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The effectiveness of natural indigo/kaolinite composite powder in the development of latent fingermarks

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Abstract

Background Composites are materials that have multiple phases and have attracted much attention as they are able to improve physical and chemical properties of an isolated material. In this sense, these composites are commonly used as key components for two purposes: coloring and improving the operational properties; besides that, they have alternative synthesis routes that respect the principles of green chemistry. Thus, this reports the development of a new composite using natural products, indigo and kaolinite, for application in papilloscopy as a new nontoxic fingermark developer.

Results The composite was obtained via green procedures and was characterized by spectroscopic and chromatographic techniques. Thus, to investigate the potential of the material as a fingermark developer, different techniques were applied such as depletion, aging, comparison with commercial powder, and development of latent fingermarks on different surfaces. Tests revealed that the composite presented good contrast and adhesion with the latent fingermarks, even after 15 days of deposition.

Conclusions This study presents a natural indigo/kaolinite composite powder that showed similar or higher efficiency when compared to the commercial fingerprint powder and was able to develop identifiable natural and sebaceous fingermarks.

Key points

- A composite was formed from eco-friendly materials.
- The composite formation follows the concepts of green chemistry and low cost.
- The composite was applied as a latent fingermark developer.

Keywords Forensic sciences, Natural indigo, Kaolinite, Latent fingermark

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Background

Patterns found in fingermarks are permanent, being considered valuable evidence that can be used to identify or exclude suspects from a crime investigation (Christofidis et al. 2018). The transfer of a fingermark to a surface depends mainly on the type of surface, the pressure, and the duration of the contact with the object (Jasuja et al. 2009). There are three main classes of fingerprints: latent, patent, or plastic. Latent fingermarks are commonly found at crime scenes, but are not visible by naked eye and therefore require treatment to become visible (Leitzke et al. 2022). This procedure is called latent fingerprint development and comprises the use of chemical or physical processes which, combined with skin secretions, make the latent fingermark visible. These techniques require chemical reagents to improve the quality of the images and facilitate the detection of latent fingerprints. Among them, the most used method is called dusting, which consists of the application of a fine powder with the aid of a specific brush and subsequent removal of powder excess (Balsan et al. 2019; Sodhi and Kaur 2001). Additional techniques to improve the visualization of fingerprints are also commonly reported, including optical methods such as absorption, UV–visible absorption, fluorescence spectroscopy, diffusion mirror imaging, and mirror imaging (Prabakaran and Pillay 2021). Besides, based on Locard's principle of mutual exchange, reliable and effective approaches that can improve the detection of latent fingermarks are increasingly necessary (Risoluti et al. 2019).

Owing to these issues, studies concerning the production of new developing powders with little or no toxicity, good adhesion, and contrast with different types of surfaces as alternatives are needed (Leitzke et al. 2022). In this sense, materials that have multiple phases have attracted much attention, as they can present superior physical and chemical properties (da Rosa et al. 2022) with a wide range of applications, such as bioimaging (Nguyen et al. 2019), medical therapy (Yang et al. 2020), photocatalysis (Wang et al. 2020), photodevices (Wu et al. 2019), sensors (Li et al. 2020), light communication (Tian et al. 2019), and forensic sciences (da Rosa et al. 2022). In contrast to commercial powders, natural dyes are biodegradable and environmentally compatible, which drives numerous studies regarding environmentally friendly developing powders (Aggarwal 2021). Accordingly, formulations containing organic materials, pigments, and dyes are commonly applied to promote color to improve the operational properties of the composite (Tracton 2006). In addition, the development of composites enlarges alternatives to physical synthesis, maintaining the principles of green chemistry (da Rosa et al. 2023). Therefore, the use of natural products, such as indigo and kaolinite, arises as interesting materials for application in forensic science as a novel fingermark developer.

Indigo is a low-cost, natural, and sustainable material obtained from the extraction of the *Indigofera tinctoria* plant and presents high potential to be used as latent fingerprint developer (Kabish et al. 2023). Thus, the use of natural indigo replacing synthetic dyes becomes interesting since synthetic dyes are one of the main pollutants of water, causing serious environmental issues (Samanta and Agarwal 2009). Therefore, in recent years, the studies regarding the use of natural indigo have attracted much the attention of the industry and the scientific community (Hossain et al. 2017). However, due to its strong pigmentation and poor adhesion, pure indigo does not contrast properly on all types of surfaces, which hinders its use as natural fingerprint developer powder. To enhance the adherence of indigo, the combination with kaolinite ($Al_2Si_2O_5(OH)_4$) rises as an interesting strategy. Kaolinite is a clay mineral that have received much attention for being one of the major components of soils and the earth's crust, being considered one of the most important mineral resources in human history, as its use has been reported since ancient times in a wide range of applications (Rivera et al. 2016). In the field of forensic sciences, it exhibits properties that can significantly contribute to improve adhesion and contrast of developing powder containing indigo as main constituent (Awad et al. 2017). Herein, this study reports the formulation of an indigo/kaolinite composite and its application in the area of papilloscopy as a developer powder for latent fingerprints (Fig. 1). To confirm the efficiency of the powder, different methods were used, including development of natural and sebaceous fingermarks from different donors on different surfaces, depletion, comparison, aging, and identification of minutiae.

Methods

Materials

Natural indigo was obtained from ETNO Botânica™ (Itamonte, Brazil). Synthetic Indigo® and Kaolinite® were obtained from Sigma-Aldrich (St. Louis, USA). Fingerprint powder developer White® was purchased from Sirchie (Youngsville, USA). Other reagents and materials were obtained from Sigma-Aldrich (St. Louis, USA), Isofar (Capivari, Brazil), and J. T. Baker (Radnor, USA) with analytical grade (≥ 99%).

Formulation of indigo/kaolinite composite

The formulation of indigo/kaolinite composite was performed according to an adapted method previously described by Modwi et al. (2018). Briefly, 0.6 g of natural indigo and 0.4 g of kaolinite were dispersed in 100 mL

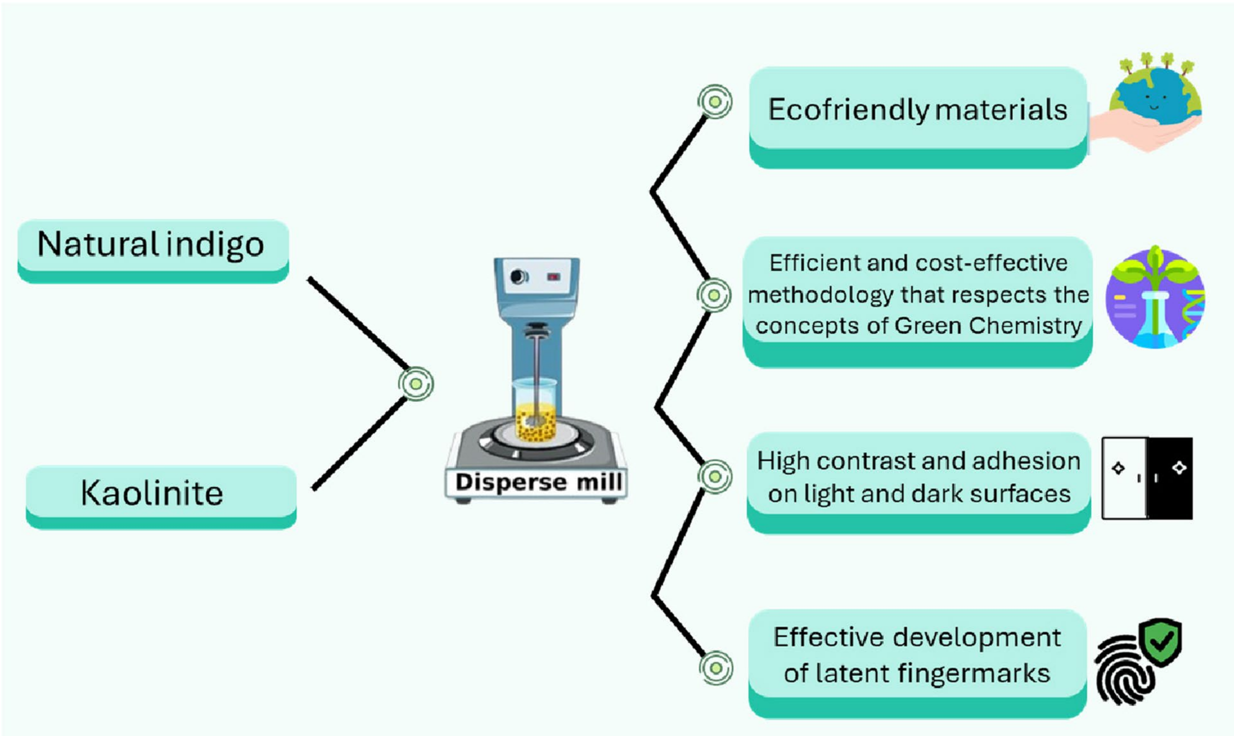

Fig. 1 Composite indigo/kaolinite graphical formulation and application process

of distilled water under sonication for 30 min. Then, the solution was added to a dispersion mill for 3 h at room temperature. To increase the physical interaction between molecules, 50 g of zirconia grinding balls was added to this mixture. The resulting material was centrifuged for 10 min at 4000 rpm, and the solid was dried in an oven at 200 °C.

Characterization

The synthetic indigo, natural indigo, and kaolinite were first investigated through ultraviolet–visible spectroscopy (UV–Vis). For this, the samples were diluted in N,N-dimethylformamide (DMF). Afterwards, these solutions were analyzed in an equipment Bel (model LGS53) performing the scanning mode between wavelengths 200 to 600 nm. Fourier transform infrared spectroscopy (FT-IR) was performed with potassium bromide (KBr — [0.5%]) in a Shimadzu spectrometer of infrared, model SPIRIT, with scanning from 4000 to 400 cm^{-1} with 45 scans and a resolution of 4 cm^{-1}. Liquid chromatography was recorded using the method adapted from Son et al. (2004), in a Thermo Scientific UltiMate 3000 UHPLC System, Waltham. The isocratic elution mobile phase consisted of a mixture of water and methanol (10:90). The analysis was performed at room temperature for 10 min with an injection volume of 10 μL, flow rate of 0.500 mL/min, and detection wavelength of 290 nm. The scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM/EDS) analyses were carried out on a JEOL JSM 6010 machine, operating at 15 kV, with a working distance of 10 mm. The samples were deposited on a stub using double-sided adhesive tape and then coated with gold. A Denton Vacuum machine was used for metallization, where the samples were exposed for 200 s to a current of 20 mA. X-ray diffraction (XRD) patterns were recorded in a D8 ADVANCE, Bruker; equipped a copper tube (Cu), wavelength of 1.5418 Å; and operated at 40 kV and 40 mA. The analysis was performed in the range between 10 and 70 at scanning speed of 0.05 min^{-1}. For scanning electron microscopy (SEM), Shimadzu equipment, model SSX-550 Superscan, was used. A glass cover slip and black plastic were used as substrates for the deposition of natural and sebaceous fingermarks and developed with the composite. The substrate was mounted on the stub with carbon tape, metallized with gold, and analyzed at 15 kV. Secondary electron imaging was used and the following analytical parameters: AccV of 15.0 kV and 4.0 probe. For particle size analysis, samples were suspended in deionized water and analyzed using a CILAS 1064 operating at particle range of 0.04 to 500 μm.

Fingermarks evaluation

Deposition and development of latent fingermarks

The deposition of latent fingermarks (natural and sebaceous) was performed according to the methodology described by Sears et al. (2012). For this purpose, fingerprints from five randomly selected donors were deposited on glass and plastic surfaces. For the revelation process, a 132 LBW brush (Sirchie, Youngsville, USA) was used, and for photographic recording, a professional camera (Canon EOS Rebel T6 18MP) was used, with the close-up + 4 58-mm lens, distance of 9 cm, focus 5.6, and automatic ISO speed photo mode. For better visualization, three white led lamps were used to improve the brightness with a black background under the fingermarks. The fingermark images were processed in the Adobe Photoshop software. All the surfaces used for deposition and development of fingerprints were washed with water and neutral soap after being photographed. All the photos taken were deleted after the publication of this work.

Depletion latent fingermarks evaluation

The depletion study followed the methodology proposed by Pacheco et al. (2021). In this procedure, sebaceous fingerprints were collected from five donors, and the fingerprints were developed using the indigo/kaolinite composite, similarly as described in the "Deposition and development of latent fingermarks" section.

Aged latent fingermarks evaluation

The fingermark aging study was conducted following the methodology of Poletti et al. (2021). Five random donors deposited five natural and five sebaceous fingerprints, all on the same day, and were developed after: 0, 1, 5, 10, and 15 days. The fingermarks were stored at room temperature in the papilloscopy room of the Laboratory of Innovation and Solutions in Chemistry at the Federal University of Pelotas during the aging process, and the fingerprints were developed using the indigo/kaolinite composite, similarly as described in the "Deposition and development of latent fingermarks" section.

Comparison of latent fingermarks developers

This investigation aimed to confirm the effectiveness of the indigo/kaolinite powder in comparison with a reference standard (Sirchie®'s commercial developer powder White®). For this purpose, the methodology of da Rosa et al. (2023) was employed. Latent natural and sebaceous fingermarks were collected from five donors. The fingermark development occurred similarly to the description in the "Deposition and development of latent fingermarks" section, where the left half was developed using the composite and the right half with the commercial powder.

Evaluation scale of latent fingermarks development

The evaluation of the developed fingermarks was performed by three independent analysts according to the scale proposed by Sears et al. (2012) (Table 1). The scores of the analysts were averaged, resulting a single final score for each fingermark located to the left of the respective image in each corresponding figure.

Results

Characterization

The UV–Vis spectra of the samples are shown in Figs. 2a and S1 (Supplementary information). Natural indigo exhibited the same absorption bands as synthetic indigo, with a peak of maximum absorption around 292 nm. A broad absorption peak in the range between 530 and 660 nm and two absorption bands at 260 nm and 287 nm were also observed. As for the kaolinite spectrum, a small absorption peak was observed at approximately 200–260 nm. Lastly, the composite spectrum exhibited bands related to both compounds.

The crystal structure of the materials was characterized through X-ray diffraction, and the XRD patterns of the natural indigo, kaolinite, and the indigo/kaolinite samples are shown in Fig. 2b. The natural indigo displayed peaks at 10.63°, 14.51°, 29.55°, and 31.01°. Furthermore, the XRD patterns of kaolinite show peaks at 12,269°, 24,921°, 26,426°, 35,164°, 36,100°, 37,866°, 38,592°, and 39,419° corresponding to crystalline planes (0, 0, 1), (0, 0, 2), (1, 1, 1), (1, 3, 0), (2, 0, 0),

Table 1 Outline grading scheme used for assessment of developed marks according to Sears et al. (2012)

Score	Level of detail
0	No evidence of mark
1	Weak development, evidence of contact but no ridge details
2	Limited development, about 1/3 of ridge details are presented but probably cannot be used for identification purposes
3	Strong development, between 1/3 and 2/3 of ridge details, identifiable fingermark
4	Very strong development, full ridge details, identifiable fingermark

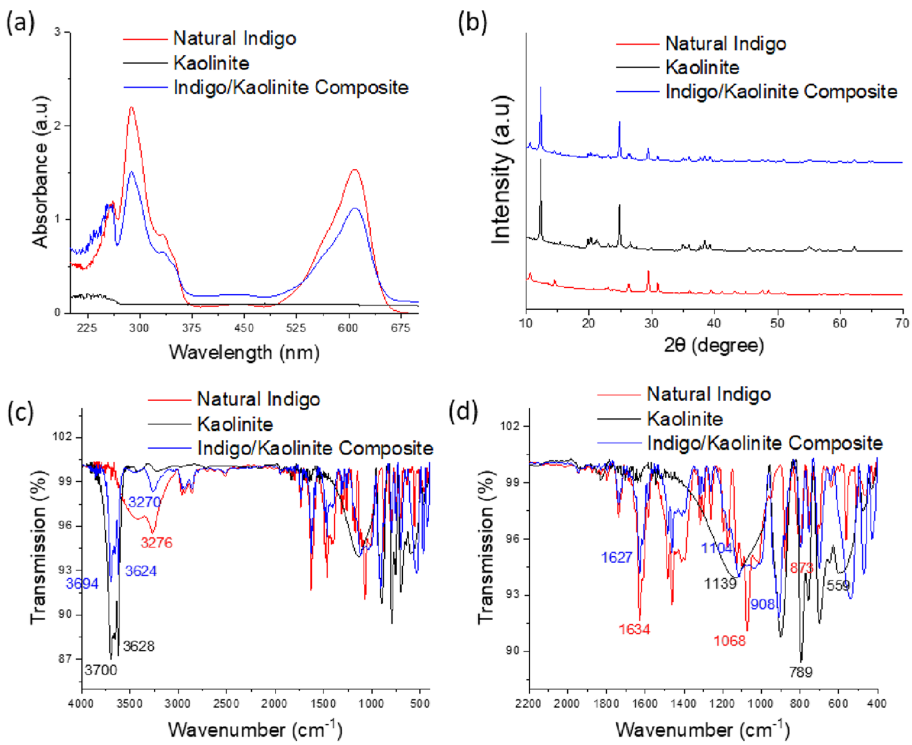

Fig. 2 **a** UV–Vis spectrum, (**b**) X-ray diffraction, (**c**) and (**d**) IR spectrum for natural indigo, kaolinite, and indigo/kaolinite composite

(0, 0, 3), (1, 3, 1), and (0, 1, 3), respectively, according to the JCPDS — International Center for Diffraction Data. Lastly, the diffractogram of the composite exhibited the diffraction patterns of both compounds.

FT-IR was performed to identify the functional groups on the surface of the samples, as shown in Figs. 2c and d and S2 (Supplementary information). For natural and synthetic indigo were observed characteristic bands at 3100–3500 cm^{-1}, 1600 cm^{-1}, 1350–1000 cm^{-1}, and 900–690 cm^{-1}. In addition, the spectrum of Kaolinite exhibited bands at 3700 and 3628 cm^{-1}, 3206 cm^{-1}, 1828 cm^{-1}, 1139 cm^{-1}, 900–400 cm^{-1}, and 559 cm^{-1}. Lastly, the composite spectrum exhibited bands related to both compounds.

The chromatograms from liquid chromatography can be seen in Fig. 3. In the chromatograms of both synthetic and natural indigo, it was possible to observe a single peak with retention times of 5.163 and 5.183 min, respectively, and two additional peaks: a first peak with a retention time of 3.010 and 3.000 min and a second peak with retention times of 3.123 and 3.140 min, respectively.

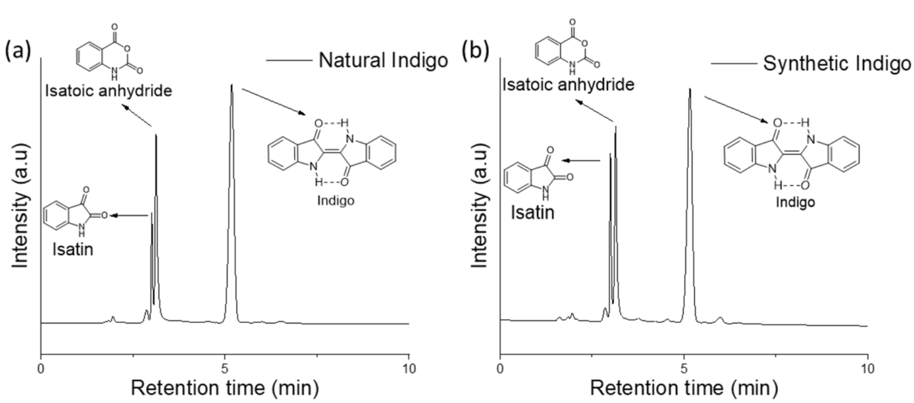

Fig. 3 Chromatograms of the natural indigo (**a**) and synthetic indigo (**b**)

Finally, the EDX analysis of the natural indigo sample revealed the presence of silicon, aluminum, potassium, chlorine, iron, sulfur, and sodium. Kaolinite primarily showed aluminum, silicon, oxygen, and carbon as constituents. Lastly, the composite exhibited elements from both compounds (indigo and kaolinite), thus indicating their coexistence. In Table S1 (Supplementary information), there are presented representative examples of the elemental composition of these compounds.

Fingermarks evaluation

Development of latent fingermarks on different surfaces

This study is a continuation of research conducted by our group, for the development of new fingerprint developers, as in the works of Leitzke et al. (2022), Balsan et al. (2019), da Rosa et al. (2022), da Rosa et al. (2023), Pacheco et al. (2021), Poletti et al. (2021), Venzke et al. (2021), Passos et al. (2021), and Lima et al. (2023). In our studies, the methodology highlights that in the deposit of fingerprints, there is no contact of the volunteers with the chemical products. Figures 4, S3, S4, S5 and S6 (Supplementary information) display the revelation of natural and sebaceous fingerprints from five donors on glass and black plastic surfaces, along with their respective classification scores as identifiable or non-identifiable fingerprints. Accordingly, an excellent pattern of fingerprint revelation was observed on the glass surface. Four natural fingerprints exhibited 1/3 to 2/3 of the ridge detail, rendering them identifiable. Only one natural fingerprint showed limited development, scoring 2. On the other hand, the sebaceous fingerprint demonstrated strong (3) or very strong (4) revelation, making all fingerprints identifiable.

Similar results were achieved on the black plastic surface. Strong development of the ridge patterns and their minutiae led to good scores for most of the fingerprints. Four natural fingerprints exhibited strong development (score 3), showing 1/3 to 2/3 of the ridge detail, allowing for fingerprint identification. Only the natural fingerprint from donor 4 and the sebaceous fingerprint from donor 1 displayed limited development of the ridge details. Factors that may have influenced this limited revelation can vary, from the force applied during deposition being insufficient in the case of donor 4 to excessive force in the case of donor 1, hindering the visualization of minutiae. On the other hand, the other four sebaceous fingerprints scored between 3 and 4.

Development of aged latent fingermarks study

In order to simulate a practical application of the composite as a developing powder, an aging study of fingermarks was conducted. Figs. 5, S7, S8, S9 and S10 (Supplementary information) illustrate natural and

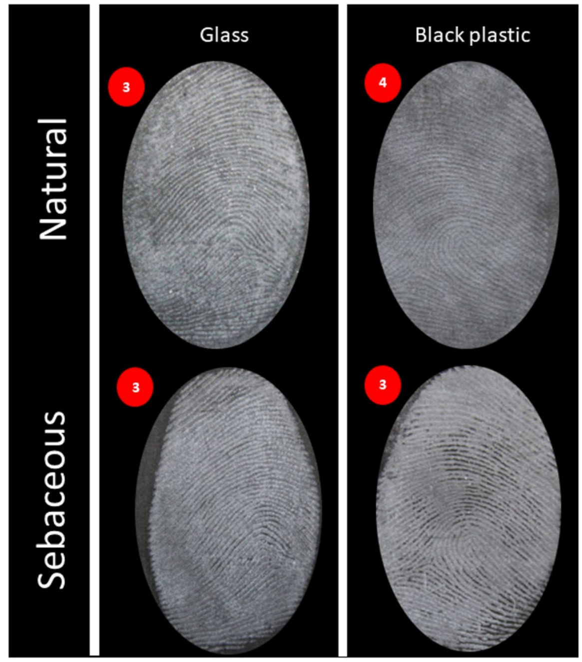

Fig. 4 Development of natural and sebaceous latent fingermarks on glass and black plastic surface from donor 3. The numbers (3 and 4) next to the fingermarks refer to the evaluation of the quality of the development according to the scale developed by Sears et al. (2012)

sebaceous fingerprints revealed on a glass surface after 0, 1, 5, 10, and 15 days. Thus, this study becomes attractive to test a potential developing powder, from which the following results can be observed: the quality of revealing natural fingerprints varied, with some showing better results on days 10 and 15, while others demonstrated superior outcomes on days 0, 1, and 5.

Development of depletion latent fingermarks study

The use of sequential fingermark depletion series, that is, the evaluation of sequential fingermarks from the same finger to generate weaker marks, is a common practice for assessing sensitivity (Almog et al. 2014). Thus, Figs. 6, S11, S12, S13 and S14 (Supplementary information) present the study of latent fingermarks deposited sequentially (1–10). By the results presented, it can be seen that the composite was able to develop identifiable sebaceous fingermarks even after 10 sequential depositions.

Comparison of latent fingermarks developers

To conduct a thorough investigation into the performance of the indigo/kaolinite composite as a potential revealing powder of latent fingermark, a study was carried out that involved comparing natural indigo, the indigo/kaolinite composite, and a commercial fingerprint

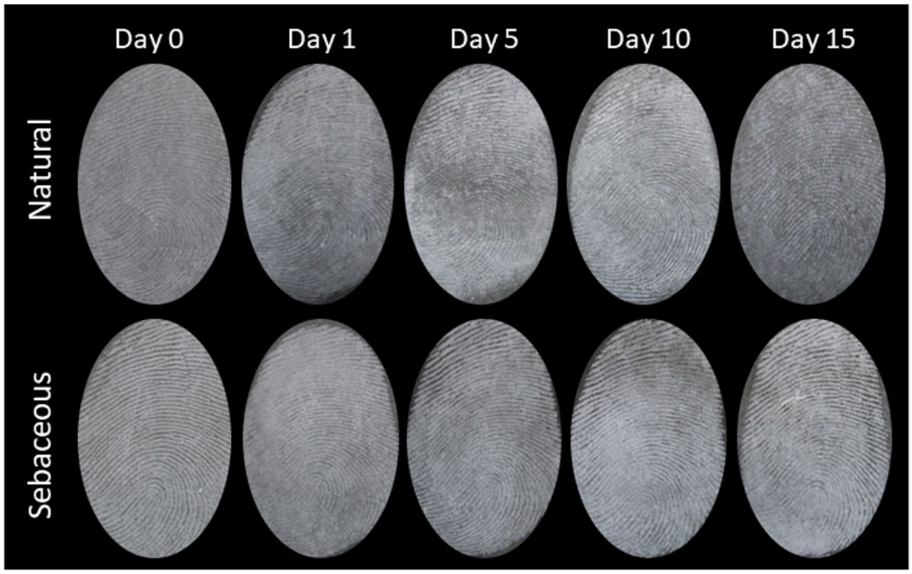

Fig. 5 Development of aged natural and sebaceous latent fingerprints on glass surface from donor 1

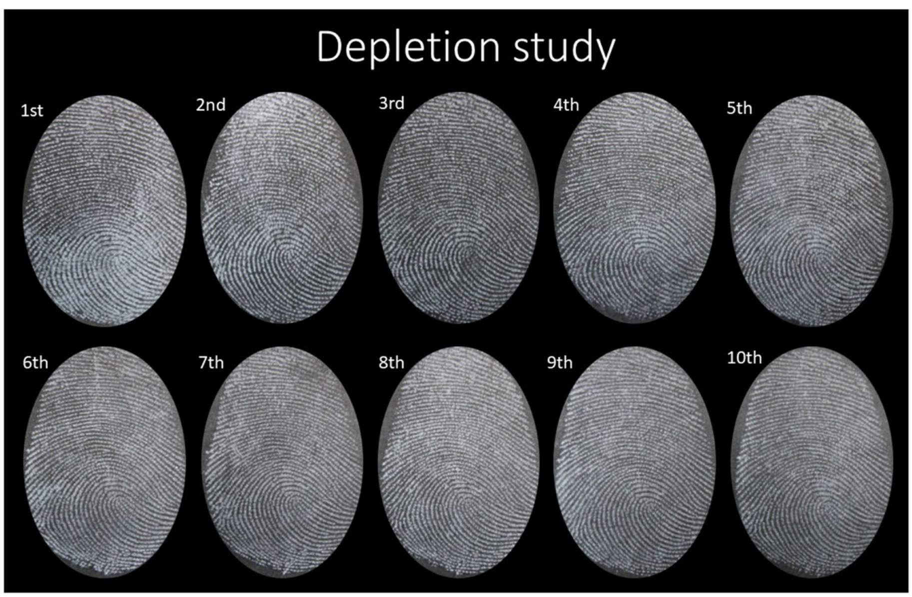

Fig. 6 Fingermarks developed on glass surface for the first until 10th impression in succession

powder (Figs. 7, S15, S16, S17 and S18 — Supplementary information). The indigo/kaolinite showed a good level of development with the possibility of identifying 3/5 natural fingermarks and 4/5 sebaceous fingermarks, while the natural indigo also developed identifiable 3/5 natural fingermarks and 2/5 sebaceous fingermarks.

Compared to the commercial fingerprint powder, it was observed that in the case of natural fingermarks of donors 1 and 2, the composite adhered better to the components of the natural fingermark than the commercial powder, since the right side developed with the commercial powder was not completely revealed, while the left side developed with the composite showed full fingermark development. The other natural fingermarks, on the other hand, showed the same level of detail for both powders, as well as the sebaceous fingermarks.

Laser particle size analysis and SEM imaging

Regarding the physical properties, the granulometric distribution is presented in Table S2 (Supplementary

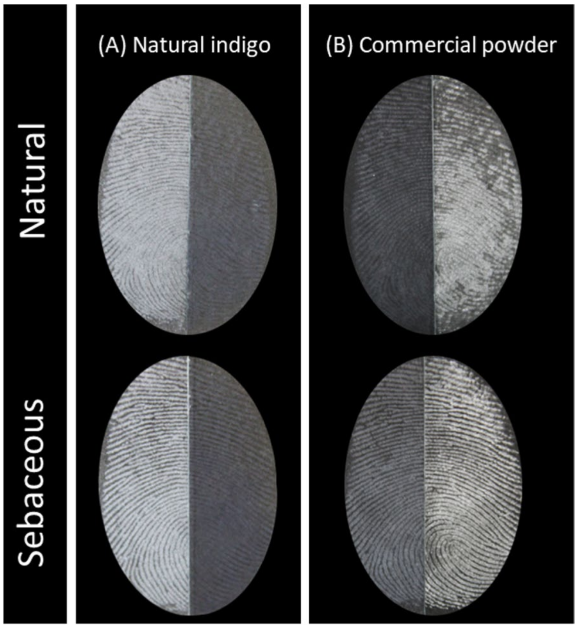

Fig. 7 Comparison of fingermarks from donor 1 developed on glass surface with the indigo/kaolinite composited (left half) and (**A**) natural indigo (right half) and (**B**) commercial powder (right half)

information). Particle size analyses of the composite revealed the lowest particle size at 10% (3.00 µm), 50% (14.37 µm), and 90% (72.97 µm) distributions. For the indigo sample, evaluation of particle size showed values at 10% (3.90 µm), 50% (32.70 µm), and 90% (48.39 µm). Through the SEM images (Fig. 8), it is possible to notice that the indigo/kaolinite composite presented better adhesion properties on the black plastic surface (Fig. 8B and D). While on the glass surface (Fig. 8A and C), there was adherence only with the compounds of the fingermark, being possible to clearly observe the lines of the dermal papillae.

Discussion

Characterization

With the UV–Vis analysis, it was possible to identify the absorption bands of indigo in the composite sample, also observing a lower intensity, possibly related to the presence of kaolinite, which exhibits lower absorption in the UV–Vis spectrum. According to the UV–Vis spectra, the two absorption bands at 260 nm and 287 nm are characteristic of carbonyl and amino groups. The lowest absorption peak and with the longest wavelength (608 nm) is

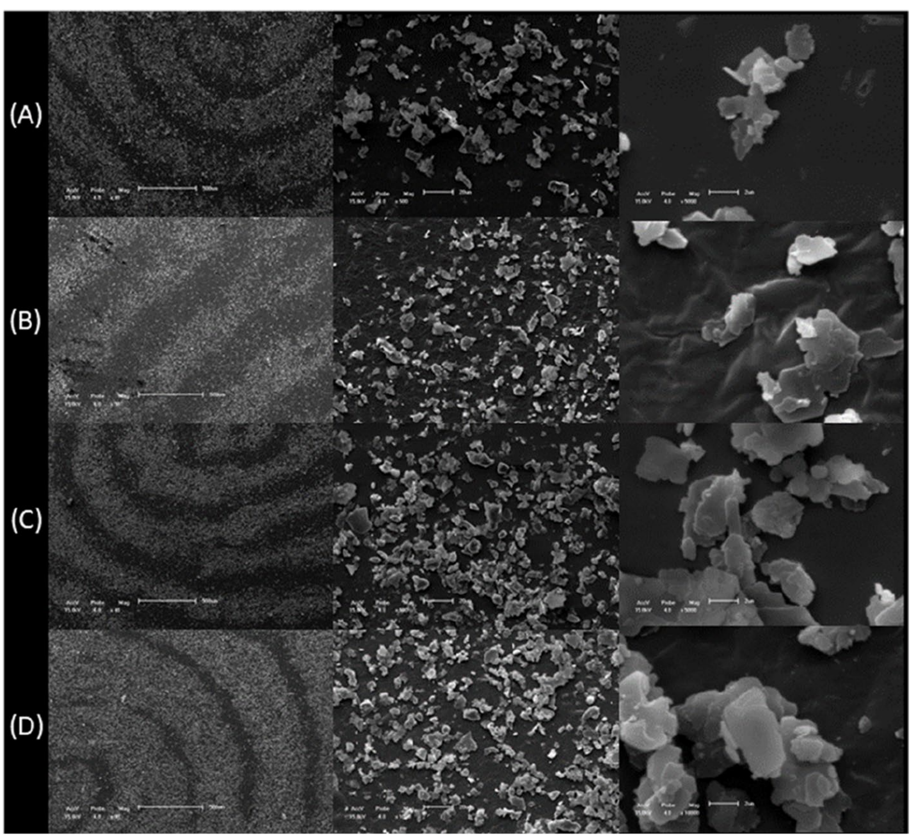

Fig. 8 SEM analysis of natural latent fingermarks developed with indigo/kaolinite composite on (**A**) glass and (**B**) plastic surfaces and sebaceous latent fingermarks on (**C**) glass and (**D**) plastic

responsible for the blue color of indigo, corresponding to the visible region (Ortiz et al. 2016). Finally, due to the indigo molecule being a large conjugated system, it results in a broad absorption peak in the range between 530 and 660 nm, which is consistent with previously reported studies (Ju et al. 2019; Sousa et al. 2008). The small absorption peak observed in the kaolinite spectrum is consistent with what has already been reported in the literature (Wang et al. 2022).

The X-ray diffraction analysis was conducted to determine whether the crystalline phases of indigo and kaolinite would remain preserved after the formation of the composite. According to Fig. 2B, it was possible to verify that the structure remained crystalline. The XRD patterns obtained for indigo confirmed its enantiomorphic orthorhombic structure with a space group P222, plane (2, 2, 2) (Bouzidi et al. 2017; Orthorhombic Space Groups 2023). Regarding the crystalline structure of indigo, the available literature is not plentiful; however, the XRD results are similar to previously described by Michels et al. (2021) and Irimia-Vladu et al. (2012). The results obtained for kaolinite agree with the literature, confirming that the kaolinite clay mineral has triclinic structure (Young and Hewat 1988).

The infrared analysis was conducted to identify the characteristic bands of natural indigo and kaolinite in the composite sample, as illustrated in Fig. 2C and D. In the infrared spectrum of both natural and synthetic indigo, it can be seen a broadband in the range between 3100 and 3500 attributed to the stretching vibration of the N–H bond of primary and secondary amines. The band at approximately 1600 cm^{-1} is related to the C=C bond and the vibration mode in the range of 1350–1000 cm^{-1} to the C–N bond of the aromatic ring. The band at 900–690 cm^{-1} can be ascribed to the C–H bond, also belonging to the aromatic ring (Wahyuningsih et al. 2017).

In addition, the spectrum of kaolinite exhibited vibration modes at 3700 and 3628 cm^{-1}, corresponding to the OH stretching vibration of interlayer water and/or of the octahedral Fe^{3+} environment in the kaolinite structure (Makó et al. 2009). The bands at 3206 cm^{-1} and 1828 cm^{-1} can be assigned to the O–H stretching and bending vibration of adsorbed water, respectively. The peak at 1139 cm^{-1} corresponds to the Si–O–Si stretching vibration. The weak peaks between 900 and 400 cm^{-1} are also related to Si–O–Si bending vibration (Wang et al. 2011), while the band at 559 cm^{-1} corresponds to the Al–O–Si deformation (Nallis et al. 2013).

Regarding liquid chromatography, as described in the literature, the most prominent peak in terms of concentration, meaning the one with the largest area and intensity, corresponds to the compound indigo (Son et al. 2004). This was reflected in the chromatograms of both synthetic and natural indigo, where a single peak with significantly higher intensity and area was observed, with retention times of 5.163 and 5.183 min, respectively. Additionally, the literature also addresses the generation of oxidation products during the photodegradation process, such as isatin and isatoic anhydride. It is widely recognized that isatin tends to display a peak of lower intensity and area, indicating a comparatively lower concentration than that of isatoic anhydride (Novotná et al. 2003).

This behavior can also be observed in the chromatograms of natural and synthetic indigo samples. Apart from the indigo-related peak, two additional peaks were observed: a less intense peak with a retention time of 3.010 and 3.000 min and a second peak with higher intensity and retention times of 3.123 and 3.140 min, respectively. Thus, chromatographic analysis confirms that natural indigo has the same composition as the synthetic indigo sample, with variations only in the concentration of degradation products.

The qualitative analysis of EDS was carried out in order to identify the elements present in the composite and verify if the formulation was obtained successfully. Thus, the elements observed in natural indigo sample are associated with the presence of residual salts and oxides in the *Indigofera* plant, while the leaves contain a significant amount of calcium and phosphorus (Abdel-Ghani et al. 2012). The EDX results of kaolinite corresponded to its chemical formula and being consistent with the literature (Sabbagh et al. 2019).

Fingermarks evaluation

Development of latent fingermarks on different surfaces

As reported, the indigo/kaolinite composite exhibited good adhesion, high contrast, and high resolution. Furthermore, the composite interacted solely with the components of the fingermark, not the surface, making the majority of fingermarks identifiable. Therefore, the obtained results indicate that the composite would be an effective fingermark powder for nonporous surfaces, especially for fingermark impressions with sebaceous secretions, due to its superior development compared to natural fingermark. This is because sebaceous fingermark deposits are composed of fatty acids that can remain adhered to surfaces for a longer period (Archer et al. 2005), and the powders exhibit much higher adhesion.

Development of aged latent fingermarks study

Generally, fingerprints found at crime scenes can be recent or old, depending on when the crime is reported and the investigation begins; therefore, it is important to age the collected fingerprints within realistic timeframes for subsequent development (Girod et al. 2012). To better simulate a routine criminal investigation and assess the sensitivity of the powder's development, tests were also performed over a period of 15 days to observe if it would still be possible to reveal identifiable fingerprints, and the results are shown in Fig. 5.

The most recent fingerprints (days 0, 1, and 5) are revealed due to the interaction of powder with the moisture present, considering that the composition of a recent fingerprint is mostly water (Poletti et al. 2021). However, over the days, part of this water evaporates. It is reported that a fingerprint loses about 85% of its weight after 15 days, mainly due to water loss (Mong, Petersen, and Clauss, 1999). During the aging process, fingerprints interact, through the van der Waals force and hydrogen bonds, with the sebaceous compounds present in the composition of fingerprints; thus, fingerprints can still be developed in an identifiable way. In this context, it can be said that throughout the days, the composition of fingerprints begins to degrade, directly affecting their quality, visualization, and, consequently, the identification of the individual (Poletti et al. 2021).

In this sense, it can be observed that natural fingermarks presented less details compared to sebaceous fingermarks. This can be justified by the aging process (0, 1, 5, 10, and 15 days), where the fingermarks undergo changes from their initial deposition until the moment of their revelation. This can be ascribed to several factors, including the amount of residue from the donor, the form of deposition, the nature of the substrate, climatic conditions, among other factors that make the revelation process challenging (Poletti et al. 2021). In sebaceous fingermarks, the development occurred uniformly, or, in the specific case of a donor, better detail was observed on initial days 0, 1, and 5, due to the better interaction of the powder with the sebaceous compounds present in fingermarks. Thus, the data suggests that the composite was able to develop natural and sebaceous fingerprints after aging for up to 15 days, maintaining efficiency and sensitivity through the period, and, therefore, being a promising powder for developing latent fingerprint.

Development of depletion latent fingermarks study

By the results presented, it can be observed that in general, the initial deposited fingermarks contained a higher amount of sebaceous secretions, resulting in limited development, except for donor 1 (Fig. 6), who exhibited excellent development quality in all deposited fingerprints. Unlike donor 2 (S11) and donor 3 (S12), where the first deposition had a high concentration of sebum, hindering complete visualization of the fingerprint. Furthermore, fingerprints with lower sebaceous content, such as those from 6 to 10, were generally revealed with good detailing, with most being identifiable. Based on these observations, the proposed material demonstrated notable sensitivity, even in relation to subtler sebaceous deposits, making it promising in a forensic context.

Comparison of latent fingermarks developers

This comparison is made possible by using the same fingermark for development with both powders. Consequently, the fingermark maintains consistent chemical composition, substrate quantity, and deposition pressure, thereby eliminating numerous variables that could influence the assessment (Sears et al. 2012). The performance disparity between the natural indigo and the composite is striking, with the composite standing out for its ability to generate a more pronounced contrast. This translates to clearer and easily distinguishable fingermarks. This enhancement can be attributed to the lack of adherence of pure natural indigo and its dark coloration, which fails to provide visible contrast on the glass surface. On the other hand, when compared to the commercial powder traditionally used by the Federal Police, it can be inferred that the composite exhibited a remarkable pattern of excellence in developing latent marks, both natural and sebaceous, on a glass surface. Its performances matched or even surpassed the results achieved using the commercial powder.

Laser particle size analysis and SEM imaging

Based on the results obtained through laser granulometric analysis, a remarkable uniformity in the particle size of the composite sample was evidenced compared to the natural indigo sample. In addition to the consistency in particle dimensions, it is noteworthy that the composite exhibited smaller particle sizes, supporting effective powder adhesion in digital printing. Thus, it can be confirmed that the efficiency of latent fingerprint development is associated with particle size, as smaller particle sizes can establish a larger contact surface with the compounds present in latent fingerprints (Wilshire 1996).

Through the observation of SEM images, it was possible to verify if the fingerprint developer powder interacted only with the components present in the fingerprint and not with the surface. Taking into consideration the SEM images obtained, it can be observed that there is little or no accumulation of dust between the lines of the papillary drawings of the fingermarks, and an identifiable fingermark can be observed. Differences in the results among surfaces can be related to distinct morphologies of the powder. Furthermore, it can be seen that adhesions in both types of fingermarks, natural and sebaceous, revealed with the composite powder on glass and plastic surfaces. According to the results, it can be observed that the papillary groove patterns developed on the glass and plastic surfaces were successfully visualized, providing satisfactory fingermark images. From the results presented and the different tests performed, it can be concluded that the indigo/kaolinite composite developed fingermarks with good visualization quality of the dermal papillae of the donors and had good adherence to the fingermark, which makes it identifiable. The indigo/kaolinite composite displayed interesting results considered in research for new developers: relatively easy process of fabrication, good adhesion on different surfaces, and non-toxicity (da Rosa et al. 2023; Pacheco et al. 2021; Poletti et al. 2021; Yuan et al. 2018).

In addition, in Fig. 9, it is demonstrated the application of the prepared powder on surfaces closer to the ones found in real cases; fingermarks were developed on different objects showing porous and nonporous surfaces such as black and white smartphones, knife, and plastic suitcase. It can be seen that in all materials evaluated, the composite allowed the enhancement of latent fingermarks on light and dark surfaces, as well as porous and non-porous, demonstrating the diverse applicability of the developed powder, making it possible to visualize fingermarks with sufficient contrast to be used for human identification purposes. In order to conclude the evaluation of this compound as a fingermark developer, the minutiae were identified. According to Farias (2010), the fingermark under analysis will only be considered as belonging to a certain individual when 12 to 20 characteristic points coincide between the fingermark under analysis and the fingermark of the person to be identified. Therefore, 12 coincident points were highlighted in Fig. 10.

Conclusions

The objective of this research was to elaborate a material composed of kaolinite, which is an abundant mineral present in kaolin, one of the most important clays present in the soil and in the earth's crust. In addition, the composite has indigo, which is a sustainable dye that can be obtained from the fermentation of the leaves of various species of indigo plants, such as those of the genus *Indigofera* ssp. Therefore, in this paper, natural and sebaceous latent fingermarks went through

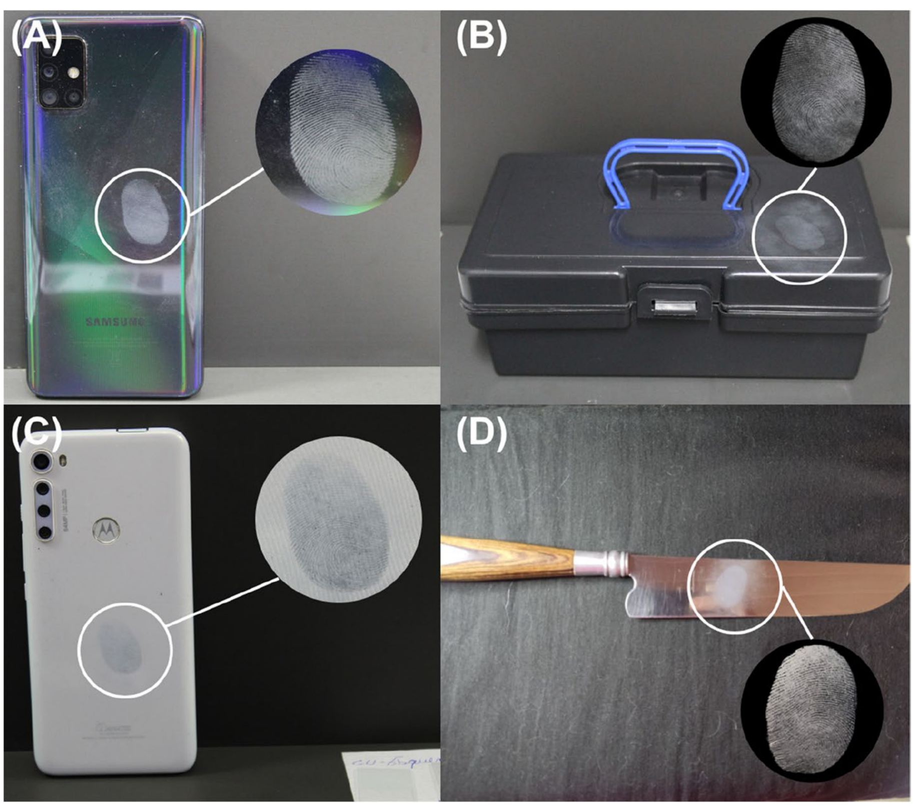

Fig. 9 Development of latent fingermarks using indigo/kaolinite composite on different objects presenting porous and nonporous surfaces such as (**A**) black smartphone, (**B**) plastic suitcase, (**C**) white smartphone, (**D**) knife

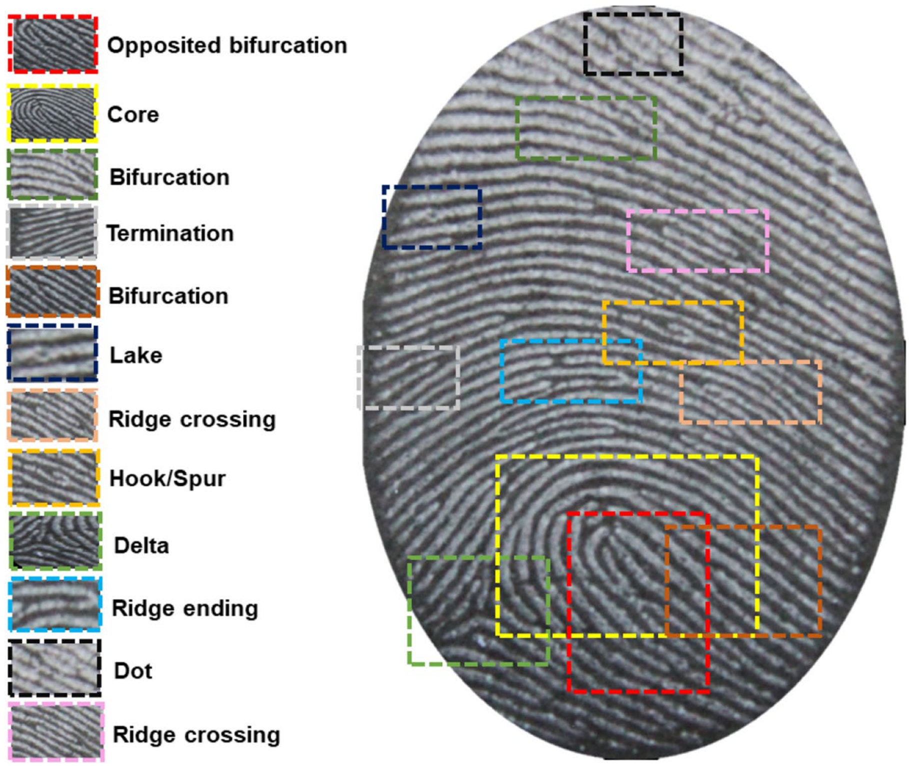

Fig. 10 Fingermark development using indigo/kaolinite composite as dusting powder and their identification of minutiae

different tests aiming to demonstrate the efficacy of the indigo/kaolinite composite as a fingermark developer. It was possible to achieve the main goal of this study, being able to develop identifiable fingermarks on different surfaces. Furthermore, it showed good development of latent fingermarks aged for 15 days, good development of fingermarks with low substrate concentration, and also showed to have the same or higher efficiency when compared to the developer powders already available in the market. Thus, the composite developed in this work provides a huge innovation to the forensic area as it is based on natural materials without any toxicity, besides proposing a methodology efficient, convenient, and cost-effective in terms of fingermark development. In summary, its ability to detect weak and faint fingermarks and its variety of application on different types of surfaces increase its usefulness in real case investigations.

Abbreviations

UV-Vis	Ultraviolet-visible spectroscopy
DMF	N,N-Dimethylformamide
EDX	Energy-dispersive spectroscopy
FTIR	Fourier-transform infrared spectroscopy
SEM	Scanning electron microscopy
XRD	X-ray diffraction spectroscopy

Supplementary Information

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Supplementary Material 1.

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Authors' contributions

AFL, conceptualization, investigation, and writing — original draft. DTP, investigation, data curation, and writing — review and editing. TP, investigation and validation. GKM, data curation, writing — review and editing. BVL, formal analysis. EVM, formal analysis. APOLI, formal analysis. CIS, data curation and visualization. JPS, data curation and visualization. DD, resources and funding acquisition. NLVC, resources and funding acquisition. CMPP, resources, project administration, and funding acquisition. All authors read and approved the final manuscript.

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Availability of data and materials

Electronic supplementary material associated with this article can be found in the online version.

Declarations

Ethics approval and consent to participate
In our study, in the deposit of fingerprints, there is no contact of the volunteers with the chemical products. Besides, there is no toxicity in the substance used. Thus, ethics approval is not applicable. Informed consent has been obtained from the participating individual.

Consent for publication
Consent to publish was obtained from each participant.

Competing interests
The authors declare that they have no competing interests.

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