EXTRUDABLE MELAMINE RESIN FOR WOOD PLASTIC

COMPOSITES

By

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EXTRUDABLE MELAMINE RESIN FOR WOOD PLASTIC COMPOSITES

ABSTRACT

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Wood plastic composites (WPCs) are usually comprised of wood particulates

and thermoplastic resins, i.e. high density polyethylene (HDPE), polyvinylchloride

(PVC), or polypropylene (PP). In this research project, a novel melamine resin was

used as a matrix for extruding WPCs. This modified melamine adhesive (Hipe®esin)

exhibits thermoplastic behavior at temperatures between 100 to130 ℃, and crosslinks

at temperatures above 150 ℃ making it possible to utilize in an extrusion system.

Mechanical properties, thermal, and creep resistance of a polymer could be increased

by crosslinking reaction. In order to prevent curing inside the extrusion system,

understanding the crosslinking behavior of the melamine resin is crucial to improve

processing and mechanical performance.

Our research examined the crosslinking behavior and the thermal properties of

the melamine resin. We also evaluated the processing and the mechanical

performance of the wood-melamine-resin composites. Utilizing differential scanning calorimetry (DSC) techniques, kinetics of the crosslinking reaction were found and the activation energy was also determined. In addition, the torque rheometry results indicated a low processing temperature between 70 to 100 ℃. The effect of wood content was also found to dramatically influence the crosslinking kinetics and the processing of the wood-filled melamine resins. A higher wood content caused a quicker curing and a lower curing temperature.

This study also evaluated the extrusion parameters including: barrel/die temperature profile and post-extrusion curing. Reducing the processing temperature from 120 to 70℃ increased the strength and modulus of composites. Additionally, 6 hours of post-extrusion curing was found to raise the bending strength of composites. On the other hand, there was a negligible affect on the flexural modulus. Water uptake of the composites was slow because of the high resistance to water attack of melamine resins. Composites that post-cured in the condition room at the room temperature presented better moisture resistance and lowest diffusion coefficients. However, samples after 6 hours post-cured at 175℃ showed the best dimensional stability.

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Dedication

This thesis is dedicated to my husband Derek, my son Eric, and all my families who

provided their emotional support throughout the years.

CHAPTER 1 PROJECT INTRODUCTION

1.1 Background

The wood plastic composites (WPCs) industry has been experiencing very important growth over the last decade. Since 1997, WPCs have experienced a 16% increase in the U.S. decking market, from 2% in 1997 to 18% in 2005. Furthermore, peak sales for WPCs in 2005 reached $702 million (Smith and Wolcott 2006). By 2011, market research experts expect the demand for WPCs will continue to grow to approximately $5.4 billion (Kim et al. 2008). Composites have been widely used in residential materials and building products, especially in many outdoor applications, including decking, fencing, landscape timbers, and railings (Clemons 2002). WPCs offer many advantages over the conventional materials. For instance, these kinds of materials have high performance in mechanical properties, such as stiffness, impact and tensile strength, low cost, and low density (Bogoeva-Gaceva et al., 2007). Compared to polyethylene (PE), the elastic modulus of wood fibers is approximately 40 times higher and the strength is about 20 times higher (Bengtsson et al. 2005).

WPCs also offer many benefits, such as reduced maintenance and moisture resistance compared to solid wood and traditional wood composites (Wolcott and Englund 1999, Hatch 2008). Additionally, toxic chemicals such as chromated copper arsenate (CCA) are currently used in pressure-treated wood by wood protection

industries. About 90% of the pressure-treated wood contains this arsenic-based compound, which is a poison and a carcinogen. This toxic chemical is impacting the environment and might cause cancer in humans. Therefore, form both the environmental and economical view, these composites can be used not only to replace chemically treated wood in exterior applications, but also as a replacement for neat plastics (Bengtsson et al. 2005).

WPCs are typically comprised of two major components, and each component presents specific purposes in the final composite. The primary components of WPCs are wood particles or other natural fiber fillers and thermoplastic resins, such as high density polyethylene (HDPE), polyvinylchloride (PVC), polypropylene (PP) or polystyrene (PS). In the final composite, wood fillers supply stiffness and strength to the WPCs. Furthermore, the polymers act as a matrix that transfers load to the reinforcement and protects it from the environmental effects. The mechanical properties of wood fibers are not as good as synthetic fibers such as glass, nylon, carbon, and Kevlar. However, the mechanical properties (as shown in Table 1.1) are still acceptable also the low cost and the low densities of wood fibers are attractive to industries. For instance, the fibers are advantageously used in the automotive industry in Europe because of increasing environmental pressures (Clemons and Caulfield

2005). Wood fibers also represent environmentally friendly alternatives to conventional reinforcing fibers.

Over the past decade, there has been extensive research focused on improving the adhesion between the wood and the plastic in order to increase the properties of WPCs. In order to improve the performance properties of WPCs, different types of chemical agents are often used to improve matrix and wood filler interaction (Bengtsson and Oksman 2006). Numerous studies have used maleic anhydride grafted polypropylene (MA-PP), maleic anhydride grafted polyethylene (MA-PE), or polymethylene-polyphenyl-isocyanate (PMPPIC) as coupling agents to modify the interface, thus forming a link between the filler and matrix (Kokta et al 1989, Felix and Gatenholm 1991). The addition of a coupling agent to composites improves the mechanical properties compared to unmodified composites.

Bengtsson et al. (2005) stated that crosslinking is another approach for modifying thermoplastic wood composites. Compared to non-crosslinked WPCs, peroxide crosslinked composites consisting of wood flour and low density polyethylene (LDPE) resulted in improved adhesion, Young's modulus, and tensile strength (Janigova et al. 2001). Numerous studies have also shown that crosslinking is directly linked to the improvement of the adhesion of matrix and wood filler, mechanical properties, creep

deformation and durability of composites (Janigova et al. 2001, Bengtsson et al. 2005, Bengtsson and Oksman 2006).

Table 1.1. Mechanical properties of synthetic and natural fibers.

Fiber	Density (g/cm^3)	Stiffness (GPa)	Strength (MPa)
Glass	2.49	70	2700
Kevlar	1.44	124	2800
Nylon-6	1.14	1.8-2.3	503-690
Softwood	1.40	10-50	100-170
Hardwood	1.40	10-70	90-180

*(Clemons and Caulfield 2005).

1.2 Research development

Today, the challenges for the WPCs industry and researchers include improving long-term load properties, durability, stiffness, and toughness. The addition of different types of coupling agents or the crosslinking reaction in reactive extrusion operations has been shown to improve the performance properties of WPCs (Bengtsson and Oksman 2006). Even today, WPCs based on thermosetting resins are not commonly used for commercial applications due to the unsuitable rheological behaviors of thermosets for preventing their application in extruding (Braun et al. 2007). Because it is based on the response to temperature, a thermosetting resin reaches its degradation without going through a fluid state when heating up to a certain temperature level (Pascault et al. 2002). However, thermosetting resins present

better performances on thermal properties, creep resistance, high-temperature strength, stiffness, and hardness because of the crosslinked 3D network structures.

Haider et al. (2009) have identified that WPCs consisting of melamine-resin exhibited higher heat resistance and heat deflection temperatures when compared to WPCs made of polypropylene (PP). For instance, tensile strength improved 30% and showed a 16% increase for the tensile modulus at room temperature. Moreover, tensile strength increased 74% and the tensile modulus also improved 29% at a temperature of $80℃$. Braun et al. (2007) also compared the properties of conventional HDPE or PP based WPCs with those of thermosetting wood composites. The WPCs consisting of thermosetting resins have better properties such as higher creep resistance, high-temperature strength, and improved stiffness and hardness. With this information, one can assume that utilizing melamine adhesive to prepare WPCs should be possible and even improve composite properties.

In this research, a novel melamine resin (Hipe[®]esin), which exhibited thermoplastic behavior at low temperatures, and crosslinked at temperatures above $150℃$, was used as a matrix for extruding WPCs. The modification of the melamine resin with thermoplastic processing range was methylolated in part and fully etherified by alcohol (Rätzsch et al. 2004). The modified melamine adhesive exhibited elastic properties in comparison to the conventional melamine resin which is brittle

and nonelastic (Pavlyuchenko et al. 2006). In addition, Braun et al. (2007) indicated that the crosslinking reaction of the resin was influenced by the presence of wood and also catalyzed by its acidity. Pizzi and Panamgama (1995) discussed the crosslinking reaction of melamine-urea-formaldehyde (MUF) resin in the presence of wood and found that cellulose took lower activation energy in comparison to the MUF resin alone. Thus, understanding the crosslinking behavior of melamine resin is important to improve processing and mechanical performance

1.3 Objectives

The goal of the following project is to investigate and determine the processing and performances of WPCs based on melamine resins. Thermal properties of melamine resin are determined first and the results are further used to come up with the extrusion processing temperatures. In order to prevent the components from disintegrating or curing within an extrusion system and to optimize the final product properties, it is crucial to know the thermal characteristics of the modified melamine polymer and the mixing and processing parameters of wood flour filled melamine resins. In addition, evaluating processing and composite performances is also a main issue for this project. Specific objectives are outlined below:

1. Determine the thermal properties and the kinetics of the crosslinking reaction for the novel melamine resin
2. Utilize torque rheometry to evaluate the mixing and processing characteristics of WPCs containing extrudable melamine resins

3. Develop an extrusion temperature profile recommendations for the wood-melamine-resin composites
4. Evaluate the processing parameters' influence on the mechanical performances of extruded wood-melamine-resin composites.

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CHAPTER 2 THERMAL STUDY AND KINETICS OF THE CROSSLINKING REACTION OF WOOD-MELAMINE-RESIN COMPOUNDS

2.1 Abstract

A novel melamine resin was used as a matrix for extruded WPCs. The modified melamine adhesive (Hipe[®]esin) exhibits thermoplastic behavior at low temperatures, and crosslinks at temperatures above 150℃, making it possible to be utilized in an extrusion system. In order to prevent curing inside the extruder, understanding the thermal transitions and curing behavior of the melamine resin is crucial to improve processing and mechanical performance. Torque rheometry was used to measure the torque and energy needed during the mixing process of the wood-melamine-resin compounds and also to characterize processing temperature and identify the curing reaction in the process.

Thermal stability of the neat melamine adhesive up to 200℃ and weight loss increased markedly in the temperature range of 400℃ to 430℃. Moreover, the curing temperature increased with increased heating rate. The torque rheometry results also indicated a low processing temperature between 70 to 100 ℃. The effect of wood content was also found to dramatically influence the crosslinking kinetics and the

processing of the wood-filled melamine resins. A higher wood content caused a

quicker curing and a lower curing temperature.

2.2 Introduction

In recent years, wood plastic composites (WPCs) have become accepted in the

market place and have received considerable attention from both the polymer and

forest products industries. WPCs have been widely used in residential building

materials such as decking, fencing, and landscape timbers, which are applications

sensitive to decay and moisture damage (Clemons 2002). WPCs are usually

comprised of wood particles and thermoplastic resins, e.g., high density polyethylene

(HDPE), polyvinylchloride (PVC), or polypropylene (PP). Even today, WPCs based

on thermosetting resins are not commonly used for commercial applications due to the

unsuitable rheological behaviors for extruding (Braun et al. 2007). Generally, a

conventional thermosetting resin reaches its degradation without going through a fluid

state when heated up to a certain temperature level (Pascault et al. 2002).

Braun et al. (2007) compared the properties of conventional WPCs with those of

thermosetting wood composites. The WPCs based on thermosetting resins enhanced

thermal properties such as higher creep resistance, high temperature strength, and

improved stiffness and hardness. In order to prevent curing within the extrusion

system, understanding thermal properties such as crosslinking behavior of the

melamine resin is crucial to improve processing and mechanical performance. In addition, curing kinetics can be used to assist in understanding the bond strength development for wood-based composites. Wang et al. (2007) also designed kinetic models of bond strength development for hot-pressing models by utilizing differential scanning calorimetry (DSC) techniques to determine the kinetics of the crosslinking reaction.

Traditionally, melamine resins have been classified as thermosetting resins. Pizzi and Mittal (1994) stated that conventional melamine resins were among the most used adhesives for wood panels; these resins have also been called melamine-formaldehyde (MF). Because of the higher resistance to water attack, MF resins have also been used as adhesives for exterior plywood and particleboard (Pizzi and Mittal, 1994). The typical chemical structure of melamine resins is shown below:

Melamine-Formaldehyde
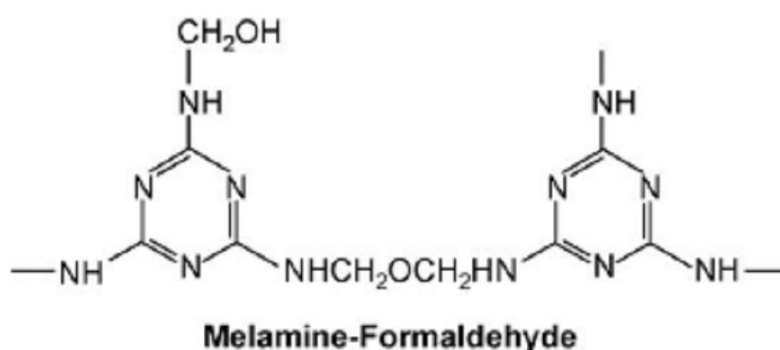
*(Kim and Kim 2006)

In this research project, a novel melamine resin was used as a matrix for extruding WPCs. This modified melamine adhesive (Hipe®esin) was developed by

Agrolinz Melamine International GmbH and exhibits thermoplastic-like behavior,

making it useable in an extrusion system. Pavlyuchenko et al. (2006) indicated that

the modification of melamine resin is based on etherification with alcohol. Mercer and

Pizzi (1993) also stated that melamine resin exhibits thermoplastic behavior with the

presence of methanol in the formalin. The modified melamine adhesive with

thermoplastic processing range is partially methylolated and fully etherified (Rätzsch

et al. 2004). Etherified melamine resin performs in an elastic manner and can be

dissolved in organic solvents. The resin is also suitable for processing into

commercial products using extrusion and injection molding intrinsic to thermoplastic

polymers (Pavlyuchenko et al. 2006). The chemical structure of transetherification of

the modified melamine resins is shown below:

$$H_2N-Tr-NHCH_2NH-Tr-... + ROH \rightleftarrows H_2N-Tr-NHCH_2NH-Tr-... + CH_3OH$$
$$NHCH_2OCH_3 \quad CH_2OH \qquad\qquad NHCH_2OR \quad CH_2OH$$

where Tr is triazine ring , R is aliphatic or aromatic substituent
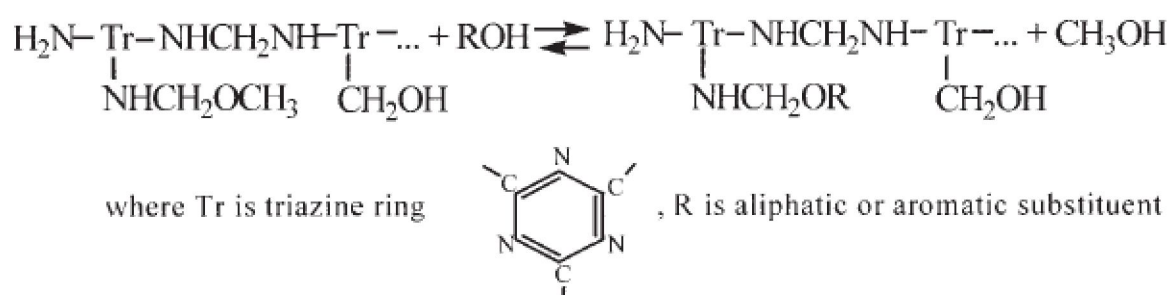
*(Pavlyuchenko et al. 2006)

Thermal analysis, which involves many analytical experimental techniques, can

measure the thermal performance of thermosetting resins as a function of temperature

(Kim and Kim 2006). The most widely used techniques for thermal analysis are DSC

and thermogravimetric analysis (TGA). In this research, TGA was used to measure

the mass change of polymers or composite materials. Thermal degradation and thermal stability were interpreted from the TGA results. Moreover, utilizing DSC techniques, kinetics of the crosslinking reaction were found and the degree of cure was also determined.

DSC has been used to analyze the cure process of thermosetting polymers, and it is also a good tool for following the polymers' curing kinetics (Alonso et al. 2004). The crosslinking reaction of the melamine resin is affected by the presence of wood and also catalyzed by its acidity. Moreover, Pizzi and Panamgama (1995) discussed the crosslinking reaction of MUF in the presence of wood and cellulose which took lower activation energy in comparison to the resin alone. Acidic groups can be found in two of the major wood components, hemicelluloses and lignin. (Bergmann et al. 2006). Comparing neutral and alkaline reaction mediums, the crosslinking reaction is very fast in acidic medium (Rätzsch et al. 2004). Increasing catalyst levels (reducing pH values) shift the onset and peak temperatures of the curing reaction to lower levels. For example, the curing peak temperature, which is 140℃, of catalyzed (pH8.15) melamine resin is lower than noncatalyzed (pH 10.2) which is 169℃ (Kohl et al. 1996).

Kohl et al. (1996) stated that heat releasing (exothermic reaction) is the cure process of most thermosetting adhesive systems. DSC exotherms indicative of the

crosslinking reaction of the melamine resin and MUF resin are evident (Pizzi and

Panamgama 1995, Kohl et al. 1996). Previous research has also identified that

commercial phenol-formaldehyde (PF) resoles typically exhibit two exothermic peaks

(Wang et al. 2007). Hydroxymethylphenols formation and condensation cause the

first exotherm, while the second exothermic peak is ascribed to elimination of

formaldehyde (Luukko et al. 2001).

Prior to extrusion, it is important to know the thermal characteristics for WPCs

based on melamine resins in order to prevent them from disintegrating or curing

inside an extrusion system. The goals of this research are not only to investigate the

wood filler levels and process parameters towards development of extruded melamine

wood flour composites, but also to investigate the thermal attributes of the novel

melamine adhesive and wood–filled melamine resins. The primary objectives of this

study were to:

1. Identify the thermal stability of the neat melamine resins using TGA
   techniques
2. Utilize DSC to evaluate the glass transition temperature of the extrudable
   melamine resins and determine the kinetics of the crosslinking reaction and
   degree of cure of the wood–filled melamine resins
3. Evaluate the rheological and curing behavior of the novel melamine resin
   (Hipe[®]esin) for WPCs utilizing torque rheometry
4. Determine the influence of wood filler levels and temperatures on the
   rheology and thermal transitions of the melamine WPCs

2.3 Materials and Methods

2.3.1 Materials

The neat melamine resin (HIPE®ESIN, type MPER 4.0 T5 E) was acquired from Agrolinz Melamine International GmbH as a dry particulate. This modified polymer exhibits thermoplastic-like viscosity at temperatures between 100 to130℃ and also make it possible to be utilized in an extrusion system. Although this melamine adhesive shows thermoplastic behavior, it still crosslinks at temperatures above 150℃.

The wood flour used was a commercial 60-mesh eastern white pine (*Pinus strobus*) obtained from American Wood Fibers®. The wood-melamine-resin compounds were mixed as 50% neat melamine resin with 50% wood flour, on a weight-basis.

2.3.2 Thermogravimetric analysis (TGA)

The neat melamine resin was analyzed for thermal degradation behavior with TGA. Thermal degradation, thermal stability, and weight loss of neat melamine resins was examined using TGA. Samples of about 10mg were placed in an aluminum crucible and exposed to a heating rate of 10℃/min over a temperature range of 30 ℃ to 600 ℃. Nitrogen gas was used as the inert purge gas in order to avoid unwanted oxidation of the sample.

2.3.3 Differential scanning calorimetry (DSC)

The glass transition (T_g) of the neat melamine and the curing kinetics of the

wood-melamine-resin compounds were determined by using DSC. T_g has been

recognized as an important physical property of a polymer. Furthermore, the T_g is a

transition of states for a polymer which can be either a semi-crystalline or an

amorphous polymer. For instance, an amorphous polymer is in glassy state when the

temperature is below T_g, and above which it is in a rubbery state (Rosen, 1993). When

the temperature is higher than its T_g, an amorphous polymer does not truly melt, but

might soften to a certain viscous flow similar to melting (Wolcott and Englund 1999).

The flow is needed during the extrusion processing since the flow might result in

good penetration of resins into wood.

a. Glass transition (T_g) of the neat melamine

DSC was used to determine the T_g of the neat melamine. Prior to DSC testing,

samples were ground with a Wiley mill using a 40 mesh screen and conditioned in a

desiccator for 24 hr at ambient temperature. DSC scans were then performed on 5 mg

samples heated from -40℃ to 100℃, which is under the crosslinking temperature of

150℃, at a heating rate of 20℃/min in hermetically sealed 40-μl aluminum crucibles.

Two cycles of heating and cooling were applied on the specimens, creating six

thermal segments, as shown in Table 2.1. The thermal cycles here are annealing and

were used to erase the influence of thermal history on the thermodynamic behavior

being measured by the DSC. In these six segments, only the endothermic reaction in

the fifth segment is meaningful for the T_g because the first heating (segment #1) was

performed to remove the thermal history and obtained the accurate results.

Table 2.1. Heating segments used for determining T_g on the DSC.

	Seg. 1	Seg. 2	Seg. 3	Seg. 4	Seg. 5	Seg. 6
Start Temp.	-40℃	Isothermal for 3 min	100℃	Isothermal for 3 min	-40℃	Isothermal for 3 min
End Temp.	100℃		-40℃		100℃	
Heating Rate	20℃/min		20℃/min		20℃/min	

b. Curing kinetics of the wood-melamine-resin compounds

DSC was also used for studying the curing kinetics of the wood-melamine-resin

compounds. Prior to DSC testing, the neat melamine resins were Wiley-milled into a

40-mesh particulate and were mixed with 60-mesh wood flour as compounds. The

compounds were conditioned in a desiccator for 24 hr and then placed in 40-μl

aluminum crucibles without lids.

In order to derive kinetic information, samples were heated from 30℃ to 250℃

using a heating rate of 2, 5, 8, 10, 15, and 20 ℃/min, following the ASTM E698

method. Sample sizes of approximately 5 mg were used for these experiments. During

this testing, exothermic reaction peaks were recorded.

During the crosslinking reaction process, a phenomenological model of cure (Eq.

2.1) could then be applied (Wang et al. 2007):

$$\frac{d\alpha}{dt} = Z \exp(-E/RT) f(\alpha) \qquad\qquad \text{Eq. 2.1}$$

Where t (s) is the time, $d\alpha/dt$ (min^{-1}) the reaction rate, Z (min^{-1}) the

pre-exponential factor, E (J/mol) the activation energy, R (8.314 J/mol K) the gas

constant, T (K) the absolute temperature, and $f(\alpha)$ the function of cure. For an $f(\alpha)$,

nth-order reaction is described in $f(\alpha)=(1-\alpha)^n$, where n is the reaction order (Harper et

al. 2001, Wang et al. 2007).

Using the nth-order, Eq. 2.1 can be rearranged into Eq. 2.2:

$$\ln(\frac{d\alpha}{dt}) = \ln(Z) + n\ln(1-\alpha) - \frac{E}{RT} \qquad\qquad \text{Eq. 2.2}$$

According to ASTM E2041, kinetic parameters Z, E and n for nth-order model

(nth-BD) might be determined from Eq. 2.2 by using multiple linear regression data

treatment. The Borchardt and Daniels method (ASTM E2041) is designated such that

all kinetic parameters are derived from one single dynamic DSC scan. However, the

results of kinetic parameters depend on heating rates (Wang et al. 2007).

The kinetic parameters can also be resolved from the multiple heating rate scan

used in ASTM E698. The E for the wood-melamine-resin compounds could be

calculated either by the Ozawa method (Eq. 2.3) or by the Kissinger method (Eq. 2.4).

As suggested by ASTM E698, the calculated E by Ozawa equation can be compared

with that by Kissinger. The exothermic peak temperatures (T_{peak}) dependencies on

multiple heating rates (β) were used to calculate the E and Z (Wang et al. 2007). In

Ozawa's method, there is a linear relationship between the logarithm of the heating

rate and the inverse of the T_{peak}. Therefore, the E could be calculated from the

resultant slope. In addition, the Kissinger method is similar to Ozawa's, which relates

to the logarithm of (β/T^2_{peak}) with the inverse of the T_{peak} (Alonso et al. 2004). Higher

E values are yielded by using the Ozawa equation than those determined by the

Kissinger equation. However, less than 4% variation was found in the estimates of E

between these two methods for phenol formaldehyde (PF) resins (Alonso et al. 2004,

Wang et al. 2007).

$$E_a = -2.19R \frac{d(\log \beta)}{d(1/T_{peak})} \qquad \text{Eq. 2.3}$$

$$E_a = \frac{Rd[-\ln(\beta/T^2_{peak})]}{d(1/T_{peak})} \qquad \text{Eq. 2.4}$$

For nth-order reaction, the Z can be calculated by using Eq. 2.5 (Wang et al.

2007).

$$Z = \frac{\beta E \exp(E/RT_{peak})}{RT^2_{peak}{}^n (1 - \alpha_{peak})^{n-1}} \qquad \text{Eq. 2.5}$$

The Z is easily obtained when assuming a first order reaction (n=1) is made

(Turcotte et al. 2005, Wang et al. 2007). Eq. 2.5 can be substituted into the first order

kinetic and yields Eq. 2.6.

$$Z = \frac{\beta E \exp(E/RT_{peak})}{RT^2_{peak}}$$

Eq. 2.6

where β= a heating rate from the middle of the range. Table 2.2 summarizes the models used in this project.

The degree of cure (α) was also determined and was calculated at the specific cure time *(t)* by normalizing the partial heat of reaction *(ΔH (t))* by the total heat of reaction (ΔH).

$$\alpha = \frac{\Delta H(t)}{\Delta H}$$

Eq. 2.7

Kinetic values calculated from the T_{peak}–β relationship were used to predict a reaction half-life at a selected temperature. The samples were aged at the selected temperature for the predicted half-life time and then cooled to room temperature and reheated to 250℃ using a heating rate of 10℃/min. According to ASTM E698, an *n*th-order reaction kinetics was confirmed for the temperature range explored, if the exothermic peak area or displacement from baseline of the aged sample is half that for the unaged sample.

Table 2.2. Summary of kinetic models, parameters, and methods.

Method	Model *f(α)*	Kinetic parameters	Standard
E698	First order *(1-α)*	*Z, E*	ASTM E698, multiple heating rates
*n*th-BD	*n*th order *(1-α)ⁿ*	*Z, E, n*	ASTM E2041, single heating rate with Borchardtand and Daniel method

2.3.4 Torque rheometry

A torque rheometer, Haake Rheomix 600 with a 69ml net chamber capacity, was used to evaluate mixing characteristics of wood-melamine-resin compounds. Two types of experiments, i. e., effect of temperatures and influence of wood filler levels, were performed in this study. No lubricants were used for this test since the goal was to investigate the natural processability of the filler and polymer. Testing was performed on a 50 g sample at a screw speed of 50 rpm until materials crosslinked.

The curing time was characterized by calculating inflection points and mid-points of the torque curves. The inflection points represent the onset of the curing reaction and the mid-points mean the middle time of the curing reaction (as shown in Fig. 2.1). In order to calculate the points, a part of the crosslinking torque curve was selected and a polynomial trend-line was developed to simulate the curve. Polynomial fits for inflection points and mid-points are shown in Fig. 2.2 and Fig. 2.3. The polynomial functions, such as; $y = 3.4859x^4 - 33.132x^3 + 114.48x^2 - 164.36x + 94.087$, were also obtained and than derived into quadratic equations. The inflection points and mid-points were calculated by using Eq. 2.8.

$$X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$
Eq. 2.8
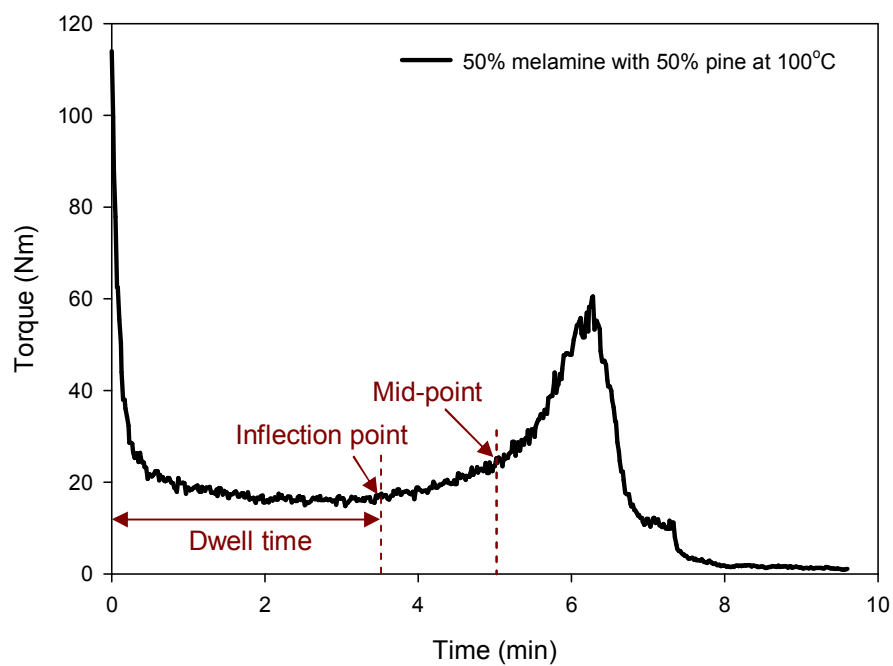
Fig. 2.1. Illustration of inflection point, mid-point, and dwell time.
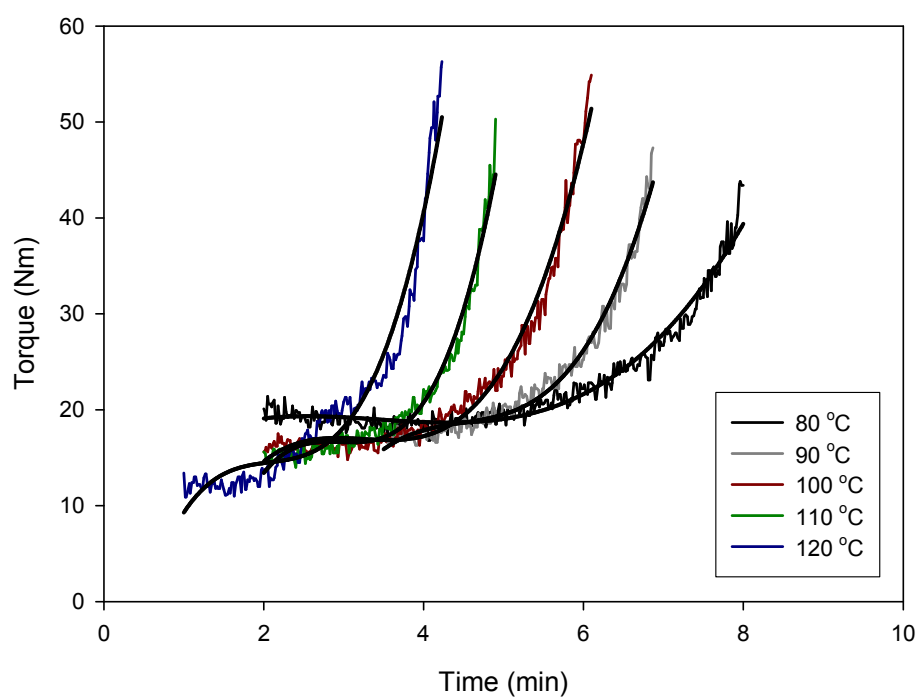
Fig. 2.2. Polynomial fits for calculating inflection points.
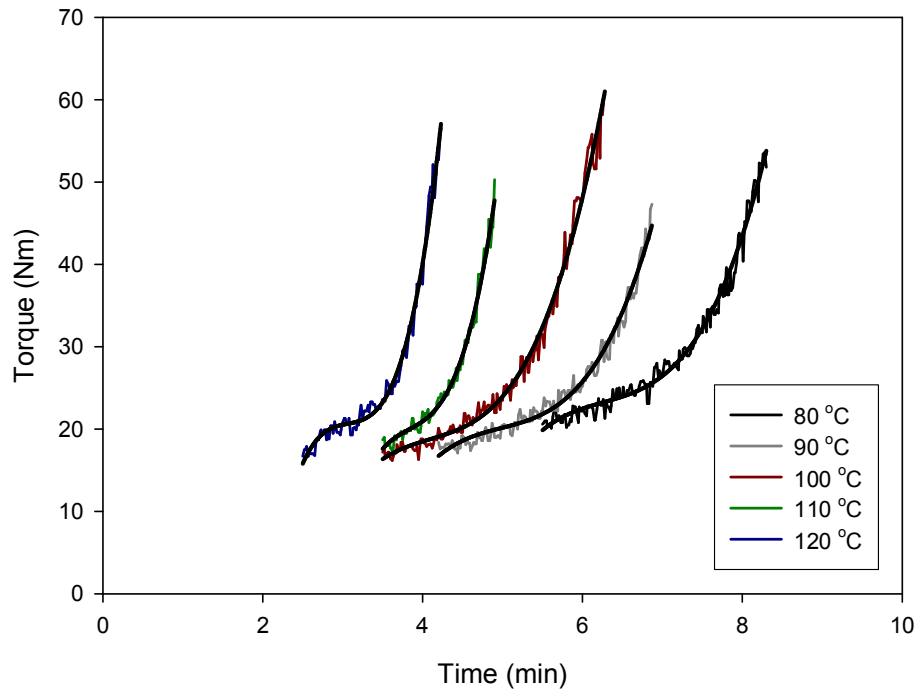
Fig. 2.3. Polynomial fits for calculating mid-points.

a. Effect of temperature

Fifty percent wood flour and 50% melamine resin (by total weight) were mixed at temperatures of 80, 90, 100,110, and 120℃. Torque data were used to evaluate the crosslinking time at different temperatures.

b. Influence of wood filler levels

Various wood fiber loadings and different melamine resin contents were mixed at a temperature of 100℃. Table 2.3 summarizes the experimental formulations for examining the influence of wood filler levels. These torque data were used to characterize the crosslinking behavior of the melamine resin at various wood filler levels.

Table 2.3. Formulations (by total weight) for examining the influence of wood filler levels in torque rheometry.

	W20	W30	W40	W50
Melamine	80%	70%	60%	50%
Wood Flour	20%	30%	40%	50%

2.4 Results and discussion

2.4.1 Thermal degradation

For all components within the formulation of extruded WPCs, the thermal degradation is important because the off-gasses from the degraded polymers or fillers within an extrusion system can result in poor adhesion between polymer and wood fillers. Using TGA, the thermal decomposition and thermal stability of the neat melamine resins were evaluated. The derivative curve is the best suited for determining the decomposition temperature for the samples, while the weight curve can be used to conclude the weight loss associated with the degradation (Brown and Laborie 2007).

TGA data with the weight loss and the derivative weight loss for the neat melamine resins are shown in Fig. 2.4 and Fig. 2.5.The neat melamine evaporated at 422.5±0.07 ℃ (as shown in Fig. 2.4), which also showed thermal stability of the neat melamine resins up to 150℃ (as shown in Fig. 2.5) (Brown 2007). The neat melamine resins started to degrade above 150℃, but less than 5% weight loss was found when heating up to 200℃. As a result, in order to prevent the off-gassing problem that

occurs within an extrusion system during processing, extrusion processing

temperatures below 200℃ can be used. Above 400℃ the weight loss increased

markedly. This can be clearly seen in the derivative of the TGA curve. The major

weight losses were observed in the temperature range of 200℃ to 430℃, which may

correspond to the structural decomposition of the resins (Kim and Kim 2006).
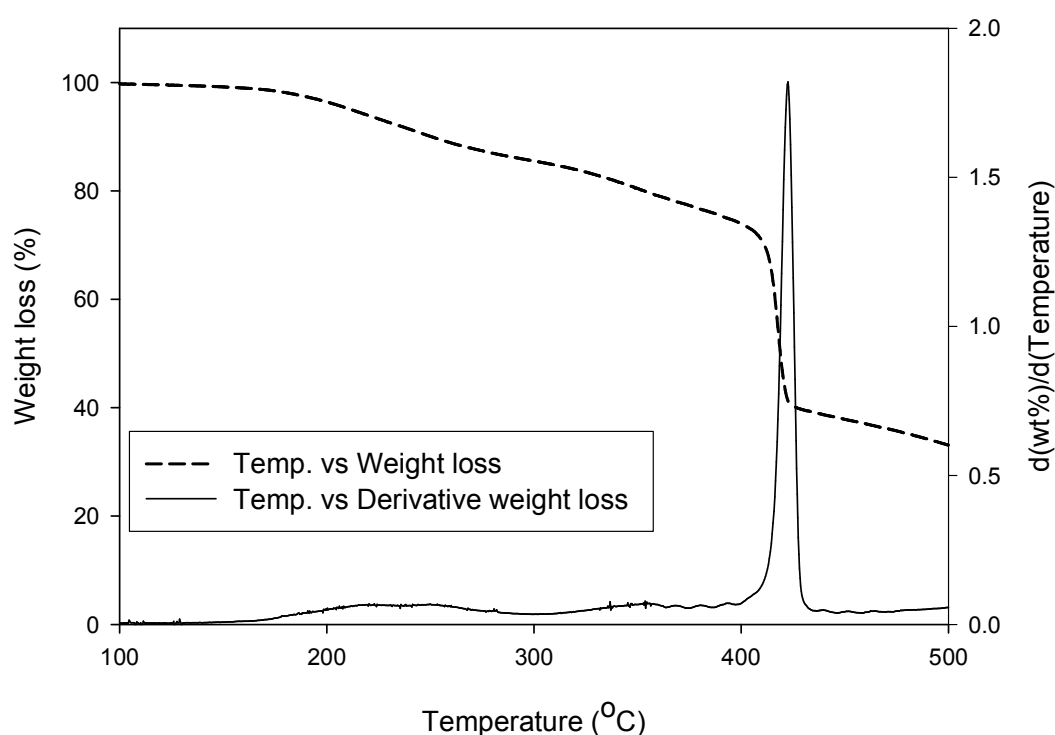
Fig. 2.4. Weight loss and derivative data of TGA of neat melamine resins at temperature range of 100 to 500℃.
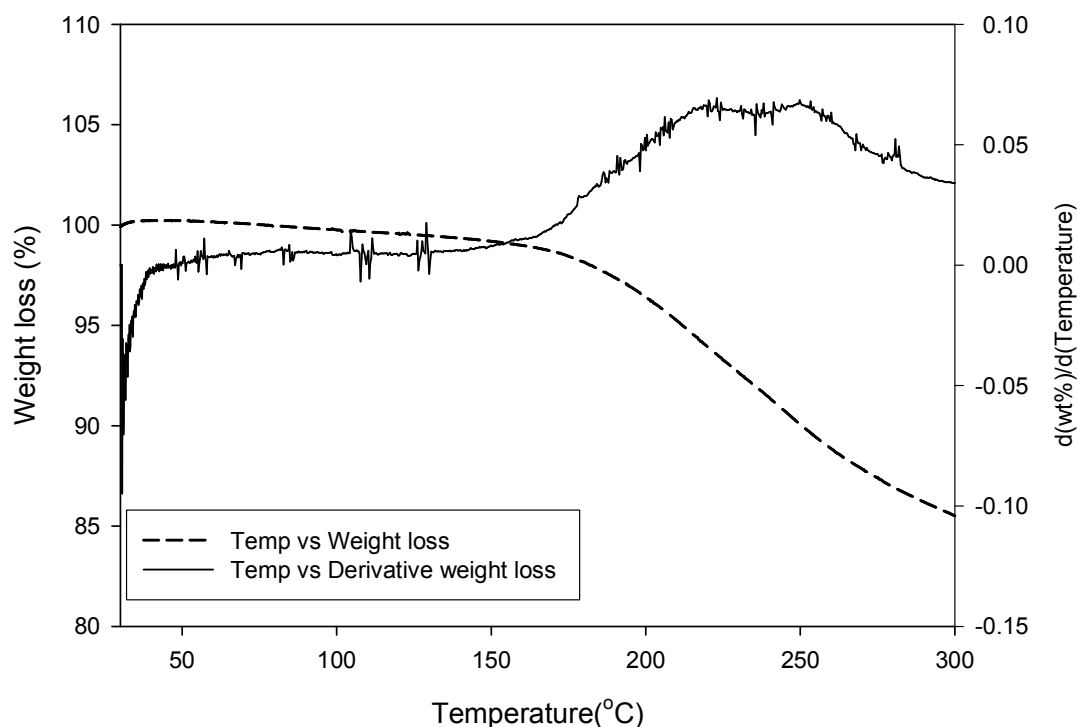
Fig. 2.5. Weight loss and derivative data of TGA of neat melamine resins at temperature range of 30 to 300℃.

2.4.2 Glass transition (T_g) of neat melamine resins

T_g has been recognized as an important physical property of a polymer and was

presented as the inflection point of the heat flow and temperature. Fig. 2.6 shows that

the multiple tests of T_g of the neat melamine resin is 34.5±0.07 ℃ at a heating rate of

20℃/min. Thus, when the temperature reaches above the T_g of the neat melamine, the

polymer becomes softer and exhibits a rubbery flow. An amorphous polymer does not

truly melt, but might soften to a certain viscous flow similar to melting (Wolcott and

Englund 1999). Although we did not necessarily use the T_g for processing information

in this case, it is still a tool to characterize the polymer for its final product behavior.

Han (2007) also stated that a very high viscosity of an amorphous polymer can be

observed at temperatures slightly above its T_g and the polymer flows when it reaches

a certain temperature which is much higher than T_g.
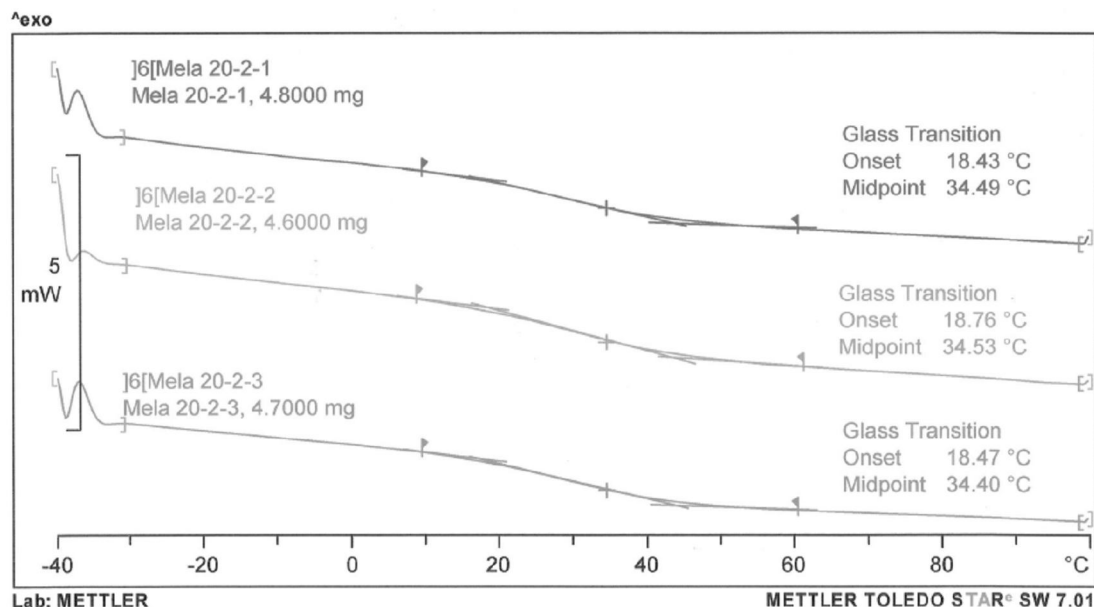
Fig. 2.6. T_g of the neat melamine resins.

2.4.3 Curing analysis of wood-melamine-resin compounds by DSC

The curing reaction curves and degree of cure obtained at various heating rates

are shown in Fig. 2.7 and 2.8. The heating rate influenced the curing behavior of the

thermosetting resins. Thus, the exothermic peak was shifted to a higher temperature

by increasing the heating rate. Wang et al. (2007) also identified that exotherms of

commercial PF resins shift to higher temperatures with increasing heating rate. Table

2.4 summarizes the experimental results as well as the maximum exothermic peak for

each heating rate (β) used to perform the calculations in the ASTM E698 method.

Degree of cure was determined at a specific cure time, which reflects the exothermic

peak temperature. The results show that the degree of cure at the peak temperature for

melamine resins at the various heating rates was approximately 45%. However, data

from Table 2.4 show that the result with heating rate of 2 ℃/min is deviated with

respect to the remaining values. The possibility might be that the behavior at the

lowest heating rate is produced by thermal decomposition of the

wood-melamine-resin compounds, which interferes with the curing reaction in the

later stages (Alonso et al. 2004).
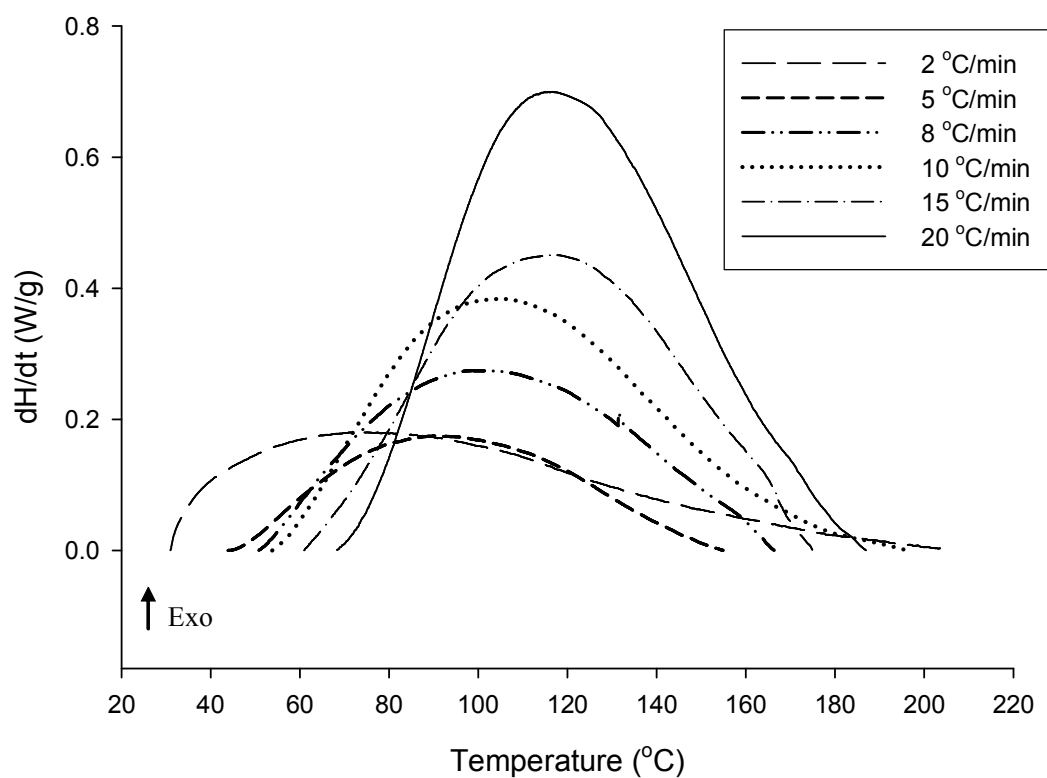
Fig. 2.7. Dynamic DSC data of wood-melamine-resin compounds at multiple heating rates.
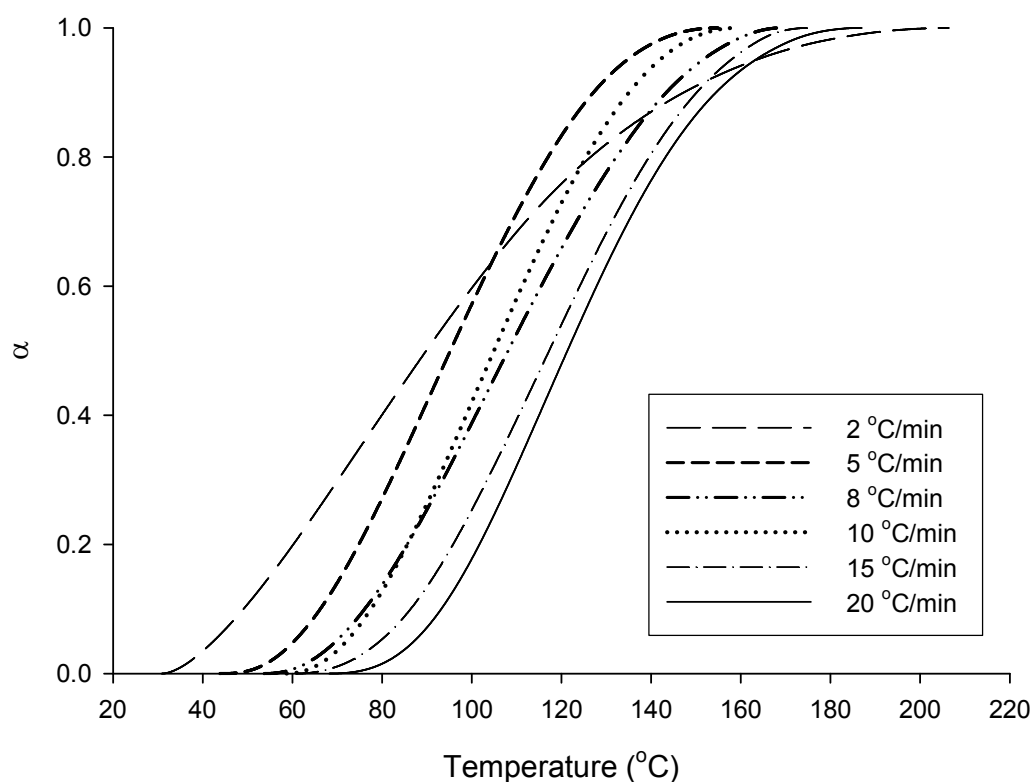
Fig. 2.8. Degree of cure (α) for wood-melamine-resin compounds.

Table 2.4. Experimental results for calculation of activation energy.

Heating Rate β (K/min)	Exothermic Peak Temp. (°C)	α (Deg. of cure at Exo. peak)	Temp. (1000/K)	$\text{Log}_{10}\ \beta$	$-\ln(\beta/T^2)$
2	74.4 (0.1)	0.36 (0.02)	4.04	0.30	10.3
5	92.2 (2.0)	0.44 (0.02)	3.77	0.70	9.55
8	101 (1.6)	0.43 (0.04)	3.65	0.90	9.15
10	104 (0.8)	0.44 (0.02)	3.60	1.00	8.95
15	112 (0.3)	0.46 (0.04)	3.51	1.18	8.60
20	117 (0.5)	0.44 (0.02)	3.44	1.30	8.35

*Standard deviation in parenthesis.

2.4.4 Kinetics of the crosslinking reaction

a. Kinetic parameters obtained from DSC ramp methods

The kinetic parameters obtained by nth-BD and E 698 models from dynamic test data for the wood-melamine-resin compounds are summarize in Table 2.5. In the Ozawa method, E could be determined from plots of the logarithm of the heating rate versus the reciprocal of the absolute peak temperature. The plot of $\log_{10} \beta$ versus $1/T$ for the wood-melamine-resin compounds was a straight line with an r^2 of 0.9952 and a slope of -1678. The E was found to be 28.0 kJ/mol, which was calculated by using Eq. 2.3.
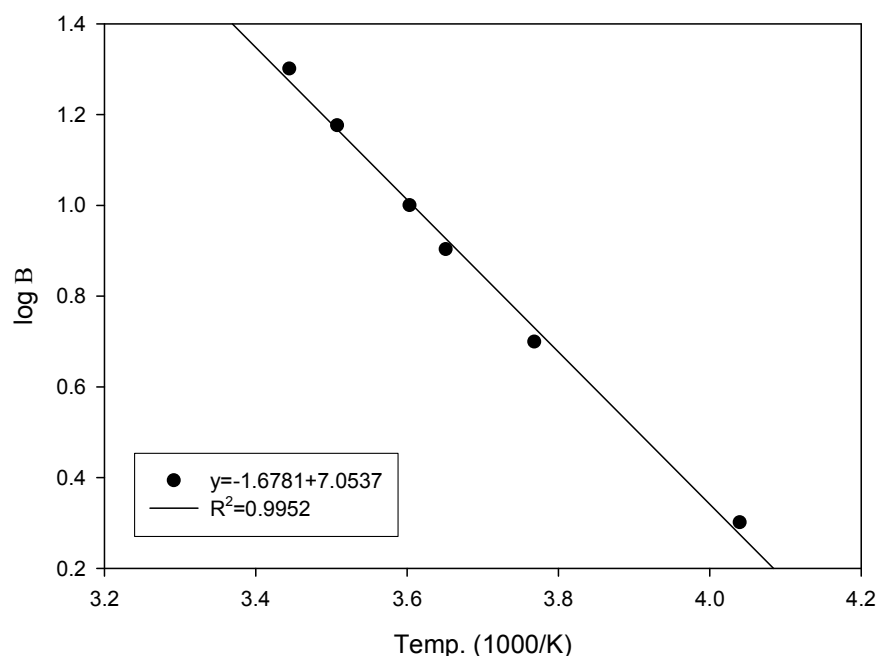
Fig. 2.9. Plot of log β versus 1/T with a slope of -1678.

In the Kissinger method, the activation energy could be determined from plots of the $-\ln (\beta/T^2)$ versus the reciprocal of the absolute peak temperature in Kelvin. The

plot of $-\ln (\beta/T^2)$ versus $1/T$ for the wood-melamine-resin compounds was a straight

line with $r^2=0.9941$ and had a slope of 3329. $E=28.0$ (kJ/mol) was calculated by

using Eq. 2.4.
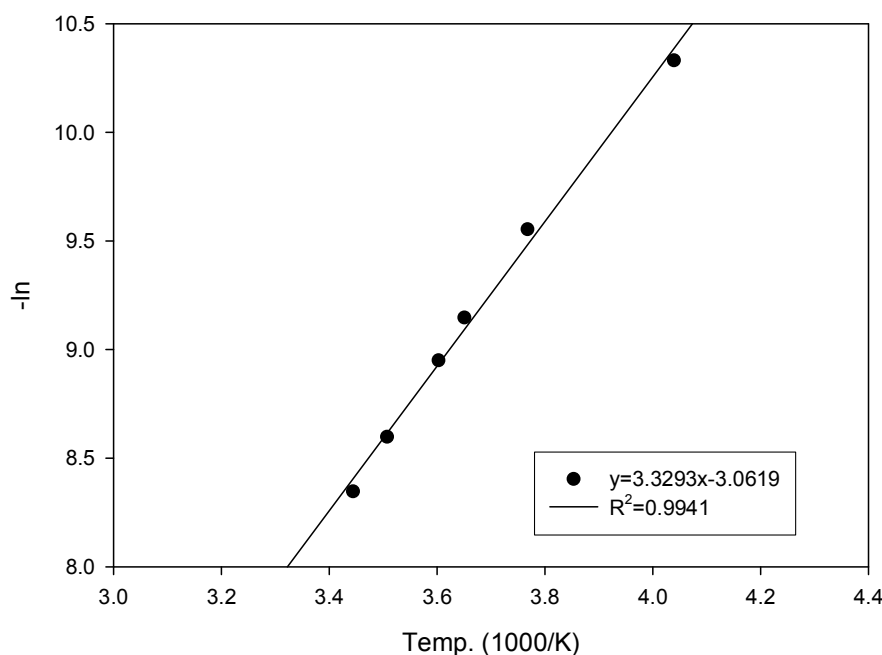
Fig. 2.10. Plot of $-\ln (\beta/T^2)$ versus $1/T$ with a slope of 3329.

Both the Ozawa and Kissinger methods give a similar E and are in agreement

with the literature (Alonso et al. 2004, Wang et al. 2007). The nth-BD employs a

single run by DSC for the overall cure process, but E 698 is no longer so. The E

determined by the nth-BD model is higher than that calculated by the E 698 (as shown

in Table 2.5). Generally, when compared with the Ozawa and Kissinger equations

used in ASTM E698, the nth-BD method is observed to overestimate the kinetic

parameters. For instance, they are 30% higher than those obtained by the E 698

method (Wang et al. 2007). Alonso et al. (2004) indicated that the reason for this

difference is due to the determination is based on a single scan by DSC. The higher E can be measured at the higher heating rates, which are 20kJ/mol at a heating rate of 2℃/min and 40kJ/mol at a heating rate of 20℃/min, respectively. This inconsistency could be explained by higher thermal lag that occurred at the higher heating rate (Wang et al. 2007).

The use of the nth-BD method is applied for obtaining the reaction order. The n (as shown in Table 2.5) determined for this wood-melamine-resin compound appears to approximate close to the first order. The results are supported by Kohl et al.'s study (1996), which reposted reaction orders of n=1.12 for the conventional acid catalyzed melamine formaldehyde resin.

Based on the E 698 method, the results of the E and Z for the modified melamine resin with a wood catalyst are lower than the conventional acid catalyzed melamine formaldehyde resin, which are E= 57.6 kJ/mol, ln Z= 15.9 1/min (Kohl et al. 1996). The data of the modified melamine resin have a better fit for extruding than that of the conventional one. For the overall cure process, the modified melamine resin can be crosslinked more easily and also take less energy.

Comparison of another thermosetting resin, which is PF resin (E= 97 kJ/mol, ln Z= 23 1/s), the E (28 kJ/mol) and ln Z (7.18 1/s) of the wood-melamine-resin compounds was much lower. This also indicates that the energy that modified

melamine resin needed in order for a crosslinking reaction to take place was lower

than PF resin (Wang et al. 2007).

Table2.5. Kinetic parameters for wood-melamine-resin compounds.

Method		E (kJ/mol)	ln Z (1/min)	n
nth-BD	2℃/min	20.4	5.72	1.06
	5℃/min	31.6	9.27	0.93
	8℃/min	33.2	10.1	1.05
	10℃/min	40.1	12.4	1.14
	15℃/min	44.1	13.8	1.18
	20℃/min	43.3	13.6	1.11
E 698		28.0	11.3	1.00

b. Half-life determination

To complete the ASTM E698 study, isothermal tests were performed on the

wood-melamine-resin compounds because this modified adhesive needs to be

catalyzed by wood to exhibit an exothermic reaction. Additionally, the exothermic

peak area from the baseline of the aged sample should be half that of the unaged

sample to confirm the test. Assuming a first-order reaction and using the above values

for E and Z, the equation to determine the half-life times is: $t_{1/2}=0.693/k$ (Turcotte et

al. 2005). The rate constant (k) for curing reaction could be calculated by Eq. 2.9:

k=Z exp-(E/RT)   Eq. 2.9

From these equations, the k was calculated as 0.0116 and $t_{1/2}$=60 (min). Also, the

temperature for a 1-h half-life was determined as 41℃. Consequently,

wood-melamine-resin compounds of about 5 mg were thermally aged at 41℃ for 60

min. The samples were then cooled to room temperature and reheated to 250℃ using

a heating rate of 10℃/min.

According to the ASTM E698, the exothermic peak area or displacement from

baseline of the aged sample should be half that of the unaged sample. If so, the

reaction kinetics are confirmed for the temperature range explored. The aged and

unaged curves of half-life test are shown in Fig. 2.11. Turcotte et al. (2005) also state

that if the kinetic parameters describe the crosslinking kinetics correctly, then the

enthalpy of the aged sample (ΔH_{aged}) should be half that of the unaged sample

(ΔH_{unaged}). The overall crosslinking average of the aged samples was:

$\Delta H_{aged} = 15.0 \pm 1.24$ (J/g)

compared to that obtained with the unaged samples:

$\Delta H_{unaged} = 29.7 \pm 1.36$ (J/g)

Since $\Delta H_{aged} = 1/2\Delta H_{unaged}$ and the exothermic peak area from the baseline of the aged

sample was half that of the unaged sample, it can be concluded that the values of the

Arrhenius parameters of the wood-melamine-resin compounds by the ASTM E698

method adequately model the kinetics of the crosslinking process.
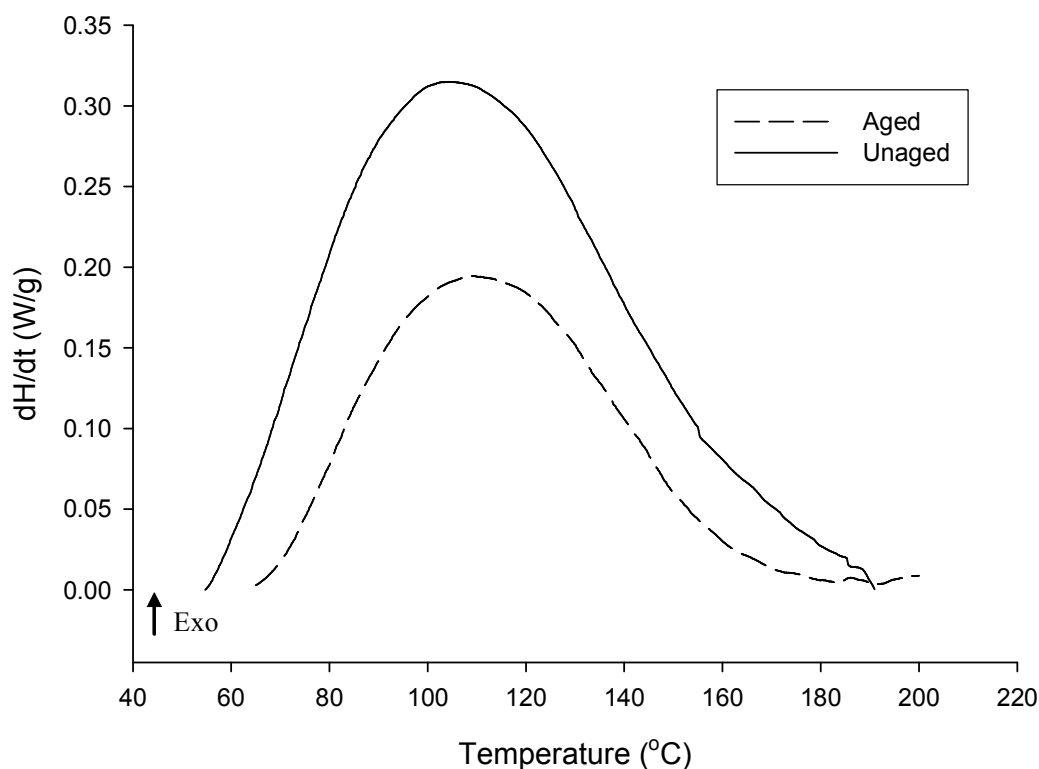
Fig. 2.11. Aged and unaged curves of half-life test obtained at a heating rate of 10℃/min.

2.4.5 Crosslinking reaction by torque rheometry

Prior to extrusion, torque rheometry was used to measure the torque and energy developed during the mixing process of the wood-melamine-resin compounds, which provides information in establishing extrusion processing parameters such as temperature profile and dwell time. The torque rheometry technique also reflects the resistance of the compound to shear deformation during processing (Villechevrolle 2008). In addition, Yang et al. (2005) noted that thermal stress and oxygen will influence the structure of the melting and also change the apparent viscosity of the material. This apparent viscosity can be related to shear stress that is similar to the

torque. In this research, only the torque and energy was determined because they represent the general mixing behavior of the wood-melamine-resin compounds. The trends shown in the following torque and energy figures are representative curves taken from a sample of three runs.

a. Influence of temperature on crosslinking reaction

At all temperatures and formulations, torque decreases rapidly after the initial higher torque associated with loading the material into the test chamber and converged to a minimum value, which corresponds to softening and mixing of the resin. The higher torque in the beginning corresponds to the time when the plunger pushed the material and the filling of the mixing chamber. The initial torque value was sporadic and thus could not be examined. After mixing, a swift rise in the torque marked the onset of curing and formed a peak. This peak represents the crosslinking behavior of the wood-melamine-resin compounds. The torques dropped again after the compounds were cured because the hardened composites had been ground into powders. Braun et al. (2007) stated that the time difference between filling and the crosslinking maximum gives the extrusion processing window.

The crosslink behavior (shown in Table 2.6) was characterized by calculating inflection points and mid-points of the torque curves. The inflection point can be indicated as the time that melamine resin starts to crosslink while the mid-point is

ascribed to mid-time of the curing reaction. In order to avoid the melamine resin

being fully crosslinked inside the screw of an extrusion system, all components

should be extruded before the inflection point. To correspond to extrusion processing,

the period before the inflection point can be reflected by the dwell time, which is also

represents the processing window. Furthermore, based on the experimental data, low

processing temperature provides the best flow characteristics and appears to be

adequate for an extrusion process. However, the processing window would be

narrower during the extrusion processing due to local heating caused by the shear

force of components within the screw area (Braun et al. 2007).

As shown in Figure 2.13, the time required to reach the onset of cure increased

as the temperature decreased. For a given processing time, curing time was reduced

by increasing the processing temperature because the polymer chains formed a 3D

network structure at a faster rate (Matuana and Kim 2007). On the other hand, the

formation of the 3D network would proceed at a slower rate when the processing

temperature is lower.

The curves of the torque energy of 50% melamine resins with 50% wood flour at

various chamber temperatures (see Figure 2.14) show the energy needed for the

mixing process. The energy here represents the work done to process the

wood-melamine-resin compounds, which is dE/dt. It is also the energy consumed

during mixing and can be stated as *WM*, where *W* is the angular velocity and *M* is the

torque. Thus, d*E*/d*t* can be also derived as d*E*= *WM* d*t*. The mechanical energy for

mixing the compounds at a given temperature and rotor speed can be determined by

integration (Supri et al. 2006). The steep slopes might reflect the crosslinking reaction

because the resin is curing and becoming more crosslinked with time and also more

energy is needed for the period. At the beginning of the curves, the higher

temperatures required lower energy, indicating a quicker softening of the melamine

resins. Moreover, the energy required to reach a crosslinking reaction increases as the

temperature decreases. After the compounds were cured the energy became constant

because the crosslinked composites became brittle and were easily ground up.

Table 2.6. Inflection points and mid-points of 50% melamine resins/50% wood flour at various chamber temperatures from torque rheometry.

	Inflection point at (min)	Mid-point at (min)
80℃	5.57 (0.15)	6.30 (0.17)
90℃	4.70 (0.08)	5.43 (0.17)
100℃	3.35 (0.10)	4.08 (0.05)
110℃	2.83 (0.06)	3.67 (0.06)
120℃	1.95 (0.06)	3.15 (0.13)

*Standard deviation in parenthesis.

Fig. 2.12. Plot of torque inflection points and mid-points in log scale versus various chamber temperatures.
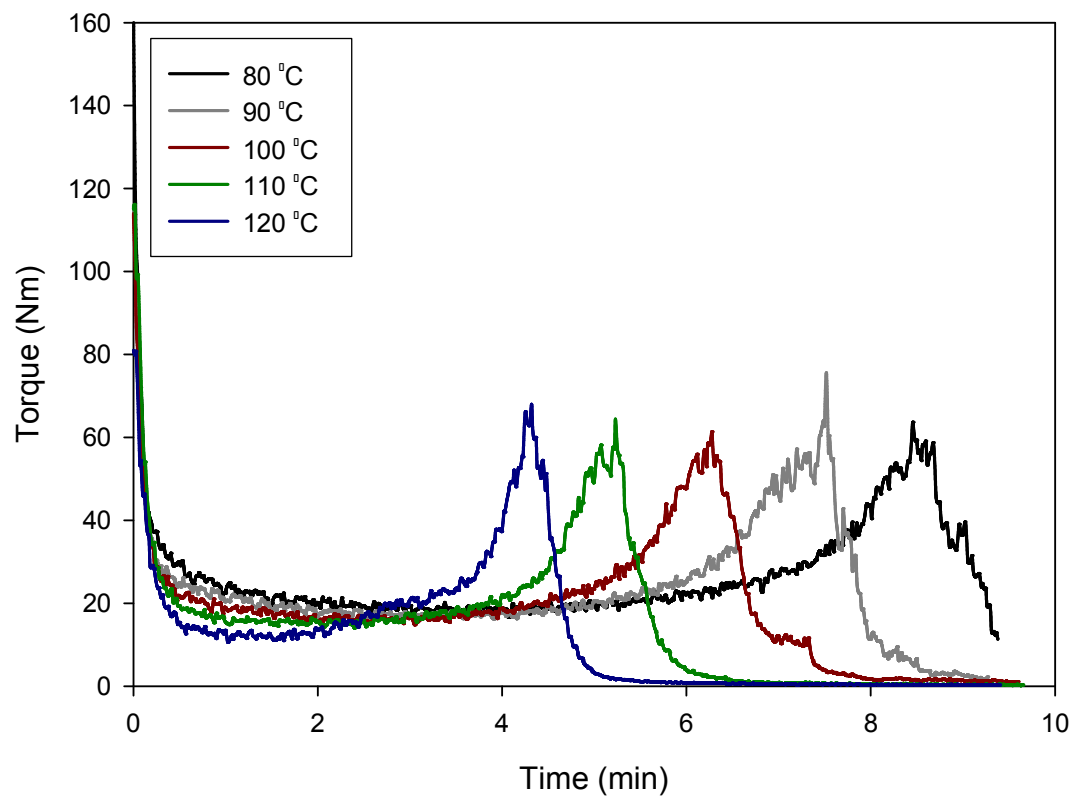
Fig. 2.13. Variation of torque with respect to time of 50% melamine resins/50% wood flour at various chamber temperatures.
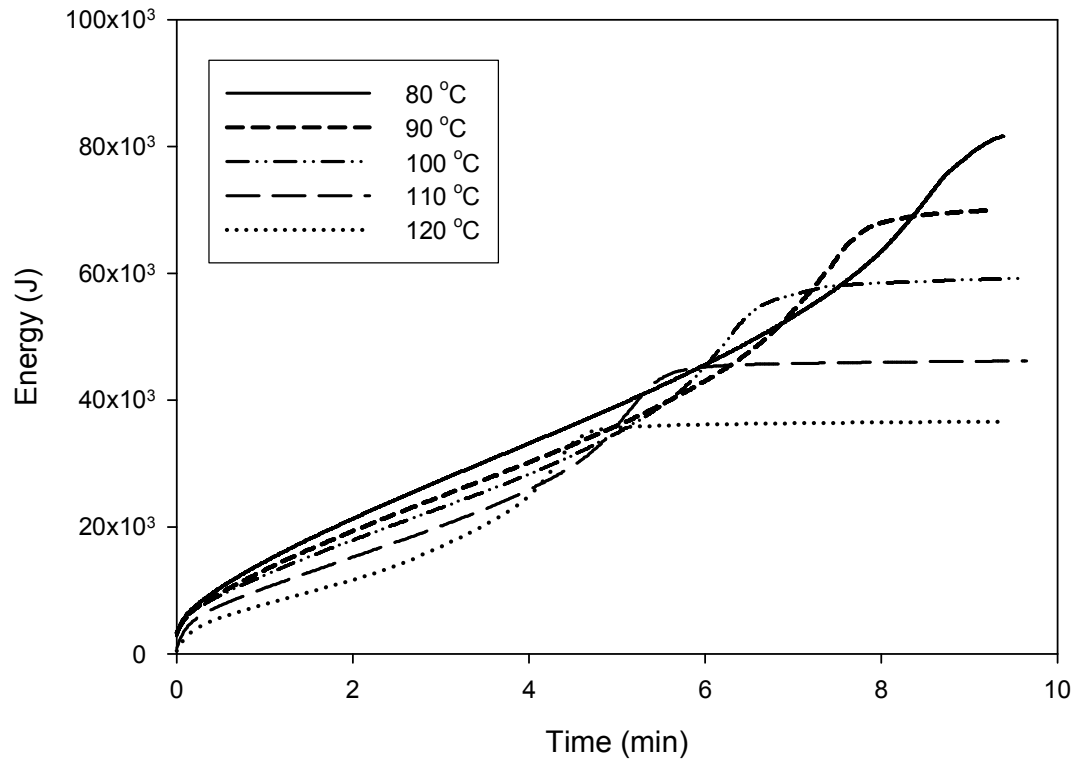
Fig. 2.14. Variation of energy with respect to time of 50% melamine resins/50% wood flour at various chamber temperatures.

b. Influences of wood filler levels on crosslinking reaction

The curing time (shown in Table 2.7) gave the processing parameters for

extruding. The addition of wood flour into the melamine matrix accelerated the curing

reaction. In Figure 2.16, it can be seen that the curing time increased as the amount of

wood flour in the composites decreased since the melamine resins were highly

catalyzed by wood (Braun et al. 2007). Similarly, the addition of wood flour into

melamine resins caused a decrease in energy. For a given processing time,

crosslinking time was reduced by increasing the addition of wood flour, primarily due

to the accelerated cure with increasing wood content. As shown in Figure 2.17, at the

same processing temperature (100℃), more energy is required to reach a curing

behavior as the amount of wood flour in the compounds decreases. Since the

crosslinking time increased as the wood flour content decreased, more thermal energy

would need to be absorbed by the wood-melamine-resin compounds in order to allow

polymers to blend together (Matuana and Kim 2007). Braun et al. (2007) stated that

the reactivity of melamine resin and wood is influenced by the acidity of wood fillers.

Therefore, the more pine fillers resulted in quicker curing and also less energy was

needed during the reactivity.

Table 2.7. Inflection points and mid-points of chamber temperatures 100℃ for various melamine resins/wood flour.

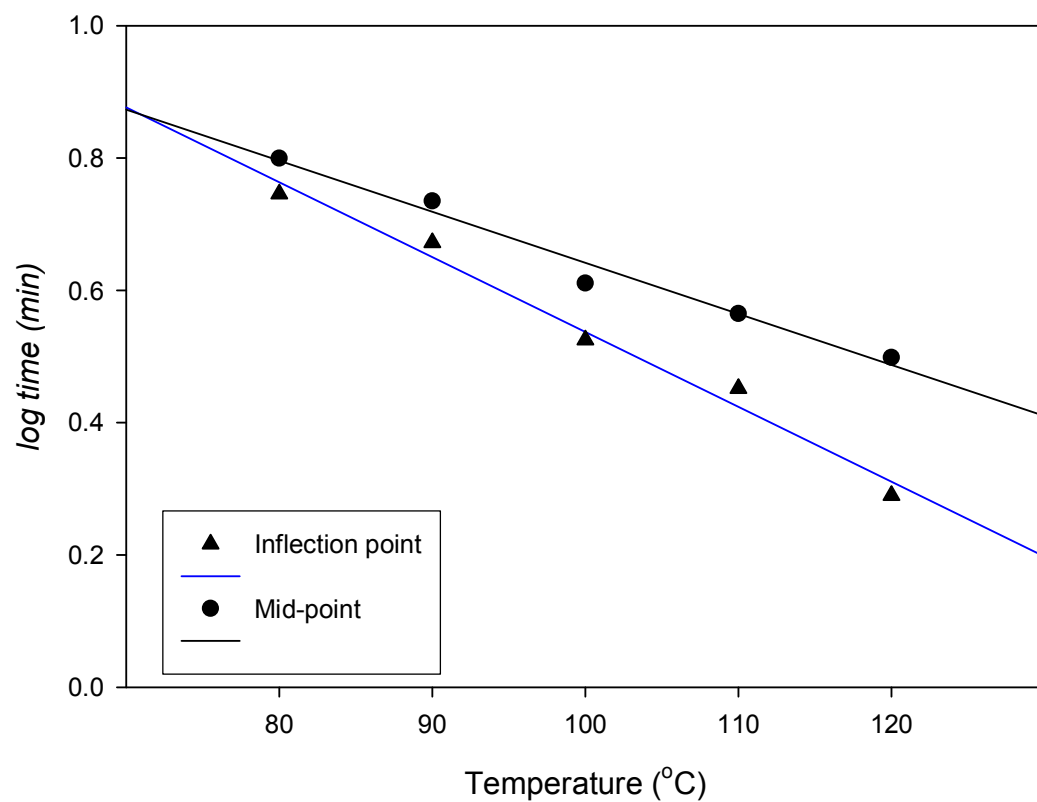|	Inflection point (min)	Mid-point (min)
20% pine with 80% melamine	26.1	44.5
30% pine with 70% melamine	10.6	19.3
40% pine with 60% melamine	4.4	12.4
50% pine with 50% melamine	3.4	4.5
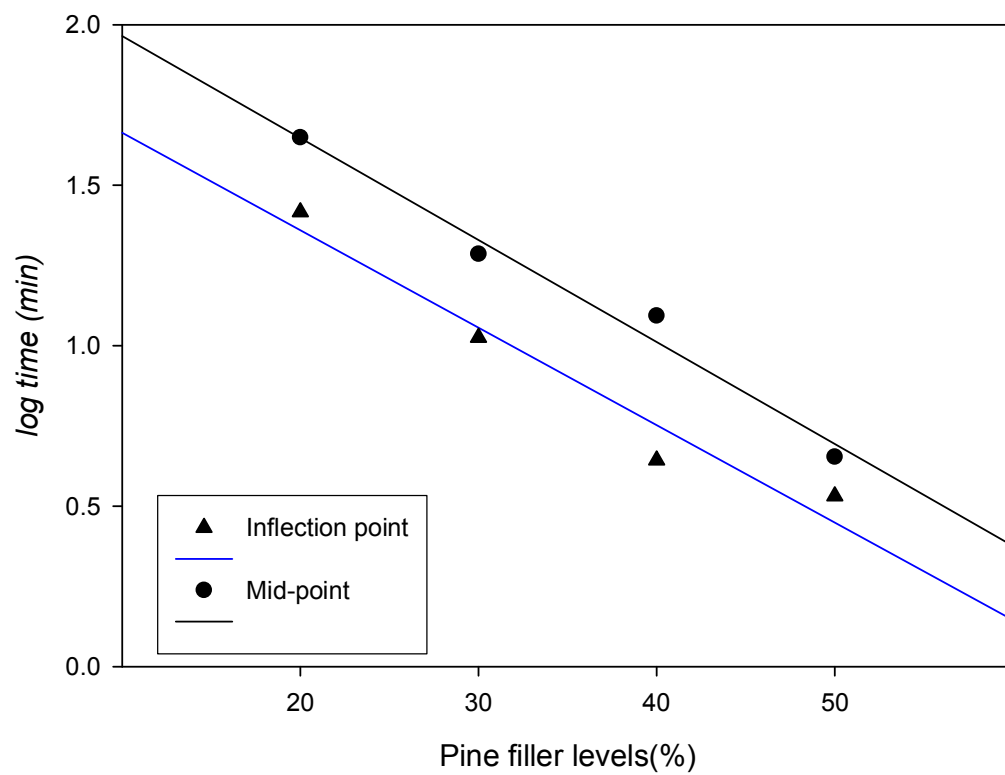
Fig. 2.15. Plot of torque inflection points and mid-points in log scale versus wood filler levels.
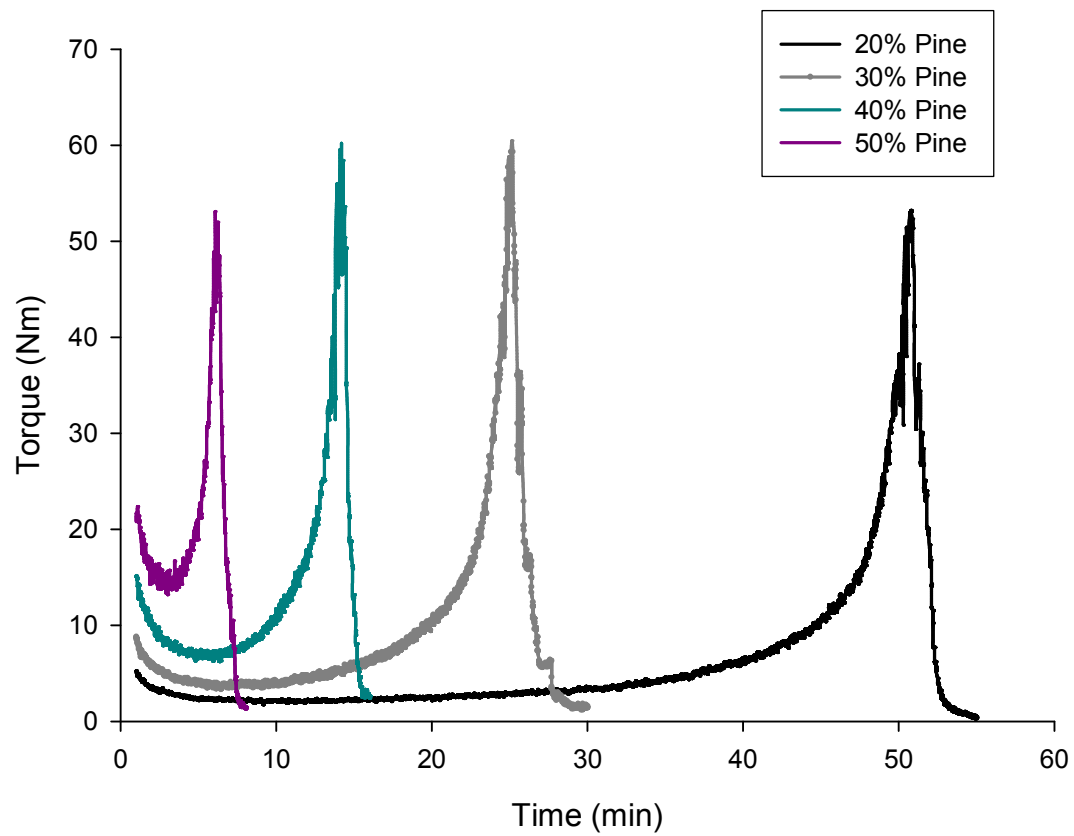
Fig. 2.16. Variation of torque with respect to time of chamber temperatures 100℃ for various melamine resins/wood flour.
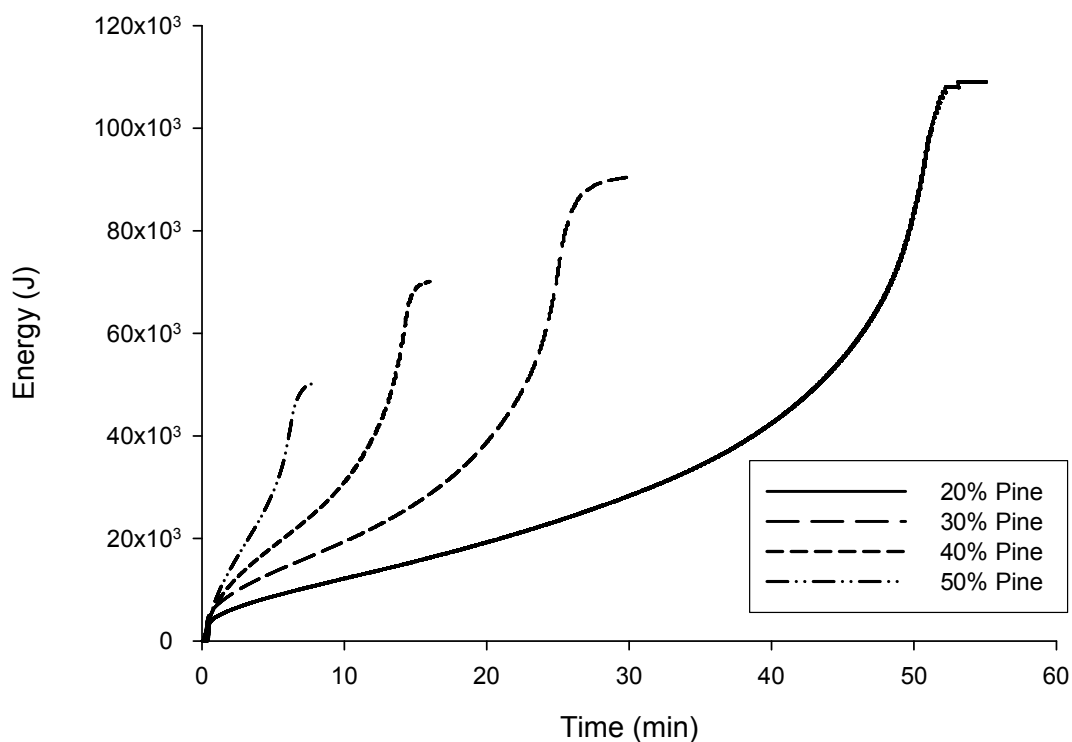
Fig. 2.17. Variation of energy with respect to time of chamber temperatures 100℃ for various melamine resins/wood flour.

2.5 Conclusion

For use in an extrusion system, the neat melamine adhesive (Hipe®esin) showed thermal stability up to 150℃ under inert atmosphere and less than 5% weight loss was found at 200℃. As a result, extrusion processing temperatures below 200℃ can be used in order to prevent the off-gassing problem that occurs and results in a poor adhesion between polymer and wood fillers. The kinetic parameters (*E*, *Z*, and *n*) of the wood-melamine-resin compounds have been determined by using DSC. The *E* and *Z* of modified melamine resin with wood catalyst are lower than the conventional acid

catalyzed melamine formaldehyde resin. Thus, it has a better fit for extruding and also

can be crosslinked more easily during processing.

The torque rheometry results indicated a low extrusion processing temperature

between 70 to 100 ℃. The effect of wood content was also found to dramatically

influence the crosslinking reaction. The quicker curing and a shorter curing

temperature could be associated with a higher wood content.

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CHAPTER 3 PROCESSING OF WOOD PLASTIC COMPOSITES: EXTRUDABLE MELAMINE RESIN (HIPE®ESIN)

3.1 Abstract

Natural fiber composites are commonly used in outdoor environments such as decking and railing. However, undesirable effects on dimensional stability and mechanical properties can be caused by poor moisture resistance of composites. Melamine resin was found to exhibit the highest resistance to water attack. In this research project, a novel melamine resin, modified melamine adhesive (Hipe®esin), was used as a matrix for extruding wood plastic composites (WPCs). This study evaluated the extrusion parameters for the wood-melamine-resin composites, including barrel/die temperature profile and post-extrusion curing. Reducing the processing temperature from 120 to 70℃ increased the strength and modulus of composites, indicating improved adhesion between polymer and wood fillers. Additionally, 6 hours of post-extrusion curing was found to raise the bending strength of composites. On the other hand, there was a negligible affect on the flexural modulus.

Water uptake of the extruded wood-melamine-resin composites was slow because of the high resistance to water attack of melamine resins. Composites that were post-cured in ambient conditions presented better moisture resistance and the

lowest diffusion coefficients. However, samples after 6 hours post-cured at 175℃

showed the best dimensional stability.

3.2 Introduction

Wood plastic composites (WPCs) are usually comprised of wood particulates

and thermoplastic resins, such as high density polyethylene (HDPE),

polyvinylchloride (PVC), polypropylene (PP) or polystyrene (PS). However, a novel

melamine resin was used as a matrix for extruding WPCs in this project. The

modified melamine adhesive (Hipe[®]esin) exhibits thermoplastic-like behavior,

making it useable in an extrusion system. Originally, melamine-formaldehyde (MF)

resins were among the most used adhesives for wood panels due to their high

resistance to water sorption. MF resins have also been used as adhesives for exterior

plywood and particleboard (Pizzi and Mittal 1994).

Crosslinking reaction in reactive extrusion operations by means of peroxide can

also modify the properties of WPCs (Bengtsson et al. 2005). The peroxide is

decomposed at high temperature during the extrusion processing, leading to the

formation of free-radicals (Berzin et al. 2000). The crosslinking reaction is caused by

radical-radical combination (Bengtsson and Oksman 2006a). Reactive extrusion is a

technology that involves the modification of polymers and chemical preparation in an

extrusion system by continuous processing (Carr et al. 1992). This technology is

mainly used to compatibilize polymer blends and also to control the rheology and

crosslinking reaction of polymers. Twin screw extruders are often used to perform

these types of reactions (Berzin et al. 2000).

Comparison of non-crosslinked WPCs, peroxide crosslinked wood/low density

polyethylene composites showed improved adhesion (Bengtsson et al. 2005). Silane

crosslinked wood-PE composites were manufactured by reactive extrusion. According

to Bengtsson et al. (2007), an addition of only 2% of silane solution during processing

was enough to achieve almost 60% degree of crosslinking. The silane solution was

comprised of vinyl-trimethoxy silane and dicumyl peroxide (12:1 w/w). Part of the

silane is grafted onto PE and wood, thus creating a crosslinked network in the matrix

with covalent and hydrogen bonding to wood. Crosslinked WPCs experienced

improvement on toughness and creep properties (Bengtsson and Oksman 2006b). In

addition, crosslinked composites absorbed less moisture during the water boiling test,

so the result can further be a proof of improved interfacial adhesion (Bengtsson et al.

2007).

Haider et al. (2009) have also identified that melamine-resin based WPCs

exhibited higher heat resistance and heat deflection temperatures when compared to

WPCs made of polypropylene (PP). For instance, tensile strength improved 30% and

there was a 16% increase for the tensile modulus at room temperature. Moreover, at a

temperature of 80℃ tensile strength increased 74% and the tensile modulus also improved 29%. Braun et al. (2007) also compared the properties of conventional WPCs containing high density polyethylene (HDPE) or polypropylene (PP) with those of thermosetting wood composites. The WPCs based on thermosetting resins have better thermal properties such as higher creep resistance, high-temperature strength, and improved stiffness and hardness.

WPCs based on thermosetting resins are still not used for commercial applications due to their unsuitable rheological behaviors (Braun et al. 2007). Kiuna et al. (2002) have stated that viscosity of a polymer increases with time while the curing reaction takes place. Moreover, thermosetting resins need more energy and temperature to soften the polymers and crosslinking reactions may occur in die zones during the extrusion processing due to the high processing temperatures. Even today, melamine resin extrusion processes in WPCs are still a novel technology. Prior to extrusion, it is important to know the process parameters for WPCs based on melamine resins in order to prevent them from disintegrating or curing inside an extrusion system.

In this research, not only mechanical performances, but also moisture resistances were determined. In general, the mechanical properties and thermal stability of WPCs can be improved by adding wood when compared to solid plastics. On the other hand,

moisture barriers of the plastic increased the water resistance of WPCs as compared to solid wood and traditional wood composites (Wolcott and Englund 1999). However, Morris and Cooper (1998) have stated that WPCs can still be attacked by fungi, exhibit a decrease in mechanical performance, and experience color change after exposure to the outdoor environment. Previous research also identified that moisture plays an important role in the fungal degradation of WPCs (Clemons and Ibach 2004). Undesirable effects on dimensional stability and mechanical properties can be caused by poor moisture resistance of WPCs (Kazemi-Najafi et al. 2007). The goals of this project are to investigate the process parameters and post-curing towards development of extruded melamine wood flour composites. The goals will be addressed through the following objectives:

1. Define a suitable temperature profile for the extrusion process
2. Utilize extrusion to manufacture melamine-based wood composites
3. Evaluate the influence of various temperature profiles on mechanical and physical properties of the final extruded composites
4. Determine the effect of post-extrusion curing on the mechanical and physical performance of the WPCs

3.3 Materials and Methods

3.3.1 Materials

The WPC formulations were composed of melamine resin, wood flour, and lubricant. Neat melamine resin (HIPE®ESIN, type MPER 4.0 T5 E) with a moisture content of 1.3% was acquired from Agrolinz Melamine International GmbH as a dry

particulate. This modified melamine adhesive exhibits thermoplastic behavior at temperatures between 100 to130℃, and crosslinks at temperatures above 150℃, making it possible to be utilized in an extrusion system.

The wood flour was a commercial 60-mesh eastern white pine (*Pinus strobes*) obtained from American Wood Fibers (Schofield, WI). A commercial lubricant, oxidized polyethylene homopolymers (OPE 629A), provided by Honeywell (Morristown, NJ), was added to the composites to improve processability.

Prior to extrusion, the wood flour was dried to a moisture content of 2% using a steam tube dryer. Wood flour, melamine resin, and lubricant were then mixed in a drum blender for 10 minutes.

3.3.2 Extrusion

A 35 mm conical counter-rotating twin-screw extruder (Cincinnati Milacron CM35) was used for WPC extrusion at a screw speed of 10 rpm. Materials were extruded into a 38×10 mm (1.5×0.4 inches) rectangular cross-sectioned profile die and a water spray cooling system was used upon exiting. Composition of the WPCs studied in this project was 50% wood flour, 47% melamine resin, and 3% OPE 629A, on a weight-basis. Additionally, six various extrusion temperatures (Temp.A to F) were used to extrude composites. These temperature profiles were derived from the

previous torque rheometry results. Processing temperatures were independently

controlled in three barrel zones, two die zones, and a screw temperature (Table 3.1).

Table 3.1. Extrusion profile for WPCs.

Temperature (℃)	A	B	C	D	E	F
Barrel Zone 1 (Feed)	102	102	102	71	66	60
Barrel Zone 2	105	105	105	80	71	64
Barrel Zone 3	110	110	105	80	71	66
Die Zone 1	116	116	105	80	80	82
Die Zone 2	140	140	121	93	88	88
Screw	116	108	102	80	71	65
Melt Temp.	120	118	109	91	82	83
Melt Pressure (psi)	590	333	342	1050	1368	1342
Screw Speed (rpm)	10	10	10	10	10	10

3.3.3 Post-extrusion curing

Post-extrusion curing was utilized since the temperature of the extrusion system

was not reaching the curing temperature range. After preliminary curing from the

processing of extruded WPCs, samples were post-cured in a convection oven at 175

℃ for 1 hour and 6 hours. After post-extrusion curing, the samples were stored in a

20℃ and 50% relative humidity conditioning room for at least 48 hours prior to any

further tests.

3.3.4 Mechanical and physical testing

a. Flexural test

Flexural tests were performed according to ASTM D790 standards. Six samples of 203×39×10 mm (8×1.5×0.4 inches) for each specimen treatment were cut and stored in a 20℃ and 50% relative humidity conditioning room at least 48 hours before the experiment. The test span, 152 mm (6 inches), was 16 times the nominal depth. A screw driven universal test apparatus was used to perform bending testing, while load and deflection were collected in real-time and used to calculate the flexural modulus of elasticity (MOE), the flexural modulus of rupture (MOR), and the strain to failure.

b. Statistical analysis

The influence of extrusion temperature profiles and post-curing on the density of the composites was analyzed by using an analysis of variance (ANOVA). The influence of density was accounted for as a covariate when the effect of density on mechanical properties was significant. In order to sort the influence of extrusion temperature profiles vs. post-curing, mechanical properties were analyzed by using an analysis of covariance (ANCOVA). In addition, $\alpha=0.05$ was utilized through SAS statistical software.

c. Water sorption: moisture resistance

Composites for water absorption tests were planed to a thickness of approximately 7 mm (0.28 inches) in order to remove the polymer-rich surface of the samples. The samples were immersed in a bath of distilled water held at room temperature for 12 weeks (2016 h). The thickness and weight were recorded at predetermined time intervals to determine thickness changes (thickness swelling) and moisture gains (water sorption). Prior to taking measurements, the samples were wiped with a towel and allowed to naturally dry in air for 5 minutes to avoid any surface water. Percentage water sorption (MC) and thickness swelling (TS) were calculated based on the following equations:

$$MC(\%) = \frac{(W_t - W_0)}{W_0} \times 100 \qquad \qquad \text{Eq. 3.1}$$

$$TS(\%) = \frac{(T_t - T_i)}{T_i} \times 100 \qquad \qquad \text{Eq. 3.2}$$

where W_0 is conditioned initial weight and W_t is the weight at time t, whereas T_i is the initial thickness and T_t is the thickness measured at time t.

In addition, the relative rates of moisture sorption for materials could be determined by comparing the Fickian diffusion constant (Rangaraj and Smith 2000). The apparent diffusion constant D_A might be calculated from the slope of the linear region as (Chowdhury and Wolcott 2007, Kim et al. 2008):

$$D_A = \pi \left[\frac{h}{4M_{sat}} \right]^2 \left[\frac{dM_t}{d\sqrt{t}} \right]^2 \qquad \qquad \text{Eq.3.3}$$

where M_{sat} is the percent of weight gain at saturation, h is the thickness of the sample,

and $dM_t/d\sqrt{t}$ is the slope taken from the weight gain versus the square root of time

relation. The apparent diffusion constant given by Equation 3.3 is one-dimensional.

However, the true diffusion constant (D) should be explained by considering a

geometric edge correction factor which was proposed by Rao et al. (1988). Hence, the

corrected diffusion constant is given by (Rangaraj and Smith 2000):

$$D = \frac{D_A}{\left(1 + \dfrac{h}{L} + \dfrac{h}{W}\right)^2} \qquad\qquad \text{Eq. 3.4}$$

where L and W are length and width of the samples.

3.4 Results and discussion

3.4.1 Processing temperatures, post-extrusion curing and mechanical performance

a. Statistical analysis of mechanical properties

The mechanical properties of the WPCs are influenced by the density (Anderson

2007). Facca et al. (2006) predicted that stiffness of composites may be increased by

increasing the composite density. The ANOVA results (as shown in Table 3.2) give

significant differences in the composite density when incorporating various

processing temperatures and post-extrusion curing conditions. Therefore, the

mechanical properties normalized to a mean density are appropriate. By using this

method any variation in properties due to changes in density can also be eliminated

(Anderson 2007).

Interpretation of the ANCOVA results (Table 3.3) for MOE suggests that either

processing temperatures or post-extrusion curing have a significant effect on MOE.

Examination of the Tukey groupings does not indicate differences between Temp.

Profile A, C, D, and, F. However, the Tukey grouping suggests that Temp. Profile E

has a significant effect on modulus. Similarly, in averaging the effect of post-curing,

the Tukey grouping also suggests a significant effect.

The results from the ANCOVA (Table 3.4) lead us to conclude that all effects for

MOR are significant. The effect of Temp. Profile is still highly significant, but less

than with MOE because the strength properties are more influenced by post-curing.

Moreover, the Tukey grouping suggests that Temp. Profile F has a significant effect

on flexure strength. The Tukey groupings also support the notion of significant

differences in strength between all post-curing. Six hours post-curing is the most

effective method on MOR.

Table 3.2. Type III ANOVA and Tukey grouping for effect of temperature profiles and post-curing on density (R^2=0.74).

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Temp. profile	5	0.09	0.02	13.4	<0.0001
Post-curing	2	0.27	0.14	106	<0.0001

Temp. profile	A	B	C	D	E	F
Tukey Grouping	A	B	B	B	A	A
Mean (GPa)	1.02	0.96	0.98	0.99	1.02	1.04

Post-curing	0 hr	1 hr	6hrs
Tukey Grouping	A	B	B
Mean (GPa)	1.08	0.97	0.96

Table 3.3. Type III ANCOVA and Tukey grouping for effect of temperature profiles and post-curing on MOE (R^2=0.81).

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Temp. profile	5	5.02	1.00	22.2	<0.0001
Post-curing	2	8.17	4.09	90.5	<0.0001
Temp.* Post-curing	10	2.66	0.27	5.90	<0.0001
Density	1	6.45	6.45	143	<0.0001

Temp. profile	A	B	C	D	E	F
Tukey Grouping	B	C	B	B	A	B
Mean (GPa)	2.68	2.14	2.57	2.63	3.03	2.55

Post-curing	0 hr	1 hr	6hrs
Tukey Grouping	C	B	A
Mean (GPa)	2.46	2.61	2.75

Table 3.4. Type III ANCOVA and Tukey grouping for effect of temperature profiles and post-curing on MOR (R^2=0.72).

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Temp. profile	5	652	130	4.71	0.0007
Post-curing	2	1991	996	36.0	<0.0001
Temp.* Post-curing	10	881	88.1	3.18	0.0016
Density	1	387	387	14.0	0.0003
Temp. profile	A	B	C	D	E	F
Tukey Grouping	BC	D	CD	AB	AB	A
Mean (MPa)	17.0	10.3	13.6	18.8	21.9	23.0
Post-curing	0 hr		1 hr		6hrs	
Tukey Grouping	C		B		A	
Mean (MPa)	10.5		18.3		23.5	

b. Effect of extrusion temperatures on mechanical properties

The suitable processing temperatures for extruded WPCs are the barrel and die temperatures that are necessary to create a good melt flow for components within the extrusion system. Extrusion temperatures below 200℃ are typically used in order to reduce wood degradation and volatile formation (Sabeb and Jog 1999). Based on our work with the wood-melamine-resin compounds in torque rheometry, the processing temperature for this melamine resin appears to require a low temperature (70 to 100℃) to prevent the melamine resin from being fully crosslinked inside the die zones of an extrusion system and subsequent breakdown of the material. The results of the torque rheometry mixing test also indicated that a longer processing window, which can provide a good flow and melt strength, was associated with a lower temperature (Chen 2009). However, materials residing in the die zones for a long time might be

damaged due to the local heating caused by the shear force of components within the screw area.

With the load and the related extension, the modulus of rupture (MOR) and the modulus of elasticity (MOE) can be calculated using the formulas provided by ASTM D790. Mechanical properties are listed in Tables 3.5 to 3.7 for the wood-melamine-resin composites extruded with different temperatures and post-extrusion curing conditions. Interpretation of this data for the composites indicates that reducing a processing temperature from 120 to 70℃ increased the MOR and the MOE. The extruding temperature strongly influenced the mechanical performances of composites: composites extruded by low temperature (temperature Profile E) presented the best MOE and MOR either post-cured in the condition room or 6 hours of post-curing. For instance, reducing the extruding temperature from 120 to 70℃ without high temperature of post-curing increased the MOR (from 6 to 18 MPa) and the MOE (from 2 to 4 GPa). Low processing temperature with 6 hours of post-curing (175℃) also increased 73% of the MOR (from 22 to 38 MPa), but had a negligible influence on MOE.

The MOR and MOE for the wood-melamine-resin composites were lowest for temperature Profile A and B in which the processing temperature was high. As shown in Figure 3.1, the dramatic decrease in MOR at a high processing temperature may be

associated with the decrease of processing melt pressure (Table 3.1). Moreover, high

temperature might affect all components pre-cured in the extruder and damage the

composites. Low processing temperature was found to increase melt pressures at the

extruder exit in order to assist the penetration of the polymer into the wood fiber voids

(Hatch 2008). Melt pressures are shown in Table 3.1 and indicate that at temperature

profiles of A and E the melt pressure are 590 and 1368 psi, respectively. However,

lower MOE and MOR in the samples extruded with Temp. F, which is the lowest

processing temperature (60 to 65℃), compared to the ones extruded at 66 to 71℃

(Temp. E) could be explained by the lower melt pressure in Temp. F. The other

reason might be that the long dwell time of the components resulted in the materials

being damaged by local heating caused by the shear force of components within the

screw area.

When comparing the silane crosslinkable polyethylene/wood flour composites

without post-curing, MOR of the wood-melamine-resin composites is lower but MOE

is 35% higher. Also, the strain at break of the wood-melamine-resin composites is

much lower (Bengtsson and Oksman 2006 b). Thus, we can conclude that the

wood-melamine-resin composites are more rigid, but also more brittle than the silane

crosslinkable polyethylene/wood flour composites. Overall, the mechanical

performances of the wood-melamine-resin composites are better than the

conventional wood-HDPE composites (as shown in Table 3.8). The extrusion

processing temperature of the wood-melamine-resin composites are also lower than

HDPE which is approximately 170℃. Thus, the processing of the

wood-melamine-resin composites is not only improves the properties but also save

some energy since low processing temperature is needed.

Table 3.5. Mechanical properties, density, and processing screw temperatures of extruded wood-melamine-resin composites at condition room post-extrusion curing.

	Screw Temp. (℃)	Modulus of Rupture (MPa)	Modulus of Elasticity (GPa)	Strain at Failure (%)	Density (g/cm^3)
Temp. 1	116	6.23 (0.27)	2.41 (0.12)	0.3 (0.05)	1.06 (0.02)
Temp. 2	108	5.20 (0.70)	1.77 (0.48)	1.1 (0.4)	0.99 (0.02)
Temp. 3	102	7.74 (0.76)	2.57 (0.18)	0.6 (0.2)	1.03 (0.01)
Temp. 4	80	11.63 (1.80)	2.60 (0.29)	0.6 (0.1)	1.07 (0.02)
Temp. 5	71	17.60 (2.36)	3.10 (0.51)	0.7 (0.05)	1.15 (0.05)
Temp. 6	65	12.77 (2.61)	2.42 (0.47)	0.7 (0.03)	1.14 (0.06)

*Standard deviation in parenthesis.

Table 3.6. Mechanical properties, density, and processing screw temperatures of extruded wood-melamine-resin composites at 1-hour post-extrusion curing.

	Screw Temp. (℃)	Modulus of Rupture (MPa)	Modulus of Elasticity (GPa)	Strain at Failure (%)	Density (g/cm^3)
Temp. 1	116	24.97 (1.37)	2.93 (0.05)	0.9 (0.1)	1.01 (0.01)
Temp. 2	108	8.05 (2.21)	2.14 (0.27)	0.6 (0.1)	0.95 (0.01)
Temp. 3	102	8.59 (1.10)	2.56 (0.24)	0.6 (0.2)	0.97 (0.02)
Temp. 4	80	17.75 (3.31)	2.48 (0.13)	0.8 (0.1)	0.94 (0.01)
Temp. 5	71	16.36 (2.87)	3.07 (0.19)	0.8 (0.2)	0.96 (0.03)
Temp. 6	65	26.45 (6.30)	2.52 (0.43)	1.1 (0.1)	0.99 (0.03)

*Standard deviation in parenthesis.

Table 3.7. Mechanical properties, density, and processing screw temperatures of extruded wood-melamine-resin composites at 6-hours post-extrusion curing.

	Screw Temp. (℃)	Modulus of Rupture (MPa)	Modulus of Elasticity (GPa)	Strain at Failure (%)	Density (g/cm^3)
Temp. 1	116	22.17 (1.34)	2.93 (0.12)	0.8 (0.1)	1.00 (0.01)
Temp. 2	108	16.79 (4.87)	2.45 (0.27)	0.8 (0.1)	0.93 (0.03)
Temp. 3	102	21.54 (3.00)	2.67 (0.16)	0.9 (0.1)	0.95 (0.01)
Temp. 4	80	33.37 (6.39)	2.91 (0.16)	1.0 (0.2)	0.94 (0.02)
Temp. 5	71	33.38 (4.14)	2.96 (0.19)	1.3 (0.3)	0.96 (0.01)
Temp. 6	65	26.40 (6.92)	2.83 (0.46)	1.2 (0.1)	1.00 (0.03)

*Standard deviation in parenthesis.

Table 3.8. Mechanical properties and density of various WPCs.

Composite	Density (g/cm^3)	MOR (MPa)	MOE (GPa)
50%WF+47%melamine+3%lubricant	0.96 (0.01)	33.4 (4.14)	2.96 (0.19)
50%WF+47%HDPE+3%CA	1.04 (0.15)	25.5 (1.00)	1.88 (0.03)
50%WF+50%HDPE	1.01 (0.20)	15.6 (1.50)	1.42 (0.04)

*WF and CA codes were used for the wood flour and coupling agent. Standard deviation in parenthesis. (Adhikary et al. 2008).

c. Influence of post-extrusion curing on mechanical properties

It is important to create an excellent curing for the melamine resins during processing since the goal of curing is to form a rigid structure of a polymer material by crosslinking of polymer chains. However, in order to prevent the polymer matrix from disintegrating or curing inside the extruder, post-extrusion curing was necessary for this research. There are two approaches that are commonly used in extruding technology. One is to try to soften mixtures and to cure all of the components within the extrusion system. The other approach is to mix or blend and form all components

in the extruder and then post-cure the composite afterwards. In this project, the materials were mixed and formed in the extrusion system and then post-cured in the oven. One hour and 6 hours post-extrusion curing were used to compare with non-post-oven-curing composites that were cured in the condition room. As shown in Figures 3.1 to 3.2, there is a 150% (in mean value) of improvement in flexural strength for composites with post-extrusion curing (6 hours) when compared to composites without post curing. Additionally, 6 hours of post-extrusion curing was found to raise the MOR more than 1 hour post-curing. However, being post-cured for a longer period (6 hours) at high temperature (175℃) was found to have a negligible effect on MOE because the polymer chains could be crosslinked at a higher degree and formed rigid and brittle 3D network structures.

Bengtsson and Oksman (2006 b) found that crosslinked polyethylene/wood flour composites that were post-cured in a 90℃ sauna for 24 hours resulted in a 15% improvement for flexural strength compared to those without post-curing. This result could be explained by the higher degree of crosslinking in the post-cured samples. The 175℃ oven post-curing used in this project seems to be an efficient treatment since samples can increase 150% in flexural strength within 6 hours of post-curing. However, the other explanation for Bengtsson and Oksman's study (2006b) could be that a high degree of crosslinking reaction mainly takes place during the higher

extrusion temperatures (165 to 200℃). In addition, the temperatures (70 to 100℃) used for extruding wood-melamine-resin composites were only to mix and form all components in the extruder. Therefore, the post-extrusion curing was crucial for the mechanical performances of the wood-melamine-resin composites.
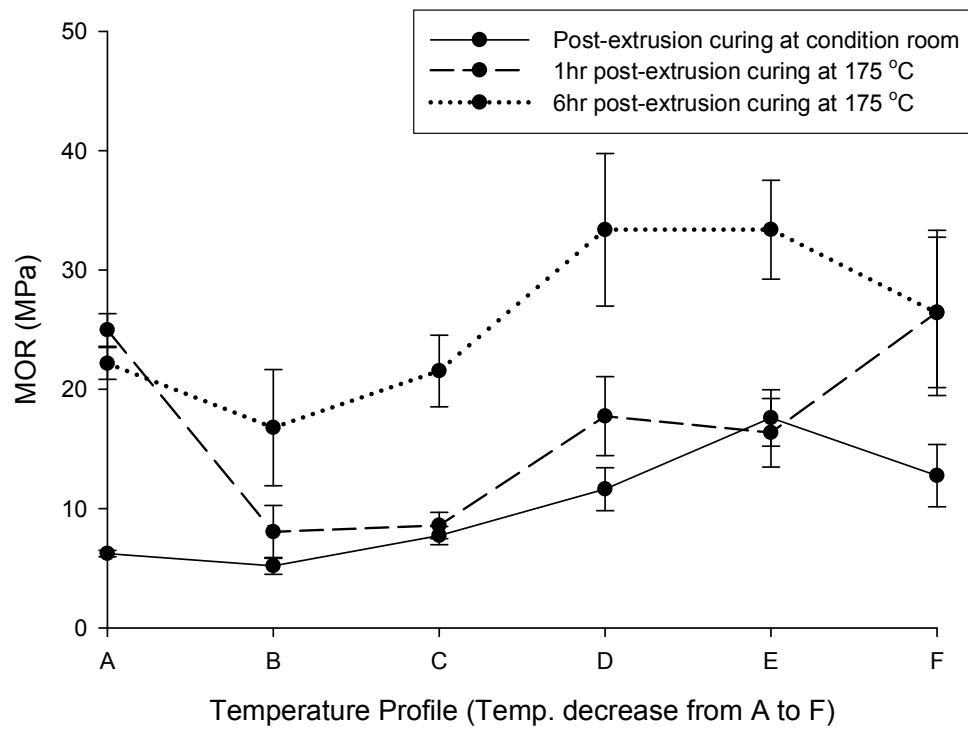

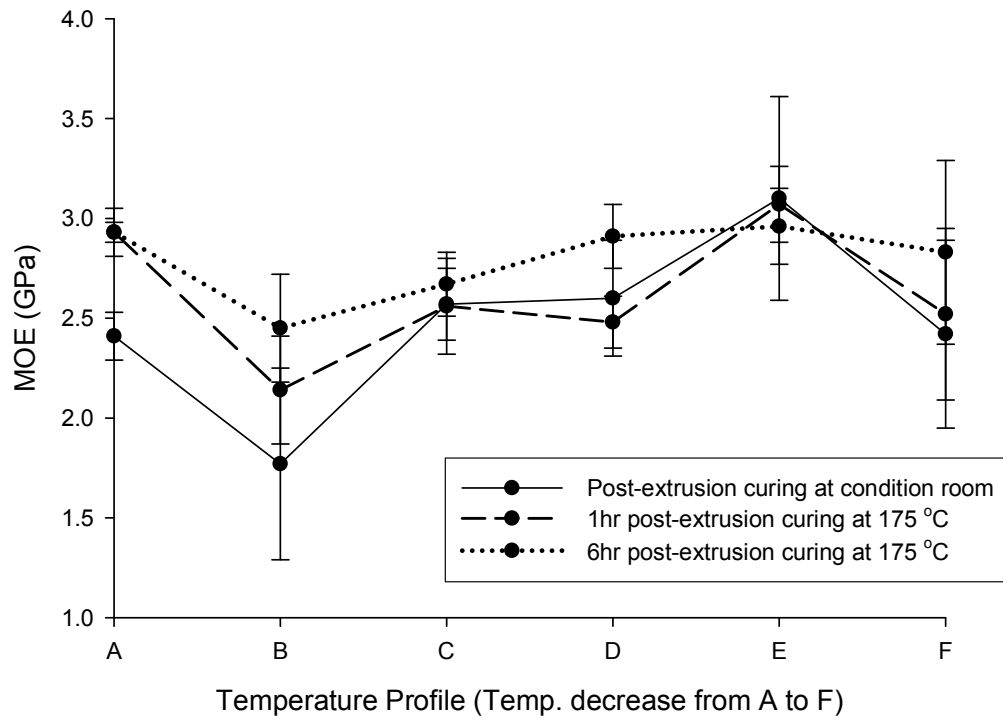**Fig. 3.1.** Modulus of rupture (MOR) of extruded wood-melamine-resin composites.

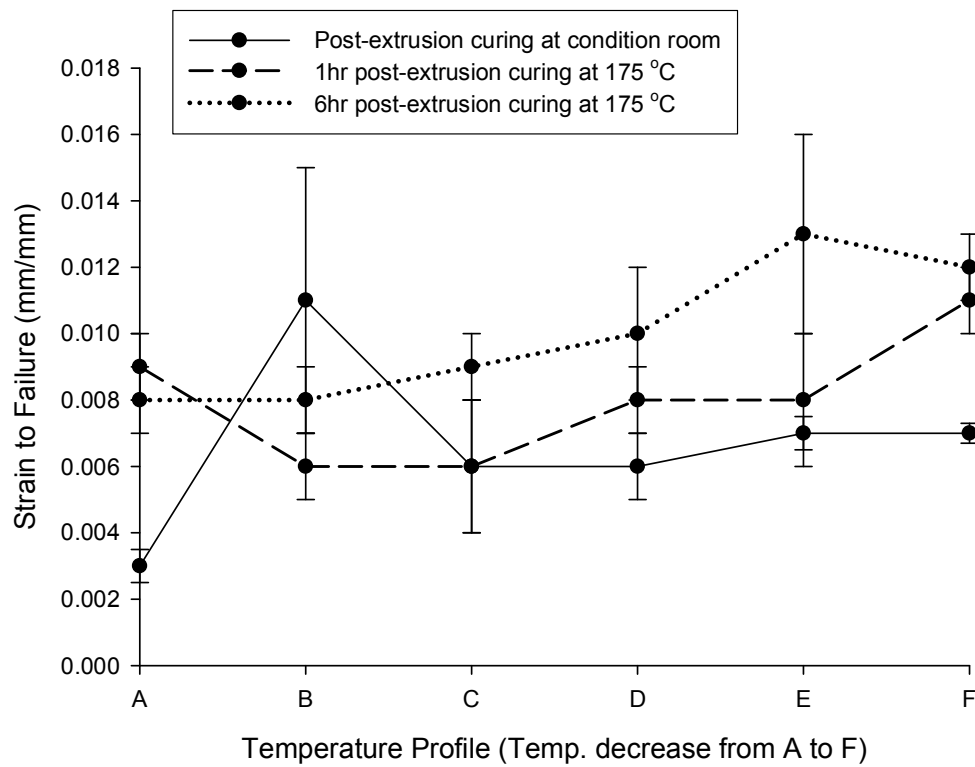**Fig. 3.2.** Modulus of elasticity (MOE) of extruded wood-melamine-resin composites.

Fig. 3.3. Strain to failure of extruded wood-melamine-resin composites.

3.4.2 Moisture resistance

Although WPCs show better durability than solid wood, a study has stated that WPCs can still be attacked by fungi, exhibit a decrease in mechanical performances, and experience color change after exposure to the outdoor environment (Morris and Cooper 1998). Previous research also identified that moisture plays an important role in the fungal degradation of WPCs (Clemons and Ibach 2004). Therefore, it is important to understand the water sorption behavior of extruded wood-melamine-resin composites in order to estimate the consequences of how much water WPCs absorbed.

a.Water sorption and diffusion

There are two major mechanisms of water sorption: one is natural sorption of the wood fillers, and the other is penetration of moisture into composites. For instance, weak bonding that gaps and flaws at the interface between wood fillers and polymers also causes the moisture sorption (Kazemi-Najafi et al. 2007). The moisture weight gain for the extruded wood-melamine-resin composites was plotted against the square root of time in Fig. 3.4. Water uptake was slow as compared with wood-HDPE and wood-PP composites with the same wood filler and polymer contents. The maximum saturation time of composites containing HDPE was 1300 h, and they also showed a longer saturation time than those made from PP (Kazemi-Najafi et al. 2007). However,

samples in this research did not reach equilibrium after 2016 hours of immersion.

Comparing the wood-PP and wood-HDPE composites, the higher water uptake of the

extruded wood-melamine-resin composites might be because of the incomplete

adhesion of wood fillers and matrix, creating gaps and flaws at the interfaces. The

results are unexpected and not in agreement with the literature on the conventional

melamine formaldehyde adhesives, since Pizzi and Mittal (1994) have stated that

resins are among the most used adhesives for exterior wood panels because of their

higher resistance to water attack.

For the moisture property tests, samples manufactured by temperature Profile F

which are related to better mechanical performances were used to for immerseion.

Comparison of various post-extrusion curing showed that those samples that were

post-cured in the condition room at room temperature had better moisture resistance

because of less voids and sorption by capillarity. It would also make sense that high

crosslinking temperature increases curing shrinkage and also causes more voids in the

composites. The diffusion constants of the extruded wood-melamine-resin composites

are presented in Table 3.8 and range from 3.61e-6 to 5.51e-6 mm^2/sec. The lowest

diffusion coefficients were found in samples stored in the condition room at room

temperature. The findings seem to support the same result and conclusion that have

been drawn for water uptake.

b. Thickness swelling

The thickness swelling of the samples (as shown in Fig.3.5) showed an opposite result to the water uptake data. Maximum thickness swelling (TS_{max}) at the end of the test was from 5 to 8% for the extruded wood-melamine-resin composites after 12 weeks immersion. The samples that experienced the highest TS_{max} were those that were post-cured in the condition room the room temperature. In addition, the highest swelling coefficient ($\beta = TS_{max} / MC_{max}$), as shown in Table 3.9, were also found with the condition room post-curing. On the other hand, even though samples after 6 hours post-cured at 175℃ absorbed more moisture, the TS_{max} was still lower than those post-cured in the condition room. A possible explanation for those results includes that high crosslinking temperature increases curing shrinkage and also causes more voids in the composites, which could raise the water uptake by capillarity. However, samples after 6 hours post-cured experienced the best mechanical performances; it also indicated that the adhesion of wood to the polymer was improved. Therefore, although wood fillers in the 6 hours of post-curing samples absorbed more water, the dimensional stability of WPCs was still good enough and did not swell more than those in the condition room post-curing.

Table 3.9. Average (standard deviation) maximum moisture content, diffusion constant, swelling coefficient, and maximum thickness swelling of extruded wood-melamine-resin composites after 2016 h of water sorption.

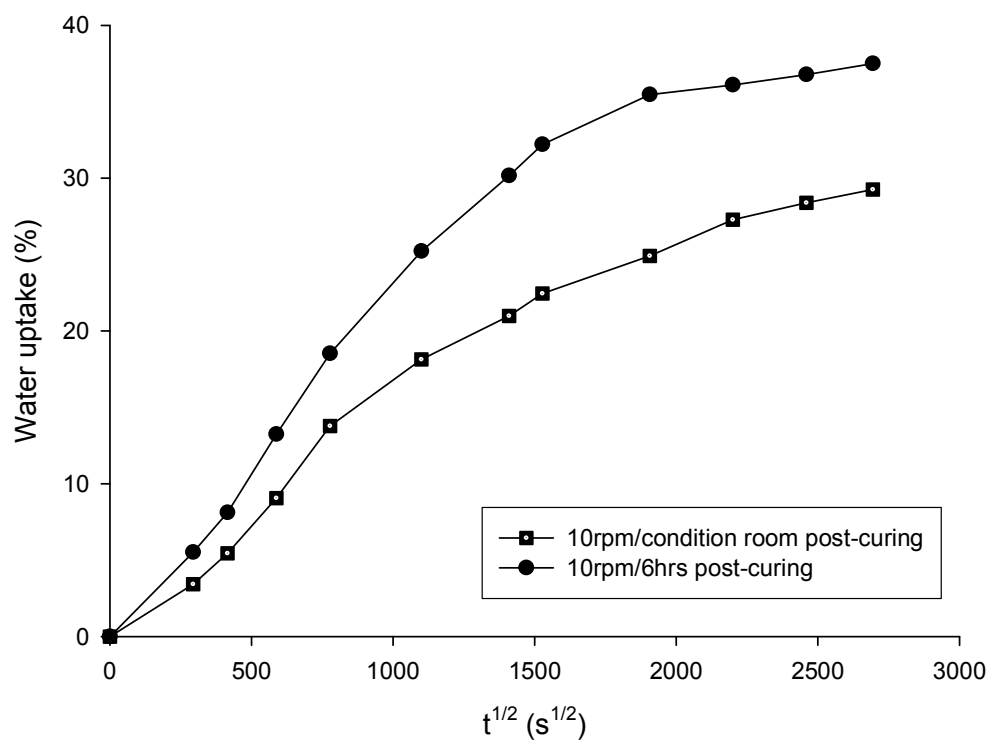| Post-curing	MC_{max} (%)	D (mm^2/sec)	β	TS_{max} (%)
condition room	29.3 (0.33)	3.61E-06	0.286	8.38 (0.31)
6 hrs	37.5 (0.44)	5.51E-06	0.160	5.99 (1.62)

*Standard deviation in parenthesis.

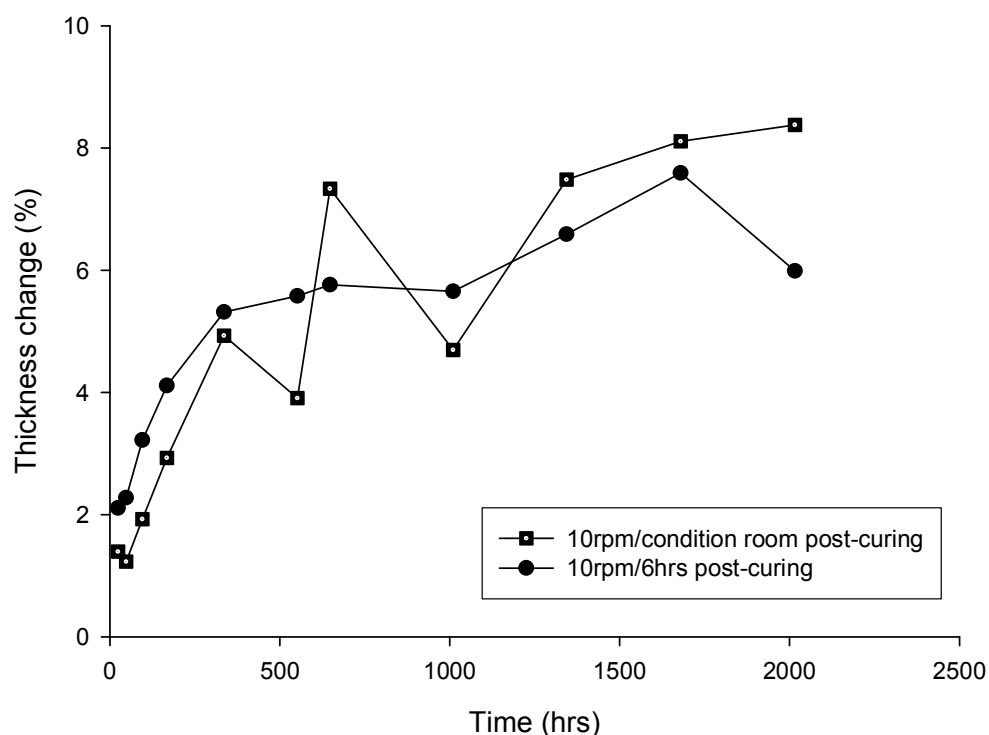**Fig. 3.4.** Water uptake of extruded wood-melamine-resin composites.

Fig. 3.5. Thickness swelling during moisture sorption of extruded wood-melamine-resin composites.

3.5 Conclusion

Mechanical performance of the extruded wood-melamine-resin composites is governed by many processing variables. Extrusion processing temperatures were found to have an effect on composite mechanical performances, while composites manufactured at lower temperature (66 to 71℃), which provided adequate melt pressure and strength to facilitate the forming of composites, exhibited an increase in flexural strength. Low processing temperature was also found to increase melt pressures at the extruder exit and to assist the penetration of the polymer into the wood fiber voids. However, reduced mechanical performances were found at processing temperatures below 65℃. Therefore, processing temperatures below 65℃

are not recommended for extruding wood-melamine-resin composites, since the

materials might be damaged by the local heating caused by the shear force of

components within the screw area for a long time. Moreover, 6 hours post-cured at

175℃ was found to increase 150% in flexural strength. Thus, the post-extrusion

curing was crucial for improving the mechanical performances of the

wood-melamine-resin composites.

In a comparison of various polymers (PP and HDPE), water uptake of the

extruded wood-melamine-resin composites was slow but absorbed more water. The

results are not in agreement with the literature on the conventional high water

resistance melamine formaldehyde adhesives. Composites that were post-cured in the

condition room at room temperature had better moisture resistance and lowest

diffusion coefficients. However, samples after 6 hours post-cured at 175℃ presented

the best dimensional stability.

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CHAPTER 4 CONCLUSIONS AND FUTURE WORK

4.1 Conclusions

Current extruded wood plastic composites (WPCs) are usually comprised of thermoplastics and have been developed for many low strength applications. The challenges for the WPCs industry and research include improving long-term load properties, durability, stiffness, and toughness. Thus, the future improvement of WPCs requires the development of higher strength and moisture resistant composites. Numerous researchers have stated that crosslinking is a technique for modifying wood composites and also improves the properties. Moreover, previous studies have found that modified melamine resin exhibits higher tensile strength, heat resistance and heat deflection temperatures in WPCs made of polypropylene (PP). The resin also shows good adhesion to wood filler. However, extrusion of WPCs consisting of melamine resin has been largely ignored due to the unsuitable polymer flow and viscosity for the extruding. The primary goals of this research were to; 1) to understand the crosslinking behaviors and mixing characteristics of the wood fiber filled melamine resins: 2) to develop an extrusion processing methodology: and 3) to determine the physical and mechanical performances for each composite with respect to processing temperatures design.

Utilizing thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques, the neat melamine adhesive (Hipe®esin) showed thermal stability up to 150℃, but less than 5% weight loss was found when heating up to 200℃. As a result, in order to prevent the off-gassing problem that occurred within an extrusion system during the processing and which resulted in   poor adhesion between polymer and fillers, extrusion processing temperatures below 200℃ can be used. During thermal dynamic testing, exothermic peaks were exhibited in all of the heat flow curves, while the curing temperature increased with increasing heating rate. The kinetic parameters (E, Z, and n) of the wood-melamine-resin compounds have also been determined by using DSC. The E and Z of modified melamine resin with wood catalyst are lower than the conventional acid catalyzed melamine formaldehyde resin. Thus, the modified melamine resin has a better fit for extruding and can also be crosslinked more easily during processing.

Torque rheometry was used to determine the processing parameters because the time difference between filling and the crosslinking maximum creates an extrusion processing window. In addition, the crosslink behavior was characterized by calculating inflection points and mid-points of the torque curves. The inflection point can be indicated as the time that melamine resin starts to crosslink, while the mid-point is ascribed to mid-time of the curing reaction. Based on the test results, a

low processing temperature between 70 to 100 ℃ provides the best flow characteristics and appears to be adequate for extrusion processing. The effect of wood content was also found to dramatically influence the crosslinking reaction, and a higher wood content caused a quicker curing and a lower curing temperature.

Extruded wood-melamine-resin composites were largely affected by extrusion processing and post-curing temperatures. Composites manufactured at lower temperature profile (approximately 70 ℃) exhibited an increase in flexural strength. Furthermore, 6 hours post-cured at 175℃ was found to promote composite mechanical properties because a rigid structure of a polymer material was formed by crosslinking reaction of polymer chains. Water uptake of the extruded wood-melamine-resin composites was slow because of the higher resistance to water attack of melamine resins when compared to high density polyethylene (HDPE) and polypropylene (PP).

This study has provided a better understanding of extruded wood-melamine-resin composites. The kinetics of the crosslinking reaction of the neat melamine adhesive (Hipe[®]esin) have been shown. Determinations were also made as to the impact of temperature, extrusion processing, and post-curing on MOE, MOR, strain to failure, and moisture resistance. Physical and mechanical properties of extruded

wood-melamine-resin composites indicate potential in durability, stiffness, and high

temperature resistance applications.

4.2 Future work

This research only addresses the initial phase of development for extruded

wood-melamine-resin composites. Further testing of various wood filler levels and

other formulations should be performed, since only one formulation was used in this

study. In addition, more study is needed to investigate the potential of these

composites with respect to impact resistance, creep resistance, cyclic weathering, and

other factors affecting composite performances.

APPENDIX A INFLUENCE OF NON-WOOD FILLERS ON CROSSLINKING

BEHAVIOR BY TORQUE RHEOMETRY

A.1 Methods and materials

A torque rheometer, Haake Rheomix 600 with a 69ml net chamber capacity, was

used to evaluate mixing characteristics of neat melamine resin with other non-wood

fillers. Testing was performed on a 50g sample at a screw speed of 50 rpm for 10

minutes.

A.2.1 Effect of temperatures on crosslinking behavior of neat melamine

100% neat melamine resin (by total weight) was mixed at temperatures of 100,

130, and 150℃ for 10 minutes. Torque data were used to evaluate the crosslinking

time at different temperatures.

A.2.2 Effect of 10% of moisture content on crosslinking behavior of neat melamine

100% neat melamine resin with 10% water (by total weight) was mixed at

temperatures of 100℃ for 10 minutes.

A.2.3 Influence of talc on crosslinking behavior of neat melamine

Fifty percent neat melamine resin with 50% talc (by total weight) was mixed at

temperatures of 100℃ for 10 minutes.

A.2.4 Influence of talc on crosslinking behavior of neat melamine

Fifty percent neat melamine resin with 50% cellulose fiber (by total weight) was

mixed at temperatures of 100℃ for 10 minutes.

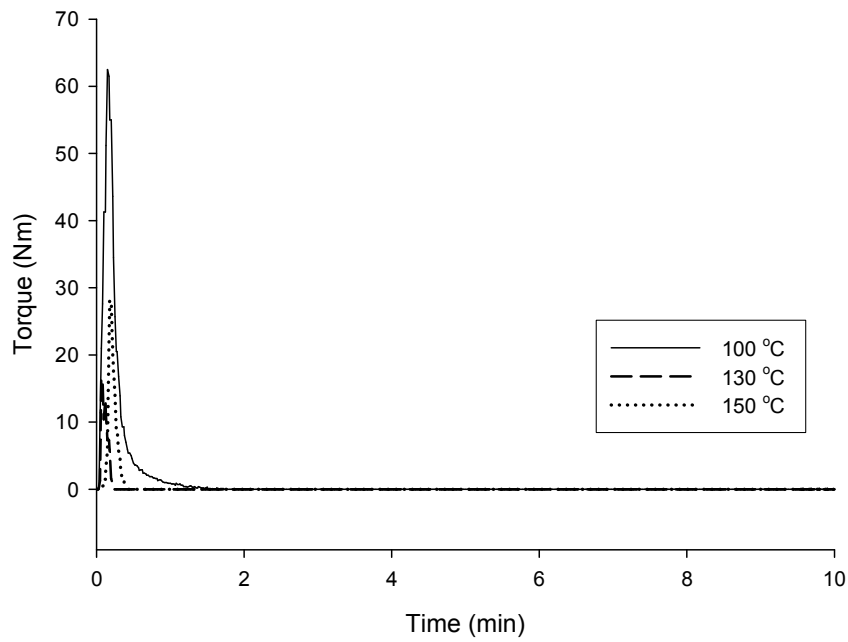**A.2 Results of torque and energy tests for neat melamine and non-wood fillers**

Fig. A.1. Variation of torque with respect to time of 100% melamine resins at various chamber temperatures.
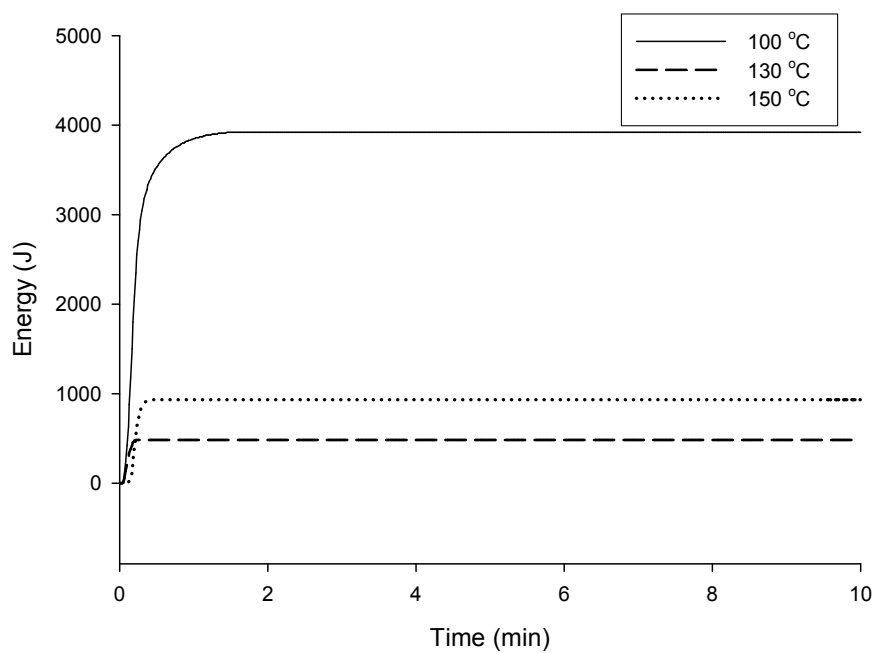
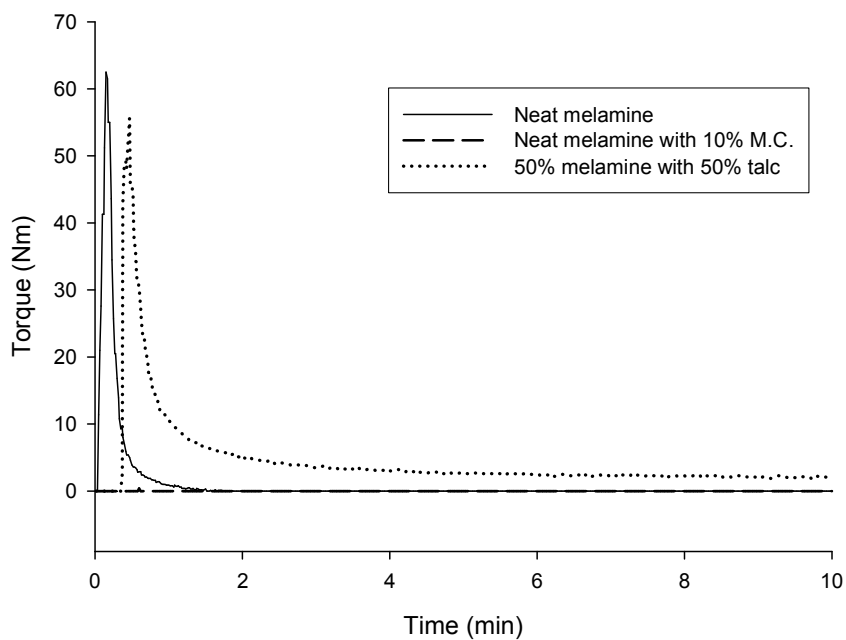**Fig. A.2.** Variation of energy with respect to time of 100% melamine resins at various chamber temperatures.

Fig. A.3. Variation of torque with respect to time of chamber temperatures 100℃ for neat melamine resins/moisture and talc.
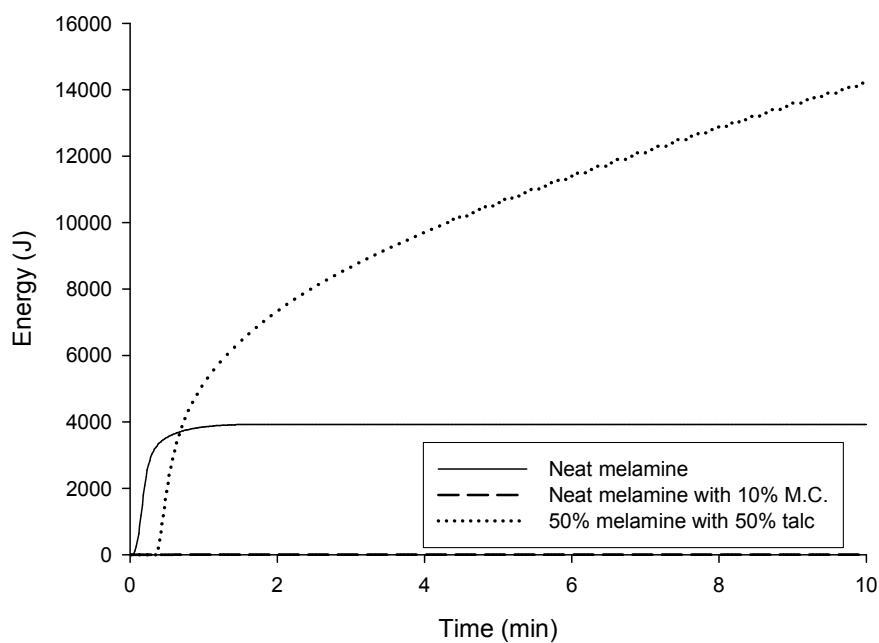
Fig. A.4. Variation of energy with respect to time of chamber temperatures 100℃ for neat melamine resins/moisture and talc.
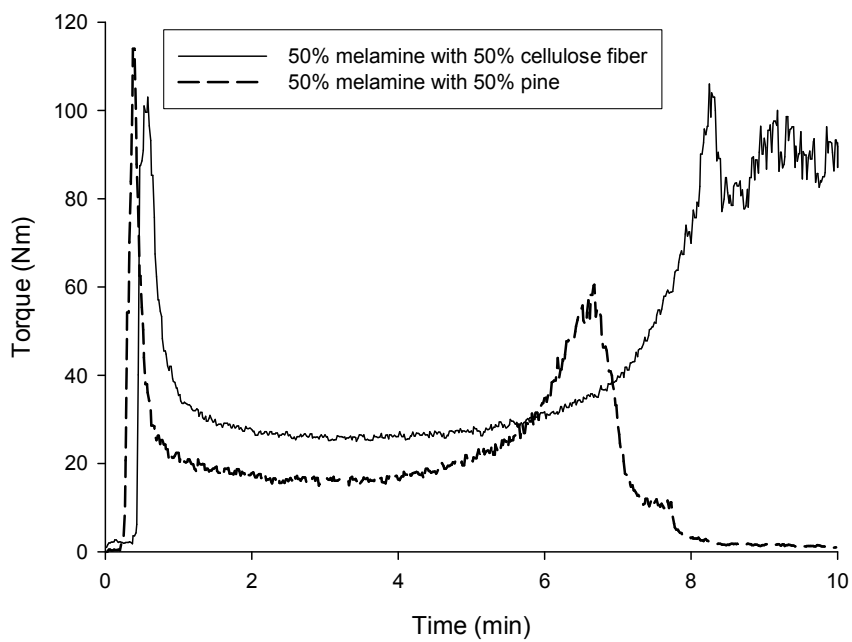

Fig. A.5. Variation of torque with respect to time of chamber temperatures 100℃ for various melamine resins/fillers.

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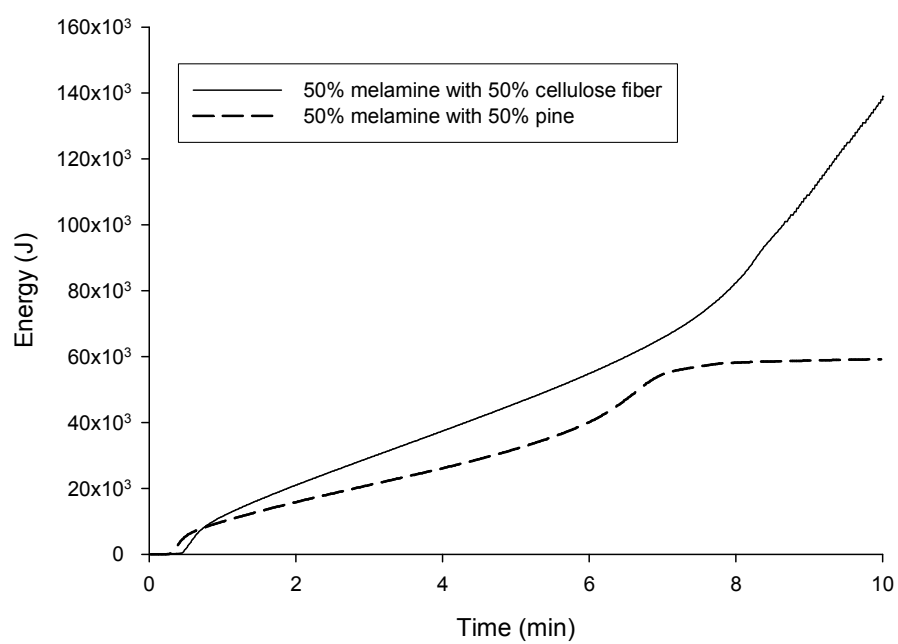**Fig. A.6.** Variation of torque with respect to time of chamber temperatures 100℃ for various melamine resins/fillers.