Journal of Hazardous Materials 187 (2011) 37–43

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Reduction of VOC emission from natural flours filled biodegradable bio-composites for automobile interior

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ARTICLE INFO

Article history:
Received 24 October 2009
Received in revised form 13 July 2010
Accepted 20 July 2010
Available online 23 August 2010

Keywords:
Volatile organic compounds
Biodegradable polymer
Thermo-extractor
Field and laboratory emission cell
20 L small chamber
Automobile interior

ABSTRACT

Various experiments, such as the thermal extract (TE) method, field and emission cell (FLEC) method and 20 L small chamber, were performed to examine the total volatile organic compound (TVOC) emissions from bio-composites. The TVOC of neat poly(lactic acid) (PLA) was ranged from 0.26 mg/m^2 h to 4.11 mg/m^2 h with increasing temperature. For both PLA bio-composites with pineapple flour and destarched cassava flour, the temperature increased from 0.30 mg/m^2 h to 3.72 mg/m^2 h and from 0.19 mg/m^2 h to 8.74 mg/m^2 h, respectively. The TVOC emission factors of all samples increased gradually with increasing temperature. Above 70 °C, both PLA-P and PLA-C composites had higher TVOC emission factors than neat PLA due to the rapid emission of natural volatile organic compounds (VOCs), such as furfural (2-furancarboxyaldehyde). PLA composites containing 30 wt% flour had high 1,4-dioxane reduction ability, >50%. The TVOC of poly(butylene succinate) (PBS) was emitted rapidly from 50 °C to 90 °C due to succinic acid from the pyrolysis of PBS. The TVOC emission factors of PLA bio-composite and PBS bio-composites were reduced using the bake-out method (temperature at 70 °C and baking time 5 h). The initial TVOC emission factors of the PLA and PBS bio-composites with pineapple flour and destarched cassava flour were reduced by the baking treatment using FLEC. The TVOC factors from PLA and PBS decreased until 5 days and were commonly maintained a relatively constant value after 5 days using 20 L small chamber. The decrease in TVOC emission showed a similar trend to that of the TE and FLEC method. This method confirmed the beneficial effect of the baking treatment effect for polypropylene and linear density polyethylene (LDPE).

1. Introduction

With the increasing problems of pollution worldwide, considerable effort is needed to reduce the consumption of petrochemical products. This also highlights the necessity of eco-friendly products, such as bio-composites, in the automotive industry. Therefore, new composite materials with the properties of current materials are needed. Bio-composites can be tailored to meet the performance requirements of car interior materials in the automotive industry such as:

- Tensile, flexural and impact properties
- Acoustic absorption
- Low odor emission and fog
- Aging resistance
- Low flammability

Recently, 'Sick Car Syndrome' has been highlighted as a problem for new cars that contain a large quantity of VOCs (volatile organic compounds) in their interior parts. Consequently, automotive makers have struggled to reduce the VOCs emitted from car interiors.

In the building field, there has been considerable research into methods to reduce TVOCs (total volatile organic compounds), such as ventilation equipment, the application eco-friendly materials and bake-out treatments. 'Bake-out' has been used to reduce the emissions of VOCs from newly installed materials, products and furnishings. This procedure is normally used to prevent building-associated illnesses caused by the out-gassing of volatile organic compounds (VOC) and formaldehyde from residual solvents in new building materials and furnishings. In this procedure, the air tem-

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doi:10.1016/j.jhazmat.2010.07.075

Table 1
Properties of the TE method.

Test condition	TE
Sample area	0.000723 m^2
Volume	0.000026 L
Loading factor (area of sample/volume, m^2/m^3)	27.81
Air change rate (h^{-1})	90
Air supply (mL/min)	39
Equilibration time	Sampling after 15–30 min
Compounds, sampling flow and total sampling	High purity N_2 gas

Table 2
Properties of the FLEC method.

Test condition	FLEC
Sample area	0.0177 m^2
Volume	0.035 L
Loading factor (area of sample/volume, m^2/m^3)	505.71
Air change rate (h^{-1})	428.57
Air supply (L/min)	250
Equilibration time	Sampling after 15–30 min
Temperature, humidity	23 ± 2.0 °C, 50 ± 5%
Compounds, sampling flow and total sampling	High purity air
Inlet air	High purity air
Background concentration	VOC: 2 μg/m^3, TVOC: 20 μg/m^3
Cleaning process	Vacuum oven or cleaning by methylene then high purity air for 1 day
Analysis method	GC/MS for VOC, HPLC for formaldehyde

perature in an unoccupied but fully furnished building is elevated while some ventilation is maintained [1–3]. The principle of this process is to drive the VOCs out of the construction materials by increasing the temperature in the building to 32–40 °C, while increasing the outdoor air exchange so that hazardous gases are emitted from the building. The procedure generally takes several days to 2 weeks, and is performed prior to occupancy. According to the results of a few pilot studies, a 60–94% decrease in the total VOC levels was achieved using a bake-out treatment [4]. To measure the TVOC and formaldehyde emission from interior materials, paints and adhesives have been studied using a range of experimental instruments. The formaldehyde concentration from wood-based panels was determined using desiccator and perforator test methods [5,6]. In the case of the TVOC and formaldehyde emission factors, a 20 L small chamber, field and laboratory emission cell (FLEC) and VOC Analyzer are used to examine the low pollution levels in indoor air [7,8]. These studies have helped reduce the emission of TVOC and formaldehyde in the construction field. Kim et al. [9] suggested that a UV coating can reduce the VOCs and formaldehyde from flooring. However, there are few reports of an analysis of automobile indoor air and biodegradable polymers using the TVOC emission reduction method.

This study examined the TVOC emission behavior of biodegradable materials to reduce the TVOC levels in car indoors using a range of test instruments. TVOC reduction was confirmed by the application of a 'bake-out' process. The optimum 'bake-out' conditions can reduce TVOC emission and prevent 'Sick Car Syndrome'.

2. Experimental

2.1. Materials

2.1.1. Biodegradable polymers

PLA was supplied by Cargill-Dow Co., USA, with an MFI and density of 15 g/10 min (190 °C/2160 g) and 1.22 g/cm^3, respectively. PBS was prepared at Ire Chemical Ltd., Korea, with an MFI and density of 25 g/10 min and 1.26 g/cm^3, respectively. Low-density polyethylene (LDPE) and polypropylene (PP) were supplied by LG Chem., Ltd. and Hyosung Co., Korea, respectively, and had a melt flow index of 24 g/10 min (230 °C/2160 g) and 1.7 g/10 min (190 °C/2160 g), respectively.

2.1.2. Natural flours

The natural flours used as reinforcing fillers, pineapple skin flour and destarched cassava root flour, were supplied by CSTRU in Thailand. The second bio-flour was prepared at the CSTRU by treating the non-destarched cassava root flour with α-amylase (2 h, 100 °C) and glucoamylase (overnight, temperature <60 °C) to remove the starch fraction (up to 69% dry weight basis), resulting in destarched cassava root flour. Tables 1 and 2 list the proximate analysis and particle size distribution of the natural flours, respectively.

2.1.3. Compounding and sample preparation

The pineapple and destarched cassava flour were oven dried at 105 °C for 24 h to adjust the moisture content to 1–3%, and then stored in sealed polyethylene bags prior to compounding. The PLA and PBS were blended with each flour in a laboratory-sized, co-rotating, twin screw extruder (Model BA-19, Bau Technology, South Korea) using three general processes: melt blending, extrusion and pelletizing. The extruder barrel was divided into eight zones with the temperature in each zone being individually adjustable.

The matrix polymer was loaded with 30 wt% of pineapple or destarched cassava flour. The temperature of the mixing zone in the barrel was maintained at 145 °C (in the case of PBS) and 185 °C (in the case of PLA) with a screw speed of 250 rpm. The extruded strand was cooled in a water bath and pelletized using a pelletizer. The extruded pellets were oven dried at 60 °C for 24 h and stored in sealed polyethylene bags to avoid moisture infiltration.

2.2. Methods

2.2.1. Thermal extractor analysis (TE)

TE analysis is used mainly to measure the TVOC and formaldehyde emitted from construction materials, such as MDF (Medium Density Fiberboard), PB (Particle Board), paints and adhesives.

Initially, to prepare the sample for TE, the extruded pellets were injection molded into test bars using an injection molding machine (Bau Technology, South Korea). The melting temperature was maintained at 145 °C and 185 °C for the PBS and PBS matrices, respectively. The injection and device pressure was 1200 psi and 1500 psi, respectively. After injection molding, the test bars were conditioned at 50 ± 5% RH for at least 24 h before testing and sealed in aluminum foil.

Fig. 1 shows the TE, inner structure of TE and a glass tube used for the experiments. Table 1 lists the properties of the TE method. The bio-composites were heated from 30 °C to 90 °C in glass tube surrounded by a heating oven using a Gerster Aux Controller 163. The air-flow of TE was controlled at 39 mL/min using high purified nitrogen gas supplied by Gerstel Airflow pneumatic and 1 L of TVOC was sampled. The gas was introduced into the inlet of the glass tube and contained the VOCs emitted from the bio-composites. The VOCs (volatile organic compounds) of the bio-composites (PLA bio-composites and PBS bio-composites) in the glass tube were sampled in Tenax TA tubes. The VOC concentrations were analyzed by gas chromatography with a mass spectrum detector (GC-MSD).

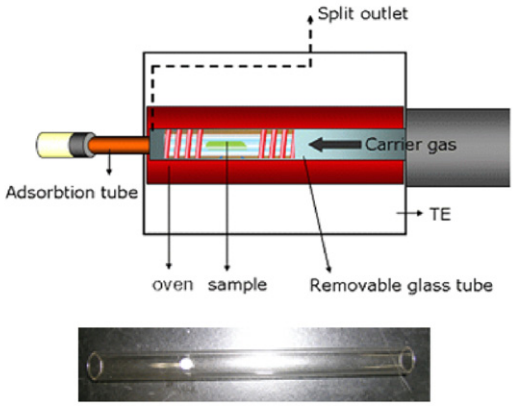
2.2.2. Field and laboratory emission cell (FLEC)

The TVOC and formaldehyde emissions of the surface materials were measured using field and laboratory emis-

① TE : width 100mm, Depth 250mm, Height 100mm

② Gerster Aux Controller 163 (temperature control)

③ Gerstel Airflow pneumatic (airflow control)



Glass tube

outer diameter:16 mm

inner diameter :13.6 mm

length : 178 mm

Fig. 1. Schematic diagram of the thermal extractor dimensions and the dimension of the glass tube.

sion cell (FLEC) techniques under the test conditions listed in Table 2.

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 of 50%. The air was introduced into the inlet of the FLEC and formed laminar flow in the slit of the FLEC [10]. After convective mass transfer of air onto the surface material, it 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. The exhaust air from the bake-out treated and untreated samples was sampled after 0, 1, 3, 5 and 7 h using Tenax TA tubes.

2.2.3. 20 L small chamber test

A 20 L small chamber was developed in Japan to determine the levels of formaldehyde and VOC emission from construction materials, paints, etc., whose performance is in compliance with the ASTM (D5116-97, D6007-96), ECA (Report No. 2, Report No. 8, Report No. 13) and ENV 13419-1 [11–16]. Before installing the samples in the 20 L small chamber, they were washed with distilled water to eliminate any pollutants and baked out in an oven at 270 °C. The 20 L small chamber was supplied with purified air at 50 ± 5% RH at a ventilation rate of 0.5ACH with an air-flow of 0.01 $m^3\,h^{-1}$. During the experiments designed to measure the emission of formaldehyde and TVOC, the inner chamber temperature was kept constant at 25 ± 1 °C. The air in the chamber of the bake-out treated and untreated samples was sampled after 0, 1, 3, 5 and 7 days using Tenax TA tubes. The TVOC (total volatile organic compound) concentrations were analyzed by gas chromatography with a mass spectrum detector (GC-MSD).

3. Results and discussion

3.1. TVOC emission for bio-composites at isothermal condition

The inner temperature of a car in Korea changes according to the seasons. The maximum internal car temperature in spring and fall is approximately 50 °C but can be as high as 90 °C in summer. Therefore, five temperatures ranging from 30 °C to 90 °C were used to determine the optimal baking treatment conditions for a car interior material. Fig. 2(1) shows the TVOC emission factors of the PLA and PLA bio-composites with the different flours. The TVOC of neat PLA was emitted from 0.26 mg/m^2 h to 4.11 mg/m^2 h with increasing temperature. In addition, for both PLA bio-composites with pineapple flour (PLA-P) and destarched cassava flour (PLA-C), the amount of TVOC emitted increased with increasing temperature from 0.30 mg/m^2 h to 3.72 mg/m^2 h and from 0.19 mg/m^2 h to 8.74 mg/m^2 h, respectively. The TVOC emission factors of all samples increased gradually with increasing temperature. It is possible that the VOCs in the composites had more active mobility at higher temperatures, which was easier to emit from the composites. Below 70 °C, all the samples had a similar TVOC emission factor. However, above 70 °C, both the PLA-P and PLA-C composites had higher TVOC emission factors than that of neat PLA due to the rapid emission of natural VOCs, such as furfural (2-furancarboyaldehyde). Table 3 shows the furfural emitted from PLA-P. However, the furfural emission factor of PLA-C was lower than that of PLA-P (Table 1). The furfural emitted from the PLA-P composite is a major VOC in the TVOC, but PLA emitted 1,4-dioxane, a known carcinogen, at approximately 3.23 mg/m^2 h at 90 °C. On the other hand, the 1,4-dioxane emission factor in PLA-P composites was 1.59 mg/m^2 h, which indicates a high 1,4-dioxane reduction ability (>50%) because the PLA composites contained 30 wt% of the flours.

Fig. 2 shows the TVOC of the PBS and PBS bio-composites with different flours. Below 50 °C, all samples had a similar TVOC emission factor. However, the TVOCs of PBS were emitted rapidly from 0.77 mg/m^2 h at 50 °C to 17.41 mg/m^2 h at 90 °C. At this temperature region, succinic acid was the major VOC in the VOCs emitted from PBS, which indicates an emission factor of approximately 7.24 mg/m^2 h at 90 °C. PBS is produced by a condensation reaction of the glycols 1,4-butanediol and aliphatic dicarboxylic acid, e.g. succunic acid [17]. Therefore, as the heating temperature approaches the melting temperature (116 °C) of PBS, more succinic acid will be emitted from the pyrolysis of PBS. However, the succinic acid of the PBS bio-composites had a relatively low emission factor due to the large amount of flour contained instead of PBS. The same was observed for the PLA bio-composites, the level of furfural from the PBS bio-composite increased gradually to above 50 °C.

Fig. 3 shows the TVOC emission factor of PLA and PBS at 70 °C according to the baking time, such as 0, 1, 3, 5, and 7 h. PLA and PBS showed a gradual decrease in the TVOC value with increasing baking time; from 6.56 mg/m^2 h to 3.69 mg/m^2 h and from 21.77 mg/m^2 h to 8.0 mg/m^2 h, respectively. This suggests that the VOC contents in PLA and PBS can be decreased by baking at 70 °C. PBS has a higher TVOC emission factor than PLA with increasing

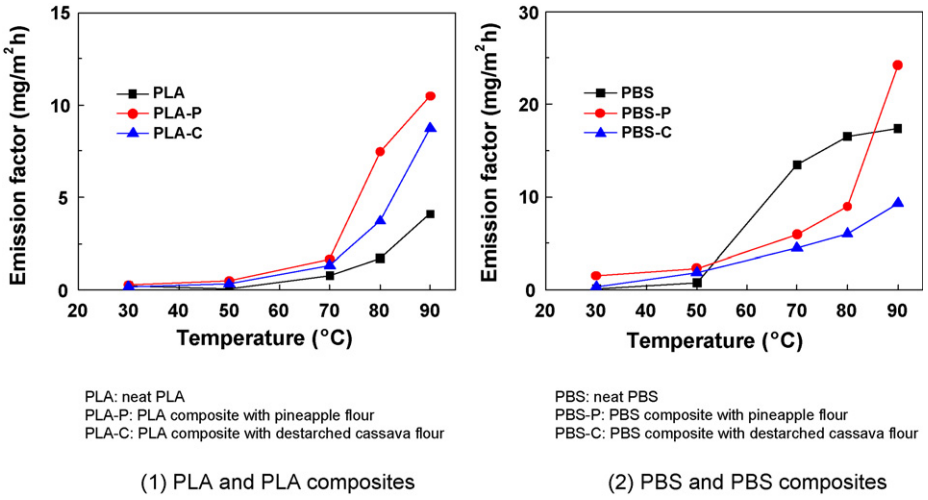


Fig. 2. TVOC emission factors of the PLA, PLA composites, PBS and PBS composites.

temperature due to the lower melting point of PBS than PLA, which undergoes pyrolysis easily. A 5 h baking time was the point of inflection in the PLA TVOC curve because the TVOC were emitted stably from 5 h (as 3.45 mg/m^2 h) to 7 h (as 3.69 mg/m^2 h). In the case of PBS, the point of TVOC inflection was more than 7 h.

Fig. 4 shows the TVOC emission factor of the PLA and PBS bio-composites after bake-out (temperature at 70 °C and baking time of 5 h). The non-baking-treated PLA-P and PLA-C emitted 4.81 mg/m^2 h and 3.08 mg/m^2 h, respectively. However, after the bake-out treatment, the TVOC emission factor of the PLA-P and -C bio-composites was 0.61 mg/m^2 h and 0.31 mg/m^2 h, respectively. In the case of the PBS-P and PBS-C bio-composites, the TVOC emission factors were 12.29 mg/m^2 h and 9.95 mg/m^2 h, respectively. However, the TVOC emission factors of the baking-treated samples were 2.08 mg/m^2 h and 1.31 mg/m^2 h. Because the TVOC reduction ratio was >80%, a positive effect of the baking treatment was observed in all samples. This bake-out method was applied to LDPE and PP, which are used as plastic green house and car interior materials. The TVOC emission factor of LDPE was higher than that of PP (194.84 mg/m^2 h vs. 17.01 mg/m^2 h). Both LDPE and PP were reduced to 66.33 mg/m^2 h and 3.26 mg/m^2 h, respectively. However, five VOCs (toluene, xylene, benzene, styrene and ethylbenzene) were not detected. It was more effective on LDPE than PP. Overall, a baking treatment can be used for LDPE and PP.

Table 3
Furfural emission factor of the PLA composites.

	30 °C	50 °C	70 °C	80 °C	90 °C
PLA-P	–	0.048	0.359	1.889	2.385
PLA-C	–	–	0.128	0.371	0.998

(–) Not detected.

3.2. VOC emission application for FLEC

The FLEC method is generally used to determine the TVOCs and formaldehyde emitted from interiors, building materials, paints and adhesives, and is very convenient due to its portability [18]. However, the FLEC method is rarely used to determine the TVOC from bio-composites used in an increasing number of fields, such as car interior materials and electronics. Therefore, the FLEC method was used to analyze the volatiles emitted from bio-composites in car interior and green house materials. To maintain a temperature of 70 °C, a heater sheet was placed at the bottom of the sample to transfer heat from the heat sheet to the specimen. The injected air was diffused onto the heated specimens at 70 °C and exhausted to the outlet with the TVOC emitted from the specimen. Fig. 5 shows the TVOC result using the FLEC method for the baking-treated PLA and PBS. In the case of PLA, the TVOC emission factor increased from 2.12 mg/m^2 h at 0 h to 3.38 mg/m^2 h at 1 h. However the VOC emission decreased gradually from 3.11 mg/m^2 h at 3 h to 1.32 mg/m^2 h

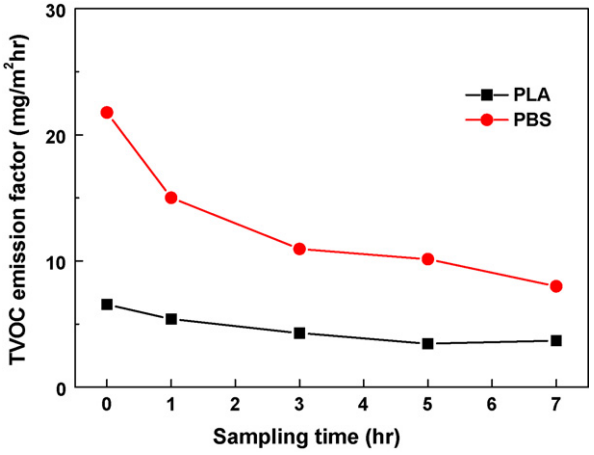


Fig. 3. TVOC emission factors as a function of the baking time.

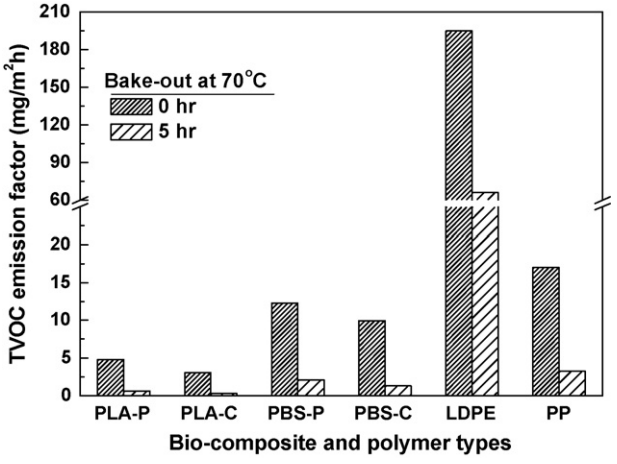


Fig. 4. Bake-out application for the PLA composites, PBS composites, LDPE and PP.

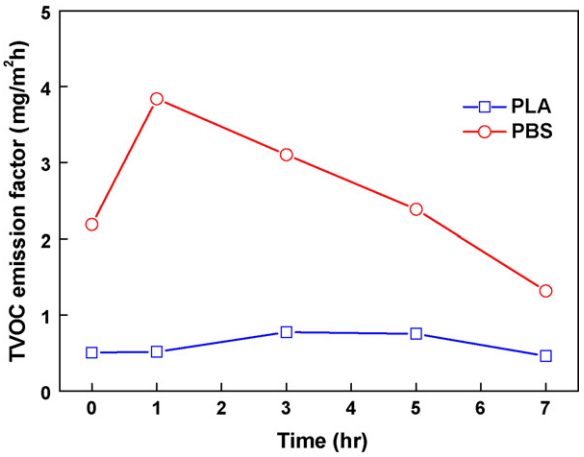


Fig. 5. TVOC emission factor using FLEC (at 70 °C).

at 7 h. The FLEC method showed that PLA has lower TVOC emission than PBS. Although FLEC has a high loading factor, the difference in the TVOC emission volume was low compared to the TE result. This is because the difference between the TE method and FLEC method was heat transfer, which might not be sufficient in the case of this FLEC method using a heat sheet. In the case of bio-composites for sufficient heat transfer, the samples were baked in a non-contamination oven at 70 °C for 5 h. The TVOC concentration from the PLA bio-composite and PBS bio-composite was determined and the results before and after baking are compared in Fig. 6. The TVOC emission factor from the FLEC method was higher than that from the TE method. There was a discrepancy in the air exchange rate in the baking-treated sample area between the FLEC and TE methods. The TE sample was tested at 90 times/h air exchange to 0.000723 m^2. However, the FLEC sample had a high air exchange rate (approximately 428 times/h to 0.0177 m^2), which mimicked the natural VOCs of TVOC emission, such as furfural. This means the natural VOCs in the bio-composites tested using the FLEC method had diffused to the surface as a result of the high air exchange. The initial TVOC emission factors of the PLA-P, and PLA-C, PBS-P and PBS-C bio-composites were 8.37 mg/m^2 h, 6.86 mg/m^2 h, 47.99 mg/m^2 h and 18.38 mg/m^2 h, respectively. However, all the baked samples showed low TVOC reduction characteristics after the baking treatment: 1.72 mg/m^2 h, 1.52 mg/m^2 h, 16.72 mg/m^2 h and 15.83 mg/m^2 h for the PLA-P, and PLA-C, PBS-P and PBS-C bio-composites, respectively. The LDPE and PP showed a TVOC

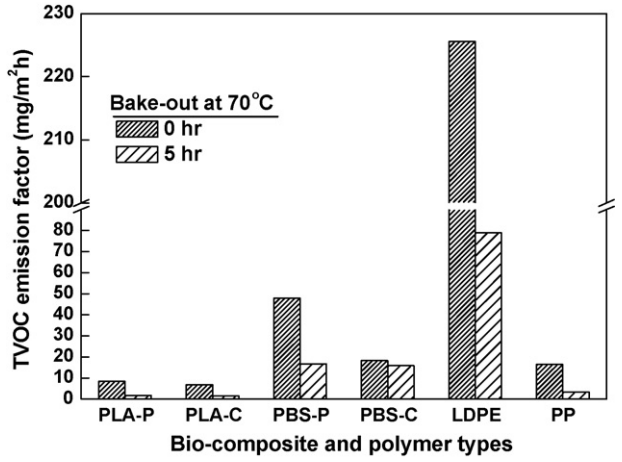


Fig. 6. Bake-out application for the PLA composites, PBS composites, LDPE and PP using FLEC.

Table 4
Five VOC emission factors of the bio-composites according to the baking time.

Baking time	PLA	PLA-P	PLA-C	PP
0 h	0.03	0.09	0.06	0.15
5 h	0.01	0.03	0.01	0.07
Baking time	PBS	PBS-P	PBS-C	PE
0 h	0.03	0.06	0.02	0.10
5 h	0.02	0.01	0.02	0.04

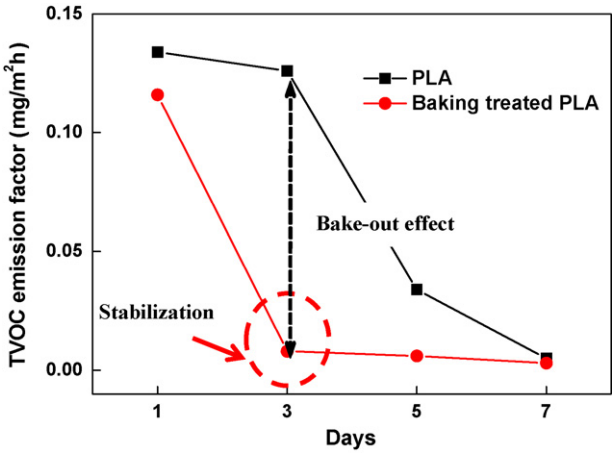


Fig. 7. TVOC emission behavior of PLA using a 20 L small chamber.

reduction effect after the baking treatment. In the case of LDPE, the initial TVOC emission factor was 225.60 mg/m^2 h but was decreased to 78.92 mg/m^2 h after the baking treatment. PP showed similar emission behavior; from 16.50 mg/m^2 h to 13.36 mg/m^2 h. In the case of LDPE and PP, no natural VOCs were emitted and the TVOC emission factor was similar to the result of the TE method. Table 4 shows the 5 VOCs emitted from the bio-composite samples. The results showed that the baking treatment using the FLEC method had a larger reduction effect on LDPE and PP than on the bio-composites.

3.3. VOC emission application for 20 L small chamber

Figs. 7 and 8 show the TVOC emission factors of PLA and PBS. The TVOC factors of PLA and PBS decreased until 5 days and remained relatively constant thereafter. These results are similar to the values mandated by the Ministry of Environment in Korea, which was

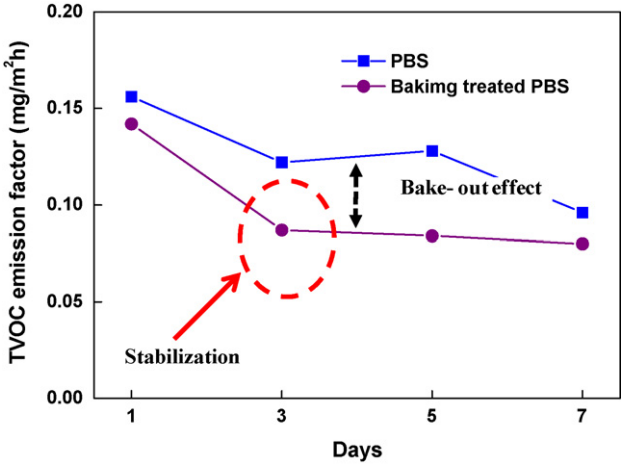


Fig. 8. TVOC emission behavior of PBS using a 20 L small chamber.

Table 5
Standard of VOCs in the Korea Air Cleaning Association.

		Interior materials	Paint	Adhesive
Most excellent	TVOC	~0.10	~0.10	~0.25
Excellent	TVOC	0.10–0.20	0.10–0.20	0.25–0.50
Good	TVOC	0.20–0.40	0.20–0.40	0.50–1.50
General I	TVOC	0.40–2.00	0.40–2.00	1.50–5.00
General II	TVOC	2.00–4.00	2.00–4.00	5.00–10.00

established for TVOC measurements from building materials, such as furniture materials, MDF (Medium Density Fiberboard) and PB (Particle Board). In the case of PLA and baking-treated PLA, the TVOC values of the initial measurement were 0.134 mg/m^2 h and 0.113 mg/m^2 h, respectively. Both PLA and the baking-treated PLA emitted at an excellent level compared to the interior material standard of the Korea Air Cleaning Association (Table 5). The TVOC of the baking-treated PLA is the most excellent grade but the untreated PLA maintained a similar emission level due to ventilation of the 20 L small chamber. Although a large decrease in TVOC emission was observed in the samples, it showed a similar trend to that of the TE and FLEC methods. The PBS samples showed slightly a higher TVOC emission factor than the PLA samples with the 20 L small chamber experiment because of the temperature difference between each experimental instrument. This difference was attributed to the 20 L small chamber being under a constant temperature (25 ± 1 °C) and not heated at 70 °C. However, a decrease in TVOC emission was observed in the PLA and PBS samples. The TVOC of the baking-treated samples decreased for 3 days and remained relatively constantly until 7 days. On the other hand, the untreated samples showed continuous TVOC emission. TVOC was emitted at a similar level to that of the baking-treated samples at 7 days. Therefore, the difference in TVOC emission from PLA and PBS with time was attributed to the bake-out effect.

To confirm the baking treatment effect on the bio-composites and other polymers, the TVOC was sampled 3 days after installing the sample in each chamber, and the samples were baked in an oven for 5 h at 70 °C. After the baking process, the samples were again installed in non-contaminant chambers. The TVOC from the samples was sampled after 3 days. Fig. 9 and Table 6 show the TVOC emission factor of the baked and unbaked bio-composite, LDPE and PP. Before baking, the TVOC of the PLA-P and PLA-C bio-composites were 0.06 mg/m^2 h and 0.05 mg/m^2 h, respectively. The TVOC reduction ratios of the PLA composites after baking were 57% and 72%, respectively. The PBS-P and PBS-C bio-composites also showed a decrease in TVOC from 0.76 mg/m^2 h to 0.17 mg/m^2 h and from 0.29 mg/m^2 h to 0.11 mg/m^2 h, respectively. This means that a

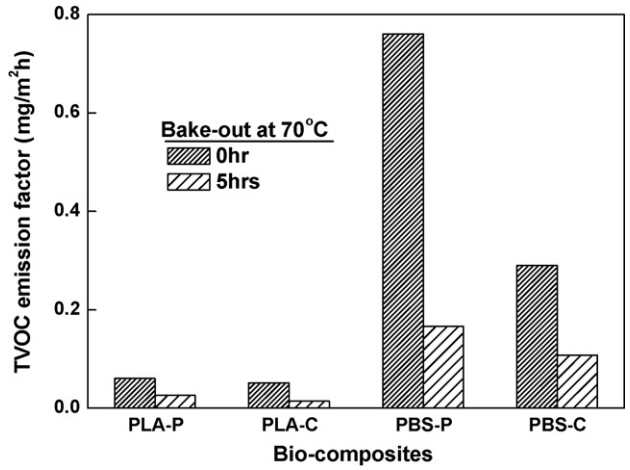


Fig. 9. TVOC emission factor of PLA and PBS composites using a 20 L small chamber.

Table 6
VOC emission factors of LDPE and PP.

	LDPE		PP	
	TVOC	Five VOCs	TVOC	Five VOCs
Non-treated	23.660	0.029	0.119	0.001
Bake-out	2.183	0.001	0.033	0.000

baking treatment is more effective on the PBS bio-composites than on PLA. LDPE showed higher TVOC emission properties than PP. The melting point of LDPE (105–110 °C) was lower than PP (165 °C). Consequently, the molecules of LDPE were broken by the increasing temperature. Therefore, LDPE molecules have volatile characteristics at relatively low temperatures, which result in higher TVOC emission factors.

4. Conclusions

In the case of TE, the TVOC emitted from neat PLA ranged from 0.26 mg/m^2 h to 4.11 mg/m^2 h according to the temperature. For both the PLA-P and PLA-C bio-composites, the TVOV emitted increased with increasing temperature from 0.30 mg/m^2 h to 3.72 mg/m^2 h and from 0.19 mg/m^2 h to 8.74 mg/m^2 h, respectively. The TVOC emission factors of all samples increased gradually with increasing temperature. Above 70 °C, both PLA bio-composites showed higher TVOC emission factors than neat PLA due to the rapid emission of furfural (2-furancarboxyaldehyde). PLA emitted 1,4-dioxane, a known carcinogen. However, 1,4-dioxane emission could be reduced significantly by adding 30 wt% flour. Below 50 °C, all the samples had similar TVOC emission factors. In contrast, the TVOCs were emitted rapidly from PBS from 50 °C to 90 °C due to succinic acid emission from the pyrolysis of PBS. PLA and PBS showed a gradual decrease in the TVOC value with increasing baking time. The TVOC emission factor of the PLA bio-composite and PBS bio-composites was reduced by more than 80% using a bake-out method (temperature at 70 °C and baking time 5 h). This method can be applied to LDPE and PP.

The TVOC emission factors of PLA and PBS were increased from 0 to 1 h using FLEC. However, the level of VOC emission at 3 h decreased gradually until 7 h. The PLA and PBS bio-composites showed a decrease in TVOC emission after baking. The TVOC emission trend of each sample was similar to the results of the TE method. LDPE and PP also showed a decrease in TVOC emission after baking.

The TVOC factors from the untreated PLA and PBS decreased until 7 days. The TVOCs were emitted stably from the baked PLA and PBS from 3 to 7 days. However, the untreated PLA and PBS showed continuous but slightly decreasing TVOC emission, which is similar to the TVOC emission level of the baked samples at 7 days. The bake-out effect was highlighted by the decrease in TVOC emission from the PLA bio-composites, PBS bio-composites, LDPE and PP.

Acknowledgement

This study was initiated by research grants (2006-A046-03) supported by the Korea National Cleaner Production Center.

References

[1] J.R. Girman, Volatile organic compounds and building bake-out, in: J.E. Cone, M.J. Hodgson (Eds.), Problem Buildings: Building-Associated Illness and the Sick Building Syndrome, Hanley & Belfus, Inc., Philadelphia, PA, 1989, pp. 695–712.
[2] J.R. Girman, L. Alevantis, G. Kulasingam, M. Petreas, L. Webber, Bake-out of an once building, in: Proceeding of the Fourth International Conference on Indoor Air Quality and Climate, vol. 1, Institute for Water, Soil, and Air Hygiene, Berlin, 1987, pp. 22–26.

[3] D.S. Etkin, Volatile Organic Compounds in Indoor Environments, Cutter Information Corp., Arlington, MA, 1996, pp. 221–228.
[4] T. Follin, Airing out pollutions, in: Proceedings of Healthy Buildings/IAQ'97, vol. 3. Healthy Buildings/IAQ'97, Washington, DC, Blacksburg, VA, 1997, pp. 353–356.
[5] S. Kim, J.-A. Kim, H.-J. Kim, H. Lee, D.-W. Yoon, The effects of edge sealing treatment applied to wood-based composites on formaldehyde emission by desiccator test method, Polym. Test. 25 (2006) 904.
[6] J.-S. Kim, Y. Eom, S. Ki, H.-J. Kim, Effects of natural-resource-based scavengers on the adhesion properties and formaldehyde emission of engineered flooring, J. Adhes. Sci. Technol. 21 (2007) 211.
[7] S. Kim, J.-A. Kim, J.-Y. An, H.-J. Kim, S. Kim, J. Park, TVOC and formaldehyde emission behaviors from flooring materials bonded with environmental-friendly MF/PVAc hybrid resins, Indoor Air 17 (2007) 404.
[8] S. Kim, J.-A. Kim, J.-Y. An, H.-J. Kim, S.-J. Moon, Development of a test method using a VOC analyzer to measure VOC emission from adhesives for building materials, J. Adhes. Sci. Technol. 20 (2006) 1783.
[9] S. Kim, J.-A. Kim, H.-J. Kim, S. Kim, Determination of formaldehyde and TVOC emission factor from wood-based composites by small chamber method, Polym. Test. 25 (2006) 605.
[10] R. Luo, Determination of water vapor diffusion and partition coefficients in cement using one FLEC, Int. J. Heat Mass Transf. 47 (2004) 2061.
[11] ASTM-D5116-97, Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products, 1997.
[12] ASTM-D6007-96, Standard Test Method for Determining Formaldehyde Concentrations in Air from Wood Products Using a Small Scale Chamber, 1996.
[13] ECA-IAQ Report No. 2, Guideline for the Determination of Steady State Concentrations in Test Chambers, Luxembourg, 1989.
[14] ECA-IAQ Report No. 8, Guideline for the Characterization of Volatile Organic Compounds Emitted from Indoor Materials and Products Using Small Test Chambers, Brussels, 1991.
[15] ECA-IAQ Report No. 13, Determination of VOCs Emitted from Indoor Materials and Products—Inter Laboratory Comparison of Small Chamber Measurements, Brussels, 1993.
[16] ENV 13419-1, Building Products—Determination of the Emission of Volatile Organic Compounds. Part 1. Emission Test Chamber Method, European Committee for Standardization, Brussels, 1999.
[17] T. Fujimaki, Processability and properties of aliphatic polyesters, 'BIONOLLE', synthesized by polycondensation reaction, Polym. Degrad. Stabil. 59 (1998) 209.
[18] K.-W. Kim, J.-Y. An, H.-J. Kim, Formaldehyde and TVOC emission according to finishing treatment onto surface materials, in: Proceedings of 57th Annual Meeting of the Japan Wood Research Society, Hiroshima, 2007, p. 81.