International Biodeterioration & Biodegradation 72 (2012) 108–113

Contents lists available at SciVerse ScienceDirect

International Biodeterioration & Biodegradation

journal homepage: www.elsevier.com/locate/ibiod

Effect of coupling reactions on the mechanical and biological properties of tropical wood polymer composites (WPC)

Md. Saiful Islam [a,*], Sinin Hamdan [a], Mahbub Hasan [b], Abu Saleh Ahmed [a], Md. Rezaur Rahman [a]

[a] Department of Mechanical and Manufacturing Engineering, Faculty of Engineering, University Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia
[b] Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology, Dhaka, Bangladesh

ARTICLE INFO

Article history:
Received 6 April 2010
Received in revised form
8 May 2012
Accepted 8 May 2012
Available online 28 June 2012

Keywords:
Wood polymer composites
Mechanical properties
Decay resistance
Coupling reaction
Methyl methacrylate

ABSTRACT

Wood polymer composites (WPCs) based on five types of selected Malaysian tropical light hardwood species were prepared using a methyl methacrylate (MMA) and hexamethylene diisocynate (HMDIC) monomer mixture at a 1:1 ratio. Before being impregnated with MMA/HMDIC, the wood species were chemically pretreated with benzene diazonium salt for the coupling reaction with wood and to increase adhesion and compatibility of the wood fiber to the polymer matrix. The monomer mixture (MMA/HMDIC) was impregnated into both the raw wood and diazonium salt pretreated wood specimens to manufacture wood polymer composites (WPC) and pretreated wood polymer composites (PWPC), respectively. Microstructural analysis (scanning electron microscopy and Fourier transform infrared spectroscopy) and mechanical (three-point bending and compression) and biological (fungal decay resistance) tests were conducted. Comparisons were made among the properties of raw wood, WPC, and PWPC. The results reveal that PWPC yielded better mechanical and biological properties compared to untreated WPC and raw wood.

1. Introduction

Recently, bio-based wood polymer composites (WPC) have been receiving considerable attention due to their low processing cost, problem-free biodegradation, and improved physical, mechanical, and biological performance. Wood is mainly composed of three polymers, namely cellulose, hemicellulose, and lignin, with a minor proportion of extractives that is subject to biodegradation. These organic polymers are readily deteriorated by environmental factors, such as light, water, temperature, and biological organisms (Hill, 2006). Modifying wood is an often-followed route to improve these properties. More precisely, modification using non-biocidal thermal, chemical, or resin treatments has been shown to have potential to improve characteristics (Kamdem et al., 2002; Lande et al., 2004; Hakkou et al., 2006). Of late, wood has been treated with a variety of chemicals such as styrene, epoxy resins, urethane, phenol formaldehyde, methyl methacrylate (MMA), and vinyl or acrylic monomers (Yalinkilic et al., 1991; Brelid et al., 2000; Chao and Lee, 2003; Islam et al., 2012a). However, it has been established that monomers and their mixtures do not form bonds with hydroxyl groups of the cellulose fibers. Instead, they simply fill the void spaces within the wood structure (Shane et al., 1995). Since most vinyl monomers are non-polar, there is little interaction between these monomers and the hydroxyl groups of the cellulose fiber. Poor chemical and physical interfacial interactions between the wood surface and chemical are two of the most important mechanisms of bond failure. Therefore, the polymer component of the WPC simply bulks up the wood structure by filling the capillaries, vessels, and other void spaces within the wood. It can therefore be deduced that if bonding was to take place between the impregnated monomers and the hydroxyl groups in the cellulose fibers, the mechanical and biological properties of WPC may be further improved. It has been noted that the interaction between hydrophilic wood fibers and polymer can be modified using coupling agents. Raw fiber has also been chemically treated with benzene diazonium salt to increase its compatibility with the polymer matrix (Haque et al., 2009). It has been established that benzene diazonium salt yields a diazo cellulose compound by the coupling reaction with hydroxyl groups of cellulose fiber (Islam et al., 2012b).

In the present work, five species of selected Malaysian tropical light hardwoods, namely jelutong (*Dyera costulata*), terbulan (*Endospermum diadenum*), batai (*Paraserianthes moluccana*), rubber (*Hevea brasiliensis*), and pulai (*Alstonia pneumatophora*) were utilized as starting materials, keeping in mind that they are

* Corresponding author. Tel.: +60 82583232; fax: +60 82583410.
E-mail addresses: msaifuli2003@yahoo.com, msaifuli2007@gmail.com (Md.S. Islam).

0964-8305/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.ibiod.2012.05.019

easily obtainable in the local forests. The major drawbacks of using these species are their high moisture uptake and biodegradation; in addition, their physical and mechanical properties change with environmental variations, which subsequently limit their use.

The hydrophilic nature of wood is the main factor responsible for moisture absorption, fungal attack, and deformation of the product. By reducing the moisture content of wood, fungal growth is inhibited (Goethals and Stevens, 1994; Donath et al., 2004, 2006; Hill et al., 2004; Mai and Militz, 2004; Mai et al., 2005). The physical, mechanical, and biological changes of wood can also be minimized by suitable chemical treatment, such as the formation of WPC, which is a promising strategy to improve wood properties (Baysal et al., 2007).

In order to overcome the hydrophilic nature of wood and to improve the adhesion and compatibility of polymers to the cellulose of wood, the wood samples were chemically pretreated with benzene diazonium salt and then impregnated with an MA/HMDIC monomer mixture to yield wood polymer composites (WPC) and pretreated wood polymer composites (PWPC). Therefore, this study examines the mechanical and biological properties of wood polymer composites (WPC) pretreated with benzene diazonium salt.

2. Materials and methods

2.1. Materials

In this study, five kinds of tropical light hardwood species, namely jelutong (*D. costulata*), terbulan (*E. diadenum*), batai (*P. moluccana*), rubberwood (*H. brasiliensis*), and pulai (*A. pneumatophora*), were collected from the local forest of Sarawak, Malaysia. Each specimen was treated with aniline ($C_6H_5{-}NH_2$), sodium nitrite ($NaNO_2$), and hydrochloric acid (HCl). The monomer mixture methyl methacrylate (MMA)/hexamethylene diisocyanate (HMDIC), at a 1:1 ratio, was used for the production of wood polymer composites. The methyl methacrylate (MMA) and hexamethylene diisocyanate (HMDC) had densities of 0.942–0.944 g mc^{-3} and 1.046–1.047 g mc^{-3}, respectively. All chemicals were AR grade products of Merck, Germany.

2.2. Synthesis of benzene diazonium salt

Benzene diazonium salt was synthesized in the laboratory with aniline and sodium nitrite in the presence of a mineral acid at 0–5 °C using the standard diazotization method (Ismail et al., 2002). The reaction scheme for synthesis of benzene diazonium salt is shown in Fig. 1. The prepared compound was used immediately after synthesis for the coupling reaction with wood species.

2.3. Specimen preparation

All wood species were felled and cut into three bolts, each with the length of 1.2 m. Each bolt was quarter sawn to produce planks of 4-cm thickness and subsequently conditioned to air-dry in a room with relative humidity of 60% and ambient temperature of around 25 °C for three months prior to testing. The planks were ripped and machined to 20 mm (L) × 20 mm (T) × 20 mm (R) specimens for decay resistance tests and ground into samples for FTIR tests.

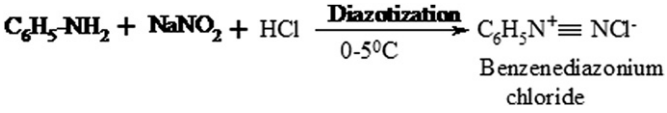

Fig. 1. The reaction scheme for synthesis of benzene diazonium chloride.

2.4. Density determination

All specimens were kept in the oven at 103 °C for 72 h before density determination. The oven-dry density of each sample was then determined by using the water immersion method (Bowyer et al., 2003). The calculation is as follows:

$$\text{Density} = \text{Mass of wood}/\text{Volume of wood} \quad (1)$$

2.5. Coupling reaction

The reaction of the diazo compound with cellulose or cellulose derivatives is known as the coupling reaction (Ibrahim, 2002). All oven-dried raw wood specimens were placed in a benzene diazonium salt solution (5 °C) containing 5 L of 5% NaOH in a reaction vessel for 30 min during pretreatment. Specimens were then removed and soaked in cold acetone to arrest the reaction. Chemically modified wood species were subsequently extracted using acetone:toluene (1:1) to remove un-reacted reagents, and subsequently oven-dried at 105 °C for 24 h.

2.6. Manufacturing of wood polymer composites

For WPC and PWPC manufacturing, oven-dried raw wood and pretreated wood specimens were placed in an impregnation vacuum chamber at a vacuum pressure of 75 mm Hg for 10 min. The respective monomer system was introduced into the chamber as the vacuum pressure was released. The specimens were kept immersed in the monomer mixture solution for 6 h at ambient temperature and atmospheric pressure to obtain further impregnation. Those were then removed from the chamber and wiped of excess impregnate. Specimens were wrapped with aluminum foil and placed in an oven for 24 h at 105 °C for polymerization to take place. The weight percentage gain (WPG) of the samples was then measured using Eq. (2):

$$\text{WPG}(\%) = [(W_i - W_o)/W_o] \times 100 \quad (2)$$

where W_o and W_i are the oven-dried weight of raw wood and monomer mixture impregnated WPC samples, respectively.

2.7. Microstructural analysis

The infrared spectra of the raw and modified wood polymer composite specimens were recorded on a Shimadzu Fourier transform infrared spectroscopy (FTIR) 81001 spectrophotometer. The transmittance range of the scan was 370–4000 cm^{-1}. The obtained spectra are described in the Results and Discussions section. The interfacial bonding between the cell wall polymer and monomer mixture was examined using a JOEL scanning electron microscope (SEM) (JSM-6701F). The specimens were first fixed with Karnovsky's fixative and then taken through a graded alcohol dehydration series. Once dehydrated, the specimens were coated with a thin layer of gold before being viewed on the SEM. The micrographs are presented in the Results and Discussions section.

2.8. Mechanical test

In order to characterize mechanical properties of manufactured composites, bending and compression tests were carried out according to ASTM D-143 (1996) using a Shimadzu universal testing