Zinc Oxide Nanoparticles in Leather Conservation: Exploring the Potential of Hydroxypropyl Cellulose/Zinc Oxide Nanocomposite as a Leather Consolidation Agent

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Abstract: This research presents a comprehensive study on the application of hydroxypropyl cellulose/zinc oxide nanocomposite (HPC/ZnO NC) as an effective consolidant in leather conservation. The critical focus is to prevent photooxidative degradation, a significant challenge in preserving historical leather artifacts. The nanocomposite was evaluated for its protective capabilities against environmental stressors like UV radiation and moisture, mechanical robustness, and potential to stabilize acid-damaged leather. The uniform dispersion of ZnO NPs in the HPC matrix was revealed as crucial for improving leather properties, which was confirmed through SEM imaging. The HPC/ZnO NC coating effectively prevented UV-induced microcracks, surface degradation and collagen denaturation. It also demonstrated enhanced mechanical resistance, inhibiting the reduction in leather’s maximum tolerable force and increasing the elongation index, even after aging. Additionally, it exhibited improved water-repellent properties and increased the pH of the leather, offering potential benefits for the treatment of acid-degraded leathers. Overall, the findings affirm that the application of HPC/ZnO NC significantly augments the physical and mechanical properties of leather, providing enhanced resistance to environmental degradation.

Keywords: leather conservation; hydroxypropyl cellulose; zinc oxide nanoparticles; nanocomposite; photooxidative degradation; mechanical properties

1. Introduction

Leather has been used for various purposes for thousands of years [1,2], but it is a perishable material that can deteriorate due to biological attacks, chemical attacks, physical factors such as temperature, humidity, and light, and improper storage and handling. Mold, mildew, insect infestation, pollutants in the air, and chemicals used in the tanning process can cause discoloration, stiffness, cracking, and a loss of strength and flexibility. Exposure to high temperatures and humidity can cause the leather to shrink and become brittle, while exposure to light can cause fading and discoloration. Storing leather in a damp or humid environment can promote mold growth, while folding or creasing leather can cause it to crack and weaken over time [3,4].

During the 19th century, the industrial revolution and rising demand brought about significant changes in the process of making vegetable leather. This included the increased use of condensed tannins, sulfur-containing compounds, and strong mineral acids like sulfuric acid, resulting in the production of unstable leathers [5]. Additionally, an increase in industrial air pollutants, which caused complex chemical processes and especially oxidation, became a major contributor to the destruction of historical objects, particularly leather [6]. These factors led to rapid chemical degradation and decay of leather products, primarily due to acid hydrolysis or acid degradation, also known as red rot. This damage
is caused by the hydrolysis of condensed tannins and leads to irreversible destruction, reducing the strength and thermal stability of the leather while increasing its acidity and creating a red color [7,8]. Unfortunately, conventional leather dressings are usually unable to improve this damage [9,10].

For a long time, various methods have been suggested and studied to address the acid degradation of vegetable-tanned leather [11–15]. These methods date back over a century. The majority of treatments and historical cases used in leather protection can be categorized based on their effectiveness into three groups: stabilizing agents, consolidation agents, and surface coatings [16]. Consolidants are commonly utilized in this field, not just for acid-damaged leather. Klucel G is the most notable, extensively used, and favored consolidating agent for leather conservation, serving a broad range of purposes [16–18].

Klucel G, known as hydroxypropyl cellulose (HPC), has been used as a conservational adhesive in leather and historical fabric conservation since the early 1980s [19,20]. It was first introduced by Cains in 1981 [21,22] for leather consolidation and has since been widely used in America and parts of Europe, especially in bookbinding conservation [16,23,24]. Klucel G is typically prepared as a solution in industrial methylated spirits (IMS), ethanol, or isopropanol, or in cellugel form [16,25]. It is commonly used for the treatment of acid degradation in protein-based materials, but there are concerns about its lack of proper efficiency and stability in acidic conditions [16]. While it causes minimal changes in the appearance of leather, it can decompose and harden over time, leading to further damage [26].

In prior research, it was found that HPC is susceptible to photooxidation, which can be addressed by optimizing its properties and rectifying its flaws [27–29]. One possible approach is to utilize it as a nanocomposite, and nano zinc oxide has demonstrated promising results in the conservation of artworks [30–32].

Nano zinc oxide (ZnO) and its composites with cellulose ethers are effective solutions for art conservation due to their unique physical, chemical, and antimicrobial properties [33–35]. ZnO nanoparticles protect artworks from UV-induced degradation and prevent biological deterioration caused by microorganisms [36–39]. However, direct application of ZnO nanoparticles can cause alterations in the original appearance. To address this issue, ZnO composites with cellulose ethers have been developed, which maintain the beneficial properties of ZnO while retaining the original aesthetics of the artwork [40,41]. These composites have shown promising results in preventing color fading and inhibiting the growth of fungi on artworks. Overall, nano zinc oxide and its composites with cellulose ethers are innovative and promising materials for art conservation.

Therefore, the aim of this study was to evaluate the efficacy of zinc nanoparticles in enhancing the properties of Klucel G, which was tested as a consolidating agent for historical leather to prevent photooxidative degradation. The investigation included analyzing various characteristics of the nanocomposite, such as its impact on tensile strength, pH level, water droplet contact angle, and changes in microstructure using ATR-FTIR spectroscopy and SEM. This research can significantly contribute to broadening the application of nanocomposites and enhancing their effectiveness in preserving historical leather artifacts.

2. Materials and Methods

2.1. Leathers

In this research, sheepskin-tanned leather with mimosa extract from Behtar Leather Co., Tabriz, Iran was utilized. Samples were obtained from the flank region of the animal and cut into 25 × 5 cm dimensions, parallel to the collagen fibers direction. To ensure consistency in sample thickness, measurements were taken at three points and compared to the mean. Any samples that deviated from the mean + standard deviation range were considered outliers and excluded from the study. Each treatment had five replicates.
2.2. Treatment Materials

In order to preserve leather, a popular consolidant called hydroxypropyl cellulose (HPC) or Klucel G was utilized. HPC was dissolved in isopropanol (Merck, Darmstadt, Germany) at a concentration of 1% and stirred for three hours. ZnO nanoparticles (purchased from US-Nano) were also dispersed in isopropanol for three hours before being added to the HPC container at a ratio of 2% (w/w). The mixture was stirred for an additional 3 h to create a nanocomposite solution (HPC/ZnO NC). The treatment involved applying two layers of the solution onto the grain layer of the leather using a brush, allowing each layer to dry before applying the next.

2.3. Accelerated Aging

To assess the effectiveness of treatments over time, an accelerated aging process was carried out using a 60 cm long black UV lamp with a UV-A range. The lamp was placed in a box and the samples were positioned 20 cm away from it. The irradiation lasted for 72 h with the temperature inside the box being maintained at around 35–40 °C. Once the process was complete, the samples were taken out of the UV box and analyzed.

2.4. Contact Angle Measurement

Contact angle measurements were performed using a Jikan CAG-10 goniometer (Jikan Co., Tehran, Iran) that was connected to JikanAssistant software Ver. 7.3.2. Five droplets of deionized water with a volume of 10 µL and an injection rate of 1 µL/s were deposited onto the surface of each sample via a syringe pump. Images of the droplets were captured after a 2 s interval. The mean value of the measured contact angles for each sample was calculated and utilized for subsequent data analysis.

2.5. Uniaxial Tensile Test

The leather samples underwent a uniaxial test following the ISO 3376 standard [42], using bone-shaped samples with standardized “large” dimensions. The SANTAM STM5 testing machine (SANTAM Co., Tehran, Iran) was used, with a jaw separation speed of 100 mm/min. To ensure statistical significance, five samples were tested, all cut perpendicular to the backbone and stretched until ultimate damage.

2.6. Colorimetry

This study examined the color changes caused by various treatments and the effects of accelerated aging conditions on the samples using an NH300 colorimeter (Shenzhen Threenh Technology Co., Ltd., Guangzhou, China) in the CIE L*a*b* space. For each sample, 5 analysis points were examined, and the average data obtained was used for further analysis.

2.7. Scanning Electron Microscopy

The scanning electron microscope (SEM) was utilized to examine the leathers and determine the thickness and microstructure of the treatment film. Samples measuring 2 mm in side length were coated with gold and inspected using the MIRA3 field emission scanning electron microscope from TESCAN in the Czech Republic.

2.8. ATR-FTIR Spectroscopy

The Nicolet 470 FTIR spectrometer and OMNIC 6.1a software (Nicolet Instrument Corporation, Madison, WI, USA) were utilized for conducting ATR-FTIR analysis. The system was equipped with a PIKE MIRacle attenuated total reflectance (ATR) accessory featuring a diamond crystal plate. The analysis was performed on the surface of leathers, with 64 scans taken at a resolution of 4 cm⁻¹ in the range of 1800–600 cm⁻¹.
3. Results and Discussion

The dispersion of nanoparticles in the HPC matrix is crucial in determining the properties of the nanocomposite. In this study, the SEM image shows that the dispersion of zinc oxide nanoparticles on the HPC matrix is uniform and well-distributed (Figure 1). This uniform dispersion can be attributed to the appropriate synthesis of the nanocomposite, which is essential for improving the properties of leather and creating a transparent film. This film can act as a protective layer, shielding the leather from environmental factors such as moisture and UV radiation, while also enhancing its mechanical and physical properties. The transparency of the film is also beneficial for leather products, as it allows the natural texture and color of the leather to be visible. The cross-sectional view provides additional insights into the thickness of the coating layer on the leather. The thickness of the coating layer is crucial in determining the durability and strength of the leather. In this study, the coating layer thickness was found to be approximately 9 µm, which is relatively high. This can be attributed to the brush treatment, which was repeated to enhance the strength of the leather. The high thickness of the coating layer can contribute to the improved mechanical and physical properties of the leather, making it more durable and long-lasting.

Figure 1. Scanning electron microscopy (SEM) images; (a): cross-sectional view of leather treated with HPC/ZnO NC, revealing the presence of a 9-micrometer film on the surface of the leather; (b): corresponding surface image of the same leather depicting a homogeneous distribution of ZnO NPs in the HPC matrix. The HPC film on the leather surface is indicated by the arrows.

Figure 2 illustrates the effect of accelerated aging on the surface of neat (untreated) and treated leather. The SEM image of neat leather shows dispersed microcracks, which are clear indicators of surface layer degradation caused by UV radiation. In contrast, the HPC-coated samples exhibit partial prevention of microcrack formation. However, the impact of UV radiation on these samples results in the deformation of the HPC film.

Conversely, the leather coated with the HPC/zinc oxide NC displays significantly minimized morphological changes on the surface of the leather. A smooth layer is still visible on the leather, indicating the effectiveness of the nanocomposite in protecting the leather from UV radiation-induced degradation. These findings indicate that the zinc oxide/HPC NC coating can effectively prevent the formation of microcracks and surface layer degradation caused by UV radiation.
When zinc oxide is added to a solution of HPC, it can protect leather from degradation by effectively absorbing and dispersing UV radiation due to its exceptional UV absorption properties [43–45]. Additionally, ZnO nanoparticles possess photocatalytic characteristics that enable them to counteract free radicals responsible for leather damage [48]. Therefore, when combined with HPC matrix, ZnO nanoparticles create a film that protects leather from photooxidation.

The chemical structure of leather was analyzed through ATR-FTIR spectroscopy (Figure 3). The spectra of leather typically show vibrations of amide I, II, and III at around 1650, 1550, and 1240 cm$^{-1}$, respectively [3,12,49]. The ratio of amide I to II peak intensities can indicate collagen hydrolysis [50,51], while the distance between their positions can indicate collagen denaturation/gelatinization [52,53]. The ratio of amide III intensity to the peak at approximately 1450 cm$^{-1}$ can indicate the collagen triple helix’s integrity [52–55]. The use of HPC increases the absorbance band intensities within the range of 900 to 1200 cm$^{-1}$, indicating various C-O vibrations in the HPC structure [27]. However, aging causes
1200 cm\(^{-1}\), indicating various C-O vibrations in the HPC structure [27]. However, aging causes a decrease in these peak intensities, indicating HPC degradation. Additionally, an increase in carbonyl vibrations around 1730 cm\(^{-1}\) can indicate HPC oxidation in these samples [27,56]. Due to overlapping peaks of collagen, HPC, and the finishing layer of leather, only the denaturation index based on the amide bands I and II positions can be verified. The difference in the position of these two peaks in the collagen FTIR spectrum is approximately 100 cm\(^{-1}\). The difference between these two peaks, known as \(\Delta \nu\), is an indicator of collagen denaturation that increases with degradation [12,50,53,57–60]. The second derivative was used to determine the precise positions of these peaks, and the \(\Delta \nu\) values for the samples before and after accelerated aging are presented in Figure 4. As illustrated in the figure, accelerated aging of both neat and HPC-treated leather resulted in increased denaturation, while HPC/ZnO NC treatment effectively prevented this change to a significant extent. The rise in \(\Delta \nu\) in the spectra of untreated leather and leather treated with HPC after accelerated aging can be noted, however, using other methods such as DSC, which can offer a better understanding of the denaturation of leathers.

Figure 3. ATR-FTIR spectra of the surface of neat and treated leathers, before and after accelerated aging (A-), following baseline correction and normalization within the range of 700–1850 cm\(^{-1}\).

Figure 5 displays the colorimetric results and pH measurements of the samples. After accelerated aging, there is not a significant difference in color changes between neat and treated leathers. The quantity of color changes resulting from accelerated aging in the samples studied is actually very similar, and there are no noticeable differences in their \(\Delta E^*\) values. The primary reason for color changes is the oxidation of condensed mimosa tannins, resulting in red leather. This is evident in the notable rise of parameter \(a^*\) following accelerated aging. Furthermore, the leather has become darker as a result of accelerated aging, which is evident in the decrease in the \(L^*\) parameter. Similarly, pH measurements do not show significant differences between the samples. However, the leather treated with HPC/ZnO NC displays an increase in pH after aging, indicating that this treatment may be useful in consolidating acid-damaged leathers.
a decrease in these peak intensities, indicating HPC degradation. Additionally, an increase in carbonyl vibrations around 1730 cm\(^{-1}\) can indicate HPC oxidation in these samples [27,56]. Due to overlapping peaks of collagen, HPC, and the finishing layer of leather, only the denaturation index based on the amide bands I and II positions can be verified. The difference in the position of these two peaks in the collagen FTIR spectrum is approximately 100 cm\(^{-1}\). The difference between these two peaks, known as \(\Delta \nu\), is an indicator of collagen denaturation that increases with degradation [12,50,53–60]. The second derivative was used to determine the precise positions of these peaks, and the \(\Delta \nu\) values for the samples before and after accelerated aging are presented in Figure 4. As illustrated in the figure, accelerated aging of both neat and HPC-treated leather resulted in increased denaturation, while HPC/ZnO NC treatment effectively prevented this change to a significant extent. The rise in \(\Delta \nu\) in the spectra of untreated leather and leather treated with HPC after accelerated aging can be noted, however, using other methods such as DSC, which can offer a better understanding of the denaturation of leathers.

Figure 4. The difference in wavenumber between amide I and II peaks can be used as an indicator of collagen denaturation. Results indicate that the use of HPC/ZnO NC prevents this change caused by accelerated aging, unlike HPC and neat leather.

Figure 5. Color index (top) and pH (bottom) changes resulting from treatment and accelerated aging.

The results presented in Figure 6 show the average water drop contact angle. The application of HPC has led to a significant increase in the contact angle of leather, from
The results presented in Figure 6 show the average water drop contact angle. The application of HPC has led to a significant increase in the contact angle of leather, from approximately 58° to 73°, indicating an improvement in its water-repellent properties. In addition, the performance of HPC has been further improved by incorporating zinc oxide nanoparticles. These nanoparticles have a hydrophobic nature, meaning they repel water. When they are added to an HPC film, they create a rough surface, which increases the contact angle of the film. This roughness prevents liquid from spreading and reduces its contact with the film. As a result, the contact angle increases, indicating greater hydrophobicity. The nanoparticles also form micro- and nanostructures that trap air and create small pockets of space between the liquid droplet and the film, further reducing the contact area and increasing the contact angle [61–63].

![Figure 6](image-url) Changes in water droplet contact angle due to treatment and accelerated aging demonstrate improved water repellency from the use of HPC. Additionally, the addition of zinc oxide nanoparticles to HPC enhances this property.

When treated with HPC/ZnO NC, the contact angle increased to around 78°, highlighting the impact of zinc oxide nanoparticles on increasing the hydrophobicity of HPC. Notably, the HPC/ZnO NC treatment exhibited a lower reduction upon aging compared to the HPC treatment, indicating that HPC/ZnO NC is more stable than neat HPC. However, accelerated aging resulted in an increase in the contact angle in neat leather, which may be attributed to the oxidation of the leather finishing layer and the augmentation of cross-links on the leather surface.

Figure 7 illustrates the results of the uniaxial tensile tests conducted on the leathers. This figure presents the maximum force at the point of failure in Newton and the amount of extension until failure in millimeter. Accelerated aging resulted in a decrease in the maximum bearable force before tearing for both neat leathers and leathers treated with HPC. However, the reduction in the tolerance threshold of the leather was less pronounced in HPC-treated samples than in neat leather. Notably, the use of HPC/ZnO NC prevented this decrease in the tolerance threshold of the leather, as no reduction in the tolerable force of the leather was observed after aging, indicating the greater stability of this leather. In terms of extension, aging caused a decrease in this index in neat leather, and HPC treatment prevented this decrease, providing relative stability to this index. However, in leathers treated with HPC/ZnO NC, not only was there no decrease in the elongation index after aging, but also a significant increase was observed. This suggests that, in addition to improving some HPC characteristics, HPC/ZnO NC treatment has also improved the mechanical resistance of leather, confirming its performance as an improved consolidant.
4. Conclusions

This study aimed to investigate the potential of using a zinc oxide/hydroxypropyl cellulose (HPC) nanocomposite as a consolidating agent for leather. The findings indicate that zinc oxide nanoparticles are uniformly distributed throughout the HPC matrix. The HPC/ZnO NC treatment applied to the leather creates a coating layer that effectively shields it from UV radiation, thus preventing the development of microcracks and surface layer deterioration. Moreover, the HPC/ZnO NC treatment exhibited superior mechanical properties, preventing the decrease in the tolerable force of the leather after aging and increasing the elongation index, confirming its performance as an improved consolidant. Additionally, the HPC/ZnO NC treatment improves the waterproofing properties of HPC and leather and prevents collagen denaturation under UV radiation. Furthermore, the treatment increases the pH of the leather, which can help control the destruction caused by acid. These findings demonstrate that the use of HPC/ZnO nanocomposites as a consolidating agent for leather significantly enhances its mechanical and physical properties and improves its resistance to environmental factors such as UV radiation and humidity. These results can contribute to the development of new and effective methods for the restoration and conservation of leather artifacts. Furthermore, future research can explore the application of these techniques on leathers that have undergone other tanning procedures.

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References
1. Koochakzaei, A.; Mallakpour, S. Identification of surface dyeing agents of two bookbinding leathers from 19th-century Qajar, Iran, using LC–MS, µXRF and FTIR spectroscopy. *Archaeometry* 2023, 65, 603–616. [CrossRef]


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