Development of Thermally Enhanced Wood-Based Materials with High VOCs Adsorption using Exfoliated Graphite Nanoplatelets for Use as Building Materials

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Wood-based materials are used to manufacture various types of panels, including particleboard, fiberboard, and plywood, and they can also be used to manufacture furniture as well as interior and exterior building materials. However, wood-based materials exhibit a number of problems, including the emission of indoor air pollutants from adhesives used during production and their inherent fire risk. To date, a number of studies have investigated the emission of indoor air pollutants, and in recent years, there has been an increasing amount of interest in the flame-retardant performance of wood-based materials. In this study, the use of carbon materials was studied to improve the flame-retardant performance of wood-based materials. A comparison was made with various methods that are currently in use. The thermal conductivity was measured by the TCi method developed by C-Therm Technologies Ltd to evaluate the energy characteristics of wood-based materials that are used as interior materials.

Keywords: Wood-based materials; Exfoliated graphite nanoplatelets (xGnP); Flame retardants; Thermogravimetric analysis (TGA); Tci

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INTRODUCTION

Wood-based materials are manufactured in various forms, such as particleboard, fiberboard, and plywood, and are increasingly being used in furniture and as interior and exterior building materials (Buchanan and Levine 1999; Buyuksari *et al.* 2010; Sathre and Gustavsson 2008; Bribián *et al*. 2011; Jeong *et al*. 2012; Wang *et al.* 2013). These materials can be applied to the inside of a building as eco-friendly materials with a wide range of decorative patterns. However, the disadvantages of doing so include the emissions of indoor air pollutants from the adhesives using (Lee and Kim 2012; Kim *et al*. 2013; Mesarič *et al*. 2013, Przepiórski *et al*. 2013) as well as the increased risk resulting from the flammable nature of wood (Kim *et al*. 2002).

The adhesives used during production of such products include melamine, urea/formaldehyde, and melamine/formaldehyde resins (Hagstrand 1999; Hematabadi *et al*. 2012; Gindl *et al*. 2003). Formaldehyde is generally used as an additive and is released as an indoor air pollutant, contaminating the indoor air. Also wood as a raw material has an ignition temperature of less than 350 °C, and therefore, improvements are being made to reduce fire hazards when wood-based materials are applied as building materials (Kim *et al*. 2002; Rowell 2013).

Recent studies have investigated the use of nanoscale reinforcing fillers to produce composite materials with exceptional flame-retardant properties (Chou *et al*. 2010; Dasari *et al.* 2013; Fang *et al.* 2013; Isitman and Kaynak 2010; Sain *et al.* 2004; Wang and Yang 2010). Nanoscale materials have a porous nature, so it is easy to carry out a variety of impregnation methods. Researchers have impregnated nanoscale materials of various types, such as silica-based materials, zeolite, montmorillonite, and carbon materials, into coating materials (Chen *et al*. 1999; Zhang *et al*. 2012; Zhao *et al*. 2013), and among these, carbon materials are also actively used in various other areas, such as the automotive industry, shipping materials industry, display materials industry, and flame retardant production (Kashiwagi *et al*. 2004; Wen *et al*. 2012; Dittrich *et al*. 2013). Carbon materials are not only flame retardant, but also have a high thermal conductivity, electrical conductivity, and adsorption performance, which contributes to the reduction in the emission of indoor air pollutants (Mesarič *et al*. 2013). If such nanoscale materials were to be applied to wood-based materials, it is thus possible to address the disadvantages of using raw wood materials. In summary, carbon materials can be used as adsorbents for indoor air pollutants and are also good flame retardants.

In this study, various wood-based materials were manufactured with the application of xGnP as a filler. xGnP was mixed with the adhesive in the case of plywood and was mixed with fibers and adhesive in the case of high-density fiberboard (HDF) (Kim *et al*. 2013; Lee *et al.* 2013). These carbon materials were characterized via thermogravimetric analysis (TGA), and a thermal extractor (TE) analysis was conducted to evaluate the adsorption of air pollutants from plywood and HDF into xGnP. The thermal conductivity of these materials was measured using a TCi analyzer, and thermal properties and air pollutants adsorption as binary properties were evaluated. In general, plywood and HDF have a low thermal conductivity and poor air pollutant adsorption when compared to the multi-functional wood-based materials that were produced in this work. The novelty of this research is in the binary assessment of the properties between applied wood-based materials with and without xGnP. As a result, the binary properties of wood-based materials were evaluated, making it possible to consider using them as building materials.

EXPERIMENTAL

Materials

In this study, plywood and fiberboard were manufactured as the two different types of wood-based materials. The carbon materials were introduced at a ratio of 5% by mass into the raw materials to improve the flame retardant performance. In this experiment, high-density fiberboard, such as that used for interior materials and furniture, was produced by applying mixing xGnP and fibers (Fig. 1). The xGnP was produced by treating a graphite surface with sulfuric acid (H_2SO_4). The material was then exposed to explosion and was crushed (Kim and Drzal 2009).

Methods

Thermal conductivity and thermal stability measurements

A TCi device (C-Therm) was used to measure the thermal conductivity of a small specimen by using the modified transient plane source (MTPS) method. In contrast with other devices, TCi is able to measure the thermal conductivity of the materials in solid,

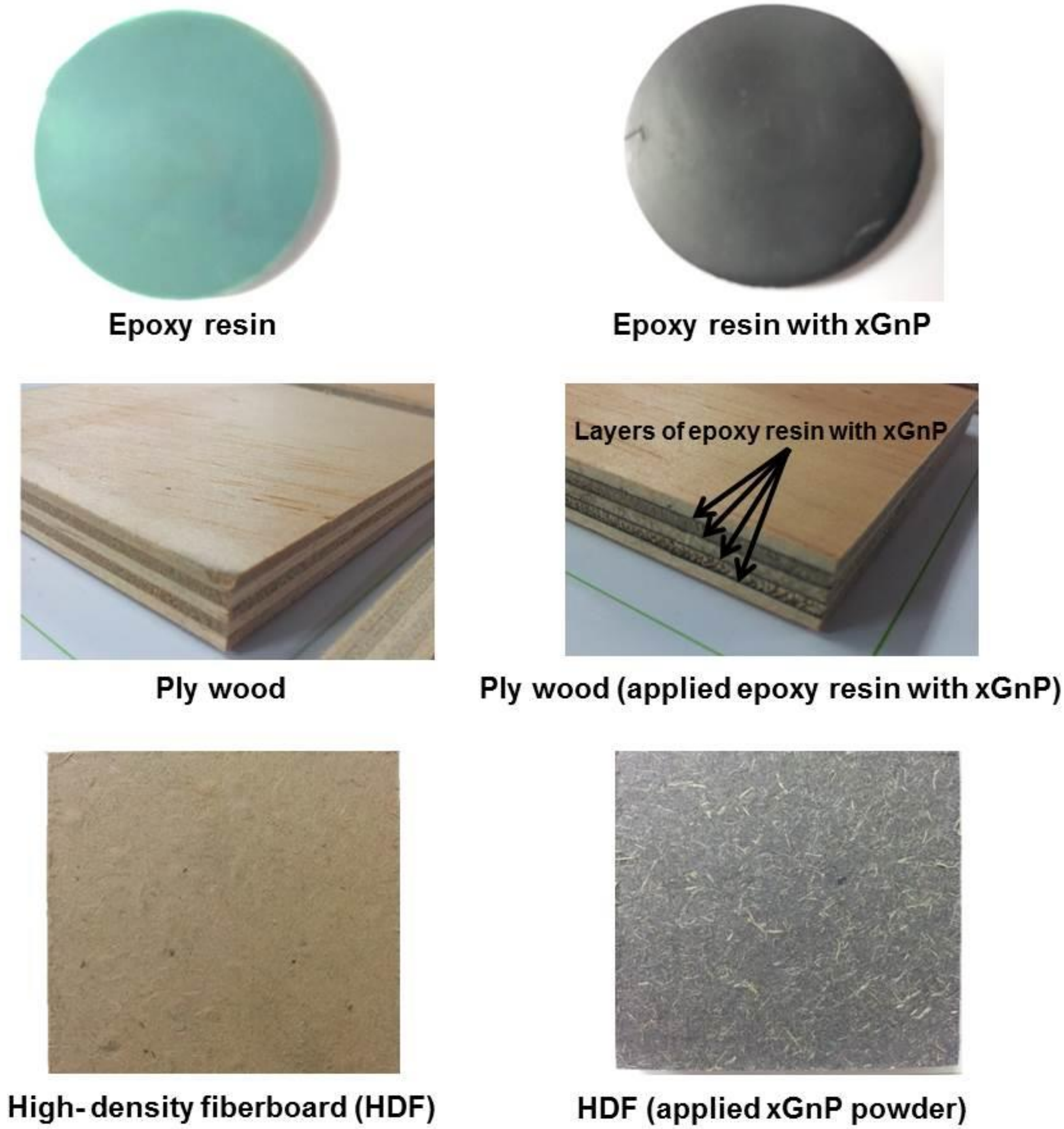


Fig. 1. Composites of xGnP mixtures

liquid, powder, and mixed states and can also measure the thermal conductivity using only one side (Kuvandykova 2010; Kuvandykova and St-Laurent 2010; Kim *et al*. 2013). The thermal conductivities of wood-based materials with various loadings were measured at room temperature (23.7 °C).

A thermogravimetric analysis (TGA) (TA Instrument; South Korea, Simultaneous DTA/TGA analyzer) was carried out to confirm the thermal stability of the samples. A differential thermal analysis (DTA) is a thermoanalytic technique that is similar to differential scanning calorimetry, which has been used for a long time to determine the transition temperature and enthalpy changes (Yang and Roy 1999). TGA was conducted to determine the mass changes of a material specimen, in terms of a given combination of time and temperature, and also to determine the pressure and gas composition of the material. The temperature was increased from 30 to 600 °C at intervals of 10 °C /min.

Thermal extractor method

A thermal extractor (TE Gerstel; Germany) was used to measure the formaldehyde and volatile organic compound (VOC) emissions at various temperatures of wood-based materials such as fiberboard, plywood, and particleboard (Lee and Kim 2012). The formaldehyde and VOCs were removed by applying a pure nitrogen gas stream with a constant flow using Tenax TA tubes and a 2,4-dinitrophenylhydrazine (DNPH) cartridge. The rate of emission of the pollutants considered the area specific emission factor, the air exchange rate ratio of the volume of clean air entering into the emission TE per hour, and the free emission TE volume measured in the same units (mg/m^2h). The thermal extraction process was applied at 25 °C.

RESULTS AND DISCUSSION

Thermal Conductivity of xGnP/Wood Composite Materials

The wood-based materials that were produced by applying xGnP were measured using thermogravimetric (TG) analysis. TG analysis measures the mass changes in the sample as a result of temperature changes. This allows for a qualitative and quantitative analysis to be conducted due to the variation of the weight curve due to the changes in the heat applied to the sample (Shin and Chung 2012). In this experiment a TG analysis was carried out to confirm the thermal stability of the xGnP/wood composite materials.

Figure 2 shows the thermal stability of the xGnP/wood composite materials that was measured using the TG analysis. The result of the TG analysis showed that the mass of all specimens decreased at temperatures from 300 to 350 °C, which is the interval course for wood combustion. The results for the untreated HDF revealed that the weight had not been reduced significantly after 350 °C. However, the results for the xGnP/HDF samples, non-treated plywood, and xGnP/Plywood composite materials each showed a second mass loss that occurred at 455.36, 445.11, and 454.45 °C, respectively. These results confirm a delay in the mass reduction ratio. The wood-based building materials made of wood fiber presented an improved flame retardant performance, and therefore, it was concluded that these results were due to the dispersion of xGnP in the raw materials. The influence of xGnP in improving the thermal transition of the wood-based materials was confirmed by conducting a thermal conductivity test using TCi.

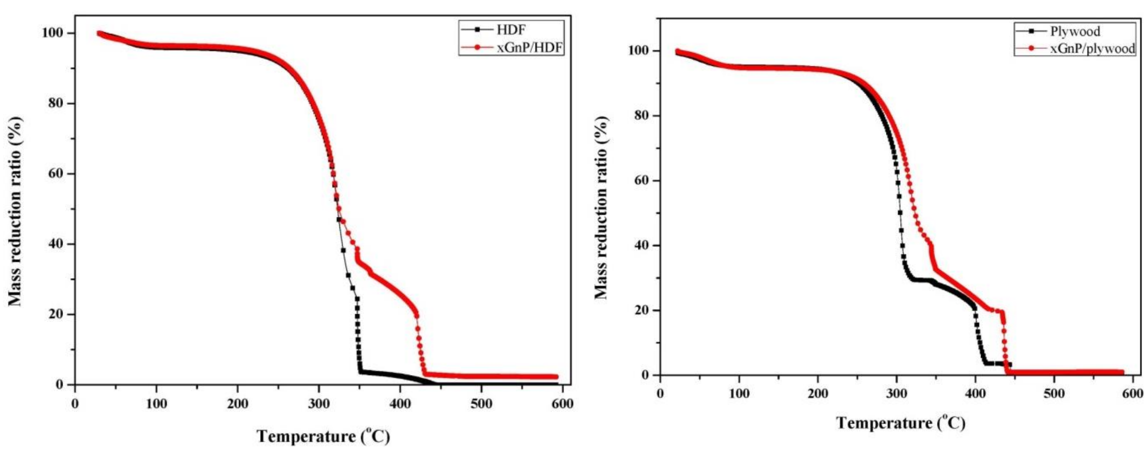


Fig. 2. Thermogravimetric analysis of the specimens

The thermal conductivity of the xGnP/HDF composites increased 4 times at 23.6 °C, as compared to pure HDF. In addition, the thermal conductivity of the plywood specimen increased 1.18 times at 23.6 °C, relative to the results for pure plywood. As expected, this indicated that mixing xGnP with the wood-based materials results in an increase in thermal transition for thermal storage during heat adsorption and release. The curve in Fig. 3 confirms the improvement in the thermal conductivity of the composite materials mixed with xGnP. As shown in the experimental results, the improvement in the thermal conductivity was higher for HDF than for plywood. When the xGnP/wood composite materials were applied as flooring materials in buildings with floor heating systems, heating energy savings were achieved in comparison to tests presented in other articles (Seo *et al*. 2011). As a result, both wood-based materials with xGnP exhibited a high thermal stability and a high thermal conductivity when comparison to wood-based materials without xGnP.

Table 1. Thermal Properties of the Specimens

Materials		Thermal conductivity (W/mK)	Thickness (mm)
Plywood	Reference	0.1133	10
	xGnP/Plywood	0.1390	10
HDF	Reference	0.1095	10
	xGnP/HDF	0.4539	10

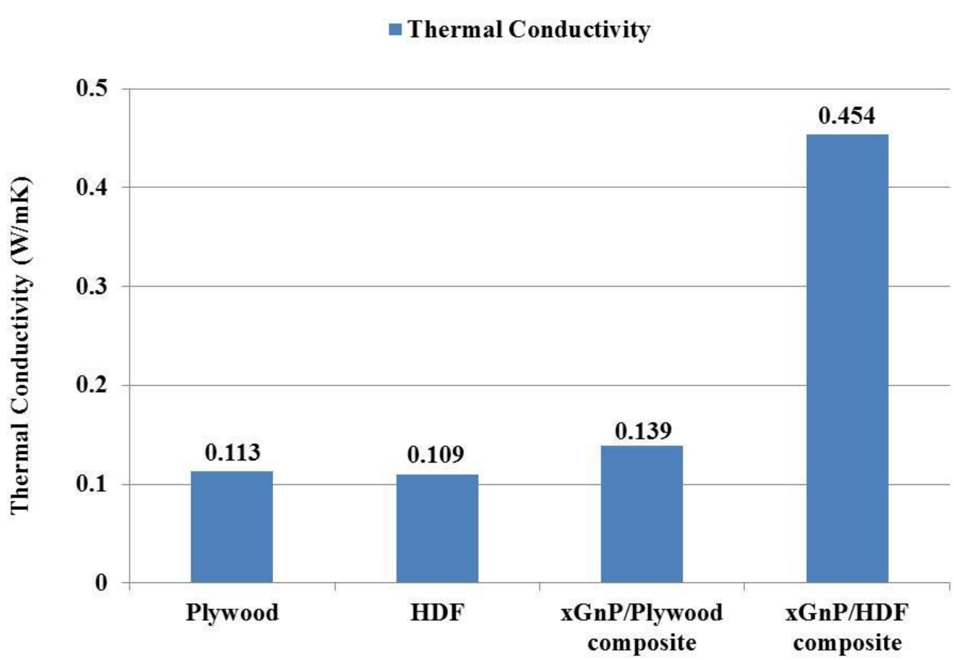
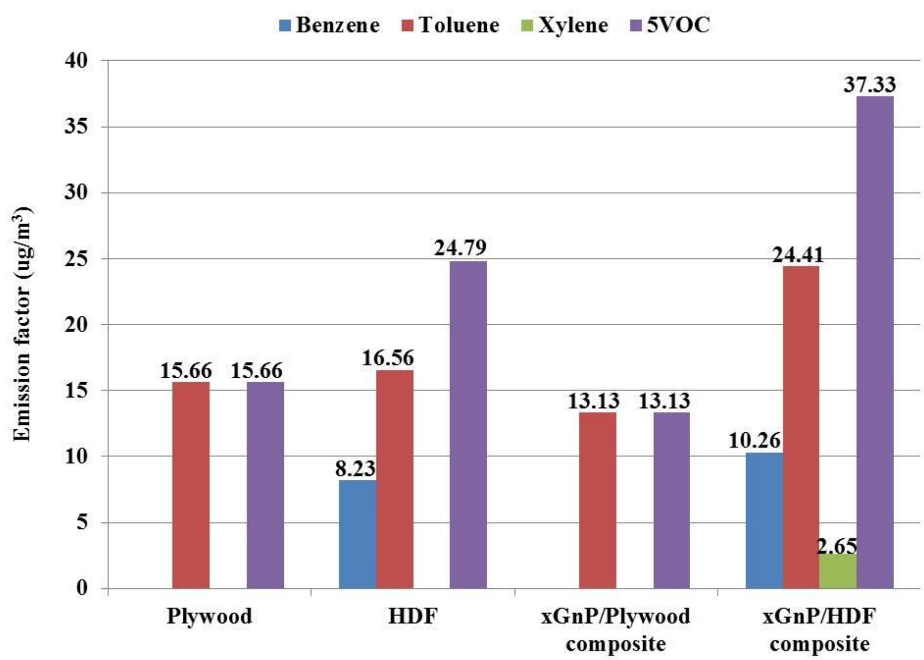


Fig. 3. Thermal conductivity of the specimens

Thermal Extractor (TE) Absorption of xGnP/Wood Composite Materials for VOCs

The VOC emissions were measured using a thermal extractor (TE). Prior to measuring the wood-based materials to which xGnP had been applied, the emission rate of the wood-based materials without xGnP was confirmed at 25 °C as a reference test, and the emission factor was determined to be 8.13 ng/(m^2h). The VOCs emitted from wood-based materials with xGnP as a porous adsorbent were then measured at 25 °C to determine their adsorption. Figure 4 shows the TVOC emission factors for the wood-based materials.

As shown in the figures, the TVOC emissions from the xGnP/wood composite materials were lower than those for untreated wood-based materials. 'Volatile organic compounds' (VOCs) is a generic name that is given to various compounds and does not refer to a single substance. Unlike common air pollutants, their source is non-specific, such as in storage facilities and in vehicle processes. When xGnP were applied in wood-based materials, the TVOC emissions were reduced. However, in the case of 5VOC emissions from xGnP/HDF, there was an increase before xGnP was applied to the HDF reference. It was determined that part of the H_2SO_4 applied during the modification of graphite had been released. H_2SO_4 had been used to increase the porosity of graphite, and during this process, the acid substances were decomposed through heat treatment as part of the H_2SO_4. Nevertheless, the amount of 5VOC emitted was 37.3 ug/m^3, and this



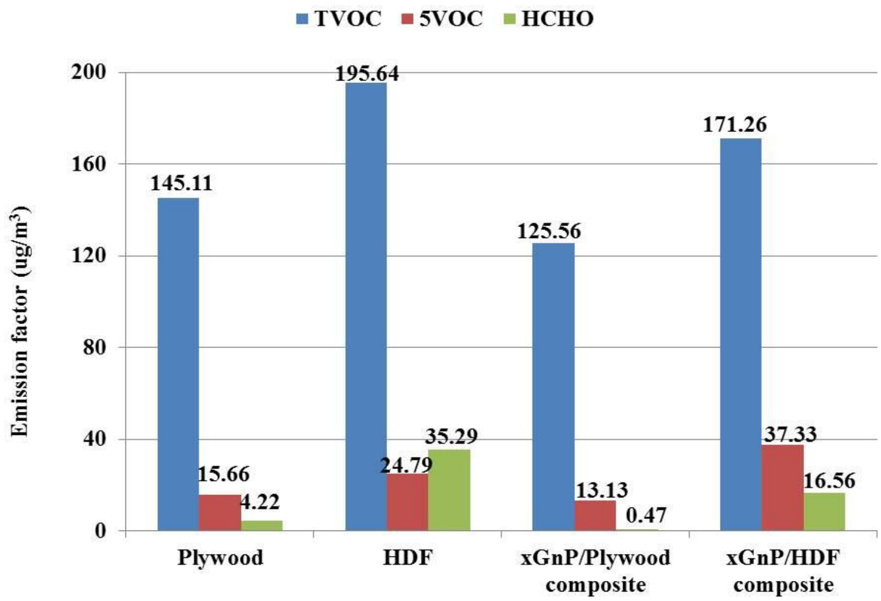


Fig. 4. TVOC emissions by type of specimen

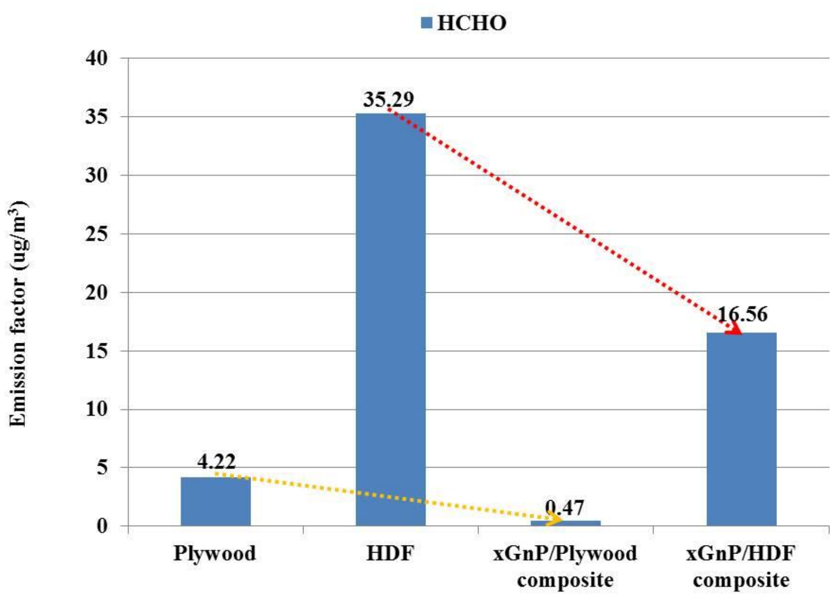


Fig. 5. HCHO emissions by type of specimen

value was significantly below the minimum value of South Korean and EU standards of VOC emissions [50 ppm (50 mg/m^3)]. Also, when considering that the decrease in the TVOC emissions, the xGnP/wood composite materials were determined to be suitable for use in interior materials that have a low level of emission of indoor air pollutants. Figure 5 shows the formaldehyde emissions according to the specimen type. The formaldehyde emitted by all specimen types did not exceed the maximum value of 0.08 ppm (0.08 mg/m^3), so we were able to determine that wood-based materials utilizing xGnP not only showed an improvement in their flame retardant performance but also expressed low levels of formaldehyde emissions.

CONCLUSIONS

The aim of this study was to rate the flame retardant performance and emission of indoor air pollutants from wood-based materials that were utilized as interior materials. The TGA method was used to determine the thermal properties of the wood-based materials, and we confirmed that the xGnP/wood composite materials exhibited improved flame retardant properties due to the delayed effects of the weight reduction when heat is applied.

The TCi method was used to confirm that the thermal conductivity also improved. Specifically, the wood-based materials that were made of wood fibers, such as HDF, displayed improved efficiency in terms of the thermal stability and thermal conductivity when compared to plywood. In addition, the TE analysis confirmed a very low level of emissions of pollutants from the material. The xGnP/wood composite materials, such as plywood and fiberboard, were subsequently estimated to be suitable for use as interior materials.

For future research, we would like to determine the optimum conditions for wood-based building materials to which xGnP are applied in order to ensure their superior performance.

ACKNOWLEDGMENTS

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF), funded by the Ministry of Science, ICT & Future Planning (2014R1A1A1064320).

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Article submitted: May 19, 2015; Peer review completed: July 20, 2015; Revised version received: August 3, 2015; Accepted; August 16, 2015; Published: September 2, 2015.
DOI: 10.15376/biores.10.4.7081-7091