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EFFECTS OF DIFFERENT ADDITIVES IN A WATERBORNE POLYACRYLATE COATING ON SELECTED SURFACE PROPERTIES OF HEAT-TREATED FINISHED WOOD

Color changes of thermally modified timber due to different formulations of polyacrylate coating were studied before and after the application of the coatings. Olive leaf extract as a natural antioxidant-bearing additive was added to polyacrylate to examine any changes in color parameters in comparison with other additives. Water contact angle, surface roughness, and the color parameters in L*a*b* coordinates were measured, and any differences (ΔE*, ΔC*, ΔH*, ΔL*, Δa*, Δb*) were also calculated after applying the formulated coats on the thermally modified wood. The results indicated that lightness decreased after coating. The Δa* value was also increased after application of the olive leaf extract to the thermally treated wood. In general, total color change (ΔE*) was increased after coating. Reduction of ΔC* was found in the coating containing TiO$_2$ with 10% antioxidant. Also, ΔH* was increased by the use of the polyacrylate coating containing TiO$_2$, compared with other coatings. Application of all of the formulated coatings on the wood surface led to improvement in the water contact angle over the evolution time. On the other hand, coating of the treated wood was responsible for the formation of a smooth surface in comparison with the uncoated thermally modified timber.

Keywords: thermally modified wood, polyacrylate coating, olive leaf extract, color change, surface roughness, contact angle

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Introduction

Thermally modified timber (TMT) is becoming an interesting constructional material for consumer uses because of its dark brown color, dimensional stability, and resistance to biodegradation [Shi et al. 2007; Saha et al. 2013]. Although TMT has many advantages, when it is exposed to an outdoor climate for a long time, there are some drawbacks, such as discolorations and loss of glossiness [Ayadi et al. 2003; Mikleĉic et al. 2015]. Also, its wettability and its surface roughness increase due to weathering. These drawbacks may affect demand for TMT. Therefore, there is a need to protect TMT against outdoor conditions, especially UV radiation and moisture. Due to rigorous environmental regulations, as well as the ease of utilization, solvent-borne coatings are more and more often replaced by waterborne clear finishes. Polyacrylate-type finishes are among the waterborne clear coatings that have a wide range of application, due to their good elasticity and sufficient chemical stability [Mikleĉic et al. 2015]. Polyacrylate finishes are popular because of their outstanding glossiness, low cost, and low content of volatile organic compounds (VOCs) [Bao et al. 2015; Bao et al. 2017]. However, the clear coatings are susceptible to penetration of UV radiation into the underlying wood, which may cause photodegradation of the wood.

From a market point of view, surface properties of coated wood are of great interest to customers due to the aesthetic aspects. These properties may be affected by the type of coating applied, as well as degradation of the coating during use.

Degradation of a coating is known to be reflected in color changes, loss of glossiness, and reduction of its flexibility [Evans et al. 2015]. To increase the resistance of clear coatings and underlying wood to UV radiation, various additives are usually added to the coatings prior to application on the wood surface. These may be pigments, UV absorbers, and also UV absorbers combined with hindered amine light stabilizers (HALS). Pigments usually reflect UV radiation or absorb it. However, they dominate the natural color of wood. Therefore, it is important to use components that can prevent photodegradation of the coating and the underlying wood and at the same time maintain the transparency of the coatings and as far as possible retain the natural color of the wood [Aloui et al. 2006]. There are reports indicating that clear coatings of wood have already increased its durability in outdoor applications [Faucheu et al. 2006]. However, Nowrouzi and Mohebby [2016], who applied a polyacrylate clear coating, found that this coating was not able to protect wood against UV radiation. Therefore, they added nano-chitosan, chitosan and nano--ZnO as well as linseed oil to prevent discoloration of the wood. They also studied the surface properties of the coated wood during natural weathering, and showed that the color change of the coated wood was less with the coatings with chitosan and nano-chitosan than with the other coatings. Also, the dynamic

contact angles of water on the wood were increased after coating. It has been shown that the properties of a coating may be affected by additives. One report observed that combined acid catalyzed lacquers and nitrocellulose lacquers had the highest resistance to water absorption [Gholamiyan et al. 2010]. In another study, Cao et al. [2012] reported that an increase in temperature during treatment decreased chroma difference (Δc^*) and enhanced total color change (ΔE^*) and hue difference (ΔH^*). However, there have been no reports on changes of thermally modified wood after coating. We will investigate changes in the properties of thermally modified wood, including color, surface roughness and contact angle, after coating.

Materials and methods

Preparation of coating

Polyacrylate waterborne clear coating (with a solid content of polyacrylate of 65% and a density of 1.05 ±0.08 g/m^3, from the Abnil Chemistry Company, Isfahan, Iran) was used in this research. Different additives were mixed with the coating. The additives were: an organic UV stabilizer, 2-(2-hydroxyphenyl)--benzotriazole[1] (Hostavin 3311, Clariant); inorganic UV stabilizers, rutile nano--TiO$_2$ (30 nm, 99.9%, Merck) and nano-ZnO (10-30 nm, 99%, Merck); and an organic antioxidant, olive leaf extract (Adonis Company, Iran). They were mixed with the coating according to the formulations described in Table 1. The additives were weighed and added to the polyacrylate, and were then mixed in an ultrasonic mixer.

Table1. Formulations of clear waterborne polyacrylate coatings

Type of coating	Additive content* (%)			
	Extract	TiO$_2$	ZnO	BTZ
Poly-	–	–	–	–
Poly- extract	10, 20	–	–	–
Poly- nano-ZnO	–	–	1	–
Poly- nano-TiO$_2$	–	1	–	–
Poly- nano-ZnO – extract	10, 20	–	1	–
Poly- nano-TiO$_2$ – extract	10, 20	1	–	–
Poly- BTZ – extract	10, 20	–	–	4
Poly- nano-ZnO – HALS	–	–	1	–
Poly- nano-TiO$_2$ – HALS	–	1	–	–
Poly- BTZ – HALS	–	–	–	4

*The additives were added to polyacrylate on a w/w basis.

[1]BTZ

Wood samples

Wood samples of *Picea sp.* with sizes of $300 \times 100 \times 25$ mm with an initial moisture content of more than 30% were modified in a heat treatment chamber (Garmin Choob Sazan Danesh Co., Iran) using a high temperature (200°C) for a holding time of 2 hours. The samples were resized to $150 \times 100 \times 20$ mm and were then conditioned at a temperature of 23 ±2°C and RH 60 ±5% for a week to achieve a moisture content of about 10%. They were then sanded with sandpaper (grit no. 120). Afterwards, the samples were double-layered with the coatings formulated according to Table 1. The coats were applied on the wood surface twice using a brush. The amount of applied coating was 200 g/m² for two layers. The coated samples were dried for 24 hours before application of the second layer. The average thickness of the coats was measured at ca. 100 ±5 µm after drying. The samples were then allowed to dry in ambient conditions (23 ±2°C, 60 ±5%) for a week before the evaluation tests were performed. At least four samples were selected for each formulation, and three spots were also marked to perform all measurements before and after coating.

Color measurement

Color coordinates were determined and compared with values of the same parameters before coating. A Sheen Micromatch Plus spectrophotometer using the CIE-Lab color measuring system was used, according to the ASTM D2224--02:2016 standard. For each sample, three readings were recorded at each spot. $L*$ expresses the lightness, and $a*$ and $b*$ are the red-green and yellow-blue coordinates, respectively. $\Delta L*$, $\Delta a*$ and $\Delta b*$ are the total changes of $L*$, $a*$ and $b*$ after coating of the wood. $C*$ denotes chroma and $\Delta C*$ is chroma difference, $\Delta E*$ is total color change, and $\Delta H*$ is hue difference. $\Delta C*$, $\Delta E*$ and $\Delta H*$ were computed using the following equations:

$$\Delta L* = L*_{coated} - L*_{uncoated} \tag{1}$$

$$\Delta a* = a*_{coated} - a*_{uncoated} \tag{2}$$

$$\Delta b* = b*_{coated} - b*_{uncoated} \tag{3}$$

$$C* = [(a*)^2 + (b*)^2]^{1/2} \tag{4}$$

$$\Delta C* = C*_{coated} - C*_{uncoated} \tag{5}$$

$$\Delta E* = [(\Delta L*)^2 + (\Delta a*)^2 + (\Delta b*)]^{1/2} \tag{6}$$

$$\Delta H* = [(\Delta E*)^2 - (\Delta L*)^2 - (\Delta C*)]^{1/2} \tag{7}$$

Contact angle

The apparent water contact angles (CA) indicate the surface free energy of the coated samples. Characteristics such as surface roughness were determined using the PGX-Goniometer contact angle system. The (distilled) water droplets

(3.5 µl) were dripped by a micro-syringe pump onto the sample surfaces, and images were then captured over 180 s of evolution time. At least three measurements were performed to determine the contact angle of water as well as the volume of the water droplets and the height of the drops on each sample. For each sample, three readings were recorded at each spot.

Roughness

A HUATEC SRT-6200 roughness meter was used to determine the roughness of the samples. Two parameters, R_a and R_z, were determined on a cut-off path line of 2.5 mm. R_a indicates an average for altitudes on the wood surface, and R_z indicates an average of 5 altitudes and 5 valleys on the wood surface along the sensor path line. The roughness was determined on surfaces of all samples with at least three readings on each sample, and in total nine readings for each coating treatment.

Results and discussion

Color changes

The color changes of the TMT samples were determined after coating with polyacrylate finishes without or with different additives. The value of Δa^* increased in the majority of the samples with additives, compared with the wood coated with polyacrylate with no additives (Fig. 1). However, the amount of variation was different according to the types of applied additives or their interactions. An increase in a^* is an indication of the color becoming reddish. Large Δa^* values were found for the coatings with BTZ and olive leaf extracts (Fig. 1c). It can be seen that all wood samples coated with polyacrylate containing nano-TiO_2 gave positive values of Δa^* after coating, except for TMT coated with the mixture Poly-nano-TiO_2-olive leaf extract 10% (Fig. 1). This means that the color of the specimens tended to take on reddish tones after coating with the polyacrylate and different additives. However, the TMT wood coated with the mixture Poly-nano-TiO_2-olive leaf extract 10% turned greenish (Fig. 1a). Also, for other formulations with nano-ZnO and BTZ, the color tendency was in the direction of red. According to the results shown in Figure 1, it can be concluded that the presence of nano-TiO_2 and of nano-ZnO produced less color variation of the samples compared with the polyacrylate-coated specimens with no additives. Also, all coats formulated with the olive leaf extracts showed a reddish tendency (except Poly-TiO_2-olive leaf extract 10%). It seems that the olive extract is responsible for the red tendency in the coats. However, interaction between additives involving BTZ is responsible for color dominance in a sample.
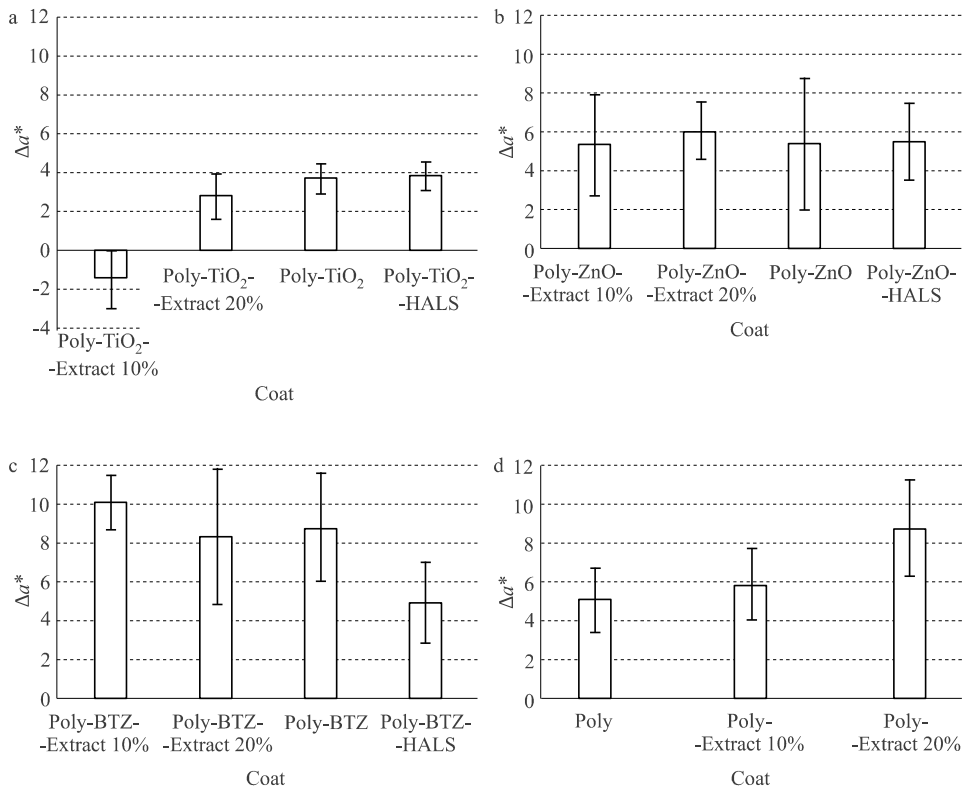
Fig. 1. Δ*a** of TMT coated with polyacrylate containing different additives

The mixing of additives into the polyacrylate changed Δ*b** in different ways (Fig. 2). An increase in Δ*b** is an indication of the color tending toward yellow, and a reduction is an indication of a change to a bluish color. As shown, the samples coated with TiO_2 show reductions in Δ*b**, which means that the color tendency is toward bluish in those samples (Fig. 2a). However, there was no clear change for nano-ZnO (Fig. 3b). For BTZ, different responses were obtained in the TMT wood color (Figure 3c), but increases in Δ*b** were found, indicating a tendency toward a yellowish color. Large Δ*b** values were found for polyacrylate with the additives BTZ and HALS and for the polyacrylate with no additives (Fig. 2c,d). It seems that the addition of the olive leaf extract reduces the color tendencies and changes it toward bluish.

The lightness of the coated samples was strongly affected by the coatings and by the additives, except for the coating having nano-TiO_2 mixed with olive leaf extract 10% (Fig. 3). As shown, Δ*L** took negative values, which means that the color became darker due to coating of the wood with polyacrylate and the additives. This darkening may be due to interaction between the wood color and the color of the polyacrylate coating [Plelit 2017].
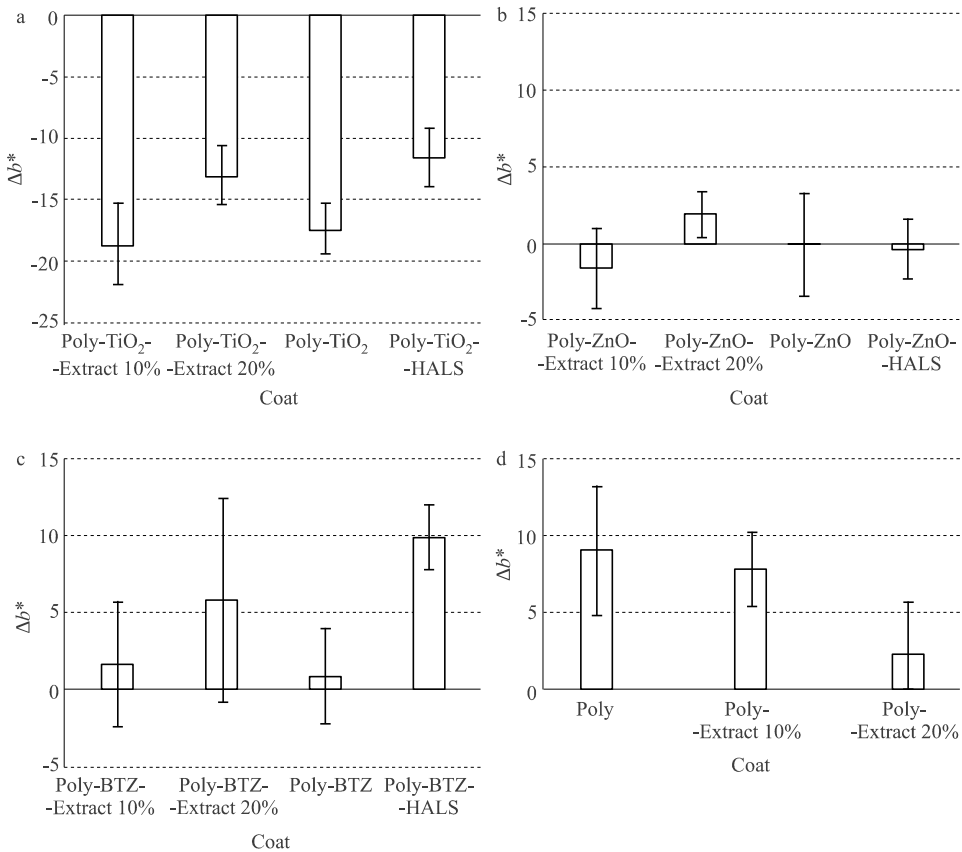
Fig. 2. $\Delta b*$ of TMT coated with polyacrylate containing different additives

The $\Delta E*$ value is an indication of total color changes in the coated TMT wood (Fig. 4). It indicates that all of the color coordinates $L*$, $a*$, $b*$ were affected by the coating. The results show that the total color change was increased in all coated samples (Fig. 4). The $\Delta E*$ changes also confirm the findings for variation in $L*$, $a*$ and $b*$ as shown above (Figs. 1-3). It is likely that TMT wood color is affected by the coating applied and the formulation. In general, $\Delta E*$ may be mostly affected by the changes in $L*$, because large variations were recorded for the lightness of the samples in comparison with $a*$ and $b*$ (Figs. 1-3). According to the observations of sample color, the samples turned to a brownish color after coating.

The chroma ($C*$) is defined mathematically as the square root of the sum of squares of the two parameters $a*$ and $b*$. The chroma indicates the quality of a color's purity, intensity or saturation. In color theory, chroma refers to the degree of vividness of a color, or how pure it is compared to its representative on the color wheel. It can also be called saturation, or color intensity. The $\Delta C*$
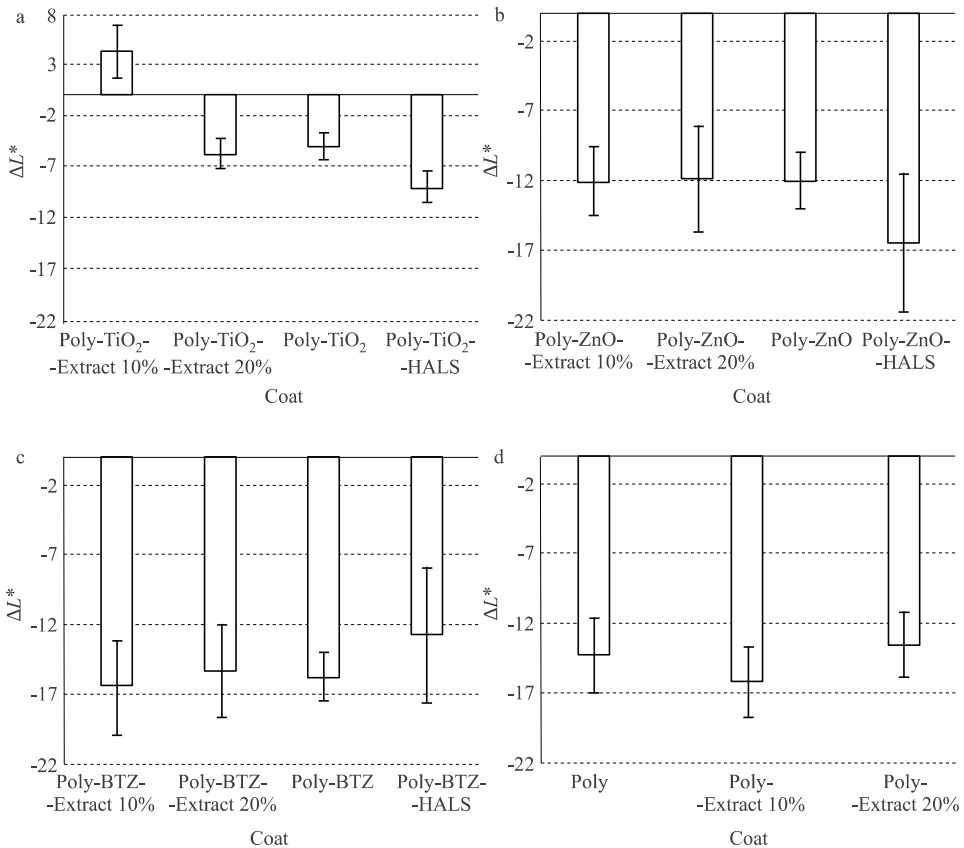
Fig. 3. ΔL^* of TMT coated with polyacrylate containing different additives

value indicates any differences in chroma before and after coating, expressing increased vividity of the wood color [Cao et al. 2012]. It shows how light or dark is the color of the coated TMT wood. The chroma of the coatings may be placed in the color zones red-yellow, yellow-green, blue-green or red-blue. Positive values of ΔC^* indicate that the color becomes more vivid and light, while for negative values the vividity is reduced and the color is changed to a darker one. According to the results, the nano-TiO_2 separately or together with olive leaf extract 10% and 20% caused reduction of the color vividity (Fig. 5a), while more vivid colors were obtained due to the addition of BTZ (Fig. 5c). Application of nano-ZnO caused less reduction in the vividity (Fig. 5b). High vividity was found for the samples coated with polyacrylate with added BTZ and olive leaf extract (Fig. 5c, d).

The ΔH^* value indicates to which color's coordinates the hue mostly tends. The results showed that the hue variation was affected by the additives (Fig. 6). High ΔH^* was determined in samples coated with polyacrylate with the additives TiO_2 and BTZ mixed with olive leaf extract, and nano-ZnO

(Fig. 6a, b, c). Pure polyacrylate produced a lower value of ΔH^* (Fig. 6d). This may be due to its intrinsic brightness.
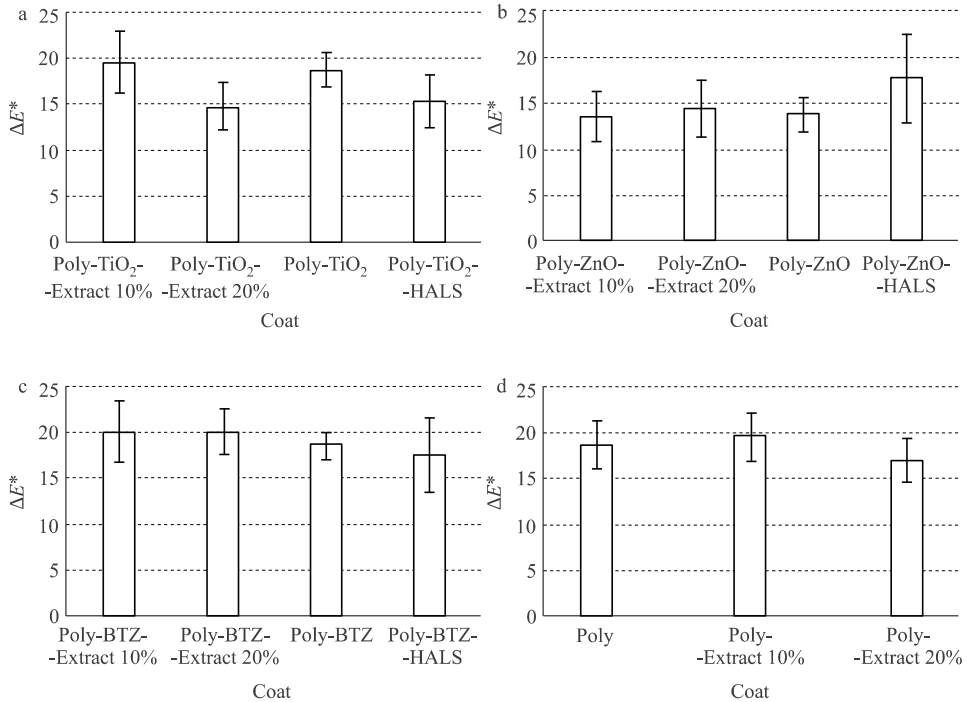

Fig. 4. Total color change of TMT coated with polyacrylate containing different additives

Contact angle

Results of water contact angle measurements are presented in Figure 7. It was found that there is a rapid decrease in the water contact angle on the uncoated TMT wood (Fig. 7d), while application of the polyacrylate coatings mixed with additives, and also with no additive, provided more stable contact angles on the coated TMT wood. Lack of changes in the water contact angle is an indication of the absence of penetration of the water into the coating and wood, as well as reduced surface tension on the wood surface. As shown, the contact angle was reduced over the evolution time on the uncoated TMT wood. This may be due to increased porosity of the thermally modified wood, produced during the heat treatment, and also probably a greater surface tension on the TMT wood. Coating of the TMT wood provided a hydrophobic surface. However, among the additives, a pronounced decrease in the water contact angle was found with BTZ (Fig. 7c). A decrease in the contact angle is an indication of the hydrophilic tendency of the wood surface, as seen with the uncoated wood and in the case of
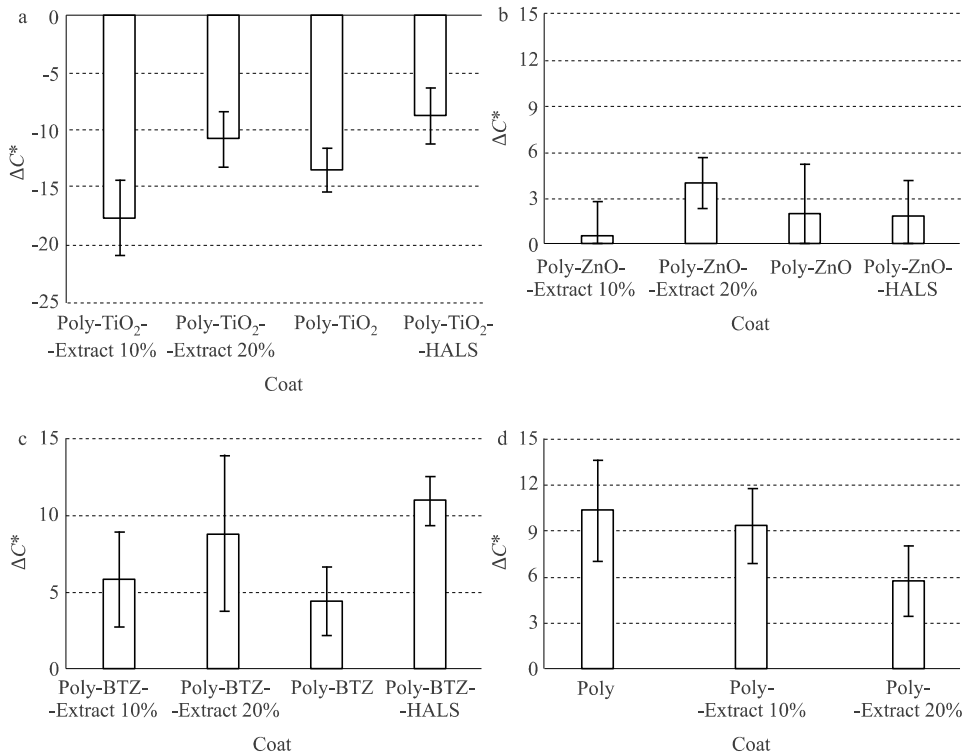
Fig. 5. ΔC^* of TMT coated with polyacrylate containing different additives
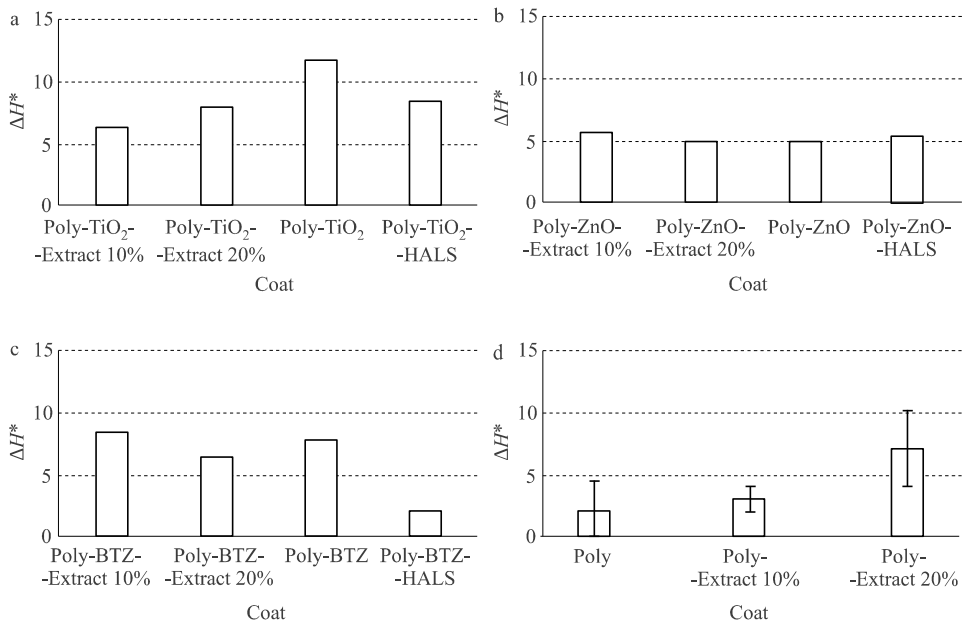

Fig. 6. ΔH^* of TMT coated with polyacrylate containing different additives

BTZ. It should be noted that thermally treated wood exhibits more hydrophobic behavior than non-modified wood. Here, all samples are thermally modified. Therefore, the porous structure of the heat-treated wood may be responsible for the decrease in the contact angle over the evolution time.
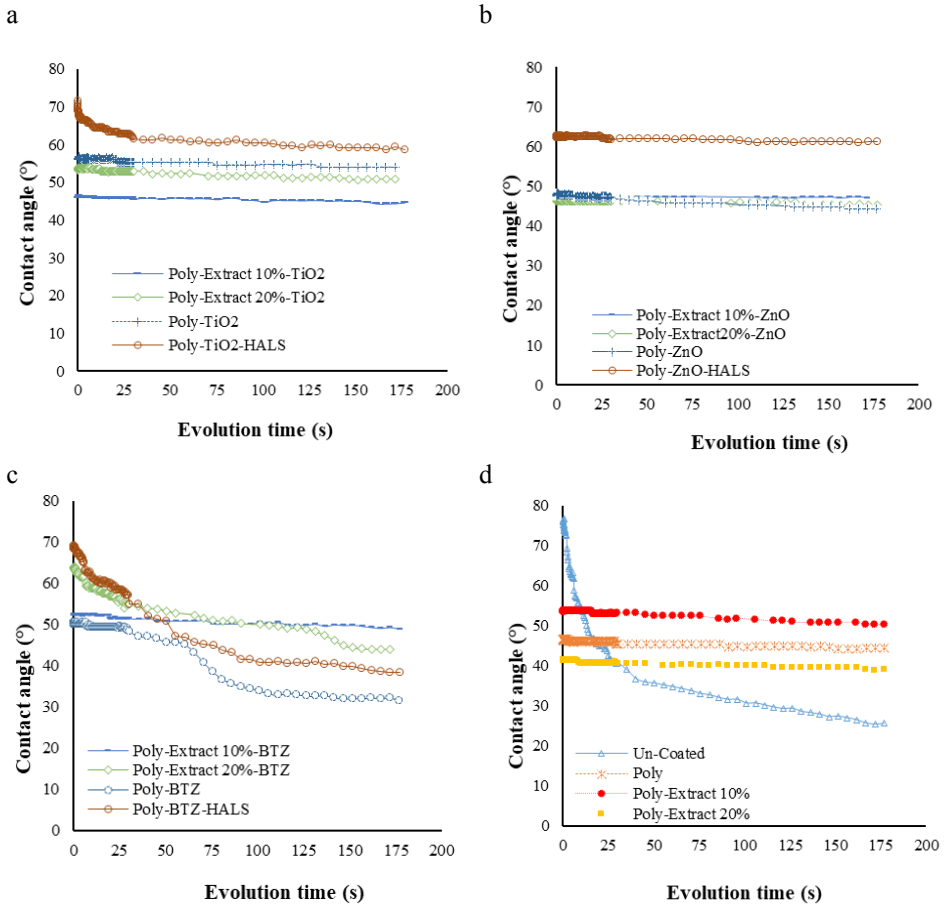

Fig. 7. Water contact angle of TMT wood uncoated and coated with polyacrylate containing different additives over the evolution time of 200 s

Changes in the volume of the water droplets during the evolution time are presented in Figure 8. As shown, there were no changes in the water volume for the coated samples in all periods. However, the water volume on the uncoated wood surface undergoes an initial increase up to an evolution time of 30 s, and then a reduction in the water volume. It seems that electrical charges require time to balance the surface tension in the water droplets on the surface of the uncoated samples due to their polymeric structure. The volume was less in the case with nano-TiO_2 added to the polyacrylate than with the other samples

(Fig. 8a). This may be due to the nano-rough surface produced on the TMT wood by the nano-TiO_2.
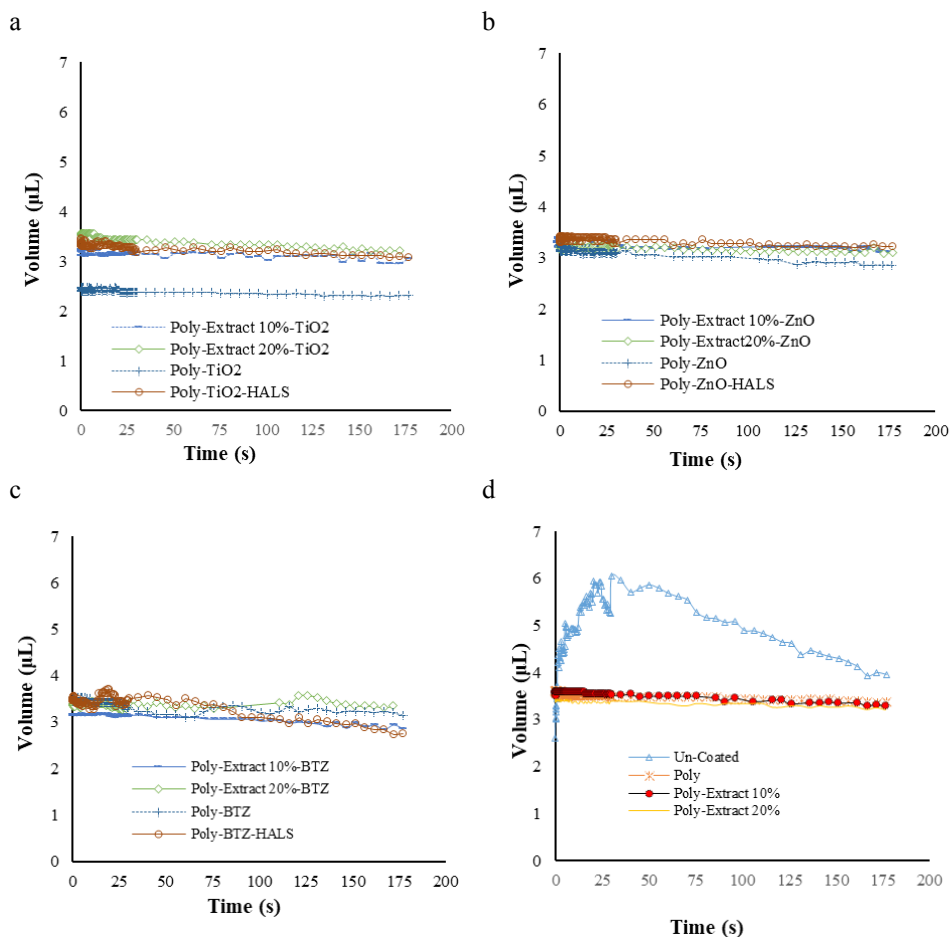

Fig. 8. Variation in water droplet volume on TMT uncoated and coated with polyacrylate containing different additives over the evolution time of 200 s

Results for the measured heights of the droplets are shown in Figure 9. It was found that the height of the water droplets reduces over the evolution time on the uncoated samples. However, there were no changes for all coated samples. Reduction of the height is an indication of surface tension and penetration of the water droplets into the wood porosities. Coating of the surface by polyacrylate with or without different additives provided a hydrophobic film on the samples that prevented penetration of the water into the wood structure.
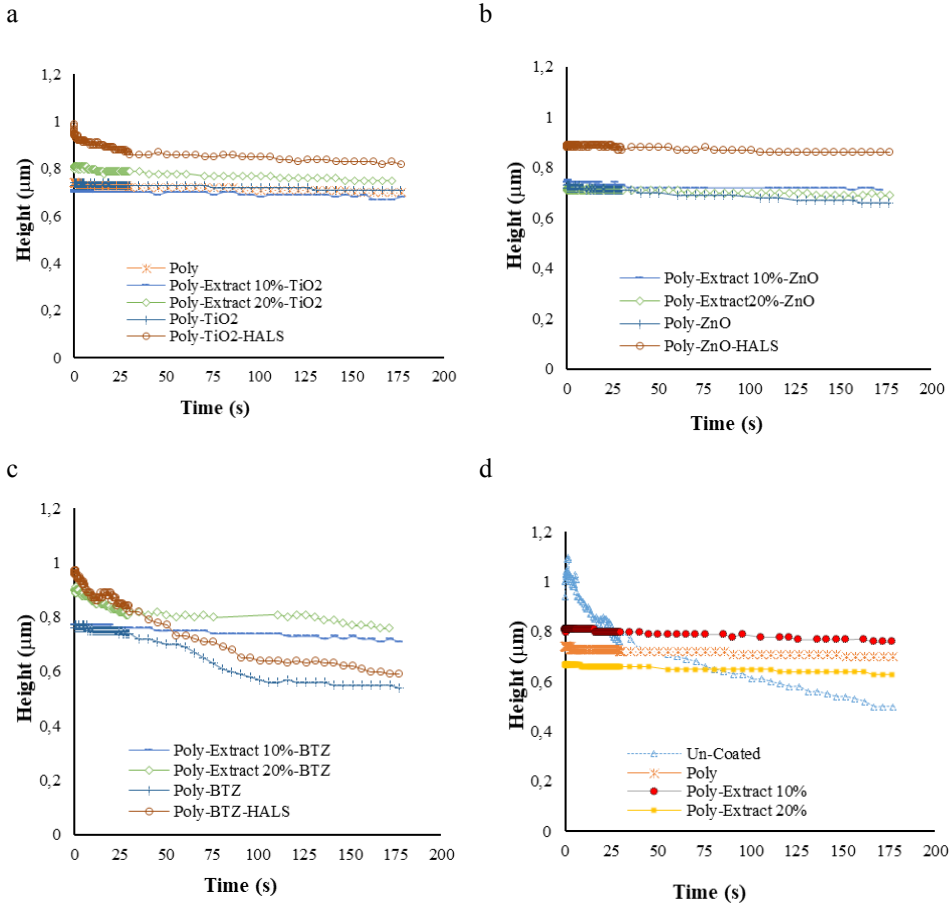
Fig. 9. Height of water droplets on TMT uncoated and coated with polyacrylate containing different additives over the evolution time of 200 s

Roughness properties

Application of the coatings on the TMT wood surface caused a clear reduction in the surface roughness (R_a) and provided a smooth surface on the coated wood samples (Fig. 10). Application of the additives in the polyacrylate coating did not affect the surface roughness in comparison with samples coated with the unmodified polyacrylate. The reduction of the surface roughness of the coated wood samples is probably related to penetration of the polyacrylate coatings into the wood pores and filling of the cell lumina. Nowrouzi and Mohebby [2016] reported that samples coated with linseed oil had the lowest surface roughness due to penetration of the oil into the wood.
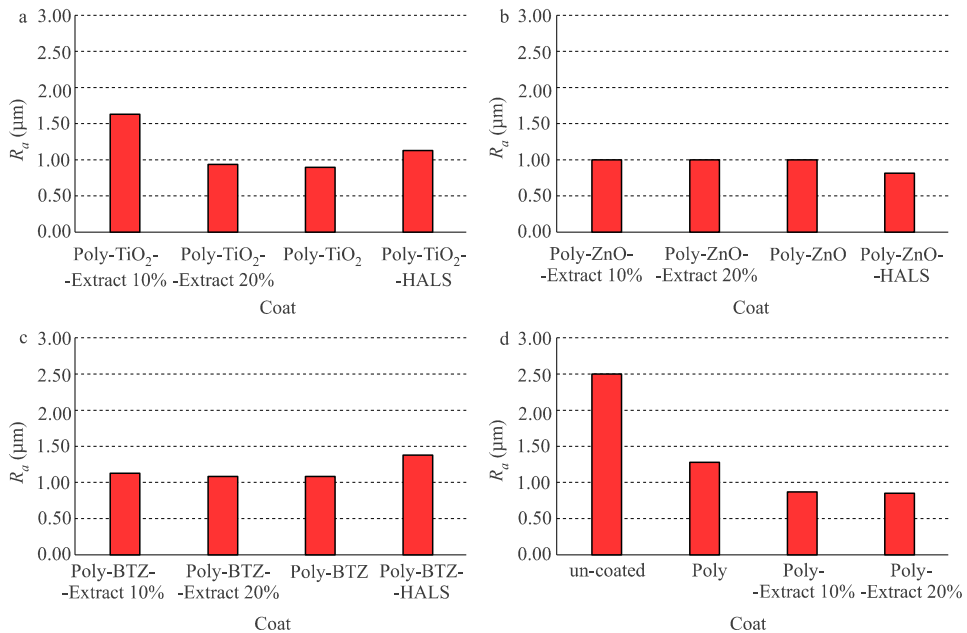
Fig. 10. Roughness properties of TMT uncoated and coated with polyacrylate containing different additives

Conclusion

The current research work was planned to study the effects of polyacrylate coating mixed with different additives on the surface properties of thermally modified wood. The following conclusions may be drawn from the results:

- Total color changes (ΔE^*) were determined in the coated samples. There was also a large change in lightness (ΔL^*) of the samples after coating. The lightness of the coated TMT wood was reduced after coating. The ΔC^* value was also reduced, and the color became darker due to coating.

- Addition of nano-ZnO and BTZ to the coating changed the ΔH^* values for the coated TMT wood less than the addition of nano-TiO$_2$.

- The coatings provided hydrophobic surfaces on TMT wood, and caused an absence of changes in water contact angle, water volume and height of the water droplets.

- Polyacrylate alone or with additives provided smooth surfaces.

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List of standards

ASTM D2224-02:2016 Standard practice for calculation of color tolerances and color differences from instrumentally measured color coordinates.

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