Original Article

Confirmation of the performance of exfoliated graphite nanoplatelets for pollutant reduction rate on wood panel



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Abstract

Exfoliated graphite nanoplatelets have been used as an additive for the improvement of a variety of properties. Nowadays, it is used as an adsorbent for pollutants, especially volatile organic compounds and formaldehyde. Additionally, exfoliated graphite nanoplatelets have been used as an additive in wood composites, because wood composites have a higher thermal conductivity than timber or typical wood-based panels. Therefore, exfoliated graphite nanoplatelets have been applied to high-density fiberboard which is a core material of wood flooring for the emission rate reduction of volatile organic compounds and formaldehyde and for increasing the thermal conductivity of wood flooring in radiant floor heating systems. Volatile organic compound emissions have been reduced significantly in wood composite boards according to the addition of exfoliated graphite nanoplatelets. The properties of formaldehyde emission and thermal conductivity decreased when 2% exfoliated graphite nanoplatelets are added to high-density fiberboard. However, these properties increased with the increase in the addition of exfoliated graphite nanoplatelets from 2% to 4%.

Keywords

Exfoliated graphite nanoplatelets, wood-based panels, formaldehyde, volatile organic compound

Introduction

In indoor environments, many additives have been applied to building materials to improve the indoor air quality. A number of studies have been conducted on wood products because they have a larger surface area than other indoor products and emit volatile organic compounds (VOCs) and formaldehyde to the indoors.^{1,2} Porous materials and bio-scavengers are used with adsorbents usually by mixing with resin or wood-flour. For the development of eco-friendly wood products, bio-scavengers have been used as chemically adsorbent materials such as tannin, soybean, CNSL, etc., but these materials only play the role of adsorbents.^{3,4} Therefore, porous materials are used as additives in wood products to improve the physical, chemical, and mechanical properties.^{5,6} Many porous materials were used as absorbents of pollutants such as zeolite and carbon materials, etc. In the case of porous materials, because zeolite and carbon materials have a large specific surface area and a suitable pore

size (3-7 nm), pollutants can be absorbed physically on the surface area and inner pores. A pore size from 3 to 7 nm can absorb carbon dioxide which penetrates into the inner pores of the zeolite and gets fixed in them.⁷

To promote the physical characteristics and chemical properties of materials, graphites have recently been used as nano-sized compounds for mixing the polymers or materials in raw materials.^{8,9}One of the nano-sized compounds, graphite, as a carbon material, is widely used as an additive in building materials or polymers to improve the strength, thermal

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Figure 1. (a) Acid intercalation and (b) exfoliation (structure of graphite).

conductivity, ductility, hardness, and flame retardancy of materials.¹⁰ In particular, it is used to improve the strength, fire-resistance performance, and pollutant adsorption in building materials.^{11,12} By covalent bonding of carbon atoms into one layer, a layer of one-atom thickness, graphene, is created, and these layers combine together to form graphite. Each of the layers has a gap of 0.335 nm and a thin plate-like structure. Therefore, graphite has excellent physical and chemical properties such as lower expansion rate, high thermal conductivity, non-affinity with other materials, chemical resistance, lubricity, and high melting point above 3500°C.¹³ Expandable graphite, a type of graphite consisting of natural graphite flakes intercalated with acid, can be expanded up to hundreds of times its initial volume at a high temperature, resulting in the separation of the graphene sheets at the nanoscopic level along the *c*-axis of the graphene layers.^{14,15} Because expanded graphite is a porous carbon material, it can be applied to building materials such as wood flooring and wood-based composites for multi-functional building materials.

In this study, exfoliated graphite nanoplatelets (xGnPs) were used as an additive with wood-flour in the manufacturing process of high-density fiberboard (HDF). HDF is used in cabinet materials such as furniture, wood flooring, housing, and other industrial products. The use of HDF for the improvement of the indoor environment has increased over the past decade. Recently, approximately 95% of wood composite products have been installed in newly constructed residential buildings in Korea. Especially, HDF is used as the core material of wood flooring.¹⁶

Melamine-urea-formaldehyde (MUF) resins are used in the manufacturing of HDF. The HDF is measured for the reduction rate of pollutant emission using a field and laboratory emission cell (FLEC), and the HDF was determined as a wood plate material using the universal testing machine (UTM) test. MUF resin is widely used as a binder of HDF, which is the raw material used in furniture manufacturing. As a porous material, graphite has been known for its adsorption performance for formaldehyde and VOCs. Therefore, xGnPs were used as additives in wood fiber for decreasing pollutant emissions. Pollutant emissions can be controlled in HDF using MUF resins by the addition of xGnPs.

Experimental

Materials

xGnPTM is prepared from sulfuric acid–intercalated expandable graphite (3806 – hammer mill type) obtained from Asbury Graphite Mills, Inc. (NJ, USA) (Figure 1). The graphite gets heated rapidly and the entrapped intercalants vaporize as a result of the coupling of conductive graphite to microwave radiation, while the graphite flakes undergo significant expansion. The result of this exfoliation process is a worm- or accordion-like expanded structure.¹⁷ After being crushed by a hammer mill, the physical properties of the graphite are as follows: carbon 98%, size 20 µm, surface area $22 \text{ m}^2/\text{g}$, sulfur 0.022%, and resistivity 0.053 Ω cm.

Preparation of wood-based composite

HDF was made by the addition of xGnPs which were added to the wood fiber by weight and MUF resin was applied. This is a thermosetting resin with a melamine content of 12%, and the wood composite boards were prepared as follows. First, wood fiber is inserted into an agitator after adding the graphite, and after the quantification of resin and additive, and graphite is then sprayed on the wood fiber. Second, resin and additive are injected and sprayed during the mixing of the wood fiber with the graphite, and then a dryer generates heat for drying the resin and the additive. Then, after drying the blended wood fiber at a moderate level, it is poured



Figure 2. Board prepared according to xGnP content: (a) 0%;(b) 2%; (c) 3%; and (d) 4%. xGnP: exfoliated graphite nanoplatelet.

into a framework to form a mat, and the mat is moved to a pressing machine for pressing and heating. The boards prepared by this process had a size $30 \times 45 \text{ cm}^2$, and the weight of the wood fiber consumed is 1148 g. Hot pressing temperature is 185° C and the pressing time 160 s. The target thickness and density of the wood composite boards are 900 kg/m^3 and 9.0 mm, respectively. Figure 2 shows that the manufactured boards darkened according to the increase in the addition of xGnPs.

Adsorption performances of formaldehyde and VOCs

An FLEC is used for the adsorption performances of formaldehyde and VOCs. This is made of stainless steel, which is acid resistant. The diameter of the FLEC is 15 cm and the maximum surface area and volume are $0.0177 \,\mathrm{m}^2$ and $0.035 \,\mathrm{L}$, respectively. When the material is placed over the FLEC, the surface of the materials becomes the bottom of the FLEC. The sample load factor is up to $506 \,\mathrm{m}^{-1}$ (area of materials/FLEC volume). Dry air (moisture content <5 ppmv) from a gas cylinder was passed through a water bubbler in an air supply instrument to obtain a relative humidity (RH) of 50%. Dry air was introduced into the inlet of the FLEC and a laminar flow was formed in the slit of the FLEC.^{18,19} Following the convective mass transfer of air onto the surface material, the air was discharged out of the FLEC. The rate of air exchange was controlled using an air pump. The air supply pump was fitted with a sensor to monitor the pressure, temperature, and RH of the air.



Figure 3. VOC concentration according to the amount of xGnPs (wt%) added.

VOC: volatile organic compound; xGnPs: exfoliated graphite nanoplatelets.

Physical and mechanical properties of HDF

Moisture content, density, thickness swelling, and water absorption were examined. Density was controlled by quality control testing, wherein each value represents the average of four samples. The three-point bending strength and internal bond strength were determined using a UTM (Hounds Co.). Each value represents the average of four samples.²⁰

Thermal conductivity

The TCi developed by C-Therm is a device used for conveniently measuring the thermal conductivity of a small sample using the modified transient plane source method. In contrast to other devices, TCi can measure the thermal conductivity of materials in the solid, liquid, powder, and mixed states. In addition, it can measure the thermal conductivity using only one side of the sample. The TCi consists of a sensor, power control device, and computer software. A spiral-type heating source is located at the center of the sensor, and heat is generated at the center. The generated heat enters the material through the sensor during which time a rapid decrease in voltage occurs at the heating source, and the thermal conductivity is calculated through the voltage-decrease data. The experiment method is given as follows.²¹

Results and discussion

Pollutant emission rate

The total volatile organic compound (TVOC) and 5VOC emissions of HDF are shown in Figure 3. The VOC emission level decreased with the addition of xGnPs to wood fiber. The TVOC emissions for the reference board and the 4% board are 4.76 and



Figure 4. HCHO concentration according to the amount of xGnPs (wt%) added. xGnPs: exfoliated graphite nanoplatelets.

 $1.10 \text{ mg/m}^2\text{h}$, respectively. The amount of TVOC emitted from the 2% board was $2.12 \text{ mg/m}^2\text{h}$, and the TVOC emissions decreased 2.5 times compared to the reference board. Even with the addition of a small amount of xGnPs, there was a significant reduction in TVOC emissions.

The 5VOC emissions also decreased with the addition of xGnPs, and there was a significant decrease with the addition of only a small amount of xGnPs. The 5VOC emission levels of the reference board and the 4% board are 0.65 and $0.12 \,\mu\text{g/m}^3$, respectively. The emission trend of 5VOC is similar to that of TVOC and the addition of xGnPs is effective in reducing 5VOC emissions.

The formaldehyde emission of HDF is shown in Figure 4. The formaldehyde emission level decreased with the addition of xGnPs (4 wt%) to wood fiber. The formaldehyde emission level of the reference board and the 4% board are 0.37 and 0.18 mg/m²h, respectively. The formaldehyde emission level of the 2% and 3% boards is higher than that of the reference board. Therefore, the formaldehyde emission level is decreased compared to the reference board when over 4 wt% of xGnps is added to the fiber.

However, in the case of 2-4 wt%, because formaldehyde emission decreased constantly according to the amount of xGnP addition, we found that wood composite, in which xGnPs were added, plays an important role in the reduction of formaldehyde. Also, the reduction rate of the 4% board is twice the value.

Physical properties

The physical properties of HDF are presented in Table 1. The density, thickness, moisture content, and

 Table I. Physical properties of HDF according to the amount of xGnPs (wt%) added

Physical property	Unit	Reference	2%	3%	4%
Density	kg/m ³	837	766	792	834
Thickness	mm	8.31	8.66	8.56	8.08
Moisture content	%	4.44	3.4	3.4	4.1
Bending strength	kgf/cm ²	529	384	315	411
Internal bond strength	kgf/cm ²	12.3	6.0	5.5	5.2

HDF: high-density fiberboard and xGnPs: exfoliated graphite nanoplatelets.



Figure 5. Thermal conductivity according to the amount of xGnPs (wt%) added.

xGnPs: exfoliated graphite nanoplatelets.

thermal conductivity values of HDF supplemented with xGnPs are similar to those of the reference board. However, in the case of 2 and 3 wt%, because of the addition of xGnPs, which prevents the formation of HDF in the manufacturing process, the overall physical properties decreased. The bending strength and internal bond strength have lower levels than those of the reference board. Especially, the internal bond strength is twice lower than that of the reference board. The strength of HDF decreased because of xGnP addition. The cohesion between the wood fibers and the thermosetting resins is reduced due to the addition of xGnPs to wood fiber. In the case of 4 wt%, the density rises to 834 kg/m^3 due to xGnPs. The high thermal conductivity of xGnPs increases the inner thermal conductivity in the formation process of a HDF. Therefore, a reduction in strength is detected in the manufactured board because xGnPs were added to the wood fiber during the making of the board. Additionally, these results showed that a small difference in the physical properties, especially density, brings about a large difference in the mechanical properties.

Thermal conductivity

The thermal conductivity of HDF is shown in Figure 5. In the case of 2%, the thermal conductivity decreased somewhat, regardless of the addition of xGnPs. The thermal conductivity of the reference board and the 2% board are 0.133 and 0.131 W/mK, respectively. This is due to the lower density of HDF than that of the reference board. Because the inner pores of HDF increased due to a low density and similar thickness compared with the reference board, the thermal conductivity somewhat decreased. However, the important aspect is that the thermal conductivity increased with the addition of xGnPs from 2 to 4 wt%due to the high thermal conductivity of xGnPs. In this study, the amount of xGnPs required to interfere with the formation of the board is more than 3%. The thermal conductivity increased compared to the reference board when over 3 wt% of xGnps was added to the fiber.

Conclusion

The VOC emission of HDF decreased. In particular, the reduction rate of TVOC is 2.5 times that of the reference board. The5VOC emission reduced considerably and the reduction rate increased by about seven times that of the reference board. From these results, the physical adsorption performance of xGnPs is acceptable. Formaldehyde emission increased with the addition of 2% and 3% xGnPs. However, when the amount of xGnPs is 4 wt%, the formaldehyde emission level decreased by twice the value. Therefore, over 5% xGnPs should be added for the reduction of formaldehyde emission. The bending strength and internal bond strength decreased because xGnPs are added to the wood fiber during the production process. Especially, the internal bond strength decreased by about twice the value. Therefore, the properties of HDF as a commercial product are not sufficient. Thermal conductivity increased with the addition of xGnPs. While the increase in thermal conductivity is small, it is confirmed that its increase is in accordance with the increase in xGnPs.

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