

Novel Approach for Preparation of Organic/Inorganic Hybrid Nanocomposites

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ABSTRACT

A new class of organic/inorganic hybrid nanocomposites has been synthesized through surface initiated emulsion grafting polymerization in the presence of modified silica particles. Well-defined polymer chains were grown from the nanoparticle surfaces to yield individual particles composed of a silica core and a densely grafted outer styrene-acrylonitrile copolymer (SAN) layer. The resulting nanocomposites demonstrated raising glass-transition temperature (T_g) and showed a good dispersion of silica nanoparticle regardless of particle content. It is because of the existence of the covalent bond between ABS chains and silica nanoparticles that increased the compatibility between the organic and inorganic phases. The interfacial interaction between the silica and the SAN phases plays a major role in controlling the microstructures and the properties of the composite materials.

Keywords: nanocomposites, ABS, silica, emulsion polymerization, grafting density.

1 INTRODUCTION

Thermoplastic resins are widely used because of their light weight and excellent moldability. However, thermoplastic resins may have poor thermal resistance, abrasion resistance and rigidity. In recent years, there has been a continuing effort to develop thermoplastic materials with improved physical properties. Specifically, research has focused on the creation of a highly moldable thermoplastic resin with good thermal resistance, abrasion resistance, modulus and rigidity.

One method of improving mechanical properties of thermoplastic resins includes adding inorganic fillers such as glass fiber, talc, and mica. However, resin composite materials prepared by blending inorganic filler and a thermoplastic resin lack a sufficient reinforcing effect because the bonding strength between the inorganic filler and the matrix resin is weak. Further, large amounts of inorganic filler may cause serious deterioration of impact strength.

In recent years, research has also focused on the effects of nanoparticles on different materials. Dispersion of very small particles in polymeric matrices is scientifically and technologically important for a variety of reasons. The preparation of nanoscale materials with unique properties represents a significant challenge. One potential advantage of a dispersed particle system is that many of its properties

are strongly dependent on the interfacial properties of the materials because the fraction of the overall materials, which is in the vicinity of the fraction of an interface, is quite high. In addition to simply providing a large interfacial area, dispersions of very small inorganic particles may have useful electronic, optical, magnetic, chemical, catalytic and unique mechanical properties [1-4].

The modification of nanoparticles by grafted polymers is a versatile technique for tailoring their properties and thus provides an effective tool to manufacture well-dispersed organic/inorganic hybrid materials. Generally, depending on the total amount and chemical composition of the tethered polymer, the choice of polymers and grafting techniques were determined. Generally, there are several techniques for attaching polymer chains onto nanoparticle surfaces, including physisorption [5], covalent attachment of end-functionalized polymers to a reactive surface ("grafting to") [6], and in-situ monomer by monomer growth of polymer chains from immobilized initiators ("grafting from") [7,8]. Among these methods, the "grafting from" approach offers the most promising route to achieve maximum structural control. This technique has been used for the preparation of thick grafted layers of high grafting density on the surface. Anionic [9], cationic [10], controlled/living, and conventional free radical polymerizations [11,12] have been successfully used to synthesize tethered polymer layers on solid substrate surfaces.

We recently became interested in utilizing well-dispersed silica sol for the preparation of novel polymer /silica nanocomposites, particularly incorporating of spherical silica particles into acrylonitrile-butadiene-styrene copolymer (ABS) and combining the excellent properties provided by inorganic nanoparticles with the versatility and easy processing characteristics of rubber-toughened thermoplastic. In order to reach a homogeneous dispersion of the nanoparticles in the polymer matrix, styrene-acrylonitrile copolymer (SAN) grafted silica hybrids were synthesized by using the surface initiated emulsion polymerization in the presence of surface modified silica. The strong covalent bonding between the silica and the SAN might be beneficial for a homogeneous dispersion of the particles in the polymer matrix. The resulting SAN/silica hybrids were then blended with polybutadiene-g-(acrylonitrile-styrene copolymer) (PB-g-SAN) to fabricate ABS/silica nanocomposites. In this article, the polymerization technique of polymer/silica nanocomposites as well as the morphological characteristics and the mechanical properties will be discussed.

2 EXPERIMENTAL

2.1 Materials

Styrene and acrylonitrile (from Aldrich) was purified by distillation under reduced pressure before use. The initiator, potassium persulfate (KPS, Kodak), and the chain transfer agent, maleic anhydride, were used as received. Stearic acid and potassium hydroxide (KOH 0.1 M) from Acros were used to prepare the potassium stearate as a anionic surfactant. Nalco 1034A (20 nm diameter silica sol, pH = 3.0) was supplied as 30 wt% aqueous dispersion by Nalco Co. (USA).

2.2 Characterization

SAN/silica hybrid nanocomposites were dried in a vacuum oven at 60 °C for several hours to minimize moisture contents in the sample and then thermogravimetric analysis (TGA) was performed with a Texas Instruments (HI-Res TGA2950) under a stream of nitrogen. Assuming that the incombustible residues were pure silica, it was found that the loss of surface moisture is around 10 wt %. About 5 mg of dried nanocomposite particles were used to examine the SiO₂ content. The sample was heated at 10 °C/min from 25 to 800 °C. Differential scanning calorimetry (DSC) measurements were carried out in the temperature range 25 to 200 °C using a Perkin–Elmer DSC-4 calorimeter. A heating rate of 20 °C/min was used. Gel permeation chromatography (GPC) was carried out on a Waters chromatograph connected to a Waters 410 differential refractometer with THF as the carrier solvent. Transmission electron microscope (TEM) analyses have been performed using a Philips Tecnai F20-ST operating at 200 kV. We carried out energy-dispersive x-ray spectroscopy (EDS) for the composition analysis of ABS/silica nanocomposites using the scanning transmission electron microscope (STEM) unit. Bruker IFS 66 v/s infrared spectrometer was used for the Fourier transform infrared (FTIR) spectroscopy analysis.

2.3 Surface Modification of Silica

Spherical silica nanoparticles with a narrow size distribution and an average diameter of 19.6 nm, determined by DLS measurement, were used to prepare polymer/nanoparticle hybrids. The immobilization of methacryloxy(propyl)trimethoxysilane (MPTS) on the silica surface was obtained by simple condensation of silanol functions as described by Phillipse and Vrij [13]. To 300 ml of the silica suspension, 23 ml of MPTS (equivalent to the concentration of silanol groups on the silica surface) was added dropwise, and stirred at room temperature during 1 h under nitrogen. To favor condensation, 100 ml of the solution were slowly distilled off under vacuum at room temperature. During the distillation, the mixture was diluted

with some isopropyl alcohol. This procedure allows to prepare surface modified nanoparticles with a radius of about 20 nm. The concentration of the suspension obtained is about 90 g of silica for 400 ml.

2.4 Synthesis and Characterization of the SAN/Silica Hybrid Nanocomposites

Surface initiated emulsion polymerization was carried out in batch at 70 °C for up to 4 h under a nitrogen atmosphere. The 10 L glass reactor fitted with a condenser was charged with silica, potassium stearate, maleic anhydride, and deionized water. Degassing was carried out for 30 min under gentle stirring before increasing the temperature up to 70 °C. The monomer and the initiator dissolved in 300 ml of deionized water were added at once to start polymerization. The chain transfer agent/monomer ratio was adjusted in order to obtain the desired molecular weight. Grafted silica particles were separated from the SAN free polymer by the Pruker and Ruhe procedure [7] with acetone, which is a good solvent for free polymer. Moreover, the SAN-grafted silica particles were carefully extracted several times with acetone and centrifuged, until no precipitate formed when the supernatant solution was added dropwise to an excess of methanol.

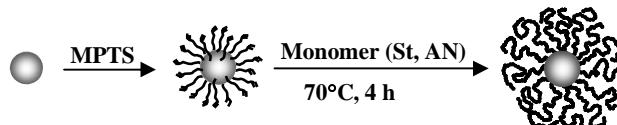


Figure 1: Synthetic steps for forming polymer/inorganic hybrid nanocomposites.

3 RESULTS AND DISCUSSION

The preparation of polymer from the silica surface has been conducted by a number of researchers. In most of the work done in this area, spherical silica particles, average diameters ranging from 100 nm up to 1 μm, were employed into the polymerization system. Therefore, the polymer-modified nanoparticles were produced instead of silica-modified polymer hybrid. In this study, we employed 20 nm diameter of silica particle to fabricate the silica reinforced polymer hybrid system. SAN/silica hybrid was prepared by two steps (Figure 1): (1) tethering a monolayer of polymerizable moieties on a nanoparticle surface and (2) conducting polymerizations in the presence of surface modified nanoparticle.

The infrared spectra of the modified and unmodified silica are shown in Figure 1. Note that the MPTS-grafted silica exhibits absorptions at 1720 and 1650 cm⁻¹. These bands, due to the C=O and C=C bonds, confirm the grafting of MPTS. Moreover, the presence of organic part on the

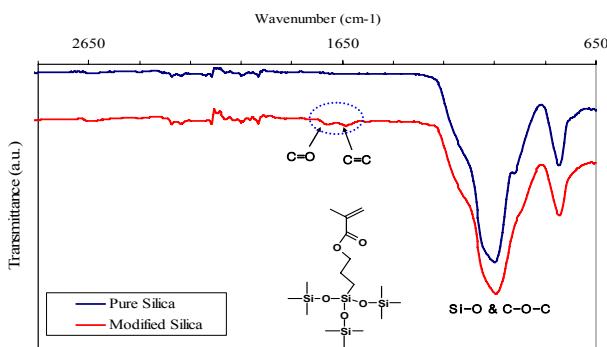


Figure 1: FTIR spectra of pure silica particles and TMPS grafted silica particles.

silica surface is confirmed by the appearance of peaks characteristic of CH functions.

The morphology of SAN/silica hybrid latex was characterized by TEM. Figure 2 shows that core-shell particles are obtained after 4 h of reaction with 20 nm silica seeds. Each silica particles is embedded inside the SAN latexes with a diameter close to 30 ± 5 nm, which seem to be strongly attached to the silica surface. Some aggregated silica nanoparticles can also be observed in EDX analysis (Figures 2). In this study, we employed the modified silica competitive without purification or redistribution step in polymerization reaction so as to develop the economically process. This aggregation, therefore, might occur during the surface modification of silica or originate from starting multitude of SAN/silica nanospheres has two or more than two cores. TEM micrographs of the silica nanocomposite material are shown in Figure 3. It can be seen that the silica nanoparticles are uniformly dispersed throughout the SAN matrix even after blending with PB-g-SAN particles.

To gain insight into the polymer growth characteristics of the surface-initiated polymerization, the surface bound

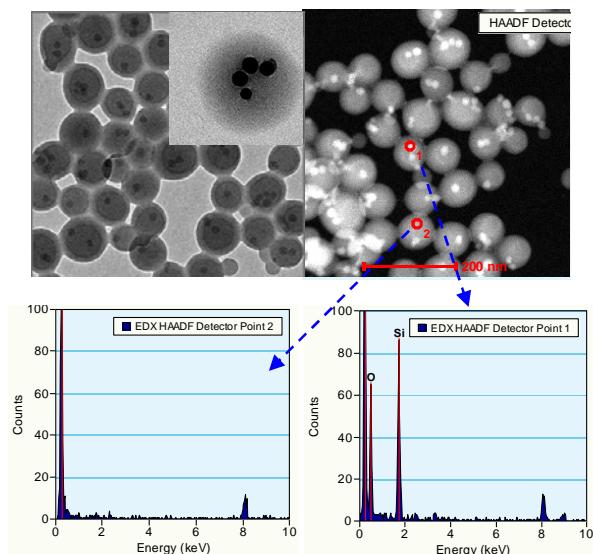


Figure 2: TEM and EDX analysis of SAN/silica hybrid latex. The diameter of MPTS-grafted silica particles: 20 nm.

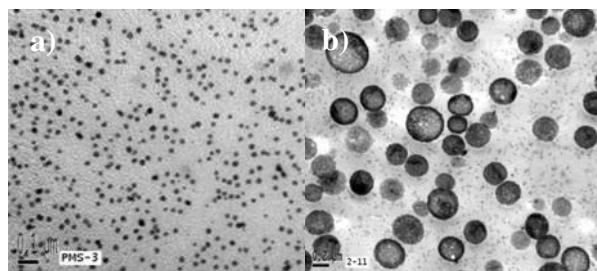


Figure 3: TEM micrographs of a) SAN/silica hybrid nanocomposite, b) ABS/silica hybrid nanocomposite.

SAN was cleaved from the silica nanoparticle surface by etching with aqueous HF (5%) for 6 h at room temperature. The results of characterization for both the detached graft polymer and the free polymer simultaneously formed from the free initiator are summarized in Table 1. It can be seen that the molecular weights (M_w) and molecular weight distributions (M_w/M_n) of the cleaved tethered polymer are slightly higher than that of the free bulk polymer. By comparison of GPC traces of cleaved SAN and free SAN (Figure 4), in the present study the silica particles used are well-defined with a spherical shape and the grafted chains have to grow in the same manner of the free chains with no effect of monomer diffusion on the silica surface.

The DSC results of SAN/silica hybrid composites with the SiO_2 content of 5, 7, 10 wt% are shown in Table 1. The effect of grafting and chain confinement due to steric crowding can be evaluated by a comparison of T_g 's of tethered and untethered SAN. For all silica content studied, the enhancement of T_g for grafted SAN was observed relative to the cleaved polymer. T_g is strongly dependent on the mobility of the polymer chain segments [14]. It is well known that the addition of a solid filler to a polymer increases the T_g if a strong attractive interactions between

Table 1: Characterization data for the SAN/silica hybrid

SiO_2 (wt%)	SAN/silica Hybrid		GPC analysis		T_g (°C)
	SAN	M_w	M_w/M_n		
5	Free SAN	127.7K	2.55	104.5	
	Tethered SAN ^a	146.7K	3.41	113.4	
7	Free SAN	185.2K	2.75	104.9	
	Tethered SAN ^a	200.5K	3.18	115.6	
10	Free SAN	127.2K	2.44	104.2	
	Tethered SAN ^a	146.6K	2.50	116.7	

^a Surface bound polymer cleaved from the silica nanoparticle surface by etching with aqueous HF (5 %) for 6 h at room temperature.

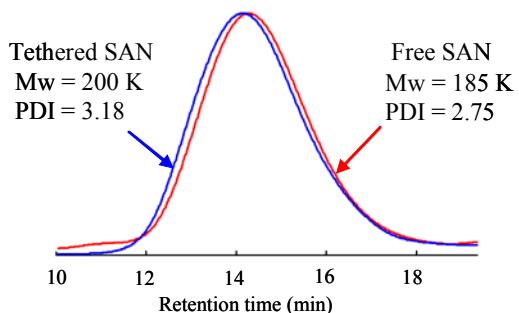


Figure 4: Comparison of GPC traces of tethered SAN and free SAN.

the polymer chain and the solid surface is present [15]. The T_g of SAN/silica hybrid increases significantly from 113.4 °C to 116.7 °C with increasing silica content, while the T_g of free SAN is 104.5 °C. The T_g increase is due to the confinement of SAN chain motion, which is imposed by the covalent bond between SAN and silica particles. The higher the silica content, the larger the restriction of chain motion, and the higher the T_g .

Thermogravimetric analysis of SAN/silica hybrid nanoparticles revealed that the amount of grafted polymer on the silica surface was ca. 81.5 % by mass (Figure 5). Contrary to most published examples where the nanoparticles are the major component (ca. 80~96 wt%), the SAN-silica nanoparticle hybrids in our system consist of 81.5 wt% SAN and 18.5 wt% silica particle. These hybrids are inorganic nanoparticle-modified polymers rather than polymer-modified nanoparticles. On the basis of weight percent of surface bound SAN and SAN molecular weight, we can also calculate a grafting density of 0.15 SAN chains/nm². This result can be compared to the MPTS grafting density of 1.92 MPTS chain/nm² on the silica surface.

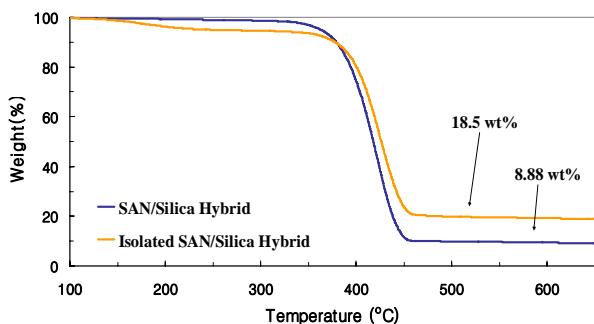


Figure 5: TGA overlay for raw SAN/silica hybrid and isolated SAN/silica hybrid.

4 CONCLUSION

A novel SAN/silica hybrid nanocomposites has been successfully prepared in aqueous media using surface-initiated emulsion polymerization. The resulting nanocomposites demonstrated increased T_g by ca. 10 °C

relative to those of free bulk SAN and showed good silica dispersion regardless of the particle content, because of the grafting and the chain extension due to the steric confinement. The interfacial interaction between the silica and the SAN phases plays a major role in controlling the microstructures and the properties of the composite materials. Further studies will be done to verify the correlation between the morphology and the mechanical properties of the ABS/SiO₂ hybrid nanocomposites.

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