Effect of Organo-Functionalized Silica Particles on the Mechanical Properties of PU

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Abstract. Monodisperse, spherical, organo-functionalized silica particles were prepared by a one-pot method. Vinyl-silica and amine-silica were prepared by the hydrolysis of tetraethyl orthosilicate in aqueous alcohol solutions with the addition of vinyl triethoxysilane and 3-aminepropyl triethoxysilane, respectively, while thiol-silica was prepared by the hydrolysis of 3-mercaptopropyl in water without ethanol. The organo-functionalized silica particles were characterized by transmission electron microscopy, scanning electron microscopy and energy dispersive spectrometer. Organo-silica particles had lower water swell by introduction of organic groups on the surface of silica particles. Afterwards, organo-functionalized silica particles were dispersed in polyurethane (PU) to improve the mechanical properties of PU. The mechanical properties of PU films were measured by universal testing machine and sclerometer. The results showed that the tensile strength, Flexural strength and hardness of PU films were obviously improved with the addition of organo-silica particles.

1. Introduction

Inorganic nanoparticles filled polymer composites have attracted a great deal of attention because of their superior properties resulting from combination of the advantages of the inorganic material and the organic polymer [1-3]. Silica nanoparticles are by far the most popular inorganic material due to their easy preparation and functionality, chemical inertia, high thermal stability and unusual mechanical properties [4, 5]. Thus, they present a wide range of application such as catalysts support, pigments, polishing material, hybrid composite materials, humidity sensors and thermal insulators [6-9].

It is seems that the incorporation of silica nanoparticles into polymers is a simple and effective method to improve the mechanical properties of polymers. Rosso et al. [10] added 5 vol% of silica nanoparticles into Araldite-F epoxy and the results showed that both the stiffness and the toughness of epoxy resin were improved with the addition of silica nanoparticles. Jeon et al. [11] found that the mechanical properties of the hybrid PU/SiO_2 nanocomposites prepared by sol-gel method were enhanced. Both the hardness and tensile properties of PU films reinforced by silica nanoparticles were increased with the increasing of silica content. Polyurethane (PU) is a versatile polymeric material due to its excellent physical properties, such as chemical resistance, elasticity, shape memory and high waterproof, and it has widely applications such as coatings, adhesives, plastics fibers, rubbers and thermoplastic elastomers [12]. However, PU could not reach the requirements of applications in some specific areas due to the low mechanical strength. The mechanical properties of PU can be obviously improved with the addition of silica nanoparticles [13, 14].

Significant improvement in mechanical properties of organic/inorganic composites can be achieved when the silica nanoparticles have a uniform dispersion in polymer matrix [15, 16]. However, the surface of silica nanoparticles is usually hydrophilic while polymer matrix is usually hydrophobic, which may cause the nanoparticles to be agglomerated in the incorporation process, leading to a poor dispersion in the polymer matrix. On the other hand, nanoparticles with high surface energy are easy to be agglomerated. The agglomeration of silica nanoparticles is a major

problem in the incorporation of nanoparticles in polymers, which limits their practical applications in polymer composites [17-19]. Consequently, surface modification is advised to improve the compatibility between silica nanoparticles and polymer matrix. A great many methods have been proposed for the functionalization of silica surface, such as grafting [20], post-synthetic modification [21] and one-step synthesis [22]. Functionalized silica nanoparticles can be prepared by one-pot method with the addition of silane coupling agents in the sol-gel process [23, 24]. Therefore, one-pot method for the preparation of functionalized silica nanoparticles is an alternative method to reduce the steps of surface modification and have many advantages such as low cost and high quality of the product. Functionally modified silica nanoparticles were synthesized by a one-step method, based on the hydrolysis of tetraethyl orthosilicate in aqueous alcohol solutions with the addition of 3-methacryloyloxypropyl trimethoxy silane in our previous study [25]. The introduction of functional groups on the surface of silica will improve the compatibility between nanoparticles and polymer matrix, leading to a better dispersion of nanoparticles in the polymer matrix.

In this study, a one-pot method was used for the preparation of organo-functionalized silica particles. Vinyl-silica and amino-silica were prepared by the hydrolysis of tetraethyl orthosilicate (TEOS) in aqueous alcohol solutions with the addition of vinyl triethoxysilane (VTES) and 3-aminopropyl triethoxysilane (APTES), respectively. Thiol-silica was prepared using 3-mercaptopropyl trimethoxysilane (MPTMS) as single silica source without other precursors. Monodisperse, spherical, organo-functionalized silica particles could be obtained. Afterwards, organo-silica particles were dispersed in polyurethane (PU) coatings via solution blending to reinforce PU. The mechanical properties of the PU/silica films were investigated.

2. Experimental

2.1 Materials

Tetraethyl orthosilicate (TEOS), vinyl triethoxysilane (VTES), 3-aminopropyl triethoxysilane (APTES) and 3-mercaptopropyl trimethoxysilane (MPTMS) were all analytical grade and purchased from Sinopharm Chemical Reagent Co., Ltd. Ethanol (99.99%, AR) and ammonia (28%, AR) were obtained from Wuxi Chemical Co., Ltd. The hydroxyl-acrylic resin (HAR), curing agent (trimer of hexanmethylene-1, 6-discocyanate, HDI-trimer) and thinner were provided by Suzhou Painting Co., Ltd. Deionized water was used throughout the experiments.

2.2 Preparation procedure

2.2.1 Preparation of the organo-functionalized silica nanoparticles

The vinyl-silica and amino-silica nanopaticles were prepared by the one-pot method. The first solution was a mixture of 5 mL TEOS and 45 mL ethanol, and the second solution was a mixture of 10 mL ammonia, 30 mL deionized water and 160 mL ethanol. Then the first solution was quickly pourer into the second solution under vigorous stirring. After 30 min, 1 mL silane coupling agent solution was added into the mixture for the surface modification of silica nanoparticles. Afterwards, the reaction was continued for 12 h at room temperature. The white precipitate was obtained through centrifugation and washed with deionized water and ethanol for three times, respectively, and then dried in vacuum at 100 ºC for 10 h. Thiol-silica was prepared by the hydrolysis of MPTMS in water without TEOS and ethanol [26]. 1 g MPTMS was added into 100 mL water under vigorous stirring until the mixture was turned to a transparent solution. Then, 0.1 mL ammonia was added to the solution and the reaction progressed during 12 h at room temperature. Pure silica nanoparticles were also prepared by the Stober method [27] for comparison.

2.2.2 Preparation of silica nanoparticles reinforced PU coatings

PU coatings reinforced by silica nanoparticles were prepared by solution blending. The hydroxyl-acrylic resin (HAR), hexanmethylene-1, 6-discocyanate (HDI) and thinner were mixed at a weigh ratio of 2:4:1 with vigorous stirring. Then, organo-silica particles were added into PU coatings and dispersed using a high-energy (JFS-900/Z, Shanghai Saijie Chemical Equipment Co., Ltd) sand milling for 3 h. Finally, curing agent HDI was added into the suspension for the curing of PU coatings. The weigh ratio of PPG, HDI and thinner was 2:4:1.

2.2.3 Preparation of PU films

The resultant homogenous PU coatings were further cured for 30 min. Then, the coatings were spread on a plastic substrate using a wet film applicator. The applicator was driven by an automatic film dauber (AFA-II, XD Env. Eng. Tech. Inc., Shanghai, China) to obtain films with precise thickness. Afterwards, the wet films were first dried at room temperature for 24 h and then roasted at 60 ºC for 2 h. Finally, PU films were peeled from the substrate carefully and used for the mechanical and thermal properties testing.

2.3. Characterization

2.3.1. Particle characterization

Fourier transform infrared spectroscopy (FT-IR) was carried out using Nicolet FT-IR Avatar 360 (Nicolet, USA) with KBr method. The morphology and particles size of silica were carried out using transmission electron microscope (TEM, Hitachi H-600-II, Japan) and scanning electron microscope (SEM, Hitachi S-4700, Japan). The element analysis of the particles was measured by scanning electron microscope appurtenance (SEM-EDS, Hitachi S-4700).

Water swell, i.e., the degree of water vapor adsorption was used to compare the surface hydrophobicity of silica nanoparticles. A constant weight of silica powder was allowed to adsorb water vapor in a closed container containing liquid water at room temperature for 7 days. It was ensured that the powder was not in direct contact with water in the container. The amount of water vapor adsorbed could be calculated by the increase in weight of silica powder [28].

$$\% swell = \frac{W - W_0}{W_0} \times 100 \quad (1)$$

Where W_0 is the original silica powder weight and W is the powder weight after water vapor absorption. This is a non-standard technique but give reproducible results.

2.3.2 Mechanical properties of PU films.

The hardness test of PU films was measured using a plastic sclerometer (LX-D, Qianzhou testing Instruments Co., Wuxi, China) according to the China National Standards GB/T 1039-79. Measurements were performed five times for each sample, and the average value was calculated.

The mechanical properties of the PU/silica films were measured using a universal testing machine (WDT20, Shenzhen KQL Testing Instruments Co., Shenzhen, China) according to our previous [29, 30]. The force transducer with a precision of ± 0.02% was made by Transcell Tech. Inc., USA and a PC was connected to the testing machine to record the results. Impact test, Flexural test and tensile test were measured according to the China National Standards GB/T 1843-1996, GB/T 9341-2000, GB/T 1040.3-2006, respectively. All measurements were measured at room temperature. The GB standards were established according to the ISO ones.

3. Results and Discussion

3.1 Preparation of organo-functionalized silica nanoparticles

In this study, organo-functionalized silica nanopaticles were prepared by a one-pot method. It was expected that the organic groups of surfactants could incorporate on the surface of silica nanoparticles, leading a good dispersion in polymer matrix. Fig. 1 and Fig. 2 show the TEM and SEM images of silica nanaparticles prepared at different conditions, respectively. It could be observed that both the pure and organo-functionalized silica have a spherical shape and a uniform size. There was also no agglomeration of organo-silica as shown in Fig.1 (b), (c) and (d). That was attribution to the space steric effect which produced by the orgaic groups located on the surface of silica reduced the agglomeration of silica nanoparticles. It seems that the Strobe method was a simple and effective route to prepare monidisperse, uniform silica particles. However, the Strobe method needs a great many of ethanol in the process. Thiol-silica was prepared by the hydrolysis of MPTMS in water without the addition of ethanol and other precursors such as TEOS. The average particles size of different silica is shown in Fig. 3. It was found that the particles size of organo-silica was larger than that of pure silica. The pure silica particles showed the smallest size (133 nm), while the thiol-silica particles showed the largest size (530 nm).

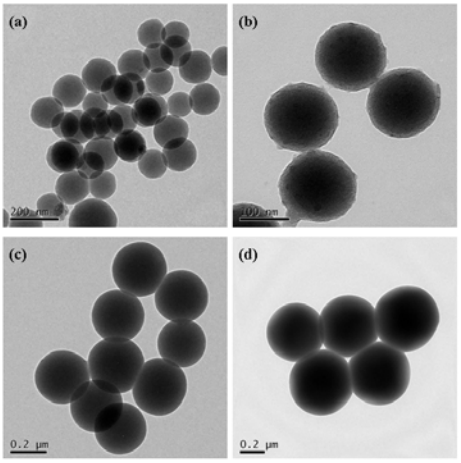

Figure.1. TEM images of organo-silica prepared at different conditions: (a) pure silica nanoparticles, (b) vinyl-silica, (c) amine-silica, (d) thiol-silica.

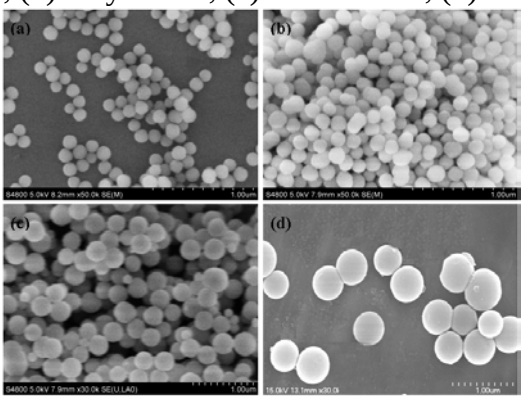

Figure.2. SEM images of organo-silica prepared at different conditions: (a) pure silica nanoparticles, (b) vinyl-silica, (c) amine-silica, (d) thiol-silica.

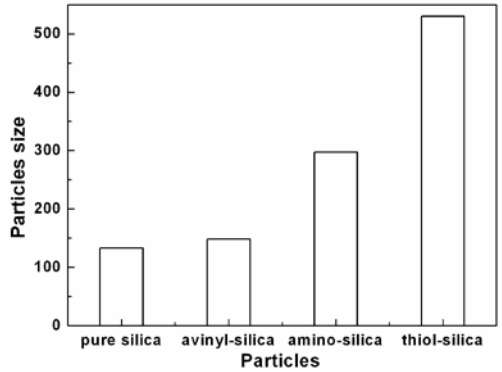

Figure.3. The average particles size of different silica.

EDS and FT-IR were employed in order to confirm that the organic groups were indeed incorporated on the surface of silica nanoparticles. Fig. 4 shows a typical EDS elemental analysis of silica nanoparticles. It could find that the content of Si element reached to 48.24 %, O element to 51.76 %, and no other element, as shown in Fig.4 (a). It was also found N, C, S element of the amino-silica, vinyl-silica, thiol-silica, respectively. That could be attributed to the organic groups of the different surfactant.

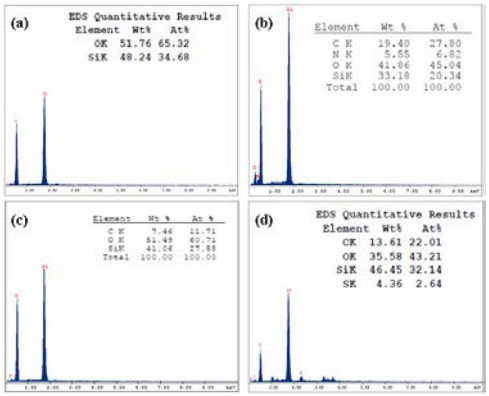

Figure.4. EDS elemental analysis of silica powders: (a) pure silica nanoparticles, (b) amine-silica, (c) vinyl-silica, (d) thiol-silica.

3.2 Water swell of silica nanoparticles

Fig.5 shows the water swell of pure silica and organo-functionalized silica. The pure silica nanoparticles showed the highest water swell (0.138 g/g), while the vinyl-silica showed the lowest water swell (0.067 g/g). It was observed that the water swell of organo-functionalized silica was lower. That could be explained by the fact that the introduction of organic groups on the silica surface made the surface more hydrophobic, leading to a lower water swell of silica. The results showed that the surface of silica was turned from hydrophilic to hydrophobic after the introduction of organic groups on the surface of silica.

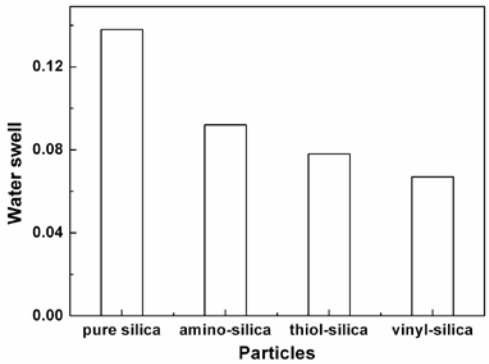

Figure.5. The water swell of pure silica and organo-functionalized silica.

3.3 Mechanical properties of PU/silica nanoparticles

It has proved that the mechanical properties of polymer could be improved with the addition of inorganic fillers. It is well-known that the major requirement of nanocomposites is to optimize the balance between the strength and toughness as much as possible. Several criterias were introduced to characterize the mechanical properties of nanocomposites, such as tensile strength, Young's modulus, impact strength, flexural strength, and hardness.

3.3.1 Tensile properties of PU/silica films

Tensile test is the most widely used method to evaluate the reinforcing effect of silica nanoparticles into PU, and accordingly tensile strength, Young's modulus and the elongation at break are three main parameters. Fig. 6 shows the tensile stress-strain curves of PU films reinforced by different silica nanoparticles and the main mechanical parameters. The results showed that the PU films reinforced by organo-functionalized silica possessed better tensile properties than neat PU. It was found that the tensile strength and Young's modulus increased with the addition of organo-functionalized silica. One the one hand, due to the large specific surface area, silica nanoparticles might have strong interaction with polymer matrix. On the other hand, the introduction of organic groups on the surface of silica could improve their dispersion in polymer matrix. So the movement of chain segments of PU matrix was limited due to the strong interfacial interaction between functional silica nanoparticles and PU, which produced high resistance against the plastic deformation, leading a great improvement in the tensile properties of PU films. Additionally, the Young's modulus and the elongation at break of the thiol-silica reinforced PU films were lower than that of PU films reinforced by amnio-silica or vinyl-silica. The tensile

strength and Young's modulus of PU films reinforced by 0.5 wt% vinyl-silica were increased up to 58.39 MPa and 2313 MPa, respectively. It is well-known that the size and sharp of particles, as well as the dispersion in polymer matrix are the major factors influencing the mechanical properties of composites. Petrovic et al. [31] reported that the tensile properties of PU could be improved more effectively by nano-size silica compared with micron-size silica.

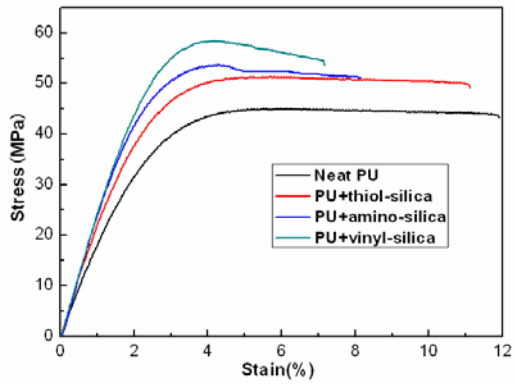

Figure.6. Tensile stress–strain curves of PU films.

3.3.2 Flexural strength and Hardness

Fig.7 (a) shows the results of flexural strength of different PU films. It was found that the flexural strength was increased with the addition of functional silica nanoparticles for samples prepared with amino-silica and vinyl-silica expect that the flexural strength was lower for sample with thiol-silica. It was attributed to the strong interfacial interaction between organo-silica nanoparticles with polymer. Silica nanoparticles was intertwisted with polymer chains, and the flexural stress could be transferred through the inorganic linking point to other polymer chains when the films under external stress. It promoted the transfer of stress at the interphase, resulting in an improvement of flexural strength [32]. Additionally, nano-size silica could have a good dispersion in the polymer matrix compared with the micron-size silica. The little deterioration in flexural strength of thiol-silica filled PU might due to lager particles size of thiol-silica.

The results of hardness measurement are listed in Fig. 7 (b). The hardness of PU films was enhanced with the addition of silica nanoparticles. Due to the large specific surface area and high surface energy, the nanoparticles could be adsorbed with polymer chain and acted as restriction sites for the movement of polymer chains. The reinforcement effect of vinyl-silica was better than thoil-silica and amino-silica. For vinyl-silica, there were functional groups C=C bonding on the surface of vinyl-silica, the PU chains could be fixed onto the silica nanoparticles by covalent bond in the curing reaction of PU [33].

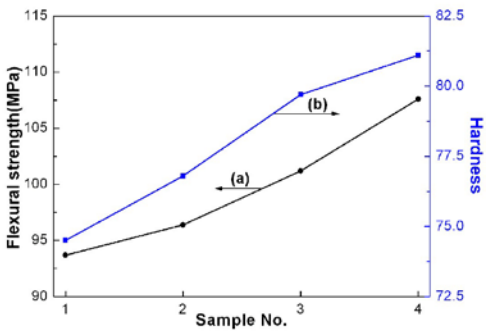

Figure.7. Flexural strength (a) and hardness (b) of PU films prepared with different organo-silica. 1: neat PU, 2: PU+ thiol-silica, 3: PU+ amine-silica, 4: PU+ vinyl-silica

3.3.4 Impact strength

The impact strength of PU films prepared with different kinds of organo-silica is shown in Fig. 8. It could be found that the addition of organo-silica nanoparticles offered a remarkable improvement of impact strength. Orago-silica nanoparticles could well-dispersed in polymer matrix, and acted as reinforcement sites which formed among the polymer chains. The impact reinforced by the incorporation of silica nanoparticles, which indicated that some energy was eliminated during the rupture of the PU films [33]. In addition, the impact strength (41.2 MPa) of vinyl-silica reinforced

PU films was higher than that of with thiol-silica (32.1 MPa) and amino-silica (36.8 MPa). It was possibly due to the particles size effect.

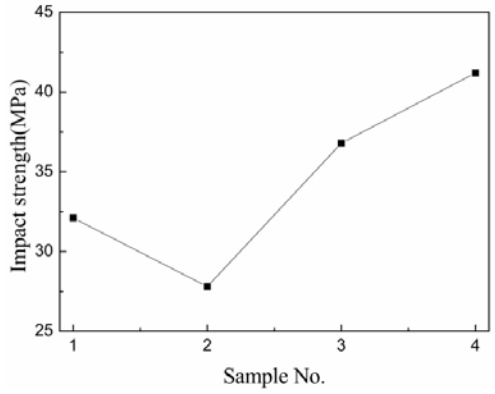

Figure.8. Impact strength of PU films prepared with different organo-silica. 1: neat PU, 2: PU+ thiol-silica, 3: PU+ amine-silica, 4: PU+ vinyl-silica.

4. Conclusion

Organo-functionalized silica nanoparticles were prepared by a one-step method. The vinyl-silica and amino-silica nanopaticles were prepared by the hydrolysis of TEOS in aqueous alcohol solutions with addition of VTEOS and ATPES, respectively. The main advantage of this method over the conventional Stober method was the introduction of organic functional groups on the surface of silica, which could improve the interaction between nanoparticles and polymer. The thiol-silica was prepared by the hydrolysis of a single organicsiloxane MPTMS in water without ethanol. The organo-functionalized silica were spherical and monodisperse. Organo-silica had lower water swell due to the hydrophobic surface by the introduction of organic groups on the surface of silica. The mechanical properties of PU films reinforced by organo-silica nanoparticles were enhanced remarkably. The results showed that the vinyl-silica reinforced PU films exhibited an higher mechanical properties than that with amnio-silica and vinyl-silica. The tensile strength, Young's modulus, flexural strength and impact strength of PU films reinforced by 0.5 wt% vinyl-silica were increased up to 58.4, 2313, 110.6 and 41.2 MPa, respectively.

Acknowledgments

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