The danger of wearing low-quality clothes. Part 1: Physicochemical characterisation DOI: 10.35530/IT.076.03.2023111

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ABSTRACT – REZUMAT

The danger of wearing low-quality clothes. Part 1: Physicochemical characterisation

Clothing has always played a vital role in people's lives, indicating social and moral status and the state of health. In a world where, for some, the appearance of a clothing product plays a much more important role than the quality of the product itself, it is necessary to know that although an item is fashionable and affordable, it may pose a real danger to health. Therefore, the main purpose of this article is to analyse, from a chemical point of view (phthalates and formaldehyde determination, FTIR measurements), the materials from which various clothing items are made and their behaviour under certain conditions (accelerated UV and visible light exposure), to highlight the danger of purchasing low-quality products. The obtained results showed that although the samples are inexpensive and look nice, they contain compounds dangerous for human health, such as phthalates and formaldehyde, which are present in materials that should not come into contact with skin and stained the material support after intensive light exposure.

Keywords: clothes, phthalates, formaldehyde, FTIR measurements, UV exposure

Pericolul purtării articolelor de îmbrăcăminte de calitate inferioară. Partea 1: Caracterizare fizico-chimică

Îmbrăcămintea a jucat întotdeauna un rol foarte important în viața oamenilor, fiind un indicator al statutului social și moral, precum și al stării de sănătate. Într-o lume în care pentru unii aspectul unui produs de îmbrăcăminte contează mai mult decât calitatea produsului în sine, este bine de știut că, deși un articol este la modă și la preț accesibil, poate reprezenta un real pericol pentru sănătate. Prin urmare, scopul acestui articol este de a analiza, din punct de vedere chimic (determinarea ftalaților și formaldehidei, măsurători FTIR), materialele din care sunt confecționate diverse articole vestimentare și comportamentul acestora în anumite condiții (expunere accelerată la UV si lumina vizibilă), cu scopul de a evidenția pericolul achiziționării de produse de calitate inferioară. Rezultatele obținute au arătat că, deși probele sunt ieftine și arată frumos, ele conțin compuși periculoși pentru sănătatea umană, precum ftalați și formaldehidă, care sunt prezenți în materiale care nu ar trebui să intre în contact cu pielea și să păteze suportul după expunerea prelungită la lumină.

Cuvinte-cheie: îmbrăcăminte, ftalați, formaldehidă, măsurători FTIR, expunere la UV

INTRODUCTION

Since ancient times, clothing has played an important role in the lives of humans, ensuring protection against environmental factors. Along with the evolution of society, there have been changes in clothing products, which are becoming increasingly complex, not only meeting protection requirements but also beautifying and acting as a form of expression. Price is often a deciding factor in the choice of clothes, but it must be taken into account that, most of the time, inexpensive clothing could pose health risks.

Textile materials can contain a wide variety of chemical compounds, depending on the type of fibres used, the manufacturing process and any finishing treatments applied [1]. Chemical finishes to textiles can greatly improve their wearability, appearance and functionality; can be durable or nondurable; and can bind different chemicals at different strengths to different fibres. To create a resistant finish and easy clothing care, chemicals are used to treat textiles, but they can generate dangerous compounds such as formaldehyde [2]. In dyeing processes, azo dyes or disperse dyes are used, but they generate aromatic amines, which have been proven to be carcinogens. Some of the chemical compounds used in textile materials can be harmful to human health or the environment [3–5]. For example, some dyes and finishes contain heavy metals or other toxic chemicals.

Phthalates have been shown to adversely affect human health, particularly in children [6–10]. Some phthalates can alter hormone levels in early life, potentially affecting reproductive health [8, 10]. A negative association between phthalate levels and thyroid hormone levels in children has also been demonstrated [11]. Epidemiologic studies have reported associations between phthalate exposure and obesity or cardiometabolic risk factors in children and adolescents [12, 13]. Accumulating evidence suggests that exposure to phthalates is negatively associated with lung function in children and with an increased risk of asthma and allergies [14].

Biometabolism in the human body is very rapid since phthalates have short biological half-lives of approximately 12 h. The first step of metabolism is hydrolysation after absorption into cells. The second step is conjugation to form a hydrophilic glucuronide conjugate, which is catalysed by the enzyme uridine 5'-diphosphoglucuronyl transferase [15]. The type of phthalate determines its toxicological fate in the body. Short-branched phthalates are often hydrolysed to monoester phthalates and then excreted in the urine, while long-branched phthalates mainly undergo several biotransformations, such as hydroxylation and oxidation, and are subsequently excreted in the urine and faeces as phase 2 conjugated compounds [16]. Studies have identified nonylphenol ethoxylate concentrations (NPEs), carcinogenic amines released from azo dyes within dyed fabric and phthalate esters in a broad range of textile clothing products [17]. A new group of chemicals, nonylphenol ethoxylates (NPEs), are used in the manufacture of textiles. The released NPEs can break down to form nonylphenols, which are bioaccumulative and toxic chemicals. The use of NPEs during the manufacture of cloth textiles can also leave residues within the final products. Formaldehyde resins are usually used in the textile industry to prevent wrinkling. Exposure to formaldehyde can irritate the skin, throat, lungs, and eyes. The International Agency for Research on Cancer (IARC) classified formaldehyde as a human carcinogen [2]. Formaldehyde mediates its toxic effects by chemically modifying vital cell components, including DNA and proteins, thereby leading to cellular dysfunction. Formaldehyde-mediated genotoxicity is caused by the formation of DNA-DNA and DNA-protein crosslinks, as well as covalent DNA monoadducts [18-21]. In recent years, there has been a very high interest in the ecological properties of textiles and chemical safety control of clothing articles to limit the negative effects of chemicals on human health. The toxicology of textiles is a subject of increasing interest because

of the presence of dangerous compounds in clothes generated from dyeing and finishing processes.

This paper aimed to determine, through chemical analyses performed in a specialised laboratory and concrete results, the health risks of low-quality, inexpensive clothes for the first time.

EXPERIMENTAL SECTION

All chemicals and reagents were of HPLC or analytical grade and purchased from Sigma Aldrich. Ultrapure water used throughout the determinations was obtained from TKA GenPure.

Sample codification

The six samples (denim overalls for children, a blue dress for children, a white dress for children, trousers, a skirt, and a belt) were bought from the Obor Market (Bucharest, Romania) and were the least expensive in their category. The seller mentioned that the skirt and the trousers were made of "ecological leather".

The samples were codified as presented in table 1.

		Table 1	
SAMPLE CODIFICATION			
No.	Sample	Codification	
1	Jean overalls for children	J	
2	Blue dress for children	D	
3	White dress for children	W	
4	Trousers	Т	
5	Skirt	S	
6	Belt	В	

The following tests were performed to characterise the samples.

Phthalate determination

All six samples were analysed according to standard EN ISO 14362-1:2017 "Textiles – Methods for determination of certain aromatic amines derived from azo colourants – Part 1: Detection of the use of certain azo colourants accessible with and without extracting the fibres" using GC equipment. Gas chromatography coupled with mass spectrometry (GC–MS 6890 N/5793 Agilent Technologies) was applied using a



Fig. 1. Images (from left to right) of sample jean overalls for children, blue dress for children, white dress for children, trousers, skirts, belt



DB-35MS capillary column (J&W®) 35 m in length with an inside diameter of 0.25 mm. Splitless injection was applied; the injector temperature was 250°C; the carrier gas was helium; the flow rate was 1 ml/min. The temperature program was as follows: 60°C (1 min) and heating at 20°C/min to 310°C (5 min). The injection volume was 1 μ l, and detection was achieved with MS.

Formaldehyde determination

For the jean overalls and blue dress, and white dress for children, the formaldehyde content was determined by a spectrophotometric method according to the SR EN ISO 14184-1:2012 "Textiles – Determination of formaldehyde – Part 1: Free and hydrolysed formaldehyde (water extraction method)". UV-visible spectrophotometric determinations were performed with a Perkin Elmer UV-Visible spectrometer, with a maximum absorption peak of formaldehyde at 412 nm.

The formaldehyde content of the trousers, skirt and belt was determined according to EN ISO 17226-2: 2019 "Leather. Chemical determination of formaldehyde content – Method using colourimetric analysis" with a Jasco 550 UV-Visible spectrophotometer.

FT-IR measurements

FT-IR-ATR measurements were performed to determine the composition of the polymeric samples (trousers, skirt and belt) using 4200 Jasco equipment.

Colorimetric measurements

To simulate sunlight conditions, the samples were exposed to UV light using a VL 6LC UV lamp with irradiation at 365 nm and to visible light using a lamp

with the following specifications: NXS-500P, 130 V AC 50 Hz7S, Adeleq.

Colourimetric measurements were made before and after UV and visible exposure, and a Data Colour DS-220 device and dedicated software were used.

RESULTS AND DISCUSSION

Phthalate determination

The results of the phthalate determination for children's clothing are presented in table 2.

Given that these are clothes for a vulnerable population (children), these compounds should not be found in the material components. In the skirt sample, dibutyl phthalate and iso-octyl phthalate were identified.

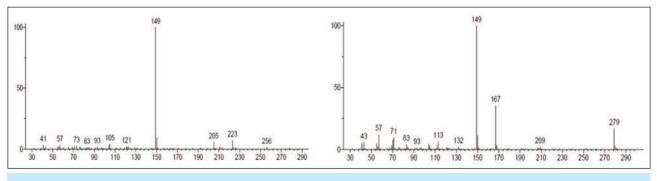
Exposure to high levels of dibutyl phthalate by inhalation can irritate the eyes, nose and throat. Exposure may also cause nausea, tearing of the eyes, vomiting, dizziness and headache. Long-term exposure may cause liver and kidney damage. Dibutyl phthalate may lead to male and female infertility and harm the development of fetuses. According to the classification and labelling (ATP15) approved by the European Union, di-iso-octyl phthalate may affect fertility and unborn children. The trouser sample contained bis(2-ethylhexyl) iso-phthalate.

This compound is considered a human carcinogen. The belt contains dibutyl phthalate and di-iso-octyl phthalate.

A recent report described increases in the incidences of hypospadias (p<0.05), cryptorchidism (p<0.05) and breast cancer (p<0.05) in the children of New Zealand soldiers who served in Malaya (1948–1960)

Table 2

PHTHALATE IDENTIFICATION AND EFFECTS ON HEALTH			
Sample	Substance	Effects on human health	
Jean overalls for children	2,4-di-tert-butyl-phenol (PRODOX 146), CAS 96-76-4	causes skin and upper respiratory tract irritation	
Blue dress for children	2,4-di-tert-butyl-phenol (PRODOX 146), CAS 96-76-4	causes skin and upper respiratory tract irritation	
White dress for children	di-iso-phthalate CAS: 27554-26-4	causes skin and upper respiratory tract irritation	





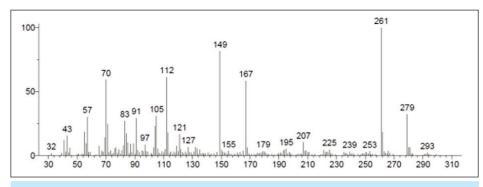
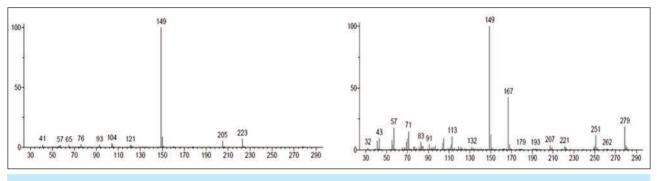


Fig. 3. MS spectrum of bis(2-ethylhexyl) iso-phthalate detected in the trouser sample





and were exposed to DBP applied daily to their clothing as an acaricide to prevent tick-transmitted bush typhus [22].

Formaldehyde determination

The results obtained for the quantitative determination of formaldehyde are presented in table 3.

The formaldehyde content obtained for the white dress sample was 5 times greater than the maximum allowed limit for the following category: textiles in no direct contact with the skin (150 mg/kg). This category was referred to because the dress also has a lining underneath. This value is extremely high for a product that is designated for children.

	Table 3		
FORMALDEHYDE CONTENT			
Sample Formaldehyde concentration (mg/k			
Jean overalls for children	8.81		
Blue dress for children	1.53		
White dress for children	769.68		
Trousers	64		
Skirt	15		
Belt	37		

Table 2

FT-IR measurements

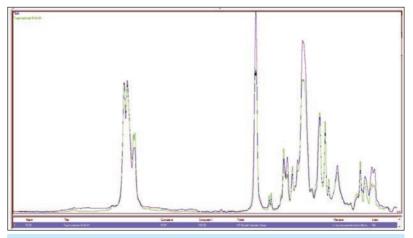
FT-IR-ATR measurements can provide useful information about the composition of a sample. Here, this technique was used to reveal the chemical profile of the samples.

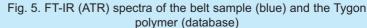
Figure 5 shows the spectrum of the belt material compared with a similar database spectrum.

Based on the information provided by the FT-IR database, regarding component identification, with an accuracy of 78.09%, the belt material was a Tygon polymer (specific for hose manufacture).

The FT-IR (ATR) spectrum of the skirt is presented in figure 6.

With an accuracy of 72.99%, the skirt sample material is a mixture of polyester and urethane. Both products are used in the clothing industry because they





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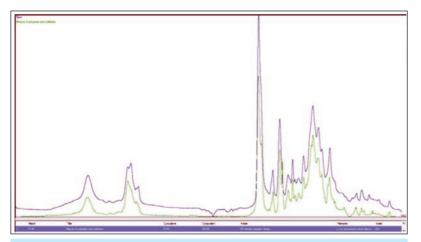


Fig. 6. FT-IR (ATR) spectra of the skirt (blue) and a mixture of polyester and urethane (database)

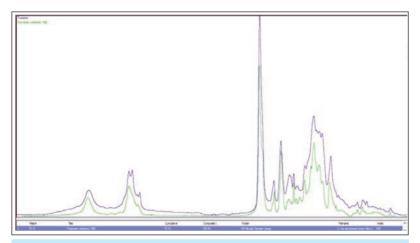


Fig. 7. FT-IR (ATR) spectra of trousers (blue) and the polyester urethane (database)

can be turned into threads and later into clothing items.

The trouser material was also a mixture of polyester and urethane, with an accuracy of 79.15%.

Colorimetric measurements

All six samples were exposed continuously for 24 hours to UV and visible light to simulate accelerated wearing in natural clothes. Colourimetric measurements were made before and after irradiation with a device that measures CieLAB parameters.

The colour parameters of the blue dress for children are presented in table 4.

			Table 4
LAB PARAMETERS FOR THE BLUE DRESS			
Sample	L*	a*	b*
D (Initial)	25.39	2.61	-16.53
D (visible light exposure)	25.91	2.83	-16.23
D (UV light exposure)	25.47	2.49	0.08

After visible light exposure, the colour parameters indicated that the colour of the blue dress sample decreased to 0.41% from the initial colour and 0.17%

from the initial colour to the green colour $(+a^*)$.

After UV light exposure, the colour parameters indicated that 0.06% of the blue dress sample changed from the initial colour to white $(+L^*)$, to red $(-a^*)$, with a value of -0.09, and finally to yellow $(+b^*)$, with a value of 14.72. In this case, it can be concluded that UV light exposure produces a yellow shift in colour for the blue dress sample.

Table 5 shows the overall values of the colour parameters of the jeans overalls before and after exposure.

After visible light exposure, the colour of the jean overalls shifted to white $(+L^*)$ with a 2.05% change from the initial value, the green $(+a^*)$ value exhibited a 0.41% change from the initial value, and the yellow $(+b^*)$ value showed a 4.29% change from the initial value.

After UV light exposure, the colour of the jean overalls sample shifted to black ($-L^*$) with a 3.04% change from the initial value, the red ($-a^*$) shifted with a -0.18% change, and the blue ($-b^*$) value shifted, with a -2.46% change from initial value.

The visible light exposure of the jean overalls produces a shift in yellow colour, and UV light exposure produces a shift in black and blue colours.

Table 5

LAB PARAMETERS FOR JEAN OVERALLS			
Sample	L*	a*	b*
J (Initial)	67.4	-5.36	-4.84
J (visible light exposure)	70.84	-4.86	0.4
J (UV light exposure)	62.31	-5.58	-7.84

No colourimetric measurements were made for the white dress because of the colour.

The colour parameters for the belt are presented in table 6.

After visible light exposure, the colour parameters of the belt sample shifts to black ($-L^*$) with a -0.83% change from the initial value, the red colour shifted

			Table 6
LAB PARAMETERS FOR THE BELT SAMPLE			
Sample	L*	a*	b*
B (Initial)	32.51	-1.56	-24.74
B (visible light exposure)	31.41	-3.55	-17.7
B (UV light exposure)	31.99	-1.62	-25.27

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 $(-a^*)$ with a -1.59% change from the initial value, and the yellow colour shifted $(+b^*)$ with a 6.88% change from the initial value.

After UV light exposure, the colour of the belt sample shifted to black ($-L^*$) with a -0.39% change from the initial value, the red colour shifted ($-a^*$) with a -0.05% change from the initial value, and the blue colour shifted ($-b^*$) with a -0.52% change from the initial value.

Visible light exposure of the belt sample produced a yellow shift in colour, and UV light exposure produced black and blue shifts in colour.

Table 7 shows the values of the colour parameters of the trousers before and after exposure.

			Table 7
LAB PARAMETERS FOR THE TROUSER SAMPLE			
Sample	L*	a*	b*
T (Initial)	21.3	0.43	-0.61
T (visible light exposure)	24.13	0.3	-0.67
T (UV light exposure)	20.96	0.37	-0.59

After visible light exposure, the colour of the trouser sample shifted to white $(+L^*)$ with a +2.33% change from the initial value, the red colour shifted $(-a^*)$ with a -0.1% change from the initial value, and the blue colour shifted $(-b^*)$ with a -0.05% change from the initial value.

After UV light exposure, the colour of the trouser sample shifted to black $(-L^*)$ with a -0.28% change from the initial value, the red colour shifted $(-a^*)$ with a -0.05% change from the initial value, and the yellow colour shifted $(+b^*)$ with a +0.02% change from the initial value.

The visible light exposure of the trouser sample produced a shift of the colour toward white, and UV light exposure produced an insignificant colour shift.

The skirt sample colour parameters are presented in table 8.

			Table 8
LAB PARAMETERS FOR THE SKIRT SAMPLE			
Sample	L*	a*	b*
S (Initial)	22.03	-0.07	-0.49
S (visible light exposure)	25.68	-0.19	-1.14
S (UV light exposure)	22.53	-0.07	-0.57

After visible light exposure, the colour of the skirt sample shifted to white $(+L^*)$ with a +2.99% change from the initial value, the red colour shifted $(-a^*)$ with a -0.09% change from the initial value, and the colour shifted toward blue $(-b^*)$ with a -0.51% change from the initial value.

After UV light exposure, the colour of the skirt sample shifted to white $(+L^*)$ with a +0.41% change from the

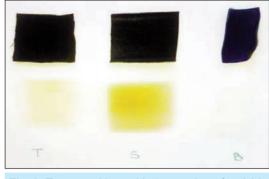


Fig. 8. Trouser, skirt and belt samples after 24 h of Vis exposure

initial value, there was no red $(-a^*)$ shift in colour, and the colour shifted to blue $(-b^*)$ with a -0.06% change from the initial value.

The visible light exposure of the skirt sample produces a shift in colour toward white, and UV light exposure produces an insignificant colour shift.

An important detail that is worth noting is that after visible irradiation, all the polymeric samples stained the support paper they were placed on, as shown in figure 8.

CONCLUSION

This article aimed to characterise (phthalate and formaldehyde determination, FTIR measurements) the materials from which six clothing items are made and their behaviour under UV and Vis irradiation. The results showed that all of these materials contain dangerous phthalates, the white dress material for children contains an enormous amount of formaldehyde, the belt material is used for hose manufacture, and the "ecological leather" is a mixture of polymers. In addition, after UV and visible light exposure, the samples change and even stain the support paper. All these aspects lead to the conclusion that consumers must choose their clothes very carefully, especially those for children, because many of them, due to the materials they are made of, represent a real danger and should not come into contact with the skin.

ACKNOWLEDGEMENTS

This work was carried out through the Core Programme within the National Research Development and Innovation Plan 2022-2027, carried out with the support of MCID, project no. 6N/2023, PN 23 26 0103, project title "Advanced functional textile materials for protection and improving the quality of life – TEX4AGE". The publication of the scientific paper is funded by the Ministry of Research, Innovation, and Digitization within Program 1 – Development of the National R&D System, Subprogram 1.2 – Institutional Performance – RDI excellence funding projects, Contract no. 4 PFE/2021.

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