Gallic Acid as a Potential Substitution for Phenol in Phenol-Formaldehyde Resin for Biocomposite Matrices

by:

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ABSTRACT

This project explores the production of new resins using gallic acid (GA) as a substitute for phenol in phenol-formaldehyde (PF) resin. A special curing schedule was made tailored to the limitations of the equipment used. Phenol was substituted with GA at various contents until the optimum ratio has been reached, which in this present study is 31% of gallic acid. The effects of co-reaction of GA and phenol with formaldehyde on mechanical, thermal, chemical and morphological properties were investigated. Test specimens were prepared by synthesising the pre-polymer at certain processing conditions and curing it in the autoclave. From the flexural test, addition of GA showed improvement in the flexural modulus and strength. The thermal properties of PF resin and GA resin were investigated by Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA) and Thermogravimetry Analysis (TGA). From the DSC result, no residual exotherm can be seen below 150 ℃ which indicates that the resin is suitable for use in natural fibre composites. Glass transition temperature (Tg) from DMA suggest that substitution of phenol with GA in production of resol resin has increased the glass transition temperature while TGA results showed that increasing GA substitution level in the compound resulted in increasing weight loss at lower temperature, and hence lower thermal stability. Based on Scanning Electron Microscopy (SEM) analysis, the flexural fracture surfaces for PF and GA resin displays no bubbles and voids present in the resin. It shows that the cure cycle proved to be successful in producing bubble-free specimens. In this study, Group Interaction Modelling (GIM) was also used to predict the Tg of the resin, which compares very well with the experimental work. Following the successful production of resin, nettle fibre was added as a reinforcing agent in producing the biocomposites. It shows that up to certain amount of nettle fibres, which is in this study 15 wt% of nettle fibres, the mechanical properties of the resin improved substantially. However, in composite systems, we can see particles and holes where fibres have pulled out upon fracture are clearly visible in the SEM images, which indicates poor interaction between fibre-matrix.

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LIST OF ABBREVIATIONS

$\emptyset_0$	Depth of the potential energy at separation distance r_o
$\emptyset$	Interaction Energy
ΔT_m	Hypothetical Temperature Increment
APP	Ammonium Polyphosphate
APS	Aminopropyl(triethoxy)silane
BM	Biomass
BTCA	Butanetetracarboxylic Acid
CNF	Cellulose Nanofibre
CNSL	Cashew Nut Shell Liquid
CO	Carbon Monoxide
CO_2	Carbon Dioxide
CPF	Cardanol-Phenol-Formaldehyde
DBS	Dibutylsebacate
DDS	Diaminodiphenylsulphone
DGEBA	Diglycidyl Ether of Bisphenol A
DMA	Dynamic Mechanical Analysis
DOS	Dioctylsebacate
DSC	Differential Scanning Calorimetry
DTG	Differential Thermogravimetry Analysis
E_{coh}	Cohesive Energy
EFB	Empty Fruit Bunch
F/Ga	Formaldehyde/Gallic Acid
FTIR	Fourier Transform Infrared Spectroscopy

GA	Gallic Acid
GDNR	Grafting Depolymerised Natural Fibre
GIM	Group Interaction Modelling
GPC	Gel Permeation Chromatography
GTA	Glycerol Triacetate
h	hours
H_C	Configuration Energy
HDPE	High Density Polyethylene
HF	Hemp Fibers
HFRUPE	Hemp Fibre Reinforced Unsaturated Polyester
H_M	Mechanical Energy
HPLC	High Performance Liquid Chromatography
HT	Hydrolysable Tannins
H_T	Thermal Energy
IFSS	Interfacial Shear Strength
IGC	Inverse Gas Chromatography
k	Boltzmann Constant
KF	Kenaf Fibre
LAP	Laprol or Oxypropylated Glycerol
LD	Laccase Doga
m	minutes
M	Molecular Weight
MAE	Microwave-Assisted Extraction
MAPP	Polypropylene-Graft-Maleic Anhydride
MMA	Methyl Methacrylate

Modar	Modified Acrylic Resins
MOE	Modulus of Elasticity
MOR	Modulus of Rupture
MY	Tetrafunctional Glycidyl Amine
N	Number of Degrees of Freedom
n_a	Avogadro Number
NaOH	Sodium Hydroxide
NH_3	Ammonium Hydroxide
NMR	Nuclear Magnetic Resonance Spectroscopy
OM	Optical Microscopy
P	Phenol
PCL	Polycaprolactone
PCL/S	Polycaprolactone/Starch
PEG	Polyethylene Glycol
PES	Polyether Sulfone
PF	Phenol-Formaldehyde
PGA	Polyglycolic Acid
PHA	Polyhydroxyalkanoates
PHB	Polyhydroxybutyrate
PIB	Polyisobutylene
PLA	Polylactic Acid
PP	Polypropylene
PP/EPDM	Polypropylene/Ethylene–Propylene–Diene–Monomer
SEBS	Poly[styrene-b-(ethylene-co-butylene)-b-styrene]
SEM	Scanning Electron Microscope

SF-PCL/S	Sisal Fibre-Reinforced Polycaprolactone/Starch
SWE	Subcritical Water Extraction
T	Temperature in K
TEA	Triethylamine
Tg	Glass Temperature
TGA	Thermogravimetric Analysis
TGAP	Triglycidyl P-Aminophenol
TGDDM	Tetraglycidyl 4,4′ Diaminodiphenylmethane
TPNR	Thermoplastic Natural Rubber
UAE	Ultrasound-Assisted Extraction
UD	Unidirectional
UPE	Unsaturated Polyester
V_W	Van der Waals Volume
θ	Debye Reference Temperature

1.0 INTRODUCTION

1.1 Background of Study

The polymer industry is one which is increasingly in the public eye, as it uses oil resources and creates a great deal of waste that pollutes the planet. Therefore, biopolymers have become increasingly important in recent years, as user nowadays are become more conscious about its effect on environment and global warming, not to mention increased cost of crude oil. Biopolymers usage should have less detrimental effect environmentally compared to the commodity plastics that use fossil-fuel [1].

Phenolic resins have been widely used in thermal insulation materials, adhesives, moulding powder, resin lamination, surface coating and composites. This is because of their excellent features such as good chemical resistance and flame retardancy, thermal and dimensional stability [2]. As such bio-based phenolic resins would be a desirable product to meet the needs of these markets.

Composite materials have also been widely adopted in a range of structural applications from automotive and aerospace to civil infrastructure and consumer goods. Traditionally they have used carbon-fibres for high mechanical performance, in terms of modulus and strength and glass-fibre for toughness or where cost dominates, or lower properties can be tolerated. However, there has been an increased interest in the use of biocomposites in recent years as the fibres are renewable and generally produced with low energy requirement, provided that agrochemical usage is minimal. Currently, numerous efforts have been focused on the use of materials from renewable resources to reinforce biocomposites. Bio-based composites are considered one of the green materials for the next generation. The market for these bio-based composites has the potential for dramatic growth with a green concept in coming years. Bio-based composites can be produced from renewable resource-based polymers in combination with fibre reinforcement for a variety of applications [3]–[5]. Generally, at present, natural fibres have been used with conventional resins, but logically the use of natural fibres and biopolymers is an obvious step to maximise the green credentials of the product [6].

Although the use of natural fibre can lead to a better environment, incorporation with petroleum-based source and the non-biodegradable polymer matrix into a composite makes it not eco-friendly enough [4]. This occurrence shows that the importance of renewable source-based resin is crucial in developing the biocomposites. The advantage of using the renewable source-based resin, for reasons other than ecological issues, can also improve the sustainability of the composite materials [7]. Therefore, evolving the bioresin from natural sources could be a good prospect for a better future in protecting the environment.

To enhance the properties of biocomposites, plant fibres or natural fibres have become an important role as a reinforcing material recently [8]–[10] . Examples of plant fibres include seed fibres (cotton), bast fibres (jute, ramie, kenaf, hemp, nettle) and hard fibres (banana fibre, agave, sisal and coir). One of the problems with plant fibres is their relatively low modulus [11]. Another is their poor adhesion to polymer resins [12]. Nettle fibres have a higher modulus than most plant fibres, due in part to their high silica content [13]. This makes them a little similar to glass fibres, and hence the modulus is good for composites. Furthermore, they are native to European countries and Asia and can be found growing in any soil, so they have the potential to be a crop plant. In an ideal world, we could use the whole plant in the manufacture of the composite, extracting the fibres and chemicals to make the resin. With nettles, for example, we could use leaves to extract gallic acid [14] and the stalks to make fibres.

In this study, phenolic resins will be modified to broaden their applications for modern composite structures. The modification consists of phenol substituted by gallic acid. Gallic acid contains a high proportion of phenolic compounds with the reactive phenolic moiety making it a potentially attractive partial substitute to petroleum-based phenol for making phenolic resin [15]–[17]. The outcome of the reactions has been modelled using Group Interaction Modelling (GIM) to predict the properties and compare it with the experimental result, the intent being to use the results to help in the design of new resins. Finally, nettle fibre will be added to the system to produce composites with the desired properties.

1.2 Problem Statement

Recent developments in manufacturing of bio-based composites from thermosetting resins have heightened the need for substituting the conventional resin materials with more environmentally friendly and/or biodegradable ones. There have been a number of studies [18]–[20] involving substitution of conventional thermosetting resins with natural materials. Previous study [21] have reported that phenol substituted gallic acid (GA) in phenol-formaldehyde (PF) resin synthesis has good effect on properties of the composite. This is a good alternative since lack of fossil supplies and effect of petroleum-based products on the environment have increased in people's awareness. GA is a type of phenolic acid that can be found in gallnuts, tea leaves, nettle and other plants [14], [22]. It consists of an aromatic ring bearing a carboxylic group (position 1) and three adjacent hydroxyl groups (positions 3,4 and 5), leaving two free sites on the ring. Details of the GA reactivity will be discussed in **Chapter 2: Literature Review**. Although some research has been carried out on using GA [23], [24], no studies have been found which use GA as a phenol substitute for incorporation with natural fibres to produce high performance biocomposites.

This project explores the production of new resins using gallic acid as a substitute for phenol in phenol-formaldehyde resin, which are then processed in an autoclave. Because no one has previously done this, a special curing schedule needs to be prepared tailored to the limitations of the equipment used. Hence, the objective of this research is to produce a modified resin as a matrix for use in natural fibre reinforced composite, specifically using nettle fibre as the reinforcing agent. Following this, there are issues that need to be fulfilled to develop this research area.

1. What are the effects of curing schedule, in particular long cure cycle of modified phenolic resin on thermal characteristics?

2. What are the effects of blend ratio of phenol and gallic acid in producing new resins on the mechanical and thermophysical properties such as flexural modulus and strength, storage modulus and tan delta?

3. What is the dispersion and morphology of gallic acid in modified phenolic resin?

4. What are the mechanical and morphological properties of nettle fibre reinforced gallic acid resin composite?

5. What is the modelling prediction in anticipated the glass transition temperature of the resin?

6. What is the best method to extract gallic acid from nettle plant and how to prove that gallic acid is present in the plant?

1.3 Objectives of the Study

The primary objectives of this thesis are:

- To co-react gallic acid and phenol to produce pre-polymer for phenolic resin synthesis.
- To develop a cure cycle that can produce a bubble(void)-free specimen. The cure cycle has to be made to tailor the limitations of the equipment.
- To investigate the capabilities of new phenolic resin that has been partially substituted by gallic acid, in terms of mechanical, thermal and morphological studies.
- To incorporate the nettle fibre as a reinforcement to produce composites.

- To extract the gallic acid from nettle leaves and stalks using suitable method, such as HPLC.
- To validate the suitability of using GIM in predicting properties of the resin with experimental work, as a future tool for resin design.

1.4 Scope of Study

To accomplish the objectives of the research, the following actions were carried out;

Initially, the modified phenolic resins were prepared with assorted amounts of gallic acid (0, 25, 50, 75 and 100 wt%). In this step, the gallic acid resin was cured in an oven at 40 ℃ (30m) - 50 ℃ (60 m) - 85 ℃ (90 m) - 125 ℃ (120 m) - 150 ℃ (120 m) as referred to previous study [25]. Unfortunately, the resins came out brittle and friable. The next curing was in an autoclave, with the same temperature and time but with addition of pressure at 7 bar throughout the process, however to no avail. A series of trials were applied in order to get an acceptable sample that is suitable for further testing. A more detailed process is discussed in **Chapter 4: Resin Development**. The resin was continuously prepared at different amount of gallic acid (31, 37, 40 and 60 wt%) to determine the maximum amount of gallic acid that can be substituted in phenol-formaldehyde resin. The resin production was stopped at 31% gallic acid, as this is the optimum amount of gallic acid that can substitute phenol in gallic acid resin in order to produce a bubble-free specimen with good mechanical properties. Thus, the final resins were set to be 1.0P (0% of gallic acid), 0.25GA (25% of gallic acid) and 0.31GA (31% gallic acid) to be investigated further. The mechanical properties of the resins were then studied by flexural test, while differential scanning calorimetry (DSC) was used to detect any residual cure present in the sample. The chemical structure of the cured resin was characterised by Fourier Transform Infrared Spectroscopy (FTIR). Next, the thermal and thermophysical behaviour of the resins were evaluated by using thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). Lastly, the morphology of fractured flexural samples was obtained using scanning electron microscope (SEM) test.

In order to compare the experimental work with prediction values, Group Interaction Modelling (GIM) was applied. This method requires good knowledge in resin chemistry to be able to predict accurately the properties of the resins. The steps involved in the use of GIM to make model predictions [26] are shown in the flow diagram in Figure 1.1. Nevertheless, these steps will normally be invisible, since properties may be predicted straight from structural input parameters via predictive equations which have been derived by means of the model processes. The necessity to limit the use of high-priced experimental screening programme led to developing a model system that is capable to predict the properties of linear polymer and recently has been extended to the three-dimensional network polymers [27]. A more detailed process on modelling the resin system in the present study is discussed in **Chapter 5: Group Interaction Modelling**.

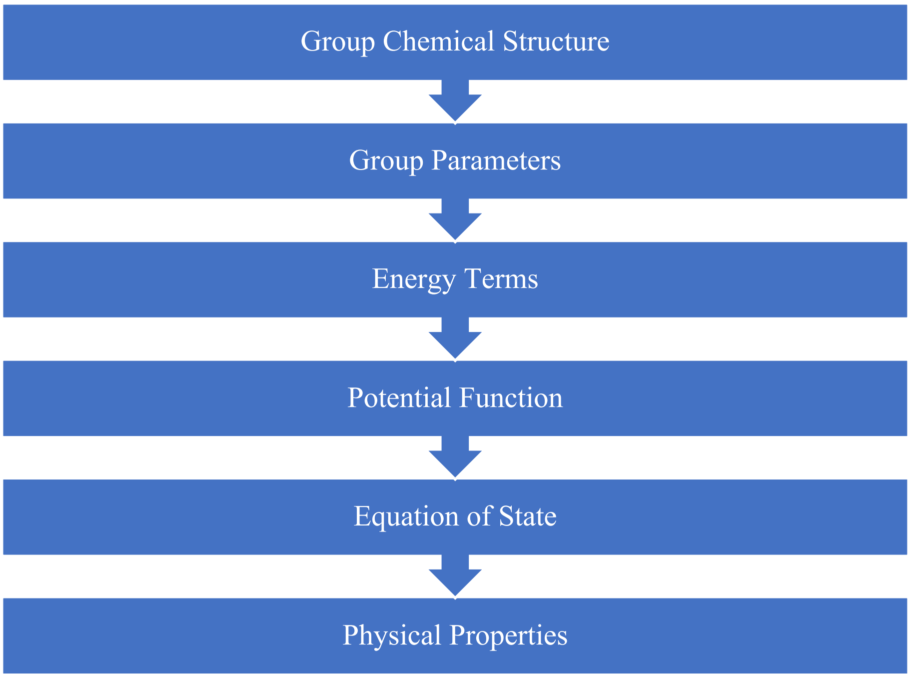


Figure 1.1 Flow Diagram of the GIM process for predicting polymer properties

What follows is the manufacturing process of biocomposite. The nettle fibre reinforced gallic acid resin at 1.0P and 0.25GA was prepared at various content of fibre, for instance 5, 10, 15 and 20 wt% of nettles. The mechanical properties of the biocomposites was determined by flexural testing. Then, the experimental value from flexural test was compared with the proposed model from this research [28], for the determination of the approximate properties of random short fibre composites. Later, the morphology of the fractured flexural surface was observed by scanning electron microscopy (SEM).

Finally, nettle stalks and leaves were extracted by Soxhlet extraction to obtain the gallic acid. The analysis of the extracted samples was done by High Performance Liquid Chromatography (HPLC).

1.5 Importance of Study

The research expects to develop a biocomposite that uses natural product that is abundantly available, low cost and renewable instead of the conventional one. Furthermore, in this study, the properties of the resin that uses gallic acid as substitution of phenol exhibit promising and comparable thermal and mechanical properties to a 100% phenol-formaldehyde resin.

2.0 LITERATURE REVIEW

2.1 Composite Materials and their Constituents

A composite material is a combination of two or more different materials with different properties, either physically or chemically, which when combined exhibit superior properties from the individual elements [29]. Over the past 80 years or so the greatest enticement for technological advances in the composite field has been in the development of reinforced plastics [30]. However, some of the advantages and disadvantages of the different types of engineering materials can be seen in these three classes for instance.

- Plastics; they are low density and lack of thermal stability but their chemical resistance to degradation of environment is temperately good. They have quite poor mechanical properties, although they can easily be fabricated and joined.

- Ceramics; possess great thermal stability and are resistant to most ordinary forms of attack although may be low in density. They are all particularly brittle, while basically very strong and rigid and it is tough to form and shape them.

- Metals; mostly are medium to high density. Many have good thermal stability and alloying process can prevent them from corrosion. Generally, they can be shaped and joined, and hence high toughness and mechanical properties.

Apart from their use in cables and ropes in tensile structures, fibres have limited value in structural applications [30]. Due to this reason, strong fibres must be combined with a matrix of metal, plastics or ceramic so that an extensive proportion of their high rigidity and tensile strength can be accessed.

This study will concentrate on polymer matrix composite, so there will be no further consideration of metal and ceramic matrix systems. For polymer composite matrices, relatively weak and ductile materials like epoxy, polyester or nylon can be used and combined with light and strong fibres to produce a strong and rigid composite which are also light and sturdy [31].

Some applications of composites can be observed in these areas;

- Aerospace - Lightweight composite materials has been used widely in manufacturing aircraft nowadays. Composite materials are being used in air frames, spoilers, tail-plane structures, fuel tanks, bulkheads, flooring, pressured gas containers, access panels, spars, air distribution ducts, seat components and so forth [32]–[37].

- Automotive engineering - To allow both energy conservation and increased motoring economy, the weight of an automobile structure needs to be compact in order to save the primary weight. This enables the designer to use smaller power plants, therefore the fuel economy or performance can be improved substantially [38]–[42].

- Bioengineering - Used in orthopaedic fracture fixation plates, mandibular and maxillary prostheses (for instance jaw remodelling) [43]–[45].

- Domestic - Injection-moulded reinforced thermoplastic and polyester moulding composites have been used extensively in manufacturing items for the domestic market such as kitchen equipment, motor cycle crash helmets, computer and television casings and tennis rackets [46].

- Sport - One can obtain composite sports gears such as boats, oars, skateboards, surf boards, archery equipment, golf clubs, cricket bats and many sorts of sports equipment. For example, the skis. Fibre composites of skis is suitable for any types of snow and easy in maintenance. For golf clubs, carbon fibre reinforced composite material is used. It is high elasticity, high strength and impact resistance, making the golf clubs being used repeatedly [47]–[49].

The main focus of interest in the present study is to reinforce the polymer matrix composite with natural fibre to produce biocomposites. In comparison with conventional composites, biocomposites use natural fibres as a reinforcing agent which are abundantly available, environmentally friendly, low cost and offer high specific properties [50], [51].

2.2 Biocomposites

In polymer science, natural fibre reinforced composite has become a promising area [38], [52]–[54]. It has gained researchers' attention because of their technical advantages like strength, lightweight and noise absorption etc. Apart from that, they are economical because of their low density, high specific properties, non-corrosive and biodegradable [55]. When compared to those of conventional fibre composite, natural fibres offer high specific properties [51]. Nevertheless, in expansion of these composites, the incompatibility of the fibres and poor resistance to moisture often lessen the prospective advantages of natural fibres and these drawbacks become a serious issue.

The addition of natural fibres in composite system, improves several mechanical properties like flexural strength, tensile strength and flexural modulus [56], [57]. Likewise, the impact strength was found to be lower than pure composite and this was because of the lignocellulosic content of the fibre.

Natural fibres have been widely used as a reinforcing agent in polymers due to their low density that can enhance the mechanical properties of materials [58]–[60] . In the work by Ramires and Frollini [25], they used sisal fibres as reinforcement in the tannin-phenolic composites, which resulted in a substantial improvement in the impact strength of the composites. However, after a certain amount of fibre was incorporated in the composites, which in this case was 50 wt%, the strength of the composite started to deteriorate. This is due to incomplete impregnation of the fibres thus leading to higher fibre-to-fibre contact in the composites.

Another study [61] demonstrated that fibre content that was higher than 15 v% reduced the modulus and strength due to poor dispersion of the fibre and voids presents in the composite. One of the alternatives to improve the fibre-matrix adhesion is to treat the fibre with suitable treatment. In this study, they treated the jute fibre with alkali treatment to remove the impurities present on the fibre. It was found that void content of the composites decreased and thus enhanced the impregnation of fibre in composite.

One of the modifications that can be implemented to enhance the properties of biocomposites is to treat the natural fibre chemically. Previous studies [62], [63] reported an increase in mechanical properties of the biocomposites when fibres were treated by alkali solution at certain concentrations. As a result, thermal stability was improved as more homogeneous materials with better resistance to thermal decompositions and also decreased the carbonaceous char formation.

Other than alkali treatment, graft copolymer of methyl methacrylate (MMA) was used on flax fibres to enhance the properties of phenolic composites [64]. Through this treatment, the tensile strength and water repellence of the composites improved compared to flax fibres without treatment.

2.2.1 Matrices for biocomposites

The matrix binds the fibres together, holding them aligned in the important stressed directions [30]. Applied loads on the composite are transferred into the fibres, establish the principle load-bearing component through the matrix. This enables the composite to withstand compression, shear forces, flexural and tensile loads. For composites with short fibre reinforcement, the capability of the composites is dependent to the matrix and the quality of fibre-matrix bond [65]. The matrix should be able to protect the fibres from mechanical damage such as abrasion and environmental attack. According to Harris [30], ductile materials will slow down or stop the cracks at broken fibres, while brittle materials depend on the fibres to act as matrix crack stoppers. The matrix gives the composite the compressive strength and in the case of fibre reinforced plastics, can be made using thermoplastic or thermoset polymers.

2.2.1.1 Thermosetting and Biopolymer Thermosetting Matrices

Thermosets are polymers that are cured into a solid form and cannot be returned to their original uncured form. They are strong and have high fatigue strength, but they are relatively brittle and low impact toughness [66] . Because the thermoset does not melt like thermoplastic, they are used extensively in high heat applications. The only drawback of thermosets is that they are hard to recycle because of their nature that they cannot be remoulded or reshaped [67][68]. Some examples of thermosetting resins used in manufacturing composites are explained in the next paragraphs.

Some epoxy resins are derived from diglycidyl ether of bisphenol A (DGEBA) and are extremely reactive to some chemical groups such as hydroxyl groups. Epoxy resins are extremely versatile materials that find use in a range of applications such as in carbon fibre composites, circuit board lamination, adhesives and electronic applications. As they are versatile, they can be mixed with a number of curing agents, for instance anhydrides, amides and amines [69]–[73]. Due to their high crosslinking degree, they tend to have low strain to failure [74], [75] but this can be enhanced by using acrylic rubber and hydroxyl-terminated butadiene, or by use of thermoplastic toughening agents such as polyether sulfone (PES) [76], [77]. It is also possible to produce epoxy resins using derivatives of plant oil in the epoxy resin formulation [78]. Such epoxidised plant oils have been synthesised, for instance epoxidised palm oil, epoxidised linseed oil, epoxidised rapseed oil, epoxidised soybean oil and many more. The derivatives of epoxidised plant oil and fatty acid become a promising material that can be used in many applications such as resins, rubbers and coatings [79]–[81].

Synthesis of a polyol and a polyvalent acid or acid anhydride produced a polymer called an unsaturated polyester resins [21][82]. They have been used currently as decorative coatings and commodity composite materials, including equipment used in industrial for instance, in making a boat, ruck roofs, tanks and many more [21]. Unsaturated polyester resins are cured with styrene as a reactive diluent in unsaturated thermosetting materials, this is general known as unsaturated polyester resin [83]. Polyester resins possess some good mechanical and electrical properties, fairly good heat and creep behaviours, chemical resistant and excellent in weak acid conditions while the disadvantages are high cure shrinkage. High styrene emission in open moulds also require special precautions when processing [84].

Polyurethane resin is a versatile material. It can be in the form of a flexible or rigid foam for use in applications such as upholstered furniture or insulation in walls, roofs [85]. Alternatively, thermoplastic polyurethane can be used in applications as diverse as medical devices, coatings, adhesives, sealants, and elastomers for use in areas such as footwear [86]. It represents a versatile thermoplastic or thermoset materials since the mechanical, thermal and chemical characteristics can be adapted as required using different polyols and isocyanates [87]. Bio-based polyols can be used instead of oil-based systems to make the material more environmentally friendly [88]. For example, castor oil and soy flours are sustainable sources that have been used as raw polyols in producing polyurethane [89], [90]. Silicon or aromatic compounds have been used for functionalising vegetable oils to broaden the applications of polyutrethane [91]. This has been used in improving the flammability of a material by using fatty acid-based polyols containing silicon [21] .

In synthesis of phenolic resins, phenol and formaldehyde are mixed and undergo a polycondensation reaction [92]. When the reaction takes place, water is eliminated as a by-product. Novolak or resole resins are produced as the main product depending on the reaction conditions whether it is acidic or basic [93]. Uses of phenolic plastics can be seen in mouldings (standard fittings, components and general utility objects both in the industrial and domestic fields), cast resins (used in decorative items such as bracelet, handles, clock cases, radio cabinets and so on due to beauty and wide color range of phenolic) and laminates (used in scientific and testing instruments, X-ray machines and many other industrial applications) [94]. Phenolic resins are combined with reinforcing fillers or fibres to support and act as a binder to the composites [95]. Phenolic resins possess good mechanical properties, resistant to heat and fire, and produce low smoke upon incineration [49], [96]. Alternatively, phenol in phenol-formaldehyde resin can also be substituted by natural phenolic materials, such as cashew nut shell liquid, lignin, tannins, gallic acid, pyrogallol and phlorogucinol, leading to production of bio-based resins [21]. In the present study, the author has chosen gallic acid as a phenol substitution to produce biocomposites, and the effect of substitution has been investigated by means of mechanical properties, thermal properties, chemical analysis and morphological study.

2.2.1.2 Biopolymer Thermoplastics for Composite Materials

Thermoplastic polymers are materials that can be moulded, melted, and remoulded without changing the physical properties. It is relatively strong and less brittle than thermoset materials, with very good impact resistance and damage tolerance. Due to its properties that can be melted, it can be remoulded and recycled easily. However, due to the high temperatures and pressures needed to melt the polymers, it is more energy intensive thus making it more expensive to process than thermosets [97]. Despite the disadvantages, a few numbers of investigations has been done to study about the suitability of thermoplastic as matrix in composite.

Due to its high strength, high modulus and high optical transparency, polylactic acid (PLA) has been a popular biodegradable polymer among scholars. Herrera et al. [98] used glycerol triacetate (GTA) as a plasticiser in PLA and blended with cellulose nanofibre (CNF) composites. When added with 20% of GTA and 1% of CNF, the degree of crystallinity was increased and the optical transparency was decreased. The presence of CNF has also improved the toughness and elongation at break from 2% to 31%.

Polyhydroxyalkanoates (PHA) is a carbon-neutral and beneficial polymer that could be manufactured from various renewable carbon sources by microorganisms. PHAs are blend with low or high molecular weight molecules in order to enhance their mechanical properties. This helps to reduce the cost of production too. Savenkova et al. [99] investigated the effect of different plasticisers on the physical properties and biodegradation characteristics of polyhydroxybutyrate (PHB) based films. It was found that between polyethylene glycol (PEG 300), laprol or oxypropylated glycerol of molecular mass 5000 (LAP), dibutylsebacate (DBS), dioctylsebacate (DOS) and polyisobutylene (PIB); Laprol was a good plasticiser for PHB produced by *Azotobacter Chroococcum 23* and for PHB containing biomass (BM). As the LAP concentration increased, the biodegradation rate of PHB decreased.

Another biodegradable thermoplastic polymer that is produced from polyester on the basis of petroleum is polycaprolactone (PCL). The miscibility of PCL is very high, such that it can be mixed with lignin and starch as well as other plastics. Furthermore, it sticks well to a variety of surfaces. It can be made easily, and is non-toxic and meltable. Di Franco et al. [100] investigated the vulnerability of polycaprolactone/starch (PCL/S) and sisal fibre-reinforced polycaprolactone/starch blends (SF-PCL/S) to various environments. Due to the hydrophobic character of PCL, PCL/S and sisal fibre composites showed hydrolytic stability in aqueous medium and in the absence of microorganisms. The composites with higher fibre content showed higher stability while low fibre content was less stable than the unfilled matrix. The strong fibre-fibre interactions cannot be achieved at low fibre content because the fibres are not close enough, but they acted as channels to promote water diffusion into the matrix and resulted in the preferential hydrolysis of the starch. As at higher fibre content, physical networks were built, so the water intake could be prevented, and the hydrolytic stability of the material could be improved.

Last but not least, Velde and Kiekens [101] made an investigation to find the most suitable thermoplastic biopolymer matrix for a flax fibre reinforced composite. Temperature and density related properties seemed to be the constraining criteria for the choice of a right polymer. As has been highlighted, the mechanical strength of the biopolymer was not very important for this particular application. In this case, polyglycolic acid (PGA) was eliminated as a candidate for composite matrix used as its density and melting point were too high in order to be energy saving. Besides, it resulted in flax degradation if processed in high processing temperatures. Due to its hydrolytic instability, its use has been limited.

2.2.2 Natural Fibres for Bio-Composites

One of the most commonly used fibre as a reinforcement in composite is glass fibre [11]. Glass fibres are low cost compared to carbon and aramid fibres and have fairly good mechanical properties [11]. Glass fibres, due to their relatively low modulus are a potential target for natural fibre systems, which can’t compete against the modulus of carbon fibres [102]. As such, comparison between glass fibres and natural fibres is an important one to determine the best approach to replacing energy intensive glass production with a natural product.

Glass fibres have disadvantages as shown in Table 2.1 below. Table 2.1 also shows that natural fibres have a number of advantages over the glass fibres.

Table 2.1 Comparison between glass fibres and natural fibres [11]

	Glass Fibres	Natural Fibres
Cost	Low, but higher than natural fibres	Low
Density	Twice that of natural fibres	Low
Recyclability	No	Yes
Renewability	No	Yes
Distribution	Wide	Wide
Energy consumption	High	Low
CO_2 neutral	No	Yes
Health risk when inhaled	Yes	No
Abrasion to machines	Yes	No
Disposal	Non-biodegradable	Biodegradable

As advantages of natural fibres outweigh the glass fibres, hence natural fibres have been chosen as a reinforcing agent in this present study. Natural fibres are classified according to their source; minerals, animals or plants [103]. Generally asbestos is a naturally arising mineral fibre (silicate-based mineral) [104]. The key properties of asbestos fibres are their electrical, thermal, and sound insulation; good fire resistance,; suitability for use as a reinforcing agent in cement, plastic, and resin, , wear and friction properties for brake linings and their chemical inertness except in acids [105]. Animal fibres commonly contain proteins [106]. Silk, feathers, wool and human hair are the examples of animal fibres [106]. Plant fibres are the main types of natural fibres and commonly used as a reinforcing agent in the composite industry. There are varieties of plant fibres such as fibre-sheaf of dicotylic plants or vessel sheaf of monocotylic plants (e.g. flax, hemp, jute, and ramie), seed fibres (cotton, kapok), and leaf fibres (coir, sisal and henequen) [107]. Table 2.2 shows the advantages and disadvantages of natural fibres and Table 2.3 shows some of the tensile properties of single fibres.

Table 2.2 Summary of Advantages and Disadvantages of Natural Fibre [108]

Advantages	Disadvantages
Recyclable	Low durability, hence need certain treatments to the fibre to cater the issue
Renewable source	Quality and availability of natural fibres is depend on certain conditions, such as origin, weather, type of soil, etc
Not expensive	Easy to absorb moisture, causes swelling
Equivalent modulus to glass fibre due to low specific weight. Favourable in applications aimed for bending stiffness	Low strength properties, such as impact strength.
User friendly, readily available	Restricted processing temperature according to type of fibres.
Good thermal and acoustic insulating properties.	Poor fire resistance and price can vary by harvest results or agricultural politics.

Table 2.3 Tensile properties of single fibres

	Young's modulus (GPa)	**Ultimate stress (MPa)**	**Strain to failure (%)**	**Density (g/cm^3)**	**Average diameter (µm)**	**References**
Stinging nettle	87 (± 28)	1594 (± 640)	2.11 (± 0.81)		19.9 (± 4.4)	[13]
Flax ariane	58 (± 15)	1339 (± 486)	3.27 (± 0.4)	1.53	17.8 (± 5.8)	[109]
Flax agatha	71 (± 25)	1381 (± 419)	2.1 (± 0.8)	1.53	15 (± 0.6)	[110]
Hemp	19.1 (± 4.3)	270 (± 40)	0.8 (± 0.1)	1.48	31.2(± 4.9)	[111]
Ramie	65 (± 18)	900		1.51		[112]
Ramie	24.5	560	2.5	1.51	34	[113]
Glass	72	2200	3	2.54		[114]

2.2.2.1 Jute Fibres

Jute fibre is produced primarily from plants in the *Genus chorchorus*, in the family *Tiliaceae* and *Malvaceae*, is one of the most commonly used natural fibres as a reinforcement in composites [115]. They are composed primarily of cellulose, hemicellulose and lignin. Jute fibre is fully biodegradable and recyclable and thus environmentally friendly [116]. They are abundantly available, low cost and high tensile strength. Numerous jute composites have been developed with different polymer matrices.

Dynamic mechanical analysis (DMA) was used by by Karaduman et al. [117] to investigate the properties of jute fibre/polypropylene nonwoven reinforced composites. Alkali solution was used to treated the surface of jute fibres to improve the fibre-matrix adhesion. The fibre content was varied from 40 to 60 wt%. From the result, it showed that the storage modulus increased with increasing content of fibres. Characteristics of interface adhesion between jute fibre and PP matrix was further analysed using adhesion efficiency factor (*A*) and reinforcement effectiveness coefficient (*C*). The result showed that higher jute fibre content led to increasing *A* values indicating that poor interface adhesion in the composites, while *C* values for the composites decreased with increase in jute fibre content suggesting poor load transfer between jute fibres and PP matrix.

Hossain and co-workers [118] extensively investigated the mechanical properties of surface modified jute fibre reinforced biopol nano phased green composites. Chemical treatments such as detergent washing, dewaxing, alkali and acetic acid treatment were performed. It could be seen from scanning electron microscopy that surface impurities, non-cellulosic substances, inorganic materials, and waxes were successfully removed resulted in cleaner and rougher surfaces. These led to better interaction of fibres with matrix for larger surface area. Higher percentage of crystalline cellulose in treated fibre was seen in the fibre bundle tensile tests and this showed that the tensile properties of the composites was improved. This can be said that composites with treated jute fibre exhibited better mechanical properties such as storages modulus, loss modulus, flexural modulus and strength compared to untreated fibre.

Jawaid et al. [119] combined oil palm empty fruit bunch (EFB)/jute fibres with epoxy resin to produce hybrid composites that is comparable to synthetic composites. It was observed that the hybrid composites exhibited better flexural strength when compared to pure EFB composites. The similar trend was also seen in flexural modulus in reference to fibres layering pattern. Impact strength of pure EFB composite was also found to improve than hybrid composites and this is because of the lignocellulosic content of the fibres. SEM showed the impact fracture surface morphology of hybrid composites were smooth indicated poor interaction between the matrix and the fibres as matrix cracking and fibre fracture can also be observed.

Jute fibre reinforced polypropylene (PP) composites were investigated by Hong et al. [120] regarding the effect of a silane coupling agent. The study showed that the fibre-matrix interaction was increased through a condensation reaction between hydroxyl groups of jute cellulose and hydrolysed silane. Mechanical properties such as tensile properties of jute/PP composites were increased too. It can be seen from dynamic mechanical analysis that reinforcing jute fibre, when combined with pure PP, enhanced the storage modulus significantly over the whole range of testing temperatures. Due to the reinforcement imparted by the fibre, resulted in allowance of stress transfer to occur at the interface.

In summation, jute fibres have been used widely as a reinforcing agent in making the composites. Numerous studies as stated above have been found using treated-jutre fibre and it shows that properties of the composites such as storage modulus, loss modulus, flexural strength and modulus improved compared to untreated jute fibre. Chemical treatment using alkali and acetic acid have been found to exhibit better fibre-matrix interaction due to removal of surface impurities, non-cellulose substances, inorganic materials, and waxes resulted in cleaner and rougher surface.

2.2.2.2 Flax Fibres

Flax fibre is a member of the *Genus linum* in the family *Linaceae* is one of the strongest bast fibres among other natural fibre [121]. It is found mostly in temperate regions and frequently used in textile markets [122], [123] . Flax has good heat conducting properties[124], [125]. However, constant creasing in the same place tends to break the fibre [121]. Currently it has been widely used in composite materials.

Zhu and co-workers [126] have studied the mechanical properties of flax fibre/tannin composites following different chemical treatments. There were five types of treatment: untreated, mercerisation (sodium hydroxide, NaOH), acetylation (butanetetracarboxylic acid, BTCA), silane treatment (aminopropyl (triethoxy) siloxane, APS), and enzyme (laccase Doga, LD). It was found that tensile properties of the composites were varied accordingly, APS > LD > BTCA > NaOH > untreated. In silane treatment, silane linkages were formed between the fibre surface and resin at elevated temperature, hence improving the interfacial adhesion strength. From the findings, they concluded that BTCA treatment was the best technique to enhance the fibre reinforcement effects.

Aydin et al. (2011) [127] performed a study to investigate the morphological, thermal and mechanical properties of short flax/fibre/polylactic acid (PLA). The untreated flax fibre/PLA composites showed higher modulus than pure PLA. Nevertheless, alkali treated fibre/PLA composites exhibited lower modulus than pure PLA. This could be due to excessive damage on fibres surfaces during alkali treatment or possibly due to the plasticising effect. Thermal properties of the PLA in the treated flax fibre composites are also affected. The glass transition temperature of the treated flax fibre composites was decreased because of the plasticisation effect. Image from SEM analysis showed that the lignin and waxes on the fibre surfaces has been removed prior to the chemical treatment on the fibre.

Manfredi and co-workers [128] studied the thermal degradation and fire resistance of flax fibre composites reinforced with polyester resin. Unsaturated polyester (UP) and modified acrylic resins (Modar) were used as matrix composites. The study showed that under thermal degradation of the Modar matrix composites, they were more resistant to temperature than the composites with UP matrix. In the cone calorimeter test, flax fibre composite developed a long gas duration, but slow growing fire compared to jute fibre that showed a quick growing but short duration fire.

Different quantity of silicones have been used to coat flax fibres and the effect on the properties such as flexural properties, dynamic modulus and loss modulus, impact toughness and notch sensitivity were studied [129]. It was found that the coating process had a strong effect on composite properties. It increased the viscosity of the silicone solution and increasing the silicone content thus improved the impact toughness of the composites. The composites with the weak interlayer showed a large drop in flexural strength and modulus similar with the degree of non-linearity of the stress-strain hysteresis loop that was found to be lower in untreated composites.

As has been discussed in this section, the other popular choice of fibre is flax fibre. The fibre has been used a reinforcing agent with thermoset and thermoplastic. Many know that incorporation of fibre into composite lead to poor interfacial adhesion with matrix. To overcome this predicament, one of the treatments used is silane treatment. Those silanes formed silane linkage between fibre and matrix hence improving the adhesion strength.

2.2.2.3 Hemp Fibres

Hemp is a variety of *Cannabis sativa* that is grown for the fibre and seeds [130]. It is an annual plant that grows in temperate climates. It has been valued for its high strength and long fibre length and has been refined into products such as hemp seed foods, hemp oil, wax, resin, rope, cloth, pulp, paper, and fuel [131].

Simultaneous influence of polypropylene-graft-maleic anhydride (MAPP) and silane-treated hemp fibres (HF) on morphology, thermal and mechanical properties of high-flow polypropylene (PP) modified with poly[styrene-b-(ethylene-co-butylene)-b-styrene] (SEBS) was studied in this paper by Panaitescu et al. [132]. The efficiency of MAPP in PP composites with HF was decreased with the addition of SEBS, thus to improve polymer-fibre interface, hemp fibres were treated with silane. After silane treatment, the thermal stability of HF was improved, and less than 2% weight loss was observed at 240 ˚C in composites with 30 wt% HF. The study showed that better dispersion of fibres and better efficiency in enhancing static and dynamic mechanical properties of PP with treated fibres resulted in superior strength and stiffness compared to untreated ones. High ability of absorption and energy dissipation and well-balanced strength and stiffness were exhibited by PP modified with SEBS and MAPP containing 30 wt% HFs.

Singh and co-workers [133] investigated the mechanical properties (tensile and flexural) of hemp fibre reinforced virgin recycled high density polyethylene (HDPE) matrix composites. It can be seen that increasing hemp content from 10% to 30% decreased the tensile strength of hemp fibre composites to 2.20 MPa compared to specimen made of 50% fresh and 50% recycled HDPE. The similar trend can also be seen in the flexural strength of the composite, in which hemp fibre content at 10%and 30%, decreased respectively between 3.82 MPa and 4.99 MPa compared to the specimen made of 50% fresh and 50% recycled HDPE. These findings showed that poor interaction of fibre-matrix, delamination of fibre and fibre tensile fracture led to poor tensile strength of the composite.

Sawpan et al. investigated the interfacial shear strength properties of treated hemp fibre reinforced polylactide (PLA) and unsaturated polyester (UPE) composites [134].

Hemp fibres were chemically treated with acetic anhydride, maleic anhydride, sodium hydroxide and silane. Furthermore, the fibre was treated using a combination of silane and sodium hydroxide. The study revealed that IFSS of PLA/hemp fibre composites increased after treatment, except in the case of maleic anhydride treatment. This was attributed to a better bonding between PLA and treated fibres, and increased transcrystallinity of the PLA. PLA/alkali treated fibre samples exhibited the highest IFSS (11.4 MPa). FTIR results showed that due to the chemical treatment on fibres, the chemical bonding between treated fibres and the UPE were improved, hence increased the IFSS of the composites. A combination of silane and sodium hydroxide treatment on hemp fibres yielded the highest IFSS, which is 20.3 MPa.

Lebrun et al. [135] manufactured unidirectional (UD) hemp/paper/epoxy and flax/paper/epoxy composites by using one or two sheets of paper at the surface of a unidirectional layer of hemp or flax fibres before moulding. Results obtained were compared with those UD composites without paper and it was revealed that the tensile strength and modulus increased when reinforced with paper layer. The strength and modulus were also increased in comparison with the base epoxy properties. Generally, the results suggested that addition of thin sheets of paper at the surface of reinforcement layers stabilised and increased the composite strength but slightly reduced the Young's modulus.

Dhakal and co-workers [136] studied the mechanical properties of polyester with hemp fibre as a reinforcing agent in in terms of water absorption. Specimens were submerged in a de-ionised water bath at 25 ˚C and 100 ˚C for different time durations. Aging conditions of both immersed and dry composite specimens were then investigated by means of tensile and flexural properties. Due to the high cellulose content, the moisture uptake level increased as the fibre volume fraction increased. Increasing moisture uptake shows that the tensile and flexural properties of hemp fibre reinforced unsaturated polyester (HFRUPE) specimens decreased. It was found that the water absorption pattern of these composites obey Fickian behaviour at room temperature, while they exhibited non-Fickian behaviour at elevated temperature.

In conclusion for hemp fibres, composites with treated fibre exhibit superior strength and stiffness properties compared to untreated fibre. Acetic anhydride, maleic anhydride and sodium hydroxide are choices to be used chemically to treat the fibre. Previous studies mentioned above showed improvement in interfacial shear strength when fibres were chemically treated. Other than that, they found that addition of thin sheets of paper at the surface of reinforcement layers improved the strength of the composites.

2.2.2.4 Sisal Fibres

Sisal fibres belong to the agave family (*Agavaceae*). The plants are able to withstand the cold of winter, hot climates and arid regions all of which are often unsuited to other crops [137] . Sisal can grow in most soil types, with the exception of clay, but it has poor tolerance to very wet or salty soil [138]. This fibre is generally used for mats, carpets, and many other reinforcement materials [139].

Orue and co-workers [140] investigated the effect of surface modifications on sisal fibre properties as well as on fibre/poly (lactic acid) (PLA) interface adhesion. For this purpose, alkali, silane and combination of both treatments were applied to sisal fibre. The effects of treatments on fibre/PLA interfacial shear strength (IFSS), fibre thermal stability, fibre wettability, morphology, and tensile properties were studied. The study showed that, after treatment, IFSS values improved at least 120%. Alkali treatment eliminated some non-cellulosic components (hemicelluloses, lignin) as confirmed by thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR). The elimination of non-cellulosic materials led to fibrillated and rough morphology as observed by optical microscopy (OM). It was found that the fibre/PLA adhesion of composites was improved regardless of the treatment used in this case study.

The effect of alkalised and silanised sisal fibres on mechanical properties of modified epoxy resin were studied [141]. Grafting depolymerised natural fibre (GDNR) that was used in modification of epoxy resin exhibited improved impact strength while composite with silanised fibre showed the highest impact strength. Flexural modulus of modified fibre composites were higher than GDNR/epoxy blend composites and increased with increasing fibre content. The flexural modulus was superior when silanised sisal fibre was added. All composites showed lower flexural strength than neat epoxy resin and the blend. Nevertheless, result showed that the composite containing silanised sisal fibre showed an improvement of flexural strength compared to the composites prepared using alkalised sisal fibre.

In the paper by Barreto et al, the sisal fibres were modified by alkali solutions of NaOH (5% and 10%) and bleached with sodium hypochlorite $NaClO/H_2O$ (1:1) at 60–75 ˚C [142]. The fibre was used as reinforcing agent in the preparation of phenolic matrix composites derived from cashew nut shell liquid (CNSL). It was observed from SEM that chemical treatment caused exposure of the cellulose structures through the separation of the fibrils and increase of the superficial area. This modification led to the improvement of fibre/matrix adhesion and resulted in more homogeneity and resistant to thermal decomposition materials. The chemical treatment improved the thermal stability of the weight loss process for sisal treated with NaOH 5% in about 12 ˚C and for sisal treated with NaOH 10% in about 18 ˚C when compared to sisal fibre in its raw state.

Sangthong et al. [143] used admicellar polymerisation of methylmethacrylate (MMA) as another method in improving the interfacial adhesion between the fibre and the polymer matrix. Sisal fibre was treated with admicellar treatment and the properties of the treated fibre was studied. Admicellar polymerisation is an innovative technique used to improve the material surface with an ultrathin polymeric film coating. Results obtained revealed that the tensile and flexural properties, in both strength and modulus, increased with increasing fibre length for both untreated and admicellar-treated sisal fibres up to the fibre length of 30 mm. Nevertheless, the trend decreased when the fibre length increased to 40 mm. Increasing fibre loading also improved both impact and hardness properties. Higher amounts of MMA were also found to give higher impact and hardness properties.

The effect of sisal fibre modified with lignin, and the correlation between fibre and phenolic composites properties were investigated by Megiatto Jr. et al. [144]. To ensure good adhesion in resole resin, sisal fibres have been chemically modified by reacting it with lignins, that were derived from sugarcane bagasse and Pinus-type wood and then hydroxymethylated. The acidic site was found to favour the unmodified/modified sisal fibres and phenolic resins as seen in inverse gas chromatography (IGC) results. This result suggested that good interaction between matrix and fibre. The IGC results also revealed that the phenolic resin has a dispersive component that was closer when compared to the modified fibres. Blocking of water passages can be seen due to the ability of the phenolic resin whereby it penetrates well into modified fibres, hence this resulted in good water diffusion in the composites. This study concluded that modification of fibres increased the storage modulus of the composites, reduce the hydrophilic character and showed almost no effect on impact strength.

One of the specialities of the sisal fibre compared to other fibre is, it grows well both in cold weather and extremely dry regions which are often irrelevant for other crops. Previous studies also mentioned the use of alkali and silane to treat the fibre. Other than those treatments, one of the scholar [143] used admicellar polymerisation which uses ultrathin polymeric film to coat the material surface. This resulted in higher tensile and flexural strength and modulus. In conclusion, fibre modification leads to better mechanical properties of the composite.

2.2.2.5 Kenaf Fibres

Hibiscus cannabinus, known as kenaf fibre is a plant in the *Malvaceae* family. It has low density, is easy to process, has high specific mechanical properties and is biodegradable [145]. Recently, kenaf fibre has been used widely as a substitution to wood in paper and pulp industry to minimise the destruction of forests, it is also used in textiles, the automotive industry and for fibre board application [145]. Kenaf fibre has also been chosen as a reinforcing agent in manufacturing composites,. with the benefits of cost, availability, recyclability, energy use and environmental considerations. This shows that kenaf fibre is a good, potential plant to reinforce polymer, both thermosets and thermoplastics.

In work by Fiore et al. [146], kenaf fibres were pre-treated in an NaOH solution (6% in weight) at room temperature for two different periods (48 and 144 h). At 48 h treatment, the fibre surface was cleaned, and impurities were removed, while a 144 h treatment time was found to deteriorate the fibre surface, and thus affected the mechanical properties of the composites. Later, the 48 h NaOH-treated-kenaf fibre was used as reinforcing agent of epoxy resin composites. The effect of the stacking sequence (i.e. using unidirectional long fibres or randomly oriented short fibres) and the chemical treatment on the static mechanical properties showed that the composites exhibited higher modulus in comparison to the pure resin. Results showed that unidirectional layers of fibres in composites exhibited higher strength than the pure resin. Furthermore, with the fibre being treated chemically with NaOH, the mechanical properties of the composites improved due to the better fibre-matrix adhesion. The dynamic mechanical analysis showed the superior properties in the storage and loss modulus, mainly influenced by the alkali treatment.

Polylactic acid (PLA) composites were synthesised by mixing PLA and kenaf fibre using dry blending, twin screw extrusion and compression moulding techniques in research by Shukor et al. [147]. The study used kenaf core fibre as a reinforcing agent with PLA as matrix, polyethylene glycol (PEG) as plasticiser, and ammonium polyphosphate (APP)as a flame retardant. The fibre was chemically treated with 3%, 6% and 9% NaOH solution separately. After that, flame retardant was added at 10, 15 and 20 phr APP to the composite in order to investigate the flammability, thermal and mechanical properties of both untreated and treated fibre in the composite. Based on the flammability test, addition of APP has increased the char residue at elevated temperature. Nonetheless, it has decreased the mechanical properties of the composites due to APP hindering the interaction between PLA and fibre. In summary, treatment of fibre with NaOH has improved the thermal properties of PLA biocomposites and diminished the formation of carbonaceous char.

Anuar and Zuraida (2011) [148] reported on the development of thermoplastic elastomer composite reinforced with 20 vol.% kenaf fibre. Polypropylene (PP) was blended with two types of impact modifier; thermoplastic natural rubber (TPNR) and polypropylene/ethylene–propylene–diene–monomer (PP/EPDM). Maleic anhydride polypropylene (MAPP) was added as in the case of treated composite due to incompatibility between matrix and reinforcement. Tensile strength for TPNR is 12% higher than the PP/EPDM matrix. The presence of kenaf fibre (KF) and MAPP had significantly increased the tensile strength of the PP/EPDM composite by approximately 81% while only 55% increment achieved in TPNR–KF–MAPP as compared to unreinforced TPNR. Furthermore, reinforcement of kenaf fibre in composites has improved both flexural properties and impact strength. This proved that KF has imparted its tensile strength to the PP/EPDM system with good interaction provided by the compatibilising agent. Fibre-matrix interaction was seen to be improved too through the images obtained from scanning electron micrographs (SEMs).

Bio-composites consisting of kenaf fibre reinforced polylactide were made-up by a carding process followed by treatment with a 3-glycidoxypropyl trimethoxy silane and hot-pressing to impregnate the fibres (Lee et al. [149]). Silane coupling agent was used on the composites to enhance modulus and heat deviation temperatures and also to reduce water swelling. When the level of kenaf loading increased, swelling was increased too, but this decreased when coupling agent concentrations increased. Mechanical properties of the biocomposites at temperatures above the glass transition significantly enhanced in comparison to the base PLA polymer. As little as 10 wt% kenaf fibre in PLA provided a heat distortion temperature in excess of 140^{o}C when mixed with the coupling agent. Incorporation of coupling agent into the composite showed little to no effect on the thermal properties such as melting temperature, glass transition temperature and crystallinity percent of PLA matrix.

In summary, kenaf fibres have been used widely as a reinforcing agent in thermoset and thermoplastic polymer, especially in tropical weather. The fibre was modified in order to improve the properties. One of the researcher [147] used kenaf core fibre and treated it with sodium hydroxide before blended it with PLA, PEG and APP. It was found that APP improved the flammability of the composites. Hence, it can be stated that surface treatment on fibre and incorporation of plasticiser in composites improved the impact strength.

2.2.2.6 Nettle Fibres

Urtica dioica, often called common nettle or stinging nettle, is an herbaceous perennial in the family Urticaceae. Nettle fibre has been investigated as a potential material to be used as a reinforcing agent in biocomposite [150], [151].

A considerable amount of literature has been published on nettle fibre. Bodros and Baley [13] performed an experiment to study the tensile properties of stinging nettle fibre. They compare it with the single fibres like flax, hemp, ramie and glass and found out that the stiffness of nettle fibre is greater than glass fibre. Due to its low density, nettle fibre can be considered as high-performance fibres. Due to that fact, nettle fibre can be a good reinforcing agent in composite materials.

To determine the effect of nettle fibre as a reinforcing agent, Fischer et al. [150] produced a composite of nettle-reinforced polylactic acid and found out that at 30wt% of nettle fibre, the tensile strength improved from 52 MPa of the pure PLA to 59 MPa. Furthermore, the modulus also increased from <3500 MPa of polylactic acid to >5000 MPa. This shows that nettle fibre can be a potential reinforcing fibre.

A previous study [152] also investigated the effect of different environmental conditions such as in river water, diesel, freezing condition, soil and sunlight on the tensile behaviour of polypropylene/nettle biocomposite. The results demonstrated the maximum reduction of tensile strength in sunlight and river water environments, while the minimum reduction was seen when samples were exposed to soil. This work is interesting and can be extended towards the study of mechanical properties of the biocomposites under various other environments.

Pokhriyal et al [153] investigated mechanical properties of Himalayan nettle fibre and unsaturated polyester resin. The Himalayan nettle is known as *Girardinia diversifolia,* a perennial herbaceous native to Nepal and India while another nettle*, Urtica dioica* is native to Europe, Asia, northern Africa and western north America [154]. This study showed that the impact strength of the composite improved when fibre was up to 15 wt%. The property started to deteriorate when fibre content was more than 15 wt%.

Another study [155] investigated the effect of surface treatment on nettle fibre using NaOH. The 2% NaOH treated composites showed higher tensile strength and modulus compared untreated ones. This treatment eliminated surface impurities on the fibre by and producing rough fibres, which improved fibre-matrix adhesion .

Paukszta et al. [156] obtained composites from PP and nettle fibre by extrusion method to study its mechanical properties. Result showed that at 10 wt% of nettle has slightly improved the Young modulus compared to unfilled PP. This is expected since higher content of natural filler lead to higher values of Young modulus.

The studies presented so far highlight the modulus of composites is greatly increased when incorporated with nettle fibre, but how about strength properties and the interaction of fibre-matrix in the composites. Further works need to be done to enhance the mechanical properties of the composites, as it has been used widely in composites manufacturing with polymer matrix. The applications of nettle fibres have no limit; for instance, in cordage industry, textile, manufacturing aircraft panels, gear wheel and other machine components [13], [151], [157]–[163]

2.2.3 Summary

The production of biocomposite from bio-based resin and natural fibre has become an interesting project for researchers. The method of combining fibres and matrix into a composite material depends very much on the ratio of both and on the scale and geometry of the structure to be manufactured. For example, most thermoplastic-based materials are made by injection moulding, while thermoset-based materials are manufactured by resin transfer moulding [164], [165]. Both methods could possibly produce a composite that contains a region in which the fibres are highly oriented and others where the degree of orientation is almost zero. This is a common problem as variations in fibre content from place to place can occur in the composite [30].

As advantages of natural fibres outweigh the glass fibres, hence natural fibres have been chosen as a reinforcing agent. In this present study, nettle fibres have a higher modulus than most plant fibres, due in part to their high silica content, thus make them a suitable option as a reinforcement in phenol-formaldehyde resin [166].

Common problems experienced in composites are the compatibility between the fibres and the matrix. This is due to poor interfacial adhesion between fibre and matrix system [167]. Therefore, many scholars have introduced treatments to the natural fibres' surfaces in order to improve the compatibility and interfacial bond strength [63], [117], [118], [140], [168]. One of the treatments is chemical treatments, such as bleaching, acetylation and use of alkali, which are found to be good at improving the matrix-fibre adhesion by cleaning the fibre surfaces and eliminating the impurities, and hence making the fibre surface rougher and interrupting moisture absorption [139], [169]–[172].

Additionally, the incorporation of natural fibre has improved the mechanical properties of the composite based on what has been reported [95], [173], [174]. This is expected since a stiffer material is introduced in to the matrix [175].

Having studied natural fibres and resin system, it is clear that nettle fibres and phenolic resins are both interesting. While it can be seen that there are a variety of natural fibres, nettle fibres have caught the author's attention as it possesses high modulus due to their high silica content. Furthermore, they are native to European countries and Asia, and can be found growing in any soil, so they have the potential to be a crop plant [176], [177]. In an ideal world, we could use the whole plant in the manufacture of the composite, extracting the fibres and chemicals to make the resin. With nettles, for example, we could use leaves to extract gallic acid and the stalks to make fibres.

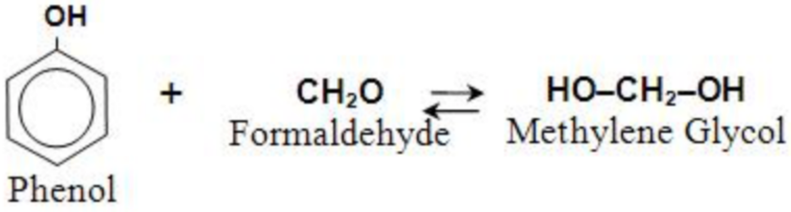
2.3 Phenolic Resins

One major benefit from phenolic resins is its fire resistance, it offers good heat and flame resistance and produces low amounts of toxic fumes when burned [178], [179]. Phenolic resin is also low cost compared to other resins such as epoxy resins [180]. Although it generates a lot of water during curing reaction, a special cure schedule might be a way overcome this problem [181].

In this present study, phenolic resin has been chosen as the matrix that will be used in the manufacturing the phenol-formaldehyde resin. Phenolic resins have low specific gravity and their density can be assorted according to the filler and moulding pressures [182]. It possesses high specific strength and the temperature range can be extended based on the intended applications [183]. They also possess good insulating properties, which makes them a good material to be used in the field of electrical insulation, specifically for standard fittings and components, where their low smoke evolution in the event of a fire is also a desirable property [184][182].

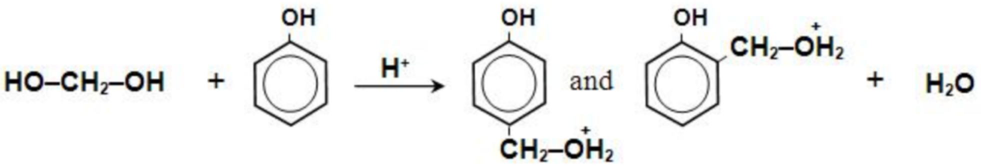
Polymerisation of phenolic resins consists of a polycondensation reaction of phenol and formaldehyde [185]. When the reaction takes place, water is eliminated as by-product. Novolak or resol resins are produced as the main product depending on the reaction conditions, whether it is acidic or basic [186].

In aqueous solution, formaldehyde exists in equilibrium with methylene glycol.

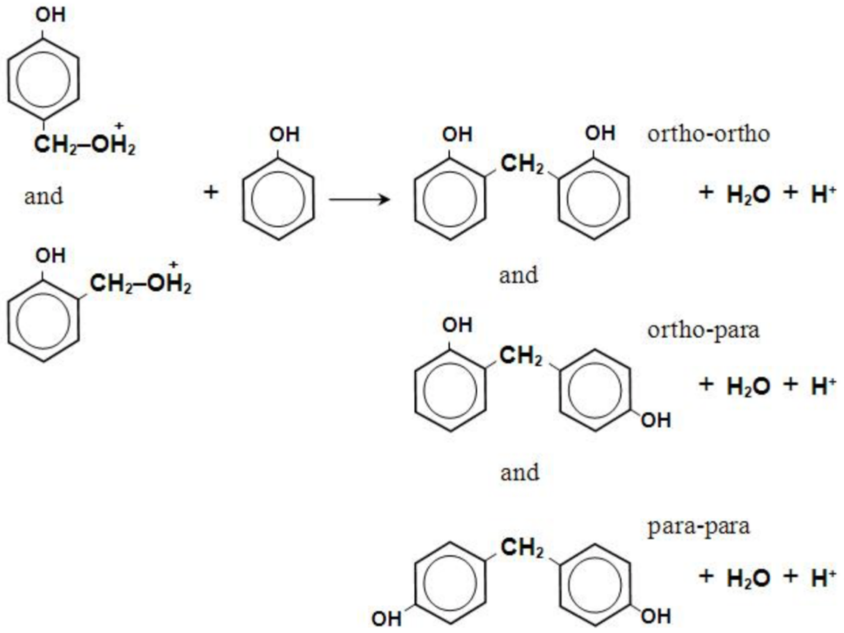


A) Polymerisation reactions of novolac resin

A molar excess of phenol to formaldehyde, and an acidic catalyst, are used in production of novolac resin. The reactions scheme below shows the possible range of polymers which start from the reaction of methylene glycol and phenol.



The reaction continues with phenol added and separation of water.

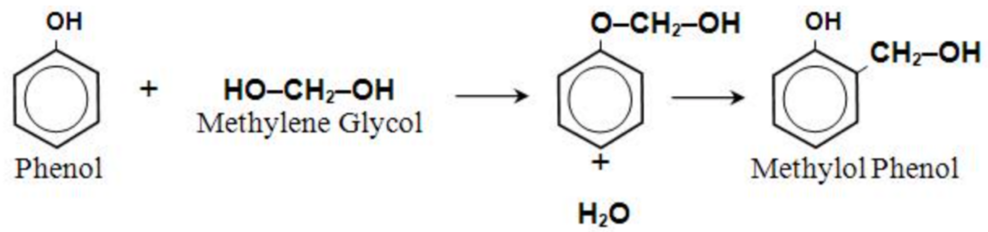


Finally, the novolac resin is unable to react further without help from a crosslinking agent, such as hexamethylenetetramine (known as hexa), to finish the curing process. That is why novolac resin is often called a 'two-stage' or 'two-step' product.

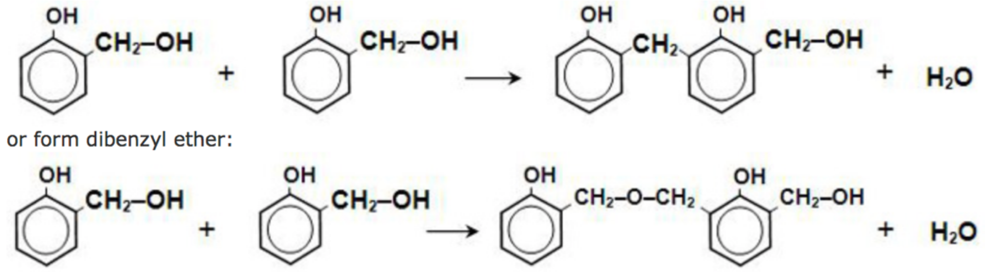
B) Polymerisation reactions of resole resin

Resole resins are produced when excess formaldehyde is used, and with addition of basic catalyst. An excess of formaldehyde gives a sufficient number of methylol and dibenzyl ether groups to complete the curing process and hence a crosslinking agent such as hexa is not needed. For this reason, resole resin is known as a 'single stage' and 'one-step' resin.

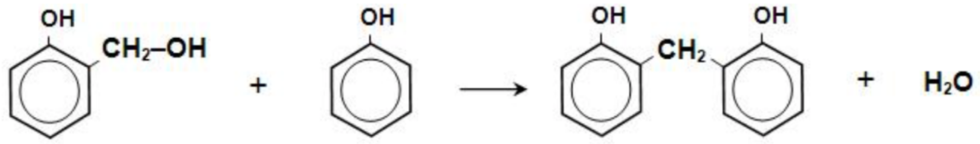
First, methylol phenols were formed from the reaction of phenol with methylene glycol;



A longer chain of methylol phenolic are produced when methylol phenol reacts with itself.



or reacts with phenol to form a methylene bridge;



**All figures above reference are from plenco.com*

2.3.1 Previous study on conventional phenolic materials

In the study conducted by Wolfrum and Ehrenstein [181], they reported that correlation between the curing, chemical structure and mechanical performance of phenolic resin was affected by the hardener percentage, which in this case was p-toluolsulfuric acid. When the concentration of the hardener increased, the average void diameters decreased but this did not affect the glass transition temperature of the resin. What affected the glass transition temperature was the curing and postcuring temperatures, whereby degree of cure has influenced the mechanical properties. Hence, when the glass transition temperature increased, fracture strain decreased.

Preparation of boron containing phenolic resin/clay (montmorillonite) nanocomposites were done by in-situ polymerisation of resole-type phenolic resins to improve its thermal stability. Thermogravimetrc (TGA) result showed that at 790 ^{o}C, the thermal degradation temperature and residual mass of cured boron-containing nanocomposites were higher when compared to the nanocomposites without boron. Nevertheless, nanocomposite with boron absorbs more moisture compared to nanocomposite without boron, as this is caused by the boric acid that was unreacted or reacted partially in the preparation process [187].

In research by Riccardi et al. [188], the kinetics of the polymerisation of phenolic resin with varied phenol and formaldehyde equilibria was studied. The type and amount of catalyst, the initial pH, the initial formaldehyde-to-phenol molar ratio and the condensation temperature was taken into account. It was found that resole with zinc acetate as a catalyst has a low reactivity value of the para phenol to ortho phenol position. As the amount of catalyst increased, the kinetic constant for the methylene glycol and ortho phenol increased. The limiting ratio for phenol/formaldehyde was 1.8, at which reaction of condensation occurred at lesser extent.

Uses of phenolic plastics can be seen in mouldings (standard fittings, components and general utility objects both in the industrial and domestic fields), cast resins (used in decorative items such as bracelet, handles, clock cases, radio cabinets and so on, due to beauty and wide color range of phenolic) and laminates (used in scientific and testing instruments, X-ray machines and many other industrial applications) [ref].

2.3.2 Phenolic Resole Resin

There is a large volume of published studies using resole as their main subject of investigation [189]–[195]. In the present study, the authors also chose resole as the main subject, as it can cure without the need of crosslinking agent, and hence a single stage of curing is sufficient to produce a polymerized resin. There are three steps involved in resole polymerisation; addition, condensation and curing [195]. Methylolphenols are produced from addition reaction of formaldehyde to phenols, then it condenses to diphenylmethanes and low molecular weight polymers. When heat is applied to the mixture of various molecular weight polymers it allows further condensation reactions and the resins form a rigid cross-linked network.

Haupt and Seller [191] studied the effect of different ratios of phenol formaldehyde in producing resole resin in terms of pH, gel time, viscosity, alkalinity, nonvolatiles, density, molecular weight, surface tension and contact angle. Some of the findings that can relate to our case study are; i) higher F:P ratios resulted in decreasing of pH due to less sodium hydroxide and ii) gel time decreased with higher F:P ratio.

Another researcher [196] discusses the effect of different ratios of F:P using the DSC analysis. They found out that when the ratio of F:P increased, the shapes of DSC signals change. The signals overlapped when at lower ratio of F:P (1.90 to 2.00) was used, while they were well separated from others at higher ratios of F:P (2.15 to 2.30). By increasing the F:P ratios, the concentration of methylol group is improved. This makes the condensation of dibenzyl ether bridge more difficult, thus large amounts of methylene and ether bridge formation takes place to produce rigid resin structure. Under the high F:P molar ratios, reactive methylol groups are formed in the resin, hence the resin cures faster than a lower F:P molar ratio does [197]. In contrast to that, Parameswaran [198] argues that formation of ether linkages reduces the strength of the cured resins, on the basis of bond energy. However, ether linkages can establish hydrogen bonds with -OH groups, and can have a positive effect on the properties of resins. However, it was unclear in the paper which properties had improved, as their research reported that the modulus of phenolic resin decreased due to a higher amount of ether linkage at P:F ratio 1:1.75.

It has been reported that optimum properties of resol resins can be accomplished when the F:P ratios are in between 1.3 and 1.4 [199]. However, more work needs to be done to prove this is actually true, as there are a lot of parameters that need to be considered such as method of curing, materials grade, catalyst used, cure schedule, pH and so on. Talking about catalysts, Shafizadeh et al. [200] demonstrated that when different catalysts were used in producing resole resins, the result of flammability varies. For instance, the flammability of sodium hydroxide (NaOH) and ammonium hydroxide (NH_3)-catalysed resins were found to be non-flammable while the triethylamine (TEA)-catalysed resin was found to burn quickly and release a lot of heat due to phenol evolving and burning in the chamber. The high degradation temperature of ammonia requires a longer time to evolve from the laminate, thus leading to a longer time for the resin to burn.

2.3.3 Modified Phenolic Resins

The modification of phenolic resins is made by partial substitution of phenol with renewable resources such as cashew nut shell liquid that contain naturally occurring phenols. Other than that, lignin is also considered as a natural substitute for phenol in phenol-formaldehyde resin due to its similar structure with phenol. Other authors as described below also proposed tannins and gallic acid as a potential substitution for phenol.

A previous study by Cardona et al. [2] investigated the effect of blends of phenolic resin (PF) with modified phenolic resins by the partial substitution of phenol with cardanol from cashew nut shell liquid in the synthesis with formaldehyde (CPF resins), in terms of mechanical and toughness properties. From the DMA result, the glass transition temperature (Tg) values, and the crosslink density, decreased when the cardanol content increased, and also with the decrease in total phenol/formaldehyde molar ratio. The best result was achieved at a molar ratio of P/F equal to 1.25 and with 40 wt% cardanol substitution of phenol. This finding showed that cardanol can be an effective substitution of phenol, and is also able to improve the toughness of the cured resins, as it is economically and environmentally friendly alternatives in the manufacture of resole phenolic resin.

Ashgari et al. [201] in their research used bark of oak (Quercus castaneifolia) as phenolic substitution in wood composite industry. In their findings, they found that tannin substituted phenol resin decreased the modulus of rupture (MOR) and modulus of elasticity (MOE) a little, but had major effect on internal bond, water absorption and thickness swelling. The drawbacks of using tannin instead of phenol are low pH, high viscosity and short gel time.

Tannin phenolic thermoset was found to have low impact strength compared to tannin phenolic composite. Incorporation of fibres have improved the impact strength of the composites together with high stiffness and lower loss modulus, indicating the good fibre-matrix interaction of the composite [25], [202]. The tannin, mentioned in previous studies showed that its structure contains natural beneficial material that can be an important factor in the area of expansion of biobased composites.

Galvez et al. [203] used gallic acid as a model of hydrolysable tannin was used to react with formaldehyde at different pH values, molar ratios formaldehyde/gallic acid (F/Ga), temperatures and reaction time. Results showed that at pH 8, molar ratio F/Ga was 2, reaction time was 4h at 60 ^{o}C were the optimum conditions in this condensation process.

2.3.4 Tannins

In this present study, gallic acid has been chosen as a partial substitution for phenol. Gallic acid is a hydrolysable tannin which will be discussed in detail in this section.

Tannins are phenolic substances made out of an exceptionally assorted gathering of oligomers and polymers. They can be found in most part in plants including the roots, leaves and natural products. There are two major types of tannins; hydrolysable and condensed tannins [204]. Condensed tannins contain flavonoid units with a number of condensation degrees while the hydrolysable ones are a mixture of simple phenols that contains ester linkages in their structure and undergo hydrolysis when dilute in mineral acids, enzyme and alkalis [204], [205]. The hydrolysable tannins are composed of both gallotannins (gallic acid and glucose) and ellagitannins (ellagic acid and glucose). Therefore, tannins can be categorised into four types which is gallotannins, ellagitannins, complex tannins and condensed tannins (Figure 2.1) [17].

(1) Gallotannins - Tannins with galloyl units or meta-depsidic derivatives which are bound to various polyol-catechin-, or triperpenoid units
(2) Ellagitannins - Tannins with at least two galloyl units that are C-C coupled together, that do not possess any glycosidally linked catechin units
(3) Complex tannins - Tannins with catechin unit bonded glycosidically to a gallotannin or an ellagitannin unit
(4) Condensed tannins - Oligomeric and polymeric proanthocyanidins formed by linkage of C-4 of one catechin with C-8 or C-6 of the next monomeric catechin

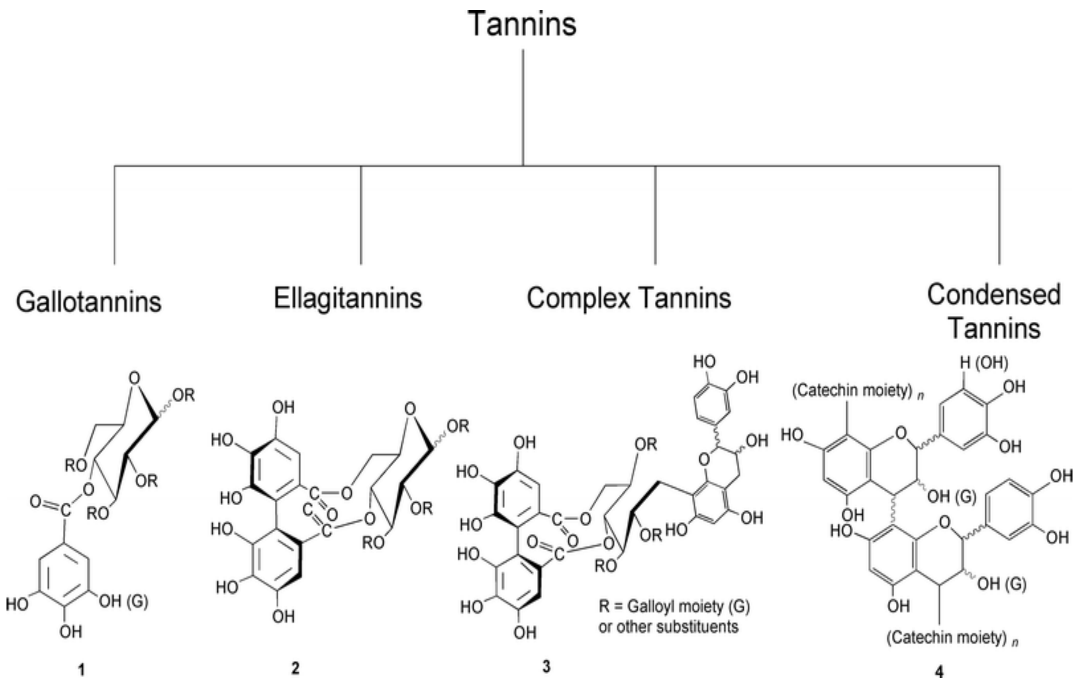


Figure 2.1 Classification of tannins. Reprinted from Tannins: classification and definition by Khanbabaee, K. and Van Ree, T., 2011, Natural Product Reports, 18(6), 641-649, DOI: 10.1039/B101061L by permission of Royal Society of Chemistry.

As a clarification, high molecular weights of natural products that have the ability to complex strongly with protein and carbohydrates are called vegetable tannins. Vegetable tannins are categorised into two major groups; hydrolysable and condensed tannins. Hydrolysable tannins (HT) are usually divided into gallotannins and ellagitannins. Gallic acid is produced from hydrolysis of gallotannins, while ellagitannins yield ellagic acid as stable dilactone [24]. Hydrolysable tannins from chestnut bark have been found to be successful in substituting phenol at amount up to 50% in the manufacture of phenolic resin [206].

HTs molecules exist largely in nature. Oxidative coupling of neighbouring gallic acid units or oxidation of aromatic rings produced variations in the compounds structural

[207]. Figure 2.2 shows the reaction which oxidative coupling reactions produce large and complex HTs [208].

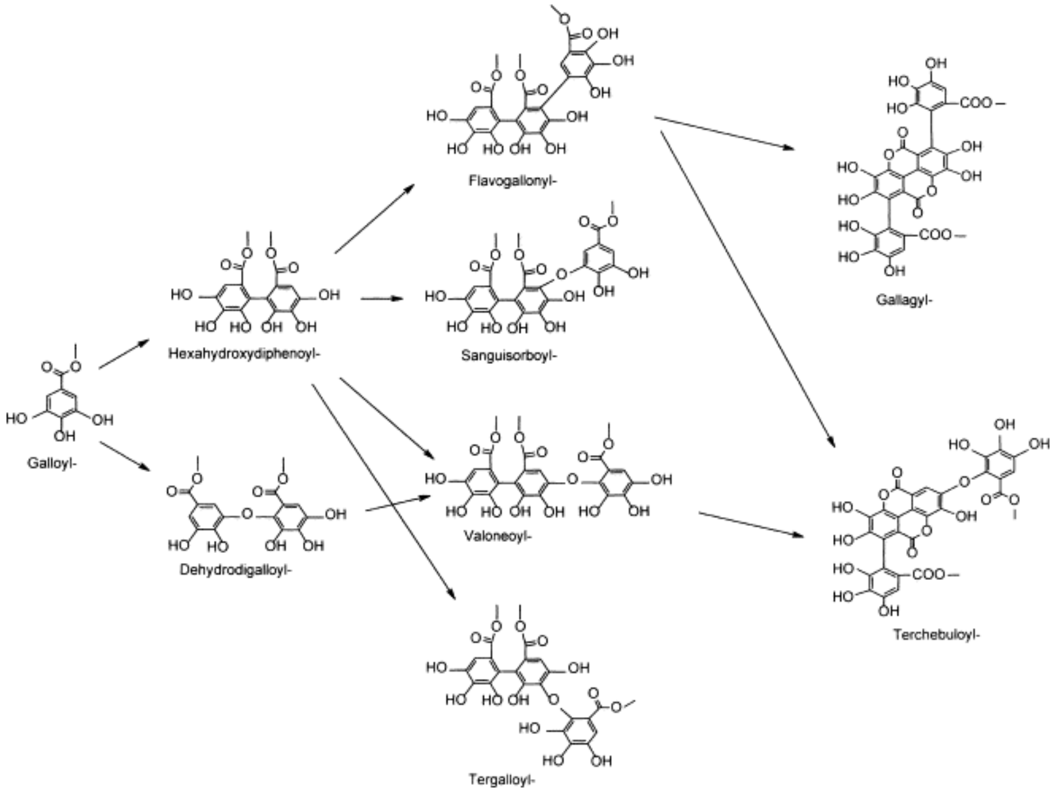


Figure 2.2 Oxidative coupling reactions between gallic acid units. Reprinted from Isolation and structure elucidation of tannins by Nonaka, G. I., 1989, Pure and Applied Chemistry, 61(3), 357-360, DOI: https://doi.org/10.1351/pac198961030357. Free Access from © 2013 Walter de Gruyter GmbH, Berlin/Boston.

Hydrolysable tannin resin formation is showed in Figure 2.3. Methylene bridge is formed when condensation of gallotannins and formaldehyde takes place. The first step is an electrophilic aromatic substitution reaction (Figure 2.3a) which is methylolation and then continued with condensation reaction. There are two mechanisms involve in this reaction which is a hydroxymethyl group with either a proton of the aromatic ring (ortho position) with one molecule of water being eliminated (Figure 2.3b) or a hydroxymethyl group with one molecule of water and one molecule of formaldehyde being eliminated (Figure 2.3c). A methylene bridge is formed in both cases. Thus, it can be said that at the ortho position, reaction of formaldehyde with a galloyl group would be able to undergo crosslinking under reaction conditions.

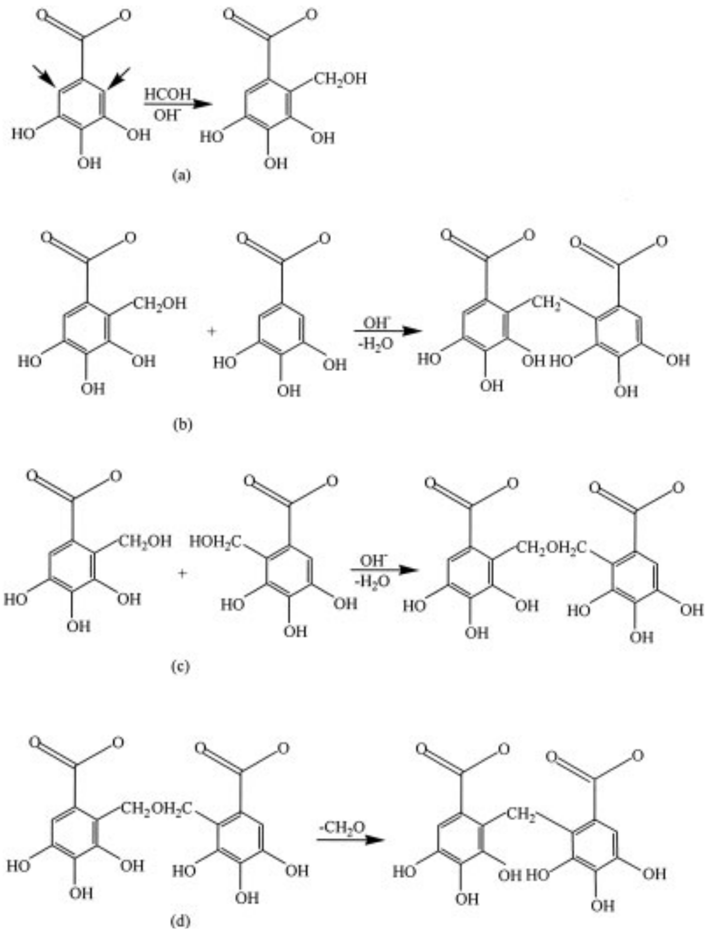


Figure 2.3 Reaction of galloyl group with formaldehyde. (a) methylolation reaction; (b– d) condensation reaction. Reprinted from Synthesis and characterization of gallic acid resin and its interaction with palladium (II), rhodium (III) chloro complexes by Can, M., Bulut, E., & Özacar, M., 2012, Industrial & Engineering Chemistry Research, 51(17), 6052-6063, DOI: https://doi.org/10.1021/ie300437u, Copyright © 2012 American Chemical Society

Reactivity of hydrolysable tannins have been investigated by Li et al. [209]. They modelled an experiment which consist of larch tannin (representing condensed tannins) and valonia tannins (representing hydrolysable tannins) and compare the properties between them. It was found that larch tannin possess greater reactivity towards formaldehyde due to the resorcinolic nuclei or pholoroglucinolic A-ring in the repeating flavonoid units (Figure 2.5) while gallic acid has lower reactivity probably due to steric hindrance caused by hydroxyl aromatic groups (Figure 2.4). To avoid this detrimental situation, and to minimise steric hindrance, resole formation was conducted under alkaline conditions. Nevertheless, gallic acid has better reactivity compared to phenol and both larch and valonia tannins and it can thus be a promising substitute for phenol especially in production of wood adhesives. Numerous studies also found that tannins are a suitable substitute for phenol in resin and adhesive preparation [210]–[212].

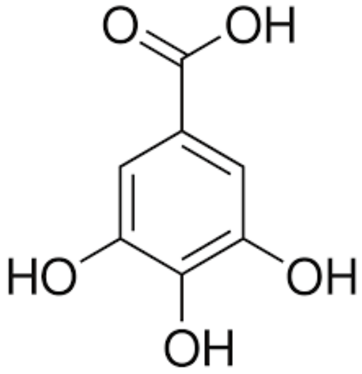


Figure 2.4 Structure of gallic acid

One of the scholars investigated tannins blends for particle board applications [213]. It shows that mechanical properties of coffee husk/hydrolysed tannin adhesive is slightly higher than coffee husk/urea formaldehyde adhesive. The adhesive also displayed improvement in water and moisture resistance. It can be concluded from this study that tannin-based resin has great potential in particle board applications. However extra works need to be done for further analysis of the resins, for instance DMA and SEM.

The other type of tannin is condensed tannin. Condensed tannins are composed of flavan-3-ol repeat units with two phenolic rings (marked A and B in Figure 2.5), which are linked by a heterocyclic ring, together with polysaccharides and sugar. Reactivity of this type of tannin is due to the A-ring phloroglucinolic or resorcinolic nuclei towards formaldehyde which can crosslink. In this case, it can be observed that rate of reaction increased compared to phenol-formaldehyde. Resin modification can be done by adding material with high tannin content, such as chestnut and mimosa, to improve the properties. Due to the molecules being large in structure, it limits the rotation around their backbone bonds, especially at high temperature, making it immobilised due to the premature gelation, and thus make the resin brittle, not stable and having a short shelf-life [21].

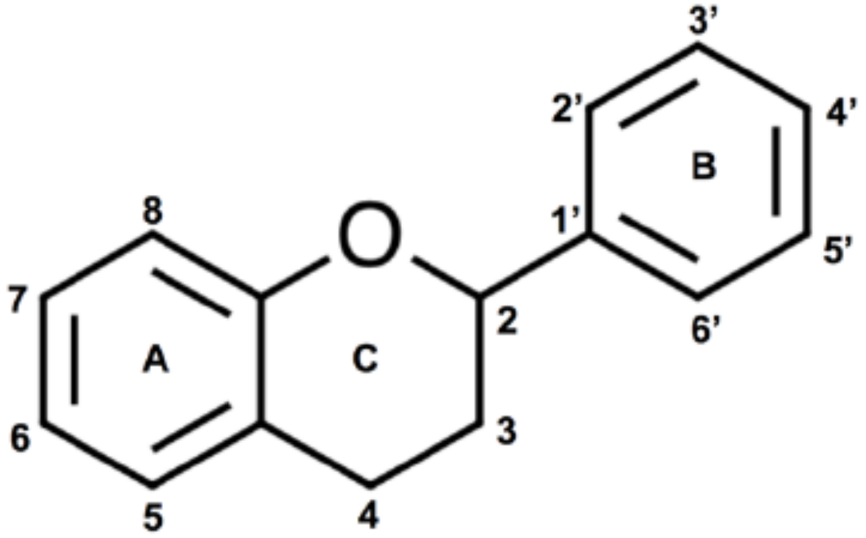


Figure 2.5 Flavonoid unit in condensed tannin [214]

The formation of condensed tannin-formaldehyde resins (Figure 2.6) can be explained by these two steps, similar to the formation of hydrolysable tannin-formaldehyde resin. The first step is methylolation, resulting in a product that is substituted in ortho- and para- positions. Activation of more original phenol can be achieved when there is two or three activating oxygen groups (i.e phloroglucinol or resorcinol) present. The next step is a condensation reaction. The methylol group of a single tannin molecule will react with another, creating an ether linkage. Water will be eliminated as a byproduct of the reaction.

The crosslinking process is difficult for tannin, whereas resole resins produce linear and regular crosslinking due to their high molecular weight. Some of the hydroxyl groups in tannin do not form crosslinks. Reactivity of the resin can be improved by using acid hydrolysis to open the polyflavinoids heterocyclic ring, and then react with nucleophilies present within the carbocation formation. For instance, tannin extracts can be incorporate in to acetic anhydride and alkaline treatment to improve the properties of tannin-based adhesives. Thus, more mobile tannin compounds are produced due to the breaking of interflavonoid bond, resulting in high level of condensation with formaldehyde. Hence, it can be concluded that the flexibility of tannin compounds is improved and they become less brittle.

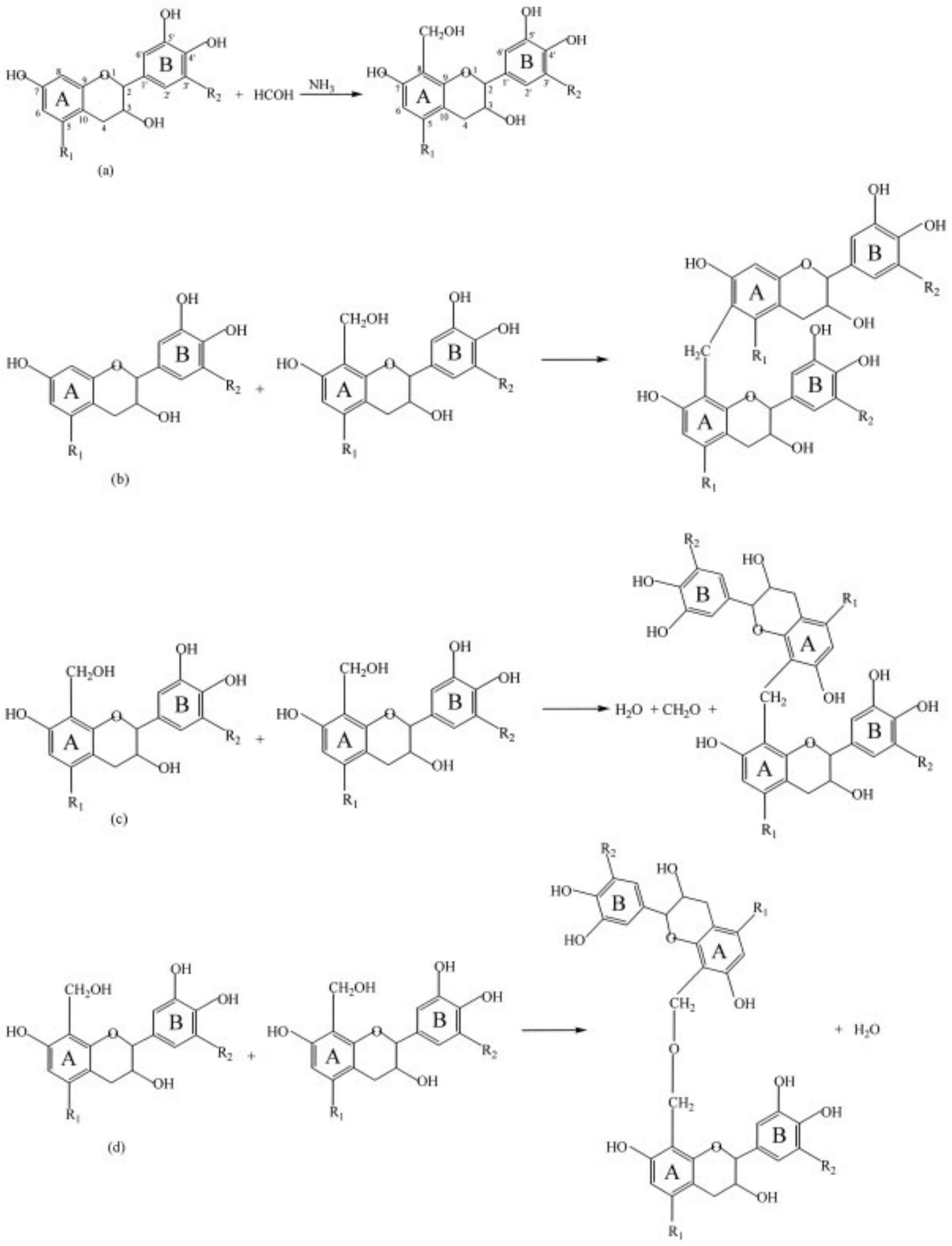


Figure 2.6 Formation of condensed tannin-formaldehyde resin (a) methylolation reaction; (b– d) condensation reaction. Reprinted from Studies on synthesis, characterization, and metal adsorption of mimosa and valonia tannin resins by Özacar, M., Soykan, C., & Şengil, İ. A., 2006, Journal of Applied Polymer Science, 102(1), 786-797, DOI: https://doi.org/10.1002/app.23944, by permission of John Wiley and Sons, license number 4695950454206

2.3.4.1 Extraction of tannins from nettle

Tannins can be found commonly in plants such as from the bark of the black wattle and the quebracho trees [215], [216] . Tannin solutions are acidic and have an astringent taste [217]–[220]. Tannin is responsible for the astringency, colour, and some of the flavour in tea [221]. Tannins occur normally in the roots, wood, bark, leaves, and fruit of many plants, particularly in the bark of oak species and in sumac and myrobalan [222], [223]. Extraction of tannin involves solvents such as water, acetone, and methanol [224]–[227]. In this present study, the selected tannin, which is gallic acid, was extracted from nettle stalks and leaves using acetone as a solvent which was later characterised by High Performance Liquid Chromatography (HPLC).

The applications of nettle have been found widely in medicine, cosmetics, herbal remedy, industry and biodynamic agriculture [228]. Nettle contains phenolic compounds in the root, stalks and leaves [14], [229]. Several studies [14], [229] have been conducted to analyse the phenolic compound present in nettle fibre. Nettle samples that were collected from different regions have been used in this investigation. Below (Table 2.4) are the summary of finding

Table 2.4 Analysis summary of phenolic compounds

	[229]				[14]											
	Prato, Tuscany				Mediterranean			Aegean			Marmara			Black Sea		
	C		W		Antalya			Aydin			Bursa			Samsun		
	L	S	L	S	R	S	L	R	S	L	R	S	L	R	S	L
Caffeic acid	🟨	🟨	🟨	🟨						🟨			🟨			
p-coumaric acid		🟨	🟨	🟨	🟨		🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨
Caffeoylquinic acid		🟨		🟨												
Chlorogenic acid	🟨	🟨	🟨	🟨						🟨			🟨			
Caffeoylmalic acid	🟨		🟨													
Rutin	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨
Quarcetin	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨		🟨	🟨	🟨	🟨	🟨
Kaempferol	🟨	🟨	🟨	🟨	🟨	🟨	🟨		🟨	🟨	🟨		🟨	🟨	🟨	🟨
Isorhamnetin	🟨	🟨	🟨	🟨			🟨				🟨			🟨	🟨	🟨
Peonidin		🟨		🟨												
Rosinidin		🟨		🟨												
Myricetin					🟨	🟨	🟨	🟨	🟨	🟨		🟨	🟨	🟨	🟨	🟨
Syringic					🟨						🟨	🟨		🟨		
Ferulic					🟨		🟨		🟨	🟨	🟨	🟨		🟨	🟨	🟨
Naringin					🟨	🟨	🟨	🟨		🟨	🟨	🟨	🟨	🟨	🟨	🟨
Ellagic acid					🟨		🟨	🟨		🟨	🟨		🟨		🟨	🟨
Fumaric						🟨						🟨	🟨			
Catechin							🟨					🟨				
Vanilic								🟨		🟨						

L, leaves; S, stalks; R, root; C, cultivated; W, wild

Another study by Proestos et al. [230] found gallic acid, syringic acid and ferulic acid in their nettle samples which were harvested from Greek origin. Moreover, numerous studies have examined stinging nettle and found gallic acid in their nettle samples [22], [231]–[235]. This can be a starting point in the present study in choosing gallic acid as phenolic precursor, as it proved to be found in nettle plant. Therefore, it would be interesting to have two things in a one plant, which is we could use leaves to extract gallic acid and the stalks to make fibres for composite applications.

2.3.5 Summary

Production of phenolic resin is challenging due to its nature, in that it produces water as a byproduct, and hence modification of the cure cycle is needed in order to get bubble-free specimen. In order to use natural products, several attempts have been done to substitute the phenol with a more environmentally friendly and low-cost material. In the present study, the author has chosen a resole resin as the main subject as it can cure without the need of crosslinking agent, hence a single stage of curing is sufficient to produce a solid resin.

In previous research, a number of researchers has raised the issue of gallic acid being a potential substitution for phenol. It can be concluded that gallic acid, which is a hydrolysable tannin can be a promising substitution due to it being reactive compared to phenol, although the reactivity is lower compared to condensed tannins due to steric hindrance. To overcome this situation, which is to reduce the steric hindrance, resole formation needs to be done in alkaline condition.

In summary, hydrolysable tannins demonstrate greater reactivity towards formaldehyde compared to phenols, while not being reactive as phlorogucinol, but still they can be a potential substitution for phenol in phenolic resin [16], [236].

2.4 Summary of literature review

In this chapter, it is shown that production of bio-based resin is possible from natural plants such as nettle, in which we could use the whole plant in the manufacture of the composite, extracting the fibres for reinforcement and chemicals to make the resin. With nettles, for example, we could use leaves to extract gallic acid and the stalks to make fibres.

Once the gallic acid has been successfully extracted from nettle plant, it can be used as a substitute for phenol in phenol-formaldehyde resin. Gallic acid was found to be more reactive compared to phenol and thus, can exhibit a resin that has better mechanical properties.

Thus, blending phenol and gallic acid was expected to achieve better properties compared to conventional phenol-formaldehyde resin. Thereafter, the good resin can be used as a matrix with nettle fibre as a reinforcement to produce the biocomposite.

3.0 EXPERIMENTAL MATERIALS AND CHARACTERISATION

The experimental details such as materials used and techniques to characterise the resins and composites are summarised in this chapter.

3.1 Chemicals

To prepare the phenol-formaldehyde (PF) and gallic acid resin, liquid phenol, gallic acid (monohydrate), potassium hydroxide from Merck, and formaldehyde (10-15% methanol) from J.T Baker were used as provided. The properties of these materials are presented in Table 3.1, which data was taken from MSDS provided from Merck.

3.2 Plant material

Stinging nettle (*Urtica dioica*) leaves were collected in Sheffield, South Yorkshire, during the period of August-September in 2018. Leaves were dried naturally and kept in a freezer to ensure the freshness of the leaves prior to use. Dried plant material was chopped and kept in paper bags before its usage.

Nettle fibre was supplied by wildfibres.co.uk. It was cut into short fibre (5-10 mm) prior to using it to make composites. The composites, reinforced with randomly oriented fibres, were obtained by adding the fibres to the liquid resin. The mixture was then cured using cure schedule as detailed in **Chapter 6: Composite Manufacturing.**

Table 3.1 Information on basic physical and chemical properties of materials used source from Merck

Name	Phenol	Formaldehyde	Gallic Acid Monohydrate	Potassium Hydroxide
CAS number	108-95-2	50-00-0	5995-86-8	1310-58-3
Appearance	Form: Liquid	Form: Liquid, clear Colour: Colourless	Form: Crystalline Colour: Beige	Form: solid
Melting point	Melting point/Range: 40-42 ℃	No data available	Melting point/Range: 251 ℃	Melting point/Range: 361 ℃
Initial boiling point and boiling range	182 ℃ at 1013 hPa	100 ℃	No data available	1320 ℃
Flash point-closed cup	79 ℃	64 ℃	250 ℃	No data available
Vapor Pressure	0.48 hPa at 20 ℃, 6.203 hPa at 55 ℃	53 hPa at 39 ℃	No data available	1 hPa at 719 ℃
Relative density at 25 ℃	1.07 g/cm^3	1.09 g/cm^3	No data available	No data available

3.3 Samples Description

These are the description of the samples mentioned in the study (Table 3.2). The synthesis of the resin and cure cycles used are discussed in **Chapter 4: Resin Development**.

Table 3.2 Description of the samples in the study

Name	Description
1.0GA	100% gallic acid (GA)
0.75GA	75%GA:25%Phenol
0.50GA	50%GA:50%Phenol
0.40GA	40%GA:60%Phenol
0.37GA	37%GA:63%Phenol
0.31GA	31%GA:69%Phenol
0.25GA	25%GA:75%Phenol
1.0P	100% phenol

3.4 Resin and Composite Synthesis

To prepare the PF resole pre-polymer, potassium hydroxide-to-formaldehyde-to-phenol were mixed to ratio of 0.2 to 1.5 to 1.0, respectively. The mixture was stirred and heated to 80°C for 60 minutes. After that, the mixture was cooled to room temperature, and water was eliminated under reduced pressure by using rotary evaporator at 45°C. For gallic acid resin, a certain amount of phenol was substituted by gallic acid. Details of the synthesis are discussed in **Chapter 4: Resin Development.**

Following the successful production of 1.0P and 0.25GA resins, composites reinforced with randomly oriented nettle fibres were prepared with the resins. The nettle fibre content varied from 5, 10, 15 and 20 wt%. Details of the preparation are discussed in **Chapter 6: Composite Manufacturing.**

3.5 Resin and Composite Characterisation

For density measurement of 1.0P and 0.25GA resin, a Mettler-Toledo MS-DNY-43 Density Kit was used. This density value is required for Chapter 6 in calculation for prediction of composite properties.

In this density calculation, a buoyancy method was used which is Archimedes' principle. A buoyant force was applied on the sample as it was immersed partially or fully in the fluid. Fluid displacement by the sample is equal to the magnitude of this force. The solid is weighed in air (A), and then again (B) in auxiliary liquid with known density. Refer to Figure 3.1 for illustrative procedure.

$$\rho = \frac{A}{A-B}(\rho_0 - \rho_L) + \rho_L \qquad (1)$$

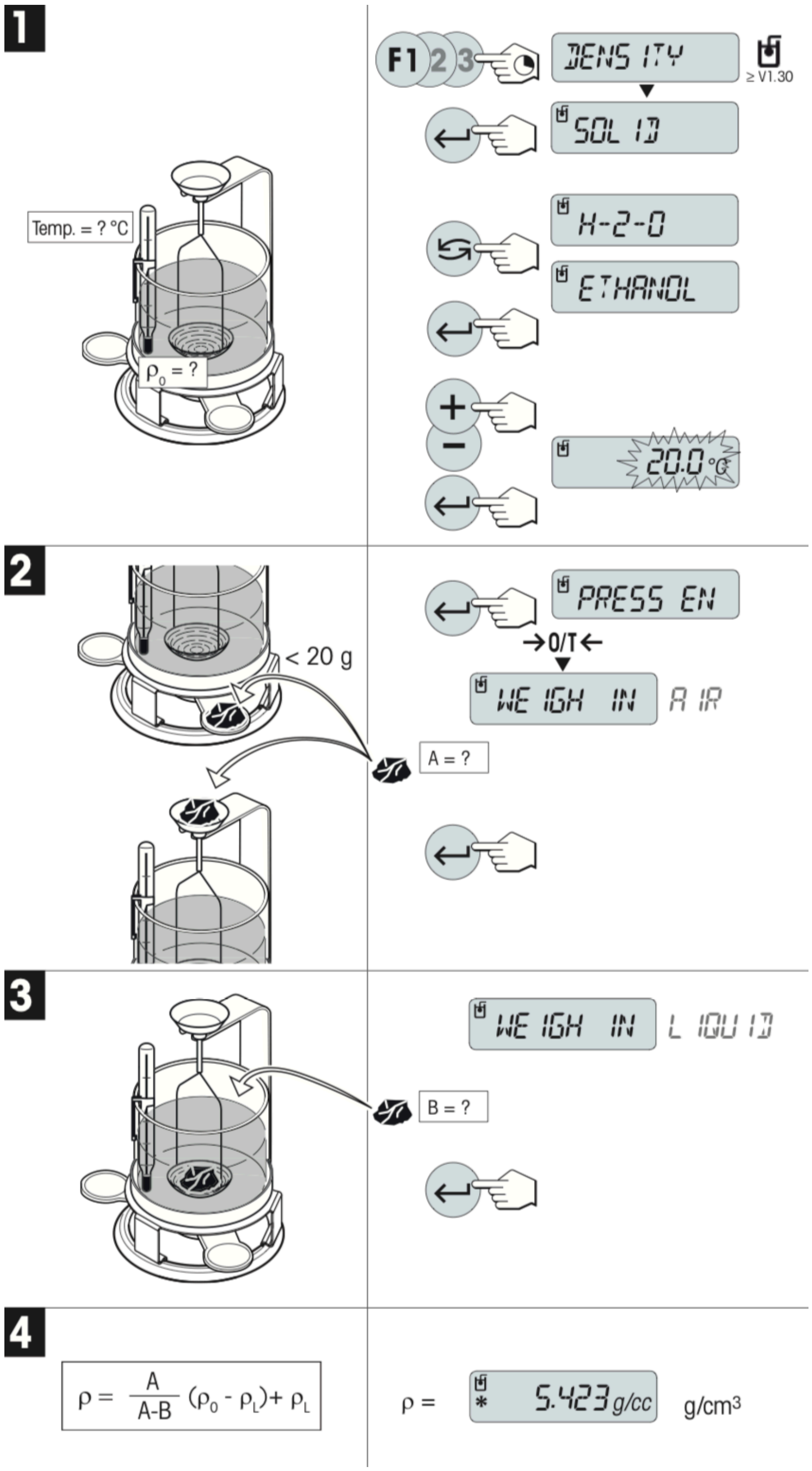


Figure 3.1 Density Determination of Solids. Reprinted from Metler Toledo manual book with courtesy of © METTLER TOLEDO. All rights reserved.

For samples magnification in order to observe bubbles and cracks in the resin, a Veho Discovery VMS-004 Deluxe 400x USB Microscope was used (Figure 3.2). . The images from this equipment are displayed in Chapter 4.

Figure 3.2 Veho Discovery VMS-004 Deluxe 400x USB Microscope. Reprinted from bhphotovideo.com; https://www.bhphotovideo.com/c/product/763007-REG/veho_VMS_004_DELUXE_VMS_004D_400x_USB_Microscope.html/%7B%7BdetailsUrl%7D%7D; © 2000-2019 B&H Foto & Electronics Corp. 420 9th Ave, New York, NY 10001

3.5.1 Thermal Analysis

3.5.1.1 Differential Scanning Calorimetry (DSC)

All DSC measurements were made by using either a Perkin Elmer DSC 6 or a DSC 4000 manufactured by Perkin Elmer. A sample of 7 to 17 mg of resin was set in an unsealed aluminium pan and heated from 25 °C to 400 °C at 10 °C/min, under a nitrogen atmosphere with the flow rate of 20 mL/min. The samples were repeated twice to produce less noise in the peak.

3.5.1.2 Dynamic Mechanical Analysis (DMA)

DMA was performed using a Perkin Elmer DMA 8000. The samples were loaded in the single cantilever bending mode in the following protocol: (a) Frequency of 1 Hz, (b) temperature range from ambient to 300 °C, (c) heating rate of 3°C/min (d) displacement of 0.05 mm.

Before cure cycle 7 was employed (see **Chapter 4: Resin Development** for cure details), all samples were tested using material pockets. The material pocket is a stainless-steel envelope that holds a powdered of otherwise intractable sample so it can be mounted in the DMA. The sample that uses a material pocket is usually powders, flakes, coatings, liquids or semi-solids. Figure 3.3 shows the sample preparation process using a material pocket. Each sample was tested twice to eliminate the noise.

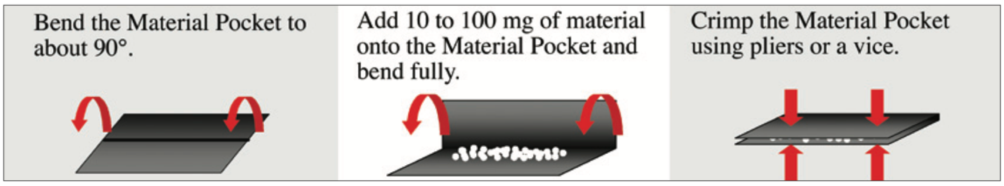


Figure 3.3 Sample preparation using the material pocket. Reprinted from PerkinElmer; https://www.perkinelmer.com/uk/lab-solutions/resources/docs/APP_007771B_03_Use_of_Material_Pockets_for_Mechanical_Analysis_of_Powders.pdf; © 2007-2011, Perkin Elmer, Inc.

3.5.1.3 Thermogravimetry Analysis (TGA)

TGA was done using a TA Instruments Q50. Nitrogen gas was set to run at 60 ml/min to provide a controlled combustion environment. The temperature was set from 0-600 °C with a ramp rate of 10 °C/min.

3.5.2 Chemical Analysis

3.5.2.1 Fourier-transform infrared spectroscopy (FTIR)

FTIR spectra of the samples were obtained using a Perkin Elmer FTIR Frontier. By using ASTM E1252, 5 mg of powder samples were mixed with about 150 mg of potassium bromide (KBr), and the mixture was pressed using hydraulic press to form a thin film at a thickness of 10-100 µm. The samples were scanned 32 times and the infrared spectra were determined in the 4000-300 cm^{-1} range. The more scans that are run, the more noise will be eliminated, leading to production of smooth peaks. A background spectrum was taken as a control before loading any samples.

3.5.2.2 High Performance Liquid Chromatography (HPLC)

The HPLC used in this study was a Shimadzu Prominence XR system, comprising of DGU-20A3 degasser, LC-20AD XR pumps (two), Sil-20A XR autosampler, CTO-10AS oven, SPD-M20A diode array detector, and CBM-20A communications bus module. The analysis was performed by the technician from the Chemistry Department with the following conditions; Samples (soluble portions of nettle stalks and leaves) were dissolved in methanol, injection size 5 µL, column used: Waters X Bridge C18 (250mm x 4.6mm), mobile phase: A=0.1%trifluoroacetic acid, B=acetonitrile, flow rate=1 mL/min, detention: UV at 270 nm.

Gallic acid was used as a reference standard in determining the phenolic compound in nettles samples.

3.5.3 Mechanical Analysis

3.5.3.1 Flexural Test

The flexural test was conducted according to ASTM D790-17, by using a Lloyd Instruments TA100. The loading rate was 2mm/min, the load cell was 500N and the span was 25 mm. The sample was prepared according to this size 50.8 mm (length), 12.7 mm (width) and 1.2-1.6 mm (thickness). This test was crucial to analyse the resistance to deformation of the material under load. Seven samples of each type were used as specimens, with the average values being recorded.

3.5.4 Morphological Study

Scanning electron microscopy (SEM) analysis was performed on the flexural fractured specimens by using a FEI Nova NanoSEM 450. In this study, no conductive coating was applied to the samples. For that reason, to prevent the samples from being damaged and charging occurring, a low accelerating voltage (1 KV) was used. A typical vacuum pressure of 10^{-5} mbar, and a working distance of about 4mm was employed. An Everhart-Thornley Detector (ETD) was then used to collect the secondary electron images for low magnification images, or a Through Lens Detector (TLD) to obtain high magnification images. The surface characterisation was then studied and analysed.

4.0 RESIN DEVELOPMENT

4.1 Introduction

Manufacturing of phenol-formaldehyde and gallic acid resin has undergone a series of studies to determine appropriate cure schedules. The initial method and processing conditions were taken from a previous paper [25] as a starting point for this project, but in this case was found to be unsuitable. It was unclear what the conditions for cure of the resin were in this paper, as the cure cycle was given without details of the necessary pressure. Therefore, possible reasons for failure of the cure cycle for this work might be because of differences in equipment (a hot press was used at high pressure to cure the composites), and material used (tannin was used as a substitution for phenol). Although some research has been carried out using gallic acid (GA) [23], [203], [236], no studies have been found which use GA as a phenol substitute, making it novel, and developing a suitable cure cycle was a time-consuming process.

Why gallic acid? Gallic acid was of interest due to a review by Raquez et. al [21]. It stated that gallic acid has better reactivity towards electrophilic aromatic substitution, compared to phenol. This can be a starting point to further investigate the suitability of gallic acid as a substitution for phenol. In this chapter, the reader will find the properties of phenol-formaldehyde resin that have been partially substituted with gallic acid and that have improved or at least yielded equivalent properties to the conventional phenolic resin that was produced as a comparison.

4.2 Synthesis and Processing

4.2.1 Pre-polymer synthesis [25]

The phenol-formaldehyde (PF) resins were synthesised with a potassium hydroxide-to-formaldehyde-to-phenol molar ratio of 0.2 to 1.5 to 1.0, respectively. Substitution of phenol with 25%, 31%, 37%, 40%, 50%, 60%, 75%, and 100% of gallic acid was performed to compare the properties with the 100% phenol in PF resin.

In synthesising PF resin, liquid phenol was dissolved in formaldehyde at room temperature. Potassium hydroxide was then added to the PF solution and was charged into a three-neck flask equipped with a reflux condenser and mixed. The mixture was stirred and heated to 80°C for 60 minutes (see Figure 4 for general setup of experiment). The reaction was performed under basic conditions, at approximately pH 10. After that, the mixture was cooled to room temperature, and water was eliminated under reduced pressure by using rotary evaporator at 45°C.

For preparation of gallic acid (GA) resin, GA were dissolved in formaldehyde at room temperature. Then, liquid phenol and potassium hydroxide were added to the three-neck flask and heated to 80°C. The mixture was stirred for 60 minutes before being placed it in rotary evaporator at 45°C to remove any water present in the resins.

The pre-polymer was made fresh prior to curing, because resole resin continues the polymerisation reaction at even ambient temperatures although at slower rates than during manufacturing.

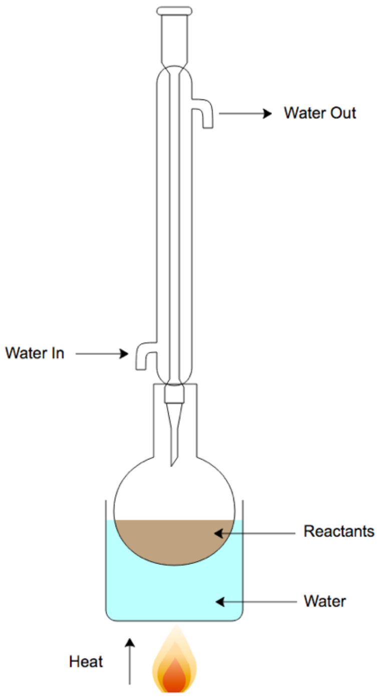


Figure 4.1 General setup for experiment.

4.2.2 Resin Processing

In this study, the biggest challenge was to produce a bubble-free specimen that leads to good properties of the resin. Phenolic resin is a condensation polymerisation process which creates water as a by-product. The water turns to steam at the cure temperature and that leads to high void content. To overcome this issue, low pressures at temperatures below the boiling point of water were used, and sustained for a period of time, to make sure bubbles have enough time to escape while maintaining the fluidity of the system. Before curing in the oven, hot press or autoclave, all samples have been dried using a rotary evaporator to eliminate water. However, further water will be generated during the remaining cure process.

In this section, the summary of all cure cycles that has been used is stated below. Resin at 25% of gallic acid was taken as a subject in comparing the results of the different cure schedules.

4.2.2.1 Trial 1

In an investigation by Ramires et. al. [25], they managed to substitute phenol with 40wt% tannin with a short cure cycle and higher pressure which is around 37 bar. A major criticism of their work is the explanation of how they cured the resin (i.e use of pressure, equipment and such) as they only described the cure cycle for composites, therefore in the first trial, resin was cured without pressure, assuming there would be enough time for the water to evaporate.

Equipment used for curing in this trial is a programmable oven and the cure schedule is, 40 ℃ (30m) - 50 ℃ (60 m) - 85 ℃ (90 m) - 125 ℃ (120 m) - 150 ℃ (120 m). Total time: 420m (=7h) [25]. Ramp rate was $2.7\ ℃/min$ [200]. Ramp rate should be slow enough to allow enough time for temperature changing between segment. Higher ramp rate could result in more voids.

Result for trial 1; the resin came out brittle and friable. A large amount of bubbles entrapped within the materials which suggest the top layer cured before the water came out. A lot of bubbles can be seen from the outer and inner surface. No further test can be done on it. Images in Figure 4.2 show the sample under digital microscope where the bubbles are obviously there.

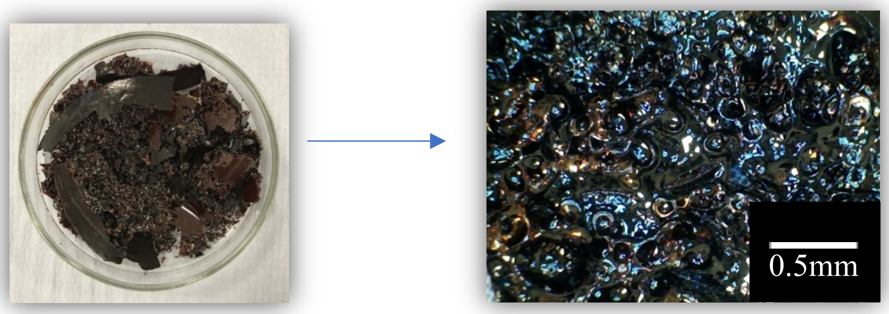


Figure 4.2 Sample's image under digital microscope for Trial 1

4.2.2.2 Trial 2

Following the unsuccessful nature of trial 1, there were two choices at that point, either increase the pressure or increase the time taken. Thus, pressure was increased to cure the samples in autoclave. A similar cure schedule has been applied as that used in the 1st trial, but with addition of a pressure of 7 bar throughout the process, with ramp rate constant at $2.7\ ^{\circ}\mathrm{C}/min$. Pressure of 7 bar was chosen as this is the maximum pressure that can be programmed on the available autoclave. Again, this reveals that the surface of the resin cured before the bulk. The resin came out shiny on the surface but puffed up like a balloon (Figure 4.3). It looked like air was trapped inside the sample. It shows that the water was unable to escape within the time and ended trapped in the resin before it cured completely. No further test is done on the sample.

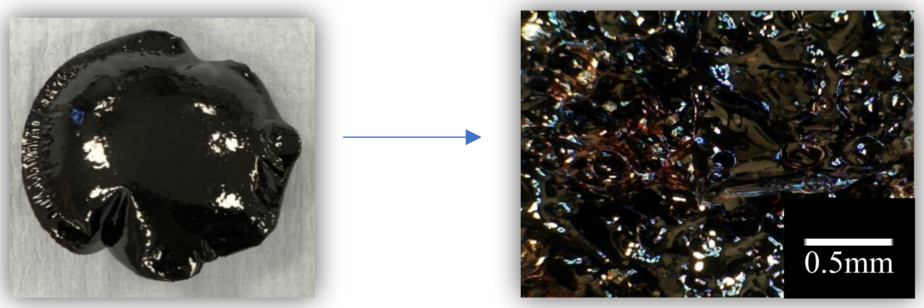


Figure 4.3 Sample's image under digital microscope for Trial 2

4.2.2.3 Trial 3

Following the unsuccessful nature of trial 1 and 2, the next cure cycle was introduced with a longer time. The cure schedule for trial 3 was modified by adding a hold at 95 ℃ for 90 minutes in the middle of the reaction. This temperature was chosen as this is below the boiling point of water, where the gel point started to occur [237], thus having the intention to allow water to be eliminated before the surface of the polymer fully gelled. It was cured in the autoclave with a cure schedule of 40 ℃ (30m) - 50 ℃ (60 m) - 85 ℃ (90 m) - 95 ℃ (90m) - 125 ℃ (120 m) - 150 ℃ (120 m), ramp rate 2.7 ℃/min, Pressure: 7 bar, Total time taken: 510m (=8h 30m). The result was that the resin's surface was dull and puffed up (Figure 4.4). The bubbles were clearly still entrapped in the material, meaning that the increased time was insufficient to facilitate full removal of the water.

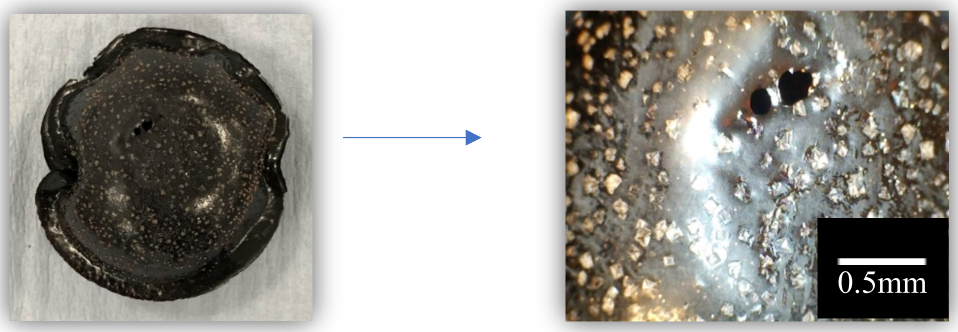


Figure 4.4 Sample’s image under digital microscope for Trial 3

4.2.2.4 Trial 4

Then, a hot press was utilised in trial 4, and the cure schedule was the same as that used previously in trial 1 [237], 75 °C (30m, 17 bar) - 75 °C (30m, 23 bar) - 85 °C (30m, 29 bar) - 85 °C (30m, 35 bar) - 85 °C (30m, 41 bar) - 95 °C (30m, 47 bar) - 105 °C (30m, 47 bar). Unfortunately, the process was aborted at 75 °C, after 45 minutes due to the sealant melting and the uncured, runny resins overflowing the hotplate. No images were taken and this approach was abandoned in favour of finding a suitable low pressure manufacturing route.

4.2.2.5 Trial 5

As only low pressures (up to 7 bar) were available in this work, it was deemed necessary to substantially increase the time available for the water to evaporate, potentially resulting in very long cure schedule. This was deemed necessary as the previous studies had all contained substantial amounts of entrapped moisture that had precluded testing of the resins mechanical properties. In this trial, the cure cycle from a previous research paper [190] was adopted. They investigated the effect of curing method on a resole type phenol-formaldehyde resins. They found out that, by keeping gel time long enough, it can help the water vapour to be released slowly leading to no bubble formation. As a result, a void-free phenolic sample was obtained. This approach necessitated a very long heating schedules (as long as 3 days) to allow slow water vapour release, preventing micro void formation. Hence, this cure cycle was applied in the current study but with some modification. The curing takes place in autoclave with similar cure schedule and constant pressure of 7 bar. It takes approximately 3 days with this cure cycle, 40 ℃ (720m) – 60 ℃ (1440m) – 80 ℃ (1440m) – 100 ℃ (600m) – 130 ℃ (60m), ramp rate 2.7 ℃/min , total time taken: 4260m (=71h). The resins came out quite brittle, but the level of bubbling was reduced compared to previous attempts. Bubbles can be seen on the outer edge and inner of the samples (Figure 4.5). Clearly this had resulted in further removal of water from the sample, however it was insufficient to fully eliminate the problem. A longer cure cycle was therefore proposed.

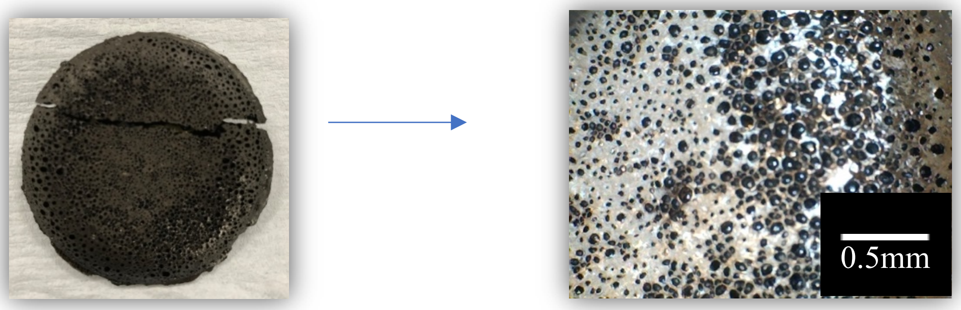


Figure 4.5 Sample's image under digital microscope for Trial 5

4.2.2.6 Trial 6

The cure schedule in trial 5 was used as a basis in trial 6, with extra holds at lower temperatures added to increase the time available for water removal. Segments were therefore added at 70 °C and 90 °C. The cure cycle is therefore, 40 °C (720m) - 60 °C (1440m) - 70 °C (1440m) - 80 °C (1440m) - 90 °C (1440m) - 100 °C (600m) - 130 °C (60m), pressure: 7 bar, total time taken: 7140m (=119h). This cure cycle takes approximately 5 days which is very time consuming. However, the resin started to show positive results, with the extra time clearly giving more evaporation and thus less bubbles in the final resin. As Figure 4.6 reveals, the sample's surface was shiny and bubbles were hardly seen.

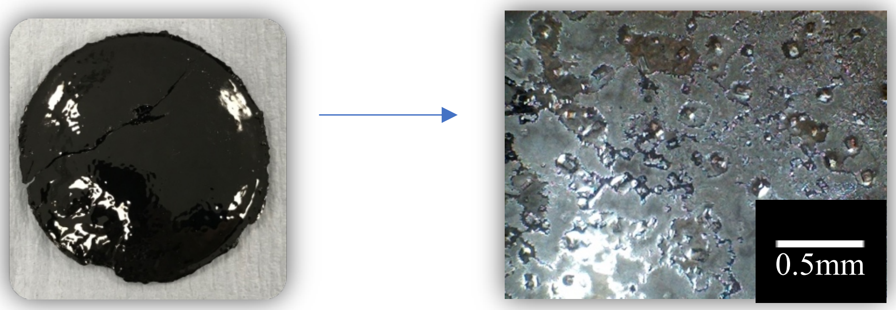


Figure 4.6 Sample's image under digital microscope for Trial 6

4.2.2.7 Trial 7

Having succeeded in producing virtually bubble free specimens in a 5 days cure schedule (Trial 6) and knowing that a 3 days cure schedule (Trial 5) was insufficient, a 4 days cure schedule was proposed in order to determine whether a reduction in time, and thus a slightly more efficient cure process, could be used. As before, the curing takes place in the autoclave with constant pressure of 7 bar and the cure cycle was modified to reduce the time of the intermediate holds from 1440 minutes to 999 minutes. Additionally, a stage was inserted at 50 °C, to facilitate further bubble removal. This gave a cure cycle of 40 °C (720m) - 50 °C (999m) - 60 °C (999m) - 70 °C (999m) - 80 °C (999m) - 90 °C (999m) - 100 °C (600m) - 130 °C (60m), total time taken: 5775m (=96.25h), ramp rate 2.7 $^{\circ}\mathrm{C}/min$. Following this cure cycle, a durable resin with no bubbles visible, and a shiny and smooth surface was obtained (Figure 4.7). The detailed image of the resin can be seen in SEM result in Section 4.5.3 that shows no micro void formation.

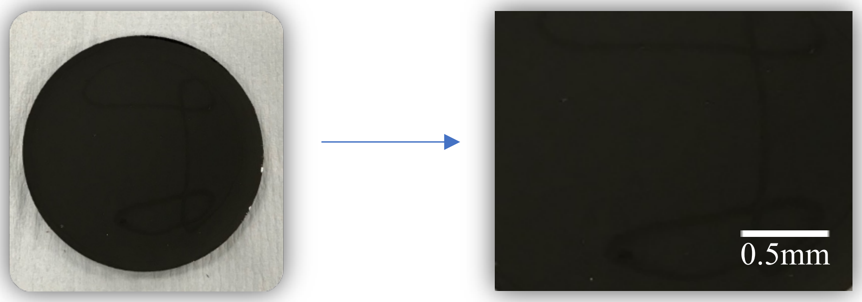


Figure 4.7 Finest sample of 0.25GA

4.2.3 Summary of cure trials

As can be seen from these results, a lot of stages were needed in order to produce a viable sample from this modified resin system. However, the optimised cure cycle, removed approximately 24 hours from the time taken in the previous cycle. The results revealed that lower values of temperature sustained for a longer time lowers the number of voids present, due to enough time being allowed for water to escape, and that the resin can be successfully cured even when the available pressure is limited to 7 bar. However, it is likely that the time taken to cure the specimens could be reduced if higher pressures were available.

4.3 Optimising the level of gallic acid substitution

The phenolic pre-polymer (1.0P) was viscous and the consistency was like honey with a dark brown colour. When phenol was partially substituted with gallic acid, the mixture became more viscous and darker. However, it was not that difficult to handle it. Initially, the modified phenolic resins were prepared with assorted amounts of gallic acid (0, 25, 50, 75 and 100 wt%). Then, more formulation was added, for instance 0.31, 0.37, 0.40 and 0.60GA, to find the optimum formulation. All the resin was cured at cure cycle number 6 and it was found that the samples still had bubbles and were not strong enough for further testing. The images for cured 0.40 and 0.60GA were quite similar to the image's samples at Trial 5, while 0.31 and 0.37GA samples looked more promising. The image of samples 0.31 and 0.37GA show similarity with image from Trial 6.

Hence, all the formulation was taken into curing at cure cycle number 7 and as a result, only 1.0P, 0.25GA and 0.31GA exhibited good properties, i.e no micro void formation, no bubbles, and no cracks on the samples. Therefore, it can be concluded that the maximum amount of gallic acid that can be substituted in phenol-formaldehyde resin is 31%, using the cure cycle number 7. All the samples after 31% of gallic acid can be neglected due to unsuitable cure cycle.

Cure cycle 6 has been used for preliminary work, while cure cycle number 7 has been adopted for all future work on the resin.

4.4 Characterisation

There were several analysis methods used to characterise the resins, such as DMA, TGA, DSC, FTIR, SEM and flexural testing. For information, not all resins underwent characterisation due to the nature of the samples, which were brittle and friable.

For preliminary works, samples at 1,0P, 0.25GA, 0.50GA, 0.75GA and 1.0GA were taken into further thermal analysis such as DSC, DMA and TGA. Mechanical testing could not be done due to the brittleness of the samples.

Due to successful production of 1.0P, 0.25GA and 0.31GA using cure cycle number 7, good samples were obtained for further testing. The testing includes DSC, DMA, FTIR, flexural test and SEM.

The equipment used for this characterisation has been explained in the previous chapter (see **Chapter 3: Experimental Materials and Characterisation**).

4.5 Preliminary Results and Discussion

This section comprises the results of the resins at 1.0P, 0.25GA, 0.50GA, 0.75GA and 1.0GA when cure schedule 6 was used.

4.5.1 DSC

Thermosetting resins contain pre-polymers that experience crosslinking processes during curing to exhibit irreversible chemical bond formation [238]–[240]. These processes eliminate the chance of the product remelting when heat is applied, thus giving the resins high thermal stability, good rigidity and hardness, and resistance to creep. Understanding the curing process enables determination of degree of cure, which is important to achieve the desired mechanical properties. The higher the degree of cure, the better the thermal resistance, higher the modulus, lower the moisture absorption, and higher the glass transition temperature should be [241], [242]. DSC is a technique that can be used to study the thermal properties of a sample when it is heated as a function of temperature [238], [243].

Chow and Steiner [244] investigated the resole resin and found endothermic peak at about 50°C. However, some other study reported that resole resin showed two exothermic peaks at 98-129℃ and 139-151℃ due to addition and condensation reactions respectively [245].

In this study, the DSC curves for resole resins with ratio of F:P = 1.5 are shown in Figure 4.8. These were obtained from the resin following cure using the standard cure schedule (number 6), with a peak temperature of 150°C. The intention was to determine whether residual cure was present (visible as an exothermic peak) as the samples were heated. In principal, this was to monitor whether the cure schedule was adequate or whether it needed to be modified to fully cure the specimens. All the samples were found to display no residual cure below 180°C, after which a cure exotherm was observed in each case, although the size of the peak was lower for the GA substituted resins. This suggests that the cure schedule was adequate for the intended application as natural fibres will degrade if heated to that level [128], [246]–[248].

It proved difficult to find Tg using the DSC data, so it was necessary to employ another technique to get this value. DMA was therefore employed.

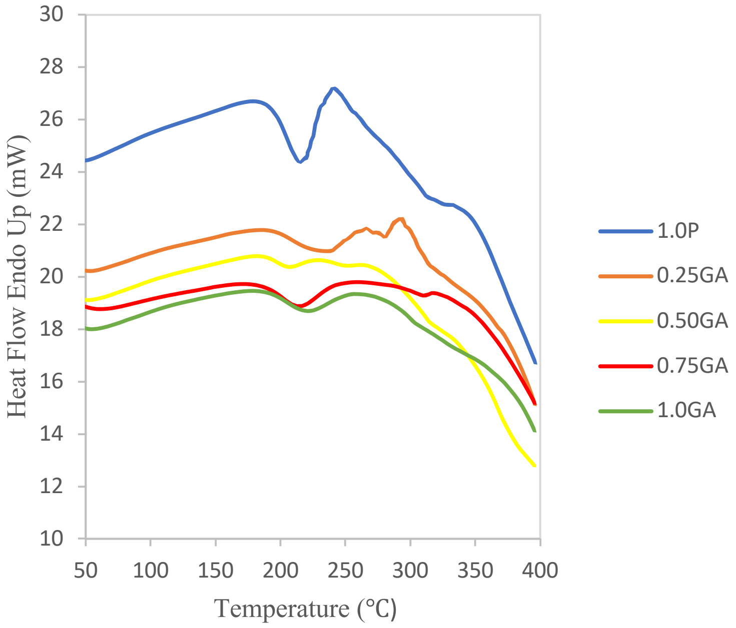


Figure 4.8 DSC thermogram of all resins

4.5.2 DMA

DMA can be described simply as a technique to study the dynamic properties when an cyclic force is applied to the sample and how the material responds to the force. One of the properties is tan delta, which is the ratio between the storage and loss moduli, which respectively show the elastic and viscous response of the material. This value is useful because it shows peaks at the point of transitions within the material, one of which is the glass transition temperature (Tg), where the polymer changes from a glassy state at low temperature to a rubbery state at high temperature. There are many points to read Tg,[249] based on the industry standards or background of the operator, for instance, the peak or onset of the rise in the tan delta curve, the onset of the E' modulus drop, or the onset or the peak of the E" modulus curve may be used. One can expect differences of up to 25°C when using these different methods to find Tg [249]. In this study, the peak in the tan delta curve is used, due to limitation of the material pocket testing geometry that was used for analysis of these resins.

Materials pockets were used due to the brittleness of the samples and thus inability to manufacture high quality bar specimens. When using material pockets, powdered samples are placed within a steel pocket to sandwich and seal the powder in place. This is then mounted in the DMA and tested normally, with a tan delta trace showing peaks were transition occurs. In this technique, the tan delta trace corresponds to the test of a monolithic material, but the modulus values are inaccurate due to the domination of the steel on this value [250].

Figure 4.9 illustrates the thermogram of tan delta of the compounds and Tg is determined from the peak of the tan delta curve. The Tg for compound 1.0P, and 0.50GA can be seen clearly at 216℃, and 235℃ respectively. This shows that increasing the gallic acid amount increases the Tg. The curve for 0.25 GA is inconclusive. For compounds 0.75GA and 1.0GA, it seems like the glass transition temperature is at least 300℃. This test has been re-run for several of the resin samples, which is 1.0P, 0.25GA and 0.31GA, employing cure schedule 7 to produce more robust resin samples that could be tested without materials pockets, and the results are presented in Section 4.5. However, this work was sufficient to show that the resin could be cured and that an acceptable Tg could be obtained.

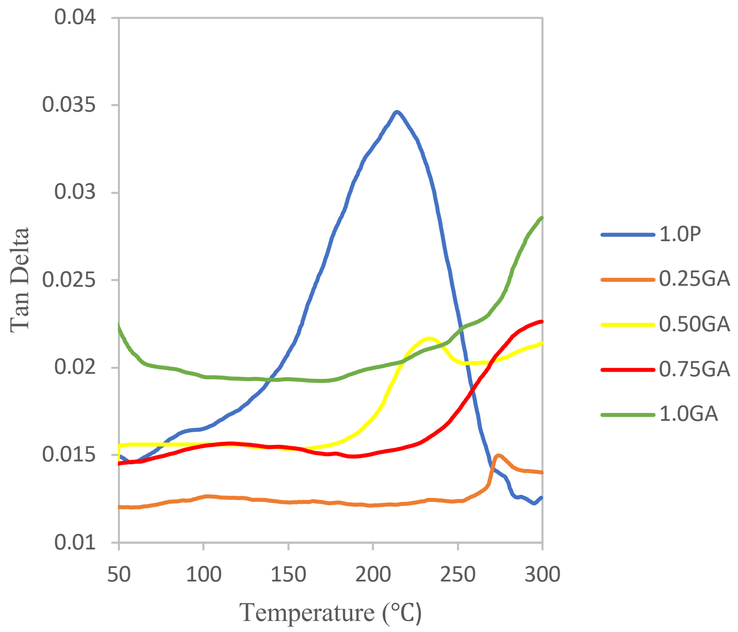


Figure 4.9 DMA testing of the resins, showing the tan delta curves for all compounds obtained using material pockets

4.5.3 TGA

TGA is an analysis technique that uses temperature to determine thermal decomposition. This technique usually involves heating, and sometimes cooling a solid sample gradually. The sample is surrounded by purge gas usually an inert gas which controls the environment. As the temperature increases, the change in weight is measured. The thermogravimetric behaviour of all samples was analysed and shown in Figure 4.10. From the graphs, it can be seen the initial decomposition temperatures of the materials decreased from 1.0P to 1.0GA. Compound 1.0P started to decompose at 350°C, followed by 0.25GA at 210°C, 0.50 GA at 180°C, 0.75GA at 160°C and 1.0GA at 150°C. This result showed that 1.0GA has the least thermal stability of the specimens which were analysed. For final residue, the amount of material left after the end of heating is 1.0P (70%), 0.25GA (66%), 0.50GA (65%), 0.75GA (61%) and 1.0GA (61%). It can be concluded that increasing gallic acid amount in the compound resulted in increasing weight loss and hence lower thermal stability which makes it challenging to substitute phenol with gallic acid for resin manufacturing. However, as the application is the use of natural fibres, which themselves have a low maximum service temperature, this lower thermal stability may not prove critical.

To obtain peak temperature related to maximum rate of weight loss, differential thermogravimetry analysis (DTG) was used. Figure 4.11 illustrates the spectra of DTG. It can be seen that a peak was detected below 250°C for gallic acid resin probably due to the loss of hydroxyl either as water or perhaps even as CO_2 or CO. While the peak at around 250°C in compounds containing gallic acid proved they exhausted carbon dioxide during heating. Constituents other than gallic acid in the compound are believed to release CO_2 at this temperature too, resulting in a high percentage of weight loss. Further loss of weight at higher temperature was probably due to oxidation of residual carbons. For 1.0P compound, this resole thermally decomposed at three temperature regions: 200-300°C, may be caused by the removal of terminal groups and further crosslinking/condensation reaction, 350-500°C (the main weight loss region for resole) corresponds to decomposition of methylene bridge into phenol and cresol homolog, and 500-600°C corresponds to further degradation of phenols to carbonaceous structure [251]. This peak is also seen to occur in the GA substituted resins, but the level is lower, due to the earlier onset of degradation in these materials.

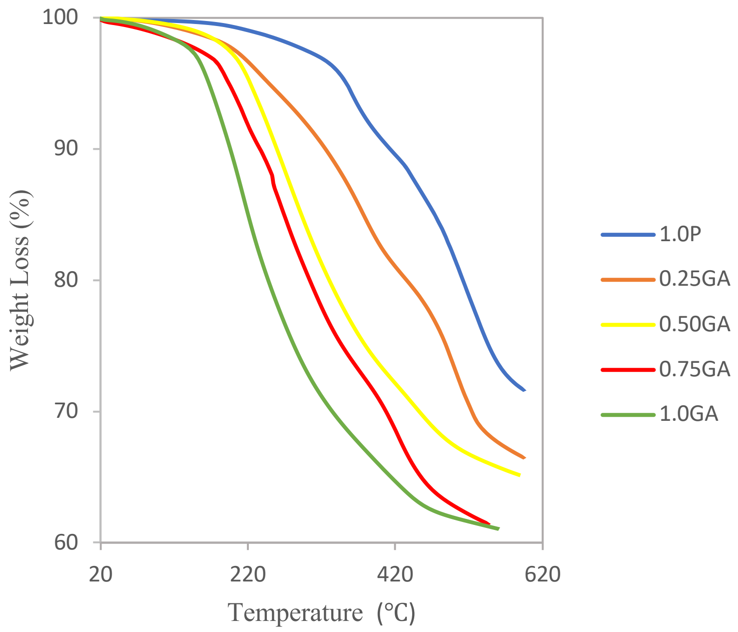


Figure 4.10 TGA analysis of all compounds

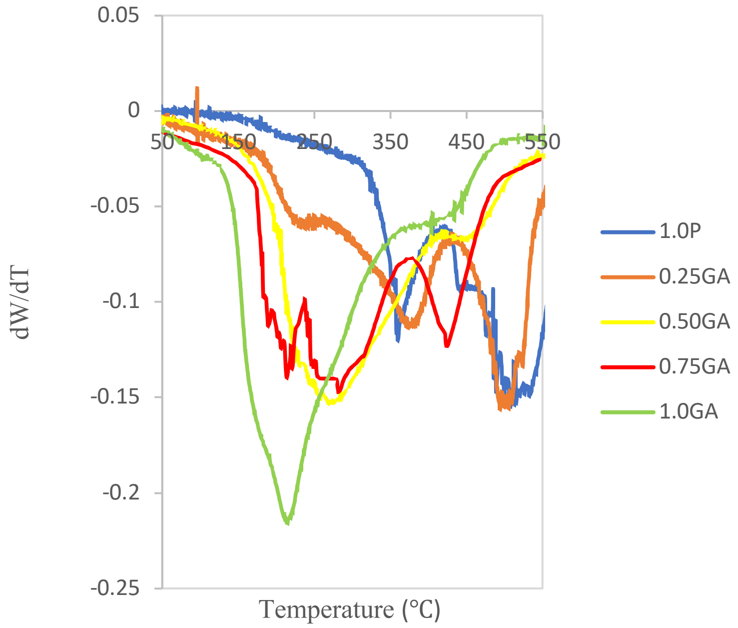


Figure 4.11 DTG analysis for all compounds

4.5.4 Summary

A series of phenol-formaldehyde resole resins were produced with gallic acid as a substitution to phenol. The influence of the gallic acid in the compounds was investigated in terms of thermal properties. Thermal behaviour of all compounds was observed by DSC, DMA and TGA. The following conclusions can be drawn. In DSC, all the samples were found to show no residual cure below 180℃. This proves that the cure schedule was suitable for the desired applications in natural composites. As it was difficult to find Tg in DSC, DMA was therefore employed. Due to the brittleness of the samples, the testing was carried out in material pockets. However, the drawback of using material pocket is it does include the modulus of the pocket as a background signal, hence it is preferable to look at just tan delta rather than changes in the modulus signal. As the gallic acid amount increased, the Tg increased significantly. However, the TGA results showed that higher gallic acid amount in the compounds resulted in increasing weight loss and hence lower thermal stability. Therefore, although the glass transition temperature rises, the thermal stability reduces as the GA content increases. Mechanical test data was necessary to complete the analysis, but this requires the production of void free specimens so that accurate bars can be cut for testing.

From these results, it can be said that gallic acid can be a potential substitution to phenol and that although the decomposition is lower than phenol-formaldehyde resin, the Tg is higher. Nevertheless, it is assumed that this will not affect the performance of the resin in the application. For further analysis in gallic acid-substitute-resin, resin at 25% and 31% gallic acid was chosen to be further analysed in thermal, mechanical, chemical and morphological properties as it gave the best samples compared to other resins when cure schedule number 7 was employed. This 0.31GA resin was successfully produced using cure cycle 7 recently, thus results for all resins that used cure schedule 7 is presented in the next section.

4.6 Resin Characterisation

This section comprises the results of the resins at 1.0P, 0.25GA, and 0.31GA when cure schedule 7 was used.

4.6.1 DSC

Figure 4.12 shows the DSC curves for 1.0P, 0.25GA and 0.31GA when cured using cure cycle 7. Although the quality of cure is better in regard to the presence of bubbling within the resin, there is a degree of residual exotherm in this material that is visible as a peak in all of the traces, centred at around 210°C. From this we can say that the resins are not fully cured. However, there is no residual exotherm below 150°C, and given that these resins are being used for natural fibre composites, the degree of cure obtained in this study is considered to be unimportant in the analysis.

One thing is fairly certain however, all the resins have quite similar onset temperature at about 175°C, so below that temperature there is no residual cure which makes it favourable for the use in natural fibre composites. It is not possible to get an accurate degree of cure using DSC, as the resins evolve large amount of water, precluding the testing of uncured resin in the DSC to obtain a base-line exotherm.

The DSC thermograms found in this study showed a single exothermic peak for all the samples. However, the findings of the current study do not support the previous research [252], in which they reported two exothermic peaks for resole resin due to high molecular weight of the PF resin. There is, however, another study that displayed a single exothermic peak for resole resin [253], in which the molecular weight of the synthesised resin is lower than the previous study. A possible explanation of these results may be the difference in the weight-average molecular weight of the resole resin, where a lower molecular weight resin leads to a single exothermic peak. Nonetheless, these results were not very encouraging as further works are needed to establish whether or not resole resin possess two exothermic peaks. However, the results of this study suggest that a single peak was found, although the molecular weight of the resin is not known.

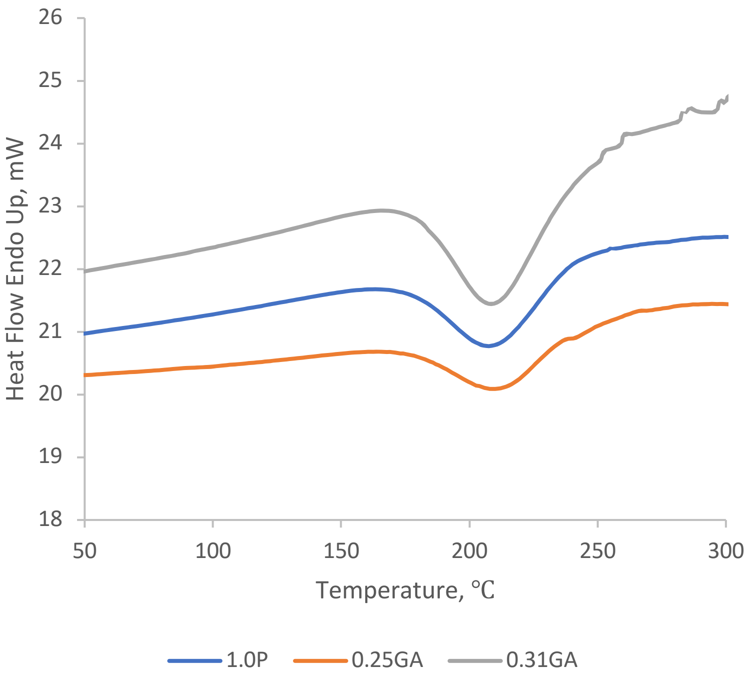


Figure 4.12 DSC curves for resins at cure cycle 7

4.6.2 FTIR

Figure 4.13 shows FTIR spectra of 1.0P, standard GA, 0.25GA and 0.31GA. The characteristic absorbances of 1.0P resin are ascribed in Table 4.1 with comparison to the literature values [254]. A peak occurred at 1600 cm^{-1} indicated that C=C band vibrations of the aromatic ring. Other than that, to characterise the formation of resole resin, a peak at 1473 cm^{-1} indicates C-H of the methylene bridge, and 1144 cm^{-1} is C-O-C of the methylene ether bridge, that were found to be present in the tested samples. This finding is consistent with the literature [255] that found bands at 1633, 1478 and 1116 cm^{-1} indicating C=C aromatic ring, C-H methylene bridge and C-O-C methylene-ether bridge respectively for resole resin. The summary of the characteristic absorbance that are present in 1.0P is displayed in Table 4.1.

Table 4.2 represents the summary of FTIR spectra of GA resin. The literature data [256] of absorption bands of GA correlates very well with the standard GA used in this study. Generally, bands in the 729-961 cm^{-1} range show the out of plane deformation vibrations of the C-H bond in the benzene aromatic rings. According to the previous research [257], these bands are relevant in monitoring the degree of crosslinking. As can be seen in GA substituted resin (0.25GA and 0.31GA), those peaks have disappeared showing that insoluble cross-linking has occurred.

Table 4.2 also displays the comparison of standard GA and 0.25GA and 0.31GA substituted resins. This GA-substituted resin has changed the FTIR spectra significantly. Initially, there were bands at 1653 cm^{-1}that corresponds to C=O stretching, however the bands disappeared in 0.25GA and 0.31GA as the regions were shifted to lower bands which are 1585 and 1575 cm^{-1} for 0.25GA and 0.31GA respectively. This is possibly due to the polymerisation process. The peak at 1454 cm^{-1} in the standard GA that indicates benzene ring, has shifted to 1440 and 1444 cm^{-1} in 0.25GA and 0.31GA, not to mention the formation of methylene bridge (-CH_2-) too. Peak at 1356 cm^{-1} shifted to 1354 for 0.25GA and 1348 for 0.31GA to indicate phenolic ring. All the bands from range 1317-1241 cm^{-1} in standard GA were combined as a peak at 1360 and 1348 cm^{-1} for 0.25GA and 0.31GA respectively. This is to represent OH group in the resin. The 1209 and 1210 cm^{-1} of GA-substituted resin denote the carboxylic acid [258]. The formation of dimethylene-ether-bridge (-CH_2-O-CH_2-) can be seen at peaks 1147 and 1142 cm^{-1} for 0.25 and 0.31GA respectively. As a summary, the important bands to observe that indicate the formation of resole resin is; 1600, 1473 and 1144 cm^{-1} as can be seen in Figure 4.13 (A), (B) and (C).

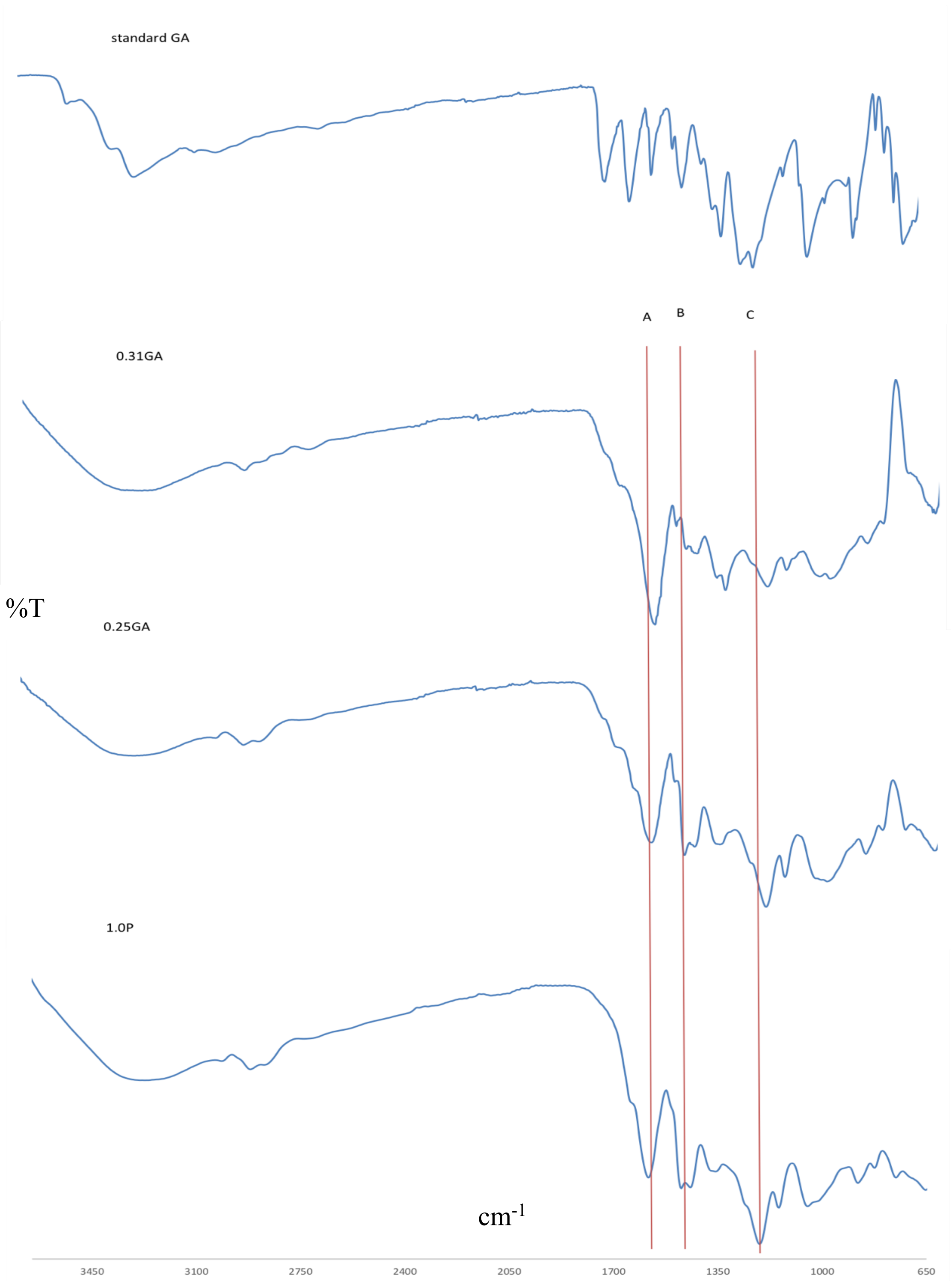


Figure 4.13 FTIR spectra of 1.0P, standard GA, 0.25GA, 0.31GA. The important bands at 1.0P, 0.25GA and 0.31GA, which is A: 1600 cm^{-1} , B: 1473 cm^{-1}, C: 1144 cm^{-1}, indicate the formation of resole resin.

Table 4.1 Functional groups and observed wavenumbers for 1.0P and their literature values [254]

Literature data of wavenumber, cm^{-1}	Observed wavenumber, cm^{-1}	Functional group
3400	3272	OH
2925	2918	in phase stretching vibration of $-CH_2-$ alkane
2850	2860	out-of-phase stretching vibration of $-CH_2-$ alkane
1610	1600	C=C aromatic ring
1480	1473	C-H aliphatic
1450	1442	C=C benzene ring obscured by $-CH_2-$ methylene bridge
1378	1360	OH in-plane
1237	1210	C-C-OH asymmetric stretch
1100	1144	C-O-C aliphatic ether
1045	1050	single bond C-O stretching vibrations of $-CH_2OH$ group
1000	1006	-C-OH
885	880	-C-H out of plane, isolated H
835	822	-C-H out of plane, para-substituted
760	755	-C-H out of plane, ortho-substituted

Table 4.2 Functional groups and observed wavenumbers for standard GA and their literature values, 0.25GA and 0.31GA

Literature data of wavenumber, cm^{-1} [256]	Observed wavenumber for standard GA, cm^{-1}	Observed wavenumber for 0.25GA, cm^{-1}	Observed wavenumber for 0.31GA, cm^{-1}	Functional group
1695	1695	*disappear*	*disappear*	*v*(C=O), *v*(CC); carboxylic acid, benzene ring
1614	1612	*disappear*	*disappear*	*v*(C-C), d_{ip}(C-H), d_{ip}(ring); benzene ring, benzene ring, benzene
1539	1538	1500	1490	*v*(C-C), d_{ip}(C-H), *v*(C-O), d_{ip}(O-H); benzene ring, benzene ring, phenolic, phenolic
1470	1454	1440	1444	*v*(C-C); benzene ring
1437	1436	*disappear*	*disappear*	*v*(C-C), d_{ip}(C-H), *v*(C-O), benzene ring, benzene ring, phenolic

1373	1356	1354	1348	v(C-C), d_{ip}(C-H), v(C-O), d_{ip}(ring); benzene ring, benzene ring, phenolic, benzene
1337	1317	*disappear*	*disappear*	d_{ip}(O-H), v(CC), d_{ip}(C-H), v(C-O); phenolic, benzene ring, benzene ring phenolic
1306	1306	*disappear*	*disappear*	v(C-O), d_{ip}(C-H), d_{ip}(O-H), d_{ip}(ring), v(CC); phenolic, benzene ring, phenolic, benzene ring, benzene
1240	1241	*disappear*	*disappear*	d_{ip}(C-H), v(C-O), d_{ip}(O-H); benzene ring, phenolic, phenolic
1202	1202	1209	1210	d_{ip}(O-H); carboxylic acid
1101	1175	1147	1142	d_{ip}(O-H), v(CC), d_{ip}(O-H); phenolic,

				benzene ring, carboxylic acid
1045	1090	*disappear*	*disappear*	*v*(CC), *v*(C-O); benzene ring, carboxylic acid
1018	1018	1030	1031	*v*(C-O), *v*(CC), *v*(C-O); phenolic, benzene ring, carboxylic acid
961	-	-	-	d_{ip}(ring), *v*(C-O); benzene, phenolic
866	865	882	3879	*t*(CH), benzene ring
791	790	*disappear*	*disappear*	*t*(CH), benzene ring
762	761	*disappear*	*disappear*	*v*(CC), *v*(C-O), d_{ip}(ring); benzene ring, carboxylic acid, benzene
729	729	*disappear*	*disappear*	*t*(C-O), d_{op}(C-H), *t*(C=O); carboxylic acid, benzene ring, carboxylic acid
Notes: *v*=stretching, *d*=deformation, *ip*=in plane, *op*=out plane and *t*=torsion				

The proposed structure of phenolic resin and gallic acid resin from this FTIR spectrum are shown below (Figure 4.14 and 4.15), which will be used in Chapter 5 for modelling in GIM.

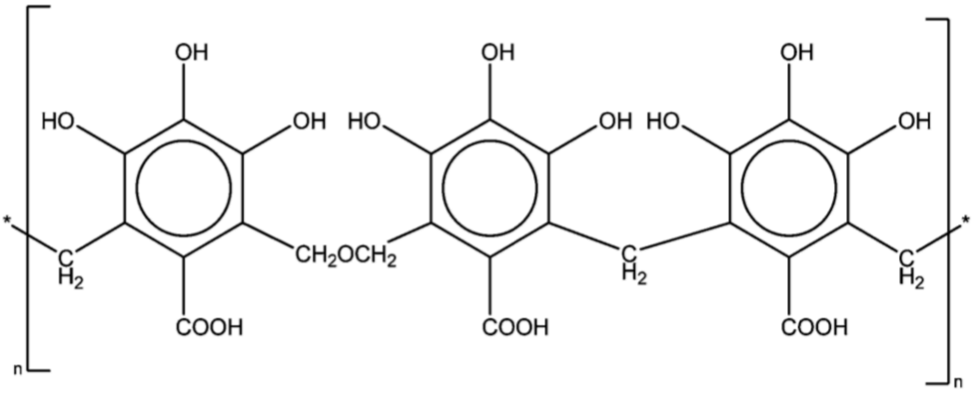


Figure 4.14 Structure of gallic acid resin. Reprinted from 'Synthesis and characterization of gallic acid resin and its interaction with palladium (II), rhodium (III) chloro complexes' by Can, M., Bulut, E., & Özacar, M., 2012, Industrial & Engineering Chemistry Research, 51(17), 6052-6063, DOI: https://doi.org/10.1021/ie300437u, Copyright © 2012 American Chemical Society

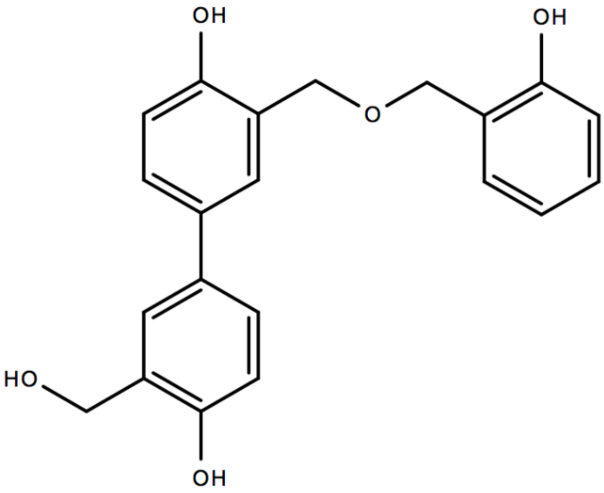
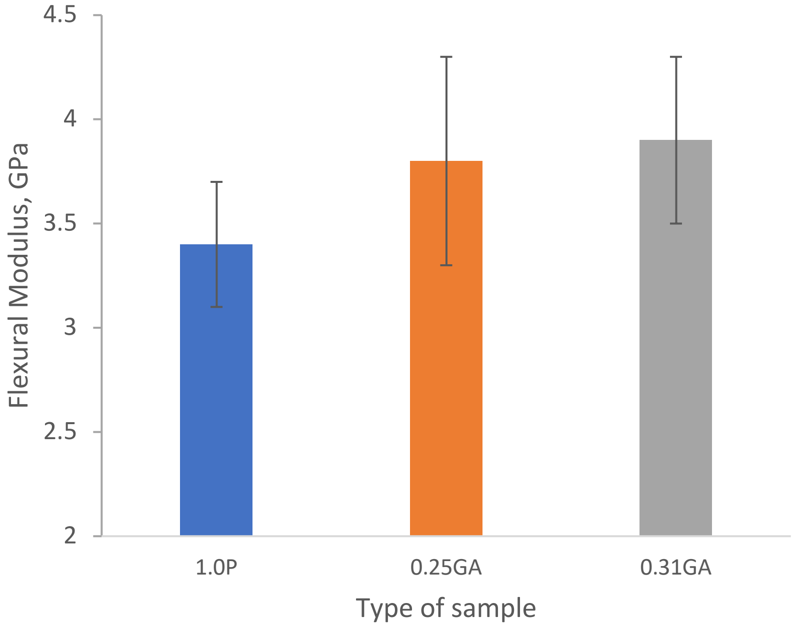


Figure 4.15 Structure of resole resin

4.6.3 Mechanical Properties

From Figure 4.16, we can see that substitution of phenol with gallic acid improved both flexural strength and modulus of the resin. The flexural modulus increased from 3.4 GPa to 3.8 GPa and 3.9 GPa for 1.0P, 0.25GA and 0.31GA resins respectively. The flexural strength also showed the similar trend in which it increased from 90 MPa for 1.0P to 94 MPa and 94.8 MPa for 0.25GA and 0.31GA resins respectively. The result shows that increasing amount of gallic acid enhanced the flexural properties of the resins. This could be due to the formation of intermolecular hydrogen bonding between OH^- of gallic acid and formaldehyde, thus enhancing the cross-linkage and decreasing the molecular mobility and free volume of formaldehyde [259]. From this data, we can see that there seems to be a trend, that the properties of the GA substituted resin is at least as high as that of the 1.0P resin.



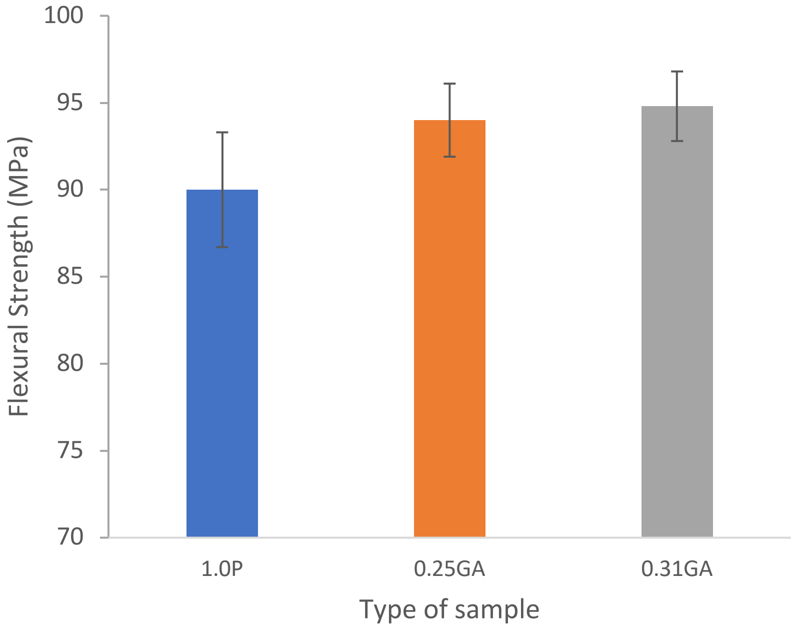


Figure 4.16 Flexural Properties of 1.0P, 0.25GA and 0.31GA. Notice that the lower value of both properties is omitted in order to improve the readability of the plot. The error bars represent ±1SD (samples tested for every set of error bars n=7)

4.6.4 Morphological study

SEM of flexural fracture surfaces of 1.0P, 0.25GA and 0.31GA resins are shown in Figure 4.17 (a), (b), (c) respectively. As can be seen in Figure 4.17 (a), the 1.0P resin had an even and smooth surface. No bubbles, cracks and voids are detected proving that the long cure cycle is suitable in producing a high-quality specimen although 1.0P resin is viscous. The long cure cycle enables the water to escape which lead to no bubbles trapped during the processing of the resin.

The similar image can also be observed in Figure 4.17 (b) and (c) where both samples displayed clean and smooth surfaces. However, there is unknown material which it is thought to be a surface contamination. It is possible that the mould used in curing the resins are not properly cleaned, thus exhibiting odd images. Nevertheless, the fracture surface of 0.25GA and 0.31GA resin shows that the mixtures are homogeneous which exhibit uniform appearance and composition throughout. Other than that, the material is brittle in nature, it is difficult to say more from these images.

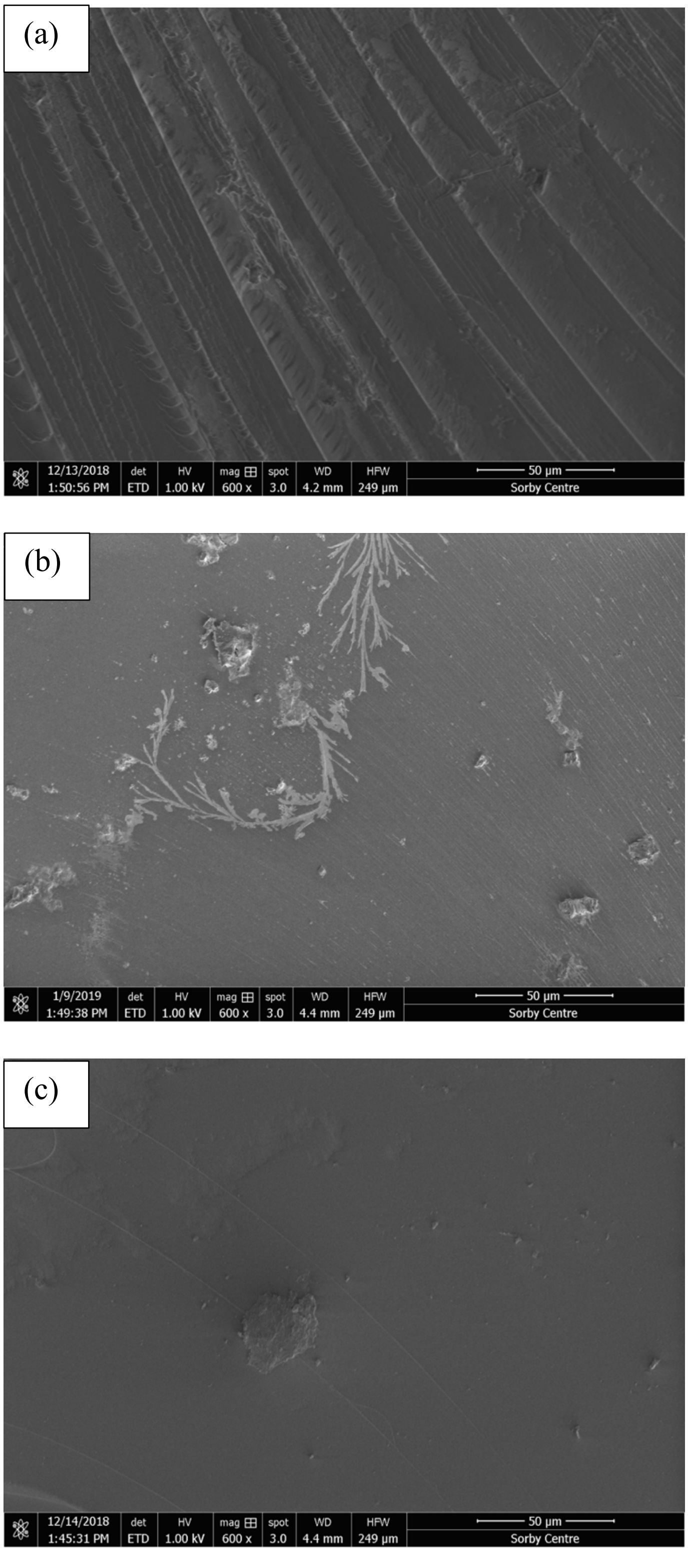


Figure 4.17 SEM micrographs of flexural fracture surface of (a) 1.0P (b) 0.25GA and (c) 0.31GA

4.6.5 Thermal properties

In the high elasticity thermoset resin, storage modulus and tan delta are essential parameters that will assists in evaluating the properties of the material. Figure 4.18 shows the storage modulus of phenolic resin and gallic acid-substituted-phenol resin. Storage modulus represents the elastic component when dynamic deformations occur. It can be observed clearly that the addition of gallic acid has increased the storage modulus of 1.0P. As the temperature increased, the storage modulus was slowly decreased, until the maximum loss at the glass transition temperature region, Tg (200-250°C). Referring to the figure, it can be seen that the storage modulus increased from 3 GPa for 1.0P to 3.4 GPa and 3.7 GPa for 0.25GA and 0.31GA respectively. The result shows that the stiffness of phenol-formaldehyde resin improved when gallic acid is added in the blends.

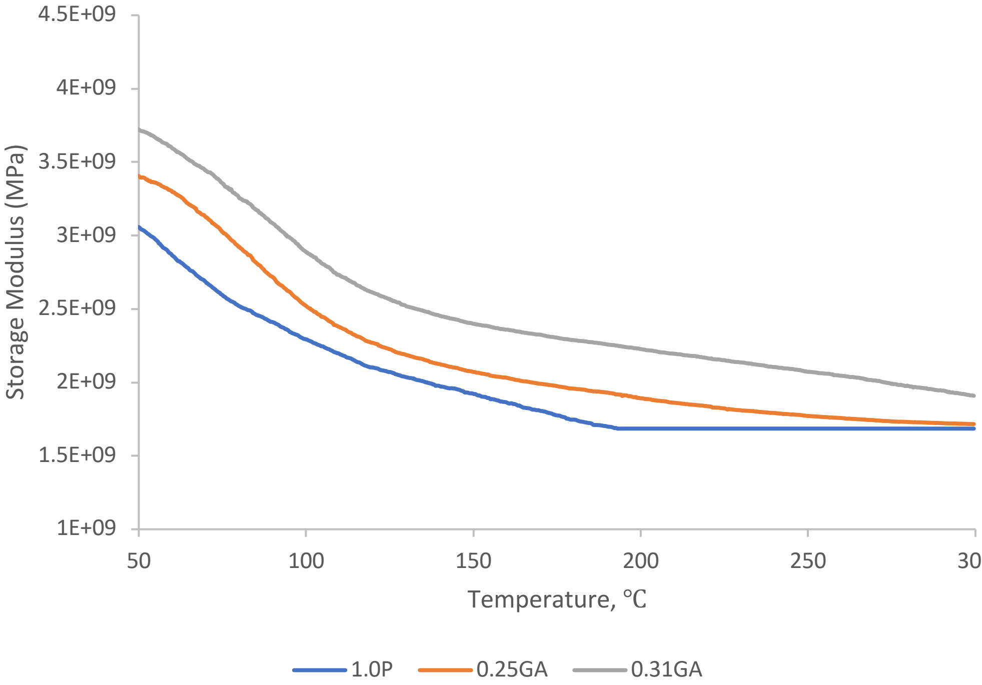


Figure 4.18 Storage modulus of 1.0P, 0.25GA and 0.31GA

Tan delta is also known as damping factor. It represents the ratio of the dissipation energy to the energy stored in the specimen during the applied alternating strain cycle. The plot of tan delta against temperature of all resins are displayed in Figure 4.19. While the tan delta curve is the ratio of the loss modulus and storage modulus, the tan delta curve commonly represents the transition state from glassy to rubbery behaviour. Thus, it can be said that the tan delta peak indicates the glass transition temperature. As demonstrated in this figure, GA substituted resin shifted the tan delta curve to higher temperature and showed an increase in the glass temperature of both the 0.25GA and 0.31GA. The glass transition temperature of 1.0P was 235℃, and it was significantly increased to 260℃ and 265℃ for 0.25GA and 0.31GA respectively. This is probably due to the increase in crosslinking density due to greater hydrogen bonding, as observed in the mechanical testing data.

The increment in crosslinking density has also contributed to the improvement in mechanical properties of the 0.25GA and 0.31GA resins. This is because increasing the crosslinking increases the number of binding chains and thus increases the stiffness of the polymer [188]. However, in TGA results discussed previously in Section 4.4.3 it was observed that the GA substituted resin possess low thermal stability which might be related to the possible impurities that exist within the GA substituted resin. There may be impurities such as residual monomer, metal ions, polymerisation solvent or oligomers, catalyst residues or other molecular weight material. There may also be more macroscopic impurities, for instance specks of degraded polymer or monomer, crosslinked gel particles, or even particles of metals from processing equipment.

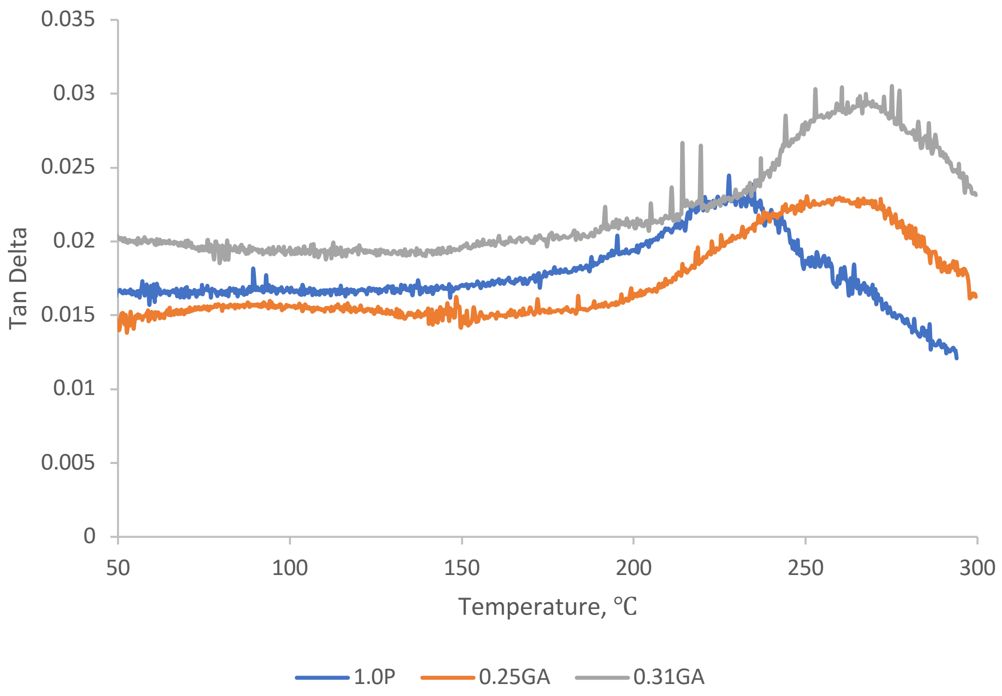


Figure 4.19 Tan Delta of 1.0P, 0.25GA and 0.31GA

4.6.6 Summary

A series of phenol-formaldehyde resole resins were produced with gallic acid as a substitution to phenol using the latest cure cycle, which is presented cure cycle trial number 7. The following conclusions can be drawn. In DSC, all the samples were found to have onset temperature at about 175°C, which means below that temperature no residual cure is detected. There is no further reactions in the desired temperature range, but there is an element of extra reactions above 175°C. This proves that the cure schedule was appropriate for the desired applications in natural composites as natural fibres would not be used at temperatures of 175°C due to thermal degradation of the fibre. The mechanical properties of 1.0P resin were enhanced when substituted with gallic acid in the range up to 31%. This is supported by the SEM image. The fractured flexural surface demonstrated that no voids, cracks and bubbles were seen from the image, although there were unknown materials that are assumed to be impurities and contamination due to not properly cleaning the mould on the image of the surface. DMA results shows that Tg of 1.0P increase when substituted with 25 and 31% of gallic acid. It shows the increment of crosslink density thus the stiffness of the resin is improved. FTIR spectra shows the absorbance peak that present in 1.0P, 0.25GA and 0.31GA with important bands to indicate the formation of resole resin, which is 1600, 1473 and 1144 cm^{-1}, C=C aromatic ring, C-H methylene bridge and C-O-C methylene-ether bridge.

From these results, it can be concluded that gallic acid can be a potential substitution to phenol as it yields good properties, of at least equivalent properties to conventional phenol-formaldehyde resin.

5.0 GROUP INTERACTION MODELLING (GIM)

5.1 Introduction

David Porter [26] has developed GIM as one of the methods to predict important engineering properties of a polymer from the chemical composition and (macro) molecular structure. This approach works by using the energetic intermolecular interaction between atomic groups in adjacent polymer chains to determine chain mobility and relate this to the mechanical properties. The energy of interaction consists of van der Waals forces between molecules, since these are the weakest bonds which distort upon the application of an external energy field, such as during mechanical distortion.

The method is based purely upon an energy balance between the negative potential energy of intermolecular forces and various positive thermodynamic energy parameters. A polymer chain is assumed to be a flexible and inextensible cylinder of circular cross-sectional area with a diameter, r. the chain is comprised of Z mer unit segments as interaction sites, each with a length, L, in the chain axis. Each chain is surrounded by six identical chains in a hexagonal packing configuration, and the separation distance between chain centres is identical to the chain diameter, r. The energy of interaction between chains is taken to be due only to nearest neighbour chain interactions, and has a magnitude of $\emptyset$ per interaction, such that a total interaction energy in a model hexagonal group is $3\emptyset$ (six interactions, two mer units per interaction). The interaction energy, $\emptyset$, becomes;

$$\emptyset = -\emptyset_0 + H_c + H_T + H_M \qquad (1)$$

$\emptyset_0 = depth\ of\ the\ potential\ energy\ at\ separation\ distance\ r_0$

$H_c = configuration\ energy$

$H_T = thermal\ energy$

$H_M = mechanical\ energy$

Parameters that are involved in GIM were taken from trusted sources [26] and are backed by experimental works. Due to the arrangement of the chemical group, each of them has been assigned their own degrees of freedom (DOF). The lower total energy the group has, the more stable the conformation is. Total energy is a sum of kinetic and potential energy between the neighbouring mer unit, and is proportional to the potential of the system $\emptyset_0$ in the lowest state of total energy.

The cohesive energy E_{coh} can be obtained using the group contribution tables, being related to $\emptyset_0$ [26].

$$E_{coh} = \frac{3}{4}\,\emptyset_0 n_a \tag{2}$$

$n_a = Avogadro\ number$

Equation (1) can be solved by including contributions to H_c, H_M and H_T. Additionally, at T_g

$$\emptyset = \emptyset_g = 0.787\emptyset_0 \tag{3}$$

$$H_c + H_T = 0.213\emptyset_0 \tag{4}$$

H_c is also related to $\emptyset_0$ according to Equation (5), which means that this estimates the extra energy associated with deviation from ideal packing. So, unless the polymer is a perfect crystal, this will have a positive value, which for an amorphous system is what we have in the equation,

$$H_C = 0.107\emptyset_0 \tag{5}$$

The energy stored in a polymer, H_M in response to an external force field must be included in the potential function in order to model non-linear bulk physical properties. $H_M = 0$ is no field is applied, i.e. no force applied.

$$H_M = \frac{N}{3} k\Delta T_m \tag{6}$$

$N = number\ of\ degrees\ of\ freedom$

$k = Boltzmann\ constant$

$\Delta T_m = hypothetical\ temperature\ increment$

The Tarasov estimation of Debye theory was used to express thermal energy (H_T) for one-dimensional chain oscillation between the neighbouring mer units. In this case, only skeletal vibrations of the polymer chain influence thermal energy [26]. Equation 7 gives the simplified form of the Tarasov estimation that can be utilise in GIM.

$$H_T = N\frac{N}{3}[T - \frac{\theta}{6.7} tan^{-1}\left(\frac{6.7}{\theta}T\right)] \tag{7}$$

$\theta = Debye\ reference\ temperature$

$N = number\ of\ degrees\ of\ freedom$

$T = temperature\ in\ K$

Equation (7) can be simplified with the assumption that the temperature is T_g, and expanding the tan^{-1} function to incorporate Equation (4) giving thermal energy at the glass transition, where $\emptyset_0$ is related to the cohesive energy through Equation (2). Equation (2) is accurate when compared to experiment for a dataset of 250 polymers. Hence, glass transition temperatures can be predicted using this equation;

$$Tg = 0.224\theta + 0.0513\frac{E_{coh}}{N} \tag{8}$$

5.2 Previous studies on GIM

A previous study by Gumen et al. [27] has shown that modelling using GIM was compelling in predicting the glass transition temperature for several epoxy resin/hardener combinations. This method can be effectively deployed to a resin blend to investigate the properties of the contribution of individual components. Using GIM, they found that the glass transition temperature of tetrafunctional glycidyl amine (MY721) cured with diaminodiphenylsulphone (DDS) was 281°C, which was comparable with the experimental value (288°C).

Foreman et al. [260] predicted the glass transition temperature for the same material as approximately 290°C. This value correlates well with the previous study though other reported values vary greatly. This can be because of the different measuring techniques and controlled transition kinetic. Exact hardener composition and the degree of cure are the essential parameters in estimating the value of glass temperature.

A recent study by Foreman et al. [261] showed the density (ρ) against temperature relationship for triglycidyl *p*-aminophenol (TGAP(MY721))/DDS, tetraglycidyl 4,4′ diaminodiphenylmethane (TGDDM(MY510))/DDS and the 50-50 blend. The density reduced with temperature gradually until the glass transition temperature was reached (~275°C) where a change in gradient was observed. Increasing in molecular motion at the large scale caused the viscoelastic polymers to move from glassy to rubbery state. Overall, the predicted values of glass temperature from GIM compare very well with experiment.

On the other hand, Tilbrook and colleagues [262] have successfully predicted polymerisation shrinkage from the modelling structure. It showed that GIM was capable of providing a suitable theoretical framework to manufacture low-shrinkage resin. It was concluded in this study that the correlation between temperature and volume changes in resin affected the polymerisation shrinkage. Hence, it would be rational to assume that polymerisation shrinkage is temperature-dependent.

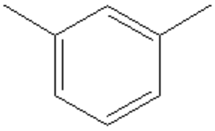
There was no study reported on prediction of properties on gallic acid substituted phenol in GIM. Thus, in this study GIM was used to predict the properties of gallic acid substituted phenol, as it can be assumed that GIM is a reliable technique for the prediction of the engineering properties of polymeric materials that can substitute time-consuming experiments.

5.3 Modelling Prediction

In this study, GIM was applied to estimate the glass transition temperature of the polymer. This approach has proven successful in a set of linear polymer [26]. GIM emphasis is on interactions between neighbouring polymer chains by using a potential function that contains a variety of thermodynamic energy terms. The set of fundamental parameters required for input into GIM is based around the representative mer unit. These are the degrees of freedom (N), the cohesive energy (E_{coh}), the Van der Waals volume (V_w), and the molecular weight (M). Initial values are taken from group contributions such as shown in Table 5.1. The degrees of freedom (N) is the most important parameters that should be taken care of.

To predict the properties of phenolic resin and gallic acid resin, a list of GIM model input parameters has been prepared using the table of group contributions. The table of group contributions of van Krevelen [26] is supplemented by values obtained using connectivity indices (see Table 5.1 for group contributions to model input parameters).

Table 5.1 Group contributions to model input parameters

Group	M (g/mol)	V_w (cc/mol)	E_{coh}(J/mol)	N (mer^{-1})
	76	43.3	25 000	4
-CH_2-	14	10.23	4 500	2
-OH	17	8	13 000	2
-O-	16	5	6 300	2
-CO-OH-	45	(19.7)	(30 500)	(4)

*Values in bracket are those with some doubt attached and are given as a starting point for calculations.

A) Phenolic Resin (1.0P)

1. Determination of phenolic mer units - unlinked

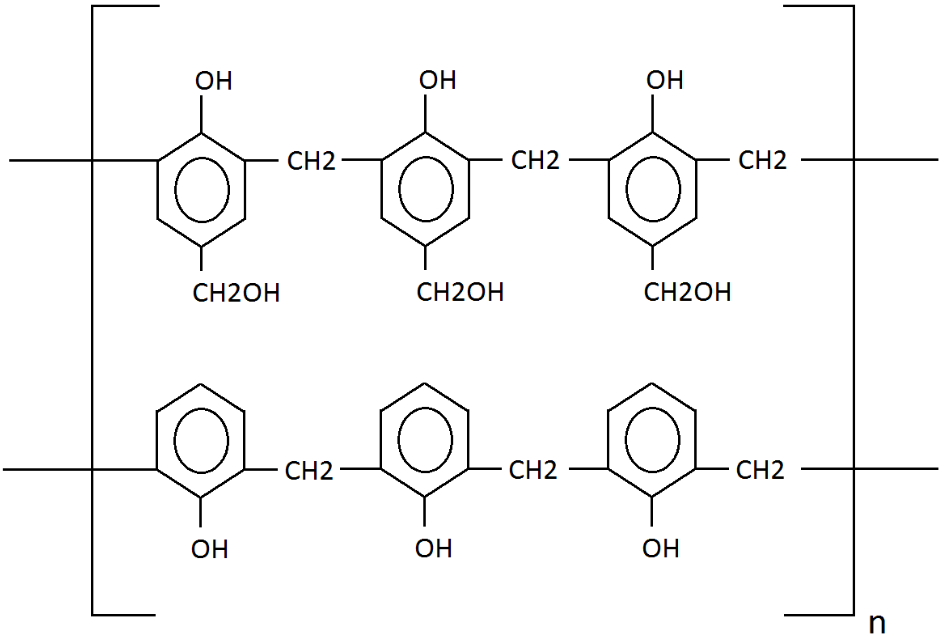


Figure 5.1 Phenolic polymer

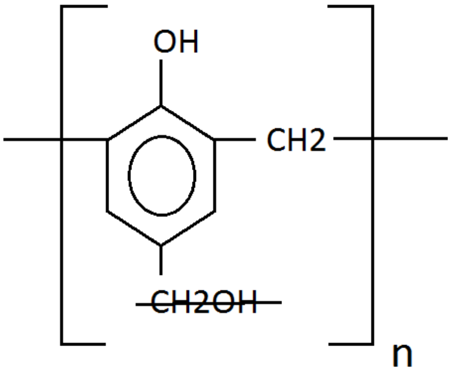


Figure 5.2 Phenolic monomer

2. Determination of phenolic mer units – linked

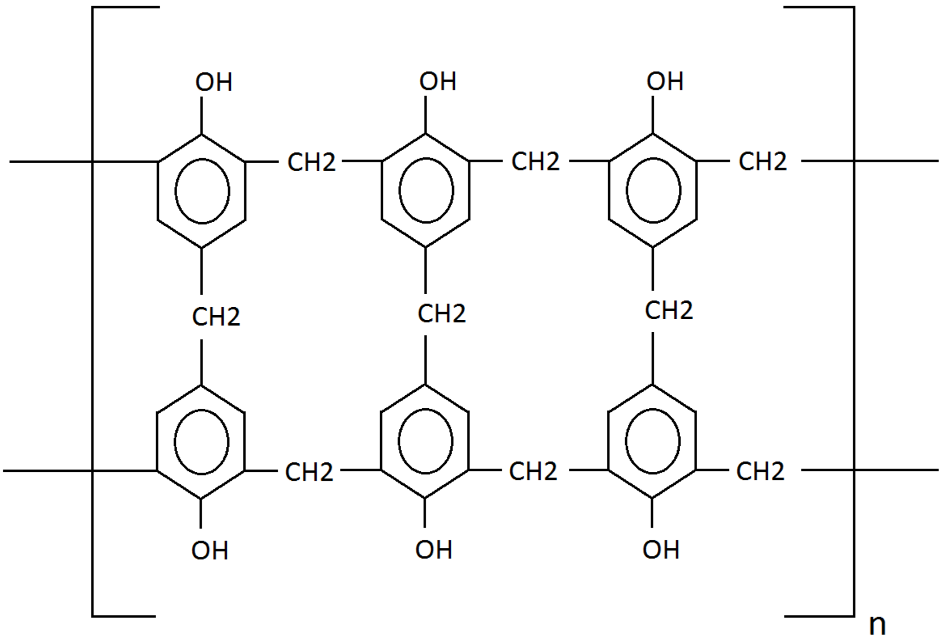


Figure 5.3 Phenolic polymer

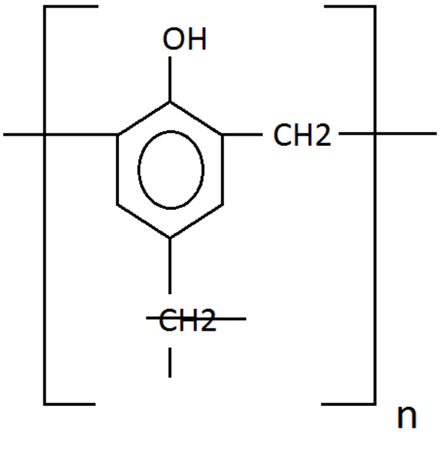
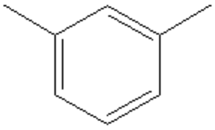


Figure 5.4 Phenolic monomer

*line (~~CH_2OH~~ and ~~CH_2~~) means half which the parameter value will be calculated half from the original value.

The parameter values for the mer units are the summation of the group contribution arising from each constituent functional group from Table 5.1. Based on structure shown in Figure 5.1-5.4, the parameter values for the relevant functional groups are constructed below (Table 5.2).

Table 5.2 Functional groups for phenolic resin

Group	M (g/mol)	V_w (cc/mol)	E_{coh}(J/mol)	N (mer^{-1})
	76	43.3	25 000	4
-CH_2-	14	10.23	4 500	2
-OH	17	8	13 000	2

The mer unit parameter values for both linked and unlinked mer units are shown below (Table 5.3).

Table 5.3 Parameter values for the monomer

Mer unit	M (g/mol)	V_w (cc/mol)	E_{coh}(J/mol)	N (mer^{-1})
Unlinked	122.5	70.645	51 250	10
Linked	114	66.645	44 750	*6*

*Notes that the N value for linked polymer is 6. The initial value of N is 9 but according to Porter [1], three degree of freedom are lost per crosslink sites, thus N_{new}= 9-3 = 6.

These parameter values are then combined fractionally to represent phenolic resins with varying degrees of crosslinking. The calculation details are shown below.

$$E_{coh1} = 44\,750\,J.mol^{-1}, E_{coh2} = 51\,250 J.mol^{-1}$$

$$N_1 = 6\,mer^{-1}\,, N_2 = 10\,mer^{-1}$$

$$\theta = 550\,K$$

$$E_{coh(x)} = (x.E_{coh1}) + ((1-x).E_{coh2})$$

$$N(x) = (x.N_1) + ((1-x).N_2)$$

$$x\ is\ 0\ to\ 1$$

By using Equation (8),

$$Tg(x) = 0.224\theta + 0.0513\frac{E_{coh(x)}}{N(x)}$$

Hence, the Tg for phenolic resin are in the range of 113-232 ℃.

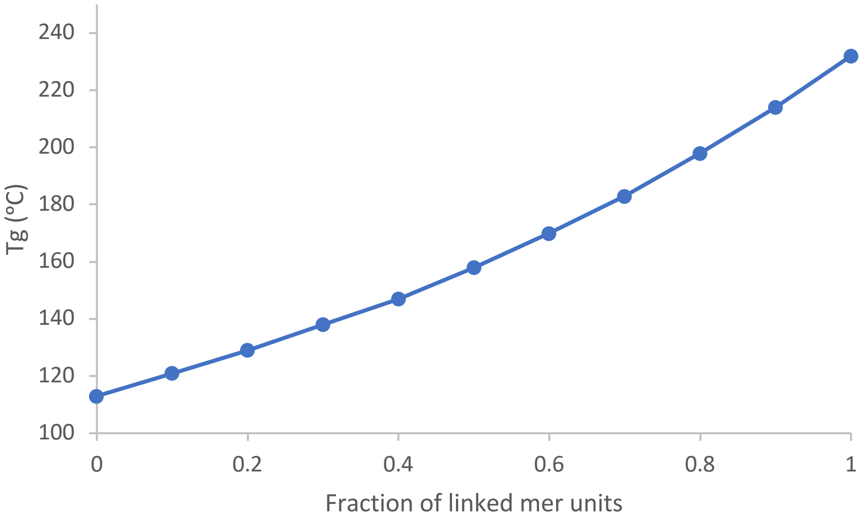


Figure 5.5 Estimation value of Tg at different crosslinking rate for phenolic resin

(*Note: the author used a Mathcad software which automated all the calculations above).*

B) Gallic Acid Resin (1.0GA) – OPTION 1

Determination of gallic acid mer unit is rather complicated because of the structure of the resin that is bulky. Selection rules for the most difficult parameter, N, for new and more complex ring structures are not yet fully developed. This means that some of the truly predictive value of the model for Tg is unavailable for the time being. However, equation (8) has the alternative use of letting a suitable value of N to be selected for use in other physical property predictions using GIM if a value of Tg can be determined either by empirical models or experimentally for a new polymer, for instance gallic acid resin. The gallic acid resin structure as proposed by Can et al. [263] is shown in Figure 4.14..

To predict Tg of gallic acid resin, the structure in Figure 4.14 is apportioned half assuming that there are two molecules which is 1) gallic acid with dimethyl ether bridge and 2) gallic acid with methylene bridge in order to produce the gallic acid resin. Thus, the final structure of gallic acid monomer is shown below (Figure 5.6).

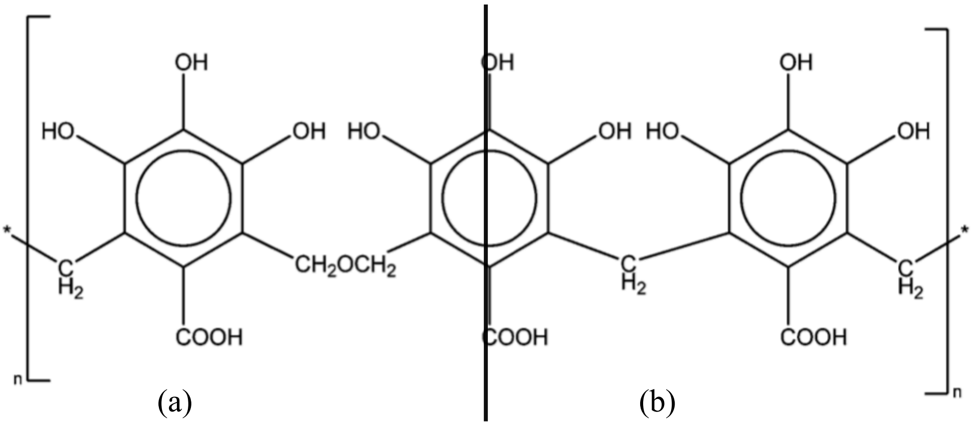
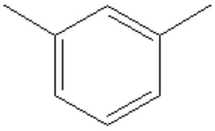


Figure 5.6 a) Gallic acid with dimethyl ether bridge b) Gallic acid with methylene bridge

The parameter values for the mer units are the summation of the group contribution arising from each constituent functional group from Table 5.1. The parameter values for the relevant functional groups for gallic acid are shown below (Table 5.4). In GIM, what matter is the actual backbone of the resin, not the side group. Hence, in this gallic acid resin, the author dismissed -OH- and -COOH- group as it is measured as the side group although it might present in the gallic acid resin.

Table 5.4 Functional group for gallic acid resin

Group	M (g/mol)	V_w (cc/mol)	E_{coh}(J/mol)	N (mer^{-1})
	76	43.3	25 000	4
-CH$_2$-	14	10.23	4 500	2
-O-	16	5	6 300	2

The mer unit parameter values for both methylene and dimethyl ether bridge are shown below (Table 5.5).

Table 5.5 Parameter values for the monomer

Mer unit	M (g/mol)	V_w (cc/mol)	E_{coh}(J/mol)	N (mer^{-1})
Methylene bridge	142	85.41	46 500	5
Ether bridge	172	100.64	57 300	11

These parameter values are then combined fractionally to represent gallic acid resins with varying degrees of crosslinking. The calculation details are shown below.

$$E_{coh1} = 46\,500\,J.mol^{-1}, E_{coh2} = 57\,300\,J.mol^{-1}$$

$$N_1 = 5\,mer^{-1}, N_2 = 11\,mer^{-1}$$

$$\theta = 550\,K$$

$$E_{coh(x)} = (x.E_{coh1}) + ((1-x).E_{coh2})$$

$$N(x) = (x.N_1) + ((1-x).N_2)$$

$$x\ is\ 0\ to\ 1$$

By using Equation (8),

$$Tg(x) = 0.224\theta + 0.0513\frac{E_{coh(x)}}{N(x)}$$

Hence, the Tg for gallic acid resin are in the range of 117-327 °C.

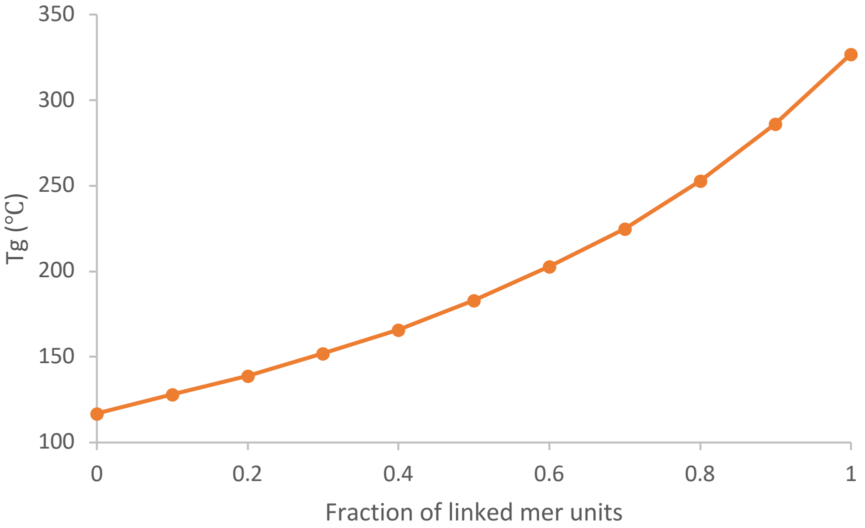


Figure 5.7 Estimation value of Tg at different crosslinking rate for gallic acid resin

(*Note: the author used a Mathcad software which automated all the calculations above).*

C) Gallic Acid Resin (1.0GA) – OPTION 2

The other possible structure of gallic acid resin that might present in this study is shown below.

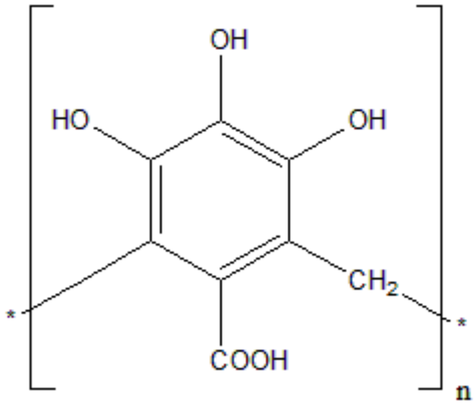


Figure 5.8 Gallic acid resin with methylene bridge

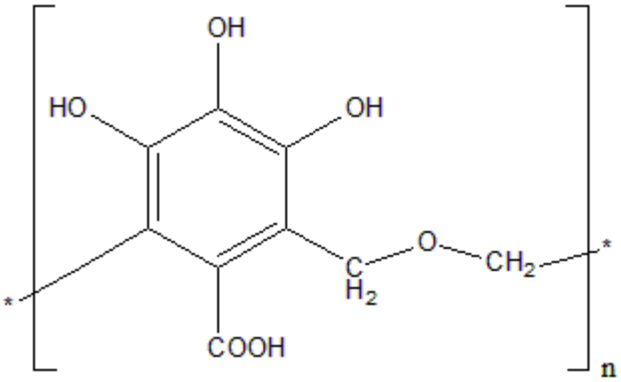
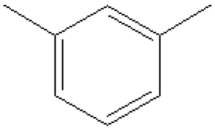


Figure 5.9 Gallic acid resin with ether bridge

The parameter values for the relevant functional groups for gallic acid are shown below (Table 5.6). In this case, all the functional group at backbone and side group has been taken into account. However, the degree of freedom was varied due to unknown proportion of methylene and ether bridge in the gallic acid resin. The distribution of values of the parameters

N in the model for glass transition temperature has been deduced by correlation of the GIM models with experimental observation of properties around Tg, and which is compatible with these approximate values. In this second option, determination of degrees of freedom was taken by summation of the degrees of freedom from the backbone groups, which are -COOH-, -CH_2-, -O- and phenyl rings, with the range given indicating before and after possible chain termination site, which means that skeletal degrees of degrees of freedom are lost at each crosslink site.

Table 5.6 Functional group for gallic acid resin

Group	M (g/mol)	V_w (cc/mol)	E_{coh}(J/mol)	N (mer^{-1})
	76	43.3	25 000	4
-CH_2-	14	10.23	4 500	2
-OH	17	8	13 000	2
-O-	16	5	6 300	2
-CO-OH-	45	(19.7)	(30 500)	(4)

*Values in bracket are those with some doubt attached and are given as a starting point for calculations.

The mer unit parameter values for both methylene and dimethyl ether bridge are shown below (Table 5.7).

Table 5.7 Parameter values for the monomer

Mer unit	M (g/mol)	V_w (cc/mol)	E_{coh}(J/mol)	N (mer^{-1})
Methylene bridge	186	97.23	99 000	10-13
Ether bridge	216	112.46	109 800	14-17

These parameter values are then combined fractionally to represent gallic acid resins with varying degrees of crosslinking. The calculation details are shown below.

$$E_{coh1} = 99\ 000\, J.mol^{-1}, E_{coh2} = 109\ 800\, J.mol^{-1}$$

$$N_1 = 10\ to\ 13\ mer^{-1}, N_2 = 14\ to\ 17\ mer^{-1}$$

$$\theta = 550\ K$$

$$E_{coh(x)} = (x.E_{coh1}) + ((1-x).E_{coh2})$$

$$N(x) = (x.N_1) + ((1-x).N_2)$$

$$x\ is\ 0\ to\ 1$$

By using Equation (8),

$$Tg(x) = 0.224\theta + 0.0513\frac{E_{coh(x)}}{N(x)}$$

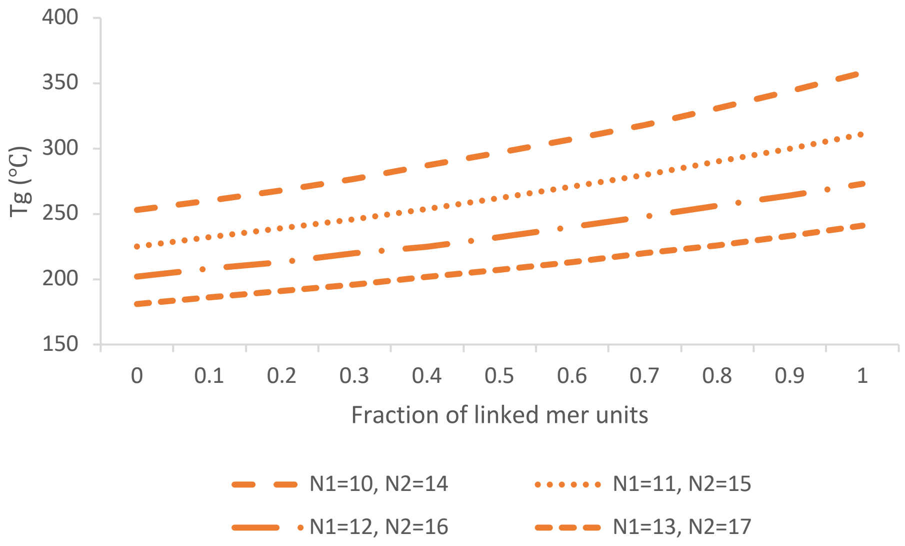


Figure 5.10 Variation of Tg values based on degrees of freedom

(*Note: the author used a Mathcad software which automated all the calculations above).*

From Figure 5.10, it shows that the lower the degree of freedom, the higher glass transition temperature is. In this case, degrees of freedom $N_1 = 11\ and\ N_2 = 15$ give comparable value with the experimental result which is 300 °C.

5.4 Results and Discussion

In order to model the polymer in GIM, first the mer unit of each reaction is determined. Once the structure is determined, the contribution of each constituent is calculated, with the value from group contributions to model input parameters. Some limitations are; information about several mer units of the polymer does not appear in the group contributions table made by Porter [26]. This is where experience and knowledge is needed to predict the values and properties of the investigated system. This is quite challenging, and some errors might occur during the calculations, it is therefore necessary to refine the model in relation to experimental measurements.

In this study, a comparison of modelled and experimental values of glass transition temperatures is given in Table 5.8. It is quite different to the measuring technique because it is a kinetically controlled transition.

Table 5.8 Modelled and experimental glass transition temperature of investigated resin systems

Glass transition temperature, T_g (^oC)	GIM	Experiment
Phenolic Resin	232	235
Gallic Acid Resin (1.0GA)	241-358	300-350

Based on Table 5.8, we can see small difference between modelled and experimental glass transition temperature of phenolic resin, but quite a difference in gallic resin. The chemical reaction of phenolic resin has been commonly studied by other researchers [195], [195], [264] thus it is not as difficult as gallic acid resin in order to propose the possible structure of the final product.

Conversely, for gallic acid resin, due to the complex reaction of gallic acid and formaldehyde, it makes it difficult to model GIM, as the final structure is unknown. In GIM, we need to modify some parameters in order to make it comparable with experimental result. The important parameters that affect the final value of glass transition temperature are degrees of freedom and cohesive energy. The lower the degree of freedom, the higher glass transition temperature. This means that crosslinking has occurred, thus restricted the chain mobility of the structures. In the other words, the lower the degree of freedom, the higher the degree of crosslinking, and therefore the higher the glass transition temperature is predicted. It is actually complicated to know what the exact proportion of each monomer is in the final product that is present in the reaction of gallic acid with formaldehyde.

GIM is used as an analytical tool to predict the possible structure of resin that is present in the reaction. The reader should bear in mind that the study is based on how good the knowledge of the resin chemistry is in order to employ the GIM-based model in terms of accuracy of the prediction. If anything is missed, it will change the overall system. Hence, there were two options that the author suggested that might be the possible structure of gallic acid resin. Further investigation of gallic acid resin can be done by investigating the resin chemistry using gel permeation chromatography (GPC) or nuclear magnetic resonance spectroscopy (NMR) to study the exact structure that is present in the resin. Likewise, further experimental work for gallic acid resin (1.0GA) needs to be done too to verify the Tg as it was very difficult to measure. This is due to the fact that the resin was continuously curing in the DMA when the temperature is increased. It was challenging to find whether the resin has been completely cured or not in the system. It is possible that the experimental value of glass transition temperature for 100% gallic acid substituted phenol is not accurate due to the nature of the samples that is unique, and it looks like the data was ‘chasing the Tg’ as the temperature increased and residual cure occurred. Or it could possibly be due to limited research facilities that cannot produce decent samples at the time of investigation.

5.5 Summary

In conclusion, GIM can be assumed as a reliable technique to predict of the thermal properties of polymer materials that can reduce the need for the time-consuming experiments. GIM can be used in either two ways; 1) model the system and validate the data through experimental work or 2) construct the modelling based on the experimental results in order to correlate between them. Both ways are valid and acceptable as it works together to achieve the comparable prediction and actual value.

In this study, the predicted glass transition temperature for phenolic resin compares very well with the experiment, assuming that full crosslinking has occurred in the reaction. For gallic acid resin, a range of glass transition temperature is produced dependent on the degree of freedom of the final product. The lower the degree of freedom, the higher the glass transition temperature. In order to know the exact proportion of what is present in the gallic acid resin, a separate study of the resin chemistry and the use of high technology equipment, for instance nuclear magnetic resonance spectroscopy (NMR) would be a tool to determine the structure of the organic molecules.

6.0 COMPOSITE MANUFACTURING

6.1 Introduction

In composite industries, natural fibres including nettle fibre are used as an option to produce green composite, as a replacement for the synthetic fibre (such as carbon fibre, glass fibre and aramid fibre). This study was focused on nettles, where the stalk (bast) fibre was used to provide the reinforcement, and the leaves were used to extract tannin materials, which is gallic acid. Then, the properties of the composite were investigated in terms of mechanical properties and morphological study.

6.2 Synthesis and Processing

Following the successful production of 1.0P and 0.25GA resins, composites reinforced with randomly oriented nettle fibres were produced. The nettle fibre content varied from 5, 10, 15 and 20 wt%. Synthesis of the composite was carried out by adding the resin to nettle fibres at the different content levels. Then, a weight is applied over the composite for 5 minutes to smooth the surface (see Figure 6.1). The composites were cured in the autoclave with cure schedule similar to resin production, which is 40 ℃ (720 min) - 50 ℃ (999 min) - 60 ℃ (999 min) - 70 ℃ (999 min) - 80 ℃ (999 min) - 90 ℃ (999 min) - 100 ℃ (600 min) - 130 ℃ (60 min), with continuous pressure of 7 bar.

For clarification, only 1.0P and 0.25GA composites with random orientation fibre were manufactured. This is because of the late discovery that 0.31GA resin worked well with the current cure schedule. Due to time constraint and equipment failure, the production of 0.31GA was not completed. The properties of the 0.31GA composites would be expected to be similar to 0.25GA composites, as there is little difference in terms of concentration and viscosity of the resin, and the mechanical properties of the two resins are very similar.

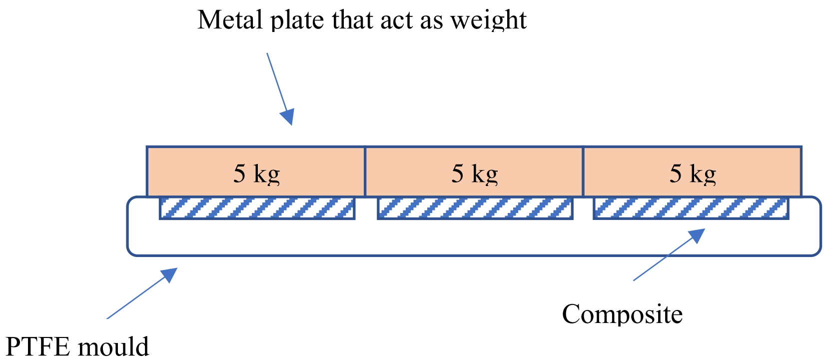


Figure 6.1 Diagram of composite preparation

6.3 Characterisation

The properties of the composites were studied using flexural testing and SEM results. Further details on the equipment used and samples measurement was explained in **Chapter 3: Experimental Materials and Characterisation.**

6.4 Results and Discussion

6.4.1 Flexural properties

The flexural properties of resin and composite are shown in Figure 6.1 and 6.2. Substitution of phenol with 25% of gallic acid shows that both flexural modulus and flexural strength of the resin without reinforcement increased (see Figure 6.2 and 6.3). This shows that gallic acid can be potential substitution for phenol in producing the composite.

The effect of fibres on the flexural modulus of the composite is shown in Figure 6.2. It can be seen that increasing nettle content has increased the flexural modulus of 1.0P and 0.25GA composite. Figure 6.2 shows the flexural modulus of 1.0P increased from 3.4 GPa to 3.6 GPa, 3.8 GPa, and 4.1 GPa at a composition of 0, 5, 10, and 15 wt% of nettles, respectively. A similar trend can be observed too for 0.25GA which increased from 3.8 GPa to 4.2 GPa, 4.3 GPa and 4.6 GPa when nettle fibre content increased up to 15 wt%. This is expected since stiffer material is introduced into the polymer matrix. This shows the material stiffness is improved when reinforcement is added, even at the low end of the fibre addition. However, after a certain content of fibre, which in this study is 20wt% of nettle, the flexural modulus started to drop slightly. This might be the point where it reached above the possible volume fraction, where the properties decrease due to insufficient resin to fully coat the fibres. These results match those observed in earlier studies [265]. Another possible reason is improper impregnation leading to dry areas. Despite the drop, nettle fibre is still considered to be a good choice as a reinforcing agent in polymer composite.

Figure 6.3 shows the influence of fibre on flexural strength. As shown in the figure, the flexural strength of 1.0P composite and 0.25GA dropped significantly once the fibres were introduced, and continued to drop progressively as the fibre content is increased from 5 to 20 wt% of nettle content in the composite. It drops from 90 MPa to 78 MPa, 70 MPa, 68 MPa and 60 MPa for 1.0P, respectively. A similar trend can also be seen for 0.25GA that drops from 94 MPa to 82 MPa, 76 MPa, 72 MPa and 65 MPa when nettle content is increased. This decrement is due to the incapability of the fibre, as it is unevenly shaped, to support stress transfer from the polymer matrix. These results agree with those obtained by Ismail et al. [266] and Yang et al. [267] that suggest a drop in flexural strength might be due to poor interfacial bonding, which produces partially spaces between fibre and polymer matrix, and as a result causes weak structure.

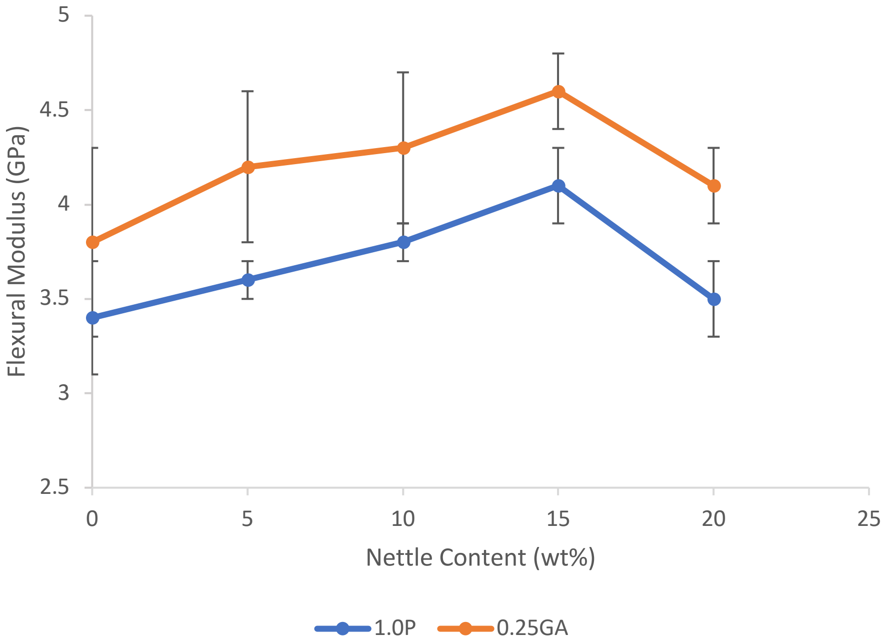


Figure 6.2 Flexural modulus of resin and composite. Notice that the lower value of flexural modulus is omitted in order to improve the readability of the plot. The error bars represent ±1SD (samples tested for every set of error bars n=7)

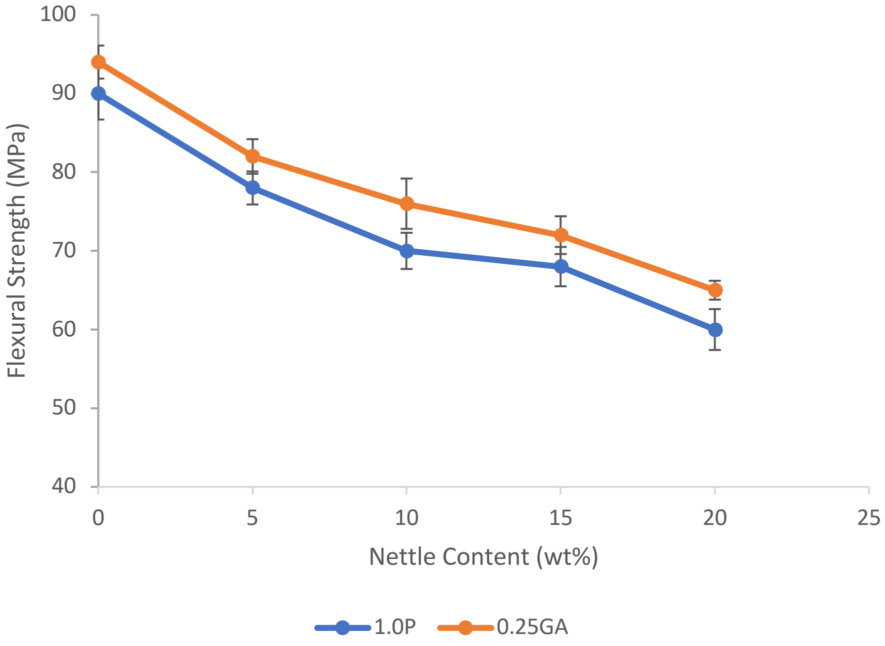


Figure 6.3 Flexural strength of resin and composite. Notice that the lower value of flexural strength is omitted in order to improve the readability of the plot. The error bars represent ±1SD (samples tested for every set of error bars n=7)

6.4.2 Prediction of Flexural Properties

For determination of estimated properties of random short fibre composites, a few models have been previously used, such as Christensen [268], Halpin-Tsai [269], and Puck and Schuermann [270].

1. Christensen Model:

$$Ec = \frac{vfEf}{3} + \frac{(1-vf)Em}{0.3} + \frac{19}{27}Em[\frac{Ef(1+vf)+Em(1-vf)}{Ef(1-vf)+Em(1+vf)}]$$

2. Halpin-Tsai Model:

$$n = \frac{3}{8}E1 + \frac{5}{8}E2$$

where,

$$E1 = Em\left(\frac{1 + \varepsilon\eta1vf}{1 - \eta1vf}\right)$$

$$E2 = Em(\frac{1 + \varepsilon\eta2vf}{1 - \eta2vf})$$

$$\eta1 = \frac{\left(\frac{Ef}{Em}\right) - 1}{\left(\frac{Ef}{Em}\right) + 2(\frac{l}{d})}$$

$$\eta2 = \frac{\left(\frac{Ef}{Em}\right) - 1}{\left(\frac{Ef}{Em}\right) + 2}$$

3. Puck and Schuermann Model;

$$Ec = vf\left[\frac{16}{45}Ef + 2Em\right) + \frac{8}{9}Em$$

Previous investigation [28] shows that the predictions of Christensen, Halpin-Tsai and Puck and Schuermann are relatively higher than experimental values. This over estimation has also been reported in several study [271], [272]. Thus, in the current study, a proposed model by Epaarachchi et al. [28] has been used to predict the properties of 1.0P and 0.25GA composites. Properties of random short fibre composites can be assumed as quasi-isotropic. As a result, the effect of aspect ratio on randomly oriented short fibre matrix can be neglected. Thus, the following formulation for randomly oriented composites, which was derived from rule of mixture is shown below;

$$Ec = (vf\left(\frac{Em}{Ef}\right))^2 Ef + \left[1 - \left(vf\left(\frac{Em}{Ef}\right)\right)^2\right] Em$$

Figure 6.4 and Figure 6.5 show the comparison of experimental and predicted value for 1.0P and 0.25GA using the proposed model above. It displays a good relationship of the suggested model with experimental result. This result also suggested that there is good adhesion between fibre-matrix in 1.0P and 0.25GA composites. However, the proposed model suggested that both modulus of 1.0P and 0.25GA have a trend of increase with increasing volume fraction. This is contradicted in the current study, as the properties of the composite start to deteriorate when the nettle content is at 20 wt%. This is probably due to the uneven application of resin and fibre, leading to non-uniform dry and wet areas of the composite.

The fibre volume fraction of the composites was determined using formulae from NetComposites [273], stated below.

$$FVF = \frac{1}{\left[1 + \frac{\rho_f}{\rho_m}\left(\frac{1}{FWF} - 1\right)\right]}$$

where;

FVF = fibre volume fraction

FWF = fibre weight fraction

ρ_c = density of composite (g/cm^3)

ρ_m = density of cured resin/matrix (g/cm^3)

ρ_f = density of fibres (g/cm^3)

The density of the fibres and matrix was obtained from the Equation (1) in Chapter 3, Section 3.5 using Mettler-Toledo MS-DNY-43 Density Kit.

The summary of the values are:

$\rho_{1.0P} = 1.35$

$\rho_{0.25GA} = 1.13$

$\rho_f = 1.51$[274]

E_m for 1.0P = 3.4 GPa,

E_m for 0.25GA = 3.8 GPa, and

E_f = 87 GPa [28]

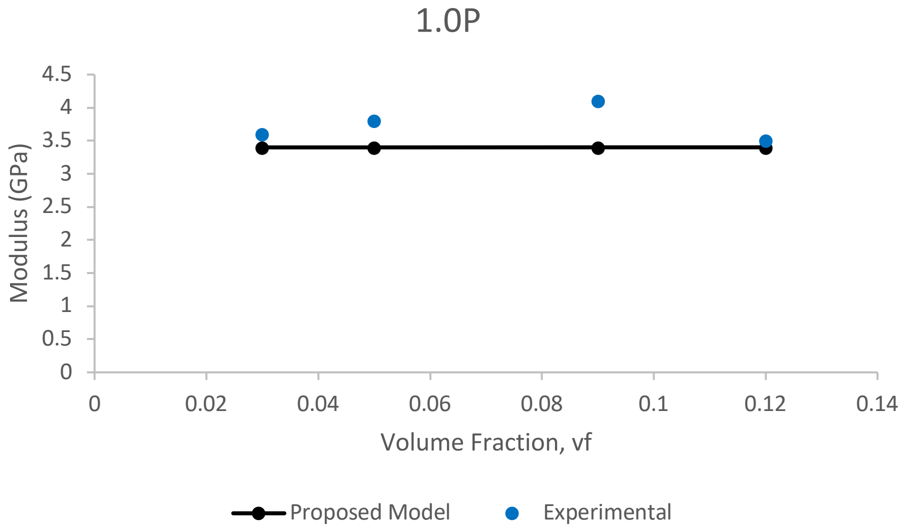


Figure 6.4 Modulus of 1.0P composite (proposed model and experimental)

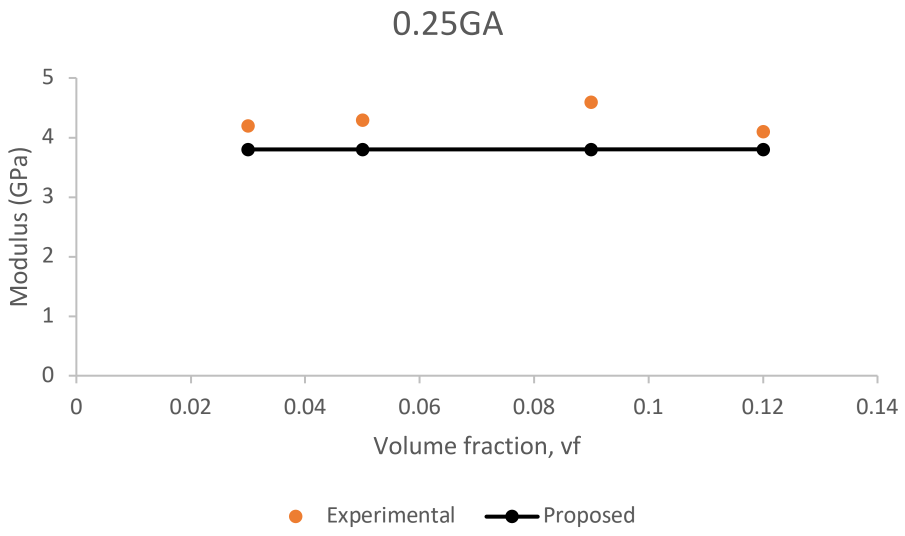


Figure 6.5 Modulus of 0.25GA (proposed model and experimental)

6.4.3 Morphological Study

Scanning electron microscopy (SEM) was used to analyse the micrographs of flexural fracture surfaces of 1.0P and 0.25GA of composites. The influence of the fibre in the composite was analysed too. From Figure 6.6 (a)-(c), we can see good interaction between fibre-matrix due to hydrophilic nature of cellulose and phenolic resin. There are no bubbles and voids indicating that the cure schedule is sufficient in removing the water in the composite system. In Figure 6.6 (d), the fracture surface reveals both distributed nettle fibre particles and holes where fibres have pulled out of the resin. The holes showed that there is a poor interface between the resin and fibres, hence lower mechanical properties of the composites were obtained. This observation at 20wt% fibre loading indicates a possible reason why the modulus and strength drop at that level, as the poor interface will limit stress transfer.

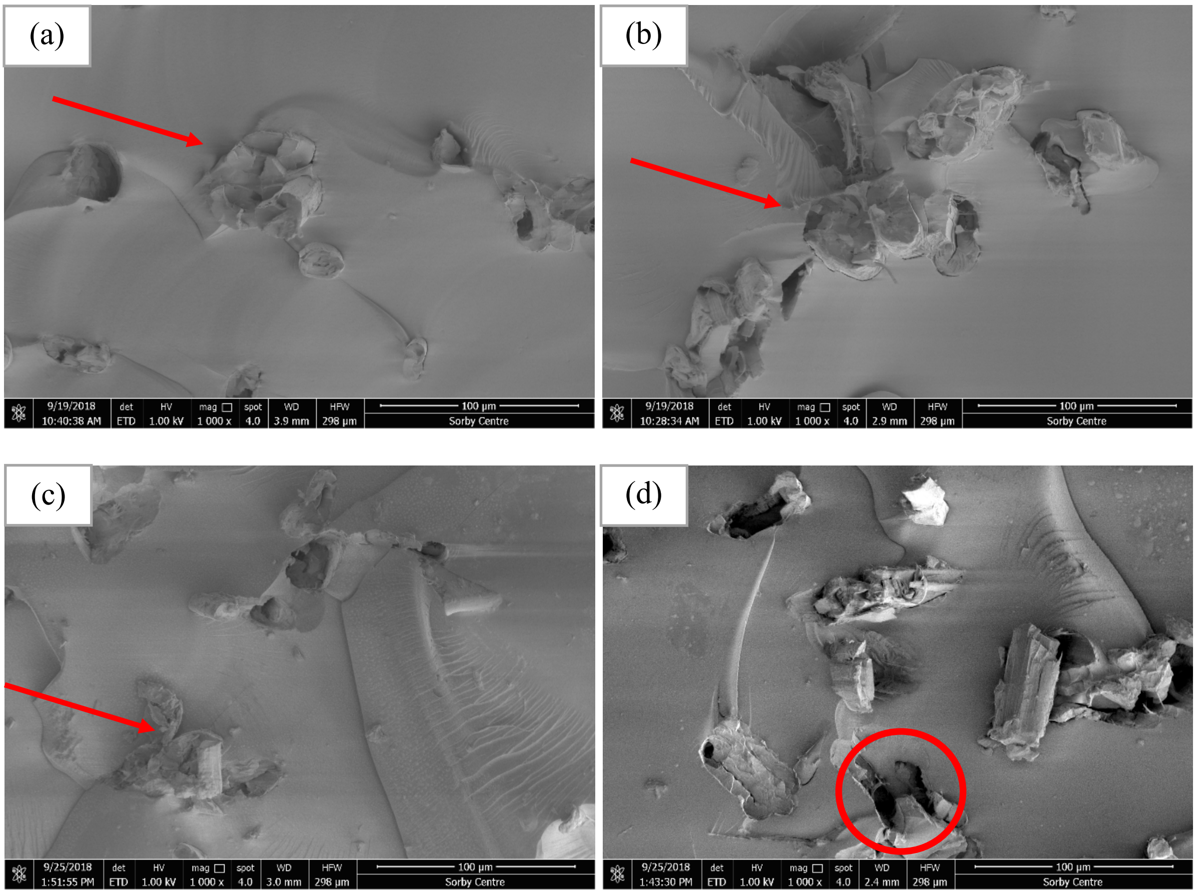


Figure 6.6 SEM micrographs of 1.0P composite at (a) 5 wt%, (b) 10 wt%, (c) 15 wt% and (d) 20 wt % of nettle. Arrow shows fibre pull out while circle indicating hole due to fibre pull out.

Figure 6.7 shows the images of flexural fracture surface of 0.25GA composites. Similar images of 0.25GA with 1.0P composites can be observed which has no noticeable voids present, indicating that the cure cycle is suitable in producing the composites. Fibre pull-out in the 20 wt% loading again shows a weak interface in the system and again accounts for the observed results. Reinforcement of polymer matrix in composites with higher content of fibre resulted in lower flexural modulus probably due to flaws present such as fibre bending, microcracks, points of tension and voids, thus leads to higher dissipation energy through friction [275].

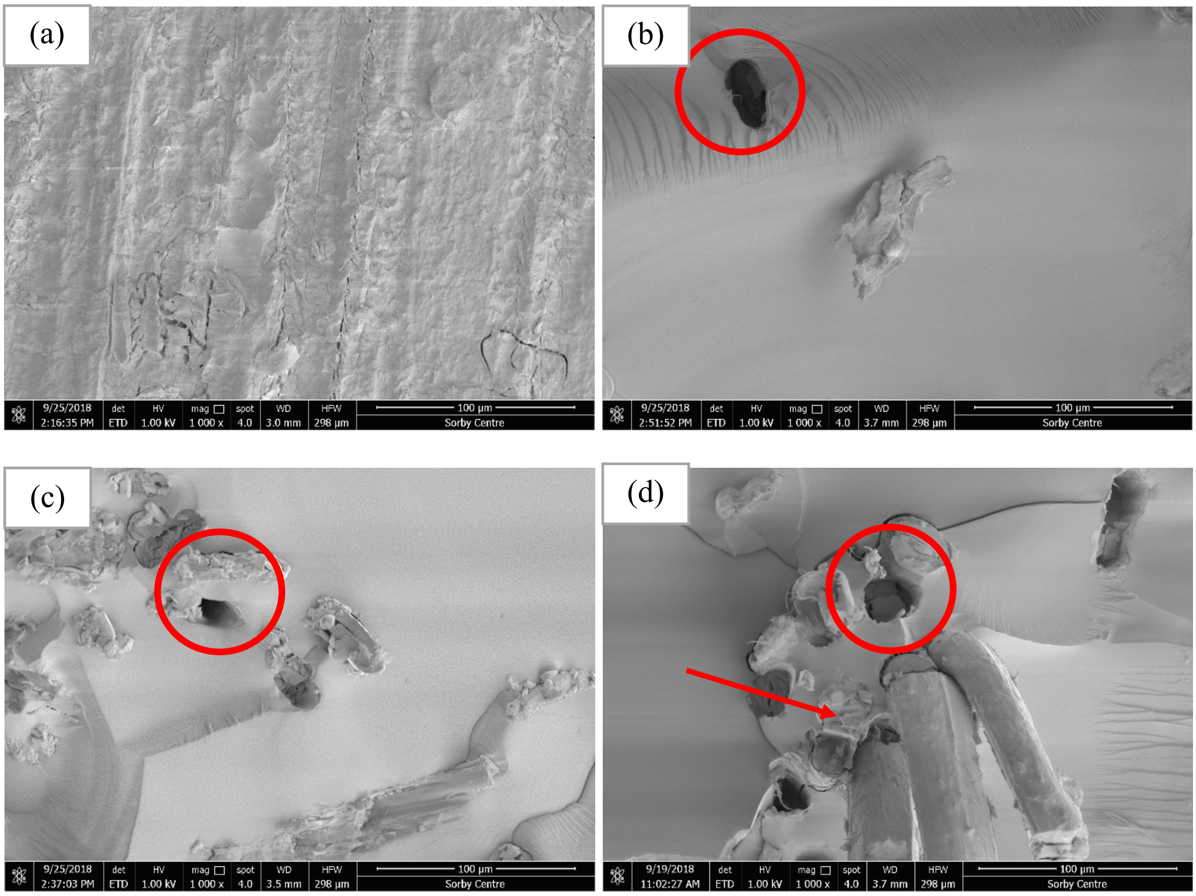


Figure 6.7 SEM micrographs of 0.25GA composite at (a) 5 wt%, (b) 10 wt%, (c) 15 wt% and (d) 20 wt % of nettle. Arrow shows fibre pull out while circle indicating hole due to fibre pull out.

Components that are rich in hydroxyl group such as hemicellulose, pectins, lignin and cellulose are commonly found in natural fibres. They are strongly polar and hydrophilic materials while the polymer is generally hydrophobic. Due to that fact, there are substantial problems of compatibility between fibre and matrix. In order to improve the poor interfacial adhesion of the natural fibre and matrix, surface modification of natural fibre is highly recommended to improve the compatibility and interfacial bond strength [276]. Bleaching and acetylation as examples of chemical treatment, and alkali treatment such as mercerisation, are found to be effective in improving the matrix-fibre adhesion. These processes increase the roughness of the fibre by eliminating the impurities from the fibre surface and disrupting the moisture absorption process [147].

Other than that, plasma treatment on the fibre might be a way to improve the mechanical properties and interface between fibre and matrix. It uses oxygen, commonly, and other gases such as carbon dioxide, carbon monoxide, nitrogen dioxide, and nitric oxide to introduce moieties on the fibre surface to make the fibre surface hydrophobic [168]. There is work ongoing within department in investigating the plasma treated in natural fibre, and it is expected to give better morphological properties of composites [277].

6.5 Summary

These findings suggest that in general, the introduction of nettle fibres resulted in a significant improvement in the flexural modulus compared with the unreinforced resin, proving that the fibres really act as reinforcement in the composites. However, it was found that the strength of the composites decreased as fibre wt% increased. It was found that the 0.25GA resin was consistently better than the 1.0P resin.

Although the study has successfully demonstrated that reinforcing the resin with nettle fibres enhanced the mechanical properties, it has certain limitations in terms of fibre content. In this study, a 20 wt% of nettle fibres resulted in a decrease of mechanical properties for both 1.0P and 0.25GA composites. This is mainly due to difficulty of impregnating a large amount of fibres, leading to dry areas. Secondly, the flexural strength decreases with increasing content of nettle fibres due to higher fibre-to-fibre contact resulted in poor interfacial bonding between the fibre and matrix [278]. More research is required to determine the efficacy of nettle fibres at certain content to show why the interface properties are poor in this loading, while they are acceptable in the case of the other composites.

7.0 CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

The present study was designed to determine the effect of gallic acid when being used as a substitute to phenol in synthesising phenolic resin. The conventional phenolic resin was derived from phenol-formaldehyde and in this case, phenol was substituted with a certain amount of gallic acid and it proved to be successful. Developing a suitable cure cycle was time consuming but in the end it was successful. The suitable cure cycle was tailored to the equipment available in the lab, with a limitation on the available pressure limiting the ability to keep water in solution within the resin. The results of this investigations show that up to 31 wt% gallic acid can be used to substitute phenol in producing a good resin, while more than that led to a brittle resin that was unsuitable for further testing. Good resin in this context means that substitution of phenol with gallic acid improved the mechanical properties of the composite. Moreover, gallic acid can be easily obtained from natural resources such as nettle, gallnuts and tea leaves.

From DSC results, it was shown that there is no residual exotherm below 150 ℃ which indicates that the resin is suitable for use in natural fibre composites. It was not, however, possible to get a degree of cure calculation due to the resins evolving large amounts of water preventing testing on curing in the DSC.

Tg from DMA suggests that substitution of phenol with gallic acid in production of resole resin has increased the glass transition temperature. This is possibly due to increasing crosslink density increasing the number of binding chains and thus increasing stiffness of the resins. However, the results are not in agreement with TGA results which show that the thermal stability of GA resins were lower than 1.0P. There may be impurities such as residual monomer, metal ions, polymerisation solvent or oligomers, catalyst residues or other molecular weight material. There may also be more macroscopic impurities, for instance, specks of degraded polymer or monomer, crosslinked gel particles, or even particles of metals from processing equipment leading to this unexpected result.

The FTIR spectrum of 1.0P was compared with literature values of bands and it was found to be matched completely. The important bands from FTIR spectra show the absorbance peaks that are present in 1.0P, 0.25GA and 0.31 GA with important bands to indicate the formation of resole resin, which are 1600, 1473 and 1144 cm^{-1}, C=C aromatic ring, C-H methylene bridge and C-O-C methylene-ether bridge.

In this study, GIM was also used to predict the properties of the resin, for instance glass transition temperature (Tg). The result of this modelling indicates that GIM is a reliable method to predict properties of the polymers, provided that one knows the resin chemistry. The results of this modelling showed that Tg for phenolic resin compares very well with the experimental work. For gallic acid resin, the structure of the resin was not known, so the accuracy of the predictions would not be as high. The author has proposed possible structures of gallic acid resin that may be present in the cured samples. Then by varying the degrees of freedom for gallic acid resin, the predicted results were found to be comparable to experimental results. The lower the degree of freedom, the higher the crosslink density, and the higher the glass transition temperature. As no other research has been carried out to support the Tg of gallic acid resin, this study has been unable to demonstrate the true value of the glass transition of gallic acid resin experimentally. However, the indications suggest that it is above 300 °C. In the current study, there is no prediction for glass transition temperature for gallic acid-phenolic resin as the resin chemistry is too complex to predict with GIM at present.

The second major finding was that, nettle fibre was found to be a good reinforcing agent to phenolic and gallic acid resin. It shows that up to certain amount of nettle fibres, which is in this study 15 wt% of nettle fibres, the mechanical properties of the resin improved substantially. The results demonstrate that incorporation of nettle fibres has improved the stiffness of the 1.0P and 0.25GA respectively. The flexural modulus was optimum at 15 wt% of nettle content. However, increasing nettle content to 20 wt% resulted in decreasing flexural modulus. Not only that, the flexural strength of both 1.0P and 0.25GA composites appeared to decrease although the flexural strength increased when compared to pure resin. This is probably due to poor impregnation of resin leading to dry areas, caused by too high a level of fibre-to-fibre contact.

Based on SEM analysis, the flexural fracture surfaces for 1.0P, 0.25GA and 0.31GA displays no bubbles and voids present in the resin. It shows that the cure cycle proved to be successful in producing bubble-free specimens. However, in composite systems, we can see particles and holes where fibres have pulled out upon fracture are clearly visible in the SEM images, which indicates poor interaction between fibre-matrix. Plasma treatment could be one of the alternatives to improve the properties of the composites.

7.2 Future Work

While it can be concluded wholly that gallic acid can be a potential substitution for phenol in manufacturing the phenol-formaldehyde resin, more work needs to be done to establish a solid case study. In this world, the objective of making greener composite is not too make it worse, which in this study, it can be said most of the properties improved when gallic acid is used. This research has thrown up many questions in need of further investigation.

- It would be interesting to assess the effect of higher pressure in curing the resins in the autoclave, probably with shorter curing time. Often, low pressure causes the bubbles of volatiles to expand and the resin, not removed from it. Void content may be reduced by increasing the autoclave pressure to counteract the vapour pressure of the volatiles, thus producing a material with better mechanical properties and fewer voids.

- Further study, especially in resin chemistry knowledge, is needed in modelling the gallic acid resin in GIM. There is so much to explore in GIM which has been previously proved successful in linear and cross-linked polymers. Its application in multifunctional-branched polymers is limited, due to its level of complexity. Thus, a series of models need to be made to predict the properties of crosslink phenolic and GA substituted resins. A detailed study about GIM would be an interesting topic to discover and to extend the earlier versions of the model.

- For better composite properties, one should consider treatment to the fibre using such techniques as plasma treatment, mercerisation, acetylation, etherification, peroxide treatment or benzoylation to improve the compatibility between fibre and matrix. Pre-treatments of the natural fibres can modify the surface chemically, clean the fibre surface from impurities, stop the moisture absorption (hydrophilic to hydrophobic) and increase the surface roughness.

- Further experimental investigations are needed to analyse the phenolic compounds in nettle. Using further HPLC studies, it would be fascinating to know which phenolic compounds are present in nettle fibres that are possibly suitable as a substitution to phenol. This would allow the actual hydrolysable tannins in the material to be employed rather than the gallic acid analogue used in the present study.

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APPENDIX

A.0 GALLIC ACID EXTRACTION FROM NETTLE

A.1 Introduction

Stinging nettle (*Urtica dioica*) is native to Europe, Asia, North America and North Africa. In order to extract the active compounds existing in nettle such as vitamins (C,B and K series), fatty acids, terpenoids, carotenes, dietary fibres, polyphenolic compounds, etc, various techniques were developed. Zekovic et al. [279] extracted the active compounds from nettle by using three methods, for instance, ultrasound-assisted extraction (UAE), microwave-assisted extraction (MAE) and subcritical water extraction (SWE). UAE uses water as solvent and sonicated for 30 minutes at ultrasonic power of 156 W. MAE was done in domestic microwave oven which has been modified and extraction takes place for 30 minutes at the power of 450 W. SWE mixes the nettle leaves with water in nitrogen pressurised vessel, which prevent oxidation. Then heating was performed at 125 °C, pressure 35 bar and 30 minutes of extraction time. Sample to solvent ratio is always 1:30. All the prepared extracts were filtered straightaway through a filter paper under vacuum and stored at 4 °C.

Another method was proposed by Ishak et al. [224], a portion of nettle was extracted with different kinds of solvents such as water, methanol and acetone. The samples were shaken at room temperatures for 8 hours and filtered before being concentrated under vacuum. In this work, they concluded that acetone is the most efficient solvent in extracting nettle chemicals.

Other researcher [280] ran the extraction at room temperature with constant shaking for 48 hours, using methanol as the solvent.

Durovic et al. [281] used Soxhlet extraction and UAE in order to obtain samples for further analysis. They used ethanol as solvent and stored the samples in refrigerator at 4 ℃ to avoid possible degradation until further analysis.

A.2 Extraction Method

In this study, Soxhlet extraction was used to extract chemicals from the nettle stalks and leaves. It was anticipated that this would contain gallic acid that could then be used to modify the resin [230]. The leaves and stalks of the nettle were dried and crushed before placing the resultant solid material inside the extraction thimble. The diagram of the extraction is shown in Figure A.1. The extraction solvent, which in this case was acetone, is placed in a distillation flask. The flask containing acetone is heated at 80 ℃, to reflux. The process starts by vapour travelling up the distillation arm and overflowing into the chamber containing the thimble. This process ensures that all the vapours from solvent are cooled and go down back to the chamber where all the solid material is. Then, the chamber that contains nettle stalks or leaves fills slowly with warm solvent. This will cause some of the desired compound to dissolve. The chamber, once full of solvent, is then automatically emptied by a siphon side arm, with the acetone returning to the distillation flask. The process was left in the laboratory, running continuously for 2 days. In each cycle, all the non-volatile soluble compounds in the nettle was extracted into the solvent. The concentrated solution of the desired compound was collected in the flask after a few cycles. This system is beneficial to the ecosystem as it prevents wastage of solvent, as only one batch of solvent is used instead of many portions in other methods.

A rotary evaporator is used after that to remove the acetone meaning that, solely the extracted compound is left in the flask.

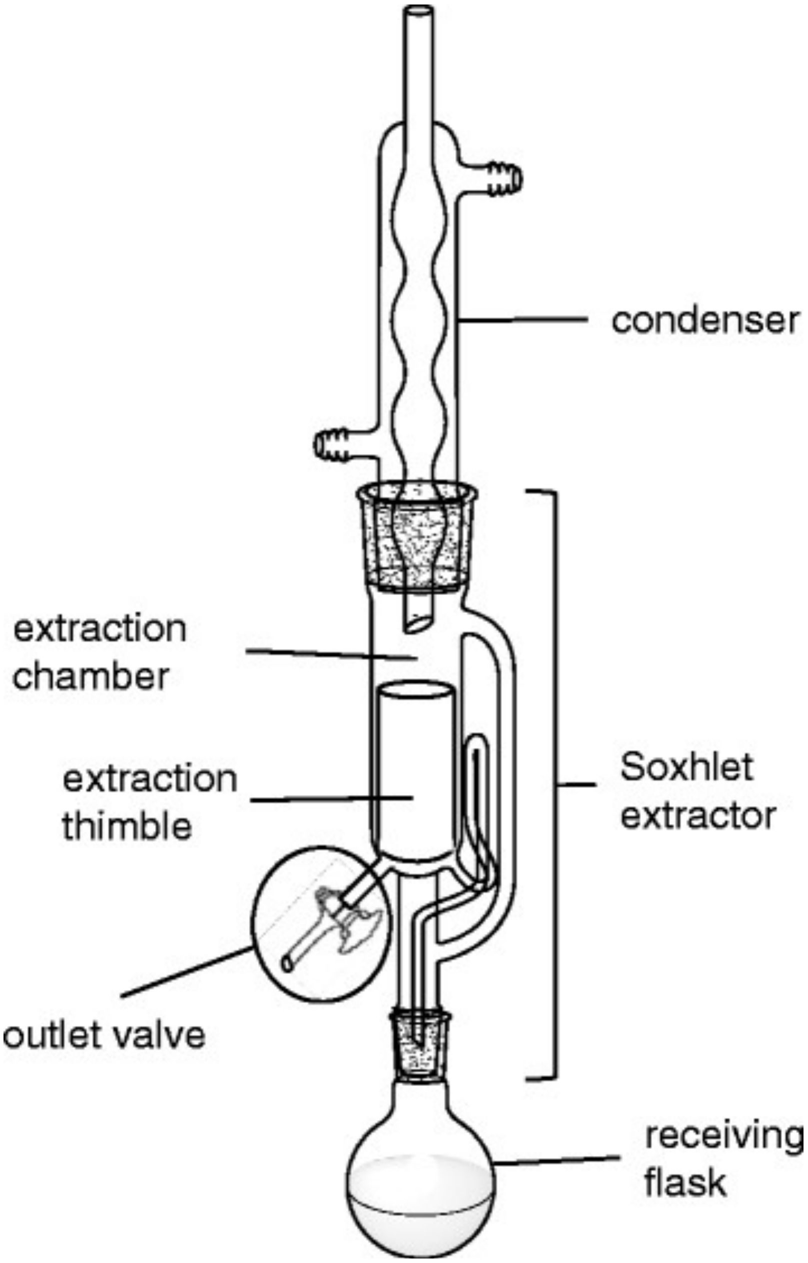

Figure A.1 Soxhlet extraction diagram. Reprinted from Practical remediation of the PCB contaminated soil by Ido *et al.,* 2015; DOI: https://doi.org/10.1186/s40201-015-0158-2; Journal of Environmental Health and Engineering [282]

A.3 Determination of Gallic Acid Content in Concentrated Nettle Stalks and Leaves

The gallic acid content of both nettle samples were analysed. Gallic acid standard was used for identification of purposes in nettle samples in this study. Samples in the tested extracts were analysed with this standard by HPLC by comparing the retention times and absorption spectra of unknown peaks with the reference standard. The parameter for HPLC analysis is listed in **Chapter 3 Experimental Materials and Characterisation**. Analysis of HPLC revealed that there was no detectable gallic acid in either nettle samples (stalks and leaves), possibly due to samples not being concentrated enough even the samples have been left for extraction for 2 days. Figure A.2 shows peak of standard gallic acid with retention time around 8.2 minutes.

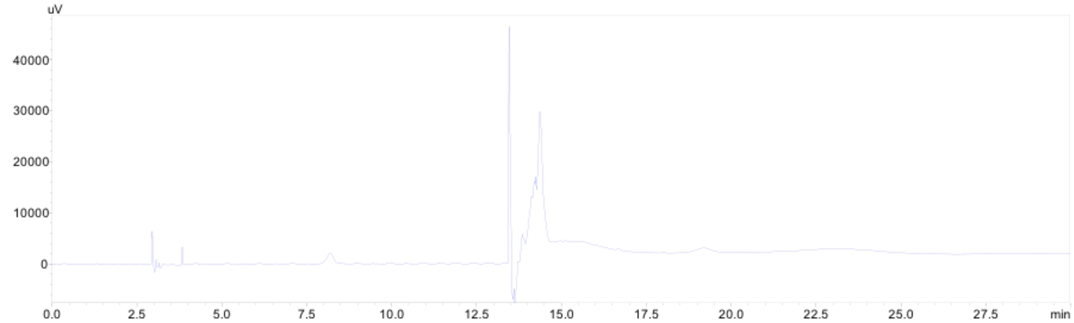

Figure A.2 HPLC of standard gallic acid peak

In Figure A.3 and A.4, it can be seen that there is no gallic acid peak detected in either nettle samples (leaves and stalks) at around 8.2 minutes, but there are unknown peaks for which no standards have been tested to compare the peak with. The composition or the extract is therefore unknown at this stage.

In an analysis of nettle samples, Otles and Yalcin [14] used series of components as standards in HPLC such as caffeic acid, vanilic acid, naringin, syringic acid, ferulic acid, myricetin, kaempferol, isorhamnetin, chlorogenic acid, catechin, rutin, fumaric acid, coumaric acid and gallic acid. The analysis of phenolic component of nettles are summarised in **Chapter 2**. Due to time constraint, it was not possible to conduct any further tests, and hence this can be a recommendation for future works.

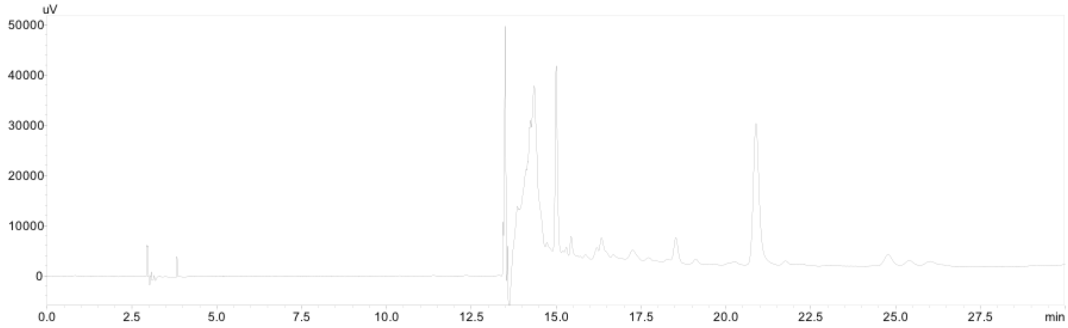

Figure A.3 HPLC of nettle leaves

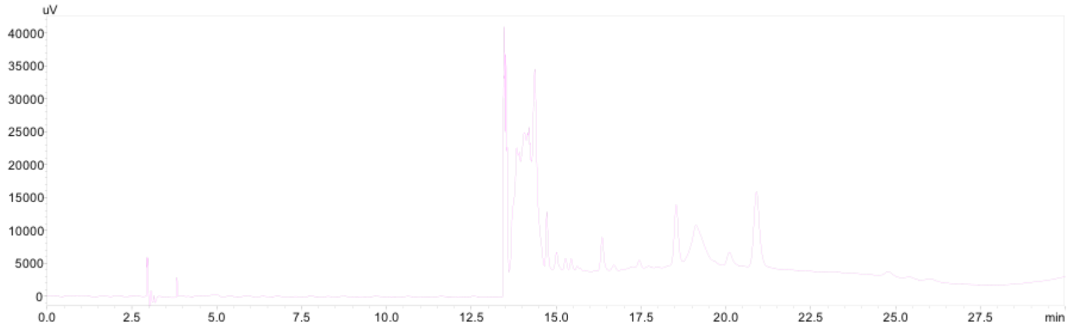

Figure A.4 HPLC of nettle stalks

It was thought from the literature that there would be gallic acid present, or at least there would be any other phenolic content. According to research [230], nettle samples from Greece were found to have syringic acid, gallic acid and ferulic acid. When nettle samples from the study region, Sheffield, were tested, there was no gallic acid found. This could be because of many reasons, such as the specimen was not concentrated enough to prove the gallic acid was there, possibly the nettles that were harvested in September were picked at the wrong time of the year. Other than that, possible degradation happened during the transportation of the samples to testing facility (as it needs to be kept in low temperature) or it is simply because there was no gallic acid present in the nettle samples from this region. A number of authors [14], [229] have reported analysis of nettle samples in their region such as Tuscany and Turkey, and have found that there were no gallic acid, syringic acid, fumaric acid, vanilic acid, or catechin (to name a few) in their nettle samples, which is similar to the findings of the current study.

In view of all that has been mentioned so far, one may suppose that the presence of gallic acid in nettle samples could be dependent on where the nettle is harvested, which part of nettles were picked (i.e leaves, root or stalk), which season is suitable to harvest nettle, the extraction method, or the specific conditions on how to store the nettles to preserve the freshness of the samples. This investigation has shown that there are unknown peaks detected in stinging nettle, hence several courses of actions could be done to determine the peaks. A series of standards, for instance, caffeic acid, vanilic acid, ellagic acid, ferulic acid and syringic acid and etc, should be used in order to compare with the unknown peaks. However, only one standard was used in this testing, which is gallic acid, which proved it is not sufficient in determining other peaks that present both in nettle stalks and leaves.

A.4 Implications for the substitution of phenol in bio-resins

As gallic acid is proven to be a potential substitution for phenol in phenol-formaldehyde resin, improving the mechanical properties that have been discussed in the current study, one should consider extracting gallic acid from nature. Some of the natural products that are rich in gallic acid are, gallnuts, witch hazel, tea leaves, apple peels, bananas, strawberries, pineapples, lemons, red and white wines [283], [284]. These products could be easily obtained, and they are low cost, which is one of the advantages of using gallic acid.

In a study which set out to determine the total phenolics in nettle, Pinelli et al. [229], found three classes of phenolics in the nettle samples; hydroxycinnamic acid derivatives (main compounds being chlorogenic acid and 2-*O*-caffeoyl-malic acid) (Figure 8.5); flavonoids (rutin, quercetin *p*-coumaryl-glucoside, kaempferol 3-*O*-glucoside, kaempferol 3-*O*-rutinoside, isorhamnetin 3-*O*-rutinoside) (Figure 8.6); and anthocyanins (peonidin 3-*O*-rutinoside, rosinidin 3-*O*-rutinoside, peonidin 3-*O*-(6'-*O*-*p*-coumaroylglucoside)) (Figure 8.7). In addition, classification of *Urtica dioica* discovered the existence of both condensed and hydrolysable tannins in the samples. This shows that there is a possibility of any of these derivatives to become a precursor for substituting phenol in future due to reactive sites of OH. However, this needs an in-depth investigation due to the complex structure of the phenolic compounds, as can be seen in Figure A.5-A.7.

In Figure A.5, it can be seen that the hydroxycinnamic acid derivatives have similarities in having many OH groups. For instance, p-coumaric acid was found to be one of the monomers that is present in lignin. Lignin has been investigated as a promising substitute for phenol in phenol-formaldehyde resin [285]–[289]. However, due to its chemical structure, it has lower reactivity than phenol. In order to improve the reactivity, several modifications can be done for example methylolation and phenolation [289]. Methylolation introduced hydroxymethyl ($-CH_2OH$) to lignin molecules in alkaline medium to modify the chemical structure of lignin therefore increase the potential reactive sites toward formaldehyde. It was found from the investigations that the modified-lignin could partially replace phenol in phenol-formaldehyde resin synthesis.

Anthocyanins are a type of flavonoid, thus it can be observed that Figure A.6 and A.7 has quite similar structure. Flavonoids are a type of condensed tannins. Condensed tannins have been found to be more reactive than hydrolysable tannins based on the study by Li et al. [290]. It was found from the FTIR results on larch tannin, the condensed tannins possess higher reactivity towards formaldehyde than valonia tannin, a hydrolysable tannin. Regardless of the finding, both larch tannin and valonia tannin can react with formaldehyde as a substitute for phenol.

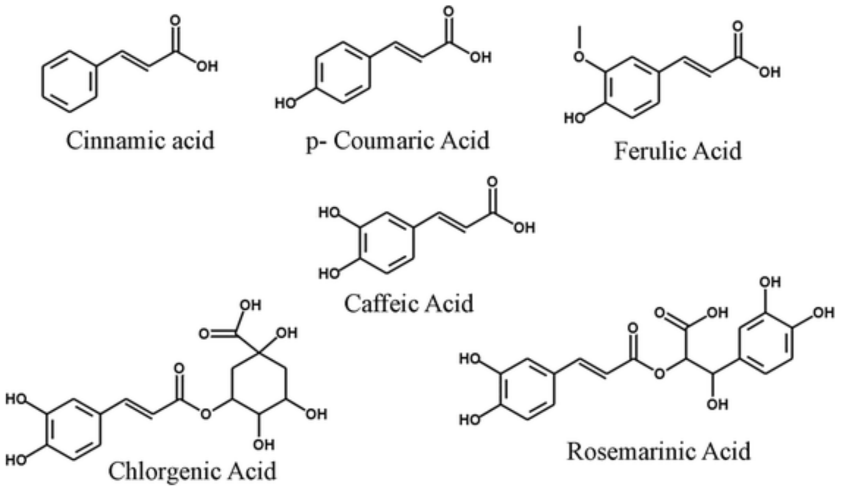

Figure A.5 Hydroxycinnamic Acid Derivatives [291]

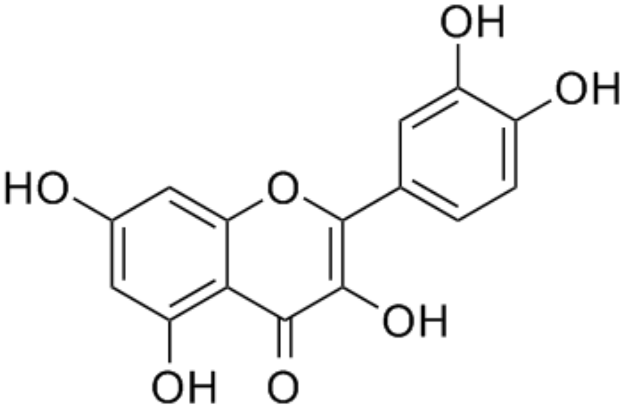

Figure A.6 Basic structure of flavonoids [292]

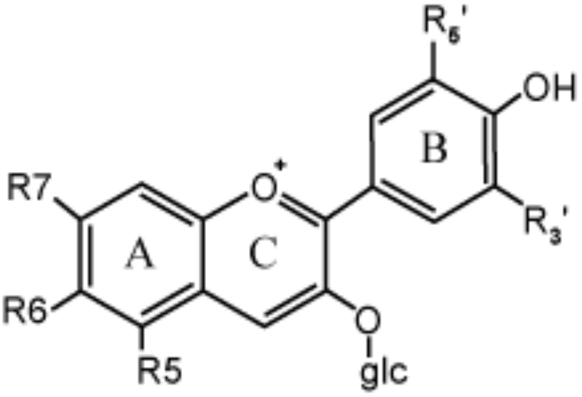

Figure A.7 General structure of flavonoids

A.5 Summary

From this chapter, the extraction of gallic acid from nettle was done by Soxhlet extraction. It was then analysed by HPLC, which found that there was no gallic acid present. This could be for many reasons, for example, possible degradation happening during the transportation of the samples to testing facility (as it needs to be kept in low temperature) or because the samples were not concentrated enough. This could also depend on the origin of nettle as some of the studies found gallic acid in their nettle while some were not.

Overall, further investigations can be taken into account to study the other phenolic compounds that may present in nettle plant that could be a potential substitution for phenol in synthesising the phenol-formaldehyde resin, other than gallic acid.