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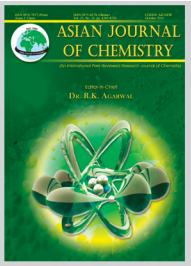

NOTE

Enhancing the Dispersity of Nano-Silica from Rice Hull Ash in Organic Solvents by Modification with a New Silane Coupling Agent Solution

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Enhancing the dispersity of nano-silica from rice hull ash in organic solvents by different γ-methacryloxypropyltrimethoxy silane (MOPTMS) solutions was investigated. The optimum solution was γ-methacryloxypropyltrimethoxy silane water solution (0.4 mol/L). 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 11.0, 11.1, 11.2, 11.2 and 11.4 g/100 mL after surface modification.

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

Enhancing the dispersity of nano-silica in organic solvents had caused intensively interesting since nano-silica well-dispersed in organic solvents could be extensively used in rubber, paint and plastic industries[1,2]. At first, most of researchers modified silica gel by surfactants to enhance its dispersity in organic solvents[3-5]. Their modified silicas could not be well dispersed in organic solvents yet[3-5]. Therefore silane coupling agent was considered as a new modification agent. Li *et al.*[6] modified nano-silica gel by silane coupling agent, anhydrous alcohol solutions. They found that silane coupling agent, anhydrous alcohol solution could enhance the dispersity of nano-silica in organic solvents and γ-methacryloxypropyltrimethoxy silane (MOPTMS) was the best among all used silane coupling agents. Li's *et al.* modified silica was not well dispersed in organic solvent. Anhydrous alcohol was costly and polluted environment.

The aim of this study was to enhance the dispersity of nano-silica in organic solvents by a low cost, unpolluted and highly efficient γ-methacryloxypropyltrimethoxy silane solution. Dibutyl phthalate (DBP) absorption number 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. Nano-silica was prepared from rice hull ash. Other reagents were analytical grade.

Selection of an optimum KH-570 solution: Thirty gram of nano-silica powders and 300 mL of water were added in a 500-mL flask. The mixture was heated at 80 ºC in water bath with stirring at 260 rpm and condensed. 80 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-methacryloxy-propyltrimethoxy 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[6]. 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[6]. The filter cakes were repeatedly washed with deionized water[6]. The filter cakes were dried at 80 ºC for 12 h to get modified nano-silica simples using different γ-methacryloxy-propyltrimethoxy silane solutions. Their dibutyl phthalate absorption numbers were measured. The optimum modification solution was selected according to the higher dibutyl phthalate absorption number.

TABLE-1
DIBUTYL PHTHALATE ABSORPTION NUMBER OF MODIFIED NANO-SILICA SAMPLES*(cm^3/g, NANO-SILICA: 2.0)

Solvent	Concentration (mol/L)						
	0.2	0.3	0.4	0.5	0.6	0.7	0.8
Water	2.7 ± 0.1[a]	3.1 ± 0.1[a]	3.4 ± 0.1[a]	-	-	-	-
Absolute alcohol	2.1 ± 0.1[b]	2.5 ± 0.1[b]	2.8 ± 0.1[b]	3.2 ± 0.1[b]	2.8 ± 0.1[b]	2.4 ± 0.1[b]	2.1 ± 0.1[b]
Acetone	2.0 ± 0.1[b]	2.3 ± 0.1[c]	2.7 ± 0.1[b]	3.2 ± 0.1[b]	2.7 ± 0. 1[b]	2.4 ± 0.1[b]	2.1 ± 0.1[b]
1-butanol	2.0 ± 0.1[b]	2.3 ± 0.1[c]	2.7 ± 0.1[b]	3.1 ± 0. 1[b]	2.7 ± 0.1[b]	2.3 ± 0.1[b]	2.0 ± 0.1[b]
1-hexanol	2.0 ± 0.1[b]	2.3 ± 0.1[c]	2.6 ± 0.1[b]	3.0 ± 0.1[b]	2.6 ± 0.1[b]	2.2 ± 0.1[b]	2.0 ± 0.1[b]
Dichloro-Methane	2.0 ± 0.1[b]	2.2 ± 0.1[c]	2.5 ± 0.1[b]	3.0 ± 0.1[b]	2.6 ± 0.1[b]	2.2 ± 0.1[c]	2.0 ± 0.1[b]
Ether	2.0 ± 0.1[b]	2.1 ± 0.1[c]	2.5 ± 0.1[b]	2.9 ± 0.1[b]	2.5 ± 0.1[b]	2.1 ± 0.1[c]	2.0 ± 0.1[b]
Carbon tetrachloride	2.0 ± 0.1[b]	2.0 ± 0.1[c]	2.4 ± 0.1[b]	2.8 ± 0.1[b]	2.4 ± 0.1[b]	2.0 ± 0.1[c]	2.0 ± 0.1[b]

*Values are means ± SD (n = 3). Values followed by the different 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 (m_1 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_2 g).

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 (OriginLab 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, dibutyl phthalate absorption number of nano-silica modified by γ-methacryloxy-propyltrimethoxy silane water solution (0.4 mol/mL) was the highest (3.4 cm_3/g). So γ-methacryloxypropyltri- methoxy 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-methacryloxypropyltri-methoxy 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.

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 (Dielectric constant)	Dispersity (g/100 mL)	
	Nano-silica	Optimum modified nano-silica
Anhydrous alcohol (24.5)	0 ± 0.0[a]	11.0 ± 0.1[a]
CH_2Cl_2 (9.1)	0 ± 0.0[a]	11.1 ± 0.1[a]
CCl_4 (2.2)	0 ± 0.0[a]	11.2 ± 0.1[b]
Cyclohexane (2.02)	0 ± 0.0[a]	11.2 ± 0.1[b]
Liquid paraffin (2.0)	0.1 ± 0.0[a]	11.4 ± 0.1[c]

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

In conclusion, the work made it clear that different γ-methacryloxypropyltrimethoxy silane solutions could affect the transparency of nano-silica. The optimum solution was γ-methacryloxypro-pyltrimethoxy silane water solution (0.4 mol/L). Dibutyl phthalate absorption number of the optimum modified nano-silica powder anhydrous alcohol solution was 3.4 cm^3/g. 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 11.0, 11.1, 11.2, 11.2 and 11.4 g/100 mL after surface modification. These results suggested that the selected optimum γ-methacryloxypropyltrimethoxy silane solution was effective.

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