UNIVERSITI PUTRA MALAYSIA

PHENOL FORMALDEHYDE RESOL RESINS WITH PLANT-BASED TANNIN FOR COMPOSITE LAMINATE APPLICATIONS

NURULDIYANAH BINTI KAMARUDIN

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By

NURULDIYANAH BINTI KAMARUDIN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the degree of Doctor of Philosophy

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DEDICATION

I would like to dedicate my thesis to my great family…

A great feeling of gratitude to my husband… who's always introduce a great support and advices…

For my lovely kids (Iman and Idlan) … whom gave me strength to get the PhD degree…

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Doctor Philosophy

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March 2021

Chair: Dayang Radiah Awang Biak, PhD
Faculty: Engineering

The use of phenol and formaldehyde in preparing resole resins had sparked some environmental concerns. This study investigated the feasibility of substituting or minimising the use of phenols and formaldehyde in the preparation of phenol formaldehyde resins by adding dissolved tannin into the formulations. The objectives of the research include assessing the effects of varying the molar ratio of phenol and formaldehyde in the preparation of phenol formaldehyde resins, evaluating the effects of minimising the use of phenol and formaldehyde and replacing it with dissolved tannin in the resins' formulation, and analysing the curing kinetics of resins and profiling the heat transfer behaviour of the composite laminate using a computational fluid dynamics software. The analyses performed in this research cover the rheological, physical, thermal, chemical and mechanical properties as well as the microscopic imaging of the produced resins and the composite laminates. The phenol formaldehyde (PF) resin shows a shear thickening behaviour at all temperature sets, *i.e.*, 40^{o}C, 60^{o}C, 80^{o}C and 100^{o}C. Water in formalin reduces the flexural and tensile properties of the PF composite laminates by 97.0% and 67.8%, respectively. The dissolved tannin reduces the amount of PF used by 20.0 % and improves the flexural and tensile properties of the PF composite laminates by 26.0% and 8.8%, respectively. Some reduction in the thermal properties of the resins were noted whilst the E_a values for both formulations were similar. Autocatalytic model can be used to represent the curing kinetics when the degree of cure is lower than 0.4 and 0.5 whilst the nth order model can be used to represent the curing kinetics when the degree of cure is higher than or equal to 0.4 and 0.5 for PF and dissolved tannin phenol formaldehyde (DTPF) resin, respectively. During curing the laminate, the heat was dissipated from the edges of the composite to the centre, while, during post curing, the heat was dispersed from the centre to the edges of the composite laminate. This study shows the feasibility of reducing the content of PF in the formulation of PF by adding dissolved tannin to the formulations. It is good to note that with the addition of dissolved tannin, the mechanical integrity of the composite laminate was improved.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
Sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

RESIN RESOL FENOL FORMALDEHID DENGAN TANIN BERASASKAN TUMBUHAN UNTUK APLIKASI LAMINA KOMPOSIT

Oleh

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Penggunaan fenol dan formaldehid dalam penyediaan gam resin resol telah menimbulkan beberapa masalah persekitaran. Kajian ini mengkaji kemungkinan untuk menggantikan atau meminimumkan penggunaan fenol dan formaldehid dalam penyediaan gam resin fenol formaldehid dengan menambahkan tanin terlarut ke dalam formulasi. Objektif penyelidikan termasuk menilai kesan memvariasikan nisbah molar fenol dan formaldehid dalam penyediaan gam resin fenol formaldehid, menilai kesan meminimumkan penggunaan fenol dan formaldehid dan menggantinya dengan tanin terlarut dalam formulasi gam, dan menganalisis kinetik pengeringan gam dan membuat profil tingkah laku pemindahan haba laminasi komposit menggunakan perisian komputasi cecair dinamik. Analisis yang dilakukan dalam penyelidikan ini merangkumi sifat reologi, fizikal, terma, kimia dan mekanikal serta pengimejan mikroskopik dari gam yang dihasilkan dan lamina komposit. Gam resin fenol formaldehid (PF) menunjukkan tingkah laku penebalan ricih pada semua suhu yang ditetapkan, iaitu, 40°C, 60°C, 80°C dan 100°C. Air dalam formalin mengurangkan sifat lenturan dan tegangan laminasi komposit PF masing-masing sebanyak 97.0 % dan 67.8 %. Tanin terlarut mengurangkan jumlah PF yang digunakan sebanyak 20.0 % dan meningkatkan sifat lenturan dan tegangan laminasi komposit PF masing-masing sebanyak 26.0% dan 8.8%. Beberapa pengurangan sifat termal gam diperhatikan sementara nilai E_a untuk kedua-dua formulasi serupa. Model autokatalitik dapat digunakan untuk mewakili kinetik pengeringan ketika tahap pengeringan lebih rendah daripada 0.4 dan 0.5 sementara model urutan ke-n dapat digunakan untuk mewakili kinetik penyembuhan ketika tahap pengeringan lebih tinggi daripada atau sama dengan 0.4 dan 0.5 untuk PF dan tanin fenol formaldehid (DTPF), masing-masing. Semasa pengeringan laminasi, panas dilenyapkan dari tepi komposit ke pusat, sementara, semasa pasca pengeringan, haba tersebar dari pusat ke tepi laminasi komposit. Kajian ini menunjukkan kemungkinan mengurangkan kandungan PF dalam formulasi PF dengan menambahkan tanin terlarut ke dalam formulasi. Adalah baik untuk diperhatikan bahawa dengan penambahan tanin terlarut, integriti mekanikal lamina komposit bertambah baik.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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Declaration by graduate student

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LIST OF ABBREVIATIONS

PF	Phenol Formaldehyde
T	Tannin Powder
DT	Dissolved Tannin
DTPF	Dissolved Tannin Phenol Formaldehyde
DSC	Differential Scanning Calorimetry
DMA	Dynamic Mechanical Analysis
TGA	Thermogravimetric Analysis
SEM	Scanning Electron Microscopy
ATR-FTIR	Attenuated Total Reflection Fourier Transform Infrared Spectroscopy
F	Formaldehyde
ParaF	Paraformaldehyde
P	Phenol
HPL	High Pressure Laminate
η	Viscosity, [cP]
τ	Shear stress, [dynes/cm^2]
G'	Storage modulus, [Pa],
G"	Loss modulus, [Pa],
OFAT	One Factor at A Time
RSM	Response Surface Methodology
k	Thermal conductivity, [W/m.K]
h_c	Convective heat transfer coefficient, [W/m^2.K]
MFK	Model Free Kinetic
ρ_c	Density Composite, (kg/m^3)
ρ_r	Density Resin, (kg/m^3)
v_r	Volume Fraction Resin to Fibre,
C_{p_c}	Specific Heat Composite, (J/kg.K)

C_{p_r}	Specific Heat Resin, (J/kg.K)
x_r	Resin weight fraction
ν_r	Volume fraction of resin
m_i	Initial mass of the samples [g]
m_f	Final mass of the samples [g]
ρ_C	Density of composite [g/cm^3]
ρ_f	Density of fibre [g/cm^3]
ΔH	Total heat flow to the sample [W]
β	Heating rate [°C /min]
H	Enthalpy [W]
T	Temperature at time, t [°C]
Q_{emit}	Emissivity power of a surface [W]
ε	Surface emissivity in the range of $(0 \leq \varepsilon \leq 1)$
σ	Stefan-Boltzmann constant [$5.67\ X\ 10^{-8}\ W/m^2.K^4$]
ϕ	Heat flux [W/ m^2]
Q_y	Heat conduction along y-axis [W]
q_y	Rate of heat transfer [W]
$k(T)$	Rate constant temperature dependent [s^{-1}]
A	Pre-exponential factor [s^{-1}]
E_a	Activation energy [J/mol]
R	Gas constant [8.314 J/mol.K]
ΔE	Change in thermal energy system [J]
E_{in}	Heat transfer from heat source [J]
E_{gen}	Heat generation during temperature rise [J]
$Q_{convection}$	Heat of convection [W]
$Q_{radiation}$	Heat of radiation [W]
Q_y	Heat of conduction along y-axis [W]

CHAPTER 1

INTRODUCTION

1.1 Introduction

Tannin is a naturally occurring polyphenolic compound extracted from the bark of trees and has been used in numerous industrial applications (Samil et al., 2005; Pizzi, 2008; Cardona & Sultan, 2015; Elbadawi et al., 2015; Yazaki, 2015; Pizzi, 2019) including for wood and leather, aerospace industries, electrical industries *etc*. Tannins are used as adhesives, for laminating, insulating or as coating materials (Pizzi, 2008; Tondi et al., 2009; Cardona & Sultan, 2015; Elbadawi et al., 2015; Pizzi et al., 2020; Antov et al., 2021). Tannin-based resin can be toughened using synthetic resin such as phenol formaldehyde (PF) (Vázquez, et al., 2002; Saleh et al. 2021). PF resole resin which is synthesised with a base catalyst is much preferred in practise due to the low cost of curing and it has excellent mechanical properties compared to the other most common resins *e.g.* urea formaldehyde, novolak and epoxy (Siddiqui et al., 2017; Yu et al., 2018). The curing process of the PF resole resin can be initiated by just heating the resole in a mould above its gel point which makes it a low cost resin compared to the other resins which require a curing agent or a hardener to cure (Mashouf et al., 2014; Tcharkhtchi et al., 2015; Siddiqui et al., 2017).

According to Grand View Research (2019) and Xu et al. (2019), the market size of PF in laminate applications for Asia Pacific increased by 17.25 % for 2007 to 2014 and is expected to grow over the forecast period until 2025 with a compound annual growth rate (CAGR) of 4.4 %. Based on a market data review for tannin, the global tannin demand was 1076.3 kilotons in 2015 and is expected to grow at a CAGR of 5.8 % from 2016 to 2025 (Grand View Research, 2019). Tannins used in the industry come from the bark of maritime pine (*Pinus pinaster*), black wattle or black mimosa (*Acacia mearnsii*), and radiata pine (*Pinus radiate*) (Yazaki, 2015; Zhou & Du, 2019). In South-East Asia, logging activities on fast growing trees such as *Acacia mangium* (a species of black wattle), and a large amount of wood waste (mainly consisting of the barks) has been produced (Yamato et al., 2006). Southeast Asia has the highest rate of deforestation which is 1.2 % of forest loss annually in 2010 (Miettinen et al., 2011). Therefore, it shows the resources for tannins come from tree barks that are abundantly available in Southeast Asia.

Tannins have been used in the tanning leather industry for centuries and is still ongoing today (Pizzi, 2019; Alhaji et al., 2020; Singh & Kumar, 2020), followed by wood adhesives (Elbadawi et al., 2015; Pizzi, 2019; Zhou & Du, 2019). Other applications of tannin are for wine, beer and fruit juice additives, ore flotation agents, cement superplasticisers and medical and pharmaceutical applications (Pizzi, 2008;

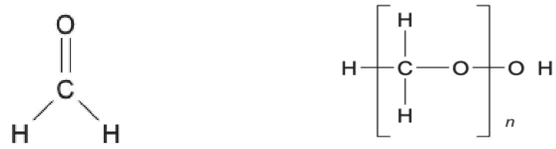
Pizzi, 2019). Based on the total volume tannin global market review of 2016 (Grand View Research, 2017), the tanning leather industry accounted for over 62 % of the total market revenue of tannin, followed by wood adhesive applications with approximately 20 % and then 28 % for the other applications including wine production, anti-corrosive primers, medical and pharmaceutical applications. Tannin also has the potential for producing laminates due to its high bonding performance (Shirmohammadli et al., 2018; Zhou & Du, 2019).

The addition of tannin to a wood adhesive (PF resin) helps to reduce the cost of resin production. The excellent bonding performance helps in reducing the brittleness characteristics of the PF resin (Cardona & Sultan, 2015; Zhou & Du, 2019). However, resin produced with the addition of tannin has high viscosity due to the presence of high molecular weight tannins in the resin and the existence of hydrogen bonding and electrostatic interactions between tannin and tannin (Hemmilä et al., 2017; Zhou & Du, 2019). Resin produced with the addition of tannin for wood adhesive has been accepted in many countries (Zhou & Du, 2019). However, research into PF resin including tannin for laminate applications is still lacking and only a few studies of laminates have been conducted on wood products. Tannin is a promising alternative bio-resource that can be used to produce laminate resin because it can provide active sites to react with formaldehyde (Jahanshaei et al., 2012) as phenol in PF resin. Therefore, this study is focused on the production of dissolved tannin phenol formaldehyde resole resin with reduced viscosity for laminating applications.

1.2 Problem Statement

Phenol formaldehyde (PF) resole resin is a well-known and versatile synthetic resin that has been in use until now. Many studies have been conducted to evaluate and improve the performance of PF resin. However, the discrepancies in the production of PF resin still exist based on previous studies. These discrepancies are:

i. Phenol formaldehyde resin (PF) is one of the oldest resin and well known as low-cost resins. PF resin is needed in industry due to it has excellent mechanical properties, thermal stability and weather resistance make it as an excellent resin and can be widely used in variety applications (Wei & Wang, 2018; Chen et al., 2019; Sandhya et al., 2019). PF resin is usually synthesised using formalin instead of paraformaldehyde (Shafizadeh et al., 1999; Poljanšek and Krajnc, 2005; Bajia et al., 2007; Christjanson et al., 2010; Zhang et al., 2013; Lin & Lee, 2018; Younesi-Kordkheili & Pizzi, 2018). This is due to the free formaldehyde monomer in formalin that leads to the higher chemical reactivity of formaldehyde with phenol to form methylol phenols compared to the large polymer molecules of paraformaldehyde that need to depolymerise before reacting with phenol as shown in Figure 1(a) and Figure 1(b) (Gardziella et al., 2010; Pilato, 2010).



n = 8-100

Formalin (a) Paraformaldehyde (b)

Figure 1.1: Formaldehyde chemical structure: a) in aqueous formaldehyde, Formalin and b) in solid powder, Paraformaldehyde with (n=4) (Kiernan, 2000)

ii. However, the synthesis of PF resin using formalin requires a longer synthesis period to achieve a desired viscosity compared to resins prepared using paraformaldehyde (Shafizadeh et al., 1999; Zhang et al., 2013; Lin & Lee, 2018). This is because formalin contains about 70 % by weight of water. During the condensation reaction, water will be generated and this condensed water needs to be removed to maintain the viscosity that is usually used in laminate resin (400 to 600 cP) and the total solid content in the PF resin is within the range of 75 to 80 % by weight (Taverna et al., 2015; Cui et al., 2017; Fleckenstein et al., 2018). Removal of the excess water is needed as the evaporation of the high water content during post-curing in an oven will lead to the formation of voids within the cured resin structure and therefore reduce the structural integrity and mechanical properties of the final product (Bajia et al., 2007; Pilato, 2010; Cardona & Sultan, 2015).

iii. The synthesis of PF resin which is a thermoset resin is an exothermic process (Gabilondo et al., 2006; Pilato, 2010; Hu et al., 2015) where heat will be released during the condensation reaction. The estimated heat of the reaction in PF resole resin production is about 670.90 ± 10.00 J/g (Sizgek, 1990; Bhattacharjee et al., 2014). Using paraformaldehyde in the formulation causes the mixture of PF liquid formed to be concentrated compared to using formalin that has a high-water content of about 70 % by weight. Low water content in the paraformaldehyde formulation is driven by the reaction process caused by the formation of methylene and ether bridges (a crosslinking process) which takes place faster, *i.e.* a high water content in the formulation hinders the formation of methylene and ether bridges (Hu et al., 2015). The rapid crosslinking in the condensation reaction generates excessive heat for which the cooling system arrangement is not adequate to properly remove the heat. This will cause the uncontrolled heat released to lead to a runaway reaction and explosion (Bhattacharjee et al., 2014; Tsai et al., 2021). In addition, the runaway reaction due the uncontrolled heat released leads to the fast polymerisation of PF resin during the synthesis period (Bhattacharjee et al., 2014). Therefore, it is important to evaluate the ratio of formaldehyde used and the operating temperature to prevent the formation of excessive heat that will affect both the viscosity and quality of the PF resin produced.

iv. PF resins are known to be brittle and have a relatively low tensile strength (Wang et al., 1997; Joseph, 2002; Sandhya et al., 2019). This property limits its applications in fibre-reinforced laminate and composite applications. Many studies have been undertaken to investigate the addition of tannins in PF resin in the production of tannin phenol formaldehyde adhesives (Moubarik et al., 2009; Hoong et al., 2010; Lee et al., 2011; Ping et al., 2011; Bertaud et al., 2012; Tahir et al., 2019; Hafiz et al., 2020). However, studies of the application and use of tannins in the synthesis of laminating resin such as tannin phenol formaldehyde type are still lacking. To illustrate, Barbosa et al. (2010) used tannin phenol formaldehyde resin in the preparation of composites reinforced with coir fibres. They found the flexural properties of the composites showed an improvement, i.e. to produce laminate composites, it requires good mechanical properties with desired values for a specific application in order to prevent cracking (Meier et al., 1977; Taverna et al., 2015; Georgia Pacific Chemicals, 2020). However, to date, as far as is known to the authors, no study has been reported concerning tannin phenol formaldehyde resin incorporated with fibreglass. Fibreglass is compatible with various type of resins and is well known to have properties of enhancing the flexural and impact strength of laminates (Parida et al., 2013). Therefore, the characteristics of laminates produced from tannin phenol formaldehyde resins combined with fibreglass were screened in this study. The characteristics of laminate resins which have a higher viscosity and solid content compared to adhesives required further evaluation in order to produce a PF resin with the addition of tannin. This is because the addition of excessive tannin to a PF resin drastically increased the viscosity of the product. Therefore, further monitoring and evaluation of the final product of laminate resins is required to maintain the good quality of the cured laminate resin.

Liquid tannin is preferred to be used to produce tannin phenol formaldehyde resin due to the increase in the reactivity of tannin and formaldehyde and the improvement of the flexural properties of the resin (Samil et al., 2005; Cardona & Sultan, 2015). However, tannins are easily found in a powder form rather than liquid form in the market to facilitate the handling process. Even though a few researchers have come up with several attempts to dissolve tannin powder (Samil et al., 2005; Hussein et al., 2011; Cardona and Sultan, 2015), however, using phenol to dissolve tannin powder in the work of Samil et al. (2005) is inappropriate due to the toxic and carcinogenic characteristics of phenol. Hussein et al. (2011) tried to dissolve tannin powder in water but only obtained coagulated tannin powder. Cardona and Sultan (2015) were able to dissolve tannin powder in a glycerol-acid solution with some dispersions of tannin powder, although the tannin solution produced was highly viscous. The highly viscous tannin leads to a highly viscous laminate resin produced, which possibly leads to difficulty in handling and spreading during the lamination process. It is known that glycerol is water soluble due to the existence of the three hydroxyl (-OH) groups (Wolfson et al., 2007). Therefore, the addition of water to glycerol can reduced the viscosity of the glycerol. In addition, water and glycerol are solvents that have the ability to bind with the tannin (Cardona & Sultan, 2015; Shrivastava et al., 2017). A water-glycerol solution with an acid catalyst (sulphuric acid) is an interesting solution that can be used to dissolve condensed tannin powder.

v. During the curing of PF resin, heat is generated from the crosslinking process *i.e.* extension crosslinking from the synthesis process to form the three dimensional networks of the cured PF resin (Hu et al., 2015). The excess heat generated will lead to air bubbles formed and trapped within the cured resin structure *i.e.* a low quality of resin is produced (Pilato, 2010). Therefore, the curing behaviour of dissolved tannin phenol formaldehyde resin needs to be monitored. The heat transfer profile during pre- and post-curing processes can be developed to access any sudden temperature increase that might affect the quality of the cured resin. The heat transfer profile also provides information concerning the temperature distribution within the cured composite to ensure that the curing temperature reaches the core composite and is able to access a suitable post-curing time with respect to the post-curing temperature of the composite laminate. The mechanical properties of the cured resin are affected by the duration of the post-curing process *i.e.* a sufficient post-curing period is important to ensure the resin is fully cured (Yahaya et al., 2014).

1.3 Objectives of the Research

This research is conducted in order to produce Phenol formaldehyde (PF) resin for bio-composite applications with the addition of tannin on woven roving fibre. The specific objectives of this research are:

1. To prepare suitable formulations that use paraformaldehyde and formalin in the preparation of phenol formaldehyde (PF) resole resin for laminate applications.
2. To analyse the dissolution behaviour of tannin and the properties of dissolved tannin phenol formaldehyde resins (DTPF) for laminate applications.
3. To evaluate suitable kinetic models and a heat transfer profile that defines the curing behaviour of the phenol formaldehyde (PF) resin produced.

1.4 Scope of Study

1. To accomplish objective (1), phenol formaldehyde (PF) resins were produced using industrial paraformaldehyde with and without the addition of formalin followed by a study of the rheological behaviour of the resins during production. The PF resins produced were laminated on to woven glass fibre and the mechanical properties of the laminated composites were compared.

2. To achieve objective (2), the dissolution of tannin powder using glycerol-water-acid solution was undertaken and the parameters involved in the dissolution process were optimised. The optimised dissolved tannin was mixed with the PF resin synthesised in objective (1) and the physical and mechanical properties of the dissolved tannin phenol formaldehyde resin and dissolved tannin phenol formaldehyde (DTPF) laminates composites were evaluated.

3. To achieve objective (3), the formulation of the screened PF and DTPF resin from objective (1) and objective (2) were used to study the cure kinetics of the

resins. The experimental data from differential scanning calorimetry (DSC) was fitted into a kinetic model to find the best fit theoretical model that was able to describe the curing behaviour of the composite laminate. The heat transfer during curing and post curing of the DTPF resin was evaluated. The surface temperature, core temperature and bottom temperature of the resin were measured. The heat transfer model of the DTPF resin during curing and post curing simulation was constructed using ANSYS simulation software.

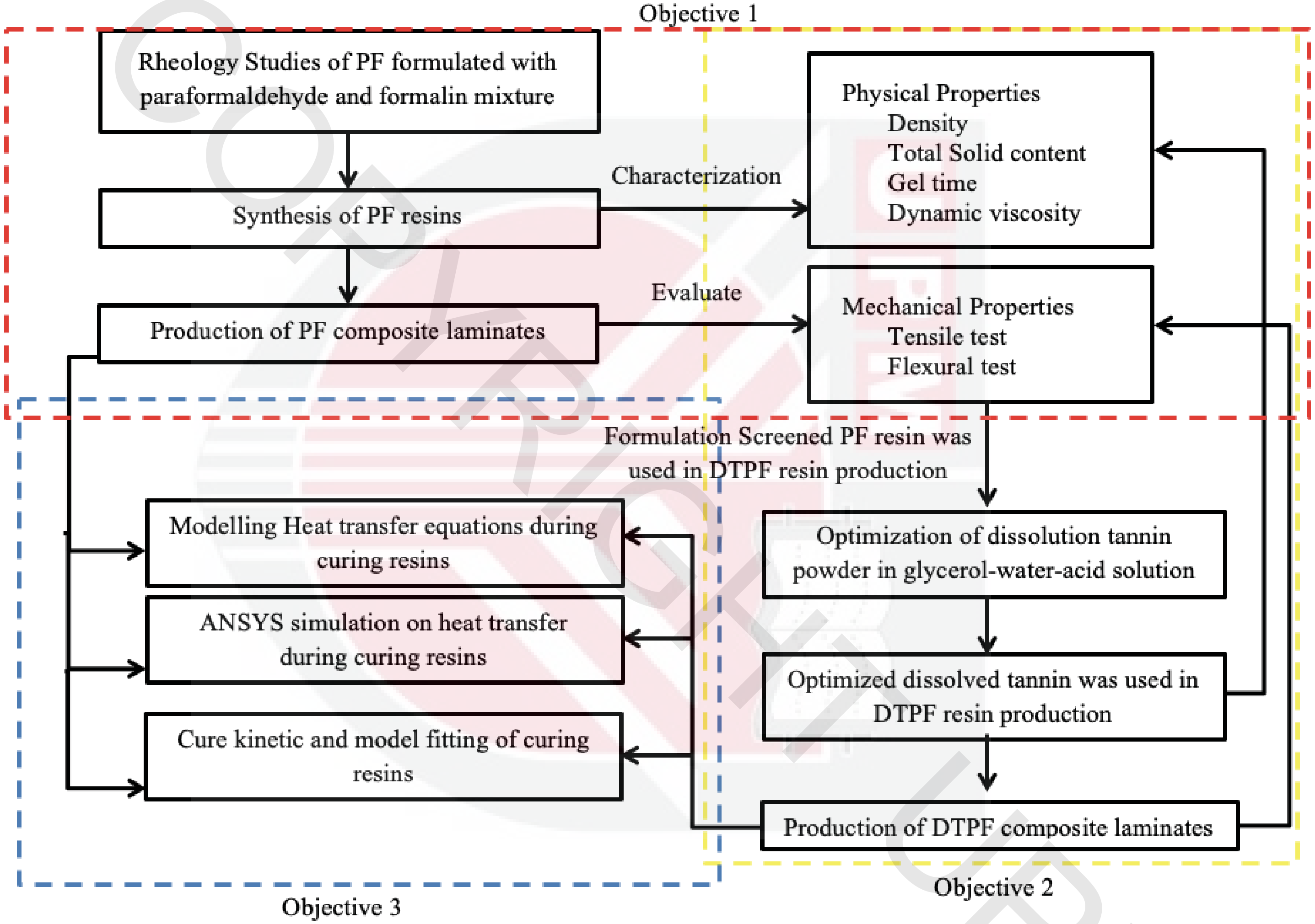


Figure 1.2: Overview of methodology

1.5 Significance of the Study

The present research work will help to understand the fluid behaviour of phenol formaldehyde (PF) resin during synthesis which is highly affected by the molar ratios of the phenol and the formaldehyde used, the synthesis temperature, the synthesis time as well as the pH of the mixture. In addition, this research work will aid in controlling and maintaining the safety of the operation of PF resin production. This is because the synthesis temperature was monitored in order to prevent the accumulation of excessive heat in the reactor which cannot be properly removed by the cooling arrangement and may lead to a runaway reaction and possibly an explosion. In addition, this research is important to ensure the introduction of defects into the cured resin structure is minimised.

1.6 Overview of the Thesis

This thesis is arranged in such a way that describes the preparation of environmentally sustainable phenolic bio-resins for bio-composite applications. This work is divided into six chapters. Chapter 1 introduces the subject matter combined with the objectives of the research. Chapter 2 discusses the literature review related to phenol formaldehyde (PF) resin and tannin addition in laminate resin. The literature review also presents general information about the background of laminates, the use and effect of tannin in PF resin production and brief information concerning the curing kinetics and heat transfer of curing resins. Chapter 3 consists of a description of the experimental approach as well as the findings with respect to the synthesis PF resin with paraformaldehyde and formalin. Chapter 4 illustrates the experimental procedure of the production of dissolved tannin phenol formaldehyde (DTPF) resins for laminate applications together with the optimisation of tannin dissolution. The effects of tannin in PF resin on the mechanical and chemical properties are discussed in detail. Chapter 5 presents the curing kinetics and heat transfer profile of curing composite laminates. The kinetic parameters are analysed and the temperature profile during curing and post curing of the composite laminate is evaluated using the ANSYS workbench. Chapter 6 refers to the overall conclusions based on the findings obtained in this study, and recommendations for future work are also given.

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