The morphology and interfacial interaction between MWCNTs and the thermoset matrix depend on the interaction between functional groups of the compatibilizer and carboxyl or amine groups of MWCNTs.

2.2.1 Mechanical Properties

The mechanical performance of nanocomposites greatly influenced by the degree of load transfer between CNTs and matrix and the dispersion of CNTs in the polymer matrix (Moses et al. 2018). The interfacial area defines the degree of load transfer and a high degree of load transfer is preferred. The poor interaction between matrix and CNTs fails to transfer the applied load. Well dispersed CNTs minimizes the stress concentration and thus distribute the load uniformly. Moreover, the heterogeneous distribution of higher loading CNTs causes agglomeration which decreases the strength and modulus of the composites. In contrast, elastic modulus mainly depends on the intrinsic properties of the matrix and filler and interaction between them rather than dispersion (Botelho et al. 2012).

Botelho et al. (2012) dispersed CNT into the phenolic resin by ultrasonication and three-roll calendar devices and CNT loading was 0.05, 0.1, 0.5, 1.0, and 2.0 wt.%. Though tensile modulus changed significantly up to 1.0 wt.%, the change was negligible above 1.0 wt.% of CNT loading. Tensile properties for both ultrasonication and roller processing techniques increased but phenolic resin/CNT processed by calendar roll showed higher tensile strength and modulus compared to the sonication. In another study, the wet and dry dispersion method was used to disperse MWCNT into phenolic resin before molding into a composite specimen (Mathur et al. 2010). Wet mixing was performed individually using novolac and MWCNT in acetone solution and mixed after sonication whereas dry mixing was performed by ball milling (10, 20, 25, 30 h) of dry phenolic resin containing 2 vol.% of CNTs without solvent before composite fabrication. The wet mixing process failed to improve the tensile strength and authored claimed that this was due to the insufficient wetting of CNTs by the resin. The dry mixing improved the tensile strength by 126% compared to the neat resin for 30 h of ball milling. The tensile strength increased gradually with the ball milling time due to the disintegration of large size CNTs.

2.2.2 Thermal Properties

In general, the addition of CNTs in phenolic resin increases the thermal stability of the nanocomposites. Carboxylated MWCNTs filler based phenolic resin composite was prepared by the in situ polymerization process and melt mixing method (Cui et al. 2008). Crosslinked phenolic resin and nanocomposites possess alike thermolysis behavior which features three thermolytic temperature zones. The first zone is (200–280 °C) where the thermal decomposition of free molecules takes place. The second zone and third zone are (310–430 °C) and (490–590 °C) respectively responsible for the decomposition of crosslinked components. These zones are responsible for the malformation of crosslinked components. While thermal stability of the polymer nanocomposites improved, the thermal stability of melt mixing nanocomposites degraded due to nanotube agglomeration. On the other hand, the carboxylated MWCNT-nanocomposite formed by in situ polymerization exhibited a higher residual weight than that prepared by the melt mixing method (Cui et al. 2008). This is due to heat removal from the surrounding by CNTs and the elimination of hot spot formation. Authors claimed that improvement on the thermostability of phenolic nanocomposites can be provided by adding a higher load of well-dispersed nanotubes instead of 1.0 wt.% of MWCNT loading. Another research also found that primary weight loss around (450–550 °C) and the secondary weight loss around (600–650 °C) due to degradation and oxidation of phenolic resin and oxidation of carbon fibers in the composite respectively (Eslami et al. 2015b). Two possible reasons for this reduction of thermal stability of the nanocomposites was assumed.

(i) At the beginning of the first stage, the phenolic resin is approximately burned off and MWCNTs and carbon fiber remain intact.
(ii) As MWCNTs are highly conductive, the heat transfer to the virgin material will increase; a slight decrease in the maximum degradation temperature of the nanocomposite (Eslami et al. 2015b).

2.3 Graphene/Phenol Formaldehyde Nanocomposites

Graphene is a planar sheet of carbon atoms and has significant potential to be used as fillers to improve the performance of phenolic nanocomposites for various applications due to their prominent mechanical, thermal, and electrical properties. Nanocomposites demonstrate significant improvement in properties at much lower loadings than conventional composites in macro/micro scale fillers. This leads to a reduction in composite weight and makes the process simpler. Recently, graphene-based fillers derived from graphene oxide (GO) are mostly used compared to other graphene-based fillers. The chemical structure of GO is shown in Fig. 5 which mostly contains hydroxyl and carboxylic acid groups. Either solvent-based or thermal-based exfoliation is an important step for better dispersion of GO-derived fillers before incorporation into a polymer matrix (Potts et al. 2011).

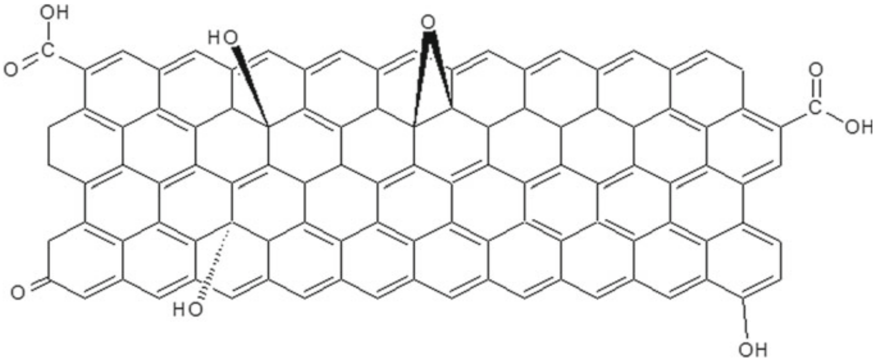

Fig. 5 Chemical structure of graphene oxide

GO-based nanocomposites are prepared by solution mixing, melt mixing, and in situ polymerization. However, coating by dispersing polymer in graphene solution followed by reduction/washing and spray/drop-casting process is also used to produce graphene nanocomposites. The GO and phenolic resin composites can be obtained by incorporating GO into phenolic resin via covalent or noncovalent interactions and GO may act as a hardener for phenolic resin in the composites. This leads to higher curing temperatures and lower heat release during the curing process of GO/phenolic composites (Si et al. 2013a). Phenol formaldehyde (PF) is extensively used in aerospace, construction, and commodity industries due to their superior flame resistance and ablative characteristics (Tao et al. 2019). The thermal stability and thermo-mechanical properties of the GO-PF nanocomposites are largely depended on the materials (GO and resin). It was reported that the thermal stability and thermo-mechanical properties of the GO reinforced PF nanocomposites improved remarkably due to the well-dispersed GO sheets in the polymer matrix and the strong interfacial interaction between the GO sheets and phenol-formaldehyde matrix (Xu et al. 2013). The polarity, molecular weight, hydrophobicity, functional/reactive groups of the polymer, graphene, and solvent greatly influence the interaction between the graphene and polymer matrix (Zhang et al. 2018).

2.3.1 Thermal Stability

The incorporation of GO increases the electrical, thermal, and flexural properties of PF composites. Yuan et al. (Yuan and Zhang 2013) studied the thermal behavior of neat PF and reduced GO (rGO)/PF composites for 10% mass loss. Uses of rGO with PF significantly improved the thermal stability of the nanocomposites showing enhanced decomposition temperature and low mass loss. While PF started to lose masses at 95 °C, no significant mass loss was evident until 300 °C for rGO/PF composites. The decomposition temperature increased with the increase of GO mass loading of 1.4–2.3 vol.%. This can be attributed to the strong confinement effect on the polymer chain mobility due to the covalently functionalized rGO sheets.

The thermal study of in situ nanocomposites of GO/PF was studied based on 5% and 15% weight loss and residual mass at 700 °C (Xu et al. 2013). The weight loading of GO in the nanocomposites was 0.25%, 0.5%, and 1% respectively. Pure PF resin showed 5% weight loss at 192 °C whereas the corresponding temperature of GO/PF nanocomposite was 235 °C for 0.25% of GO loading and increased to 247 °C for 1% GO loading. A similar trend was found for the 15% weight loss of pristine resin and nanocomposites. However, the decomposition of the pure resin and nanocomposites does not vary significantly and independent of graphene loading. A very small increase of around 2% in decomposition temperature was found for 0.5% GO loading compared to PF resin. The Tg of pure PF resin was 229 °C but initial decomposition started at 191.7 °C which was lower than its Tg. In contrast, GO nanocomposites showed decomposition at about 100–300 °C which is close to their Tg (Xu et al. 2013; Si et al. 2013b). It gives an inference that GO/PF composite displayed better thermostability in 15% weight losses compared to pure PF resin. Further increase in temperature weakens the interfacial interaction with pure resin and can break the PF. The thermal stability of GO/PF nanocomposite was comprehensively enhanced by in situ polymerization especially with 0.25% of GO due to the increased interfacial interaction between GO and PF polymer matrix (Xu et al. 2013).

2.3.2 Mechanical Properties

Dynamic mechanical analysis (DMA) of the in situ polymerized GO/PF composite was reported by Xu et al. (2013). The experiment showed that the storage modulus of GO/PF increased significantly compared to pure PF. The high mechanical modulus of GO and the reinforcing effect of GO in the PF matrix caused the significant increment of the storage modulus of GO/PF. Strong interfacial bonding was formed by the active groups of GO with the PF matrix which limits the molecular chain mobility of PF. The increases in GO content in the nanocomposites reduced the Tg of GO/PF. This was due to the aggregation of excess GO in the matrix and poor dispersion of GO weakened the interaction between GO and PF matrix. In another study, phenolic resin reinforced with GO was prepared and their mechanical properties were investigated (Zhou et al. 2013). The tensile strength and Young's modulus were found to be increased with GO content. When 0.5% GO was added to the composites, the tensile strength and Young's modulus increased by 39% and 23% respectively. A small improvement in mechanical properties was found after 0.5% of GO loading. Similar behavior was also reported in another study (Zhao et al. 2019). Higher loading of GO caused agglomeration and poor dispersion was obtained. The storage modulus of the composites also showed improvement with the GO loading.

3 Applications of Phenolic Nanocomposites

3.1 Aerospace Industry

To the construction of aircraft and spacecraft, one of the fastest grounds gaining materials is fiber-reinforced polymer composite material. Their use as primary structural materials in recent years in several technology-demonstrator front-line aerospace projects across the globe has provided confidence to their acceptance as prime materials for aerospace vehicles. The aerospace structure must meet some requirements such as fuel sealing, easy maintenance of the equipment, durability, and safety standards for the passenger carriage. The space environment (vacuum, radiation, and thermal cycling) needs to be appropriate for spacecraft. The advancement of computational power and the usage of fiber-reinforced polymeric materials made significant changes in material selections and the manufacturing of aerospace structures. The powerful computational tools along with CAD modeling and computer interfaces remove the complexity in manufacturing (Mangalgiri 1999).

Despite some limitations, the use of composite materials saves around 30% weight in making aerospace components. These developments in aerospace technology have been influenced by using different thermoset and thermoplastic polymeric matrices. Some of the widely used matrices in the aerospace application and their properties are listed in Table 1 (Mangalgiri 1999).

Phenolic composites are used in the different component fabrication of aerospace. The main applications with examples of phenol-based nanocomposites in the aerospace industry are presented in Table 2.

3.2 Automobile Industry

Phenolic nanocomposites have higher tensile and flexural properties due to the high interfacial bonding between phenol resin and fillers. Additionally, the phenolic resin has low flammability, smoke properties, and excellent resistance to degradation under extreme thermal operating conditions in addition to their low density, water-repelling properties, low thermal conductivity, and high strength. These properties together make it a safe and cost-effective material of choice in the automotive industries (Bafekrpour et al. 2013a). Generally, long fiber reinforced phenolic nanocomposites are compatible with automobile parts due to less joining and faster productions. The strength acquired by distributing the tensile strength by the specific density exceeds that of steel and aluminum. Natural fiber-reinforced nanocomposites are widely implemented in automotive and aerospace industries due to the reduction in vehicle weight. It is assumed that, in the future, the fiber-reinforced composite will reduce approximately 15% weight of automobiles (Asim et al. 2017).

Different parts of automotive are produced from phenol-based nanocomposites. Carbon nanotubes/phenolic nanocomposites are suitable for electrostatic dissipation

Table 1 Characteristics of the most familiar thermoset polymeric matrices used in the aerospace industry (Mangalgiri 1999)

Epoxies	Phenolics	Polyester
Most popular	Cheaper	Cheap
80% of total composite usage	Easy to use Lower viscosity	Easy to use
Moderately high temp.	High-temperature usage	Popular for general applications at room temp
Low shrinkage (2–3%)	More shrinkage	High shrinkage (7–8%)
No release of volatile during curing	Release of volatiles during curing	
Can be polymerized in several ways giving varieties of structures, morphology and a wide range of properties	Inherent stability for thermal oxidation Good fire and flame retardance Brittle than epoxies	Good chemical resistance Wide range of properties but lower than epoxies Brittle Low T_g
Good storage stability to make prepregs	Less storage stability difficult to prepreg	Difficult to prepreg
Absolute moisture (5-6%) causes swelling, and degradation of high temp properties	Absorbs moisture but no significant effect of moisture in working service range	Less sensitive to moisture than epoxies
Density 1.1–1.4 gm/cm^3	Density 1.2–1.4 gm/cm^3	Density 1.1–1.4 gm/cm^3
Tensile Modulus 2.7–5.5 GPa	Tensile Modulus 2.7–4.1 GPa	Tensile Modulus 1.3–4.1 GPa
Tensile strength 40–85 MPa	Tensile strength 30–60 MPa	Tensile strength 40–85 MPa

Table 2 Application of phenolic nanocomposite in the aerospace industry

Applications	Examples
Thermal protection	Space reentry vehicles Rocket nozzles Surfaces of the rocket, space vehicles Combustion chambers of rocket engines
Aircraft interiors	Sidewalls Partitions Ceiling panels Stow bins General aircraft interiors applications Environmental control system ducting

because of their conducting characteristics and mainly used as a fuel line in most modern vehicles (Corp et al. 2003). Carbon/phenolic nanocomposites are also used in the Chevrolet Corvette Stingray floor pan and recently being used in entry-level vehicles too. It had been used in the roof and the hood to take the weight off the front and the high panels of the vehicle to drive the center of gravity down. Carbon/phenolic nanoribbons can be used for electric vehicle batteries as high energy density cathodes. Graphene oxide/phenolic nanocomposites are used for corrosion and scratch resistance automobile applications (Corp et al. 2003). Additionally, they are used as a drive mechanism, catalytic converters, the inner and outer power train, suspension, exhaust systems, braking systems, lubrication, tires, and body parts.

3.3 Electronics Applications

Nanotechnology is deeply embedded in the design of advanced devices for electronic and optoelectronic applications. The dimensional scale for electronic devices has now entered the nano range. The utility of phenol resin-based nanocomposites in these areas is quite diverse involving many potential applications. Phenolic nanocomposites are used in chemical sensors, electroluminescent devices, electrocatalysis, batteries, smart windows, and memory devices (Tyagi and Tyagi 2014). Another potential application includes photovoltaic (PV) cells and photodiodes, supercapacitors, printable conductors, light-emitting diodes (LEDs), and field-effect transistors. Some other uses of phenolic nanocomposites are electromagnetic interference shielding, transparent conductive coatings, electrostatic dissipation, electromechanical actuators, and various electrodes (Singh et al. 2008).

3.4 Flame Retardant Phenolic Nanocomposites

The lightweight rime-like structure of carbon/phenolic nanocomposites are used for their flame retardant properties. It was found that the network structure of carbon fiber- nanometer-scaled porous phenolic (NCF-NP) nanocomposite has a low density and low thermal conductivity. Under the arc-jet wind tunnel simulation environment, it has impressive flame retardant property exceeding 2000 °C (Singh et al. 2008). The anisotropic thermal and mechanical characteristics of the NCF-NP nanofoams are suitable for applications such as high-temperature fire-retardants in the field of advanced buildings and aerospace thermal protection.

3.5 Construction Applications

Phenolic nanocomposites are also used in various construction materials to improve their physical and chemical properties. The functions of phenolic nanocomposites in constructions are discussed below:

- Improvement of reinforcing steel regarding corrosion and deterioration and improvement of the strength of concrete.
- Phenolic nanocomposites are used to repel dampness, dust, fingerprints, and bacteria in construction components.
- Thermal insulation and UV protection.
- In new-generation photovoltaic cells and panels.
- In waterproofing materials, paints, glues, and sealants for high quality and durability.
- Unreinforced phenolic polymer composites are being used for non-load-bearing applications such as trimmings, cladding, kitchenware, etc.

4 Recycling of Phenolic-Nanocomposites

4.1 Phenolic Resin Recycling

Thermoset plastics are very popular in the automotive, construction, aerospace, electrical, and electronics industries because of their hardness, good corrosion resistance, and high-temperature resistance. In 2010, approximately 4.9 and 8.3 million tons of waste thermoset plastic were produced in America and the European Union, and 1.1 million tons of waste thermoset plastic were produced in Japan in 2012 (Yang et al. 2019). The Japanese production of plastics was reported to be 15.2 million tons (Ozaki et al. 2000). Due to the highly cross-linked structure of thermoset plastic, it is very difficult to recycle them. There are three methods of recycling composite materials as shown in Fig. 6.

Thermoset resins cannot melt or solubilized like thermoplastic resins because thermosets resins cross-link after curing. Chemical recycling is also known as feedstock recycling and can be more effective for the linear structure of phenolic resin and supercritical methanol mixture is used the reacting solvent here (Ozaki et al. 2000). After the phenolic resin is recycled, the hardener is added to it, and then it is heated up to restore the rigid networked configuration. The flow chart of chemical recycling

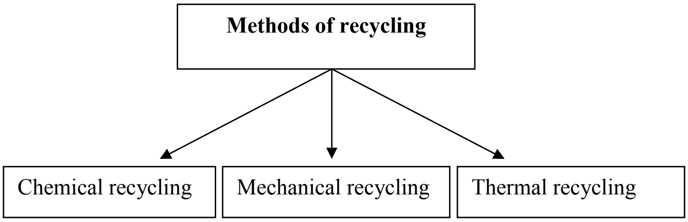

Fig. 6 Different methods of recycling composites materials

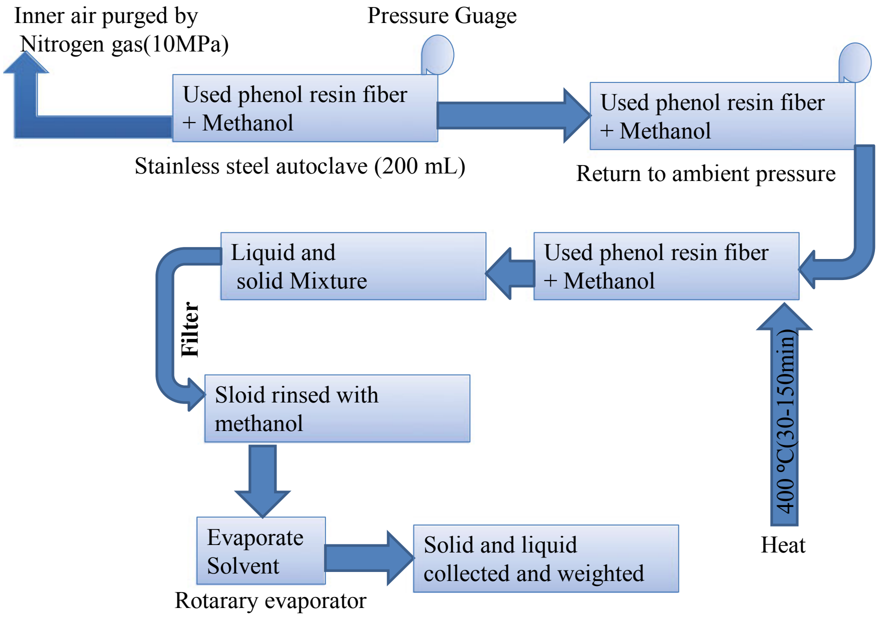

Fig. 7 Chemical recycling of phenolic resin (Ozaki et al. 2000)

steps of a novolac type phenol-formaldehyde resin is shown in Fig. 7 (Ozaki et al. 2000).

Phenolic materials are crushed into powder form in mechanical recycling (Yang et al. 2019). The flow chart of the mechanical recycling steps of a novolac type phenol-formaldehyde resin is shown in Fig. 8 (Yang et al. 2019).

4.2 Recycling of Carbon from Phenolic Resin-Carbon Nanocomposites

Recycling of carbon fiber from phenolic resin-carbon nanocomposites is very difficult. There is only available procedure is called thermal depolymerization. In this method, the phenolic resin-carbon nanocomposite is superheated in an oxygen-free chamber. The reinforced material is thus burned away which breaks the bonds and the freed carbon can then be collected and reused [27].

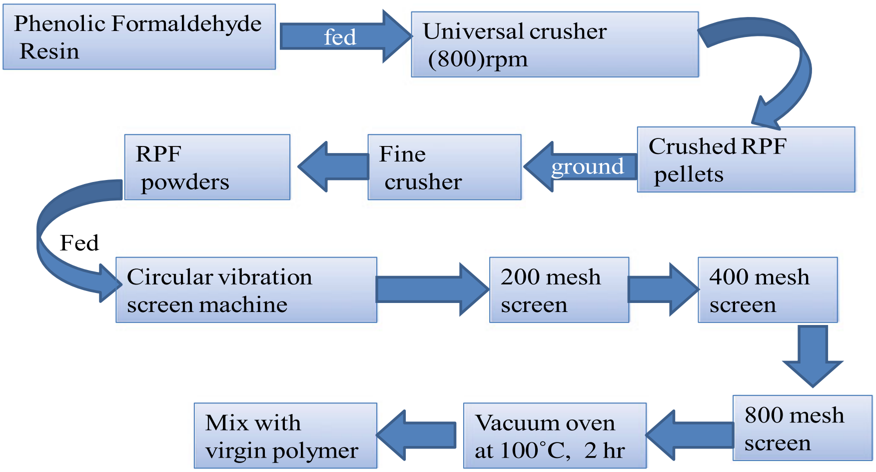

Fig. 8 Mechanical recycling of phenolic resin (Yang et al. 2019)

5 Conclusion and Future Perspective

Phenolic resin nanocomposites are a remarkable part of composite materials due to some distinctive characteristics. Phenolic nanocomposites provide higher surface area and better thermal properties. Phenolic resin reinforced nanocomposite possesses enhanced toughness without sacrificing stiffness or optical clarity. It also exhibits better mechanical characteristics, thermal and oxidative stability, and barrier behavior. Excellent fire-retardant characteristics of phenolic resin nanocomposites enable this material suitable for automobile, aerospace, electronics, construction, flame retardancy, marine, environmental, and many other applications.

Different efforts have been carried out to improve the performance of the phenolic nanocomposites. The major focus was given to the modification of nanofiller to improve the interaction between fillers and matrices. It is expected that with the rapid development in nanomaterials, new applications of phenolic based nanocomposites will emerge in the future with improved characteristics. The modification of the fabrication method can also contribute to the development of phenolic nanocomposites with multi functionalities.

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Fire Retardant Properties of Bio-phenolic Hybrid Composites

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Abstract Bio-phenolic based hybrid composites are used in engineering applications due of their better specific stiffness, strength, environmental resistance and thermal insulation properties. However, these composites cannot match the flammability resistance requirements for the high performance applications. Hence, numerous studies have attempted to enhance their fire retardant properties without deteriorating the physico-mechanical properties. Different approaches have been investigated to enhance the fire-retardant properties, such as the blending of phenolic resin with other polymers, addition of fillers, intumescent fire retardant coatings and chemical modification of the fibres. This article briefly presents an overview of the

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M. Jawaid and M. Asim (eds.), *Phenolic Polymers Based Composite Materials*, Composites Science and Technology,
https://doi.org/10.1007/978-981-15-8932-4_7

fire-retardant properties of the polymers, fibres and composites and the corresponding tests and standards involved. Recent studies on the improvement of fire-retardant characteristics of bio-phenolic hybrid composites with fillers were discussed.

Keywords Polymer composites · Bio-phenol · Fire-retardant properties · Fillers

1 Introduction

Polymeric composites reinforced with natural fibres are considered to substitute the synthetic fibres due to their lower density, low cost, abundant availability and biodegradability (Senthilkumar et al. 2018). However, the natural fibre reinforced composites are yet to find their use in high performance applications like aircraft and aerospace vehicles owing to their inferior mechanical properties (Chandrasekar et al. 2019) and poor flammability resistance to fire. Among the polymers, phenolic resin has better thermal insulation properties and fire retardation characteristic or low flammability. The superior flammability resistance or fire retardant characteristic of the phenolic resin is due to the following reasons: (i) high degree of cross-linking-in which the carbonyl linkage in the polymeric chains occur due to the oxidation of methylene groups and release of water due to the phenol-phenol condensation and (ii) release of volatile constituents such as CO, CO_2, and their ability to form char which acts as a thermal barrier (Kim et al. 2018; Mohd Asim et al. 2018a).

1.1 Fire Retardation Properties of the Natural Fibres, Polymer and Composites

Fire retardation is the ability of the material to slow down combustion, prevent flame propagation, less release of volatiles, reduction in the smoke volume, and high resistance to ignition (Kim et al. 2018; Jang et al. 2000). Thermogravimetric analysis (TGA) is the most widely used method for understanding the flammability properties of the natural fibres. In TGA, natural fibres are incinerated between 30 and 800 °C in a closed chamber filled with nitrogen. Thermograms and derivative thermograms which display the mass loss % as a function of temperature provide information on the thermal decomposition characteristic of constituents in the natural fibres. Natural fibres such as kenaf, flax, palm, jute, sisal, etc. are made up of cellulose, hemicellulose, lignin, pectin, moisture and waxes (Chandrasekar et al. 2017). These constituents are volatile compounds and decompose at elevated temperatures when subjected to fire. Thermal decomposition of the natural fibres occur in two or three stages depending on the fibre structure, fibre composition, density, etc. For a typical natural fibre, initial weight loss occurs between 80 and 100 °C which is due to the evaporation of moisture followed by decomposition of hemicellulose in the range of

200–260 °C, lignin between 160 and 400 °C and cellulose between 300 and 600 °C (Kim et al. 2018).

The fire retardant characteristic of the polymers and their composites reinforced with natural or synthetic fibres is determined from the following tests: (1) Limited Oxygen Index (LOI), (2) Underwriter's Laboratory-94 (UL-94)—vertical and horizontal burn experiments, (3) Cone calorimetry test and (4) Smoke density measurements (Table 1).

Polymers used as matrix material in the bio-composites are classified into thermoset and thermoplastic respectively. Tables 2 and 3 present the LOI % and HRR of the widely used thermoset and thermoplastic resins as matrix in the composite.

Table 1 Fire retardation tests (Laza et al. 2008; Marliana et al. 2016)

<table>
<tr><td><i>LOI test</i></td><td colspan="2"><i>UL-94 vertical burn test</i></td></tr>
<tr><td>• ASTM D2863
• Minimum oxygen concentration required to burn 50 mm length or burn for 3 min
• $\text{LOI}\% = 100 \times [O_2]/([O_2] + [N_2])$</td><td colspan="2">• ASTM D3801
• V-0: burn time <10 s per sample and sum of burn time for five samples ≤ 50 s
• V-1: burn time for combustion 30 s and the sum of the after-flame times for the five samples ≤ 250 s and flame could not ignite cotton below the specimen
• V-2: If flame drops and ignites the cotton</td></tr>
<tr><td><i>UL-94 horizontal burn test</i></td><td><i>Cone calorimetry</i></td><td><i>Smoke density measurement</i></td></tr>
<tr><td>• ASTM D635
• Flame time from 25 mm (free end) to 100 mm
• $V = 60L/t$, where V is the burning rates (mm/min), L is burned length (mm), and t is the time of burning (s).</td><td>• ASTM E1354
• A 50 kW/m^2 heat flux is applied to the sample
• Heat release rate (HRR), Mass loss rate (MLR), Smoke production rate (SPR) and critical time were measured.</td><td>• French Standard NF X 10-702
• Test is performed for 20 min, under flaming and non-flaming conditions in the NBS chamber
• Maximum smoke density (D_{max}) and area under the smoke density vs time curve in the first 4 min of the test (VOF4) were measured</td></tr>
</table>

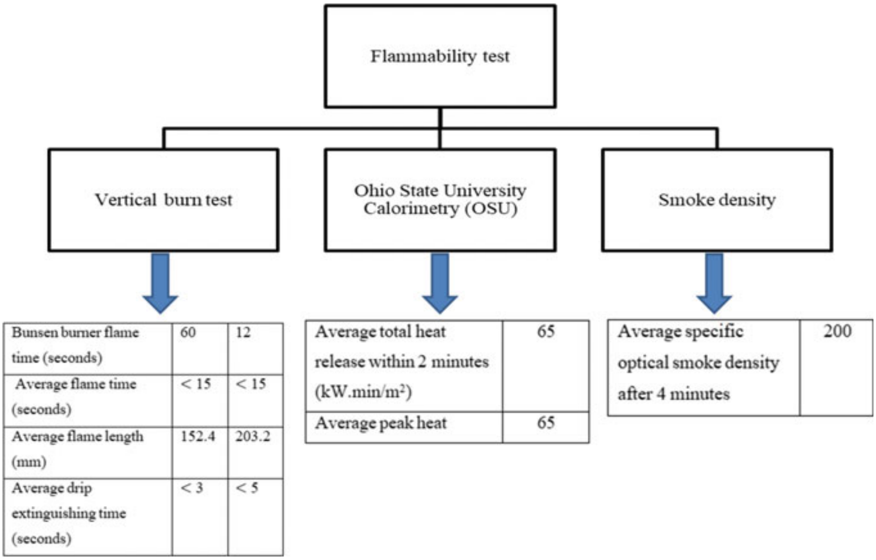
Table 2 LOI% of various polymers (Chapple and Anandjiwala 2010; Prabhakar et al. 2015)

Type of resin	Resin	LOI%
Thermoset	Phenolic	25–57
	Epoxy	23–27
	Vinyl ester	20–23
Thermoplastic	Polycarbonate	26
	Polylactic acid	21
	Polypropylene	17
	Polyethylene	17
	Polystyrene	18
	Polyvinyl chloride	23–45

Table 3 HRR of various thermoplastic polymers from the Cone calorimetry test (Prabhakar et al. 2015)

Type of resin	Resin	HRR (W/cm^2)
Thermoplastic	Polycarbonate	42.9
	Polylactic acid	27.2
	Polypropylene	150.9
	Polyethylene	140.8
	Polystyrene	110.1
	Polyvinyl chloride	42

Fibre reinforced composites to be used in interior furnishing of the aerospace and automotive vehicles are expected to fulfill their standard through the fire test. For instance, Fig. 1 shows the minimum fire retardation requirements for composites application to the interior furnishing of the Aircraft as per the Code of Federal Regulation (CFR) 25.853 (Kim et al. 2018).



Bunsen burner flame time (seconds)	60	12
Average flame time (seconds)	< 15	< 15
Average flame length (mm)	152.4	203.2
Average drip extinguishing time (seconds)	< 3	< 5

Average total heat release within 2 minutes (kW.min/m^2)	65
Average peak heat	65

Average specific optical smoke density after 4 minutes	200

Fig. 1 Fire retardation requirements of composites in interior furnishing as per the Code of Federal Regulation (CFR) 25.853

2 Enhancing Fire Retardation Properties of the Composites

Flammability of the composites is influenced by the individual constituents such as type of fibre and matrix, density, thermal conductivity, etc. (Kozlowski and Wladyka-Przybylak2008). In general, fire retardant properties of the bio-composites can be enhanced by the following methods (Chapple and Anandjiwala 2010):

- Blending phenolic resin with other thermoset resins that has lower flammability resistance
- Incorporation of flame retardant fillers into the polymer matrix
- Intumescent flame retardant coating on the polymer composites
- Fibre treatment with various reagents

2.1 Hybrid Composites

In a study by Laza et al. (2008), pure epoxy (E) and pure phenolic resin (P) were designated as 100E and 100P while the hybrid composite resin blend was designated as 80E/20P, 60E/40P 50P/50E, 60P/40E, 80P/20E. D_{max} and VOF4 from the smoke density experiment for 100E is 20 and 6.5 and for 100P is 289 and 682 respectively. Increasing phenolic resin in the blend led to the decline of D_{max} and VOF4 indicating improvement in the fire retardation characteristic of the hybridization effect in the composite.

Chiu et al. (2000) performed LOI test on unsaturated polyester resin (UP) blended with various proportions of phenolic resin (P) as UP0P100, UP40P60, UP60P40, UP20P80 and UP0P100. LOI was approximately 20.2% and 26.5% for the pure UP and phenolic resin. Hybrid composites possessed intermediate LOI values. As the phenolic resin% was increased in the resin blend, LOI % was found to increase in the order: UP0P100 < UP60P40 < UP40P60 < UP20P80 < UP0P100. In a recent study, Marliana et al. (2016) has shown that flame retardation of the UP/phenolic resin can be improved by the addition of kenaf into the resin blend. Cellulose, hemicellulose and lignin in the kenaf undergo thermal degradation at elevated temperatures above 200 °C unlike the UP resin which undergoes thermal decomposition at lower temperature. In particular, lignin in the kenaf fibre also adds to char and improves the fire characteristics of the composite. Similarly, UP resin burnt rapidly and did not come under V-0, V-1 and V-2 classification in the UL-94 vertical test. As the phenolic resin was increased in proportion of 10, 20 and 40%, hybrid composites came under the V-1 category.

Asim et al. (2018b).studied the effect of hybridization of PALF on the flammability properties of kenaf fibre reinforced phenolic composites. From the vertical UL-94 test, they indicated that as kenaf fibre was replaced by the PALF at 30, 50 and 70 wt%, flammability of the hybrid composites dropped to V-1 from V-0. In case of horizontal UL-94, the burn rate for kenaf/phenolic composite increased from 13.6 mm/min to 18 mm/min when the PALF was added up to 70 wt%. The significant difference in their individual constituents such as cellulose, hemicellulose and lignin was found to be an influencing factor in combustion behavior of the PALF/kenaf/phenolic hybrid composite.

2.2 Flame Retardant Fillers

Phenolic resin based composites were widely used in thermo-structural applications due to its exceptional thermal stability and fire resistance. Nonetheless, incorporation of different additives and fire retardants would enhance the flammability of resulting nano composites. Table 4 shows the various types of fillers with the fire-retardant properties.

According to Prabhakar et al. (2015), fire retardant fillers which induce flammability resistance to the composite fall under five different mechanisms as shown in Table 5.

Table 4 Commonly used flame retardants based on their functional elements (Prabhakar et al. 2015)

S. No	Classification of retardants	Examples
1.	Mineral flame retardants	*Metal hydroxide*: Aluminium tri-hydroxide ($Al(OH)_3$), Magnesium di-hydroxide ($Mg(OH)_2$), Antimony trioxide (Sb_2O_3) and Expandable graphite
		Hydroxycarbonates
		Borates: Zinc Borate
2.	Halogenated flame retardants	*Organochlorine*: Chlorinated paraffins and Antimony trichloride
		Organobromine: Polybrominated diphenyl ethers, Hexabromocyclododecanes and Tetrabromobisphenol-A
3.	Nitrogen containing flame retardants	Melamine, Melamine cyanurate, Melamine polyphosphate and Ammonium polyphosphate
4.	Phosphorous containing flame retardants	Ammonium polyphosphate, Chlorophosphates, Bromophosphate
5.	Silicone based flame retardants	Silicones, Silanes, Silsequioxane, Silica and Silicates
6.	Nano-sized Additives	Carbon nanotube, montmorillonite (nanoclay), vermiculite, and perlite *Metallic oxide*: Magnesium oxide (MgO), Zinc oxide (ZnO), and Ferric oxide (Fe_2O_3), Titanium oxide (TiO_2)

Table 5 Fire retardation mechanism of various fillers

Description	Physical dilution	Chemical interaction	Inert gas dilution	Thermal quenching	Protective coatings
Fillers	Talc and microspheres	Organobromines	Metal hydroxides, metal carbonates and nitrogen producing compounds	Metal hydroxides and carbonates	Phosphorous containing compounds and intumescent systems
Mechanism	Acts as heat sink and increases heat capacity	Dissociates into radical species that curbs chain propagation and branching in combustion	Releases large volume of non-combustible gases during combustion and dilutes the oxy gen supply	Release of water molecules due to endothermic reaction and quench the polymer during the combustion	Forms a char layer on the polymer surface, slows down pyrolysis and hinders the release of volatiles due to combustion

2.2.1 Studies on Phenolic Based Nanocomposites

Bahramian (2013) investigated the effect of graphite nano crystals (3 wt% and 5 wt%) on the flammability of graphite/novolac phenolic composites. Cone calorimetry results revealed that addition of graphite at 3 and 5 wt% exhibited 41% and 58% lower HRR (heat release rate) respectively compared to pure phenolic samples. Theoretical results were significantly closer to the experimental HRR. At 2.5×10^6 W/m^2 external heat flux condition the surface erosion or ablation rate for neat phenolic, 3 and 5 wt% of graphite nano-composites are 0.0184, 0.0164 and 0.0153 mm/s respectively. From the SEM analysis, it has been noticed that uniform char formation is mainly due to proper arrangement of graphite layers and thereby enhanced the thermal stability and lower the flammability at elevated temperatures.

High energy consumption in construction sector is mainly due to inefficient insulating materials with poor thermal performance. Organic thermal insulators such as phenolic foam board, extruded polystyrene foam board and polystyrene foam board were extensively used due to its thermal insulation, wear resistance and lower cost (Xu et al. 2012). Phenolic foam based insulators exhibited better thermal insulation performance compared to other wall insulators. Hence, it is termed as “King of Insulators” (Zhou et al. 2020). Neat phenolic resin is brittle in nature and the hydroxyl and methylene groups of its molecular structure can be easily oxidized. These impediments limit the application of neat phenolic resin at elevated temperature. Hence, phenolic resin can be modified with different nano fillers and fire retardants to enhance the fire resistant behavior. Most commonly used fire retardants are boron, silicones, nitrogen and phosphorous based fire retardants. Zhou et al. (2020) studied the effect of adding aluminum diethylphosphinate (ADP) and melamine on the fire performance

Table 6 Effect of fire retardants on the flammability of phenolic composites (Zhou et al. 2020)

Mass fraction (%)		UL-94	LOI
Neat Phenolic (100)		V-2	30.0
Melamine	Aluminum Diethylphosphinate		
2	–	V-1	30.8
4	–	V-0	32.1
6	–	V-0	31.6
8	–	V-1	30.4
–	5	V-1	31.0
–	10	V-0	33.1
–	15	V-0	34.6
–	20	V-0	32.3
3	10	V-0	34.6
3	15	V-0	34.8
4	**10**	**V-0**	**35.8**
4	15	V-0	34.4
5	10	V-0	34.1
5	15	V-0	34.0

of phenolic resin through limiting oxygen index (LOI) and vertical combustion test (UL-94) for thermal insulation applications. Table 6 shows the results of LOI and UL-94. From the results it is observed that addition of ADP (10 wt%) and melamine (4 wt%) shows higher LOI and achieved UL-94 V-0 grade. Further increase in flame retardant content declined the flame retardancy.

Flame retardants together with nano filler modified phenolic resin based nanocomposites possess excellent mechanical, thermal and fire retardant properties compared to composites without nano fillers. Hassan et al. (2017) studied the influence of ammonium polyphosphate on the flame retardant behavior of nanoclay filled phenolic/polyester nano composites. Unsaturated polyester resin was blended with the phenolic resin in order to achieve superior mechanical and fire retardant properties through effective interpenetrating polymeric networks. Limiting oxygen index (LOI) and vertical combustion test (UL-94) were utilized to investigate the flame retardant behavior of the nanocomposites. Hybrid nano composites with 30 phr ammonium polyphosphate showed V-1 grade with LOI of 29.2%. Robert et al. (2015) also highlighted that incorporation of 3 wt% and 10 wt% nanoclay or MMT into the chopped silica fiber/addition curable propargylated phenolic novolac (ACPR) improved the LOI from 64 to 69%. Higher flame resistance of MMT/polymeric nano composites is due to the dispersion and exfoliation of MMT, which strengthen the polymeric network by forming a silicate barrier and protects the composite as follows: (a) obstructs the evaporation of volatile compounds during combustion and (b) inhibits the diffusion of oxygen into the composite during the combustion (Shahroze et al. 2019).

Table 7 Effect of different wt% of Tetraethoxysilan on the fire performance of phenolic nanocomposites (Chiang and Ma 2004)

Tetraethoxysilan (wt%)	UL-94	LOI
0	V-1	32
20	V-0	35
40	V-0	37
60	V-0	40
80	V-0	43

Polymeric nanocomposites possess excellent thermal and fire resistant properties compared with fiber reinforced polymeric composites due to restriction in polymeric chain movement by nano sized fillers (Leszczyńska et al. 2007). Generally, the compatibility between inorganic additives and polymeric matrix is poor. It can be improved through organic modification of additives using organic surfactants. Organically modified nano fillers play a vital role in improving the wetting characteristics with the matrix. Also, it reduces the surface energy of the inorganic host (Alexandre and Dubois 2000). On the other hand, hybridizing organic and inorganic materials combine the advantage of individual constituents and it has received much attention in recent years. The most commonly used inorganic materials are titania, alumina and silicone (Chiang and Ma 2004). These materials are termed as "Ceramers" or "Ormosils" (Wilkes et al. 1985; Schmidt 1986). The hybrid organic-inorganic nano composites can be produced through sol-gel process at the molecular level. A coupling agent is required to form a covalent bond in between the constituents. "Ceramers" are well known for their thermal and flame retardant behavior. Incorporation of nano ceramers in the phenolic resin would improve the flame retardancy (Mark and Wen 1995). Chiang et al. investigated the effect of adding Tetraethoxysilan on the fire performance of phenolic resin through limiting oxygen index (LOI) and vertical combustion test (UL-94). The hybrid phenolic/silica ceramer has been synthesized by sol-gel process (Chiang and Ma 2004). The results are shown in Table 7.

Table 7 shows that addition of tetraethoxysilan significantly improved the flame resistance. Increase in silicone content enhanced the LOI compared to neat phenolic resin. Also 80 wt% of silicone based phenolic composites exhibited UL-94, V-0 grade. Hence, this hybrid ceramer can act as a green flame retardant.

Nanoclay filled polymeric composite exhibited outstanding properties at a much lower weight or volume fraction. For instance, it was found that at less than 1 wt% of clay content, the nano- composites showed higher thermal stability and low heat release rate compared to virgin polymer (Zhu and Wilkie 2000). Nanoclay modified phenolic composites has declined the peak heat release rate. However, there is no significant effect on Limiting oxygen index and UL-94 classification (Wang et al. 2010).

3 Conclusion

The need for new structural elements motivates the research in the field of fire-retardant biocomposites. Thermal properties of biocomposites play a vital role in the usage of composites in thermo-structural applications. Many industries are aiming in the development of fire-retarded materials. For instance, in the electronics industry, there is a need for developing flame retarded and flexible, recyclable/biodegradable circuit boards. They have successfully demonstrated the use of phosphorus-based fire retardants in the instrument housings and the application of ceramers in cable coatings to prevent short circuit. Phenolic based composites have a combination of properties that make them attractive for engineering applications requiring flammability resistance. Methods to obtain phenolic based bio-composites with better flame retardant properties have been discussed and the flame retardant mechanisms have been elaborated. New multifunctional additives and processing techniques that can improve fire-retardant characteristic of the biocomposites could make them suitable for the thermo-structural applications.

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Mechanical, Structural, Thermal and Tribological Properties of Nanoclay Based Phenolic Composites

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Abstract Phenolic resins are brittle at room temperature, hence to obtain suitable properties such as enhanced mechanical, thermal, etc., the phenolic resins are preferred to incorporate with fiber and/or filler. The phenolic based composites could be used to make complex geometries as they possess high strength and stiffness with high impact properties; hence, they would be the best alternative for metals. Furthermore, phenolic resins are well resistant to burning. It produces lesser smoke and toxic fumes, so they could be utilized in construction and building materials where high-temperature resistance is required. Therefore, numerous methods have been used to enhance the fire, mechanical, physical, etc., properties of phenolic resins by incorporating different sizes of fillers and/or fibers. However, the dispersion of nanoclay in the polymer matrix can limit the efficiency of composites. This chapter highlights the recent research works done on mechanical properties, X-ray diffraction, Fourier transform infrared spectroscopy, differential scanning calorimetry, thermogravimetric analysis, and tribological properties of nanoclay based phenolic matrix composites. Also, it explored how these properties were managed.

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M. Jawaid and M. Asim (eds.), *Phenolic Polymers Based Composite Materials*, Composites Science and Technology,
https://doi.org/10.1007/978-981-15-8932-4_8

Keywords Phenolic matrix · Nanoclay · Mechanical properties · Thermal properties · X-Ray diffraction · Fourier transform infrared spectroscopy analysis

1 Introduction

Commercially for the first time, the thermoset based phenolic resins synthesized in 1907. The phenolic resins are available in two different forms, such as (i) resole and (ii) novalac. These differences are made based upon (i) maintaining the ratio of phenol (P) and formaldehyde (F) and (ii) the polymerization reaction environment during synthesizing (Kakati and Deka 2007). The molar excess of phenol ($F/P < 1$) produces novolac resin, while the molar excess of formaldehyde ($F/P > 1$) produces resole resin.

Among the thermosetting resins, the phenolic resins are easy to produce at a low cost. Besides, these resins have excellent properties such as (i) good fire performance (ii) suitable thermal insulation property (iii) good dimensional stability and (iv) good chemical and corrosion resistance. Hence the phenolic resins can be used in various applications, such as (i) electrical related systems (ii) household appliances (iii) wiring equipment (iv) coatings (v) wood-based products, etc. (Zhou et al. 2008; Gardziella et al. 2013; Kim and Kim 2004; Eesaee and Shojaei 2014).

It is well known that fibers and fillers can be used to enhance the specific properties of composites. When the resin price increased to a double-digit percentage, the usage of fillers has been increased and became more significant. According to the size of filler, it can be classified as a micro filler (range of particle size is 10^{-6} m), and nanofiller (range of particle size is 10^{-9} m) and these fillers are dispersed into the matrix, which is called as micro composites and nanocomposites, respectively (Tolinski 2009).

The performance of the polymeric matrix composites can be enhanced by incorporating a few percents of nanoparticles, e.g., <5 wt%. The nanoclays or silicate layers are the most widely used fillers in polymeric matrix composites. It may be attributed to the fact that these nanoclays are from natural mineral; also, it offers excellent thermal and mechanical properties (Abrisham et al. 2020).

Nowadays, the usage of electronics/electrical instruments and automobiles (i.e., motor vehicles) is rapidly increasing. It is expected that the nanocomposites to provide specific engineering properties. Hence, the demand for using the nanocomposites is found to be increased; for example, the demand may increase from one billion dollars (in the year 2006) to a hundred billion dollars (by the year 2025) (Jeyaraj et al. 2019; Mansor and Akop 2020). There are many reasons for having such positive forecasts. When the filler size reduces to sub-micron size in resin, the composite could deliver unusual and enhanced properties. For example, the organically modified nanoclay can exhibit favorable properties, which is ascribed to its high aspect ratio. A common filler may have an aspect ratio of around 100 or less. But the organically modified nanoclay fillers can have an aspect ratio of above 1000. Since the nanoclay offers a high aspect ratio, the nanoclay/polymeric matrix composites could be suggested in high barrier applications, e.g., food packaging (Choudalakis and Gotsis 2009). The nanoclay particles also can provide better dimensional stability, when compared to the traditional micro fillers (Pasquini and Addeo 2005).

Besides, the organically modified nanoclay fillers would produce improved stiffness at lower filler loadings without losing their essential properties. The montmorillonite (MMT) clay is the most studied and commercialized among the nanofillers (Sherman 2007; Ramasubramanian 2007). Hence, the nanoclay based fillers are attracted by many researchers, scientists, and manufacturers. However, the dispersion of nanoclay in the polymeric matrix would be a prerequisite to obtaining the enhanced properties from their composites (Kornmann et al. 1998). Nevertheless, the researchers are facing difficulties in terms of dispersing the nanofillers. In order to achieve an effective dispersion, the nanoclay sheets have to be exfoliated by physically or chemically, to separate them into the individual layers (Ramasubramanian 2007; Sherman 2007).

FRP is commonly referred to as fiber-reinforced polymer composites. In general, the fibers are acting as load-carrying members, whereby the resins used to retain the position of fiber orientation. Moreover, the resin protects the fibers from the environmental attacks (Zhou et al. 2008; Senthilkumar et al. 2018; Kerni et al. 2020). Hence, fibers and/or nanoclay fillers are used together to enhance the properties of polymeric matrix composites synergistically. For example, Asim et al. (2018) examined the thermal properties of a phenolic matrix reinforced with pineapple leaf and kenaf fiber. The authors have improved the thermal properties by hybridizing the natural fibers in the phenolic matrix. Likewise, mechanical and physical properties of sugar cane bagasse/oil palm empty fruit bunch/phenolic matrix were also improved (Ramlee et al. 2019).

It is observed from the literature that most of the works have been done on thermoset and thermoplastic-based composites reinforced with nanoclay and/or fibers (Kornmann et al. 2005; Subramaniyan and Sun 2006; Zulfli and Shyang 2010; Nagendiran et al. 2007). However, the phenolic based composites are found to be limited since the phenolic matrix has a three-dimensional molecular structure before it cures (Ishida et al. 2000; Wu et al. 2002). Therefore, in this chapter, previous works from the phenolic composites reinforced with nanoclay and/or fibers have been highlighted involving mechanical, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermal and tribological properties.

2 Mechanical Properties of Nanoclay Based Phenolic Composites

One of the basic requirements of a composite is that it should have some desirable properties such as mechanical, thermal, physical, chemical, etc., relating to the intended application. According to Easaee et al., the nanoclay could be used to enhance the mechanical properties of glass fiber reinforced plastic composites, most importantly, their stiffness (Eesaee and Shojaei 2014). In an interesting work, Zhou et al. observed the combined effect of carbon fiber and nanoclay on the flexural properties of carbon fiber/nanoclay/phenolic composites. For example, the flexural properties (flexural strength and modulus) were more than doubled when adding 25wt% of carbon fibers into the phenolic matrix. Further, 17% and 10% of improvement in flexural strength and modulus have been observed from their composites due to the addition of nanoclay (5%) (Zhou et al. 2008).

In another interesting study, Pappas et al. showed the enhanced properties of tensile modulus, fracture strength, and strain to failure in montmorillonite clay/phenolic matrix composites. It was ascribed to complete dispersion of clay, which was obtained at 2.7% of clay by mass (Pappas et al. 2005). Singh et al. formulated hybrid phenolic composites containing $BaSO_4$, Kevlar fiber, lapinus fiber, nanoclay, and graphite. According to their study, impact strength and hardness were observed a significant drop by increasing nanoclay and lapinus fiber in phenolic matrix with a lesser amount of aramid fiber and graphite. These reductions were found due to the existence of intrinsic structural discontinuities in composites. The hardness and the impact strength reached the highest magnitude at 2% of nanoclay addition, and the lowest value observed at 2.5% (Singh et al. 2013a).

Interestingly in another study (Eesaee and Shojaei 2014), the tensile and flexural properties were reached the higher magnitudes at 2.5% of nanoclay addition in glass fiber/phenolic matrix composites (shown in Fig. 1). It was ascribed to the existence of improved interfacial adhesion between the phenolic resin/clay and the glass fiber, which would restrict the movement of the polymer chain at the polymer-nanoclay interface.

Singh et al. formulated hybrid PF composites containing $BaSO_4$, kevlar fiber, lapinus fiber, nanoclay, multiwalled carbon nanotubes (MWCNTs), and graphite. The authors illustrated that the flexural properties and the tensile strength were enhanced by decreasing the contents of (i) nanoclay (ii) multiwalled carbon nanotubes and (iii) lapinus fiber in the phenolic matrix. In contrast, (i) kevlar fiber and (ii) graphite contents were higher. On the other hand, the tensile modulus of these composites was found to be increased by increasing the content of nanoclay (Singh et al. 2013b). Asaro et al. compared the flexural properties of carbon fiber/phenolic resin with the addition of unmodified clay and modified clay (5 wt%. of bentonite). The flexural strength and flexural modulus, which get decreased as the fiber volume fraction are reduced since the mechanical properties are primarily provided by the carbon fiber (Asaro et al. 2016). Table 1 illustrated some of the works from the different researchers on nanoclay based phenolic matrix composites and also highlighted the observations measured by varying the nanoclay content.

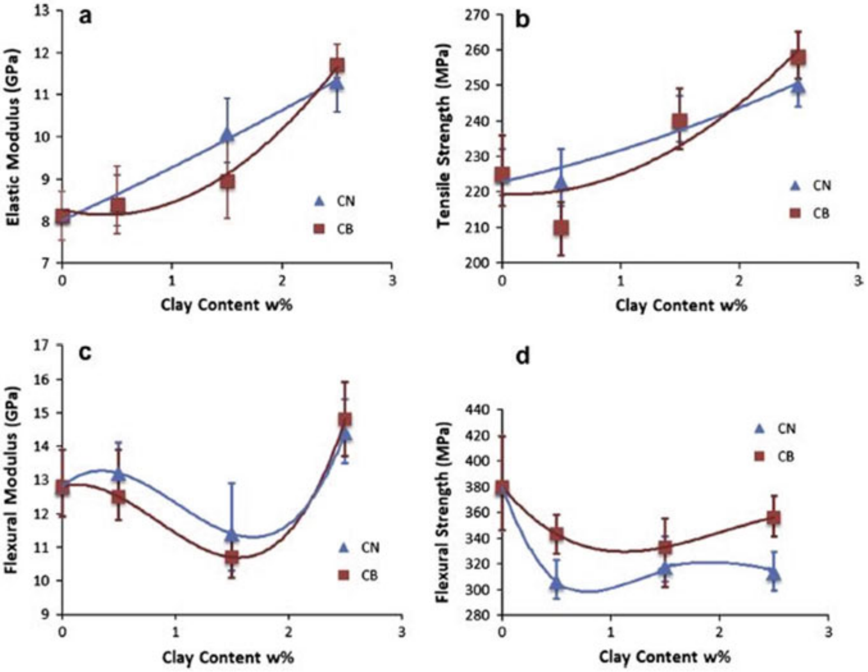

Fig. 1 Tensile and flexural properties of glass fiber/phenolic matrix composites (*CN = natural montmorillonite; CB = organically modified montmorillonite) (Eesaee and Shojaei 2014) (Reused with permission, Licence number: 4841721192720)

3 X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) Analysis of Nanoclay Based Phenolic Composites

Many researchers examined the XRD and the FTIR tests for polymeric matrix composites as a function of adding nanoclay and evaluated their suitability in different applications for day-to-day life. Singh et al. used the X-ray diffraction method to observe the exfoliation of nanoclay in kevlar fiber/lapinus fiber/graphite/phenolic matrix hybrid composites. The XRD plot revealed that there were no peaks observed between 2° to 5°, due to the uniform dispersion of nanoclay in phenolic matrix hybrid composites. For the sake of comparison, the pure cloisite 30B nanoclay was also subjected to XRD analysis, which showed the silicate reflection at 4.81° (2θ) (Singh et al. 2013a). Similarly, in another work, Kaynak and Tasan have compared the diffraction peaks of Rheospan clay and phenolic/Rheospan (0.5–1.5%) composites. The results revealed a complete exfoliation of Rheospan clay in phenolic resin and were assured by the disappearance of their peaks from the angle of 3.4° (shown in Fig. 2) (Kaynak and Tasan 2006).

Table 1 Effect of nanoclay adding on mechanical properties of phenolic matrix composites

Composite details	Observation	Reference
E-glass/nanoclay/phenolic; Nanoclay: 2.5, 5 and 7 wt%	Flexural modulus (MPa): 7.5 > 2.5 > 5 (high shear mix (HS)) Flexural strength (MPa): 2.5 > 7.5 > 5 (HS) Compressive strength (MPa): 7.5 > 2.5 > 5 (HS) Interlaminar shear strength (MPa): 7.5 > 2.5 > 5 (HS)	(Kabakov et al. 2011)
Phenolic/nanoclay; Nanoclay: 0.5, 1 and 1.5%	Flexural strength (MPa): 0.5 > 1>1.5 Charpy impact strength (kJ/m^2): 1.5 > 0.5 > 1 Fracture toughness (MPa/$\sqrt{m}$): 0.5 > 1.5 > 1	(Kaynak and Tasan 2006)
Phenolic/glass fiber/carbon black/nanoclay; Nanoclay: 0 and 5 wt%	Flexural strength (MPa): 0 > 5 Flexural modulus (GPa): 0 > 5 Flexural distortion at break (%): 0 > 5	(Kato et al. 2006)
Bakelite/Cloisite 30B nanocomposites wt% of clay: 0, 2.5, 5 and 10	Hardness (GPa): 10 > 5>2.5 > 0	(Solyman et al. 2017)
addition curable propargylated phenolic novolac (ACPR)/silica fiber/Cloisite 30B; Closite 30B varied from 1 to 10%	Optimum mechanical properties were observed at 3% loading of closite 30B. However, the properties were found to be decreased at higher loading of closite 30B	(Robert et al. 2015)

In other research work, the disappearance of peak at 4.81° was observed from the Bakelite/Cloisite 30B nanocomposites. It indicated that the platelets were become singular and found to be exfoliated due to the increased spacing between their platelets. Because the Bakelite resin entered into the nanoclay layers and produced their separation (Solyman et al. 2017). Another study illustrated the diffraction peak at 7.15° for original bentonite and was disappeared for modified bentonite. This is due to the increase in interlayer distance in modified bentonite when compared with unmodified bentonite. (Asaro et al. 2016).

In another work, the researchers (Lei et al. 2010; Fang et al. 2014) compared the exfoliation behavior of nanoclay (NaMMT) in two different resins, such as phenol-formaldehyde and phenol-urea-formaldehyde. NaMMT shows a strong peak at 2θ value 7, with d spacing 1.26 nm. However, the 2θ peak for NaMMT shifted to a lower angle with the d-spacing of 1.47 nm for NaMMT/phenol-formaldehyde composites. On the other hand, the authors stated that the nanoclay was thoroughly exfoliated in phenol-urea-formaldehyde resin. The difference in the behavior is due to the different structure of the polymers.

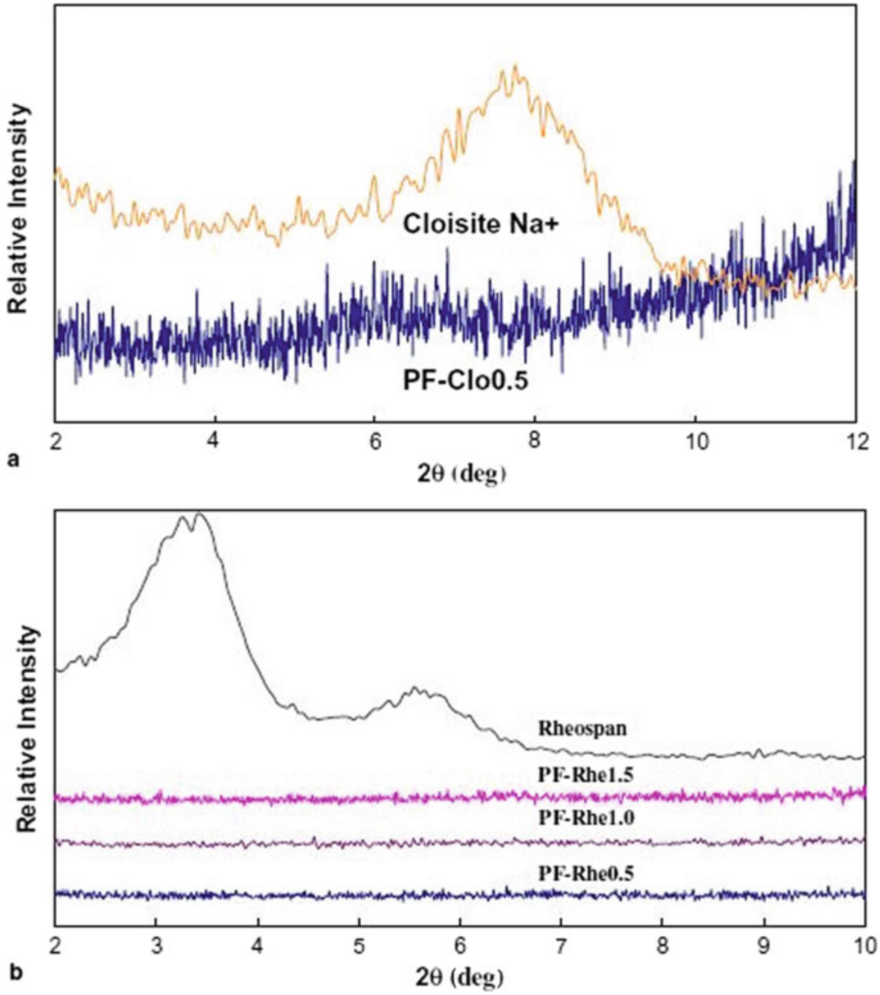

Fig. 2 XRD plots of Rheospan clay and phenolic/Rheospan composites (Kaynak and Tasan 2006) (Reused with permission, License number: 4841730742534)

Many earlier studies reported that properties (e.g., thermal and mechanical) of polymeric matrix composites could be improved by introducing a small amount of nanoclay in the matrix. Thus, understanding the bonding characteristics between the matrix and the nanoclay is essential (Chan et al. 2011). Amongst the characterization tools, the Fourier transform infrared spectroscopy (FTIR) would be the most powerful technique to obtain the details of (i) structure of individual materials (ii) composition of polymer mixtures and (iii) formation of new bonds in between the polymer and nanomaterials (Mohamed et al. 2017).

Table 2 Types of bond and their functional groups, wavenumber (Mohamed et al. 2017)

Type of bond	Details of functional groups	Wavenumber (cm^{-1})
Single bond	O–H, C–H, and N–H	2500–4000
Triple bond	C≡C, C≡N, X=C=Y (C, O, N, S)	2000–2500
Double bond	C=O, C=N, C=C, N=O	1500–2000
Fingerprint region	C–Cl, C–O, C–N, C–C	650–1500

In general, the FTIR spectra can be used to analyze four different types of bonds, such as (i) single bond (ii) triple bond (iii) double bond and (iv) fingerprint region. Table 2 gives some necessary details of bonds and their wavenumber.

The compatibility of nanoclay in fumed silica/phenol formaldehyde composites was studied using FTIR spectra analysis (Lai et al. 2017). The authors observed a peak between 1500 and 1650 cm^{-1} for phenol-formaldehyde (PF), phenol-formaldehyde/fumed silica composites (PF/FS), and nanoclay/silica/phenol formaldehyde composites (PF/FS/clay). The peak of PF/FS/clay composites was broader compared to the PF and PF/FS composites. This is attributed to the breaking of the C=C bond into the C–C bond. Therefore, hydroxyl groups can attach to the C atoms, and hence, the compatibility of the clay with PF/FS composites was found to be enhanced. In another research study, researchers used nanoclay as a reinforcing fillers in wood/PF adhesives. They also analyzed the effectiveness of using montmorillonite and organomodified montmorillonite by comparing their FTIR spectra. Both montmorillonite and organomodified montmorillonite showed similar absorption peaks at 3926, 3428, 1637, 1044, 521, and 470 cm^{-1}. However, the organomodified montmorillonite exhibited new peaks at 2929 and 2853 cm^{-1}; due to the C–H stretching vibrations of the organic intercalation agent. Besides, the modified montmorillonite provided (i) the enhanced compatibility with PF and (ii) the dispersion of nanoclay layers in the PF matrix was improved (because the cations in montmorillonite were exchanged with organic ammonium ions). Table 3 gives observations made by the researchers due to the addition of nanofillers in the phenolic matrix (Wang et al. 2017).

4 Differential Scanning Calorimetry and Thermogravimetric Analysis of Nanoclay Based Phenolic Matrix Composites

The differential scanning calorimetry (DSC) can be used to evaluate variations in cure reaction and glass transition temperatures (T_g) in phenolic resins with the addition of nanoclay. Choi et al. studied the curing behavior of phenolic resin and their nanocomposites such as (i) phenolic resins (ii) phenolic/montmorillonite (iii) phenolic/dodecyl ammonium-modified montmorillonite (iv) phenolic/octadecyl ammonium-modified

Table 3 Summary of observations made by the researchers due to the addition of nanoclay in phenolic matrix composites using FTIR spectra

Composite details	Observation	References
addition curable propargylated phenolic novolac (ACPR)/silica fiber/Cloisite 30B; Closite 30B varied from 1 to 10%	Owing to the diminishing of C≡C, the peak at 2120 cm^{-1} was disappeared at ACPR/silica/Cloisite 30B10%, while a new peak appeared at 1736 cm^{-1} It was ascribed to the substantiating curing of ACPR	(Robert et al. 2015)
Natural bentonite, nanoclay, and TiO_2 nanoclay nanocomposite	*Natural bentonite* 3600–3700 cm^{-1}: due to montmorillonite-rich smectite clay 3220 cm^{-1}: N–H stretching 540 and 753 cm^{-1}: Si–O–Al symmetric vibrations 836 and 915 cm^{-1}: Al–Mg–OH bending vibrations 3620 and 1034 cm^{-1}: OH stretching and Si–O bending *Nanoclay* 2940 and 2850 cm^{-1}: asymmetric and symmetric vibration of methylene groups $(CH_2)_n$ of the aliphatic carbon chain The shape of the FTIR curve changed due to the increased gallery spacing *TiO_2 nanoclay nanocomposite* Ti^{4+} ions were found to be deposited between the clay platelets Sharp peaks were observed due to the addition of (i) bentonite and (ii) TiO_2 500 cm^{-1}: Ti–O stretching	(Ghodke et al. 2012)

montmorillonite and (v) phenolic/benzyldimethyloctadecylammonium-modified fluorohectorite. Interestingly, the samples studied (i.e., both modified and unmodified) showed no differences in exothermic peaks. This is because the organosilicates has no effect on the curing behavior of phenolic resin(Choi et al. 2000).

In another study, the curing characteristics of neat phenolic and phenolic/Na^+ -montmorillonite (NaMMT) composite compared by using the DSC. Also, they reported two significant differences between the phenolic and phenolic/NaMMT composites in terms of (i) the pH values and (ii) the level of intercalation. The intercalation caused changes in curing characteristics of the phenolic matrix and exhibited some differences between the phenolic and NaMMT/phenolic in terms of showing the different number of peaks (Lei et al. 2010). Researchers investigated the differences in curing behavior of neat phenolic and MMT/phenolic composites using the DSC technique and reported that the differences were minimal (shown in Fig. 3). However, the MMT/phenolic composites showed three exothermic peaks in the DSC

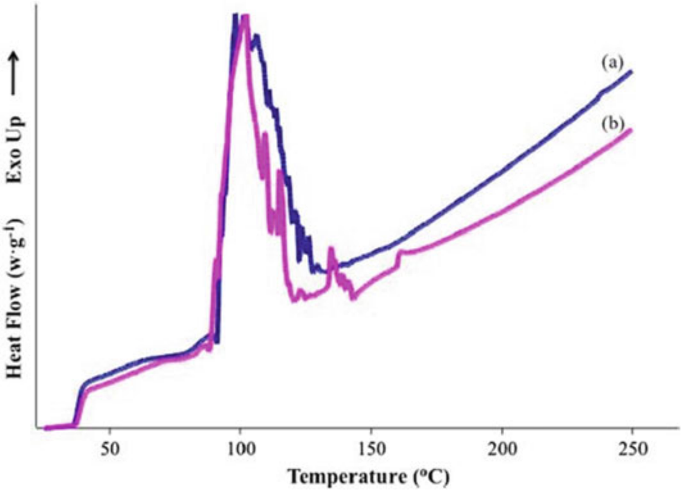

Fig. 3 DSC plots of neat phenolic and MMT/phenolic composites (Fang et al. 2014) (Reused with permission, License number: 4841740117490)

plot when compared to the neat phenolic since the composites blocked the mass and the heat transfer, which delayed the curing (Fang et al. 2014).

Byun et al. studied the thermal stability of phenolic resin (resole type) modified with ω-amino acid modified montmorillonites (KLC6M). The concentration of 6-aminocaproic acid-modified MMT (C6M) (layered silicate) was varied from 1 to 5%. Only marginal changes in the thermal stability of the composites observed with the incorporation of MMT. This is because the phenolic resin itself had excellent thermal stability (Ho Yun Byun et al. 2001). Chiang et al. reveal that increasing the content of the coupling agent (3-glycidoxypropyltrimethoxysilane) in phenolic resin/SiO_2 composites increases the char value. The enhancement in char values provided three distinct advantages such as (i) the combustible gas generation was reduced (ii) the exothermicity was decreased and (iii) the thermal conductivity of burning material was impeded (Chiang et al. 2003). Pappas et al. illustrated that phenolic resin/nanoclay (2.7% by mass) composites retained the thermal stability up to 225 °C when compared to the phenolic resin (Pappas et al. 2005).

Rangari et al. reported that the 2% Cloisite 10A clay/phenolic resin nanocomposites undergoes decomposition at 455 °C while the phenolic resin decomposes at 443 °C. The increase in thermal stability of the nanocomposites was explained by (i) the catalytic action of nanoclay on crosslinking and (ii) the high cell density of the resin due to the addition of nanoclay. Also, the researchers studied the DSC analysis for the above-said nanocomposites and reported that the nanocomposites had the T_g of around 282 °C. This value is marginally higher than the neat phenolic resin (270 °C). The addition of nanoclay was attributed to causing higher crosslinking; hence the T_g of the Cloisite 10A clay/phenolic composites was found to be enhanced (Rangari et al. 2007). In another work, the thermal stability of nanoparticles (i.e., reactive rubber nanoparticles and cloisite 30B) reinforced with phenolic matrix examined by using TGA and DSC techniques. It was observed that the composites reinforced with nano fillers both the reactive rubber nanoparticles and cloisite 30B showed 10 to 20% of enhancement in thermal stability than the neat phenolic resin (Solyman et al. 2017).

According to Jiang et al. the thermal decomposition temperature (T_d) of nanocomposites depended on the chemical structure of the organic modifiers. Hence the montmorillonite/phenolic resin/benzyldimethylphenylammonium chloride (B2MP-MP) (organic modifiers) nanocomposites possessed higher T_d (783 K); it was attributed to (i) benzyl and (ii) phenyl groups in the organic modifier (Jiang et al. 2006). In another interesting study by Zhou et al. states that with the increasing content of nanoclay in a phenolic resin, the T_g was found to be shifted to the higher temperature. For example, the T_g of the phenolic resin was increased from 207 °C (at 0 wt% of nanoclay) to 247 °C with the incorporation of 5wt% of nanoclay. Besides, the authors have compared the T_g of phenolic resin with the epoxy resin using similar nanoclay content. It showed that the improvement was less than 10 °C (i.e., increased ~60 to ~70 °C). The results revealed that the phenolic resin showed higher T_g than the epoxy resin due to (i) the existence of strong interfacial interaction between the phenolic resin and the silicate nanolayers and (ii) the phenolic resin has a different structure than the epoxy resin (Zhou et al. 2008).

To obtain improved thermal stability, the researchers combined boron with nanoclay/phenolic resin composites. Montmorillonite was modified with organic modifiers, such as (i) benzyldimethylhexadecylammonium chloride (BH) (ii) benzyldimethyphenylammonium chloride (BP), and (iii) benzyltriethylammonium chloride (BE). Results were indicating that boron-based nanocomposites exhibited higher thermal degradation temperature. This, however, was not the case after the boron was removed. Amongst the composites, BP based composites possess higher residual weight % from the TGA analysis (Wang et al. 2008). Table 4 illustrated a list of work made by the different researchers on nanoclay based phenolic resin composites.

Table 4 Reported studies on the thermogravimetric analysis of nanoclay based phenolic composites

Details of resin	Details of filler	References
Resole-type	Organophilic clay	(Kato et al. 2006)
Resol type phenolic resin/asbestos cloth	Cloisite 15A	(Bahramian and Kokabi 2009)
Novolac phenolic resin	Clay Cloisite Na^+	(Zhang et al. 2010)
Kevlar-lapinus fiber/phenonlic resin	Multiwalled carbon nanotube and nanoclay	(Singh et al. 2014)

5 Tribological Properties of Nanoclay Based Phenolic Composites

Polymer composites comprised of filler and/or fiber reinforcements are often used in friction and wear-based applications, mainly these composites are acted as sliding elements. In earlier days, metallic materials were used as sliding elements. New developments are being made to utilize the polymer-based composites, both in extreme loading and higher temperature conditions. For example, tribo-couple from the automobile component, which is subjected to operate in both high load with high-temperature conditions (e.g., 120 °C). Hence, the polymer matrix composites are preferred to fulfill (i) an excellent wear resistance and (ii) low friction characteristics. However, it depends upon the required application, and the polymer matrix composites have to function differently. For example, clutch or brake pad needs (i) a high coefficient of friction and (ii) low wear. This, however, is not the case for gear components (Friedrich et al. 2005).

It is well known that the incorporation of nanoparticles in the matrix would increase the mechanical properties of the polymeric matrix composites. Besides, the size of the particles is also playing a vital role to optimize the properties. For example, both toughness and stiffness simultaneously. Since the nanoparticle possesses three-dimensional interphase, it can cover the huge interfacial area in the matrix (Karger-Kocsis and Zhang 2005). Several studies were established that the addition of nanofillers in matrix significantly improves the wear performance of polymeric matrix composites. Since the particle size of nanofillers is <100 nm, the performance of the nanofilled composites significantly different than the micron-sized filled composites (Friedrich et al. 2005).

A comparative study was performed on the friction coefficient of glass fiber/silicon carbide/phenolic resin and carbon fiber/silicon carbide/phenolic resin composites. The composites reinforced with carbon fiber showed better friction coefficient to composites reinforced with glass fiber. It may be attributed to the existence of a difference in tribological properties of glass and carbon fiber. Also, the carbon fiber possessed anti-friction property, while the glass fiber encouraged friction characteristics (Kompozitih 2017). In another study, researchers fabricated hybrid composites comprised of (i) Kevlar fiber (2.5–10 wt%) (ii) Lapinus fiber (20–27.5 wt%) (iii) nanoclay (1–1.375 wt%) (iv) multi-walled carbon nanotube (1–1.375 wt%) (v) graphite (2.25–3 wt%) (vi) $BaSO_4$ (50 wt%) and (vii) phenolic resin (15 wt%). Comprehensively it was reported that the composites reinforced with 1.375 wt% of nanoclay and 1.375 wt% of multi-walled carbon nanotube with an adequate amount of fibers showed the best performance in tribological characteristics (Singh et al. 2013b).

6 Conclusion and Future Perspective

In the past decade, the researchers have used different types of fillers (e.g., kaolinite, mica, montmorillonite, chlorite, bentonite) and studied their mechanical, thermal, Physico-chemical properties, etc. with the addition of phenolic resin. Nevertheless, dispersing the nanofillers in the phenolic matrix was the most critical issue. In this chapter, the quality of dispersion of nanoclays and/or different fillers by varying their content in phenolic resin are given. Also, the interaction between the nanoclay and/or fibers with phenolic are discussed with the help of characterization techniques such as mechanical, thermal, tribological, X-ray diffraction, and Fourier transform infrared spectroscopy.

Besides, in the upcoming years, the number of research works from the nanoclay and/or fibers reinforced phenolic composites should be increased. Based upon the performance and the low cost to buy, the phenolic based composites should remain in the prominent position amongst the thermoset based composites.

Since the phenolic based composites possess higher impact strength, stiffness, and strength, it could act as an alternative material for metals. Besides, the phenolic composites have good in fire performance and good in chemical and corrosion resistance. Hence the possibility of utilizing the phenolic based composites in civil and construction industries by way of increasing safety and diminishing the price.

Acknowledgements This research was entirely supported by King Mongkut's University of Technology North Bangkok (KMUTNB), Thailand through Grant No. KMUTNB-64-KNOW-001. Therefore, all the authors at this moment express their sincere appreciation to the KMUTNB.

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Nanofibrillated Cellulose Based Bio-phenolic Composites

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Abstract Phenolic composites are well known for their excellent resistance to corrosion, heat and combustion. Bio-based phenols or plant-derived phenol, on the other hand, has been promising renewable and environmentally friendly substitute to petroleum derived phenols. Due to some notable disadvantages of biophenol (i.e. poor design flexibility and brittleness of the materials among others), several effective attempts have made to overcome the problem by incorporating nano-sized cellulose fibre as reinforcement materials in bio-phenolic composites. The modified phenolic resins have been fabricated with nano-fibrillated cellulose (NFC) to produce bio-composites that possess superior mechanical, thermal and electrical properties. The combination of NFC from kenaf, jute, sisal, pineapple leaf fibre (PALF), flax, and hemp with phenolic matrices will produce composite materials that can compete and invade markets currently dominated by carbon and glass fibre reinforced composites especially in construction and automotive applications. Due to its abundancy and renewability, embedding NFC with phenolic polymer will solve numerous environmental problems. In fact, wide varieties of NFC based bio-phenolic composites have been innovated using various advance synthesis processes. This chapter is intended to present an overview on the attributes of NFC from various sources and its effects on the properties of bio-phenolic composites. The bio-based phenolic matrix synthesis and composite processing technique are also discussed herein.

Keywords Nanocellulose · Nanofibrillated cellulose · Natural fibre · Phenols · Biocomposites

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M. Jawaid and M. Asim (eds.), *Phenolic Polymers Based Composite Materials*, Composites Science and Technology,
https://doi.org/10.1007/978-981-15-8932-4_9

1 Introduction

Phenolic materials are made of the low molecular weight precursors, either of conventional novolacs or resoles in which the cured network produce good heat-resistant, flame-retardant, and dielectric composites (Ning and Ishida 1994). Due to its inexpensive fabricating process and raw materials, they have been widely used in various industrial applications includes household, construction, and electrical facilities. To reduce the dependence on fossil fuel, the use of an eco-friendly bio-based polymers shall be prioritised in the future design of both structural and non-structural composites.

Lignin, as one of the major cell wall elements in plants, not only plays a major role in the transport of water and nutrients and protects the plant against microorganisms, but it also provides skeletal support for the plant. Due to their structural similarity, lignin is used as the alternative to petroleum-based phenol (Li et al. 2010). Wood and agricultural industries produce tonnes of residue which can be converted into renewable biomass resource for the production of bio-phenols (Wang et al. 2009). The presence of a large number of distinct functional groups in the structure of lignin structure allow this macromolecule to undergo numerous modifications. However, these bio-phenolic resins exhibit some notable disadvantages related to low shelf-life, poor design flexibility and the brittleness of the materials (Kanchanasopa et al. 2001). Fortunately, these problems can be potentially overcome by incorporation of natural micro/nano-sized fibres with some chemical modifications.

Despite high-tech development of synthetic or manmade fibres (i.e. aramid, carbon, and glass), natural fibres such as pineapple leaf, flax, kenaf, jute, hemp, and sisal have also attracted renewed interest in the research of green composites due its low cost, biodegradability, sequestration of carbon dioxide, ease of separation as well as having low density and relatively excellent specific strength properties (Sanjay et al. 2016). These natural fibres, or so called bio-fibres, are often linked to the emerging use of nanocellulose (NC), as an ideal candidate of reinforcement material due to its ability to exploit the strength and high stiffness of cellulose crystals in a composite application (Fareez et al. 2020). Apart of plant sources, NC can also be naturally obtained from algae, and tunicate while some NC are synthesised by a bacteria (i.e. *Acetobacter* sp.), which in this case it is known as bacterial cellulose (Ya'acob and Aziz 2017). In fact, there are other several terms used to describe NC, which mainly refers to their morphological structures and synthesis processes and the most commonly used term are nanofibrillated cellulose (NFC) and cellulose nanocrystals (CNC). In this chapter, we adopt the generic term 'nanocellulose' to describe a nanometre scale cellulose and NFC as of non-acid hydrolysed and fibrous type of NC.

The concept of using NFC as a reinforcement material in bio-phenolic composite is pioneered from one of the composite products called "Papreg". It is a phenolic resin impregnated paper-based laminate with high toughness and high tensile properties of plant fibre network structures developed in 1940 and 1950. The nanopaper laminates which contains phenolic resin content of 35 wt%, demonstrated an excellent tensile strength and modulus of 188 MPa and 18.6 GPa, respectively (Lee et al. 2014b), and it was used in various applications that includes aircraft structures. Although the name seems to be unpopular nowadays, the design of such green chemistry product and the sustainability and eco-efficiency of nanocellulose have led the extensive research of these materials in the development of the next generation of biocomposites.

This chapter is split into two sections; the first section briefly discusses properties of NFC, followed by a section reviewing NFC as a reinforcement material in phenolic bio-composites covering the synthesis process of biophenols and the manufacture process of the biocomposite. The potential of NC as reinforcement material in the high-performance structural applications of NFC-reinforce phenolic bio-composite is critically assessed in this chapter.

2 Bio-based Phenolic Matrix Synthesis

Plant biomass contains a significant amount of a polyphenolic macromolecule called lignin of up to 30–40% of its dry weight. Therefore, several efforts have been made to enhance the isolation of lignin as a feedstock for the production of bio-based phenolic compound (Zhang et al. 2016). Lignin can be harvested and isolated by means of various methods such as delignification with organic solvent, alkaline pulping, liquefaction, hydrolysis, and pyrolysis. Delignification is an organosolv process using organic solvent that is considered to be more cost efficient and environmental-friendly method. This process is commonly employed in both laboratory (pilot plants) and industrial scale. Organosolv extraction has been used to extract lignin for biophenol production. For example, Wang et al. (2009) had successfully extracted lignin from white pine sawdust by organosolv extraction using hot-compressed ethanol–water co-solvent at 180 °C with ethanol–water solvent (1:1 wt/wt). With such parameters, the resulting lignin yield and purity were recorded at 26% and 83%, respectively. Through condensation polymerization process as catalysed by sodium hydroxide, phenol–formaldehyde resol resins extracted from the synthesized lignin display a varying replacement ratio from 25 to 75% (wt/wt) with petroleum-based phenol. Furthermore, the author suggests that the ratio should be less than 50% (wt/wt).

Besides that, alkaline pulping process such as soda pulping and kraft pulping is also considered as potential pulping process for non-woody materials. Essentially, these processes facilitate the extraction of lignin, hemicelluloses and cellulose to improve the quality of the pulp. Kraft pulping is known for one of the major pulping processes in the world. Kraft lignin, which is isolated from kraft black liquors, acts as fuel to generate energy for the pulping process especially in the paper industry. Another study by Ibrahim et al. (2011) had highlighted the potential of lignin biophenols from oil palm biomass as a substitute to petroleum-based phenols. Kraft and soda pulping of oil palm biomass generate large amounts of black liquor as a by-product. The precipitated lignin in the black liquor was filtered and dried in order to remove the impurities. Recovered lignin can then be used as biophenol or to be partially incorporated into phenolic resins such as phenol formaldehyde resin.

Liquefaction is also one of the useful and viable techniques to extract the bio-phenol from agricultural and wood waste. Tymchyshyn and Xu (2010) had first reported the synthesis process of phenol formaldehyde resins from sawdust and cornstalks by means of hot-compressed water, suggesting a novel green approach production of the bio-phenolic compounds. To isolate pure phenolic compounds, direct liquefaction of these biomass fibres was conducted at a temperature range of 250–350 °C in the presence of 2 MPa H_2. As a result, a significant number of phenolic compounds such as 2-methoxy-phenol, 4-ethyl-2-methoxyphenol, and 2,6-dimethoxy-phenol, were obtained with concentration of up to 80%. All these phenolic compounds can be further modified to fabricate the bio-phenol resins. Besides, with the same extraction process, Zhao et al. (2010) had successfully produced phenol–formaldehyde resins derived from lodgepole pine barks. In comparison to a commercial and lab phenol–formaldehyde resin, the biophenol-formaldehyde resins were found to have higher polydispersity indices and higher average molecular weights, but with shorter gelling times. Therefore, the viscosity of the biophenol-formaldehyde resins was notably higher than the lab phenol-formaldehyde resin and the commercial phenol-formaldehyde resin.

The biophenol can also be produced by addition of bio-oil with the commercially available phenol formaldehyde which then known as bio-oil phenol formaldehyde. According to Cui et al. (2017), bio-oil from renewable biomass was obtained by using fast pyrolysis. The synthesized bio-oil was then used for the manufacture of phenol formaldehyde resin. Results indicated that bio-oil phenol formaldehyde resin with the addition of 20% bio-oil produces an outstanding performance on bending strength. It was also reported the bio-oil addition could enhance the fire resistance and the brittleness of phenol formaldehyde resin and that explained by the modification on the crosslinking degree with increased formation of more hydrocarbon chains in phenol formaldehyde resin.

Since crude lignin has fewer reactive sites than phenol, incorporation of crude lignin directly into the phenol formaldehyde is always a challenge. The additional hydrolysis of lignin could be a good alternative to this issue. In the study done by Zhang et al. (2016), a bio-phenol-hydroxymethylfurfural resin was produced from hydrolysed lignin as bio-phenol where glucose is used as a precursor. This bio-phenol-hydroxymethylfurfural resin was developed through a resinification reaction between hydroxymethylfurfural and phenolated hydrolysed lignin under constant pressure, in the presence of Lewis acid catalysts, with up to 85% yield. It is also worth to note that, to avoid carcinogen toxicity of formaldehyde as declared by the World Health Organization's (WHO), its uses in bio-composites has tremendously been reduced.

3 NFC as Reinforcement Material in Phenolic Composites

NFC from renewable biomass received much interest as an alternative to micro-sized reinforcements in high-performance composites (Lee et al. 2014a; Norrrahim et al. 2018; Yasim-Anuar et al. 2019). Numerous studies have demonstrated the reinforcement of phenol-formaldehyde composites by NFC shown a great improvement on the properties. The application of NFC into the phenol formaldehyde matrix is usually benefited to increase the composite strength. This can reduce the dependency on petroleum-based phenol formaldehyde while simultaneously lowering overall formaldehyde concentrations (Atta-Obeng et al. 2013). Nakagaito and Yano (2004) discovered the impregnated of NFC from kraft fibre with phenolic resin to improve the mechanical performance of composites. It was proven that the presence of NFC in phenolic composites positively improved the mechanical strength.

3.1 NFC Attributes Affecting Polymer Composite Properties

Cellulose is indeed the stiffest and strongest component of the plant fibre which consists of a linear polymer of 1,4 β-glucan dioxide ($C_6H_{11}O_5$). A broad range of ranking parameters, like the plant/wood sources, cellulose volume fraction, fibril geometry, the degree of delignment, the removal effects of hemicellulose, cellulosic orientation, polymer matrices, porosity, or interfacial properties of the composites made should be considered to provide an understanding of the NFC's structure underlying relationship with the bio-polymer composites (Jonoobi et al. 2015). There are many established studies indicating the systemic rise of the modulus of elasticity as determined by the cellulose content, likewise fibre-reinforced composites tensile strength's depends on their fibre content, but there are other factors that are significantly influence that properties, notably their fibre-matrix adhesion (Leitner et al. 2007).

As mentioned above, the origin of cellulosic fibres determines the morphology of the produced NFC, owing to the nature of the individual plant cell wall (e.g. primary or secondary). Its size depends on several factors including the cellulose source, the exact conditions of hydrolysis and the ionic strength (Spence et al. 2010). Indeed, its dimensions are usually based not just on the concentration, reaction temperature, type and time of treatment, but it is also dependent on the various plant source of cellulose. It has been recorded that each varied sources of cellulose had varied geometrical characteristics of: length (L), cross section (D), and aspect ratio (L/d) (Kalia et al. 2011). Hence, these attributes affect the NFC thermal and mechanical properties, that will be discussed in the later section (Gan et al. 2020).

There are various sources of plant fibres which can be mainly categorized into 6 types: leaf, bast, straw, grass, seed, and wood (Ramamoorthy et al. 2015). Lignocellulose (cellulose, hemicellulose and lignin) is the main chemical components of plant fibres and the amount of these components varies between the sources, age and type of the plant. Cotton fibre, for example, has the highest cellulose volume and coir fibre has the lowest lignin content. Therefore, NC materials from different native sources may exhibit varying ability in improving the mechanical strength of a bio-composite (Le Bras et al. 2015).

Furthermore, the cellulose orientation of NFC, comprising of anisotropic cellulose fibrils in longitudinal direction, demonstrated greater elastic modulus when compared to CNC, due to the retained cellulose scaffold within the composites. Meanwhile, cellulose volume fraction is one of the key factors in determining the cellulose orientation (Frey et al. 2018). Therefore, although the mechanical characteristics of sheets of homogenised NFC are lacking a desired orientation, they are clearly superior to Kraft's paper in both tensile strength modulus and elasticity properties. This discrepancy is believed to be due to the fact that individual nanofibrils are more resistant and rigid and NFC are closer intertwined by nature. A potential explanation for the observed improvement in mechanical properties is the isolation in fibril bundles or individual fibrils from the cell wall network. The hydrogen bonds would be more readily bound to the cellulose fibrils during solvent evaporation when it is in a suspension rather than when it is still intact in the primary cell wall network that is prior to the homogenisation process. The former forms an interconnected network that produce NFC with high strength and elastic modulus (Leitner et al. 2007). For example, bast fibres such as jute, hemp and kenaf when compared to other fibre types due to higher degree of polymerization in the bast fibres (Ramamoorthy et al. 2015).

The humidity in cellulosic substances, especially paper, has been shown to affect tensile properties. Generally, the greater the cellulose's crystallinity, the lower the moisture level (Panchal et al. 2019). Water vapor transmission rate (WVTR) of the NFC cast films, for example, is lower when compared to the hand sheets provided by the unprocessed pulp as the bond network has a considerable effect on barrier properties (Kalia et al. 2011). A high moisture content in a bio-composite is anticipated to lead to significantly less strength because of the increased in the hydrogen binding effects of water (Haslach 2009).

For instance, Kasmani and Samariha (2019) reported that by reducing the moisture content in the mechanical pulping from 4 to 8% of NFC for newspaper production, a significant increase in the tensile strength, burst strength, air resistance, brightness and whiteness of the paper were observed. Meanwhile the tear strength, roughness and opacity had declined due to the efficient and optimum moisture of cationic starch adsorption within the fibre network. These cation charges bind with anion surfaces thus decreasing inter-fibre gaps through hydrogen bonding resulting to elevated strength and air permeability. It was also noted that NFC has higher dielectric property in contrast to algae cellulose of *Cladophora* due to the high porosity of *Cladophora* cellulose that resulted in air entanglement, which then increased its dielectric loss. *Cladophora* was more crystalline with low-and moderate-sorption power compared to NFC. The higher the crystallinity degree, the lower the water is absorbed and that is evidenced by the X-ray diffraction (XRD) analysis of *Cladophora*, resolved at the narrow peaks of 14 and 16° (Le Bras et al. 2015). It is worth pointing out that NFC do have excellent dielectric properties that can be used for electrical insulation purposes, such as in cable insulation, but the effectiveness of this property, again depends by the source of the NFC and its morphological features (Gaspar et al. 2014).

3.2 NFC-Reinforced Biophenolic Composite Processing Technique

Processing techniques have quite a major influence on the final properties of the composites. It was shown that the adhesion and dispersion of NFC and polymer matrix are important in order to obtain good mechanical properties of composites. Generally, three ways are used to prepare the NFC composites as shown in Table 1. Composites of NFC are usually prepared through solvent casting technique. This method requires mixing and drying process. Even though this technique is the most successful technique on producing homogenous mixture of NFC in composites, it is less suitable to be used in large scale production of NFC composite. Research on NFC composites production from cellulose often used this technique to mix with polyurethane (Seydibeyoğlu and Oksman 2008). Atta-Obeng et al. (2013), for example, had prepared the micro crystalline cellulose (MCC)-reinforced phenol formaldehyde composites. It was produced by mechanically mixing MCC with the aqueous phenol formaldehyde at room temperature for 10 min. However, the particulate nature of MCC at loadings was found to be greater than 10% and yielded a viscosity that would not be practical during industrial application.

In situ enzymatic polymerization of phenol is another approach used to manufacture composites with TEMPO-oxidized NFC (Li et al. 2010). In this technique, phenol was polymerized using horseradish peroxidase in the presence of TEMPO oxidized NFC. The composite was found to be insoluble in organic solvents, although the individual components were soluble. This finding is considered an remarkable

Table 1 Production methods of NFC composites

Method	Findings	References
Solvent casting	-Most common technique applied. -Less suitable to be used in large scale production of composites.	(Chang et al. 2012; Seydibeyoğlu and Oksman 2008)
Melt blending	-Most interesting technique in industrial processing of composites. -Final product can be easily shaped by blow molding or compression molding. -Some challenges when using NFC in extrusion processes due to aggregation.	(Herrera 2015; Norrrahim et al. 2013; Oksman et al. 2003; Norrrahim et al. 2018)
Film stacking	-Main technique for the construction of fiber-reinforced polymers. -High volume production ability and short cycle times. -Need to consider the maximum pressure before the damage of the fibers and the structure.	(Raquez et al. 2013)

enhancement in the manufacture of the NFC-reinforced biophenolic composites, without the intensive processing usually required for the dispersion of the NC.

Besides, there are several other approaches as shown in Table 1 such as melt blending and film stacking can be used to prepare NFC-phenol composites. However, to the best of our knowledge, there is still lack of reports on the fabrication of NFC-biophenolic composites prepared by these approaches. Composites production research usually revolves around solvent casting method, but melt-blending method has gained interest especially in large scale industrial manufacturing since the final product can be easily shaped by compression moulding (Herrera et al. 2015).

Injection moulding is also can be considered to prepare the NFC-phenol composites method used to produce composites with complex shapes and excellent, surface smoothness. This method is suitable to be used for polymer granules or mixtures of polymer granules with reinforcements, which will be heated within a metallic barrel (Hemanth et al. 2015). For composites, injection moulding was applied after the reinforcements was incorporated in the polymer matrix by other compounding methods, typically extrusion and internal melt blending (Kargarzadeh et al. 2017; Mahmood et al. 2017). The main role of injection moulding is to mould the final shape of the composites. Similar like injection moulding, a compression moulding was also applied after polymers and reinforcements were compounded by other methods. This method involves the use of stationary and movable moulds to produce composites with desirable shape. Composites is placed between the moulds, then selected heat and pressure are applied to obtain desired shaped composites.

3.3 Mechanical Properties of NFC-Reinforced Biophenolic Composite

Paper-based laminates are laminated sheets of resin-impregnated paper into solid plates. As discussed earlier,' Papreg' is among the first phenolic resin-impregnated paper-based laminate that has produced with an remarkably high tensile strength (Stamm 1956). Another biophenolic cellulose-based composite with high strength was fabricated back in 2005 which having nano-order-unit web-like structure. The production was done by immersing different types of kraft pulp cellulose species (Lodgepole Pine (*Pinus contorta*): 50%; White Spruce (*Pinus glauca*): 40%; and Douglas Fir (*Pinusmenziesii*): 10% mixture of dry mat into phenol-formaldehyde resin. The Young modulus (E) and bending strength (σ_b) of phenolic resin binder composites has been found to achieve values of up to 19 GPa (145 g/cm) and 370 MPa (280 g/cm^2), respectively, which was an exceptional mechanical features for such fibre composites (Nakagaito and Yano 2005).

Phenol-formaldehyde-modified cellulose polymers are considered as thermoset which are relatively less hydrophilic thus less problematic. Commonly, the process of Resin Transfer Moulding (RTM) is used to impregnate phenol-formaldehyde as it is low in viscosity thus the wetting of the fibres will be more suitable and easier to handle (Kalia et al. 2008). Nakagaito and Yano (2008) showed that the nanocomposite mechanical properties could be further increased if NFC first were treated with a base or when the NFC mat is made with freeze-drying instead of oven-drying methods. These findings were validated by measurements of the coefficient of thermal expansion (CTE) relative to the fibre content, indicating a high thermal expansion restriction rate below 60% (wt/wt) of fibre content. One of the essential properties of cellulose composites is the low CTE which observed at 10 ppm/K, indicating the successful strengthening of the composite.

NFC from sugar beet also possess an excellent reinforcement property when it is introduced into polyvinyl alcohol (PVA) and PF resin matrix. A composite with 10% resin contents of phenol-formaldehyde obtained the best mechanical efficiency with a tensile strength, elasticity modulus and break elongation of 127 Mpa, 9.5 GPa and 2.9%, respectively. The composite was consisted of water-soluble PVA, and phenol-formaldehyde with diluted aqueous suspensions of cellulose fibrils [cellulose content of around 0.5% (wt/wt)]. In order to achieve a homogenous fiber content, both amount of polymer added to cellulose suspension and the evaporation time was optimized. They discovered that treatment of the high-pressure homogenizer of sugar beet cellulose leads to nanofibril disruption of cell walls forming solid cellulose sheets after they are dried out. This study also shows that phenol-formaldehyde is able to provide more interfibrillar link to the NFC network, enhancing tensile strength (Leitner et al. 2007). Nakagaito and Yano (2008) also reported that, when compared to the original flax fiber, NFC composites of phenol-formaldehyde combined with flax-g-poly(MA) demonstrated improved mechanical properties with Modulus of Rupture (MOR), Modulus of Elasticity (MOE) and Stress at the Limit of Proportionality (SP) were at 112.8, 5248.,0 98.4 N/mm^2 respectively. Due to the high toxicity properties of formaldehyde, a suitable substitute would be preferred in the polymerization of biophenols. A unique treatment done by Li et al. (2010) via 2,2,6,6-tetramethylpiperidinyloxy radical (TEMPO) with oxidized NFC using horse radish peroxidase (HRP) enzyme was performed. They recorded higher thermal stability of the novel composite compared to biophenols alone. This research represents a major improvement in the development of nanocomposites without lengthy extensive treatment required for NC dispersion in the composites. Table 2 shows NFC based bio-phenolic composites from several plant origin and its mechanical properties.

4 Conclusion and Future Perspective

The development of high-performance engineering materials with sustainable or renewable features has received much attention to both academicians and industrialists. NFC from natural fibres are often regarded as ideal candidate reinforcement because of their low cost, low density, renewable resource origin and biodegradability. In NFC composites, the cellulosic fibres work as reinforcement by giving strength stiffness to the structure while the polymer deals with the adhesiveness and to hold the fibres in place so that suitable structural component can be made. It

Table 2 NFC of various plant origins for biophenol composite application

Origin of cellulose	Treatment	Process	Properties	References
Kraft pulp cellulose species Lodgepole Pine (*Pinus contorta*): 50%; White Spruce (*Pinus glauca*): 40%; and Douglas Fir (*Pinusmenziesii*): 10%	Dried mats were immersed in methanol-diluted PF resin while pulp mats were immersed in PF resin various concentrations at 20 °C for 96 hr.	Hot press	λ: 19 GPa σ_b: 370 MPa, with a density of 1.45 g/cm^2	(Nakagaito and Yano 2005)
Sugar beet pulp chips 0.5 % wt.	Diluted aqueous suspensions of cellulose fibrils were combined with water-soluble PVA and PF resin.	Hot press	λ: 127 MPa T: 9.5 GPa ε: 2.9 %	(Leitner et al. 2007)
Natural flax fibers (*Linum sitatissimum*)	Flax-g-poly(MA) added as reinforcing agent and PF as binding agent	Hot press	T: 235 N	(Kalia et al. 2008)
Lodgepole Pine (*Pinus contorta*): 50%; White Spruce (*Pinus glauca*): 40%; and Douglas-fir (*Pinus menziesii*): 10%.	Dried cellulose were immersed in methanol for 12 hr and subsequently immersed in PF / methanol solution with a solid content of 62 % wt. for 48 hr.	Hot press	λ: 16 GPa CTE: 10 ppm / K	(Nakagaito and Yano 2008)
Undried cellulose from wood pulp	Enzymatic polymerization of phenol using horse radish peroxidase (HRP)	TEMPO	Higher thermal stability, no solubility in organic solvents, and fracture on the surfaces formed with phenol polymerization into oxidized nanocelluloses were indicative of increased toughness in comparison polyphenol alone.	(Li et al. 2010)

*Where σ_b = Bending strength, T = Tensile strength, λ = Young's modulus, ε = Elongation at break, CTE: coefficient of thermal expansion also displays satisfactory thermal and dynamic properties and could be thus considered as an alternative to conventional buildings materials such as ceramic bricks, aggregates, partitioning materials, timber wood, and concrete. Apart from that, NFC reinforced bio-phenolic composites can be used in transportation, chemical equipment and machinery construction, electrical and electronics equipment, fishing rods and storage tanks. Plus, they can be exploited into various sport applications such as golf clubs and tennis rackets to jet ski, and also in aircraft, missile, spacecraft and marine components. Future studies should focus more on understanding the importance of nano-size reinforcement of NFC, of different sources and the varying effect of its distribution in a bio-phenolic composite.

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Natural Fibers Based Bio-phenolic Composites

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Abstract The increase in the demands of eco-friendly martial goes on increasing day by day, which results in shifts of researcher's interest in bio-phenolic based composites. Bio-phenolic resin comes out to be the most use thermoset resin which receives great attention in the past few decades. This book chapter provides a discussion on recent development in the bio-phenolic based resin and their composites. Starting from the history of phenolic resin back to its discovery (i.e. in 1907 by Baekeland providing synthesis process for industrialization) and shifting towards the bio-phenolic resin. Discussion on two important phenols i.e. novolaks and resoles also been done, including their synthesis process and effect of the molecular ratio of formaldehyde/phenol. Present work discusses about the major synthesis process mainly hydrothermal liquefaction and pyrolysis process for extraction of bio-oil from the biomass. Moreover, different separation techniques use to extract bio-phenol from bio-oil also been discussed. An important source of biomass used to extract bio-phenol is also stated and the major sources found by the different researchers are seed, wood, fiber shell, bagasse, empty fruit bunches, cashew nut shell liquid, palm oil, and coconut shell tar waste. After that, some of the important characterization techniques used to characterize the bio-phenolic resin are also discussed.

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M. Jawaid and M. Asim (eds.), *Phenolic Polymers Based Composite Materials*, Composites Science and Technology,
https://doi.org/10.1007/978-981-15-8932-4_10

Keywords Natural fibers · Bio-phenolic resin · Composites · Polymers · Biodegradable materials · Mechanical characterization

1 Introduction

In today's world, there is an increasing demand for component materials that are durable, reliable, lightweight, and with mechanical properties that are significantly better than those of the traditional materials. Various new materials were continuously developed through the stage of the twentieth century and composites have identified as one of the materials, which revolutionized the concept of high strength and thermal stability. Composite can be defined as synergetic amalgamation of two or more different materials which results in a product with superior properties than its parental components. Bones, wood, muscle, tissue, teeth, etc. are common examples of composites that are found in nature. The major categorization of composite material is related to the matrix component are metal matrix composites, ceramic matrix composites, and polymer matrix composites. In the present work, the major focus is one on polymer matrix composite (PMC). If we further categories the PMC based on the polymer are biodegradable (Sanjay et al. 2018; Zhang et al. 2011; Sanjay et al. 2019a, b; Chhavi et al. 2017) and non-biodegradable polymer matrix composites. Green composites are a special class of bio-composites (Verma et al. 2019a, b, c) that catch the attention as an alternative solution to petroleum-derived materials which cause several environmental problems. The focus of the researchers from a couple of past decades shifted towards eco-friendly materials due to formaldehyde emissions, growing awareness of biodegradability, depleting petroleum resources, green chemistry, and manufacturing. Utilization of bio-based resin which may be derived from agro-waste fit into this category, however, 100% replacement cannot be achieved. In the case of green composites, both reinforcement and matrix are derived from natural renewable resources. Green composites (Deepmala et al. 2018) are named as green because of their sustainable and degradable properties so it can be simply decomposed without causing any harm to the environment. Nowadays different experiments and research are performed to enhance mechanical and other desirable properties of green composites so that their applications can be expanded. Furthermore, the polymer is also classified as thermoplastic and thermosetting depending upon their properties. Thermoplastic polymers are those which can reshape under high temperature and pressure while thermosetting cannot change their shape due to dense cross-linking bonds. In this chapter special types of biodegradable green polymer matrix composites (or we can say green composites) are been studied i.e. bio-phenolic composites reinforced with natural fibers. Biophenoic polymer comes under the thermosetting category. Phenolic resin-based composites have application in different fields such as adhesives, particleboard, molded product, insulators, coating, painting, etc. (Alma and Basturk 2006; Amen-Chen et al. 2002a, b; Wang et al. 2009). But to replace the phenolic resin with bio-phenolic become major challenges for the researchers and many attempts also done in this area. Non-petroleum product such as biomass becomes the major sources of bio-phenolic production. Palm oil, wood, coconut shell tar, tannin, etc. are the major potential source of biomass from which bio-phenolic resin can be derived.

This chapter covers detailed review of work carried out related to bio-phenolic based resin/composites, especially those polymer composites in which natural fibers used as reinforcement/fillers. It also included brief description of the history of phenol from discovery to the industry level. Two important classifications of phenol i.e. novolak and resole are also been discuss. Further synthesis bio-oil from the biomass through hydrothermal liquefaction and pyrolysis process is also stated. Then phenolic resin extraction processes from these bio-oils are also studied. Sources of biomass for phenolic compounds are also studied and some of the major sources are seed, wood, fiber shell, bagasse, empty fruit bunches, cashew nut shell liquid, palm oil, and coconut shell tar waste. Natural fiber, their properties with advantages and disadvantages and characterization techniques applied to characterize the bio-phenolic were also discussed in this chapter.

2 Phenolic Resin

2.1 History: Discovery to Industrialization

Phenolic resins have a history of past 100 years or more, tracing back to 1907 where the patent of production of phenolic resin was filed by Dr. Baekeland. His patent was “method of making insoluble products of phenol and formaldehyde” which describes the method for mass production of phenolic resin (Baekeland 1907) and named it Bakelite. Pressure and filler were used to eliminate foaming (Ostwald 1907). Whereas the discovery of this resin occurred in 1872 JFWA Baeyer while studying the dyes discovered the new colourless resin by reacting phenol and formaldehyde (Baeyer 1872). But was not able to crystalline it. Kleeberg in 1891 crystalline the colourless resin by cross-linked with hydrochloric acid but unable to characterize the solid material obtained after cross-linking. Another aspect is recycling the phenolic resin also increasing in today’s world concerning the growing environmental issue. Some have work on chemical recycling using water phenol solution at the supercritical or subcritical condition as the reactive solvent. Whereas mechanical recycling involves powder formation of bio-phenolic resin/composite through crushing and then used as filler material for other plastics fabrication. In thermal one bio-phenolic resin/composite is used as the fuel material to provide energy as having good calorific value in different industries. Other researchers were also looking for the application of phenolic resin in the field of preservation of wood, insulators, paint, cloth buttons, etc. But unable to develop the mass production technology for manufacturing in industries. On the other hand during the early 20th and late 19th-century electricity was introduce, which increased the demands of fabrication of good quality insulators. The current demand for during that time was fulfilled by the natural resin shellac produced in India but has limited supply. On the other end, Dr. Baekeland was performing number of the experiment to determine the potential of phenolic resin. Inflammable, inert nature to alkali & acid, insoluble and strong with lightweight were important properties of phenolic resin stated by him. And finally, the mass production synthesis process for phenolic resin for industrial production was discovered by Dr. Baekeland in 1907. Finding was reported in American chemical society meeting in 1909 (Knop et al. 1989). Parallel to phenolic discovery, the establishment of other industry i.e. plastic industry making their debut in the early twentieth century. In 1910 commercial production of phenolic resins mainly novolak and resoles were started. In Germany Bakelite Gesellschaft and in USA General Bakelite Company are the major production unit. The major ingredients of phenolic resin were phenols and formaldehyde.

Synthesis of phenolic resins involves several parameters like the molecular ratio of formaldehyde to phenol; catalyst nature (acidic, metal salt, basic); thermosetting/thermoplastic resin, etc. Two types of resins are formed when formaldehyde reacts with phenol that is novolaks (novolacs) and resoles (resols) (Bao et al. 1999; Kopf 2002). Synthesis of resole is done under basic condition having formaldehyde/phenol ratio >1 curable through heating. Synthesis of resole resins is fabricated when the formaldehyde/phenol ratio is between 3:1 to 1.2:1 at 80–90 °C (in an alkali solution having a pH of 9–12). The most commonly used alkalis are NaOH, $Ca(OH)_2$ and $Ba(OH)_2$. The fabrication process involves two steps: the first step involves the addition reaction in which formaldehyde is added on phenolate anions results in the formation of hydroxyl methylated phenols. Formaldehyde, when dissolved in water results in composed of methylene glycol telomers, is CH_2O. Phenol under alkali medium results in the formation of phenoxide anion having three resonance structures (obtain when negative charge delocalize to para and ortho position). This phenoxide anion vulnerable to electrophilic aromatic substitution to form mono, di and tri methylolated phenols with methylene glycol under alkali medium; the second step is condensation reaction which results in chain growth and cross-linking. Condensation occurs through quinine methide intermediates (Jones 1946; Haider et al. 2000) which is reactive and unstable substance. It immediately reacts with phenoxide anions result in the formation of dimethlene ether of methylene bridges. Further in dimethylene ether bridges converted into methylene bridges i.e. more satiable by eliminating formaldehyde (Kim et al. 1996). Whereas for novolaks formaldehyde/phenol ratio < 1 under the acidic condition with cross-linking agents (Wendler and Frazier 1996).

Phenol which is one of the raw material for the manufacturing of phenolic resin synthesize from the cumene process over benzene drive from petroleum (Emmanuel 2011). This is one of the drawbacks of the phenolic resin as petroleum products are non-renewable sources and have environmental issues. Therefore research has been shifted towards bio-phenolic resin i.e. use of bio-phenol. Biomass can be one of the alternative or production phenols (Connor and Piskorz 1994). Important advantages of biomass over petroleum are renewable and eco-friendly nature. Moreover, atmosphere carbon balance is also maintained as green plants are the source of biomass that use carbon from the atmosphere and return back after burning. A major prominent source of biomass is agriculture waste, animal wastes, crops, etc. (Demirbas 2004).

Bio-oil extracted from biomass contain phenolic compounds chiefly singly phenolic ring with alcohol, carboxylic acid or aldehyde, and some oligomeric polyphenols. Mainly obtain from the decomposition of lignin constitute 18–40% mass of dry wood (Amen-Chen et al. 2001). Guaiacols are yield as a by-product after softwood lignin pyrolysis, whereas, syringols and guaiacols are yields as a by-product after hardwood lignin pyrolysis. Syringol and guaiacols act as the precursors for phenol formation by cracking of methoxy group on the aromatic rings (Shen et al. 2010).

2.2 Production of Bio-oils from Biomass and Extraction of Bio-phenolic

Hydrothermal liquefaction (HTL) and pyrolysis are the two main synthesis processes to produce bio-oils from biomass. After manufacturing bio-oil different technology are been applied on bio-oil to separate bio-phenols. Out of these solvent extractions and molecular distillation are mostly used. This section will discuss out the two-synthesis process of bio-oils and some of the separation techniques.

(a) **Hydrothermal liquefaction (HTL)**: In this process, water is used as a solvent kept at high pressure and temperature to maintain water at supercritical state. The biomass produces liquid bio-oil when treated at moderate temperature (250–400 °C) and pressure (50–200 atmospheres) (Huber et al. 2006). At this high-pressure solvent get penetrated into the biomass structure result in fragmentation of biomass. The process involves cracking of long carbon chain thermally and simultaneously removal of oxygen through dehydration and decarboxylation. Figure 1 represents a block diagram for the extraction of bio-oil from wood. HTL produces bio-oil as the primary product and solid residue, soluble inorganic compounds and bio-char as secondary products. The advantages of the HTL process are low cost, use of a single reactor and simplicity as compared to pyrolysis. On the other hand, a large amount of char and a wide range of by-products make this process non-selective (Huber et al. 2006).

(b) **Pyrolysis**: In this process, mainly lignocellulosic derivatives thermally decomposed to produce bio-oil under oxygen-deficient environment. In today's era, pyrolysis is been considered as a prominent technology to transform biomass into bio-oils (Demirbas 2007). The most commonly used biomasses are bagasse, beechwood, straws, seedcase, municipal solid waste and woody biomass (Asadullah et al. 2007; Demiral and Sensoz 2008; Mohan et al. 2007; Aho et al. 2008; Karaosmanoglu and Tetik 1999; Jensen et al. 2001) (refer to Fig. 2 for the detailed process). This process is further classified into slow and fast depending upon the heating rate. Both are carried out in the inner atmosphere whereas another classification where hydrogen medium is used is hydro pyrolysis & water medium hydrous pyrolysis. The heating rate is further increased then it is termed as the last pyrolysis in which bio-oil production is higher as

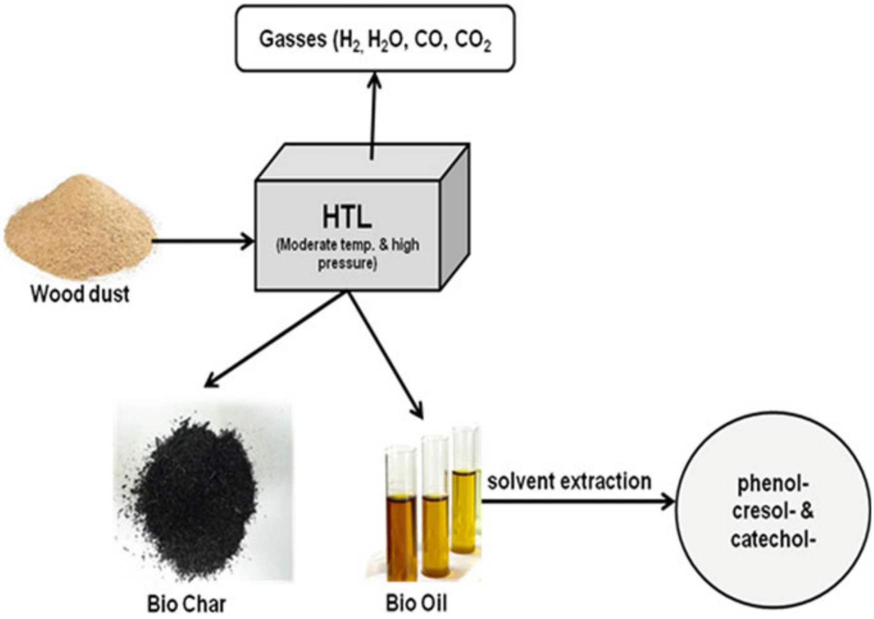

Fig. 1 Represent block diagram for extraction of bio-oil from wood through HTL

compared to the other two [about 75% (Demirbas 2000)]. Another classification is done on the basis of catalyst i.e. non-catalyst and catalyst pyrolysis.

(c) **Extraction of bio-phenol from bio-oil**: After the production of bio-oil from HTL or pyrolysis phenols are been extracted through separation techniques. Guaiacol, syringol, cresols and other phenol products can be extracted from bio-oils. Some of the important techniques are distillation, solvent extraction, absorption, pervaporation and column chromatography. In solvent extraction, the products of pyrolysis or HTL are dissolved into the solvent (solvent are selected on the bases of the target product). Most commonly solvents are alcohols, water, dichloromethane, alkaline, toluene, ketones, etc. Now a day's switchable hydrophilicity solvents (Solvent with completely absorb water in the presence of CO_2 and vice-versa) (Jessop et al. 2011) and supercritical CO_2 (Patel et al. 2011) are the major areas of studies. In solvent extraction, supercritical fluid extraction (SFE) (Reverchon and De Marco 2006) comes out to be the most attractive method. Column chromatography (Zeng et al. 2011) separates bio-phenol by employing aluminium oxide and silica gel as a stationary phase. On the other end depending upon the polarity of the bio-oils selection of the mobile phase is done. The separation occurs on the basis of absorption capabilities o the bio-oils components onto the stationary phase. In the distillation process (Czernik and Bridgewater 2004) separation of the bio-oil component occurs on the basis of different volatilities. Components of bio-oil can be separated by

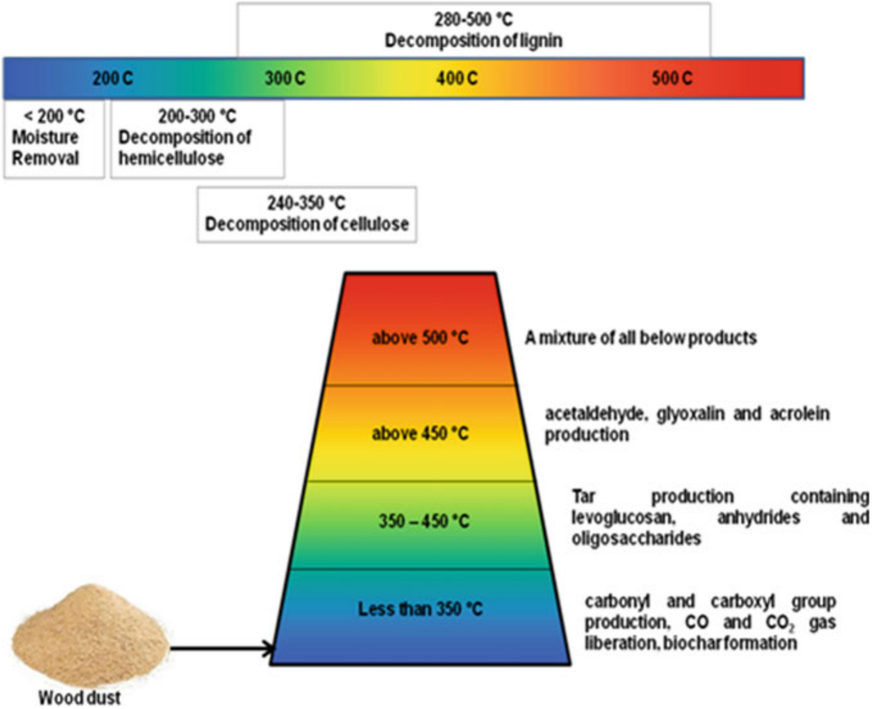

Fig. 2 Represent flow diagram of pyrolysis of wood dust

employing a vacuum, steam, atmospheric pressure, and molecular distillation techniques. Out of these molecular distillations getting more interest.

2.3 *Resources for Bio-phenol*

Now a day's replacement of petroleum-based phenols is been replaced with bio-phenols to maintain the balance. Environment issue, greenhouse gasses, increasing-price of petroleum come out to be a major reason for shifting the interest towards biodegradable phenolic resins. The major raw materials for the bio-phenolic resin is phenol which should to biodegradable. The major source of bio-phenol comes from agro-waste, industrial waste, and plants. Natural phenol may be extracted from lignin, nutshell liquid, palm oil tannin, coconut shell tar or by agriculture waste such as bagasse and wheat straw. Previously agriculture waste was only utilized as fertilizer only; but from the past decade, it was found that seed, wood, fiber shell, bagasse, and empty fruit bunches were rich in phenols derivatives (Md Kawser and Farid Nasir 2000; Kozlowska et al. 1983; De Marino et al. 2007; ZahradNíkOVá et al. 2008; Wasserman and Dawson 1945; Leal et al. 1994). Major phenols derivative which may be obtained from these compounds are guaiacols, catechol, cresol, eugenol, etc. These phenols obtained from natural resources may be utilized to synthesis the different polymeric (polyurethane, epoxy resins, polycarbonates, etc.) based composites.

Cashew nut shell liquid (CNSL) obtained from cashew nut is a viscous reddish-brown liquid having honeycomb structure having alkyl phenolic compounds where benzene ring is substituted with long unsaturated alkyl side-chains (Gallezot 2012; Lichtenthaler and Peters 2004). CNSL is an agro-industrial waste having a mixture of phenols and after separation process cardol, anacardic acid, cardanol, 2-methylcardol (Calò et al. 2007) are obtained with some unidentified polymers. Out of this cardol and cardanol have potential applications in the synthesis of bio-phenolic resin (Lomonaco et al. 2013; Kasemsiri et al. 2011; Besteti et al. 2014; Huang et al. 2012). Pyrolysis, solvent extraction, and supercritical CO_2 are major extraction process employed by different researchers. Another source is lignin which is an aromatic polymer found in the cell walls of secondary thickened cells. The main components of lignocellulosic biomass are lignin, cellulose, and hemicellulose in which 40% is lignin. Lignophenols extraction from lignin involves many processes such as pyrolysis, ultrasonic irradiation, thermo-chemical methods, the solid-state fermentation, etc. (Effendi et al. 2008; Bu et al. 2012). Another potential biomass for phenols is tannins present in different wood species across the southern hemisphere (Pizzi 2008). Researchers are also found that the source of novolac (Peña et al. 2010) and resole adhesive which have applications as wood adhesives (Ramires and Frollini 2012). Valoneic, hexahydroxydiphenoic, avogalonic and nonahydroxytriphenoic are obtained from the hydrolysis of tannins. Similar extraction processes are used as applied for other biomasses. Another potential source of bio-phenols is palm oil obtained from palm trees mainly cultivated in Southeast Asia. Mesocarp and kernel are the two types of oils from the palm tree. The agro-waste obtained from palm oil industries are rich in lignocellulosic material (Goh and Lee 2011; Sabiha-Hanim et al. 2011) having 20–30% lignin and 60–80% cellulose (Goh et al. 2012). Which makes is a good source of phenolic compounds. Major phenolic components obtained from the pyrolysis of palm oil are cresol, guaiacol, eugenol, cresol, and syringol. Coconut shell tar waste is also a major renewable biomass. It is obtained by the distillation of coconut shells and also the source of active carbon in plastics. It is tarry oil having an unpleasant odour with dark brown in colour. After distillation, the residue further treated and free carbon is filtered from the tar (Ikeda et al. 2002). Then it is used to polymerize and having major content of phenolic components (Lochab et al. 2014).

3 Natural Fibers

Now a day’s one o the important source of reinforcement for composites material comes out is natural fibers. Increasing demand for natural fibers may be addressed to sustainability development. Today’s problem of increasing environmental safety and biodegradability of composite products are coming out of the major challenges for the plastic industries. Therefore the concept of green composite in which both matrix and reinforcement material is completely biodegradable comes into play. In this chapter review of the bio-phenolic resin-based composite has been done which are reinforced with natural fiber. Therefore natural fiber becomes one of the raw materials for fabrication PE resin. Easy availability, abundance in nature and low processing cost are the major advantages of natural fibers as compared to synthetic fiber (Arpitha et al. 2017; Madhu et al. 2019). Furthermore, the extraction of natural fiber required less man-power and energy as compared to synthetic fibers. Moreover, the density of synthetic fiber such as glass fiber (about 2.4 g/cm^3) as compared to natural fibers (about 1.2–1.6 g/cm^3) results in lower weight composites. Natural occurring fibers come under three classifications namely: vegetable fibers which as composed of cellulose or lignocellulose; Animal fibers which as composed of protein; and Mineral fibers which as composed of minerals. The major source of fibers in vegetables are fruits, leaf, wood, stalk, seed, grasses, etc.; in animals are wool, hair, silk, etc.; and in minerals are asbestos, wollastonite, fibrous brucite, etc. (Aziz and Ansell 2004; Huda et al. 2006; Kicinska-Jakubowska et al. 2012). Major constituents of vegetable fibers are lignin, cellulose, pectin, hemicelluloses and other unwanted impurities (oil, wax, etc.) (Bledzki and Gassan 1999). Plant fiber has a complex chemical structure by nature. The chemical structure basically consists of micro-fibril crystalline cellulose bonded together by lignin or hemicelluloses. Out of the above constituent, major is cellulose which has 40–45% total weight plant fiber, made up of glucose units in the long chain. The mechanical properties of plant fiber (P-F) highly depend upon the content of cellulose. P-F obtained through woody and non-woody plants through many techniques such as mechanical exploitation, chemical treatment, or many combine process. Moreover, the crystallinity of cellulose also play an important role, higher crystalline cellulose has high stiffness (Reddy and Yang 2005). But their major limitation is hydrophilic in nature i.e. water absorption characteristics. But it plays an important role in the biodegradability of P-F. The presence of the hydroxyl group plays an important role in the hydrophilic nature of these fibers. Sometimes these fibers are also surface-treated to get rid of these impurities. Surface treatment also improves the interfacial bonding between fiber and matrix by increasing surface roughness (Liu et al. 2005; Mahjoub et al. 2014; Manimaran et al. 2017; Athith et al. 2018; Sanjay et al. 2019a, b). Natural fibers come under thermoplastics and show higher elongation percentage as compare to synthetic fibers. Bast and leave fibers in P-F show the lowest elongation as compared to the others. Natural fiber has applications in almost every field technology like aerospace, automobile, electronics, packaging, plastics industries, etc. In 2010, the total market of natural fiber composites reaches $2.1 billion with an annual growth of 15%.

4 Bio-phenolic Resin

Increasing environmental issues of hazardous plastic waste and their recycling issue draw the attention of industrialists and researchers toward green composites in which matrix and reinforcement both should be biodegradable. Therefore the attention of researchers is over bio-phenol and it derived bio-phenolic resin nowadays. As discussed earlier also that bio-phenolic resins are obtained by reaction between bio-phenol and formaldehyde, mostly condensation polymers were obtained. Acidic or basic catalysts such as oxalic acid, sulphuric acid, sodium hydroxide, etc. were used to initiate the synthesis process. Finally result in the formation of methylol which is water-soluble derivatives o resoles or novolac resin having high relative mass. Well known example PE resin obtained from cardanol and HCHO has been known from the nineteenth century. But due to low thermal stability and tensile strength (O'Connor and Blum 1987) get less importance. The replacement of some optimum percentage of phenol with cardanol is become essential to overcome the disadvantages of pure PF based resin and achieve specific properties. The presence of cardanol less than 15 wt% in the phenolic resin may result in an enhancement in chemical and mechanical properties such as tensile impact and flexural strength (Vemula et al. 2008). Hydroxymethyation between phenol and lignin in the presence of alkali and formaldehyde results in the formation of lignin phenolic formaldehyde (LPF) copolymer (Alonso et al. 2011; Ibrahim et al. 2011). There may be about 50% replacement of phenol with lignin due to less thermal stability of LP resin. In some studies phenol obtain from kraft pine, anthraquinone/soda flax, and sulfonated SL) were also replaced with lignin to form lignin novolac phenolic resin (Tejado et al. 2007). Similar properties of a lignophenolic thermoset may be obtained as that of a phenolic thermoset. Such as the behavior of bio-composite fabricated from lignophenol extracted from sugarcane bagasse is similar to that of phenol resin (Faulstich de Paiva and Frollini 2006). Lignophenolic resin reinforced with sisal fiber also has good adhesive properties. Oil palm EFB based bio-phenol has higher bonding strength as compared to phenolic formaldehyde resin and has lower kinematic viscosity over 21 days storage time (Ibrahim et al. 2007). This resin can replace commercial phenol (1:1) resin. The bio-phenolic resin obtained from coconut shell tar has 240% higher lap shear strength as compare to phenolic formaldehyde resin (Manjula et al. 1985). These works can confirm that bio-phenol based resin can able to replace the petroleum-based phenolic resin without any compromising the properties. Good adhesive properties of Lignophenolic resin can be attributed to higher hydroxyl to methoxy group ratio (Zhang et al. 2013; El Mansouri and Salvadó 2006) and lower molecular weight of resin which seeps easily into the pores of the binding substrate to form better cross-linked channels. To facilitate the reaction of phenol with formaldehyde, the presence of phenolic rings having large no of free aromatic positions and activating the hydroxyl group to facilitate the electrophilic attraction. Therefore condensed tannins are more preferred as compared to hydrolyzable tannins in the synthesis of bio-phenol.

5 Characterization of Bio-phenolic Resin/composites

In the development of composite materials starting from selection/designing of resin to its final application stage characterization techniques play an important role in each stage. The process of development of bio-phenolic resin/composites involves analyzing of bio-phenolic resin by molecular dynamic simulation. The chemical structure of phenolic resin has a 3-D crosslink of phenols through methylene bonds. To get the optimum mechanical properties relationship between its structures is required with mechanical properties. But on the other hand, bio-phenolic thermoset has a complex structure and their higher-order structure is not fully understood which a new prominent area of research is also. To study the molecular dynamic of resin computer simulation should be more effective. We can analyze/developed the stress–strain behavior of the main chain and predict the response of the chain. But still, no such strong methodology is developed for accurately modelling of thermoset chain. In present scenario modelling of the 3-D phenolic structure by varying cross-linked degree and study their effect of mechanical properties can be evaluated. After curing the hardened material it may be analyzed with the X-ray technique. In X-rays, small-angle X-rays scattering (SAXS) and wide-angle X-rays scattering (WAXD) may play an important role. These techniques will give some information on the structure by calculating the electron density distribution of atoms. SEM morphology and simple X-ray only provide the picture of the void, filler distribution and phase separation of the cross-section. But there are no such studies on the superstructure of phenolic resin. Another important technique to determine the cross-linking structure of bio-phenolic resin/composites by studying the methylene bond (Abdellaoui et al. 2015; Kozlowski and Wladyka-Przybylak 2008). In this technique, the sample is placed into a magnetic field and the detail of the electronic structure of that molecule and its functional group will be known. PF resin phenol makes N-methylene bridge, which can be represented by peaks: at 30–45 ppm represent methylene bridge and at 45–70 represent intermediate structure. Dynamic mechanical analysis is another material characterization technique that may be used to determine the glass transition technique of the biodegradable polymeric composites. In this technique modulus (both storage and loss) of the material is being calculated at various temperatures and temperature at modulus suddenly starts decreasing are known as glass transient temperature (Jain et al. 2018, 2019) (change its stage from solid to viscous fluid). Moreover, the crystallinity of lamina can also be measure from the shift in the glass transient temperature (T_g). With an increase in crystallinity T_g shift towards higher temperature range and vice versa. The study of cross-linking bonds can be done through Fourier-transform infrared spectroscopy (FTIR). Cross-linking bonds & the presence of the functional group can be examined by this type of technique through the study of absorption/transmittance peaks at different wavelengths. There are also other mechanical characterization techniques used to determine the failure behavior of bio-phenolic resin/composites such as tensile, impact, flexural, creep and torsion tests. These tests are sometimes also used to generate the mathematical model between mechanical properties and composition of composites. Thermo-gravimetric analysis and DSC are other important tools for the thermal characterization of biomaterials and composites (Verma and Singh 2016, 2019; Verma et al. 2016, 2017, 2018a, b, c, 2019a, b, c, 2020a, b).

Acknowledgements Monetary support from the All India Council for Technical Education (AICTE) and Department of Science and Technology (DST), India is gratefully acknowledged.

Conflicts of Interest There are no conflicts of interest to declare

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Physical, Mechanical, Thermal Properties of Bio-phenolic Based Composites

Tamil Moli Loganathan, Ibrahim Burhan, Saifuddin Kumar Bin Abdullah, Mohamed Thariq Hameed Sultan, Salvinder Singh A/L Karam Singh, and Umaradli Amran

Abstract Phenolic, a thermoset polymer are among the most adaptive materials utilized by hundreds of industries. Phenol reacts with formaldehyde under either acidic or basic (alkali) conditions for formation structure of novolac and resol phenolic resin. Bio-phenolic or known as modified phenolic was introduced due to formaldehyde was assessed carcinogen with genotoxicity; harmful for respiratory system. This review article is intended to present an overview on the phenolic, types and chemical structure and extraction of phenolic resin from CSNL. In addition, flammability, fire retardancy, phenolic resin, physical, mechanical and thermal properties of bio-phenolic composites especially natural fibers reinforced phenolic

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M. Jawaid and M. Asim (eds.), *Phenolic Polymers Based Composite Materials*, Composites Science and Technology,
https://doi.org/10.1007/978-981-15-8932-4_11

composites were discussed. When natural fibers reinforced with phenolic resin the polar structure of lignin in the natural fiber will provide better fire resistance properties of the composites. Moreover, natural fiber which is hydrophilic, will improve the compatibility of it physical properties with hydroxyl groups presented in phenolic resin. In addition, this work is also support the ongoing research on bio-phenolic composites and phenolic bio-composites in order to development of green sustainable products.

Keywords Bio-phenolic · Cashew nut shell liquid (CSNL) · Flammability · Physical · Mechanical · Thermal properties

1 Introduction

Phenolic resins continue to be the versatile system of resins, featuring either a stables, thermoplastic composition of novolac, which cures either in thermal, acidic or special basic conditions with additional source of hardener such as hexamine, or resole which composed of higher formaldehyde to phenol (F/P) molar ratio. Phenolic resin is produced in tremendous amount worldwide with its volume exceeding 5 million metric tons per annum (Pilato 2010). It remain as one of the predominant bonding agents which is used in various applications, for examples, bonding of wood, metals, glasses, and paper. It also surpass most of other polymer resins in term of cost-effectiveness.

Most phenolic resins are produced via condensation reaction between phenol and formaldehyde. However, for certain applications, modifications of the resin may be done via substitution of phenol with substituted phenols (i.e. resorcinol, cresols, and cashew nutshell liquid (CNSL)), or replacement of formaldehyde with other aldehydes (i.e. furfural, gluteraldehyde, and glyoxyl). Selection of suitable polymerization parameters results in the optimum distribution of molecular weight and residual monomeric content which essential for maximum reaction efficiency. Most of phenolic resins are supplied in the form of unmodified and modified novolac and resole resin products, such as powders, lumps, flakes, pastilles, and water or solvent-based liquids.

Phenol and formaldehyde reaction in basic or acidic media, and at different mole ratio of formaldehyde to phenol would produce different types of phenolic resins as shown in Fig. 1. Heat-responsive resole phenolic resins are produced when basic medium, and greater or equimolar ratio of formaldehyde to phenol are used. On the other hand, a novolac resins are produced via polymerization in acidic medium with the used of less than equimolar of formaldehyde to phenol ratio. Several natural products such as lignin, tannin, CNSL and starch have been used to partially substituted phenol. Furfural, furfural alcohol and soy were used to replace the solvent, whereas linseed oil and tung oil were utilized as modifiers. Table 1 demonstrated the raw materials and their roles of substitution in phenolic resin formulation.

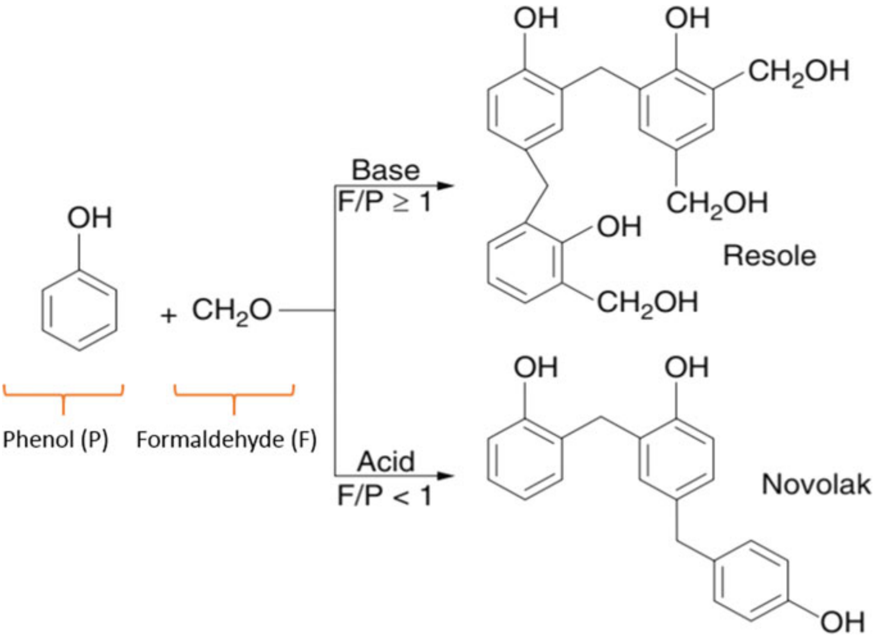

Fig. 1 Basic chemistry of structure of resole and novolac formation from Phenol Formaldehyde (Pilato 2010)

Table 1 Role of natural products in phenolic resins preparation (Pilato 2010)

Raw material	Source	Substitute of	Resole	Novolak
Lignin	Bagasse wood	Phenol	Adhesive, coatings	Co-react
Tannin	Argentina, Australia, Chile, and South Africa	Phenol	Adhesive	Co-react
Cashew	Brazil, China, India	Phenol	Adhesive	Friction
Starch	Cellulose	Phenol	Co-react	Co-react
Furfural, furfuryl alcohol	Oats, corn cobs	Solvent, reactant	Foundry	Abrasives
Tung oil, linseed oil	Plants	Modifier	Electrical laminates	Friction
Soy	Soy bean	Co-reactant and modifier	Adhesive	–

1.1 Why Bio-phenolic?

The World Health Organization (WHO) has classified formaldehyde as a carcinogenic material which possess genotoxicity. Vaporization of phenol is hazardous to the skin, eye, and respiratory and central nervous system. In addition, phenol prices are subjected to the fluctuation of crude oil prices and often on increasing trend especially when petroleum crisis occurs. Besides, the depletion of fossil sources has also increase the demand for petrochemical. Hence, there are efforts to replace petrochemical-based phenol and formaldehyde with renewable alternatives from bio-derived products to decrease the dependency on the non-renewable fossil sources. Cashew nut shell liquid (CNSL) is a sustainable bio-based product derived from the refinery of cashew nuts, it is used to partially or fully replace phenol component in the production of phenolic resins. Tannin is a naturally occurring phenolic resin produced by plants such as myrtle, wattle and pine, and it can be polymerized via crosslinking with formaldehyde and hexamine to become thermosetting resin (Lomonaco et al. 2017). Tannin is preferred due to its availability, fast curing, non-toxic, and cheap. Apart from tannin and cashew shell nut oil, substances such as soy, furfural, tung oil and linseed oil without corresponding adverse production performance are examined for economic savings. Phenol costs vary between USD 1100 and 1450 while CNSL costs about USD 200–300 per metric tons, depending on the processing and content added to it.

1.2 Cashew Nut Shell Liquid (CNSL) Derived Phenolic Resins

The predominant phenolic derivatives available in CNSL are anacardic acid, cardanol and cardol (Balgude and Sabnis 2014; Paramashivappa et al. 2001; Sharma et al. 2020) as shown in Figs. 2 and 3. CNSL possessed phenolic nature and unsaturation on its side chain, offers reaction sites on its aromatic ring and also on the side chain. Hydroxyl group of CNSL reacts with active methylene such as formaldehyde or hexamine via addition polymerization at the side chain. There are only little publications on the preparation of phenolic resins derived from CNSL.

Similar with conventional phenolic resins, novolac and resole types CNSL-derived phenolic resins can be produced using acid and base catalysts, respectively. Figure 4 illustrates the preparation of novolac and resole types CNSL-based phenolic resins. It was reported that the addition of CNSL resulted in a decrease in tensile strength but an increase in impact strength (Venkatachalam et al. 2016). Novolac phenolic resins are thermoplastic resins that have molecular weight ranging from 500 to 5000, and glass transition temperature (T_g) of 45–70 °C (Knop and Pilato 2013). Novolac resin is used extensively in heated molding compounds because it offers heat resistance, meanwhile resole resin releases water vapor or/and gases when heated for curing, lead to formation of unwanted porosity or voids. Other researchers isolated

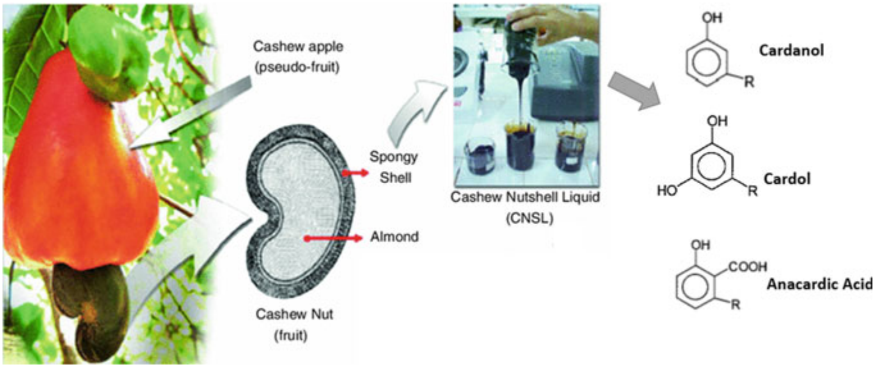

Fig. 2 Phenolic constituents extraction from CNSL adapted from (Balgude and Sabnis 2014)

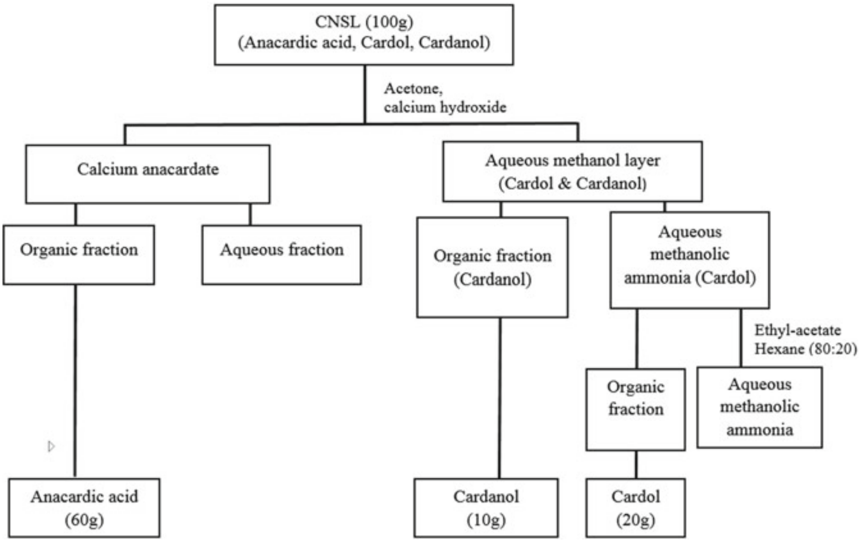

Fig. 3 Flowchart of preparation of CNSL-derived anacardic acid, cardol and cardanol

16 phenolic compounds from CNSL, and most of them possess strong antibacterial activity (Kanehashi et al. 2015). Cardanol isolated from CNSL can be prepared into cardanol-phenol–formaldehyde (CPF) resin by mixing cardanol with phenol before crosslinked with formaldehyde (Pola 2010). It was found that the increase in cardanol has led to the increased in fracture toughness and flexural strength, but decreased in the flexural modulus of the cured resins (Cardona and bin Hamid Sultan 2016).

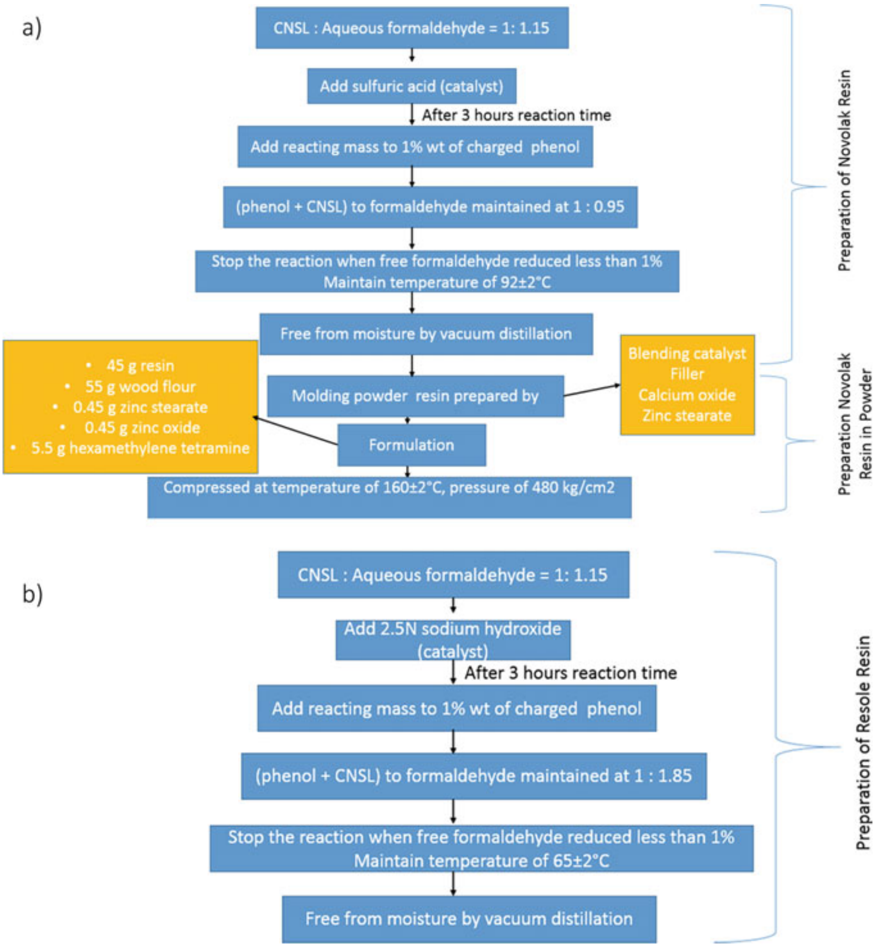

Fig. 4 Flowchart of preparation of **a** novolac and **b** resole resins from CNSL

2 Phenolic Resins in Aircraft Application

One of the main features of thermosetting phenolic resin is its capacity to resist mechanical deformation at high temperature. Cured phenolic resin provides rigidity that maintain dimensional stability and structural integrity, even under severe conditions. Therefore, phenolic resin could cater the demands for foundry, frictional, refractory and aerospace industries which involve in high temperature environments.

Due to its inherently low inflammability and relatively low generation of smoke, phenolic resin is widely used in manufacturing of mass transit, mining, and tunnel construction sectors (Knop and Pilato 2013). Limiting oxygen index (LOI) of phenolic resin was found to be around 25, hence it is regarded as a “slow burning”. This makes phenolic resin to be suitable for structural applications, although it might produce high amount of smoke when burning. However, phenolic resins have some limitations which include low toughness and generation moisture via condensation polymerization.

A fire resistance ranking presented in number of studies and reviews, concluded that phenolic > polyimide > epoxy > polyester and vinylester (Horrocks and Kandola 2005). Char formation is key to low flame retardance and good fire performance. Char ‘locks’ the available carbon, less smoke may form, and if it is formed, the char will act as a barrier to their release. Water only releases at over 400 °C in case of highly crosslinked material and decomposition begins at above 500 °C. This is why phenolic resin should be examined by differential thermal analysis (DTA). The amount of char will depend on phenol structure, initial linkage structures and a tendency to crosslinking during decomposition and methane, acetone, carbon monoxide, propanol and propane are the major decomposition of phenolics (Heath 2017).

In comparison with other potential matrix materials, phenolic-based synthetic composites provide a good fire performance at a reasonable cost. The inherent and distinctive characteristics of phenolic resins rather than other polymeric matrices are, low flammable, low smoke, low flame propagation, high ignition delay, low heat release and high oxygen index (Wang et al. 2018). However, its brittleness has significantly limited its application. Higher shrinking during curing, high fragmentary behavior and surface cracking are the major drawbacks for phenolic thermoset (Sreekala et al. 2000). In order to meet the fire performances of composite panels for interior aircraft, three flammability criteria have been required by the Federative Aviation Regulations, including vertical burn results, heat release and smoke density measurement.

3 Natural Fibers Reinforced Phenolic Composites

In a natural fiber reinforced phenolic composite, high polarity phenolic resin forms very strong hydrogen bonds between the hydroxyls groups, meanwhile, strong van der Waals and dipole—dipole forces develop and cause chemical reactions between resin and fiber to occur. Polar structure of lignin in natural fiber could react with phenolic resin and increase thermal resistance of the composites. Moreover, that natural fiber which is hydrophilic, will improve the compatibility of it physical properties with the phenolic resin. The hydrophilic nature of natural fiber is one of the major constraints in natural fiber reinforced composites, especially when incorporation with hydrophobic matrix materials. Therefore, poorly compatible between interfaces of fiber-matrix will eventually reduce the final performance of composites (Shaha et al. 2011). Many researchers have developed treatments to alter the topography of fiber surface which then improve the compatibility, interlocking and adhesion between the matrix and fiber. However, when natural fibers are reinforced with phenolic resin, hydroxyl groups present in resin are bonded to the hydroxyl groups available in the natural fibers promoted to forming a very strong hydrogen bonds by development dipole–dipole and van der Waals force (Abdullah et al. 2019). This formation of bonding significantly reduced the moisture content by fact that water molecules (H_2O) will bonded with the accessible hydroxyl groups on the surface of the fiber, by reducing the availability to the matrix. Subsequently, produced voids in the composite when the water is evaporates. Therefore, it necessary to dry the fiber at suitable temperature based on evaporation on water molecules in TGA result, to avoid this consequence. The advantages of using phenolic as a natural fiber matrix reinforcement are their processing temperature and production process. The phenolic resin powder is processed by temperatures of approximately 150 °C, but hemicellulose, cellulose and lignin deterioration starts with over 180 °C. However, in natural fiber reinforced thermoplastic-matrices composites, the thermal stability of the fibers often limits the maximum processing temperature to 180 °C, which then limits the choice of thermoplastic polymers.

Flammability is a key parameter, which usually limits the application of a composite, especially for natural fiber-based composites. In practical applications, one of the main issue surrounding the natural fiber reinforced composites is it susceptibility to heat and flame damages. Thus, information on the thermal decomposition and fire properties of the natural fibers, matrix polymers, and the final composite products is need to be known for selection of materials before being used in any application (Kim et al. 2018). Furthermore, appropriate flame retardants have proven to improve their thermal stability and fire resistance effectively. Although natural fibers have diverse advantages, their low fire resistance represents a critical restriction for natural fiber reinforced composites in engineering applications. In particular, the presence of celluloses in plant fibers and hydrocarbon in polymers is highly inflammable, influencing the properties of composite flammability. It is a challenge to keep a balance between the physical and mechanical properties with the fire performance of the composites. Not long ago, the fire properties of natural fiber reinforced composite have been less focused compared to the physical and mechanical properties, but recently they have received deserved attention (Lee et al. 2014).

Cellulose, hemicellulose, lignin, and pectin and waxes are the major components of plant fibers, with traces of secondary and inorganic metabolites (Kim et al. 2018). Kozlowski et al. reported that lignin-rich fibers like hemp and flax, exhibited lower releases of heat than leaf fibers, such as abaca and cabuya (Kozłowski and Władyka-Przybylak 2008). In addition, Barbosa et al. (2010) found that high lignin content (48%) in coir fiber has provides high concentration of aromatic ring which increases fiber compatibility with phenolic matrix. Recent studies have shown that impurities or chemical substances of the fiber surface can also affect the inflammability of the fibers. High production of carbonaceous char during thermal decomposition of the composites can be caused by high crystallinity of fiber and highly oriented fibrils, which also increases inflammability. The use of natural fibers as reinforcement in phenolic composites overcomes brittleness and enhances mechanical properties and dimensional stability of the composites.

Natural fibers have been extensively used as reinforcements or fillers in polymer-matrix composites. Researchers and manufacturers are attracted to the natural fibers availability, low cost, processing flexibility, and high specific stiffness. There are two categories of plants that produced the natural fibers, i.e. primary and secondary. Primary plants are plants that are planted to produce the fibers, meanwhile secondary plants produced the natural fiber as by-products. Examples of primary plants are hemp, jute, kenaf, and sisal. On the other hand, coconut, coir, oil palm, and pineapple are examples of secondary plants.

Sreekala et al. produced oil palm fiber reinforced phenol formaldehyde (PF) composites (Sreekala et al. 2004). They studied the thermal and mechanical properties, and biodegradation of the composites. It was found that the mechanical properties of the composites decreased upon thermal ageing. Greater decrement of mechanical properties showed by composite samples that was subjected to radiation ageing. However, mechanical strength of composites which treated with alkali, acetylation, acrylonitrile grafting, silane, isocyanate, and permanganate had increased when immersed in water.

Agarwal et al. studied the effects of different treatments on the thermal behavior of oil palm empty fruit bunch (EFB) fibers (Agarwal et al. 2000). They investigated the stress relaxation behavior of EFB fiber reinforced PF composites, and hybrid composites reinforced by EFB and glass fibers. Effects of fiber loading, physical ageing, treatment of fiber and level of strain on the stress relaxation behavior were determined. The rate of relaxation of the composites showed at different time intervals was computed to explain gradual changes in relaxation mechanisms. Treatment on the lignocellulosic fibers had led to formation of lignin-cellulose complex that improve thermal stability of the fibers.

Grass fiber reinforced PF composites were studied by researchers (De et al. 2007). The grass fiber was subjected to water leaching, and alkali treatment at different concentrations of sodium hydroxide (NaOH). Alkali treated fiber showed lower water absorption and swelling compared to water leached fiber. Alkali treated fibers also produced composites with higher tensile and flexural strengths. Alkali treatment imparted stronger bonding between grass fiber and PF. Thermal stability of alkali treated fiber composites were also higher than the water leached fiber composites. Morphological analysis of the composite samples fractured surface revealed lesser fiber pull-out showed by alkali treated fiber PF composites in comparison to water leached fiber composites.

Joseph et al. carried out a comparative study on mechanical properties of PF composites reinforced with glass and banana fibers (Joseph et al. 2002). Different fiber length and loading were used to produce the composites. The density of glass reinforced composite was higher than the banana reinforced composite due to the higher density of glass fiber than that of banana fiber. The interfacial shear strength of banana fiber was higher than that of glass fiber, indicated that banana fiber is more compatible with the resole PF resin. The tensile, flexural and impact properties of both composites were affected by fiber length and loading. The optimum length for glass and banana fibers to obtain the maximum mechanical properties was 40 and

30 mm, respectively. Meanwhile, the tensile, flexural, and impact strengths of glass and banana PF composites were increased with fiber loading.

Sisal fiber reinforced novolac PF composites were studied by researchers (Mu et al. 2009). The sisal fiber was subjected to heat, alkali, heat-alkali, isocyanate, cyanoethylation and silane coupling treatments. Different fiber/PF ratios (5, 10, 15, 20, and 25 wt%) were used. Two different methods, i.e. direct mixing and polymerization filling were performed to produce the composites. Treated sisal fiber composites showed greater mechanical properties (impact and bending) than the untreated fiber composites. For the method, polymerization filled composites possessed higher impact and bending strengths compared to direct mixed composites. Silane coupling treatment had produced composites with the highest impact and bending strengths. It was also found that treated fibers and polymerization filled composites had lower water absorption than that of untreated, and direct mixed composites.

Mishra et al. studied the compatibility of banana, hemp and sisal fibers esterified using maleic anhydride on the mechanical and swelling properties of the fibers reinforced novolac PF composites (Mishra et al. 2000). It was found that the water and steam absorptions were reduced in the maleic anhydride treated fibers composites when compared to the untreated fibers composites. Besides that, the mechanical properties such as Young's modulus, flexural modulus, impact strength and hardness were higher in the treated fibers composites than that of untreated fibers. Thus, maleic anhydride served as a compatibilizer between the natural fibers with novolac type PF resin.

Emanuel and Sinha carried out a comparative study on jute, and glass fibers reinforced cashew nut shell liquid (CSNL)-based resole resin composites (Emanuel and Sinha 2014). They found that the tensile strength of glass fiber (3400 MN/m^2) was higher than that of jute fiber (442 MN/m^2). At 50% fiber loading, the flexural strength of glass fiber-reinforced composite (72.30 MPa) was higher than that of jute fiber-reinforced composite (51.18 MPa). Besides that, at the same fiber loading the Izod impact strength of the glass fiber-reinforced composite (4.82 J/cm^2) was also higher than that of jute fiber-reinforced composite (3.04 J/cm^2).

Ozturk investigated the effect of basalt and hemp fibers loading on the mechanical properties of the fibers reinforced novolac PF composites (Ozturk 2005). The fiber loading was set at 20, 32, 40, 48, 56 and 63 vol%. The tensile strength of basalt/PF composite increased when fiber loading was increase up to 32 vol%, but it decreased at higher fiber loading. However, the flexural strength of basalt/PF composite decreased when the fiber loading was increased. The highest impact strength for basalt/PF composite was obtained at 48 vol% fiber loading. For hemp/PF composite, the tensile and elongation at break increased when the fiber loading was increased to 40 vol% (optimum). Meanwhile the flexural strength of the hemp/PF composite increased as the fiber loading increased to 48 vol% (optimum). The values for tensile and flexural decreased beyond the optimum fiber loading for the respective properties. Impact strength of hemp/PF composite showed increment with the increased in fiber loading. The research also studied the hybrid hemp/basalt/PF composites at designated hemp:basalt ratios (1:0, 0.95:0.05, 0.82:0.18, 0.68:0.32, 0.52:0.48, 0.35:0.65, 0.18:0.82 and 0:1). It was found that, the tensile strength of hemp/basalt/PF composites decreased when basalt fiber loading was increased. Meanwhile the maximum values for the flexural and impact strengths of the hemp/basalt/PF composite were obtained at hemp:basalt ratio of 0.52:0.48 and 0.68:0.32, respectively.

Sugarcane bagasse was used to reinforce phenolic and lignophenolic composite in a research conducted by Paiva and Frollini (2002). Phenol and lignophenolic (substituted with 40 wt% sugarcane bagasse-derived lignin). The impact strength of the composite increased when higher volume fraction of fiber was used. Mercerization and esterification of the bagasse fibers did not led to significant increase of impact strength. Comparable properties of composite were still obtained although the petroleum-based phenol was partially replaced with lignin.

Swamy et al. studied the properties of areca fiber reinforced PF composites. Adhesion tensile strength, water absorption and degradability of the composites were investigated. Composite was prepared using areca fiber:PF weight ratio of 1:0.1, 1:0.2, 1:0.3, 1:0.4, and 1:0.5. It was found that the tensile strength increased from the ratio of 1:0.1 to 1:0.4, but decreased back at 1:0.5. The highest bending strength was obtained at the ratio of 1:0.2. Increased in the loading of PF had decreased the water absorption of the composites. Less than 12.5% of the composites were degraded within 60 days.

Date palm reinforced phenolic composite has been studied by (Kashizadeh et al. 2019). The tensile strength and modulus of the composite were found to be 30.25 MPa and 3.0 GPa, respectively. Meanwhile, the composite flexural strength and modulus were 73.25 MPa and 5.9 GPa, respectively. The impact strength of the composite was 85 J/m^2. After the fiber was treated with alkali (6% NaOH solution), the composite produced had increased in tensile, flexural and impact strength by 19%, 14%, and 140%, respectively.

3.1 Physical Properties

The presence of void content in the composites reduces the mechanical and physical features of the composites significantly. The void present in the composites, owing to trapped air or other volatiles exist during the impregnation of fibers into the matrix or during the manufacture of fiber reinforced composites. The void content is relative to incompatibility between fiber and matrix and incomplete matrix wetting of fibers. However, it has been found that, hybridization of natural fibers (oil palm EFB composite with jute) able to reduce the content of void(Jawaid et al. 2011). By reducing the load transfer factor, the void dismisses the composite's integrity. On the other hand, control as minimum the presence of void appearance in composite fabrication. Equation (1) is illustrated the calculation of void content in the composite materials accordance with ASTM D 2734–91.

$$V_p = 100 - M_d\left(\frac{r}{d_r} + \frac{g}{d_g}\right) \tag{1}$$

where V_p is the void content of the composite (%), M_d is the measured density of the composite (g/cm^3), r is the resin content (wt%), d_r is the resin density (g/cm^3), d_g is the fiber density (g/cm^3) and g = fiber content (wt%).

According to Mwaikambo and Ansell (Mwaikambo and Ansell 2003), untreated unidirectional composites showed the highest porosity followed by composites reinforced with alkali treated hemp mat reinforced with CNSL. The overall decrease in porosity of alkali treated hemp mat composites and untreated hemp mat composites is due to the increased molding pressure, whereas unidirectional alkalized composites show slight increases in porosity with increasing molding pressure.

3.2 Mechanical Properties

Some of the natural fibers acting as reinforcement in phenolic resin tabulated in Table 2. Researchers found that mercerization (alkali treatment) using NaOH 10%, esterification (succinic anhydride) exhibited improvement on fiber/matrix interfacial

Table 2 Natural fiber reinforced phenolic composites

Matrix	Fiber	Treatment	Findings	References
Phenolic Lignophenolic	sisal	Untreated NaOH solution (10%) for 1 h esterification ionized air	Mercerized and esterified fibers improved the interfacial adhesion	Faulstich de Paiva and Frollini (2006)
Phenolic formaldehyde resins (PF) Phenolic formaldehyde resins modified with Cardanol (CPF)	Sawdust fibers			Pola (2010)
Bio-phenolic	Flax	Esterification	More moisture retardant	Zhu et al. (2013)
Tannin resin	short coir fibers	30–70% fiber (w/w)	Improvement in impact strength Excellent adhesion for fiber/matrix interface	
Bio-phenolic (CSNL)	hemp	8% NaOH Nonwoven fiber mats and unidirectional fiber composites	The hemp–CNSL interface is more coherent for the untreated than the alkali treated fiber (SEM)	Mwaikambo and Ansell (2003)

adhesion, however, it did not induced improvement in impact properties by sugarcane reinforced with the same matrices (Faulstich de Paiva and Frollini 2006).

In general, phenolic resin presented low tensile strength and low elongation at break, due to the brittleness characteristic of this resin (Milanese et al. 2011). The integration of natural fibers into phenolic composites helps to reduce the high brittleness of the composites and improve mechanical features and dimension stability (Torres-Tello et al. 2017). Some modification made by the researchers to overcome this challenges. Amran et al. reduced the resin brittleness and increases of impact strength as much as 77.7% by addition of 35 wt% epoxidised natural rubber into synthesized bio-phenolic by oil palm empty fruit bunch (EFB) fibers (Amran et al. 2015). A researcher found that Cardanol has shown a positive effect, since the composites with cardanol and sawdust fibers have demonstrated great flexibility and higher strength with a high temperature of glass transition (Pola 2010) rather than with Phenolic formaldehyde resins (PF), that commercial phenol formaldehyde can be effectively replaced by Phenolic formaldehyde resins modified with Cardanol (CPF).

Mwaikamboo and Ansell found that, because of the presence of lignin in untreated hemp fiber surface, the interfacial bonding with hemp surface and phenoloc based CNSL was stronger than untreated fiber and more compatible than the treated alkaline surface (Mwaikambo and Ansell 2003). Most researchers reported that the strength and stiffness of composites increased after alkalization compared to untreated fiber (Bachtiar et al. 2008; Das and Chakraborty 2009; Shahzad 2012). The content of cellulose increases slightly at lower NaOH levels and decreases at greater NaOH levels (Mwaikambo and Ansell 2006). Furthermore, the tensile strength and stiffness increase to a limited level with increasing NaOH concentration. However, researcher indicate that surface roughening by alkali treatment enhances fiber matrix adhesion by mechanical interlocking and the increasing number of hydroxyl groups, particularly with thermoset matrices, which contain functionally charged polar groups(Bisanda and Ansell 1991). On the other hand, researchers that study the effects of untreated and chemical modified oil palm fiber reinforced phenol composites has stated that fiber is more hydrophobic due the surface modification, which reduces interaction with PF resin, leading to a reduction in interface between (Sreekala et al. 2000). In other word, the hydrophilicity of the fiber can therefore be reduced by chemical modifications, thus reducing interfacial adhesion.

Few variables, like chemicals concentration, temperature and soaking duration, should be taken into account for chemical treatment and the results directly influence thermal and mechanical properties, biodegradability and thus adhesion between the matrix and the fiber. Barreto et al. (2011) found that chemical treatment caused exposure of cellulose structures, observed by separation of fibrils and increased surface area. This modification was important for improving bio-composite fiber adhesion matrix, which resulted in thermally more homogeneous and resistant materials.

3.3 Thermal Properties

When exposed to fire and high intensity heat sources, natural fiber reinforced composites are subjected to thermal decomposition. Although preventing the ignition of a fire is the first precautionary step, but another measure that can be done is to extend the material's ignition time. Ignition time is commonly depends on the heat intensity, oxygen density and the air flow in the location. However, once the ignition of fire started, the fire propagation rate need to be reduced to prevent. The rate of fire spreading is widely tested using fire propagation test such as the cone calorimeter (ASTM E1354 or ISO 5660) (Molaba et al. 2018) and lateral ignition and flame spread test (LIFT) (Gatien et al. 2019). Fire propagation is affected by the total heat liberated, and fire spread for fuel (Lee et al. 2014).

Meanwhile, to study the thermal behavior of the composites, methods such as thermogravimetric analysis (TGA), different scanning calorimetry (DSC), and dynamic mechanical analysis (DMA) are used. TGA is used to determine the mass loss due to the increase in temperature. The thermal decomposition of lignocellulosic components of natural fibers is normally began with decomposition of hemicelluloses, followed significant dropped in mass due to pyrolysis of cellulose, and lastly lignin at the highest temperature. DSC helps to determine the stages of thermal decomposition and other important parameters, for examples, glass transition, oxidation, level of crystallinity, and melting temperature. Heat and fire cause a material to rupture and degrade, hence loses its strength. DMA can be used to observe the time-dependent deformation behavior at very small amplitude. Thus, it could provide information such as Young's or storage modulus, loss modulus, tan δ, and mechanical loss factor, as a function of deformation (Lee et al. 2014).

Flammability of a material is an important factor to be addressed before it is being use in any applications. For natural fiber reinforced composites, the flammability of both reinforcement and matrices could contribute to the overall flammability of the composites. Hence, it is crucial to determine the flammability of the composite, in order to make sure that it is suitable for desired applications. According to Horrocks and Kandola, the fire resistance of some thermosetting resins in ascending order is vinyl ester < polyester < epoxy < bismaleimide < polyimide < phenolic (Horrocks and Price 2008).

One of the critical limitations of natural fiber is its low resistance of fire. This is due to the existence of cellulose in plant fibers and hydrocarbon-based polymers which increase the flammability of the natural fiber reinforced composites (Kim et al. 2018). Unlike thermoplastics, cured thermosetting polymers did not undergo melting phase when subjected to high temperature. Phenolic resin is a thermosetting polymer which contain three-dimensional crosslinked molecular structures that make it unable to melt. The burning of thermosetting polymers occurs in several stages, i.e. heating, decomposition, ignition, and combustion (Azwa et al. 2013). At the initial heating, both thermoplastics and thermosets undergo modification of molecular structure. Further heating decomposes the polymers via breaking of molecular bonds, and produce volatile substances at pyrolysis stage. Formation of free radicals through the bond scission and flammable products under high temperature ignite the polymer in the atmospheric environment. Phenolic polymer has inherent flame resistance and it yields char during combustion. Phenolic resin releases water due to condensation of phenol-phenol, and oxidation of methylene groups which bridged the phenols leads to formation of carbonyl linkage. Extensive decomposition of phenolic polymer liberates carbon monoxide (CO), carbon dioxide (CO_2), and other volatiles substances, and ultimately char is produced (Kim et al. 2018).

The presence of flax fiber in thermosetting polymer matrix composite was found to reduce the heat release rate (HRR), total heat release (THR), and smoke production in comparison to the neat polymer (Chai et al. 2012). The horizontal and vertical burning rates of the composites have also been decreased via the addition of flax fiber (Chai et al. 2012). Molaba et al. studied the thermal properties and flammability of flax fiber reinforced phenolic composites. The flax fiber was treated with alkali and silane. Meanwhile, diammonium phosphate was used as a fire retardant. The addition of fire retardant had reduced the HRR and smoke production rate of the composite. However the decomposition temperature of the composite was lowered. After aged at high temperatures, the tensile strength of both untreated fiber and fiber treated with flame retardant composites was decreased, but the decrement is more prominent in the latter. The modulus of elasticity of the composite without flame retardant increased after aged at higher temperatures.

Zhang et al. used milled recycled phenolic foam as a fire retardant incorporated into flax reinforced phenolic medium-density fiberboard (MDF) composites (Zhang et al. 2018). They studied the effect of size (40–60, 60–80, and 80–120 mesh) and proportion (0, 10, 20, 30 and 40 wt%) of the phenolic foam particles on the physical, mechanical and thermal properties of the composites. The mechanical properties of the composites decreased when the size and proportion of the particles were increased. The flammability of the composites was remarkably reduced when the size of the particles was decreased, and its proportion was increased. The composite produced with 30 wt% of phenolic foam particles showed the optimum flame retardancy with the smallest HRR, total smoke production, and smoke production rate. The LOI value of the control composite sample with no addition of flame retardant was 26.4%, meanwhile the LOI value for the composite produced at the optimum flame retardant parameter (particle size = 80–120 mesh; proportion = 30 wt%) was 37.3%.

Thermal properties and flammability of natural fibers and phenolic resin, tabulated in Table 3. The thermal and fire properties of date palm fiber reinforced phenolic composite has been studied by (Kashizadeh et al. 2019). The thermal properties and flammability of untreated and alkali (6% NaOH solution) treated fiber composites were determined. The alkali treatment had decreased the decomposition temperature of the composite. However, the treated fiber composite yielded higher char formation than that of untreated fiber composite. This was due to the removal of hemicellulose in the treated fiber during alkali treatment which increased the weight proportion of lignin in the fiber that ultimately led to production of higher carbon residue. The alkali treatment on the date palm fiber did not significantly improved the flammability of the composite when compared to that of untreated fiber.

Table 3 Thermal properties and flammability of natural fibers and phenolic resin

Fiber	Lignin content	Glass transition, T_g (°C)	Melting, T_m (°C)	Pyrolysis, T_p (°C)	Ignition, T_c (°C)	LOI (%)	References
Wool		NA	No melting	245	600	25.2	(Thakur and Thakur 2014)
cotton	1	NA	No melting	350	350	18.4	
Flax	3	NA	No melting	371	NA	NA	
Hemp	6	NA	No melting	346	NA	NA	
EFB	17						
Kenaf	18						(John and Thomas 2012)
Phenolic		300	No melting	440–520	614	25	(Kozłowski and Władyka-Przybylak 2008)
Polycarbonate						27	
Polyamide						43	

Tao et al. investigated the thermal properties and flammability of pine flakes reinforced PF composite filled with calcium carbonate ($CaCO_3$) as a fire retardant (Tao et al. 2019). The $CaCO_3$ was deposited on the pine flakes by in-situ reaction of calcium chloride ($CaCl_2$) and sodium carbonate (Na_2CO_3) with different molarity (0.5 and 1.0 M). The LOI and flame retardancy of the composites increased as the molarity of the reactants was increased. From TGA-DTG analysis, the thermal decomposition of composites treated with $CaCO_3$ lowered in comparison to the untreated composite. The TGA analysis also showed a layer of char accumulated on the treated pine surface which increased the flame retardancy of the composites. At 0.5 M of reactants, the internal bonding strength of the composite slightly decreased, but its modulus of elasticity (MOE) and modulus of rupture (MOR) increased significantly by 182.9% and 63.5%, respectively.

The thermal properties and flammability of woven coconut tree leaf sheath (CLS) reinforced PF composites was studied by Bharath and Basavarajappa (2014). The CLS was treated with 5% NaOH solution and used for the production of the composites by 60% volume fraction. The flammability of the composites was determine using UL94 (horizontal and vertical) and LOI tests. The alkali treated composite showed decrement in mass loss and flame propagation rates. The treated CLS composite required higher oxygen for ignition compared to that of untreated CLS composite.

Jang et al. investigated the flammability of paper sludge reinforced PF composites treated with different flame retardants (Jang et al. 2000). They used phosphate flame retardants containing halogen (tris 2-chloroethyl phosphate (TCEP), tris 2-chloropropyl phosphate (TCPP), SFR-300 (SFR)), halogenated flame retardant Ethylene-bispentabromo-diphenyl (EBPED)), and inorganic flame retardant Aluminium trihydroxide (ATH) and magnesium hydroxide (MH)). All flame retardants except the inorganic flame retardants exhibited significant flame retardancy on the composites. Combination of flame retardants EBPED/ATH had reduced the flammability of the paper sludge PF composite to the level of V-0 class. Although ATH did not showed significant flame retardancy when used as a single flame retardant, but it showed good synergism in retarding flame when combined with phosphate flame retardants and EBPED.

Marliana et al. studied the thermal and fire properties of kenaf fiber reinforced unsaturated polyester (UP) and phenol formaldehyde (PF) composites (Marliana et al. 2016). Kenaf fiber (20 wt%) was used to reinforced different proportion blends of UP and PF (UP/PF). Increased in PF content had linearly increased the char yield of the composites. The flammability of the composites was characterized via UL94 and LOI tests. The value of LOI increased with the increased in PF proportion, and the flame retardancy improvement was supported by the UL94 test. However, the mechanical properties of the composites deteriorated with the increased in PF content.

The thermal properties and flammability of pineapple leaf (PALF) and kenaf (KF) fibers reinforced PF composites were studied by (Asim et al. 2017). The composites were produced using untreated and alkali treated fibers. They found that the thermal properties of the composites reduced when the fiber loading was increased. Among all of the composites produced, treated 50% KF composite showed the highest Tg value followed by treated 50% PALF composite. This was due to good interfacial bonding between the fibers and matrices. Vertical and horizontal UL94 tests showed that neat phenolic polymer possessed the highest fire resistant. When PALF and KF was incorporated into the phenolic matrices, the fire retardancy decreased. Compared to PALF, KF showed higher fire retardancy. The fiber treatment however, did not significantly improve the fire retardancy of the composites.

3.4 Limiting Oxygen Index (LOI)

The Limiting Oxygen Index (LOI) measured according to ASTM D-2863 test is an excellent indicator to compare the flame retardance of fiber. LOI is the lowest oxygen concentration, as a volume percentage, which supports flaming burning of the material in an oxygen–nitrogen mixture. a polymer with a higher LOI would have lower flammability.

Based on the research carried out by (Jaafar et al. 2015) on thermal properties of bio-phenol formaldehyde composites reinforced with empty fruit bunch fiber at (5, 10, 15 and 20%), the weight losses occurred at 100 and 260 °C as an indication of water evaporation and lignocellulosic degradation. Ruseckaite and Jiménez (2003) has also shown that the sample with the highest filling content has a critical weight loss in comparison with that with the smallest filler sample. On the other hand, (Rashid et al. 2017) investigated the thermal properties of untreated, underwent treatment and alkali treated sugar palm fiber with phenolic, found that no significant differences in term of thermal analysis of TGA. Faulstich de Paiva and Frollini (2006) investigated the thermal stability of unmodified and mercerization (10%NaOH) sisal fibers reinforced with phenolic as well as lignophenolic composites and found that thermal stability natural fiber reinforced composites lower than their respective thermosets due to the fact that the first fibers had decomposed below thermosets at temperatures. The weight loss of unmodified fiber is larger compared to the treated fiber indicating that their lower hygroscopicity compared to unmodified fiber (Fahim and Chand 2008). Mercerization resulted extraction of hemicellulose partially, which is highly hydrophilic and acts as water absorber. The properties of phenol resin, untreated sisal/phenol and thermally-treated sisal (72 h at 60 °C) / phenolic composites were investigated by (Milanese et al. 2012). The sisal/phenolic composite was more stable than sisal fiber, yet less stable than the corresponding resin.

4 Conclusions and Future Perspective

The inherent and distinctive characteristics of phenolic resins are, low flammable, low smoke, low flame propagation, high ignition delay, low heat release and high oxygen index. However, its brittleness has significantly limited to structural application. Incorporating natural fibers into phenolic composites enables the composites to overcome the high brittleness and allows the improvement of mechanical properties. Enhancing phenolic composites properties with natural fibers in terms of strength, brittleness, toughness is critically important in order to expand its potential use in many fields such as landscape, architecture, automotive and aircraft industries. Furthermore, the fabrication of high-performance engineering materials, with low flammability, higher index of LOI, improved thermal resistance, seems to receive more attention from academics and industrialists globally. When natural fibers reinforced with phenolic resin the polar structure of lignin in the natural fiber will provide better fire resistance properties of the composites. Moreover, that natural fiber which is hydrophilic, will improve the compatibility of it physical properties with hydroxyl groups presented in phenolic resin. In this review article, provides valuable information on bio-composites phenolic resin for further investigation on its application. In addition the chemical structure and derivative of bio-phenolic from CNSL explained. As a future work, it is recommended to use bio-phenolic composites structural and non-structural applications.

Acknowledgements The financial aid for this research is supported by MOHE under TVET (T-ARGS) grant. The authors would like to express their gratitude and sincere appreciation to the Research and Innovation Center, Jabatan Pendidikan Politeknik Kolej Komuniti (JPPKK), Politeknik Banting Selangor (PBS) and Department of Aerospace Engineering, Faculty of Engineering, Universiti Putra Malaysia (UPM) for the close collaboration in this research.

Declarations of Interest The authors declare that there is no conflict of interest.

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Thermal Properties of Phenolic Composites

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Abstract Phenolic resin based natural, synthetic and nano composites are widely used in composite structures at elevated temperature and wall insulators. Thermal stability of natural fibers can be improved with phenolic resin. However, higher thermal stability can be achieved with effective surface treatments. Carbon fiber reinforced phenolic resin can be efficiently utilized in high temperature application due to its thermal stability and low coefficient of thermal expansion. On the other hand, Phenolic foams with different nano fillers can be utilized as thermal insulators due to its low thermal conductivity. This is mainly attributed to the lower volume fraction of solid phase in the material. Addition of nano fillers in the phenolic resin showed outstanding multifunctional properties compared to traditional polymeric composites. Researchers reported that nano clay, carbon and graphene based nano composites showed outstanding thermal stability. Functionalization or advanced treatments (Ultraviolet-ozone) enhanced the degradation temperature of the phenolic based nano composites.

Keywords Phenolic resin · Natural fiber · Synthetic fiber · Thermal stability · Thermal conductivity · Thermal insulation

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M. Jawaid and M. Asim (eds.), *Phenolic Polymers Based Composite Materials*, Composites Science and Technology,
https://doi.org/10.1007/978-981-15-8932-4_12

1 Introduction

Phenolic resin is a thermoset polymer and it exhibits brittle nature at room temperature (Frollini et al. 2013). Generally, phenolic resin can be efficiently utilized in high temperature application and thermal insulators. The raw materials for phenolic resin (phenol and formaldehyde) were derived from non-renewable resources. Nonetheless, substitution of these raw materials from non-fossil based resources would be an interesting and effective research in terms of cost and environmental perspective (Razera and Frollini 2004). The most commonly used bio-phenolic resins are lingo phenolic resin, tannin–phenolic resins and cardanol-based resins, which are derived from natural resources. The main advantage of phenolic resin compared to other thermoset or thermoplastics are chemical resistance, thermal insulation, thermal stability, flame resistance and excellent adhesive properties (Asim et al. 2018b).

Fibers and fillers are incorporated while preparing phenolic composites. Different organic and in-organic fillers can be used to enhance a specific characteristic for the intended applications. Incorporation of nano particles into the polymers showed improvement in various properties. Nanofillers such as carbon nanotube (CNT), graphene based fillers and nanoclay are commonly used to improve the thermal stability, fire resistance (Asim et al. 2018b; Frollini et al. 2013). On the other hand, fibrous reinforcement can improve the mechanical and impact properties of phenolic resin. Natural fibers (kenaf, pineapple, Coir, banana, sugarcane, etc.) and synthetic fibers (Carbon, glass and kevlar) can act as a load carrying member.

Thermal performance of a composite structure can be investigated through several ways such as thermo gravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and thermal conductivity measurement. Thermal stability of the material refers to its ability to maintain desire mechanical strength and stiffness at a given temperature. Thermo Gravimetric Analysis (TGA) is a widely used technique to investigate the thermal stability through mass loss, when it is subjected to higher temperature. The degradation can be classified into three stages such as initial degradation, major degradation and final degradation. Higher char residue content is a measure of higher thermal stability with lower degradation rate (Naveen et al. 2019a; Jesuarockiam et al. 2019).

Composites are a typical viscoelastic material. Mechanical deformation can be noticed at higher temperature. Dynamic mechanical analysis (DMA) measures the viscoelastic properties such as storage modulus (E'), loss modulus (E'') and damping factor (Tanδ). Storage modulus is associated with "Stiffness" and it measures the rigidity of the polymeric structure at higher temperature. Loss modulus indicates the amount of dissipated heat energy. Tanδ is the ratio of loss modulus and storage modulus. Higher Tanδ value exhibits the non-elastic behaviour of the composite, while lower value indicates better stiffness and elasticity (Jesuarockiam et al. 2019).

Generally, in buildings the walls are the main structural elements that receive heat directly from the surrounding atmosphere. An efficient thermal insulator would reduce the transmission of heat between two surfaces with different temperatures in order to minimize the energy consumption. The major parameters regarding the thermal insulation performance are usually evaluated through the thermal conductivity (W/mK). It can be measured using a thermal constants analyzer. Nowadays, thermal insulation performance in the building sector has become an interesting research to researchers concerned about energy consumption. Phenolic resin based composites can act as an efficient thermal insulator (Ramlee et al. 2019).

This chapter addresses the effect of reinforcing natural and synthetic fibers on the thermal stability, dynamic mechanical analysis and thermal conductivity of phenolic composites. Also, the influence of different nano-fillers on the thermal performance of nano phenolic composites has been addressed.

2 Thermal Properties of Natural Fiber Reinforced Phenolic Composites

Thermal degradation properties of the phenolic resin and the phenolic composites reinforced with the various natural fibres have been studied with the help of thermograms (Weight loss % vs. Temperature) and derivative thermograms (DTG) obtained from the thermo gravimetric analysis (TGA). It could be noticed from Table 1 that pure phenolic resins undergo thermal decomposition in single stage. Phenolic resins have better thermal stability over the other resins as visible from their far higher initial degradation temperature (IDT), final degradation temperatures (FDT) and residue or char.

Thermal decomposition of the natural fibre reinforced phenolic composite takes place in two or three stages (Table 2) compared to the single stage for the pure phenolic resin (Table 1). Incorporation of natural fibres into the phenolic resin reduces thermal stability of the composite in two ways: (i) fibre constituents degrades at lower temperature than the phenolic resin, (ii) fibre constituents like moisture, lignin, hemicellulose are volatile compounds and disappears at temperatures between 200 and 500 °C, hence leading to lower residue %than the pure phenolic resin (Table 2). As the incineration temperature inside the chamber containing fibre/resin mixture increases from room temperature to elevated temperatures between 800 and 1000 °C, constituents of both the fibre and resin decompose at different temperatures: (i) Initial weight loss occurs 100 °C is due to the removal of moisture from the fibre, (ii) intermediate weight loss between 305 and 410 °C is associated with the degradation of hemicellulose, cellulose and lignin of the fibre and (iii) final weight loss above 500 °C is loss of benzene rings in the PF resin (Rashid et al. 2017; Joseph et al. 2008). In a recent study, Faulstich de Paiva and Frollini reported that weight loss % of the sisal/PF composite was significantly lower than the raw sisal fibre in the temperature ranging from 100 to 800 °C (Faulstich de Paiva and Frollini 2006). Furthermore, residue % for the sisal fibre increased from 19.6 to 39.4% for the sisal/PF composite (Milanese et al. 2012). This implies that fibre degradation at the elevated temperature is slowed down due to the presence of phenolic resin. Phenolic resin has better compatibility with the natural fibre due to the presence of polar hydroxyl groups

Table 1 Thermal degradation properties obtained from TGA of various phenolic resins

Material	Thermal decomposition stages	IDT ($^{\circ 52}$C)	FDT ($^{\circ 52}$C)	Residue (%)	References
Novolac-type phenolic formaldehyde resin (PF)	1-stage	420.73	–	55.97	Eslami et al. (2015)
Resorcinolformaldehyde (RF)		299	990	48.92	Faulstich de Paiva and Frollini (2006)
Glyoxal–phenolic resin		150–250	800	–	Frollini et al. (2013)
Phenol formaldehyde		400	1195	51.47	Gupta and Jha (2018)

Table 2 Thermal degradation properties obtained from TGA of the natural fibre reinforced phenolic composites

Material	Thermal decomposition stages (°C)	IDT (°^{52}C)	IMDT (°C)	FDT (°C)	Residue (%)	References
Sisal/Glyoxal–phenolic composite	2-stages	300–600	–	800	15	Frollini et al. (2013)
PALF (50 wt%)/Novolac-type phenolic formaldehyde		283.64	–	391.38	29.22	Eslami et al. (2015)
Kenaf (50 wt%)/Novolac-type phenolic formaldehyde		293.14	–	447.99	24.23	
Grewiaoptiva/phenol formaldehyde		337	-	989 53	46.26	Gupta and Jha (2018)
Eucalyptus wood fibre/phenolic foam	3-stages		150–500	>500	34.95	Megiatto et al. (2008)

Table 3 Peak temperature from the DTG of PF composites reinforced with untreated and banana treated fibres

Banana/PF composite	Peak temperature (°C)			
	Peak 1	Peak 2	Peak 3	Peak 4
Untreated	46	302	405	510
Alkali	84	309	392	511
Silane	82	311	397	535

in their structure. Hence, phenolic resin has better wetting characteristic than the hydrophobic thermoplastic and other thermoset polymers. Hence, natural fibre is protected from the thermal degradation when used as reinforcement in the phenolic resin.

In case of the phenolic foam, degradation occurs in 3 stages compared to the single stage observed in the conventional phenolic resin. Initial degradation occurs at temperatures less than 150 °C followed by the intermediate stage between 150 and 500 °C in which and final stage beyond 500 °C (Table 2). Also, the char reduced from 35.81 to 34.95% after reinforcing the phenolic foam with 6 wt% Eucalyptus wood fibres (Rojo et al. 2015).

In order to compensate the loss in thermal stability due to the incorporation of natural fibres into the phenolic resin, fibre treatments with various reagents have been attempted by researchers. Table 3 shows the peak degradation temperature from the DTG for the PF composite reinforced with the untreated and treated banana fibres (Joseph et al. 2008). It is clear from Table 3 that composite with treated fibres possessed higher peak degradation temperature than the counterpart with the untreated fibres.

Similar observations on the shift in peak degradation temperature for the composite reinforced with the treated fibres were reported by other researchers (Asim et al. 2018a; Rojo et al. 2015). Another reason for the improvement in thermal stability of the PF composite with treated fibres is the substantially lower weight loss % than the composite with untreated fibres. This observation was made for the Alkali treated sisal/PF composites at degradation temperatures ranging from 100 to 500 °C (Faulstich de Paiva and Frollini 2006). In addition to the good wetting characteristic of the phenolic resin, alkali treatment of the sisal fibre further enhanced the interfacial adhesion between the fibre and matrix leading to better thermal properties.

DMA is a unique characterization technique in which the composite is subjected to both heat and mechanical load simultaneously. Viscoelastic properties of a material such as storage modulus, loss modulus and damping factor (tan ∂) are measured from DMA. Storage modulus provides information on the stiffness and fibre-matrix interfacial adhesion (Shahroze et al. 2019), while loss modulus highlights the extent of crosslinking in the polymer matrix and the energy dissipation characteristic (Joseph et al. 2010). Changes in glass transition temperature (T_g) of the composites can be identified from the damping factor. Cole–cole plot drawn between the loss modulus and storage modulus provides information on fibre-matrix interfacial bonding and fibre dispersion characteristic within the polymer matrix. Imperfect semi-circular shape indicates good wettability of the fibre with polymer matrix.

Ramires et al. (2010) studied the effect of curing temperature on sisal/glyoxal-phenolic composite. Composite with curecycle temperature lower than 150$^{\circ 52}$C exhibited increased storage modulus while the loss modulus and Tanδ were lower indicating better fibre-matrix adhesion.

According to Asim et al. (2018a) storage modulus increased with the reinforcement of PALF and kenaf fibres into the phenolic resin. Increase in peak loss modulus, imperfect semi-circular shape and shifting of glass transition temperature demonstrated the improvement in fibre-matrix adhesion due to the fibre treatment with silane. Similar trend on fibre loading was reported for date palm/phenolic composites in a recent study (Asim et al. 2020). Improvement in storage modulus for sisal/phenolic composite due to the fibre treatment was indicated by Megiatto et al. (2008) in their study. According to them, reaction between the hydroxymethyl groups in lignin and pre polymer phenolic rings resulted in strong fibre-matrix interfacial bonding characteristic which was also confirmed from their microscopic images.

Sreekala et al. (2005) varied the fibre loading by 30–50 wt% in the phenolic resin and reported that damping increased with the fibre loading while the peak loss modulus and T_g declined at 40 wt% indicating poor fibre-matrix adhesion at higher fibre loading. Since the fibres were used in chopped form, increased fiber-to-fiber contact at higher fibre loading can cause fibre agglomeration and uneven dispersion of the fibres within the matrix. These factors are detrimental to the mechanical properties and fibre-matrix adhesion of the composite.

3 Thermal Properties of Synthetic Fiber Reinforced Phenolic Composites

Carbon fiber reinforced phenolic composite has been widely used as a thermal protection system in the aerospace structures. Also, it acts as ablative material in the re-entry vehicle structure (RVS) due to its excellent properties such as low coefficient of thermal expansion, thermal insulation and thermal stability. RVS consist of internal carbon/epoxy shell to bear the mechanical loads, whereas outer carbon/phenolic shell resists the thermal loads. Filament wounded carbon/phenolic shell was cured in the autoclave through the following steps. (i) Phenolic resin impregnated carbon fiber was wound around the carbon/epoxy mandrel to the required thickness. (ii) Breather layer was wrapped around the carbon/phenolic shell to achieve uniform distribution and avoid resin bleeding. (iii) In order to avoid voids, carbon/phenolic composites along with carbon/epoxy mandrel was sealed in a vacuum bag with vacuum pump. (iv) Eventually, the composite shell has been cured in the autoclave. USIM software can be efficiently utilized to study the thermal stability of carbon/phenolic structure of RVS. Also this software can be used to study the effect of aerodynamic loads on the thermal performance (Coefficient of thermal expansion, thermal diffusivity and specific heat) of composite structure (Gupta and Jha 2018).

Carbon aerogels possess excellent thermal stability and low thermal conductivity which makes it suitable for thermal protection system, particularly for aerospace applications. Seraji et al. (2018) have developed the hybrid glass/rock wool fiber based phenol–formaldehyde composite aerogels and investigated the thermal performance. The hybrid glass/rock wool/phenol–formaldehyde composite aerogels were made through sol–gel polymerization under solvent saturated vapor atmosphere. Pyrolysis process was employed to transform the fabricated polymeric aerogels into rock wool/carbon and glass/carbon composite aerogels. The obtained results indicated that at 2.5 Wt% of wool fiber content of the rock/carbon aerogels showed higher thermal stability (643 °C) compared to glass/carbon composite aerogels (620 °C).

Ahmadijokani et al. (2019) investigated the effect of adding short carbon fiber on the thermal and dynamic mechanical analysis of phenolic based composites for brake pad applications. The fabricated composites contains 77 vol% of fixed masterbatch (Matrix: Phenolic resin, Fiber: Aramid and glass fiber). The remaining 23 vol% consists of barite and carbon fiber.PAN (polyacrylonitrile) type carbon fiber was used with different vol% (0–4%). From the observation, it was found that inclusion of 4 vol% of carbon fiber enhanced the thermal stability and storage modulus.

Yang et al. (2018) studied the thermal properties of hollow glass microsphere/phenolic resin composites. Spherical shaped hollow glass microsphere is an in organic powder, which holds excellent properties such as low thermal conductivity, low density and chemical stability. It has been extensively used in building, aerospace and oil gas exploitation (Herrera-Ramírez et al. 2017). Phenolic resin exhibited higher flame retardancy compared to other organic materials. Also, it releases very less toxic gases and smoke. Phenolic resins act as a binder in the hollow glass microsphere (HGM)/phenolic resin (PR) composites. The samples were made with different mass ratio of PR/HGM. The thermal conductivity results revealed that increase in mass ratio of PR/HGM (0.7 to 1.3) enhanced the thermal conductivity from 0.0723 to 0.1024 W/mK. Reduction in HGM content might be the reason for higher thermal conductivity at PR/HGM mass ratio of 1.3. From the thermogravimetric analysis it has been reported that the PR/HGM samples at 0.7 mass ratio exhibited higher char residue at 700 °C which indicates higher thermal stability. Hollow phenolic microspheres possess outstanding thermal properties. Liu et al. (2009) introduced a facile method to fabricate the hollow phenolic microspheres (HPM) through in situ polymerization. The particle size was measured through SEM (Scanning Electron Microscope) and the average particle size was 500 μm. Thermogravimetric analysis results have shown that the decomposition temperature of HPM was 420 °C. The residual weight was 62% at 800 °C, indicating the thermal stability of HPM. DSC results revealed that the glass transition temperature (Tg) of HPM was 200 °C.

Generally, inorganic materials are non-combustible, whereas foamy organic materials possess excellent thermal insulation properties. In particular, organic foams were extensively used as a thermal insulator in buildings due to its low thermal conductivity and light weight. The most commonly used organic foams are phenolic foam, polyurethane foam and polystyrene foams (Sayadi et al. 2016). However, the organic

Table 4 Literature's on the thermal performance of synthetic fiber/phenolic composites

Fibers	Matrix	Properties	References
Carbon fiber	Phenolic resin	Coefficient of thermal expansion, thermal diffusivity and specific heat	Ramlee et al. (2019)
Glass/carbon	Phenol–formaldehyde	Degradation temperature, thermal stability	Rashid et al. (2017)
Rockwool/carbon			
Short carbon fiber	Phenolic resin based masterbatch	Thermal stability, storage modulus and loss modulus	Razera and Frollini (2004)
HH Hollow glass microsphere	Phenolic resin	Degradation temperature, thermal stability	Rojo et al. (2015)

foams hold poor fire retardant properties. Hence, developing an efficient wall insulator with higher flame resistance has become an interesting research. Hybridizing organic and inorganic materials will take the advantage of both constituents and produces an efficient thermal insulator with flame resistant behavior.

Wang et al. (2014) utilized this HPM as a filler in the phenolic resin derived carbon foams. Also, phenolic based carbon samples in the absence of HPM were fabricated to compare the thermal conductivity. The obtained results revealed that HPM filled carbon foams exhibited 49% lower thermal conductivity compared to phenolic based carbon samples at room temperature. On the other hand, at 800 °C carbon foams showed 35% lower thermal conductivity, which makes it suitable for thermal insulation application compared to phenolic based carbon samples. This is mainly attributed to the lower volume fraction of solid phase in the carbon foams. Table 4 shows the reported research on the thermal properties of synthetic fiber/phenolic composites.

4 Thermal Properties of Nano Phenolic Composites

Novel polymeric nano composites have been widely used in high temperature application and thermal insulators. This is mainly due to its multifunctional properties such as higher mechanical properties, fire resistance, lower thermal conductivity and higher thermal stability. Incorporation of inorganic nano additives in the polymeric system exhibits outstanding multifunctional properties compared to traditional polymeric composites. Nanofillers such as nanoclay, carbon nanotube, silica and graphene are commonly used nanofillers. Incorporation of nano particles into the polymers showed improvement in various properties. The enhancement in properties of the nanocomposites depends on (i) the polymer matrix (ii) the type of nanofiller selected (iii) nanoparticle orientation (iv) particle aspect ratio (v) particle concentration, etc.

Eslami et al. (2015) investigated the influence of adding MWCNT (multi walled carbon nanotubes) on the thermal properties of carbon fiber reinforced phenolic composites. Initially, different weight percentage of MWCNT (0, 0.25, 0.5,1 and 2 Wt%) was incorporated into the phenolic resin through ultra-sonication. Then the MWCNT modified phenolic resin was mixed with the carbon fiber manually and bulk moulding compound (BMC) has been made. Eventually, the BMC paste was placed in the hot press. The pressure and temperature were maintained at 10 bar and 170 °C for 5 h. In order to achieve effective cross linking the composite samples were post cured at 200 °C for 2 h. Thermal stability was investigated through thermogravimetric analysis and the results showed that addition of MWCNT upto 1Wt % enhanced the thermal stability and degradation temperature (7%), However, further addition of MWCNT didn't show much improvement due to aggregation.

Bahramian (2013) investigated the effect of graphite nano crystals on the thermal stability of graphite/novolac phenolic composites. DSC (Differential Scanning Calorimetry) results revealed that the peak of the curve associated with nano composites were shifted to higher temperature compared to virgin phenolic samples. Similar results were observed in thermogravimetric analysis (TGA), whereas the weight loss was found in between 300 and 550 °C for all the composite specimens. However, addition of graphite nano crystals slightly enhanced the thermal stability. Cone calorimetry results showed that incorporation of graphite at 3 and 5 Wt % exhibited 41 and 58% lower HRR (heat release rate) respectively compared to pure phenolic samples. SEM analysis, revealed that uniform char formation is mainly due to proper arrangement of graphite layers and thereby enhanced the thermal stability of the graphite/phenolic nano composites.

Nanoclay consists of several layer of mineral silicates (tetrahedral $[SiO_4]^{4-}$ or octahedral $[AlO_3(OH)_3]^6$) that are arranged in a layering sequence. Montmorillonite (MMT) nanoclay fall under group of 2:1 phyllosilicate clay which has been extensively used for the past 50 years, Owing to its inexpensive, easily available, large surface area and well-understood chemistry to form organically modified MMT (OMMT). Hassan et al. (2017) studied the influence of adding ammonium polyphosphate on the thermal stability of nano clay (MMT) (montmorillonite) filled phenolic/polyester nano composites. Unsaturated polyester resin was blended with unsaturated phenolic resin in order to achieve superior mechanical and thermal properties through effective interpenetrating polymeric networks. Addition of 30 phr ammonium polyphosphate exhibited higher thermal stability compared to other nano composites.

Discovery of graphene gained more attention due to its outstanding mechanical properties (Strength: 130 GPa, Modulus: 1TPa) and thermal stability (Naveen et al. 2019a). Few layers of graphene were stacked together with high aspect ratio and forms GNP (graphene nanoplatelets) and it possess a 2D planar structure. Researchers found that GNP acts as a potential filler in the polymeric composites. This is mainly due to its higher mechanical properties, thermal stability, chemical resistance, availability and cost effectiveness. (Naveen et al. 2019b)The GNP could efficiently transfer the stress and improves the load carrying capability due to large specific surface area. At an optimal GNP loading in the polymeric composites enhanced the thermal stability properties of polymers. GNP is widely used as a nano filler in polymeric nano composites for advanced applications such as sensors, super capacitors and batteries. Researchers reported that graphene based nano composites showed outstanding properties compared to clay or carbon filler based nano composites (Eda and Chhowalla 2009).

Shaheryar et al. (2017) studied the thermal stability of GNP/Carbon fiber/barium phenolic composites. Ultraviolet-ozone (UV-O3) treatment was used to achieve better dispersion of GNP. GNP (0.3 Wt%) was mixed with phenolic resin using a mechanical stirrer. Then GNP modified phenolic resin was coated over the carbon fiber using hand lay-up process. GNP coated carbon fiber were stacked together in a compression mould and cured in a vacuum oven. TGA results indicated that composites containing treated GNP showed higher thermal stability and lower degradation rate. This is attributed to fact that efficient covalent linkages (containing functional groups of GNP) hinder the molecular chain mobility and also due to the interfacial compatibility.

High energy consumption in construction sector is mainly due to inefficient insulating materials with poor thermal performance. Organic thermal insulators such as phenolic foam board, extruded polystyrene foam board and polystyrene foam board were extensively used due to its thermal insulation, wear resistance and lower cost. Phenolic foam based insulators exhibited better thermal insulation performance compared to other wall insulators. Hence, it is termed as “King of Insulators”. Virgin phenolic resin is brittle in nature and the hydroxyl and methylene groups of its molecular structure can be easily oxidized. These drawbacks limit the application of neat phenolic resin. Hence, it can be modified with different nanofillers to improve the multifunctional properties. Zhou et al. (2020) studied the effect of adding aluminum diethylphosphinate and melamine on the thermal performance of phenolic resin through Thermo-gravimetric analysis (TGA). The Table 5 shows the results TGA.

T5%, T10% and T_{dmax} in Table 5 indicate the temperature at 5, 10 wt % and maximum weight loss rate, respectively. From the results it is observed that addition of melamine (4 wt %) the phenolic resin (without Aluminum Diethylphosphinate) showed higher thermal stability, whereas addition of 10–15% of Aluminum Diethylphosphinate (without melamine) exhibited better thermal stability. On the other hand, the Wt % of fillers plays a vital role on the thermal stability of hybrid melamine and aluminum diethylphosphinate filled phenolic composites. Addition of 3Wt % melamine and 10 Wt % aluminum diethylphosphinate showed higher residual content of 59.5% and thermal stability compared to other hybrid combinations. Table 6 shows the reported literature’s on the thermal performance of nano/phenolic composites.

Table 5 Effect of nano additives on the thermal stability of phenolic composites

Mass fraction (%)		T5% (°C)	T10% (°C)	T_{dmax} (°C)	Char Residues at 800 (wt %)
Neat Phenolic (100)		178	313	550	51
Melamine	Aluminum Diethylphosphinate				
2	–	133	231	559	57
4	–	268	426	560	64
6	–	206	331	566	53
8	–	198	306	340	42
-	5	151	300	562	52
-	10	147	299	557	55
-	15	177	329	561	52
-	20	121	305	467	49
3	10	121	265	570	59.5
3	15	125	256	560	50.7
4	10	155	299	559	57.7
4	15	137	281	559	52.2
5	10	138	271	559	54.3
5	15	176	303	561	49.5

Table 6 Literature's on the thermal performance of nano/phenolic composites

Fibers	Nanofiller	Matrix	Properties	References
Carbon fiber	MWCNT	phenolic resin	Degradation temperature and thermal stability	Wang et al. (2014)
-	Graphite nano crystals	phenolic resin	Thermal stability and heat release rate	Yang et al. (2018)
-	Montmorillonite (MMT)	phenolic resin/polyester	Thermal stability	Zhou et al. (2020)
Carbon fiber	Ultraviolet-ozone treated Graphene nanopletelets	Barium phenolic resin		Shaheryar et al. (2017)

5 Conclusions and Future Research

The effect of reinforcing natural/synthetic fibers and the effect of incorporating nano fillers on the thermal stability, dynamic mechanical analysis and thermal conductivity of phenolic composites were investigated. Addition of natural fiber in the phenolic resin has declined the thermal stability due to the natural chemicals. However, different surface treatment enhanced the degradation temperature of the resulting composites. Phenolic resin based aerogels and foams possess higher thermal stability. Several organic and inorganic materials can be hybridized to achieve higher degradation temperature and fire resistance. Addition of nano fillers in the phenolic resin improved the thermal stability and insulation properties. However, identifying optimal Wt (%) to achieve better thermal performance is a challenging task. Hence extensive research is required about the fictionalisation of nano fillers and identifying optimum Wt (%) of potential nano filler in the phenolic resin for high temperature applications and wall insulators.

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Mechanical Performance of Fire Retardant Coated and Uncoated Okra/Agave Americana Hybrid Fibre Reinforced Phenolic Composites

Nadendla Srinivasababu

Abstract Several numbers of fibres were collected from long back and examined for making clothes and were reported in the literature. In that popularly used green vegetable okra plant and agave Americana fibres were taken in the proportion of 60:40% to prepare composites using phenolic resin. Fibres were coated with phosphorous based fire retardant chemical applied manually and dried in an oven till the complete moisture vanishes by ensuring the fibre dryness. Then the composites were made with the fire retardant coated hybrid fibres as reinforcement. Fabricated composites were subjected to a heating cycle at different temperatures as per the specification of the industry. Tensile, three-point bend and impact composite specimens were tested according to ASTM standards for determining their mechanical performance and know the impact of fire retardant coating on reinforcement and their compatibility with the phenolic resin. Further, the reddish-brown color of the resin created difficulty in the fabrication of the composites. Photograph of the tested composites was taken to visualize the alignment of fibres in the matrix, fibre-matrix bonding, and fibre pull out and reported in respective sections. From the results, it is concluded that fire retardant coated phenolic composites had shown inferior performance when compared with uncoated okra-agave Americana hybrid fibre composites.

Keywords Phenolic resin · Fire retardant coating on okra-agave americana hybrid fibre · Mechanical properties and impact of fibre retardant coating

1 Introduction

In present days synthetic polymers were ubiquitous to fulfill several needs in different sectors. Leo H. Baekeland developed and economical method in 1907 to convert resins into mouldable parts through the application of heat and pressure and was

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M. Jawaid and M. Asim (eds.), *Phenolic Polymers Based Composite Materials*, Composites Science and Technology,
https://doi.org/10.1007/978-981-15-8932-4_13

evidenced by several patents. Phenolic resins occupied a comparable extent on par with the polyester or polyurethanes in the market. High infusibility, more temperature resistance, flame retardance are important considerable parameters for the expansion of the phenolic resin usage in the market (Knop and Pilato 1985).

For improving flame retardancy (Li et al. 2016) Layered Double Hydroxide (LDH) was introduced into the phenolic resin. They found that the sisal fibre phenolic composites showed a 60% reduction in total heat. Further, bio-based silicone modifier was introduced into the resin for enhancing electrical resistance and reducing sorption behaviour.

Dialdehyde available in natural sources was used to prepare glyoxal phenolic resin reinforced with sisal fibre composites. Irrespective of curing cycle 1 or 2, sisal fibre phenolic composites had shown impact strength of one order of magnitude (Elaine et al. 2010).

Pineapple, kenaf fibre reinforced Novoloc phenol formaldehyde composites were prepared (Asim et al. 2018) to determine dynamic mechanical, thermal, and flammability properties. Untreated and chemically treated kenaf fibre composites showed better flame retardance than pineapple leaf fibre phenolic composites.

Untreated, thermally treated Brazilian plain weave sisal fabric of 2.4 mm thick at 60 °C up to 72 h, was reinforced (33 wt%) into Cascophen RS 216 M synthetic phenolic resin to prepare composites by compression molding (Milanese et al. 2012). Sisal-phenolic composites showed tensile, flexural strength of 25 MPa, 11 MPa respectively.

Macromolecule tannin was abundantly available in natural sources. So, this was used to synthesize tannin-phenolic resin. Here tannin 50 wt % was used as a substitute of phenol and coir fiber was reinforced into it and the composites were fabricated to assess impact, dynamic mechanical thermal, and water sorption analysis (Barbosa et al. 2010). At 60 wt % of coir fibre, the composites had shown high impact strength.

Thermal stability of unmodified and modified sisal fibre reinforced phenolic and lignophenolic composites were made and subjected to TGA, DSC, DMTA analysis (Faulstich et al. 2006). Mercerized and esterified fibres had good interfacial adhesion with the matrix. High temperatures (200 °C) were limited by thermal stability of lignocellulosic fibres.

Graft copolymerization of flax fibres was done using methyl acrylate through Fenton's reagent (Kalia et al. 2008). Phenolic composites reinforced with these fibres have bear tensile, the compressive load of 235,814 N respectively.

Tensile, flexural, impact, dynamic mechanical, and thermal analysis of jute woven fabric phenolic composites were investigated in respect of orientation of fibre and fabric characteristics (Eliton S de Medeiros et al. 2005). Type III fabric composite has shown tensile strength, modulus of 59.4 MPa, 7.1 GPa respectively. In the case of bending Type IV fabric composites showed 165.6 MPa flexural strength and 11.3 GPa flexural modulus. The impact strength of 13 kJ/m^2 was shown by Type IV fabric phenolic composites. In all the cases 0° orientation of fabric had given the highest value as described above.

Treated coir fibre 20 mm length: glass in 1:2 composition phenolic composites made by hand lay-up followed by compression molding produced (Mithil Kumar et al. 2009) high tensile strength of 74.58 MPa and modulus of 9.91 GPa when compared with other compositions results in their work.

Sugarcane bagasse reinforced lignophenolic composites were prepared (Jane and Pavia 2002). In unnotched Izod impact test mercerized bagasse lignophenolic composites showed an impact strength of 24.9 J/m. From the literature review, it was understood that the authors had put their efforts into understanding the mechanical, thermal, and flammability of the composites with various matrices to be specific phenolic resin for studying the fire resistance nature of them. So, in the present work, the author has attempted to prepare uncoated and fire retardant coated okra/agave Americana composites according to the ASTM standards. The prepared composites were subjected to tensile, bending, and impact loading conditions. The impact of fire-resistant coating of the composites under the above mechanical test results was compared with the uncoated okra/agave Americana hybrid fibre reinforced phenolic composites.

2 Materials, Fabrication and Testing

This section describes the materials used and sequential steps followed for making composites along with the testing procedures are described.

2.1 Materials

Okra, agave Americana fibres were received from the locally available agricultural market. Phenolic resin is a room temperature curing resin with dark brown and was kindly given by M/s Romit Resins Pvt. Ltd., Panvel, Raigad District, Maharashtra, India. Para toluene sulphonic acid was used as a catalyst for the resin. In this experimentations, resin and catalyst were mixed in a proportion of 100:20 parts.

2.2 Fabrication of Composites

Long back established wet layup method was used for the preparation of the composites. Initially, okra, agave Americana fibres were placed in a heating oven at a temperature of 85 °C up to 2 h and allowed to cool in an oven. The cooled fibres were taken out from the oven and cut as per the required dimensions of the pre-prepared mold. The resin mixture was coated as a thin layer over the mold and rolled using using ‘small washer roller’ procured from M/s Carbonblack Composites, India.

Pre-weighed okra, agave Americana fibres of 60%, and 40% respectively were dipped up to three minutes in the bowl having resin mixture through fingers and completely wet fibre bunch was kept in the mold without deviating fibres alignment.

Then, the mold is covered with polyester film and a load of 392.4 N was applied and the excess resin from the mold is squeezed out. The main issue arose during the alignment of fibres in the respective specimen mold due to the dark brown color of the resin mixture. The mold was allowed at room temperature till the next day i.e. 24 h. Cured specimens were taken out from the mold but they were relatively soft. So, a heating cycle of 60, 80 °C 2 h each and at 100 °C 1 h was applied for better curing of the composites followed as per the specifications of the supplier.

In another stage, the above-mentioned proportion of fibres were dipped separately and manually in a dilute phosphorous based fire retardant chemical purchased from Safechem Solution Pvt. Ltd., Faridabad, India. Fibres were taken out from the about 66% fire retardant solution after 26 h and allowed to dry in a room. These fibres were kept in an oven at a temperature of 80 °C, 120 °C up to 1 h, and 2 h respectively. Dried fibres were used to prepare the phenolic composites in similar lines as described earlier. When the composites were taken out from the mold, it was observed that fibres were not fully bonded to the phenolic resin mixture. This was confirmed after a series of experiments conducted on the fire retardant coated fibre reinforced phenolic composites. All the composite specimens were ground with a belt grinding machine which produces straight edges.

2.3 Testing of Composites

Okra, agave Americana hybrid fibre reinforced phenolic composite tensile test specimens prepared according to ASTM D638-14 was tested on Computerized Tensometer at a crosshead speed of 4 mm/min. Phenolic hybrid composites were kept in a three-point bend fixture to perform the flexural test as per ASTM D790-17 at a speed of 2.6 mm/min using a Tensometer. During both the tests care was taken and the specimen was arranged correctly to minimize slip during the test. Notch was cut on the set of composites specimens and the Charpy impact test was conducted on the specimens according to ASTM D6110-08. In all the tests five samples were tested and the average value of each test properties was determined.

3 Results and Discussion

Okra, agave Americana hybrid fibre reinforced phenolic composites specimens' possessed slight variation in its thickness and width along its length. So, each dimension of the specimen i.e. width, the thickness was measured with digital Mitutoyo micrometer at section 1-1 (left side of the specimen), section 2-2 at centre, and section 3-3 (right side of the specimen) and the average value was taken. This procedure was followed for uncoated and fire retardant coated composite specimens. Tables 1, 2, 3, 4, 5, and 6 show the specimen dimensions data and calculated average

Table 1 Okra-Agave Americana hybrid fibre reinforced phenolic composites—tensile test specimen dimensions

Specimen No.	Width (mm)			Average width (mm)	Thickness (mm)			Average thickness (mm)
	Left section 1-1	Center section 2-2	Right section 3-3		Left section 1-1	Center section 2-2	Right section 3-3	
1	13.933	13.378	13.541	13.617	5.103	5.037	5.045	5.062
2	14.078	14.233	14.056	14.122	4.015	3.608	3.650	3.758
3	13.737	14.142	13.702	13.860	4.072	4.075	4.027	4.058
4	13.351	13.632	14.031	13.671	4.113	4.024	3.976	4.038
5	14.074	12.925	14.202	13.734	4.158	4.109	3.976	4.081

Table 2 Fire retardant coated Okra-Agave Americana hybrid fibre reinforced phenolic composites—tensile test specimen dimensions

Specimen No.	Width (mm)			Average width (mm)	Thickness (mm)			Average thickness (mm)
	Left section 1-1	Center section 2-2	Right section 3-3		Left section 1-1	Center section 2-2	Right section 3-3	
1	13.239	13.739	13.431	13.470	5.315	5.327	5.209	5.284
2	14.930	14.905	14.434	14.756	5.272	5.340	4.827	5.146
3	15.249	14.074	14.301	14.541	5.234	5.308	5.326	5.289
4	15.172	14.452	14.631	14.752	5.332	5.319	5.051	5.234
5	12.135	12.810	14.252	13.066	5.451	5.232	5.155	5.279

Table 3 Okra-Agave Americana hybrid fibre reinforced phenolic composites—flexural test specimen dimensions

Specimen No.	Width (mm)			Average width (mm)	Thickness (mm)			Average thickness (mm)
	Left section 1-1	Center section 2-2	Right section 3-3		Left section 1-1	Center section 2-2	Right section 3-3	
1	13.112	12.931	13.353	13.132	4.158	4.249	4.150	4.186
2	13.620	13.731	13.339	13.563	4.157	4.146	4.029	4.111
3	13.035	12.724	12.940	12.900	4.143	4.047	4.077	4.089
4	14.139	14.216	14.052	14.136	5.440	5.535	5.538	5.504
5	13.733	14.438	14.951	14.374	5.550	5.023	5.553	5.375

Table 4 Fire retardant coated Okra-Agave Americana hybrid fibre reinforced phenolic composites—flexural test specimen dimensions

Specimen No.	Width (mm)			Average width (mm)	Thickness (mm)			Average thickness (mm)
	Left section 1-1	Center section 2-2	Right section 3-3		Left section 1-1	Center section 2-2	Right section 3-3	
1	14.739	14.719	14.875	14.778	5.135	5.223	5.317	5.225
2	15.011	13.937	15.358	14.769	5.425	5.200	5.319	5.315
3	14.955	14.757	13.734	14.482	5.113	5.256	5.056	5.142
4	14.701	14.254	14.711	14.555	5.476	5.639	5.510	5.542
5	14.850	13.906	14.116	14.291	5.531	5.631	5.348	5.503

Table 5 Okra-Agave Americana hybrid fibre reinforced phenolic composites—impact test specimen dimensions

Specimen No.	Width (mm)			Average width (mm)	Thickness (mm)			Average thickness (mm)
	Left section 1-1	Center section 2-2	Right section 3-3		Left section 1-1	Center section 2-2	Right section 3-3	
1	14.111	14.035	14.655	14.267	5.526	5.529	5.430	5.495
2	14.551	13.976	14.335	14.287	5.432	5.444	5.432	5.436
3	13.559	14.070	14.037	13.889	5.435	5.458	5.456	5.450
4	13.738	13.857	13.974	13.856	5.416	5.431	5.502	5.450
5	14.130	14.105	14.044	14.093	5.325	5.318	5.239	5.294

Table 6 Fire retardant coated Okra-Agave Americana hybrid fibre reinforced phenolic composites—impact test specimen dimensions

Specimen No.	Width (mm)			Average width (mm)	Thickness (mm)			Average thickness (mm)
	Left section 1-1	Center section 2-2	Right section 3-3		Left section 1-1	Center section 2-2	Right section 3-3	
1	14.344	14.657	14.350	14.450	5.524	5.278	5.124	5.309
2	15.112	15.111	14.207	14.810	5.434	5.173	5.238	5.282
3	15.040	15.538	15.607	15.395	5.121	5.138	4.948	5.069
4	14.925	14.707	14.818	14.817	5.457	5.135	5.135	5.242
5	15.112	14.537	15.129	14.926	5.009	4.959	4.942	4.970

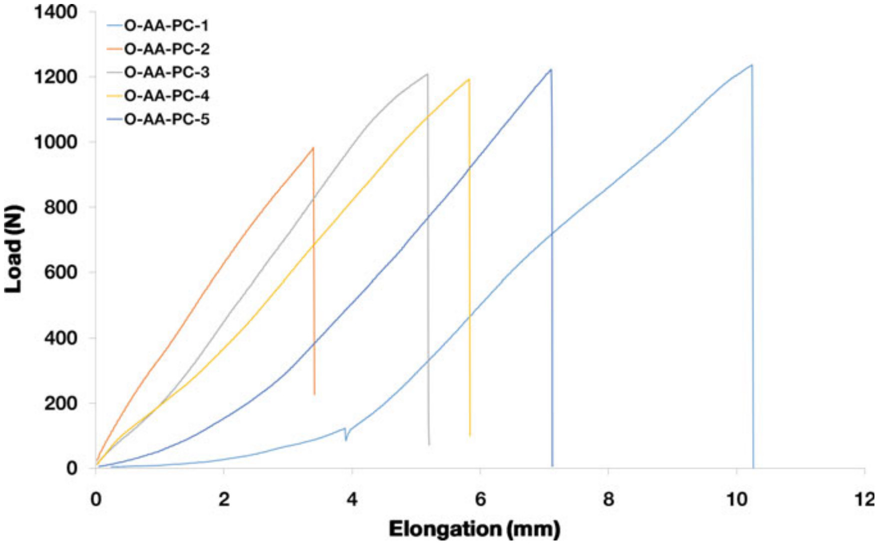


Fig. 1 Load elongation graph of okra, agave Americana hybrid fibre reinforced phenolic composites under tensile test

value of phenolic fibre composites for each test specimen viz. tensile, bending, and impact.

Uncoated and fire retardant coated okra-Agave Americana hybrid fibre reinforced phenolic composites load vs. elongation data during the tensile test was shown in Figs. 1and 2 respectively. Uncoated hybrid fibre (21 wt %) phenolic composites exhibited tensile strength, modulus of 20.28 MPa, 0.279 GPa respectively due to good bonding between reinforcement and matrix, Fig. 3. From Fig. 4, it was observed that the alignment of the fibres was changed in the composite specimens that might be resulted in a decrease in strength in the longitudinal direction than that of the anticipated values. Whereas fire retardant coated hybrid fibre composites had shown a decrease in tensile properties when compared with the earlier composites and fibre pullout was seen from Fig. 5. Uncoated composites tensile strength, the modulus was 3.72 times, 2.25 times more than fire retardant coated phenolic composites. This clearly from the fact that the partial non-bonded fibres with the resin which is identifiable from Fig. 6. But all the uncoated hybrid fire phenolic composite specimens were failed due to tension only and there was no fibre pull out observed.

Impact of fire ammonium polyphospahate (APP) retardant on the mechanical performance of polypropylene wood fibre composites was described (Zhang et al. 2012). Though the compatibilizer was used to achieve bonding between reinforcement and matrix, a decrease in the trend of tensile strength and elongation was observed.

In a three-point bend test uncoated hybrid fibre composites reasonably good strength and modulus of 20.43 MPa and 2.58 GPa respectively. Whereas fire retardant coated composites had shown 13.22 MPa, 0.89 GPa of flexural strength, and

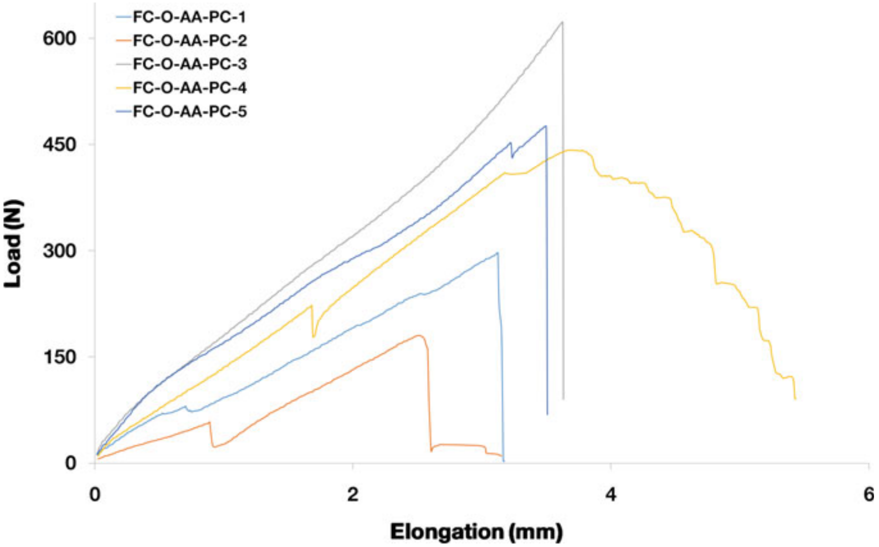
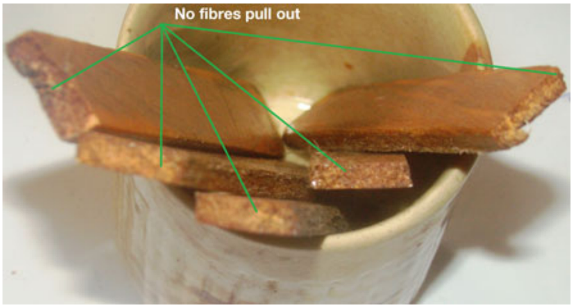


Fig. 2 Load elongation graph of fire retardant coated okra, agave Americana hybrid fibre reinforced phenolic composites under tensile test

Fig. 3 Tensile tested okra, agave Americana hybrid fibre reinforced phenolic composites specimens with a view from top—specimens' positioned in a cup



modulus respectively. The results of load vs. elongation of all the uncoated and coated fibre composite specimens were graphically shown in Figs. 7and 8 respectively. Reinforcement in fire retardant coated hybrid fibre composites reached to the bottom layer of the matrix and was observed from Fig. 9. During the bend test also uncoated fibre phenolic composites flexural strength and modulus were superior to coated fibre composites. Each specimen during the test was failed in its outermost layer which was anticipated. Though the specimens failed at the applied load during the flexural test, the misalignment of fibres was observed clearly in the prepared composites from Fig. 10.

Charpy impact strength against uncoated and fire retardant coated fibre reinforced phenolic composites was shown in Fig. 11. Here fire retardant coated fibre composites impact strength (3.9 kJ/m^2) was slightly higher than that of the uncoated fibre

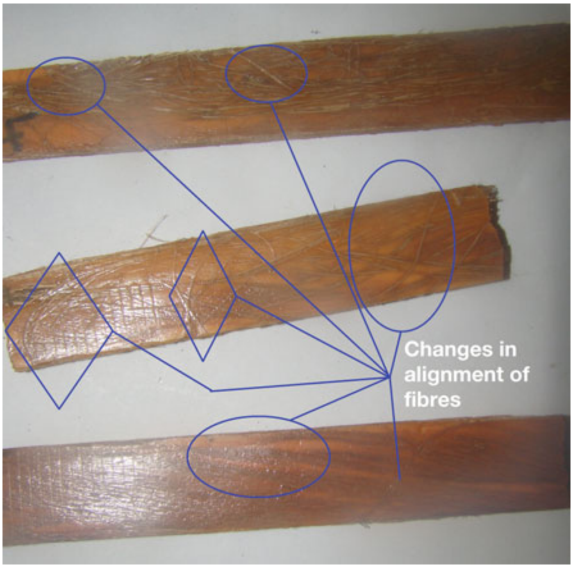


Fig. 4 Okra, agave Americana hybrid fibre reinforced phenolic composites specimens showing misalignment of fibres

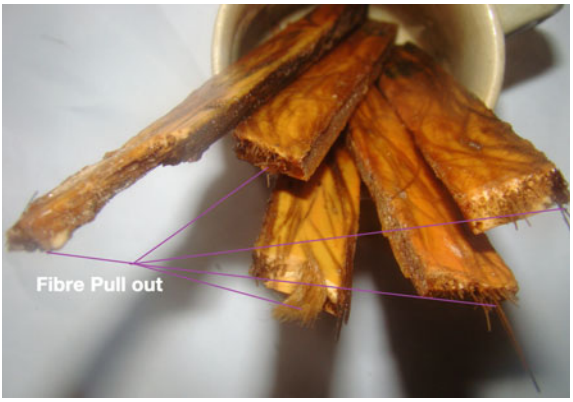
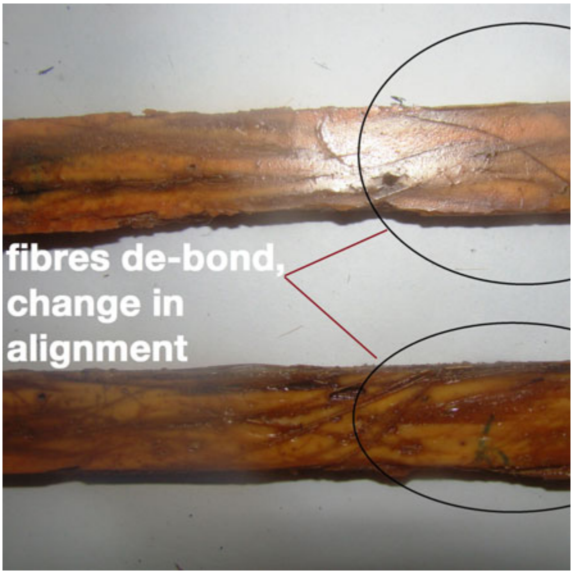


Fig. 5 Tensile tested fire retardant coated okra, agave Americana hybrid fibre reinforced phenolic composites with a view from top—specimens' positioned in a cup

phenolic composites (3.38 kJ/m^2). The type of failure observed in the uncoated hybrid phenolic composites specimens is 'C'. Notch cut on the specimen along with a clear fractured surface was recognized from Fig. 12. obviously, due to de-bonding fibre pull out after the impact test was showed by fire retardant coated phenolic composites and was shown in Fig. 13.

Fragile surface adhesiveness between the fillers, matrix, and cavities formed within the sample was responsible for a decrease in impact strength with an increase in the amount of filler APP resulted in a decrease in impact strength (Zhang et al. 2012).

Fig. 6 Impact of fire retardant coating on fibres: de-bonding from the matrix



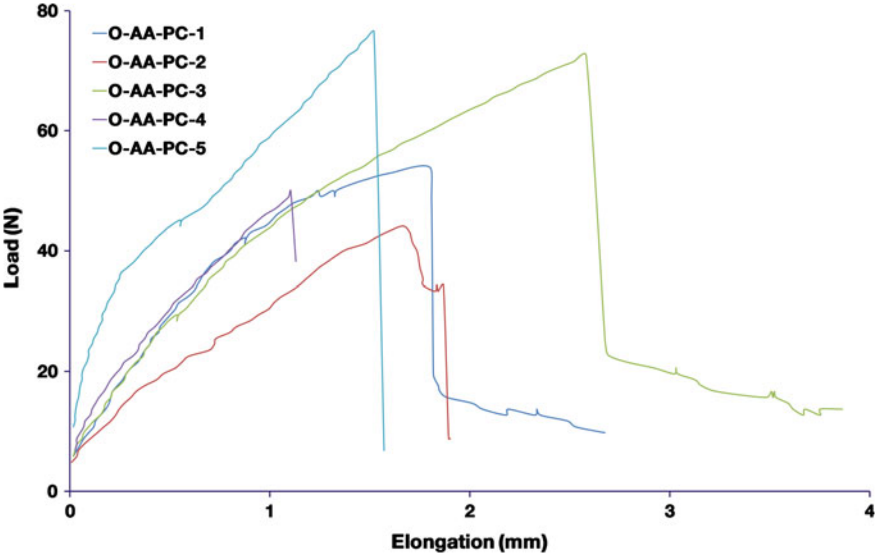


Fig. 7 Load elongation graph of okra, agave Americana hybrid fibre reinforced phenolic composites under three-point bend test

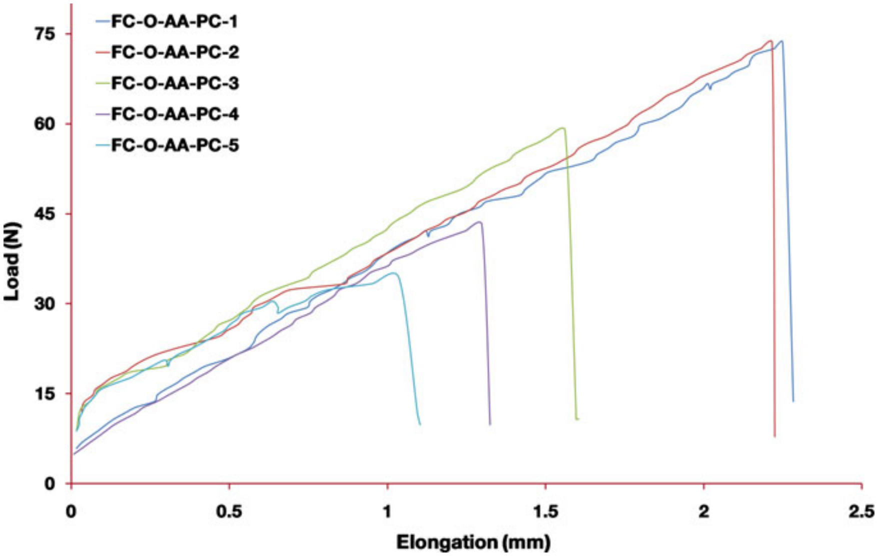


Fig. 8 Load elongation graph of fire retardant coated okra, agave Americana hybrid fibre reinforced phenolic composites under three-point bend test

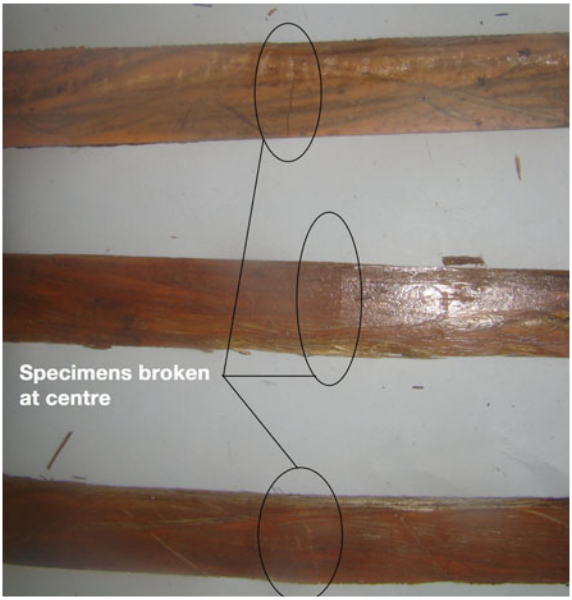


Fig. 9 Failure phenomena in three-point bend test of okra, agave Americana hybrid fibre reinforced phenolic composites

Fig. 10 Failure phenomena in three-point bend test of fire retardant coated okra, agave Americana hybrid fibre reinforced phenolic composites

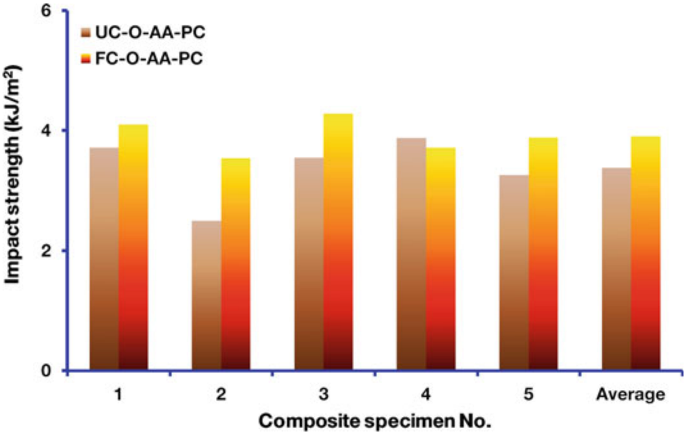


Fig. 11 Comparison in impact strength of uncoated and fire retardant coated okra, agave Americana hybrid fibre reinforced phenolic composites

4 Conclusions

Okra, agave Americana fibre reinforced phenolic composites were successfully prepared and tested for mechanical properties. But the fire retardant coating on the fibres had resulted in poor adhesion with the matrix used in this work and similar kind of results reported by the researchers were also compared. To the possible extent,

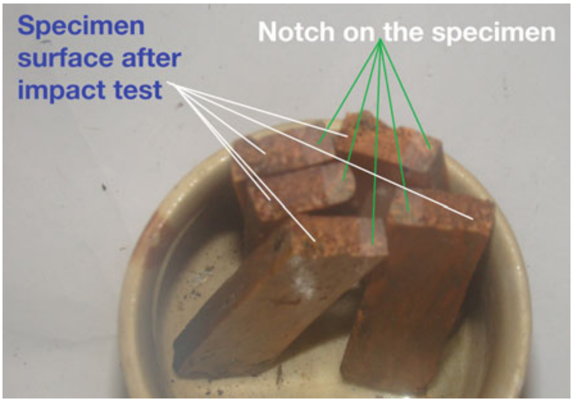


Fig. 12 Fracture surface of okra, agave Americana hybrid fibre reinforced phenolic composites

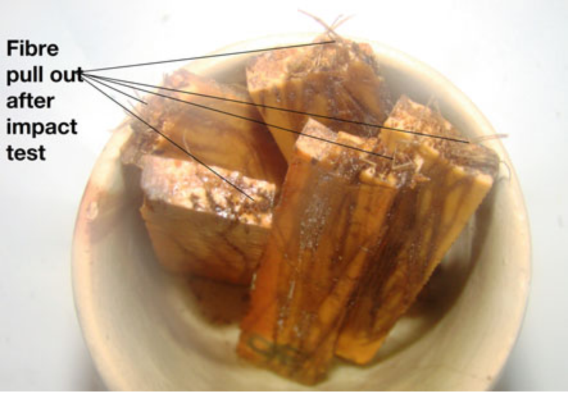


Fig. 13 Fracture surface of fire retardant coated okra, agave Americana hybrid fibre reinforced phenolic composites

the author had taken effort in the alignment of the fibres in the longitudinal direction through the resin was dark brown which creates blur/invisibility. Although it is very slightly more, fire retardant coated hybrid fibre composites had shown impact strength of 3.9 kJ/m^2 when compared with uncoated okra, agave Americana fibre composites.

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