Enhancement of impact strength of poly (methyl methacrylate) with surface fine-tuned nano-silica

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Abstract. Highly dispersible nanoparticles in organic solvent always receive wide interests due to their compatibility with polymer materials. This paper reported a kind of isopropanol alcohol silica dispersion which obtained using a method of azeotropic distillation. The isopropanol alcohol dispersed silica (IPADS) were treated with coupling agents to fine-tune their surface properties. Polymethyl methacrylate (PMMA) was then used as a research object to test the compatibility between IPADS and polymer. UV-vis spectra indicate that IPADS would reach its high compatibility with PMMA if coupling with trimethoxypropylsilane (PTMS). Followed experiments on PMMA proved that the high compatibility can prominently enhance the impact strength about 30%. The results may provide reference both for nano-silica modification and better understanding of nano-enhanced materials.

1. Introduction
Nanomaterials had been broadly applied in polymer composites to improve their performance, such as strength, thermal stability, electrical properties and optical properties [1-3]. Nano-silica is one of the most widely used nanomaterials because of its low cost and potential application in different fields including paints, catalysis, etc. Mostly, the surface of silica was modified by varied types of coupling agent to improve their compatibility with polymers, like oleic acid, methyltriethoxysilane, etc [4-6]. The coupling agents also help nanosilica to form complex with polymers hence increase their performance [7-10]. This also provide an important step to stop agglomerates and lower the intersurface energy between silica and polymer [5, 11-13]. For this purpose, different modification methods were highlighted in recent literature [14].

PMMA complexed with SiO₂, ZnO, CeO₂ had been studied to improve performances of high transparency, better mechanical strength, ultraviolet resistance, and the like [3, 15-20]. However, many existed works didn’t fully get rid of the defects of agglomerate while fabricating a composite. The core problem is low interface compatibility. Herein nano-silica was surface modified with three kind of silane coupling agents in order to improve their interface compatibility with PMMA. The results were further test by UV-vis spectrum and the impact strength of PMMA. The water dispersed nano-silica was firstly transferred into isopropyl alcohol phase by a simple method of azeotropic distillation. Three kinds of coupling agent were selected to improve surface property of nano silica. The final test of silica modified PMMA bulk confirmed that nano-silica can effectively improve the...
performance of PMMA in light transmission and impact strength.

2. Experimental section

2.1. Materials
Isopropyl alcohol (IPA, ≥ 99%), Benzoyl peroxide(BPO, ≥ 99%) was purchased from Sinopharm Chemical Reagent Co., Ltd. Aqueous silica sol (25 wt% in water) was purchased from Jiangyinguolian Chemical Industry Co., Ltd. Hydrochloric acid (36%~38%) was purchased from Xinyang Chemical Reagent Co., Ltd. Methyl methacrylate (MMA, ≥99%) was purchased from Tianjin Kermel Chemical Reagent Co., Ltd. 3-chloropropylmethyldimethoxysilane (CPMDMS, ≥ 95%), 3-chloropropyltrimethoxysilane (CPTMS, ≥98%), trimethoxypropylsilane (PTMS, ≥ 97%) was purchased from Aladdin Chemical Co., Ltd. All chemicals were used as received without further purification.

2.2. Preparation of IPA dispersed silica nanoparticles (IPA-DSN) and its surface modification
The pH of 20g aqueous silica was adjusted to 2.0 by 5 N HCl and added to a 500 mL distillation flask which equipped with a magnetic stir bar. Then silica sol mixed with 180 g IPA for azeotropic distillation in order to remove water. When the boiling point of distillate raised from 80.4°C to 82.4°C, the transition finished, keeping on the distillation until the left silica sol in flask was about 45 g. The distillation product was subsequently purified by 220 nm millipore filter.

A round bottom flask which equipped a reflux condenser and a magnetic stir bar was charged with 40 g IPA-DSN (10 wt% is silica) and required silane coupling agents (about 20 wt% to silica mass). The mixture was heated to 75°C for 4h to finish nanoparticles surface modification.

2.3. Preparation of nano-enhanced poly (methyl methacrylate)
The four- necked flask containing MMA (50 g) and BPO (initiator, 0.25 g) was heated to 85°C in oil bath for 20min under nitrogen. Modified IPA-DSN was added under vigorous stirring to form a clear dispersion. Then the four- necked flask was rapidly taken to water bath under 40°C. The dispersion was applied a vacuum environment to remove residual IPA until the boiling point of the dispersion reached 100°C. At last, the PMMA serum was cured at 65°C for 2 h and 50°C for 12 h.

2.4. Sample characterization
Dynamic light scattering (DLS) data was record by Malvern Instruments ZEN1600 series; FTIR data was collected on Lambda 750 S which was purchased from PerkinElmer; Transmission electron microscopy (TEM) was performed with JEM-2100F STEM/EDS working at a voltage of 160 kV; TG was taken on Power-Compensation Differential Scanning Calorimeter which was purchased from PE; UV / visible spectroscopy were measured by UV-8800 series which was produced by Jiangsu Skyray Instrument Co., Ltd; Impact strength test was performed on XJJ-50.

3. Results and discussion
FTIR spectra in figure 1 confirm the silane coupling agent is partly grafted on the surface of nano silica. Detailed analysis is described as follows. Firstly, there is a strong absorption band at 800 cm⁻¹, which corresponds to the C-Si stretching vibration or Si-O-Si stretching vibration in silica sol. The absorption band in 1630 cm⁻¹ corresponds to the O-H stretching vibrations of water, and 2960 cm⁻¹ indicates the stretching vibration of asymmetric C-H bond. After treated by CPMDMS(spectrum b) or CPTMS(spectrum c), two new absorption peaks appear at 698 and 1415 to 1440 cm⁻¹, corresponding to the C-Cl stretching vibrations of halogenated hydrocarbon and alkyl group in coupling agent. A strong absorption band is enhanced at 2960 cm⁻¹, indicating that there are alkyl groups on the surface of silica sol, which has been modified by PTMS (spectrum d).

However, FTIR is not sufficient to confirm our aimed product since some peaks are relatively weak. So the modified IPA-DSN was test by thermal gravimetric (TG) analysis, additionally. The TG plot
(figure 2a) showed an initial weight loss of 1.38% up to 89.5°C due to the adsorbed water molecules in silica which had been modified by CPMDMS. The weight loss increased significantly near 300°C, indicating the decomposition of organic part on silica surface. The followed TG plots (figures 2b and 2c) present similar results. Above all, it can be concluded that CPMDMS, CPTMS and PTMS are successfully grafted onto silica sol.

We also did a quantitative calculation of the grafting rate based on TG data (table 1), which had listed the number of grafting rate per square nanometer. The grafting rate could be calculated by equation (1),

$$\eta = \frac{\alpha}{M - 60} N_A \left( \frac{4\pi}{3} \left( \frac{d}{2} \right)^3 \rho \right)^{-1} \pi d^2$$

where $\alpha$ is the weight loss of the sample (measured by TG), $N_A$ is the Avogadro constant, $d$ is average diameter of nanosilica particles, $\rho$ is density of silica and $M$ is the molecular mass of coupling agents.

| Coupling Agent | CPMDMS | CPTMS | PTMS |
|----------------|--------|-------|------|
| Weight loss    | 10.17% | 12.04%| 5.01%|
| Grafting Rate(N/nm²) | 3.73 | 3.90 | 2.16 |
Furthermore, the quality of original silica dispersion is highly essential for nanocomposites so that we test it with DLS (table 2). It is obvious that the particle size (ca 17 nm) has not been much affected after dealing with silane coupling agent, so was its size distribution (demonstrated by PDI data).

Table 2. The DLS data of IPA-DSN.

| Nano-silica Sample | Unmodified | CPMDMS | CPTMS | PTMS |
|--------------------|------------|--------|-------|------|
| Average Size       | 17.2       | 18.1   | 17.6  | 16.6 |
| PDI                | 0.23       | 0.228  | 0.235 | 0.187 |

Figure 3. TEM image of (a) water dispersed nanosilica, (b) IPA-DSN. (c) modified silica sol by CPMDMS.

Images of transmission electronic microscopy (TEM, figure 3) also present the same results, of which with the original particle size of water dispersed nanosilica was about 10nm. Its size didn’t have much change after transferred into IPA and modified by silane coupling agent (figures 3b and 3c). The result was coincident with DLS data and demonstrates the high quality of our nano silica materials.

Because PMMA is a kind of ultra transparent materials, it is very convenient to observe agglomeration of nano silica via transmittance. For this reason, UV / visible spectrum was applied as one of methods to judge the compatibility (figure 4). It is obvious that the light transmittance of PMMA modified by PTMS present the highest transmittance among the three, which means silane coupling agent which contain propyl groups have better compatibility with MMA.

Figure 4. UV-vis spectrum for nanosilica modified-PMMA.

Figure 5. Impact strength of prepared PMMA.

Additionally, the impact strength of PMMA further confirm the result acquire by UV-vis spectrum (figure 5). The most transparent sample which tailored by PTMS receive best mechanical performance. Nevertheless, the sample which was tailored by other two silane coupling agents also have great enhancement on impact strength compared to the unmodified one.

4. Conclusions
In this work, we have made three main contributions. 1) We have successfully transferred nanosilica into IPA phase without further aggregation. 2) Three kinds of silane coupling agent were applied to improve surface properties of IPA-DSN. The grafting efficiency was demonstrated by IR and TG
measurement. 3) It is clear that IPA-DSN which has been modified by different coupling agent can improve the impact performance of PMMA without much changing of its transmission. There was also a comparison of three kind of as-used silane agents. The propyl group can improve the compatibility between PMMA and nanosilica better than other two functional groups. Above all, this study may provide reference for future work of fabricating nano doped composite materials.

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