Preparation of Inorganic Filler Modified Epoxy Resin Adhesive and Study on Its Compatibility with UDMH

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Abstract. Epoxy resin adhesive have many advantages that other adhesives do not have, and are widely used in various fields. At the same time, it is also a thermosetting resin with high crosslinking density. Its cured product is brittle, low impact strength, and easy to crack. These shortcomings limit the further application of epoxy resin. This article takes the plugging agent of UDMH as the starting point. Epoxy resin adhesive toughened and modified with two kinds of inorganic fillers, nano-titania and micro-alumina, were prepared and study the compatibility of modified epoxy resin adhesive with UDMH. It is found that under certain conditions, the silane coupling agent KH570 can undergo a grafting reaction with the hydroxyl groups on the surface of nano-TiO₂ to improve its lipophilic and hydrophobic properties, and the effect is better than KH560, KH550; Through FT-IR, SEM, TG and other characterization methods, it is found that when the content of coupling agent is 15%, the effect of surface modification is the best. In the preparation of two kinds of inorganic filler modified epoxy adhesives, it is found that when the content of nano-TiO₂ is 3%, the toughening effect is the best, and the impact strength can reach 36.78 KJ/m²; When the content of micro alumina is 60%, the toughening effect is best, and the impact strength can reach 28.43 KJ/m². In general, the toughening effect of using nano-TiO₂ is significantly better than that of alumina. In the study of the compatibility of the two kinds of filler modified epoxy resin adhesives with UDMH, it is found that when nano-titanium oxide is used as the filler, the compatibility of epoxy adhesive and UDMH is improved. However, when micro-alumina is used as the filler, the compatibility of epoxy resin adhesive and UDMH becomes worse.

1. Introduction
UDMH has the characteristics of high specific impulse, high combustion temperature, high density, etc. [1], and can be used as a combustion agent and a variety of oxidants to form a spontaneous combustion liquid propellant. It occupies an extremely important position in the research, design, testing, and use of rockets, missiles, and spacecraft. However, UDMH not only has the above advantages, but also has the characteristics of being flammable, explosive, and corrosive. During use, transportation and storage, it is easy to cause corrosion in the storage tank, sealing flange, pipeline interface, welding seam and other parts, and then cause leakage. In order to avoid major safety accidents, when the unsymmetrical dimethyl hydrazine propellant accidentally leaks, it is the first to carry out emergency and rapid plugging
treatment to prevent the leakage of unsymmetrical dimethyl hydrazine. This can effectively guarantee the safety of personnel, equipment, and facilities, and minimize losses.

The current emergency plugging methods include welding plugging method, plug wedge sealing method, mechanical plugging method, sticking plugging method, etc. [2]. Obviously, for the plugging of the flammable, explosive and corrosive hydrazine fuel, the welding plugging method, the plug-wedge sealing method, and the mechanical plugging method all have certain problems and cannot be used safely for a long time. However, the plugging method can make up for the deficiencies of the above methods and meet the requirements of people's practicability, safety and economy. The key is the plugging adhesive.

Among many adhesives, epoxy adhesives are widely used in aerospace, automotive, microelectronics, precision machinery because of their low curing shrinkage, high bonding strength, good material compatibility, good corrosion resistance, and low cost. However, its high internal stress and brittleness after curing also limit its wider use [3]. In order to make up for the lack of brittleness of the epoxy resin system, the most effective method is to toughen the epoxy adhesive [4].

There are many methods of toughening modification, such as thermoplastic resins [5~7], rubber elastomer toughening [8], thermotropic liquid crystals [9], and nanoparticles [10~11]. This paper uses nano-TiO$_2$ particles and micro-sized micro-alumina inorganic fillers to toughen the epoxy adhesive. On the basis of satisfying its mechanical properties, the compatibility of the modified epoxy adhesive with UDMH is studied.

2. Experimental

2.1. Determine the best type and content of coupling agent for modified nano-TiO$_2$ and Characterization of modified nano-TiO$_2$ particles

The presence of hydroxyl groups on the surface of nano-TiO$_2$ will produce hydrogen bonding, and then agglomeration will occur, which is not conducive to the uniform distribution of titanium dioxide in the liquid in the nano-sized state. The coupling agent reacts with the surface of the nano material to reduce its surface energy, so that the nano titanium dioxide reduces agglomeration in the epoxy resin adhesive [12-13].

The experimental method for confirming the best coupling agent type: Measure 100 mL of anhydrous ethanol in a three-necked flask, weigh a certain amount of dried nano-titanium dioxide into a three-necked flask containing anhydrous ethanol, and ultrasonically disperse for 25 min. Stir in a constant temperature water bath at 70°C for 20 minutes to make the nanometer titanium dioxide powder uniformly dispersed in absolute ethanol. Then slowly drop 10 mL of absolute ethanol solution containing KH570 (15% by mass) into the three-necked bottle, react at constant temperature for 1.5h under the condition of rapid stirring, cool at room temperature, filter with suction, wash, and dry for 8h in a thermostat at 80°C, to obtain hydrophobically modified nano titanium dioxide powder. The preparation steps of silane coupling agent KH560, KH550 modified nanometer titanium dioxide are the same as above. After three kinds of modified nano-titania were prepared, the modified nano-titania was characterized by lipophilicity [14] and Fourier infrared (FT-IR).

The experimental method for confirming the optimal coupling agent content: The method is similar to the above method for determining the type of coupling agent. The experiment uses the best coupling agent with content (mass fraction) of 10%, 15%, and 20% to modify nano-titanium dioxide and characterize the modified nano titanium dioxide with lipophilicity, thermogravimetric analysis (TG), scanning electron microscope (SEM), etc.

2.2. Preparation of nano-titania and micro-alumina modified epoxy adhesive

The corresponding modified epoxy adhesive is prepared by adding different kinds of inorganic fillers with different contents. The mass of E-51 epoxy resin is 100 parts, and the curing agent is a self-made amine room temperature curing agent. The specific formula refers to the following table 1.
Table 1. The formula of epoxy adhesive

| Number | E-51 | Diluent | Coupling agent | Filler | Filler content | Curing agent |
|--------|------|---------|----------------|--------|---------------|--------------|
| 1      | 100  | 20      | 3              | -      | 0             | 25           |
| 2      | 100  | 20      | 3              | Nano-TiO\(_2\) | 3             | 25           |
| 3      | 100  | 20      | 3              | Nano-TiO\(_2\) | 5             | 25           |
| 4      | 100  | 20      | 3              | Micron-Al\(_2\)O\(_3\) | 40            | 25           |
| 5      | 100  | 20      | 3              | Micron-Al\(_2\)O\(_3\) | 60            | 25           |
| 6      | 100  | 20      | 3              | Micron-Al\(_2\)O\(_3\) | 80            | 25           |
| 7      | 100  | 20      | 3              | Micron-Al\(_2\)O\(_3\) | 100           | 25           |

Preparation method of nano titanium dioxide modified epoxy adhesive:
(1) Weigh 100 parts of E-51 epoxy resin in a 50mL clean cup, add 20 parts of AGE diluent and 3 parts of KH570 coupling agent dropwise to it, and stir until uniform;
(2) Add 3 parts of nano-TiO\(_2\) powder to the colloid, vibrate ultrasonically and stir the colloid until uniform with a glass rod;
(3) Add 25 parts by mass of homemade amine curing agent to the colloid, vibrate ultrasonically and stir evenly with a glass rod;
(4) Refer to the above steps for blank test and configuration of adhesive samples with 5% nano-TiO\(_2\) filler.

Preparation method of micron alumina modified epoxy adhesive:
The preparation process of micron Al\(_2\)O\(_3\) modified epoxy adhesive refers to the preparation process of nano-TiO\(_2\) modified epoxy adhesive, and the specific ratio refers to Table 1.

2.3. Study on the mechanical properties of modified epoxy adhesive
Strength is the most important mechanical parameter of epoxy adhesives, among which impact strength can be used to characterize the toughness of the cured product of the adhesive [15].

Experimental method: The epoxy adhesives numbered 1-7 are cast according to the sample size specified in GB/T2571-2008 "Resin Casting Impact Test Method", and 5 samples of each epoxy adhesive are prepared. After the sample is completely cured for one week, the impact strength test is performed [2].

Experimental sample: Using non-notch impact, the span is 60mm, and the size is (80±2) mm×(10±0.5) mm×(4±0.2)mm, as shown in Figure 1:

![Figure 1. Dimensional drawing of the sample](image)

2.4. Study on the compatibility of modified epoxy adhesive with UDMH
Prepare epoxy resin according to Table 2 below, and after curing, put it into a nitrogen-filled container containing colorless and transparent UDMH according to a certain quality. The soaking temperature is 25℃, and the soaking time is 1d, 3d, 5d, 7d, 9d, 11d, 13d, 15d, and then take it out. Use filter paper to absorb the surface liquid, and then measure its mass change rate, and judge its compatibility with UDMH by mass change.
Table 2. Proportion of adhesive

| number | E-51 Diluent | Coupling Agent | Filler         | Filler content | Curing agent |
|--------|--------------|----------------|----------------|----------------|--------------|
| 1      | 100          | 20             | 3              | -              | 25           |
| 2      | 100          | 20             | 3              | Nano-TiO$_2$   | 3            | 25           |
| 3      | 100          | 20             | 3              | Micron -Al$_2$O$_3$ | 60          | 25           |

3. Results and discussion

3.1. Determination of Coupling Agent Type and Content and Characterization of Modified Nano-TiO$_2$

3.1.1. Determination of the type of coupling agent:

(1) The characterization results of lipophilicity are shown in Table 3,

Table 3. The lipophilicity of 15% content of KH570, KH560, KH550 modified TiO2

| Coupling Agent | the Amount of ethanol /mL | Lipophilic Degree /% |
|----------------|---------------------------|----------------------|
| KH570          | 0.02                      | 0.2                  |
| KH560          | 1.07                      | 9.7                  |
| KH550          | 0.08                      | 0.8                  |
|                | 0.07                      | 0.7                  |

After surface treatment of the nano titanium dioxide powder, the hydroxyl groups on the surface will be coated with a layer of organic coupling agent, which becomes a lipophilic and hydrophobic non-polar surface, thus exhibiting strong non-wetting in aqueous solution. The better the modification effect, the more modified nano titanium dioxide particles floating on the water surface. According to the above table, the lipophilicity of KH570 is better than the other three. Analyzing the reasons, the main reasons are the following reactions:

\[
\begin{align*}
\text{CH}_3\text{═C(CH}_3\text{)COO(CH}_2\text{)}_3\text{Si(OCH}_3\text{)}_3 & \quad \longrightarrow \\
\text{CH}_3\text{═C(CH}_3\text{)COO(CH}_2\text{)}_3\text{Si(OH)}_3 & \\
\text{CH}_3\text{═C(CH}_3\text{)COO(CH}_2\text{)}_3\text{Si(OH)}_3 \text{+HO} \quad \text{(TiO}_2\text{)}_n & \quad \longrightarrow \\
\text{CH}_3\text{═C(CH}_3\text{)COO(CH}_2\text{)}_3\text{Si} \quad \text{O} \quad \text{(TiO}_2\text{)}_n
\end{align*}
\]

The above reaction leads to a decrease in the number of hydroxyl groups on the surface of the titanium dioxide, which makes the hydrophilicity of the titanium dioxide powder decrease and the lipophilicity is stronger [16].

Through the lipophilicity experiment of nano-TiO$_2$ particles modified with 15% content of different coupling agents, we can judge that the modification effect of KH570 is better than other types, so it is best to use KH570 under this experimental condition.

(2) Fourier transform infrared spectroscopy (FT-IR) characterization
Figure 2 is the infrared spectra of nano titanium dioxide particles before and after modification with silane coupling agent KH570. Among them: line a represents the infrared spectrum of silane coupling agent KH570, line b represents the infrared spectrum of nano titanium dioxide particles modified by silane coupling agent KH570, and line c represents the infrared spectrum of nano titanium dioxide particles not modified by KH570. The absorption peak at 3342.22 cm\(^{-1}\) in line b corresponds to the stretching vibration peak of the hydroxyl group-OH of the TiO\(_2\) particles. The absorption peaks at 1706.13 cm\(^{-1}\) and 1091.64 cm\(^{-1}\) in the c line are the C=O and Si—O stretching peaks of the silane coupling agent KH570, respectively, indicating that KH570 was successfully grafted onto the surface of nano-TiO\(_2\). The characteristic peak of C=O at 1706.13 cm\(^{-1}\) indicates that KH570 first undergoes hydrolysis, then dehydrates and condenses to form oligomers, and then undergoes dehydration reaction with the -OH on the surface of the nanoparticles to form partial covalent bonds. Then the coupling agent is coated on the surface of the nanoparticles to improve their hydrophobicity. The absorption peak at 1091.64 cm\(^{-1}\) is the characteristic peak of Si—O—Si, indicating that after the hydrolysis of some coupling agents to form —OH, they condense with each other to form oligomers.

Through FT-IR infrared spectroscopy analysis, it can be analyzed that the silane coupling agent KH570 has indeed reacted with the hydroxyl-OH of the nano-TiO\(_2\) particles, the grafting is successful, and the reason analysis is correct.

3.1.2. The content of coupling agent is determined:
(1) The characterization results of lipophilicity are shown in Table 4,

| Coupling agent content /% | The amount of ethanol /mL | Lipophilicity degree /% |
|---------------------------|---------------------------|------------------------|
| 0                         | 0.02                      | 0.2                    |
| 5                         | 0.71                      | 6.6                    |
| 10                        | 0.85                      | 7.8                    |
| 15                        | 1.07                      | 9.6                    |
| 20                        | 0.42                      | 4.0                    |
It can be analyzed from Table 4 that when the dosage of KH570 coupling agent is 15%, the lipophilicity of nano-titanium dioxide is the largest. After the surface of nano titanium dioxide particles is modified, it will show strong non-wetting in aqueous solution. When the surface tension is greater than the weight of the powder, it will float on the water. The better the modification effect, the more floating nanoparticles. When the amount of KH570 coupling agent exceeds a certain value, the siloxane anion generated by the hydrolysis of the silane coupling agent will attack the Si atoms in the molecule of the silane coupling agent bonded with titanium dioxide, bridging the particles, and causing the powder to flocculate. Therefore, under this reaction condition, the optimal amount of silane coupling agent is 15%. Within this range, the silane coupling agent reacts with the hydroxyl groups on the surface of the titanium dioxide to reduce the hydroxyl groups on the surface of the titanium dioxide and increase the lipophilicity of the titanium dioxide.

(2) Thermal weight loss analysis (TG)
Figure 7. TG curve of nano-TiO$_2$ modified by 20% coupling agent

It can be seen from Figure 3 that the mass loss of unmodified nano-TiO$_2$ particles is 6.10% when the temperature is below 200°C, which is mainly caused by the evaporation of water adsorbed on the surface of the nano-particles; In the mass loss range of 200°C to 600°C, the mass loss of the modified nano-TiO$_2$ particles is about 1%, which is mainly caused by the reduction of the hydroxyl groups on the surface of the nano-TiO$_2$ particles.

It can be seen from Figure 4 that the mass loss of unmodified nano-TiO$_2$ particles is 0.94% when the temperature is below 200°C, which is mainly caused by the evaporation of water adsorbed on the surface of the nano-particles, and the adsorption amount is reduced compared with the previous group. The hydrophobicity of the particle surface has been improved; In the mass loss range of 200°C to 600°C, the mass loss of the modified nano-TiO$_2$ particles is about 2.03%, which is mainly caused by the combustion of the KH570 coupling agent grafted on the surface of the nano-TiO$_2$ particles.

It can be seen from Figure 5 that the mass loss of unmodified nano-TiO$_2$ particles is 0.76% when the temperature is below 200°C, which is mainly caused by the evaporation of water adsorbed on the surface of the nano-particles, and the adsorption amount is reduced compared with the previous group. The increase in the amount of coupling agent is beneficial to the improvement of hydrophobic and lipophilic performance; In the mass loss range of 200°C to 600°C, the mass loss of the modified nano-TiO$_2$ particles is about 2.14%, which is mainly caused by the combustion of the KH570 coupling agent grafted on the surface of the nano-TiO$_2$ particles. The degree of grafting has increased compared to the previous group.

It can be seen from Figure 6 that the mass loss of unmodified nano-TiO$_2$ particles is 0.64% when the temperature is below 200°C, which is mainly caused by the evaporation of water adsorbed on the surface of the nano-particles, and the amount of water adsorption is reduced compared with the previous group. Indicating that the increase in the amount of coupling agent is still conducive to the improvement of hydrophobic and lipophilic properties; In the mass loss range of 200°C to 600°C, the mass loss of the modified nano-TiO$_2$ particles is about 3.01%, which is mainly caused by the combustion of the KH570 coupling agent grafted on the surface of the nano-TiO$_2$ particles. The degree of grafting is still increasing compared to the previous group.

It can be seen from Figure 7 that the mass loss of unmodified nano-TiO$_2$ particles is 1.20% when the temperature is below 200°C, which is mainly caused by the evaporation of water adsorbed on the surface of the nano-particles, and the amount of water adsorption is increased compared with the previous group. The modification effect is not enhanced, but weakened; In the mass loss range of 200°C to 600°C, the mass loss of the modified nano-TiO$_2$ particles is about 2.11%, which is mainly caused by the burning of the KH570 coupling agent grafted on the surface of the nano-TiO$_2$ particles. The degree of grafting is
on the contrary compared with the previous group. The decrease indicates that too much KH570 coupling agent inhibited the progress of the reaction.

Based on the above 5 pictures, it can be analyzed that when the content of KH570 coupling agent is 15%, the modification effect of nano-TiO2 particles is the best, and its hydrophobic performance is the best, and the amount of grafted KH570 coupling agent is also the largest. However, if the optimum content is exceeded, the modification effect will decrease. Analyzing the reason, it may be that too much KH570 coupling agent has undergone hydrolysis and self-condensation reaction has occurred, which affects the modification effect.

Through the FT-IR and TG characterization methods, it can be concluded that the KH570 coupling agent with a content of 15% has the best effect of modifying nano-TiO2.

(3) Scanning electron microscope analysis (SEM)

The modified and unmodified nano-TiO2 particles were scanned under the VEGE II XMU electron microscope, and Figure 8 and Figure 9 were obtained respectively. Comparing the two images, it can be found that the particle size of the modified nano-TiO2 particles is much smaller than that of the unmodified nanoparticle, indicating that the agglomeration phenomenon has been effectively suppressed and the modification was successful.

![Figure 8. The particle size of unmodified nano-TiO2 particles](image1)

![Figure 9. The Particle size of modified nano-TiO2 particles](image2)

### 3.2. Preparation and mechanical properties characterization of modified epoxy adhesive

| Number | 1  | 2  | 3  | 4  | 5  | 6  | 7  |
|--------|----|----|----|----|----|----|----|
| Filler | TiO2 | TiO2 | Al2O3 | Al2O3 | Al2O3 | Al2O3 |
| Content | 3% | 5% | 40% | 60% | 80% | 100% |
| Impact Strength (KJ/m²) | 13.91 | 36.78 | 29.32 | 18.29 | 28.43 | 24.34 | 19.41 |

From Table 5, the average impact strength of each numbered sample can be obtained. The impact strength of No. 1 sample can reach 13.91 KJ/m², No. 3 can reach 36.78 KJ/m², and No. 5 can reach 28.43 KJ/m². Whether it is nano-TiO2 or micron Al2O3, the added filler has significantly better impact strength than the sample without filler.

When the content of nano-TiO2 is 3%, the impact strength of the sample is the largest, which is 264.4% of the unmodified epoxy adhesive. Analyzing the reason, when adding nano-TiO2 during the curing process, the -OH on the surface of TiO2 can react with the active hydroxyl groups and epoxy active groups on the epoxy resin, which changes the structure of the epoxy resin to a certain extent. At the same time, because of the presence of the coupling agent, the interface bonding between the nanoparticle
and the matrix is stronger, which is conducive to the stress transfer between the nanoparticle and the matrix, and enhances the toughness of the sample. When the addition amount of nano-TiO$_2$ exceeds 3%, the distance between the nano-particles will become too close, causing agglomeration, which will make it lose the advantage of large specific surface area and have a negative impact on toughening; at the same time, when subjected to external force, the material There are too many silver streaks and excessive plastic deformation, which then evolve into excessive cracks, resulting in a decrease in the toughness of the material [17].

When the addition amount of micron Al$_2$O$_3$ is less than 60%, the impact strength of the modified epoxy adhesive increases with the addition amount. The reason for the analysis may be that the added Al$_2$O$_3$ filler can absorb part of the external impact and improve its impact strength. When the added amount exceeds 60%, the impact strength of the modified adhesive does not increase, but decreases. Analyzing the reason, it may be due to the excessive addition of micron Al$_2$O$_3$, which causes the viscosity of the colloid to be too large, which reduces the crosslinking density and the surface of the filler cannot be completely wetted by the epoxy resin.

3.3. Study on compatibility of modified epoxy adhesive with UDMH

By regularly weighing the changes in the mass of the samples, we can see that the masses of the three groups of samples all show a certain increasing trend. Analyzing the reason, it may be because the molecules of unsymmetrical dimethyl hydrazine enter the three-dimensional network structure of the epoxy adhesive, which increases the quality of the epoxy adhesive. Among them, the mass increase rate of epoxy adhesives with nano-titanium dioxide is the smallest, followed by no fillers, and the largest with micron alumina. Therefore, it can be judged that the epoxy adhesive with nano-TiO$_2$ has the best compatibility, and the micro-alumina has the worst compatibility. Analysis of the reason may be due to the small particle size of nano-titanium dioxide, which is blocked on the mesh of the three-dimensional network structure, which makes the mesh smaller and prevents the UDMH molecules from entering the mesh. The macroscopic phenomenon is that the mass increase rate of adding nano titanium dioxide filler is better than that without filler; the particle size of micron alumina is larger, unlike nano titanium dioxide which has a bonding effect with epoxy glue. There are gaps between it and epoxy glue, and these gaps allow more unsymmetrical dimethyl hydrazine to enter the cured epoxy glue.
4. Conclusion
In this thesis, based on the plugging agent of UDMH, two inorganic fillers, nano-titania and micro-alumina, were prepared to toughen modified epoxy adhesives. The compatibility of modified epoxy adhesive with unsymmetrical dimethyl hydrazine was studied. Among them, the surface of nano-titanium oxide was also modified, and the modification conditions and processes were studied. Get the following main conclusions:

(1) Under certain conditions, the silane coupling agent KH570 can have a graft reaction with the hydroxyl groups on the surface of nano-titanium dioxide to improve its lipophilic and hydrophobic properties. Through FT-IR, SEM, TG and other characterization methods, it is found that when the content of coupling agent is 15%, the effect of surface modification is the best.

(2) In the preparation of two inorganic filler modified epoxy adhesives, it was found that when the content of nano titanium dioxide is 3%, the toughening effect is the best, and the impact strength can reach 36.78 KJ/m². When using micron alumina for toughening, when the content is 60%, the toughening effect is the best, and the impact strength can reach 28.43 KJ/m². In general, the toughening effect of using nano-sized titanium dioxide is significantly better than that of alumina.

(3) In the study of the compatibility of two filler-modified epoxy adhesives with unsymmetrical dimethyl hydrazine, it was found that when nano-titanium oxide was used as a filler, the compatibility of epoxy adhesive with unsymmetrical dimethyl hydrazine was improved. The compatibility of epoxy adhesive with micron alumina becomes worse.

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