1

RESEARCH ARTICLE

A Review on Phenolic Resin and its Composites

Mohd Asim[a], Naheed Saba[1a], Mohammad Jawaid[2a*,b], Mohammad Nasir[c], Mohammed Pervaiz[d] and Othman Y. Alothman[2b]

[a]*Laboratory of Biocomposite Technology, Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia;* [b]*Department of Chemical Engineering, College of Engineering, King Saud University, Riyadh, Saudi Arabia;* [c]*School of Industrial Technology, Universiti Sains Malaysia, 11800 Penang, Malaysia;* [d]*Centre for Biocomposites and Biomaterials Processing (CBBP), Faculty of Forestry; University of Toronto.33 Willcocks St., Toronto, ON. M5S 3B3, Canada*

Abstract: ***Background:*** Phenolic resins received greater attention from academic researchers and made prestigious status among all thermoset resins. Several effective attempts have made to explore different synthesis processes of producing phenolic in more useful and advanced way. Since the date of innovation, huge varieties of biocomposites and composites products have been produced for various applications.

Methods: Among all types of Phenolic resin related applications, Phenolic resin molding compounds have been used for highest utility products due to better mechanical strength, resistance, long-term reliability and cost effectiveness.

Results: Currently, modified phenolic resins are broadly used in the fabrication of synthetic/natural fiber reinforced composites in order to replace metals and ceramics on industrial level owing to its superior mechanical, thermal and electrical properties. This review article is intended to present an overview on the phenolic chemistry, curing process, structure, synthesis and its properties.

Conclusion: The present review article also aims to cover the reported research works on modified phenolic, and bio-phenolic resins, and their diverse industrial applications to support the ongoing research and development in green sustainable commercial products.

1. INTRODUCTION

Polymers are a large group of molecules or macromolecules, which are formed by the combination of many smaller molecules. These smaller units are termed as monomers and the group of monomers when is being converted into polymers. In fact, the word "polymer" has a Greek origin meaning "many members" [1]. Thermoset polymers characteristics like, mechanical properties, temperature resistance and they are perceived to be more durable. The thermoset polymers are expensive and have moderate production. Thermoset resin and thermoset reinforced composites are characterized by unique property, as they cannot be reshaped or reformed on curing due to the formation of highly cross-linked web [2]. Moreover, it cannot be re-cured by using temperature, pressure and light irradiation. A variety of thermosets such as melamine formaldehyde, urea formaldehyde, phenol formaldehyde, resorcinol formaldehyde, polyurethane, polyesters, and epoxies are known [3, 4]. In spite of the appearance of many types of thermosets, having high mechanical performance and thermal stability in some aspects, phenolic resins keep hold of industrial and commercial interest [5].

The higher flexibility for desirable design and better performance products for industries and research are met by phenolic high strength, high modulus, durability, and better thermal and chemical resistance [6, 7]. The focus on natural fibre-reinforced polymer composite materials is swiftly rising in terms of their manufacturing applications and elementary research [8, 9]. Until now several attempts were made by the researchers in order to explore different processing methods for phenolic thermosets. Moulding ,techniques such as compression molding, transfer molding and injection molding are widely accepted as the easiest methods for the processing of materials and end products [3, 10].

*Address correpondence to this author at the Laboratory of Biocomposite Technology, Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia; E-mail: jawaid_md@yahoo.co.in

2. PHENOLIC RESIN

Japan is well aware about phenolic resin since century, but during the technology period (1911-1930), European countries such as Germany and USA had started its domestic production. First commercial production of phenolic resin started by Rütgerswerke AG at Erkner near Berlin on May 25, 1910 [11]. During World War II, Japan enhanced its research on phenolic resin and come with fruitful results, to expand their application range [12].

In early stage, Beakeland achieved success in producing biocomposite with natural fibres and synthetic fibres materials reinforced phenolic resins composites, paper or cotton impregnated composites as well as wood fibre molding materials. Until now, plastic industries have contributed as important material industries by developing million tons polymeric materials including epoxy and phenolic resin and fibres reinforced biocomposites based on both thermoset and thermoplastic resins. Phenolic resins are being produced nearly 6 million tons/year worldwide and it is found to be one of the largest consuming resins, even of its certain limitations, like brittleness and shrinkage. Phenolic resin is well known as binder for a range of substrates like fibres, wood, glass substrate, metallic component, paper, rubber, etc. It displays better characteristics and is cost effective as compared to most of the other polymeric resin system. Phenolic resins have been deeply studied for commercial purpose and still there is no substitute of phenolic in stability and heat-resistance quality [13].

Several conferences were reported to admit the production of phenolic resins worldwide. In Belgium, Baekeland's birth place, the centennial conference commemorating the ''Heat and Pressure'' patent of 1907 occurred in 2007. In 2009, conference held in Berlin on thermoset 2009, the first production and sale of phenolic resin to Siemens that was produced in Erkner, Berlin. In 2010 china held SAMPE centennial conference in Shanghai to celebrate the huge production of phenolic resins in Germany in May of 1910 and in October 1910 in US.

In 2011, Japan held a conference Baekeland 2011 to acknowledge the centennial celebration for the production of phenolic resins in Japan [14]. Many researchers [15, 16] reported that phenolic resins are capable to fulfil many desirable characteristics, such as superior mechanical strength, heat resistance, dimensional stability, as well as, high resistance against various solvents, water and acids. Moreover, phenolic resins are naturally flame resistant and generate less smoke on ignition, in comparison to epoxies [17].

Phenolic resin cannot substitute epoxies and polyimides which are giving very well performance in advanced engineering areas. But phenolic based composites still find a huge market in thermo-structural application in the aerospace industry due to good heat and flame resistance, excellent ablative properties and low cost [11]. A huge amount of phenolic resins are used to apply in coatings, adhesive, composite wood materials, industry laminates, paper impregnation and reinforced by fibres to make high performance composite products. Phenolic resins are quite prominent polymer among composite fields for structural stability and thermo-structural stability applications. Phenolic resins are applica-

ble for all kinds of thermoset applications but particularly they are suited in specific areas such as aerospace, as aerospace required high quality of thermo-mechanical performed components [11]. Both resole and novolac resins are cured on different temperature and optimum pressure during production to acquire a void free component [18].

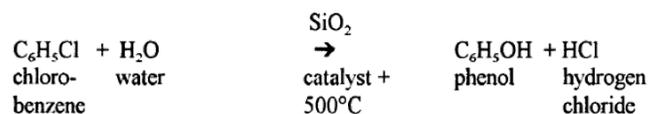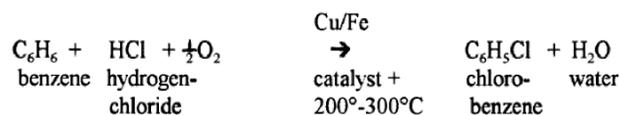## 3. STRUCTURE, CHEMISTRY, AND SYNTHESIS OF PHENOIC RESIN

Phenolic compounds are a family of aromatic compounds, and are directly bonded with hydroxyl group. Its character is different from alcoholic groups, it performs like weak acidic groups and easily dissolve in sodium hydroxide but insoluble in sodium carbonate. Moreover, phenol is easily dissolved in polar organic solvents, but lesser soluble in aliphatic hydrocarbons. Appearance of phenols is as a colorless solid like prism, and some are in liquid like alkylphenols. It changes its color when it comes in contact to air, or if it contains iron or copper [19]. Typical physical properties of phenolic resin are tabulated in Table **1** [19].

Phenol is extracted from the fractional coal tar and by different synthesis processes. There are many commercial processes that are being used in industrial synthesis process for making phenols. Some of the processes that are very common in industries such as Dow, Raschig and Cumene are given in detail in Fig. (**1**) [20].

Dow Process

$$C_6H_5Cl + NaOH \xrightarrow[4000\ psi]{300°C} C_6H_5OH + NaCl$$

chloro benzene sodium hydroxide → phenol sodium chloride

Raschig Process

$$C_6H_6 + HCl + \tfrac{1}{2}O_2 \xrightarrow[200°-300°C]{Cu/Fe\ catalyst\ +} C_6H_5Cl + H_2O$$

benzene hydrogen-chloride → chloro-benzene water

$$C_6H_5Cl + H_2O \xrightarrow[500°C]{SiO_2\ catalyst\ +} C_6H_5OH + HCl$$

chloro-benzene water → phenol hydrogen chloride

Cumene Process

$$C_6H_6 + CH_2=CHCH_3 \xrightarrow{AlCl_3\ catalyst} C_6H_5CH(CH_3)_2$$

benzene propylene cumene

$$C_6H_5CH(CH_3)_2 \xrightarrow{O_2} C_6H_5\ COOH \xrightarrow{acid} C_6H_5OH + CH_3COCH_3$$

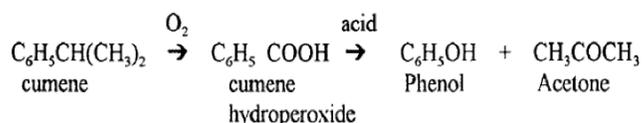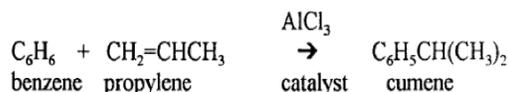cumene cumene hydroperoxide Phenol Acetone

Fig. (1). Synthesis processes.

3.1. Chemistry of Phenolic Resins

Currently, several types of phenolic resin are available such as resole resins, novolac resin and many more. These resins are closely related to the phenolic resins like benzox-

Table 1.   Physical properties of phenols [19].

Name		MW	MP °C	BP°C	PK$_a$25°C
Phenol	**Hydroxybenzene**	**94.1**	**40.9**	**181.8**	**10**
o-Cresol	1-methyl-2-hydroxybenzene	108.1	30.9	191	10.33
m-Cresol	1-methyl-3-hydroxybenzene	108.1	12.2	202.2	10.10
p-Cresol	1-methyl-4-hydroxybenzene	108.1	34.7	201.9	10.28
p-tert. Butylphenol	1-tert-butyl-4-hydroxybenzene	150.2	98.4	239.7	10.25
p-tert. Octylphenol	1-tert-octyl-4-hydroxybenzene	206.3	85	290	-
p-N onylphenol	1-nonyl-4-hydroxybenzene	220.2	-	295	-
2,3-Xylenol	1,2-dimethyl-3-hydroxybenzene	222.2	75	218	10.51
2,4-Xylenol	I ,3-dimethyl-4-hydroxybenzene	222.2	27	211.5	10.60
2,5-Xylenol	1,4-dimethyl-2-hydroxybenzene	222.2	74.5	211.5	10.40
2,6-Xylenol	1,3-dimethyl-2-hydroxybenzene	222.2	49	212	10.62
3,4-Xylenol	1 ,2-dimethyl-4-hydroxybenzene	222.2	62.5	226	10.36
3,5-Xylenol	1,3-dimethyl-5-hydroxybenzene	222.2	63.2	219.5	10.20
Resorcinol	1 ,3-dihydroxybenzene	110.1	110.8	281	-
Bisphenol-A	2,2-bis(4-hydroxyphenyl)propane	157.3	157.3	-	-

azines and cyanate esters. A simple description in Fig. (**2**) has shown reaction of phenol with formaldehyde under both basic and acidic conditions revealing versatile characteristics of phenolic resins. Molar ratio of formaldehyde to phenol with acid and base has its different contribution [21]. Resol resins can either be fluid, firm or in solution form, and are produced under basic state with a surplus of formaldehyde to phenol. Resol is heat reactive and it is catalyzed in specially ester, acid, base and thermal conditions.
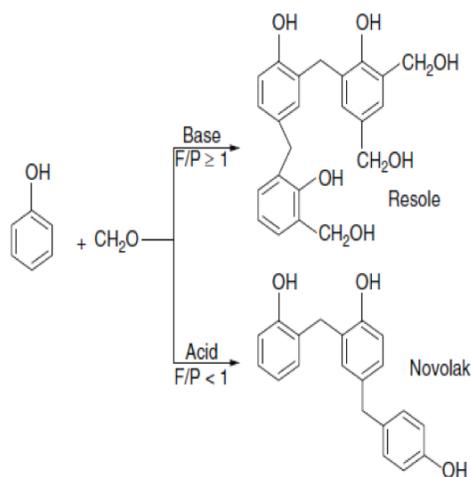

Fig. (2). Preparation of resole and novolak [14].

3.2. Synthesis of Phenoic Resins

Resole phenol-formaldehyde resin is a water soluble methylol (-CH,OH) bearing thermoset. The final thermoset material can initiate the curing process by just heating the resole in a mold above its gel point. The formed resole resins have reactive methylol and hydroxyl groups, when resol get temperature, it starts to make larger chain of molecules and cross link with methylene without the use or addition of a curing agent. The phenol-formaldehyde resin resinification reaction is a typical polycondensation reaction since water is given off as a by-product.

The polymerization process of phenol-formaldchydc novolac resin is carried out in the presence of an acid catalyst such as oxalic acid, sulfuric acid, hydrochloric acid, formic acid, and aromatic sulfuric acids. Sulfuric and oxalic acids are only in common use. In the ratio of phenol and formaldehyde, formaldehyde is use comparative low in ratio (phenol: formaldehyde 1:0.8) to delay the gel process. First stage of polymerization is carried out by heating the mixture for 2-4hours at reflux, with water removal at temperatures as high as 160°C. The second stage is crushing the cooled low-molecular weight molten intermediate and blend with hexamethylene tetramine (HEXA) (in powder form) to produce a molding compound. Heating the novolac resins to about 165°C in a mold, the HEXA decomposes to provide the formaldehyde necessary for the final curing. Novolac phenolic resins have an infinite shelf life under normal storage conditions [19].

The rising cost of adhesives raw materials and pressure of the future scarcity of petro-chemicals have led the research to investigate the use of renewable resource as natural products. Some natural materials like tannin and lignin are the most suitable substitutes of phenol in phenol formaldehyde [22]. M. Wang *et al*. [23] extracted lignin from white pine sawdust by using organosolv-extraction method with hot compressed ethanol-water co-solvent to produce resol-

type phenolic resins. Lignin is applied as replacement of petroleum-based phenol resin. H. Ishida [24] studied about Benzoxazine-based phenolic resin. He searched volumetric expansion upon polymerization through this class of phenolic resin. Molecular packing influenced by inter- and intramolecular hydrogen bonding are consequences of volumetric expansion, many other identified intensifying monomer and spiro-ortho compounds resins show high potential for both structural/engineering applications. R. Yadav *et al.* [25] worked based on cardanol, novolac-type phenolic resin developed by using response surface methodology (Fig. **3**) to optimized reaction conditions. When the cardanol was condensed with formaldehyde, Maximum extent of conversion was predicted.
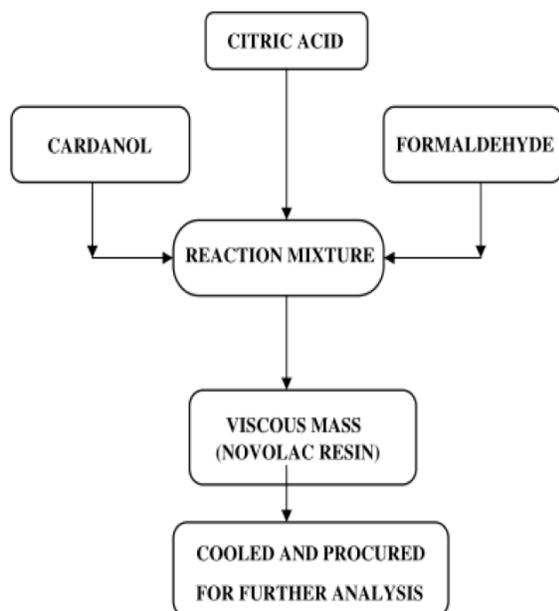

Fig. (3). Preparation chart of cardanol-based novolac resin [25].

T. Horikawa *et al.* [26] examined synthesized phenol–formaldehyde resins (PF) with the addition of organic substances such as ethylene glycol (EG), 1,6-hexanediol (1,6HD), polyethylene glycol (PEG), etc and PF's extracted carbonized materials. The influence of temperature on the carbonization, organic additive species, and the chemical addition percentage in synthesizing the PF resins on the pore formation of the carbonized PFs was also investigated. S. Serkar *et al.* [27] prepared a lignin modified phenolic resin by the replacement of phenolic with lignin at different weight percentage. 50% lignin replacement with phenol showed best result of adhesive strength, having temperature for curing lignin modified phenolic resin same to the pure phenolic resin (resol). Lignin modified phenolic resin showed better thermal stability than resol. M. Turunen *et al.* [28] studied on PFs resol resins and its modification. Lignin-based chemicals, urea, and starch were used as modifiers. In comparison of unmodified PF resin, wheat-starch-modified resins showed higher exothermic curing reactions. Bindu *et al.* [18] studied the novel Phenolic (novolac type) resins contain maleimide groups. Mixture of phenol and N-(4-hydroxy phenyl) maleimide (HPM) with formaldehyde was synthe-

sized by the polymerization method in the presence of an acid medium. They recommended low temperature reaction for prevention of the melt flow of resin during molding on high temperature.

4. CURING PROCESS OF PHENOLIC RESIN

Phenolic resins are in demand from several types of industries, as their different types of applications and products influence the way of producing materials. Phenolic resins are very much dependent of the properties of solvents. Researchers claimed that three phases which effect the cuing process during curing are formaldehyde and phenol ratio next, prepolymer formation or chain growth and last the crosslinking or curing process [29]. Selections of solvent affect the rate of dissolvability of phenolic resin and its chain reactions. The Phenolic chain reactions are fully associated with the curing process, quality and time. Though, chain reactions are matters of concern, phenolic resin could get very less research on curing process[30, 31] and most of the researches are associated with novolac resin.

Prepolymers are two types which can differentiate by their pH values. Novolacs exist in acidic pH region while resols exist in alkaline pH region. These types of resins consist of mono or polynuclear hydroxymethyl phenols (Fig. **4**). These are inactive on normal temperature but after reaching optimum temperature it start to react three dimensional cross linkage, and convert into insoluble and infusible polymer [32]. Mark-Houwink-Sakurada (MHS) equation determined to random and found value of α acetone, tetrahydrofuran, and aqueous 1N NaOH solution. It indicated enhancement in value of exponent α due to wide molecular weight distribution and resulting successive precipitational fractionation. In acetone, values of α are 0.5 and 0.28 for high ortho novolac and random novolac respectively. MHS value α of phenolic novolac type resin is much higher in comparison of branched one [33]. Due to many branches and reactive methylol end group, resol shows more complicated structure than novolac. Extensive research study was still going on resol chain reaction with different solvents as well as curing reactions. Though many researches on curing process have been done including gel time, temperature, hardener proportion, and resin pH [34, 35]. Many solvents like ethanol and acetone are being used for phenolic resin. While, methanol showed higher curing rate and good cross linkage density of phenolic resin [33].
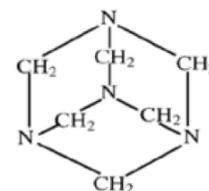

Fig. (4). Chemical structure of Hexamine-Hardener [36].

Raman spectroscopy is one of the suitable techniques for monitoring online curing progression of Phenolic resin in various conditions. Monni *et al.* [37] studied about curing process of phenolic resin on different degree of condensation on various temperature and time. Raman band changes its

character of intensity and function of curing time and temperature as spectral region. Although, curing of phenolic resins and its structure are very complex. Phenolic process has shown on the base of Raman band by revealing its intensity like at 1500– 1400 cm^{-1}, at 1300–1296 cm^{-1}, at 1050– 995 cm^{-1}, and at 950– 920 cm^{-1}.

The characteristic of Phenolic resin was shown in Fig. (**5**) with help of FTIR by using the literature reviews. These wavelengths were helpful to locate the components of the condensation reaction of phenol and formaldehyde. The reaction mixture spectra and comparative studies of phenol, formaldehyde and Phenolic resin have been shown in between the wavelength from 4000–650 cm^{-1} at every 3 minutes for a total of 180 minutes. The characteristic peaks of phenol diminished at 1594, 1498, 1224, 1170, 999.7, and 748.8 cm^{-1} with increasing reaction time and methylene and hydroxymethyl group enhance the absorbance bands. Some peaks revealed at 1594 and 1498 cm^{-1} corresponded to the C=C aromatic ring vibrations, other peaks at 1224 and 1170 cm^{-1} corresponded to the C-C-O asymmetric stretch and C-H in plane deformations.
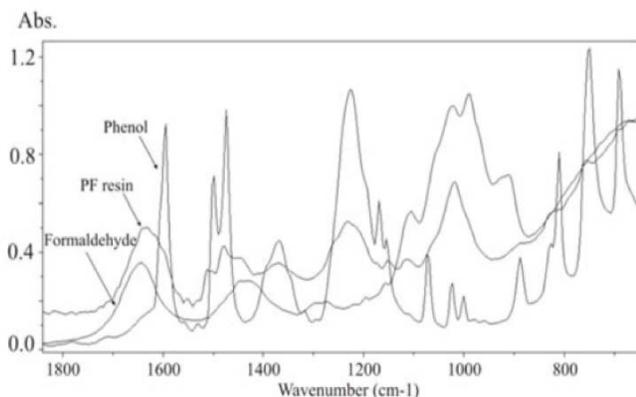

Fig. (5). FTIR image of curing process.

The peak at 1370 cm–1 corresponded to the phenol O-H in plane bend and also detected for phenol-formaldehyde resin. The width of the band at 1370 cm–1 revealed the presence of O-H than C-H or C-C bond. In the beginning of the process, the formaldehyde aqueous solution was added into the reactor, therefore the characteristic peaks of methylene glycol C-O, O-H, and C-H bends at 1108 cm–1, 1023 cm–1, and 992 cm–1 were observed in the first spectrum, respectively. After the reactor content heated to preferred temperature a sharp decrease of phenol and formaldehyde peaks was observed as a result of the reaction [32].

Occurrence of nano-clay (unmodified and modified montmorillonite) in phenolic resin also influences the curing reaction of biocomposites. The bonding can be easily seen by DSC and FT-IR. Acidic character of clay promotes oxidation reaction of resol resin, and benzophenone structure justified by the band at 1650cm-1, approved the presence of carbonyl behaviour [38]. Curing temperature and pH value under reaction condition of phenol and formaldehyde affect the characteristics of final products.

5. COMMERCIAL APPLICATION OF PHENOLIC RESIN

In commercial production, only plastics cover around 18-20% of the world production (approx.I00-120 million tonnes) such as Phenolic formeldehyde, epoxy resin, urea formaldehyde resins, melamine resin, furan, and unsaturated polyester resins as well as thermosetting polyurethane, acrylate, and silicone resins.

In Western Europe, distribution of thermoset resin such as phenolic, amino, epoxy, and unsaturated polyester resins proximately data are mentioned (Fig. **6**), the distribution is on the basis of the productions Figures (100 %) in Europe, such as 49 % urea resins, 22% Phenolic resin, 14% unsaturated polyester resins, 8 % epoxy resin, 6 % melamine resins, and 1 % furan polymers (based on furfuryl alcohol).

Phenolic resin has been commercialized by using large variety of applications and developments of new products for different purposes. There are many applications of phenolic resin based on products and components; however, the technical and industrial potential of this thermosets is far from fatigued.
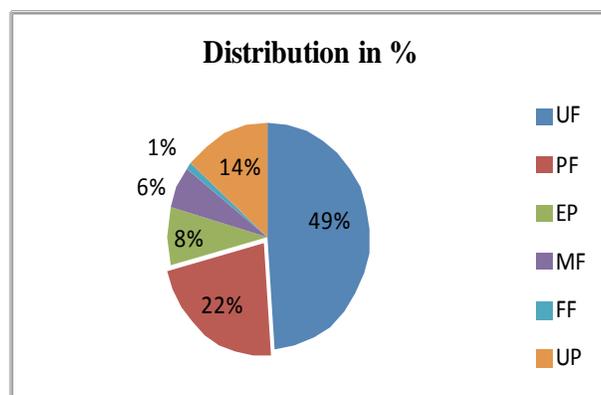

Fig. (6). Thermosets production in Europe.

In many areas, phenolic resins display a very important role in luggage carrying systems, electric appliance and components [39, 40] and in power production. Some fields of usage and type of thermosetting synthetic resin including, urea, unsaturated polyester, phenol-formaldehyde, epoxy resins and melamine are given in Table **2**, based on types and aspects in their application technology [41].

Phenolic resin products are widely accepted in automobile parts. Phenolic resins are known for heat resistant, very consistent and vey advance in hybrid technologies. Many Phenolic components are used in automobile components, and additional expansion of applications is expected. Mechanical and structural parts of automobiles are used fibreglass reinforced Phenolic composites for primarily uses,

Because, these composites are superior in dimensional constancy, mechanical strength, chemical resistance and heat resistance among other factors, and are more commercial than thermoplastic composites.

Table 2.   Fields of application for thermosets selection.

Fields of use	Synthetic resin				
	UF	PF	UP	EP	MF
Automotive construction and accessories		x	x		x
Aircraft construction		x	x	x	
Wood materials processing	x	x			
Building industry (above ground, subterranean, streets		x	x		x
Mechanical engineering and equipment construction	x	x	x	x	x
Abrasives industry	x	x		x	
Foundry industry, refractories, steel	x	x		x	
Paint and adhesives industry	x	x	x	x	x
Electrical and lighting industry	x	x	x	x	x

Natural fibre reinforced phenolic resins are being rapidly used in fire retardant areas, and are found suitable to replace metal because of its light weight and low cost abilities shown in Fig. (**7**).

Fig. (7). Phenolic resins applications [12].

Phenolic resin products are light in weight and are of low cost, hence grabbing more attention from automobile producers and for additional functions (Fig. **8**). Certain modification in phenolic resin has been made to achieve required characteristics for specific applications, such as silicone/phenolic modified resins, rubber/phenolic modified resins, and aromatic/Phenolic modified resins. These materials showed various improved properties such as high mechanical strength, high dimensional stability, high creep resistance, abrasion resistance, heat resistance, and resistance to various chemicals.

It can be used in producing cooling pumps, and different components for the supporting machine pulley, brake pistons, and many more. In addition, long fibre reinforced phenolic composites skill and heat indulgence technology developed components in blanket parts, high-pressure pump components, fuel injector components, EGR components (exhaust gas recirculation), and fuel pump components.

6. ADVANTAGE OF PHENOLIC OVER THERMO-PLASTIC

Thermoset resins are extremely cross-linked resins that are known for its stability by using temperature, pressure, and/or light irradiation. Thermoset materials are highly cross-linked dense materials, useful for high-mechanical and physical strength materials for industrial purposes, with high mechanical modulus and strength, physical durability and stability towards thermal stress and chemical resistance [2, 4]. Interestingly, phenolic resins have individual advantages compared with other conventional thermoplastic or thermoset resins, including [36, 42, 43, 44].

- Exceptional adhesive properties
- High rigidity
- Excellent dimensional stability at high temperatures
- Excellent thermal properties
- Excellent mechanical strength and high durability
- Excellent flame resistance
- Heat insulation properties
- Highly cross linked thermoset
- Efficiency in glue-bond formation
- Chemical stability

7. GREEN OR SUSTAINABLE PHENOLIC RESIN

Researchers draw their efforts to make green sustainable chemistry to indicate growing worldwide environment concerns, based on deposition of plastics wasted materials and plastics recycling procedure. Even though, phenolic resins are being synthesized from natural resources such as trees and plants to address the growing concerns about expected fuel resource exhaustion. The three most general methods of recycling are chemicals recycling (feedstock recycling), material recycling and thermal recycling. Recycling methods have both strengths and weaknesses; usage of method should be chosen according to the principle or circumstances.

Fig. (8). Products by Phenolic molding compounds and Phenolic resin [12].

In the case of thermoset polymers such as epoxy, phenolic etc, there are no researches and industries recycled chemical on large scale. Goto *et al*. [45] invented an advance chemical recycling process that is mainly focused phenolic resin yields for the first time. This chemical recycling process is considered as nearly 100% recovery of used resins (linear structure), and are produced by using the water-phenol mixture in either new supercritical or sub-supercritical condition as the reacting solvent. The process takes 10-20 min of reaction time to complete decomposition. Recycled resin added with hardener and heated up to re-stored rigid networked configuration of phenolic resin. The recycled resin has novolac-type phenolic resin structure. The molecular weight of recycled resins smaller and curing time is lesser as compared with the general novolac type phenolic resins, [12]. In mechanical recycling, phenolic materials were crushed into powder form. Mechanical process and reused as fillers or additives in new materials effects to flow ability, gel time, and mechanical properties of the materials. In thermal recycling, coals are replaced to phenolic waste materials for using as alternative of solid fuel. It is combustible and has good calorific value, and most of the industrial wastage of phenolic resins has been used in cement plants. Therefore, recycling methods are desirable and should be established with the evaluation method of quantitative and objective [46].

Green Phenol Technology Research Association established with Research Institute of Innovative Technology for the Earth (RITE) have been working together to conduct research into the manufacturing process of phenol (green phenol) to counter global warming and oil resources. Growth-independence bioprocess based on genetic engineering obtained green phenol from non-edible biomass. Some non-edible plant resources such as rice straws and corn stems are being converted into green phenol by using sugar mixture (saccharification) and fermentation technique. This process saves energy and the synthetic processes are also ecofriendly, to make green environmentally polymers [47].

8. MODIFICATION OF PHENOLIC RESIN

Phenol–formaldehyde resol resins were modified by using lignin-based chemicals such as starch, and urea. Profound effects on the structures of the resins of the reactions and molar masses of modifiers at addition stage have been observed. The modifier corn starch and lignin accelerated condensation as compared to resin without a modification reagent. Enhanced molar masses and high ratios of methylene bridges to the sum of free ortho and para aromatic groups verify modification of resins [28]. Ammonium lignin sulfonate (30 wt%)) as filler in the formulation of lignin–phenol–formaldehyde resol resins improved thermal stability than PF commercial resin [48]. Zhang *et al* [49] modified the phenol–formaldehyde resin by copolymerization, by producing four types of bio refinery residues such as the ethanol, the butanol, the xylitol and the lactic acid residues. Bioethanol bio-refinery excess exhibited high reactivity due to large amount of hydroxyl group, and lower content of polysaccharide, so it provided more activity and greater potential to partially substitute phenol in PF resin comparing with other residues. Matsushita *et al*. [50] studied that surface characteristics of phenol-formaldehyde resin with lignin enhance consumption of lignin as a sustainable organic materials. In other research [51], on the characterization of lignin to integrate into phenolic resins such as phenol–formaldehyde by using technical lignin such as kraft, lingo-sulfonate, soda-anthraquinone, organosolv, and ethanol process lignin, characterized by elemental analysis, functional groups analysis, molecular weight distribution, Mannich reactivity and other techniques. Reactivity of lignin by Mannich reactivity and UV-spectroscopy showed that Kraft and soda-anthraquinone lignins were more reactive toward modification than the other studies. These lignins act as better bio raw materials for lignin-based phenol–formaldehyde resins.

Ionic liquids have also been tested as reactant agents or co-extenders in the reaction to phenolic or connected generating modified phenolic resin. By the polymerization of benzoxazine in the existence of ionic liquid, hybrid prepared of polybenzoxazine (PBa) and ionic liquids (ILs), as 1-butyl-3-methylimidazolium tri-fluoro-methane-sulfonate (BMICF3SO3), are produced. Hybrid layer found 20 wt% BMICF3SO3 content had much better mechanical strength and elongation at break in comparison of pure PBA film. DMA and TGA revealed, the hybrid film had higher Tg and degradation temperature [52].

Preparation of IL-phenol resin hybrids by polymerization of phenol and formaldehyde followed by immediate crosslinking between phenol polymer chains using para-toluene sulfonic acid in ionic liquid is an ''in situ'' method [53]. In this procedure, high ion-conducting ionic liquid of 1-ethyl-3-methylimidazolium bis(tri-fluoro-methane-sulfonyl) amide [EMI][TFSA] with a value of 8.4x10-3 S cm-1 at 30°C results highly ion-conductive ionic liquid-phenolic resin hybrids. Resulted hybrid film was softer, elastic and significantly dissimilar than pure phenolic resin. Conductivity value of phenolic film containing 20 wt% showed 1.0x10-3 S cm-1 at 30°C, and it is relatively higher as compared to the value of [EMI][TFSA]. Thermal stability was also much higher than pure phenolic resin. A.V. Itter *et al*. [54] studied on the reaction of novolac with phenylene bisoxazolines (PBOs) to introduce in aerospace and electronics industries. Mechanical and thermal properties obtained on curing at 140°C for 2 h with a Tg of 195°C. The advance resin provides high compressive and shear strength properties with fibre reinforcement, which shows a great possibilities to initiate superior technology for interior aircraft applications [14].

9. FIRE RETARDANT PHENOLIC RESIN

Origin of most of the polymers is petroleum-based, due to this, they are highly flammable/combustible [55] On the basis of fire resistant, researchers [56, 57] compared some polymers and made order of that polymers such as Phenolic > Polyimide > Bismaleimide > Epoxy > Polyester and vinyl ester.

Flammability properties of the composites are totally different from the component materials and its composites structure. Flammability properties depend on type of matrix polymer, and the type of fibre separately and also adhesion between the fibres and the matrix [58, 59]. During burning, char formation of matrix polymer shows its flammability characteristics such as Phenolic resin; a highly cross-linked polymer, polyvinyl chloride; cross-linking process occur during the decomposition process, and casein, a protein-based biopolymer, form char during combustion [59, 60]. Formation of char is exhausted of possible flammable volatiles and it work as heat obstacle between the heat source and lower layers of the polymer. Blend of resin improve poor flame retardant value with polymers having good flame retardant value [61]. Unsaturated polyester resin blended with a phenolic resin, blended resin improved heat resistance and reduce heat releasing smoke and toxic gas emissions [62, 63].

10. PHENOLIC COMPOSITES

In fibre reinforced composites, the 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 [64]. Natural fibre phenolic composites show various sport applications such as golf clubs and tennis rackets to jetski, and also in aircraft, missile, spacecraft and marine components. They are also used in transportation, chemical equipment and machinery construction, electrical and electronics equipment, fishing rods and storage tanks. Carbon fibres reinforced phenolic composites are highly acceptable to produce as a responsible component in various industries

and are also applicable on high temperature [65]. Mechanical properties of the composite from phenolic resin and carbon fibres with length of 25mm are, flexural strength, 247 MPa; modulus, 27.6 GPa; impact resistance 110 and 91 KJ/m2 justified the application of this composite material in the automotive, leisure, [44].

Sulaiman *et al.* [36] studied about the effect of hardener on mechanical properties of carbon reinforced phenolic resin composites. 15% hardener in composite has showed highest flexural strength, tensile strength and hardness. The tensile strength, flexural strength and hardness for 15% hardener are 411.9 MPa, 51.7 MPa and 85.4 HRR respectively. Research study elaborated its application in manufacturing of aerospace and automotive components and in other leisure industries.

D.C. Wang *et al.* [66] studied about improving thermal stability by making biocomposite with reinforcement of boron and clay with phenolic resins. Boron-containing phenolic resin/clay (montmorillonite) nanocomposites were prepared using in situ polymerization of resol-type phenolic resins, and are characterized by transmission electron microscope (TEM), showing partially exfoliated clay platelets, while, thermo gravimetric analysis (TGA) showed thermal decompositions and residual weight at 790 °C of cured boron-containing nanocomposites. The residual weight was much higher than only clay with phenolic nanocomposite.

Park *et al* [76] studied about phenol formaldehyde-based resole thermosetting resin reinforced ceramic-based fillers(SLG) composite, to investigate fatigue behavior. Fatigue behaviors and viscosity tests revealed that the optimal addition of SLG is (35wt %), and its addition reduces the cost by 50% but fracture toughness was reduced only by 20% as compared to the pure phenolic resin; however, fire resistance of resin extremely increased.

In other research study, the NaOH treated hemp fibres reinforcement cashew nut shell liquid polymer composite manufactured by hand lay-up compression moulding technique [70]. Two types of fibre arrangement have been used in composites, nonwoven fibre mats and unidirectional fibre mat. Some testings such as tensile properties, porosity and fracture surface topography of the composites were analyzed. The unidirectional fibre composites exhibited the best mechanical properties and lowest porosity. Except for untreated nonwoven hemp composites, enhancement of moulding pressure resulted in a decrease in the mechanical properties [70]. In other findings, sisal fibers were modified by two different methods; alkali solutions with various NaOH concentrations and bleached with sodium hyplochlorite NaClO/H2O (1:1) at 60–75°C, are reinforced in phenolic matrix composites derived from cashew nut shell liquid (CNSL). Sisal composite treated with 5% in 12°C improved its thermal stability in compare of untreated fibre composite [71]. Additionally, oil palm fibres reinforcement in phenol formaldehyde resins also been studied, to explore the effects of treated fibers on the mechanical performance of phenolic composites [72]. Scanning Electron Microscopy (SEM) and IR studies revealed that treated fibres reinforced phenolic composite showed excellent impact properties, reduced hydrophilic character of fibre and strong covalent bond formation between fibre and polymer [72].

11. HYBRID PHENOLIC COMPOSITES

Hybrid composites are proved to create equilibrium consequence within the fibres incorporated in the composite materials [79]. Reinforced fibre may be either natural fibres or synthetic fibres. The amalgamation of renewable and synthetic materials emerges to be the excellent structural materials, in order to substitute the costly and non-renewable synthetic fibre [80]. Structural natural fibre hybrid composites, proposed for indoor use, are usually made by low-cost adhesive which is unable to sustain moisture, while outdoor grade composites are composed of thermosetting resin and less hydrophilic fibres, that is higher in cost but stable to moisture. Physical and mechanical performance of structural natural fibre composite can be improved further by improving the properties such as impurities and hydrophobic nature of natural fibre especially agro-based fibre using chemical modification techniques [81, 82].

In hybrid composite, both agricultural and wood based [83, 84, 85] and wastes [86] as reinforcement have shown promising effect on the upgrading of mechanical properties of resulting hybrid composites. Reported research on composites and hybridization of natural/natural fibres, natural/synthetic fibres and synthetic/synthetic fibres in a single matrix are tabulated in (Table **3**). Mechanical properties (tensile, flexural, and impact) of jute/cotton reinforced novolac type phenolic hybrid composites were investigated as a function of fibre orientation and roving/fabric characteristics [87]. Results of the hybrid composite were strongly inclined by test direction and roving/ fabric characteristics. Glass fibre and oil palm EFB fibre reinforced phenol formaldehyde hybrid composite was also investigated by other researchers [16]. Performance of the composites was found to get improved by the glass fibre addition. When, volume fraction of oil palm EFB fibre increases density, hardness and impact strength of the resulting hybrid composite reduced. Glass fibre reinforced phenolic hybrid composites showed better values compared to oil palm composites. In other research, the advantages of combining high-modulus glass fibres with banana fibre reinforced phenolic resoles hybrid composite to develop high-performance, cost-effective, lightweight hybrid composites, were investigated [88]. Moreover, the mixed hybrid composite of both fibres, having glass fibre mounted in periphery as it is hydrophilic, and banana fibres in middle of composite, showed much higher tensile strength nearly 62.9% than for a bi-layer composite of both fibres. They also studied environmental durability properties of banana/glass hybrid composites [89, 90].

Kumar at al [91] investigated mechanical properties of coir/glass fibers based hybrid composites, showing that tensile properties increased with increasing fibre content. The effect of surface modification of fibres on the mechanical properties was also studied. Alkali treatment based coir composites showed improvement significantly. Varada Rajulu and Devi [92, 93] investigated mechanical properties such as tensile, compressive and flexural properties of glass/ridge gourd/phenolic hybrid composites. In other studies, mechanical properties of alkali treated sisal/glass reinforced phenol formaldehyde (PF) hybrid composites have been studied [94]. Researchers elaborated that hybrid composites reinforced in PF resulted composites having encouraging mechanical and water absorption properties [95].

Table 3.   Reported study on natural/synthetic fibre reinforced phenolic hybrid composite.

Type of Phenolic Resin	Type of Reinforcement	References
Hybrid		
Phenol formaldehyde	Banana fibres /Glass fibres	[42]
Phenol formaldehyde	Kenaf iber/ Flax fiber	[67]
Resol type phenolic resin	layered silicate	[68]
Resol type phenol-formaldehyde	Cotton,/Sisal /Sugarcane fibres	[69]
Phenolic Resin	Glass/Oil palm fibres	[16]
Biocomposites		
Phenol-based cashew nut shell liquid (CNSL)	Hemp fibre	[70]
Phenol-based cashew nut shell liquid (CNSL)	sisal fibers	[71]
Urea Formaldehyde	Kenaf Fibre	[43]
Phenol Formaldehyde	Oil Palm Fibre	[72]
Phenolic Resin	Jute fibre	[73]
Synthetic fibres		
Phenolic matric	Vapour grown carbon fibre	[74]
Phenolic resin	Carbon fibers	[44]
Phenol Formaldehyde	E-spheres	[75]
Phenolic Resin	Ni-Plated Carbon Fiber	[76]
Phenolic resin	Silica	[77]
Boron-containing Phenolic resin	Nano clay	[78]
Phenolic Resin	Carbon fibre	[36]

12. APPLICATION OF FIBRE REINFORCED PHENOLIC COMPOSITES

Fibre-reinforced phenolic composites globally accepted since last century. Among all renounced thermosets, as a resin, phenolic resin works better than epoxy and polyester resins In 1930s, commercially natural fibres reinforced polymer composite used in aero research [98]. First, flax fibre/phenol formaldehyde matrix composite was fabricated for aircraft construction. Development of natural fibres reinforced composite was increasing dramatically; however, in 1940s, glass fibre reinforcement for plastic laminates produced and increased use in airplanes and boats. Phenolic composites showed higher tensile and flexural properties due to the high interfacial bonding in phenolic composites [97]. Regeneration of natural fibres as reinforced Phenolic composites have a very good status in technical applications of industries [98, 99].

Long fibre reinforced phenolic composites are suitable to automobile parts, the strength obtained by distributing the tensile strength by the specific gravity, exceeds that of steel and aluminium. Long-fibre reinforced phenolic compounds have the potential for new and broader applications as resin materials to replace metals. The fibre orientation and the methodology applied for the fabrication of composites play important role in improving the mechanical strength. Potential applications of long fibre reinforced phenolic composites are aircraft parts and industrial machine parts including automobile [12]. Phenolic reinforced composites are found as resistance to ignition, low smoke generation, high temperature resistance and strength, these characteristics are widely accepted in aircraft, transportation and construction industries [100].

Phenolic resin based composites show extensive functional applications from past decades, such as engine parts, electronic instrumentation enclosures, and pump-related component. Phenolic composites are also known as binders for frictional material, such as brake linings, disc pads, clutch facing, brakes pads and its components due to high strength, high heat resistance, high flexibility, vibration-damping properties, and water-repelling properties.

Fig. (**7**) and Fig. (**8**), clearly show versatile usage of phenolic products. Phenolic composites are being used in many applied fields such as innovative packaging, mechanical apparatus, composite wall and flame resistant materials.

Fig. (9). Several types of aircraft applications [101].

Natural fiber-reinforced composites are widely accepted in automotive and aerospace industries, due to reduction in weight and lesser density which reduces vehicle weight; to replace steel and aluminium. In future, fibre reinforced composite will reach approximately 15% weight of automobile weight [102, 103]. Natural fibre reinforced phenolic rein composites find markets in thermo-structural applications in the aerospace shown in Fig. (**9**) and railway industries, because of its good heat, flame resistance, excellent ablative properties and low cost. Many innovative research, based on phenolic products and its applications in various fields continue the potential to cope with the ever-changing requirements and challenges of advanced technology [5, 41, 104].

CONCLUSION AND FUTURE PERSPECTIVE

Phenolic thermosets polymers provide high mechanical performance to keep hold of industrial and commercial interest, and exceed to most of the other polymeric resin systems. The structure of phenolic resin and its curing process is very complicated and found to be depending on temperature and the curing time. Phenolic resins use for various types of materials such as fibre, wood, glass, metal, paper, rubber, etc. owing to their lower cost and characteristics feature. The modification of phenolic resin is critically important to improve its brittleness, toughness, wear, and compatibility with natural fibres and to widespread its practical applications in many areas of outdoor, construction buildings, engineering, and technology sectors. Moreover, it seems that fibre reinforced phenolic composites gaining more attention from the academicians and industrialists globally for the manufacture of high-performance engineering materials with fire resistance capacity. The introduction of natural fiber reinforcement in the epoxy matrices as an alternative to metallic parts, results in lower density, weight, and cost, accompanied with the better renewability and biodegradability. Natural fiber-reinforced phenolic composite displayed better physical, mechanical, and thermal properties for manufacturing of high-performance automotive and aerospace products and their components. This review article provides valuable literature information for further investigations on phenolic resin, its chemistry, curing process and its derivatives. In this review, we elaborated study of novel natural/synthetic fibre reinforced phenolic composites as compared with other thermosets composites. The future work would be the production of innovative phenolic and bio-phenolic resins and its curing characteristics. Green composite materials with biodegradable phenolic resin possessing higher physical, mechanical and thermal properties will enhance attention span for both structural and non-structural applications.

LIST OF ABBREVIATIONS

MP	=	Melting point
MW	=	Molecular weight
BP	=	Boiling point
PK_a	=	Acid dissociation constant

REFERENCES

[1]   Saldívar-Guerra, E.; Vivaldo-Lima, E. Introduction to Polymers and Polymer Types. *Handbook of Polymer Synthesis, Characterization, and Processing.* **2013,** pp. 1–14.
[2]   Raquez, J. M.; Deléglise, M.; Lacrampe, M. F.; Krawczak, P. Thermosetting (Bio)materials Derived from Renewable Resources: A Critical Review. *Prog. Polym. Sci.* **2010,** *35,* 487–509.
[3]   Saldívar-Guerra, E.; Vivaldo-Lima, E. *Handbook of Polymer Synthesis, Characterization, and Processing*; **2013.**
[4]   Naheed saba, Mohammad Jawaid, Othman Y Alothman, Hassan, M. P. and A. H. Recent Advances in Epoxy Resin,natural Fiber-Reinforced Epoxy Composites and Their Applications. *J. Reinf. Plast. Compos.* **2015,** 1–24.
[5]   Nair, C. Advances in Addition-Cure Phenolic Resins. *Prog. Polym. Sci.* **2004,** *29,* 401–498.
[6]   Gourichon, B.; Deléglise, M.; Binetruy, C.; Krawczak, P. Dynamic Void Content Prediction during Radial Injection in Liquid Composite Molding. *Compos. Part A Appl. Sci. Manuf.* **2008,** *39,* 46–55.
[7]   Guilleminot, J.; Comas-Cardona, S.; Kondo, D.; Binetruy, C.; Krawczak, P. Multiscale Modelling of the Composite Reinforced Foam Core of a 3D Sandwich Structure. *Compos. Sci. Technol.* **2008,** *68,* 1777–1786.
[8]   Abdellaoui, H.; Bensalah, H.; Echaabi, J.; Bouhfid, R.; Qaiss, A. Fabrication, Characterization and Modelling of Laminated Composites Based on Woven Jute Fibres Reinforced Epoxy Resin. *Mater. Des.* **2015,** *68,* 104–113.
[9]   Kozłowski, R.; Władyka-Przybylak, M. *Flammability and Fire Resistance of Composites Reinforced by Natural Fibers*; **2008**; Vol. 19, pp. 446–453.
[10]   Saba, N.; Jawaid, M.; Alothman, O. Y.; Paridah, M.; Hassan, A. Recent Advances in Epoxy Resin, Natural Fiber-Reinforced Epoxy Composites and Their Applications. *J. Reinf. Plast. Compos.* **2015,** 0731684415618459-.
[11]   Qureshi, S. P.; Resins, G. Phenolic Resins. **2001,** *21,* 120–125.
[12]   Hirano, K.; Asami, M. Phenolic Resins — 100 Years of Progress and Their Future. *React. Funct. Polym.* **2013,** *73,* 256–269.

[13]   Wang, M.; Wei, L.; Zhao, T. Cure Study of Addition-Cure-Type and Condensation–addition-Type Phenolic Resins. *Eur. Polym. J.* **2005**, *41*, 903–912.

[14]   Pilato, L. Reactive & Functional Polymers Phenolic Resins : 100 Years and Still Going Strong. *React. Funct. Polym.* **2013**, *73*, 270–277.

[15]   Trindade, W. G.; Hoareau, W.; Megiatto, J. D.; Razera, I. a T.; Castellan, A.; Frollini, E. Thermoset Phenolic Matrices Reinforced with Unmodified and Surface-Grafted Furfuryl Alcohol Sugar Cane Bagasse and Curaua Fibers: Properties of Fibers and Composites. *Biomacromolecules* **2005**, *6*, 2485–2496.

[16]   Sreekala, M. S.; George, J.; Kumaran, M. G.; Thomas, S. The Mechanical Performance of Hybrid Phenol-Formaldehyde-Based Composites Reinforced with Glass and Oil Palm Fibres. *Compos. Sci. Technol.* **2002**, *62*, 339–353.

[17]   Saba, N.; Jawaid, M.; Paridah, M. T.; Al-othman, O. Y. A Review on Flammability of Epoxy Polymer , Cellulosic and Non-Cellulosic Fiber Reinforced Epoxy Composites. *Polym. Adv. Technol.* **2015**.

[18]   Bindu, R. L.; Reghunadhan Nair, C. P.; Ninan, K. N.Phenolic Resins Bearing Maleimide Groups: Synthesis and Characterization. *J. Polym. Sci. Part A Polym. Chem.* **2000**, *38*, 641–652.

[19]   A. Knop, L. A. P. Raw Materials. In *Phenolic Resins Chemistry, Applications and Performance*; Springer-Verlag Berlin Heidelberg GmbH, **1985**; pp. 5–23.

[20]   Goodman, S. H. Phenol-Formaldehyde Resins. In *HANDBOOK OF THERMOSET PLASTICS*; Ibeh, C. C., Ed.; NOYES PUBLICATIONS W&wood. New Jersey. U.S.A., **1998**; pp. 23–71.

[21]   Pilato, L. *Phenolic Resins : A Century of Progress*. 1ˢᵗ edition, USA, **2010**.

[22]   Vázquez, G.; Antorrena, G.; González, J.; Mayor, J. Lignin-Phenol-Formaldehyde Adhesives for Exterior Grade Plywoods. *Bioresour. Technol.* **1995**, *51*, 187–192.

[23]   Wang, M.; Leitch, M.; (Charles) Xu, C. Synthesis of Phenol–formaldehyde Resol Resins Using Organosolv Pine Lignins. *Eur. Polym. J.* **2009**, *45*, 3380–3388.

[24]   Ishida, H.; Low, H. Y. A Study on the Volumetric Expansion of Benzoxazine-Based Phenolic Resin. *Macromolecules* **1997**, *30*, 1099–1106.

[25]   Yadav, R.; Devi, A.; Tripathi, G.; Srivastava, D. Optimization of the Process Variables for the Synthesis of Cardanol-Based Novolac-Type Phenolic Resin Using Response Surface Methodology. *Eur. Polym. J.* **2007**, *43*, 3531–3537.

[26]   Horikawa, T.; Ogawa, K.; Mizuno, K.; Hayashi, J.; Muroyama, K. P Reparation and Characterization of the Carbonized Material of Phenol – Formaldehyde Resin with Addition of Various Organic Substances. *Carbon N. Y.* **2003**, *41*, 465–472.

[27]   Sarkar, S.; Adhikari, B. Lignin-Modified Phenolic Resin: Synthesis Optimization, Adhesive Strength, and Thermal Stability. *J. Adhes. Sci. Technol.* **2000**, *14*, 1179–1193.

[28]   Turunen, M.; Alvila, L.; Pakkanen, T. T.; Rainio, J. Modification of Phenol-Formaldehyde Resol Resins by Lignin, Starch, and Urea. *J. Appl. Polym. Sci.* **2003**, *88*, 582–588.

[29]   Alonso, M. V.; Oliet, M.; Pérez, J. M.; Rodríguez, F.; Echeverría, J. Determination of Curing Kinetic Parameters of Lignin-Phenol-Formaldehyde Resol Resins by Several Dynamic Differential Scanning Calorimetry Methods. *Thermochim. Acta* **2004**, *419*, 161–167.

[30]   Chen, Y.; Shew, C. Y. Theoretical Studies of the Conformational Behavior of Chain Molecules Containing Polar Groups: Simulations of a Poly(vinylidene Fluoride) Model. *J. Mol. Model.* **2003**, *9*, 379–389.

[31]   Bin Wang, Mingzhu Liu, Yong Chen, Rui Liang, S. C.; Jin, S. Effect of Metal Ions and pH Values on the Conformational Transition of the Copolymer Chain in Aqueous Solutions. *J. Appl. Polym. Sci.* **2006**, *104*, 1714–1722.

[32]   Poljanšek, I.; Krajnc, M. Characterization of Phenol-Formaldehyde Prepolymer Resins by in Line FT-IR Spectroscopy. *Acta Chim. Slov.* **2005**, *52*, 238–244.

[33]   Guo, C.; Zhou, L.; Lv, J. Effect of Solvent on the Chain Conformation and Cure Behavior of Phenolic Resin. *Polym. Polym. Compos.* **2013**, *21*, 449–456.

[34]   Park, B. D.; Riedl, B.; Kim, Y. S.; So, W. T. Effect of Synthesis Parameters on Thermal Behavior of Phenol-Formaldehyde Resol Resin. *J. Appl. Polym. Sci.* **2002**, *83*, 1415–1424.

[35]   Wolfrum, J.; Ehrenstein, G. W. Interdependence between the Curing, Structure, and the Mechanical Properties of Phenolic Resins. *J. Appl. Polym. Sci.* **1999**, *74*, 3173–3185.

[36]   Sulaiman, S.; Yunus, R.; Ibrahim, N.; Rezaei, F. Effect of Hardener on Mechanical Properties of Carbon Fibre Reinforced Phenolic Resin Composites. *J. Eng.* **2008**, *3*, 79–86.

[37]   Monni, J.; Niemelä, P.; Alvila, L.; Pakkanen, T. T. Online Monitoring of Synthesis and Curing of Phenol-Formaldehyde Resol Resins by Raman Spectroscopy. *Polymer (Guildf).* **2008**, *49*, 3865–3874.

[38]   López, M.; Blanco, M.; Vazquez, a.; Gabilondo, N.; Arbelaiz, a.; Echeverría, J. M.; Mondragon, I. Curing Characteristics of Resol-Layered Silicate Nanocomposites. *Thermochim. Acta* **2008**, *467*, 73–79.

[39]   A, B. Zähelastisch Und Flammfest. *Kunststoffe* **1995**, *8*, 1142–1144.

[40]   Böttcher A, P. LA. Phenolic Resins for FRP Systems. *SAMPE J* **1997**, *33*, 35–39.

[41]   Knop, A. G. · L. A. P. · A. Thermosets: Overview, Definitions, and Comparisons. In *Phenolic Resins: Chemistry, Applications, Standardization, Safety and Ecology*; Knop, A. G. · L. A. P. · A., Ed.; Springer-Verlag Berlin Heidelberg GmbH, **1999**; pp. 109–121.

[42]   Joseph, S.; Sreekala, M. S.; Oommen, Z.; Koshy, P.; Thomas, S. A Comparison of the Mechanical Properties of Phenol Formaldehyde Composites Reinforced with Banana Fibres and Glass Fibres. *Compos. Sci. Technol.* **2002**, *62*, 1857–1868.

[43]   Chiang, T. C. Mechanical Properties of Kenaf Fibre Reinforced Urea Formaldehyde Resin Composites. **2013**.

[44]   Srebrenkoska, V.; Bogoeva-gaceva, G. Composite Material Based on an Ablative Phenolic Resin and Carbon Fibers. **2009**, *74*, 441–453.

[45]   J. Goto, T. K. 3rd International Symposium on Network Polymers. In *Baekeland 2011 Symposium*; **2011**.

[46]   Santorelli, J. G. and M. Recycling. In *phenolic resin: A century of progress*; Pilato, L., Ed.; Springer-Verlag Berlin Heidelberg, **2010**; pp. 514–521.

[47]   Gou, Y. plastic age of planet. *Plast. Age.***2010**. *58*, 107–110.

[48]   Alonso, M. V.; Oliet, M.; Dom??nguez, J. C.; Rojo, E.; Rodr??guez, F. Thermal Degradation of Lignin-Phenol-Formaldehyde and Phenol-Formaldehyde Resol Resins : Structural Changes, Thermal Stability, and Kinetics. *J. Therm. Anal. Calorim.* **2011**, *105*, 349–356.

[49]   Zhang, W.; Ma, Y.; Wang, C.; Li, S.; Zhang, M.; Chu, F. Preparation and Properties of Lignin-Phenol-Formaldehyde Resins Based on Different Biorefinery Residues of Agricultural Biomass. *Ind. Crops Prod.* **2013**, *43*, 326–333.

[50]   Matsushita, Y.; Wada, S.; Fukushima, K.; Yasuda, S. Surface Characteristics of Phenol – Formaldehyde – Lignin Resin Determined by Contact Angle Measurement and Inverse Gas Chromatography. **2006**, *23*, 115–121.

[51]   Mansouri, N. El; Salvad, J. Structural Characterization of Technical Lignins for the Production of Adhesives : Application to Lignosulfonate , Kraft , Soda-Anthraquinone , Organosolv and Ethanol Process Lignins. **2006**, *24*, 8–16.

[52]   Takehiro Kawauchi, Minori Ohara, Shoko Hirai, T. T. Preparation of Polybenzoxazine/Ionic Liquid Hybrids. *Chem. Lett.* **2008**, *37*.

[53]   Ogoshi, T.; Onodera, T.; Yamagishi, T.; Nakamoto, Y.; Kagata, A.; Matsumi, N.; Aoi, K. Transparent Ionic Liquid-Phenol Resin Hybrids with High Ionic Conductivity. *Polym. J.* **2011**, *43*, 421–424.

[54]   A. Von Itter, B. S. Evonik Degussa Calidur™ Literature. In *SAMPE Fall Technical Conference, Wichita*; **2009**.

[55]   Aji, I. S.; Sapuan, S. M.; Zainudin, E. S.; Abdan, K. Kenaf Fibres as Reinforcement for Polymeric Composites: A Review. *International Journal of Mechanical and Materials Engineering*, **2009**, *4*, 239–248.

[56]   Thiruchitrambalam, M.; Alavudeen, a.; Venkateshwaran, N. Review on Kenaf Fiber Composites. *Rev. Adv. Mater. Sci.* **2012**, *32*, 106–112.

[57]   Saba, N.; Jawaid, M.; Paridah, M. T.; Al-othman, O. Y. A Review on Flammability of Epoxy Polymer , Cellulosic and Non-Cellulosic Fiber Reinforced Epoxy Composites. *Polym. Adv. Technol.* **2016**, *27*, 577–590.

[58]   Horrocks, A.R. and Kandola, B. K. Flammability and Fire Resistance of Composite. In *Design and Manufacture of Textile Composites*; Woodhead, Cambridge., **2005**; pp. 330–363.

[59]   Kandola, B.K. and Kandare, E. Composites Having Improved Fire Resistance. In *Advances in Fire Retardant Materials*; Horrocks, A.R. and Price, D., Ed.; Woodhead, Cambridge., **2008**; pp. 398–442.

[60]   Hirschler, M. M. Chemical Aspects of Thermal Decomposition of Polymeric Materials. In *Fire Retardancy of Polymeric Materials*; Grand, A.F. and Wilkie, C. A., Ed.; CRC Press, Boca Raton, **2000**; pp. 28–79.

[61]   Kandola, B.K. and Nazare, S. An Overview of Flammability and Fire Retardancy of Fibre Reinforced Unsaturated Polyester Composites. In *Proceedings of Fibre Reinforced Composites Conference*; Port Elizabeth., **2007**.

[62]   Chiu, H.T., Chiu, S.H., Jeng, R.E. and Chung, J. S. A Study of the Combustion and Fire-Retardance Behaviour of Unsaturated Polyester/Phenolic Resin Blends. *Polym. Degrad. Stab.* **2000**, *70*, 505–514.

[63]   Chapple, S.; Nandjiwala, R. Flammability of natural Fiber-Reinforced Composites and Strategies for Fire Retardancy : A Review. J. Thermoplast. Compos. Mater. **2010**, 23, 871-893.

[64]   Jawaid, M.; Khalil, H. P. S. A.; Bakar, a. A.; Khanam, P. N. Chemical Resistance, Void Content and Tensile Properties of Oil Palm/jute Fibre Reinforced Polymer Hybrid Composites. *Mater. Des.* **2011**, *32*, 1014–1019.

[65]   Fritz, W. Belgrade, ,. In *in Proceeding of the first seminar on carbon materials*; Vinča, Yugoslavia, 1985; p. 10.

[66]   Wang, D.-C.; Chang, G.-W.; Chen, Y. Preparation and Thermal Stability of Boron-Containing Phenolic Resin/clay Nanocomposites. *Polym. Degrad. Stab.* **2008**, *93*, 125–133.

[67]   Ozturk, S. Effect of Fiber Loading on the Mechanical Properties of Kenaf and Fiberfrax Fiber-Reinforced Phenol-Formaldehyde Composites. *J. Compos. Mater.* **2010**, *44*, 2265–2288.

[68]   Kayank, C.; Tasan, C. Effects of Production Parameters on the Structure of Resol Type Phenolic Resin/layered Silicate Nanocomposites. *Eur. Polym. J.* **2006**, *42*, 1908–1921.

[69]   Aranguren, M. I.; Reboredo, M. M.; Za, C. N. Resol – Vegetable Fibers Composites. **1999**, 1832–1840.

[70]   Mwaikambo, L. Y.; Ansell, M. P. Hemp Fibre Reinforced Cashew Nut Shell Liquid Composites. *Compos. Sci. Technol.* **2003**, *63*, 1297–1305.

[71]   Barreto, A. C. H.; Rosa, D. S.; Fechine, P. B. A.; Mazzetto, S. E. Properties of Sisal Fibers Treated by Alkali Solution and Their Application into Cardanol-Based Biocomposites. *Compos. Part A Appl. Sci. Manuf.* **2011**, *42*, 492–500.

[72]   Sreekala, M. S.; Kumaran, M. G.; Joseph, S.; Jacob, M. Oil Palm Fibre Reinforced Phenol Formaldehyde Composites : Influence of Fibre Surface Modifications on the Mechanical Performance. *Appl. Compos. Mater.* **2000**, *7*, 295–329.

[73]   Maffezzoli, A.; Calò, E.; Zurlo, S.; Mele, G.; Tarzia, A.; Stifani, C. Cardanol Based Matrix Biocomposites Reinforced with Natural Fibres. *Compos. Sci. Technol.* **2004**, *64*, 839–845.

[74]   Patton, R. D.; Pittman, C. U.; Wang, L.; Hill, J. R.; Day, a. Ablation, Mechanical and Thermal Conductivity Properties of Vapor Grown Carbon Fiber/phenolic Matrix Composites. *Compos. - Part A Appl. Sci. Manuf.* **2002**, *33*, 243–251.

[75]   Onlinefirst, C. M.; Queensland, S.; Composites, E. F.; Queensland, S. Fracture Toughness of Phenol. **2009**, 1–14.

[76]   Park, S.-J.; Jang, Y.-S. Interfacial Characteristics and Fracture Toughness of Electrolytically Ni-Plated Carbon Fiber-Reinforced Phenolic Resin Matrix Composites. *J. Colloid Interface Sci.* **2001**, *237*, 91–97.

[77]   Chiang, C. L.; Ma, C. C. M. Synthesis, Characterization, Thermal Properties and Flame Retardance of Novel Phenolic Resin/silica Nanocomposites. *Polym. Degrad. Stab.* **2004**, *83*, 207–214.

[78]   Byun, H. Y.; Choi, M. H.; Chung, I. J. Synthesis and Characterization of Resol Type Phenolic Resin / Layered Silicate Nanocomposites. **2001**, 4221–4226.

[79]   Asim, M.; Abdan, K.; Jawaid, M.; Nasir, M.; Dashtizadeh, Z.; Ishak, M. R.; Hoque, M. E. A Review on Pineapple Leaves Fibre and Its Composites. *Int. J. Polym. Sci.* **2015**, 1–17.

[80]   Da Silva, R.V.; Aquino, E.M.F.; Rodrigues, L.P.S.; Barros, A. R. . Development of a Hybrid Composite with Synthetic and Natural Fibers. *Matéria (Rio J.)* **2008**, *13*, 154–61.

[81]   Kabir, M. M.; Wang, H.; Lau, K. T.; Cardona, F. Chemical Treatments on Plant-Based Natural Fibre Reinforced Polymer Composites: An Overview. *Compos. Part B Eng.* **2012**, *43*, 2883–2892.

[82]   Thiruchitrambalam, M.; Alavudeen, a; Athijayamani, a; Venkateshwaran, N.; Elaya Perumal, a. Improving Mechanical Properties of Banana / Kenaf Polyester Hybrid Composites Using Sodium Laulryl Sulfate Treatment . *Mater. Phys. Mech.* **2009**, *8*, 165–173.

[83]   Harnnecker, F.; Santos Rosa, D. dos; Lenz, D. M. Biodegradable Polyester-Based Blend Reinforced with Curau?? Fiber: Thermal, Mechanical and Biodegradation Behaviour. *J. Polym. Environ.* **2012**, *20*, 237–244.

[84]   Ku, H.; Wang, H.; Pattarachaiyakoop, N.; Trada, M. A Review on the Tensile Properties of Natural Fiber Reinforced Polymer Composites. *Compos. Part B Eng.* **2011**, *42*, 856–873.

[85]   Mohanty, a. K.; Misra, M.; Hinrichsen, G. Biofibres, Biodegradable Polymers and Biocomposites: An Overview. *Macromol. Mater. Eng.* **2000**, *276–277*, 1–24.

(86)   Maleque, M. A.; Atiqah, A.; Talib, R. J.; Zahurin, H. New Natural Fibre Reinforced Aluminium Composite for Automotive Brake Pad. *Int. J. Mech. Mater. Eng.* **2012**, *7*, 166–170.

(87)   De Medeiros, E. S.; Agnelli, J. A. M.; Joseph, K.; De Carvalho, L. H.; Mattoso, L. H. C. Mechanical Properties of Phenolic Composites Reinforced with Jute/cotton Hybrid Fabrics. *Polym. Compos.* **2005**, *26*, 1–11.

(88)   Seena Joseph, M. S. Sreekala Peter Koshy, S. T. Mechanical Properties and Water Sorption Behavior of Phenol–Formaldehyde Hybrid Composites Reinforced with Banana Fiber and Glass Fiber. *J. Appl. Polym. Sci.* **2008**, *109*, 1439–1446.

[89]   Joseph, S.; Oommen, Z.; Thomas, S. Environmental Durability of Banana-Fiber-Reinforced Phenol Formaldehyde Composites. *J. Appl. Polym. Sci.* **2006**, *100*, 2521–2531.

[90]   Joseph, S. and Thomas, S. Electrical Properties of Banana Fiber-Reinforced Phenol Formaldehyde Composites. *Appl. Polym. Sci.* **2008**, *109*, 256–263.

[91]   Kumar, N. M.; Reddy, G. V.; Naidu, S. V.; Rani, T. S.; Subha, M. C. S. Mechanical Properties of Coir/Glass Fiber Phenolic Resin Based Composites. *J. Reinf. Plast. Compos.* **2008**, *28*, 2605–2613.

[92]   DEV, A. V. R. R. R. Flexural Properties of Ridge Gourd/ Phenolic Composites and Glass/Ridge Gourd/Phenolic Hybrid Composites. *J. Compos. Mater.* **2008**, *42*, 593–601.

[93]   Rajulu, a. V.; Devi, R. R. Compressive Properties of Ridge Gourd/Phenolic Composites and Ridge Gourd/Phenolic/Glass Hybrid Composites. *J. Reinf. Plast. Compos.* **2007**, *26*, 1657–1664.

[94]   Mu, Q.; Wei, C.; Feng, S. Studies on Mechanical Properties of Sisal Fiber/phenol Formaldehyde Resin in-Situ Composites. *Polym. Compos.* **2009**, *30*, 131–137.

[95]   Jawaid, M.; Abdul Khalil, H. P. S. Cellulosic/synthetic Fibre Reinforced Polymer Hybrid Composites: A Review. *Carbohydr. Polym.* **2011**, *86*, 1–18.

[96]   Bishopp, J. A. The History of Redux♦ and the Redux Bonding Process. *Int. J. Adhes. Adhes.* **1997**, *17*, 287–301.

[97]   Kalia, S.; Kaur, B. S. K. I. *Cellulose Fibers: Bio- and Nano-Polymer Composites*; **2011**.

[98]   Cicala, G.; Cristaldi, G.; Recca, G.; Ziegmann, G.; El-Sabbagh, A.; Dickert, M. Properties and Performances of Various Hybrid Glass/natural Fibre Composites for Curved Pipes. *Mater. Des.* **2009**, *30*, 2538–2542.

[99]   Ochi, S. Mechanical Properties of Kenaf Fibers and kenaf/PLA Composites. *Mech. Mater.* **2008**, *40*, 446–452.

[100]   A. Knop, L. A. P. *Chemistry, Applications and Performance*; 1st ed.; Springer-Verlag Berlin Heidelberg GmbH, **1985**.

[101]   Halim, Z.; Zainudin, E. S.; Mustapha, F.; Haris, M. Y.; Laila, D.; Zahari, R. Preliminary Review of Biocomposites Materials for Aircraft Radome Application. *Key Eng. Mater.* **2011**, *471–472*, 563–567.

[102]   Zampaloni, M.; Pourboghrat, F.; Yankovich, S. a.; Rodgers, B. N.; Moore, J.; Drzal, L. T.; Mohanty, a. K.; Misra, M. Kenaf Natural Fiber Reinforced Polypropylene Composites: A Discussion on Manufacturing Problems and Solutions. *Compos. Part A Appl. Sci. Manuf.* **2007**, *38*, 1569–1580.

[103]   Mohanty, A. K.; Drzal, L. T.; Misra, M. Novel Hybrid Coupling Agent as an Adhesion Promoter in Natural Fiber Reinforced Powder Polypropylene Composites. *J. Mater. Sci. Lett.* **2002**, *21*, 1885–1888.

[104]   Ghosh, N. N.; Kiskan, B.; Yagci, Y. Polybenzoxazines—New High Performance Thermosetting Resins: Synthesis and Properties. *Prog. Polym. Sci.* **2007**, *32*, 1344–1391.