



## Investigation of Nano Silica Ball Core-Poly(Styrene-Acrylonitrile-Methyl Methacrylate) Shell Hybrid Compounds<sup>†</sup>

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Silica core-copolymer shell hybrid compounds have been synthesized by copolymerization of styrene, acrylonitrile (AN) and methyl methacrylate (MMA) on the surface of  $\gamma$ -methacryloxy propyl trimethoxy silane ( $\gamma$ -MPS) modified nano silica ball (NSB). The core-shell materials were characterized by scanning electron microscope, Fourier transform infrared spectroscopy and thermo gravimetric analysis. The results show that the particle size distribution of new core-shell structured materials can be tuned by control of the core and the shell contents. The core-shell hybrid materials can also be adjusted to form the only one single spherical phase with the diameter of 200 nm. The addition of the core-shell hybrid materials to clearcoat enhances the anti scratch property.

**Key Words:** Hybrid nanocomposite, Nano silica ball, Poly(styrene-AN-MMA), Core-shell composite, Clearcoat.

### INTRODUCTION

Organic/inorganic hybrid materials have attracted great interest because they exhibit complementary physicochemical properties<sup>1-3</sup> and can be adjustable through the control of functionality of the components<sup>4,5</sup>. Compared to pure polymers, core-shell hybrid nanocomposites are claimed to exhibit markedly improved properties, such as strength, adhesion, durability, flame retardancy, electrical conductivity, barrier performance, abrasion resistance depending on type and content of nanoparticles used<sup>6-8</sup>. In the present work, we have synthesized new nano silica ball core-poly(styrene-AN-MMA) shell structured materials. The core-shell materials were characterized by SEM, FTIR and TGA. The aim of this study is to systematically investigate the synthetic method of core-shell hybrid materials and understand the application of them to coating fields.

### EXPERIMENTAL

**Synthesis method of nano silica ball core-poly(styrene-AN-MMA) shell hybrid compounds:** The synthesis of hybrid materials was performed in two steps. The colloidal nano silica ball (NSB) particles were synthesized by sol-gel synthesis reported elsewhere (step 1). The colloidal nano silica ball particles with large number of exposed hydroxyl group reacted with  $\gamma$ -MPS *via* hydrolysis, association and conden-

sation process by Stober method<sup>9</sup> to form NSB- $\gamma$ -MPS. Copolymerization of the  $\gamma$ -MPS on nano silica ball with acrylonitrile, styrene and methyl methacrylate monomer was performed at water solvent environment (step 2).

**Step 1:** Synthesis of NSB- $\gamma$ -MPS polymer: 500 mL ethanol was taken in a conical flask. 4 mL ammonium hydroxide was added to ethanol and stirred at room temperature. 30 mL tetraethylorthosilicate (TEOS) was added to above mixture and stirring was continued for 5 h at 450 rpm.  $\gamma$ -MPS was added in four sets changing volume as 5, 10, 15 and 20 mL. The sample was stirred for 12 h at room temperature and then dried at 60 °C.

**Step 2:** Synthesis of nano silica ball core-poly(styrene-AN-MMA) shell hybrid compounds: The polymer of NSB- $\gamma$ -MPS (5 g) was taken in a conical flask and mixed with 150 mL distilled water and 2.2 mL MMA, 2.3 mL styrene, 1.3 mL AN. Heated at 40 °C and stirred at 450 rpm for 0.5 h. Potassium persulfate (0.218 g) and sodium metabisulfite (0.109 g) were dissolved in 15 mL water and added to the above mixture drop wise. The mixture was stirred for 12 h. The polymer product was filtered, washed with distilled water and dried at 60 °C. The materials prepared were given for physicochemical characterization.

**Characterization:** The inorganic core-shell materials were examined on a SEM (FEI Quanta 200) at 25 kV and 20,000 magnifications. Particle size was analyzed by scattering

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method (Malvern Instruments Ltd). The polymeric materials were well characterized by Fourier transform infrared spectroscopy (FTIR, Spectrum GX, Perkin Elmer Co. Ltd.) using KBr self supported pellet technique. The thermo gravimetric (TG) data were obtained from thermo gravimetric analysis (TGA, Mettler TG50 Thermobalance) performed under a nitrogen atmosphere over a temperature range of 20-900 °C at a heating rate of 5 °C/min.

**Application of core-shell compounds to acrylic/melamine automotive clearcoat:** The substrate used throughout experiments was steel panels containing zinc phosphate pretreated layer, electro-coated layer, basecoated layer and clearcoated layer. After application of core-shell compounds to conventional acrylic-melamine clearcoat nano scratch test was conducted. The clearcoat formula for the test was: butyl acetate (5 %): xylene (5 %):tinuvin-400/tinuvin-200 (1.5 %, BASF SE): Setalux 1756W-65 (45 %, Nuplex Co. Ltd.): Setulux 91772SS-60 (20 %, Nuplex Co. Ltd.): Setamine US 138 BB-70 (15 %, Nuplex Co. Ltd.): Batsilon OL-10 (0.5 %, Bayer AG): Solvesso #100 (9%). The scratch resistance of clearcoats was evaluated using by a nano-scratch tester (Open Platform CSM Instruments Co. Ltd., Switzerland)<sup>10,11</sup>. During the test, scratches are made on the sample with a sphere-conical stylus (tip radius 2 μm) which is drawn at a constant speed across the sample, under a constant load or more commonly, a progressive load with a fixed loading rate. For the test, the normal force acting on the clearcoats surface is gradually increased from an initial load of 1.0 mN with a scanning load speed to 30 mN by 1 mm/min for the comparison of relative scratch damages occurring in clearcoats. As the increase of the normal force acting on clearcoat, the point of first fracture (Lc, mN) was compared.

## RESULTS AND DISCUSSION

**Synthesis of nano silica ball:** In the beginning, nano silica ball (NSB) was synthesized by sol-gel process<sup>6</sup>. The polymerization of NSB-γ-MPS and styrene-AN-MMA mixture was performed in two steps to form nano silica ball core-poly(styrene-AN-MMA) shell structured hybrid materials. The colloidal nano silica ball particles with large number of exposed hydroxyl group reacted with γ-MPS *via* hydrolysis, association and condensation process by Stober method<sup>7</sup>. The exposed hydroxyl groups on nano silica ball can react with methoxy groups of γ-MPS to produce NSB-γ-MPS particles during modification. Copolymerization of the γ-MPS on nano silica ball and styrene-AN-MMA mixture yields the hybrid composite. Fig. 1 shows the SEM images of nano silica ball core-poly(styrene-AN-MMA) shell structured hybrid materials synthesized. The average size of nano silica ball was tunable in the range 10-50 nm by the control of sol-gel process. The spherical nano silica ball (30 nm) became 38 nm after the reaction of γ-MPS. Finally, the average size of nano silica ball core-poly(styrene-AN-MMA) shell structured hybrid materials increases to 200 nm. Fig. 2 shows the particle size distribution of nano silica ball core-poly(styrene-AN-MMA) shell hybrid compounds synthesized. After the copolymerization of NSB-γ-MPS and styrene, acrylonitrile and methyl methacrylate one single sphere phase with mean diameter 182.3 nm (width 76 nm) was observed. Fig. 3 shows the TGA thermogram of nano

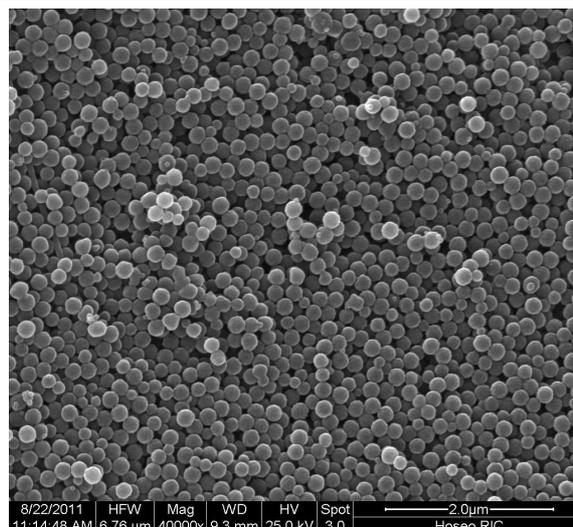


Fig. 1. SEM images of nano silica ball core-poly(styrene-AN-MMA) shell hybrid compounds

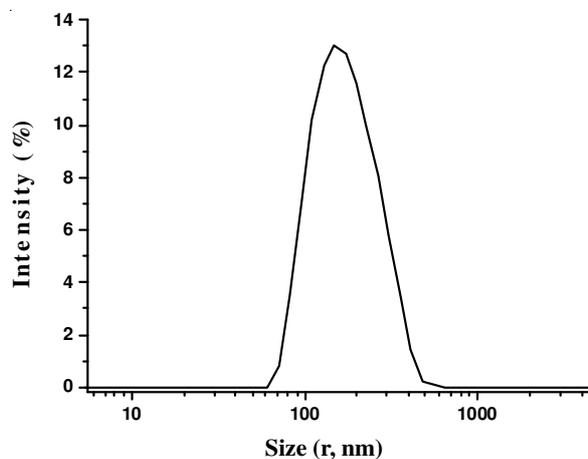


Fig. 2. Particle size distribution of nano silica ball core-poly(styrene-AN-MMA) shell hybrid compounds

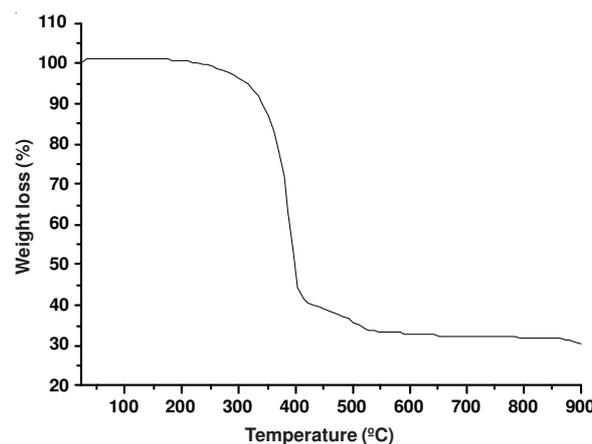


Fig. 3. TGA thermogram of nano silica ball core-poly(styrene-AN-MMA) shell hybrid compounds

silica ball core-poly(styrene-AN-MMA) shell hybrid compounds. As the temperature of nano silica ball sample increases by 5 °C/min from room temperature to 900 °C, the first weight loss observed at 300 °C by 5 % is assigned due to the water or ethanol or ethoxy groups isolated in the matrix and OH groups on the surface. The first weight decrease by 65 % due to

decomposition of copolymer is observed at 300-400 °C. The second weight decrease by 10 % due to decomposition of copolymer is observed at 400-550 °C. Based on the TGA analysis, it is suggested that the organic/inorganic hybrid materials are composed of 30 % nano silica ball inorganic part and 70 % copolymer part. In order to confirm the chemical modifications of the nano silica ball (NSB) surface, the FTIR spectra of nano silica ball and nano silica ball core-poly(styrene-AN-MMA) shell hybrid compound were compared (Fig. 4). After copolymerization, strong absorption bands at 1720, 1494 and 1300  $\text{cm}^{-1}$  are observed. The absorption band at 1720, 1300  $\text{cm}^{-1}$  are attributed to stretching vibrations of C=O and C-O of ester bond in MMA<sup>12</sup>. The band at 1494  $\text{cm}^{-1}$  is attributed to C=C bond vibrations of styrene. The weak bands at 2963 and 2933  $\text{cm}^{-1}$  are assigned to -CH<sub>3</sub> and -CH<sub>2</sub>, respectively<sup>12</sup>. The band at 2250  $\text{cm}^{-1}$  due to nitrile bond is weakly observed. Fig. 5 shows the panoramic images of clearcoats deformed by lateral forces and point of first fracture ( $L_c$ , mN) as the content of core-shell compounds increases to clearcoat. The point of first fracture ( $L_c$ ) increases 16 % from 7.96 to 9.25 mN after application of core-shell compounds by 5 wt % to conventional clearcoat, which indicates the increase of surface hardness and anti scratch property.

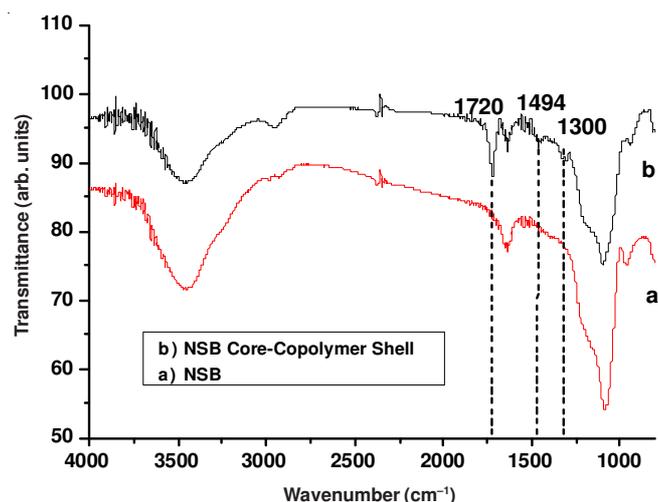


Fig. 4. FTIR of (a) nano silica ball (NSB), (b) nano silica ball core-poly(styrene-AN-MMA) shell hybrid compounds

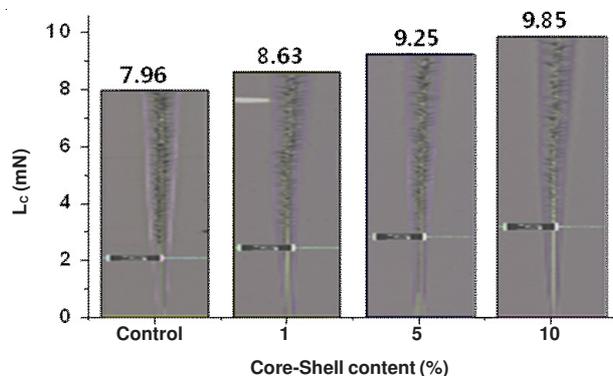


Fig. 5. Panoramic images of clearcoats deformed by lateral forces and point of first fracture ( $L_c$ , mN) as the content of core-shell compounds increases

## Conclusion

Nano silica ball (NSB) core-poly(styrene-AN-MMA) shell hybrid compounds have been synthesized by continuous reaction in order of sol-gel process to form nano silica ball, hydrolysis, association and condensation process to form NSB- $\gamma$ -MPS and copolymerization of NSB- $\gamma$ -MPS and styrene, AN and MMA to form the core-shell hybrid compounds. After the copolymerization one single sphere phase of core-shell compound with mean diameter 182.3 nm (width 76 nm) was observed. Based on the thermogravimetric analysis, we suggest that the organic/inorganic hybrid materials are composed of 30 % nano silica ball inorganic part and 70 % copolymer part.

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