

SYNTHETIC AND NATURAL DYEING OF WOOD FIBERS IN WOOD-PLASTIC COMPOSITE

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1 Introduction

It is well known that color of wood-plastic composite (WPC) changes to lighter after outdoor exposure. Adding pigment is a general remedy to obtain long-lasting appearance of WPC products. In textile industry, direct and reactive dyes are synthetic dyes which are suitable for cellulosic dyeing. They not only provide colors to textiles but also protect them from photo-degradation and light fastness. Recently, use of natural dye becomes an interest in textile industry due to environmental concern. There is no much literature reported on dyeing wood flour used in WPC and their influence on physical and mechanical properties. The aim of this work is thus to improve appearance of wood-plastic composite by dyeing delignin wood flour with two types of synthetic dyes and one natural dye from *Caesalpinia sappan* bark. Influences of dyes on integrity of wood fibers and WPC's mechanical properties with dyed wood fibers were investigated.

2 Experimental

2.1 Materials

Rubber wood (*Hevea brasiliensis*) sawdust was ball milled and sieved (200-500 mesh size) to be 31-74 micron in particle size. High density polyethylene (HDPE, MFI of 20 g/10 min) was kindly supplied by PTT Chemical Public Co Ltd., Thailand. Maleated polyethylene (MAPE, maleic anhydride content of 0.9 wt%) was purchased from DuPont, USA. Solophenyl Bodeaux 3 BLE (C.I. Direct Red 83.1) and Novacron Red C-2G (C.I. Reactive Red 281)

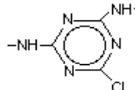
were supplied by Huntsman (Guangdong) Ltd. *Caesalpinia sappan* bark was received from a local mill. Other chemicals used were; Sodium chlorite, Acetic acid, Sodium sulphate, Sodium carbonate anhydrous, and Aluminium sulphate. All materials were used as received.

2.2 Removing lignin and dyeing

Method to remove lignin by Sodium chlorite (NaClO₂) was performed following P.A. Ahlgren *et al.* [1]. Sodium chlorite (NaClO₂) of 0.3 g and glacial acetic acid of 0.1 ml, per 1 gram of dry wood and liquor ratio of 15:1 were used to remove lignin from wood. Bleaching temperature was set at 70°C for 8 hrs. Treated wood flour was washed in distilled water until pH of water was 7. Original and delignin wood flour were determined lignin content in accordance to TAPPI T 222 om-98 (Klason lignin).

Table 1. Characteristics of synthetic dyes.

Trade name	Scientific name	Main functional group	λ_{max} (nm)
Solophenyl Bodeaux 3 BLE	CI Direct Red 83.1	Amide, Sulphonate, Metal complex	519
Novacron Red C-2G	CI Reactive Red 281	MCT ¹ /VS ² /VS	514

¹ MCT : monochlorotriazine ; 

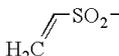
² VS : vinyl sulphone ; 

Table 1 presents characteristics of two types of synthetic dyes used in this study. Delignin wood flour was dyed with CI Direct Red 81.3 of 1% on weight of fiber (%o.w.f.) at liquor ratio 10:1 using Sodium sulphate as salt electrolyte. Delignin wood flour was dyed with CI Reactive Red 281 of 1%o.w.f. at liquor ratio 4:1 using Sodium carbonate and Sodium chloride to increase dye affinity.

Caesalpinia sappan bark was grinded into small pieces and boiled in water (1:10 weight ratio, 80°C, 4 hrs) to receive dye solution (red). Delignin wood flour was dyed with dye solution using Aluminium sulphate 1.5%o.w.f. to improve dye affinity.

In all dyeing process, delignin wood flour was dyed with upper 60% absorption ratio of the origin natural dye solution, which concentrations of dye solution before and after dyeing process were determined using a UV/VIS Spectrophotometer (PG Instruments Ltd.).

Table 2. Sample codes and their compositions.

Sample Code	Compositions	Compositions ratio
HDPE	HDPE	100
MA-HDPE	HDPE : MAPE	100 : 15
W-WPC	HDPE : Original wood : MAPE	40 : 60 : 6
D-WPC	HDPE : Delignin wood : MAPE	40 : 60 : 6
DR-WPC	HDPE : Direct dyed wood : MAPE	40 : 60 : 6
RT-WPC	HDPE : Reactive dyed wood : MAPE	40 : 60 : 6
SP-WPC	HDPE : Sappan dyed wood : MAPE	40 : 60 : 6

2.3 Preparation of wood-plastic composite (WPC)

Before compounding, wood flour were dried in an air-circulating oven at 80°C for 24 hours. Composites were prepared by compounding HDPE 40 wt% and wood 60 wt% with MAPE (6 wt% of fibers) as coupling agent in a twin screw extruder

with a temperature profile of 150, 160, and 180°C from feeding to die. Original wood, delignin, direct-dyed, reactive dyed, and Sappan-dyed WPC are denoted as WPC, D-WPC, DR-WPC, RT-WPC, and SP-WPC, respectively. Sample compositions are presented in Table 2. Extrudate were pelletized into pellets and injection molded into tensile and flexural specimens using an injection molding machine with nozzle temperature of 180°C and mold temperature of 40°C.

2.4 Characterization and testing

Fiber integrity in all composites was characterized by Fourier transform infrared spectrophotometer (FTIR) and Thermogravimetric analyzer (TGA). FTIR spectra of sample were recorded on a Vertex 70, BRUKER in range 4,000-400 cm⁻¹ using KBr disc. Spectra were obtained using 32 scan and a resolution 4 cm⁻¹. TGA measurements were analyzed using TGA/DSC1 STAR System, Mettler Toledo. Temperature program for tests were run from 40°C to 700°C at heating rate 10°C/min in nitrogen atmosphere (20 ml/min).

Tensile test was performed according to ASTM D-638-03 using LR 50 K universal testing machine (Lloyd Instrument) equipped with 50 kN load cell and a crosshead speed of 5 mm/min. Ten measurements of each sample code were conducted to calculate the average and its standard deviation. Flexural test was performed according to ASTM D-790-03 using LR 50 K universal testing machine (Lloyd Instrument) equipped with 50 kN load cell. Specimens were deflected in three-point loading mode until failure or until 5 percent strain was reached in the outer surface of test specimen with a crosshead speed of 1.8 mm/min.

Morphology of composites was studied from their fracture surface by means of scanning electron microscopy (JSM 5410 LV). Samples were prepared by immersing specimen in liquid nitrogen and then breaking them. The fractured surfaces were sputter-coated with gold for observation.

3 Results and discussion

3.1 Content of lignin

After Chlorite treatment, Klason lignin was removed about 70 wt% of original lignin content. In Fig.1, the reduction of lignin in wood flour was confirmed by FTIR showing disappearance of the characteristic peaks of lignin at wave number of 1,600-1,500 cm^{-1} which is aromatic skeleton vibration [2].

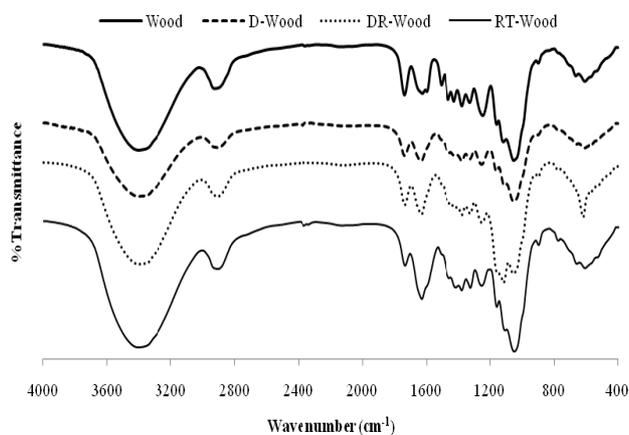


Fig.1. FTIR spectra of original and modified wood fibers.

Fig. 2 indicates normalized FTIR peaks of lignin (Lignin index), which was calculated using the following equation:

$$\text{Lignin index} = \frac{I_{1507}}{I_{1738}} \times 100 \quad (1)$$

where I is a peak intensity of FTIR spectra. The peak intensities at 1,507 cm^{-1} of lignin were normalized with the peak at 1,738 cm^{-1} of hemicellulose (unconjugated C=O) [3]. This peak was chosen as a reference peak because it slightly changed after treatment with acid or dyes. It is seen that lignin in modified wood flour were in the same range.

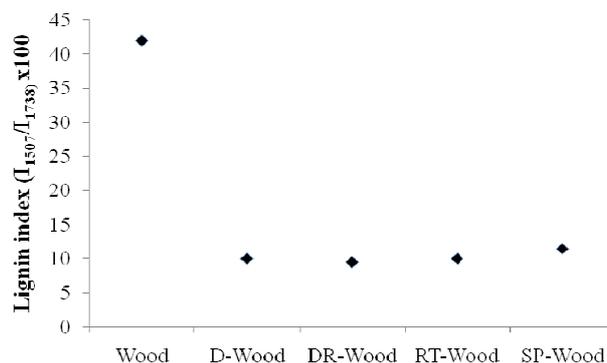


Fig.2. Lignin index of wood and modified wood.



Fig 3. Color of wood and modified wood fibers.

Delignin wood flour had significantly lighter color compared to original rubber wood flour. After dyeing, synthetic dyed wood flour was bright red while Sappan dyed one was dark red as seen in Fig.3.

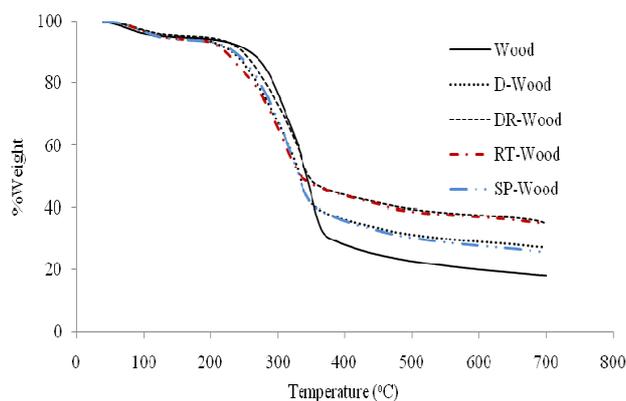


Fig 4. TGA thermograms of wood and modified wood fiber composites.

3.2 Integrity of wood fibers from TGA

From TGA as shown in Fig.4, it is found that WPC with original wood flour started to decompose at higher temperature than delignin and dyed WPC. This result indicates that the acid chlorite treatment weakened celluloses even though it could remove lignin sufficiently [4]. Compared among dyed WPC, RT-WPC had the lowest onset degradation temperature. The reason was dyeing wood flour with reactive dye had to be done in alkali condition for good dye fixation on fiber surfaces. The alkali dyeing condition weakened celluloses further after acid chlorite treatment. In contrast, DR-WPC had the highest onset degradation temperature and SP-WPC had higher onset degradation temperature than D-WPC. In direct dyeing process, celluloses were swelling and then direct dyes could form hydrogen bonding to fibers or even be embedded between them. This action could strengthen damaged celluloses from acid chlorite treatment. For Sappan

dyeing process, Aluminium sulphate (dye mordant) in water could form gelatinous precipitate of aluminium hydroxide ($Al(OH)_3$) that helps Sappan dye to adhere to the cellulose fibers by rendering the pigment insoluble. These thin layers could improve thermal stability of these dyed fibers compared to naked delignin fibers, and also strengthens fibers by dye fixation with mordant as well.

3.3 Mechanical properties and morphology

It is found that mechanical properties of delignin WPC were lower than original WPC due to weakened celluloses from severe acid chlorite treatment. After dyeing, tensile (Fig.5) and flexural (Fig.6) moduli of dyed composites were back to closed to those of non-dyed composites. However, delignin and synthetic dyed composites were weaker in term of tensile strength, especially reactive dyed composites. Sappan dyed composites presented the best properties among them from fiber strengthening from mordant as discussed in TGA. Thus, dyeing condition had influence on mechanical properties of dyed wood composites. SEM micrographs in Fig.7 show that good dispersion of wood fibers was obtained with the presence of MAPE. Nevertheless, there were voids around wood fibers observed in synthetic dyed composites implying coupling agents did not wet fibers as well as non-dyed composites. White traces on dyed wood fiber surfaces identified by XRF were Sodium chloride. These salts were resulted from incomplete washing to remove them from wood fibers.

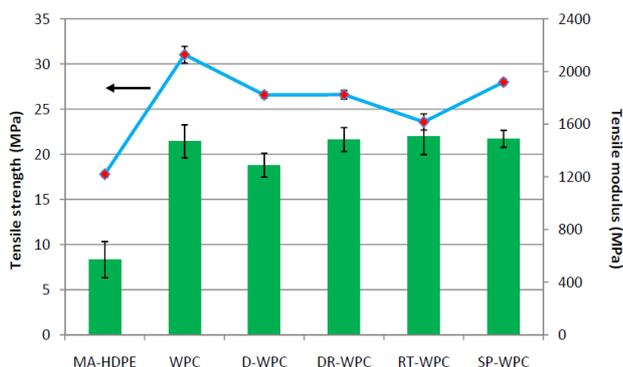


Fig.5. Tensile properties of HDPE and WPC.

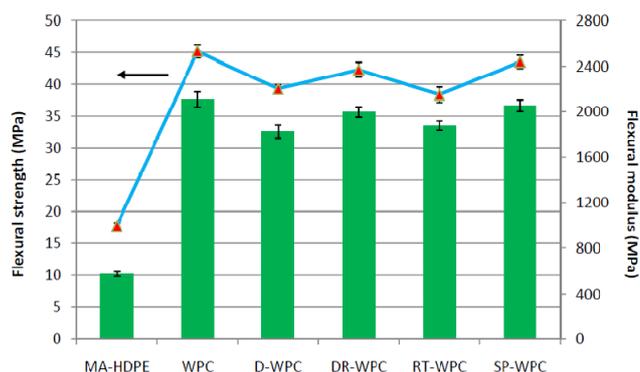


Fig.6. Flexural properties of HDPE and WPC.

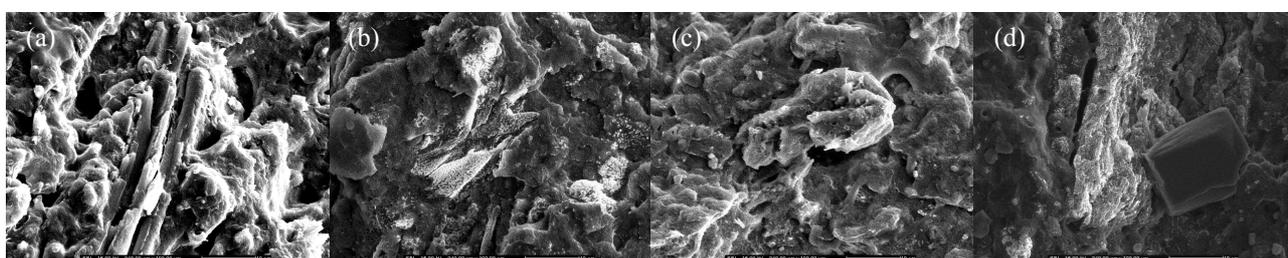


Fig.7. SEM micrographs of WPC specimens; a) WPC ; b) D-WPC, c) DR-WPC ; d) RT-WPC.

4 Conclusions

Lignin was removed from rubber wood flour 70 wt% after the acid chlorite treatment. After chlorite treatment, Young's modulus and flexural modulus of delignin wood composites were lower due to celluloses was damaged during the acid treatment. Dyeing wood flour with different types of dyes affected not only appearance of wood composites but also their mechanical properties. Natural dye WPC presented the best mechanical properties among the dyed WPC due to dyeing process which is less hostile to wood fibers.

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