Development of a coating with UV protection for leather finishing in the automobile industry

Desarrollo del recubrimiento para protección a los rayos UV del acabado del cuero para la industria automotriz

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Abstract

Due to continuous use and environmental factors (humidity and continuous exposure to the sun), the leather upholstery experiences cracking, discoloration and possible yellowing. The above factors significantly decrease the life of leather upholstery in cars. The objective of this work is to synthesize zinc oxide nanoparticles, which have optical properties that allow it to absorb UV radiation and then incorporate them into a polymeric matrix to develop a coating with UV protection for leather finishing in the automobile industry. The particles of zinc oxide were synthesized by the sol-gel method to obtain a nanometric particle size, the method represent a low-cost synthesis method, without the use of surfactants and easily scalable. With monoethylene glycol was formed a stable colloid with the zinc oxide nanoparticles and the polymer matrix. Finally, the final leather finishing obtained for the automotive industry has greater resistance to bending, also thermal stability was improved. In consequence, the lifetime of the leather finishing has improved.

UV radiation, Zinc oxide nanoparticles, Leather finishing

Resumen

Debido al uso continuo y los factores ambientales (humedad y exposición continua al sol), la tapicería de cuero experimenta grietas, decoloración y posible amarillamiento. Los factores anteriores disminuyen significativamente la vida útil de la tapicería de cuero en los automóviles. El objetivo de este trabajo es sintetizar nanopartículas de óxido de zinc, que tienen propiedades ópticas que le permiten absorber la radiación UV y luego incorporarlas en una matriz polimérica para desarrollar un recubrimiento con protección UV para el acabado del cuero en la industria automotriz. Las partículas de óxido de zinc se sintetizaron mediante el método sol-gel para obtener un tamaño de partícula nanométrica, este método representa un método de síntesis de bajo costo, sin el uso de tensoactivos y fácilmente escalable. Con monoetilenglicol se formó un coloide estable con las nanopartículas de óxido de zinc y la matriz polimérica. Finalmente, el acabado final del cuero obtenido para la industria automotriz tiene mayor resistencia a la flexión, también se mejoró la estabilidad térmica. En consecuencia, la vida útil del acabado del cuero ha mejorado.

Radiación UV, Nanopartículas de óxido de zinc, Acabado de cuero

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Introduction

Currently, the impact of UV rays in humans has focused on how it causes damage to the structure of collagen, but there are few references of the impact that UV radiation has on leather finishing materials (A. J. Bailey, 1980). In the bibliography, the inclusion of inorganic compounds such as carbon materials and metal oxides to polymeric matrices improves mechanical properties and thermal resistance to leather finishing (Pavel, 2011). Zinc oxide has an excellent absorption of UV radiation material (L. Wallenhorst, 2018), so it is widely used in the manufacture of sunscreens.

The synthesis of metal oxides by the Sol-Gel method implies: simplicity, low cost, reliability, repeatability, relatively simple synthesis conditions (low synthesis temperatures, minimum evaporation loss, minimum contamination), favourable optical properties, higher surface area, greater purity, better microstructural control of metal particles and narrower distributions of particle and pore (J. F. De Lima, 2012).

Many leather finishing use polyurethanes (C. Niculescu, 2012) like film protectors because they have high abrasion resistance, superior hardness, elastomeric properties, good chemical resistance, tensile strength, high extensibility at low temperature and properties that are simple to modify. In this work, a mixture of polyurethane resins and dispersants (provided by leather finishing industry), a polymeric matrix, with inserts of zinc oxide nanoparticles was used as the finishing material and applied by the spray coating technique.

Methodology

For the synthesis of nanoparticles of ZnO is necessary a five-step method, as indicated by (S. Jurablu, 2015) and the modifications made by (Valencia-Rodríguez, 2018).

Solubility and solvent-polymer matrix compatibility tests of the nanoparticles were performed in: 1. Isopropanol, 2. Polyethylene glycol, 3. Ethanol, 4. Ethanol-water mixture (1:1), 5. Monoethylene glycol, 6. Methanol and 7. EEP (ethyl 3-Ethoxypropionate).

5 layers of the polymer matrix, nanoparticles, and pigment (provided by the company) were applied (by pressure gun), with and without nanoparticles. It was dried in a convective heating oven at 90 °C for 3 minutes. Previous tests were exposed to solar radiation for 70 days, and it was considered an unexposed reference sample.

All materials were characterized by X-ray diffraction UV-Vis spectroscopy, diffuse reflectance UV-Vis spectroscopy, Scanning electron microscopy (SEM), Raman spectroscopy, Fourier transform IR spectroscopy, Thermogravimetric analysis (TGA) and Chronoamperometry. Evaluation of the colour difference (ΔE^*), in applied samples to leather finishing, were with a colorimeter.

Results

The samples were prepared by the sol-gel method using different pH's (Figure 1 and 2) the results confirmed the wurtzite hexagonal phase whose characteristic peaks are located at 32.24°, 34.42°, 36.25°, 47.54°, 56.84°, 62.86° and 68.76° corresponding to the diffraction planes (100), (002), (101), (102), (110), (103) and (112). With Graphic 1 it follows that the sample analysed has no impurities and small particles have good crystallinity. Graphic 2 also indicates wurtzite phase without impurity residues but the peaks in the diffractogram of the oxide indicates a lower degree of crystallinity. The previous results are due to the pH of synthesis, 9 and 11, respectively (L. Li, 2010), (Thambidurai, 2017).

Graphic 1 Diffractogram of ZnO nanoparticles synthesized via sol-gel at pH 9

Source: own work [OriginPro 9]

Graphic 2 Diffractogram of ZnO nanoparticles synthesized via sol-gel at pH 11
Source: own work [OriginPro 9]

Graphic 3 represents the absorption spectra by UV-Vis spectroscopy, with an absorption band at 370 nm. The presence of the highest absorption peak at 355.78 nm is observed, which confirms the presence of zinc oxide nanoparticles in the solution (Pavel, 2011), (W. A. G. Bruls, 1984). Also, the Graphic 3 corresponds to the ZnO obtained by method at pH 11, it is observed that the wurtzite phase is also obtained without residues of impurities. The peaks of this diffractogram are less intense, so this material has a lower degree of crystallinity than the previous one (at pH 9). Direct banned band energy was calculated from the Planck equation (Eq. 1) taking as reference the peak of greatest absorption obtaining $E_{gap} = 3.49$ eV.

Graphic 3 UV-Vis absorption spectrum of ZnO nanoparticles
Source: own work [OriginPro 9]

$$E_{gap} = h\nu = \frac{hc}{\lambda} \quad (1)$$

Where:

- h = Planck constant (6.626×10^{-34} joules).
- c = speed of light ($c = 3 \times 10^8$ m/s).
- λ = peak absorption wavelength (3.557836×10^{-7} m).

Considering the diffuse reflectance UV-Vis spectroscopy, the sample absorption coefficient (at pH 9 and 11) for each wavelength was estimated and it was graphed $(\alpha\lambda\nu)^2$ vs $(\lambda\nu)$ (Graphic 4), for energy estimation forbidden band with Kubelka-Munk model for which $E_{gap} = 3.25$ eV was obtained. For both cases, the value is close to that reported in the bibliography for the ZnO, $E_{gap} = 3.37$ eV (M. Shaban, 2016). Forbidden band energy is influenced by several nanoparticle factors such as morphology, particle size, composition and the presence of defects (oxygen vacancies), (A. K. Zak, 2011).

Graphic 4 Kubelka Munk graph of ZnO synthesized by the sol-gel method at pH 9
Source: own work [OriginPro 9]

Graphic 5 shows that the peak of the highest intensity of the spectrum was located around 438 cm^{-1} and is due to the E_2 (high) mode, which is a typical Raman peak of the wurtzite ZnO phase (Golzary, 2014). The spectrum shows peaks around 213.12 cm^{-1} , 326.94 cm^{-1} , 336.67 cm^{-1} , 436.67 cm^{-1} , 559.51 cm^{-1} , 583.44 cm^{-1} which are also attributed to the wurtzite phase. For zinc oxide in the wurtzite phase, 6 first-order vibrational modes are expected, assigned as A_1 , E_1 , $2E_2$ Y $2B_1$ (C. A. Arguello, 1969). Modes A_1 and E_1 are polar and break in optical transverse (TO) and longitudinal optical (LO) phonic modes. The modes E_2 (E_1^{LOW} , E_2^{HIGH}) are non-polar and active in the Raman spectrum.

The band observed around 213.12 cm^{-1} is attributed to the E_2^{LOW} mode of the ZnO in the wurtzite phase. The vibrational modes that appear around 336.67 cm^{-1} and 436.67 cm^{-1} in our spectrum are attributed to modes $A_1(\text{TO})$ and E_2^{HIGH} (associated with oxygen subnet in ZnO) of the wurtzite phase. The band that appears in 583 cm^{-1} is attributed to the ZnO mode $A_1(\text{LO})$ of the wurtzite phase (al. H. Z., 2002). The peak observed in 326.94 cm^{-1} is attributed to the second-order Raman process characteristic of the wurtzite phase. The signal marked with an asterisk is attributed to the formation of $\text{ZnO}(\text{OH})_2$ (P. Kumar, 2018).

Graphic 5 Raman spectrum of the ZnO sample synthesized at pH 9

Source: own work [OriginPro 9]

Graphic 6 corresponds to the infrared spectrum of synthesized ZnO, the signal observed in 452 cm^{-1} is characteristic of the stretching vibrations of the Zn-O bond (Soto-Robles, 2017), (Prasad, 2018).

Graphic 6 The infrared spectrum of synthesized ZnO

Source: own work [OriginPro 9]

Graphic 7 shows the TGA results of the ZnO. It can see three stages of weight loss. The total weight loss of 9% for nanoparticles dried for 2 h at 60°C . In the first stage, a small amount of weight loss (1.5%) is observed at temperatures below 141°C , which is considered as the dissociation of weakly bound solvent molecules, such as methanol (D. Sun, 2007). The second stage is between 141°C and 386°C , in which the most significant weight loss is observed, in this range 6.2% is lost, and this stage is followed by the third stage of weight loss in which a slow weight loss was observed until reaching 9% of weight lost at 600°C . The second stage can be attributed to acetate ions which are difficult to remove during washing and to the possible presence in a smaller amount of $\text{Zn}(\text{OH})_2$ (al. L. L., 2018).

Graphic 7 TGA of ZnO nanoparticles synthesized via sol-gel

Source: own work [OriginPro 9]

Figure 1 (a, b, c and d) show that the nanoparticles have a homogeneous and spherical shape. The formation of nanoparticle clusters is observed in better detail in the Figure. In the four micrographs presented, it is observed that the size of the nanoparticles that form the clusters is less than 100 nm.

Figure 1 SEM micrographs of ZnO nanoparticles
Source: own work [JEOL SU 3500 SEM Hitachi]

Graphic 8 shows the impedance spectrum corresponding to the films made with prepared solutions of 0.1%, 0.3% and 0.5% w/w ZnO in methanol. It is observed that as the concentration increases the resistance of the film decreases. The same trend is followed in Graphic 9 which corresponds to the spectrum of films made with solutions of ZnO AL 1%, 3% and 5% w/w, in methanol. This corroborates the semiconductor capacity of the material, the higher the concentration, the better the conductivity.

Graphic 8 Electrochemical Impedance Spectrum of ZnO particles at concentrations 0.1%, 0.3%, 0.5% in methanol
Source: own work [OriginPro 9]

Graphic 9 Electrochemical Impedance Spectrum of ZnO particles at concentrations 1%, 3%, 5% in methanol
Source: own work [OriginPro 9]

Graphics 10, 11, 12 and 13 describe the chronoamperogram of the film formed with 0.3%, 1%, 3% y 5% w/w ZnO in methanol, it is observed that at a higher concentration of ZnO the amount of UV light it absorbs is less. This is because the ZnO disperses the incident radiation on the film. It is also observed that when the concentration of the nanomaterial is increased, the absorption intensity remains constant, which encourages believing that it can be irradiated with UV light for long periods.

Graphic 10 Chronoamperogram of a 0.3% w/w ZnO film in methanol
Source: own work [OriginPro 9]

Graphic 11 Chronoamperogram of a 1% w/w ZnO film in methanol
Source: own work [OriginPro 9]

Graphic 12 Chronoamperogram of a 3% w/w ZnO film in methanol
Source: own work [OriginPro 9]

Graphic 13 Chronoamperogram of a 5% w/w ZnO film in methanol
Source: Own work [OriginPro 9]

It was decided to use monoethylene glycol as a dispersing phase for the ZnO nanoparticles, due to the non-formation of agglomerates in the films applied on the substrates, as shown in Figure 2.

Figure 2 Application of the first coating layer with nanoparticles dispersed in a) Monoethylene glycol, b) Polyethylene glycol, c) Ethanol-water mixture
Source: own work [Microsoft Office Word]

The samples applied to leather finishing were exposed to solar radiation for 70 days, and it was considered an unexposed reference sample. The evaluation of this samples was with a colorimeter, colour difference (ΔE^*), as show in Table 1.

Number of layers applied on the substrate	1	2	3	4	5
Colorimetric parameter evaluation, b^*	Δb : 9.52	Δb : 8.38	Δb : 6.26	Δb : 3.04	Δb : 2.69

Table 1 Application of films, with ZnO nanoparticles synthesized via pH 9 sol-gel, in leather substrate, dispersed in monoethylene glycol
Source: own work [VHX-7000 Series Digital Microscope]

Conclusions

The sol-gel method represents a simple synthesis method with low cost and high productivity ZnO. UV-Vis spectroscopy with diffuse reflectance and chronoamperometries confirmed the good absorption of UV radiation from the synthesized ZnO. The sample irradiated by sunlight that contained ZnO nanoparticles in the leather finish was preserved in a better state than the one that did not contain nanoparticles. The addition of ZnO nanoparticles to the leather finish layers greatly improved their mechanical properties and thermal stability. The Δb value was reduced by 74%, a value of 2.69 was obtained for this parameter, which is only 0.69 units above the maximum allowed value (Δb : 2).

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