Staff Sergeant Daria Śmigiel-Kamińska

Forensic Laboratory, Gdańsk Province Police Headquarters Specialist, Department of Chemistry and Biology

Damaging effect of corrosive substances on textile products and fibres in the view of forensic analyses

Summary

A trace evidence in the form of a fiber or textile product gains greater evidential usefulness if it is damaged due to the use or destructive factors. Hence, an intensive examination of destructive processes influenced by either physical or chemical factors may significantly help in determining the type of a product, circumstances and the course of a criminal incident.

The aim of conducted studies was to test the influence of selected corrosive substances on morphology of textile products and fibres, and to conclude whether despite the changes inflicted by the used substances, there was a possibility of subjecting the fibres to identification and comparative tests in order to objectively conclude about the course of an incident in its criminal aspect.

The results of conducted studies allowed to characterize the influence of used corrosive substances on textile products and single fibres, varying in qualitative composition and structure. Undoubtedly, the present study does not cover all the aspects of undertaken issue and opens the door to further considerations in the context of observed chemical reactions. Such studies would likely contribute to developing new research methodologies of fibre microtraces analyses.

Keywords microtraces, fibres, textile products, corrosive substances, fibre destruction

Introduction

The 60's and 70's brought to Poland a significant interest in small particles in the context of forensic analyses. In 1972, at the Symposium dedicated to microtraces held in Warsaw, such particles were defined as "invisible or hardly visible to the naked eye particles of matter or mechanical features measurable by microanalytical techniques only" [1, 2].

Chemical microtraces most commonly analyzed in forensic laboratories include fibres, glass, paints and metal alloys.

Fibres are commonly found on a daily basis, coming mainly from clothing products. Depending on the type and intended use, clothing can be made from natural or chemical fibres. Chemical fibres include: i) manmade fibres – produced in the processes that modifies the structure of natural biopolymers, e.g. viscose fibres made of cellulose and mineral resources or fibreglass, and ii) synthetic fibres – made of polymers not found in nature, e.g. polyamides and polyesters [3].

Forensic analysis of individual fibres leads to determination of characteristics of their

physicochemical structure, based on which fibres are identified, i.e., classified into specific types, varieties and ranges of textile products [3]. Lack of difference between the evidence and comparative fibres shown in tests, indicates that these fibres are similar or compliant, and that they come from similar or identical source. A trace evidence in the form of a fibre or a textile product gains greater evidential value if it becomes damaged from the use or as a result of destructive factors. Hence, an in-depth examination of destructive processes governed by either physical or chemical factors, may significantly help to determine the type of a fibre product (yarn, thread, fragment of knitted item or fabric), circumstances and the course of a criminal incident [4–8].

Course of study and analysis

Research experiment

The aim of the present study was to assess changes in the structure of textile products and in morphology

(vertical view) of individual fibres. Experimental material has been chosen, based on market research in terms of preferences in textile products [9] and population studies of particular type fibre distribution [10].

The study involved samples 10 x 10 cm of the following textile products:

- gray wool knit made of thread with plait type "S" (right-handed plait);
- blue cotton fabric made of blue thread with plait type "Z" (left-handed plait) and white thread with plait type "Z" (left-handed plait);
- black polyamide knit made of thread with plait type "S" (right-handed plait);
- black polyester fabric made of thread with plait type "Z" (left-handed plait);
- brown polyacrylonitrile knit made of thread with plait type "S" (right-handed plait);

The experimental part involved the use of corrosive substances selected based on the following criteria: i) ease of access and ii) widespread use by criminal offenders in Poland. Five agents have been selected:

- 36% hydrochloric acid, P.P.H. STANDARD;
- 98% sulphuric acid (IV), POCH;
- 65% nitric acid (V), POCH;
- sodium hydroxide, the main component of agent (in a form of gel) with brand name "Kret", GLOBAL POLLENA S.A;
- sodium hypochlorite, a component of agent with brand name "Domestos", Unilever Polska Sp. z o.o. According to manufacturer's description the agent consists of sodium hypochlorite (4,8 g/100 g),
 5% bleaching agents based on chloride, nonionic surfacants, soap, and fragrance composition.

Samples of particular types of textile products were positioned on the glass surface. Subsequently, individual samples were treated with 5 ml hydrochloric acid, sulphuric acid (IV), nitric acid (V), sodium hydroxide and sodium hypochlorite. Such material was left under the hood, at room conditions for 24 hours. Each sample was prepared in three repetitions to eliminate the possibility of accidental effects.

Research equipment

Stereomicroscopes: Leica Mz9 with reflected illumination and transmitted white illumination (6.3x – 16x magnification) and OLYMPUS SZX 12 with reflected illumination (10x – 90x magnification) were used to observe changes on the surface of textile products.

Research microscopy and scanning electron microscopy techniques were used in order to observe morphological changes in fibers, including damages resulting from conducting the experiment.

Wet microscope slides immersed in liquid with refractive index $n^{20}_{D} = 1.516$ were examined using

OLYMPUS PROVIS AX-70 research microscope. Observations were performed in transmitted white light (BF), phase contrast (PH), white polarized light (PO) and ultraviolet light (UV), at a magnification of 100x and 200x.

Research material samples were placed on the electron microscope stage, and subsequently coated with gold (for 3 minutes) in the atmosphere of argon. Coating was performed with BioRad Polaron Division sputter coater. Prepared samples were analysed using Philips XL40 scanning electron microscope, by applying SE detector (81x – 2,626x magnification).

Studies involving the use of OLYMPUS SZX 12 stereoscopic microscope, OLYMPUS PROVIS AX-70 research microscope and Philips XL40 scanning electron microscope were carried out at Chemistry Department of the Central Forensic Laboratory of Police in Warsaw.

Study results

The subject of present study involved morphological changes occurring in textile products and single fibres, due to the effects of corrosive substances. Further studies of the end products would allow for chemical interpretation of observed processes.

36% hydrochloric acid

No changes in the appearance of textile products and morphology of single fibres were observed in case of natural fibres (wool and cotton) or synthetic fibres (polyamide, polyester, polyacrylonitrile).

However, the cotton fibres were observed to have acquired increased brittleness and fragility (decreased mechanical resistance) (Fig. 1–3; Fig. 1 Cotton, from the left – not affected by corrosive substance, affected by hydrochloric acid [stereomicroscope image]; Fig. 2 Cotton, from the left – not affected by corrosive substance, affected by hydrochloric acid [material microscope image]; Fig. 3 Cotton, from the left – not affected by corrosive substance; affected by hydrochloric acid [scanning electro microscope image]; see Polish version).

98% sulphuric acid

Sulfuric acid was found to have a destructive effect on all textile product types. A textile product made of wool degraded completely due to sulphuric acid treatment, transforming into brown – colored pliable mass (Fig. 4 Wool, from the left – not affected by corrosive substance, affected by sulphuric acid [stereomicroscope image]; see Polish version). The knit structure was partially preserved, however no single fibres could be found.

A discoloration was observed in the case of cotton fabric, with visible areas of yellowish - brown

and black color. Microscopic transmitted light imaging of a sample collected from black - colored area revealed that carbonization reaction was not completed. The original color of the material (blue) was still visible. Sulfuric acid increased fragility of cotton product, resulting in its partial degradation. Within the preserved parts, original plait was still visible and threads of the weft and warp remained distinguishable. Additionally, cotton products became swollen, which made it impossible to isolate individual fibres, but their morphological features remained preserved (Fig. 5-7; Fig. 5 Cotton, from the left - not affected by corrosive substance, affected by sulphuric acid [stereomicroscope image]; Fig. 6 Cotton, from the left - not affected by corrosive substance, affected by sulphuric acid [material microscope image]; Fig. 7 Cotton, from the left – not affected by corrosive substance, affected by sulphuric acid [scanning electro microscope image]; see Polish version).

Sulfuric acid treatment caused dissolving of the fibres of polyamide textile products. Preserved pieces of fabric were characterized by red, fragile edges with a plastic material appearance, which morphed into black knit with original morphology (Fig. 8 Polyamid, from the left – not affected by corrosive substance, affected by sulphuric acid [stereomicroscope image]; see Polish version).

Sulfuric acid has shown to have similar effect on the fabric made of polyester fibres and on the wool knit made of polyamide fibres. At the site of corrosive substance application, the dissolving of fibres was observed. The edges of the preserved parts of research material were characterized by plastic material–like, pinkinsh–purple appearance and they were fragile. Within the formed mass, an original, black – colored material was visible, which was amenable to separation of single polyester fibres with preserved morphological features (Fig. 9 Polyester, from the left – not affected by corrosive substance, affected by sulphuric acid [stereomicroscope image]; see Polish version).

Under the action of sulfuric acid, the textile product made of brown polyacrylonitrile fibres turned into yellow, pliable substance. Microscopic imaging revealed the presence of fibre clusters within the formed substance. The observed fibres were swollen and impossible to be dissected (Fig. 10 Polyacrylonitrile, from the left – not affected by corrosive substance, affected by sulphuric acid (stereomicroscope image); see Polish version).

65% nitric acid

The destructive effect of nitric acid was observed in the case of wool products as well as products made of polyacrylonitrile fibres.

After treatment with a corrosive substance, the gray wool knit dissolved, resulting in formation of brown pliable mass with no characteristics typical of wool

fibres. The edges of the preserved research material consisted of a substance similar to brown, plastic – like material, with visible, partially dissolved wool fibres (Fig. 11 Wool, from the left – not affected by corrosive substance, affected by nitric acid [stereomicroscope image]; see Polish version). Microscopic image of a knit sample collected from the above area, obtained from a scanning electron microscope, revealed the presence of morphological elements typical of wool fibres (so called roofing tiles) (Fig. 12 Wool, from the left – not affected by corrosive substance, affected by nitric acid [scanning electro microscope image]; see Polish version).

At the site of nitric acid treatment of brown knit made of polyacrylonitrile fibres, the formation of a substance resembling an orange plastic material was observed (Fig. 13 Polyacrylonitrile, from the left – not affected by corrosive substance, affected by nitric acid [stereomicroscope image]; see Polish version) Fragments of knit which retained the original structure became discolored. Dissected fibres did not exhibit any morphological changes in the structure (Fig. 14 Polyacrylonitril, from the left – not affected by corrosive substance, affected by nitric acid [scanning electro microscope image]; see Polish version).

Nitric acid caused discoloration of cotton fabric (Fig. 15 Cotton, from the left – not affected by corrosive substance, affected by nitric acid [stereomicroscope image]; see Polish version) as well as changed the original color of the fabric made of polyester fibres (Fig. 16 Poliamid, from the left – not affected by corrosive substance, affected by nitric acid [stereomicroscope image]; see Polish version), and the knit made of polyamide fibres (Fig. 17 Polyester, from the left – not affected by corrosive substance, affected by nitric acid [stereomicroscope image]; see Polish version). However, the conducted study indicated that no morphological changes occurred to either textile products or single fibres.

Sodium hydroxide and sodium hypochlorite

Sodium hydroxide and sodium hypochlorite applied on wool knit sample caused stiffening and thickening of the material's structure, resembling "felting effect". However, neither of the agents affected the morphology of wool fibres (Fig. 18 Wool, from the left – not affected by corrosive substance, affected by sodium hydroxide, affected by sodium hypochlorite [stereomicroscope image]; see Polish version).

Cotton fabric subjected to the action of sodium hydroxide and sodium hypochlorite showed discoloration. Increased fragility of cotton fibres was observed, without having any effect on fibres' morphology (Fig. 19 Cotton, from the left – not affected by corrosive substance, affected by sodium hydroxide, affected by sodium hypochlorite [stereomicroscope image]; see Polish version).

Other textile products, i.e. knits made of polyamide or polyacrylonitrile fibres, or polyester fabric did not show any morphological changes. Microscopic image obtained from a scanning electron microscope demonstrated that the used agents, after evaporation of the solvent, crystallized on the surface of single fibres (Fig. 20 Polyacrylonitril, from the left – affected by sodium hydroxide, affected by sodium hypochlorite [scanning electro microscope image]; Polish version).

Discussion

The conducted study allowed for characterization of the influence of selected corrosive substances on textile products and single fibres varying in qualitative composition and structure. A performed experiment allowed for initial morphology assessment of the obtained pieces of evidence in the form of fibres, with respect to forensic analyses.

Based on the obtained results it can be stated, that the most destructive effect on textile products and fibres was that of 98% sulphuric acid, which dissolved four out of five research material samples. In the case of samples treated with sulphuric acid there was no possibility of analyzing morphology of individual fibres. Cotton fabric underwent the process of fibre crumbling and swelling; however preserved fibre fragments retained their shape of a spirally twisted ribbon, characteristic of cotton fibres.

65% nitric acid dissolved two out of five study material samples, causing destruction of single fibres morphology in the case of wool and polyacrylonitrile. The sample of cotton fabric treated with nitric acid underwent discoloration, whereas polyamide and

polyester knit samples showed a change of the original color. The above mentioned processes did not alter morphology of individual fibres.

The action of sodium hydroxide and sodium hypochlorite was apparent in the case of cotton fabric samples – discoloration and increased fibre fragility, and wool knit samples – stiffening and thickening of the structure. From a forensic analysis point of view it is important, that the above processes did not result in changes to single fibres morphology. Conducted study did not show any destructive effect of sodium hydroxide and sodium hypochlorite on the remaining research material samples.

36% hydrochloric acid showed the least destructive impact on research samples. This type of acid affected only cotton, increasing its fragility and tenderness, but with no changes to the appearance or single fibre morphology of a textile product.

The conducted experiment facilitated the observation of morphological changes or lack of such changes in selected textile products and individual fibres. Undoubtedly, the present study does not cover all the aspects of the undertaken issue and opens the door to further considerations in the context of the observed reactions taking place inside fibres.

Described experiments will likely contribute to developing new research methodologies of fibre microtraces analyses and they will expand the view on capabilities of forensic fibre analyses.

Source

Figs. 1-20: author

Translation: Rafat Wierzchosławski