ORIGINAL PAPER

SUPERHYDROPHOBIC COATINGS BASED ON CELLULOSE ACETATE FOR PINEWOOD PRESERVATION

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Abstract. *This study deals with the investigation of the preservation of cellulose acetate based micronized particles (ZnO and TiO_2) for the artificial wood preservation. The protection of wood artifacts has raised serious problems, due to the main factors that affect the wood structure, such as low temperature, fire and microbiological agents. These factors act on the wood structure and induce some degradation processes, such as discoloration, fragility and unsightly appearance. The capacity of these new composites used as a coating for wood was investigated on young and aged wood samples. First, it was tested the aspect of the samples after treatment and the colorimetric measurements have confirmed that all consolidates doesn't significantly influence the color of the samples. Then, the mechanical character of the samples has demonstrated that the presence of the cellulose acetate has increased the resistance of the samples, even in the case of the aged samples. The efficacy of the treated samples to wet environment has confirmed that all the composites used as coating created a hydrophobic surface that has the role to protect the wood surface against long-term exposure to environmental changes.*

Keywords: *superhydrophobic coatings; cellulose acetate; micronized particles; wood preservation*

1. INTRODUCTION

Over the centuries wood has been used for houses and ships building, and over time many attempts have been made to protect the wood against destructive agents in order to prolong their useful life [1]. Wood is one of the oldest materials in the humanity history that has been used for thousands of years for fuel, as a construction material, for furniture and paper [2, 3]. The major problem of wood artifacts is related to the aging process which is closely dependent on passage of time and deterioration through environmental factors, such as climatic factors (weathering), wood-destroying organisms (insects, fungi, microorganisms) [4-6]. Climatic differences are associated with the changes in the moisture content of wood; which are mainly governed by the relative humidity of the surrounding air, every change in humidity affecting the wood structure [7]. Due to these destructive factors, there is a huge need for treatments that helps wood conservation.

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One effective way to prevent wood's degradation processes is to apply coating protective layers by chemical modification of the wood surface [8, 9]. Presently, there is an increasing interest in the improvement of coatings for wood and their performance in outdoor applications [10]. The coating must be able to prevent or limit the deterioration effects of the environmental factors and to ensure the maintenance of the wood's aesthetical appearance.

In order to prevent the wood degradation processes, the researchers have used some conservation treatments with different compatible materials [2, 11-13]. In the last several years, biodegradable polymeric materials have been used in order to protect the wooden artifacts or artworks. In the first stage, the solid polymer is dissolved into a solvent in order to treat the degraded wooden structure, filling the voids resulted by degradation. In the second stage, after the solvent evaporation, the polymer remains fixed in the wooden structure improving the internal cohesion and the mechanical strength of the treated wooden material [14].

Cellulose acetate (CA) is one of the most important esters of cellulose and was obtained by acetylation of cellulose from a variety of sources, such as wood pulp or bacterial cellulose. An advantage of this polymer is the fact that it can be processed into a variety of forms (e.g. for films, membranes or fibers), depending on the area of application. This polymer presents several properties which make it suitable for conservation/restauration of wood artifacts, such as high flexibility, good elongation at break, biodegradability, moderate hydrophobicity, environmentally friendly and protection against insects [15-20].

Cellulose acetate has also excellent resistance to degradation by ultra violet light and does not readily discolor when exposed to light or heat [21]. Due to these important advantages, cellulose esters coatings, like CA have been used in the last several years in various costumer products, such as: electronic displays, pharmaceutical products and food packaging. In a recent paper, an environmentally friendly coating based on cellulose acetate has been successfully obtained with the capacity to be water resistant and oil resistant in order to be used in food related and non-food related applications [22]. Also, in the last years has been reported that cellulose esters are used for bonding leather, paper, and wood [23, 24].

In the last years, it has been demonstrated that micro and nanomaterials play a key role in cultural heritage, new and efficient systems being created and tested on wood, such as metallic oxides (ZnO, TiO_2, CuO) [25-27]. These materials have the capacity to insert in the wood channels along the microfibrils, with local agglomerated formations, preserving the wood [2]. It was demonstrated that these metallic oxides applied on wood samples improves mechanical resistance, restoring the weathering resistance of wooden surface (water impermeability and UV radiation) [14, 28, 29].

This paper aims to obtain new composites based on cellulose acetate and micronized particles; and to test these composites on wood samples (young and aged specimens) in order to create a new solution for preservation of old artifacts.

2. MATERIALS AND METHODS

2.1. MATERIALS

Wooden materials

In the present study, some pinewood parts without knots were cut at about 7x3x1 cm and used, without drying beforehand, for the future tests. The selected samples of wood were

brushed in three layers on all sides with the solution obtained below (Fig. 1) and some of the samples were aged by thermal treatment (100°C for 24).

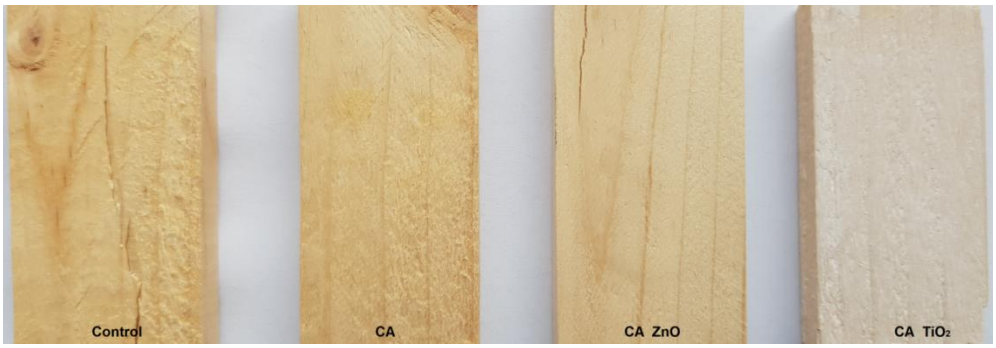


Figure 1. Aspect of the samples after applying the treatment.

Solutions preparation

In order to obtain the cellulose acetate (CA) solution, 1 g of CA was dissolved in 100 ml glacial acetic acid/water (70/30) and the mixture was homogenized under mechanical stirring for 6 hours at room temperature. Then, 4 wt% ZnO and TiO_2 micronized particles, respectively were added to the CA solution and continually stirred until the particles were dispersed. The prepared solutions were applied on the pinewood items by brushing (CA, CA_ZnO and CA_TiO_2).

2.2. METHODS

In order to study the *major functional groups* of the solutions, Fourier transformed infrared spectroscopy (ATR-FTIR) has been achieved with a Portable FTIR spectrometer Interspec 300-X, in the range of 4000–400 cm^{-1}, 32 scan, and resolution 4 cm^{-1}.

The *dimensions of the ZnO and TiO_2 particles* were measured using a Novex Microscope BBS that offers the possibility of investigating the samples in transmitted light at amagnification between 4–100×. The equipment had a digital video camera attached (Axiocam 105, Carl Zeiss, Oberkochen, Germany) which, by the microscope software (ZenPro), allowed real-time data acquisition.

The *deposition of the particles* on the wood surface was recorded with CM700D spectrophotometer (KONICA MINOLTA) (Japan) under a D65 light source and an observer angle of 10°. The differences in a*, b* and the total color differences ΔE^*_{ab} were calculated. The CIELab chromatic parameters chosen for the study were chromatic coordinates a* and b*, with the following significance: coordinate a* ranges in value from +60 (red) to -60 (green) and b* from +60 (yellow) to -60 (blue) [20]. The total color differences ΔE^*_{ab} was calculated using equation (1).

$$\Delta E^*_{ab} = [\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}]^{1/2} \quad (1)$$

where L^* is the lightness and a^* and b^* represent the color coordinates under any testing condition.

The colorimetric investigation has been recorded for the untreated and treated specimens with CA, CA_ZnO and CA_TiO_2 micronized particles.

Mechanical Testing Measurements have been recorded with a Silver Schmidt Proceq test hammer, type L-0.735 Nm impact energy, according to ASTM C805. The strength range of the hammer is from 10–100 N/mm^2. For each sample, ten replicates at distance of minimum 10 cm were recorded with the hammer positioned at 90° downward and the result (rebound number value - Q) is calculated as the average of the readings, in order to find a relationship between surface hardness and compressive strength [30]. The compressive strength was calculated using equation (2).

$$\text{Compressive strength} = 2.77 \times e\hat{}(0.048 \times Q) \quad (2)$$

In order to evaluate the water resistance of wood samples several methods has been carried out:

Water Absorption Test has been carrying out in order to investigate the water repellency of the wood samples, this parameter being closely related to the degree of deterioration of the artifacts. This method offers information about the quantity of water absorbed by a material immersed in distilled water at room temperature. In the first step, all the samples have been dried in an oven for 8 hours at 40ºC, this low drying temperature will prevent the deterioration of any organic substances employed in the case of treated samples. After drying, the samples were left at room temperature to cool, and then weighed (W_1). Once the samples were completely dried and the constant mass recorded, were placed in a tray filled with distilled water for 24 hours. Then the samples were removed from the water, wiped with a towel and weighed (W_2) [31]. The water absorption (WA) was calculated using formula (3).

$$WA = \frac{W_2 - W_1}{W_1} * 100 \quad (3)$$

Also, the *water absorption rate* (WAR) of the samples was investigated and correlated with the results obtained from the water absorption test. Water absorption rate of the samples was determined after the immersion in distilled water at room temperature for 1 hour to 20 hours. The samples were initial weighed (W_i) with a precision of 0.001 g and then immersed in distilled water. At the end of the immersion periods, the samples were removed from the distilled water, the surface water was wiped off, and wet weight values were determined (W_f) [32]. Water absorption rate was calculated using the following equation (4):

$$\text{WAR} = \frac{W_f - W_i}{W_i} * 100 \quad (4)$$

Another way to understand the water permeability of the wood samples, and thus the degree of deterioration in weathering conditions refers to *Humidity Test*. Firstly, all the samples have been immersed in a tray filled with distilled water for 30 minutes and after that the samples were weighed (W_t). Then, the samples were dried in an oven for 1 hour at 60ºC and then were let for 12 hours at room temperature [31]. After 12 hours, all the samples were weighed (W_0) and the humidity (H) was calculated according to equation (5).

$$H = \frac{W_t - W_0}{W_0} * 100 \quad (5)$$

Contact angle was carried out in order to investigate the hydrophobicity of the treated and untreated sample. The sample was placed on a right surface and then 60 µl were dropped at a single point on the sample surface. After the drop has reached the surface, pictures were taken at a distance of 5 cm from 20 to 20 seconds for 1 minute, in order to calculate the

contact angle at different times. The contact angle was calculated according to Buahom P. [33] using DropAnalysis plugin in ImageJ.

3. RESULTS AND DISCUSSION

The major functional groups of the obtained solutions were identified by FTIR. The observed vibrational peaks are characteristic of cellulose acetate, similar to other literature data reported below (Fig. 2).

Fig. 2 shows the FT-IR spectra of CA film, CA_ZnO film and CA_TiO_2 film. The spectra of CA confirms the presence of major absorption features appeared at 1713 cm^{-1} (–C=O), 1361 cm^{-1} (–CH_2), 1223 cm^{-1} (C–O), 1027 cm^{-1} (C–O–C) and 900 cm^{-1} (–CH). Also, the bands appeared at 2907 cm^{-1} (–CH_2) and 3453 cm^{-1} (–OH) which are characteristic bands of CA [34]. In the case of CA_ZnO spectra, it can be observed the characteristic bands of ZnO between 400 and 700 cm^{-1} [35]. Also, the O–H stretch appears in the spectrum at 3074 cm^{-1} and moderate levels of absorption in the region covering 1536–1425 cm^{-1} imply the presence of an aromatic ring [36]. The presence of CA is confirmed by the bands appeared at 1027 cm^{-1} (C–O–C) and 900 cm^{-1} (–CH). In the case of CA_TiO_2, the intense peak at 647 cm^{-1} is assigned to the Ti-O stretching band, which is the characteristic peak of TiO_2 [37].

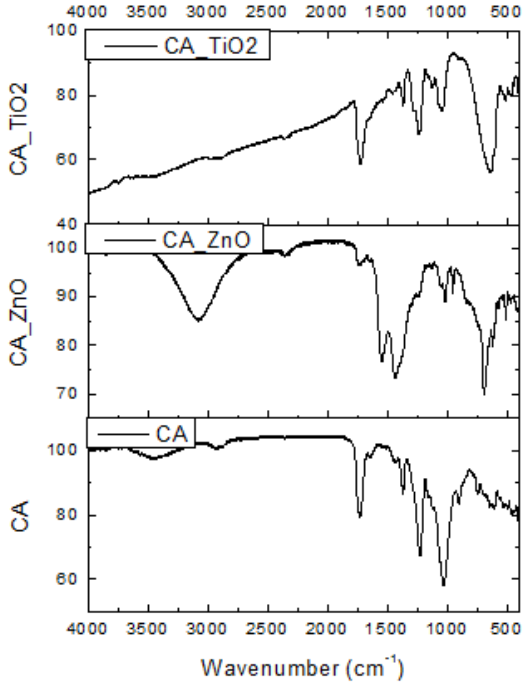
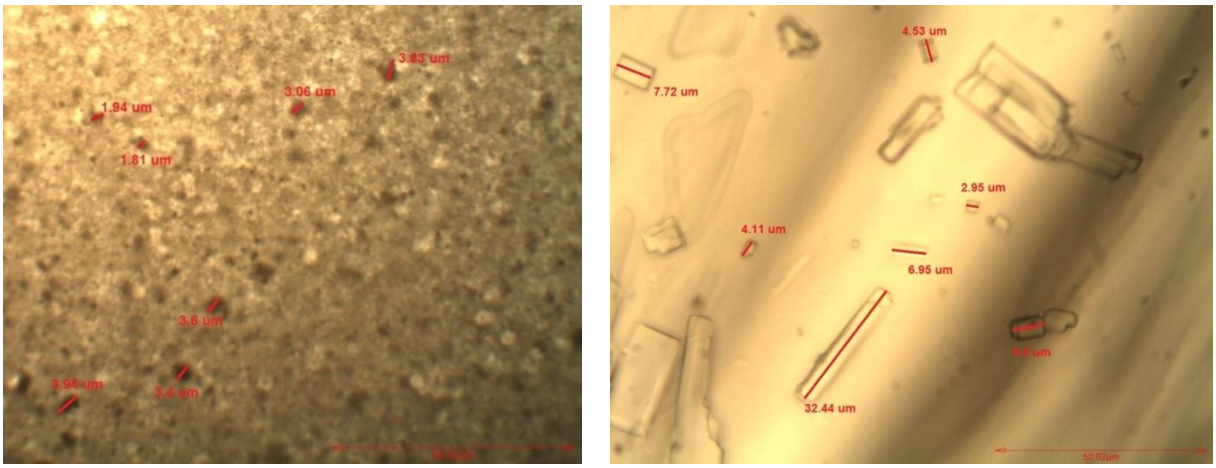


Figure 2. FTIR spectra of the CA film, CA_ZnO film and CA_TiO_2 film.

Fig. 3 shows the dimensions of the TiO_2 and ZnO particles, both materials present micronized particles, with dimensions between 0.1 µm – 100 µm. In the case of the CA_TiO_2 film, there are particles with dimensions between 1.8 µm and 3.5 µm, while in the case of CA_ZnO film, particle size has a wider spectrum between 3 µm and 8 µm.



a b

Figure 3. Optical microscopy of the CA_TiO_2 (a) and CA_ZnO films (b).

One of the main criteria of consolidation is to prevent dimensional changes and maintain the original appearance of the artefact [2]. Regarding this aspect, the chromatic parameters of the samples before, after the treatment and after the ageing of the samples by thermal treatment were investigated in order to test the efficiency of the new materials as consolidates (Fig. 4).

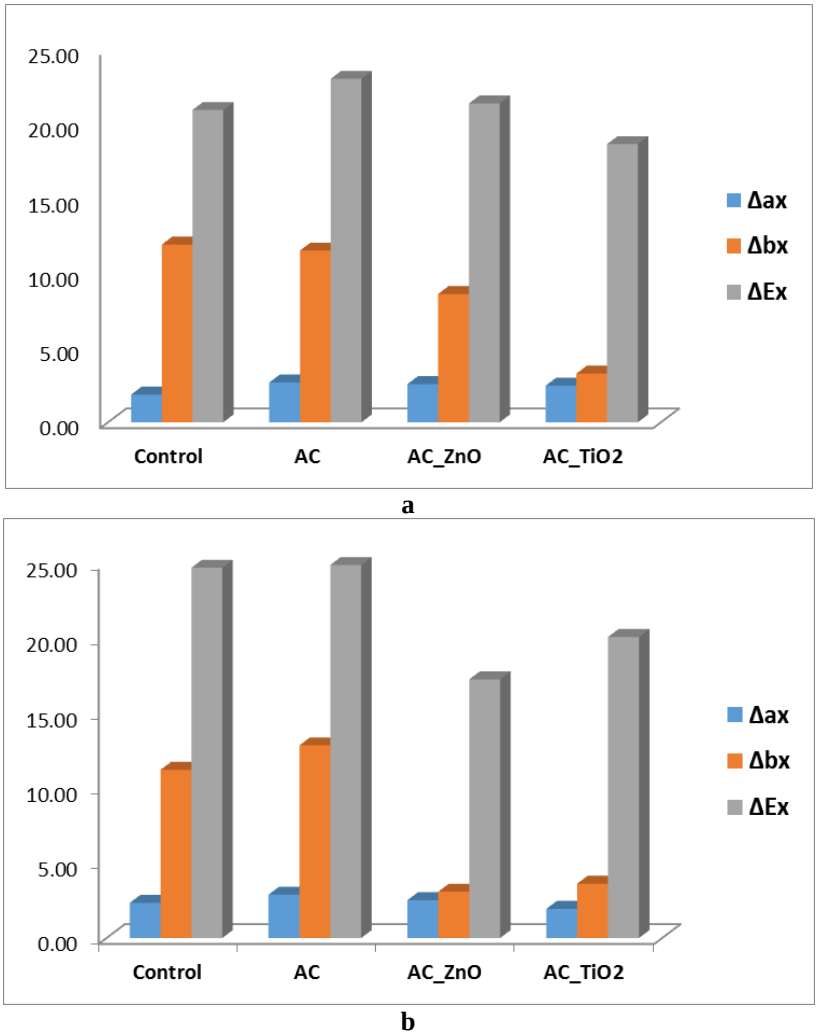


Figure 4. Chromatic parameter of the samples before ageing (a), after thermal treatment (b).

In the case of the young samples treated with the new materials (Fig. 4a), it can be observed that there are no differences in the case of a* coordinate. In the yellow-blue interval (b*) some changes in color can be observed, mostly in the case of the samples treated with the new materials containing micronized particles, but the Δb* parameter is not higher than 8, so the samples are moderately stable. Also, the total color differences ΔE^*_{ab} confirms that the surface of the samples treated with these particles shows the greatest differences compared to control, but these differences are acceptable because the differences are between 3 and 5, what means that the consolidate doesn't significantly influence the color of the samples.

When the samples were exposed to thermal treatment (Fig. 4b), it can be observed that the tendency remains, the samples treated with the solution containing TiO_2 and ZnO particles show differences in color, but not significant differences. These differences are due to the presence of the micronized particles that slowly influence the color of the wood surface. Since, the values of all the treated samples are below 8, it demonstrated that the treatments are suitable for future investigations.

Mechanical measurements were recorded with Silver Schmidt hammer in order to evaluate the mechanical properties of the wood samples (compressive strength). The rebound number measurements treated samples before and after the thermal treatment are shown in Fig. 5. The measurements of rebound number have been taken and then the compressive strength was determined according to ASTM C805 [38].

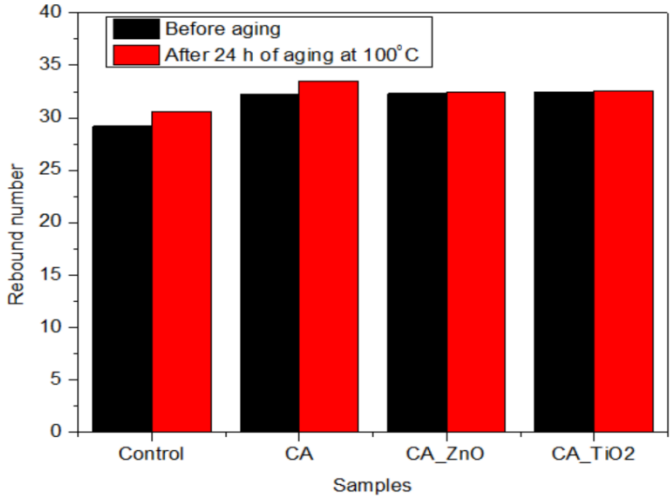


Figure 5. Mechanical strength for the untreated and treated samples before ageing and after thermal treatment.

It could be observed that by comparison with the control samples (before and after ageing), all the treated samples presented higher compressive strength values (Fig. 5) correlated with an increased rebound number (Fig. 6). The addition of the micronized particles on the samples surface enhanced the durability of wood compared to the untreated, due to the role of these particles in reinforcing the wood. The aged wood appears more rigid and stronger than young wood because of its stable physical behavior and relatively constant cell size [2].

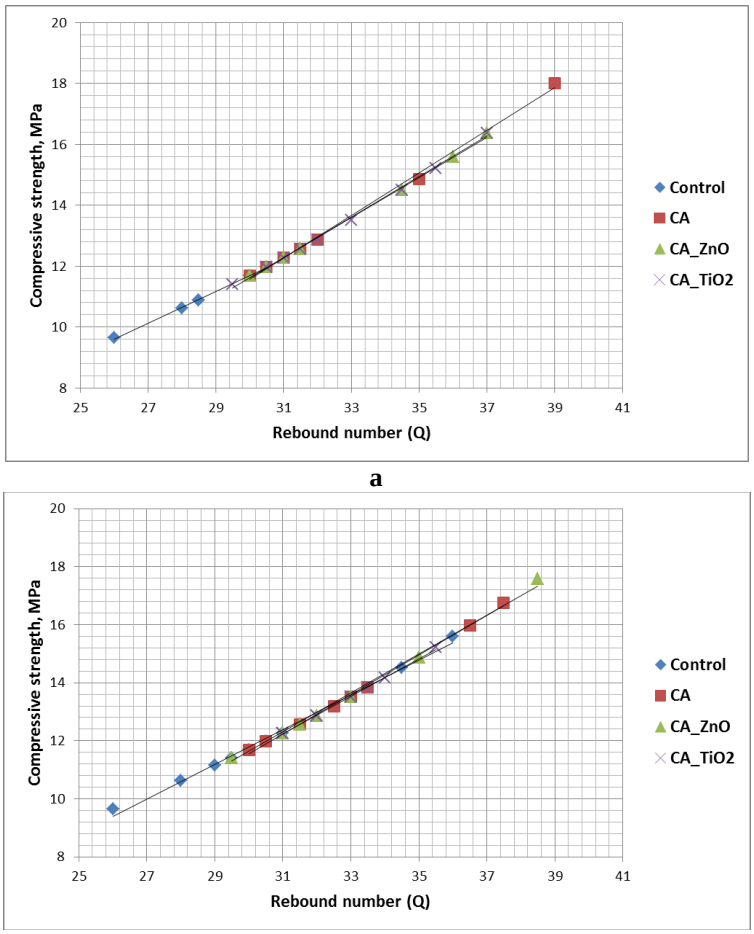


Figure 6. The compressive strength vs. rebound index relationship for wood samples untreated and treated samples before (a) and after thermal treatment (b).

One of the most important characteristics of the wood objects is their behavior to wet environment. A good consolidate has to protect the wood against humidity, mostly in the case of an aged wood, because this wood is much less sensitive to humidity variations than a younger wood [39]. Both water absorption and humidity capacity of the untreated and treated wood samples were investigated. In Figs. 7 and 9, it can be observed that compared to control the treated samples presented a lower water absorption and humidity percent, respectively. Also, the water absorption rate (Fig. 8) suggests that the wood samples treated with CA and micronized particles presented the lowest absorption in time, the control sample presenting the higher absorption rate. This could be explained by wood chemical composition, the wood fiber contains high hydrophilic content (cellulose and hemicelluloses), which are responsible for the high water absorption of natural fibers, since they contain numerous accessible hydroxyl groups [32]. The treatment proposed in this paper, suggests that the use of chemical coating has successfully created a hydrophobic surface that has the role to protect the wood surface against long-term exposure to environmental changes. The obtained results suggest that the treated samples offer a good hydrophobic character to the wood surface.

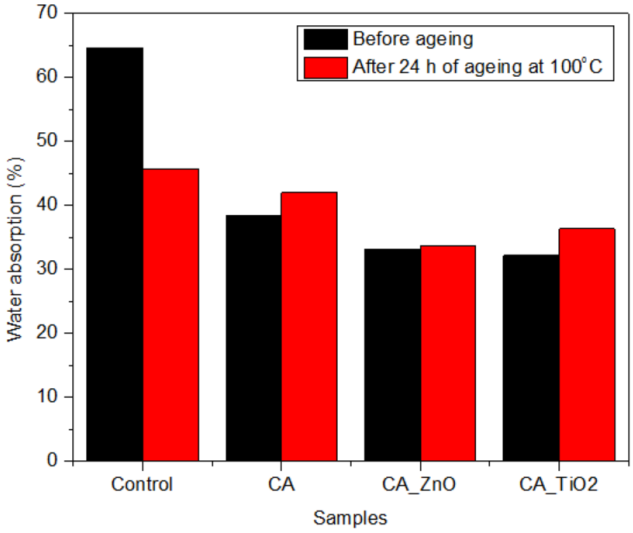


Figure 7. Water absorption of the untreated (control) and treated samples before and after ageing.

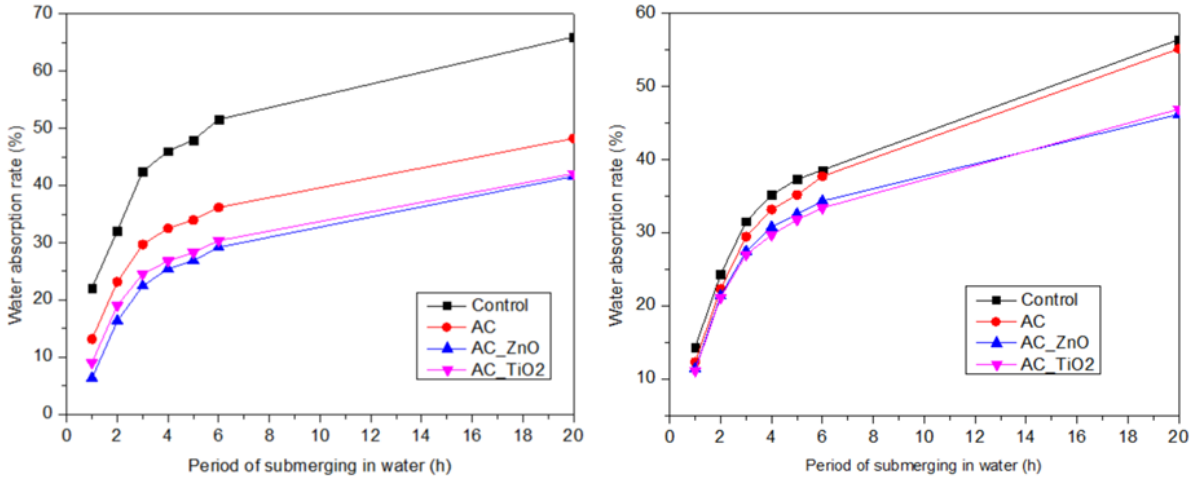


Figure 8. Water absorption rate of the untreated and treated samples before (a) and after ageing (b).

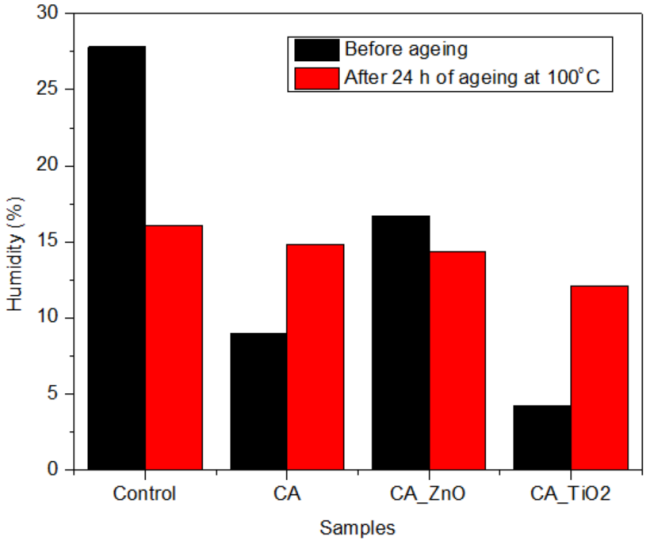


Figure 9. Humidity of the untreated (control) and treated samples before and after ageing.

Also, the behavior to wet environment of the samples can be investigated by contact angle measurements; the higher is the value of the contact angle, the greater is the hydrophobicity of the surface. According to the obtained results, it can be confirmed that the treated samples present a higher hydrophobicity comparing with the untreated sample, and the best value of the contact angle was achieved by the sample treated with CA_TiO_2 before and after ageing (Fig. 10). This suggests that the incorporation of TiO_2 particles on the polymeric matrix contributed to the increase of water contact angle, in order to generating high hydrophobicity.

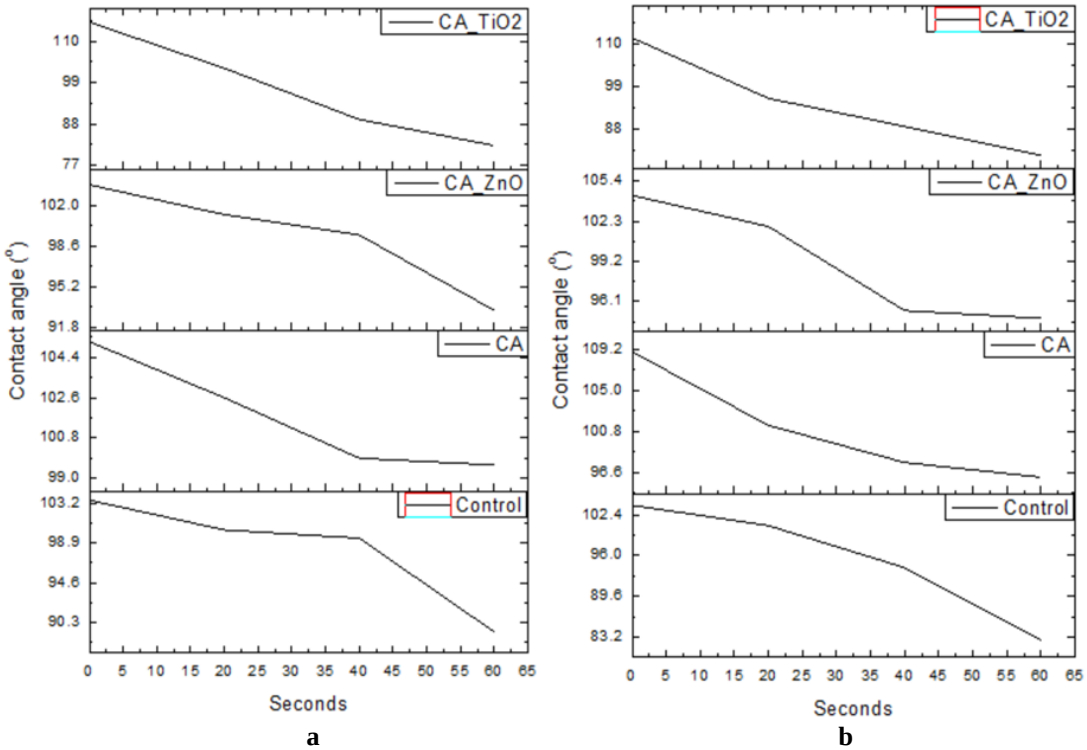


Figure 10. Contact angle of the control and treated samples before (a) and after ageing (b)

4. CONCLUSIONS

This study aimed to test the potential of biodegradable composites based on cellulose acetate and composites from cellulose acetate based ZnO and TiO_2 micronized particles, applied on the pinewood samples (young and aged specimens), as a new solution for preservation of some artificial wooden parts.

The values obtained on colorimetric measurements have confirmed that all consolidates doesn't significantly influence the color of the samples, confirming that the used materials do not significantly change the color of wooden objects. The hardness test reveals that the presence of the polymer increases the mechanical properties of the samples, even in the case of the aged samples.

Also, the behavior of the untreated and treated wood parts (younger and aged) to wet environment was tested. The results suggest that the all the three new materials used as coating has successfullly created a hydrophobic surface that has the role to protect the wood surface against long-term exposure to environmental changes. The hydrophobic character of the treated samples was confirmed also by contact angle measurements, CA_TiO_2 presenting the higher value of the contact angle.

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