Mechanical and thermal properties improvement of unsaturated polyester resin by incorporation of TiO$_2$ nanoparticle surface modified with titanate

Chaohua Jiang $^1$, Chen Jin $^1$, Min Wei $^1$, Sheng Yan $^2$ and Da Chen $^1$

$^1$ Jiangsu Key Laboratory of Coast Ocean Resources Development and Environment Security, Hohai University, Nanjing, Jiangsu 210098, People’s Republic of China

$^2$ College of Material science and engineering, Nanjing University of Technology, Nanjing, Jiangsu 211800, People’s Republic of China

E-mail: chenda@hhu.edu.cn

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Abstract

Unsaturated polyester resin (UPR)/titanium dioxide (TiO$_2$) nanocomposites were obtained by the incorporation of TiO$_2$ nanoparticle surface modified with titanate in the UPR. The mechanical properties, thermal behavior, anti-ultraviolet aging properties and composite microstructure were tested. The results show that TiO$_2$ nanoparticles have a good compatibility with the UPR matrix. When the contents of TiO$_2$ and titanate coupling agent are 4% and 3% respectively, the impact strength, flexural strength and heat deflection temperature of the composites are 16.28 kJ m$^{-2}$, 63.23 MPa, and 70.3 °C, respectively, which increase by 890.5%, 77.5% and 23.7% compared with pure UPR. The incorporation of modified TiO$_2$ nanoparticles in the UPR enhances the anti-ultraviolet aging properties of the composites. When 4% TiO$_2$ nanoparticles are added to the UPR, the impact strength retention rate improves by 29.8% compared with pure UPR at 60 days. Strengthening and toughening effects with the incorporation of TiO$_2$ can be achieved by forming a flexible interface layer between the TiO$_2$ and UPR matrix because of the higher rigidity, excellent bonding and compatibility of the TiO$_2$.

1. Introduction

Unsaturated polyester resin (UPR) is one of the most commonly used thermosetting resins available globally. UPR can become an insoluble and infusible thermosetting material after solidification, but it shows poor mechanical properties. Furthermore, as a thermosetting material, UPR is extremely brittle, which restricts its application in products that require high impact and fracture strength. Many researchers have attempted to overcome this problem by using a thermoplastic elastomer, inorganic filler and nanoparticles [1–3]. In recent years, nanoparticles are being used as an advanced filler to improve the mechanical properties of the UPR. Nanoparticles have advantages, such as a large specific surface area, a high unsaturation and a prominent nanoscale effect. The incorporation of inorganic nanoparticles in resin improves the stiffness, hardness, creep behavior, and heat stability of the matrix simultaneously, with a large reduction in output cost. Different types of nanoparticles, such as CaCO$_3$ [4, 5], SiO$_2$ [6, 7], Al$_2$O$_3$ [8, 9], ZnO [10, 11], Cu/Cu$_2$O [12, 13], and TiO$_2$ [14, 15] are used to improve the UPR performance. The nanoparticles can fill the cavities in the resin and decrease the total free volume, which lead to a significant toughening and improvement in mechanical properties, heat resistance and combustion performance for the UPR composites.

Among different nanoparticles used to improve properties of UPR, TiO$_2$ is probably the most interesting and the most investigated metal-oxide. Preparation of TiO$_2$ in anatase and rutile forms is inexpensive and quite efficient. Furthermore, TiO$_2$ nanoparticles have unique properties, such as non-toxicity, good chemical and electrical properties, good compatibility with various materials, high photocatalytic activity, high refractive index, and the ability to absorb ultraviolet (UV) light [14]. It also has a good dispersivity and weatherability,
which may allow for an improvement in the mechanical properties and ageing resistance performance of UPR. Xiao et al. [15] produced the UPR/TiO2 composite by incorporation of 27 nm TiO2 particles. The results showed that when the TiO2 content was 4%, the tensile strength and modulus of elasticity of the composites increased by 47% and 22%, respectively, compared with pure UPR. Evora et al. [16] added 36 nm TiO2 into UPR to obtain UPR/TiO2 composites by an ultrasonic effect. They found that the nanoparticles were well dispersed in the resin and the addition of TiO2 could improve the fracture toughness of the composite. When the content of TiO2 was 1%, 2% and 3%, the fracture toughness of the composite increased by 57%, 42% and 41%, respectively, compared with the plain sample. However, the fracture toughness decreased slightly when the TiO2 content exceeded 3%, possibly because of particle agglomeration. Goodarzi et al. [17] formed a polyacrylate layer on the surface of the TiO2 through a copolymerization reaction, and then added the modified TiO2 into UPR to obtain UPR/TiO2 composites. When the TiO2 content was 0.5%, 1% and 1.5%, the composite impact strength increased by 19.5%, 28.1% and 53.7% respectively, compared with the pure resin because of a better interfacial bonding force between the modified TiO2 particles and the resin matrix.

Weather resistant multi-orifice plates made from composite materials, such as UPR composite, are applied mainly to the edges of coal yards, bulk cargo yards, or desert green belts to reduce the wind force and to suppress dust flying. An excellent mechanical strength, heat resistance, ageing resistance, and simple forming process for composite materials are needed, and especially for durability against various climatic conditions, such as a dusty and plateau climate. To achieve the desired properties of a polymer nanocomposite for modern dust prevention, more studies need to be carried out. In this paper, an attempt has been made to investigate the effect of TiO2 surface modification with titanate on the mechanical properties, heat resistance and UV aging resistance of UPR composite. Furthermore, Scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy were used to analyze the strengthening and toughening mechanism of TiO2/UPR composites.

2. Materials and method

2.1. Materials
Commercially available 191 UPR (Oasis Composite Material Co., Ltd China), was used as a matrix. Its solid content was 63%–69%. The acid value of UPR was 18–24 mg g⁻¹ and its viscosity was 0.25–0.60 Pa.s at 25 °C. Titanate coupling agent NXT-102 was provided by Nanjing Xiangfei Institute, China. Commercially available 30 nm rutile TiO2 (99.5% purity, 3.9 g cm⁻³ density) was provided by Nanjing Haitai Materials Co., Ltd China. UV-P was used as a UV absorber in UV aging resistance tests.

2.2. Sample preparation
2.2.1. Surface modification of TiO2
Titanate NXT-102 was prepared as a 1% petroleum ether solution. After drying and calcining, the TiO2 was placed into the solution and mixed uniformly until all the petroleum ether was volatilized at 60 °C. Afterwards, samples were dried at 110 °C for 2 h. The coupler content was 1%, 2%, 3% and 4% by weight of TiO2.

2.2.2. Preparation TiO2/UPR nanocomposites
Different contents of TiO2 by weight of UPR with and without surface modification were placed into a certain amount of UPR. After stirring and even dispersion, a 1% curing agent of methyl ethyl ketone peroxide and a 0.2% accelerator of cobalt iso-octoate were added. The composite material was injected into molds after good mixing and then was solidified at room temperature. After post curing treatment, the samples were placed into an oven at 45 °C for 2 h and then at a constant temperature of 95 °C for 3 h. The samples were allowed to cool naturally.

2.3. Test method
2.3.1. Impact strength
The impact strength test of the TiO2/UPR composites were carried out according to GB/T2571-1995. The width and thickness of the samples were 10 mm and 4 mm, respectively. The impact strength of the composite materials was calculated from:

\[
\alpha_k = \frac{A}{b \times h},
\]

where \(\alpha_k\) is the impact strength of the composite material (kJ/m²); \(A\) is the energy consumed by the impact sample (mJ); \(b\) is the width of the middle of the notch sample (mm); \(h\) is the thickness of the middle of the notch sample (mm).
2.3.2. Flexural strength
The flexural strength test of the TiO$_2$/UPR composite was measured according to GB/T2570-1995. The length and span of the TiO$_2$/UPR composites were 80 mm and 60 mm, respectively. The width and thickness of the samples were 10 mm and 4 mm, respectively. The test speed was 2 mm min$^{-1}$. The flexural strength of the composite materials was calculated from:

$$\sigma_f = \frac{3P \times L}{2bh^2}$$

where $\sigma_f$ is the flexural strength of the composite material (MPa); $P$ is the failure load or the maximum load (N); $L$ is the span of the material (mm); $b$ is the width of the composite sample (mm); $h$ is the thickness of the composite sample (mm).

2.3.3. Heat resistance
The heat resistance is reflected by a heat deflection temperature in this study. The heat deflection temperature of sample was measured based on GB1634-79. The maximum flexural normal stress of the sample after load application was 18.5 kg cm$^{-2}$ and the heating rate was 2 $^\circ$C min$^{-1}$.

2.3.4. UV aging resistance
An accelerated artificial aging test was used to test the UV aging resistance. Samples were placed in a self-made UV-irradiation device to carry out the UV irradiation test (figure 1). A straight tubular type-I fluorescent UV lamp was used as the light source; the lamp power was 20 W and the lamp wavelength was 300–400 nm. The distance between the sample and lamp tube was 30 cm. After an irradiation time of 3, 7, 14, 28 and 60 days, the impact strength of the sample was tested, and the test results consisted of an average of five replicate tests.

2.3.5. Fourier transform Infrared (FTIR) spectroscopy
The FTIR spectrum was obtained by using a NEXLS 670 infrared spectrometer (Niocllet Company) and the KBr compression method.

2.3.6. Scanning electron microscopy (SEM)
Impact fracture surfaces of samples with different coupling agent contents were coated with gold and analyzed. A JSM-6360 SEM (JEOL, Japan) was used to test the sample microstructures.

3. Results and discussion

3.1. Impact strength
The effects of different TiO$_2$ contents with and without surface modification on the composite impact strength is shown in figure 2. The composite impact strength increases initially and then decreases with an increase in TiO$_2$ content. When the content of unmodified TiO$_2$ is 2%, the impact strength reaches a maximum, and then the curves go down as the TiO$_2$ amount increases constantly. At a maximum, the impact strength increases by 92.3% compared with that of pure UPR. Incorporating modified TiO$_2$ greatly improves the impact strength compared with unmodified TiO$_2$. When the content of modified TiO$_2$ is 3% and the coupling agent is 4%, the maximum value of the impact strength of the composite is 16.28 kJ m$^{-2}$, which improves by 890.5% and 415.0% compared with pure UPR and UPR with the addition of 2% modified TiO$_2$, respectively. Therefore, the addition of TiO$_2$
improves the impact strength of the composite significantly. In addition, adding modified TiO₂ presents a better toughening effect.

The addition of rigid inorganic filler TiO₂ will cause a stress concentration effect, which easily triggers matrix yielding around the particle. This behavior will absorb a large amount of deformation work, and result in composite toughening. Shang et al [18] explained that the addition of TiO₂ improved the mechanical properties of the composite for a similar reason. Existing inorganic TiO₂ particles will prevent crack growth because the inorganic particles are less likely to produce a large expansion deformation. Under a large tensile stress, partial interfacial debonding between matrix and inorganic particles will form holes around the interface, which will deactivate cracks and avoid the development of destructive cracks. Yield and interfacial debonding that are produced by stress concentration need to consume extensive energy, and thus a toughening effect can be attained.

There are more physical and chemical defects on the nanoparticle surface because of a larger specific surface area. More opportunities exist for nanoparticles to create physical or chemical bonding with polymer chains, and thus the contact area between the matrix and nanoparticles increases. Composites will produce more microcracks that absorb more impact energy when suffering from shock. However, fine nanoparticles are easy to reunite because of small-size effort. When the nanoparticle content exceeds a certain level, the composite strength will decrease because of nanoparticle agglomeration [19]. Kango et al [20] has verified that an adequate chemical modification of the nanoparticle surface was effective to prevent agglomeration, decrease surface tension and improve the interaction of nanoparticles with the polymer matrix. Therefore, surface modification with a titanate coupling agent makes it difficult for TiO₂ to recombine and the TiO₂ disperses uniformly in the matrix, which yields a better toughening effect.

3.2. Flexural strength

Figure 3 shows the relationship between the TiO₂ nanoparticle content and the composite flexural strength. A similar behavior as shown for impact strength of the UPR composite is observed. An excessive amount of TiO₂ will reduce the composite flexural strength. This result agrees well with the work of Xu et al [21]. Without coupling agent treatment, the optimal improvement achieves 35.10 MPa in composites when the TiO₂ content is 1.0%. A further increase in the TiO₂ content above 1.0% leads to a gradual reduction in flexural strength of the composite, mainly because of nanoparticle agglomeration. When the content of modified TiO₂ and coupling agent is 4.0% and 3.0%, respectively, the flexural strength reaches a maximum of 62.30 MPa, which increases by 77.5% compared with the UPR addition of 1.0% unmodified TiO₂. Goodarzi et al [17] drew a similar conclusion, where the introduction of 1.5% modified and unmodified TiO₂ increased the flexural strength by 53.65% and 37.1%, respectively.

Figure 2. Relationship between the content of TiO₂ nanoparticle modified with different titanate contents and the impact strength.
3.3. Heat resistance
The effects of the TiO$_2$ with and without surface modification on the composite heat deflection temperature are shown in figure 4. The nanocomposites have better heat resistance than that of pure UPR. The optimal value of unmodified TiO$_2$ is 4\% with a corresponding deflection temperature of 68.1 °C, which increases by 19.9\% compared with pure UPR. The further increase in TiO$_2$ decreases the deflection temperature. The optimal content of modified TiO$_2$ is 4.0\% and the titanate content is 3.0\%. The corresponding deflection temperature is 70.3 °C, which increases by 23.7\% compared with the pure UPR. Therefore, the addition of TiO$_2$ can increase the UPR heat resistance significantly.

Figure 3. Relationship between the content of TiO$_2$ nanoparticle surface modified with different titanate contents and the flexural strength.

Figure 4. Relationship between the content of TiO$_2$ nanoparticle surface modified with different coupling agent contents and the heat deflection temperature.
This result agrees well with previous studies [15, 22–25]. Zou et al [22] found that the heat deflection temperature of polypropylene random resin with 4% modified TiO₂ nanoparticles improved by 27.8% compared with the pure resin. Jiang [23] mentioned that the heat deflection temperature of the TiO₂/epoxy resin composite increased up to a maximum and then decreased as the amount of TiO₂ increased. The maximum heat deflection temperature was 161.1 °C, which increased by 112.1% compared with the pure resin. Investigations by Tijana et al [24] and Xiao et al [15] showed that the incorporation of modified TiO₂ nanoparticles increased the glass transition temperature (Tg) in the range from 10.0% to 18.2%. The increase in Tg with the addition of modified TiO₂ nanoparticles indicates a reduced polymer segmental mobility at the interface of the polymer/nanoparticles then a higher composite heat resistance [25–27]. Kaushal et al [28] considered that characteristics of the small nanoparticles, such as a higher rigidity than epoxy, a high specific surface area, and a sufficient particle–matrix adhesion, should be credited for the interfacial interaction improvement. With a better interfacial interaction, it is difficult for matrix macromolecular chains to move during heating, and thus, the heat-deflection temperature increases. However, a continuous increase in number of nanoparticles leads to an increase in the probability of collisions, and thus, an increase in agglomeration. Therefore, the physical and chemical crosslinking of nanoparticles weakens and the interfacial bonding decreases, which will decreases the heat resistance of nanocomposites.

3.4. UV aging resistance

The relationship between the retention rate of the impact strength and the ageing time is shown in figure 5. The impact strength retention rate of the sample with 4% TiO₂ is 80.5%, which is higher than that of the pure UPR sample of 29.8% at 60 days. TiO₂ is similar to a light screener; it can reflect or absorb UV light, which sets up a barrier between polymer and light sources and prevents the entrance of any UV light, which protects the polymer.

A light screener of UV-P with 0.1% content was chosen to enhance the anti-UV performance of the composites. The impact strength retention rate of the sample with 4% TiO₂ and 0.1% UV-P separately is approximately 96.3%, which is higher than that with 0.2% UV-P addition at 60 days. The corresponding improvement rate is 52.4% compared with pure UPR. UV-P can change light energy into heat energy to avoid a photo-oxidation reaction of materials, and thus play a role in stabilizing light. At the same time, UV-P can create a synergistic effect with TiO₂ as a light screener.

3.5. Characterization of TiO₂ nanoparticle surface modified with titanate

The molecular formula of the titanate coupling agent NXT-102 is i-C₃H₇OTi[OPO(OC₈H₁₇)₂]₃. It contains two different functional groups, namely, a low-carbon alkoxy group of C₃H₇O– at one end, which is easily hydrolyzed and has an inorganic affinity. A dealkylation reaction can be caused by a C₃H₇O– reaction with the hydroxyl
hydrogen on the TiO$_2$ surface, which forms an adsorption layer of coupling agent molecules on the matrix surface. The other end is a long carbon chain alkoxy group, which is an organophilic substance. Its polarity is weak and compatible with UPR resin, which can connect with the matrix resin through a chemical reaction or physical winding.

Figure 6 shows the FTIR spectrum of TiO$_2$ with and without surface modification. For TiO$_2$ nanoparticles modified with coupling agent NXT-102, an obvious C–H group belt caused by the long-chain alkyl group in the titanate structure is seen at 2850–3000 cm$^{-1}$. After surface modification, a more flexible interfacial layers between the TiO$_2$ nanoparticles and UPR matrix is formed with interfacial adhesion, which increases the matrix toughness and provides a stress transfer function, which improves the impact strength. When titanate are used to as surface modifiers for TiO$_2$, hydrophilic groups are bound easily to the hydroxyl groups on the TiO$_2$ surface to form chemical bonds. The number of hydroxyl groups on the TiO$_2$ surface is reduced, thus particle aggregation is reduced and the lipophilicity and dispersity in the organic matrix improves \[29, 30\]. More uniform TiO$_2$ nanoparticle dispersions exist after surface modification because of good interfacial bonding, and thus the flexural strength improves. Meanwhile, more physical junctions existence between TiO$_2$ nanoparticles and macromolecular chains, which improve the compatibility of the TiO$_2$ with matrix. The heat deflection temperature increases with an increase in interfacial bonding.

3.6. SEM analysis

The fracture surface of the impact sample was sprayed gold and the fracture morphology was observed by SEM. Figure 7(a) reveals three obvious regions of the fracture, namely, an initial stage, such as compressing, cracking, and bending of materials; a crack-growth stage accompanied by interfacial debonding, torsion, and drafting; and, an end stage that includes split separation and fragment throwing. The crack-growth stage occupies approximately half of the total destruction area. In this stage, a large-scale stripping phenomenon can be observed. Rapid crack growth results in extensive damage in a local region, which shows typical brittle characteristics. The effect of crack-tip passivation by TiO$_2$ addition is easily visible from figure 7(b). Special comb-like tearing damages are observed and the fracture roughness is higher than that of the pure UPR sample in figure 7(a). An apparent plastic deformation and a shearing belt are observed because of matrix yielding caused by stress concentration. Figure 7(c) shows a good bonding between the matrix and the TiO$_2$ surface modified by 1% coupling agent. The TiO$_2$ nanoparticles and internal stress distribute uniformly compared with the sample without modification by the coupling agent. Large tears without dimples show a typical brittle fracture as shown by the fracture morphology for TiO$_2$/UPR composites with 1% coupling agent treatment. Fracturing of the TiO$_2$/UPR composites with 3% coupling agent is very rough as shown in figure 7(d). An orientation beam and multiple microcavity cavitation zone are formed on a raised sheet layer. Many tiny cracks and dimples are formed on the fracture, which indicate that this was a ductile fracture.

Therefore, toughening and reinforcing by TiO$_2$ nanoparticle incorporation can be achieved by forming an interface between the TiO$_2$ and the UPR. When composites are subjected to an impact load, an interfacial transfer load and then rigid TiO$_2$ particles bear the main load and achieve reinforcing. The interface disperses the impact energy and the TiO$_2$ nanoparticles stop cracks and absorb energy to achieve toughening \[21\].

Figure 6. FTIR spectrum of TiO$_2$ nanoparticle surface modified with and without titanate.
4. Conclusions

The mechanical properties, heat resistance, anti-UV aging performance, and strengthening and toughening mechanism of TiO$_2$/UPR composites with and without coupling agent treatment were investigated. The following conclusions were drawn.

1. Incorporation of the modified TiO$_2$ nanoparticles in UPR causes an increase in the composite mechanical and thermal performance. When the TiO$_2$ and titanate contents are 4% and 3%, respectively, there is a good compatibility between the nanoparticles and the UPR matrix. The impact strength, flexural strength, and heat deflection temperature of the composites are 16.28 kJ m$^{-2}$, 63.23 MPa, and 70.3 °C, respectively, which increase by 890.5%, 77.5%, and 23.7% compared with the pure UPR, respectively. Incorporation of modified TiO$_2$ nanoparticles in the UPR enhances the anti-UV aging properties of the composites.

2. Strengthening and toughening effects with TiO$_2$ incorporation can be achieved by forming a flexible interfacial layer between the TiO$_2$ and UPR matrix because of a higher rigidity, excellent bonding and good compatibility of TiO$_2$. With a continuous increase in TiO$_2$ content, the compatibility between the nanoparticles and the matrix weakens and the interfacial bonding decreases, which decreases the composite performance, such as impact strength and heat deflection temperature.

3. After surface modification, a more flexible interfacial layer is formed between the TiO$_2$ nanoparticles and the UPR matrix, which increases the matrix toughness and provides a stress transfer function that results in an improvement in impact strength. A more uniform dispersion exists for the TiO$_2$ nanoparticles after surface modification because of a better interfacial bonding, and then the flexural strength increases. An increased number of physical junctions exist compared with that without surface modification between the TiO$_2$ nanoparticles and the macromolecular chain resulting in difficult movements of the TiO$_2$ during heating, which increases the heat resistance.
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ORCID iDs

Da Chen  https://orcid.org/0000-0003-4246-632X

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