An Optimization Method for Analyzing the Dispersibility of KH550 Modified Nano-Ag/TiO₂ in Urea-formaldehyde Resin

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Abstract
Nano-TiO₂ and KH550 had a bonding effect that allowed the nano-surface to be covered with a layer of monomolecular film, greatly weakening the adsorption force and surface energy between nano-TiO₂. In this paper, the authors analyse the Dispersibility of KH550 Modified Nano-Ag/TiO₂ in Urea-formaldehyde Resin. The dispersibility of the modified nano-Ag/TiO₂ improved significantly, and the precipitation time of the n-hexane solution was prolonged by 15 times and it was stable in ethanol. The modified Ag/TiO₂ kept the crystal diffraction characteristics of the original powder and TiO₂ remained an anatase type, indicating that the photocatalytic performance could be maintained through the modification treatment. The modified Ag/TiO₂ dispersed better in urea-formaldehyde resin and the agglomeration phenomenon was significantly reduced. The addition of nano-Ag/TiO₂ had little effect on the curing time and viscosity of urea-formaldehyde resin.

Key words: Surface modification, composite resin, Urea-formaldehyde resin, nano-Ag/TiO₂.

1. INTRODUCTION
The Urea-formaldehyde resin adhesive is simple in its manufacturing process, featuring low cost, good wettability, and high bonding strength. It is widely used in wood-based panel manufacturing industry, accounting for approximately 80% of the total amount of the Chinese adhesive (Xia, 2009). However, the wood-based panel produced from the urea-formaldehyde resin contains free formaldehyde that will be slowly released during use, seriously polluting the indoor environment, and is harmful to human health; its use scope is limited. Therefore, the research into reducing the release of formaldehyde has become one of the hot spots for the research of the urea-formaldehyde resin adhesive.

Nano-TiO₂ is a N-type semiconductor catalyst which produces electron-hole pairs under the irradiation of ultraviolet light to form active hydroxyl and superoxide ions with the surface O₂ and H₂O. It can react with formaldehyde to produce CO₂ and H₂O and reduce the formaldehyde emission (Sun, 2010; Xu, 2013). The researches of V. Jovanović et al. have shown that compared with the formaldehyde emission of the micro-TiO₂-urea-formaldehyde resin composite material, that of nano-TiO₂-urea-formaldehyde resin composite material was reduced by 3/4 under γ irradiation. Xia Songhua added 0.05% nano-TiO₂ in urea-formaldehyde resin and prepared plywood: the free formaldehyde content of the urea-formaldehyde resin decreased 77.8%, the bonding strength of the plywood increased 155%, and the formaldehyde emission decreased 68.3%.

However, the photocatalytic effect of nano-TiO₂ was notable in ultraviolet light, but poor in natural light, weak light and dark conditions (Shie, 2008), which limited the scope of its use. The loading of nano-Ag on the TiO₂ surface could solve this problem. On the one hand, as the shallow trap captures photogenerated electrons, nano-Ag extended the lifetime of the photogenerated carriers and improved the photocatalytic activity of TiO₂. On the other hand, the reaction activity of the nano-Ag was high and it had a synergistic effect with (Wang, 2015). However, the surface of nano-TiO₂ was hydrophillic and oleophobic. It was difficult to dissolve in organic solvent. The nano-TiO₂ doped with Ag was more polar and agglomerate to form agglomerates with larger sizes, which would seriously affect its practical application effect. In order to prevent this phenomenon, the means such as an addition of dispersant (Wang, 2012), surface modification and ultrasonic dispersion were often used for auxiliary treatment (Zhou, 2015).

The silane coupling agent KH550 was used to modify the surface of the nano-Ag/TiO₂ and improve its dispersibility in organic solvent. Afterwards, the modified nano-Ag/TiO₂ composite urea-formaldehyde resin was prepared to study the effect of nano-Ag/TiO₂ addition on the properties of the composite resin. Its characteristics were detected and its reaction mechanism was explored using the field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR).
2. MATERIALS AND METHODS

2.1. Materials
The Nano-Ag/TiO$_2$ purchased from XuanchengJingrui Nano Material Co., Ltd. (China), was an anatase type, with an average particle size of 20~30nm and a silver loading of 1%; the KH550 coupling agent (γ-chloropropyltriethoxysilane) was purchased from Dow Corning Investment Co., Ltd. (USA); the anhydrous ethanol was purchased from Beijing Chemical Factory (China), with analytical pure grade; the urea-formaldehyde resin was purchased from Henan Binhai Industry Co., Ltd. (China), with a solid content of 55%.

2.2. Preparation method
2.2.1. Coupling agent modification of nano-Ag/TiO$_2$: Configured the KH550 ethanol solution with a mass fraction of 20%, 8%, and 72%, respectively for KH550, deionized water and anhydrous ethanol, added glacial acetic acid to adjust the pH value to be 4, weighed 5g of nano-Ag/TiO$_2$ and added it into 200 mL of anhydrous ethanol, fully stirred it, ultrasonic dispersion for 10min, added 4mL of KH550 ethanol solution, fully stirred it, ultrasonic dispersion for 10min. The solution then reacted for 2h at 60°C. The modified nano-Ag/TiO$_2$ was statically cooled down for centrifugal separation (5000r/min, 10min), and was followed by the modified Ag/TiO$_2$ being dispersed and washed by anhydrous ethanol ultrasonic. Lastly it was centrifuged three times to obtain the modified nano-Ag/TiO$_2$.

2.2.2. Preparation of modified urea-formaldehyde resin: 1g of unmodified nano-Ag/TiO$_2$ and 1g of modified nano-Ag/TiO$_2$ were weighed and added into 100g of urea-formaldehyde resin respectively for high-speed shear emulsification for 30 min to obtain the composite urea-formaldehyde resin.

2.3. Testing and characterization
2.3.1. Dispersibility test: The Ag/TiO$_2$ was, before and after modification, dried in a vacuum oven for 48h. 0.2g of nano-Ag/TiO$_2$ powder was, before and after modification, weighed and placed in a 25mL of graduated cylinder, and a certain volume of ethanol and n-hexane were added and dispersed after 10min of ultrasound. The settling of the powders was observed and the elapsed time of the supernatant solution was recorded.

2.3.2. Effect on the viscosity of the urea-formaldehyde resin: the viscosity of the urea-formaldehyde resin, urea-formaldehyde resin added with the unmodified nano-Ag/TiO$_2$ and the urea-formaldehyde resin added with the modified nano-Ag/TiO$_2$ were measured respectively by using the BookfieldDV2T LV Rotational Viscometer of the USA. The measurements were accurate to 1mPa.s.

2.3.3. Effect on curing time: 50g of the urea-formaldehyde resin, urea-formaldehyde resin added with the unmodified nano-Ag/TiO$_2$ and the urea-formaldehyde resin added with the modified nano-Ag/TiO$_2$ were weighed respectively and added into 2 mL of 2.5% ammonium chloride solution and stirred uniformly. 10g of resin was removed from the tube (25 mm in inner diameter and 150 mm in length). The tube was placed in a water bath at 100°C and the liquid level of the sample in the test tube was 20 mm below the boiling water surface to start timing. The mixture was stirred until the resin suddenly hardened and the length of time was recorded.

2.3.4. FTIR analysis: The unmodified, modified nano-Ag/TiO$_2$ and urea-formaldehyde resins added with the unmodified and modified nano-Ag/TiO$_2$ respectively were dried in a vacuum drying oven with infrared spectroscopy carried out by using Nicolet Avatar 330 Fourier Transform Infrared Spectrometer.

2.3.5. FESEM analysis: The Urea-formaldehyde resin: urea-formaldehyde resins added with the unmodified and modified nano-Ag/TiO$_2$ were dried in a vacuum drying oven. The dried film was cut into 5mm*5mm sheets to be attached to the objective table and sprayed with gold field via the vacuum ions. The JEOL JSM 6301F field emission scanning electron microscope was used to observe and determine the surface morphology characteristics.

2.3.6. XRD analysis: The unmodified and modified nano-Ag/TiO$_2$ were dried in a vacuum oven to obtain a powder sample. The crystal phase was analyzed using a Bruker D8 ADVANCE X-ray diffractometer manufactured by Bruker Company, USA. The scan range was 10 ~ 80°, with target-turning speed of 2°/min.

3. RESULTS AND ANALYSIS

3.1. Dispersibility of modified nano-Ag/TiO$_2$
The organic solvents with different polarities such as n-hexane and ethanol were selected to detect the
dispersion stability of the nano-Ag/TiO$_2$ before and after modification. In n-hexane, the supernatant of the unmodified nano-Ag/TiO$_2$ suspension became clear after 2min and the significant precipitation occurred, while the supernatant of the modified nano-Ag/TiO$_2$ suspension became clear after 30min and the precipitation occurred due to the surface of the Ag/TiO$_2$ being grafted with organic functional groups as well as the weakened polarity, and the dispersibility was improved obviously in n-hexane. However, the grafted surface of the Ag/TiO$_2$ was still incomplete and a large number of hydroxyl groups were still on the surface, resulting in the rapid settlement of the particles in the n-hexane. The ethanol solution of the unmodified nano-Ag/TiO$_2$ showed the precipitation after 6h, and the modified nano-Ag/TiO$_2$ showed stable dispersion in ethanol because a result of the space barrier generated from the organic long chain grafted on the surface of the modified TiO$_2$ prevented the agglomeration between the particles to enhance the dispersibility. In addition, the amino group in KH550 was hydrophilic and as such the modified nano-Ag/TiO$_2$ could be stably dispersed in the polar solvent ethanol.

**Table 1. Effect of Modification Treatment on Dispersibility**

<table>
<thead>
<tr>
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<th>Precipitation time in n-hexane</th>
<th>Precipitation time in ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nano-Ag/TiO$_2$</td>
<td>2min</td>
<td>6h</td>
</tr>
<tr>
<td>modified nano-Ag/TiO$_2$</td>
<td>30min</td>
<td>&gt;24h</td>
</tr>
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</table>

3.2. FTIR analysis of the modified nano-Ag/ TiO$_2$

**Figure 1. FTIR spectra of nano-Ag/TiO$_2$ and modified nano-Ag/TiO$_2$**

Fig. 1 showed the FTIR spectra of the nano-Ag/TiO$_2$ and modified nano-Ag/TiO$_2$. It could be seen from the figure that 3422 cm$^{-1}$ was the stretching vibration peak of the surface hydroxyl group OH (-OH) of nano-TiO$_2$, 1626 cm$^{-1}$ was the OH bending vibration peak of the TiO$_2$ absorption water, and the wider vibration absorption band appearing at 500-700 cm$^{-1}$ was the characteristic absorption peak of Ti-O-Ti. The obvious absorption peak of the organic group appeared in the spectrum of the modified nano-TiO$_2$, the characteristic absorption peaks of the methyl group (-CH$_3$) and methylene group (-CH$_2$-) appeared at 2925 cm$^{-1}$ and 2850 cm$^{-1}$ respectively, and the bending vibration absorption peak in the amine group plane and C-N bond stretching vibration peak appeared at 1635 cm$^{-1}$ and 1127 cm$^{-1}$ respectively. The Si-O-Ti characteristic absorption appeared at 972 cm$^{-1}$ and 934 cm$^{-1}$ indicating that the bonding between nano-TiO$_2$ and KH550 occurred and KH550 was successfully grafted onto the surface of nano-Ag/TiO$_2$.

3.3. XRD analysis of nano-Ag /TiO$_2$
Fig. 2 showed the XRD spectra of nano-Ag/TiO$_2$ (A) and modified nano-Ag/TiO$_2$ (B). Before modification, the anatase absorption peaks of TiO$_2$ appeared for Ag/TiO$_2$ when 2θ was at 25.3 °, 37.7 °, 48.0 °, 53.7 ° and 62.2 °. Meanwhile, the characteristic absorption peak of Ag appeared when 2θ was at 35.9 °, 40.3 °, 55.1 ° and 59.1 ° indicating that the elementary substance Ag was adsorbed on the TiO$_2$ surface. The XRD spectrum of the modified nano-Ag/TiO$_2$ was mostly unchanged and the crystal diffraction characteristic of the original powder remained. TiO$_2$ was still an anatase crystal form and it did not change to other crystalline forms ensuring its good photocatalytic effect.

3.4. Effects on the performance of urea-formaldehyde resin

<table>
<thead>
<tr>
<th></th>
<th>Viscosity</th>
<th>Curing time</th>
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</thead>
<tbody>
<tr>
<td>Urea-formaldehyde resin</td>
<td>97</td>
<td>86</td>
</tr>
<tr>
<td>Urea-formaldehyde resin added with unmodified nano-Ag/TiO$_2$</td>
<td>103</td>
<td>86</td>
</tr>
<tr>
<td>Urea-formaldehyde resin added with modified nano-Ag/TiO$_2$</td>
<td>114</td>
<td>84</td>
</tr>
</tbody>
</table>

The addition of the nano-Ag/TiO$_2$ could increase the viscosity of the urea-formaldehyde resin. Compared with the blank group, the viscosity of the urea-formaldehyde resin added with the unmodified nano-Ag/TiO$_2$ increased by 6 mpa·s, and the viscosity of the urea-formaldehyde resin with the modified nano-Ag/TiO$_2$ increased by 17 mpa·s. The mechanism of the nano-Ag/TiO$_2$ increasing the viscosity of the urea-formaldehyde resin was not only because that the addition of solid nano-Ag/TiO$_2$ made the solid content of the urea-formaldehyde resin increase, resulting in increased viscosity; but also because that a large number of hydroxyls existing at the nano-Ag/TiO$_2$ surface and Amino groups existing in KH550 grafted on the surface of the modified nano-Ag/TiO$_2$ could form a hydrogen bond or van der Waals force with the hydroxyl and amino groups of the urea-formaldehyde resin. The force between the molecules increased and the viscous resistance increased when the molecules moved relative to each other. Thus, the viscosity increased.

The addition of the nano-Ag/TiO$_2$ had little effect on the curing time of the urea-formaldehyde resin. Compared with the blank group, the curing time of the urea-formaldehyde resin added with the unmodified nano-Ag/TiO$_2$ was unchanged, it was 86 s. The curing time of the urea-formaldehyde resin with the modified nano-Ag/TiO$_2$ was reduced by 2 s and measured at 84 s. This may be due to the small amount of nano-TiO$_2$ added and only physical mixing. There was no chemical reaction affecting the resin structure and enough to cause changes in the resin curing time.

3.5. FESEM characterization of composite UF resin
Fig. 3-a, 3-b and Fig. 3-c, 3-d showed the distribution FESEM diagrams of the unmodified nano-Ag/TiO$_2$ and the modified nano-Ag/TiO$_2$ in the urea-formaldehyde resin respectively. It could be seen from Figures a and b that nano-Ag/TiO$_2$ existed in the urea-formaldehyde resin in the form of larger aggregates, and the interface was clear. This was because that the polarity of nano-Ag/TiO$_2$ doped with Ag was strong, the particles had high surface energy and were easily agglomerated, and the nano-Ag/TiO$_2$ was physically dispersed in the urea-formaldehyde resin. There was no urea-formaldehyde resin coating layer, so the interface was clear. It could be seen in Figures c and d that nano-Ag/TiO$_2$ significantly improved its dispersibility in urea-formaldehyde resin, which was due to the dehydration condensation of KH550 and the hydroxyl on the surface of TiO$_2$. The modified TiO$_2$ particles turned from the hydroxyl-containing hydrophilic surface into the organic functional groups-containing surface, which not only reduced the surface energy effectively, but also the electrostatic repulsive effect of the KH550 molecular chains improved the dispersibility of the nano-TiO$_2$ particles significantly. Simultaneously, the amino groups in the modified nano-Ag/TiO$_2$ surface silane coupling agent reacted with the active groups in the resin to form a good interfacial bonding between the modified nano-Ag/TiO$_2$ and the resin.

3.6. FTIR analysis of urea-formaldehyde resin

Fig. 4. FTIR spectra of urea-formaldehyde resin (a), urea-formaldehyde resin added with nano-Ag/TiO$_2$ (b) and urea-formaldehyde resin added with modified nano-Ag/TiO$_2$ (c)
Fig. 4 showed the FTIR spectra of urea-formaldehyde resin (a), urea-formaldehyde resin added with nano-Ag/TiO_2 (b) and urea-formaldehyde resin added with modified nano-Ag/TiO_2 (c). As shown in the figure, 3300-3500 cm\(^{-1}\) was the characteristic absorption peak of the stretching vibrations of -NH, -NH\(_2\) and -OH, and 1650-1630 cm\(^{-1}\) and 1520-1600 cm\(^{-1}\) were the characteristic absorption peaks of amide bands I and II. 1397 cm\(^{-1}\) was the characteristic absorption peak of the deformation vibration of methylene, 1253 cm\(^{-1}\) was the asymmetrical stretching vibration characteristic absorption peak of -C-O-. 1110-1000 cm\(^{-1}\) was the absorption peak of hydroxymethyl and ether bond, and 780-800 cm\(^{-1}\) was the characteristic absorption peak of the skeleton vibration of the Uron ring. In conclusion, a, b, and c all displayed the functional group characteristic peaks of the urea-formaldehyde resin, indicating that TiO\(_2\) had no effect on the formation of the urea-formaldehyde resin. Compared b, c curves and a curve, the characteristic absorption peaks of Ti-O-Ti appeared at 500 cm\(^{-1}\) and there were only increases or decreases of intensity for other peaks indicating that the addition of TiO\(_2\) had no significant effect on the chemical properties of the urea-formaldehyde resin.

4. CONCLUSION

Nano-TiO\(_2\) and KH550 had a bonding effect that allowed the nano-surface to be covered with a layer of monomolecular film, greatly weakening the adsorption force and surface energy between nano-TiO\(_2\). The dispersibility of the modified nano-Ag/TiO\(_2\) improved significantly, and the precipitation time of the n-hexane solution was prolonged by 15 times and it was stable in ethanol.

The modified Ag/TiO\(_2\) kept the crystal diffraction characteristics of the original powder and TiO\(_2\) remained an anatase type, indicating that the photocatalytic performance could be maintained through the modification treatment.

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