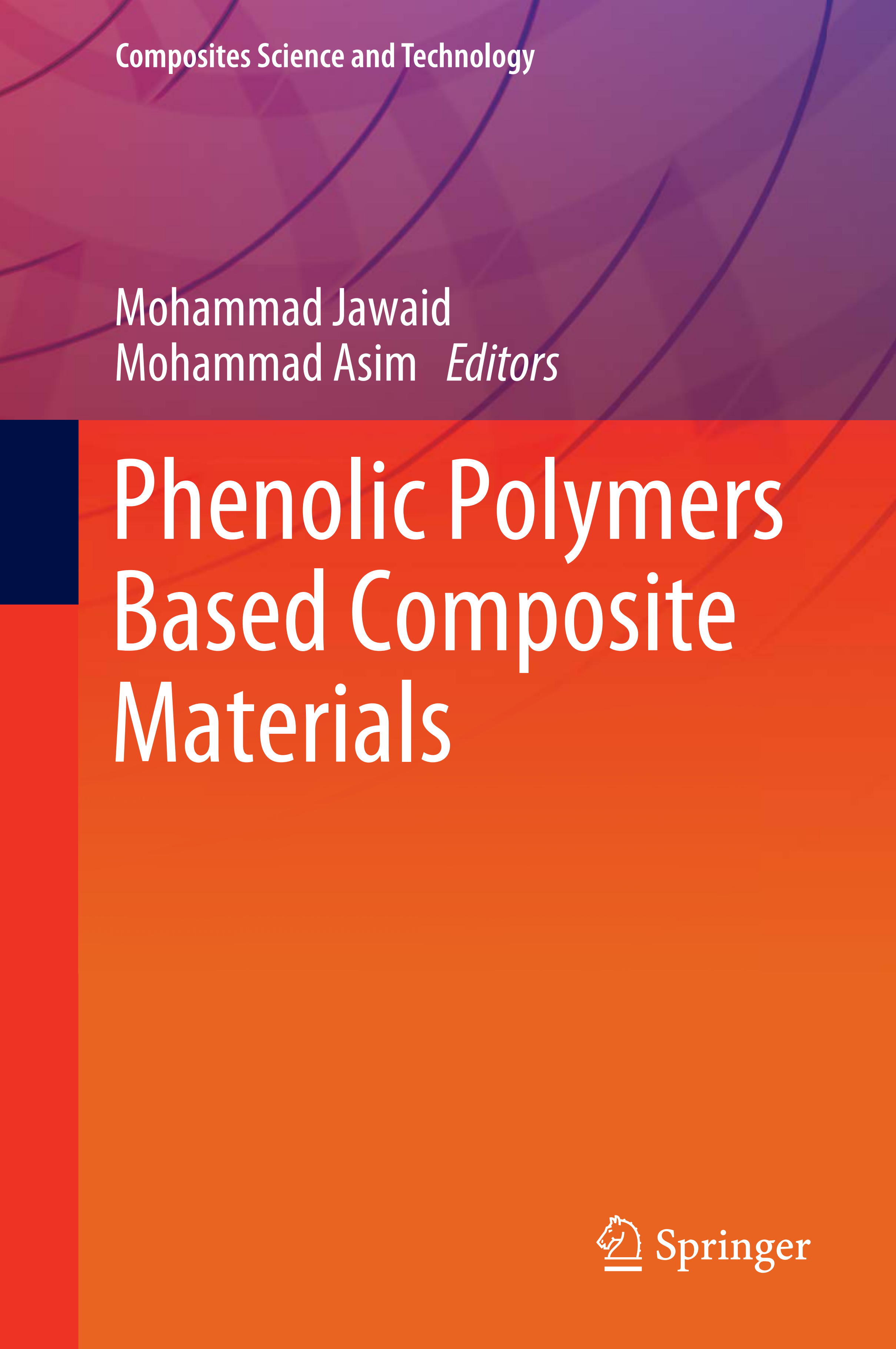

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Mohammad Jawaid
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Phenolic Polymers Based Composite Materials

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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

Contents

About the Editors

Dr. Mohammad Jawaid is currently working as High Flyer Fellow (Professor) at Biocomposite Technology Laboratory, Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia, Serdang, Selangor, Malaysia, and also Visiting Professor at the Department of Chemical Engineering, College of Engineering, King Saud University, Riyadh, Saudi Arabia, since June 2013. Dr. Mohammad Jawaid received his Ph.D. from Universiti Sains Malaysia, Malaysia. He has more than ten years of experience in teaching, research and industries. His area of research interests includes hybrid reinforced/filled polymer composites and advance materials. So far, he has published 37 books, 65 book chapters, more than 350 peer-reviewed international journal papers and several published review papers under top 25 hot articles in science direct during 2013–2018. He also obtained two patents and five copyrights. H-index and citation in Scopus are 51 and 11838, and in Google scholar, H-index and citation are 60 and 16232. He is founding Series Editor of Composite Science and Technology Book, and Springer Proceedings in Materials from Springer Nature. He is also International Advisory Board member of Springer Series on Polymer and Composite Materials. His five published review papers under hot cited articles in science direct during 2016–2019. He is reviewer of several high impact ISI journals (90 journals).

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Phenolic Resin and Its Derivatives

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

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

Keywords Thermosetting resins · Novolac · Resole · Crosslinking bonds

1 Introduction

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

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Table 1 Applications for phenolic resins

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

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

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

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

2 Polimerization

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

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

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

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

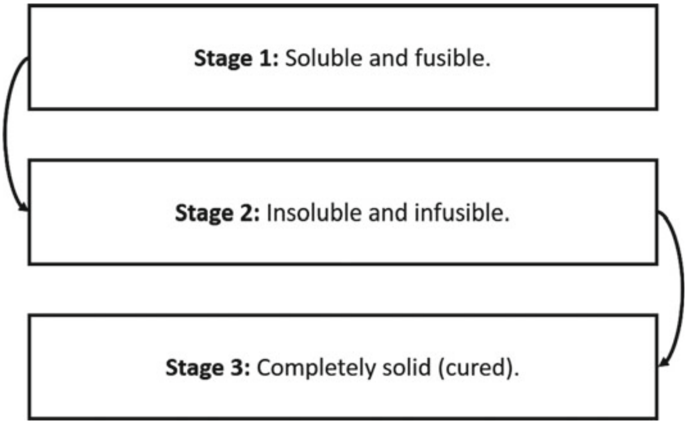

Fig. 1 Curing process of a phenolic resin composite

3 Classification of Phenolic Resins

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

Resoles or single stage resins.

Novolacs or two stage resins.

3.1 *Novolac*

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

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

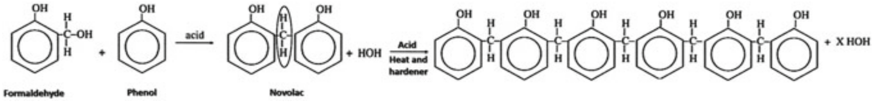

Fig. 2 Synthesis of novolac resins

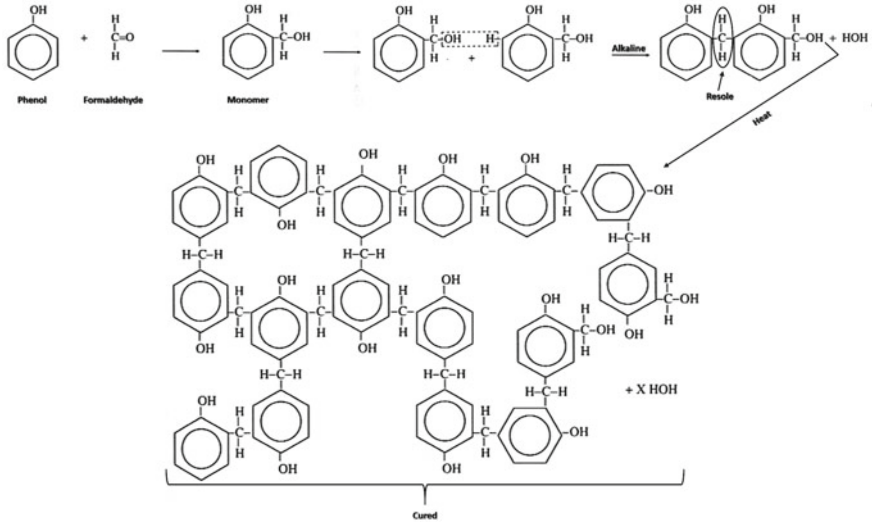

Fig. 3 Synthesis of resole resins

3.2 Resoles

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

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

3.3 Others

3.3.1 Bisphenol-A

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

3.3.2 Bisphenol-F

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

3.3.3 Polybenzoxazine

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

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

4 Use of Phenolic Resin in Composite Matrices

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

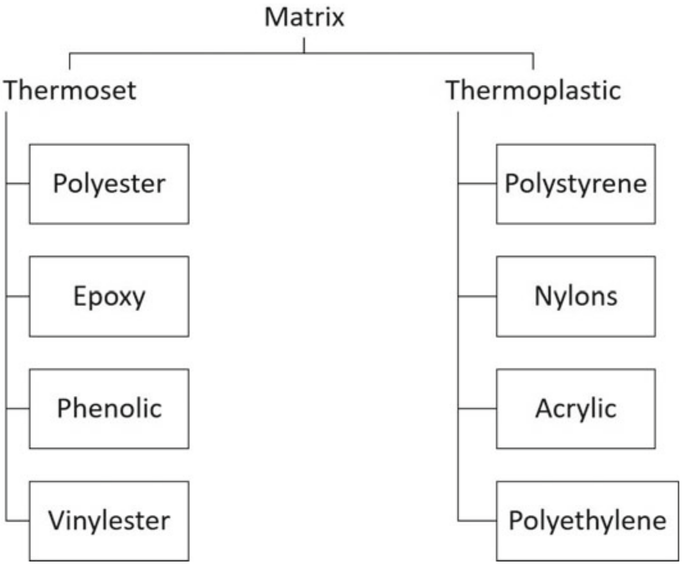

Fig. 4 Classification of polymeric matrices

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

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

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

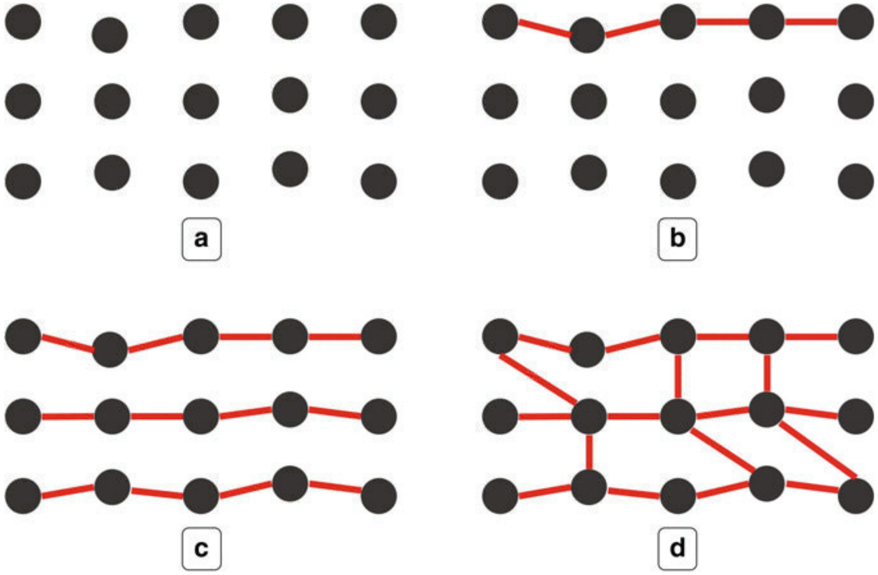

Fig. 5 Thermosets crosslink during the curing process

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

5 Conclusion and Future Perspective

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

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Synthesis of Bio Phenolic Polymer and Its Properties

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

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

List of abbreviations

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

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