Beyond the surface: a closer look at the stratigraphy of synthetic-coated fabrics in fashion collections and commercial samples through optical microscopy

Para além da superfície: um estudo sobre a estratigrafia de tecidos com revestimentos sintéticos em coleções de moda e amostras comerciais através de microscopia ótica

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Abstract

Synthetic-coated fabrics, often made of short-life expectancy coatings, namely plasticised poly(vinyl chloride) (p-PVC) and thermoplastic polyurethane (TPU), are challenging to preserve. These materials are poorly studied within the conservation field, and there is a lack of research and solutions for their preservation. This study aimed to provide insight into the yet unknown variability of p-PVC and TPU-coated fabrics in fashion collections. The subtle differences in layer construction and morphology were investigated in a selected set of materials to unveil production methods and better understand delamination damages, namely peeling and flaking. Optical microscopy provided primary material assessment, complemented by ATR-FTIR for molecular identification. A wide variability of synthetic-coated fabrics was reported and connections between morphology, production methods and delamination damages were suggested. Optical microscopy proved to be a powerful tool in the study of the stratigraphy of coated fabrics, enhancing material knowledge for more informed conservation decisions.

KEYWORDS
Thermoplastic polyurethane
Poly(vinyl chloride)
Coatings
Cross-section
Synthetic textiles
Heritage conservation

Resumo

Os tecidos revestidos, frequentemente compostos por revestimentos efémeros, como o poli(cloreto de vinilo) plastificado (p-PVC) e o poliuretano termoplástico (TPU), são materiais de difícil preservação. Estes materiais são ainda pouco estudados na área da conservação, existindo uma lacuna de investigação e soluções para a sua preservação. Este estudo visa demonstrar a variabilidade dos tecidos revestidos com p-PVC e TPU em coleções de moda. As diferenças subtis na construção e morfologia das camadas de um conjunto de materiais foram investigadas, para desvendar métodos de produção e melhor compreender danos causados por destacamento, nomeadamente *peeling* e *flaking*. Os materiais foram analisados por microscopia ótica, complementada por ATR-FTIR para identificação molecular. A ampla variabilidade destes tecidos é apresentada e sugerem-se relações entre morfologia, métodos de produção e danos por destacamento. A microscopia ótica provou ser uma ferramenta vantajosa neste estudo, permitido um avanço no conhecimento para decisões de conservação mais informadas.

PALAVRAS-CHAVE
Poliuretano termoplástico
Poli(cloreto de vinilo)
Revestimentos
Corte estratigráfico
Tecidos sintéticos
Conservação do património

Introduction

A coated fabric is characterised as a multilayer construction composed of two or more layers, in which at least one should be a textile fabric and another a substantially continuous polymeric layer. The bonding of these layers occurs by means of their own adhesive properties or by an additional adhesive layer [1]. The application of a coating layer to a textile fabric significantly influences the external characteristics and physical properties of the final product [2] by granting a new aesthetic, such as a highly glossy or leather-like appearance, or additional technical or functional properties, including flame retardancy or fire-resistance, waterproofness, and improved solvent and abrasion resistance [2-3].

Fabrics have been coated for several centuries with the natural materials available, such as linseed oil, wax emulsions, and natural rubber [3-6]. More recently, in the nineteenth and twentieth centuries, advances in chemistry and textile technology allowed the development of new semi-synthetic and synthetic polymer materials, several of which came to be used as fabric coatings, and new processing coating techniques [3-4, 7]. Synthetic-coated fabrics paved their way into several industries and fields due to their broad range of physical and chemical properties and the ability to be tailored-made to meet specific requirements, including casual and sports apparel, protective clothing, household textiles and transports [2-4].

Many items made of synthetic-coated fabrics have become collectable pieces, and their presence in modern museum collections worldwide has significantly increased as a reflection of their widespread application in several fields, technological development, and artistic and societal preferences over time. Examples include garments, shoes and accessories in costumes and fashion [8-13], upholstery furniture in product design [14-16] and even spacesuits in astronautics [17]. However, the conservation of synthetic-coated fabrics presents a significant challenge due to the lack of awareness of their presence in museum collections, possibly related to the many visual looks that these fabrics can assume, and the lack of studies in the field; diverse production methods that result in complex and composite materials, many times combining natural and synthetic materials; and a large variety of ageing behaviours. In addition, these materials often have a shorter life expectancy compared to traditional fabrics and textiles, making their preservation particularly difficult [7-8, 11, 18]. All these factors pose challenges to identifying and recognising synthetic-coated fabrics as priority materials in museum collections preservation.

Synthetic-coated fabrics can be composed of several layers of different materials. As coatings, several semi-synthetic and synthetic polymers have been applied to fabrics, including cellulose nitrate (CN), cellulose acetate (CA), synthetic rubbers, acrylics, poly(vinyl acetate), plasticised poly(vinyl chloride) (p-PVC) and thermoplastic polyurethane (TPU) [3-4]. Many of these materials, such as CN, CA, p-PVC and TPU, are already known by the conservation community for their unstable and ephemeral nature, which leads to early signs of deterioration and premature loss of iconic objects [7, 18-19]. In addition, and further contributing to the complexity of these materials, additives can be incorporated into their formulation to confer specific properties, including plasticisers, anti-ageing additives (light and heat stabilisers, antioxidants), fillers and colouring agents, which can significantly influence the deterioration of the material [7, 20]. Regarding the fabric substrate, a wide range of natural and synthetic fabrics can also be used, including cotton, polyester and polyamide, in knitted, woven and non-woven constructions [2-4].

Numerous application techniques have been developed throughout the last decades to produce coated fabrics, which can be categorised on a different basis, such as equipment used or the form of the coating material [3]. Concerning how a coating is applied to a fabric substrate, two important techniques can be distinguished: the direct and the indirect coating methods. The direct coating is the oldest method and is still applied today. It consists, as the name indicates, of the direct application and homogeneous spreading of a coating compound onto a fabric, which can be achieved by means of different techniques such as spraying, knife coating or a roller system [2-4]. This method is usually not suitable for open-structure fabrics, such as knitted ones, as penetration of the coating compound into the fabric might occur, or for stretchy fabrics, as they need to be pulled flat for proper coating application [3-4]. Alternatively, these fabrics can be coated by the indirect method, also known as transfer coating. Instead of applying the coating directly onto a fabric, it is first applied onto a release paper, which acts as a temporary support, and spread using the same techniques as in the direct method. Coating and release paper are then laminated to a fabric substrate either by the adhesive properties of the coating itself or by adding an adhesive layer (tie-coat) before introducing the fabric. The final step is the removal of the release paper [2-4]. Resin penetration into the fabric is low or non-existent with this method since the coating is usually in a film form when it comes into contact with the substrate [2, 4].

The transfer coating method was an important development in the coated fabrics industry, especially for producing imitations of leather, as it offered several advantages over the direct method. It has been applied to fabrics at least since the 1940s [21], followed by continuous advancements that shaped the machinery and materials used [22-27]. This method was first developed to overcome a particular limitation of CN as a coating - its low viscosity, which at the time could only be applied to tightly woven and thus more expensive fabrics to avoid excessive penetration [28]. The transfer method allowed for a more versatile and less expensive coating process, enabling the application of thinner coating layers to virtually any fabric of choice, even the simpler, low-cost and open-structure ones. As it minimised coating penetration, it allowed the production of fabrics with improved hand and suppleness [2, 4, 28-29]. Additionally, transfer coating facilitated embossing using customised patterned released paper, ideal for simulating leather texture [2, 28]. While CN, CA, and PVC were mentioned in early transfer-coating patents in the 1940s [21-27], not all synthetic compounds were readily compatible with the method once introduced to the market. Polyurethanes, for example, started to be applied to fabrics in the 1950s by the direct method as a two-component system [29-30], although their application by the transfer method was only possible in the 1960s with the development of the one-component system [30-32]. This formulation offered greater stability, longevity, and ease of application, resulting in high-quality, durable, and resistant coatings [29-32].

Despite the challenge synthetic-coated fabrics represent, these materials are still poorly studied within the conservation field, and adequate conservation strategies for their preservation are still lacking. The first research steps into this subject were taken by the Glossy Surfaces research project (2020-2023), an international consortium of museums (MoMu, Belgium; MUDE, Portugal; MET, USA) and research centres (DCR LAQV-REQUIMTE, Portugal; Centexbel, Belgium), entirely focused on the study and preservation of synthetic-coated fabrics in fashion collections from the 1960s until now. Within this timeframe and collection type, there are few existing studies researching these materials, most of which have resulted from the Glossy Surfaces project. These studies have mainly focused on identifying the chemical composition and damages of the synthetic-coated fabrics. TPU and p-PVC were found to be the most prevalent coating materials [8, 33], especially ester-based and aromatic TPUs [8-10]. These polymeric materials have been on the market as coatings ever since the mid-twentieth century [5, 34], due to their highly appreciated physical properties and for being particularly excellent options for rainwear and imitations of leather, namely TPUs [2]. Cotton, polyester, polyamide and leather were the most commonly found fabric substrates, the latter predominately identified within the domain of footwear and accessories [10]. Regarding damages of the synthetic coatings, several have been identified and reported, the most common patterns being blooming (mostly caused by adipic acid [9-10]), stickiness, peeling, flaking and cracking [8, 35]. França de Sá et al. also identified blooming as being the main damage for ester-based aromatic TPUs, while ester-based aliphatic coatings were more prone to stickiness when deteriorated [10]. Nevertheless, no studies were found within the conservation field that explored the variability of these materials based on manufacturing processes and their possible influence on the observed damages.

The present study started during the Glossy Surfaces project. It aims to fill this knowledge gap by providing new insight into the variability of p-PVC and TPU-coated fabrics in the context of fashion collections, the two most found coating compositions during the project. Although the Glossy Surfaces project covered the period from the 1960s until now, the present study focused on the timeframe from the 1970s until the present decade. Production methods were unveiled based on the analysis of the layer construction and morphology of the coated fabrics, and their possible impact on damages was explored, namely flacking and peeling. This study focused on the visual analysis of the cross-sections through optical microscopy (OM) as the main source of information, aiming at developing a first-step characterisation methodology that could be easily implemented by most museums and cultural institutions holding these materials in their collections. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was used as a complementing tool. This research is a step forward in advancing the knowledge of synthetic-coated fabrics within fashion collections and in developing suitable conservation strategies.

Materials and methods

Sample selection

During the Glossy Surfaces project, a representative set of more than 100 synthetic-coated fabric samples from fashion museum collections worldwide was collected for analysis. It included clothing, shoes, and accessories covering the period from the 1960s until now, different stages of deterioration, and the most common damage patterns. Most of these samples did not show a complete stratigraphy of the coated fabrics since collecting full cross-sections from fashion museum items poses particular difficulties, especially from footwear, due to the lack or even inexistence of hidden areas to collect samples unnoticed and without damaging the integrity of the item.

From the Glossy Surfaces set of samples, a minor set showed a complete cross-section, which was crucial for the present study, and was further analysed. In addition, several case study fabrics and items, donated or acquired and with no cultural value, were included in the research, from which it was possible to collect the complete stratigraphy without worrying about potential damages. Custom-made coated fabrics produced by Centexbel (Ghent, Belgium) were also included in the study for comparison. These samples were composed of ester-based TPU coatings, both aliphatic (Impranil DSL/1, Covestro AG, Leverkusen, Germany) and aromatic (Laripur S860, COIM, Milan, Italy), with no additive added to the formulation. Both TPU coatings were directly applied to polyester and cotton fabrics and transfer-coated to a leather substrate.

In total, the set analysed in the present study comprised c. 70 samples, composed of TPU and p-PVC-coated fabrics from the 1970s until now. It was not possible to include complete cross-section samples of items from the 1960s in this research. The set analysed included unaged and aged materials showing the most common damage patterns (blooming, stickiness, flaking, and peeling) in different stages of deterioration (slightly deteriorated, deteriorated and severely deteriorated).

Sample characterisation

Empirical assessment

A first evaluation of the properties of the selected samples was conducted under low magnification using a stereomicroscope. The samples were observed and manipulated for an initial assessment of the different layers regarding number, thickness, colour, pliability, and overall appearance. The level of attachment of the layers was also evaluated, in particular to determine the possible presence of an adhesive layer.

Samples from fashion museum items were only slightly manipulated to avoid destruction and the need to collect more samples for future analysis. However, samples from the acquired or donated case study fabrics and items were manipulated and deconstructed with the help of tweezers and scalpers for a better understanding of the properties of the different layers. This destructive analysis was possible due to a larger amount of material available for sampling and the absence of historical value.

Optical microscopy imaging

The top surface and cross-section of all samples were observed under reflected (incident) light in brightfield, darkfield, cross-polarized and fluorescence modes. The method for sample preparation for analysis and to acquire cross-section images is described elsewhere [10].

The images presented are representative of the coated fabrics analysed, which, as previously described, included samples from museum items and non-cultural materials. Due to the limited size of museum samples, it was more difficult to obtain clear cross-section images. Thus, most of the images presented are from representative non-cultural materials, allowing for better visualization of the stratigraphy since there were no size limitations for sample collection. Table 1 provides a detailed description of the sample cross-sections presented in this study.

Micrographs were acquired using an Axioplan 2ie Imaging system (Zeiss, Germany) equipped with an incident halogen (tungsten-halogen light source, HAL 100) and UV radiation (mercury light source, HBO 100) illuminators and coupled with a DXM1200F digital camera and ACT-1 control software (Nikon, Japan). The samples were analysed using ocular lenses with a magnification of 10x and Epiplan objective lenses with magnifications of 5× and 10× for a total optical magnification of 50× and 100×, respectively. The scales for all objectives were calibrated within the Nikon ACT-1 control software. Fluorescence microscopy images were acquired with blue-violet light (Zeiss Filter set 05 – excitation BP 395-440 nm, beamsplitter FT 460 nm, emission LP 470 nm) and ultraviolet light (Zeiss Filter set 02 - excitation G 365 nm, beamsplitter FT 395 nm, emission LP 420 nm).

Table 1. Description of the origin of the sample cross-sections presented in this study.

Table/Figure		**Origin**
Table 2	a)	Runaway jacket (2000) from the Museu do Design e da Moda – MUDE
	b)	Commercial fabric bought in 2022 (Lisbon, Portugal)
	c)	Sample donated by Rossimoda (Venice, Italy)
	d)	Commercial fabric bought in 2022 (Lisbon, Portugal)
	e)	Ready-to-wear purse (2000) from the Palais Galliera – Musée de la Mode de la Ville de Paris
Figure 1	a)	Commercial fabric bought in 2022 (Lisbon, Portugal)
	b)	Ready-to-wear shorts (1996) from the ModeMuseum – MoMu
Figure 2	a)	Ready-to-wear dress (1970) from the Museu do Design e da Moda – MUDE
	b)	Ready-to-wear jacket (c. 2020) donated to the Glossy Surfaces project, naturally aged and damaged by flaking
Figure 3	a)	Commercial fabric bought in 2022 (Lisbon, Portugal)
	b)	Ready-to-wear jacket (1990s) from the André Courrèges Archive
	c)	Ready-to-wear parka bought at a second-hand store (Brussels, Belgium) in 2022, naturally aged and damaged by stickiness
Figure 4	a)	Ready-to-wear jacket donated to the Glossy Surfaces project (2010), naturally aged
	b)	Commercial fabric bought in 2023 (Lisbon, Portugal)
Figure 5	a)	Commercial fabric bought in 2023 (Lisbon, Portugal)
	b)	Commercial fabric bought in 2022 (Lisbon, Portugal)
Figure 6	a)	Commercial fabric bought in 2022 (Lisbon, Portugal)
	b)	Ready-to-wear jacket (c. 2010s) donated to the Glossy Surfaces project, naturally aged and damaged by peeling
Figure 7	a)	Ready-to-wear jacket (c. 1990s), donated to the ModeMuseum – MoMu
	b)	Ready-to-wear jacket (unknown date), donated to the ModeMuseum – MoMu
Figure 8	a)	Ready-to-wear jacket (c. 2020) donated to the Glossy Surfaces project, naturally aged and damaged by flaking
	b)	Ready-to-wear jacket (c. 2010s) donated to the Glossy Surfaces project, naturally aged and damaged by flaking
	c)	Fabric (c. 2010s) donated to the Glossy Surfaces project, naturally aged and damaged by flaking

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR)

Attenuated total reflection Fourier transform infrared spectroscopy (ATR FTIR) was used to determine the chemical composition of the top coating, substrate and, whenever present and possible to analyse, the intermediate layer(s) of the samples. In the present study, ATR-FTIR was only used as a complementing tool for a more informed establishment of connections between material composition and visual characteristics observed under the OM regarding the layer construction, morphology and damages.

ATR-FTIR was carried out with the Handheld Agilent 4300 spectrophotometer (Agilent, USA), equipped with a ZnSe beam splitter, a Michelson interferometer and a thermoelectrically cooled DTGS detector. Spectra were acquired with a diamond ATR interface, 128 scans and a resolution of 4 cm^{-1} in the spectral region between 4000 and 650 cm^{-1}. This ATR interface allows the analysis of samples with a minimum size of 200 microns. Background spectra were collected between every acquisition. Spectral analysis was performed using Omnic32 and OriginPro 8 software.

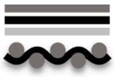
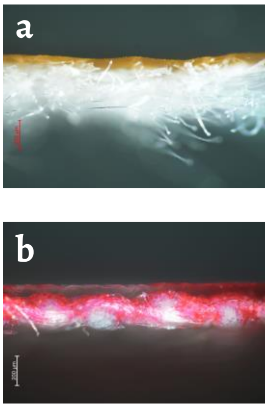
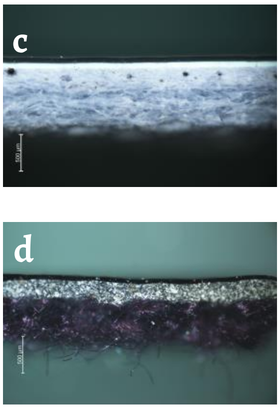
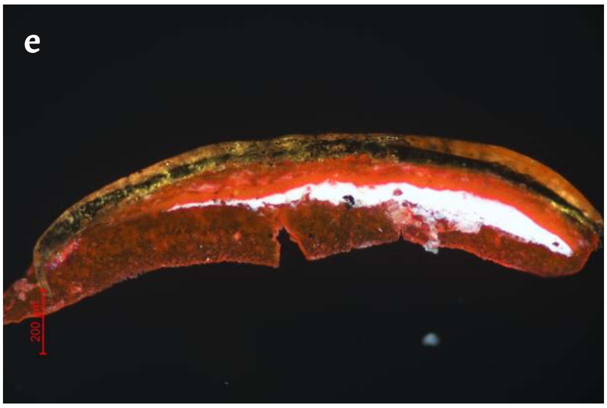
Results and discussion

Layer construction: visible and hidden layers

As expected, the analysed set of coated fabric cross-sections showed a variable number of layers under visible light (Table 2). The most common stratigraphy were two-layer constructions, solely composed of a top polymeric coating on a fabric substrate (examples a and b), or three-layer, which also included an additional intermediate coating layer between these two (examples c and d). Coated fabrics with more complex layer build-ups composed of four or more layers, as shown in Table 2 (example e), were less commonly found.

The thickness of the analysed samples also varied, even between coated fabrics with similar layering construction, i.e., the same number of layers. It varied from very thin (less than 1 mm), such as lightweight raincoats (Table 2, example b), to thicker, like some imitations of leather (example d) or coated leathers (example c), the latter more often found in footwear and accessories. The relationship between thickness and the number of layers is not a straightforward one. It is a complex interplay that is influenced by the desired aesthetic, suppleness, and function of the final product. Additionally, the production method employed might also play a role, as will be delved into in more detail in the following chapter.

Table 2. Microscopy images of cross-section examples of synthetic-coated fabrics (see Table 1) under cross-polarized visible light, showing a varied number of layers: two (a and b); three (c and d) and more than four (e).

Cross-sections			
Number of layers	2	3	≥ 4
Scheme			
Examples			

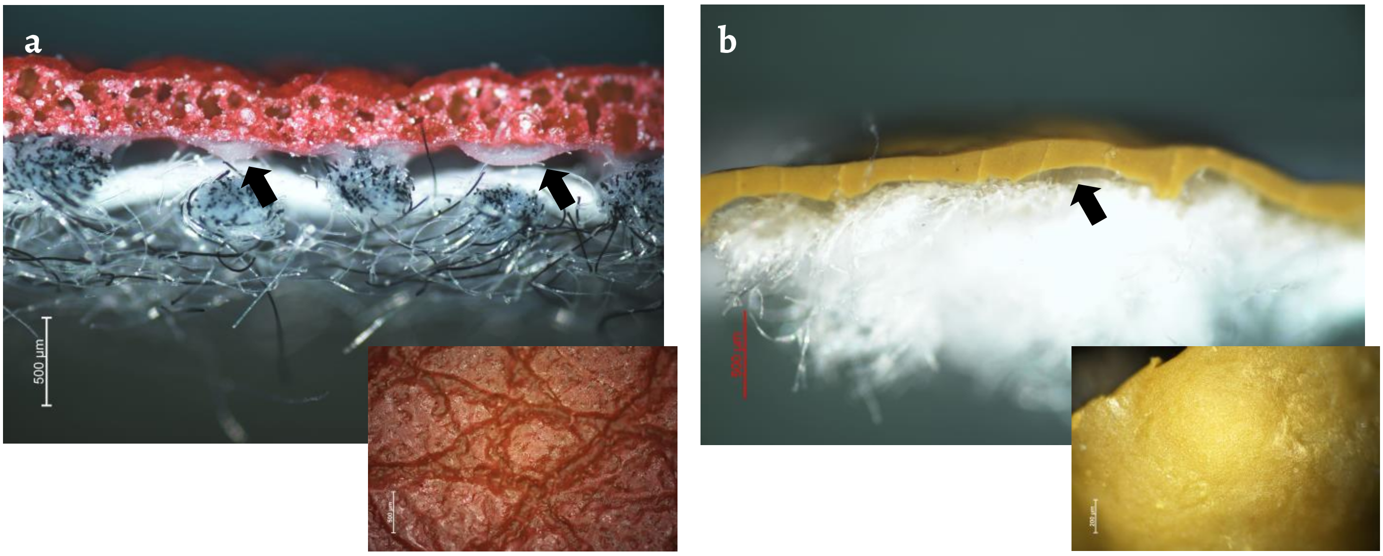


Figure 1. Microscopy images of: *a-b)* two cross-section examples of synthetic coated fabrics (see Table 1) under cross-polarised visible light composed of three layers, in which the intermediate one (arrows) was possibly added for adhesive purposes. Insets: top views of the respective coated fabric.

As observed in Table 2, each layer might play a different role in the final aesthetic and properties of a coated fabric. The colour might be introduced either by the top coating layer (examples a and d), an intermediate layer if present (example c), or even by the fabric substrate (example b). On the other hand, when a glossy finish is desired, it is, in most cases, obtained by an uncoloured top layer, as observed in Table 2 (examples b, c and e).

In addition, intermediate layers might be added for adhesive purposes, i.e., to promote the bond between the coating layer(s) and the fabric substrate [4]. Examples of such layers visible under visible light are shown in Figure 1 (highlighted by black arrows).

The presence of this layer indicates that the coated fabrics might have been produced by the transfer coating method, as will be discussed in more detail in "Coating morphology" section. As observed in these images, the level of contact of this type of layer with the substrate varies, as the adhesive might be more (Figure 1b) or less (Figure 1a) impregnated within the fibres of the substrate. In the latter, the observed voids between the two layers might be seen as weak points in the fabric structure, which can lead to future damage at this interface, particularly delamination.

However, in most cases, adhesive layers are particularly difficult to detect under visible light for their transparency and thinness, and for frequently being impregnated within the fibres of the fabric substrate. To overcome this limitation, samples were also observed under blue-violet and ultraviolet radiation to detect fluorescence in case the layers had different fluorescence properties under these wavelengths (Figure 2). In some cases, as observed in Figure 2a, an additional layer was detected due to its distinctive fluorescence (right, highlighted by an arrow), while being barely visible under visible light (left). This sample was composed of a TPU coating and, while it was not possible to analyse the adhesive layer with the used techniques, it is likely composed of the same material for compatibility [32].

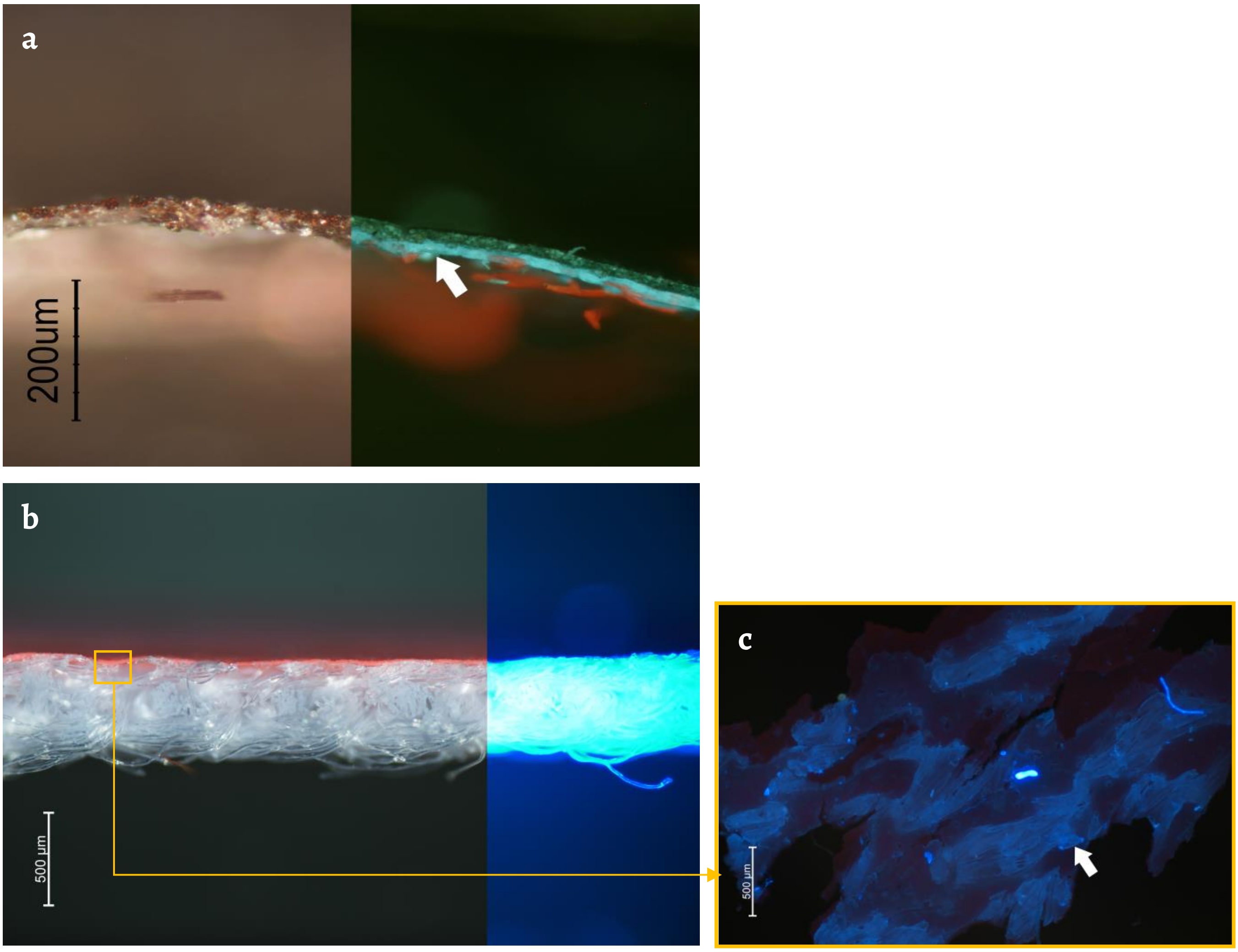


Figure 2. Microscopy images of two synthetic coated fabrics examples (see Table 1) composed of an intermediate layer, possibly added for adhesive purposes, only detectable under fluorescent illumination: *a)* cross-section of the dress sample under visible (left) and blue-violet (right) lights; and jacket sample: *b)* cross-section under visible (left) and ultraviolet (right) lights and *c)* bottom side of the top coating under ultraviolet light (arrows highlight the presence of the detected intermediate layer).

Unaged polyurethane is known for showing some fluorescence under both blue-violet and ultraviolet lights, corresponding to longer and shorter wavelengths, respectively, which can be attributed to the presence of aromatic structures and amide groups in its network, along with a predominance of non-oxidized forms [36]. However, previous studies have demonstrated that the fluorescence properties of several polymers, natural and synthetic, can suffer modifications due to ageing [37-41]. Particularly for polyurethane, observations with fluorescence microscopy showed that the fluorescence intensity of the material strongly increases with ageing, as a consequence of the formation of new fluorophores such as oxidised species and new conjugated bonds [36, 42]. However, the stronger fluorescence observed for the intermediate layer in Figure 2a compared to the top coating is believed to not be related to its more advanced deterioration state, but rather due to a more straightforward chemical formulation, possibly with fewer additives, such as pigments and fillers, since its function is to promote the bonding between the upper coating and substrate and not an aesthetic one. The presence of additives like pigments is also known to strongly influence the fluorescence properties of a material [43-45], which, in this case, might be masking the intrinsic fluorescence of the polymer.

This hypothesis is corroborated by the overall observations on the fluorescent properties of the analysed set of TPU-coated fabrics. Most of the analysed TPU top coatings showing colour did not particularly fluoresce under blue-violet or ultraviolet wavelengths, while the transparent TPU top coatings of most highly glossy coated samples strongly fluoresced under the same illumination conditions. Moreover, the reference coated-fabric samples custom-made by Centexbel composed of ester-based TPU coatings (both aliphatic and aromatic) with no additives incorporated into the formulation, also exhibited strong fluorescence. However, it is important to highlight that the same observations did not apply to coated fabrics composed of p-PVC coatings, as these did not show fluoresce properties under the same illumination.

Some of the analysed coated-fabric samples were composed of other layers that also showed a strong fluorescence, as the fabric substrate in Figure 2b, which disguised the presence of an additional intermediate layer. Several factors can influence the fluorescence properties of a fabric, including the chemical composition of the fibres, additives, treatments, and degradation [46]. If the destruction of the sample is possible, the substrate can be removed from the sample for further examination of the bottom side of the remaining coating layers(s), as shown in Figure 2c. In this case, clues of an additional layer were found, through the observation of traces of a heterogeneously spread material (white arrow) with a distinct fluorescence.

Coating morphology, chemical composition and processing techniques

As previously described, there are several manufacturing techniques to produce synthetic-coated fabrics. However, for the present research, the way a coating is applied to the fabric was considered of the most relevance, which is mainly done through the direct and transfer coating methods.

As previously mentioned, the direct method is not suitable for stretchy and open-structure fabric, like knitted ones, making it possible to discard this technique in the presence of such fabric substrates. The direct application and spreading of a coating on a fabric substrate leads to the formation of a compact continuous film that sinks into the weave of the fabric [3-4]. Figure 3a shows an example of a coated fabric produced by this method in which these characteristics can be easily observed.

On the other hand, the so-called transfer coating method can be used for the coating of knitted fabrics or others with open and stretchable constructions. The principle of this method can be summarised by the application and spreading of the polymer coating onto a release paper to form a continuous film, followed by the application of additional layers such as adhesive ones, lamination to the fabric substrate and removal of the release paper [2-4]. An example of a coated fabric produced by this method is shown in Figure 3b. Since the fabric substrate usually only comes into contact with the coating layer(s) after the latter is already in a film form, resin penetration tends to be low or even inexistent, as opposed to the direct method [2, 4]. In addition, the presence of an adhesive layer, also known as tie-coat, to promote the bond of the coating to the substrate is a good indicator that the coated fabric might have been produced by this method. Such a layer is not needed when a coating is directly applied since its sink-in into the fibres of the substrate is usually enough for good adhesion.

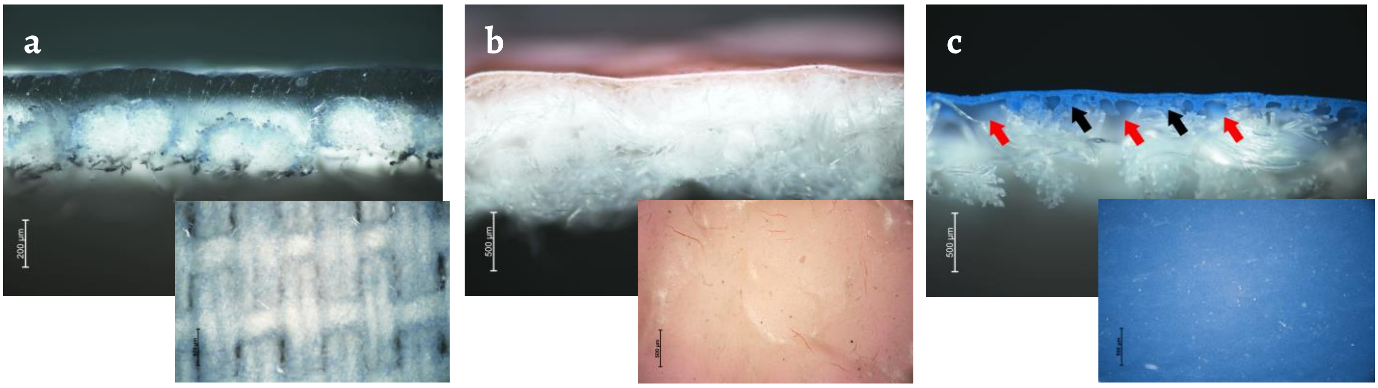


Figure 3. Microscopic images of cross-section examples of coated fabrics (see Table 1) under cross-polarised visible light possibly produced by: *a)* direct method; *b-c)* transfer coating method with complete and partial curing of the coating before lamination of the fabric substrate, respectively (red arrows indicate voids, while black arrows highlight contact areas between the coating and substrate). Insets: top views of the respective coated fabric.

However, coatings that are only partially penetrated within the weave of the fabric were also found, as the example shown in Figure 3c. At the interface between coating and substrate, voids can be observed (red arrows), i.e., areas of no contact between the layers, suggesting that the coating was possibly not applied by the direct coating method as it would have been fully impregnated within the fibres, as the example in Figure 3a. Instead, the coated fabric was more likely produced by the transfer coating method, although the coating was possibly only partially dried upon lamination of the fabric substrate, leading to the observed partial penetration of the coating into the fabric (black arrows), which does not usually occur with this method. The voids observed in this fabric can be pointed out as weak areas in its structure that might be more prone to future damage as, for example, humidity might be trapped in here, causing an imbalance between the layers and triggering the chemical deterioration of the coating [47].

Microporous coating structures were also detected within the analysed samples, obtained by different production techniques such as foamed and coagulation methods.

Examples of foam coatings are presented in Figure 4, in which the cells of the foams are clearly distinguished. These coatings usually have a leather-like appearance and tend to be bulkier than the compact continuous coatings, resulting in coated fabrics with an opaque look, and a soft and cushioned feel. Foam coatings are usually directly applied to the substrate although its penetration into the weave of the fabric does not occur. This method is thus suitable for woven and knitted fabrics, even the ones with relatively open constructions, that typically cannot be coated by the more conventional direct coating technique [4, 48]. Furthermore, the low penetration of the foam makes it possible to preserve the original properties of the fabric, like the soft drape [48]. These coating structures were found in both TPU and p-PVC-coated fabrics.

Other examples of microporous coating structures were detected, corresponding to coated fabrics with a soft and spongy feel, composed of porous TPU layers (Figure 5). These materials are distinguished from the foam coatings observed in Figure 4 by the reduced cell size. The observation of the samples under blue-violet and ultraviolet radiation provides finer image resolution than visible light due to shorter wavelengths [49], which proved useful in exposing more clearly the microporous structure of these samples (Figure 5b, right) for comparison with the literature [50-52].

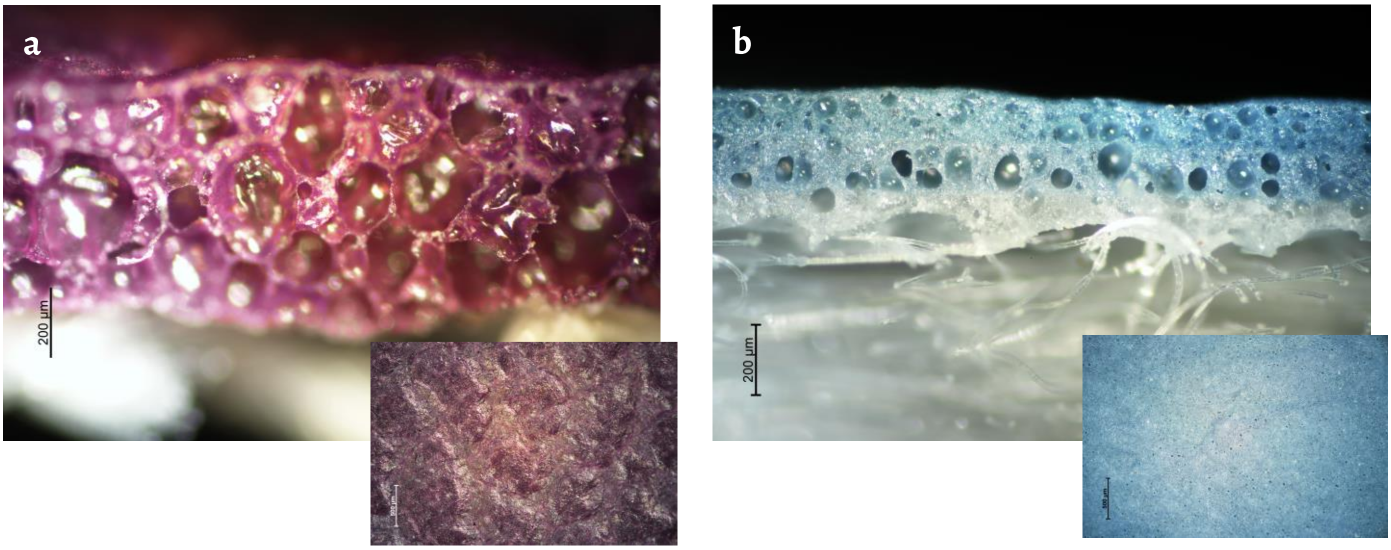


Figure 4. Microscopic images of two cross-section examples of coated fabrics (see Table 1): *a)* jacket and *b)* commercial fabric, under darkfield visible light composed of a foam coating. Insets: top views of the respective coated fabric.

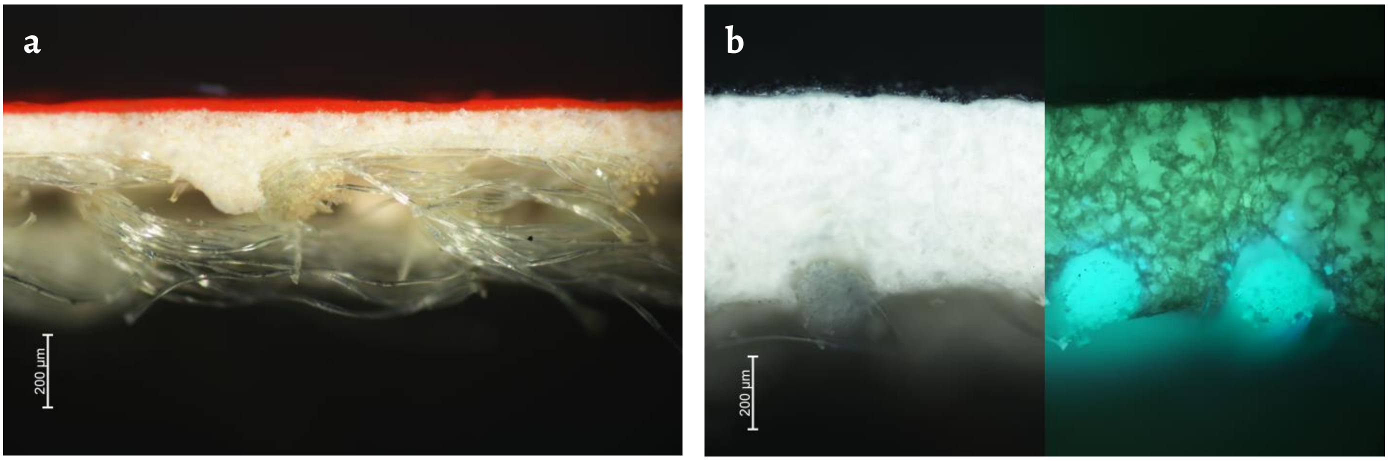


Figure 5. Microscopic images of two cross-section examples of synthetic-coated fabrics (see Table 1) composed of coatings with a microporous structure, possibly produced by the coagulation method: *a)* sample one under cross-polarized visible light; *b)* sample two under cross-polarized visible light (left) and blue-violet (right) radiation.

These microporous-coated fabrics might have been produced by the so-called coagulation process, in which polyurethane is the preferred polymer to produce breathable fabrics and imitations of leather [2, 4, 52]. This procedure can be performed through a direct or transfer coating method and polyurethane can be coagulated by a wet or dry procedure. The principle of the wet coagulation technique is solvent exchange: the TPU, non-soluble in water, is dissolved in a water-soluble solvent, such as dimethylformamide (DMF), followed by an aqueous treatment for the dilution/extraction of the organic solvent, resulting in a progressive phase-separation and subsequent precipitation or coagulation of the TPU and formation of pores [2, 4, 51]. The addition of additives, such as pigments, is particularly difficult with this process since they might also be removed during the solvent extraction step [2]. On the other hand, phase-separation and coagulation of the TPU can also be achieved through the dry-coagulation method or thermocoagulation, based on the controlled evaporation of the solvents in which the TPU is dissolved, in this case commonly a mixture of methylethylketone/toluene in water [2, 4, 51]. Additional layers might be added to the top of the coagulated TPU to impart colour or other properties through the conventional transfer coating method.

The observation of the examples in Figure 5, particularly the lack of pigmentation of the microporous coating and its penetration within the weave of the fabric, indicates that the TPU coating might have been directly applied to the fabric.

Some of the analysed samples also showed coatings with microporous-like structures that seemed to have a composite nature, as indicated by the difference in fluorescence intensity observed under ultraviolet radiation (Figure 6). These layers might correspond to a nonwoven fabric, composed of different fibre types that fluoresce differently, flame laminated to the fabric substrate and coated on top with a polymeric compound, possibly by the transfer coating method. Other possibilities, particularly the ones in which impregnation of the coating into the substrate is observed, might be for the coating layer to be composed of a mixture of polymer resins or of a polymer resin, such as TPU, filled with heterogeneous fibre particles, the latter also identified by Meyer et al. [53]. However, further characterisation of these samples is needed to better understand their composition.

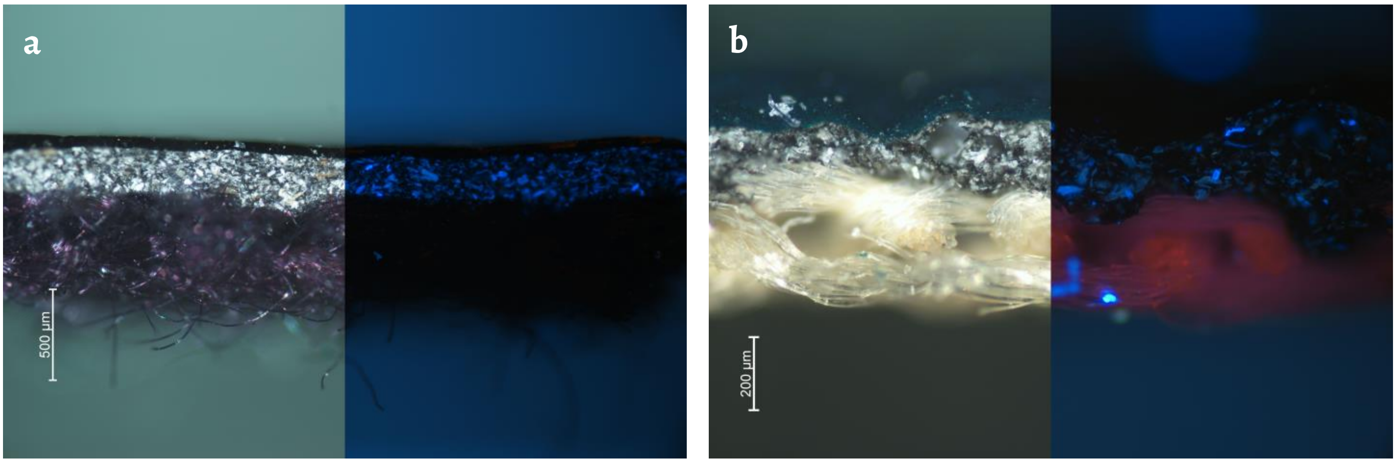


Figure 6. Microscopic images of two cross-section examples of coated fabrics (see Table 1) composed of coatings with a microporous structure, possibly composed of a nonwoven fabric laminated to the substrate or of a mixture of resin/resin or resin/fibre particles: *a)* and *b)* under cross-polarized visible light (left) and ultraviolet (right) radiation.

Flaking and peeling patterns: preliminary observations on TPU-coated fabrics

Flaking and peeling have been reported as common deterioration patterns in synthetic coated fabrics found in museum collections, leading to drastic visual changes and the eventual complete loss of the affected items [8-9]. A brief definition was presented by França de Sá et al. to describe both damages [8], though there is still a lack of knowledge on the possible causes for their occurrence.

In a coated fabric, both peeling and flacking are characterized by a delamination phenomenon caused by a bonding failure. In the case of peeling, the coating layer(s) completely detach in large fragments, while mostly maintaining their overall flexibility. On the other hand, flaking is usually preceded by cracking, leading to fragmentation in smaller-sized pieces of the coating layer(s), resembling small islands, and their subsequent detachment.

The set of analysed samples from items affected by flaking and peeling was only composed of TPU-coated fabrics. In most cases, the delamination observed in both damage patterns occurred at the interface between the coating layer and substrate. However, it is also described in the literature that interlayer delamination might also occur, i.e., separation at the interface between two coating layers due to, for example, insufficient heat during application [4].

As previously described and exemplified in Figure 1a and Figure 3c, flaws in the bonding between the coating and substrate, i.e., areas of no contact, can be weak points in the structure of the coated fabric that are more prone to damage [47]. Humidity might be trapped in these voids, promoting the chemical deterioration of the coating at this interface, which can lead to delamination. The larger the weak point, the more extended the delamination between the layers: large weak points might lead more likely to peeling, while smaller weak points might lead to flaking instead. In addition, due to the composite nature of the coated fabrics, variations in humidity might also cause a differentiated expansion/contraction of the several layers, promoting the delamination phenomenon.

Peeling was mostly observed in thin-coated fabrics with a 2-layer construction (Figure 7), i.e., composed of only a coating and fabric substrate layers. As observed in Figure 7a, it was also noted an overall reduced contact between the coating and fabric layers, suggesting a production through the transfer coating method, as the direct one would have led to an increased impregnation of the coating [3-4]. However, the lack of an adhesive layer to ensure proper bonding between the two layers resulted in a large weak point at this interface and consequent delamination of the coating in large pieces.

On the other hand, flaking was detected in both thin and thicker coating layers on the set of analysed fabric samples (Figure 8).

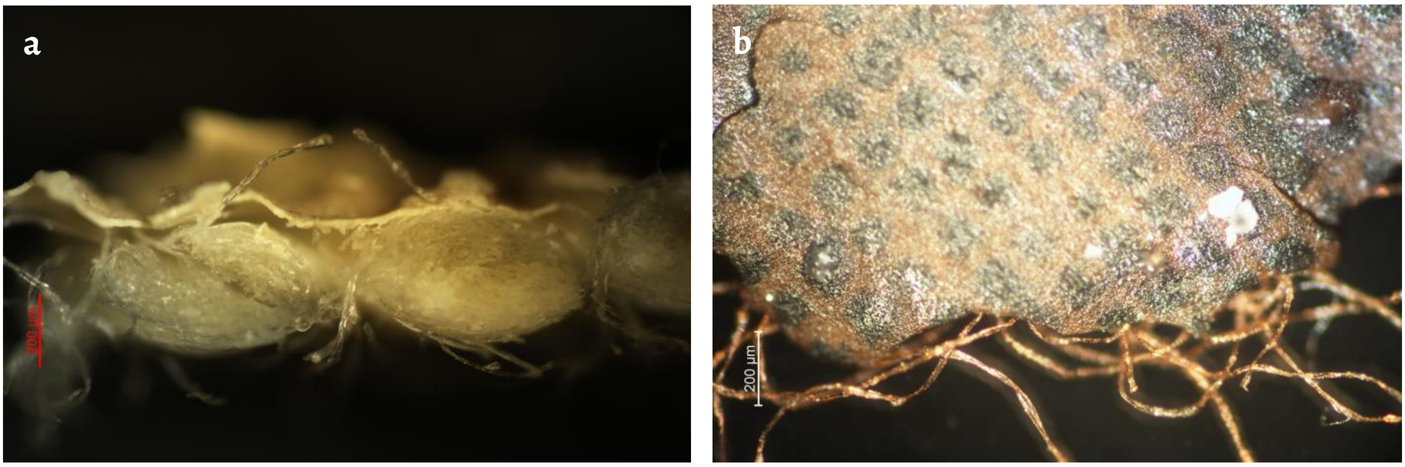


Figure 7. Microscopy images of two examples of thin-coated fabrics (see Table 1) damaged by peeling under darkfield visible light: *a)* cross-section; *b)* top-view.

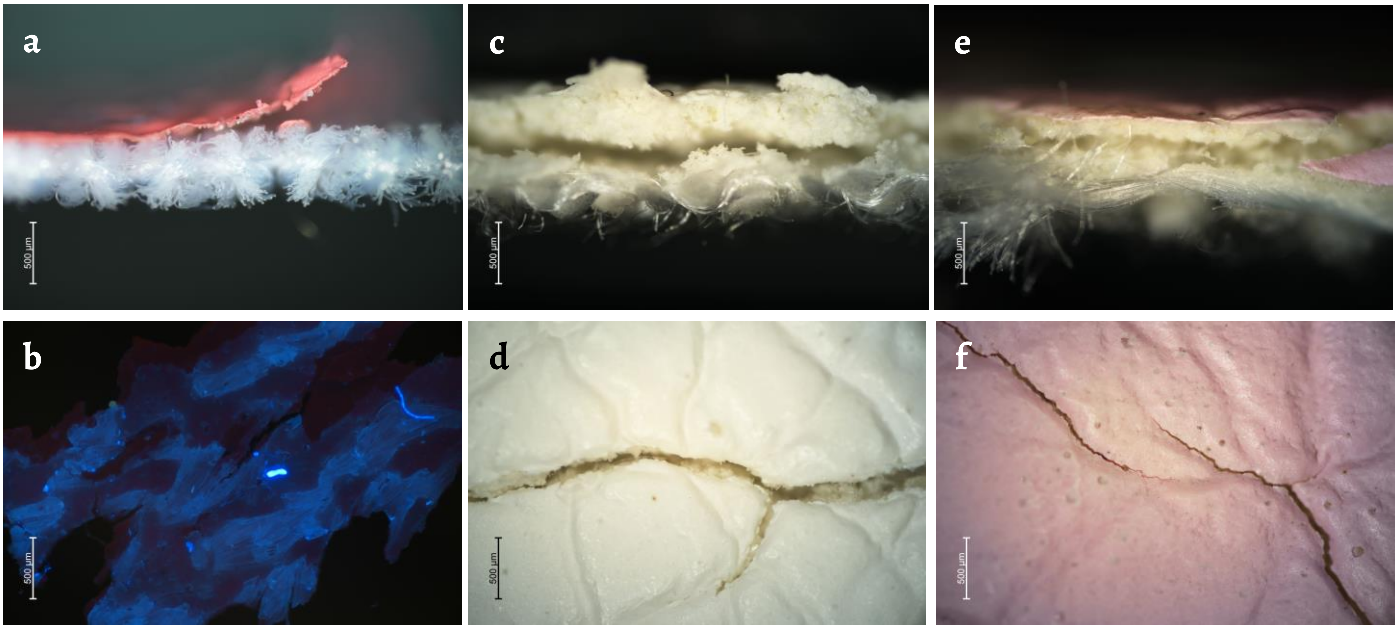


Figure 8. Microscopy images of three examples of synthetic-coated fabrics (see Table 1) damaged by flaking: *a)* cross-section under cross-polarised visible light and *b)* bottom side of the top coating of the same sample under ultraviolet radiation, in which traces of an adhesive layer are visible; *c* and *e)* cross-section and *d* and *f)* respective top-view of two coated fabrics with leather-like textures under darkfield visible light.

Opposingly to peeling, most fabrics with thin coating layers showing flaking were composed of an adhesive intermediate layer (Figure 8a-b). The improvement of the bonding strength between the coating and fabric substrate possibly prevented the detachment of the coating in large fragments. However, the cracking and detachment in smaller fragments does not seem to have been completely prevented by the presence of this adhesive layer, as it might not be homogeneously spread, as the example observed in Figure 8b (corresponding to the bottom of the top coating from the sample shown in Figure 8a), leading to only a partial bonding and areas of no contact between the layers. Extensive physical handling and/or wear of an item might also promote flaking, as it leads to mechanical damage like cracking and subsequent detachment of the broken fragments. In addition, the chemical deterioration of a TPU coating, mainly caused by hydrolysis for the ester-based and photooxidation for the ether-based [54], might also promote cracking of the material, due to internal breakage of chemical bonds that weaken its cohesion and integrity.

Flaking was also found in thicker TPU-coated fabrics, composed of microporous structures and leather-like textures (Figure 8c-f). In these examples, the cracking phenomenon leading to flaking also seemed to have been promoted by the texture of the coated fabric, as the net of embossed grains created a path for a facilitated spreading of a net of cracks throughout the entire surface of the coating, especially the deeper the embossing (Figure 8d and Figure 8f).

Conclusions

The present study reported for the first time the variability of p-PVC and TPU-coated fabrics in fashion museum collections. The construction and morphology of the layers of a selected set of samples were investigated through a straightforward methodology mainly based on a visual assessment by optical microscopy, complemented by infrared spectroscopy (ATR-FTIR) for the identification of material composition. Visual clues were found that enabled the indication of the manufacturing processes used in the production of the coated fabrics analysed. In addition, preliminary results of the detailed observation of delamination damages, namely flaking and peeling, suggest their connection to production methods.

The analysed set of samples showed great variability in terms of the number of layers, thickness, transparency, colour, and morphology. The most common number of layers identified were two and three-layer constructions, composed of a fabric substrate coated with one or two coatings, respectively. In addition, it was possible to identify different coating morphologies, such as compact and microporous structures. The latter are characterized by the presence of a cell structure which can be further divided, depending on the size of the cell, into foamed (bigger size) and coagulated coatings (smaller size). Microporous structures can also be achieved by other means, such as a nonwoven fabric or a composite coating layer comprising a polymer resin filled with fibre particles.

Several methods are described in the literature to produce a coated fabric, but only the distinction between a direct and indirect application of a coating to the fabric substrate was considered relevant for the present study. Coated fabrics produced by the direct coating method usually result in coatings that sink into the weave of the fabric, which can be easily identified when observing a cross-section, that can have either a compact or microporous structure. For this reason, this method is usually not suitable for open-structure fabrics, such as knitted ones, unless a foamed or coagulated coating is applied. On the other hand, coated fabrics produced by the indirect coating method, also known as transfer coating, tend to show a well-defined coating layer that does not sink into the fabric since it is usually in a film form when laminated to the substrate. Intermediate adhesive layers are frequently present in coated fabrics produced by this method. In addition, it is important to highlight that the production of coated fabrics might not be restricted to one method only and that several techniques can be applied to obtain the desired final product.

Fluorescence microscopy proved to be particularly useful in the detection of additional layers with distinctive fluorescence, namely the TPU intermediate layers added for adhesive purposes. The finer resolution of these images also allowed for a better understanding of the morphology of the coatings, particularly of coagulated structures, which helped determine production methods.

Delamination issues, such as flaking and peeling damages, were investigated in TPU-coated fabrics and preliminary results show a connection to the production methods of the materials. Peeling seems to be particularly common in coated fabrics with two-layer constructions, i.e., with no adhesive layer, produced by the transfer coating method. The reduced contact between the coating and substrate layer leads to a large weak area at this interface, causing their separation in the long term. On the other hand, flaking seems to be a more complex delamination phenomenon in which several factors might play a role. It is usually preceded by cracking, which can be caused, individually or in combination, by the physical handling and/or wear of the material and the chemical deterioration of its coating. Although coated fabrics with flaking tended to show a better bonding strength between coating and fabric than the ones with peeling, flaws at this interface were still found, i.e., areas of no contact or voids, which are possibly more prone to physical and chemical damage. These voids are weak points in the structure of the fabric where cracking, followed by delamination by flaking, might be more likely to occur. Additionally, coated fabrics with leather-like textures seem to be particularly prone to flaking, as the net of embossed grains seemed to create a path for a facilitated spreading of a net of cracks throughout the entire surface of the coating.

It was also concluded in this research that it is not possible to distinguish p-PVC and TPU-coated fabrics merely through visual assessment, which highlights the need for further molecular analysis for proper identification of the material. However, the present study proved the value of a simple observation-based approach for a first assessment of the synthetic-coated fabrics present in fashion museum collections. The detailed observation of the subtle differences in their structure and morphology contributes to the increased knowledge about these materials which will hopefully pave the way for the development of informed and suitable conservation strategies for their long-term preservation.

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