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Development of a new sampling method by carbon-nanotube-based gecko tape for pyrolysis-gas chromatography/mass spectrometry

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ABSTRACT

Carbon-nanotube-based gecko tape is a material that emulates the adhesive mechanism of geckos. This adhesive, which has excellent adhesive strength and heat resistance, was used as a sampling tool for collecting and holding samples for pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) to facilitate the sampling of small amounts of powder samples. Polystyrene and an acrylonitrile-butadiene-styrene copolymer were analyzed by Py-GC/MS using gecko tape. The resulting pyrograms were different from those normally obtained, and the composition of the pyrolysis products was changed. Based on these results, the thermal decomposition of samples analyzed using gecko tape was discussed, and the suitability of gecko tape as a sampling tool for Py-GC/MS was evaluated.

1. Introduction

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) is widely used in the field of polymer analysis [1], and is very useful because small, insoluble solid samples can be directly introduced into the GC/MS apparatus without pretreatment. This technique is utilized not only for simple identification and compositional analysis, but also for detailed structural analysis [2–4]. Furthermore, the technique may be augmented with methods such as double-shot pyrolysis and thermochemolysis, also known as thermally assisted hydrolysis and methylation [5–7]. However, if the sample size is very small, it can be difficult to place in a sample cup or transfer to the pyrolyzer.

A method to address this practical problem is to collect and hold powder samples using a sampling tool such as adhesive tape. Characteristics required for such sampling tools are adhesiveness and heat resistance. Furthermore, the tool must be fabricated from a material that will not contaminate the sample, must not emit interfering compounds, and must not decompose at the pyrolysis temperature of the samples. Based on these factors, we focused on gecko tape, which is a new adhesive material [8–10]. Geckos have a fine seta structure on their toes, and the setae have a hierarchical structure (Fig. 1, right), with each seta dividing into branches called spatulas. Adhesion is caused by van der Waals forces between the setae and the adherent. Gecko tape, which emulates the adhesive mechanism of geckos, is made of carbon nanotubes (CNTs). The CNT fibers are aggregated to each other, and are aligned vertically to emulate the toe structure of geckos (Fig. 1, left). Gecko tape adheres to samples by van der Waals forces, and does not contaminate them because it is composed of CNTs alone. Furthermore, it exhibits excellent heat resistance.

In this study, two different polymer materials were analyzed by Py-GC/MS using gecko tape as a sampling tool, and its suitability was evaluated by comparing the resulting Py-GC/MS pyrograms with those obtained using conventional methods.

2. Materials and methods

2.1. Materials

Polystyrene (PS) (UV1-4001, polystyrene standard sample, Frontier Lab, Japan) and acrylonitrile-butadiene-styrene copolymer (ABS) (Sanplatec Co., Ltd.) were used as samples.

Gecko tape (Nitto Denko Co., Ltd.) was used as a sampling tool for collecting and holding the samples. The size of gecko tape was approximately 3 mm long, 3 mm wide, and 1 mm thick, and its weight was 38 ± 3 μg.

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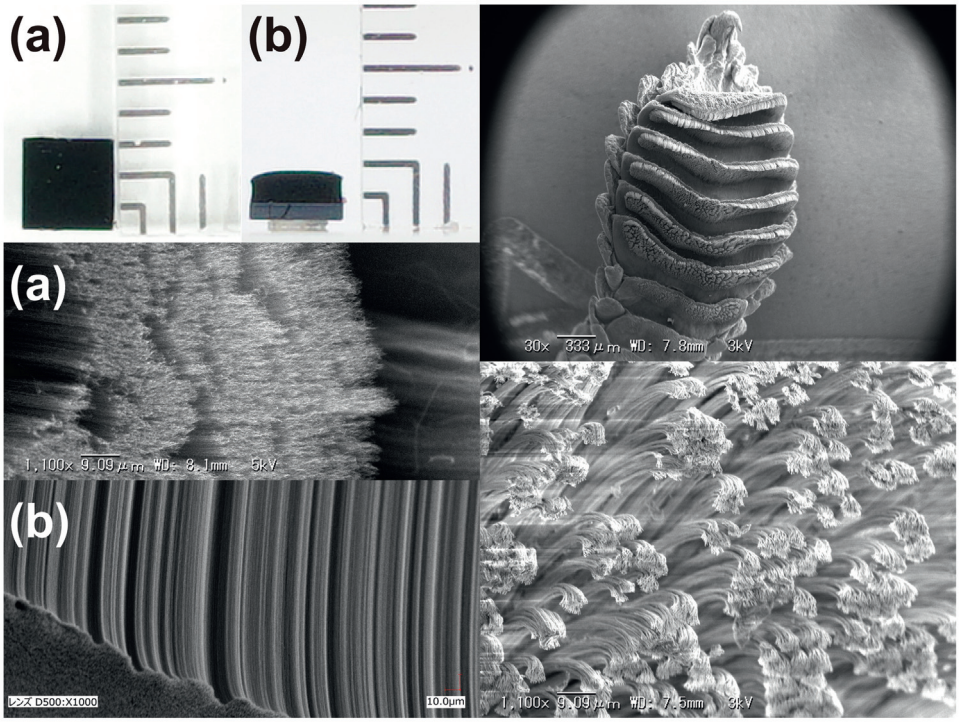

Fig. 1. Photographs and SEM images. Left: gecko tape top (a) and side (b). Right: a gecko toe.

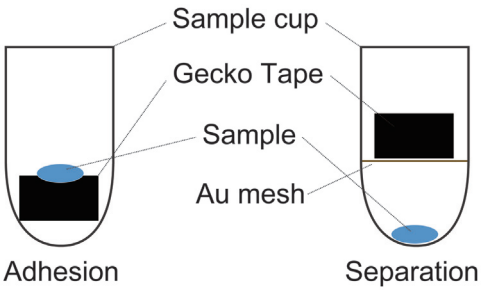

Fig. 2. Normal and separated sample/gecko tape.

2.2. Py-GC/MS measurement

Py-GC/MS measurements were performed using a EGA/PY-3030D multi-shot pyrolyzer (Frontier Lab, Japan), a 7890 B gas chromatographer (Agilent Technologies, Inc. Japan), and a 5977A MSD mass spectrometer (Agilent Technologies, Inc.). A stainless steel Ultra ALLOY-1 (MS/HT) capillary column (0.25 mm i.d. × 30 m, Frontier Lab, Japan) coated with 0.25 μm 100% dimethylpolysiloxane was used for separation. Gecko tape was heated to 800 °C in a helium atmosphere prior to use in order to remove contaminants. The sample (ca. 20 μg) was adhered to clean gecko tape and placed in a glass sample cup on the pyrolyzer at near ambient temperature. The sample cup was then introduced to the furnace, and then the temperature program of the gas chromatographer oven was initialized. The sample was pyrolyzed at 500 °C or 550 °C. The temperature of the pyrolyzer interface and injector was set at 280 °C. The initial temperature of gas chromatograph oven was set at 40 °C and held for 5 min, then increased at 12 °C/min from 40 to 320 °C, and held for 10 min at 320 °C. The flow rate of the helium gas was 1.0 mL/min and the injection was performed in split mode at a 1:20 ratio. All pyrolysis products were identified by mass spectrometry. The mass spectrometry electron ionization (EI) energy was 70 eV, and the scan range was from m/z 29 to 800 with a one second cycle. Perfluorotributylamine (PFTBA) was used to tune the mass spectrometer. The EI mass spectra were acquired in total ion-monitoring mode. The temperatures of the interface and the source were set at 280 and 230 °C, respectively. Agilent Mass Hunter Work-

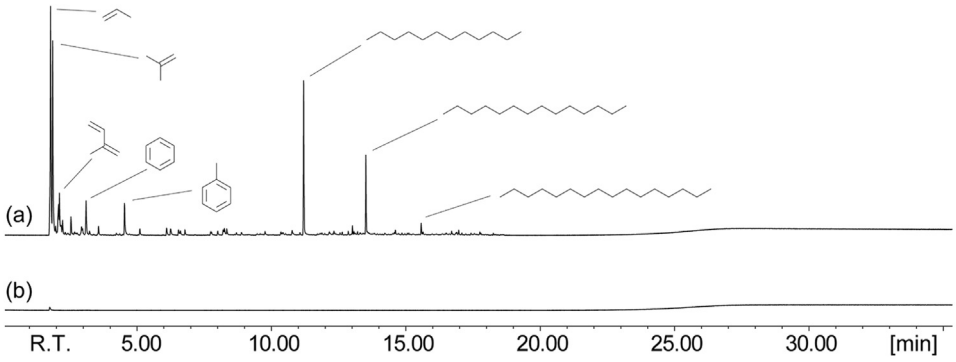

Fig. 3. Total ion chromatogram of gecko tape (a) before and (b) after decontamination.