Titanium dioxide (TiO₂), in the crystal form of rutile with high refractive index, 2.7, is one of the most important inorganic pigments. In the recent years nano TiO₂ has attracted interest as an inorganic material for nanocomposites. It is used for the development of photocatalysts, semiconductors in solar cells and for the protection of materials from UV damage. To achieve high UV absorbing efficiency of TiO₂ nanoparticles into polymer matrix and to yield a better compatibility with polymeric materials surface treatment of TiO₂ nanoparticles with 3-glycidyloxypropyltrimethoxysilane (GLYMO) in a polyacrylic clear coating was investigated. The grafting of GLYMO on the TiO₂ nanoparticles surface was characterized with TGA and FTIR techniques. The stability of TiO₂ nanoparticles in a acrylic clear coating was evaluated by zeta potential measurement. Microstructural analysis of nanoparticles was done by SEM and the influence of surface treatment on stability of nanoparticles in dispersion and acrylic coating was analysed. Finally the UV absorption effectiveness of acrylic clear coating with treated nanoparticles of rutile TiO₂ was measured to determine the effect of improved dispersion. The performance of nanocomposite coatings was demonstrated through accelerated weathering by gloss measurement. The results showed that surface treatment of TiO₂ nanoparticles with GLYMO improves nanoparticles dispersion and preserves UV protection of the acrylic clear coating.

Keywords: titanium dioxide, nanoparticles, polyacrylic clear coating, surface treatment, GLYMO, UV protection

1 INTRODUCTION

Architectural coatings are usually used to enhance the durability of wood in exterior environment. Inorganic UV absorbers are often used in coatings formulations, since they increase polymer stability. TiO₂ possesses a lot of attracting advantages, like thermal stability and long-term life time, compared to traditional organic UV absorbers.

There are two limitations of using TiO₂ as UV absorber. First, TiO₂ particularly in anatase crystal form and less in rutile form exhibits strong photocatalytic behavior when absorbing UV-rays, which is harmful for the photosstability of polymer materials. As a result, TiO₂ nanoparticles as catalyst can create , which can produce highly reactive free radicals and exert strong oxidizing power.

Second, for producing suitable nanocomposites, it is necessary to disperse the nano-particles without agglomeration in organic binders. Due to their extremely large surface-area/particle-size ratio, nano-particles have high tendency of agglomeration. Many efforts have been taken in order to overcome the problem of agglomeration. Polymeric dispersants containing different functional groups are usually used in order to prevent the high tendency of nanoparticles to form aggregates in the wet state of coating and in the dry paint film. Polyacrylic acid, polyacrylamide and their copolymers are widely used to disperse inorganic particles in the wet state of coating and in the dry paint film.
SiO₂ shells onto TiO₂ particles by seeded sol–gel process of tetraethyl silicate (TEOS) in ethanol. The use of different coupling agents such as trialkoxysilanes for surface modification of nanoparticles is recommended. For example, Ukaji et. al. coated thin aminoethylamino-propyltrimethoxysilane layers onto TiO₂ particles in ethanol by adding silane during ball-milling dispersing procedure. Shafi et. al. coated octadecyltrihydrosilane layers on TiO₂ surfaces in heptane by ultrasonic irradiation. M. Sabzi et. al. showed that surface treatment of TiO₂ with aminopropyl trimethoxysilane improves nanoparticles dispersion and UV protection of the urethane clear coating.

The purpose of this study was to investigate the influence of TiO₂ nanoparticles surface modification by different wt. % of 3-glycidyloxypropyltrimethoxysilane on transparency and UV absorbing efficiency of polyacrylic coating.

2 EXPERIMENTAL WORK

2.1 Synthesis of TiO₂ nano crystalline particles in rutile crystal structure and preparation of a dispersion

TiO₂ nanoparticles with rutile crystal structure were prepared by co-precipitation method which is described elsewhere. Deagglomerated rutile nanoparticles were prepared as dispersion in water and propilenglycol in high-energy horizontal attrition mill.

2.2 Surface modification of TiO₂ nanoparticles in dispersion with silane coupling agent

As silane coupling agent we used 3-glycidyloxypropyltrimethoxysilane (GLYMO) with chemical formula which is a bifunctional organosilane, possessing reactive organic epoxide and hydrolyzable inorganic methoxysilyl groups. It bounds chemically to both inorganic material and organic polymers. According to the producer in the presence of water the methoxy groups hydrolyze to form reactive silanol groups which bound to inorganic substance.

We prepared dispersions of TiO₂ nanoparticles grafted with GLYMO according to the following procedure. First, TiO₂ nanopowder in dispersion with wetting and defoaming agent was milled for 1.5 hour at 25 °C with organic surface active agent with zirconia balls 1 mm diameter. Than silane coupling agent of different concentrations was added as shown in Table 1 and the dispersion was milled additionally for 1 hour at the same conditions.

2.3 Preparation of clearcoat with integrated rutile crystalline nanoparticles of TiO₂

We prepared clearcoat in the laboratory as described elsewhere. Water based dispersions of TiO₂ nanoparticles were than added to clearcoat of 0.6 wt. %, stirred at approximately 1000 rpm for 20 minutes and prepared for the testing.

2.4 Characterization of the samples

Surface morphology of coated sample was studied by scanning electron microscopy (SEM, ZEISS Gemini Supra 35 VP), with a maximum resolution up to 5 nm. Nanoparticles were dried on brass holders by adhesive carbon band with thin layer of gold. The samples were placed in the vacuum chamber of the instrument and then were examined at various magnifications. Grafting of GLYMO on TiO₂ nanoparticles was analysed by FT-IR. The infrared spectra of original and modified TiO₂ were conducted using a FT-IR spectrometer (PERKIN ELMER Spectrum 100) and thermogravimetrical analysis by TGA/DSC 1, METTLER TOLEDO.

Zeta potential was obtained to investigate the surface character of original TiO₂ and TiO₂ modified with GLYMO. The electro-phoretic mobility data, measured also by Zetasizer Nano series HT by of the dispersions were transformed into ζ-potential according to (eq. 1):

\[ \zeta = -\frac{4\pi\eta\mu}{\varepsilon} \]

where ε is a dielectric constant of the dispersing medium and η the solvent viscosity. pH was measured by pH meter (Mettler Toledo).

UV–VIS transmittance of modified samples was measured for estimating UV-shielding ability and transparency. 0.6 wt. % of surface treated TiO₂ nanoparticles was integrated into acrylic clear coating and 200 μm films were prepared. The different free film systems (coating-UV absorber) were analysed by UV–VIS spectrophotometer Varian Cary 100. The film transmittance was measured in the wavelength range 280 to 720 nm.

At the end, wood blocks measuring 15 × 7 cm² (longitudinal × tangential) × 0.5 cm width were cut from air dried boards from the specie pine. Two layers of clear coat of thickness of 200 μm were applied on pine blocks. Coated wood plates were used to assess weathering exposure degradation (QUV accelerated weathering tester, Q – PANEL LAB PRODUCTS). Simulation of exterior use was done by six weeks weathering by an
optimised cycle defined: 4h at (60 ± 3) °C and 4h water shower at (50 ± 3) °C. Only light of the solar type was activated on the QUV with sources type UVA-340 nm\(^2\). Gloss at 60° was measured by Micro-TRI-gloss (Byk Gardner).

3 RESULTS AND DISCUSSION
3.1 SEM characterization

The size of the nanoparticles, grafted with GLYMO was analysed by scanning electron microscope (SEM). SEM images at two different magnifications of sample C are shown on Figure 1. Agglomeration tendency of TiO\(_2\) nanoparticles in the dispersion cannot be determined because of the preparation of the sample, however we assume, that some agglomerates are probably present as seen on SEM image. Individual particles can be identified, which appears to be polydisperse in size but below 100 nm.

3.2 TGA analysis

To estimate the amount of GLYMO grafted on nanoparticles, the various percentage of GLYMO – grafted nano-TiO\(_2\) particles were analyzed by TGA technique. Figure 2 shows the TGA curves of untreated TiO\(_2\) nanoparticle, GLYMO alone and treated TiO\(_2\) nanoparticles with different percentages of GLYMO. For untreated nanoparticles (sample A), the weight loss from 120 till 600 °C is almost negligible and is probably due to desorption of physisorbed water\(^27\). For GLYMO alone the weight loss begins at 120 °C and ends at 200 °C. As can be seen for sample B, C and D, the various weight percentages of GLYMO grafted nanoparticles show sharp weight loss, beginning near 220 °C, continues till 620 °C, which is a consequence of oxidative thermal decomposition of grafted GLYMO as quantitatively shown in Table 2. The largest amount of grafted GLYMO was in the case of sample C.

![Figure 1: SEM image of sample C with inserted image at higher magnification](image1.png)

**Figure 1:** SEM image of sample C with inserted image at higher magnification

**Slika 1:** SEM posnetek vzorca C z vstavljenim posnetkom pri višji povečavi

![Figure 2: TGA curves of untreated TiO\(_2\) nano-particle (sample A) and treated TiO\(_2\) nano-particle (sample B–D). The composition of all samples is described in Table 1.](image2.png)

**Figure 2:** TGA curves of untreated TiO\(_2\) nano-particle (sample A) and treated TiO\(_2\) nano-particle (sample B–D). The composition of all samples is described in Table 1.

**Slika 2:** TGA krivulje površinsko neobdelanih (vzorec A) ter površinsko obdelanih (vzorec B–D) nanodelcev TiO\(_2\). Sestava vseh vzorcev je podana v Tabeli 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>GLYMO:TiO(_2) (%)</th>
<th>Weight loss caused by grafting of GLYMO</th>
<th>The amount grafted/added GLYMO (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>B</td>
<td>0,1</td>
<td>1,00</td>
<td>67</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>11,40</td>
<td>76</td>
</tr>
<tr>
<td>D</td>
<td>2</td>
<td>20,20</td>
<td>67</td>
</tr>
<tr>
<td>GLYMO</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

**Table 2:** TGA-based weight losses caused by grafting of GLYMO and the amount grafted/added GLYMO of various GLYMO – grafted nanoparticles TiO\(_2\). The composition of all samples is described in Table 1.

![Table 2: Izguba mase vzorcev nanodelcev TiO\(_2\) ter razmerje vezani/dodani GLYMO površinsko obdelanih in neobdelanih z GLYMO glede na TGA analizo. Sestava vseh vzorcev je podana v Tabeli 1.](image3.png)

**Table 2:** Izguba mase vzorcev nanodelcev TiO\(_2\) ter razmerje vezani/dodani GLYMO površinsko obdelanih in neobdelanih z GLYMO glede na TGA analizo. Sestava vseh vzorcev je podana v Tabeli 1.

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<th>Sample</th>
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<th>Weight loss caused by grafting of GLYMO</th>
<th>The amount grafted/added GLYMO (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>B</td>
<td>0,1</td>
<td>1,00</td>
<td>67</td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>11,40</td>
<td>76</td>
</tr>
<tr>
<td>D</td>
<td>2</td>
<td>20,20</td>
<td>67</td>
</tr>
<tr>
<td>GLYMO</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
</tbody>
</table>

3.3 FTIR spectroscopy

The hydroxyl groups on the surface of the TiO\(_2\) nanoparticles (TiOH) are reactive sites for the reaction with alkoxy groups of silane compounds, however corresponding bands are not present in spectrum of unmodified TiO\(_2\), since it was dried at 130 °C for 24h. The efficiency of silane grafting on TiO\(_2\) nano-particles was determined by Fourier transform infrared spectroscopy (FTIR). Figure 3 shows normalised FTIR spectra of unmodified TiO\(_2\) nanoparticles (sample A), grafted TiO\(_2\) nanoparticles with GLYMO (sample B – D), GLYMO alone and GLYMO with addition of water. In the spectra of all TiO\(_2\) nano-particles the broad band between 400 and 800 cm\(^{-1}\) correspond to Ti–O–Ti network. GLYMO posseses two functional groups: epoxi and metoxysilyl, which both hydrolize and condensate. Epoxy band in FTIR spectra is preserved, while the intensity of Si-O-Me band is decreased. Also two bands of hydroxyl groups appear at ~3300 and ~1640 cm\(^{-1}\), because of hydrolysis of Si-O-Me groups. In spectra of
GLYMO with addition of water peak at 1050 cm\(^{-1}\) appears, which we can assign to formation of Si-O-Si groups. Compared with the spectrum of non-modified TiO\(_2\), FTIR spectrum of GLYMO modified sample exhibits some new characteristic absorption peaks. Peak at \(\sim\)1200 and 1093 cm\(^{-1}\) which belongs to Si-O-Me groups\(^{28,29}\), was observed in the spectra of samples C and D, however not in the spectrum of sample B, which indicates that only in the case of sample B complete hydrolysis and condensation of GLYMO takes place. In contrast to GLYMO spectrum, we cannot observe in GLYMO modified TiO\(_2\) spectra peak at 914 and 1254 cm\(^{-1}\) which corresponds to epoxi group\(^{30–34}\). We presume that the epoxi group reacts with -OH groups which were formed by the hydrolysis of metoxysilyl groups. The broad bend at \(\sim\)1050 cm\(^{-1}\) represent the Si-O-Si bond is observed which indicates the formation of Si-matrix\(^{35}\). The small peak in spectra of samples B – D at around 930 cm\(^{-1}\) reconfirms condensation reaction between methoxysilyl groups of GLYMO and the TiO\(_2\) surface hydroxyl groups\(^{36,37}\).

To sum up, Si-O-Me groups of GLYMO have reacted completely only in the case of sample B, in samples C and D are still present. Epoxi groups of GLYMO have reacted completely in all GLYMO modified TiO\(_2\) nanoparticles samples. The results of FTIR analysis confirm that Si-O-Si network has been formed probably around the TiO\(_2\) nanoparticles and in small amount Si-atoms of GLYMO are bound to TiO\(_2\) surface. Similarly, F. Bauer and coauthors reported about a polymerization-active siloxane shell formed around the nanoparticles Al\(_2\)O\(_3\), when surface treated by GLYMO\(^{37}\). The reaction of GLYMO with TiO\(_2\) nanoparticles leads to different kind of stabilization of nanoparticles in the dispersion as suggested by the producers of GLYMO, since they claim that in the presence of water the methoxysilyl groups hydrolyze to form reactive silanol groups which bound to inorganic substance\(^{24}\).

3.4 pH and \(\zeta\)-potential measurement

pH and \(\zeta\)-potential measurement were used to quantify the conditions leading to the stability of TiO\(_2\) dispersions. Relevant values of the pH – measurements and \(\zeta\)-potential of unmodified and modified TiO\(_2\) with GLYMO are collected in Table 3 and in Figure 4. The pH variation from 4.6 to 5.9 upon adsorption of GLYMO was detected. An increase of the pH from 5.6 up to 5.94 when increasing GLYMO/TiO\(_2\) from 0 to 1 (sample A, B and C) was accompanied with an increase of \(\zeta\)-potential from \(\sim\)33 to around \(\sim\)39 mV, with subsequent increase in colloid stability. We assume that TiO\(_2\) surface is probably mostly covered with modifier in monolayer. As ratio GLYMO/TiO\(_2\) increases to 2, the pH decreases to 5.43, resulting in decrease in zeta potential to -35.5 mV. We predict that the reason for decrease in pH and \(\zeta\)-potential is the excess amount of GLYMO or formation of multilayer on TiO\(_2\) surface as observed by E. Ukaji et. al.\(^8\). It is supposed that thicker layer could be formed due to subsequent growth of layer to dimers, oligomers, and polymers.

Table 3: pH values for TiO\(_2\) dispersions, in the presence of different amounts of GLYMO (sample A–D). The composition of all samples is described in Table 1.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5.60</td>
</tr>
<tr>
<td>B</td>
<td>5.78</td>
</tr>
<tr>
<td>C</td>
<td>5.94</td>
</tr>
<tr>
<td>D</td>
<td>5.43</td>
</tr>
</tbody>
</table>

3.5 Ageing behaviour

Artificial weathering results in surface degradation of the coatings, which affect the appearance of the coating.
Figure 5: Gloss measurement vs. irradiation time in a QUV apparatus for the exterior use clearcoatings with different UV absorbers, samples A–D, with their composition described in Table 1.

Slika 5: Meritve sijaja v odvisnosti od časa izpostave v UV komori za premaz za zunanj uporabo z različnimi UV absorberji, vzorci A–D, njihova sestava je podana v Tabeli 1.

is the information on photostabilisation performances of UV absorbers. M. Beyer and C. Jobos investigated the use of nano-scale light absorbers in water based glaze for outdoor applications. They showed that TiO₂ proved to be effective additives in concentration 0,25 – 4 wt. % TiO₂.

For outdoor weathering simulation of clearcoating gloss measurement during the exposure in QUV chambre for six weeks are displayed in Figure 5. Figure 5 shows gloss 60° vs. time of exposure in QUV chambre for clearcoating with modified TiO₂ nanoparticles of different wt. ratios of GLYMO/TiO₂. The results illustrated that addition of GLYMO decreases the gloss 60°. During accelerated weathering the gloss changes are strongly correlated with the degradation level of the surface coating. In some composite materials the polymer around the filler particles will degrade due to the particle catalytic effect. The accelerated weathering with water spray induced the washing out of degradation products on the coatings surface and consequently a fresh surface was further exposed. During the accelerated weathering a pronounced loss of gloss was observed for coatings formulated with nanoparticle UV absorber. We can conclude that the surface treatment of TiO₂ nanoparticles with GLYMO reduces the gloss 60° of acrylic coating before exposure to accelerated weathering. The gloss change after six week exposure to accelerated weathering is the smallest in the case of sample C, which shows that the UV efficiency was improved the most, when ratio GLYMO/TiO₂ was 1.

4 CONCLUSIONS

Surface modification and characterization of TiO₂ nanoparticle with GLYMO at different wt. percentages as an additive in a polyacrylic clear coating were investigated. TGA and FTIR analysis show that grafting of GLYMO on the nano-particles has occurred successfully. According to ζ-potential measurements the most stable TiO₂ nanoparticle dispersions are with ratio GLYMO:TiO₂ 0,1 and 1. At the end, artificial weathering results confirm that surface treatment of TiO₂ nanoparticles with GLYMO with ratio GLYMO:TiO₂ = 1 improves nanoparticles dispersion and consequently its transparency the most and improves UV protection of acrylic clear coating.

Acknowledgement

The authors acknowledge the financial support from the Ministry of Higher Education, Science and Technology of the Republic of Slovenia through the contract No. 3211-10-000057 (Center of Excellence Polymer Materials and Technologies).

5 REFERENCES

14 S. Farrokhpay, A review of polymeric dispersant stabilisation of titania pigment, Advances in Colloid and Interface Science, 151 (2009), 24–32
16 A. M. El-Toni, S. Yin, T. Sato, Control of silica shell thickness and microporosity of titania–silica core–shell type nanoparticles to depress the photocatalytic activity of titania, J. Colloid Interface Sci. 300 (2006), 123–130
22 M. Sabzi, S.M. Mirabedini, J. Zohuriaan-Mehr, M. Atai, Surface modification of TiO₂ nano-particles with silica coupling agent and investigation of its effect on the properties of polyurethane composite coating, Progress in Organic Coatings 65 (2009), 222–228
23 J. Godnjavec, B. Znoj, P. Venturini, A. Žnidarič, The application of rutile nano-crystalline titanium dioxide as UV absorber. Inf. MIDEM, 40 (2010) 1, 6–9
26 SIST EN ISO 11507:2002
34 http://www.thefreelibrary.com/Insitu+monitoring+of+the+curing+of+epoxy+resins+by+DSC,+FTIR+and...-a0216041185
41 M. V. Cristea, B. Riedla, P. Blancheta, Enhancing the performance of exterior waterborne coatings for wood by inorganic nanosized UV absorbers, Progress in Organic Coatings, 69 (2010), 432–441