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Comparison of decay resistance of wood and wood-polymer composite prepared by in-situ polymerization of monomers



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ABSTRACT

Fast-growing plant wood Populus ussuriensis Kom, and Micheliamacclurel wood were respectively modified by formation of wood-polymer composite to improve their decay resistance. Two functional monomers, glycidyl methacrylate and ethylene glycol dimethacrylate, added with a few Azo-bisisobutryonitrile as initiator, and maleic anhydride as catalyst, were first impregnated into wood cell lumen under a vacuum-pressure condition, and then in-situ polymerized into copolymers through a catalyst-thermal treatment. The decay resistances of untreated wood and wood-polymer composites were assessed by weight loss and compared by SEM observations. SEM and FTIR analysis indicated that the in-situ polymerized copolymers fully filled up wood cell lumen and also grafted onto wood cell walls, resulting in the blockage of passages for microorganisms and moisture to wood cell walls. Thus, the decay resistance of poplar wood-polymer composite and Micheliamacclurel wood-polymer composite against brown rot fungus and white rot fungus in terms of weight loss achieved 3.43-3.92% and 1.04 -1.33%, improved 95.06-95.18% and 95.10-95.35% than those of untreated poplar wood and Micheliamacclurel wood, respectively; and also respectively higher than that of boron-treated wood. The SEM observations for the decayed poplar wood, Micheliamacclurel wood and their corresponding treated wood also showed the remarkable improvement of decay resistance of wood after such treatment, which effectively protected wood from degradation by fungi.

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1. Introduction

Wood possesses porous structure consisting of various cell walls, which are mainly composed of biopolymers, i.e., carbohydrate polymers of cellulose and hemicelluloses and phenolic polymers of lignin. Such special structure and chemical components render wood desirable for a broad variety of end uses where wood is superior to a number of other materials (Sèbe and Brook, 2001). However, depending on end applications, wood, especially fast-growing plant wood and low-quality wood like poplar wood (PW) and *Micheliamacclurel* wood (MW), have some undesirable properties. In particular, the fact that wood is vulnerable to degradation when exposed to microorganisms and susceptible to change in dimension under different moistures, often result in wood to be an ineffective material for long-term utilization. For the poor durability of wood, many attempts are made based on physical or chemical treatments to improve its disadvantages (Obataya et al., 2001). However, these treatments are normally designed based on the improvement of one disadvantage, such as preservatives to improve its decay resistance and reagents or coating treatments to improve its dimensional stability (Schniewind and Arganbright, 1984). And the preservatives, especially waterborne preservatives are normally leachable, resulting in the damage of environment (Obanda et al., 2008). Thus, to explore another modification way that can not only improve most of the wood durability, but also be friendly to environment under the situation of society attaching more attention to environment, is necessary.

In order that fungal attack can occur on wood, it is essential that the substrate can be metabolized by the fungi, and that the substrate has a moisture content above a certain threshold level (of the order of 20% moisture content) under relative mild temperature (20–30 °C) (Rowell, 2005). In other words, randomly lacking of each random factor, the microorganisms could not attack

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wood (Hill et al., 2006). Thus, suitable chemical modification seems to be effective to improve decay resistance of wood. In fact, several studies have reported that the chemical modification of wood was able to provide protection against fungal attack (Hill et al., 1998; Larsson et al., 2000; Rowell et al., 2009). A chemical modification reaction involves the formation of a chemical bond between a reagent and the cell wall polymers of wood. In almost all cases, this reaction occurs between the hydroxyl groups of these polymers and the reagent molecules. Such a reaction leads to a change in the chemical and physical properties of the substrate. For example, the acetylation of wood results in the substitution of hydrophilic hydroxyl groups with hydrophobic acetyl groups. In addition, the bonded adduct occupies additional space in the cell wall, over and above which was occupied by the proton of the hydroxyl group. Thus, the enzymes associated with metabolizing the cell wall polymers are unable to recognize the substrate because the hydroxyl groups have been substituted; the moisture content of the cell wall is not sufficiently high for fungal attack to occur; blocking of the cell wall micropores by bonded adduct prevents access to the cell wall interior. All these modifications contribute to the improvement of decay resistance of the chemically modified wood.

One normal way of chemical modifications on wood to improve wood durability is fabrication of wood-polymer composite (WPC) through in-situ formation of polymer from unsaturated monomers within wood pores (Hill et al., 2005; Habu et al., 2006). The resultant polymer can both strength the mechanical properties of wood and defer or stop wood matrix from being attacked by water or microorganisms (Hill et al., 2005). Such multifunctional treatment can help avoid the potential disadvantages of the above modifications and strengthen the wood (Yalinkilic et al., 1999; Kartal et al., 2004; Habu et al., 2006). Thus, the method became an environmentally friendly wood modification process.

However, most monomers employed can rarely enter into wood cell wall to react with hydroxyl groups and just polymerize in wood cell lumen without grafting with wood matrix (Furuno et al., 1992; Li et al., 2011a), resulting in weak chemical combination between the two phases and large numbers of hydroxyl groups still available. Thus, these monomers are unable to effectively reduce the moisture content within wood cell wall and correspondingly improve the durability of wood (Yildiz et al., 2005). Consequently, various functional monomers have been explored to improve wood durability (Zhang et al., 2005, 2006), including allyl 2,3 epoxy propyl ether (Solpan and Güven, 1995), glycidyl methacrylate (Devi et al., 2003; Kartal et al., 2004; Li et al., 2011a), and polyglycerol (Soulounganga et al., 2004). These monomers normally improved the decay resistance of wood. However, in this study, a novel chemical system constituted by two functional monomers, glycidyl methacrylate (GMA) and ethylene glycol dimethacrylate (EGDMA) is first explored on the assumption that they could polymerize within wood cell lumen and react with hydroxyl groups on wood matrix and thus improve interfacial compatibility between the two phases. Thus, the effect of such treatment on decay resistance of wood should be mainly examined.

2. Materials and methods

2.1. Raw materials

All chemicals were purchased in China. Chemicals without purification: analytical grade glycidyl methacrylate (GMA) and analytical grade maleic anhydride (MAN) (Nanjing Jiulong Chemical Industry, Nanjing, and Tianjin Kermel Chemreagent, Tianjin), ethylene glycol dimethacrylate (EGDMA), and 2,2-azobisisobutyronitrile (AIBN) (Shanghai Chemical Reagent Factory, Shanghai). Poplar lumber (*Populus ussuriensis* Kom) was obtained from the original plantation areas in Maoershan located in the northeast of China. *Micheliamacclurel* wood was obtained from 'Yulin original plantation area' located in Guangxi province of China. The two types of wood were labeled as PW and MW. Test samples of 20 mm by 20 mm by 10 mm (radial by tangential by longitudinal) were further cut from the lumbers and then oven-dried at 105 °C for constant weight. The oven-dried density of the poplar wood and *Micheliamacclurel* wood is about 0.40 \pm 0.05 g/cm³ and 0.60 \pm 0.05 g/cm³, respectively.

2.2. Preparation of WPC

The expected reactions are presented in Fig. 1. AIBN as an initiator was dissolved in MMA and GMA/EGDMA (2:1 M ratio) monomers with 0.5 wt% concentration of AIBN in each solution. Six percent of MAN (mass ratio, MAN: GMA/EGDMA) as a catalyst was dissolved in several drops of acetone and then mixed with the above monomers. PW and MW were vacuum/pressure impregnated with these solutions separately (ca. 0.08 MPa for 20 min, then 0.8 MPa for 20 min). Then, the two types of the treated woods were wrapped in aluminum foils and separately oven-dried at 110 °C for 8 h (Li et al., 2011a, 2012). The resultant modified wood was coded PW-PGE-C and MW-PGE-C, respectively (P is for polymer and C is for composite). The prepared samples were stored in a vacuum desiccator containing phosphorus pentoxide for further use.

The conversion rate and weight percent gain of the samples due to the reaction are, respectively, calculated according to the following two equations:

$$C(\%) = \left[\left(W_p - W_u \right) / (W_i - W_u) \right] \times 100 \tag{1}$$

where: *C* is the conversion rate, W_p is the oven-dried weight of wood after final polymerization treatment, W_i is the wet weight of wood after impregnation, and W_u is the corresponding oven-dried weight of unmodified wood samples.

$$WPG(\%) = \left[\left(W_p - W_u \right) / W_u \right] \times 100$$
⁽²⁾

where WPG is the weight percent gain.

2.3. Characterization of the microstructure and analysis

Polymer distribution within wood was demonstrated by environmental scanning electron microscopy (ESEM) Instrument (QUANTA 200, FEI Inc., Hillsboro, USA). The sample was cut with a surgical blade and the sample was mounted on sample holders with a double-sided adhesive tape, and then gold sputter-coated.

FTIR spectra (KBr technique) were recorded with the instrument Magna-IR560 E.S.P (Thermo Nicolet Inc., Madison, USA). Each type of treated and untreated poplar samples were ground to powder by means of a disintegrator (100-mesh screen). The samples were extracted in a soxhlet extractor with acetone for 24 h and benzene-ethanol (2/1 by vol.) for 24 h, and then subsequently dried to constant weights (Li et al., 2011a). The resolution ratio was 4 cm⁻¹ and 40 spectra were accumulated.

2.4. Evaluation of decay resistance

The decay test was carried out according to the "Chinese forest industry standard - Laboratory methods for the toxicity test of wood preservatives on decay fungi (LY/T 1283–1998)", which is referred to the international fungal decay test, JIS K 1571-Qualitative standards and testing methods of wood preservatives. (Japanese Industrial Standards (JIS), Japanese Standards Association, Tokyo, JIS, 1998) (Furuno et al., 2003).

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