An Investigation of Wood-Plastic Novolac Modified by Biomass Pyrolysis Oils

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ABSTRACT: *The possibility of using water insoluble fraction from biomass pyrolysis oil as additive in synthesis of Wood-Plastic novolac has been proved by using Differential Scanning Calorimetry (DSC) and Fourier Transformed Infra Red (FT-IR) spectroscopy. Synthesis of novolac with different concentrations (10, 20 and 30 wt %) of water insoluble fraction were performed. It was found that mechanical properties were improved by using water insoluble fraction as additive. However, furthe increasing amount of water insoluble fraction, the mechanical properties of wood-plastic novolac were decreased. When the amount of water insoluble fraction in wood-plastic novolac was 10%, the flexural strength of wood-plastic novolac was 57.8 MPa, tensile strength was 29.5 MPa. The performance and thermal behavior of novolac were characterized by DSC and TG.*

KEY WORDS: *Biomass, Pyrolysis, Novolac, Preparation.*

INTRODUCTION

Wood Plastic Composite (WPC) is a kind of composite materials, consisting of thermoplastic resins, wood flour and additives. Wood flour is the most common organic filler used in WPC, with the aim to decrease cost and enhance performance of WPC. Demand for WPC has been steadily increasing in the past decade, with a market demand of 1.95 billion kg in 2006 [1]. Thus, WPC producers are forced to seek other non-wood sources to supply the increasing raw material requirement and protect timber resources.

Phenolic resins are typically cross-linkable polymeric resins widely used as adhesive agent. Because phenol is produced primarily from petroleum, its price and availability are linked to that of petroleum. Consequently, phenolic resins are relatively expensive. A number of attempts have thus been made in recent years to at least partially substitute the petroleum-based phenol in phenolic resins with inexpensive phenols derived from lignocellulosic wastes such as bark, sawdust, wood chips and the like[2-5].

Pyrolysis of biomass materials is known to produce a complex mixture of phenolic compounds and aldehydes which are derived primarily from the lignin and cellulose contained in the feedstock. We consider that biomass pyrolysis oil(bio-oil) trends to polymerization automatically in storage. Therefore, such a complex mixture of compounds may be used as additive in synthesis of novolac resins after thermal treatment. To our knowledge, there is little published information about using biomass pyrolysis oil as a filler of WPC.

In this work, we have investigated the possibility of synthesis of novolac composite using water insoluble fractions from biomass pyrolysis oil, wood flour and PS as starting materials. Resins obtained have been characterized by several techniques.

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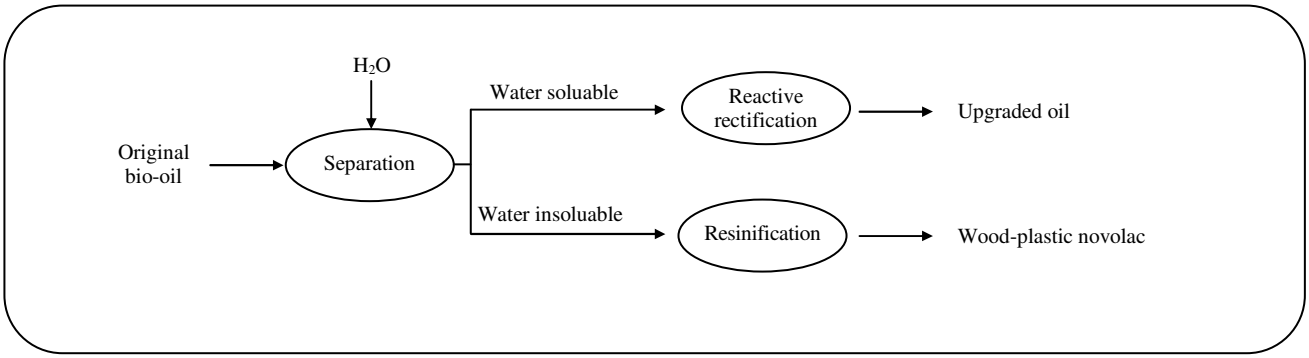

Fig. 1: Scheme for utilization of pyrolysis oils.

EXPERIMENTAL SECTION

General

Plastics used in the study were recycled high density Poly Ethylene (PE) and Poly Styrene(PS). Wood flour used in the study was derived from various scrap wood from wood processors. The moisture content of wood flour was about 8%, and the particle size was less than 0.15mm. The fast pyrolysis bio-oil from biomass used in experiment was the same as literature [6,7]. IR spectra (max in cm^{-1}) were obtained on a MAGNA-IR 550 spectrophotometer. Gas chromatography-mass spectrometry (Agilent 6890N/5973N) was conducted to analyze the composition of bio-oil. The separation was realized on a column of HP-5, 30 m × 0.25 mm ×0.25 um.

The mechanical properties like flexural strength and tensile strength were tested. Flexural strength is maximum bending stress developed in a specimen just before it cracks or breaks in a flexure test. Tensile strength measures the force required to pull a specimen to the point where it breaks, and is measured in units of per unit area or pascals(Pa). Flexural and tensile impact tests were performed on the WPC composites according to ASTM D 790 and ASTM D 638, respcetively.

Water absorption test was conducted in accordance with ASTM D 570-98, in which the specimens were immersed in water for 24 h at a temperature 23±1 °C. The weight gain was then measured after being removed from the water.

Thermal analysis was carried out with Pyris Diamond (Perkin-Elmer) Differential Scanning Calorimeter (DSC). A 5-10 mg sample was sealed in a medium pressure capsule pan and scanning temperature range from 25 to 200 °C was employed for thermal characterization. The sample crucibles were heated at 10 °C min^{-1}.

TG analysis was carried out with Netzsch409PC, temperature range from 25 to 700 °C was employed for thermal characterization. The sample crucibles were heated at 20 °C min^{-1}.

Experimental setup and procedure

The operation procedures were shown in Fig. 1.

Separation of original bio-oil was based on the fractionation of the bio-oil with water into water soluble and insoluble fractions. In a typical operation, 200 mL bio-oil(232.0 g) was added slowly as drops in 100 g H_2O with constant stirring. Then, it resulted in a phase separation, 73.0 g water insoluble fractions was obtained. Main components in original bio-oil [7] and water insoluable fractions was illustrated in Table 1.

From Table 1, it was determined that formic acid in bio-oil(soluble in water phrase) could possible convert into ester and separate from bio-oil through reactive distillation. Bio-oil upgrading by means of ethyl ester production in reactive distillation was in our previous work[6]. Moreover, it was indicated that fraction quantity of phenolic compounds and aldehydes(Vanillin and 4-Hydroxy-2-methoxycinnamaldehyde) was increased in water insoluble fractions. Therefore, in this paper, we tried to use water insoluble fractions as additive in wood-plastic composite production after thermal treatment.

Fig. 2 shows the process of synthesis of Wood-Plastic Composite (WPC) substitute by water insoluble fraction from biomass pyrolysis oils. Water insoluble fraction was added in several concentrations (10, 20 and 30 wt %) in synthesis of WPC. Wood flour, plastic and water insoluble fraction were used for profile extrusion by a conical counter-rotating Twin-Screw Extruder (TSE). Along with the conical counter-rotating TSE, the die was

Table 1: Main components in original bio-oil[7] and water in soluble fractions.

Original bio-oil		insoluble fractions	
Composition	wt%	Composition	wt%
Formic acid	7.69	Phenol,-3-methyl-	2.598
Hydroxybutyric acid	2.31	Phenol, -2-methoxy-	7.644
Toluene	5.00	Phenol, -4-ethyl-	3.869
Benzoic acid, 3-Methyl	1.15	Phenol,-2-methoxy-4-methyl-	4.259
1,2-Benzenedicarboxylicacid	1.22	1,2- Benzenediol,-3-methyl-	1.602
2-Cyclopentane-1-one, 3-methyl	1.42	Hydroquinone	0.928
4H-Pyran-4-one, 2,6-dimethyl-	2.15	Phenol,-4-ethyl-2- methoxy-	2.823
Acetophenone, 1-(4-hydroxy-3-methoxy)	1.00	1,2- Benzenediol, -4-methyl-	2.473
Benzaldehyde, 2-hydroxyl	1.85	2-methoxy-4-vinylphenol	2.196
Benzaldehyde, 3,5-dimethyl-4-hydroxyl	1.92	Vanillin	4.251
		Phenol,-2-methoxy-4-(1-propenyl)-	6.501
		4-Hydroxy-2-methoxycinnamaldehyde	5.930

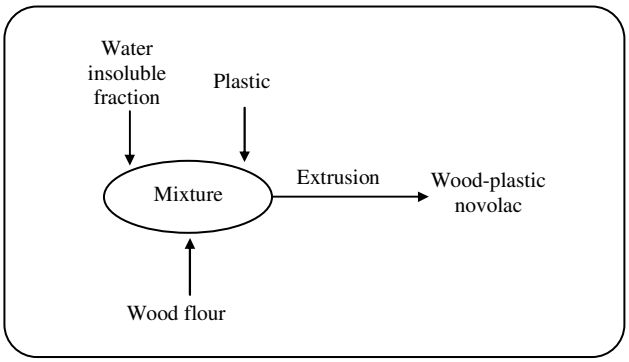

Fig. 2: Scheme for synthesis of wood-plastic composite.

an important part of the WPC product extrusion system. The die was heated using cartridge heating elements. After the cooling tank, the WPC profile went through a cutoff saw that can cut the WPC panels to the desired lengths.

Average temperatures in the extruder barrel and die were maintained at 120 °C and 170 °C. The extruder pressure was maintained at approximately 700 bar.

RESULTS AND DISCUSSIONS

Synthesis of novolac composite from different kinds of thermoplastic

The mechanical properties of WPC panels were shown in Table 2. WPC is a kind of composites with fillers as reinforcing materials. It can be seen that PS is suitable thermo-plactic filler compared with PP. WPC used PP as filler showed the worst properties as shown in Table 2. With the increase amount of PS, the mechanical properties of WPC promoted dramatically.

Synthesis of novolac composite in different ratio of water insoluble fraction

In previous GC-MS analysis, it was determined that the pyrolysis oils from biomass materials produce a complex mixture of phenolic compounds and aldehydes, especially richer in water insoluble fractions. Therefore, in this study, we tried to use such mixture as additive in synthesis of novolac composite.

Table 3 shows the properties of novolac composites in different ratio of water insoluble fraction. Values of flexural strength and tensile strength of WPC with water insoluble fraction were slightly greater than those of specimen without addition of water insoluble fraction. In addition, 10% dosage in novolac conposite possessed the highest mechanical properties, with a flexural strength of 57.8 MPa and tensile strength 29.5 MPa.

Results of density and moisture absorption are also given in Table 3. It is found that the density of the WPC panels ranges from 1210 to 1280 kg/m^3. With the decreasing amount of wood flour, the water absorption of WPC also decreased. The different performance is caused by the large difference between the wood flour. The moisture absorption in wood flour is mainly due to water absorption

Table 2: Properties of novolac from different kinds of thermoplastic.

Sample[a]	Density (g/cm^3)	Moisture absorption (%)	Flexural strength (MPa)	Tensile strength(MPa)
PP	1.17	2.63	14.2	10.2
1/2PP+1/2PS	1.15	1.95	19.6	13.7
PS	1.25	1.85	48.7	24.3

a) m(thermoplastic):m(wood flour):m(water insoluble fraction) = 40 : 50 : 10

Table 3: Effect of substitute ratio on novolac resins.

m(PS):m(wood flour): m(water insoluble fraction)	Density (g/cm^3)	Moisture absorption (%)	Flexural strength (MPa)	Tensile strength (MPa)
40:60:0	1.21	2.35	43.5	23.3
40:50:10	1.25	1.85	48.7	24.3
40:40:10	1.23	1.76	57.8	29.5
40:40:20	1.27	1.78	52.3	25.6
40:40:30	1.28	1.92	45.2	25.6

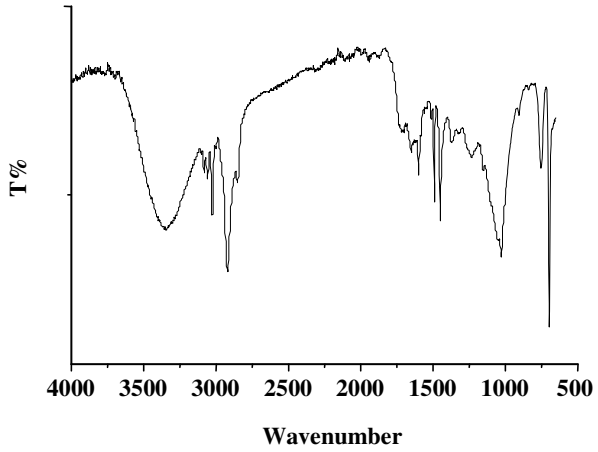

Fig. 3: IR spectra of novolac composite modified by water insoluble fraction.

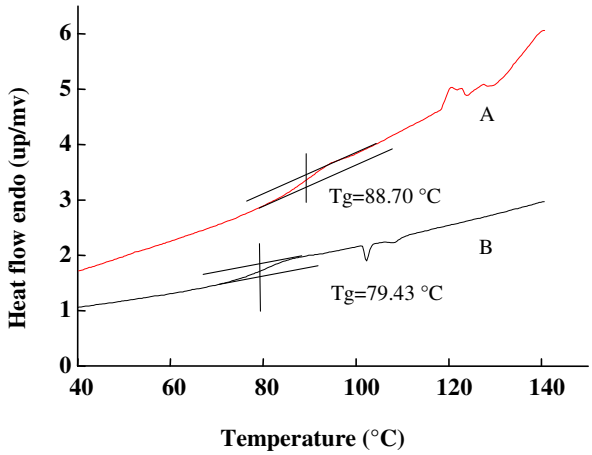

Fig. 4: DSC thermograms of different kinds of novolaks (A : without water insoluble fraction; B : 20 % dosage of water insoluble fraction)

by cellulose and hemicelluloses depends on the number of free hydroxyl groups thus the amorphous regions are accessible by water [8].

Characterization of WPC

Fig. 3 shows the FT-IR spectra of novolac composite modified by water insoluble fraction. The spectral region between 3500cm^{-1} and 3250cm^{-1} has been assigned to hydroxyl groups originating mainly from cellulose of wood flour. The spectral region between 1050cm^{-1} and 1023cm^{-1} has been assigned to C-O groups in wood cellulose.

Fig. 4 gives DSC analysis of novolacs. It can be seen that the glass transition temperature is changed from 88 °C for sample A to 79 °C for sample B. This change must be attributed to the biomass pyrolysis oil presence in novolac because they are not present in reference spectra (sample A).

Fig. 5 shows TG thermograms of WPC samples, and different data can be obtained in Table 3. It can be noticed that all thermograms represented in Fig. 5 are of similar shape. The thermal degradation of mechanism of WPC included two stages. The first step was from 200 to 380 °C, and it included the decomposition of wood flour and water insoluble fraction. WPC with more water insoluble fraction decomposed more easily than WPC

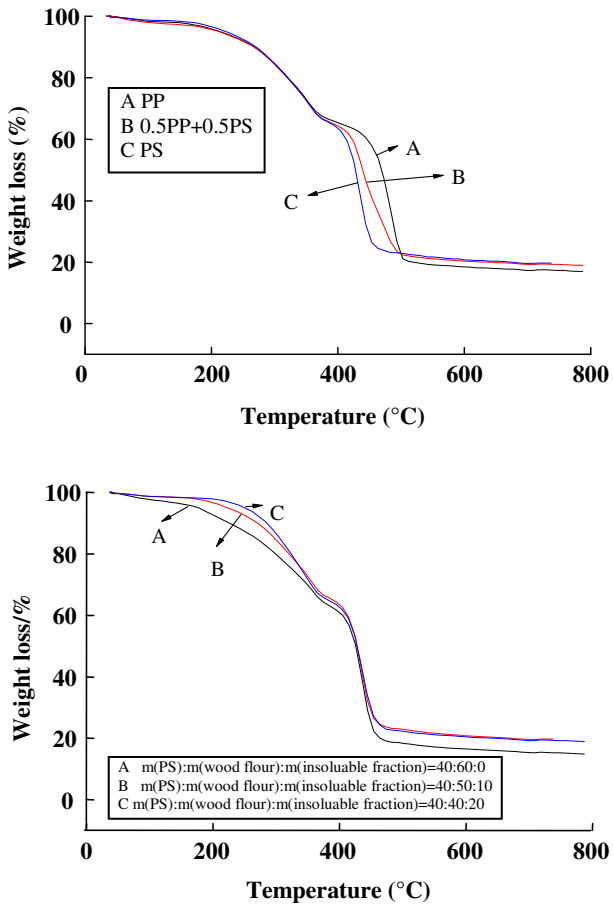

Fig. 5: TG curves of different kinds of novolacs.

without water insoluble fraction. The second decomposition curves of three samples were of different shape. The stage began around 400 °C with a weight loss of about 40%. The weight loss was due to the decomposition of recycled plastic. The thermal degradation step was in agreement with the results reported in the literature [9]. All the novolacs did not showed much weight loss under 200°C. This means that composite product had good thermal stability.

CONCLUSIONS

1. Synthesis of Wood-Plastic novolac using biomass pyrolysis oil as additive was studied in this paper.

2. It was found that the suitable amount of water insoluble fraction in Wood-Plastic novolac was 10%. In this optimum condition, the flexural strength of Wood-Plastic novolac was 57.8 MPa, tensile strength was 29.5 MPa.

3. The novolacs modified by water insoluble fraction did not showed much weight loss under 200 °C. This means that composite product had good thermal stability.

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