

Characteristics of a Reddish Residual Soil (Hwangtoh) finishing material with water-soluble adhesive for residential building

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ABSTRACT

This study manufactured an environmental finishing material composed of Reddish Residual Soil, water and water-soluble resin. The objective was to make an environmental finishing material with an optimum ratio and evaluate its usability for wall applications. The viscosity of the Reddish Residual Soil finishing material was altered with water. Finishing material with a higher water content had better application abilities than with a low viscosity. But over 1.3 wt.% water blending with Reddish Residual Soil and a vinyl type water-soluble adhesive resulted in an unsuitable application of flowing on a substrate. The manufactured finishing material that was suitable for wall applications was not only evaluated for physico-mechanical properties like impact testing, wet abrasion testing and internal bonding testing, but also testing environmental properties such as emission of formaldehyde, TVOC, far infrared radiation and radon.

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1. Introduction

The construction industry has developed rapidly since 1960. Construction materials for buildings have changed from natural materials to petrochemical materials to meet the demands for greater airtight seals to save energy. But building and furnishing materials may emit various volatile organic compounds (VOCs) into the interior air of the building [1]. Due to the toxicity of these volatile organic compounds and their severe impact on human health, it is necessary to use low level emitting materials instead [2]. VOCs are generally composed of BTEX (benzene, toluene, ethylbenzene and xylene) and halogenated hydrocarbons [3]. Wolkoff [4] mentioned that it is necessary to know the characteristic of the primary and secondary emissions from building materials. The free (non-bound) VOCs are primary emissions because of low molecular weights, and can emit from solvent residues, additives and non-reacted raw products, e.g. monomers. Secondary emissions are bound VOCs, caused by chemical or physical reactions, and several of these are emitted or formed by different processes under special chemical or physical conditions. These types of VOCs have caused sick-building syndrome (SBS) in humans.

Wood-based panels contain formaldehyde-based resins, panels such as particleboard (PB), medium density fiberboard (MDF), the veneer of widely raw materials of furniture, flooring, housing and other industrial products. Formaldehyde resin in these wood-based panels emits formaldehyde, which is toxic and is associated with possible health hazards. Therefore, European and Northern American governments have imposed regulations limiting the emissions of formaldehyde from building materials [5].

Radon (²²²Rn) is a naturally occurring radioactive gas, present in all rocks and soils, and is a cancer-causing agent that cannot be seen, smelled or tasted. Its presence in a home can pose a danger to the health of the residents. Radon is the leading cause of lung cancer among non-smokers. Extensive epidemiologic studies have linked inhalation of the radioactive decay products of radon to an increased risk of lung cancer and approximately 21,800 lung cancer deaths are attributed [6] to radon annually in the United States (US).

Thus, environmentally friendly indoor construction materials with a limited affect on human health are needed, having low emissions, but still maintaining structural integrity. In South Korea, Reddish Residual Soil (Hwangtoh) has been traditionally used to make beds, dye clothing and treat red tide matter because of its high far infrared emissions resulting in an anti-biotic characteristic. The Reddish Residual Soil was weathering soil, consists of 40–80% clay minerals and various minerals such as quartz, feldspar, hornblende, goethite and gibbsite, from rocks to changed soil

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Table 1
Physical properties of Reddish Residual Soil.

	Grain size	Porosity	Water content	Color	Tensile strength	Compressive strength
Value	Under 0.002 mm	About 50%	About 40–45	Red or yellow	3–10 kg/cm ²	15–50 kg/cm ²

from a chemical weathering effect [7]. The physical properties of Reddish Residual Soil are listed in Table 1.

The objective of this study was to investigate the feasibility of Reddish Residual Soil as an indoor finishing material, maintaining structural soundness and having low emissions. We conducted physico-mechanical property tests such as internal bonding strength, wet abrasion tests and impact tests of the finishing material, and tested for various emissions including formaldehyde, TVOC, 5 VOCs and radon.

2. Experimental

2.1. Preparation

The particle size of the Reddish Residual Soil was about 270 μm, obtained from San-chung in Korea. The vinyl type water-soluble adhesive was donated by Okong Co., Ltd. (South Korea), with a viscosity of 15,000 cP and 58% solid contents. The adhesive was blended with Reddish Residual Soil and water, whose ratio is listed in Table 2.

2.2. Test methods

2.2.1. Physico-mechanical properties

The viscosities of the Reddish Residual Soil finishing materials were evaluated with a Brookfield Model DV-II+Pro viscometer (Brookfield Engineering Laboratories, Inc., MA, USA) with spindle No. 4 at 22 ± 1 °C. Containers of the same cylinder-shape and 500 mL-capacity were used to reduce the effect of resistance by the surface.

The internal bonding test was conducted by a Universal Testing Machine (Zwick Co.) to investigate the internal bonding strength of a sample of the Residual Soil finishing materials with different blending ratios, according to KS F 4715 [8]. Before the internal bonding test, each individually manufactured component of the Reddish Residual Soil finishing material was coated, with an approximate thickness of 2 ± 0.5 mm, on mortar substrates prepared as 70 × 70 × 20 mm slabs. After curing, the middle of each piece was grooved to a size of 40 × 40 mm, in order to show the top face of the substrate board. The grooved part in the middle of the sample was fixed with a jig that was about 1 kg in weight, using a type 2 epoxy resin to prepare for the internal bonding test. The maximum tension loading value and internal bonding strength, T (N) and I (N/mm²), respectively, of the manufactured samples were computed for a test specimen as follows:

$$I = \frac{T}{1600} \quad (1)$$

Wet abrasion tests have been useful in evaluating the abrasion resistance of attached coatings in wet conditions. The wet abrasion test for this study used gypsum board (430 × 170 × 6 mm), with each face being coated by a sample of the Reddish Residual Soil finishing material with a thickness of 2 mm. After curing, the samples were experimented on using an Wet Abrasion Scrub Tester (Sheen Co.) that was a gardner straight type washerability machine at 37 ± 1 cycle/min, 300 times.

The impact test was conducted to check cracks on a sample of the Reddish Residual Soil finishing material when the plummet (W_2 -500) fell from 30 cm over a coated mortar board, with those of the top face of the sample tested 3 times in different positions. This experiment was conducted with a sand bottom, according to KS F 2221 [9].

2.2.2. Environmental characteristics

A 20 L small chamber was developed in Japan to investigate the emission levels of formaldehyde and TVOC (total volatile organic compound) from furniture raw materials, paints and adhesives, with performance set to ASTM [10,11], ECA [12–15] and ENV 13419-1 [16]. Although there are larger chambers, the 20 L chamber

Table 2
The ratio of a sample of the of the Reddish Residual Soil finishing material.

Sample	Soil	Vinyl type water-soluble adhesive	Water
A	1	1	0.7
B	1	1	1.0
C	1	1	1.3
D	1	1	1.6

Table 3
Test conditions in the 20 L small chamber method.

Variables	Condition
Chamber volume	20 L
Sample size	0.0432 m ² (0.147 m × 0.147 m × 2)
Air flow rate	0.01 m ³ h ⁻¹ .
Ventilation rate	0.5 h ⁻¹
Sample loading factor	2.16 m ² /m ³
Temperature	25 ± 1 °C
Humidity	50 ± 5%

Table 4
Sampling condition in the 20 L small chamber method.

	Formaldehyde	VOCs
Sampler	2,4-DNPH Cartridge (Supelco, USA)	Tenax-TA (Supelco, USA)
Air flow rate	167 mL/min	167 mL/min
Total volume	10 L	3.2 L

was used in this study because it has been standardized in Korea. The 20 L small chamber was supplied with purified and humidified air at a ventilation rate of 0.5ACH through an air-flow of 0.01 m³ h⁻¹. The temperature of 25 ± 1 °C and 50 ± 5% relative humidity (RH) inside the chamber were kept constant. The test was conducted using two samples of size 0.147 × 0.147 m (total 0.0432 m²) at a sample loading factor of 2.16 m² m⁻³. The test conditions are shown in Table 3. Test pieces, all sealed with seal boxes, were set in the chamber, and the air inside the chamber was sampled after 12 h. Sampling conditions are shown in Table 4. Throughout the measurements, the air temperature and RH inside the test chamber, which was ventilated at 0.5/h, were kept constant at 25 ± 1 °C and 50 ± 5%, respectively. Aldehydes were analyzed by HPLC, and TDS/GC-MS was used for VOCs, as shown in Tables 5 and 6. In this paper, TVOC was defined as the conversion of all areas of the peaks between C₆ and C₁₆ to concentrations using the toluene response factor. A peak area under 10 was defined as the limit of detection. The sample gas was taken by Tenax-TA and 2,4-DNPH cartridge 7 days after the sample specimens were installed into the 20 L small chamber, according to the regulation of the Ministry of Environment, Korea.

The calculation of the emission factor (EF) from some materials is defined in ASTM D5115. Generally, two technical terms are used to describe the rate of emission from materials to test emission concentration, EF and ER, which are related as follows:

$$ER = A(EF) \quad (2)$$

where ER is the emission rate (mg/h), A is the source area (m²) and EF is the emission factor (mg/m² h).

ER can be considered for both area sources and non-area sources, but EF is applied as mass/mass/time or in the case of caulk beads, mass/length/time [17].

The far infrared radiation (FIR) test of a sample of the Reddish Residual Soil finishing material (40 × 40 × 3 mm) was conducted in the range of 5–20 μm at 40 °C using a Fourier Transformation Infrared Spectrometer (Midac Co., M2410-C), to investigate emissivity and emission power after each dried sample was attached to a heating system. A rack was constructed with the top and two sides containing FIR sources. The FIR sources were constructed from a ceramic-coated sheet of aluminum, and the opposite side of the sheet was heated by an electric heater.

Table 5
Analysis conditions for formaldehyde.

Variables	Condition
HPLC	Agilent HP1100
Detector	UV/Vis 365(Bw.30), ref. 590(Bw.10)
Column	Supelco C18. 4.6 × 250 mm
Mobile phases	Acetonitrile:water = 45:55
Analysis time	25 min
Injection volume	20 μL
Column temperature	40 °C
Mobile phase flow rate	1.0 mL/min

Table 6
Analysis conditions for VOCs.

Variables		Condition
TDS		Perkin Elmer ATD400
GC/MS		HP6890/Agilent5973
Column		RTX-1 (105 m × 0.32 mm × 3 μm)
Carrier gas and flow		He (99.99%)
Temperature program		40 °C (5 min) → 70 °C (5 min) → 150 °C (5 min) → 200 °C (5 min) → 220 °C (5 min) → 240 °C (5 min)
MS condition	Mode	EI (Electron ion)
	Electron energy	70 eV
	Detection mode	TIC (scan), m/z: 35/350

The radon concentration of the manufactured finishing material was detected using a Model 1027 professional continuous radon monitor (Sun Nuclear Co., USA) that is classified as a Continuous Radon Monitor (CRM) testing device [18–22]. The radon detector had been installed in a space (300 × 300 × 300 mm) consisting of six gypsum boards coated by a sample of the Reddish Residual Soil finishing material. This test was maintained at 50 ± 5%, 23 ± 1 °C for 7 days.

3. Results and discussion

3.1. Physico-mechanical properties

The water contents of the samples of Reddish Residual Soil finishing materials with 0.7(A), 1.0(B), 1.3(C), 1.6(D) with relating viscosities is shown in Fig. 1. Samples A and B were 1640 cP and 1120 cP, while samples C and D were 280 cP and 164 cP, with low viscosity and increasing water content. Generally, the higher the water content in a sample of the manufactured Reddish Residual Soil finishing material, the better the application ability because of lower viscosity. But when coated on the substrate, sample C and D were observed to be flowing, proving to be unsuitable for real world application. Considering its application ability, Sample B was well suited to be a component of the Reddish Residual Soil finishing material.

Fig. 2 shows the internal bonding strength of each sample according to its mixture ratio. Sample A was 0.3 N/mm², but the internal bonding strength of samples B, C and D increased with an increasing water ratio in the Reddish Residual Soil and vinyl type water-soluble resin mixture, 1.3, 1.2, 1.2 N/mm², respectively. These values satisfy the Korea Standard of interior paint specification of 0.4 N/mm². Because of the low viscosity of the manufactured finishing materials, there was enough adhesion between substrate and sample.

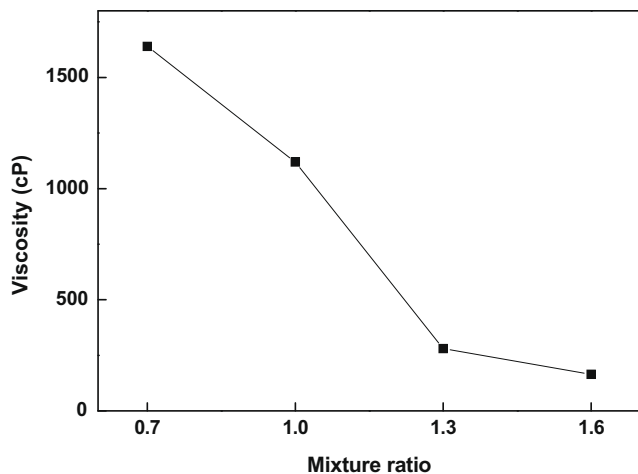


Fig. 1. Viscosity of samples.

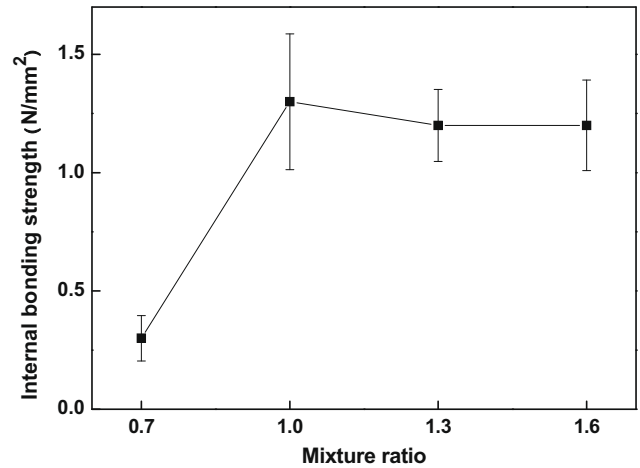


Fig. 2. Internal bonding strength of samples.

Problems that appeared with all of the samples were not observed after wet abrasion testing and impact testing (Fig. 3 and 4). Impact strength sample A and B incurred some cracking because of lack of application technique, and did not crumble and crack after the plummet fell on top of the samples.

Sample B was the top sample of the Reddish Residual Soil finishing materials with various water contents when taking into consideration the physico-mechanical aspects.

3.2. Environmental characteristics

The formaldehyde emission factors of sample B was detected by a 20-l small chamber using 2, 4-DNPH cartridges that were

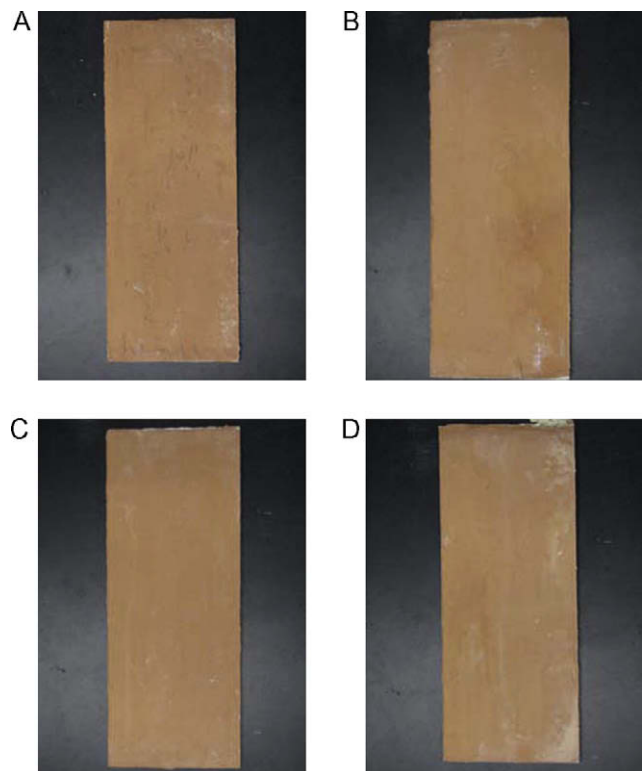


Fig. 3. Wet abrasion test of samples.

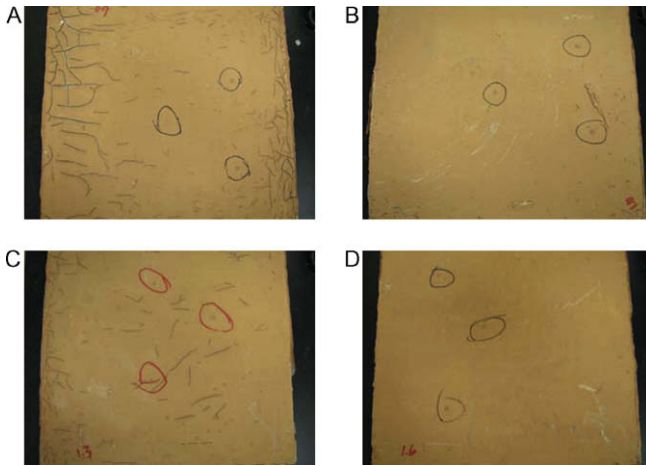


Fig. 4. Impact test of samples.

sampled after 1, 3, 5 and 7 days, as mandated by the Ministry of Environment, Korea. Formaldehyde was emitted at about 0.003–0.005 mg/m² h from sample B during the experimental period shown in Fig. 5. The emission factors of sample B were stable, the first day value of sample B was about 0.003 mg/m² h, and the value of the last day was 0.004 mg/m² h. This value is a comparatively low emission rate compared to other finishing materials [23]. In this paper, TVOC was defined as the conversion of areas of all peaks between C₆ and C₁₆, relative to concentrations of the toluene response factor. The TVOC emission gas from sample B was collected using Tenax-TA tubes (Supelco, USA) for 7 days. The TVOC emission factor for sample B, between C₆ and C₁₆, are shown in Fig. 6. The TVOC emission rate was 0.11 mg/m² h of TVOC on the first day. Sample B exhibited a stable reduction in TVOC emission rates from about 0.09 mg/m² h to about 0.05 mg/m² h after 3 days. VOCs, such as benzene, styrene, toluene, ethylbenzene and xylene are known to be harmful. However, TVOC was calculated by including organic compounds between C₆ and C₁₆, some of which are harmless or unknown. Thus, the total sum of the emission rate of benzene, styrene, toluene, ethylbenzene and xylene, the five main aromatic hydrocarbons (5 VOCs), was separated from TVOC. Fig. 7 shows the 5 VOCs emission rate of sample B. The curve of the 5 VOCs was similar with TVOC, approximately 0.0045 mg/m² h after first days, then stable at about 0.0023 mg/m² h. The emission rate values after 3 days of formaldehyde, TVOC

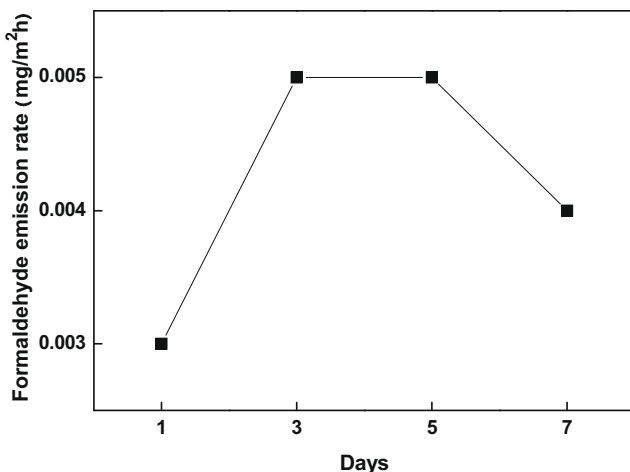


Fig. 5. Formaldehyde emission rate of sample B.

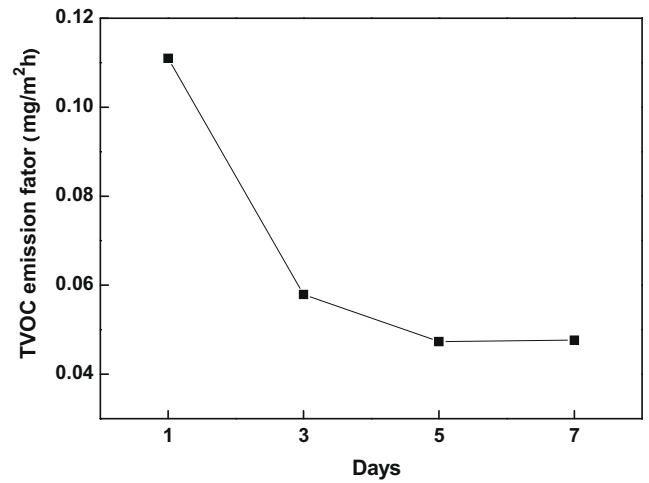


Fig. 6. TVOC emission factor of sample B.

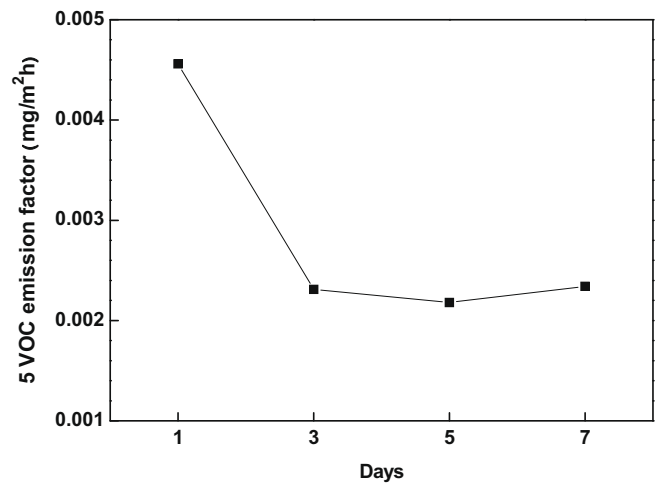


Fig. 7. 5 VOC emission factor of sample B.

and the 5 VOCs of sample B were compared to the Korea Clean Association standard (Table 7) [24]. Sample B had a superior emission grade. Because of the low emission levels from sample B, it can be considered as an environmentally friendly finishing material.

The emissivity and emission power of sample B was 0.92 and 3.71×10^2 W/m², which had high far infrared characteristics due to the Reddish Residual Soil. Thus, it is also good for human health, as referred to in the introduction. The far infrared results of this sample of the Reddish Residual Soil finishing material was similar with another Reddish Residual Soil finishing material for indoor wall wood construction [25].

The radon emission from sample B during the experimental period is shown in Fig. 8. According to the standard of the Ministry of Environment of the Republic of Korea, the radon emission concentration of indoor air is harmless if it is below 4 pCi/l. The radon of sample B emitted around 2.2–3.8 pCi/l, which decreased over time, confirming that the radon concentration level of sample B was not high enough to affect human health.

Public interest in healthy housing with eco-friendly materials has sharply increased recently. Reddish Residual Soil finishing material is a representative healthy and eco-friendly material with properties of high absorbency, and self-purification. It has been suggested that hwangtoh could possibly be used as an admixture

Table 7
Sample B and finishing material standard of Korea Clean Association.

	Sample B			Superior		
	HCHO	TVOC	5VOCs	HCHO	TVOC	5VOCs
Emission rate	0.005	0.058	0.002	Under 0.03	Under 0.25	Under 0.075
	Excellent			Good		
Emission rate	0.03–0.12	0.25–0.50	Under 0.15	0.12–0.40	0.50–1.5	Under 0.45
	General I			General II		
Emission rate	0.40–2.00	1.50–5.00	Under 1.5	2.00–4.00	5.00–10.00	Under 3.00

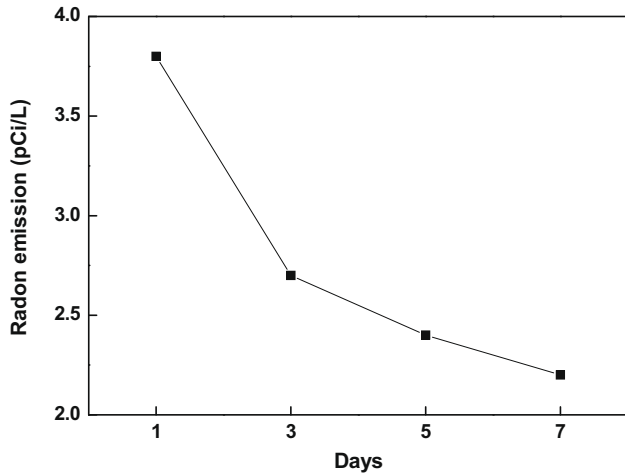


Fig. 8. Radon emission of sample B.

for enhancement of concrete's mechanical properties[26]. Application of this material as a whole substitute material rather than a partial replacement for ordinary portland cement would have a significant influence on the development of healthy housing with eco-friendly material and the reduction of carbon dioxide emissions.

4. Conclusions

The following conclusions can be made based on the results of this investigation.

The objective of this study was to investigate the feasibility of Reddish Residual Soil as an indoor finishing material, maintaining structural soundness and having low emissions. The viscosity of the Reddish Residual Soil finishing material was altered with water. Finishing material with a higher water content had better application abilities than with a low viscosity. But over 1.3 wt.% water blending with Reddish Residual Soil and a vinyl type water-soluble adhesive resulted in an unsuitable application of flowing on a substrate. With this blending ratio to finishing ratio, there was not only an internal bonding strength of about 1.3 N/mm², but the standard of wet abrasion and impact strength by the KS was satisfied. Environmental properties of Sample B of the Reddish Residual Soil finishing material had low emission characteristics of formaldehyde, TVOC and 5 VOCs, about 0.005, 0.06 and 0.002, respectively. The finishing material had high far infrared emissivity and emission power, which is good for health. The sample also had a low radon emission concentration, lower than levels considered to affect human health.

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References

- [1] Gustaffson H. Building materials identified as major emission sources for indoor air pollutants – a critical review of case studies. Document D10. Stockholm, Sweden: Swedish Council for Building Research; 1992. ISBN 91-540-5471-0.
- [2] Commission of the European Communities. Effects of indoor air pollution on human health. Report EUR 14086 EN; 1991.
- [3] Afshari A, Lundgren B, Ekberg LE. Comparison of three small chamber test methods for the measurement of VOC emission rates from paint. *Indoor Air* 2003;13:156–65.
- [4] Wolkoff P. Photocopiers and indoor air pollution; atmospheric environment 2001;33:2029–30.
- [5] Kovvouras PK, Koniditsiotis D, Petinarakis J. Resistance of cured urea-formaldehyde resins to hydrolysis. *Horzforschung* 1998;52:105–10.
- [6] National Research Council. Health effects of exposure to radon BEIR VI. Washington (DC): National Academy Press; 1999. p. 15.
- [7] Hwang JY, Jang MI, Kim JS, Cho WM, Cho BS, Kang SW. Mineralogy and chemical composition of the residual soils (Reddish Residual Soil) from South Korea. *J Mineralogical Society of Korea* 2000;13(3):147–63.
- [8] KS F 4715. Wall coatings for thin textured finishes; 2007.
- [9] KS F 2221. Test method of impact for building boards; 1999.
- [10] ASTM-D5116-97. Standard guide for small-scale environmental chamber determinations of organic emissions from indoor materials/products; 1997.
- [11] ASTM-D6007-96. Standard test method for determining formaldehyde factors in air from wood products using a small scale chamber; 1996.
- [12] ECA-IAQ report no. 2. Guideline for the determination of steady state concentrations in test chambers. Luxembourg; 1989.
- [13] 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.
- [14] ECA-IAQ report no.13. Determination of VOCs emitted from indoor materials and products—inter laboratory comparison of small chamber measurements. Brussels; 1993.
- [15] ECA-IAQ report no. 16. Determination of VOCs emitted from indoor materials and products—second inter laboratory comparison of small chamber measurements. Brussels; 1995.
- [16] ENV 13419-1. Building products—determination of the emission of volatile organic compounds—part 1: emission test chamber method. Brussels: European Committee for Standardization; 1999.
- [17] Kim S, Kim JA, An JY, Kim HJ, Kim SD, Park JC. TVOC and formaldehyde emission behaviors from flooring materials bonded with environmental-friendly MF/PVAc hybrid resins. *Indoor Air* 2007;17(5):404–15.
- [18] EPA. Protocols for radon and radon decay product measurements in homes. EPA 402-R-92-003; 1993.
- [19] EPA. Indoor radon and radon decay product measurement device protocols. EPA 402-R-92-004; 1992.
- [20] EPA. Large building Radon manual. EPA 600-SR-97-124; 1998.
- [21] EPA. National radon proficiency program. EPA 402-R-012; 1997.
- [22] EPA. Radon proficiency program. EPA 402-R-95-013; 1996.
- [23] Kim S, Kim HJ, Moon SJ. Evaluation of VOC emissions from building finishing materials using a small chamber and VOC analyzer. *Indoor Built Environ* 2006;15(6):511–23.
- [24] Kim S, Kim JA, Kim HJ, Kim SD. Determination of formaldehyde and TVOC emission factor from wood-based composites by small chamber method. *Polym Test* 2006;25:605–14.
- [25] An JY, Kim KW, Kim S, Oh JK, Kim HJ, Park MJ. *J Korea Soc Wood Sci Technol* 2007;35(6):100–7.
- [26] Yang K-H, Hwang H-Z, Kim S-Y, Songd J-K. Development of a cementless mortar using hwangtoh binder. *Build Environ* 2007;42:3717–25.