X-ray and infrared spectroscopy study on contamination of asbestos in Thai commercial cosmetic talc powder product

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Abstract. It is well-known that asbestos such as asbestosis and mesothelioma is a fiber causing lung diseases. Talc is used for commercial applications for example paints, plastics, papers, ceramics, construction materials, and cosmetics. It is well-known that the cosmetic talc powder is used for preventing diaper rash as a deodorant. The sampling in this work has been done from various commercial products in Thailand. Their microstructure and elemental composition are analyzed using a scanning electron microscope coupled with an energy dispersive X-ray spectrometer (SEM-EDS). A small-angle X-ray scattering (SAXS) and infrared spectroscopy (IR) based on synchrotron radiation are also carried out to determine their phase composition and functional groups. It has been found that fibers with asbestos-like shapes are present in some samples. The main composition of oxygen, silicon, and magnesium in samples are in the form of the functional groups that associate with absorption band in the range of 3600-3700 cm\textsuperscript{-1} of IR spectra. It is proposed that there are 6 from 17 samples that possibly have asbestos contamination.

1. Introduction

Talc is an industrial raw material that has unique physical and chemical properties, such as hydrophobicity, organophilicity, lamellarity, softness, chemical inertness, high thermal stability, low electrical conductivity, heat resistance, wide particle size distribution, high specific surface area, oil absorption, and polymer absorption capability. However, these features depend on their parent rock types and origin. It is shown that talc which is extracted from various localities shows the difference in mineralogical chemical and physical properties. It is used in many industrial applications including cosmetics, pharmaceuticals, textiles, papers, food, plastics, ceramics, paints, and pesticides [1-5].
Talc is a clay mineral that consists of a hydrated magnesium silicate sheet with the ideal chemical formula of Mg$_2$Si$_2$O$_5$(OH)$_4$ [1-2, 4]. Moreover, its structure frequently contains small amounts of iron and other trace metals. Talc is widely used as talc powder which is a household product sold globally for use in personal hygiene (baby and feminine powders) and cosmetics [4] as shown in Figure 1.

![Figure 1. Cosmetic talc powder.](image)

It has been reported that talc powder tends to be contaminated with asbestos fibers [6-10] which contribute to certain types of diseases such as asbestosis and mesothelioma [11]. In Thailand, it has been reported that asbestos contamination has been found in commercial body soothing powders which can result in lung inflammation and talc pneumoconiosis [12].

Asbestos is classified as a carcinogen material of the Catalog 1 by the World Health Authorities [13-15]. Several works showed the fiber's toxicity depended on its morphological size, chemical-physical characteristics, surface reactivity, and biopersistence [16-22]. Asbestos is a collective name given to a variety of naturally occurring complex, crystalline, fibrous silicate minerals. Asbestos fibers have a needle-like or sometimes flexible structure that may vary widely in the micron to millimeter ranges. Asbestos minerals are classified into serpentine and amphibole groups. Serpentines have a leafy or layered structure consisted of fine fibers. The leaves consist of alternate layers of silicate tetrahedron (SiO$_4$), which are held together by hydroxide groups (OH), and magnesium ions. Chrysotile, Mg$_3$Si$_2$O$_5$(OH)$_4$, is only one mineral of this group. It has a very small diameter, tubular, very soft, and bendable. Amphibole has a chain-like crystal structure which stipulates their fibrous nature. They have a larger diameter, straight, firm, and hard, but elastic. This group includes amosite (Fe$^{2+}$)$_2$(Fe$^{3+}$)$_2$Mg$_3$Si$_2$O$_{22}$(OH)$_2$, crocidolite; Na$_2$Fe$^{2+}$Mg$_3$Fe$^{3+}$Si$_5$O$_{22}$OH$_2$, anthophyllite; Mg$_7$Si$_8$O$_{22}$OH$_2$, tremolite; Ca$_9$Mg$_3$Si$_3$O$_{22}$OH$_2$, and actinolite; Ca$_9$Mg$_2$Fe$^{2+}$Si$_6$O$_{22}$OH$_2$ [23].

It is well-known that SEM-EDS, XRD, and IR methods are important non-destructive tools for the characterization of materials. It is revealed that morphology, structural, and chemical features of various asbestos minerals have been verified through investigation using a variety of analytical methods, such as electron microscopy [23-32] and infrared spectroscopy [23, 26, 33-35]. SAXS is also applied to determine the structure of the element component in minerals [36-40].

This study reports on the determination of contamination of asbestos in talc using synchrotron facilities for the first time. The morphology, microstructure, and elemental composition are characterized using SEM-EDS, SR-SAXS, and SR-FTIR. The safety of using Thai commercial talcum powder has been discussed.
2 Experimental

2.1 Sample
The two samples of talc powders (STD N1 and STD N2) contained with asbestos are used as the reference. Other 17 samples (N3 to N19) are commercial products (including in-country manufacturing and import products) in Thailand.

2.2 Methods

2.2.1 SEM-EDS. Microstructure and elemental composition are characterized using SEM SU350 (Hitachi, Japan) coupled with EDS Ultimax40 (Oxford Instruments, UK) at Coax Group Corporation Ltd. (Headquarter) (Bangkok, Thailand). The system is operated at 5 kV accelerating voltages, in 30-50 Pa vacuum, and using the AZtec Automated program for analysis. Each sample, three X-ray were corrected.

2.2.2 SR-SAXS. Phase composition is determined using a synchrotron radiation-small angle X-ray scattering (SR-SAXS) at the Synchrotron Light Research Institute (SLRI; Nakhon Ratchasima, Thailand). It utilizes from a bending magnet at the photon energy between 6-9 keV, the calculated photon flux density of about $10^{11}$ photons/sec/0.1% Bending magnet/mrad²/mm², and exposure time of 240 s. The diffraction pattern is obtained from 0º to 40º 2 Theta (2θ).

2.2.3 SR-FTIR. The samples are performed at synchrotron-based FTIR (Fourier Transform Infrared) microspectroscopy. Each sample is prepared using a diamond anvil cell which is a high-pressure cell permitting to operate and adjust under a microscope for transmission studies. The functional groups of the sample composition are evaluated as spectral data and collected at an infrared microspectroscopy beamline (BL4.1 Infrared Spectroscopy and Imaging) at the Synchrotron Light Research Institute (SLRI; Nakhon Ratchasima, Thailand). Spectra were acquired with an SR-FTIR (Hyperion 2000, Bruker Optics, Ettlingen, Germany) coupled with an Infrared microscope (Hyperion 2000, Bruker) using the 36x IR objective lens with an MCT (Mercury cadmium telluride) detector cooled with liquid nitrogen over the measurement range from 3800 to 3000 cm⁻¹. The measurements are performed in transmission mode, using an aperture size of 20×20 μm² with a spectral resolution of 4 cm⁻¹, with 64 scans co-added. Spectral acquisition and instrument control are performed using OPUS 7.5 (Bruker Optics Ltd, Ettlingen, Germany) software.

3 Results and discussion
The element composition of samples obtained by using SEM-EDS is reported in Table 1. It is shown that O (26.8 to 38.1), Si (8.1 to 19.1), and Mg (5.5 to 11.9 wt%) are the main composition of samples. Small amount of Mg (0.3 wt%) is detected only in sample N19. Ca is found only in samples N1 (4.6) and N2 (6.8 wt%). A large amount of Al is found in samples N17 and N19. K (N17 and N19), Ti (N8, N17, N18, and N19), Fe (N1, N17, N18, and N19), and Zn (N6 and N11) are detected in some samples. Na and P also present only in samples N19 and N17, respectively. However, a large amount of C in all samples is suggested to be coming from surrounding contamination.

Due to the main compositions of asbestos are O, Si, Mg, Fe, and Ca. It is implied that N1 and N2 contain actinolite and tremolite, respectively. The results imply that many kinds of asbestos are possibly
contained in samples: chrysotile and/or anthophyllite (N1-N11 and N16); amosite (N17 and N18); and crocidolite (N19).

Table 1. Elemental composition of samples.

| Sample | C   | O   | Si  | Al | K | Ti | Na | Mg | Fe | Ca | Zn | P |
|--------|-----|-----|-----|----|---|----|----|----|----|----|----|---|
| N1     | 33.7| 35.3| 15.8| 1.3| - | -  | -  | 9.3| 29 | 46 | -  | - |
| N2     | 36.6| 32.4| 16.3| -  | - | -  | 8.0| 68 | -  | -  | -  | - |
| N3     | 35.0| 36.9| 16.4| 0.4| - | -  | 11.5| -  | -  | -  | -  | - |
| N4     | 35.8| 37.2| 16.1| 0.5| - | -  | 10.6| -  | -  | -  | -  | - |
| N5     | 31.4| 37.8| 19.0| -  | - | -  | 11.9| -  | -  | -  | -  | - |
| N6     | 33.7| 37.7| 17.0| 0.2| - | -  | 11.0| -  | -  | 0.4| -  | - |
| N7     | 37.7| 36.2| 15.9| -  | - | -  | 10.2| -  | -  | -  | -  | - |
| N8     | 34.8| 37.1| 16.0| 0.3| 1.2| 10.7| -  | -  | -  | -  | -  | - |
| N9     | 33.8| 38.1| 17.1| -  | - | -  | 11.1| -  | -  | -  | -  | - |
| N10    | 38.7| 35.6| 15.6| 0.3| - | -  | 10.0| -  | -  | -  | -  | - |
| N11    | 50.2| 26.8| 8.1 | -  | - | -  | 5.5 | -  | 9.8| -  | -  | - |
| N12    | 35.4| 35.1| 18.0| 0.2| - | -  | 11.4| -  | -  | -  | -  | - |
| N13    | 36.3| 35.3| 17.1| 0.2| - | -  | 11.3| -  | -  | -  | -  | - |
| N14    | 35.4| 35.4| 17.2| 0.5| - | -  | 11.5| -  | -  | -  | -  | - |
| N15    | 40.5| 33.4| 15.8| 0.4| - | -  | 9.9 | -  | -  | -  | -  | - |
| N16    | 36.8| 32.7| 19.1| -  | - | -  | 11.5| -  | -  | -  | -  | - |
| N17    | 38.9| 32.9| 11.5| 8.0| 2.6| 2.0| 5.7| 23 | -  | -  | -  | 0.3|
| N18    | 37.7| 31.6| 14.4| 0.6| 1.2| 8.4| 60 | -  | -  | -  | -  | - |
| N19    | 35.4| 35.7| 12.4| 8.6| 3.4| 2.3| 0.3| 3.1| -  | -  | -  | - |

Figure 2 shows morphologies of straight and firm fibers of amphibole-group asbestos in the reference samples (N1 and N2). A small amount of this type of particle is found in N4 and N17 which is proposed to be anthophyllite and amosite as characterized by EDS. SEM can reveal contamination of the small fibrous with a length of 1-2 µm in samples. However, the fibrils of chrysotile may be beyond the resolution limit of SEM. The characterization based on only chemical composition and morphology may give wrong information due to the contribution of other phases including talc, anthophyllite, etc.
SAXS is a primary characterization tool that can provide structural information describing how large molecules are shaped and organize in any sample. Nevertheless, it is a new method to identify the presence of asbestos in talc powder. It is shown fully characterizing mineral assemblage, provides information about the bulk purity, gives information about the origin of the talc deposit and the associated risk, and indicates if problematic levels of any phase are present. Nonetheless, it is cannot distinguish asbestos from non-asbestos forms of the same mineral. The limit of detection may be too high and may give false-negative results if it used as a screening method.

The phase of reference and talc powder samples are shown in Figure 3. It is shown that SAXS is an analytical technique that measures the intensities of the X-ray scattering by a sample as a function of the scattering angle, the same as the X-ray diffraction technique. In previous research which characterized using the XRD technique based on synchrotron radiation, it is reported that the main pattern of chrysotile is present at 2θ of 12.2 and 24.4°, while amphibole is at ~10.6° [41-44].

FTIR spectroscopy is a powerful tool to qualify and quantify organic substances in the solid, liquid, or gaseous state. However, many sampling techniques require pre-treatment of samples in order to obtain high-quality spectra. It allows solid or liquid samples to be measured with only minimal sample preparation. Because other minerals, including nonasbestos amphiboles, also absorb within these wavelength bands, IR is not always definite for identifying asbestos. The use of an FTIR spectrophotometer improves dramatically the sensitivity and selectivity. With synchrotron light, IR microspectroscopy allows measuring samples at high spatial resolution. Computer-assisted analysis of spectra offers the possibility to reduce matrix interferences and to compare different spectra. It is typically available for testing. However, it is cannot distinguish asbestos from non-asbestos forms of the same mineral, this method is subject to interferences with other minerals, and the detection limit is unknown, up to the samples.

The IR spectra of the reference and talc powder samples are shown in Figure 4. It is shown that absorption bands in the infrared spectra associated with asbestos fibers are all present in the range of 3600-3700 cm⁻¹ which correspond to specific hydroxyl bands: the O-H stretching vibration band of the hydroxyl group surrounded by 3Mg3(Mg3-OH)2[23-26, 33-35].
Figure 3. Phase composition of samples using SR-SAXS.

Figure 4. IR spectra of the samples.

The results show that some samples possibly contain asbestos, especially N5, N12, and N17 are the same characteristic as N1, while N4, N10, and N15 correspond to N2. By comparing the information of asbestos morphology, elemental composition, molecular structure, and functional group, it is proposed that there are 6 from 17 samples that possibly have asbestos contamination. The contamination can result from the mining process and production. Asbestos is present in some Thai commercial talc-powder products but not all. It is highly recommended that they should be used with caution.
Further works using other techniques such as Near-IR spectroscopy, TEM (Transmission electron microscopy), XRD, particle size analysis, thermal degradation, and Raman spectroscopy would be done in order to find out more details.

4 Conclusion
Asbestos contamination in Thai commercial talc-powder products has been analyzed using SEM-EDS, SR-SAXS, and SR-FTIR. The main composition of oxygen, silicon, and magnesium in samples are in the form of the functional groups that associate with absorption band of IR spectra. According to information on morphology, elemental composition, molecular structure, and functional group obtained from these techniques is proposed that there are 6 (such as N4, N5, N10, N12, N15, and N17) from 17 samples that possibly have asbestos contamination.

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