

A Novel Waterborne Acrylic Coating Incorporation TiO_2 Nanoparticles Modified With Silane Coupling Agent and Ag/zn Zeolite: Mechanical Properties, Thermal Stability, Artificial Weathering Durability and Antibacterial Activity

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Abstract

Effect of rutile TiO_2 nanoparticles modified with 3-(trimethoxysilyl) propyl methacrylate silane - TMSPM (m- TiO_2) and Ag/Zn zeolite on the properties, and durability of acrylic waterborne coatings was studied. The obtained results indicated that m- TiO_2 nanoparticles and Ag/Zn zeolite could disperse regularly in the acrylic polymer matrix. Consequently, the abrasion resistance of the acrylic coating was improved in the presence of m- TiO_2 or/and Ag/Zn zeolite. The abrasion resistance of the acrylic coating depended on the content of m- TiO_2 nanoparticles as well as the initial TMSPM content for modification of rutile TiO_2 nanoparticles. The abrasion resistance of the acrylic coating filled by m- TiO_2 was higher than that of the acrylic filled by unmodified TiO_2 nanoparticles. The acrylic coating filled by 2 wt.% TiO_2 modified with 3 wt.% TMSPM had the highest abrasion resistance value, leveling off at 187.16 L/mil. The abrasion resistance of acrylic coating reduced with increasing too high initial TMSPM content for TiO_2 modification and m- TiO_2 nanoparticles content. The starting temperature of weight loss of acrylic coating filled by m- TiO_2 was lower than that of the neat acrylic coating. In comparison with the m- TiO_2 nanoparticles, the Ag/Zn zeolite particles showed a lower improvement for acrylic coating properties, i.e. abrasion resistance, weathering durability, but the Ag/Zn zeolite particles expressed an excellent antibacterial activity. Hence, combination of the m- TiO_2 nanoparticles and Ag/Zn zeolite particles could enhance the properties of the acrylic waterborne coatings. The acrylic coating filled by 2 wt.% m- TiO_2 nanoparticles and 1 wt.% Ag/Zn zeolite particles illustrated high abrasion resistance, good weather durability, and superior antibacterial activity for both of negative gram bacteria (*E. Coli*) and positive gram bacteria (*S. Aureus*). This coating is promising for environmental friendly building materials application.

Introduction

Organic coatings have been using widely to protect and decorate for various materials. In outdoor applications, they are exposed to a lot of factors such as UV radiation, temperature, humidity, oxygen, ozone, bacteria, fungi, etc. The UV light is considered as a main contributor of polymer degradation. Polymer coatings are photo-degraded as Norrish type I and type II reactions presented in Scheme 1 [1].

Scheme 1.

Hence, organic UV absorbers (such benzophenone and benzotriazole derivatives) [2], photo-stabilizers (hindered-amine light stabilizers - HALS) [3, 4] or nanoparticles (ZnO, TiO_2 , etc.) [5, 6] have been used to enhance lifetime of organic coatings. These photo-stabilizers can stabilize the organic coating with different mechanisms. There are two major mechanisms: removing free radicals and absorbing UV rays to minimize UV available for polymer matrix absorption [7]. The utilization of organic photo-stabilizers shows sometimes several drawbacks, like poor compatibility (especially with waterborne polymer) and decomposition upon UV exposure. Besides, the organic photo-stabilizers are hazardous chemicals which are pollutants. In comparison with organic photo-stabilizers, the inorganic photo-stabilizers are more stabilized and less toxic. For example, TiO_2 and ZnO are used in sunscreen cream [8]. Furthermore, the

photo-properties of ZnO and TiO₂, which help nanoparticles act as photo-stabilizers or photo-catalysts, depended on their morphology and structure. It was reported that the ZnO nanoparticles could act both of photo-stabilizer and photo-catalyst [9-11]. Chen et al. reported that the rutile TiO₂ nanoparticles could act as a photo-stabilizer that prevented polymer matrix from photo-degradation while the anatase TiO₂ nanoparticles increased photo-oxidation of polymer matrix [12]. Consequently, the rutile TiO₂ (R-TiO₂) nanoparticles have been selected to improve weather durability of polymer coating. A lot of publications reported the R-TiO₂ nanoparticles contributed to enhance weather durability of polymer coatings [9, 12-15].

Recently, in order to protect environment, renewable and friendly-environmental materials have been interested by experts and scientists. The solvent-borne coating systems with high volatile organic compounds (VOCs) have been replaced by low or zero VOCs coating systems such as waterborne coatings [9-11, 16, 17]. There are 85 wt.% of waterborne binders used in the architectural paint industry [18]. Thanks to their small size and huge specific surface, the R-TiO₂ nanoparticles can absorb a large amount of UV irradiation (up to 95 %) at small content, i.e. 2 wt.% [9]. Accelerated weathering test results showed that the waterborne acrylic coating filled by 2 wt.% R-TiO₂ nanoparticles was less degradable than the neat coating. After 720 hours of aging test, the weight of R-TiO₂ filled coating lost 17 % while the loss weight of the neat coating reduced by 20 % [9]. However, the aged R-TiO₂ filled coatings based on the acrylic polymer emulsion had black spots on their surface with high R-TiO₂ nanoparticles content due to R-TiO₂ nanoparticles agglomeration [16]. Surface of R-TiO₂ nanoparticles contains a lot of hydroxyl groups and thus forming hydrogen bonds among R-TiO₂ nanoparticles. Hence, the R-TiO₂ nanoparticles agglomeration produced hydrophilic areas. These areas accelerated hydrolysis reaction of polymer matrix upon condensation process in aging test and thus deteriorated coatings' surface [16]. Effect of R-TiO₂ nanoparticles on the properties of coatings were reported by a lot of researches. H. Shen et al. used TiO₂ sol and paraffin emulsion as coating for Scots pine sapwood. Thanks to the negative effects from UV and water of TiO₂/paraffin emulsion, the weathering resistance performance of wood was improved [19]. To enhance dispersion ability of R-TiO₂ nanoparticles in polymer matrix, the surface of R-TiO₂ nanoparticles was modified with organic compounds like silane coupling agents [20]. After surface modification, the R-TiO₂ nanoparticles could disperse better and more stable in the polymer matrix than the unmodified R-TiO₂ nanoparticles [20]. Lihui Xuan *et al.* modified TiO₂ nanoparticles surface with ethenyltrimethoxy silane (A171). The modified TiO₂ nanoparticles improved thermal stability, mechanical properties (flexural, tensile and impact properties) and UV resistance of wheat straw fiber/polypropylene composite [21].

Organic coatings have been affected not only by weather factors such humidity, UV radiation, temperature, etc. but also by microorganisms leading to biodegradation of coating. Therefore, anti-microorganism property has been required for organic coating. Up today, microorganisms' antibiotic resistance is one of the most problematic issues of daily life. Infections caused by antibiotic-resistant germs are difficult, and sometimes impossible, to treat. In order to reduce infections, preparation of

antimicrobial coatings is one of approaches. S.S. Dunne *et al.* indicated that antimicrobial coatings could reduce healthcare-associated infections [22]. Hence, antibacterial agents are added into component of coating formulas. It was demonstrated that R-TiO₂ nanoparticles could inhibit *E. Coli* growth in liquid cultures [15]. In comparison with the R-TiO₂ nanoparticles, the antibacterial activity of the anatase TiO₂ (A-TiO₂) nanoparticles was higher [23]. The A-TiO₂ nanoparticles can kill bacteria based on reactive oxygen species (ROS) which is produced photo-catalytic activities of the A-TiO₂ nanoparticles upon UV exposure [24]. As a result, a side effect of the A-TiO₂ nanoparticles as well as antimicrobial agents acting as photo-catalyst (like the ZnO nanoparticles) is to enhance photo-degradation of polymer coatings. Silver nanoparticles have highly antibacterial ability [26]. The antibacterial property of silver nanoparticles could be improved by zeolite particles and thus, the silver-zeolite particles have been applied in various polymer composite materials [27]. Moreover, the silver-zeolite particles combined with zinc were investigated synergistic effect on the antibacterial properties of the polymer composite materials [28]. The acrylic composite containing Ag/Zn zeolite particles could against different kinds of germs [29].

As mentioned above, the researches on the coating have mainly focused to the R-TiO₂ nanoparticles or Ag/Zn zeolite particles adding to the polymer coatings. There is lack of the information on combination R-TiO₂ nanoparticles modified with silane coupling agent and Ag/Zn zeolite particles. In order to preparation of the coating having high weather durability and good antibacterial activity, in this work, both m-TiO₂ nanoparticles and Ag/Zn zeolite were introduced into waterborne acrylic. The effect of the R-TiO₂ nanoparticles modified with silane coupling agent (TMSPM) and Ag/Zn zeolite particles on the properties (the abrasion resistance, thermal stability, accelerated weathering test and antibacterial activities) of coating based on acrylic emulsion polymer was investigated.

Experimental

Materials

Rutile TiO₂ nanoparticles (Kronos 2360, purify of 92 %, South Korea) have average particle size of 160 nm and density of 3.9 g/cm³. The 3-(trimethoxysilyl)propyl methacrylate silane (TMSPM) with purity of 98 % was supplied by Sigma-Aldrich. Its formula is illustrated as follows.

Acrylic emulsion resin Plextol R 4152 (Synthomer, USA) with a solid content of 49 ± 1 %. Ethanol 99.7 %, ammonia solution 25 %, etc. were obtained from Vietnam. Ag/Zn zeolite particles (Irgaguard B5000 commercial name) having elemental composition 0.44 % Ag and 1.46 % Zn, was purchased from BASF (Germany). The Ag/Zn zeolite particles have size range of 200-500 nm (Fig. 1).

Modification of TiO₂ nanoparticles

Rutile TiO₂ (R-TiO₂) nanoparticles were modified with TMSPM as our previous publication [20]. The TMSPM was added in the flask containing 100 mL ethanol and 1 mL ammonia at 50 °C for 60 min on a magnetic stirrer with the stirring speed of 400 rpm. Next, 5 g R-TiO₂ was introduced to TMSPM/ethanol

solution. The mixture was stirred continuously with 400 rpm speed for 120 min at 50°C and followed by stirring in high-speed (15000 rpm) for 30 min. The solid part was obtained by centrifugation at room temperature with 6000 rpm speed and then it was rinsed by ethanol five times. The residue of TMSPM after the surface treatment process of R-TiO₂ nanoparticles was taken away from the solid part by Soxhlet process for 4 h in the water/ethanol solution (1/1, v/v). The modified R-TiO₂ nanoparticles were obtained after drying in a vacuum oven at 80 °C for 4 h. The unmodified and modified TiO₂ nanoparticles were abbreviated as u-TiO₂ and m-TiO₂, respectively. FESEM images of unmodified and modified TiO₂ nanoparticles were presented in Fig. 2.

As can be seen in Fig. 2, the size of TiO₂ nanoparticles was 100-200 nm. The modification of TiO₂ nanoparticles did not influence on size of TiO₂ nanoparticles. The modified TiO₂ nanoparticles were less agglomeration in comparison with the unmodified TiO₂.

Preparation of acrylic composite coatings

Acrylic coating formulas were prepared according to following steps. In the first step, the unmodified or modified TiO₂ nanoparticles or Ag/Zn zeolite particles were dispersed in distilled water using ultra-sonication for 1 h. Next, acrylic emulsion polymer introduced into the above mixture which was stirred on a magnetic stirrer for 15 min at room temperature with a speed of 300 rpm before ultra-sonication for 1 h.

The acrylic coatings were applied on the glass by film applicator (Erichsen model 360) with 120 µm wet thickness (equivalent with 30µm ± 2 µm dried thickness). The investigated coatings were kept at room temperature until completely drying and conditioned at 25 °C ± 2 °C, relative humidity of 50 % ± 5 % for at least 48 h before further characterizations.

Accelerated weathering test

Accelerated weathering test of acrylic coating formulas was carried out in UV CON 327 chamber (Atlas, United State) according to ASTM G154-12a standard using UVB 313 lamp (313 nm, 0.49 Wm⁻²nm⁻¹) and operated exposure cycle condition of 8 h of UV irradiation at black panel temperature of 70 °C (± 3 °C), then followed by 4 h of condensation at 50 °C (± 3 °C). All samples before and after testing were dried at 50 °C in vacuum oven for 24 h before analysis.

Analysis

Mechanical properties

The abrasion resistance of acrylic coating samples was carried out at room temperature by falling sand abrasion test according to ASTM D968-15. The abrasion resistance of investigated coatings was determined as formula: $A = V/T$ with V was volume of sand used (L) and T was thickness of coating (mil).

Thermo-oxidation stability

Thermogravimetric analysis diagrams of investigated coatings were recorded by Labsys TG/DSC1600, TMA (Setaram, France) with heat rate of 10°C/min, from room temperature to 600 °C in air atmosphere.

Morphology

Field emission scanning electron microscopy (FESEM) images of investigated coatings were captured by FESEM S4800 (Hitachi, Japan). The investigated coating's surface was coated by a very thin platinum layer to avoid the charging effect caused by the nonconductive nature of coatings.

Infrared spectra (IR)

The functional groups in investigated coatings upon the accelerated weathering test were analyzed on a FTIR NEXUS 670 spectroscopy (Nicolet, USA) (detector DTGS-KBr, resolution of 4 cm⁻¹ and 16 scans) in air atmosphere.

Weight loss

The weight loss (Δm_t) of investigated samples after accelerated weathering test was determined as the difference between the weights of the samples (dried in vacuum oven at 50 °C until reached the constant weight) before (m_0) and after (m_t) accelerated weathering test as below formula: $\Delta m_t = (m_0 - m_t) * 100 / m_0$

Gloss measurement

The gloss at 60° angle of the formula coatings upon the accelerated aging process was measured according ISO 2813:2014 using Erichsen Picogloss (model 503). The gloss retention was calculated by the ratio of a gloss of aged coating in comparison with the gloss of the initial coating.

Antibacterial test of investigated coating

The antibacterial activity of investigated coating was determined according to ISO 22196:2007 method. Briefly, bacteria from the stock tube were inoculated onto slanted agar and incubated at 35 °C for 24 h. From this test tube, the bacteria were again inoculated into a new inclined agar tube and cultured at 35 °C. Using a sterile culture rod transferred a ring of activated control bacteria in slant agar. The control bacteria were uniformly dissolved and the bacterial cell solution was diluted in 1/500 NB medium to a density of 10⁶ cells/mL. This solution was used to contaminate the test samples. Place each prepared test specimen in each sterile petri dish with the test surface facing up, and place 0.4 mL of the previously prepared bacteria on the surface of the specimen. Cover the top with a thin film of size (40x40) mm and gently press the membrane to spread the bacterial fluid evenly to the edges. Infected samples were incubated at 35 °C for 24 h, then the number of viable bacteria was determined by colonization.

The antibacterial activity of investigated coating (R) was determined as below formula: $R = (U_t - U_o) - (A_t - A_o)$. In there: U_o and A_o were log average number of initial viable bacteria on control surfaces and coated surface, respectively. The U_t and A_t were log average number of viable bacteria on control surfaces and coated surface, respectively, after 24 h testing.

Results And Discussion

Mechanical properties of acrylic coatings

Organic modification of nanoparticles' surface is considered as one approach to improve the compatibility of nanoparticles with polymer matrix leading to enhancing some properties of polymer coatings. The efficiency of enhancement of mechanical properties for acrylic coatings depends on nature and content of TMSPM used to modify TiO_2 nanoparticles. The acrylic coatings filled by 2 wt.% nano TiO_2 (in comparison with solid part of acrylic resin), which was modified with different TMSPM content, were prepared as mentioned in experimental section. The TiO_2 nanoparticles modified with 1, 3, 5, 10 and 20 wt.% TMSPM (in comparison with nano TiO_2) were abbreviated as m- TiO_2 -1, m- TiO_2 -3, m- TiO_2 -5, m- TiO_2 -10 and m- TiO_2 -20. The abrasion resistance of acrylic coatings filled by m- TiO_2 modified with various TMSPM content was displayed in Table 1.

As can be seen in Table 1, the unmodified and modified TiO_2 nanoparticles improved the abrasion resistance of the acrylic coating. The acrylic coating filled by 2 wt. % TiO_2 nanoparticles modified with 3 wt.% TMSPM had the highest abrasion resistance. However, the abrasion resistance value of acrylic coatings filled by TiO_2 nanoparticles modified by higher TMSPM content was lower than that of the acrylic/m- TiO_2 -3 coating. These obtained results were similar with the results determining the abrasion resistance of the acrylic coatings filled by ZrO_2 nanoparticles modified with TMPSM [31].

Thank to small size, the nanoparticle could be filled into defects in coating structure, consequently, the coating's structure became more tightly [15, 17, 30]. Due to the difference of nature and structure, the nanoparticles and polymer matrix are poorly compatible, leading to the agglomeration of the nanoparticles in the polymer matrix [2]. Silane coupling agent grafted on the surface of the nanoparticles acted as a bridge between nanoparticle and polymer matrix [6]. Hence, the dispersion of the nanoparticles modified with silane coupling agent in polymer matrix was improved. However, the efficiency of the silane coupling agent grafted on the surface of the nanoparticles was reduced when using high silane coupling agent content [20, 31]. The reason was that in the modification process, the silane coupling agent reacted with the hydroxyl groups on the nanoparticles' surface to produce a layer of silane coupling agent. This new-formed layer covered the surface of nanoparticles and thus preventing silane coupling agent grafting continuously onto the TiO_2 nanoparticles. The silane coupling agent residues could be polymerized and thus forming the third phase in coating [20, 31]. Hence, using the nanoparticles modified with high silane coupling agent content could reduce the regularity of the acrylic coatings. It means that the abrasion resistance of the acrylic coatings was lower in comparison with the coatings filled by TiO_2 nanoparticles

modified with TMSPM content over 3 wt.%. As from obtained results, the TiO₂ nanoparticles modified with 3 wt.% TMSPM was chosen for further studies.

The abrasion resistance of investigated acrylic coatings depends on size and content of modified TiO₂ nanoparticles. The acrylic coatings filled by different content of TiO₂ nanoparticles modified with 3 wt.% TMSPM (m-TiO₂-3) were prepared as mentioned in experimental section. The abrasion resistance of investigated coatings containing 0.5; 1; 2 and 4 wt.% m-TiO₂-3 was performed in Table 2.

As can be seen from Table 2, the abrasion resistance of the acrylic coating grew up with increasing content of m-TiO₂-3 nanoparticles. However, the acrylic coating filled by 4 wt.% m-TiO₂-3 nanoparticles had a lower abrasion resistance value in comparison with the acrylic coating filled by 2 wt.% m-TiO₂-3 nanoparticles. When the acrylic coating filled by the low m-TiO₂-3 nanoparticles content, the silane coupling agent could establish a good phase interaction between the nanoparticles and polymer matrix. The m-TiO₂-3 nanoparticles could fill into defects of acrylic coating leading to be tighter coating's structure (as discussed above). In addition, the m-TiO₂-3 nanoparticles also acted as a reinforcing agent. As a result, the mechanical properties of the acrylic coating were improved. However, using high content of m-TiO₂-3 nanoparticles could lead to the agglomeration of the nanoparticles and the decrease in the phase interaction between the nanoparticles and polymer matrix [29]. Hence, the abrasion resistance of acrylic coating reduced. As can be seen from obtained result, the acrylic coating filled by 2 wt. % m-TiO₂-3 nanoparticles reached the highest value of abrasion resistance. Therefore, using 2 wt. % m-TiO₂-3 nanoparticles was suitable content for the acrylic coating. The acrylic coating filled by 2 wt. % m-TiO₂-3 was selected for further studies.

The effect of Ag/Zn zeolite content on the abrasion resistance of the acrylic coating filled by 2 wt. % m-TiO₂-3 nanoparticles was also evaluated. The abrasion resistance of the acrylic coating filled by 2 wt. % m-TiO₂-3 nanoparticles combined with different Ag/Zn zeolite particles content was displayed in Table 3.

As can be seen from Table 3, the abrasion resistance of the acrylic coating increased in the presence of Ag/Zn zeolite particles in comparison with the neat acrylic coating. However, the Ag/Zn zeolite particles caused the reduction in the abrasion resistance of the acrylic coatings filled by 2 wt. % m-TiO₂-3 nanoparticles. The abrasion resistance of the acrylic coating decreased as increasing Ag/Zn zeolite content particles. The Ag/Zn zeolite was inorganic compound and thus having higher hardness in comparison with the acrylic polymer. Therefore, the Ag/Zn zeolite particles could improve mechanical properties of acrylic coating. However, the zeolite has a porous structure, consequently, the Ag/Zn zeolite particles could influence on the structure of acrylic coating filled 2 wt.% m-TiO₂-3 nanoparticles. As a result, the abrasion resistance of the acrylic coatings filled by both m-TiO₂-3 nanoparticles and Ag/Zn zeolite particles was reduced.

Morphology of acrylic coatings

As mentioned above, the properties of the acrylic coatings were affected by size and content of m-TiO₂-3 nanoparticles and Ag/Zn zeolite particles. Their size and the morphology of the acrylic coating can be observed in FESEM images of the coatings' cross surface (Fig. 3).

Fig. 3 showed a poor dispersion of the unmodified TiO₂ (u-TiO₂) nanoparticles in the polymer matrix (Fig. 3 (a,b)). The agglomeration of the u-TiO₂ nanoparticles could be seen obviously (Fig. 3.b) while the m-TiO₂ nanoparticles could disperse more regularly in the polymer matrix. The size of the m-TiO₂ nanoparticles in the acrylic coating was about 100 nm (Fig. 3.d) which was similar with the size of initial m-TiO₂ nanoparticles (Fig. 2.b). The u-TiO₂ nanoparticles tend to agglomerate together producing large clusters which are more stable status in comparison with single particles because of its high surface energy. In addition, TiO₂ nanoparticles and acrylic polymer are different in nature leading to poor compatibility of nano TiO₂ and polymer matrix. Furthermore, hydroxyl groups on the surface of the TiO₂ nanoparticles could form hydrogen bond among TiO₂ nanoparticles [16]. However, when the TiO₂ nanoparticles were modified with TMSPM, amount of hydroxyl groups on the surface of m-TiO₂ nanoparticles decreased. Moreover, the silane coupling agent could act as a bridge between TiO₂ nanoparticles and polymer matrix. Consequently, compatibility of m-TiO₂ nanoparticles with acrylic polymer matrix was improved [20, 31]. It means that dispersion of m-TiO₂ nanoparticles in polymer matrix was enhanced. As a result, the properties of acrylic coating filled m-TiO₂ nanoparticles were higher than those of the acrylic coating filled u-TiO₂ nanoparticles.

The FESEM images of the cross-surface of the acrylic coating filled Ag/Zn zeolite particles and Ag/Zn zeolite particles combined with m-TiO₂ nanoparticles indicated that these particles could disperse regularly in polymer matrix. The size of Ag/Zn zeolite particles dispersed in the acrylic coating was 200 nm.

Antibacterial activity of acrylic coatings

The antibacterial activity for *Escherichia Coli* and *Staphylococcus Aureus* of the acrylic coatings filled by 2 wt. % m-TiO₂-3 nanoparticles and different content of Ag/Zn zeolite particles was presented in Table 4.

As can be seen from Table 4, the acrylic coatings filled by m-TiO₂-3 nanoparticles did not kill *E. Coli* bacteria. The obtained results seemed to be conflicted with other publication [15]. The reason was that TiO₂ nanoparticles can kill bacteria because of their photo-catalytic properties. Under UV irradiation, TiO₂ nanoparticles indicated the photo-catalytic properties and producing reactive oxygen species (ROS) such *OH, hydroperoxide, etc. [35]. The new-former ROS are able to kill bacteria. It means that the TiO₂ nanoparticles showed antibacterial activity with light (UV) irradiation. Therefore, in this test, the acrylic

coatings filled by m-TiO₂-3 nanoparticles had insignificant antibacterial activity. The same result was reported by Ashrafi and his coworkers [38].

However, the acrylic coating filled by both m-TiO₂-3 and Ag/Zn zeolite particles showed a high antibacterial activity. The antibacterial activity of acrylic coatings grew up with increasing Ag/Zn zeolite particles content. The acrylic coating filled by both m-TiO₂-3 and 1 wt.% Ag/Zn zeolite particles could kill 99.99 % *E. Coli* bacteria after 24 hours of testing. It could be seen that there was no difference in antibacterial activity between the coating filled by 1 wt.% Ag/Zn zeolite particles and that by 2 wt.% Ag/Zn zeolite particles because most of all bacteria were killed. As the mechanism antibacterial of metal like Ag, Zn, etc., the metal could kill bacteria due to ion metal and ROS (which was produced by the oxidation-reduce of metal) [35]. Therefore, the metal content is enough to produce the necessary ROS and most bacteria will be killed.

The antibacterial activity of the acrylic coatings filled by 2 wt. % m-TiO₂-3 nanoparticles and different content of Ag/Zn zeolite particles for *S. Aureus* was similar for *E. Coli* (Table 5). The Ag/Zn zeolite particles played a role of antibacterial agents in acrylic coatings. The antibacterial activity of investigated coatings grew up with rising Ag/Zn zeolite particles content. However, the antibacterial activity of acrylic coating filled by 2 wt.% Ag/Zn zeolite particles was insignificantly in comparison with that of the acrylic coating filled by 1 wt.% Ag/Zn zeolite particles. Hence, 1 wt.% Ag/Zn zeolite particles in acrylic coating was selected for further studies.

Thermo-oxidation stability of acrylic coatings

Thermogravimetric analysis (TGA) diagrams of the acrylic coating without TiO₂ nanoparticles, with modified TiO₂ nanoparticles, and modified TiO₂ nanoparticles combined with Ag/Zn zeolite particles were presented in Fig. 4. The temperatures at which 5, 50 and 90 % weight of samples lost (T₅, T₅₀ and T₉₀, respectively) were displayed in Table 6.

As could be seen from Fig. 4, the TGA diagrams of the acrylic coatings could be divided into three periods. In the first period, from ambient temperature to 240 °C, the weight of all acrylic coatings was fairly stable (the weight loss of the acrylic coatings was zero). However, from 240 °C, the weight of the acrylic coating filled by m-TiO₂-3 nanoparticles started to reduce slightly. The weight loss also occurred in the neat acrylic coating and acrylic coatings filled by m-TiO₂-3 nanoparticles combined with Ag/Zn zeolite particles at the temperature over 240 °C. The starting temperature of weight loss of the investigated acrylic coatings could be arranged as follow: Acrylic/m-TiO₂-3 < Acrylic/m-TiO₂-3/1 wt.% Ag/Zn zeolite < acrylic. The reason may be thermal transport increased during heating process of acrylic coatings in the presence of nanoparticles [36]. However, the acrylic coating filled by Ag/Zn zeolite particles which have the microporous structure, more or less, reduced the thermal transport. Although the weight loss of the neat acrylic coating occurred later in comparison with the acrylic/m-TiO₂-3 coating, the weight of neat acrylic coating showed a faster reduction. The T₅ (which is assigned with

temperature in which 5 wt. % weight of materials lost) of acrylic/m-TiO₂-3 coating was higher than that of the neat acrylic coating, 319.54 °C for the former and 318.16 °C for the later. The T₅ of acrylic/m-TiO₂-3/1 wt.% Ag/Zn zeolite coating was the lowest. It was explained that m-TiO₂-3 nanoparticles could make acrylic coating structure become tighter and less defect (as mention in above) and limit permeation of oxygen into the coating. Thus, the T₅ of acrylic coating filled m-TiO₂-3 was improved. Besides, the microporous zeolite structure made coating structure became less tight, having more defects. Moreover, due to reducing T₅ of acrylic coating [37].

In the second period, the weight of acrylic coating reduced sharply. Most of the acrylic coatings lost weight in this period due to breaking and thermo-oxidation degradation of the polymer chains. The dTGA diagrams of the acrylic coatings indicated the temperature corresponding to maximum degradation rate were 350.8 °C, 372.01 °C and 364.15 °C for the neat acrylic, acrylic coating filled by m-TiO₂-3 nanoparticles and acrylic coating by filled m-TiO₂-3 nanoparticles combined with Ag/Zn zeolite particles, respectively. The weight loss was caused by the degradation of organic parts in acrylic coating. If heating temperature was higher than 400 °C, the weight of samples was unchanged.

Weathering durability of acrylic coatings

Infrared spectroscopy analysis

In aging process, polymer coatings are exposed to UV irradiation, heat and high humidity. Polymer degradation can be obtained in chemical changes firstly before other symptoms. Therefore, monitoring chemical changes of functional groups of polymer upon accelerated weathering test is very necessary to propose the mechanism of polymer degradation. Infrared (IR) spectroscopy is a sensitive method which can identify and quantify functional groups in the polymer coating. The IR spectra of investigated acrylic coatings before and after accelerated weathering test (36 cycles) were shown in Fig. 5. It was obvious that the absorptions in the IR spectra of aged acrylic coatings were clearly significant changed in comparison with IR spectra of the initial acrylic coatings. For instance, the absorption located at the wavenumber of 3440 cm⁻¹ (corresponding to hydroxyl stretching) was bigger for the acrylic coating filled by m-TiO₂-3 nanoparticles, Ag/Zn zeolite particles and TiO₂ nanoparticles combined with Ag/Zn zeolite particles. It could also be observed that shoulder peak located at 1780 cm⁻¹ appeared during aging process for all of acrylic coatings. While the absorptions located at 2925 and 1450 cm⁻¹ (which were assigned to C-H of alkane stretching and bending) and absorption located at 1150 cm⁻¹ (which was characteristic of C-O of ester group) indicated in reversion. The change in the wavenumber of some functional groups in acrylic coatings were displayed in Table 7.

Carbonyl index (CI) and photo-oxidation index (PI) are usually used to evaluate the degradation degree of polymer coatings [1, 34]. The CI and PI of acrylic coatings were calculated on the basis of absorptions' intensity which was corresponding to hydroxyl groups, carbonyl groups, and C-H (of alkane groups) as below formulas [34]:

$$PI = A/B \text{ (1)}$$

$$CI = C/B \text{ (2)}$$

There: A, B, C represents of hydroxyl, C-H (alkane) and carbonyl peak heights, respectively.

The CI and PI of acrylic coatings with different compositions during the accelerated weathering test were presented in Fig. 6 and Fig. 7.

As can be seen from Fig. 6, the CI of the acrylic coatings grew up upon aging test. The neat acrylic coating had the highest increase in CI among investigated acrylic coatings. Their CI of the samples could be arranged as neat coating > acrylic/(Ag/Zn zeolite) > acrylic/m-TiO₂-3/(Ag/Zn zeolite) > acrylic/m-TiO₂-3. It means that the weather degradation of acrylic coatings filled by m-TiO₂-3 nanoparticles was the lowest among investigated coatings. In other word, the weather resistance of acrylic coating was improved in the presence of m-TiO₂-3 nanoparticles.

Fig. 7 indicated that the PI of investigated acrylic coatings rose during aging process. The acrylic/(Ag/Zn zeolite) coating had the highest increase of PI. This value of the neat acrylic coating slightly increased in the first periods of aging process which was followed by sharply increasing. After 36 cycles (432 hours) of the artificial aging test, the increase in PI of the investigated acrylic coatings was in order: neat coating < acrylic/m-TiO₂-3/(Ag/Zn zeolite) ~ acrylic/m-TiO₂-3 < acrylic/(Ag/Zn zeolite). However, the CI of the neat acrylic coating illustrated the highest increase due to the difference of degradation mechanism of neat acrylic coating in comparison with acrylic composite coatings. This is needed further studies to propose mechanism degradation for the acrylic coating.

Weight loss of acrylic coatings

Under effect of aging process, the chemical functional groups of the acrylic coatings will be changed. The polymer chain scissions were caused by photo-degradation reaction, hydrolysis and erosion, etc. to produce low weight molecules. As a result, the weight (thickness) of acrylic coatings was decreased. It was reported that thickness loss of polymer coating was 5 – 25 μm/year upon natural aging test [33]. Hence, monitoring weight change of polymer coating during accelerated weathering test is one of simple methods to evaluate polymer degradation degree [2, 9, 10, 15, 16]. The weight change of the investigated acrylic coatings with different compositions upon the aging process was illustrated in Fig. 8. It was clear that the weight of neat acrylic coating reduced upon aging test. For the rest investigated acrylic coatings, the weight of the composite acrylic coatings increased in the first 72 hours of the aging which was followed by decreasing in the weight of investigated acrylic coatings. After 36 cycles of the aging test (equal 432 hours), the weight loss of investigated acrylic coatings could be arranged as follow: Neat acrylic coating > Acrylic coating filled Ag/Zn zeolite > Acrylic coating filled m-TiO₂ > Acrylic filled m-TiO₂.

The reason of different weight changes among investigated acrylic coatings was degradation mechanism. For acrylic polymer, the acrylic polymer chain was degraded to form free radicals as Norrish type I and type II (as scheme 1) upon UV irradiation. And then, these free radicals continuously attacked to the polymer chain to produce chain propagation [1]. Consequently, scissions of the polymer chain were

occurred to form low molecular weight products [15]. In addition, the acrylic polymer was hydrolyzed at the condensation periods [9, 16]. As a result, the molecular weight of neat acrylic coating was reduced. However, in the presence of TiO₂ nanoparticles, the degradation mechanism of acrylic composite coating had a little difference in comparison with the degradation mechanism of neat acrylic coating. The TiO₂ nanoparticles produced charge particles (such as electron and holes containing positive charge) under UV irradiation effect. After that, oxygen and water molecules were attacked by electro-particles to produce active free radicals and charged particles. These active parts attached onto the acrylic polymer chains. This was the reason of the investigated coatings' weight increase in the beginning period of aging process [32].

In comparison with the neat acrylic coating, the weight loss of the acrylic coatings filled by both m-TiO₂ nanoparticles and Ag/Zn zeolite particles was lower. It was explained by inorganic nanoparticles which made the coating structure becoming tighter (as discussion mentioned above). In addition, the inorganic nanoparticles could absorb UV irradiation and thus decreasing amount of UV rays exposing to polymer chains. In other word, the inorganic particles acted as a photo-stabilizer. Therefore, this was, more or less, one of the causes of the low weight loss of acrylic composite coatings.

Gloss changes

The surface properties of investigated acrylic coatings will be changed under the effect of the accelerated aging test. The gloss is one of the characteristic properties of the acrylic coating surface. The weathering degradation of the acrylic coating can be evaluated through the gloss retention of investigated samples [2, 6]. The gloss retention of investigated acrylic coatings having different compositions during the accelerated weathering test were demonstrated in Fig. 9. It is clear that the gloss retention at 60° angle of the acrylic coatings reduced during the accelerated aging process. After 36 cycles (432 hours) of the accelerated aging test, the gloss retention of the investigated coating could be arranged as Neat acrylic ~ Acrylic/(Ag/Zn zeolite) < Acrylic/m-TiO₂/(Ag/Zn zeolite) < Acrylic/m-TiO₂.

Under effect of the accelerated aging process, the surface of the investigated polymer coating became rougher due to the erosion of aging process [2, 6]. Therefore, the gloss of the investigated coatings was decreased in comparison with that of the initial coatings. On the base of the gloss retention, the acrylic/m-TiO₂ coatings showed the highest weathering resistance (As above discussion). However, in presence of the Ag/Zn zeolite particles which had size range of 200-500 nm, the structure of acrylic coating became less tight in comparison with the acrylic coating filled m-TiO₂ nanoparticles.

Conclusion

The role of rutile TiO₂ nanoparticles modified by silane coupling agent and Ag/Zn zeolite particles in acrylic waterborne coating was investigated. The obtained results indicated that unmodified rutile TiO₂ nanoparticles could enhance the abrasion of acrylic coating. The abrasion of acrylic coating reached the highest value with 2 wt.% TiO₂ nanoparticles modified 3 wt.% TMSPM (m-TiO₂-3), leveling off at 187.16

L/mil. The SEM images showed that the m-TiO₂-3 nanoparticles could disperse regularly in acrylic polymer matrix. Hence, the weather resistance of coating filled m-TiO₂-3 nanoparticles was best among the investigated coatings. However, the acrylic coating filled m-TiO₂-3 nanoparticles had a lower starting weight loss temperature in comparison with neat acrylic coating. In comparison with the acrylic coating filled m-TiO₂-3 nanoparticles, the acrylic coating filled Ag/Zn zeolite particles was lower improvement for acrylic coating properties, namely, thermal stability, abrasion resistance and weathering durability but the acrylic coating filled Ag/Zn zeolite particles could express excellent antibacterial activity. The acrylic coating filled 1 wt.% Ag/Zn zeolite particles could kill 99 % bacteria after 24 hours (for both negative gram (*E. Coli*) and positive gram (*S. Aureus*) strains). The acrylic coating filled both of m-TiO₂-3 nanoparticles and Ag/Zn zeolite particles indicated a high abrasion resistance, a good weather durability, and a strong antibacterial activity. This composite coating showed promising out-door applications for the construction and architecture.

Declarations

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Conflict of interests The Authors declare that there are no competing interests associated with this article.

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Tables

Table 1. Abrasion resistance of acrylic coatings filled 2 wt.% TiO₂ modified with various TMSPM content

No	Sample	Abrasion resistance (L/mil)
1	Acrylic	84.06 ± 4.74
2	Acrylic/u-TiO ₂	135.37 ± 5.42
3	Acrylic/m-TiO ₂ -1	174.17 ± 6.00
4	Acrylic/m-TiO ₂ -3	187.16 ± 9.36
5	Acrylic/m-TiO ₂ -5	142.24 ± 4.59
6	Acrylic/m-TiO ₂ -10	128.34 ± 3.29
7	Acrylic/m-TiO ₂ -20	125.31 ± 4.04

Table 2. Abrasion resistance of acrylic coatings filled by different contents of TiO₂ nanoparticles modified with 3 wt.% TMSPM

No	Samples	Abrasion resistance (L/mil)
1	Acrylic/0.5 wt.% m-TiO ₂ -3	158.04 ± 4.27
2	Acrylic/1 wt.% m-TiO ₂ -3	173.10 ± 6.18
3	Acrylic/2 wt.% m-TiO ₂ -3	187.16 ± 9.36
4	Acrylic/4 wt.% m-TiO ₂ -3	173.32 ± 9.63

Table 3. Abrasion resistance of acrylic coating filled by 2 wt. % m-TiO₂-3 nanoparticles combined with different Ag/Zn zeolite particles content

No	Samples	Abrasion resistance (L/mil)
1	Acrylic/1 wt.% Ag/Zn zeolite	166.91 ± 5.76
2	Acrylic/ m-TiO ₂ -3/0.5 wt.% Ag/Zn zeolite	179.29 ± 9.96
3	Acrylic/ m-TiO ₂ -3/1 wt.% Ag/Zn zeolite	175.85 ± 6.51
4	Acrylic/ m-TiO ₂ -3/2 wt.% Ag/Zn zeolite	169.33 ± 5.46

Table 4. Antibacterial activity of acrylic coatings for *Escherichia Coli*

Result of bacteria array			Antibacterial activity R
Incubation time	0 h	24 h	
Samples	Log (Average CFU/cm ²)	Log (Average CFU/cm ²)	
Glass (control)	4.00 ± 0.04	4.03 ± 0.05	-
Acrylic/m-TiO ₂ -3	4.00 ± 0.04	4.03 ± 0.05	< 0.1
Acrylic/m-TiO ₂ -3/0.5 wt.% Ag/Zn zeolite	4.00 ± 0.04	1.52 ± 0.05	2.51 ± 0.1
Acrylic/m-TiO ₂ -3/1 wt.% Ag/Zn zeolite	4.00 ± 0.04	0.04	3.99 ± 0.05
Acrylic/m-TiO ₂ -3/2 wt.% Ag/Zn zeolite	4.00 ± 0.04	0.04	3.99 ± 0.05

Table 5. Antibacterial activity of coating formulas for *Staphylococcus Aureus*

Result of bacteria array			Antibacterial activity
Incubation time	0 h	24 h	
Samples	Log (Average CFU/cm ²)	Log (Average CFU/cm ²)	R
Glass (control)	4.08	4.01 ± 0.05	-
Acrylic/m-TiO ₂	4.08	4.00 ± 0.05	< 0.1
Acrylic/m-TiO ₂ -3/0.5 wt.% Ag/Zn zeolite	4.08	1.72 ± 0.03	2.29 ± 0.08
Acrylic/m-TiO ₂ -3/1 wt.% Ag/Zn zeolite	4.08	0.38 ± 0.01	3.63 ± 0.06
Acrylic/ m-TiO ₂ -3/2 wt.% Ag/Zn zeolite	4.08	0.04 ± 0.01	3.97 ± 0.06

Table 6. TGA parameter of acrylic coatings having different compositions

Samples	T ₅ (°C)	T ₅₀ (°C)	T ₉₀ (°C)	T _{max} (°C)
Acrylic	318.16	356.21	394.14	350.8
Acrylic/m-TiO ₂ -3	319.54	372.96	409.66	372.01
Acrylic/m-TiO ₂ -3/1 wt.% Ag/Zn zeolite	311.08	365.57	404.66	364.15

Table 7. IR absorption changes of functional groups in acrylic coatings before and after accelerated weathering test

IR wavenumber (cm ⁻¹)	Characteristics of functional groups	Before	After	Observation
3440	O-H stretching	+	+	Increase
2925	C-H stretching (in alkane group)	+	+	Decrease
1780	C=O stretching (in acid group)	-	+	Appearance
1730	Carbonyl stretching	+	+	Unclear change
1450	C-H bending in alkane	+	+	Decrease
1150	C-O stretching	+	+	Decrease
Note: "+" absorption; "-" no absorption				

Figures

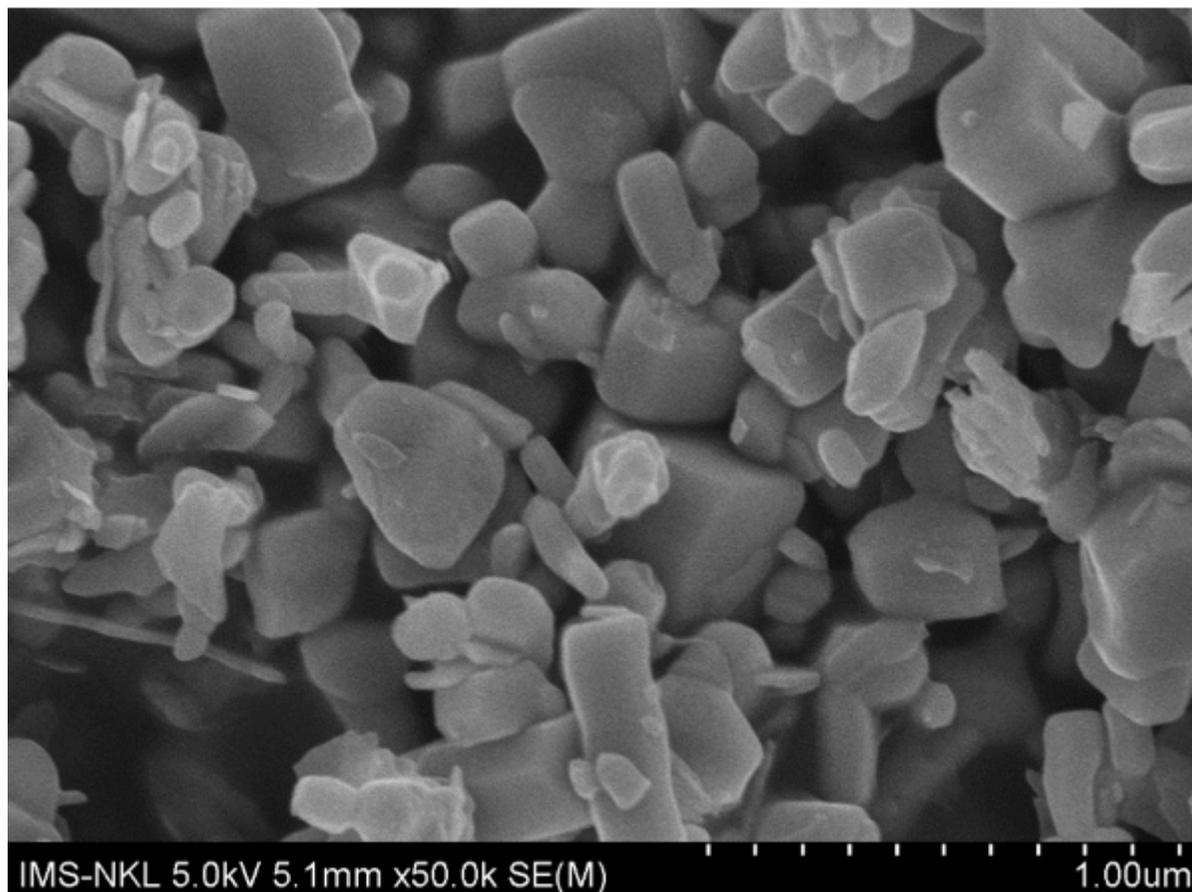


Figure 1

FESEM image of Ag/Zn zeolite particles

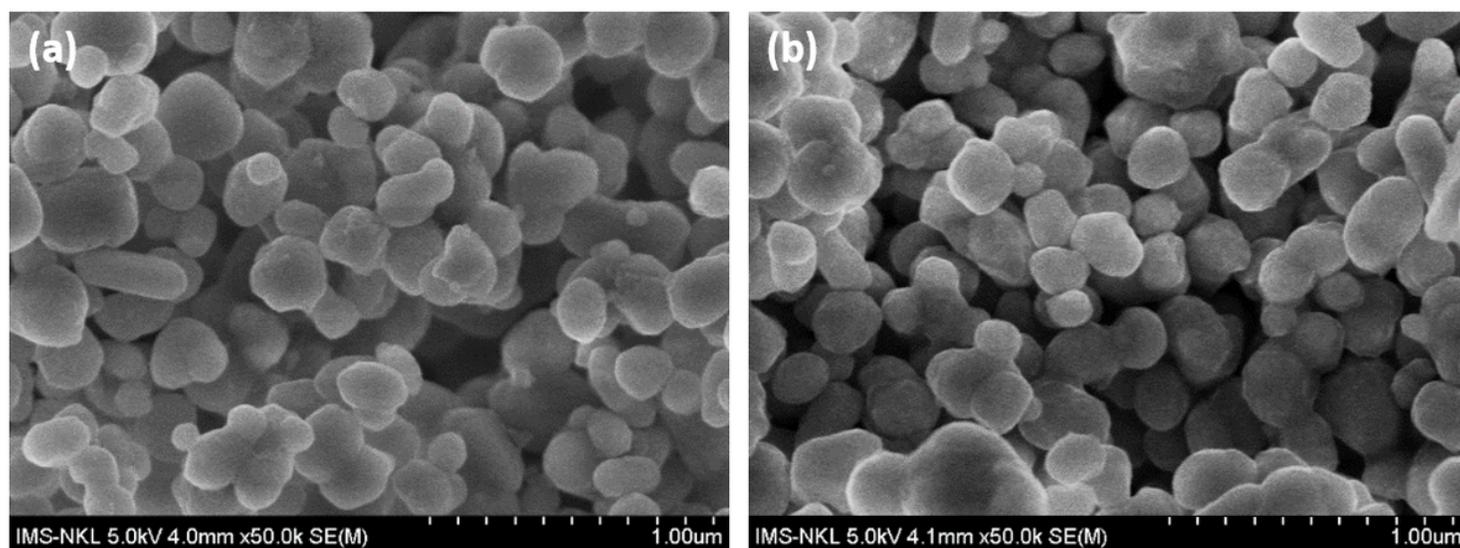


Figure 2

FESEM images of TiO₂ nanoparticles unmodified (a) and modified with 3% TMSPM (b)

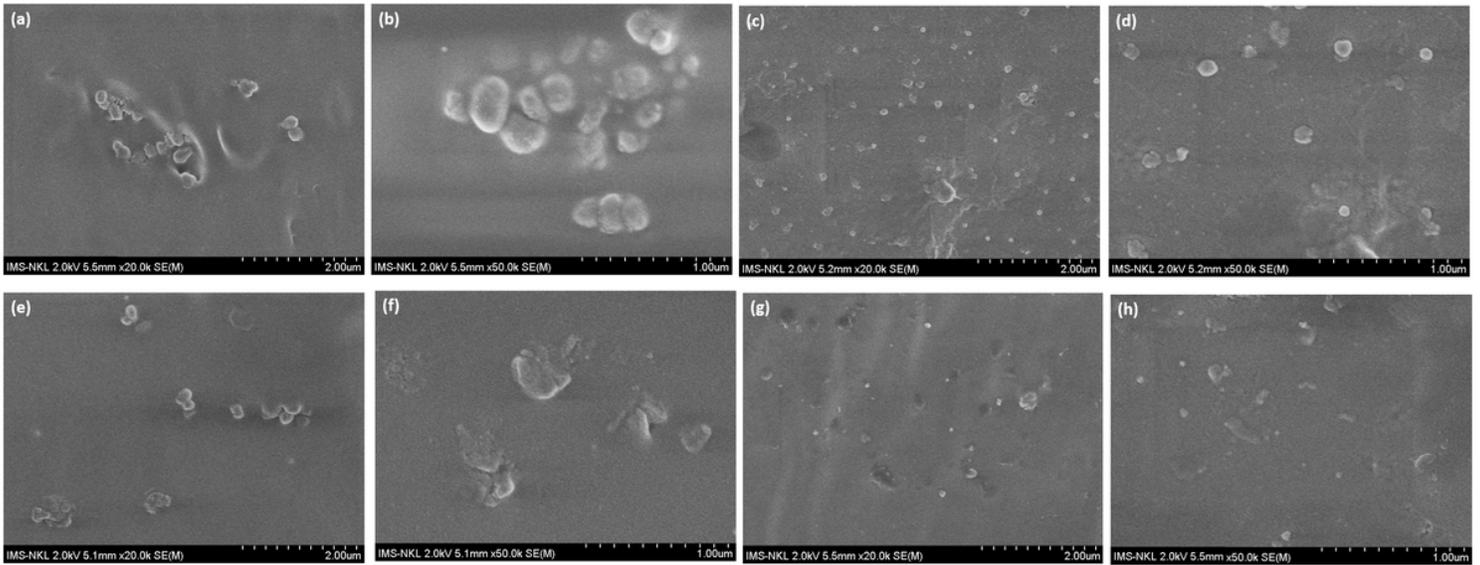


Figure 3

FESEM images of cross surface of investigated acrylic coatings filled unmodified TiO₂ (a, b), modified TiO₂ nanoparticles (c, d), Ag/Zn zeolite particles (e, f), modified TiO₂ nanoparticles combined with Ag/Zn zeolite particles (g, h)

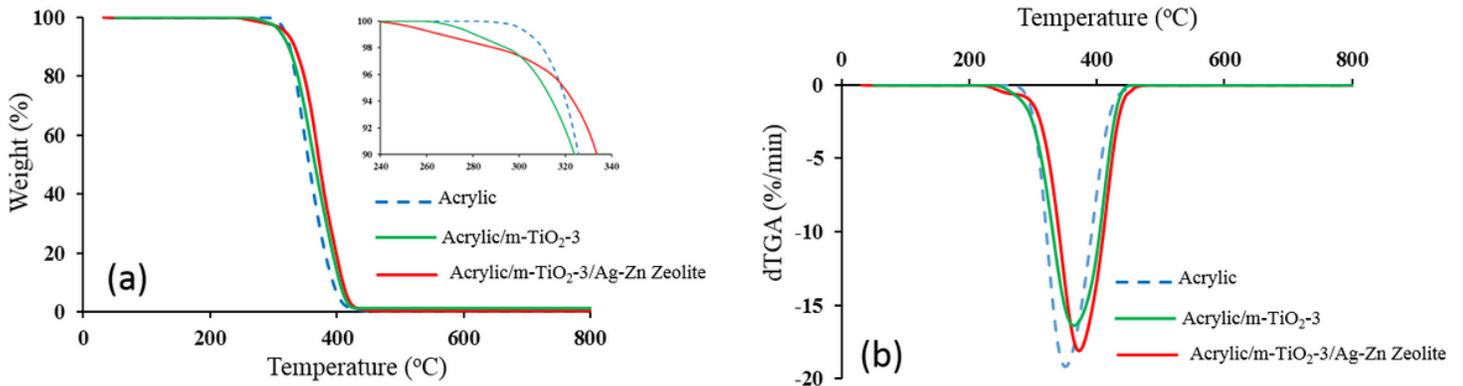


Figure 4

TGA (a) and dTGA (b) diagrams of acrylic coatings without TiO₂ nanoparticles, with modified TiO₂ nanoparticles, and modified TiO₂ nanoparticles combined with Ag/Zn zeolite particles

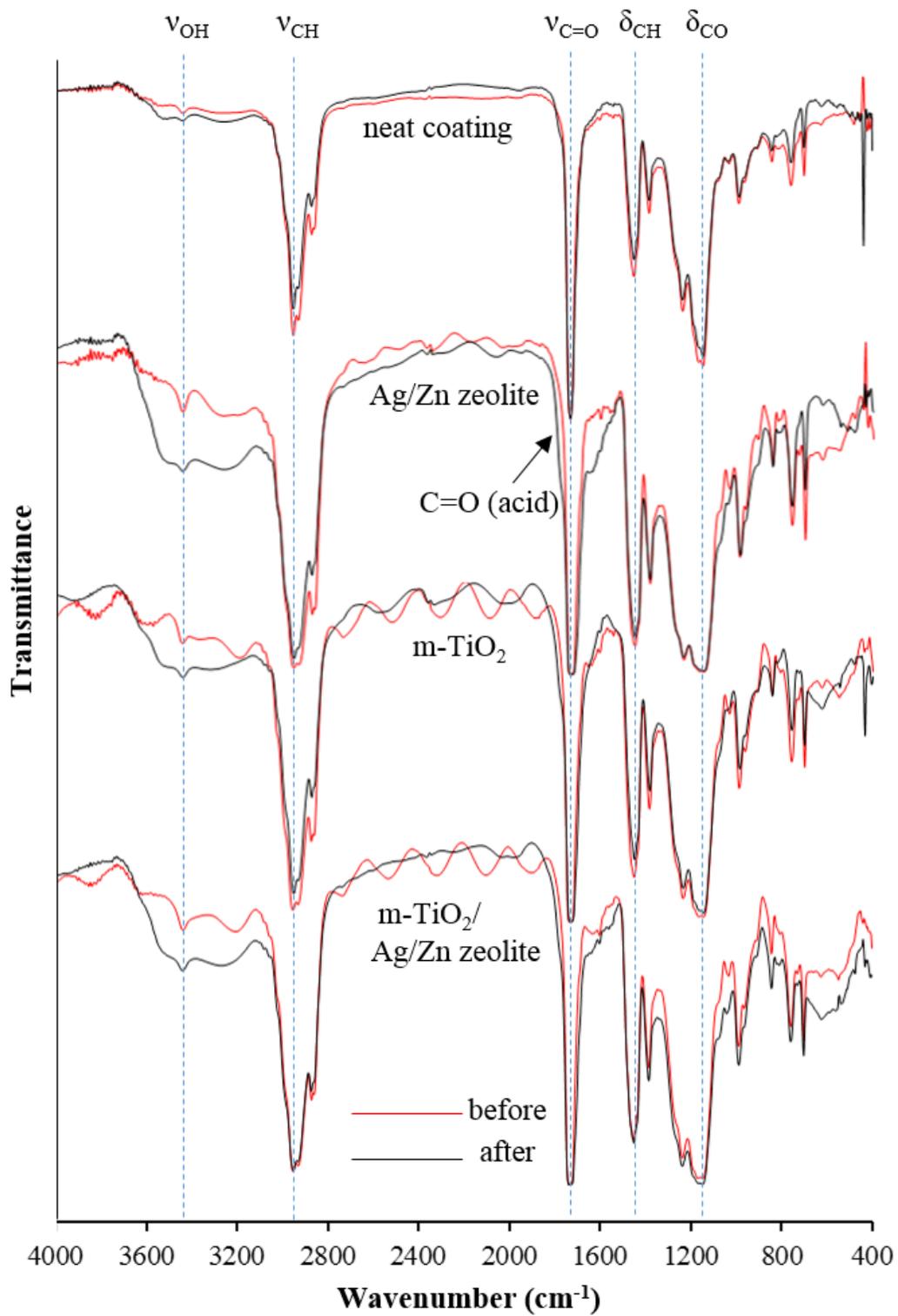


Figure 5

IR spectra of acrylic coatings with different composition before and after (36 cycles - 432 hours) accelerated weathering test.

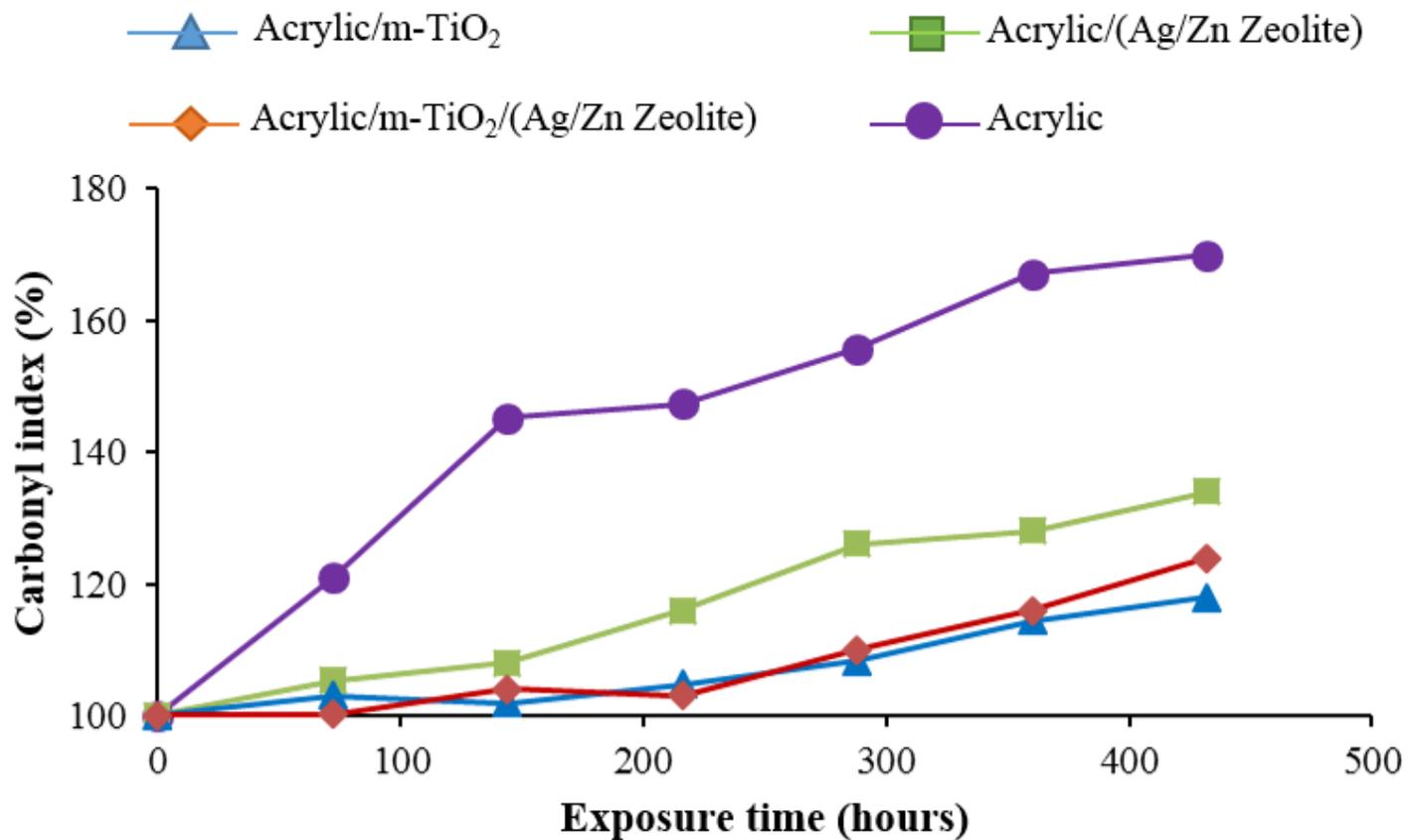


Figure 6

Carbonyl index of investigated acrylic coatings with different compositions during accelerated weathering test

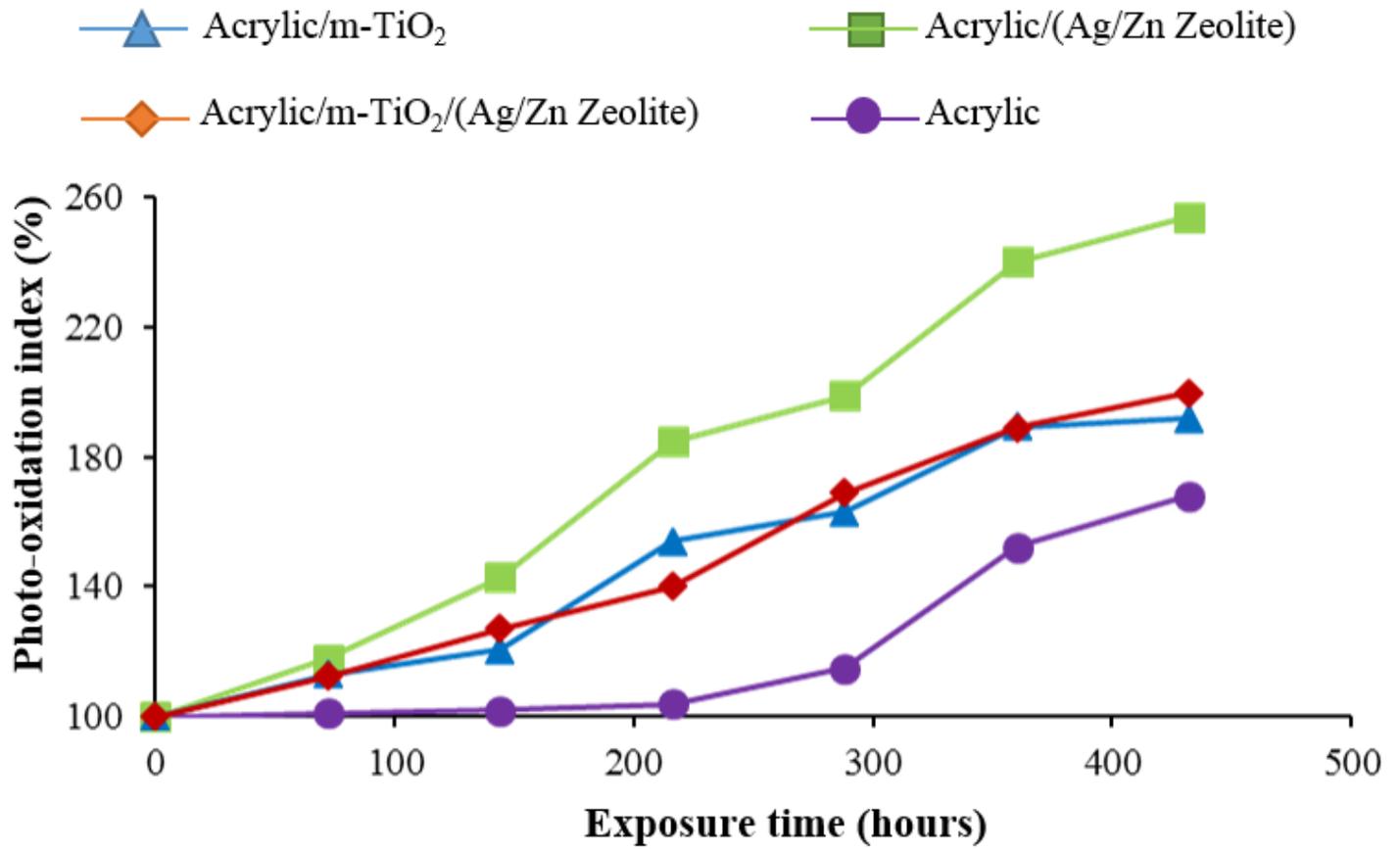


Figure 7

Photo-oxidation index of investigated acrylic coatings with different compositions during accelerated weathering test

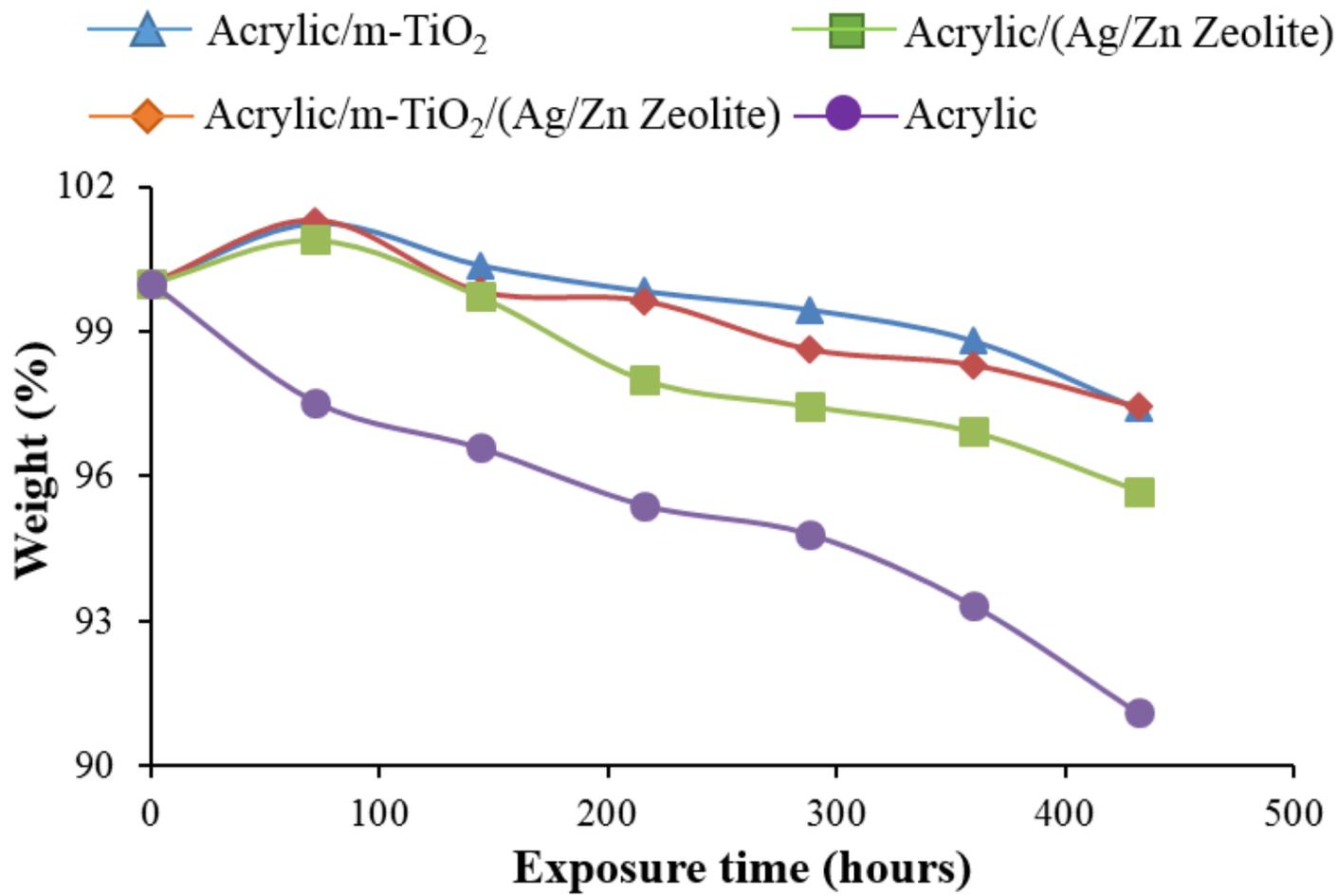


Figure 8

Weight loss of investigated acrylic coatings with different compositions upon accelerated weathering test

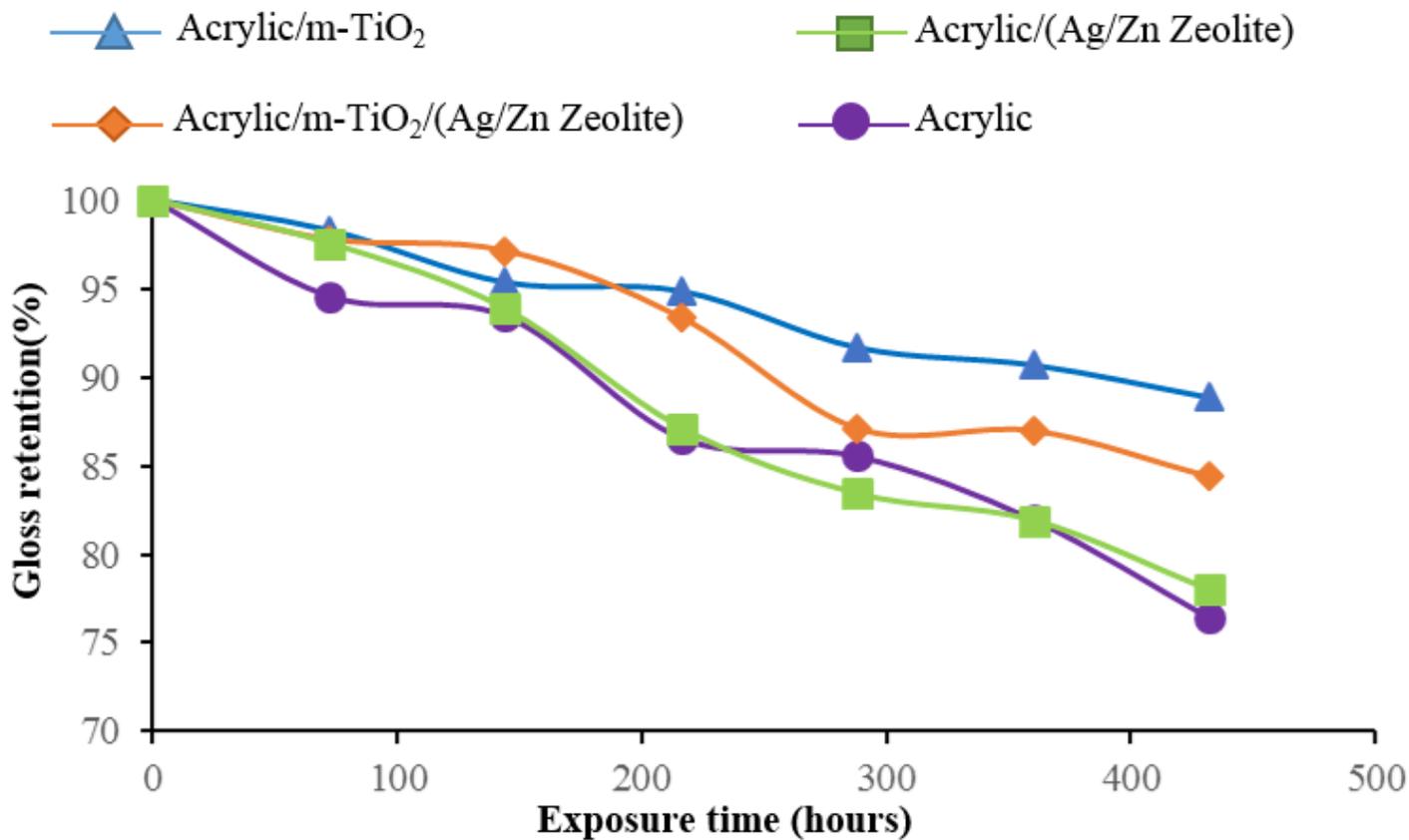


Figure 9

Gloss retention at 60o angle of investigated acrylic coatings upon accelerated weathering test

Supplementary Files

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