

Isocyanate-modified Nano-SiO₂ and Corresponding Process Optimization

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Abstract. Nano-SiO₂ is hydrophilic, and the surface of nano-SiO₂ should be modified to improve its dispersion in a polymer matrix. Here, triallyl isocyanurate was selected to modify the surface of the nano-SiO₂ powders. Because the reaction between isocyanate groups (-NCO) and hydroxyl groups (-OH) on surface of the nano-SiO₂ does not need any pre-treatment, one single and simple step can facilitate the graft. By optimizing the specific modification process via orthogonal experiments, optimal processing conditions that yield good graft modification effects are obtained. This enhances the lipophilicity of the nano-SiO₂. The Fourier-transform infrared spectrometer (FTIR) results indicate that the isocyanate groups (-NCO) in triallyl isocyanurate and the hydroxyl groups (-OH) on surface of the nano-SiO₂ undergo a chemical reaction. Further, the precipitation data show that modified nano-SiO₂ is well dispersed in the organic phase, and its hydrophobic property is strong. This fulfills the goal of modifying nano-SiO₂ powders.

1. Introduction

SiO₂ is a non-metal functional material that is odorless, non-toxic and pollution-free. Due to its special particle sizes, nano-scale SiO₂ has features such as small particle sizes and high specific surface area. It also has surface effects, small-size effects, quantum-tunneling effects, macroscopic quantum tunneling effects and special photoelectric effects. As a result, nano-SiO₂ is often used as an effective insulating material, a catalyst carrier, a gas filter, or a high-grade paint filler. It is widely applied in rubbers, plastics, coatings, oil paint, or cosmetics [1–6].

Figure 1 shows that on the surface of SiO₂, there are unsaturated residual bonds and hydroxyl groups (-OH) in different bonding states. While adjacent hydroxyl groups (-OH) are connected via hydrogen bonds, hydrogen atoms in isolated hydroxyl groups show strong electropositivity, and they tend to attract electronegative atoms. This can facilitate a dehydration condensation reaction with any molecule containing a hydrogen group. The presence of surface hydroxyl groups facilitates chemical adsorption including hydrogen bonds with water. Meanwhile, the compatibility between the nanoparticle and the polymer matrix is poor because the nanoparticle atoms are in a highly active state, have a relatively high specific surface energy, and easily agglomerate. Consequently, nanoparticles that are dispersive and polymer-compatible with a uniform particle size distribution is an active area of research—especially in processing the surface hydroxyl groups (-OH) [7–8].



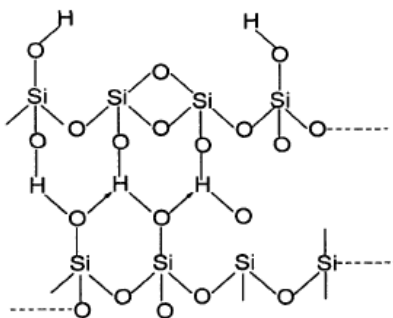


Figure 1. A schematic view of the SiO₂ surface.

There are currently many nano-SiO₂ surface modification processes, but each process has its own disadvantages [9–12]. For example, while the modification method utilizing silane coupling is easy to use, the related large-scale production is discouraged due to the expensive price of the silane-coupling agent. Modification using polymer graft polymerization offers poor grafting efficiency due to the existence of homo-polymerization, which influences the mechanical performance of the material. Moreover, esterification can hydrolyze the ester groups resulting in relatively poor thermal stability.

This research utilizes the chemical reaction between the isocyanate groups (-NCO) in triallyl isocyanurate and the hydroxyl groups (-OH) on the surface of the nano-SiO₂ to modify the surface of the nano-SiO₂. The modified surface of the nano-SiO₂ has acrylate groups, which isolate nano-SiO₂ particles from each other to prevent agglomeration and produce stably modified nano-SiO₂. Meanwhile, the modified system may further undergo a polymerization reaction to fabricate nano-SiO₂ composites.

Though studies on the inorganic nanomaterials using isocyanate for modification have been reported previously [13], these studies often use two-step reactions. Most commonly, toluene diisocyanate (TDI) is used as the modifier and the isocyanate groups (-NCO) undergo a grafting reaction with the hydroxyl groups (-OH) in the nano-SiO₂. Another -NCO group is then utilized for connection to the various desired groups. Therefore, this method is relatively complicated, and the grafting efficiency is affected by the process parameters. Here, triallyl isocyanurate was used to modify nano-SiO₂ resulting in outstanding advantages including no need for pre-treatment. That is, the acrylate groups with chain-extending polymerization ability can be connected to nano-SiO₂ in a single step. As a result, the processing process is simplified with superior grafting modification effects.

2. Experiments

2.1. Major Experimental Reagents and Instrument

2.1.1. *Major reagents in the experiments.* The major reagents used in this research are listed in Table 1.

Table 1. Experimental reagents.

Name	Size	Manufacturer
Nano-SiO ₂	Particle size 15±5 nm	Shenzhen Jingcai Chemical Industry Co., Ltd.
Toluene	Analytically pure	Xilong Chemical Co., Ltd.
Acetone	Analytically pure	Guangzhou Haizhu Chemical Reagent Co. Ltd.
Absolute ethyl alcohol	Analytically pure	Tianjin Yongda Chemical Reagent Co. Ltd.
Triallyl isocyanurate	Analytically pure	Sinopharm Chemical Reagent Co. Ltd.
Dibutyltin dilaurate	Analytically pure	Tianjin Fuchen Chemical Reagent Factory
High purity nitrogen	Purity ≥ 99.99%	Foshan MS Gas Co. Ltd.

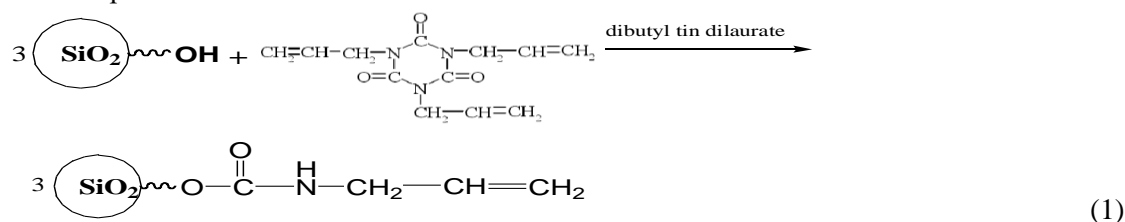
2.1.2. Major instrument in the experiments. The major instrumentation used in this research is shown in Table 2.

Table 2. Experimental instrument.

Name	Style	Manufacturer
Digital thermostatic water bath	HH-2	Jintan Fuhua Instrument Co. Ltd
Power electric mixer	JJ-1	Jintan Honghua Instrument Factory
Water-cycling vacuum pump	SHZ-D(III)	Gongyi Yuhua Instrument Factory
Electric centrifuge	TDL-50	Jintan Medical Instrument Factory
Numerical control ultrasonic cleaning machine	KQ-200DB	Kunshan Ultrasonic Instrument Co. Ltd
Electronic analytical balance	GR-200	A&D (Guangzhou) Company Limited
Electric blast drying oven	101-1AS	Shanghai Xunneng Electric Device Co. Ltd.

2.2. Specific Experimental Method

The number of hydroxyl groups (-OH) on surface of the nano-SiO₂ is reduced by using the isocyanate groups (-NCO) in triallyl isocyanurate to react with the hydroxyl groups (-OH) on surface of the nano-SiO₂. Meanwhile, it is possible for the nano-SiO₂ to undergo the chain-extension reaction by introducing the acrylate groups into the surface of the nano-SiO₂. The specific reaction principles and procedure are explained as follows.



(1) The nano-SiO₂ was placed on a watch glass, and then dried in 100–130°C oven for 2-6 hours.

(2) The dried nano-SiO₂ was added to a flask with toluene. This was dispersed with shaking and ultrasonication for 20–50 min, which made the nano-SiO₂ be evenly dispersed.

(3) The triallyl isocyanurate and dibutyltin dilaurate were then added for reaction at 50–90°C under N₂ aeration and stirring for 0.5–5 hours, after which, the reaction solution was cooled to room temperature.

(4) The reaction system was centrifuged, and the precipitate was washed with acetone, suction-filtered, and heated at 80°C for 8 h to obtained the well-dispersed nano-SiO₂ product.

2.3. Tests and Characterization Methods

2.3.1. IR characterization. The reaction conditions between isocyanate groups (-NCO) in triallyl isocyanurate and hydroxyl groups (-OH) on surface of the nano-SiO₂ were determined via the KBr method and FTIR (manufacturer: Nicolet; stype: FTIR-850; test range: 4000 cm⁻¹–900 cm⁻¹, precision: 0.01 cm⁻¹). This technique characterized the structure of the nano-SiO₂ before and after modification.

2.3.2. Calculation method of percentage grafting. The grafting percentage is used as the parameter to compare the modification effects of triallyl isocyanurate on nano-SiO₂. Specifically, the weight of nano-SiO₂ before and after modification is measured (W₁ is the weight of the SiO₂ modified by triallyl isocyanurate, and W₂ is the weight of nano-SiO₂ before modification). The percentage grafting of the reaction is calculated: (W₁–W₂)/W₂×100%.

2.3.3. Precipitation experiment

2.3.3.1. Precipitation in water. Nano-SiO₂ before and after modification were weighed and placed in different tubes. After deionized water was added to each tube, the tubes were vibrated and ultrasonic-dispersed for 30 min to observe the precipitation of nano-SiO₂ in water. If the modified nano-SiO₂ precipitates in water, then it is very hydrophilic, and the amount of residual -OH groups on its surface is relatively large, indicating that the modification effect is not ideal. In contrast, if there is no significant precipitation in water, then the lipophilicity of the modified nano-SiO₂ is good and the amount of residual -OH groups on the surface is small indicating a good modification effect.

2.3.3.2. Precipitation in ethyl alcohol. Nano-SiO₂ before and after modification were weighed and placed in different tubes. Ethyl alcohol was then added into each tube, and the tubes were vibrated and ultrasonic-dispersed for 30 min to observe the precipitation condition of nano-SiO₂ before and after modification in the ethyl alcohol. If the modified nano-SiO₂ is evenly dispersed in the ethyl alcohol, then its lipophilicity is good, and the amount of residual -OH groups is small indicating good modification. In contrast, if the modified nano-SiO₂ precipitates in the ethyl alcohol, then its hydrophilicity is good and the amount of residual -OH groups is relatively large indicating poor modification.

3. Results and discussion

3.1. Analysis of IR Spectra

Figure 2 shows an IR spectrum of the nano-SiO₂ before modification, and Figure 3 shows the IR spectrum of nano-SiO₂ modified by triallyl isocyanurate. Figure 2 shows that the absorption peak near 1118 cm⁻¹ corresponds to the asymmetric stretching mode of the Si-O-Si bond; the absorption peak at 3462 cm⁻¹ is attributed to the stretching vibration of the hydroxyl groups (-OH) on the surface of the nano-SiO₂ as well as the hydroxyl groups (-OH) in the physically adsorbed water. The absorption peak at 1636 cm⁻¹ is generated due to the bending vibration of the hydroxyl groups (-OH) in the physically adsorbed water on surface of the nano-SiO₂.

Figure 3 shows the IR spectrum of the nano-SiO₂ modified by triallyl isocyanurate. The stretching vibration of the hydroxyl groups (-OH) still exists at 3462 cm⁻¹, but the antisymmetric stretching vibration of the C-H bond occurs near 2955 cm⁻¹ indicating the existence of organic materials on the SiO₂ surface. This also shows that triallyl isocyanurate is already grafted to the SiO₂ particles. Further, the adsorption peak at 1636 cm⁻¹ shows a decreasing trend compared to Figure 2, which indicates that fewer hydroxyl groups (-OH) on surface of the nano-SiO₂ were modified by triallyl isocyanurate.

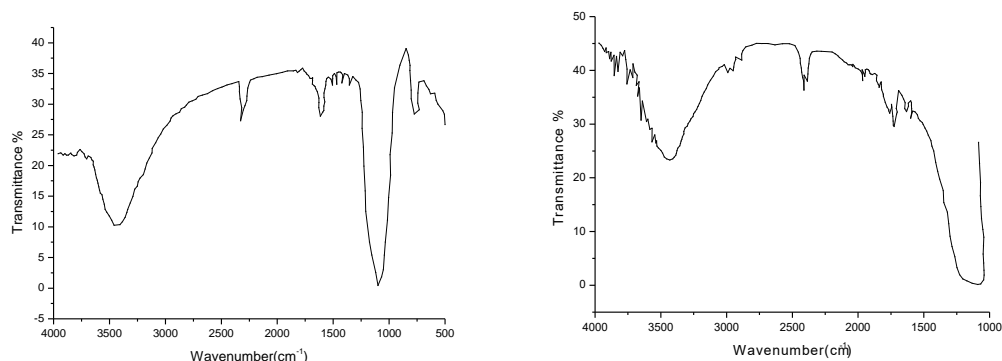


Figure 2. IR spectrum of nano-SiO₂ before modification. **Figure 3.** IR spectrum of nano-SiO₂ after modification.

3.2. Level and Factors of Orthogonal Experiments

We used time (h), temperature (°C) and the weight ratio of triallyl isocyanurate to the nano-SiO₂ to

identify the optimal processing conditions. We compared the percentage grafting and evaluated the modification effect of triallyl isocyanurate on the nano-SiO₂. We also used a three-factor, four-level orthogonal experiment. The factors and levels can be found in Table 3, and the orthogonal experiment design is illustrated in Table 4.

Table 3. Factor level table.

Run	Time/h	Temperature/°C	Weight ratio of triallyl isocyanurate to nano-SiO ₂
1	1.5	50	1:0.6
2	2	60	1:0.8
3	3	70	01:1
4	4	80	1:1.2

Table 4. Orthogonal experiments.

No.	Time/h	Temperature/°C	Weight ratio of triallyl isocyanurate to nano-SiO ₂	Percentage grafting/%
Exp. 1	1.5	50	1:0.6	5.1
Exp. 2	1.5	60	1:0.8	7.5
Exp. 3	1.5	70	1:1	15.1
Exp. 4	1.5	80	1:1.2	16.3
Exp. 5	2	50	1:0.8	6.1
Exp. 6	2	60	1:0.6	8.2
Exp. 7	2	70	1:1.2	16.0
Exp. 8	2	80	1:1	18.6
Exp. 9	3	50	1:1	6.3
Exp. 10	3	60	1:1.2	9.4
Exp. 11	3	70	1:0.6	16.9
Exp. 12	3	80	1:0.8	19.7
Exp. 13	4	50	1:1.2	5.9
Exp. 14	4	60	1:1	10.7
Exp. 15	4	70	1:0.8	13.3
Exp. 16	4	80	1:0.6	15.4
Avg. 1	11.000	5.850	11.400	
Avg. 2	12.225	8.950	11.650	
Avg. 3	13.075	15.325	12.675	
Avg. 4	11.325	17.500	11.900	
Range	2.075	11.650	1.275	

Figures 4, 5, and 6 illustrate the effect of reaction time (h), temperature (°C), and the weight ratio of triallyl isocyanurate to the nano-SiO₂ on the percentage grafting of the nano-SiO₂, respectively. Typically, a greater range has a larger influence on the level variation of each factor. If the range is small, then the influence of the level variation of the specific factor on the experimental result is also small. The range analysis results show that the order of the influence of the three factors on the nano-SiO₂ modified by isocyanate groups (-NCO) is: temperature > time > the weight ratio of triallyl isocyanurate to the nano-SiO₂. The best conditions are 3 h, 80°C, and a 1:1 weight ratio of triallyl isocyanurate to the nano-SiO₂ (Table 4).

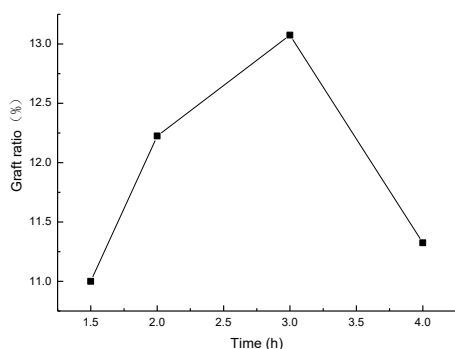


Figure 4. Influence of time on percent grafting.

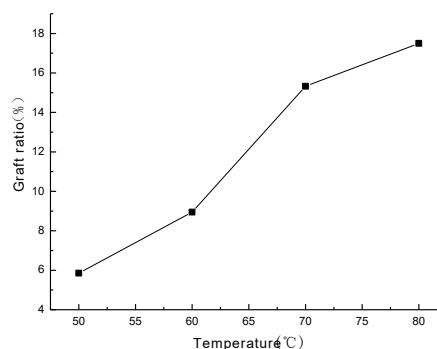


Figure 5. Influence of temperature on percent grafting.

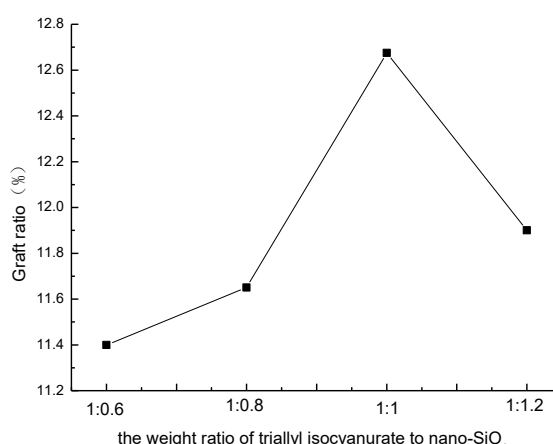


Figure 6. The influence of the weight ratio of triallyl isocyanurate to nano-SiO₂ on the percentage grafting.

3.3. Precipitation Data

Precipitation experiments were performed with nano-SiO₂ modified by triallyl isocyanurate under the optimal conditions as well as control nano-SiO₂ before modification as described in section 2.3.2. Then, 0.1 g nano-SiO₂ before and after modification were weighed and placed in dry and clean tubes a and b, respectively (nano-SiO₂ before modification was placed in tube a, and the nano-SiO₂ after modification was placed in tube b). Then, 10 mL de-ionized water was added to tubes a and b, respectively, and dispersed with sonication for 30 min to observe the precipitation of nano-SiO₂ before and after modification in the water. Similarly, 0.1 g nano-SiO₂ before and after modification were weighed and placed in dry and clean tubes c and d, respectively (the nano-SiO₂ before modification was placed in tube c, and the nano-SiO₂ after modification was placed in tube d). Then, 10 mL ethyl alcohol was injected into tube c and tube d, respectively, and dispersed with 30 min of sonication to observe the precipitation of nano-SiO₂ before and after modification in the ethyl alcohol.

3.3.1. Precipitation experiments in water. Figure 7 shows that unmodified SiO₂ can be dispersed evenly in the water (tube a) to form a suspension solution. No precipitates were found on the bottom of the tube indicating that a large amount of hydrophilic groups (-OH) exist on the surface of unmodified SiO₂, and the unmodified SiO₂ shows strong hydrophilicity. In contrast, the nano-SiO₂ modified by triallyl isocyanurate totally floats on the water surface (tube b). This is due to the capillary effect. A thin layer of water film is attached to the wall of the tube above the water level in the tube. The modified nano-SiO₂ is hydrophobic because the modified nano-SiO₂ is attached to the water film. This indicates that the amount of hydrophilic groups (-OH) on surface of modified SiO₂ is greatly reduced.

3.3.2. Precipitation experiments in ethyl alcohol. Figure 7 shows that the unmodified SiO_2 in ethyl alcohol precipitates quickly (tube c), and the upper layer of the solution in tube c is clear indicating that the unmodified nano- SiO_2 has low lipophilicity. The number of hydrophilic groups ($-\text{OH}$) on the surface of the unmodified nano- SiO_2 is relatively large. Meanwhile, the nano- SiO_2 modified by triallyl isocyanurate may be dispersed evenly in ethyl alcohol (tube d) to form a suspension solution indicating that the modified nano- SiO_2 shows reduced hydrophilicity, and the number of hydrophilic groups ($-\text{OH}$) on its surface decreases.

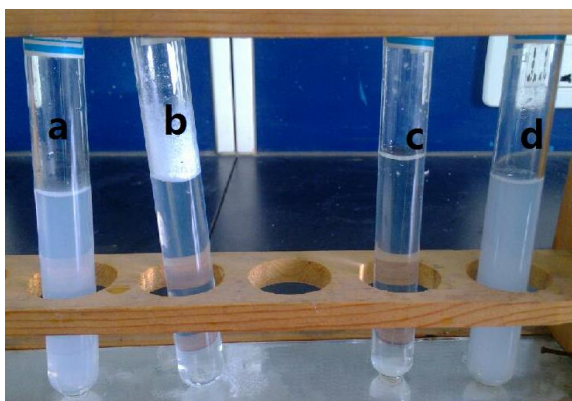


Figure 7. Precipitation data

Figure 8 shows the precipitation conditions of SiO_2 -containing ethyl alcohol obtained from tube c and tube d after being placed in 10 mL measuring cylinders, respectively. For every 30 min, the precipitation volumes of solution c and solution d were recorded. In particular, curve A shows the precipitation conditions of nano- SiO_2 modified by triallyl isocyanurate, and curve B shows the precipitation condition of unmodified nano- SiO_2 . The figure shows that the modified powder has a significantly smaller precipitation rate than unmodified powder due to the reduction in its hydrophilicity. After 2.5 hours, the precipitation of the modified powder basically stops, and the precipitation volume of the modified powder is greater than that of the unmodified powder.

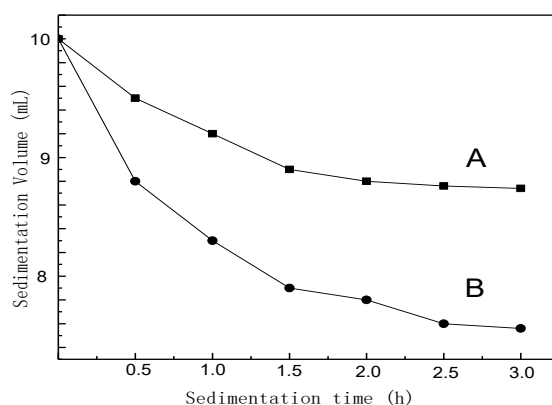


Figure 8. Variation of the precipitation volume of nano- SiO_2 in ethyl alcohol before and after modification.

Clearly, many hydroxyl groups ($-\text{OH}$) exists on surface of the nano- SiO_2 before modification, and the unmodified nano- SiO_2 shows strong hydrophilicity and tends to aggregate in the organic phase. Moreover, unmodified nano- SiO_2 has large nano- SiO_2 particles that precipitate relatively fast. The small particles precipitate fast at the beginning and these induce large particle precipitation. After modification, the number of hydroxyl groups ($-\text{OH}$) on the surface decreases, and the modified nano- SiO_2 is lipophilic. They then disperse uniformly. After precipitation, the modified nano- SiO_2

precipitates very slowly, and it eventually reaches a dynamic equilibrium. The precipitation volume is constant throughout.

4. Conclusions and issues future work

(1) The IR data indicate that under these experimental conditions, isocyanate groups (-NCO) in triallyl isocyanurate and hydroxyl groups (-OH) on the surface of the nano-SiO₂ undergo a chemical reaction. The number of hydroxyl groups (-OH) on the surface of the nano-SiO₂ is reduced.

(2) The optimal conditions for triallyl isocyanurate modification of the nano-SiO₂ is 3 h at 80°C with a 1:1 weight ratio of triallyl isocyanurate to nano-SiO₂.

(3) The precipitation experiments show that the modified nano-SiO₂ has an extremely strong hydrophobicity, and it can be dissolved in organic solvent indicating that the number of the hydroxyl groups (-OH) on surface of the nano-SiO₂ is greatly reduced.

Acknowledgments

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