



The role of organic and inorganic UV-absorbents on photopolymerization and mechanical properties of acrylate-urethane coating

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ABSTRACT

In this study, the kinetic of photopolymerization reaction, mechanical properties and the morphology of UV curable acrylate urethane coating were investigated. Coatings consisting of 2 wt.% of tinuvin 384, R-TiO₂, A-TiO₂ and ZnO were fabricated. Loading of 2 wt.% of Tinuvin 384 organic UV absorbent was found to decrease the conversion of acrylate double bonds, gel fraction, relative hardness and abrasion resistance of the coating. R-TiO₂ nanoparticles showed insignificant impact on the conversion of acrylate double bonds but improved mechanical properties of the coating. A-TiO₂ and ZnO enhanced both the conversion of acrylate double bonds and mechanical properties of the coatings. A mechanism of photopolymerization reaction of UV-curable acrylate urethane coating in the presence of inorganic UV absorbents has proposed. Nanoparticles were dispersed well in a polymer matrix, with a size of about 50–200 nm.

1. Introduction

Acrylate resins are widely used in exterior and interior coating applications thanks to high transparency, remarkable glossiness and chemicals, and weathering resistance [1–4]. However, the acrylate-based-solvent resins used for coatings suffer from the emitting a large amount of toxic organic solvents in which limit its application due to the environmental issues. Therefore, water-based resins and UV-curing technique have been addressed as an environmental-friendly solution [4–10]. Several efforts have been performed to improve the drawbacks of the acrylate resins. For example, the coating of acrylate resin by fluorine groups by means of solvent polymerization resulted in a higher

hydrophobicity, chemical resistance, glass transition temperature and thermal stability [11]. Inorganic fillers such as SiO₂, TiO₂, ZnO, ZrO₂, Ag, and their hybrid materials were suggested as a superior additive to improve not only the mechanical, thermal [12–15], UV-shielding [16], weathering and anti-corrosion properties [17,18] but also provided remarkable antibacterial and self-cleaning properties [19–22].

Outdoor coatings degrade under some weathering circumstances such as ultraviolet radiation, heat, oxygen, and moisturized condition in which this degradation depends on the nature, structure and the components of the coating [23,24]. The weathering stability of the coating can be improved by adding organic and inorganic UV-absorbents into the coatings. For example, the addition of Tinuvin 384 and Tinuvin 292

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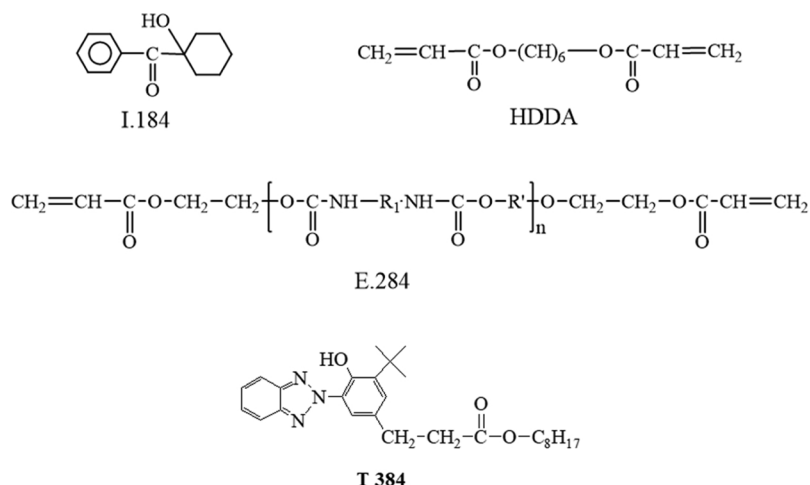


Fig. 1. The structural formula of I184, HDDA, E284 and T 384.

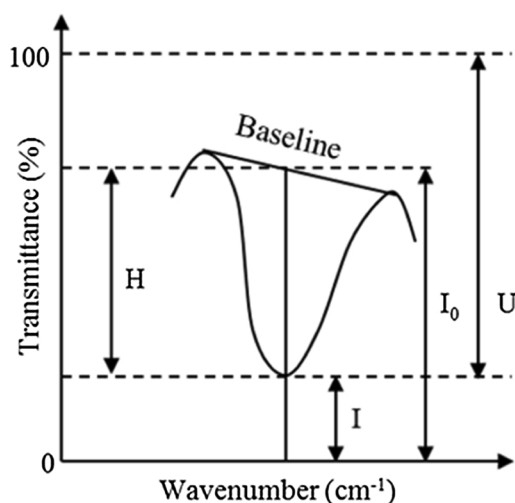


Fig. 2. The relationship between I_0 and I with H and U .

into the solvent-based acrylic polyurethane coatings resulted in higher outdoor service time from 2 to 3 times [1]. Similar results were obtained with inorganic nanoparticles (R-TiO₂, ZnO) as UV absorbers [4,16,17]. However, several studies also revealed that in the presence of additives, the crosslinking process of the thermosetting resin system was influenced [25–30]. In the case of the epoxy matrix, Fe₃O₄ nanoparticles could act as bridge interconnecting molecules, and thus reduced the total free volume and increased the cross-linking density [25,26]. In this direction, to study the cure kinetics of epoxy/amine system, Fe₃O₄ nanoparticles were used as nanocarriers for loading of the acid functional group [27], amine functional group [28,29], or hydroxyl functional group [28,30]. It was reported that the reaction of acid functional groups with amine groups of curing agent could possibly deactivate the hardener [27]. Whereas, the presence of hydroxyl and amine groups might access to epoxy groups leading to an increase in the amount of curing heat [28]. H. Yari et al. have reported that SiO₂ nanoparticles caused an incomplete curing process of the acrylic melamine clearcoat, leading to a lower crosslinking density compared to the pure clearcoat and enhanced weathering performance of clearcoats. This is because the SiO₂ nanoparticles absorbed or scattered the harmful incident UV rays, protecting the clearcoat against weathering degradation [31]. For UV curable systems, the effect of some additives on the photocrosslinking process has also been investigated. X. Allonas et al. have successfully synthesized organozirconiums from zirconium and organic fluorides and used them as the peroxy radical scavengers

against oxygen inhibition [32]. In our previous work [22], it was shown that although the Fe₃O₄-Ag hybrid nanoparticles acts as UV absorbers, but at low concentrations (0.1%), they affected insignificantly on the kinetics of UV curing reaction of acrylate epoxy resin system.

The influence of organic and inorganic UV absorbers such as Tinuvin 384, nano R-TiO₂, nano A-TiO₂ and nano ZnO on the cross-linking of the UV curable acrylate-urethane resins has not been reported in the literature. Therefore, here, the curing reaction of the coatings in presence of UV absorbers additives is quantitatively investigated by IR spectroscopy, gel fraction and relative hardness assessment. The morphology and abrasion resistance of the prepared coatings are also evaluated.

2. Experimental

2.1. Materials

1-Hydroxy-cyclohexyl-phenyl-ketone, Irgacure 184 (I.184) as a photoinitiator was purchased from CIBA. 1,6-Hexanediol diacrylate (HDDA, 80%) as a diluent was ordered from Sigma Aldrich. Ebecryl 284 diacrylate urethane resin (E284) was received from Allnex, Belgium. 2-(2-hydroxy-3-tert-butyl-5-propionic axit isooctyl este) -2H-benzotriazol (T 384) as an organic UV absorber was purchased from CIBA. The structural formula of I184, HDDA, E284 and T 384 were presented in Fig. 1.

Rutile TiO₂ (R-TiO₂), Anatate TiO₂ (A-TiO₂) and ZnO nanoparticles as inorganic UV absorbers were obtained from Sigma Aldrich (Singapore).

2.2. Preparation of samples

The optimal selected content of the UV absorbers, 2 wt%, according to former studies [1,4,16], was dispersed in HDDA using a PTC-25 supersonic bath (Switzerland) for 3 h. Then, the dispersants were stirred with E284 and I.184 using an Ika RW16 basic mixer (England) for 30 min. The ratio of E284:HDDA:I.184 was chosen 55:45:3. Coatings with a thickness of ~25 μm were prepared on KBr pellets for IR spectroscopy. A sheet of coating was casted on a Teflon film with a size of 100 × 100 × 10 mm for UV-vis spectroscopy, gel fraction and FE-SEM analyses. In addition, samples with the dimension of 100 × 100 × 2 mm were prepared on glass sheet for relative hardness and abrasion resistance measurement using a spiral film applicator (Erichsen model 358). The coatings were exposed to UV radiation of a medium-pressure mercury lamp (250 mW/cm²) at room temperature, in the presence of air in FUSION UV equipment (Model F300S, USA). The samples were passed several times under the light with a web rate

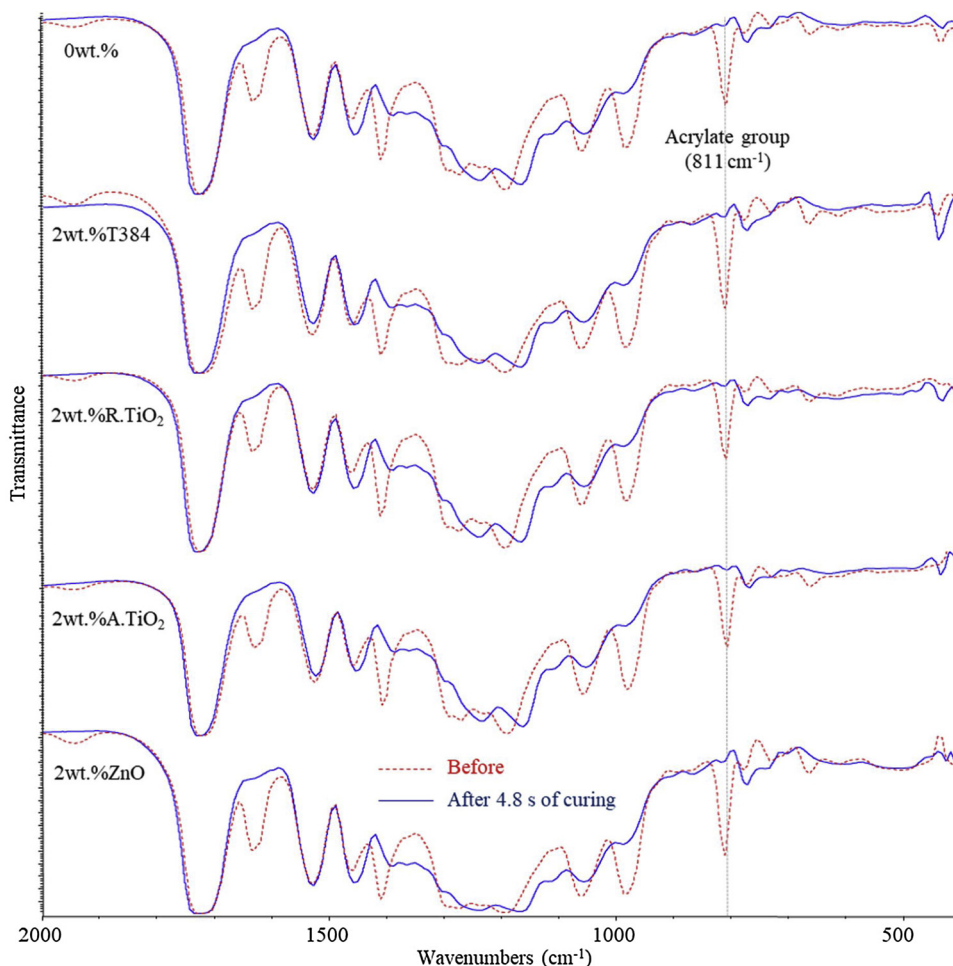


Fig. 3. IR spectra of the UV-curable acrylate urethane coatings in the absence (0 wt.%) and presence of 2 wt.% UV absorbers (T384, nano R-TiO₂, nano A-TiO₂ or nano ZnO) before and after 4.8 s of UV exposure.

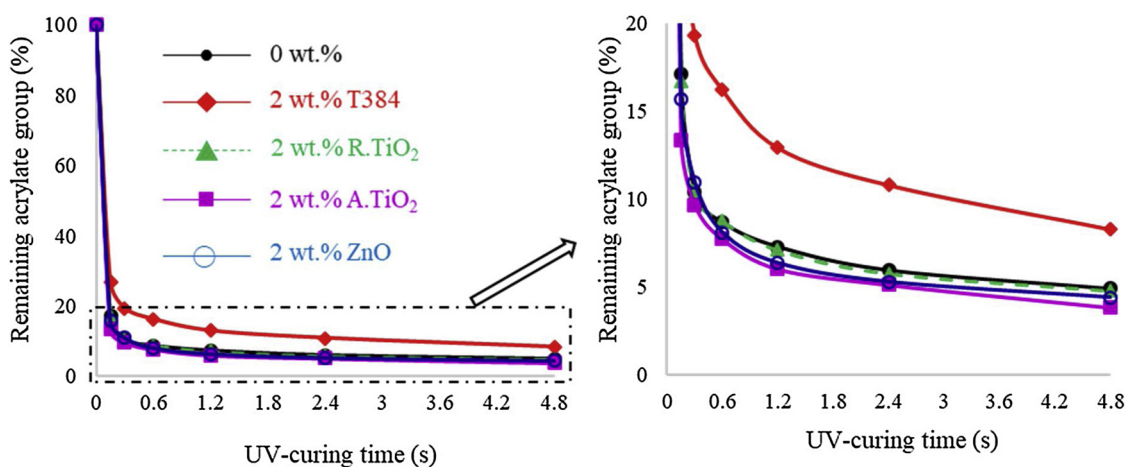


Fig. 4. Conversion of the acrylate double bonds during the UV exposure.

between 5 and 40 m/s and the exposure time is thus calculated. For example, for a web rate of 40 m/s, exposure time is calculated, was 0.15 s.

2.3. Characterization

2.3.1. IR spectroscopy

IR spectroscopy was conducted using an FT-IR spectrometer

(NEXUS 670 from Nicolet). Experiments were carried out on the same position of each sample at various time for the UV exposed samples [19]. To eliminate the effect of changes in the coating thickness, carbonyl band at 1730 cm⁻¹ was chosen as the reference band.

The optical density (D) of groups was estimated by the following formula:

$$D = \log(I_0/I) = \log[1 + H/(100-U)] \tag{1}$$

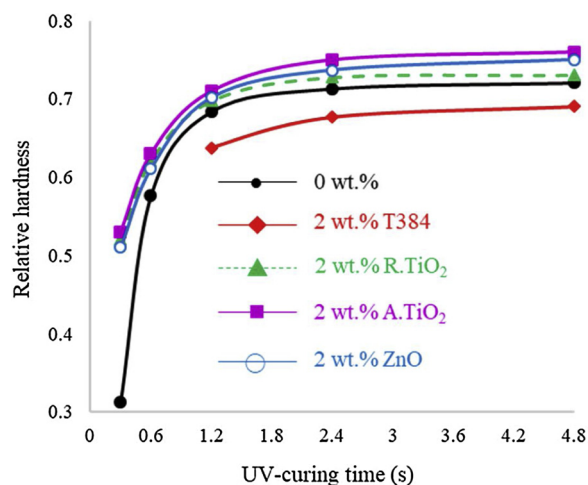


Fig. 5. Variation of relative hardness of the coatings without (0 wt.%, solid circle) and with 2 wt.% UV absorbers of T384, R-TiO₂, A-TiO₂ and ZnO.

The relationship between I_0 and I with H and U was showed in Fig. 2 where H and U were calculated by using the software of FTIR spectroscopy.

Remaining acrylate group (%) was calculated by dividing the ratio of optical density of acrylate group and optical density of reference carbonyl group at the reaction time t ($D_{811 \text{ cm}^{-1}}/D_{1730 \text{ cm}^{-1}})_t$ by the ratio of optical density of acrylate group and optical density of reference carbonyl group at the initial time 0 ($D_{811 \text{ cm}^{-1}}/D_{1730 \text{ cm}^{-1}})_0$, then multiply by 100.

2.3.2. UV-vis spectral analysis

The UV-vis spectra were recorded in the absorbance mode using a UV-vis spectrophotometer (GBC, CINTRA 40, USA)

2.3.3. Gel fraction analysis

The cured coating samples were carried out in a Soxhlet tool in accordance with the ASTM D 2765 in acetone for 24 h to analyze the gel fraction of the coatings [22]. The gel fraction (%) was calculated by dividing the weight of insoluble film part (which was heated at 50 °C until the sample reached to a completely dry state) by the weight of the initial coating sample (before the analysis), then multiply by 100.

2.3.4. Determination of mechanical resistance

The relative hardness of the cured coatings was determined using a

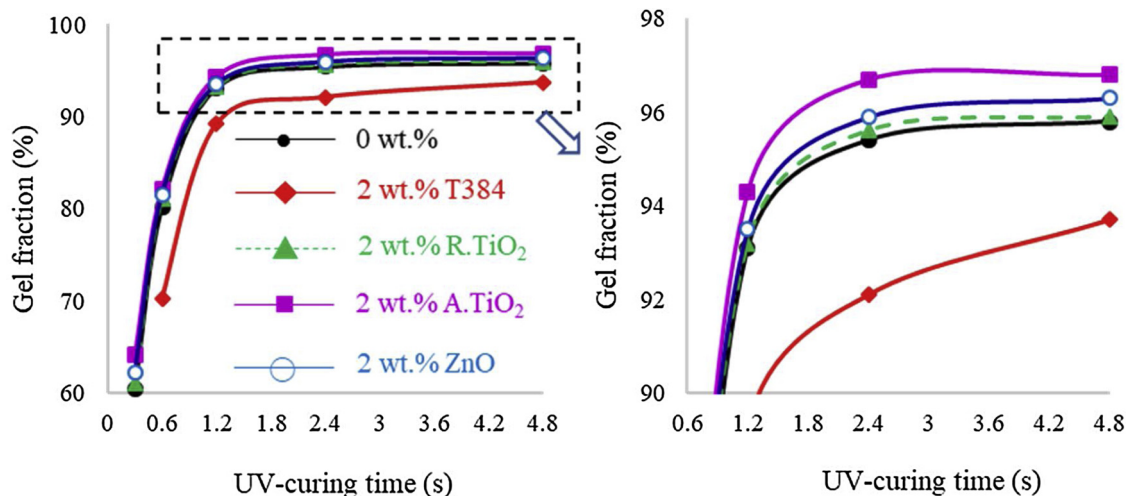


Fig. 6. Variations of gel fraction of the coating without (0 wt.%), with 2 wt.% UV absorbers of T384, R-TiO₂, A-TiO₂ and ZnO.

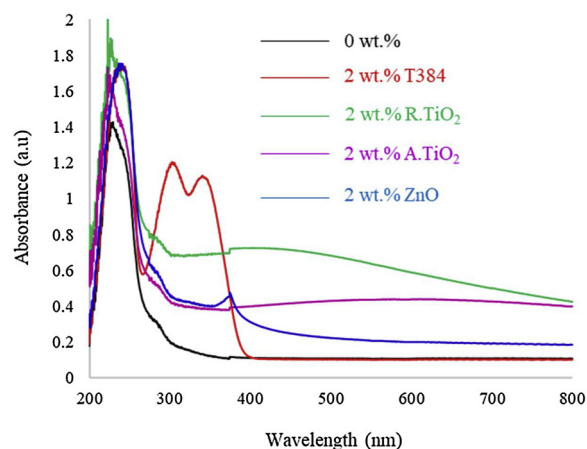


Fig. 7. UV-vis spectra of the the reference coating and coatings containing 2 wt.% UV absorbers of T384, R-TiO₂, A-TiO₂ and ZnO.

Pendulum Damping Tester (ERICHSEN, model 300) according to the Persoz Standard (NF T 30-016). The relative hardness was calculated by dividing the absolute hardness by the hardness of standard glass, which was 425 s.

Abrasion resistance of the coatings was assessed using the abrasive falling methods, according to the ASTM D968. All samples were determined triplicate and the data were presented as average values.

2.3.5. Morphology analysis

The morphology of the coatings was analyzed using a scanning electron microscope S- 4800 (Hitachi, Japan) (FE-SEM). The surface of the sample was coated with a thin layer of carbon.

3. Results and discussion

3.1. Kinetic of photopolymerization of acrylate urethane coating in the presence of UV absorbent

IR spectroscopy was conducted to evaluate the photocrosslinking polymerization reaction of the acrylate urethane coating in the presence of UV absorbers by analyzing the changes of IR absorption density of acrylate double bonds. IR spectra of the UV-curable acrylate urethane coatings in the absence (0 wt.%) and presence of 2 wt.% UV absorbers such as T384, nano R-TiO₂, nano A-TiO₂ and nano ZnO before and after 4.8 s of UV exposing time were presented in Fig. 3. The intensity of the IR peaks at 1632, 1409, 984 and 811 cm⁻¹

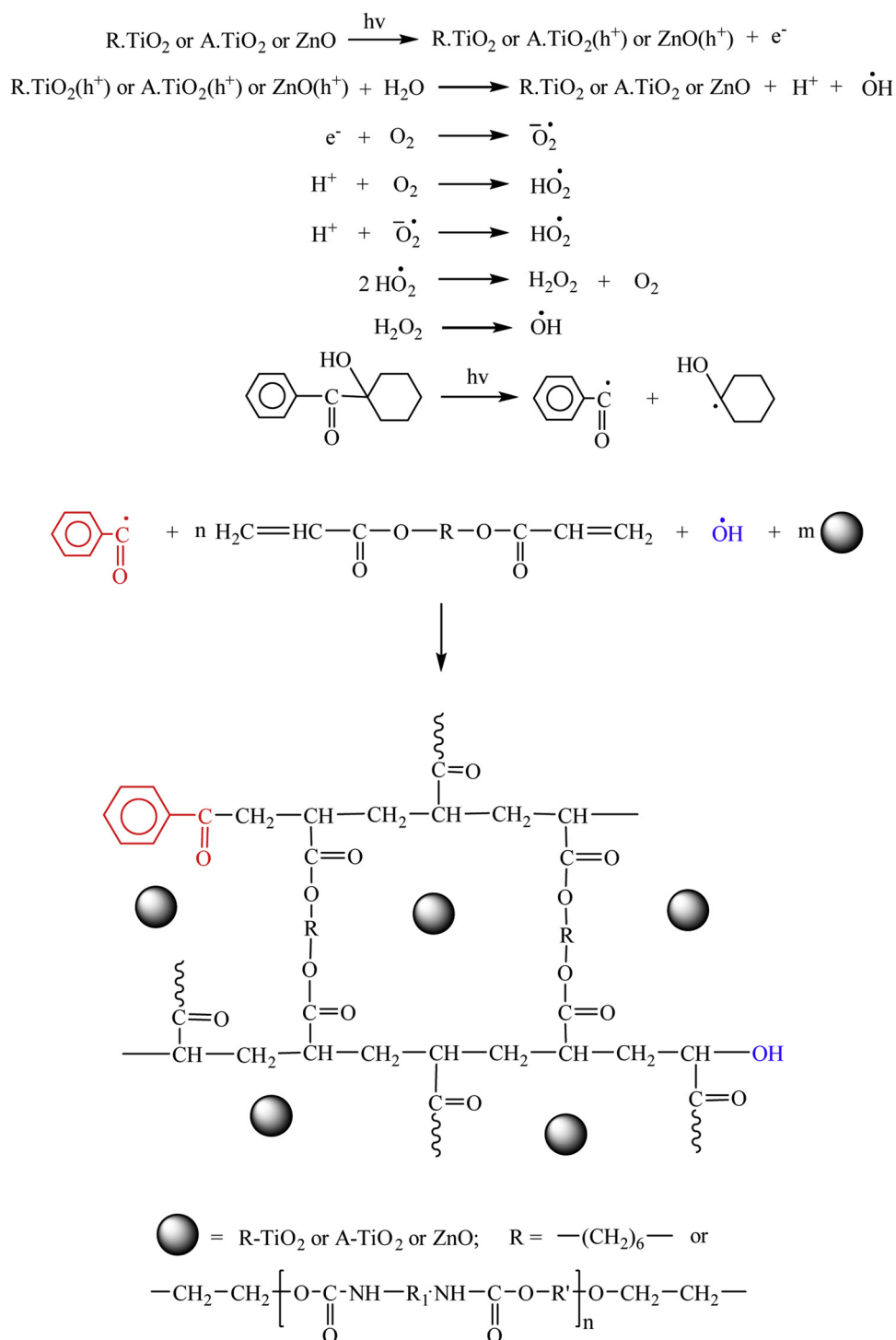


Fig. 8. Proposed mechanism of photocrosslinking polymerization reaction of UV-curable resin system based on photoinitiator I.184, HDDA, E.284 in the presence of inorganic UV absorbents.

assigning to acrylate double bonds of HDDA and E284 was decreased due to the curing polymerization process.

The IR peak at 811 cm^{-1} was selected to study the conversion rate of the acrylate double bonds during the crosslinking process, and as seen in Fig. 4, it was clearly decreased. As can be seen from Fig. 4, the conversion in the acrylate double bonds was occurred quickly (in the first 0.15 s) and then slowed down. The highest conversion rate of the acrylate double bonds was taken place at the coating containing 2 wt.% nano A-TiO₂ and the lowest with 2 wt.% T384. After 4.8 s of UV exposing, the acrylate double bonds seemed to reach a maximum value

of 95.1, 91.7, 95.2, 96.2 and 95.6% for the coating 0 wt.%, 2 wt.% T384, 2 wt.% R-TiO₂, 2 wt.% A-TiO₂ and 2 wt.% ZnO, respectively. Thus, UV absorbents influenced the conversion of acrylate double bonds at different levels depending on their nature.

3.1.1. Hardness assessment

The hardness of the coatings in thermoset resins is a useful parameter to evaluate the conversion of the curing reaction since the more crosslinking would result in harder composite. The variation of relative hardness of the coatings was shown in Fig. 5. As seen, the relative

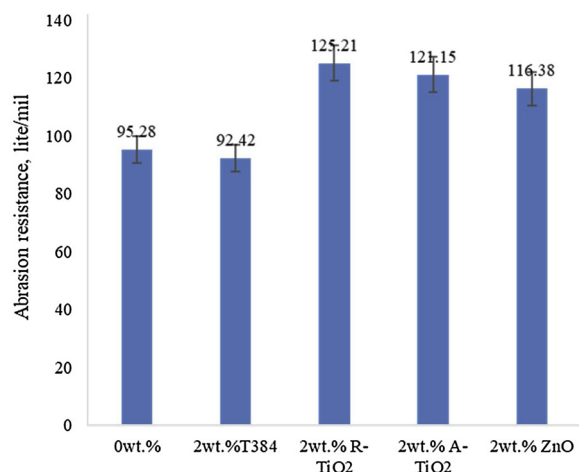


Fig. 9. Influence of UV absorbers on the abrasion resistance of the coatings.

hardness increased rapidly in the first 1.2 s of the reaction before slowing down. The hardness of the coating containing 2 wt.% T384 was possible to measure after 1.2 s of UV exposure time, while the other coatings were hardened after only 0.3 s of the curing. The hardness of the coating containing 2 wt.% inorganic UV absorbers (R-TiO₂, A-TiO₂ and ZnO) was higher, while the hardness of the coating containing 2 wt.% organic UV absorbent (T384) was lower compared with that of the neat coating (without UV absorbent). After 4.8 s of crosslinking reaction, the relative hardness of the coatings reached the highest value of about 0.72, 0.69, 0.73, 0.76 and 0.75 for the coating without and with 2 wt.% UV absorbers of T384, nano R-TiO₂, nano A-TiO₂, and nano ZnO, respectively. The addition of the inorganic UV absorbers into the coating formulation increased slightly the coating hardness while in the presence of the organic UV absorbent (T384), the hardness was decreased.

3.1.2. Gel fraction analysis

Gel fraction analysis can give further information regarding the

photopolymerization reaction in presence of UV absorbers. The gel fraction results are presented in Fig. 6. As seen, the gel fraction of the coatings without and with 2 wt.% inorganic nanoparticles R-TiO₂, A-TiO₂ and ZnO appeared after 0.3 s of the initiating of the reaction. However, the coating containing 2 wt.% T384 featured a gel fraction after 0.6 s of curing. The gel fraction increased rapidly in the first 2,4 s, then it slowed down. In the presence of 2 wt.% A-TiO₂ and ZnO, the gel fraction of the coatings was increased while significant change was not seen for the coatings containing 2 wt.% R-TiO₂. In addition, the gel fraction of the coating containing 2 wt.% organic UV absorbent (T384) decreased, in comparison with that of the coating without UV absorbent. The gel fraction of the coatings reached a maximum value of about 95.8 (without UV absorbent), 93.7 (T384), 95.9 (R-TiO₂), 96.8 (A-TiO₂), and 96.3 % (ZnO) after 4.8 s of the initiating the reaction. Thus, UV absorbers affected on the gel fraction of the coating.

The UV-vis spectra of the examined coatings are shown in Fig. 7. As seen, the coating without UV absorbent featured only 2 UV absorbance peaks in the range of 200–300 nm which assigned to C=O group (at 234 nm) of the polymer matrix and benzene ring (at 275 nm) of photoinitiator I 184 while light absorbance range of the coatings containing UV absorbers were appeared in a broader range. The coating containing T384 absorbed strongly the UV radiation in the two ranges: (1) from 200–300 nm and (2) from 300 to 400 nm which are assigned to T384. The nano R-TiO₂ and A-TiO₂ filled coatings absorbed light radiation in both UV and visible light ranges but UV light absorbance of the R-TiO₂ filled coating was found to be stronger. Coating loaded with 2 wt.% ZnO showed also two UV absorbance peaks: (1) at about 240 nm and (2) at 375 nm but those were significantly weaker than that of the T384 coating.

It is known that the characteristic of photoinitiator was very sensitive to UV radiation [33], under the effect of UV radiation of a medium-pressure mercury lamp in FUSION UV equipment, photoinitiators I.184 was decomposed into free radicals, and then the free radicals reacted with acrylate double bonds and initiated the photocrosslinking polymerization reaction. Primarily, in the first 0.15 s of UV exposure, the content of photoinitiators was high (about 3%) and the curing system was relatively flexible (low viscosity), therefore, the

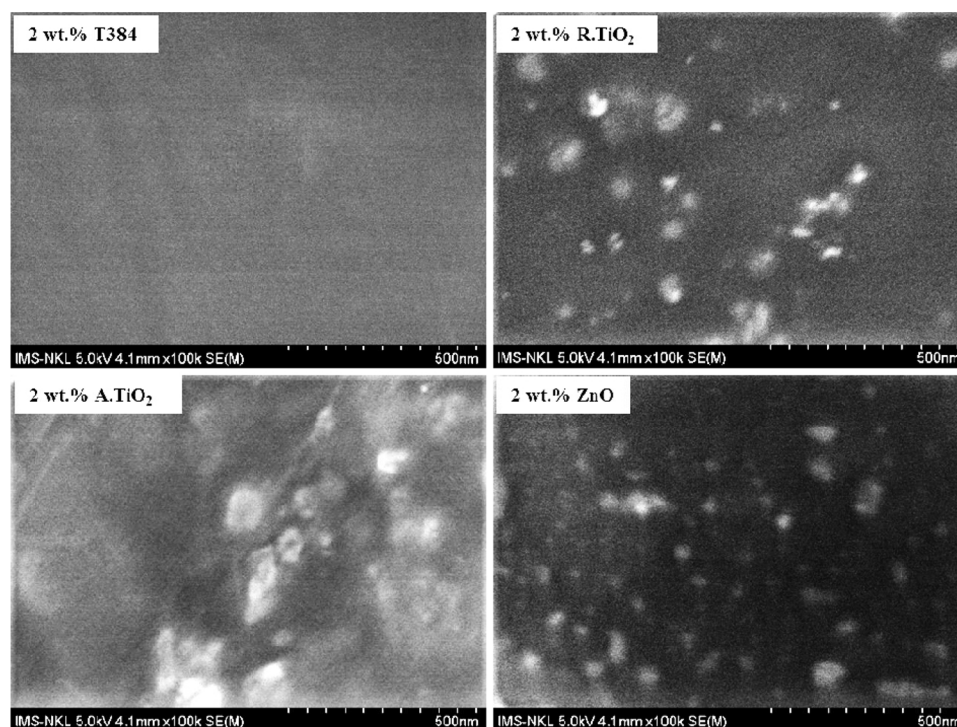
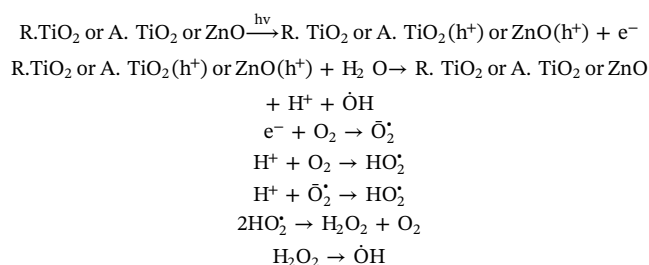


Fig. 10. The FE-SEM images of the coatings containing UV absorbers.

reaction of the acrylate double bonds was negligibly affected by UV absorbers. However, the concentration of the photoinitiators and the acrylate double bonds reduced rapidly by the time, and thus the conversion of the acrylate double bonds was decreased. In the presence of 2 wt. % organic UV absorbent (T384), the conversion of the acrylate double bonds was reduced. This can be explained by the fact that the T384 absorbed the UV radiation which in turn preventing the UV energy absorption of the photoinitiators. In the case of the presence of 2 wt.% inorganic UV absorbents (nano R-TiO₂, nano A-TiO₂ or nano ZnO), the conversion of the acrylate double bonds was influenced by both UV shielding and photocatalytic of the inorganic UV absorbents. The UV absorption intensity of the inorganic UV absorbents was found weaker than that of T384. On the other hand, when absorbing UV energy, an electron jumped from the valence band to the conduction band resulting in the formation of an electron-hole pair. These electron and positive hole reacted to hydroxyl groups, water and oxygen molecules on the nanoparticles' surface to generate free radicals ($\cdot\text{OH}$) [4,16] which could also initiate the crosslinking polymerization reaction. Photocatalytic reactions of the generation of free radicals $\cdot\text{OH}$ can be presented as follows:



Photocatalytic activity of the nanoparticles used in the study was arranged in order: A-TiO₂ > ZnO > R-TiO₂ [16,34]. The low UV shielding of R-TiO₂ nanoparticles was compensated by its photocatalysis. Therefore, the impact of R-TiO₂ nanoparticles on the conversion of acrylate double bonds was not remarkable. However, the photocatalytic activity of A-TiO₂ and ZnO nanoparticles was found much stronger, wherein $\cdot\text{OH}$ free radicals initiated the curing reaction leading to the increase of the conversion of acrylate double bonds.

On the basis of the obtained analytic results of the acrylate double bonds conversion, the variations of the relative hardness and gel fraction of UV cured acrylate urethane resin system in the absence and presence of organic and inorganic UV absorbents, it can be identified that photocrosslinking polymerization of the coatings was remarkably influenced by the presence of the UV absorbents. The mechanism of photopolymerization reaction of UV curable acrylate urethane resin system in the presence of inorganic UV absorbents (R-TiO₂ A-TiO₂ and ZnO) was shown in Fig. 8.

3.2. Abrasion resistance and morphology of the coatings

The influence of UV absorbents on the abrasion resistance of coatings is presented in Fig.9. As seen, the incorporation of the inorganic UV absorbents into the polymer matrix increased the abrasion resistance of the coating from 95.28–125.21, 121.15 and 116.38 lite/mil for the incorporation of 2 wt.% UV absorbent of nano R-TiO₂, nano A-TiO₂ or nano ZnO, respectively. The incorporation of 2 wt.% organic UV absorbent (T384) decreased slightly the abrasion resistance from 95.28–92.42 lite/mil. To corroborate the variation of abrasion resistance in the coating, FE-SEM images of the coatings containing UV absorbents are shown in Fig. 10. As seen, all the coatings had tight structures without comparable defects and cracks. Nanoparticles were dispersed uniformly in the polymer matrix, with a size of about 50–200 nm. The abrasion resistance of the nanocomposite coatings was enhanced by tough nanoparticles which revealed a higher hardness. Among them, R-TiO₂ featured the highest value, therefore its

corresponding nanocomposite showed a higher abrasion resistance than the nanocomposite containing A-TiO₂ and ZnO one. The abrasion resistance of the coating containing T384 was reduced due to the softening effect of the T 384.

4. Conclusion

The curing conversion, gel fraction and relative hardness of the acrylate urethane coatings tailored with organic and inorganic UV absorbents such as Tinuvin 384, R-TiO₂, A-TiO₂ and ZnO were studied quantitatively. Findings revealed a reduction of conversion of acrylate double bonds, gel fraction, relative hardness and abrasion resistance for the coating blended with T384. The influence of R-TiO₂ nanoparticle on photocrosslinking polymerization was found fairly negligible, however, noticeable improvement in mechanical properties of the coating was seen. Loading of A-TiO₂ and ZnO particles to the resin led to an increase in both the conversion of acrylate double bonds and mechanical properties. The effect of TiO₂ and ZnO on the photocatalytic activity of these coating dealing with antibacterial and pollutant removal under UV radiations will be investigated in the next step of this project. The chemical interactions between nanoparticles with resin matrix will be also investigated in depth by using an atomic force microscopy coupled with infrared spectroscopy (AFM-IR) according to our recent reported approaches [1,35–37].

CRediT authorship contribution statement

Thien Vuong Nguyen: Writing - review & editing. **Phuong Nguyen-Tri:** Conceptualization. **Sohrab Azizi:** Writing - original draft. **Tran Chien Dang:** Investigation. **Duc Minh Hoang:** Investigation. **Thu Ha Hoang:** Investigation. **Thi Linh Nguyen:** Investigation. **Thuy Thi Le Bui:** Investigation. **Viet Hung Dang:** Methodology. **Ngoc Linh Nguyen:** Investigation. **The Tam Le:** Investigation. **Thi Ngoc Linh Nguyen:** Investigation. **Quoc Trung Vu:** Resources. **Dai Lam Tran:** Project administration. **Thi My Linh Dang:** Investigation. **Le Trong Lu:** Supervision.

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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