Communication

Green Composites from Thiophene Chalcones and Rice Husk Lignin: An Alternative of Powder for Latent Fingermark

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Abstract: This study reports a route to obtaining a novel and cost-effective rice husk-derived lignin/thiophene chalcone green composite for application in forensic science as a fingermark developer through high energy milling. The material was properly characterized by UV-Vis, IR, fluorescence, X-ray diffraction and scanning electron microscopy. The product provided clear and sharp images of latent fingermarks with minimal background staining, revealing all ridge details. Thus, the composite presented good performance as a fingermark developer, becoming an interesting alternative to being applied as a technological, reproducible and renewable product.

Keywords: fingermark; lignin; forensic; green chemistry

1. Introduction

Fingerprints have been used as a method of human identification since ancient times due to their uniqueness to each individual and have become fundamental in crime scene investigations as circumstantial evidence for suspect identification [1,2]. When the fingermarks are found in latent form, it is necessary to use a development technique. Currently, there are numerous methodologies, which can be classified into physical or chemical techniques, depending on the type of substrate in which the latent fingermark (LFM) is found [3].

The development of hybrid materials containing two or more phases to generate increased physical and chemical properties is an approach that has been continuously applied in different fields of science [4]. Accordingly, there has been an increasing search for this class of material for fingermark development [5]. As an example, the use of lanthanide doping to obtain core–shell nanoarchitectures [6] and Europium ions doped with calcium hydroxy stannate can be cited [7]; both are studied as fingermark-revealing materials in different surfaces. Other hybrid materials, such as red fluorescent carbon dot powder [8] and doping of Li^+ to improve the luminescence permittivity of green nanophosphor $CaWO_4$:Tb_3^+, are also reported [9]. In this scenario, rice husk is an interesting waste material that can be used for the biosynthesis of gold nanoparticles [10] or for lignin extraction [11]. Moreover, organic molecules, such as curcumins [12] and chalcones [13], have also been efficiently applied in LFM development.

In nature, lignin usually forms ether or ester bonds with hemicellulose that is associated with cellulose. Therefore, these natural polymers build a complex and valuable

lignocellulose polymer [14]. Among the available natural precursors, rice husk has attracted attention due to presence of silica (SiO_2), resulting in a natural organic–inorganic composite, since it also contains cellulose, hemicellulose and lignin [15]. Furthermore, the structural components of lignin make it an attractive resource for value-added products, including carbon fibers, resins, polymers and chemical commodities. Due to the presence of SiO_2, the rice husk lignin (RHL) has already been used as a residual source to obtain silica nanoparticles/curcumin pigment fluorescent composites for the development of latent fingermarks [16]. Similarly, as a potential candidate to be used as latent fingermarks revealers, the use of chalcones is also reported. In particular, the presence of α, β-unsaturation lead at special coloration can be interesting for the development of a novel composite [13]. The application of powders to latent fingermarks has been long established as an effective and reliable method for developing latent fingermarks both in crime scenes and in laboratories. Most studies have focused on the development—or optimization—of conventional detection techniques [17]. Nevertheless, fundamental issues still need improvement and the actual efficiency of detection sequences remains hard to assess when considering non-supervised items (approximately 50% of fingermarks escape detection) [18,19]. The development of new materials to detect LFM through clean chemistry, with low cost of production, high sensibility and low toxicity, seems to be an interesting alternative. Herein, this work describes the development of a novel and green hybrid composite of RHL and thiophene chalcone for application as an LFM development technique.

2. Material and Methods

2.1. Preparation of Rice Husk Lignin and Chalcone Composite

All solvents and reagents used in the synthesis were obtained from Sigma-Aldrich Co., St. Louis, MO, USA. Lignin from rice husk was obtained as previously reported [20]. The chalcone was prepared by mixing 2-acethylthiophene and 4-dimethylaminobenzaldehyde in a solution of sodium hydroxide dissolved in ethanol, which was left stirring at room temperature for 4 h. The solution was then placed in a refrigerator and the precipitate obtained was filtered and washed with cold ethanol, resulting in the pure 4-(4-(dimethylamino)phenyl)-1-(thiophen-2-yl)but-3-en-2-one. For the composite preparation, a solution containing distilled water, chalcone and RHL was added to a dispersing mill for 3 h at room temperature. After this period, the solution was centrifuged and dried in an oven at 50 °C.

2.2. Characterization

All samples were characterized by infrared spectroscopy and a spectrophotometer. Infrared spectra were recorded on a Shimadzu (Japan) infrared spectrophotometer with Fourier transform (FTIR), model IRSpirit, with KBr pads with readings from 400 to 4000 cm^{-1} and 45 scans. The spectroscopic analysis in the ultraviolet/visible (UV-Vis) were performed by a Bel Photonics (Italy) spectrophotometer, model UV-M51, using glass cuvettes with solutions in methanol at a concentration of 10 μM. Absorbance was read at an interval between 200 and 600 nm. The emission spectral profile measurement of chalcone was carried out using a TECAN (Switzerland) Infinite 200PRO spectrofluorometer. The experiment was carried out at 10^{-3} M concentration in MeOH. For scanning electron microscopy, Shimadzu equipment, model SSX-550 Superscan, was used. A glass cover slip was used as a substrate for the deposition of a natural fingermark and developed with the prepared RHL/chalcone. The substrate was mounted on the stub with carbon tape, metallized with gold and analyzed at 15 kV.

2.3. Fingermark Deposition

Glass substrates were used for deposition of fingermarks. Eight donors washed their hands and waited 30 min to perform the deposition. After the deposition, LFM was kept at room temperature for 24 h to simulate a real casework. The development was carried out by powder dusting method using brushes for the development and cleaning of the

excess of powder (132LBW and CFB100 from Sirchie®). Photographs were taken with a semi-professional Canon camera, model EOS Rebel T6, with a distance of 9 cm and focus 5.6.

3. Results and Discussion

Figure 1a shows the UV-Vis spectrum of chalcone, RHL and RH/chalcone composite. A band between 260 and 340 nm related to chromophore groups of conjugated and unconjugated phenolic compounds present in lignin with maximum absorption at 280 nm are observed. For the two samples containing chalcone, an intense band between 360 and 480 nm with maximum intensity at 430 nm can be noticed, transmitting an intense orange coloration, as evidenced in the fingermarks exhibited in Figure 2. The analysis was performed at the same concentration for all samples, but because the compound RHL/Chalcone is a mixture of the m/m ratio of the other compounds, there was a variation in the bands. Furthermore, the composite sample presented respective bands previously described, indicating that the RHL acquired the orange coloration, which is attractive for the LFM development. Although chalcone exhibits high fluorescence emission, as presented in Figure 1b. With the use of lignin for composite preparation along with chalcone, it was not possible to observe this property in the final product.
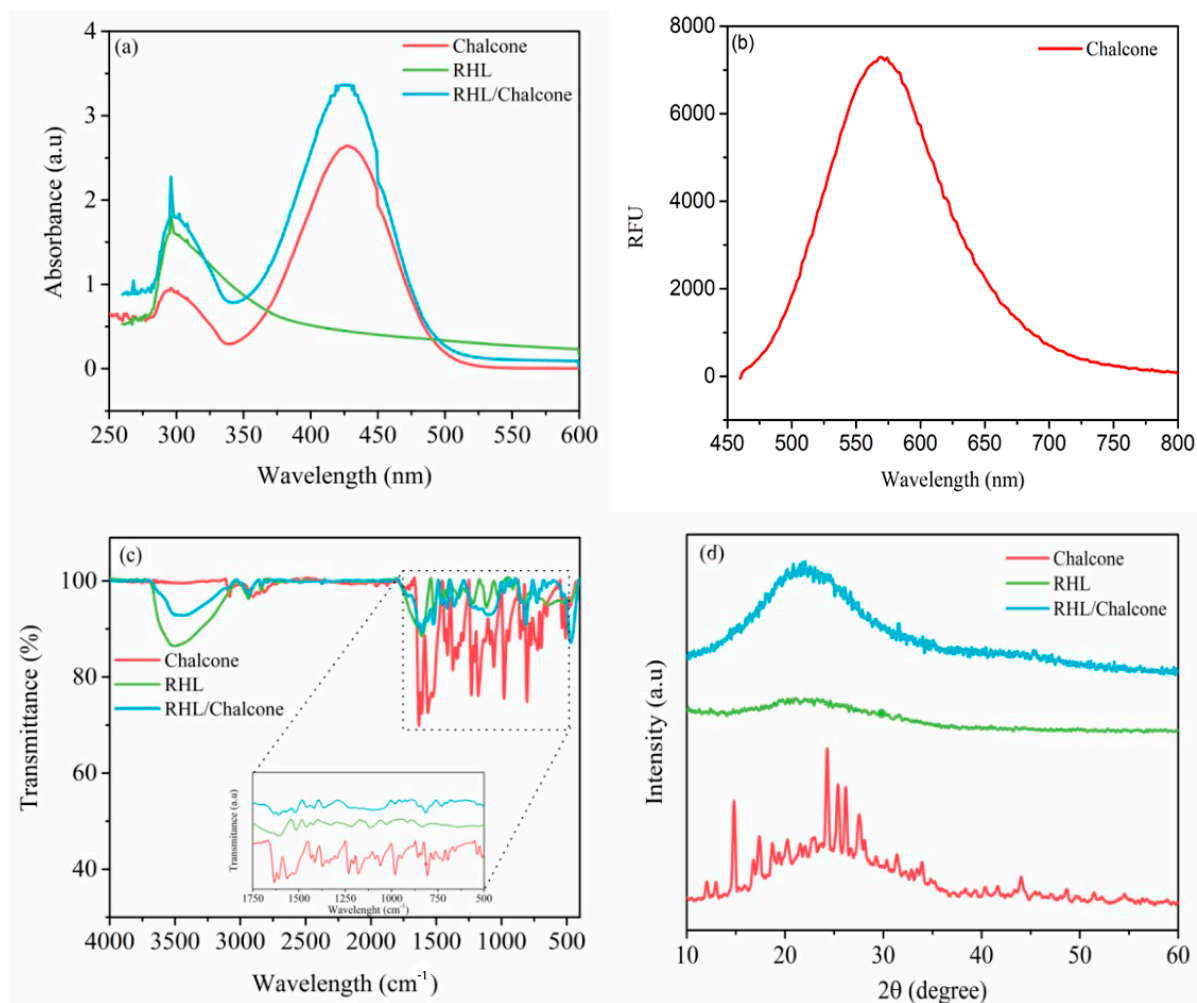
Figure 1. (**a**) UV-Vis spectrum; (**b**) Fluorescence spectrum; (**c**) IR spectrum and (**d**) X-ray diffraction for chalcone, RHL and RHL/chalcone.
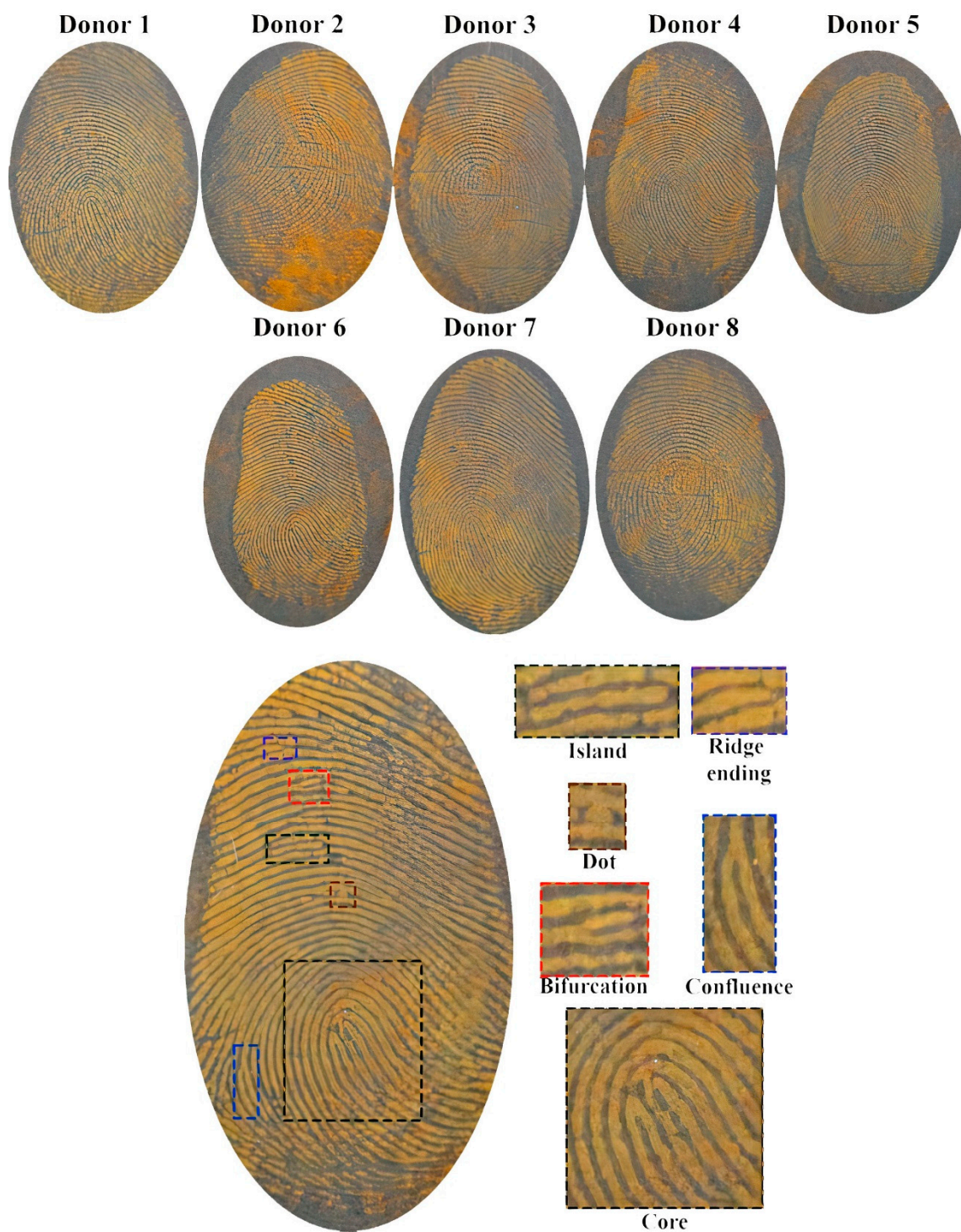
Figure 2. Fingermark development using RHL/chalcone as dusting powder and their identification of minutiae.

The IR spectrum of the samples are shown in Figure 1b. The typical bands associated with different types of hydrocarbons in reaction to vibrations of C-H bonds in CH_3 and CH_2 groupings are observed between 2800 and 3000 cm^{-1}. In the region from 500 and 2000 cm^{-1}, the RHL presented bands at 1712 cm^{-1}, corresponding to unconjugated carbonyl in a guaiacyl (G) unit; 1589–1591 cm^{-1} aromatic ring in guaiacyl and syringyl (S) units; 1417–1421 cm^{-1} C-H stretching in G and S rings in the plane; 1325–1327 cm^{-1} C-O stretching in S units; 1267 cm^{-1} C-O stretching in G units; 1219–1226 cm^{-1} C-C, C-O and C=O stretching in G units; 1159–1161 cm^{-1} C=O stretching in ester grouping; 1126–1128 cm^{-1}

aromatic ring stretching in G units; 1091–1095 cm^{-1} C-O stretching in secondary alcohols or aliphatic ethers; 1033–1039 cm^{-1} C-O stretching in methoxyl grouping; and 835–839 cm^{-1} out-of-plane C-H stretching in G and S units [21]. The chalcone exhibited bands at 1820 and 1600 cm^{-1} related to the carbonyl C=O functional groups, which are assigned to axial strain vibrations, C=C bonds at 1650 cm^{-1} and a strong band between 1650 and 1450 cm^{-1} related to aromatic rings. Similarly, for RHL/chalcone, the aforementioned overlapping of the bands was noticed.

The crystal structure of the materials was further studied by X-ray diffraction and the XRD patterns of chalcone, RHL and chalcone/RHL are shown in Figure 2c. As expected, the results for chalcone reveals several sharp and intense peaks, indicating the existence of long-range structural order within the solid state [22]. Differently, the diffractogram of RHL showed the typical amorphous characteristic of lignin, with a large band at approximately 2θ = 22°. For the RHL/chalcone sample, the predominance of the amorphous characteristic was maintained, with no evident peaks observed in the XRD pattern.

The images of the fingermark development are shown in Figure 2, clearly evidencing the existence of drawings belonging to the dermal papilla of each donor. According to the Sears classification, the fingermark can be classified as very strong development, full ridge details and identifiable fingermarks [23]. Additionally, due to the high coloration of the material, a good contrast differentiating the fingermark from the substrate was obtained. In addition, the powder can also be applied on other surfaces, as in Figure 3, where it is possible to observe fingermarks developed on glass, cardboard and ceramics. The scanning electron microscopy (SEM) images of the fingermarks were developed with RHL/chalcone, as shown in Figure 4.

Figure 3. Fingermarks developed with RHL/chalcone on objects, such as (**a**) cell phone (glass); (**b**) box (cardboard); (**c**) mug (ceramic).
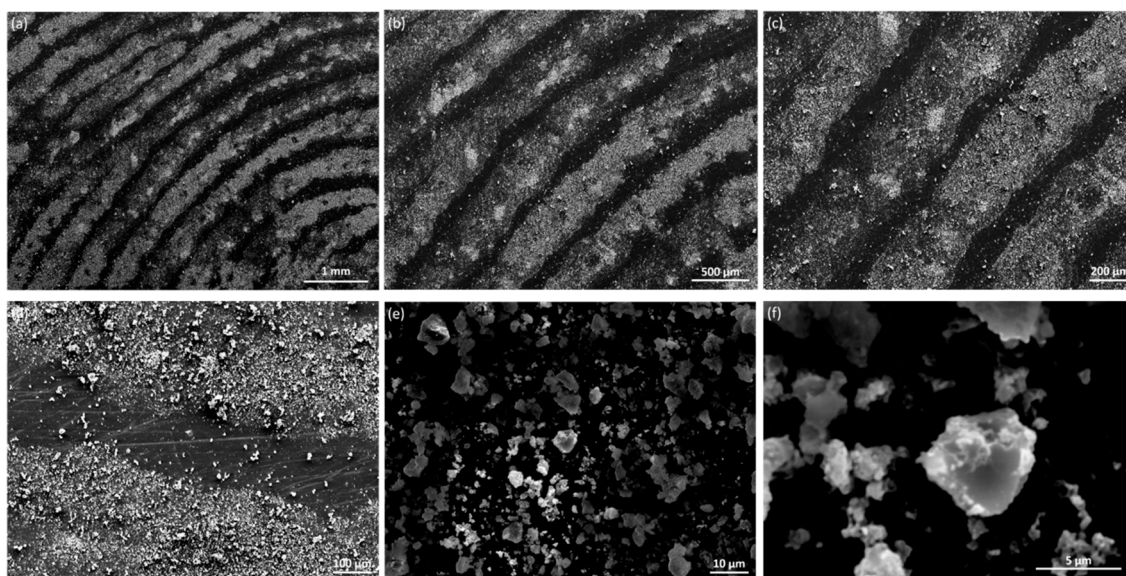
Figure 4. (**a–f**) SEM images of fingermarks developed with RHL/chalcone.

Through the SEM images, it noticed that there is little or no dust accumulation between the lines of the fingermark designs, resulting in high-qality image formation. Moreover, on the fingermark lines, small circular holes can be observed, which are result of the pores from human sweat glands. Thus, the material exhibitted small rounded crystals morphology, which might be related to the crystal structure of chalcones and the conglomerate shape usually found during lignin formation [24]. Furthermore, these results demonstrate that the RHL/chalcone powder do not overaccumulate in the regions where the particles are stacked in the fingermark, avoiding excessive powdering, which can make the visualization difficult [25].

Thus, a new composite was obtained from a fluorescent chalcone and rice husk lignin. This material was characterized by UV-Vis, IR, fluorescence, X-ray diffraction and scanning electron microscopy. The chalcone used presents fluorescence, but the final product with the presence of lignin does not. However, the compost was applied efficiently to develop fingermarks that could be used for human identification. The material also showed adherence to fingermarks and different surfaces. Scanning electron microscopy confirms that the material shows affinity for fingermarks and not with the surface. Thus, the proposed material is an interesting alternative for the area of papiloscopy, which can be obtained on a large scale and also offers a certain level of sustainability due to the use of lignin from rice husk, which otherwise would be a waste product.

4. Conclusions

A simple, rapid and cost-effective approach was presented for visualizing LFM on different surfaces. The novel hybrid rice husk lignin/chalcone composite resulted in clear and sharp images of LFM with minimal background staining, revealing all ridge details. Moreover, the developing powder presented good reproducibility and can be easily prepared in large quantities. In terms of future perspectives, an investigation with a greater number of donors, evaluating different aging times and fabricating fluorescent developing powders would be worthwhile. Additionally, this material can promote siginificant advances in the area of papiloscopy as a development powder, especially in emerging countries, contributing to forensic sciences and case elucidation.

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