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Phenolic Polymers Based Composite Materials

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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

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and nanocellulose fibres, thermosets and thermoplastics. Dr. Asim has published more than 35 international journal papers, three review papers, four book chapters and four conference proceedings.

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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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 its physical properties with hydroxyl groups presented in phenolic resin. In addition, this work also supports the ongoing research on bio-phenolic composites and phenolic bio-composites in order to develop green sustainable products.

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

1 Introduction

Phenolic resins continue to be the versatile system of resins, featuring either a stable, 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 is 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 remains as one of the predominant bonding agents which is used in various applications, for examples, bonding of wood, metals, glasses, and paper. It also surpasses most of other polymer resins in terms 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, glutaraldehyde, and glyoxyl). Selection of suitable polymerization parameters results in the optimum distribution of molecular weight and residual monomeric content which is 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, novolac resins are produced via polymerization in acidic medium with the use of less than equimolar of formaldehyde to phenol ratio. Several natural products such as lignin, tannin, CNSL and starch have been used to partially substitute 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.

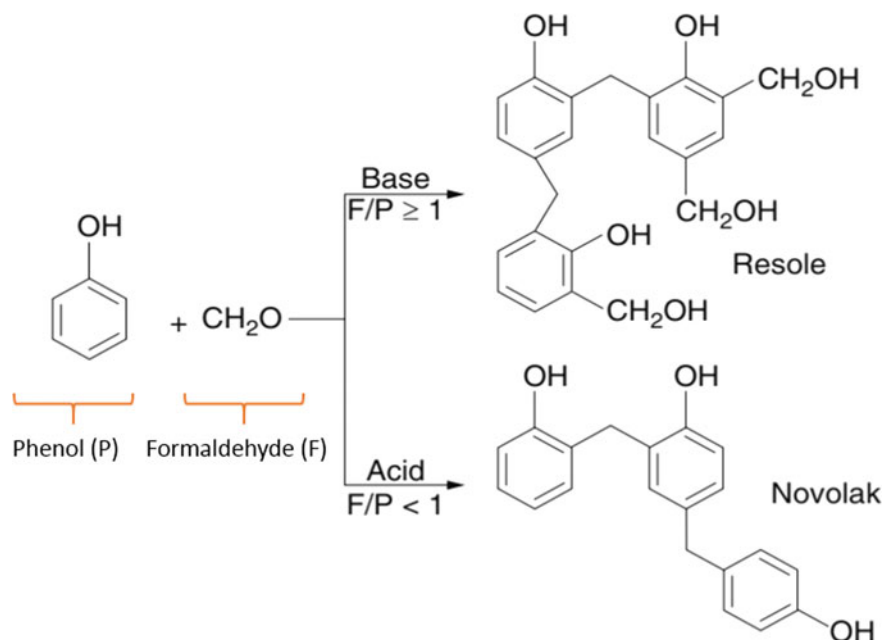


Fig. 1 Basic chemistry of structure of resole and novolak formation from Phenol Formaldehyde (Pilato 2010)

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

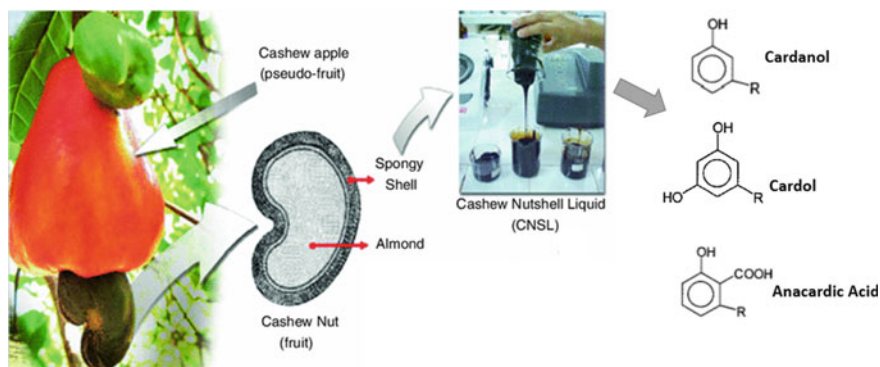


Fig. 2 Phenolic constituents extraction from CNSL adapted from (Balgude and Sabnis 2014)

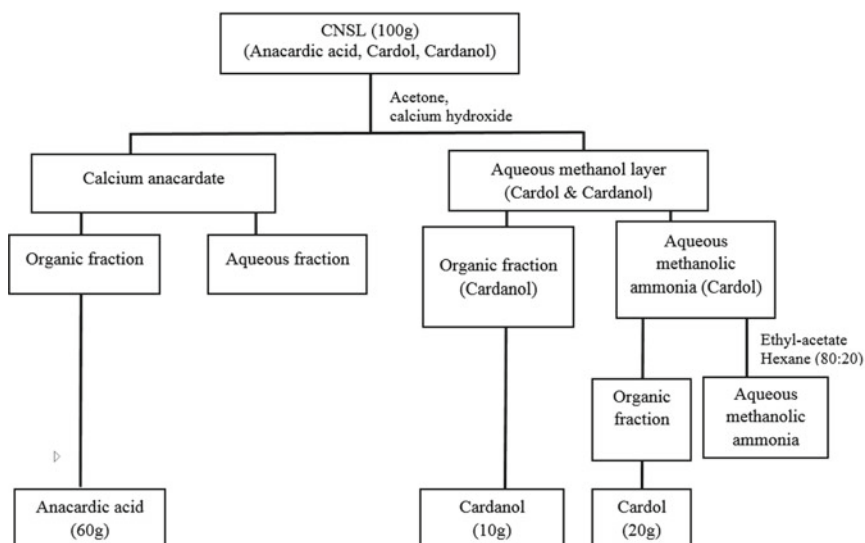


Fig. 3 Flowchart of preparation of CNSL-derived anacardic acid, cardol and cardanol

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).

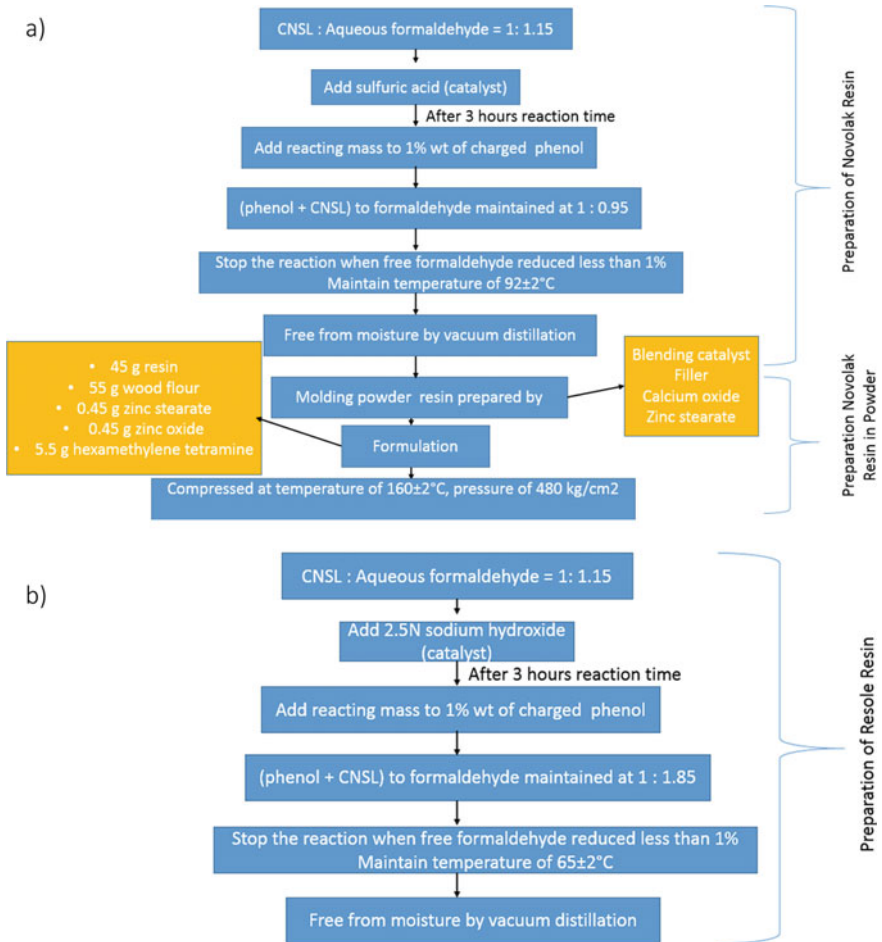


Fig. 4 Flowchart of preparation of a novolac and b resolite resins from CNSL

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 vinyl ester (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 its 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 its 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). Kozłowski 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 Władysław-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/m²) was higher than that of jute fiber (442 MN/m²). 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/cm²) was also higher than that of jute fiber-reinforced composite (3.04 J/cm²).

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/m². 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.

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

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 (CNSL)	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).

Mwaikambo and Ansell found that, because of the presence of lignin in untreated hemp fiber surface, the interfacial bonding with hemp surface and phenolic 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, $\tan \delta$, 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 (CO₂), 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 Władysław-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 determined 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-bis(pentabromo-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 show 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 reinforce 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 its 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.

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