

자동차용 펠트로부터 방출되는 휘발성 유기화합물의 저감 연구

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Reduction of Volatile Organic Compounds Emitted from Automobile Felt by Activated Carbon and Hollow Core/Mesoporous Shell Carbon Ball

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나노카본볼과 활성탄을 혼합하여 자동차용 펠트에서 발생하는 휘발성유기화합물의 흡착성능을 시험하였다. 자동차에서 발생하는 휘발성유기화합물의 양을 측정하는 최적의 분석방법으로 고성능 액체크로마토그래피와 가스크로마토그래피를 활용하였다. 새로 생산된 펠트에서는 포름알데히드가 0.3~6.0 ppm 존재하였으나 상온에서 14일 동안 숙성시키면 0.2~0.5 ppm으로 감소하였고, 아세트알데히드도 0.2~3.0 ppm에서 0.2~0.4 ppm으로 감소하였다. 새로 생산된 펠트에서 발생하는 총 휘발성유기화합물은 8.49 $\mu\text{g}/\text{TP}$ 로 일본자동차협회의 허용치에 비하여 약 26배나 높게 관측되었으나, 나노카본볼과 활성탄 혼합물 0.2 wt%를 펠트에 첨가시키면 0.32 $\mu\text{g}/\text{TP}$ 이하로 저감할 수 있었다.

Nano carbon balls (NCBs), activated carbons (ACs) and their mixture (new carbon mixtures, NCMs) were used to reduce volatile organic compounds (VOCs) emitted from the automobile felt. The optimum analytical method to measure the trace amount of the VOCs, including formaldehyde and acetaldehyde, has been established by utilizing high performance liquid chromatography (HPLC) and gas chromatography (GC). The levels of formaldehyde and acetaldehyde released from newly produced felt were in the ranges of 0.3~6.0 ppm and 0.2~3.0 ppm, respectively. After 14 days of aging at the room temperature, however, their levels were still in the ranges of 0.2~0.5 ppm and 0.2~0.4 ppm, respectively. By applying NCMs of 2 wt% to the automobile felt, the amount of the total volatile organic compounds (TVOCs) was reduced under the chronic inhalation minimum risk level of 0.32 $\mu\text{g}/\text{TP}$.

Keywords: nano carbon balls, activated carbons, automobile felt, VOCs, adsorbent

1. Introduction

Emissions of volatile organic compounds (VOCs), extensively used as solvents, refrigerants, aerosol propellants and raw materials, are one of the most delicate environmental problems currently faced by chemical industries. VOCs are known as pollutants that contribute to smog generation, greenhouse effect and ozone layer depletion, and some are even considered toxic and hazardous to human health. VOCs including formaldehyde and acetaldehyde released from the automobile felts can irritate human respiratory system and evoke many physical symptoms such as headaches, nausea, dizziness and allergies[1-4]. The potential health risk exists due to the toxic nature of such compounds. Although the threshold concentration of formaldehyde recognized by passengers in the vehicle is 0.83 ppm[5], the minimum risk level (MRL) of the

chronic inhalation is 0.03 ppm[6]. In consequence, passengers exposed to sub-ppm levels of such VOCs may get sick without any odor perception[5-7]. Since the symptoms can be more seriously recognized by the passenger in the new automobile, minimization of VOCs released from the new automobile felt is of major interest to contemporary society.

Japan automobile manufacturers association (JAMA) and automobile companies established the indoor concentration level guideline of VOCs in the automobile cabin (Table 1), promoted a voluntary approach to reduce VOC levels in vehicle cabins, and announced to apply it to the new commercial vehicles from the year 2008[8]. Generally, big automobile companies strictly limit VOCs emission from automobile parts such as dashboard, fabric and felt etc. Despite of many efforts to reduce VOCs emission from the felt, non-woven cloth, used for damper or shock absorbent in the automobile, only a few studies regarding the indoor air quality of automobile were carried out for practical application[9-11]. Several studies to eliminate VOCs in atmosphere by adsorb-

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Table 1. VOCs Indoor Concentration Level Guideline by Automobile Manufacturer

Entry	Substances	Indoor concentration guideline value[8]	Target value
1	Formaldehyde	100 $\mu\text{g}/\text{m}^3$ (0.08 ppm)	0.08 $\mu\text{g}/\text{TP}$
2	Acetaldehyde	48 $\mu\text{g}/\text{m}^3$ (0.03 ppm)	0.04 $\mu\text{g}/\text{TP}$
3	Xylene	870 $\mu\text{g}/\text{m}^3$ (0.20 ppm)	
4	Toluene	260 $\mu\text{g}/\text{m}^3$ (0.07 ppm)	
5	Ethyl benzene	3800 $\mu\text{g}/\text{m}^3$ (0.88 ppm)	TVOCs : 400 $\mu\text{g}/\text{m}^3$ or 0.32 $\mu\text{g}/\text{TP}$
6	Styrene	220 $\mu\text{g}/\text{m}^3$ (0.05 ppm)	
7	Di- <i>n</i> -butyl phthalate	220 $\mu\text{g}/\text{m}^3$ (0.02 ppm)	
8	Di-2-ethylhexyl phthalate	120 $\mu\text{g}/\text{m}^3$ (7.6 ppm)	
9	Tetradecane	330 $\mu\text{g}/\text{m}^3$ (0.04 ppm)	

ents such as activated carbons[12-15], carbon fibers[1,16,17], and mesoporous silica materials[2,18-20] were also reported.

This study aims at the effective reduction of VOCs released from the automobile felt and the accurate analysis of the trace amount of VOCs. To reduce VOCs emission, nano carbon balls (NCBs), activated carbons (ACs) and their mixture (new carbon mixtures, NCMs) were applied into the felt. Adsorption of VOCs released from the felt was analyzed by using high performance liquid chromatography (HPLC) and gas chromatography (GC). The amount of the total volatile organic compounds (TVOCs) was calculated by summing the amount of individual volatile organic compounds.

2. Experiment

2.1. Preparation of Test Pieces for the Analysis of Aldehyde Gases

In the analysis of typical aldehyde gases, the automobile felt (Feltech Co., Japan) was first kept at the room temperature for 14 days. Then the test pieces (TPs) of 8 cm \times 10 cm \times 1 cm were prepared. 5 TPs (4 g each) were analyzed by the following procedure 1) silicon chip (Aldrich, USA) and clamp was connected to the tedlar bag (SKC Inc., USA) of 5 L, 2) the bag was washed out twice with pure nitrogen gas (99.9%), 3) TPs were placed inside the bag, 4) the bag was filled with pure nitrogen gas of 4 L and was kept at 65 $^{\circ}\text{C}$ in dry oven, 5) after thermal treatment for 2 h, the bag was connected to 2,4-dinitrophenyl-hydrazine (DNPH) cartridge (Aldrich, USA), 6) the total gas was pumped out at 100 mL/min from the bag to the cartridge by ADPEC pump, 7) and acetaldehyde and formaldehyde eluted with acetonitrile (Aldrich, USA) of 10 mL were analyzed by HPLC (Waters 600, USA) using C_{18} column (250 \times 4.6 mm, 5 μm particles) and UV photodiode array detector.

2.2. Preparation of Test Pieces for the Analysis of TVOCs

For the measurement of TVOCs, the 5 test piece was also prepared from the automobile felt. The size and weight of each TP were 8 cm \times 10 cm \times 1 cm and 4 g, respectively. Two-way glass chamber and stainless chamber in same size were constructed for the analysis. Pure nitrogen (99.9%) was supplied with a mass flow controller into the first glass chamber, and the outlet of the second stainless chamber was

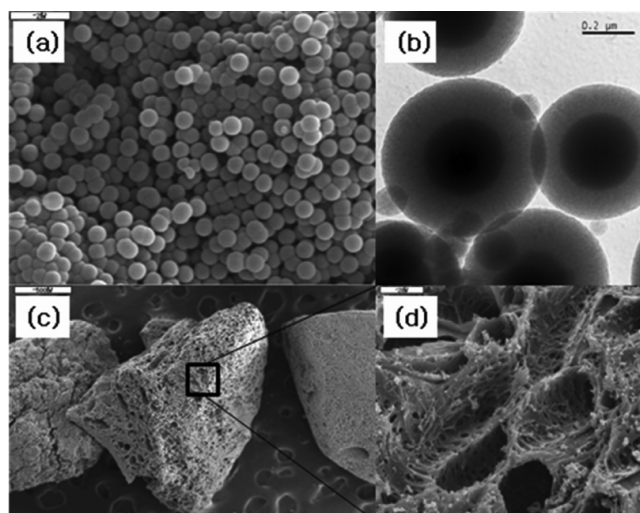


Figure 1. (a) SEM Image of NCBs, (b) TEM Image of NCBs, (c) SEM Image of ACs, and (d) SEM Image of pores in ACs.

Table 2. Composites and Physico-chemical Data of NCBs, ACs and NCMs Mixtures

Materials	Material composition	BET surface area (m^2/g)	Pore size (nm)
NCBs	Carbon/Silica/ H_2O = 57.1/41/1.9	1230	2~4
ACs	Coconut activated carbon	1275	0.5~500
NCMs	Mixture of NCBs and ACs (1 : 9)	1255	0.5~500

connected to Tenax-TA column (Alltech Associates Inc., USA). A 5 L tedlar bag, containing TPs, was placed in the glass chamber. The nitrogen gas was introduced into the glass chamber along with the heat treatment at 65 $^{\circ}\text{C}$ for 2 h in a dry oven. Subsequently, all the gases adsorbed into Tenax-TA column were analyzed by GC (Hewlett Packard 5890 series-II, USA) with the optimized analysis condition (UV photodiode array detector, UV-A column, temp: 40 to 250 $^{\circ}\text{C}$, rate 15 $^{\circ}\text{C}/\text{min}$).

2.3. Removal of VOCs and Aldehyde Gases from the TPs

The starting materials inserted into the felt were commercially available coconut ACs and NCBs. Figure 1 represents the SEM and TEM images of NCBs and ACs used for the adsorption study. The surface area of NCBs was 1230 m^2/g , slightly smaller than that of ACs, and the molar composition of NCBs were carbon/silica/ H_2O = 57.1/41/1.9 as shown in Table 2. The manufacturing process to produce NCBs can be found elsewhere in the literature[21-24]. NCBs and ACs were first separately used as adsorbing materials for the removal of VOCs released from the automobile felt. Then the mixture of NCBs and ACs, designated as new carbon mixtures (NCMs), was also utilized for the adsorption study. Based on the precedent abatement experiment for various gases, the optimum ratio of NCBs to ACs was 1 : 9 by weight. Once the NCMs was scattered uniformly into the TPs, the TPs were kept in zipper storage bag for the experiment.

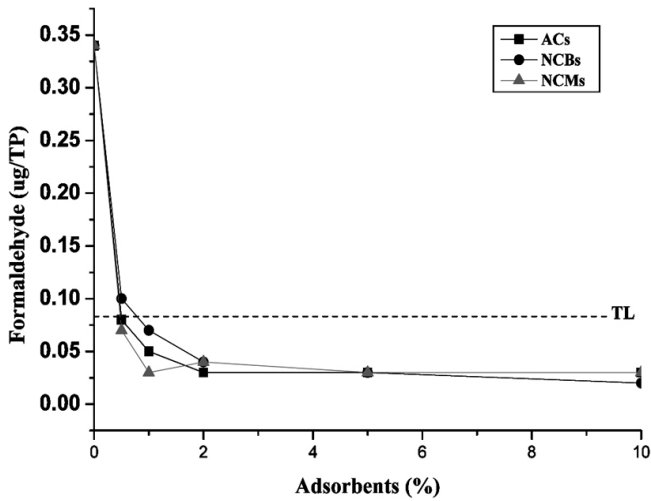


Figure 2. Reduction of formaldehyde released from the felt after introduction of adsorbents.

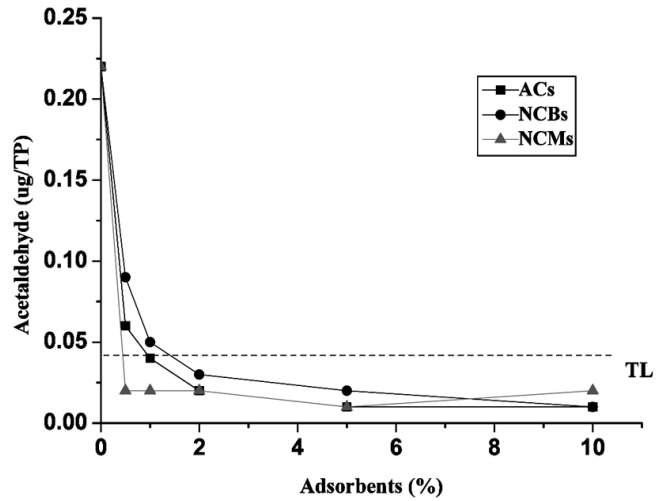


Figure 3. Reduction of acetaldehyde released from the felt after introduction of adsorbents.

3. Results and Discussion

From the morphology analysis, NCBs were almost mono-dispersed spherical particles with core-shell structure, as shown in Figure 1, and micro pores were found to be well developed in ACs. Figure 2 shows the reduction of formaldehyde after introduction of adsorbents, ACs, NCBs and NCMs, into the felt at the room temperature (25 °C). After 14 days of aging at the room temperature, the level of formaldehyde released from the incipient felt was 0.35 ppm (or 0.35 $\mu\text{g}/\text{TP}$) without the application of any adsorbent. When NCBs of 0.5 wt% were applied into the felt, the formaldehyde release decreased to 0.1 ppm. With the same amount of ACs, the formaldehyde release decreased to 0.07 ppm. It should be noted that the application of 0.5 wt% NCMs, a mixture of NCBs and ACs, showed somewhat enhancement in the reduction of the formaldehyde release. This synergetic effect can be more clearly seen when the amount of NCMs applied to the felt increased to 1 wt%, resulting in about 93% reduction of the formaldehyde release.

Figure 3 shows the reduction of acetaldehyde after introduction of adsorbents at the room temperature. Without any adsorbent, after 14 days aging at the room temperature, the level of acetaldehyde released from the original felt was observed to be 0.23 ppm. Although decreased to 0.09 ppm with 0.5 wt% NCBs and to 0.06 ppm with 0.5 wt% ACs respectively, the levels of the acetaldehyde release were still much higher than the target. However the application of 0.5 wt% NCMs into the felt dramatically reduced the acetaldehyde release down to 0.02 ppm, satisfying the allowable level of the acetaldehyde release. The addition of more NCMs nearly affected the reduction capacity of the acetaldehyde release.

Figure 4 shows the reduction of TVOCs in the glass chamber system after introduction of adsorbents at the room temperature. When the tedlar bag was employed instead of two-way glass chamber or stainless chamber, the initial level of TVOCs after baking at 65 °C for 2 h was somewhat higher. Nonetheless, without any adsorbent, the level of TVOCs released from the original felt was 8.49 ppm, about 26 times

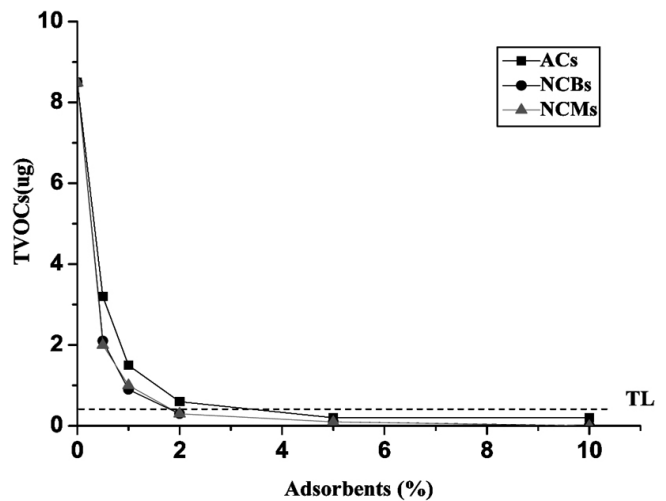


Figure 4. Reduction of TVOCs released from the felt after introduction of adsorbents.

higher than the target level of 0.32 ppm. NCBs and NCMs showed similar performance, while ACs were less effective, in the reduction of the TVOCs release. It was observed that the level of the TVOCs release could be lower down under the target level by either NCBs or NCMs of 2 wt%.

4. Conclusions

To reduce emissions of volatile organic compounds from new automobile felts, new test methods to measure the extremely low concentrations of VOCs released from the felt were established. The concentrations of VOCs released from the original felt were varied. After 14 days of aging at the room temperature, the levels of acetaldehyde and formaldehyde were 0.2~0.5 ppm and 0.2~0.4 ppm, respectively. To reduce VOCs levels, NCBs, ACs and NCMs were applied into the felt. With the application of 0.5 wt% NCMs, the levels of formaldehyde

and acetaldehyde decreased by more than 80%. With the application of 2 wt% NCMs, the level of TVOCs released from the felt decreased under the target level of 0.32 $\mu\text{g}/\text{TP}$.

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References

1. K. L. Foster, R. G. Fuerman, J. Economy, S. M. Larson, and M. J. Rood, *Chem. Mater.*, **4**, 1068 (1992).
2. R. S. Guerrero and A. Sayari, *Environ. Sci. Technol.*, **41**, 4761 (2007).
3. M. E. Davis, A. P. Blicharz, J. E. Hart, F. Laden, E. Garshick, and T. J. Smith, *Environ. Sci. Technol.*, **41**, 7152 (2007).
4. T. Schupp, H. M. Bolt, and J. G. Hengstler, *Toxicology*, **206**, 461 (2005).
5. J. E. Amoore and E. Hautala, *J. Appl. Toxicol.*, **3**, 272 (1983).
6. M. Krzyzanowski, J. J. Quackenboss, and M. D. Lebowitz, *Environ. Res.*, **52**, 117 (1990).
7. B. N. Tam and C. M. Neumann, *J. Environ. Manage.*, **73**, 131 (2004).
8. JAMA Press Releases (<http://www.jama-english.jp>), March 31 (2006).
9. T. Hayashi, M. Kumita, and Y. Otani, *J. Chem. Eng., Jpn.*, **32**, 72 (2006).
10. T. Hayashi, M. Kumita, and Y. Otani, *Environ. Sci. Technol.*, **39**, 5436 (2005).
11. M. Sugiura and K. Fukumoto, *J. Mater. Sci.*, **29**, 682 (1994).
12. L. Jing, L. Zhong, L. Bing, X. Qibin, and X. Hongxia, *Chin. J. Chem. Eng.*, **16**, 871 (2008).
13. N. Ozturk and T. M. Bektas, *J. Hazard. Mater. B*, **12**, 1555 (2004).
14. X. S. Zhao, Q. Ma, and G. Q. Lu, *Energy Fuels*, **12**, 1051 (1998).
15. S. Carlos-Cuellar, P. Li, A. P. Christensen, B. J. Krueger, C. Burrichter, and V. H. Grassian, *J. Phys. Chem. A*, **107**, 2350 (2003).
16. M. P. Cal, M. J. Rood, and S. M. Larson, *Energy Fuels*, **11**, 311 (1997).
17. A. Stein, Z. Wang, and M. A. Fierke, *Adv. Mater.*, **20**, 1 (2008).
18. K. Kosuge, S. Kubo, N. Kikukawa, and M. Takemori, *Langmuir*, **23**, 3095 (2007).
19. J. Yang, T. T. Zhuang, F. Wei, Y. Zhou, Y. Cao, Z. Y. Wu, Z. J. H. Zhu, and C. Liu, *J. Hazard. Mater.*, **162**, 866 (2009).
20. S. O. Lee, S. J. Kitchin, K. D. M. Harris, G. Sankar, M. Dugal, and J. M. Thomas, *J. Phys. Chem. B*, **106**, 1322 (2002).
21. S. B. Yoon, K. N. Sohn, J. Y. Kim, C. H. Shin, J. S. Yu, and T. H. Hyeon, *Adv. Mater.*, **14**, 19 (2002).
22. S. B. Yoon, J. Y. Kim, J. H. Kim, Y. J. Park, K. R. Yoon, S. K. Park, and J. S. Yu, *J. Mater. Chem.*, **17**, 1758 (2007).
23. Y. Kim, S. B. Yoon, and J. S. Yu, *Chem. Commun.*, **21**, 790 (2003).
24. J. K. Lee, S. Y. Han, S. K. Park, Y. K. Park, and C. W. Lee, *Korean J. Chem. Eng.*, **22**, 42 (2005).