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NOTE

Improving the Dispersity of Nano-silica from Rice Hull Ash in Organic Solvents by a New γ-Methacryloxypropyltrimethoxy Silane Solution

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Improving the dispersity of nano-silica from rice hull ash in organic solvents by different γ-methacryloxypropyltrimethoxy silane solutions was investigated. The possible principle of the solvent polarity influencing the dispersity of nano-silica in organic solvents was proposed. The optimum solution was γ-methacryloxypropyltrimethoxy silane water solution (0.4 mol/L). The transparency of the optimum modified nano-silica powder anhydrous alcohol solution (0.1 wt. %) was 91.4 %. The dispersity of nano-silica in anhydrous alcohol, CH_2Cl_2, CCl_4, cyclohexane and liquid paraffin increased from 0, 0, 0, 0 and 0.1 to 11.2, 11.3, 11.4, 11.4 and 11.6 g/100 mL after surface modification.

Key Words: Dispersity, Nano-silica, Organic solvents, Water, Transparency.

Most of researchers modified silica gel by surfactants to improve its dispersity in organic solvents recently[1-4]. Their modified silicas could not be well dispersed in organic solvents yet. Therefore silane coupling agent was used as a new modification agent[5]. Li *et al*. modified nano-silica gel by silane coupling agent anhydrous alcohol solutions. He found that silane coupling agent anhydrous alcohol solution could improve the dispersity of nano-silica in organic solvents and γ-methacryloxypropyltrimethoxy silane was the best among all used silane coupling agents[5]. Li *et al*.[5] modified silica was not well dispersed in organic solvent. The objective of this study was to improve the dispersity of nano-silica in organic solvents by a cheap, unpolluted and highly efficient γ-methacryloxypropyltrimethoxy silane solution. The transparency of nano-silica anhydrous alcohol solution was used as an index of evaluating the modification effect. The dispersity of nano-silica and the optimum modified nano-silica in many organic solvents such as anhydrous alcohol, CH_2Cl_2, CCl_4, cyclohexane and liquid paraffin were compared.

γ-Methacryloxypropyltrimethoxy silane was purchased from the Nanjing Crompton Shuguang Organosilicon Company in China. Other reagents were analytical grade.

Selection of an optimum KH-570 solution: Three gram of nano-silica powders and 30 mL of water were added in a 50-mL flask. The mixture was heated at 80 ºC in water bath with stirring at 250 rpm and condensed. 8 mL of γ-methacryloxypropyltrimethoxy silane carbon tetrachloride solution, γ-methacryloxypropyltrimethoxy silane ether solution, γ-methacryloxypropyltrimethoxy silane dichloromethane solution, γ-methacryloxypropyltrimethoxy silane 1-hexanol solution, γ-methacryloxypropyltrimethoxy silane 1-butanol solution, γ-methacryloxypropyltrimethoxy silane acetone solution, γ-methacryloxypropyltrimethoxy silane anhydrous alcohol solution and γ-methacryloxypropyltrimethoxy silane water solution (the concentration of these solutions from 0.2 to 0.8 mol/L respectively except the concentration of γ-methacryloxypropyltrimethoxy silane water solution from 0.2 to 0.4 mol/L because γ-methacryloxypropyltrimethoxy silane water solution was saturated when its concentration came to 0.4 mol/L) was added to the flask at 3 mL/min by a constant flow pump respectively[5]. The mixtures were treated by an Ultrasonic Cell Muller at 90 W for 15 min after they reacted for 100 min. Finally the mixtures were centrifuged at 3000 rpm for 10 min and filtered through Whatman ashless filter paper[5]. The filter cakes were repeatedly washed with deionized water[5]. The filter cakes were dried at 80 ºC for 12 h to get modified nano-silica simples using different γ-methacryloxypropyltrimethoxy silane solutions.

Different modified nano-silica samples (1 g, respectively) were grinded into powders for 1 min using a JYL-A110 Muller. These modified nano-silica powder anhydrous alcohol solutions (0.1 wt. %) were treated by an Ultrasonic Cell Muller at 90 W for 10 min. They were used to measure the transparency of modified nano-silica samples on an UV-VIS spectrophotometer at 500 nm. The optimum modification solution was selected according to the higher transparency[6].

TABLE-1
TRANSPARENCY OF MODIFIED NANO-SILICA SAMPLES *(TRANSPARENCY OF NANO-SILICA: 5.5 %)

Solvent	Concentration (mol/L)						
	0.2	0.3	0.4	0.5	0.6	0.7	0.8
Water	30.6 ± 0.1[a]	74.7 ± 0.1[a]	91.4 ± 0.1[a]	-	-	-	-
Absolute alcohol	8.3 ± 0.1[b]	19.9 ± 0.1[b]	40.5 ± 0.1[b]	85.9 ± 0.1[b]	40.5 ± 0.1[b]	16.8 ± 0.1[b]	8.3 ± 0.1[b]
Acetone	5.5 ± 0.1[b]	13.9 ± 0.1[c]	30.6 ± 0.1[b]	85.9 ± 0.1[b]	30.6 ± 0. 1[b]	16.8 ± 0.1[b]	8.3 ± 0.1[b]
1-butanol	5.5 ± 0.1[b]	13.9 ± 0.1[c]	30.6 ± 0.1[b]	74.7 ± 0. 1[b]	30.6 ± 0.1[b]	13.9 ± 0.1[b]	5.5 ± 0.1[b]
1-hexanol	5.5 ± 0.1[b]	13.9 ± 0.1[c]	23.2 ± 0.1[b]	62.8 ± 0.1[b]	23.2 ± 0.1[b]	11.2 ± 0.1[b]	5.5 ± 0.1[b]
Dichloro-methane	5.5 ± 0.1[b]	11.2 ± 0.1[c]	19.9 ± 0.1[b]	62.8 ± 0.1[b]	23.2 ± 0.1[b]	11.2 ± 0.1[c]	5.5 ± 0.1[b]
Ether	5.5 ± 0.1[b]	8.3 ± 0.1[c]	19.9 ± 0.1[b]	51.6 ± 0.1[b]	19.9 ± 0.1[b]	8.3 ± 0.1[c]	5.5 ± 0.1[b]
Carbon tetrachloride	5.5 ± 0.1[b]	5.5 ± 0.1[c]	16.8 ± 0.1[b]	40.5 ± 0.1[b]	16.8 ± 0.1[b]	5.5 ± 0.1[c]	5.5 ± 0.1[b]

*Values are means ± SD (n = 3). Values followed by the different superscript letter in the same column are significantly different ($P \leq 0.05$)

Comparison of the dispersity of nano-silica and the optimum modified nano-silica in many organic solvents: Nano-silica powder and the optimum modified nano-silica powder samples (mL g, respectively) and an organic solvent (50 mL, such as anhydrous alcohol, CH_2Cl_2, CCl_4, cyclohexane and liquid paraffin respectively) were added and stirred in a 100 mL measuring cylinder. The supernatants were discarded. The sediments were dried and weighed (m_2g).

The dispersity of the sample in the organic solvent was calculated according to eqn. (1):

$$\text{Dispersity of the sample} = \frac{m_1 - m_2}{50} \times 100 \text{ (g/100 mL)} \quad (1)$$

Statistical analysis: Statistical analysis was carried out using ORIGIN 7.5 (Origin Lab Inc., USA).

Determination of the optimum KH-570 solvent: Carbon tetrachloride, ether, dichloromethane, 1-hexanol, 1-butanol, acetone, anhydrous alcohol and water were selected as γ-methacryloxypropyltrimethoxy silane solvents because they were common solvents and their polarity and dielectric constant increased in turn. As shown in Table-1, the transparency of nano-silica modified by γ-methacryloxypropyltrimethoxy silane water solution (0.4 mol/mL) was the highest (91.4 %). So γ-methacryloxypropyltrimethoxy silane water solution (0.4 mol/mL) was optimum. When γ-methacryloxypropyltrimethoxy silane water solution (0.4 mol/mL) and nano-silica dispersed in water were mixed up, the modification reaction was easy to carry out because nano-silica was hydrophilic. When γ-methacryloxypropyltrimethoxy silane organic solution and nano-silica dispersed in water were mixed up, the modification reaction was difficult to carry out because the polarities of nano-silica and organic solvent were reverse. When the concentration of γ-methacryloxypropyltrimethoxy silane solution increased, the transparency of different modified nano-silica increased at first and then decreased. It was due to fact that the modification reaction could not carry out completely when the concentration of γ-methacryloxypropyltrimethoxy silane solution was too low and there was steric hindrance on the surface of nano-silica when the concentration of γ-methacryloxypropyltrimethoxy silane solution was too high.

Comparison of the dispersity of nano-silica and the optimum modified nano-silica in many organic solvents: The data of the dispersity of nano-silica and the optimum modified nano-silica in many organic solvents (such as anhydrous alcohol, CH_2Cl_2, CCl_4, cyclohexane and liquid paraffin, these solvents were selected because they were common solvents) were listed in Table-2. The dispersity of nano-silica in these organic solvents was poor. The optimum modified nano-silica was well dispersed in these organic solvents. The fact may be explained using the polarity theory. Nano-silica is polar and hydrophilic. Organic solvents were apolar and hydrophobic. According to the principle of "the similar, the soluble", nano-silica was not well dispersed in organic solvents. When -Si-R groups were connected with the surface of nano-silica, the optimum modified nano-silica became apolar and hydrophobic. The optimum modified nano-silica could be well dispersed in organic solvents.

TABLE-2
DISPERSITY OF NANO-SILICA AND THE OPTIMUM MODIFIED NANO-SILICA IN MANY ORGANIC SOLVENTS*

Organic solvent	Dispersity (g/100 mL)	
	Nano-silica	Optimum modified nano-silica
Anhydrous alcohol	0 ± 0.0[a]	11.2 ± 0.1[a]
CH_2Cl_2	0 ± 0.0[a]	11.3 ± 0.1[a]
CCl_4	0 ± 0.0[a]	11.4 ± 0.1[b]
Cyclohexane	0 ± 0.0[a]	11.4 ± 0.1[b]
Liquid paraffin	0.1 ± 0.0[a]	11.6 ± 0.1[c]

*Values are means ± SD (n = 3). Values followed by the different superscript letter in the same column are significantly different (P ≤ 0.05)

In summary, the work made it clear that different γ-methacryloxypropyltrimethoxy silane solutions could affect the transparency of nano-silica. The transparency of the optimum modified nano-silica powder anhydrous alcohol solution (0.1 wt. %) was 91.4 %. The dispersity of nano-silica in anhydrous alcohol, CH_2Cl_2, CCl_4, cyclohexane and liquid paraffin increased from 0, 0, 0, 0 and 0.1 to 11.2, 11.3, 11.4, 11.4 and 11.6 g/100 mL after surface modification.

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