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Assessment of influence of silane modified zirconia nanoparticle content on weather resistance of water-borne acrylic coating

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Abstract. Water-borne acrylic resin has attracted much attention thanks to its environmetally friendly, high weather stability, good mechanical properties, high toughness. It is widely used in coatings, ships, bridges, locomotives, etc. In this work, the effect of ZrO_2 nanoparticles content which were modified with (3-glycidyloxypropyl)triethoxysilane (GPTS) on the weather resistance of the acrylic emulsion coatings was tested and discussed. The change in functional groups, carbonyl index value, gloss, weight and morphology of the coatings before and after accelerated weathering test was investigated. The obtained results showed that the GPTS modified ZrO_2 nanoparticle content had a significant effect on the characteristics of acrylic emulsion coatings. The 2 wt.% content of GPTS modified ZrO_2 nanoparticles exhibited a highest efficiency in improvement of weather resistance of acrylic emulsion coatings. This result indicated that acrylic emulsion coating filled by the GPTS modified ZrO_2 nanoparticles is potential for outdoor applications.

Keywords: modified zirconia, acrylic emulsion coating, weather resistance, ZrO_2 nanoparticle, (3-glycidyloxypropyl)triethoxysilane, nanocoating.

Classification numbers: 2.3.1, 2.5.2, 2.9.4.

INTRODUCTION

Recently, nanocoatings based on polymer matrices and inorganic nanoparticles have garnered attention from scientists and producers due to their exceptional advantages, including high transparency, reflective index, hardness, elastic modulus, tensile strength, and thermal stability. Incorporating nano-additives such as zinc oxide [1], titanium oxide [2], graphene oxide [3], zirconium oxide [4, 5], silica [6], etc., can significantly enhance the properties of coatings due to their high specific surface area [7]. Among these nanoscale additives, zirconium oxide

(ZrO_2) nanoparticles exhibit excellent physical, chemical, and mechanical properties [8, 9]. By appropriately dispersing ZrO_2 nanoparticles into the polymer matrix, the coatings' transparency, reflective index, hardness, elastic modulus, tensile strength, and thermal stability can be improved [5, 10 - 14]. However, the compatibility between the organic phase and inorganic nanoparticles is often a challenge, leading to defects in the coatings [10]. Surface modification of inorganic nanoparticles using silane coupling agents has emerged as a useful solution to enhance compatibility [5, 7, 15, 16]. This process involves hydrolyzing alkoxy groups of silane coupling agents in solvents, which then react with hydroxyl groups on the nanoparticles' surface. The resulting organic functional groups act as bridges between the nanoparticles and polymer matrix, leading to improved dispersion and enhancement of the polymeric coating's properties. Studies have confirmed that the functionalization of ZrO_2 nanoparticles with silane agents significantly increases mechanical and corrosion protection in epoxy coatings [7]. It also enhances the transparency, mechanical, and thermal properties of UV-curable poly(urethane-acrylate) (PUA) coatings [5].

Water-borne acrylic resins possess excellent properties, such as high UV resistance, good weather stability, color stability, environmental friendliness, and low cost [2, 6]. In our previous report, we found that ZrO_2 nanoparticles modified with 3-(trimethoxysilyl)propyl methacrylate silane positively influenced the abrasion resistance of acrylic emulsion coating [16]. While acrylic emulsion coating exhibits good weather stability, there is still a need to explore the appropriate content of ZrO_2 nanoparticles modified with organosilane coupling agent to further enhance the weather resistance for outdoor applications. Thus, this study investigated various contents of ZrO_2 nanoparticles modified with 3 wt.% of GPTS, including 0.5, 1, 2, and 5 wt.% compared to the weight of acrylic resin. The characteristics (functional groups, carbonyl index, gloss retention, weight loss, and morphology) of acrylic emulsion nanocoating containing GPTS-modified ZrO_2 nanoparticles were studied and discussed, both before and after accelerated weathering tests [16].

2. MATERIALS AND METHODS

2.1. Materials

The GPTS modified ZrO_2 nanoparticles (m-ZrO_2) were obtained basing on the modification of commercial ZrO_2 nanoparticles (particles < 100 nm, Sigma) with (3-glycidyloxypropyl) triethoxysilane) (GPTS, Sigma) in ethanol solution. The weight ratio of GPTS/ZrO_2 was 3/100. Acrylic polymer dispersion Plextol R 4152 (solid content of 49 ± 1 %) was provided by Synthomer, USA. Other chemicals were analytical and obtained from Vietnam.

2.2. Preparation of acrylic emulsion nanocoatings

The acrylic nanocoatings contained various m-ZrO_2 content were prepared as follows. 2 g of m-ZrO_2 were dispersed in 9.01 g of distilled water in ultrasonic tank at 25 ^oC for 60 mins. Next, this mixture was introduced into 90.09 g of acrylic polymer dispersion Plextol R 4152 and was magnetically stirred for 15 mins and ultrasonicated for 60 mins at room temperature. The nanocoating was then prepared on the cleaned substrates (glass and steel) by a film applicator (Erichsen 360) with the wet thickness of 120 μm. The sample was kept at room temperature for 5 days to completely dry and then stored at 25 ^oC and 50 % relative humidity for at least 2 days before further study. The acrylic emulsion nanocoating contained 2 wt.% of m-ZrO_2 was obtained and abbreviated as AmZ2.0. The acrylic emulsion nanocoatings contained 0.5, 1, and 5 wt.% of m-ZrO_2 were similar prepared and abreviated as AmZ0.5, AmZ1.0, AmZ5.0.

2.3. Accelerated weathering test

The accelerated weathering test of samples was carried out using a UV CON 327 chamber (United State). The samples were tested according to ASTM G154-12a with UVB 340 lamp (340 nm, 0.89 W/m^2) for 24 cycles. Each cycle included 8 h of UV irradiation at 70 ^{o}C, and 4 h of humidity condensation at 50 ^{o}C. After every 6 cycles, the samples were withdrawn and determined of the Infrared (IR) spectra (Nicolet iS10, Thermo Scientific, USA), gloss (ISO 2813:2014, Erichsen Picogloss (model 503)), weight loss (IKA, Germany) and morphology (Field Emission Scanning Electron Microscopy (FESEM), S4800, Hitachi, Japan). The carbonyl index (CI) was calculated according to method reported in Ref. [17].

$$\mathrm{CI} = \frac{A_{1725}}{A_{1450}} \tag{1}$$

where, A_{1725} and A_{1450} are the absorbance of carbonyl group and methyl group at 1725 cm^{-1} and 1450 cm^{-1}, respectively.

3. RESULTS AND DISCUSSION

3.1. IR spectra of the acrylic emulsion nanocoatings

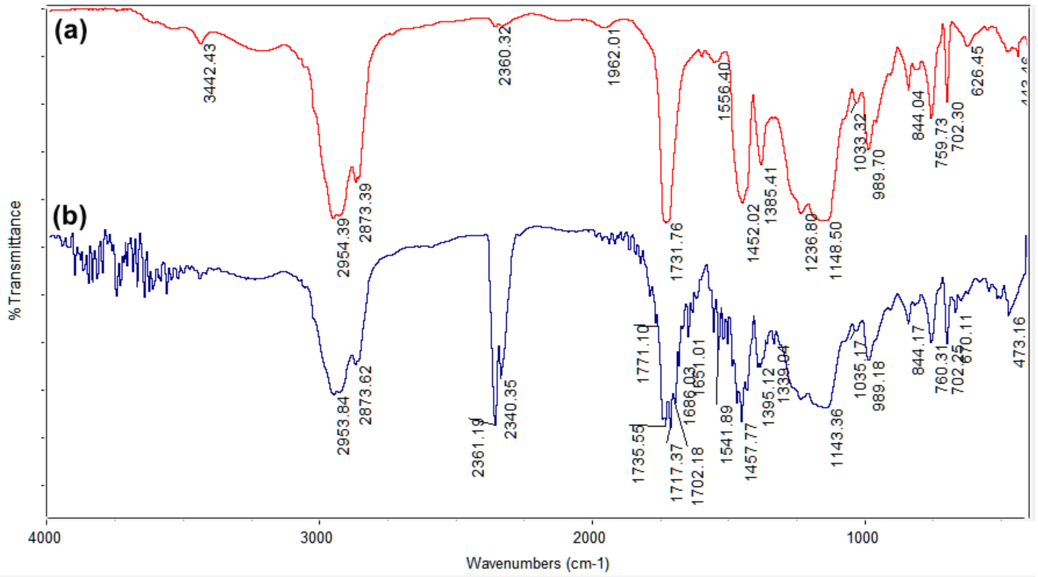

Figure 1. IR spectra of acrylic emulsion coating before (a) and after (b) accelerated weathering test.

Figures 1 and 2 display the IR spectra of acrylic emulsion coating and acrylic emulsion nanocoating containing 0.5 wt.% m-ZrO_2 before and after accelerated weathering test. The IR spectra of other nanocoatings showed similarities to the AmZ0.5 sample, hence they are not included here. Observing Figure 1, new peaks in the range of 1400 - 2400 cm^{-1}, characteristic of stretching vibrations of C=C and C=O linkages in low molecular weight products like ketones, aldehydes, acids, and alkanes, appeared in the IR spectrum of acrylic emulsion coating after 24 cycles of accelerated weathering test [5, 18, 19]. This indicates the degradation of the acrylic matrix due to UV irradiation and humidity condensation. In contrast, no new peak was observed in the IR spectrum of the AmZ0.5 sample after the accelerated weathering test (Figure 2). Comparing the IR spectrum of acrylic emulsion coating after aging (Figure 1b) with that of the AmZ0.5 sample after aging (Figure 2b), there were distinct differences, especially in the peaks at 1450 - 1800 cm^{-1}. This suggests that the neat acrylic emulsion coating underwent more significant weather-induced decomposition compared to the AmZ0.5 nanocoating. This result can be attributed to the uniform dispersion of m-ZrO_2 nanoparticles in the acrylic emulsion coating, acting as a UV shielding agent that protects the acrylic matrix from the impact of UV rays and humidity. This finding confirms the enhancement of weather resistance of acrylic emulsion coating in the presence of m-ZrO_2 nanoparticles.

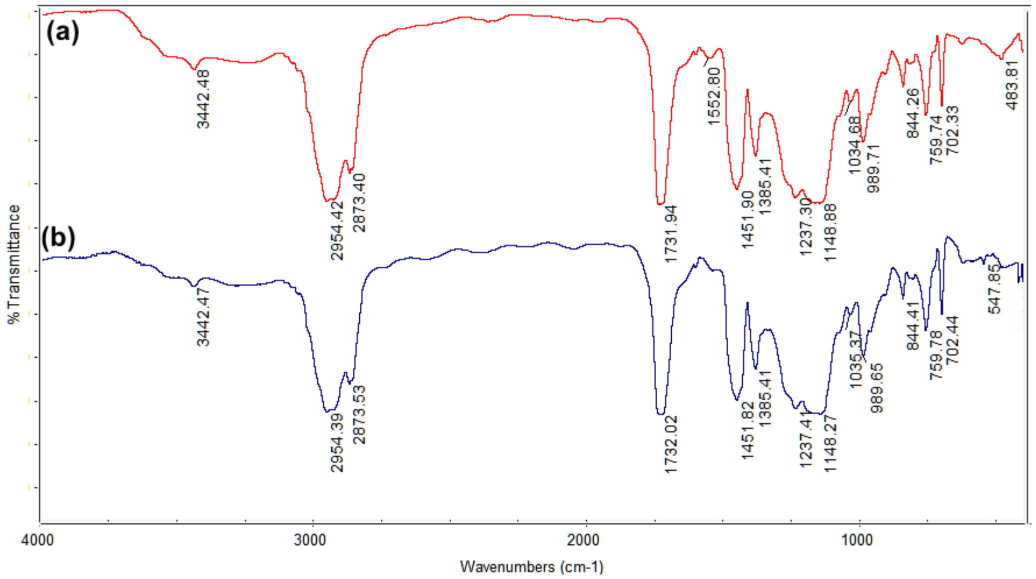

Figure 2. IR spectra of acrylic emulsion nanocoating contained 0.5 wt.% of m-ZrO_2 (AmZ0.5) before (a) and after (b) accelerated weathering test.

3.2. Carbonyl index of the acrylic emulsion nanocoatings

The carbonyl index (CI) values of neat acrylic emulsion coating and acrylic/m-ZrO_2 nanocoatings after accelerated weathering test were listed in Tables 1 and Figure 3. From Tables 1 and Figure 3, it can be seen that the CI values of acrylic emulsion coating and acrylic/m-ZrO_2 nanocoatings increased after 6 - 24 cycles of accelerated weathering test. This revealed that the content of carbonyl group in the coating samples increased as increasing time of aging test. The CI value of all acrylic emulsion coatings is largest after 24 cycles of aging test. This suggested that acrylic emulsion coating was degraded the most strongly under the impact of UV lamp and humidity. The acrylic chains were cut by photo-reactions and hydrolysis-reactions [1, 20]. In the presence of m-ZrO_2 nanoparticles, the CI values of the acrylic/m-ZrO_2 nanocoatings were lower than that of the neat acrylic emulsion coating. The CI values of acrylic emulsion nanocoatings only increased 16 - 28 % while that of the acrylic emulsion coating increased 34 % after 24 cycles of testing. This means that the weather resistance of the acrylic/ m-ZrO_2 nanocoatings was higher than that of the acrylic emulsion coating. As increasing content of m-ZrO_2 nanoparticles in polymer matrix, the CI value had a tendency of decrease at the same time of withdrawn sample. This exhibited the role of m-ZrO_2 nanoparticles as UV shielding agent as above discussed.

Table 1. CI value (in unit) of acrylic emulsion coating and acrylic/m-ZrO_2 nanocoatings after accelerated weathering test.

No.	Sample	0 cycle	6 cycles	12 cycles	18 cycles	24 cycles
1	Acrylic resin	1.60	1.68	1.89	2.00	2.14
2	AmZ0.5	1.53	1.68	1.73	2.00	1.96
3	AmZ1.0	1.93	2.11	2.18	2.32	2.46
4	AmZ2.0	1.71	1.78	1.86	1.95	2.02
5	AmZ5.0	1.94	2.06	2.14	2.17	2.24

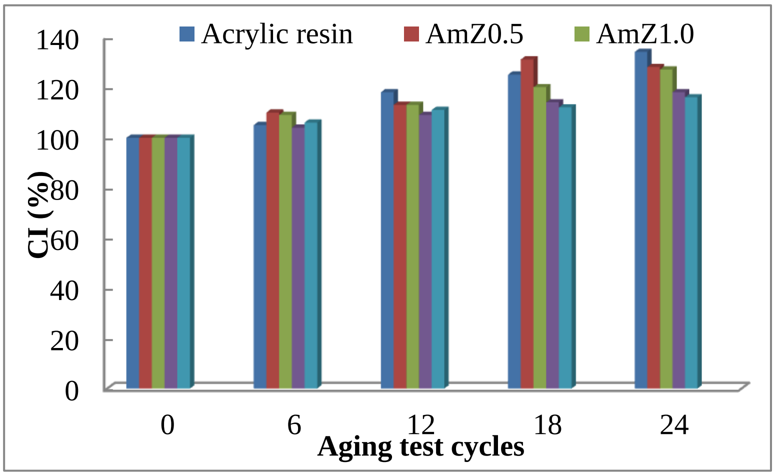

Figure 3. Graph of CI value (in percentage) of acrylic emulsion coating and acrylic/m-ZrO_2 nanocoatings after accelerated weathering test.

3.3. Weight loss of acrylic emulsion nanocoatings

Figure 4 presents the weight retention of neat acrylic emulsion coating and acrylic/m-ZrO_2 nanocoatings obtained during accelerated weathering test process. It can be seen that the weight retention of samples decreased as increasing aging time. This is due to the loss of low molecular weight compounds which were formed by the degradation of acrylic resin under the impact of UV irradiation and humidity condensation [2]. However, all samples have weight retention higher than 93 % after 24 cycles of aging test. It suggested that acrylic emulsion coating and acrylic/m-ZrO_2 nanocoatings have high weather stability. The weight retention of acrylic/m-ZrO_2 nanocoatings was higher than that of neat acrylic emulsion coating at the same aging time. For instance, the weight retention of acrylic emulsion nanocoatings, AmZ0.5, AmZ1.0, AmZ2.0 and AmZ5.0 was 93.7 %, 94.6 %, 95.6 %, 95.7 % and 96.7 % after 24 cycles of aging test. This means that m-ZrO_2 nanoparticles improved the weather resistance of acrylic emulsion coating. This result is in agreement with IR and CI results. At the early cycles of testing, the nanocoating contained 1 wt.% of m-ZrO_2 nanoparticles had highest weight retention. This is thanks to the excellent dispersion of m-ZrO_2 nanoparticles in acrylic emulsion coating at the content of 1 wt.%. When using low content of m-ZrO_2 nanoparticles (0.5 wt.%), it maybe not enough to shield UV-rays for acrylic resin matrix, thus, the effectiveness in reduction of weight loss of acrylic resin was lower as compared to using higher content of m-ZrO_2 nanoparticles. In general, when increasing m-ZrO_2 nanoparticle content in the nanocoatings, the weight loss of the nanocoatings was decreased after 24 cycles of aging test.

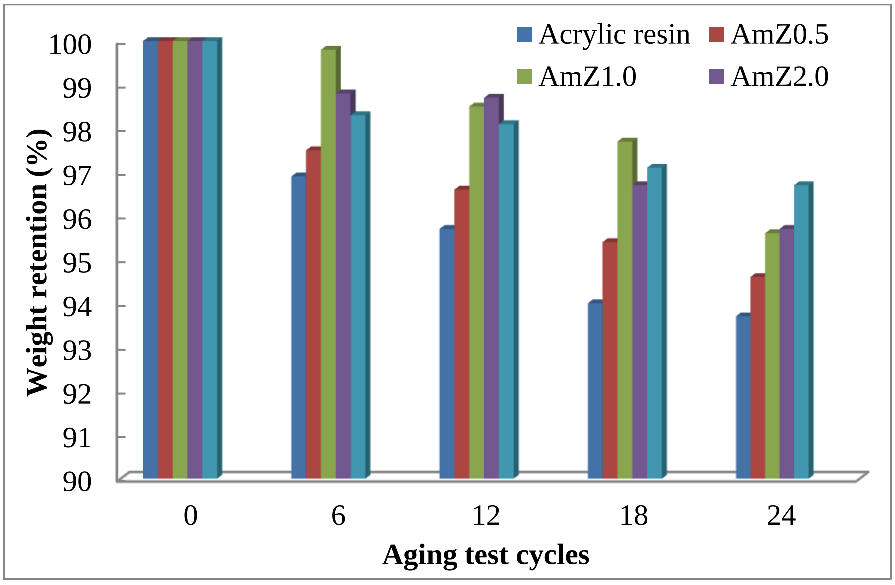

Figure 4. Graph of weight retention of acrylic emulsion coating and acrylic/m-ZrO_2 nanocoatings after accelerated weathering test.

3.4. Morphology of acrylic emulsion nanocoatings

The surface SEM images of neat acrylic emulsion coating and acrylic/m-ZrO_2 nanocoatings after 24 cycles of accelerated weathering test was shown in Figure 5. At the magnification of 500 times, it can find that the surface of acrylic emulsion coating and acrylic/m-ZrO_2 nanocoatings was relatively smooth without cracks or holes. This is evidence for high weather stability of acrylic based coatings. There are some fragments which were the low molecular weight products degraded from acrylic resin by UV irradiation and humidity condensation impact [2, 19]. At the magnification of 50,000 times, it can be seen the microstructure of the neat acrylic emulsion coating and acrylic/m-ZrO_2 nanocoatings. There were some micro-pores on the surface acrylic emulsion coating while the nanoparticles were appeared in microstructure of the nanocoatings. The size of m-ZrO_2 nanoparticles was ranged from 100 - 200 nm (Figure 5k).

When dispersed in acrylic emulsion coating, the nanoparticles adhered with resin matrix, however, they were agglomerated to each other. The micro-holes could be observed on the surface of AmZ0.5 nanocoating while the nanoparticles were dispersed well on the others. This is the reason for the reduction in weight of the nanocoatings at the low content of m-ZrO_2 nanoparticles as above discussed.

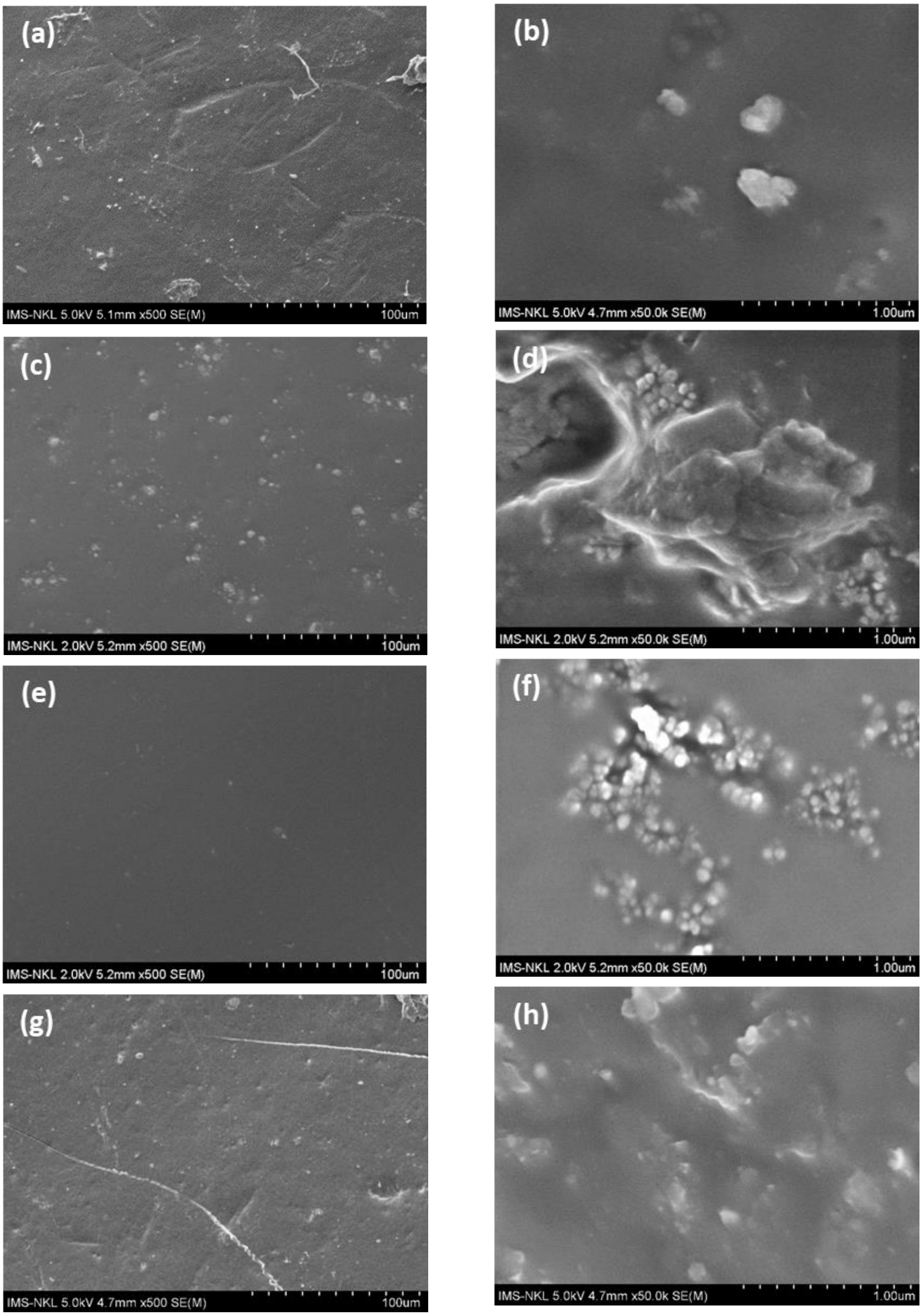

Figure 5. Surface SEM images of acrylic emulsion coating (a, b), AmZ0.5 (c, d), AmZ1.0 (e, f), nanocoatings after 24 cycles of accelerated weathering test and the SEM image of m-ZrO_2 nanoparticles (k).

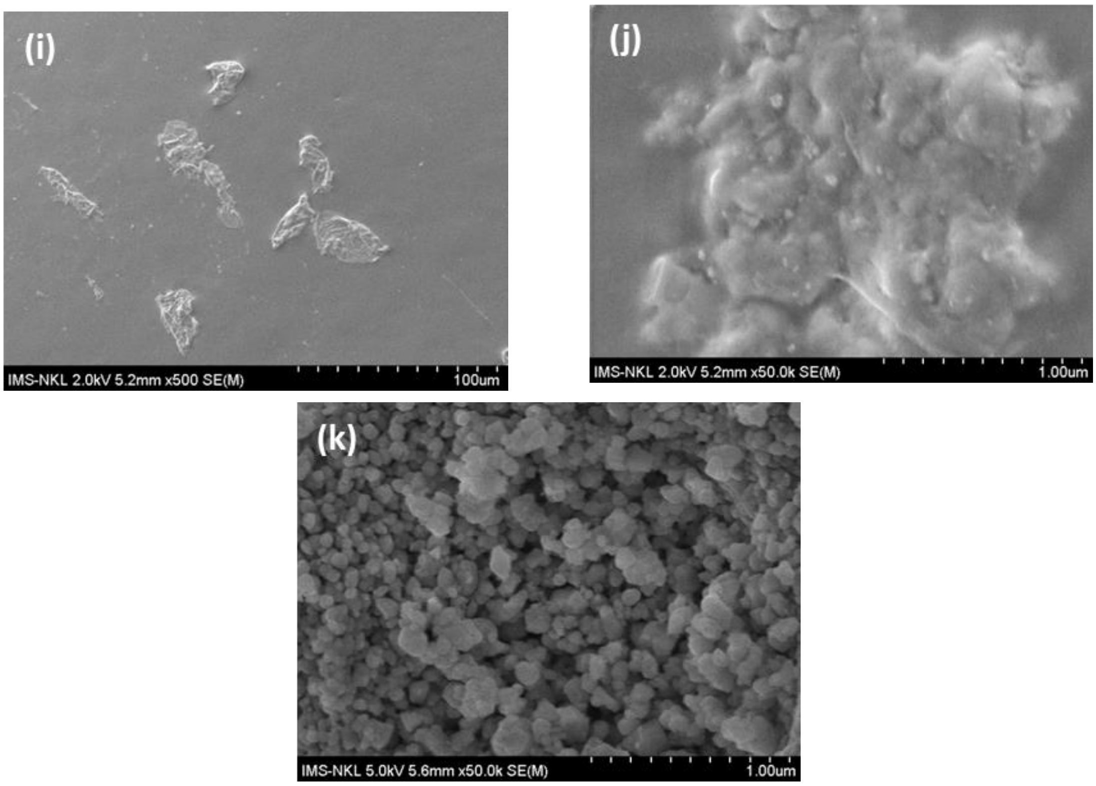

Figure 5 (continue). Surface SEM images of acrylic emulsion AmZ5.0 (i, j) nanocoatings after 24 cycles of accelerated weathering test and the SEM image of m-ZrO_2 nanoparticles (k).

3.5. Gloss of acrylic emulsion nanocoatings

The gloss retention of neat acrylic emulsion coating and acrylic/m-ZrO_2 nanocoatings according to accelerated weathering testing time was listed in Table 2.

Table 2. Gloss retention of acrylic emulsion coating and acrylic/m-ZrO_2 nanocoatings after accelerated weathering test.

No.	Sample	0 cycle	6 cycles	12 cycles	18 cycles	24 cycles
1	Acrylic resin	100	97.6	93.9	91.7	88.4
2	AmZ0.5	100	96.4	93.4	91.6	89.2
3	AmZ1.0	100	98.3	95.4	94.9	91.7
4	AmZ2.0	100	98.6	97.5	94.0	93.7
5	AmZ5.0	100	97.6	95.8	96.1	95.4

From Table 2, the gloss retention of samples had a tendency of decrease when increasing testing time. This trend is also observed for polyurethane/silane modified ZnO particles coating [1] and acrylic/rutile-TiO_2 coating [2]. The reduction of gloss of samples is due to appearing degradation products of acrylic resin and defects on surface of coatings as shown in Figure 5. The gloss retention of acrylic/m-ZrO_2 nanocoatings was higher than that of neat acrylic emulsion coating. This suggested that m-ZrO_2 nanoparticles enhanced the gloss of acrylic resin during aging test process thanks to the limitation UV degradation of acrylic resin matrix. The 0.5 wt.% of m-ZrO_2 nanoparticles exhibited lowest efficiency in the improvement of gloss loss of acrylic emulsion nanocoatings as compared to other samples. The same trend with weight retention was observed for the gloss retention of acrylic/m-ZrO_2 nanocoatings as increasing m-ZrO_2 nanoparticles content.

4. CONCLUSIONS

This paper mentions the effect of GPTS modified ZrO_2 nanoparticles content on weather resistance of acrylic emulsion coating. The obtained results confirmed that m-ZrO_2 nanoparticles improved significantly the weather resistance of coating. The absence of new peaks in the IR spectrum, the lower CI values, weight loss and higher gloss retention of acrylic/m-ZrO_2 nanocoatings are evidences for this enhancement. The CI values of the nanocoatings increased 16 - 28 % lower than that of the neat acrylic emulsion coating (increased 34 %) and the weight retention, gloss retention of the acrylic/m-ZrO_2 nanocoatings increased as increasing m-ZrO_2 nanoparticles content after 24 cycles of testing. The surface of acrylic emulsion coating and acrylic/m-ZrO_2 nanocoatings was relative smooth after 24 cycles of impact of UV irradiation and humidity condensation. There were some micro-pores on the surface acrylic emulsion coatings while the nanoparticles were appeared in microstructure of the nanocoatings. The m-ZrO_2 nanoparticles dispersed regularly in the acrylic matrix play role of UV shielding agent for the acrylic nanocoatings.

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CRediT authorship contribution statement. Nguyen Thuy Chinh: Investigation, Formal analysis, Writing-original draft preparation. Dao Phi Hung, Nguyen Anh Hiep: Methodology, Formal analysis, Validation. Nguyen Xuan Thai: Investigation. Thai Hoang: Conceptualization, Funding acquistition, Writing-Reviewing and Editing, Supervision, Project administration.

Declaration of competing interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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