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Short Communication

Types and Health Hazards of Fibrous Materials Used as Asbestos Substitutes

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ABSTRACT

Asbestos has been banned in many countries but many countries, including developing countries, are still using asbestos or materials containing asbestos. Substitute materials have been studied and developed over a long period of time because of the hazards of asbestos, and many people have recently shown interest in the hazards of substitute materials. However, comprehensive information about the types of asbestos substitutes, their use and health hazards, and references for the protection for the health of workers is limited. The purpose of this study is to provide people in the related industries with information on the types and health hazards of fibrous materials that can be used as asbestos substitutes. According to the patent resources from the United States and Europe, fibrous materials have been used to develop asbestos-free products since before 1980. Recently, the health hazards of asbestos substitutes have been assessed and many additional researches are required. However, only some of the substitute materials have been assessed for health hazards, and health hazard data has not been sufficient in many cases. Therefore, efforts should be made to minimize workers' exposure to substitute materials that do not contain asbestos.

1. Introduction

The World Health Organization (WHO) estimates that about 125 million people are exposed to asbestos at worksites around the world, and more than 107,000 people die of asbestos-related diseases, including lung cancer, mesothelioma, or asbestosis, due to occupational exposure to asbestos [1]. Substitute materials have been studied and developed over a long period of time because of the hazards of asbestos, and many people have recently shown interest in the hazards related to such substitute materials.

Fibrous materials may be considered as an alternative to asbestos. There are many kinds of fibrous materials, which can be largely classified into synthetic fibers and natural fibers. Synthetic fibers can be classified into organic and inorganic fibers; synthetic organic fibers include polyamide fiber, polyolefins fiber, polyester fiber, polyurethane fiber, and polyvinyl fiber, and synthetic inorganic fibers include glass filaments, glass wool, refractory ceramic fibers, rock wool, and slag wool fiber. Natural fibers include natural organic fibers such as cotton and hemp and natural inorganic fibers such as attapulgite, erionite (*zeolite*), nemalite (fibrous brucite), sepiolite, and wollastonite [2].

According to patent resources in the United States and Europe, asbestos substitutes have constantly been developed since before 1980 [3–31]. An asbestos-free drywall joint compound was developed in 1975 [3], an asbestos-free tape sealant was developed in 1979 [4], and an asbestos-free friction material was developed in 1980 [5]. An asbestos-free gasket was developed in 1982 [7] and a method of manufacturing an asbestos-free glass fiber reinforced product was developed in 1983 [10]. Flexible sheet material suitable for use in the manufacture of asbestos-free gaskets was developed in 1985 [15] and a method of manufacturing aramid-containing friction materials in 1986 [16]. In 1996, a fiber-reinforced building material was developed using sepiolite [26]; in 2002, a press pad composed of an asbestos-free material was developed [29].

The International Social Security Association provides information on asbestos substitute materials through a technical report [32]. The report classifies types of asbestos use into eight categories which are raw asbestos in bulk, asbestos in powder, asbestos in liquid or pastes, asbestos in sheet or board, asbestos in woven or braided goods, asbestos in a resin or plastic matric, asbestos in cement, and asbestos in asphalt or bitumen. According to the report

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of the International Social Security Association, mineral wool and ceramic fibers can be used as an asbestos fiber substitute for insulation or soundproofing, while sheets and boards containing asbestos can be substituted with synthetic vitreous fibers or clay instead of asbestos, and textile containing asbestos can use polyethylene fiber, polypropylene fiber, polyamide fiber, carbon fiber, and glass fiber instead of asbestos. Asbestos cement products can use cellulose, polypropylene fiber, polyvinyl alcohol fiber, aramid, and glass fibers instead of asbestos. Cellulose, polypropylene fiber, polyvinyl alcohol fiber, aramid, and glass fibers can be used as an asbestos fiber substitute for asbestos cement products.

In addition to the development of asbestos substitute materials, a series of studies have also been conducted in regard to the hazards of fibrous materials. Erionite fiber, which is a mineral fiber, causes malignant mesothelioma and has been classified into Group 1 (carcinogenic to humans) by the International Agency for Research on Cancer (IARC) [33]. Also, refractory ceramic fibers are classified into Group 2B (possibly carcinogenic to humans) by the IARC [34] and Group A2 (suspected human carcinogen) by the American Conference of Governmental Industrial Hygienists (ACGIH) as it can cause lung fibrosis [35]. The WHO has assessed the hazards of 14 types of asbestos substitute materials, including para-aramid, attapulgite, and carbon fiber [36]. Also, Harrison et al [37] has discussed the health hazards of para-aramid, polyvinyl alcohol, and cellulose in comparison to chrysotile. According to this literature, the major characteristics related to the health hazards of fiber are its dose, dimensions (especially diameter), and durability. National Institute for Occupational Safety and Health has recently presented a research roadmap for a broad understanding of the health hazards of asbestos fiber and other elongate mineral particles [38]. This roadmap suggests that studies related to the toxic effect, occupational exposure, and development of methods of measurement and analysis of asbestos fibers and elongate mineral particles are required.

This study discusses the types of fibrous materials that can be used as asbestos substitute materials, the development of asbestos-free products, and the health hazards of fibrous materials to provide information for the protection of health of workers in the related industries.

2. Materials and methods

Literature on the types and characteristics of asbestos substitutes, the development status of asbestos-free materials, and the health hazards of asbestos substitutes was reviewed for this study. To examine the types and characteristics of asbestos substitutes, this study referenced literature on chemical and physical properties and morphology [2,3,11,13,26,31,33,34,39–41]. The resources on the development of asbestos substitutes referred to the cases of asbestos substitutes that have been certified internationally based on patent resources from the United States and Europe. According to the United States Geological Survey report on the worldwide asbestos supply and consumption, the United States and Europe imported more than 80% of worldwide asbestos production during 1920∼1960 [42], which caused high levels of asbestos-related disease in the United States and Europe [43,44]. As a result of searches on the patent site (Google patents, https://patents.google.com), there were many patents for asbestos substitutes in the United States and Europe. The development status of building materials, friction materials, gaskets, joint sheets, and fabrics that are free of asbestos was identified by patent resources [3–31]. Literature on the hazard assessment of asbestos substitutes has referenced hazard assessment report of asbestos substitutes prepared by the WHO through an workshop of expert group [36], IARC's carcinogen assessment resources on fibrous materials [33,34,39], and ACGIH's resources on threshold limit values (TLVs) [41]. The participants in the WHO workshop evaluated the health hazards and carcinogenicity of asbestos substitutes based on epidemiological evidence, studies in experimental animals, *in vitro* short-term tests, physicochemical properties, and biopersistence. The workshop decided to group asbestos substitutes roughly into hazard groupings of high, medium, and low. These hazard groups should be considered in relation to each other and did not have reference to formal criteria or definitions, as such. The IARC evaluated the carcinogenicity of some silicates and synthetic vitreous fibers based on studies of cancer in human, studies of cancer in experimental animals, physicochemical properties, persistence and biodegradability, other data relevant to evaluation of carcinogenicity and its mechanism. ACGIH evaluated the carcinogenicity of synthetic vitreous fibers based on studies of cancer in humans, studies of cancer in experimental animals, physicochemical properties, and other data relevant to evaluation of carcinogenicity.

3. Results

3.1. Types and characteristics of fibrous materials

The asbestos substitute materials known so far include synthetic fibers such as man-made vitreous fibers (synthetic vitreous fibers) and para-aramid and natural inorganic fibers such as attapulgite, sepiolite, and wollastonite. Man-made vitreous fibers refer to inorganic fibrous materials made with glass, rocks, minerals, slag, or processed inorganic oxides [34]. Para-aramid, which is a widely known asbestos substitute material, is a type of polyamide fiber similar to nylon fibers. This material is mostly used to improve the strength, durability, and heat resistance of synthetic materials. It is light enough to be used within the aviation and sports industries, and it is also used to reinforce fiber for synthetic materials, thermoplastic materials, tires, and rubber products. It is used as an asbestos substitute material for automotive friction materials and gaskets [39]. Natural inorganic fibers such as attapulgite, sepiolite, and wollastonite have been used as a substitute for asbestos in building materials and friction materials [3,11,13,26,31].

Attapulgite is a hydrated magnesium aluminum silicate mineral [40]. Attapulgite is elongated in structure and similar to the mineral structure of amphibole group. It is known as “palygorskite” in mineralogy, but it is more widely known as “attapulgite” [39]. Attapulgite has been used as an asbestos substitute material for building materials and friction materials as asbestos has been found to be hazardous [3,13].

Sepiolite is a clay mineral composed of hydrated magnesium silicate. Structurally, it is similar to attapulgite, but it has one more SiO_4 tetrahedron when compared to attapulgite. Sepiolite is an elongated and lath-like structure of crystals. The length of fibers varies according to the location of sepiolite sediments [39]. The elongated particles of sepiolite improve its usability as a viscosity improver and sedimentation preventer.

Wollastonite is a calcium silicate mineral that is chemically inert, but it can be decomposed in concentrated hydrochloric acid. With its unique cleavage property, it breaks into thin lath-like shapes or needle-like particles. Wollastonite is mostly used for ceramic, plastic, rubber, asbestos substitute, paint, and coating products, and wollastonite with a high aspect ratio (10: 1 to 20: 1) is used to reinforce plastic and rubber and as a functional filler and an asbestos substitute material [39].

Erionite is a fibrous hydrated aluminosilicate mineral in the zeolite group. Erionite is similar to amphibole in shape, but it has different physicochemical structures. Erionite exists in the form of a bundle of fibers [33]. Natural erionite has not been mined or distributed for commercial purposes since the late 1980s and has been substituted with nonfibrous synthetic zeolite.

3.2. Development of asbestos-free materials

Asbestos has been widely used for building materials, automotive and industrial friction materials, gaskets and joint sheets, and asbestos fabrics [45]. For building materials, 10–20% asbestos is mixed with cement, pulp, sand, plaster, etc. to make cement corrugated sheets, cement flat boards, cement gypsum boards, and autoclaved cement extrusion panels. For automotive and industrial friction materials, 10–20% chrysotile is mixed with synthetic resin, metal powder, etc. to make brake lining, brake pads, clutch lining, clutch facing, and special brakes for railroads or cranes. In the case of gaskets and joint sheets, 30–40% chrysotile is mixed with synthetic resin, fiber, etc. For asbestos fabrics, asbestos is the main component (90% or greater asbestos content) to make asbestos yarns, asbestos ropes, asbestos tapes, asbestos packing, asbestos cloths, and asbestos gloves.

As the hazards of asbestos have been known since before 1980, products using asbestos substitute materials have been consistently developed. Table 1 lists the development of asbestos-free products using asbestos substitute materials based on the patent resources from the United States and Europe.

With regard to building materials, attapulgite, cotton, mineral fiber, polyacrylamide, polypropylene, polyvinyl alcohol fiber, sepiolite, and slag wool have been used to develop asbestos-free building materials such as boards and sheets, drywall joints, fiber reinforced products, inorganic sheets, and joint compounds [3,6,10,11,18,21,26,31].

Friction material area is one of the areas that has actively developed substitutes as asbestos was widely used for automotive brake lining, mechanical clutches, and brake pads for machine tools. In the realm of friction materials, aramid, aromatic polyamide, attapulgite, carbon fiber, ceramic fiber, cotton, glass fiber, mineral wools, and silica fiber have been used to develop asbestos-free friction materials such as brake lining and pads, brake shoes, clutch facing, clutch lining, clutch surfaces, and press pads [5,9,13,16,29,30].

For gaskets and joint sheets, aramid fiber, aromatic polyamide fiber, cellulose fiber, ceramic fiber, nylon fiber, and vitreous fiber have been used to develop asbestos-free gaskets or joint sheets [7,12,14,15,24,25].

For fabrics, cotton fiber, glass fiber, ceramic fiber-containing paper (strand), texturized fiber glass roving or yarn, and acrylic fiber have been used to develop asbestos-free fabrics such as tape sealants, rope packing, yarns, and other fabrics [4,8,17,20].

Other aramid fiber, polytetrafluoroethylene fiber, carbon fiber, and metallic alloy fiber have been used to develop asbestos-free sealing materials, diaphragms, electroconductive substrates, and valve packing [19,22,23,27,28].

3.3. Health hazards of fibrous materials

The major factors of toxicity of fibers are in the fiber sizes, fiber durability, and fiber types [46]. In terms of the size of a fiber, fibers thinner than 3 μm can reach lower airways, while fibers longer than 5–10 μm can stay in the lungs longer than other shorter fibers. Also, the length of fibers which macrophage can remove is about 16–17 μm. Considering the durability of fibers, a fiber generally undergoes the process of fragmentation (latitudinal breakage) or splitting (longitudinal breakage) in the human body. Both fragmentation and splitting can increase the number and surface area of fibers, but shorter fibers resulting from fragmentation are easily removed by macrophage. In the case of splitting, it does not affect the removal by macrophage. When considering the types of fibers, it is known that amphibole asbestos stays in the lungs longer than the serpentine chrysotile.

Considering the health hazard of asbestos fibers by size, asbestosis is most closely related to the size of fibers that are 2 μm or longer and 0.15 μm or thicker in diameter, while malignant mesothelioma is most closely related to the number of fibers that are 5 μm or longer and 0.1 μm or thinner in diameter. In the case of lung cancer, it is most closely related to the number of fibers that are 10 μm or longer and 0.15 μm or thicker in diameter [47].

The WHO assessed the hazards of 14 kinds of asbestos substitute materials, including para-aramid, through a workshop conducted by experts in the field [36]. This workshop classified the hazards of asbestos substitute materials into three steps—high, medium, and low—and the major factors of hazards were health hazards related to lung cancer, malignant mesothelioma, and asbestosis.

Table 2 lists the results of hazard assessment of asbestos substitute materials by the WHO and the classification of carcinogens by IARC and ACGIH. According to the assessment results of the WHO, p-aramid fibers have respirable fibers with similar dimensions as carcinogenic fibers and had effects on the lungs in an animal testing. As it also has biopersistence, its hazards were rated medium. Respirable attapulgite fiber is highly hazardous when it contains long fibers, but shorter fibers are less hazardous. In the respiratory testing on animals, longer fibers caused tumors, whereas shorter fibers did not. Carbon fibers were 5–15 μm in diameter and mostly nonrespirable in the industrial sites with low hazards, and cellulose was also mostly nonrespirable and not hazardous. However, respirable cellulose fibers were found to be indeterminate due to insufficient data.

Table 1
Examples of asbestos substitutes used in development of asbestos-free materials.

Type of materials	Use	Asbestos substitutes
Building materials	Boards & sheets, drywall joint, fiber reinforced product, inorganic sheet, and joint compound	Attapulgite, cellulose pulp, cotton, mineral fiber, hydroxypropyl methyl cellulose, polyacrylamide, polypropylene, polyvinyl alcohol fiber, sepiolite, silica fume pulp, and slag wool
Friction materials	Brake lining & pad, brake shoe, clutch facing, clutch lining, clutch surface, and press pad	Aramid, aromatic polyamide, attapulgite, carbon fiber, ceramic fiber, cotton, glass fiber, metal fiber, mineral wools, silica fiber, steel wool, wood pulp, and woven fabric (heat-resistant yarn)
Gasket & joint sheet	Gasket and joint sheet	Aramid fiber, aromatic polyamide fiber, cellulose fiber, ceramic fiber, nylon fiber, phenolic fiber, and vitreous fiber
Fabrics	Tape sealant, rope packing, yarn, and other fabrics	Cotton fiber, glass fiber, ceramic fiber-containing paper (strand), texturized fiber glass roving or yarn, and acrylic fiber
Others	Sealing, damping, and separating Diaphragms (fibrous sheet) Electroconductive substrate Valve packing	Aramid fibers and polyaramide Polytetrafluoroethylene (PTFE) fiber and inorganic fiber, Carbon fiber (or graphite fiber), inert mineral fiber and PTFE fiber Carbon and metallic alloy fiber

Table 2
Health hazard and carcinogenicity of some fibrous materials.

Materials	Health hazard & carcinogenicity	
	WHO	IARC (ACGIH)
p-Aramid fibers	Medium	Group 3
Attapulgite fibers		
Long fibers, >5 μm	High for long fibers	Group 2B
Short fibers, <5 μm	Low for short fibers	Group 3
Carbon fiber	Low	—
Cellulose fibers	Low for not respirable, indeterminate for respirable	
Continuous filament glass fibers	Refer to synthetic vitreous fibers	Group 3 (A4)
Erionite fibers		Group 1
Glass wool fibers	Refer to synthetic vitreous fibers	Group 3 (A3)
Graphite whiskers	Indeterminate	—
Magnesium sulfate whiskers	Low or indeterminate	—
Polyethylene fibers	Indeterminate	—
Polypropylene fibers	Indeterminate	—
Polyvinyl alcohol fibers	Indeterminate	—
Polyvinyl chloride fibers	Indeterminate	—
Potassium octatitanate fibers	High	—
Refractory ceramic fibers	Refer to synthetic vitreous fibers	Group 2B (A2)
Rock wool fibers	Refer to synthetic vitreous fibers	Group 3 (A3)
Sepiolite fibers	—	Group 3
Slag wool fibers	Refer to synthetic vitreous fibers	Group 3 (A3)
Synthetic vitreous fibers	High for biopersistent, low for nonbiopersistent	—
Wollastonite fibers	Low	Group 3
Xonotlite fibers	Low	—

ACGIH, American Conference of Governmental Industrial Hygienists; IARC, International Agency for Research on Cancer; WHO, World Health Organization.

Graphite whiskers, in terms of dimensions, are highly respirable with a long half-life in the lungs but findings were indeterminate due to insufficient data. Magnesium sulfate whiskers did not cause tumors in limited studies and they are very quickly removed from the lungs. Overall, the hazard was assessed as low or indeterminate. Polyethylene, polyvinyl chloride, and polyvinyl alcohol fibers were also found to be indeterminate due to insufficient data. In the case of polypropylene fibers, they could be respirable in the production process and respirable polypropylene fibers showed high biopersistence after intratracheal administration, but did not show fibrosis in the subchronic test. Overall, polypropylene fibers were found to be indeterminate due to insufficient data. In the case of potassium octatitanate fibers, they were found to be highly hazardous. They are exposed as a respirable fiber at industrial sites, cause mesothelioma when injected into intraperitoneal organs, and show evidence of genetic toxicity and biopersistence. In Table 2, synthetic vitreous fibers include continuous filament glass fibers, glass wool fibers, refractory ceramic fibers, rock wool fibers, and slag wool fibers. The major factors that determine the hazards of synthetic vitreous fibers are the dimensions, biopersistence, and physicochemical properties of fiber. The hazards of synthetic vitreous fibers vary from high to low; the materials with biopersistence were found highly hazardous, while other materials were found less hazardous. Natural wollastonite contains respirable fibers but found to be less hazardous because workers are mostly exposed to short fibers occupationally, and it did not cause tumors in chronic toxicity assessment. In the case of xonotlite, it did not cause tumors in an intraperitoneal implantation research. Its chemical components are similar to those of wollastonite, but it is more quickly removed from the lungs.

According to IARC's classification of carcinogens, p-aramid fibers are classified into Group 3 which is not classifiable because it is carcinogenic to humans. Attapulgite has insufficient evidence of carcinogenicity in humans, but a study of samples containing fibers that are 5 μm or longer showed occurrence of malignant tumors and mesothelioma in animal testing; however, no significant increase in the occurrence of tumors was observed for fibers that are shorter. IARC classifies attapulgite fibers that are 5 μm or longer into Group 2B (possibly carcinogenic to humans) and shorter fibers into Group 3 (not classifiable as to its carcinogenicity in humans) [39]. Also, erionite fibers that cause malignant mesothelioma and are carcinogenic to human are classified into Group 1 [33]. With respect to fire-resistant ceramic fibers, there is insufficient evidence of carcinogenicity in humans, but there is significant evidence of lung cancer and malignant mesothelioma in the long-term inhalation test of mouse. Therefore, fire-resistant ceramic fibers are classified into Group 2B (possibly carcinogenic to humans) [34].

ACGIH classifies some synthetic vitreous fibers according to their carcinogenicity and recommends the TLV. Fire-resistant ceramic fibers are classified into the A2 group (suspected human carcinogen), and the recommended TLV is 0.2 f/cc. Also, glass wool fibers, rock wool fibers, and slag wool fibers are classified into the A3 group (confirmed animal carcinogen with unknown relevance to human), and the recommended TLV is 1 f/cc [35].

4. Discussion

As the hazards of asbestos have been known to many people, substitute materials have been studied and developed over a long period of time, and many people are also concerned about the hazards of substitute materials. Some fibrous materials have been assessed for health hazards, but there are some materials that may be carcinogenic to humans or may affect the health of humans. IARC classifies erionite fibers into Group 1 (carcinogenic to humans) and fire-resistant ceramic fibers and attapulgite fibers that are 5 μm or longer into Group 2B (possibly carcinogenic to humans). Recently, the WHO assessed the hazards of 14 kinds of asbestos substitute materials, including attapulgite and potassium octatitanate fibers. As a result of the assessment, attapulgite was classified as highly hazardous as it can cause tumors when the fibers are long. Potassium octatitanate fibers were also classified as highly hazardous. They can be exposed as respirable fibers at industrial sites and cause mesothelioma when injected into intraperitoneal organs, and there is evidence of genetic toxicity and biopersistence. In the case of synthetic vitreous fibers , biopersistence fibers were classified as highly hazardous, while nonbiopersistence fibers were classified as low hazard. para-Aramid has a medium level of hazard as it is similar in the size of fibers that are known to be carcinogenic and may be exposed as respirable fibers. Also, carbon fibers, wollastonite, xonotlite, and short attapulgite fibers have low hazard. Polyethylene fibers, polyvinyl chloride fibers, polypropylene fibers, and graphite whiskers were not assessed due to insufficient data. Assessment of these asbestos substitute materials has been limited and further studies are needed in the future. It is necessary to develop building materials and friction materials using substitute materials that can replace the carcinogenic asbestos. However, fibrous materials include materials that may be carcinogenic and may affect health. Only some substitute materials have been assessed for health hazards, and there are materials that do not have sufficient assessment data. For this reason, there are still many materials for which occupational exposure limits have not been established yet. Therefore, efforts should be made to minimize workers' exposure to substitute materials that do not contain asbestos.

Conflicts of interest

The author declares that there is no conflict of interest.

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Appendix A. Supplementary data

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