# Effect of Titania and Zinc Oxide Particles on Acrylic Polyurethane Coating Performance

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The outer environment, especially UV portion of solar radiation and water (in the form of moisture or rain) has an adverse effect on the surface appearance of heat-treated wood. Exposure to UV triggers the chain scission reactions which change the intrinsic properties of heat-treated wood and discoloration of wood surface. Repeated temperature and humidity variations cause swelling and shrinking of wood surface, which consequently creates cracks and fissures exposing wood's sub superficial layers to atmospheric agents. Therefore, wood industries move towards the development of coatings in order to protect the heat-treated wood while retaining wood's natural look. Water based acrylic polyurethane coatings are highly efficient, non toxic and durable coatings with upgraded film properties. In this study, an attempt is made to improve the performance of these coatings by incorporating natural antioxidant (bark extract) and inorganic UV absorbers (nano and micro titania and nano zinc oxide) into the coatings. The main objectives of this study are to investigate the wetting and penetration characteristic of these new coatings on the wood surface and to study coating thickness variation with weathering time. The Sessile-drop method and fluorescence microscope are used for this investigation. The wettability of different coatings applied to heat-treated jack pine early wood and late wood is compared. The results show that there is a significant difference between the contact angle of early wood and late wood for acrylic polyurethane coating containing titania micro particles. The contact angle between water and coated wood surface reveals that the degree of orientation of the coating materials increases as the weathering time increases. The penetration characteristics of all the three coatings are found to be very poor. In addition, the relationship between the coating thickness and the UV exposure time are studied for three different water based acrylic polyurethane coatings. It is found that the coating thickness decreases with increasing weathering time and a tissue deformation beneath the coating surface takes place during weathering.

Key Words: Weathering, Heat-treated jack pine, Acrylic polyurethane coating, Wetting, Fluorescence microscopy, Titania and zinc oxide particles.

## 1. Introduction

Heat-treated wood is a new value added product with improved biological resistance, dimensional stability, and an attractive darker color [1-4]. Changes in the intrinsic properties of heat-treated wood as a result of exposure to outer environment especially to UV portion of solar radiation and water (in the form of moisture or rain) often cause serious problems in appearance of the surface due to the occurrence of chain scission reactions. Moreover, the repeated temperature and humidity variations of the ambient environment subject the wood to wet and dry cycles which result in swelling and shrinking, consequently, creates cracks and fissures [5-12]. These in turn lead to the exposure of the wood's sub superficial layers to atmospheric agents and the progressive degradation of the wood surfaces and sub surfaces. These facts forced wood industries to move towards the development of a non toxic transparent coating for UV protection of heat-treated wood [7, 13]. Coating selection for exterior use often requires a balance between aesthetic (clear coatings) and protection (colored coatings) for a particular application. Water based acrylic polyurethane coatings are highly efficient, non toxic and durable with upgraded film properties [14-16] and applied widely in the recent years due to growing environmental concerns. Though the polymer itself is non toxic and durable in outer environment, incorporation of UV absorbers and HALS is necessary for the development of transparent coatings which most of the time are toxic in nature. Increasing pressure of the environmental legislation to reduce the VOC content of the coatings has compelled the development of non toxic organic and inorganic UV absorbers. Among the inorganic UV absorbers titanium dioxide and zinc oxide have a long history of color protection [17-19]. The natural antioxidant (bark extract) on the other hand is a new additive and no information was found in the literature citing their application as coating additive and their effectiveness in prevention of wood discoloration. The effect of natural antioxidant in prevention of wood coloration is the subject of another paper [20]. In this study, an attempt was made to improve the performance characteristic of acrylic polyurethane by incorporating them with a natural antioxidant (bark extract) and inorganic UV absorbers (nano and micro titania and nano zinc oxide). In order to assess the performance of these modified coatings, it is necessary to study their wetting and penetration characteristics into wood and changes occurring at the wood and coating interface due to weathering induced by UV.

The service life (durability) of coated-wood surface depends on the chemical composition of coating material, properties of the wood surface (type of species, early wood and late wood region, sap wood or heart wood etc) and the interaction between the coating materials with the wood at their interface [21-23]. This interaction is primarily reflected in the wetting and spreading of the coating material over the wood surface during its application and it determines the contact area and smoothness of the coating layer.

The fluorescence microscope is a very important tool to determine the penetration characteristic of different coatings into wood cells. The penetration behavior is well correlated with the adhesion performance of coatings to the wood surface. Also, the changes in the wood-coating interface taking place due to weathering can be characterized using fluorescence microscopy. This analysis gives valuable information on the interaction between wood and coating [23]. In this paper, the effects of additives on the wetting and penetration characteristics of polyurethane coating and on the wood degradation due to weathering are presented. The coating thickness change with the increasing weathering time is also discussed.

## 2. Materials and Methods

### *2.1. Wood Surface Preparation*

In this study, commercially available heat-treated (210°C) jack pine wood has been used for all the tests. The wooden boards with tangential surfaces were randomly chosen from the lot obtained from ISA industry. The wooden panels were then planed followed by sawing.

### *2.2. Preparation of Coatings*

The acrylic-polyurethane coating was used as a base during the present study. This coating was modified using different additives such as organic antioxidant (bark extract), inorganic UV absorbers (micro titania particles obtained from Sigma Aldrich, nano titania and nano zinc oxide obtained from MK Nano). Alone or different combinations of these additives were utilized. The formulations of different coatings are presented in Table1.

Table1 Summary of the composition of the four coating formulations

| **Composition** | **Coatings** | | | |
|---|---|---|---|---|
| | **A** | **B** | **C** | **D** |
| Other components | √ | √ | √ | √ |
| Inorganic UV absorbers | none | Titania micro particles<5µm | Titania nano particles~50nm | Zinc oxide nano particles~30nm |
| Organic UV absorber and HALS | √ | √ | √ | √ |
| Natural Antioxidant | none | √ | √ | √ |

### *2.3. Accelerated Weathering Test*

28 jack pine samples were coated with two layers of the coatings tabulated in Table1. Seven samples were prepared for each coating. 6 of these samples were exposed to accelerated weathering test and one sample for each coating was kept as a reference. The reference samples were protected from the light exposure.

Accelerated weathering test was conducted in Atlas Xenon Weather-Ometer (with a daylight filter, irradiation 0.35W/m2 at 340nm, BPT 63±3°C and continuous light cycle with 102min light and 18 min specimen spray with light). All the above mentioned samples were exposed to UV light for different time span with maximum exposure time of 1500h. A sample for each coating was taken out after 72h, 168h, 336h, 672h, 1008h and 1500 h exposure.

### 2.4. Contact Angle Tests

The contact angle tests were performed using FTA200 sessile-drop system. FTA200 consists of a measurement platform and a frame grabber (video capture) card and a computer. With the help of a computerized syringe pump, 15µL drop of a desired liquid was placed on the wood sample and the images were captured using high resolution camera for a predetermined time. The contact angle measurement of liquid/wood system and data analysis was carried out using the image analysis software FTA32. All the contact angle experiments were carried out at room temperatures. In this study, only tangential surface of wood was examined and the contact angle experiments were executed along the veneer grain direction in order to study the affinity of the coatings towards tangential surface of heat-treated jack pine. The contact angles of water and coated jack pine surface were also measured before and after weathering. The surface tension of the liquid coatings was measured by pendant drop method using the FTA32 software. At least 6 measurements were carried out for each coating.

### 2.5. Fluorescence Microscopy Test

For fluorescence microscopy tests, 2cm×2cm×1cm blocks were sawn from the wood specimens before and after they are subjected to accelerated weathering test. Then, they were immersed in water for at least an hour in order to soften the surface prior to microtoming. After, 15µm thick sections were cut perpendicular to the surface by using sliding microtome in the region of wood-coating interface in both axial and radial directions. The staining of sections was performed in the following manner. All sections were stained with a 0.5% aqueous solution of Toluidine Blue to enhance the contrast of the wood tissue. To examine the depth of penetration and the pattern of distribution of the coating, sections were also stained with 1% Sudan IV solution prepared in 95% ethanol [24]. The resulting turquoise color of the wood cell walls contrasts well against the red color of the coating. Stained sections were mounted in glycerol on a glass slide and examined with a polaroid digital microscope consisting of a Nikon eclipse 600 camera with various zoom lenses. The coating thickness was measured from the light micrographs of radial sections using Wincell software and at least 30 measurements were carried out to find the average thickness of the coating.

## 3. Results and Discussions

### 3.1. Wetting of Wood Surfaces by Coatings Materials

The contact angle measurements of coating materials on the wood substrate are essential for understanding the adhesion, spreading and penetration characteristics of coatings [25]. As reviewed by Rijckaert et al. [21] the bulking effect of the coating polymers in the cell voids and cell wall structure may improve the dimensional stability, check resistant of the wood surface and penetration of the paint into the wood rays and cell lumens provides some mechanical strength to the wood.

Figure 1 compares the early wood and late wood dynamic contact angles for the acrylic polyurethane coating containing bark extract and titania micro particles. Late wood has a higher contact angle at all the times compared to that of the early wood. The porosity (big cell lumen and thin cell wall) of the early wood region is higher than that of the late wood region (thicker cell wall and smaller cell lumen). Higher porosity results in larger contact area between coating material and early wood which leads to better wettability, consequently, lower contact angle (Figure 1(a)). The wettability manifests itself not only through penetration of the liquid into the substrate and the spreading of the liquid on the substrate. The spreading on the early wood region is faster than the spreading on the late wood region. In order to comprehend the penetration characteristic of this coating, the images were taken using a fluorescence microscope in early and late wood regions along the wood-coating interface. Figures 1 (b) and (c) show that the penetration into both early wood and late wood regions is poor but there is good adhesion between cell wall and the coating for both. While there is one or two cell layer penetration in early wood region almost no penetration is observed in late wood region.

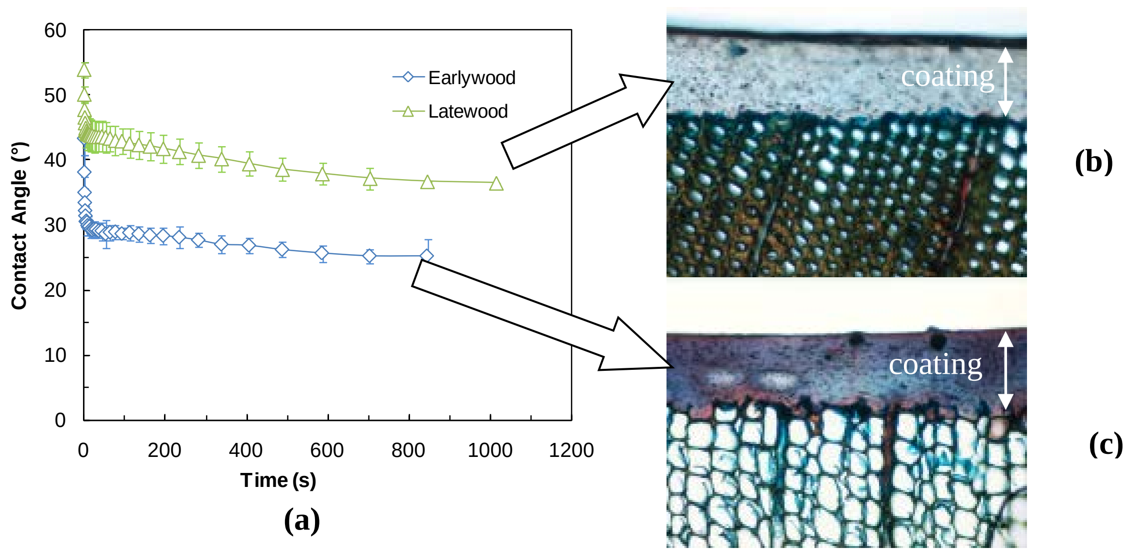
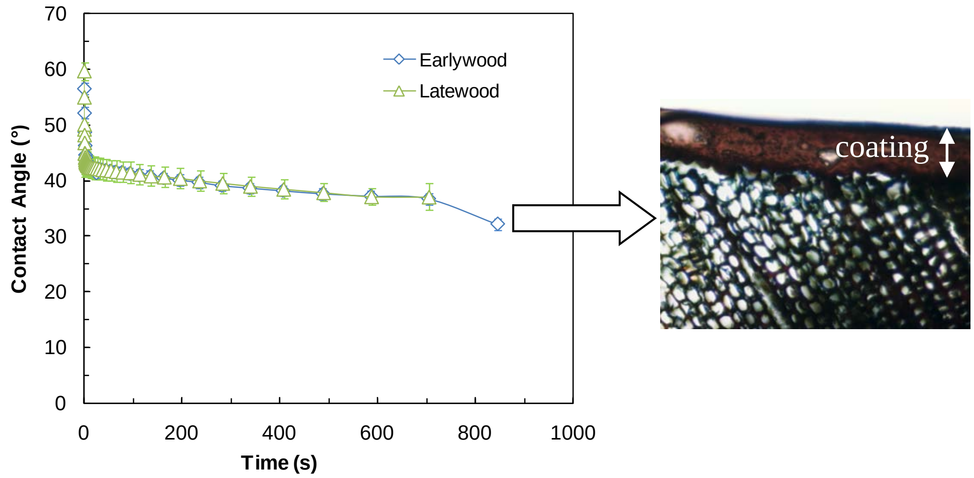



**Figure 1** Acrylic polyurethane coating containing bark extract and titania micro particle **(a)** comparison of contact angle change with time on early wood and late wood regions; penetration characteristic of **(b)** late wood **(c)** early wood jack pine studied with  fluorescence microscope




(b)

(a)

**Figure 2** Acrylic polyurethane coating containing bark extract and titania nano particles **(a)** comparison of contact angle change with time on early wood and late wood regions; penetration characteristic of **(b)** early wood jack pine studied using fluorescence microscope

No considerable difference in dynamic contact angles was observed between early wood and late wood regions coated with the acrylic polyurethane coating containing bark extract and titania nano particles (Figure 2 (a)). Spreading was also similar on both early wood and late wood jack pine for this coating. This is probably due to the presence of nano particles. Fluorescence test results show low penetration in the early and late wood region for both coatings. This is in agreement with the results of wetting test (Figure 2(b)).

Also, there wasn’t any significant difference in the dynamic contact angles of early wood and late wood jack pine and the acrylic polyurethane coating containing bark extract and zinc oxide nano particles (Figure 3(a)). However, the initial contact angle was higher in late wood region compared to that of the early wood region. The difference in the penetration characteristic of this coating in late wood and early wood regions is clearly shown in Figure 3 (b) and (c). The coating penetrates up to 4-5 cells in the early wood region but there is almost no penetration in the late wood region. Penetration results seem to be in conflict with the contact angle test results. As already mentioned above, the contact angle depends not only on the penetration but also on spreading. There is almost no spreading on early wood whereas spreading is very high for late wood for this coating. This might explain the observed contrast between the contact angle and penetration data.

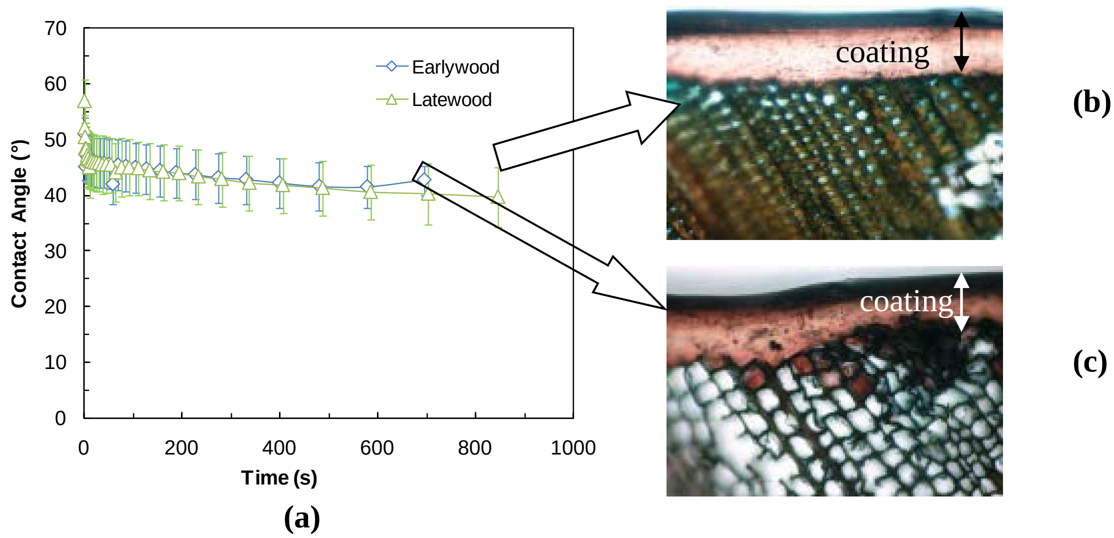



**Figure 3** Acrylic polyurethane coating containing bark extract and zinc oxide nano particles **(a)** comparison of contact angle change with time for early wood and late wood region; penetration characteristic of **(b)** late wood **(c)** early wood jack pine studied using fluorescence microscope

The only difference between the three coatings is the size and type of the incorporated nano particles. The overall comparison of the contact angle, penetration and spreading characteristics of these three coatings revealed that the coating containing titania micro particles wetted the surface most and coating containing zinc oxide nano particle containing wetted the surface least. This can be directly related to the surface tension results (Figure 4) obtained for these coatings. The lowest surface tension was measured for coating containing titania micro particles whereas highest surface tension was measured for coating containing zinc oxide nano particles. Although the highest penetration in the early wood region was observed for the coating containing zinc oxide nano particles compared to those of the coatings containing titania particles (micro and nano), the spreading of the former coating was found to be less comparatively less due to higher surface tension resulting in the highest contact angle at all times compared to the contact angles measured using other coatings.

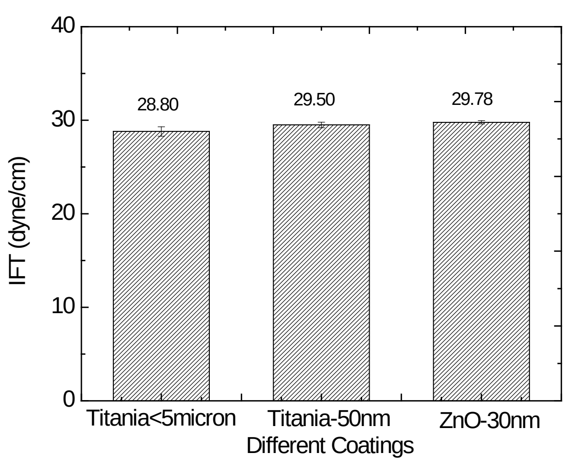


**Figure 4** Comparison of surface tension of acrylic polyurethane coating containing titania micro particles, titania nano particles and zinc oxide nano particles (IFT- interfacial tension between liquid coating and air)

### 3.2. *Contact Angle of Water and Coated-Wood Surface*

The weathering factors not only affect wood surfaces but they are also responsible for physical alteration of coatings. The wetting of the coated-wood samples by water is a simple but insightful measure of water penetration into the wood substrate through coatings. These measurements can indicate possible surface property modification of coated-wood due to weathering.

The contact angle change with time was found to be nonlinear for all the four coated and heat-treated jack pine surfaces before weathering (Figures 5 to 8). Figure 5 demonstrates the contact angle change of wood substrates coated with the coating containing only organic UV absorbers as a function of time before and after weathering at different times. The initial contact angle before weathering was lower than the initial contact angle after aging for 72h and 1500h and the contact angle before weathering changed very fast for initial 500s and reaches to 0 within 1250s. The initial contact angle after 72h of aging increased significantly comparing to that of the wood which was not subjected to the accelerated aging (before weathering 49.79 and after 72h of weathering 61.53) and the contact angle changed gradually with time with a slope of almost 0.02 and even after 2500s the contact angle was 8.43°. Though the initial contact angle after 1500h of weathering increased to 65.01° the contact angle changed drastically and approached to 0 within 150s. Usually, contact angle decreased with weathering but for this coating it increased, probably, due to the fact that this is a day light-cured coating. Therefore, the coating was cured by the cross linking between the polymers with increasing weathering time and the film hardened resulting in increased contact angle (decrease in wetting). After 1500h of weathering the significant change of the contact angle was due to the degradation of the coating surface and small crack formation at the surface.

For the acrylic polyurethane coating containing titania micro particles, the contact angle changes very fast and reaches to zero within 750s (Figure 6) whereas the acrylic polyurethane coating containing titania nano particles, the contact angle approaches to zero within 1250s (Figure 7) but the acrylic polyurethane coating containing zinc oxide nano particles exhibits highest resistance to water and complete wetting takes place only after 2000s (Figure 8). This is due to the higher degree of orientation of the acrylic polyurethane coating containing zinc oxide nano particles. As seen from the contact angle tests, the particle size of the inorganic UV absorber has an effect on the degree of orientation of the acrylic polyurethane coatings. The initial contact angles of water on all the three coated-wood surfaces were observed to increase with weathering time. Also, the contact angles at all times were found to be higher after subjected to 1500h of weathering compared to those observed after 72h of weathering for all the coatings studied. After 72h and 1500h of weathering, the contact angle change with time was found to be linear for all the three coatings except for an initial short period. The increase in contact angle after weathering is due to the amorphous nature of the coating material with a low degree of orientation at the initial stage. With the exposure to the lower wavelengths of solar radiation, these meta-stable chain orientations regroup to form a stable state resulting in increased degree of orientation. As explained previously, highest degree of orientation was observed for the acrylic polyurethane coating containing zinc oxide nano particles which resulted in highest contact angle after 1500h of weathering for all times compared to other two coatings. So it can be concluded from the above results that inclusion of natural antioxidant togather with inorganic UV absorbers improved film properties of the acrylic polyurethane coating.

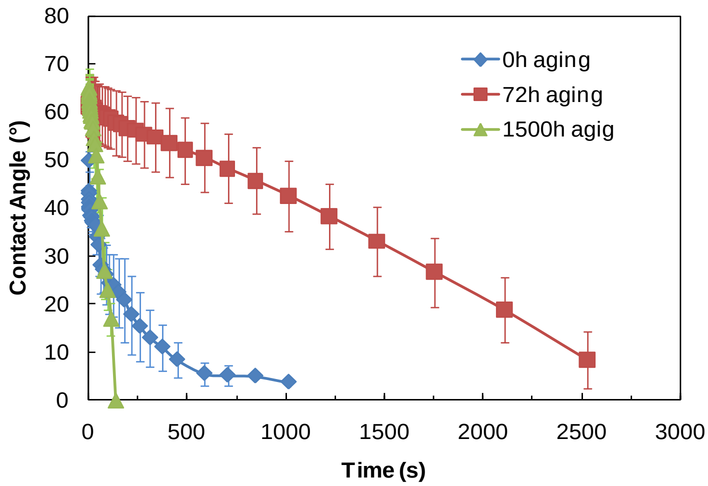



**Figure 5** Dynamic contact angle of water for different weathering times on jack pine surface coated with the acrylic polyurethane coating containing only organic UV absorbers

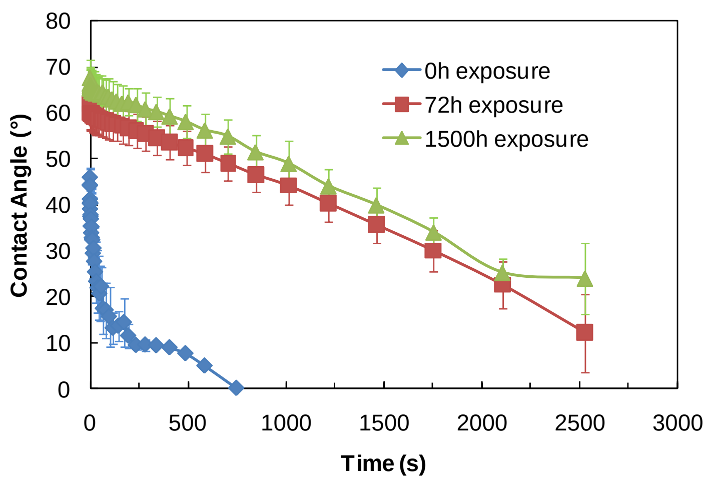



**Figure 6** Dynamic contact angle of water for different weathering times on jack pine surface coated with the acrylic polyurethane coating containing titania micro particles

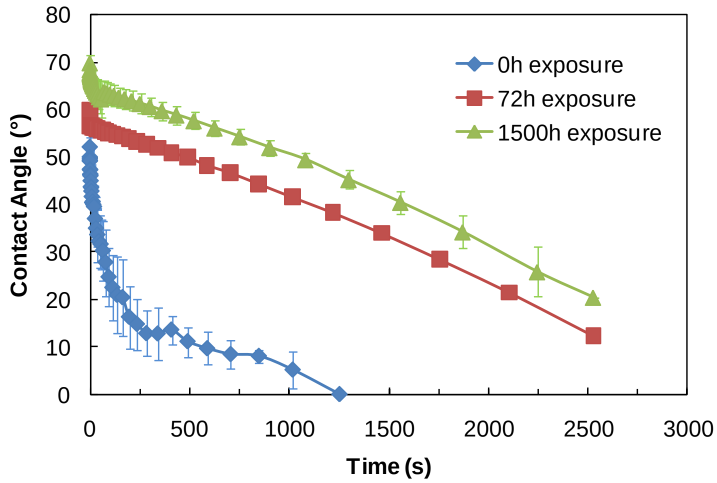



**Figure 7** Dynamic contact angle of water for different weathering time on jack pine surface coated with the acrylic polyurethane coating containing titania nano particles

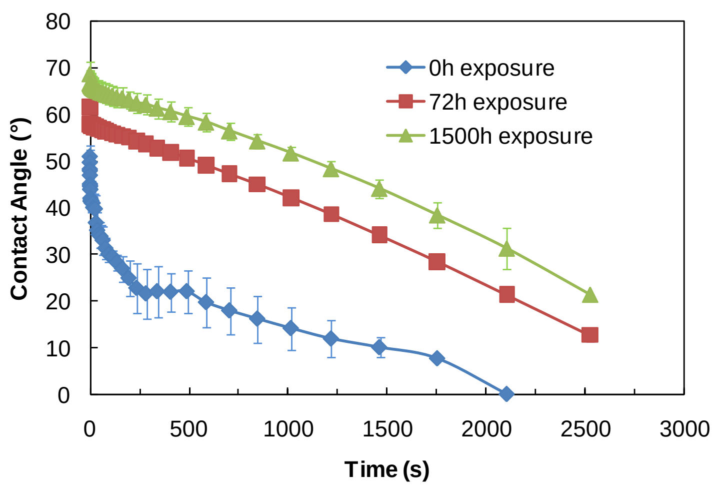



**Figure 8** Dynamic contact angle of water for different weathering time on jack pine surface coated with the acrylic polyurethane coating containing zinc oxide nano particles

### *3.3. Fluorescence Microscopy Assessment of Weathering of Coated-Wood*

The light microscopy of transverse sections of coated-wood provides useful information on the distribution of the coatings by observing relatively large areas at low magnification, thus enabling a comparison of coated-wood surfaces at different weathering times. Light microscopy observations also facilitate the evaluation of penetration characteristic of different coatings in early wood and late wood regions and coating thickness change with weathering. The coatings applied on wood were not visible under light microscopy. Wood samples were stained with a suitable dye as recommended by Singh and Dawson [24] in order to get an estimate of the depth of penetration into wood tissues. The radial sections were used to measure the coating thickness above the wood surface tissue for different weathering times for understanding the weathering effects on coating thickness.

The light microscope (LM) pictures before weathering shows good adhesion between outer layer of wood cells and the acrylic polyurethane coatings for both late wood (Figure 1 (b), 3 (b) and 9 (a)) and early wood (Figure 1(c), 2(b), 3(c) and 9(a)) regions though very poor penetration is observed for all. For early wood, only the outer early wood cells which are cut open over the full length and occasionally one layer below are filled. This phenomenon is well explained by de Meijer [23] as the paint flow over a short distance through the open end of a longitudinal tracheid. The occurrence of this kind of penetration depends on the angle of longitudinal tracheids and properties of the coatings such as viscosity and surface tension [21]. The late wood cells are hardly cut open forming a smooth cell layer and the coatings rest on the smooth late wood surface resulting in even paint layer whereas an unevenness is observed for early wood region (Figure 3(c) and 9(a)) for these coatings. The coatings mainly penetrate through the ray cells and tracheids adjacent of these ray cells in the late wood region are occasionally filled with coating due to the longitudinal flow through fenestiform pits [22]. The radial surface section (Figure 9 (b)) shows that the coating flow in the ray cells takes place through the parenchyma cell for jack pine whereas slight penetration is observed through ray tracheid cells.

After 672h of weathering, coating detachment takes place in the early wood region due to the degradation of the cells beneath the coating layer showing poor protection capacity of the coating against weathering (Figure 9c). From the radial section, it can be clearly seen that the coloration of the weathered cells becomes darker and slightly towards violet which is mainly caused by the lignin depletion in those cell layer during weathering (Figure 9c). Similar result is observed after 1500h weathering, however, the extend of degradation is more significant and the coating fully detaches from the wood surface in both early wood and late wood regions as shown in Figure 9d**.**

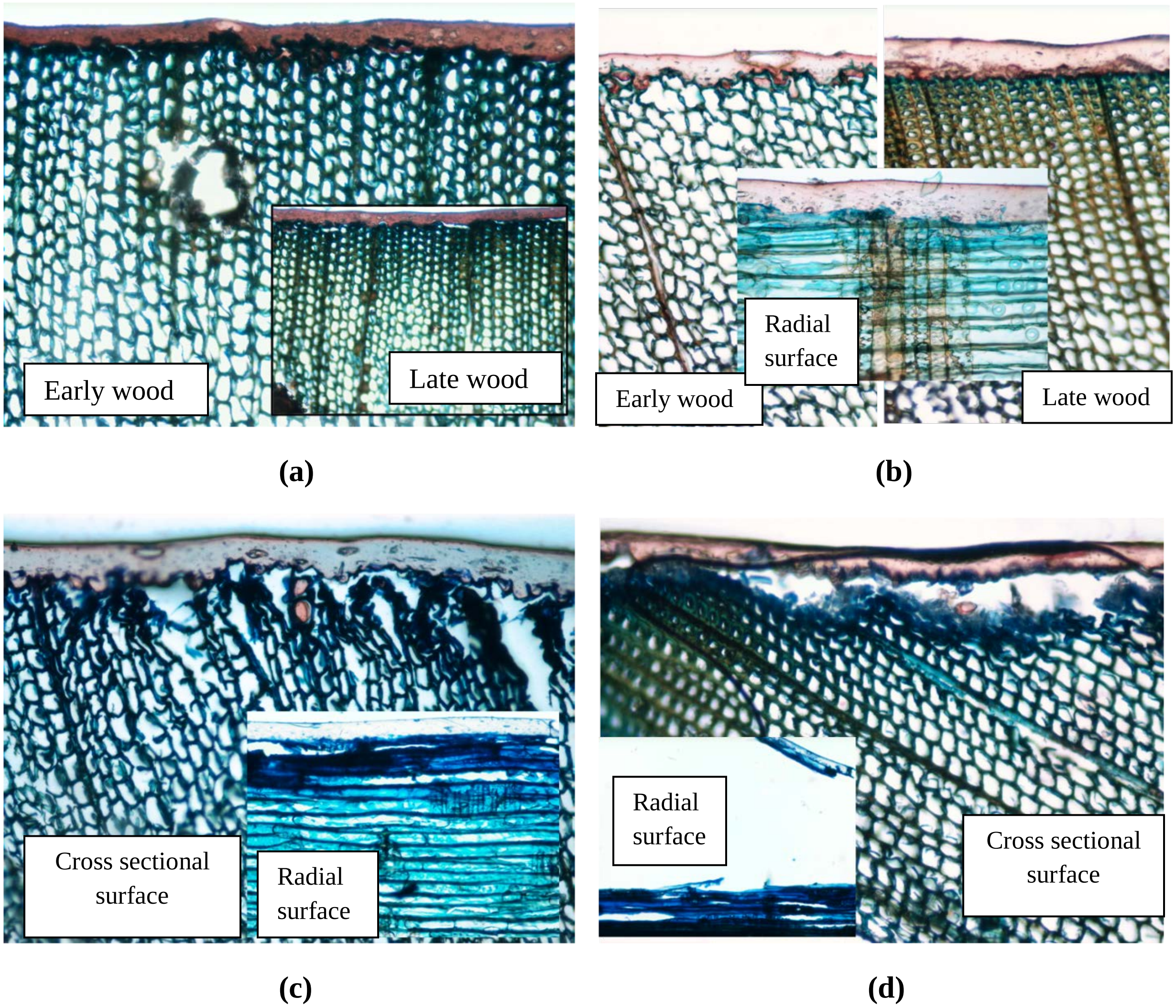



**Figure 9** Light micrographs from transverse and radial sections through faces of heat-treated jack pine wood coated with the coating containing organic UV absorbers (a) before weathering (b) After 72h of aging (c) After 672h of aging (d) After 1500h of weathering

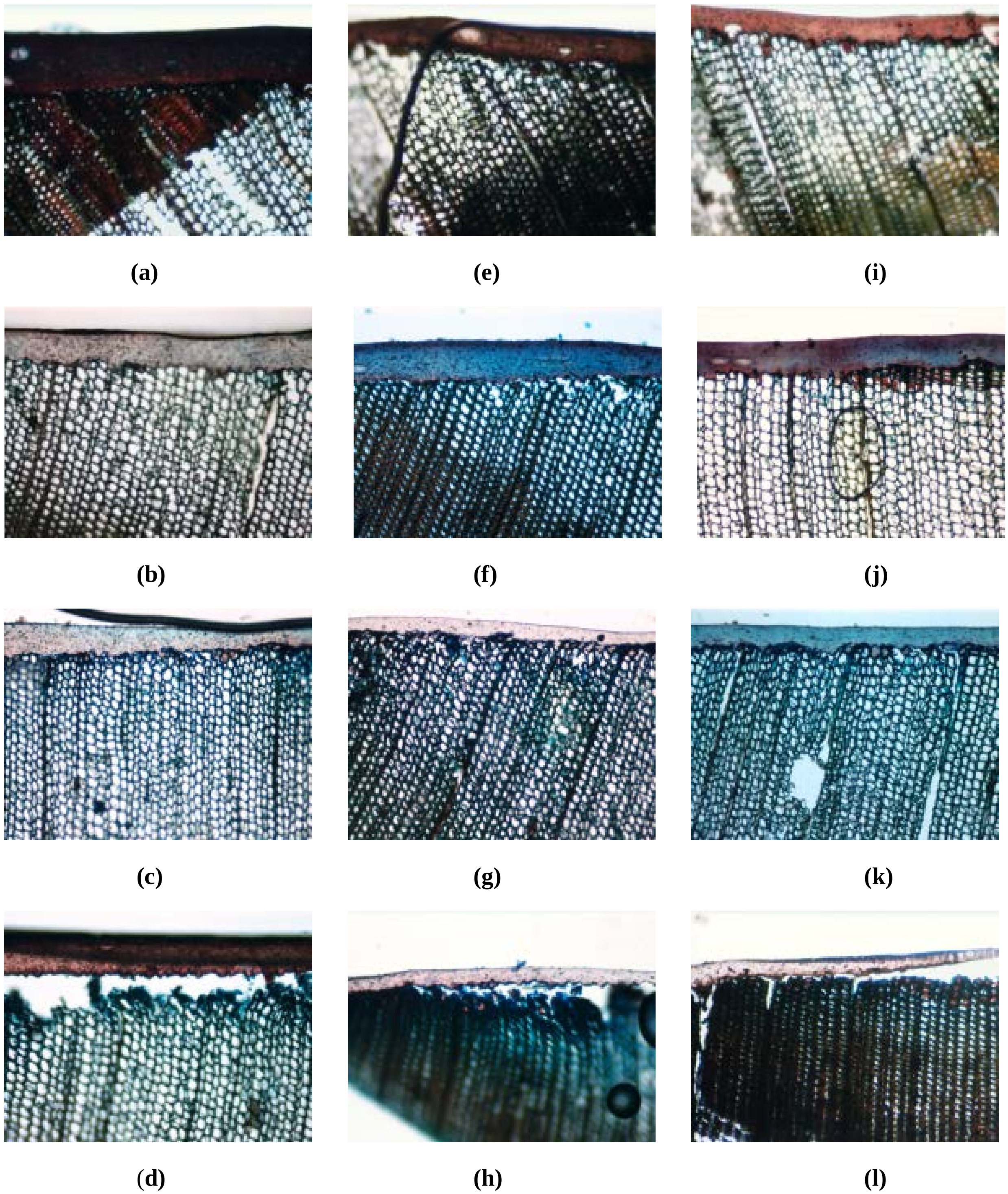



**Figure 10** The light micrographs of transverse section of the coating containing titania micro particles and wood interface for different weathering time **(a)** before weathering, **(b)** after 72h of weathering, **(c)** 672h of weathering, **(d)** 1500h of weathering, the coating containing titania nano particles and wood interface for different weathering time **(e)** before weathering, **(f)** after 72h of weathering, **(g)** 672h of weathering, **(h)** 1500h of weathering and the coating containing zinc

oxide nano particles and wood interface for different weathering time **(i)** before weathering, **(j)** after 72h of weathering, **(k)** 672h of weathering, **(l)** 1500h of weathering

The light micrographs of the three modified coatings have been compared for different weathering time in Figure 9. The acrylic polyurethane coating containing titania micro particles (Figure 10 (a)-(d)) protects well up to 672h of weathering (Figure 10c) and no change is observed up to this time. After 1500h (Figure 10d), weathered-wood micrograph shows that the degradation has started. Early wood cells just beneath the coating surface degrade due to weathering and after this time coating fails to protect the wood surface from weathering. However, the late wood is affected less compared to early wood. The acrylic polyurethane coating containing titania nano particles (Figure 10(e)-(h)) protects less compared to the acrylic polyurethane coating containing titania micro particles as it can be seen from light micrographs. The degradation of cell layer just beneath the coating surface has started after 672h (Figure 10(g)) of weathering for early wood region. Therefore, repainting is needed after this time for this coating. After 1500h (Figure 10(h)) of weathering, although high degradation is observed for late wood region, the early wood degrades at much faster rate than late wood. The acrylic polyurethane coating containing zinc oxide nano particles (Figure 10(i)-(l)) also protects jack pine well against weathering and no changes in the cell layer below the coating are noticed up to 672h (Figure 10(k)) of weathering. However, after 1500h (Figure 10(l)) of weathering, the degradation starts but it is less severe than those of the other two coatings. Certainly improved protection characteristics were observed for all the three modified coatings in comparison of the base coating (coating containing only organic UV absorbers).

The delamination of all the three coatings from wood surface after 1500h of weathering is mainly due to the separation of wood cells from each other at or near to the wood coating interface. Also, it is observed that one or two layers of wood cells remain attached to the coating surface after delamination (after1500h of weathering). This suggests a failure within wood tissue which causes the delamination of the coatings [26]. The main cause of coating failure as revealed by the light microscopy images (Figure 9 and 10) is the cell separation due to destruction of lignin in the middle lamella region [26] and not the loss of coating adhesion to the wood surface.

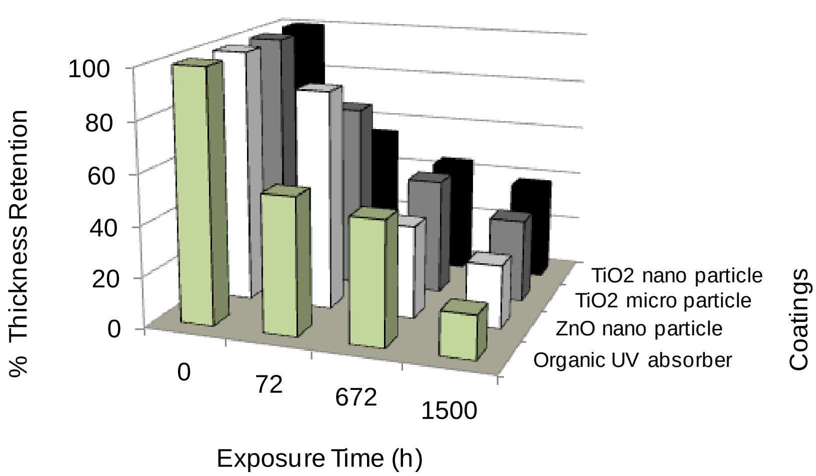



**Figure 11** Percentage of coating thickness retention with increasing weathering time

The protective characteristic of any coating depends highly on its thickness. If the coating is thin a part of the surface remains unprotected due to the porous nature of wood. If it is very thick the possibility of blistering increase. Therefore, an optimum coating thickness is necessary. Figure 10 compares the percentage of coating thickness retention of all the four coatings before and after 72h, 672h and 1500h of weathering**.** It is very clear from this figure that the coating thickness decreases with increasing weathering time and becomes almost 1/3$^{rd}$ of the initial thickness after 1500h of weathering for all the four coatings. This results show that coating erosion takes place due to weathering. After 72h of weathering, the acrylic polyurethane coating containing zinc oxide nano particles retains most its thickness whereas the acrylic polyurethane coating containing organic UV absorbers shows the lowest thickness retention at this stage. After 672h of weathering, all the four coatings retain almost similar coating thicknesses. After 1500h of weathering, the lowest thickness retention is observed for the acrylic polyurethane coating containing organic UV absorbers. Although the highest coating thickness retention is observed for the acrylic polyurethane coating containing titania nano particles, this coating has comparatively poor protective characteristic as shown by LM micrographs. The highest coating erosion at the end of 1500h of weathering was observed for coating containing organic UV absorbers.

The coatings penetration depths are not discussed further because the penetration is generally poor for all the four coatings. Mostly the coatings stay on the wood surface and form a film rather than penetrating in to the wood structure.

## 4. Conclusions

There was a significant difference between the contact angle of acrylic polyurethane coating containing titania micro particles and early wood or late wood jack pine whereas for the other two coatings no difference in contact angle has been observed in early wood and late wood regions. The contact angle of the acrylic polyurethane coating containing zinc oxide nano particles/jack pine showed highest value at all times compared to that of the other two coatings. This can be attributed its high surface tension. Coating containing titania micro particles has the lowest surface tension. The degree of orientation due to cross linking between polymers under the influence of light increases initial contact angle of coated-wood surface with water during weathering for all the three coatings. Coating erosion which takes place due to the photodegradation of polymeric material of the coating during weathering is an important phenomenon noticed for all coated-wood surfaces. Highest change in the coating thickness was observed for ZnO nano particle coating. Very poor penetration characteristic of all coatings was another important phenomenon revealed by fluorescence microscopy tests. The photodegradation effect on the cell layer just beneath the coating after 1500h of weathering was observed for all coatings but for the acrylic polyurethane coating containing titania nano particles the degradation started within 672h of weathering. Therefore, it can be said that this coating is less effective than the other two coatings for protecting heat-treated jack pine surface. The delamination is mainly due to the separation of wood cells from each other as a result of degradation of lignin during weathering and not to the adhesion loss of the coating material from the wood surface.

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