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Surface Degradation of CeO_2 Stabilized Acrylic Polyurethane Coated Thermally treated Jack Pine during Accelerated Weathering

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Abstract

The thermally treated wood is a new value-added product and is very important for the diversification of forestry products. It drew the attention of consumers due to its attractive dark brown color. However, it loses its color when exposed to outside environment. Therefore, development of a protective coating for this value added product is necessary. In the present study, the efficiency of CeO_2 nano particles alone or in combination with lignin stabilizer and/or bark extracts in acrylic polyurethane polymer was investigated by performing an accelerated weathering test. The color measurement results after accelerated weathering demonstrated that the coating containing CeO_2 nano particles was the most effective whereas visual assessment suggested the coating containing CeO_2 nano particles and lignin stabilizer as the most effective coating. The surface polarity changed for all the coatings during weathering and increase in

contact angle after weathering suggested cross linking and reorientation of the polymer chain during weathering. The surface chemistry altered during weathering was evaluated by ATR-FTIR analysis. It suggested formation of different carbonyl byproducts during weathering. The chain scission reactions of the urethane linkages were not found to be significant during weathering.

Key Words: Surface degradation, thermally treated jack pine, Acrylic polyurethane, Accelerated Weathering, CeO_2 nano particles, Color change, Wetting, ATR-FT-IR analysis

1. Introduction

Wood is a biological material which is susceptible to weathering and biological attack in external environment if not protected [1-11]. The thermally treated wood has improved durability against biological attack and also improved dimensional stability which reduces the fissures and crack formation on the surface [12-15]. It also changes the appearance of wood to a very attractive darker color which is in high demand among consumers, but its color is not stable during weathering without protection [16-18]. In order to protect the thermally treated wood from weathering, a durable, transparent or semitransparent and non toxic coating is needed to retain the wood's natural texture and look as well as the environment friendliness of the thermally treated wood [16-20].

Recently, acrylic polyurethane coatings have been widely used because of their high durability against weathering and also for their non toxic nature [17-18, 21-23]. From durability point of view, colored products are often added to coating materials, but this affects negatively the aesthetic nature of the end product. The transparency of the coating material is the most important factor for thermally treated wood from consumer's perspective so that its attractive darker color is preserved for decorative purposes. But, transparent coatings allow sunlight to reach to the wood surface which enables the onset of the photochemical reactions leading to change of color and loss of gloss of the surface [22-23]. To overcome this shortcoming of transparent coatings, UV absorbers are added as an additive to the coating formulations. The UV absorbers can be organic or inorganic in nature or can be combinations of both. The commercially available organic UV absorbers are very effective but mostly produced from petroleum by products which have adverse effect on environment. In addition, their life spans are

limited due to continuous destruction of active molecules (migration, leaching, photochemical activity).

Inorganic UV absorbers have been used since long time and silica, titania and zinc oxide are most commonly used inorganic UV absorbers [16, 24-26]. On the other hand, numerous researches are directing towards the ceria containing materials due to their wide ranges of applications in solid oxide fuel cells (SOFCs), catalysis, luminescent materials, gas sensors, polishing materials, and ferromagnetic oxides and so on [27-31]. Cerium oxide has almost the same band gap as that of titania (3.0-3.2eV) and shares the same classical UV absorption mechanism. Under UV light both cerium oxide and titania molecules get excited by absorbing a photon which creates an electron-hole pair [29].

In case of titania, these electron hole pairs migrate to the surface of the particles and eventually react with oxygen, water or hydroxyls to form free radicals. This process is known as photocatalysis and thus titania particles are not able to prevent the weathering of wood. On the contrary, cerium oxides are photocatalytically inactive in nature. The electron-hole pair formation is much lower than that of the titanium oxide due to the presence of higher localized electron in cerium oxide (4f orbital in case of cerium oxide in comparison to 3d orbital for titanium oxide) which leads to more ionic cerium-oxygen bonding. In addition, the electron-hole pair recombines very fast before it can migrate to the particle surface because of the crystal defects and oxido-reduction reaction. Also, cerium oxide has a lower refractive index than that of titanium oxide and is rather transparent to visible light compared to titanium oxide and zinc oxide. Therefore, it seems that it is advantageous to use CeO_2 as UV absorber in coating material; however, it's very high catalytic activity [31] constitutes a major drawback.

There are several techniques which can easily quantify the coating degradation during weathering. The color measurement and visual assessment are two very simple yet powerful techniques to characterize weathered surface in order to study the discoloration and formation of some cracks or checks on the coated weathered surface. The coating adhesion is a prerequisite to coating's performances. If the coating does not adhere well to the surface, coating failure due to blistering or crack formation is evident. The surface polarity changes with weathering for these coatings were studied by contact angle tests with water. This test can give information about water penetration rate through the coatings. The water penetration rate can give an idea about coating degradation during weathering. Also penetrated water usually degrade wood surface more severely by leaching the oxidation photoproducts formed during weathering and also leads to coating delamination from the wood surface. The FT-IR technique is very useful to measure the chemical changes takes place during weathering and widely applied to study the coating degradation.

2. The main objective of this study is to delay the discoloration of thermally treated wood during accelerated weathering by application of an efficient transparent coating. In this paper, the effectiveness of CeO_2 nano particles in acrylic polyurethane coating for the protection of thermally treated jack pine is reported. The protective characteristics of CeO_2 alone or along with lignin stabilizer and/or bark extract against weathering have been compared with those of organic UV absorbers and HALS by comparing their quantified color measurements as well as visual assessments. The adhesion characteristics of the coatings containing CeO_2 nano particles are reported as well in this paper. The chemical modifications of coating containing CeO_2 nano particles after different weathering time were characterized by ATR-FTIR and

were compared with those of organic UV absorber containing coatings.**Materials and Methods**

2.1. Wood Surface Preparation

In this study, commercially available jack pine samples (sap wood) thermally treated at 210°C was used for all the tests. The wooden boards with tangential surfaces were randomly chosen from a lot obtained from Les Industries ISA, Normandin, Quebec, Canada. The wooden panels were then planed and sawed. The test panels were selected carefully by avoiding knots and cracks and, any other visible defects. The dimension of the wood samples used in the accelerated weathering test was 20cm×7cm×1.9cm which is according to the sample holder size. Also each sample was divided into three parts which contains different coatings.

2.2. Preparation of Coatings

Sunlight-cured two component water borne acrylic-polyurethane (Bayer Corporation) coating was used for this study as the base. The weight ratio of the two components of acrylic polyurethane was 2.33:1. Organic UV stabilizers (Tinuvin123 and Tinuvin1130 obtained from CIBA specialty chemicals), organic antioxidant (bark extract, synthesized in the laboratory), CeO_2 nano particles (obtained from BYK Chimie) and lignin stabilizer (obtained from CIBA specialty chemicals) were used as additives. Alone or different combinations of these additives were tested. The additives were added to the coatings while stirring continuously in order to get a homogeneous mixture. All the additives used in this study were either water soluble or they were dispersed in water. The formulations of different coatings are presented in Table1.

2.3. Accelerated Weathering Test

49 samples (6.6cm×7cm×1.9cm) were coated with three layers (same coating applied three times on each sample with a drying period in between applications) for all the coatings. The coatings were applied by brush along the grain direction of the thermally treated wood samples. The dry coating thickness was 100μm in average which is determined from the Fluorescence Microscographs of wood-coating cross sections. Seven samples were prepared for each coating. Six 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/m^2 at 340nm, BPT 63±3°C and continuous light cycle with 102min light and 18 min specimen spray with light). All the samples were exposed to UV light for different times. The maximum exposure time was 1500h. A sample for each coating was taken out after 72h, 168h, 336h, 672h, 1008h and 1500 h exposure. These exposure periods were chosen in order to achieve a good distribution as from previous experience; the degradation is faster at the beginning of the exposure period.

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

temperature. 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 thermally treated jack pine. The tangential surface is chosen since the UV weathering tests are also carried out on this surface. 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. Color Measurement

The color of all the samples was measured before and after the weathering test using Datacolor CHECK® spectrocolorimeter with diffuse illumination 8° viewing in conformance with CIE publication No.15.2 (Colorimeter based on D65 light source by simulating day light). The CIE L*, a*, b* coordinates were characterized by three parameters. L* axis represented the lightness and it varies from 100 (white) to 0 (black). a* and b* were the chromaticity indices where +a* was the red, -a* was the green, +b* was the yellow, -b* was the blue directions. The color differences were calculated using the equations [1] to [3] and the total color difference was calculated from equation [4] for each sample.

$$\Delta L = L^*_{after\ weathering} - L^*_{before\ weathering} \quad [1]$$

$$\Delta a = a^*_{after\ weathering} - a^*_{before\ weathering} \quad [2]$$

$$\Delta b = b^*_{after\ weathering} - b^*_{before\ weathering} \quad [3]$$

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad [4]$$

2.6. *FT-IR Analysis*

The chemical modifications of the coated wood samples due to weathering were examined by FT-IR spectroscopy. IR spectra were collected in the wave number range of 550-4000 cm^{-1} and all the spectra were recorded at 4 cm^{-1} resolution. Each time 20 scans were carried out prior to the Fourier transformation. All spectra were collected using a diamond micro-ATR crystal (Jasco FT/IR 4200). The incident angle of the crystal was 47˚ corresponding to an analysis depth of 0.2-5 µm, depending on the wave number. This ensured that the recorded FT-IR spectra were solely for the coating and there was no interaction with wood. The diameter of the actual analysis area was approximately 30µm. All spectra were analyzed using Jasco spectra manager software.

3. Results and Discussions

3.1. Contact Angle of Coatings on Wood Surface

The wetting characteristics of different coatings on thermally treated jack pine revealed that the contact angle of the coating with CeO_2 nano particles was lowest (better wetting) compared to other coatings (Figure 1). This resulted in better interaction of this coating with thermally treated wood compared to all other coatings. This also means that this coating can more easily be applied to thermally modified wood compared to all other coatings under consideration during this study. This was due to the lowest solid content of this coating (Table1) compared to all other coatings. Also the CeO_2 nano particles were small enough to penetrate through the pores of the wood surface (which are usually in micrometer range) resulting in higher wetting. However, the contact angles of all the coatings were below 90° which means that they all have good contact with jack pine wood. For all the coatings, contact angle started changing as soon as coating materials came in contact with wood surface. After approximately 10 s, the contact angle reached to an

equilibrium point for all the coatings. Similar trend was reported by Meijer and Militz [32] who found equilibrium contact angles after 50s on untreated wood for acrylic and alkyd paints. The coating with bark extract showed slightly higher equilibrium contact angle compared to coating with CeO_2 nano particles and almost similar equilibrium contact angle with coating containing CeO_2 nano particles and lignin stabilizer. Bark extract and lignin stabilizer containing coating exhibited slightly higher contact angle compared to the coating containing bark extract. The highest equilibrium contact angle was observed for the coating with CeO_2 nano particles, lignin stabilizer and bark extract whereas the coating containing CeO_2 nano particles and bark extract showed slightly lower contact angle than the former coating (Figure 1). Higher contact angle means less wetting which also means lower adhesion between coating and wood. The difference in contact angle was mainly due to the difference in percentage of solid (additives) in the coating materials (Table 1). Increase in solid percentage increases the viscosity of the coating which eventually results in higher contact angle and decrease in wetting. The results are well supported by the finding of Petric et al., [33] who reported that good wetting of modified wood (oil heat-treated and DMDHEU-modified scots pine) by waterborne coatings opens up possibilities to use environment friendly waterborne coatings on modified wood surface.

The contact angle test of the coating/thermally treated jack pine is an easy method to analyze the affinity of the coatings towards thermally treated surface. This gives an insight about coating penetration and spreading on the thermally treated surface which is directly related to the flow ability of the coatings. This also provides information about how easily can a coating be applied on the surface. Higher contact angle means lower adhesion and less penetration and spreading of a coating on the surface. This also means that coating application on the surface is more difficult.

3.2. *Color Measurement*

In this section color differences are presented for different weathering times for coated and thermally treated jack pine samples. Color measurement is a quantitative assessment of visual evaluation. In this section, color measurements for coatings containing organic UV absorbers; bark extracts; and lignin stabilizer are included only for comparison purposes. The details of these coatings were published previously by S. Saha et al. [18].

All the coatings became greener (Fig 2a) after weathering. The highest change in the red-green index was observed for PUA with organic UV absorbers. Lowest change in the same index was observed for coating containing CeO2 and lignin stabilizer. Coating containing only CeO_2 nano particles also showed very low variation in red-green index. The coatings containing CeO_2 nano particles and bark extract; only bark extract; CeO_2, bark extract and lignin stabilizer showed same variation of the red-green index after 1500h of weathering as coating containing only CeO_2 nano particles. Other than coatings containing only CeO_2 nano particles; only lignin stabilizer; and organic UV absorbers which pertained bluish nature after 1500h of weathering, all other coatings became more yellowish. Coatings containing bark extracts alone and only CeO_2 nano particles showed lower changes in yellow-blue index compared to other additives studied. On the other hand, coating containing UV absorbers showed highest change in the same index. All the other coatings showed moderate changes in that index. With increase in weathering time all the coated wood became lighter in color. There was a significant increase in lightness index for initial 168h of weathering and thereafter the lightness index increased slowly for all the coatings with the exception of coating containing UV absorbers. After 1500h of weathering, coating containing CeO_2 nano particles exhibited the same lightness index variation as coating containing bark extract which showed also the lowest change in that index compared to other coatings. The

coating containing CeO_2 nano particles and lignin stabilizer showed slightly higher change in the same index compared to former two coatings whereas coating containing UV absorbers pertained highest change in lightness index compared to all the other coatings. The other three coatings exhibited moderate change in the lightness index.

The total color change exhibited similar trend as lightness index change for all the coatings. Coating containing UV absorbers showed the highest color change whereas coatings containing only bark extract; only CeO_2 nano particles; CeO_2 nano particles and lignin stabilizer showed the lowest color variation after 1500h of weathering. The color change was significant for initial 168h of weathering for all the coatings and thereafter it changed slowly. The coatings containing lignin stabilizer; CeO_2 nano particles and bark extract; CeO_2 nano particles, bark extract and lignin stabilizer showed moderate total color change after 1500h of weathering. The color change of coated wood surfaces was due to the degradation during weathering. Higher degradation resulted in more color change. From the color measurement data it is very clear that coating containing CeO_2 nano particles is as effective as coating containing bark extracts for the protection of thermally treated jack pine although the concentration CeO_2 nano particles was only 18% (solid %) of that of bark extract in the acrylic polyurethane coatings. This was probably due to the higher surface area of the nano particles compared to higher particle size of the bark extracts or CeO_2 nano particles might be more effective than bark extracts for the protection of thermally treated jack pine from exterior environment.

Custódio and Eusébio [34] reported similar color change trend for acrylic varnishes on pine and iroko wood. They also found that acrylic varnishes with light stabilizers and colorants were more effective than the acrylic varnishes without either colorant or light stabilizers. Nejad and Cooper [35] in a very recent study recommended that transparent coatings generally not to be used for

exterior application on Oil-heat-treated wood which was previously also reported by Fiest [36]. But the recent study showed that transparent coating with proper stabilization could be very effective in exterior application. Aloui et al., [24] also reported similar statement as they found clear coatings stabilized with transparent iron oxide was highly effective in accelerated weathering on untreated wood compared to the base coating.

3.3. Visual Assessment

The visual evaluation for the color change of coated wood is more practical from consumer's point of view compared to color measurement. Because the coatings developed during this study were transparent or semitransparent in nature. Therefore, the color measurement mostly depends on the wood color. Since wood is a non-homogeneous biological material, the color varies between the same species e.g., late wood and early wood, sapwood and heartwood, different regions of origin, and even within the same tree wood. Also it is impossible to incorporate all the non-homogeneity that can be observed in naked eye to the color measurement which is the average of 9 different points on coated wood surface. In this section the uncoated thermally treated wood is used as the control because the main objective of this study is to protect thermally treated wood from weathering. The uncoated wood started changing its color from the beginning of weathering test and became completely white after 672h of weathering (Figure 3) whereas degradation started for the coating containing only lignin stabilizer after 672h of weathering (Figure 3). Although acrylic polyurethane coating containing CeO_2 nano particles exhibited very low total color change (almost similar to that of coating containing bark extracts) during color measurement, it was clear from visual evaluation that it was not as effective as the coating containing bark extracts. The coating containing CeO_2 nano particles showed a very high protective characteristic (less color change) until 1008h of weathering, but the degradation was

evident at the sides after 1500h of weathering. On the other hand, the coating containing CeO_2 nano particles and lignin stabilizer showed better protection at the end of 1500h of weathering compared to the coating containing CeO_2 nano particles, and very small degradations at the sides of thermally treated wood were evident for the former coating. For the coatings containing CeO_2 nano particles and bark extracts; CeO_2 nano particles, bark extracts and lignin stabilizer high protection against weathering was observed up to 1008h of weathering, but high degradation was evident at the end of 1500h of weathering. Highest color change was observed for coating containing organic UV absorbers from visual assessment as well as color measurement.

Jamsa et al [3] reported visual assessment of color change of coated heat-treated wood under natural weathering. They used different commercially available coatings on heat-treated wood and found that highly pigmented opaque coatings were best to be used in exterior application. They also found crack formation on the coated heat-treated wood surface. Small cracks were observed in present study for uncoated wood from the beginning of the aging period and after 1008h of aging for acrylic polyurethane with organic UV absorbers. But for other coatings, even after 1500h of aging no cracks were observed. Fufa et al., [37] reported heavy color loss of untreated spruce coated with acrylic stain containing titania nano particles after 47 days of natural weathering whereas uncoated wood started losing its color after 10 days of natural weathering.

3.4. Contact Angle of Water and Coated-Wood Surface

The contact angle change is directly related to the degradation of the surface. The contact angle change is faster when there are cracks or checks on the surface. Contact angle between water and

coated-wood surface for different weathering times is a simple yet insightful measure of surface modification due to weathering [17]. These results are shown in Figure 4.

The contact angles changed non linearly with time for all the four coatings before weathering. For the coating containing CeO_2 nano particles, contact angle changed very fast and within 750s of contact between water and coated surface a complete wetting took place. The trend of contact angle change was similar for the coating containing CeO_2 nano particles and bark extracts, but complete wetting (zero contact angle) took place after 1250s of contact between water and this coating. For the acrylic polyurethane containing CeO_2 nano particles and lignin stabilizer coated thermally treated jack pine, the contact angle changed very fast for initial 500s and after that it changed gradually with time and approached to zero after 1750s of contact. On the other hand, the contact angle between water and bark extract, CeO_2 nano particles and lignin stabilizer containing acrylic polyurethane coated wood surface decreased gradually with time and reached to zero after 2500s of contact time. This difference observed in time required to reach complete wetting for different coatings was due to the different degree of orientation of the acrylic polyurethane due to the additives. Before weathering, the highest degree of orientation was observed for coating containing bark extract, CeO_2 nano particles and lignin stabilizer whereas lowest cross linking took place for coating containing CeO_2 nano particles. After weathering, the initial contact angle increased for all the coatings and contact angle changed in a linear manner with time for all the coatings except for short initial period. Other than coating containing only CeO_2 nano particles, for all the other three coatings, contact angles after 1500h of weathering were higher than the contact angles after 72h of weathering. This increase in contact angle after weathering was probably due to the amorphous nature of the acrylic polyurethane coatings with lower degree of orientation of acrylic polyurethane coatings which when exposed to lower

wavelengths of solar radiation regrouped to form a stable state of chain orientation [17, 22]. The highest degree of cross-linking after 1500h of weathering was observed for coating containing CeO_2 nano particles and lignin stabilizer. So the contact angle change proved to be a very important tool to study the degradation of coated thermally treated wood. Similar contact angle trend results were reported by Hora [38] before weathering for coated wood surface. After weathering the contact angle change was more rapid than before weathering for his study. But in the present study we found opposite results. This is due to the differences in coatings properties.

3.3. FT-IR Analysis

Before the weathering test, all the coated samples were cured at 23°C and 15% humidity (laboratory condition) for one week. The effects of different additives on chemical changes of acrylic polyurethane coatings were analyzed using ATR-FT-IR. The FT-IR spectra of the acrylic polyurethane coating containing CeO_2 nano particles coated wood panels before and after weathering for different exposure times are shown in Figures 5(a) and 5(b). The assignments of the bands were performed based on the literature FT-IR data for acrylic-polyurethane system that is well documented [18, , 39-45].

Before the detailed analysis, each spectrum was normalized at the CH bending frequency (1451cm^{-1}) in order to emphasize the oxidation of the polymer matrix [18, 41]. As reported by Perrin et al. [40], CH bending frequency must decrease slightly due to the partial oxidation of the CH_2 in the α-NH position. Semi-quantitative measurements were carried out to comprehend the effect of different additives (Figures 6- 11) on the weathering of acrylic polyurethane coating. As already discussed by Saha et al. [18], increase in absorption in the carbonyl region (1670-1770 cm^{-1}) for acrylic polyurethane coating containing bark extract suggested the formation of several oxidation photoproducts mainly the carboxylic acid (peak at 1715 cm^{-1}) while a decrease in

absorption was observed for the acrylic polyurethane coatings stabilized with organic UV absorbers (Figure 6). For the coating containing CeO_2 nano particles, decrease in absorption of carbonyl group was observed for initial 72h of weathering which might be due to the depletion of these photoproducts with the water spray during accelerated weathering test. An increase in the same absorption band thereafter was due to the accumulation of carbonyl photo products on the surface of weathered wood. Also Figure 5b clearly shows that, with increase in weathering time, the C=O stretching of ester at 1720 cm^{-1} becomes broader which was due to the overlapping of different carbonyl photoproducts formed during weathering. Carbonyl photoproducts formed either through the direct chain scission or by the radical induced processes upon exposure to the artificial weathering conditions [18, 44]. Significant decrease of the absorption in the region of 1605-1670 cm^{-1} (H-bond and C=O stretching of the urethane) was another noticeable phenomenon for all the three stabilized acrylic polyurethane coating as shown in Figure 7. The decrease in the absorption at 1640 cm^{-1} was due to the conversion of urea to urethane linkages [41]. The extent of absorption intensity loss in this region was the highest for the acrylic polyurethane coating containing bark extract and a very high loss was also observed for the acrylic polyurethane coating with CeO_2 nano particles. However, relatively small change was observed for the acrylic polyurethane coating stabilized with organic UV absorbers (Figure 7). Usually a significant loss in the amide II band (1530 cm^{-1}, as a result of mixed vibration involving C-N and N-H mode), often reported due to the chain scission reaction of the urethane linkages [18, 39]. However, a small loss in intensity of amide II band (1530 cm^{-1}) was detected for all the three stabilized coating (Figure 8) during the present study. The lowest loss of the urethane group was observed for the acrylic polyurethane coating containing organic UV absorber due to the presence of HALS type UV stabilizer which extends the coating durability as

well as the UV absorbers lifetime [18]. The loss of the acrylate double bond (at 1407 cm^{-1}) was attributed to the oxidation reactions initiated by free radicals (Figure 9) [46].

The asymmetric CH group disappeared faster than the symmetric CH group for the acrylic polyurethane coatings with organic UV absorbers or bark extracts. Slight increase in absorption of symmetric and asymmetric CH was noticed for the acrylic polyurethane coating containing CeO_2 nano particles after 72h of weathering (Figure 10). The decrease of 3341 cm^{-1} for initial 72h of weathering for all the three coatings was due to the cross linking between urethane groups whereas increase thereafter suggested formation of polyurea (Figure 11). Maximum increase in the polyurea stretching was observed for the coating containing CeO_2 nano particles. With the increase in weathering time broadening of N-H vibration indicated overlapping of different N-H vibrations.

From the FT-IR analyses, it seemed that the coating containing organic UV absorbers was most stabilized and should be the most durable during accelerated weathering test. However, from the accelerated weathering test results, it was evident that the acrylic polyurethane coating containing bark extract or CeO_2 nano particles and lignin stabilizer were the most effective coatings from the aesthetic and durability point of view. Similar observation was found by S. Saha et al., [18]. This might be explained by considering the fact that all the acrylic polyurethane coatings used in this study are transparent or semitransparent in nature. Therefore, these coatings cannot prevent the sunlight to reach to the wood surface completely which eventually commences the photodegradation reaction on the wood surface.

4. Conclusions

In this study acrylic polyurethane coating was modified by adding CeO_2 nano particles alone or together with bark extracts and lignin stabilizer. These modified coatings showed better protective characteristic on thermally treated jack pine compared to the coatings containing organic UV absorbers.

The contact angle change of these modified coatings and thermally treated wood system suggested that coatings started spreading together with penetration through the pores as soon as it came in contact with wood surface. This phenomenon took place within a very short time and the contact angle reached to an equilibrium point. The decrease of contact angle after this point was due to diffusion of the coatings through the pores of thermally treated wood which was almost negligible. The lowest contact angle was found for coating containing CeO_2 nano particles. The accelerated weathering test certainly degrades all the modified as well as unmodified coatings. But the coatings modified with bark extract or CeO_2 nano particles showed much better protection of wood surface compared to the coating containing organic UV absorbers. Thus it can be concluded that CeO_2 nano particles are better than the organic UV absorbers in protecting the thermally treated jack pine. Formation of different carbonyl products during weathering was evident from ATR-FTIR analysis. The chain scission of urethane linkages was negligible during weathering.

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Table 1 Description of the coatings

Coating	Description	Solid content (%)	Reference
Acrylic polyurethane with organic UV absorber	The base coating + Tinuvin123 + Tinuvin1130	26.85	[18]
Acrylic polyurethane with bark extract	The base coating + bark extract	26.33	[18]
Acrylic polyurethane with lignin stabilizer	The base coating + lignin stabilizer	26.33	[18]
Acrylic polyurethane with CeO_2	The base coating + CeO_2 nano particles~30nm	25.39	Present study
Acrylic polyurethane with CeO_2 and bark extract	The base coating + CeO_2 nano particles~30nm + bark extract	26.23	Present study
Acrylic polyurethane with CeO_2 and lignin stabilizer	The base coating + CeO_2 nano particles~30nm + lignin stabilizer	26.23	Present study
Acrylic polyurethane with CeO_2, bark extract and lignin stabilizer	The base coating + CeO_2 nano particles~30nm + bark extract + lignin stabilizer	27.06	Present study

List of Figures

Figure 1 Contact angle of different coatings/thermally treated wood system

Figure 2 Comparison of acrylic polyurethane coatings stabilized with different additives (a) red-green index, (b) yellow-blue index, (c) lightness index, and (d) total color change.

Fig 3 Thermally treated jack pine coated with different coatings for different weathering time

Figure 4 Dynamic contact angle of water for different weathering times on thermally treated jack pine surface coated with the acrylic polyurethane coating containing (a) only CeO_2 nano particles, (b) CeO_2 nano particles and bark extracts, (c) CeO_2 nano particles and lignin stabilizer, and (d) CeO_2 nano particles, bark extract and lignin stabilizer

Fig 5 ATR–FT-IR analysis of acrylic polyurethane coating containing CeO_2 nano particles and lignin stabilizer for different exposure times (a) 1800–650cm^{-1} and (b) 3800–2600cm^{-1}

Figure 6 Buildup of oxidation products during accelerated weathering of acrylic polyurethane coatings stabilized by different additives

Figure 7 Diminution of H-bond and C=O stretching of the urethane during accelerated weathering of acrylic polyurethane coatings stabilized by different additives

Figure 8 Change in urethane group of stabilized acrylic polyurethane coatings during weathering

Figure 9 Loss of acrylate double bond of acrylic polyurethane coating during weathering

Figure 10 Changes in CH stretching of stabilized acrylic polyurethane coatings during accelerated weathering

Figure 11 Changes in hydroxyl group during accelerated weathering for stabilized acrylic polyurethane coatings

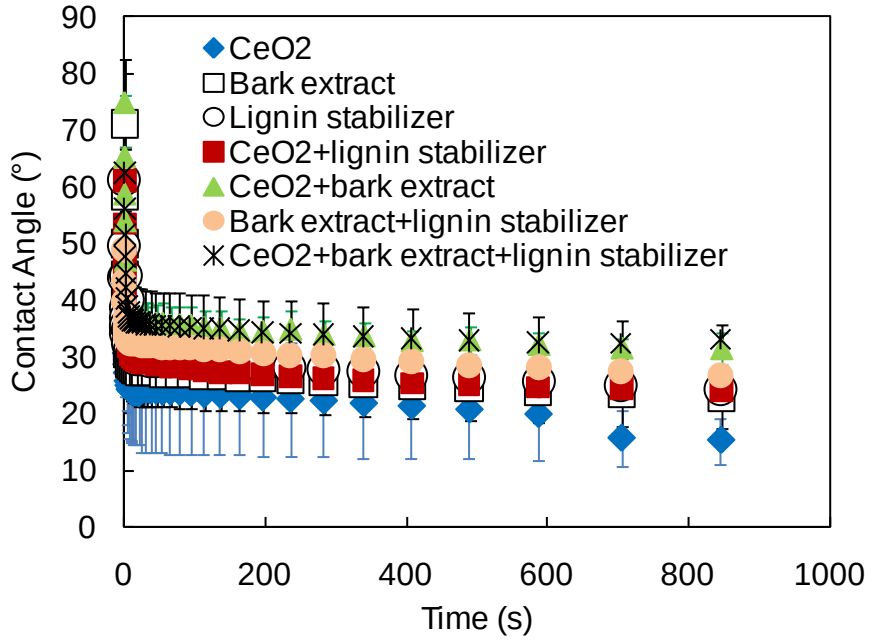
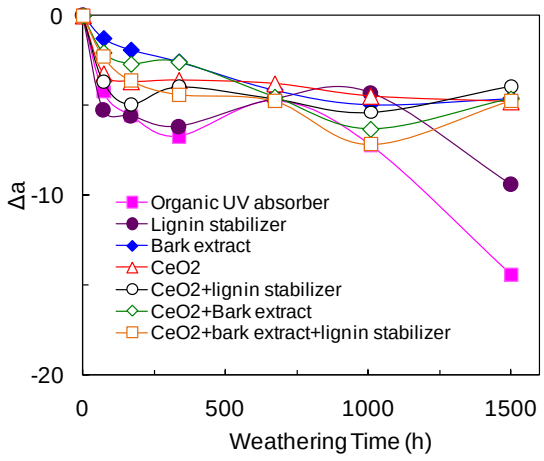
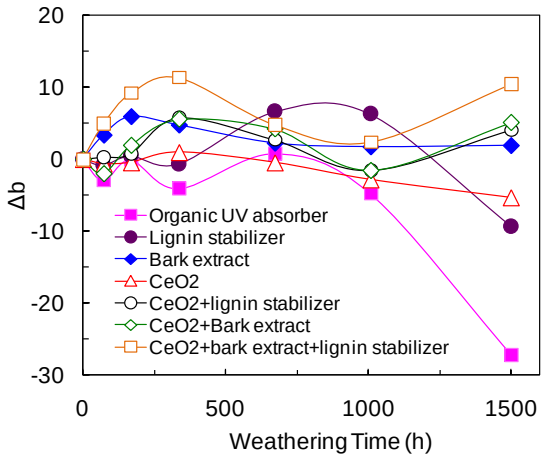

90
80
70
60
50
40
30
20
10
0
Contact Angle (°)
0
200
400
600
800
1000
Time (s)
CeO2
Bark extract
Lignin stabilizer
CeO2+lignin stabilizer
CeO2+bark extract
Bark extract+lignin stabilizer
CeO2+bark extract+lignin stabilizer

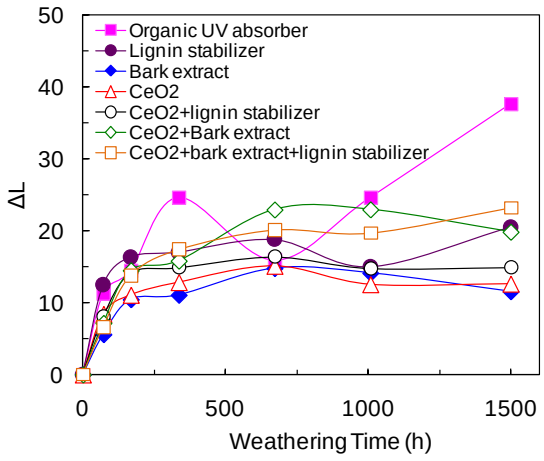
Figure 1



(a)



(b)



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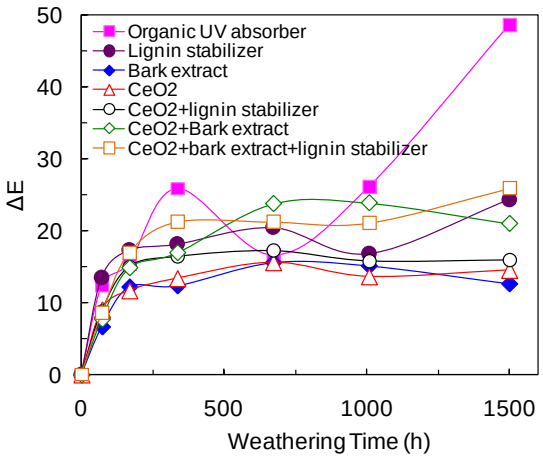


(d)

Figure 2

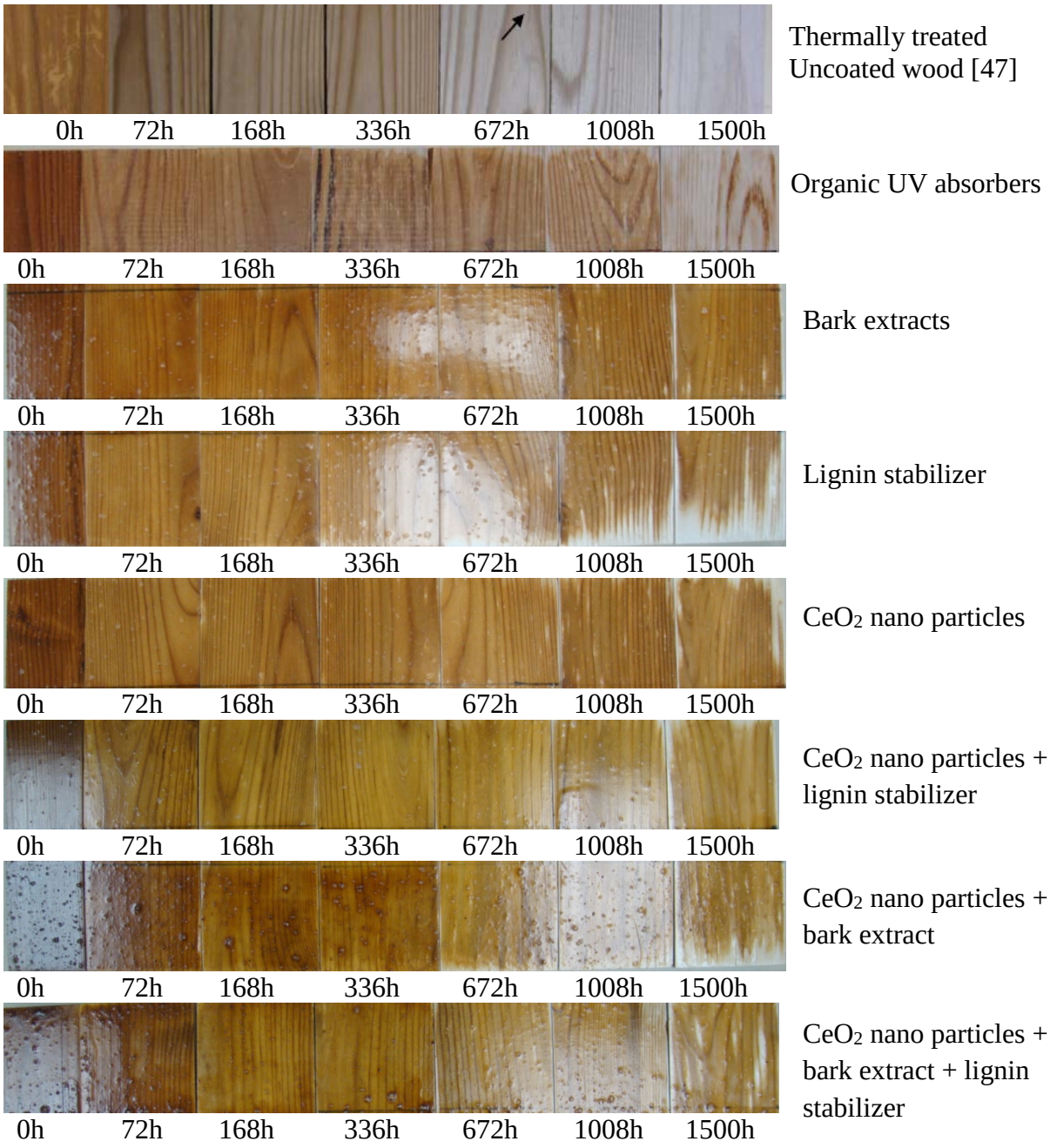
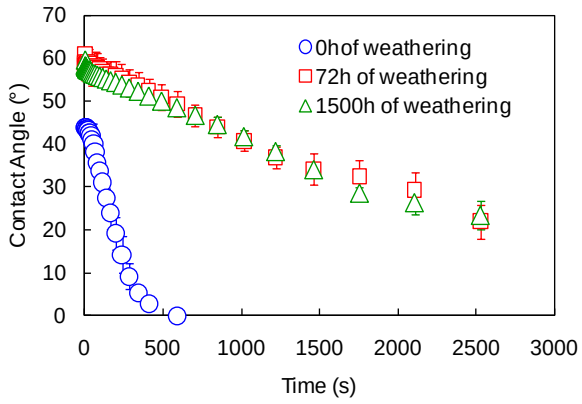
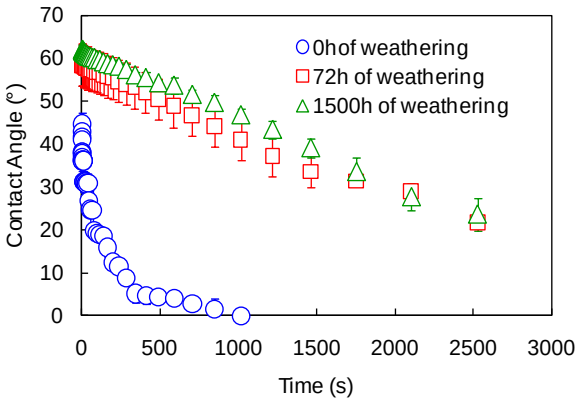

Thermally treated Uncoated wood [47]
0h 72h 168h 336h 672h 1008h 1500h
Organic UV absorbers
0h 72h 168h 336h 672h 1008h 1500h
Bark extracts
0h 72h 168h 336h 672h 1008h 1500h
Lignin stabilizer
0h 72h 168h 336h 672h 1008h 1500h
CeO2 nano particles
0h 72h 168h 336h 672h 1008h 1500h
CeO2 nano particles + lignin stabilizer
0h 72h 168h 336h 672h 1008h 1500h
CeO2 nano particles + bark extract
0h 72h 168h 336h 672h 1008h 1500h
CeO2 nano particles + bark extract + lignin stabilizer
0h 72h 168h 336h 672h 1008h 1500h

Figure 3



(a)



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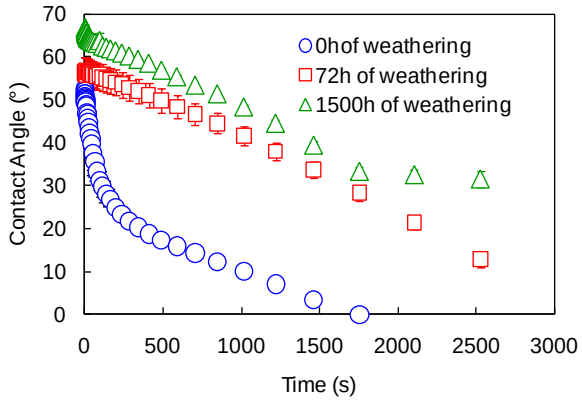
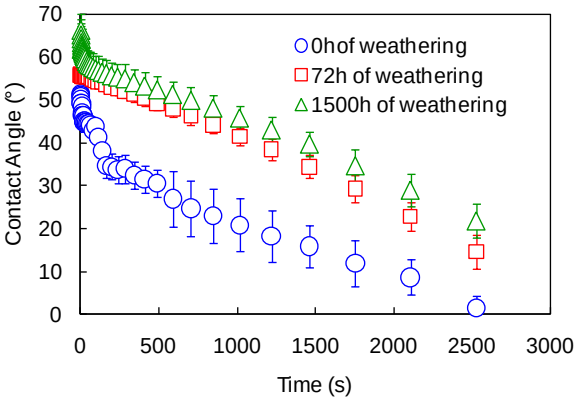
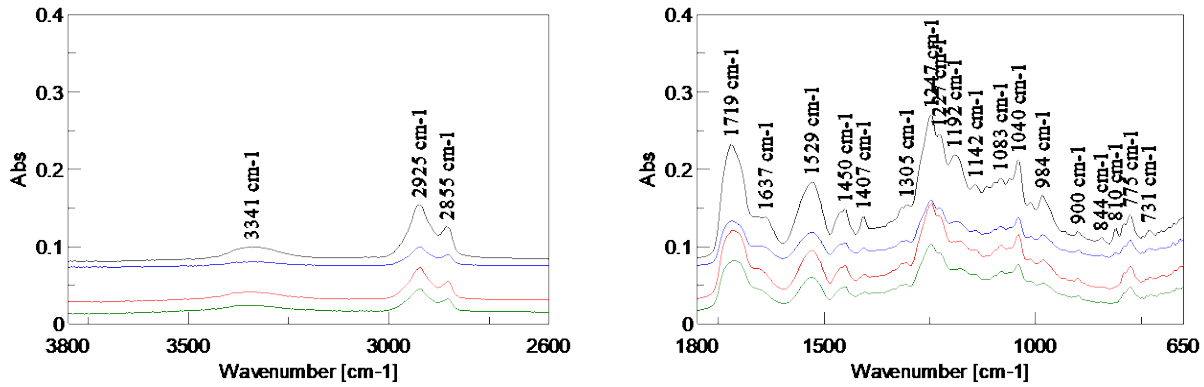


(c)



(d)

Figure 4


Abs
0.4
0.3
0.2
0.1
0
3800
3500
3000
2600
Wavenumber [cm-1]
3341 cm-1
2925 cm-1
2855 cm-1
1800
1500
1000
650
1719 cm-1
1637 cm-1
1529 cm-1
1450 cm-1
1407 cm-1
1305 cm-1
1192 cm-1
1142 cm-1
1083 cm-1
1040 cm-1
984 cm-1
900 cm-1
844 cm-1
775 cm-1
731 cm-1

(a) (b)

Figure 5

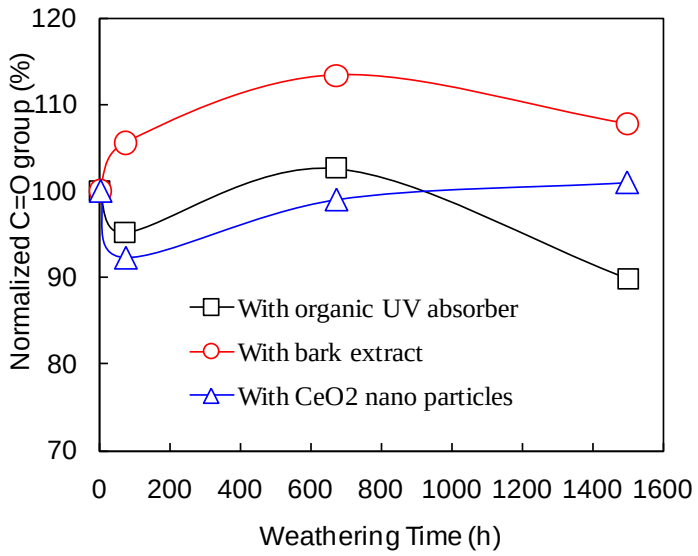

120
110
100
90
80
70
Normalized C=O group (%)
0
200
400
600
800
1000
1200
1400
1600
Weathering Time (h)
With organic UV absorber
With bark extract
With CeO2 nano particles

Figure 6

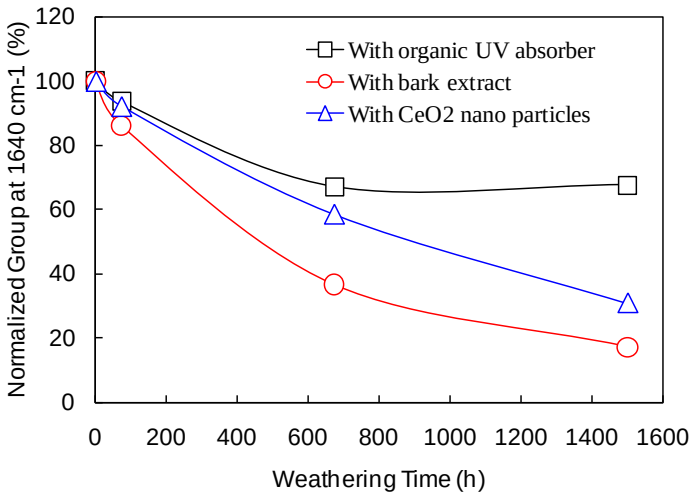

Normalized Group at 1640 cm-1 (%)
120
100
80
60
40
20
0
0
200
400
600
800
1000
1200
1400
1600
Weathering Time (h)
With organic UV absorber
With bark extract
With CeO2 nano particles

Figure 7

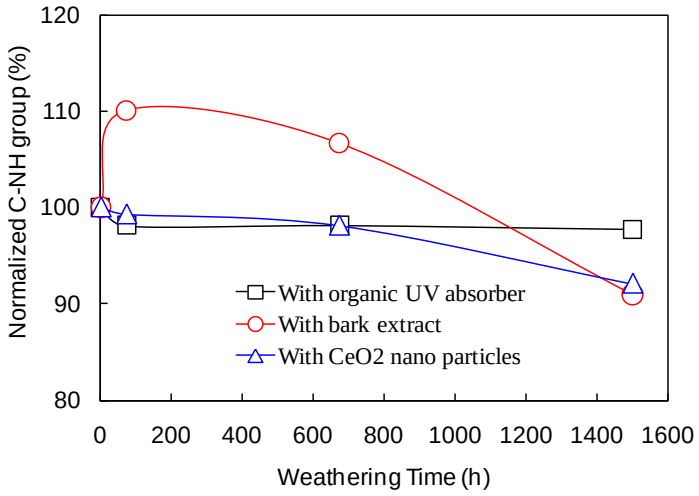

120
110
100
90
80
Normalized C-NH group (%)
0
200
400
600
800
1000
1200
1400
1600
Weathering Time (h)
With organic UV absorber
With bark extract
With CeO2 nano particles

Figure 8

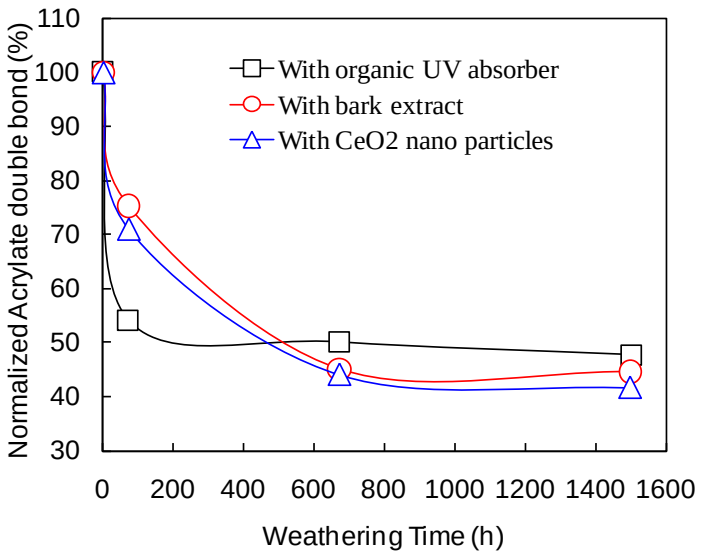

Normalized Acrylate double bond (%)
110
100
90
80
70
60
50
40
30
0
200
400
600
800
1000
1200
1400
1600
Weathering Time (h)
With organic UV absorber
With bark extract
With CeO2 nano particles

Figure 9

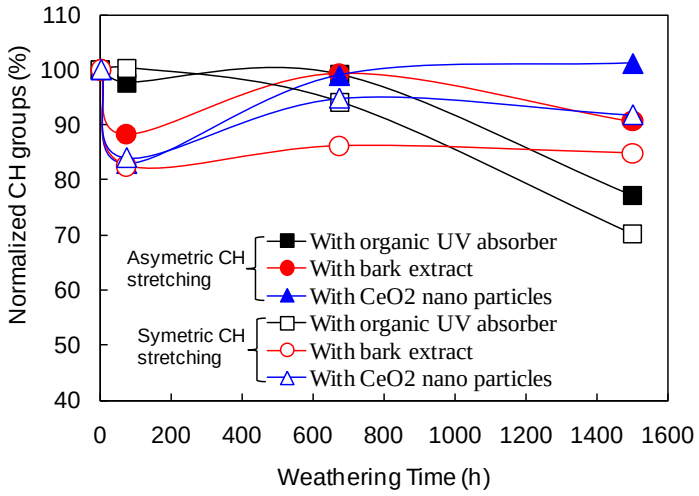

Normalized CH groups (%)
110
100
90
80
70
60
50
40
0
200
400
600
800
1000
1200
1400
1600
Weathering Time (h)
Asymetric CH stretching
With organic UV absorber
With bark extract
With CeO2 nano particles
Symetric CH stretching
With organic UV absorber
With bark extract
With CeO2 nano particles

Figure 10

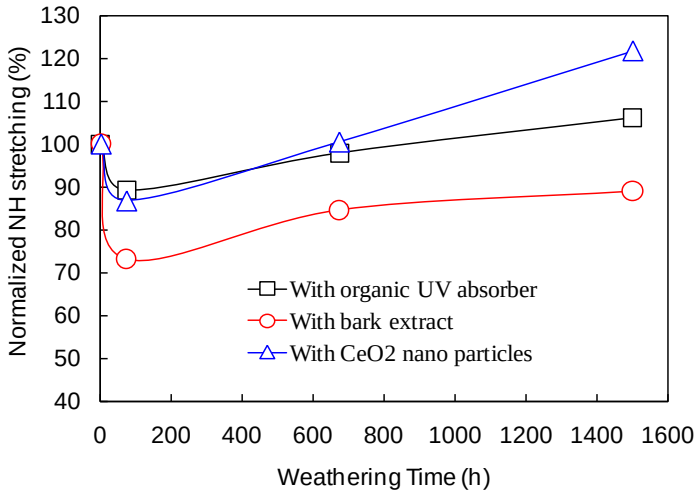

Normalized NH stretching (%)
130
120
110
100
90
80
70
60
50
40
0
200
400
600
800
1000
1200
1400
1600
Weathering Time (h)
With organic UV absorber
With bark extract
With CeO2 nano particles

Figure 11