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Thermal Extractor Analysis of VOCs Emitted from Building Materials and Evaluation of the Reduction Performance of Exfoliated Graphite Nanoplatelets

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Key Words
Graphite · Porous · xGnP · Thermal extractor · VOCs

Abstract
This study evaluated the amount of volatile organic compounds (VOCs) emitted from building materials, such as wallpaper, paint, adhesive and wood-flooring material, using a thermal extractor (TE). To evaluate the performance of TE on VOCs emissions of building materials according to temperature variation, all specimens were measured at two temperatures: 25°C and 35°C. Through emission results, the acceleration effect on the diffusion of VOCs in the material at the elevated temperature and the feasibility of TE on VOCs emission test according to temperature variation were confirmed. In addition, exfoliated graphite nanoplatelets (xGnP) made by using shape modification process to improve porosity of graphite, which can remove VOCs by sorption was applied to materials. The adsorption amounts of VOCs by exfoliated xGnP were evaluated at 35°C with each specimen. The xGnP as a porous material had an effect on the material emissions; the emission amounts were reduced. The emission tests were conducted with the same exposed surface area for each specimen. As the temperature increased, VOCs emission rates increased from approximately 2 to 5 times. And the adsorption performance of xGnP showed that the reduction percentage of VOCs was 9% to 81%.

Introduction

People spend on an average almost 90% of their time indoors, which presents a higher risk of inhalation of air pollutants than when spending time outdoors. It has been reported in recent years that many people, after spending some time in new buildings or newly renovated housing, complained of symptoms of illness, such as headaches, irritation of the nose, nausea, skin disorders and fatigue. Sick building syndrome (SBS) is a serious problem of poor

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air quality, and is caused by indoor contaminants in the home and work place [1–4]. SBS symptoms that are experienced by a building's occupants may be caused by volatile organic compounds (VOCs), which are known to be emitted from building materials and furnishings [5–8].

In order to reduce VOCs and formaldehyde emitted from building materials and furnishings, bake-out technology has been developed, and conducted in buildings prior to occupancy. The theoretical concept of the bake-out is to remove VOCs out of the material into the indoor air, by raising the temperature. The elevated temperature accelerates the diffusion of VOCs in the material, and decreases the amount of VOCs adsorbed, resulting in lowering the equilibrium partition coefficient, thereby allowing VOC content to rapidly reduce [9–13].

In previous studies, bake-out has disadvantages of causing damage to the plywood flooring was the largest concern because the plywood flooring is directly heated by the floor heating system. However, they found no material damage in the investigated residential housing units even though the floor temperature reached 37°C [14]. Usually, plywood flooring that is available in Korean market is designed to resist high temperatures. This is because the range of thermally comfortable floor surface temperatures for Koreans is somewhat higher because of the Korean habit of sitting on the floor [15]. Several studies determined that the comfortable floor surface temperature in Korea ranged from 28.1°C to 38.8°C. From those results, there is no damage on building materials by heating at 38.8°C [16,17]. Accordingly, bake-out is generally implemented at 35°C to prevent the damage of building materials and to reduce formaldehyde and VOCs by contractors in Korea.

In addition, porous materials with nanoscale pores are widely used to remove chemical species in a gas or liquid phase through their excellent adsorption capacities [18,19], which are closely related to the large internal surface areas and pore volumes that are generally associated with porosity. For practical industrial use, adsorptivity is one of the most important properties of porous materials with similar surface chemistry [20].

Among carbon nanomaterials, graphite is a layered material consisting of one-atom-thick sheets of carbon. The carbon atoms are bonded covalently in a hexagonal arrangement within the layer, and these layers are bonded to each other by weak van der Waals forces. The α-spacing between the carbon layers is 0.335 nm. Since the van der Waals forces are relatively weak, the material can be expanded by high temperature up to hundreds of times its initial volume, resulting in separation of the graphene sheets at the nanoscopic level along the c axis of the graphene layers [21–23].

Generally, a 20-L chamber method is used in Korea to determine the area specific emission factor of VOCs emitted from building products, which is calculated from the small emission test chamber concentration, by considering the passing air flow rate and surface area at 25°C. However, the 20-L chamber method needs 1–28 days depending on experimental purpose, which is not suitable to determine the effect of temperature variation on VOCs emissions [24,25]. In addition, the 20-L chamber method is designed to measure products of panel type, thus there are some problems with measuring products of powder type. The difficulty of 20-L chamber experiment for materials in powder form has already been described in a previous work by two of the present authors [26].

In this study, the emission of VOCs from building products was measured by using a thermal extractor (TE), which was applied at 25°C and 35°C to evaluate the feasibility of TE on VOC emission test according to temperature variation. In addition, the improvement of porous property of exfoliated graphite nanoplatelets (xGnP) compared with natural graphite was evaluated, and the adsorption performance of xGnP for removal of VOCs from the building products was also examined using the TE experimental method.

Experimental

Thermal Extractor Analysis of Materials

TE analysis was used mainly to measure the VOCs and formaldehyde emitted from construction materials, such as medium density fibreboard (MDF), particleboard (PB), paints, adhesives and floorings. The TE experiment has the advantage that can be installed particle- or powder-type materials due to its minimal specimen requirement. In addition, the TE method can be conducted at the desired temperature from room temperature to 350°C by an adjustable oven in the TE.

In this study, testing temperature was adjusted to 25°C which was the room temperature of the laboratory. Therefore, the tests were carried out at two temperatures, 25 ± 1°C and 35 ± 1°C, with a relative humidity (RH) of 55 ± 10% and the 35°C was set to fit the bake-out effect to confirm the acceleration effect of the diffusion of VOCs in the material at the elevated temperature. The gas was introduced into the inlet of the TE glass tube, which contained the VOCs emitted from the specimens. The VOCs emitted from the specimens in the glass tube were

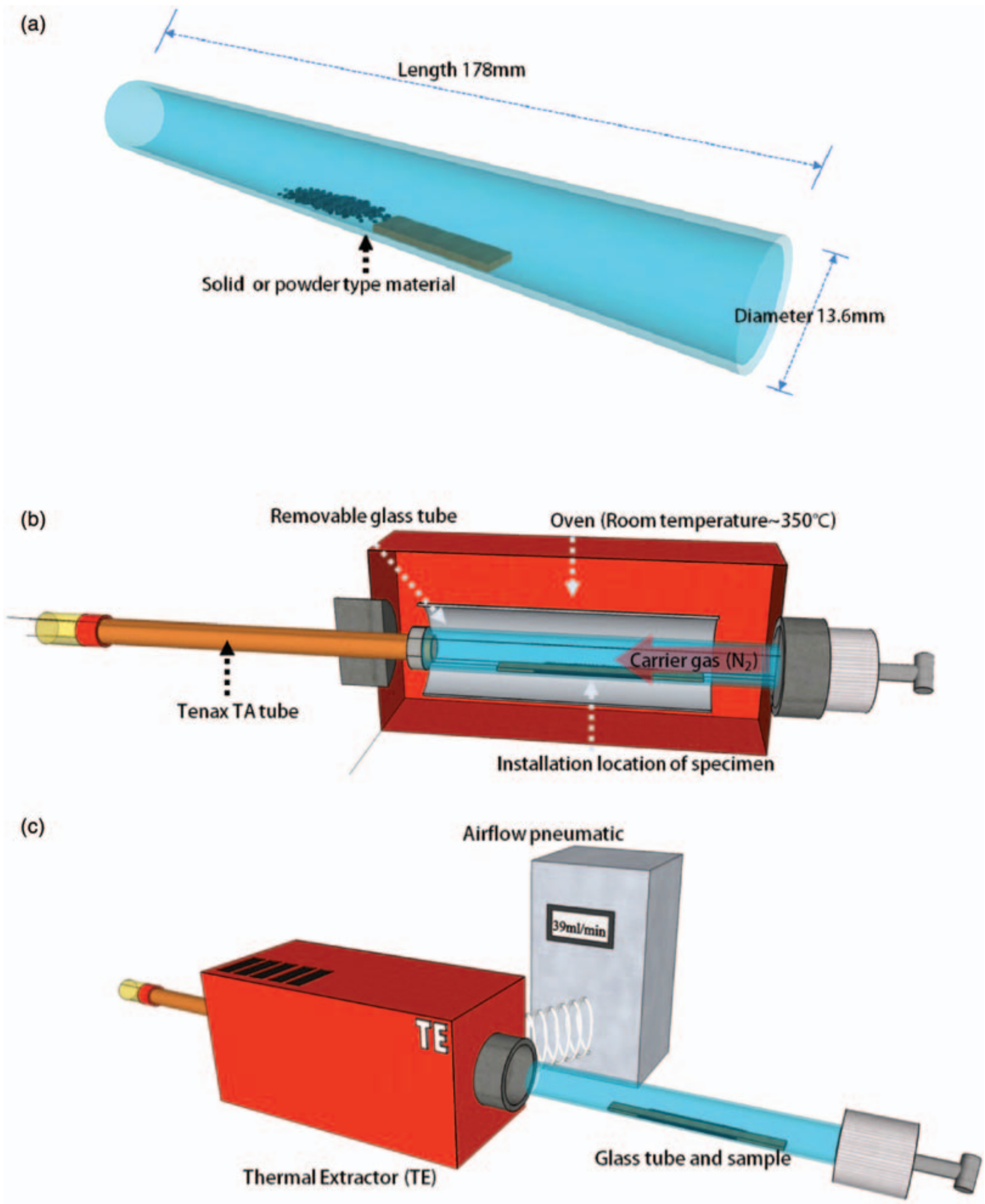

Fig. 1. Schematic diagram of the thermal extractor (TE): (a) glass tube and installation of specimen; (b) inner structure of TE; (c) the composition of the TE analysis apparatus.

sampled by Tenax TA tubes. The sampling volume was 1 L. Air sampling was performed at a flow rate of 39 mL min^{-1} for approximately 30 min by Gerstel Air flow pneumatic. Due to the low volume of the glass tube and high nitrogen gas flow, the air exchange rate was 90 h^{-1}. VOC concentrations were analysed by a gas chromatography-mass spectrum detector (GC-MSD). Figure 1 shows the TE, inner structure of the TE, and a glass tube used for the experiments.

In addition, to confirm the adsorption performance of xGnP for removal of VOCs from building materials, the comparison experimental were conducted at 35°C condition in accordance with the presence or absence of xGnP with each building material.

Materials

Specimens used in the experiments were purchased in the market as commercial products, namely paint, wall

Table 1. Types of specimens

Category	Material
Wall paper	PVC Wall paper 1
	PVC Wall paper 2
Paint	Water-borne paint
	Oil-based paint
Adhesive	Phenol-based resin
	PVAc (polyvinyl acetate) resin
Furnishing materials	MDF (medium density fibreboard)
	PB (particle board)
Wood-flooring materials	Plywood flooring
	Laminate flooring

paper, adhesive, furnishing materials and wood flooring materials. Each specimen type is shown in Table 1. All specimens were modified to expose the same exposed area of 0.0005 m^2, and were placed in a glass extraction tube of the TE.

As an absorbent material, xGnP was prepared from sulphuric acid-intercalated expandable graphite (3772) (obtained from Asbury Graphite Mills, NJ), by applying a cost and time effective exfoliation process that was initially proposed by Drzal's group [21,22].

Sulphuric acid-based graphite intercalated compounds (GICs) were fabricated from natural graphite through chemical oxidation in the presence of concentrated sulphuric acid. Expanded graphite is generally produced by using sulphuric acid-based GICs which are widely used for the exfoliation process, because they can give high expansion volume during the thermal treatment. The expanded graphite maintains a layered structure similar to that of natural graphite flake but produces very wide size range of pores and nanosheets with very high aspect ratio [27,28]. In this study, to obtain a uniform powder of xGnP, two different milling types were performed to break down the structure of expanded graphite: hammer-mill-type and fluid mill-type.

Analysis of Property Improvement on the Porosity of Modified Graphite

To determine the improvement of the porosity of the modified graphite, the morphology of natural graphite, expandable graphite, expanded graphite and exfoliated graphite was observed by scanning electron microscopy (SEM, JEOL JSM-6360A) at room temperature. An SEM with an accelerating voltage of 12 kV and working distance of 12 mm was used to collect SEM images. The samples were coated with a gold coating of a few nanometers in thickness. In addition, the Brunauer–Emmet–Teller (BET) surface area of each of the modified graphite was measured using an auto N_2 absorption instrument.

Results and Discussion

Porous Properties of the Modified Graphite

The morphology of the graphites in accordance with the modification process was confirmed by SEM analysis. Sulphuric acid-based graphite was fabricated from natural graphite, through chemical oxidation in the presence of concentrated sulphuric acid. In this morphology, the layers of graphite were clearly shown, when compared to before the sulphuric acid treatment. Figure 2(c) shows the worm- or accordion-like expanded structure of graphite intercalated compounds, which were exfoliated up to about 500 times their initial volume by rapid heating in a microwave environment. The multi-pore structure is observed from high magnification ($\times 50$) of the expanded graphite. Pulverisation using a hammer mill or fluid-energy mill processor was employed to break down the worm-like structure and to reduce its size, resulting in individual graphite nanoplatelets of <10 nm in thickness with an average diameter of 15 mm, as shown in Figure 2(d). This means that through the graphite modifying process the natural graphite became a highly porous material, with high specific surface area.

The specific surface area of the exfoliated graphite nanoplatelets was analysed by BET analysis. Consequently, we determined the improvement of porosity. One gram of natural graphite represented 1.1985 m^2 of surface area, but the expanded graphite showed approximately 25 times the surface area of natural graphite. However, we confirmed that the exfoliated graphite nanoplatelets bore a reduced specific surface area after the graphite exfoliation process. In spite of the decrease of specific surface area, the hammer mill-type of xGnP had more than 17 times the specific surface area of natural graphite. In addition, the total pore volumes of graphites were also increased, and various volumes of pores were generated through the modifying process compared with natural graphite. The results showed the values of natural, expandable, expanded, fluid energy-mill type and hammer mill type of 0.004621, 0.005567, 0.095333, 0.059891 and 0.081583 $m^3 g^{-1}$, respectively. In particular, after the exfoliate process, the decrease in the amount of total pore volume of the hammer mill type xGnP was lower than the fluid-energy mill type of xGnP. As a consequence of these results, the hammer mill-type of xGnP was used as

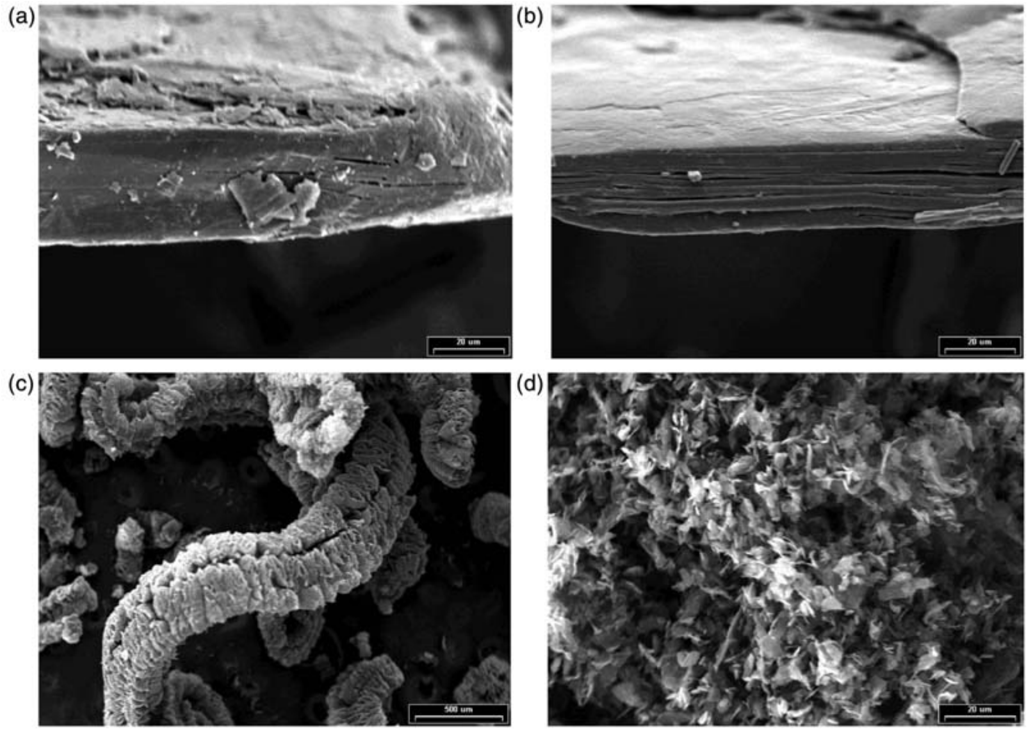

Fig. 2. Morphological changes of graphite according to the modifying process: (a) natural graphite; (b) expandable graphite; (c) expanded graphite; (d) xGnP.

an absorbent in our TE experiments, because of its higher porous property. The results of BET analysis are shown in Table 2 and Figure 3.

Table 2. The results of BET analysis

Type of graphite	Specific surface area ($m^2 g^{-1}$)	Total pore volume ($m^3 g^{-1}$)
Natural graphite	1.1985	0.004621
Expandable graphite	1.1207	0.005567
Expanded graphite	30.8898	0.095333
xGnP (Fluid energy-type mill)	18.5498	0.059891
xGnP (Hammer mill type)	20.4055	0.081583

The Effect of Temperature Change on VOCs Emissions

To evaluate the accuracy of evaluation performance of TE according to temperature variation, experiments were conducted at two specific temperatures: 25°C and 35°C. Figure 4 shows the variation of VOCs emissions with temperature change.

At a temperature of 25°C, most specimens showed low emission rates under $5\,mg\,m^{-2}\,h^{-1}$, except for plywood flooring. However, as the temperature increased, VOCs emission rates increased from approximately 2 to 5 times. This is because VOCs are volatile substances that are sensitive to temperature, and the activation of volatile compounds in each material was elevated by an increase in temperature. In particular, plywood flooring showed significantly high emission rate in the state of room temperature and the growth rate of VOCs at elevated temperature was also higher than the others, approximately 550%. The reason of highest emission rate from the plywood flooring is due to the species. Generally, softwood emits abundant natural VOCs. Thus, it seemed that the emission amount of natural VOCs emitted from plywood flooring was detected in TE test sampling process.

Previous studies reported the changes in emission with temperature, and concluded that the emitted substances were temperature dependent [29–31]. Temperature variations did not have a significant effect on the emissions of VOCs with a lower boiling point, but had a stronger effect on VOCs at a higher boiling point [32]. As shown in Figure 4, the VOCs emission rates from building materials were significantly affected by temperature. Through the previous studies and this paper, the acceleration effect of VOCs at elevated temperature was confirmed. In addition, the accuracy of evaluation performance of TE was also confirmed according to temperature variation.

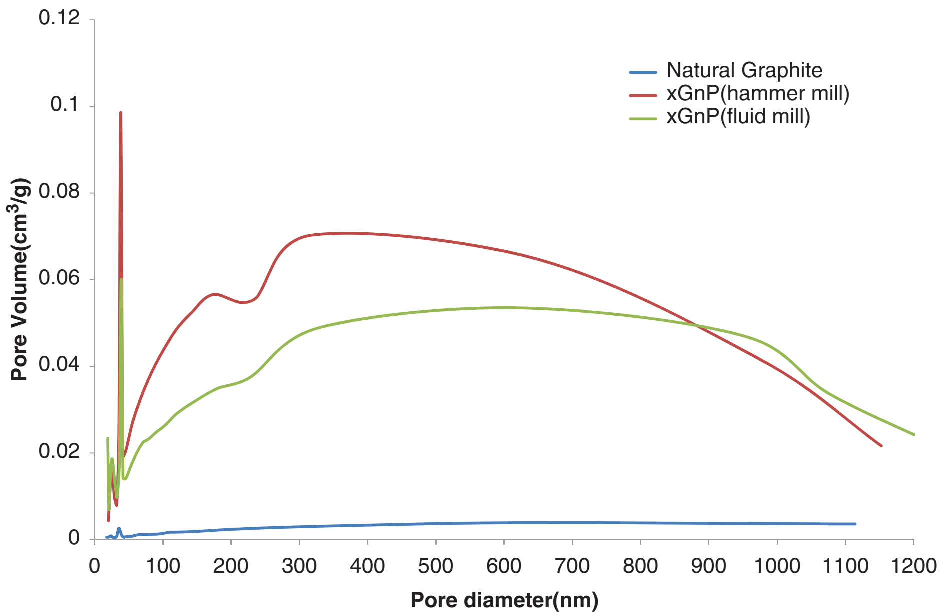

Fig. 3. Dispersion of pore volume and diameter of natural graphite and xGnP.

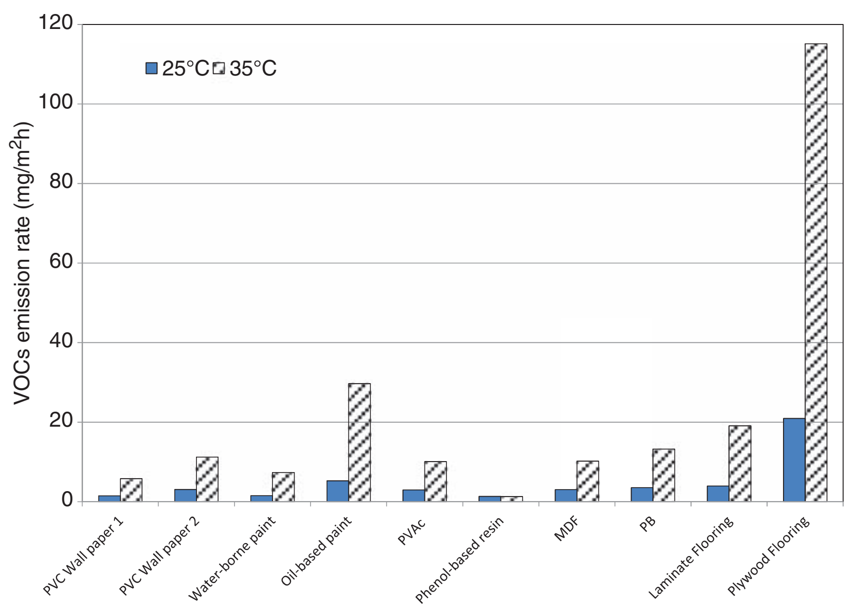

Fig. 4. VOCs emission rate from building materials according to temperature variation.

The Adsorption Performance of xGnP for VOCs

Each specimen was installed with 0.1 g of xGnP as adsorbent material at 35°C, to determine the adsorption performance of xGnP. Figure 5 shows the TVOC emission factors of specimens containing xGnP at 35°C, compared with the sample that did not contain xGnP.

In case of wall papers, the emission rate of PVC wall paper 1 and PVC wall paper 2 decreased about 82% and 46% when TE test were performed with xGnP. However, the reduction amount of VOCs showed similar value as much as 4.75 and 5.19 $mg\,m^{-2}\,h^{-1}$. These results were caused by the use of a similar raw material of PVC in the wall papers.

In case of paints, the emission rate of oil-based paint decreased about 9%, which released a large amount of VOCs. On the other hand, the decreased rate of water-borne paint showed about 76%. These test data showed that the components and emission amounts of VOCS

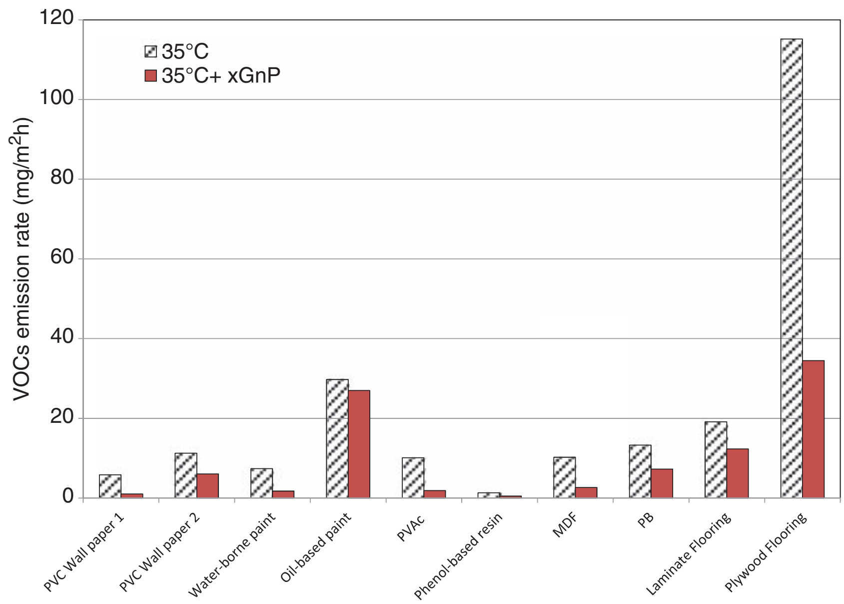

Fig. 5. The variation of VOCs emission rate according to the addition of the absorbent material.

Table 3. The results of VOCs emission values and reduction rates ($mg\,m^{-2}h^{-1}$)

Material	VOCs emission rate at 25°C	VOCs emission rate at 35°C	VOCs emission rate at 35°C with xGnP	Reduction rate (%)
PVC Wall paper 1	1.492	5.781	1.032	82.14
PVC Wall paper 2	3.058	11.232	6.038	46.24
Water-borne paint	1.532	7.354	1.729	76.49
Oil-based paint	2.239	29.710	26.995	9.14
Phenol-based resin	1.326	1.287	0.494	61.63
PVAc resin	2.963	10.075	1.849	81.64
MDF	3.051	10.233	2.2665	73.94
PB	3.526	13.232	7.251	45.20
Plywood flooring	20.945	115.173	34.482	70.06
Laminate flooring	3.958	19.085	12.317	35.47

emitted from paints had led to the differences in the VOCs emission rates.

In case of adhesives, PVAc showed higher reduction rate of VOCs rather than phenol-based resin. Due to the insufficient emission rate of phenol-based resin, the reduction amount showed was also lowered.

In cases of wood-based products, MDF, PB and laminate flooring showed reduction percentages of VOCs were to 35–73%. However, the reduction amount of plywood flooring was much higher than other wood-based products. Table 3 shows all VOCs emission result values.

Figure 6 shows the improved capacity of adsorption/absorption in porous media. The gap of graphite sheet layer help reduction of VOCs, and expanded and exfoliated graphite can improve the VOCs removal performance because of its increased fine porosity. In addition, the growth porosity of xGnP can produce the reduction performance of a porous media. The capillary condensation and micro-pore of xGnP play a key role physicochemically as a scavenger.

According to the results, the adsorption performance of xGnP was evident in all experiments, and the reduction range of VOCs was confirmed to be 9–81%. In particular, the emission rate of the PVAc resin decreased by approximately 82% through the addition of xGnP. The emission amount of VOCs for plywood flooring showed the highest amount of reduction, with a value of $80.69\,mg\,m^{-2}\,h^{-1}$. As the results, VOCs emission rate

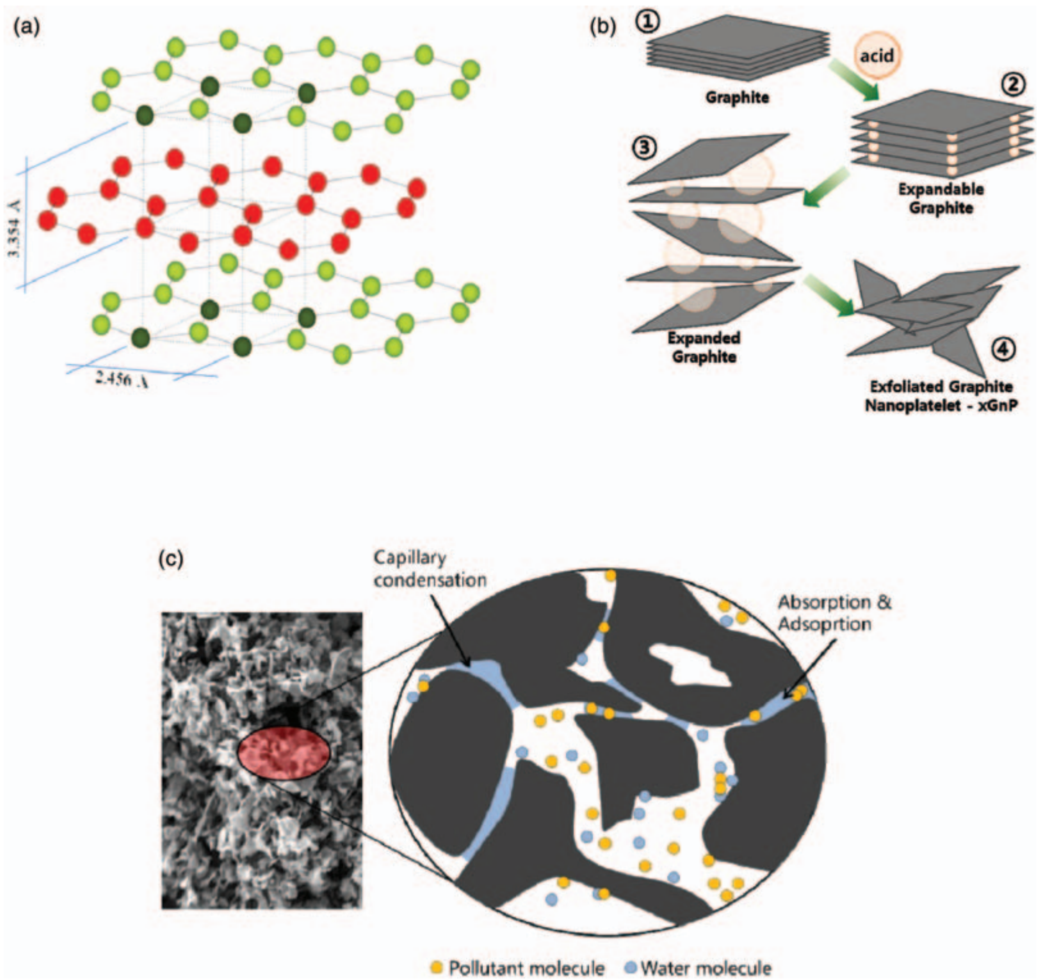

Fig. 6. Improved capacity of adsorption/absorption in porous media: (a) structure of graphite; (b) expansion and exfoliation process of xGnP; (c) water vapour effect on contaminant adsorption/absorption in porous media.

from building materials was affected by xGnP as an absorbent. Thus, the adsorption performance of xGnP was confirmed using TE method.

Conclusion

The variation of emission rate from building products with an increase in temperature was confirmed by using TE analysis. The difference according to the temperature variation was clearly shown, and the results of experiments confirmed TE analysis to be a useful test method for measuring building materials at desired temperature. In addition, the TE method is applicable to powder-type specimens, which shows that it is possible to evaluate the adsorption performance of powder specimens accompanied by porous materials. Another benefit of TE analysis is that a small size or small amount of specimen is adequate for the TE analysis, due to the minimal specimen requirement. The results of the experiments to determine the adsorption performance of xGnP were in accordance with expectation. Thus, it is expected that xGnP can be applied to building materials such as wood flooring and wood-based composite, after surface treatment, to provide low-emission building materials.

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