Thermogravimetric analysis and dynamic Young's modulus measurement of N, N-dimethylacetamid impregnated wood polymer composites (WPC)

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Abstract

All wood species were mercerized with N, N-Dimethylacetamid impreganation. The FT-IR show the enhance absorption at 1419 cm⁻¹(-C-/CH₃) and 1267 cm⁻¹ (-N-/ CH₃) stretching band confirmed the polymerization reaction. Thermogravimetric investigation of wood polymer composites indicates a better thermal stability in comparison with the raw wood. Dynamic Young's modulus of WPC was significantly increase compare the raw ones. After polymerization SEM show the porous cells of raw wood filled by the monomer which gave better stability of WPC. The XRD analysis indicate that the crystallinity of WPC increased which due to an increased the stiffness and the thermal stability of the composites.

Keyword: Wood, Thermal properties, Thermal analysis, Non-destructive testing.

1. Introduction

The development of polymeric composite materials, especially using lignocellulosic fibers, has received increasing attention. This is interesting from the environmental and economical viewpoint, as lignocellulosic fibers such as sisal, wood and coir are obtained from renewable resources. Previous researchers have demonstrated that lignocellulosic materials properties (such as dimensional instability due to moisture and low durability due to biodegradation) can be improved by chemical modification using etherification, esterification, cyanoethylation, oxidation and diazonium salt coupling reaction [1-10]. Chemical modification of wood is defined as chemical reaction involving functional groups of wood-based component and a simple single chemical reagent that forms a covalent bond with the wood-based components [11-12]. Dicarboxilic acid anhydrides such as phthalic (PA), maleic (MA) and succinic (SA) anhydrides have been used to esterify the lignocellulosic materials with the aim to produce a thermoformable product [13]. The advantages of lignocellulosic fibers are high specific modulus, light weight and low cost. On the hand, wood like other natural fiber is hygroscopic and exhibits a tendency to be in moisture equilibrium with the relative humidity of the surrounding atmosphere, either by taking up moisture from or giving out moisture to the atmosphere. Wood fibers absorb moisture as the cell wall polymers contain hydroxyl or other oxygenated groups that attract moisture through H-bonding. Taking advantage of the plentiful reactive groups present, modification of cell wall using proper surface modifier can be made to increase the scope of utilization of the natural fibers as reinforcement [14-151.

Mercerization is one of the most conventionally used treatments for natural fibers to modify its surface properties so that it can be successfully employed in composite formation [16]. Available literature pertaining to alkali treatment of many natural fibers reveal that the process removes one of the cementing materials,

hemicelluloses, depending on the concentration of the alkali used, time and temperature of treatment etc. The thermal and weathering studies have been reported on many other natural fibers and their composites [17-21]. However, there is no work on the tropical wood mercerization with N,N-Dimethylacetamid monomer impregnation.

The present paper, wood specimen was mercerized by 5% NaOH solution than impregnated by N,N-Dimethylacetamid. Microstructures of the composites were observed by using Fourier transform infra red (FTIR) and scanning electronic microscope (SEM). Thermal and dynamic Young's modulus were determined and compared.

2. Materials and Methods

2.1. Materials

Five wood species were collected for this study. Among them are the softwoods *Eugenia Spp*, *Artocarpus Rigidus*, *Artocarpus Elasticus* and *Xylopia Spp*, and the hardwood *Koompassia Malaccensis*. Chemicals used to treat these wood species were 5% NaOH and N,N-Dimethylacetamid (Merck, Germany). The purity grade of the chemicals was 99%.

2.2. Specimen preparation

Five wood species were felled and each tree was cut into three bolts of 1.2m long. Each bolt was quarter sawn to produce planks of 4cm thickness and subsequently conditioned to air-dry in a room with relative humidity of 60% and ambient temperature of around 25° C for one month prior to testing. The planks were ripped and machined to 340 mm (L) x 20 mm (T) x10 mm (R) specimens for the free-free vibration test.

2.3. Manufacturing of treated wood composites

Raw wood specimens were soaked into 5% sodium hydroxide solution using an autoclave. The temperature and pressure used were $120^{\circ}C$ and 85 kPa, respectively, for 2 hours. Sodium hydroxide soak specimens were then impregnated by N,N-Dimethylacetamid using a vacuum chamber at $25^{\circ}C$ and 60cm Hg to convert into wood polymer composite.

2.4. FT-IR spectroscopy analysis

The infrared spectra of the raw woods and WPC were recorded on a Shimadzu Fourier Transform Infrared Spectroscopy (FTIR) 81001 Spectrophotometer. The transmittance range of the scan was 370 to 4000 cm⁻¹.

2.5. Thermogravimetric analysis (TGA)

All raw wood and WPC sample were analyzed using a Perkin Elmer thermal analyzer. All measurements were made under a nitrogen flow (30ml per min), keeping a constant heating rate of 10° C per min and using an alumina crucible with a pinhole.

2.6. The free- free flexural vibration testing

Determination of the dynamic Young's modulus (E_d) was carried out using the free-free flexural vibration testing system as shown in Fig. 1. The specimen was held with AA thread according to the first mode of vibration. The specimen with an iron plate bonded at one end was set facing the electromagnet driver, and a microphone

was placed at the centre below the specimen. The frequency was varied in order to achieve a resonant or natural frequency. The E_d was calculated from the resonant frequency by using the following equation,

$$\vec{E}' = \frac{4\pi^2 f^2 l^4 A\rho}{I (m_n)^4}$$

Where $I = bd^3/12$, *d* is beam depth, *b* is beam width, *l* is beam length, *f* is natural frequency of the specimen, ρ is density, *A* is cross sectional area and *n*=1 is the first mode of vibration, where m_1 =4.730



Figure 1: Schematic diagram of free-free vibrational testing

2.7. Scanning electron microscopy analysis (SEM)

The specimens were first fixed with Karnovsky's fixative and then taken through a graded alcohol dehydration series. Once dehydrated, the specimen was coated with thin layer of gold before viewed on the SEM. Scanning Electron Microscope (JSM-6701F) supplied by JEOL Company Limited, Japan. The micrographs, taken at a magnification of 150X, are presented in the results and discussions section

2.8. XRD analysis

XRD analysis for raw wood and wood polymer composites (WPC) were performed with a Rigaku diffractometer (CuK α radiation, λ =0.1546 nm) running at 40 kV and 30 mA.

3. Results and discussions

3.1 Fourier transform infrared spectroscopy analysis

The IR spectrum of raw wood and WPC are shown in figure 2. The spectrum of the raw wood shows the basic structure of all wood samples i.e. strong broad OH stretching ($3300-4000 \text{ cm}^{-1}$), C-H stretching in methyl and methylene groups (2800-3000 cm⁻¹) and a strong broad superposition with sharp and discrete absorptions in the region from 1000 to 1750 cm⁻¹ [22].Comparing the spectra of holocellulose and lignin

reveals that the absorptions situated at 1508 and 1600 cm⁻¹ are caused by lignin, and the absorption located at 1734 cm⁻¹ is caused by holocellulose; this indicates the C=O stretch in non-conjugated ketones, carbonyls and in ester groups[22].



Figure 2. IR spectrum of raw wood and WPC

The region between 1800 and 1100 cm⁻¹ compares bands assigned to the main components from wood such as cellulose, hemicelluloses and lignin. The clear differences can be detected in the infrared spectra for raw wood and WPC bands and their location.

A decrease in the intensity of the O-H absorption band at 3424 cm^{-1} indicates that the hydroxyl group contents in WPC were reduced after mercerization with monomer impregnation. The higher xylan content in raw wood is evidenced by a stronger carbonyl bands at 1734 cm⁻¹, for polymerize wood, this being shifted to a lower wave number value at 1570 cm⁻¹. The absorption at 1419 cm⁻¹(-C-/CH₃) and 1267 cm⁻¹ (-N-/ CH₃) stretching band confirmed the polymerization reaction.



Figure 3. Mercerization of wood specimens with polymerization reaction. **3.2 TGA Analysis**

The thermal stability of wood is a very important parameter in the production of wood polymer composites. Wood is used as a filler material to improve mechanical strength in plastic that are processed at temperature below 200° C [23]. In thermogravimetric tests on raw wood it is common behavior for dehydration process, in which 5-8% of absorbed water is removed. According to the literature, it has been established that there is no degradation up to 160° C [24]. Above this temperature the thermal stability gradually decreases, and decomposition takes place. Figures 4(a-e),

5(a-e) and table.1 represent the thermogravimetric curves obtained by the dynamic scans for raw wood and WPC.

The thermogravimetric analysis of raw wood and WPC indicated that a loss of water started for both raw and WPC samples from 10° C up to 150° C. The chemical N, N-dimethylacetamid impregnated WPC improves the thermal stability of wood, showing the evidence that the initial and final decomposition temperature (T_i, T_f) of all WPC is higher than that of raw wood. Analysis of the activation energy can be helpful in reaching conclusions about the thermal stability of WPCs. The larger the activation energy, the greater is the stability. The present calculation is based on the Broido equation and measured from the TGA thermograms of all raw wood and WPC [25]. The activation energy can be obtained from a plot of ln k versus 1/T. The linear plots are shown in Fig. 5(a-e) and the value for activation energy is given in Table 1. The value of activation energy of WPC was higher compared with raw wood. Table 1: Thermal Characteristics of Raw Wood and WPC

T_m- temperature corresponding to the maximum rate of mass loss

T_i- temperature corresponding to the beginning of the decomposition

T_f- temperature corresponding to the ending of the decomposition

 W_{Ti} , W_{Tm} and W_{Tf} –mass loss at T_i , T_m and T_f

Sample		T _i	T _m	T _f	W _{Ti}	W _{Tm}	W _{Tf}	Activation
		(°C)	(°C)	(°C)	(%)	(%)	(%)	Energy
								Ea
								(J/ ⁰ K)
Artocarpus	Raw	201	332	419	98.96	64.73	32.67	33.11
Elesticus	wood							
	WPC	210	269	622	97.89	77.16	38.17	73.49
Artocarpus	Raw	211	340	388	99.67	56.45	30.63	25.79
Rigidus	wood							
	WPC	215	277	537	98.16	63.46	33.68	34.99
Xylopia Spp	Raw	212	341	420	98.78	56.15	29.85	27.04
	wood							
	WPC	225	285	630	98.39	64.35	41.16	30.14
Koompassia	Raw	212	355	403	98.99	57.91	30	16.12
Malaccensis	wood							
	WPC	213	301	576	98.06	59.94	22.51	41.34
Eugenia Spp	Raw wood	214	340	443	99.77	60.32	27.51	19.17
	WPC	218	285	521	98.48	70.68	44.35	28.68



Figure 4 (a) TGA curve of Artocarpus Elasticus raw wood and WPC



Figure 4 (b) TGA curve of Artocarpus Rigidus raw wood and WPC



Figure 4 (c) TGA curve of Xylopia Spp raw wood and WPC



Figure 4 (d) TGA curve of Koompassia Malaccensis raw wood and WPC



Figure 4 (e) TGA curve of Eugenia Spp raw wood and WPC



Figure 5 (a) Temperature dependency of the decomposition rate of the *Artocarpus Elasticus* raw wood and WPC



Figure 5 (b) Temperature dependency of the decomposition rate of the *Artocarpus Rigidus* raw wood and WPC



Figure 5 (c) Temperature dependency of the decomposition rate of the *Xylopia Spp* raw wood and WPC



Figure 5 (d) Temperature dependency of the decomposition rate of the *Koompassia Malaccensis* raw wood and WPC



Figure 5 (e) Temperature dependency of the decomposition rate of the *Eugenia Spp* raw wood and WPC

3.3. Dynamic Young's modulus measurement

The stiffness of the raw wood and WPC, from the free-free flexural vibration testing system is shown in Fig. 6. Ten specimens were used for each species. The mercerization upon polymerization increased the Young's modulus, as seen in all species which was according to the other researcher [8]. Although the increment in activation energy was significantly affected by the polymerization (see Table 1), but the elastic properties showed significant changes only in *Artocarpus elesticus*.



Figure 6. E_d of raw wood, WPC for all species

3.4 Scanning electron microscopy analysis (SEM)

Figure 7 shows the SEM micrograph for the raw wood and WPC. The micrograph of raw wood (*Artocarpus rigidus*) shows dramatically changes after polymerization as shown by the WPC. This is in accordance with the drastic increase of activation energy and final decomposition temperature of WPC after polymerization (Fig. 4a-e, table-1). However, before mercerization with polymer the raw wood showed big pores inside. On the other hand, after polymerization the SEM micrograph of WPC showed all hole was filled by monomer and the waxy substance removes from the sample which was according to our other works [26].



Figure 7. SEM micrograph of raw wood (A) and WPC (B)

3.5. XRD analysis

The X-ray diffraction patterns of raw wood fiber and WPC are given in figure 8-9 respectively. As seen in figure.8 the patterns of raw wood fiber exhibit only one well defined 2θ peak at 22.0° , which are due to cellulose [27]. It is observed in figure 9 the WPC exhibited four broad 2θ peaks at 42.08° , 43.68° , 49.23° and 72.67° which are due to increasing polymerization. The effect of chemical modification of lignocellulosic materials on their crystallinity has been investigated by various researchers [27]. The reagent first react with the chain ends on the surface of crystallites, as it cannot diffuse into the crystalline region, resulting in the opening of some of the hydrogen-bonded cellulose chains. It was clear that the mercerization with monomer impregnation increased the crystallinity of WPC, which is due to an increased removal of the fiber amorphous constituents.

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Figure 8. X-ray diffraction of raw wood fiber.



Figure 9. X-ray diffraction of WPC

4. Conclusion

In this paper N, N-Dimethylacetamid wood polymer composites have been studied. FT-IR spectra indicate the occurrence of chemical impregnation of wood by reacting with organic N, N-Dimethylacetamid. The enhanced absorption at 1419 cm⁻¹(-C-/CH₃) and 1267 cm⁻¹ (-N-/ CH₃) stretching band confirmed the polymerization reaction. Mercerization with monomer impregnation of wood species makes it thermally more stable over certain temperature range during this study. The stiffness of the WPC was significantly increase compared with raw wood. The X-ray diffraction patterns of WPC indicate that the crystallinity increase with monomer loading.

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