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Porous nonhierarchical CeO$_2$-SiO$_2$ nanocomposites for improving the ultraviolet resistance capacity of polyurethane coatings

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Abstract

Polyurethane (PU) coating degrades quickly under the irradiation of ultraviolet (UV). Thus, increasing the durability of the coating is necessary. In this study, porous CeO$_2$-SiO$_2$ nanocomposites (CS-NCs) were used to disperse into the PU matrix. The CS-NCs were prepared by a sol-gel combustion method using polyvinyl alcohol as precursors. Prepared nanocomposites were characterized by x-ray diffraction (XRD) analysis, Fourier transform infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM) as well as Energy dispersive x-ray (EDX) mapping analysis. Next, the prepared nanocomposites were employed for the preparation of PU coatings. The loading of nanoparticles was varied between 0.1% and 2.0%. These coating properties were investigated by using FTIR and UV–vis spectroscopy. As also in this study, these coatings were subjected to UV exposure with accelerated weather testing. The structural changes were characterized by applying FTIR analysis and measuring gloss and color deviation. The results indicate that incorporating nanocomposites into the polymer matrix improves the UV-durable properties of the PU matrix.

1. Introduction

Polyurethane (PU) has been used in many applications such as transportation, furniture, automotive, and textile industries because of its excellent coating properties [1–4]. Recently, the PU coating market increases [5], which attracts more intention from scientists. Even though PU coatings are relatively durable, prolonged exposure to ultraviolet (UV) irradiations, high temperature, humidity, oxygen, and some pollutants lead to coating degradation [6, 7]. As a result, the lifetime of the coating reduces significantly. Therefore, the demands for exploring methods to improve the PU coating’s performance are urgent. Regarding this, polymer composites, in comparison to polymers alone, have more superior properties. There are two methods of preparing the polymer composite. The first method is based on π–conjugated systems with band gaps capable of absorbing UV photons, such as ureido-pyrimidone and coumarine-based [8]. It was reported that the π–conjugated system could be easily tailored into polyurethane chains both as chain ends and/or chain extenders [9]. However, the drawback of these materials is their gradual decomposition under prolonged UV exposure [10, 11].

On the other hand, the second method uses inorganic nanoparticles as additive particles such as CeO$_2$, ZnO, TiO$_2$, Fe$_3$O$_5$, or graphene. These inorganic materials have higher chemical stability, and they are successfully applied in PU formulations with UV-resistance capacity [7, 12–18]. In those potential candidates, CeO$_2$ nanoparticles are particularly of interest because of special properties like high stability at normal temperature, high hardness, and non-toxicity. This material has a bandgap of about 3.2 eV, which is the largest UV absorption
spectrum [12, 19, 20]. For example, Dao et al (2011) pointed out that, with a relatively small amount of CeO₂ nanoparticle, the UV absorption property of the thin epoxy film was noticeably improved [15]. Unfortunately, inorganic nanomaterials systems often have the disadvantage of difficulty evenly disperse in membranes due to the strong self-agglomeration of small particles. Besides, CeO₂ particles have low calcination thermal stability. Even a small change in sintering temperature has a large change in surface area and catalytic activity of CeO₂ [21]. Therefore, efforts have been made to obtain a more stable and uniform distribution of CeO₂ by adding different oxides like TiO₂, SiO₂ [22]. Notably, SiO₂ materials offer holes in their structures which can trap the electrons induced by UV photons, converting them into heat energy. Hence, the polymer’s photo-induced degradation is suppressed [23].

Herein, this study describes a simple method to synthesize nonhierarchical CeO₂-SiO₂ nanocomposites (CS-NCs) using the gel combustion method using polyvinyl alcohol (PVA). PVA was preferred to use in this study because of its superior properties such as inexpensive, biodegradable, and non-toxic materials. Besides, PVA helps the homogeneous distribution of the metal ions and inhibits their segregation/precipitation from the solution [24, 25]. Furthermore, PVA was also selected as a complexing agent that reduces the agglomeration effect of metal ions. Then, PU/CeO₂-SiO₂ coatings were prepared as a functional coating for the automotive industry. This prepared polymer coating was exposed to 700 h of accelerated artificial weather. The bonding configuration of the coating was investigated using FTIR spectroscopy. To the best of our knowledge, the CS-NCs have not been used in any coating polymer before. This strategy offers a promising application such as coatings for automobiles and other industries such as furniture and wood.

2. Experimental section

2.1. Materials

Unless otherwise stated, all chemicals were used without further purification. All chemicals employed for the preparation of CS-NCs were poly(vinyl alcohol) (PVA, M = 145 000 g mol⁻¹, 99%, Merck), cerium(III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O, 99%, Merck), tetraethyl orthosilicate (Si(OC₂H₅)₄, 99%, Merck), 25% ammonium hydroxide solution (NH₄OH, Merck) and acetic acid (CH₃COOH, 99%, Merck). Chemicals employed for preparing polyurethane films were a diisocyanate (Desmodur® Z 4470 MPA/X), two acrylic polyls (Acrylic AC-3252 and Olester AO-529), an inorganic UV-absorber (rutile TiO₂), and other organic solvents. They were obtained in industrial qualities from commercial sources, such as BASF Vietnam, TOP Solvent Vietnam, Evonik Singapore, Covestro Hongkong, and Hunan Chemical China.

2.2. Preparation of CeO₂-SiO₂ nanocomposites

The CeO₂-SiO₂ nanoparticle was synthesized by the gel combustion method. In a typical procedure, 0.434 g of Ce(NO₃)₃·6H₂O and 0.208 g of Si(OC₂H₅)₄ (1:1 molar ratio) were added to 55.8 ml of 5.0% PVA solution. The pH level was adjusted to 4.0 by adding 1 M CH₃COOH and 25% NH₄OH solutions. The mixture was stirred at 80 °C for 4 h until a homogeneous gel was formed. The gel was dried at 105 °C for 2 h. Then the prepared material, which is calcined at 650 °C for 8 h before being calcinated at 550 °C, 650 °C, 750 °C, and 850 °C for 2 h. Then the prepared material, which is calcined at 650 °C, was used to prepare PU coatings.

2.3. Preparation of the PU coatings

100 g of the powder mixture was prepared in a typical procedure as follows. A polyol (Acrylic AC-3252, 30.0 wt%), an additive (higher fatty acid amide, 0.4 wt%), and a mixture of solvents (15.0 wt%, including xylene, Topsol A100/A150, Shellsol A100/A150, cyclohexanone, propylene glycol methyl ether acetate, butyl carbitol, and diethylene glycol butyl ether) were added to a flask (the used chemicals are summarized in table S1 (available online at stacks.iop.org/MRX/8/056405/mmedia)). The mixture was stirred at 1200 rpm to obtain homogeneity. After that, the stirring speed was lowered to 500 rpm. Zirconium silicate (200 g), rutil TiO₂ (20.0 g), and an appropriate amount of CS-NCs were added. The mixture was stirred for 4 h. The powders were passed through a sieve with a pore size of 37 μm.

A mixture of two polyls (AC-3252, 38.5 wt% and Olester AO-529, 40.5 wt%) was placed into a flask. The mixture was stirred at 1200 rpm for 20 min. Then, an additive (2-dimethylamino ethyl methacrylate, 0.035 wt%) and a catalyst (dibutyltin dilaurate, 0.010 wt%) were added. After that, 16.5 wt% of solvent mixture (Solvesso, propylene glycol methyl ether acetate, and bisphenol A diglycidyl ether) and 4.46 wt% of the powder mixture prepared from the previous step were added. Next, isocyanate (Desmodur® Z 4470 MPA/X, 20.0 g) and a mix of solvents (xylene, Topsol A150, Shellsol A150, butyl acetate) were added, followed by stirring until a homogenous mixture with a viscosity of 12.5 m²/s was obtained. The mixture was sprayed onto ABS panels using an automotive paint gun, aged 15 min before dried at 80 °C for 30 min furnishing the corresponding films with thicknesses of 24.5 ± 0.9 μm (table S4).
2.4. Analytical and test methods

X-ray diffraction (XRD) analysis was performed on a Bruker D8 Advance equipment applying Cu (Kα) as the radiation source. The morphology of nanocomposites was characterized using Scanning Electron Microscopy (SEM) on a Hitachi S-4800 microscope (Japan). Energy dispersive x-ray (EDX) mapping analysis was conducted employing a 2100 HSX JEOL (Japan). UV/Vis-DR spectroscopy was undertaken on a Cary UV-5000 spectrophotometer. Fourier transform infrared spectroscopy (FTIR) was carried out employing a Bruker Equinox 55 spectrometer (Germany). The color deviation was measured on a Chroma Meter CR-400 Konica Minolta INC (Japan). The QUV accelerated weathering test was carried out according to ASTM D4587 standard.

3. Results and discussions

3.1. Characterization of prepared CeO$_2$-SiO$_2$ nanocomposites

3.1.1. XRD analysis

The crystal structures of CeO$_2$-SiO$_2$ nanocomposites were characterized by XRD analysis (figure 1). XRD pattern of an annealed sample at 550 °C reveals a slightly broad peak at 2θ ~22.0° infers initial evolution of crystalline phase of SiO$_2$ cristobalite. As the calcination temperature increases, the peaks become sharp and intensify, which introduces the modification of amorphous to complete crystalline phase \[22\]. In general, the higher the calcination temperature, the higher crystallinity because when crystallites gain enough energy, they can orient themselves to possess the highest atomic packing density and inevitably minimize surface energy \[26\].

In this study, energy further provided when the calcination temperature ignites the gel’s components and begins the thermal decomposition of PVA, nitrate, and ethyl. According to our previous studies and other authors, PVA is starting to decompose at a temperature of about 130 to 450 °C \[27–30\]. However, to remove the carbon residual completely, the annealing temperature needs to reach around 600 °C \[27, 31\]. This study result shows that the best crystallization performance obtains at 650 °C (figure 1). If we keep increasing the temperature, the crystal structure will be decomposed to form different phases. As can be seen, typical peaks assigned to the cristobalite phase of SiO$_2$ were observed at 21.9, 28.4, and 36.1° (JCPDS no. 01-077-8627), which are at planes (101), (102), and (200), respectively \[32, 33\]. However, at the temperature higher than 750 °C, the peak at 21.9° decrease the intensity along with the appearance of two small peaks at 2θ ~20.8° and 23.3° (figure S1). This indicates the transformation of the SiO$_2$ cristobalite phase to the SiO$_2$ tridymite phase \[33\]. Similar observations were also reported in some literature \[21, 22\].

In addition to SiO$_2$, XRD results reveal peaks assigned to the cerianite phase of CeO$_2$. The peaks responsible for the CeO$_2$ cerianite phase were observed at 28.7, 33.2, 47.4, and 56.1° or planes (111), (200), (220), and (311), respectively \[34, 35\]. These peaks are ascribed to the face-centered cubic (fcc) crystal structure of cerianite with the Fm-3m space group (JCPDS no. 00-054-0593) \[36\]. The absence of any other noticeable trace peaks for the
under the action of weathering pressures bonding force between PU is feeble, micro-cracks start to occur at the interface junction and continue to extend much smoother structure with little evidence of microscopic cracks at any content of nanocomposites. Since the happens because the CS-NCs have a high surface polarity, making it easy to form aggregation in the PU. strong interfacial interaction between CS-NCs and PU could enhance the tensile strength. The interaction results in cracking or delamination of the coating.

3.1.2. FTIR analysis, SEM image, and EDX mapping of CeO$_2$-SiO$_2$ nanocomposites

The bonding configuration of the CS-NCs prepared at 650 °C (i.e., CS650) was investigated using FTIR spectroscopy (figure 2(a)). CS650 was selected because the best crystallization performance is obtained at the calcination temperature of 650 °C. At this calcination temperature, there is no residual of carbon, and the CeO$_2$, SiO$_2$ crystalline phases were clearly observed without as in figure 1. The FTIR spectrum shows a peak at approximately 1071 cm$^{-1}$ and a shoulder at about 1200 cm$^{-1}$, corresponding to Si–O–Si asymmetric stretching vibration [37, 38]. Almeida and Pantano stated that the peak and the shoulder originate from this vibration’s transverse and longitudinal optical components, respectively [39]. The FTIR result also exhibits a band at about 790 cm$^{-1}$, assigned to Si–O–Si stretching vibration [37, 40]. Previous literature often reported bands between 3500–3200 cm$^{-1}$ and 1600–1500 cm$^{-1}$ attributed to stretching and bending vibrations of adsorbed water molecules, respectively [41, 42]. However, these bands were not observed in this study, suggesting the complete removal of water molecules adsorbed on the surfaces of nanocomposites. According to Ho et al the Ce–O stretching bands are expected to be 400 to 450 cm$^{-1}$ and not distinguishable from silica stretching modes [43]. However, figure 2(a) indicates that the band of Si–O–Si asymmetric stretching vibration in CeO$_2$–SiO$_2$ at 1071 cm$^{-1}$ shifted. This probably causes by the influence of CeO$_2$ on the SiO$_2$ structure or due to the attachment of electropositive cerium ions to highly electronegative oxygen of silica nanoparticles [44, 45].

The morphology of the CS-NCs was analyzed by scanning electron microscopy. Figure 2(b) shows the SEM image of the nanocomposites calcined at 650 °C, which are monodisperse and highly porous. These prepared materials were used to disperse into the PU matrix.

According to the EDS layered images and compositional analysis, Ce, Si, and O atoms were found homogeneously dispersed in the nanocomposites (figure 3).

3.2. Impact of CeO$_2$–SiO$_2$ nanocomposites on the properties of PU coating’s surface

The polyurethane formulation in this study is typical for protective applications in the automotive industry. The prepared coatings were named according to their loading levels 0%, 0.1%, 0.25%, 0.5%, 0.75%, 1.0%, 1.5% and 2.0% (i.e., PU0, PU0.1, PU0.25, PU0.5, PU0.75, PU1.0, PU1.5 and PU2.0, respectively).

Figure 4(a) shows SEM images of pure PU coating whereas figures 4(b)–(e) corresponding to composites with 0.25, 0.5, 1.0, and 2.0 wt% contents of CS-NCs, respectively. As can be seen, the nanocomposites (white dots) well dispersed in the PU matrix. By using a similar coating preparation method (figure S2), the other nanomaterials are also reported to be successfully dispersed into polymer matrix [13, 17, 46, 47]. One may notice from figure 4, the presence of CS-NCs reduces fractures of the PU hybrid coatings. The coatings exhibited a much smoother structure with little evidence of microscopic cracks at any content of nanocomposites. Since the bonding force between PU is feeble, micro-cracks start to occur at the interface junction and continue to extend under the action of weathering pressures (i.e., oxygen, UV, temperature, water) [48]. The propagation of cracks results in cracking or delamination of the coating (figure 4(a)). When the coat has the presence of CS-NCs, the strong interfacial interaction between CS-NCs and PU could enhance the tensile strength. The interaction happens because the CS-NCs have a high surface polarity, making it easy to form aggregation in the PU.

![Figure 2](image-url)
However, adding too many CS-NCs would cause it to agglomerate heavily in the PU, which leads to a decrease in tensile strength [49]. Chang et al described that the high content of inorganic embedded nanoparticles might increase the brittle failure of polymer structure [50]. However, this study results suggest that, with the content of

![Figure 3. EDS layered images and compositional analysis of CeO$_2$-SiO$_2$ nanocomposites.](image)

| Element | % wt. Experimental | % wt. Theoretical |
|---------|--------------------|-----------------|
| Ce      | 59.66              | 60.34           |
| Si      | 12.37              | 12.07           |
| O       | 26.22              | 27.59           |

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CS-NCs up to 2.0 wt%, the mechanical properties of the coating remain properly. Besides, the satisfactory level of dispersion of the nanocomposites enhances the uniformity at lower contents of the CS-NCs. At higher content of the nanocomposites (> 1.0 wt%), random occurrence of large particles on the surface of PU coatings (white dots in figures 4(d), (e)) causes by the strong self-agglomeration of small particles.

3.3. Impact of CeO$_2$-SiO$_2$ nanocomposites on the UV–vis absorbance of polyurethane films

Figure 5 showed the UV–vis absorption spectra of the CS-NCs embedded in the PU matrix from 280 nm to 500 nm. Pure PU coating (i.e., PU0) and PU hybrid coatings (i.e., PU0.1, PU0.25, PU0.5, PU0.75, PU1.0, PU1.5, and PU2.0) exhibited similar absorption in the selected region. The absorption peak is at about 344 nm, and the shoulder at about 400 nm. This absorption band belongs to UV$_A$ radiation [51]. At relatively low content of CS-NCs, the absorption band shifted to UV$_A$ range may cause by the characteristic of CeO$_2$ particles [51]. The
UV absorption capacity is enhanced gradually by increasing the CS-NCs content from 0.1 wt% to 1 wt% except for PU1.0 and PU1.5. As we discussed in section 3.2, the higher content of materials may cause nanomaterial agglomeration. At the content of CS-NCs larger than 1 wt%, some large particles can be observed (figures 4(c), (d)). The presence of large particles may affect the absorption capacity of the coating. As a result, absorption capacity may not linearly increase as the content of CS-NCs. Introducing CS-NCs into the PU coating may anticipate having a wide application as outdoor coatings.

3.4. Impact of CeO$_2$–SiO$_2$ nanocomposites on the UV-resistance properties of the films

The coating PU1.0 was chosen for the functional group investigation by FTIR spectroscopy. Figure 6 shows the FTIR spectra of the coating during 700h of UV exposure testing. The modification of bands of PU clear coat can be seen in this figure. In the figure, the spectra were obtained by measuring the spectra of the coatings at different times. Accordingly, 0h represents the PU1.0 coating before the UV exposure test, and 100h, 300h, 400h, 500h, 600h, and 700h indicates the exposure time of the PU1.0 coating under UV irradiation.

In these spectra, bands related to the nanocomposites were not observable, as more intensive peaks overlapped them. It is seen that a weak band exists in the range of 2250–2300 cm$^{-1}$, which is indicative residual isocyanate group (-NCO) of polyisocyanate (hardener) in cured clear coat at the beginning (0h) [52, 53]. It indicates that the presence of nanoparticles delayed the curing process or indicating that the reaction is not complete. Overall, the monitoring of FTIR spectra changes indicate different trends in the decomposition of the blank and nanocomposites-embedded polyurethane films’ structure. As shown in the figure, bands are assigned to different functional moieties C=O vibration modes around the 1700 cm$^{-1}$ region. Generally, the greater the order of the C=O bond, the higher the wavelength of the band. Thus, the vibrational bands at 1685, 1681, and 1676 cm$^{-1}$ correspond to the NH–(C=O)–NH of polyurea, while the vibrational modes at 1724 and 1719 cm$^{-1}$ provide a strong indication of polyurethane C=O stretching. This was described in previous studies such that the bands in the range 1635–1703 cm$^{-1}$ are assigned to the ordered C=O structures, while those in the range 1703–1735 cm$^{-1}$ are classified as the less-ordered C=O structures [54, 55]. Under prolong UV irradiation, the coating appears to undergo some molecular changes as indicated by the increase of the 1724 and 1719 cm$^{-1}$ bands together with the increase of both 1685, 1681, and 1676 cm$^{-1}$ stretching modes. This can be explained by the chain scission of the PU coating led to the re-association of polyurea molecular segments [6]. The other possibility can happen at the coating’s surface, and some species are oxidized, leading to the formation of carbonyl groups, particularly the formation of polyurea [56].

The FT-IR spectrum presents a characteristic band between 3100–3500 cm$^{-1}$ which is assigned to stretching vibrations of H-bonded –NH groups [10, 57, 58]. This band’s intensity decreasing with increasing UV irradiation illustrates the loss of urethane structure [10]. Interestingly, this study results show that there was a slight change in that band (figure S3). The N–H stretching at 3370 cm$^{-1}$ becomes broader, indicating overlapping different

![Figure 6. FTIR spectra of the coating PU1.0 during 700h of the UV exposure testing.](image-url)
Another interesting feature is the appearance of a band at 2862 cm$^{-1}$, attributed to C–H$_2$ stretching. This band seems to increase after 700h of exposure. Besides, the aliphatic chains were observed at 2862 cm$^{-1}$ (−CH$_2$−H stretching) and 1454 cm$^{-1}$ (−C−H bending). The bands at 1238, 1137, 1064, 962, and 764 cm$^{-1}$ (i.e., found the fingerprint region of the polymer [57]) related to the C−O bonds also slightly increased (figure S3). The explanation for these changes starts from the adsorption of air oxygen molecules on the PU coating surface [59, 60]. Then, the formation of corresponding organic radicals (R-NH·, R-CH$_2$-CH$_2$·, R-CH-OO·) results in the cleavage of the C-N and C-O bonds. This process releases gases, which are majorly comprised of CO$_2$ and CO with a minority of H$_2$, CH$_2$O, and HCN. Furthermore, hydrophilic groups, such as aldehydes, carbamates, carboxylic acids, amino esters, and peresters, are formed [6]. Gradually, it results in the formation of damages on the polyurethane surface, including voids, cracks, and blisters. Overall, it leads to changes in material properties, such as increased surface roughness and loss of gloss, tensile strength, and color.

General decomposition pathways of polyurethane films damaged by UV lights are illustrated in figure 7 [60]. The presence of nanoparticles in the polymer matrix can prevent the degradation of polymer structures by several mechanisms to a certain degree. One can be the absorption, reflection, and scatter the UV light of the nanoparticles. These activities reduce the amount of UV light that initiates the degradation of the polymer matrix. Furthermore, nanoparticles can mobile or trapped electrons in the conduction band combine with fast charge recombination of positive holes, and electrons in the conduction band will quench the charge-separated state and decay the destructive energy of UV radiation [61]. Nanoparticles can further expand the range of applications where the particles below 20 nm in diameter. This size is unable to scatter light in the visible spectrum but retaining its UV-shielding properties. Thus, these materials would allow for optically clear composites that still offer effective UV irradiation protection [14, 62]. The dispersion of nanoparticles into the...
PU coating matrix can initiate the reorganization of the coating. It can result in further changes in different material properties, such as mechanical strengthen, gloss, color, surface roughness, and wettability.

Figure 8 shows the color differences and gloss of the PU coatings embedded with different concentrations of CS-NCs. The color differences in prepared PU coatings under prolonged UV exposure are demonstrated in figure 8(a). Due to the self-light-yellow color of the CeO₂ particles [17], as can be clearly seen from the figure, color deviation tends to rise with increasing content of the nanocomposites (figure 8(a), table S2). However, the content of the CS-NCs only ranges from 0.1 wt% to 2.0 wt%, so that the color difference is negligible. Generally, the deviation rate of the color change for PU0 was the highest (table S2). In comparison, the deviation rates of PU0.1 to PU2.0 are lower and are comparable to each other. Under the prolonged exposure to UV irradiations, the color of the polymer deviated gradually, which was mainly caused by the slow deterioration of the residual resin matrix of the coating surface [63]. Figure 8(a) indicates that PU coatings in this study show an exceptional UV resistance against discoloration during accelerated weathering tests. As an example, Jalili and Moradian

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Figure 8. Changes in (a) color difference and (b) gloss of the PU coating embedded with different percentages of the nanocomposites during the UV exposure testing.
reported $\Delta E$ values of 2–4.8 for nano-silica embedded PU coats under 200 h of QUV weathering, while Saadat-Monfared et al reported $\Delta E$ values of 1–1.2 for nano-ceria embedded PU coats in 700 h of weathering exposure [64, 65]. This difference is a strong indicator of the efficiency of CS-NCs as a UV absorber in the PU coat.

The loss of gloss of polyurethane films is mainly attributed to the increase of surface roughness due to the formation of surface damages [66]. Again, the blank polyurethane coating $PU_0$ showed the fastest decline rate, followed by $PU_2.0$ (figure 8(b)). In comparison, $PU_0.1$ and $PU_1.5$ revealed a comparable rate of gloss loss, which was followed by $PU_0.25$ to $PU_1.0$. From 400 to 700 h, the loss of gloss for $PU_1.5$ to $PU_0.1$ increased remarkably, possibly due to the formation of damages on the surface. The gloss of nanocomposite-embedded PU hybrid coating remains at 93 GU for $PU_0$, $PU_0.1$, and $PU_0.25$ (table S3), which increases to 95 GU for $PU_0.5$ before gradually declining to 89 GU for $PU_2.0$ (figure 8(b), table S3). The loss of gloss shows a trend to keep decreasing due to the effect of UV irradiation. However, this study results indicated that the presence of CS-NCs in PU coating significantly reduces the PU surface damages with 0.25–1 wt% of nanocomposites.

The result implied that too low content or too high nanomaterial content also affects the loss of gloss. The possible explanation for this can be the UV absorption capacity of the coating. With too low content of the nanomaterials, the PU coating rapidly degrades because of the weathering pressure (i.e., UV irradiation, water, temperature). On the other hand, too high content of the nanomaterial can produce a large amount of radical, which also degrades the PU matrix. CeO$_2$ absorbed the light radiation in UV irradiation which helps electrons jump from the valance band to the conduction band resulting in the production of an electron-hole pair. Then these positive holes and electrons can attack the water, oxygen to form free radicals. When the formed free radicals are too high, the coating cannot handle making the fast degradation. The general mechanism can be presented in figure 9 as follows:

3.5. Comparison with other works

Table 1 shows some of the most recent similar studies. In general, nanomaterials are preferred to synthesize with the sol-gel combustion method using a number of different gel systems. The technique is simple, and inexpensive chemicals can be used. Using green and economical synthesis methods is trending at present. As also from table 1, single nanomaterials such as SiO$_2$, CeO$_2$ show promising effects. Therefore, the synthesis of the nonhierarchical CeO$_2$-SiO$_2$ nanocomposites in this study creates a synergistic effect. The use of CeO$_2$-SiO$_2$ nanocomposites in PU has not been reported before.

4. Conclusion

To summarize, the incorporation of CeO$_2$-SiO$_2$ nanocomposites in polyurethane films’ structure shows several beneficial impacts. The coatings embedded with the nanocomposites retained the value gloss and color during 700h of the UV exposure. The prepared hybrid PU coating shows an exceptionally low value of color difference. Besides, the presence of CeO$_2$-SiO$_2$ nanocomposites reduces the effect of UV irradiation on the roughness of the PU coating. Overall, the nanoparticle’s optimal concentration in the polyurethane film was in the range of 0.25–1.0 wt%.
| Material                        | Synthesis method                  | Content of material in the polymer coating (% wt.) | Application                                      | References |
|--------------------------------|-----------------------------------|--------------------------------------------------|-------------------------------------------------|------------|
| Lignin/ZnO Composites         | Precipitation method              | 0.2–1.2                                          | UV resistance                                   | [49]       |
| SiO$_2$ nanoparticles          | Readily usable                    | 3.5–15.17 in PU                                  | Mechanical improvement                          | [67]       |
| CeO$_2$ nanoparticles          | Auto-combustion method            | 0.1–1 in epoxy                                   | UV resistance                                   | [15]       |
| CeO$_2$ nanoparticles          | Combustion method                 | —                                                | Adsorption                                      | [51]       |
| CeO$_2$-Fe$_3$O$_4$@SiO$_2$ nanocomposites | Sol-gel combustion method   | 0.1–2 in PU                                      | Thermal stability and UV resistance             | [68]       |
| CeO$_2$ grafted carbon nanotube | Reducing and mixing method        | 1.0                                              | Enhance corrosion barrier                       | [69]       |
| Nonhierarchical CeO$_2$-SiO$_2$ nanocomposites | So-gel combustion method | 0.1–2 in PU                                      | UV resistance                                   | Present work |

- not reported.
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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflicts of interest

The authors declare no conflict of interests.

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