Photocatalyst Immobilization On Vegetable-tanned Bovine Leather: A Methodology Development

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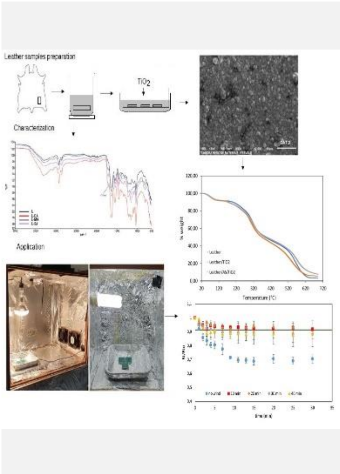

Aiming to achieve self-cleaning properties, this work evaluated the use of polycarboxylic acids as chemical binders for TiO_2 immobilization on leather surfaces. A methylene blue photocatalyst activity indicator ink (PAII) was used to test the photocatalytic activity of the leather samples. The change in color ink was registered through digital images and evaluated by RGB spectra. Through an innovative methodology, the researchers used a wind tunnel to investigate the strength of the bond between the catalyst and the leather surface. The samples were characterized through SEM and FTIR-ATR. The results demonstrate that polycarboxylic acids act like binders between collagen fibers and TiO_2 particles, increasing photocatalyst mass deposition and consequently, photocatalytic activity. The wind tunnel was an easy-to-use and reliable methodology, however, indicated the lower resistance of surface-catalyst bonding. It was also demonstrated that the use of *paii* on the leather surfaces was an efficient methodology, which can measure the photocatalytic activity with good reproducibility.

Introduction

Leather is a material widely used in our daily lives and due to its high moisture absorption and organic matter, it is suitable for microorganism growth [1]. The incorporation of nanomaterials is often used to achieve functionalities such as self-cleaning, photocatalytic, and antimicrobial surfaces in fibers or fabrics [2]. Different methodologies have been used to immobilize photocatalysts into leather [3]. One of the main challenges of these methodologies is the bond fragility between the photocatalysts and the surface, which can be easily damaged or removed by abrasion and washing [4]. In this work, polycarboxylic acids were used as binders to immobilize TiO_2 on leather surfaces, achieving self-cleaning properties.

Material and Methods

Polycarboxylic Acid (PA) Treatment

Samples (4 x 4 cm^2) of bovine vegetable-tanned leather were immersed in succinic acid solutions, in the presence of NaH_2PO_2 as a catalyst (4%wt), according to the parameters: concentration (1%, 3%, and 5% wt), immersion time (1h, 3h, and 5h), and curing temperature (30°C).

The leather samples were immersed in an aqueous solution of TiO_2 5 g L^{-1}, previously sonicated for 30 min, for 1 h. After photocatalyst deposition, the samples were dried at room temperature.

Leather samples characterization

The leather samples were analyzed using a Fourier transform infrared (FTIR) and thermogravimetric analysis (TGA).

Photocatalytic Activity of Leather Samples

A methylene blue photocatalyst indicator ink (*paii)* was prepared according to [5], and 2 mL was placed on the leather sample surface. The photocatalytic activity was evaluated by *paii* reduction using a solar simulation lamp. The color decay was registered through digital images, being analyzed by *Image J* software, to obtain a blue color fraction of the RGB (red, green, blue) spectral colors. The method measures the change in the normalized value of the blue fraction B_t (1).

$$B_t = \frac{RGB_{blue}}{RGB_{blue} + RGB_{red} + RGB_{green}} \qquad (1)$$

To eliminate the effects of variation in the initial paint shade, the data were adjusted by B_t/B_{t0}, where Bt_0 is the measure of the normalized blue fraction at t=0. Tests were conducted in a wind tunnel to assess the resistance of the photocatalyst layer immobilized on the leather surface. The wind speed was approximately 5 $m.s^{-1}$ and the exposure time ranged from 10 to 40 minutes.

Results and Discussion

FTIR/-ATR analysis

Figure 1 shows that, in the presence of PA, no changes were observed in the collagenic structures of leather samples.

On cotton fibers, a band at 1700 cm^{-1} showcased the binding between the -OH groups of cellulose and the carboxylic groups of the binders through an esterification reaction [6].

Thus, the spectra of leather samples treated with PA suggest the esterification processes of leather collagen with the carboxylic groups of succinic, citric, and maleic acids.

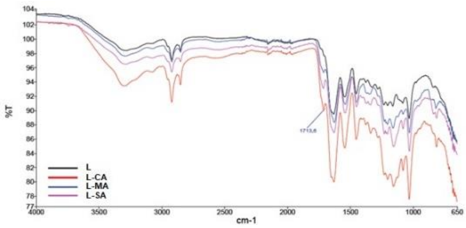

Figure 1: FTIR of leather samples

TG analysis of leather samples

The TG curves of treated and untreated leather are shown in Fig 2. Although the shape of TG curves looks quite similar, a difference in residual yields can be observed. Succinic acid treatment resulted in a higher residual yield, indicating that PA favors TiO_2 immobilization, leading to an improved mass deposition.

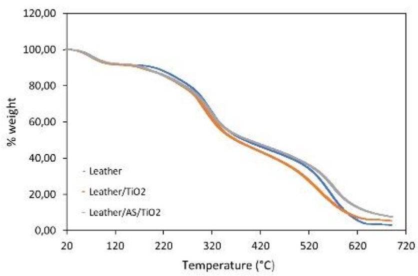

Figure 2: TGA curves of leather samples

Photocatalytic Activity of Leather Samples

The leather samples showed increased photocatalytic activity after being immersed in succinic acid for 1 hour, resulting in 30% photoreduction in just 30 minutes of irradiation. Values of approximately 16% and 12% were obtained for samples immersed for 2 h and 3 h, respectively. (Figure 3).

An increase in succinic acid concentration results in a decrease in photocatalytic activity, which is evident from Figure 3. When the concentration is at 5%, a.nd the immersion times are 2 hours and 1 hour, the activity is comparable to the degradation achieved without the acid (around 7% degradation), as shown by the blue line.

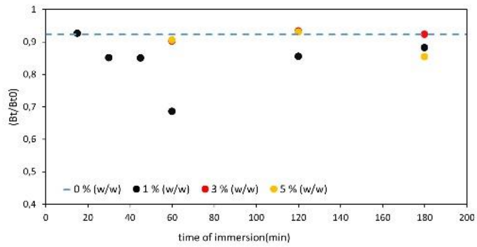

Figure 3: Comparison of (Bt/Bt0) Comparison of (Bt/Bt0 values after immersion in succinic acid solution at different concentrations (%wt) and times

The photocatalytic activity decreases in leather samples exposed to wind for 10 minutes or more, becoming similar to untreated samples. This could be explained by the loss of TiO_2 mass during wind exposure, which reduces photocatalytic activity

Conclusions

In this study, TiO_2 was immobilized on the leather surface using succinic acid as a chemical binder. FTIR-ATR and TGA analysis confirmed that PA binds to collagen fibers without damaging the leather structure, improving mass deposition and photocatalytic activity. A new paii methodology was used for measuring photocatalytic activity on leather surfaces with good reproducibility. The optimal conditions for succinic acid treatment were determined to be immersion in a 1% (wt.) solution for 1 hour, followed by curing at 30°C. Although it has been established that polycarboxylic acids act as binders on TiO_2 immobilization onto collagen fibers, a wind tunnel test revealed that the longer the exposure time to wind, the lower the photoactivity became, and this was correlated with a decrease in the amount of photocatalyst mass on the surface.

References

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