

Synthesis and Characterization of Nanosilica Ball–PMMA Hybrid Composites

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ABSTRACT: Organic–inorganic hybrid materials are one of the most attractive topics, which deals from fundamental researches to practical applications. In the present research, we have studied the polymerization of methyl methacrylate (MMA) on the surface of γ -methacryloxy propyl trimethoxy silane (γ -MPS) modified nanosilica ball (NSB). The polymeric materials were characterized by scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), and thermo gravimetric analysis (TGA). The results show that new core-shell structured materials, NSB core-PMMA shell composites, have been synthesized. The core-shell hybrid materials can be adjusted to form only a single spherical phase. The addition of the core-shell hybrid materials to the clearcoat enhances the surface hardness and antiscratch property. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: nanosilica ball (NSB); methyl methacrylate (MMA); core-shell composite; antiscratch; clearcoat

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INTRODUCTION

Organic–inorganic hybrid materials have attracted great interest for many years because they exhibit complementary physicochemical properties^{1–5} and can be tunable through the control of size or functionality of the components.^{1–10} The organic part in the hybrid materials usually improves the flexibility, whereas the inorganic part is responsible for hardness.^{1,4,5} The modified nanosilica-acrylate composites were found to form crosslinks through UV curing and revealed a distinct improvement in the surface mechanical properties.^{3,11} Mori et al. reported that the complexation of amine modified silica nanoparticles and a weak acidic poly(acrylic acid) caused a pH-responsive property.¹² When thin films formed by spin coating of amine containing colloidal silica and poly(acrylic) hybrid materials, the refractive index was tunable by the silica fraction.⁶ Inorganic coatings produced by gas phase or vacuum deposition onto polycarbonate sheets allow a protective top layer for high density digital versatile disc systems (HD-DVD).¹³ Hybrid glasses based on silyl components and methyl methacrylate, prepared by sol–gel process, showed an increase of the elastic modulus and hardness values by increasing the inorganic content.¹⁴ The research regarding the building applications of polyacrylate/silica nanocomposite has been spotlighted since the uniform dispersal of nano-SiO₂ in the polymer can improve the strength and the climate-resistance of the polymer materials.^{10,15}

Polymer latexes with inorganic components can be used in a wide variety of applications such as paints, inks, adhesives, cosmetics, flame retardants, and papers.^{15–18} Particularly, the complexation of polymethyl methacrylate (PMMA)/silica materials has been widely studied because the hybrid materials can be applicable to electronic devices, high refractive index materials, electroluminescent materials, solar cells, and thin film transistors.^{19–25} Understanding of the structures and dynamics of polymer–silica interfaces should aid the design of materials with improved mechanical and optical properties.^{21–25} Compared to pure polymers, polymeric nanocomposites are claimed to exhibit markedly improved properties, such as modulus, strength, stiffness, flame retardancy, dimensional stability, electrical conductivity, barrier performance, solvent and heat resistance, wettability, and dyeability depending on the type and content of nanoparticles used.^{19–26}

The basecoat/clearcoat systems for vehicles were introduced in the early 1980s. The clearcoat is the coating layer that forms the last interface against the environment. It carries the biggest part of the technical performance and must be able to resist environmental mar caused from acid rain, bird droppings, and car wash machines. The clearcoat in combination with the basecoat forms the automotive topcoat, which gives the vehicle its appearance. The driving forces for clearcoat development

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are cost of material and process, appearance, etch, and scratch resistance and the environmental footprint. Many studies have, therefore, been carried out to increase performances of such clearcoats when they are exposed to aggressive and harsh conditions. Such conditions are usually simulated in the laboratory and are known as accelerated physical and chemical aging tests.^{24–27} Scratch resistance is considered as the most important criterion for ranking the performances of basecoat/clearcoat automotive paint systems. Nanosized-alumina, -titania, -ceria and -silica materials are applied to clearcoats to increase scratch resistance of the vehicle.^{27–31} Recently, we reported that inorganic–organic hybrid materials such as vinyl-nano-sized silica ball increase the glossy retain effect in the acrylic-melamine clearcoats.²⁷ In the present work, we have synthesized core-shell hybrid materials using nanosilica ball (NSB), γ -methacryloxy propyl trimethoxy silane (γ -MPS) and methyl methacrylate (MMA). Even though PMMA provides excellent optical property and compatibility with the conventional acryl-melamine clearcoats, there is no direct covalent linkage between NSB and PMMA. So, γ -MPS was introduced as a chemical binder between NSB and MMA.^{6,26} The polymeric materials were characterized by scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), and thermo gravimetric analysis (TGA). The aim of this study is to systematically investigate the synthetic method of core-shell hybrid materials and to access the enhancement of scratch resistance in clear coating material for the clear coating materials.

EXPERIMENTAL

Synthesis Method of NSB- γ -MPS-PMMA Core-Shell Complexes

Commercially available ethanol (Samchun pure chemicals, Korea), ammonium hydroxide, γ -methacryloxy propyl trimethoxy silane (γ -MPS, Dow Corning), tetraethylorthosilicate (TEOS, Aldrich), MMA (Aldrich), potassium persulfate ($K_2S_2O_8$, Aldrich) and sodium metabisulfite ($Na_2S_2O_5$, Aldrich) are used without further purification. All the chemicals used are of analytical grade.

Step 1: Synthesis of NSB- γ -MPS in ethanol solution

- 500 mL ethanol was taken in a conical flask.
- 4 mL ammonium hydroxide was added to ethanol and stirred at room temperature.
- 30 mL TEOS was added to above mixture and stirring was continued for 5 h at 450 rpm.
- γ -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 NSB- γ -MPS-MMA in water solution

- The polymer of NSB- γ -MPS (10 g) was taken in a conical flask and mixed with 150 mL distilled water and 17.12 mL MMA. Heated at 40°C and stirred at 450 rpm for 30 min. 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–organic hybrid materials were examined with SEM (FEI Quanta 200) at 25 kV and 20,000 magnifications. Particle size was analyzed by the scattering method (Malvern Instruments). The polymeric materials were well characterized by Fourier transform infrared spectroscopy (FTIR, Spectrum GX, Perkin Elmer) 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⁻¹.

Scratch Test

The scratch resistance of the clearcoats was evaluated using a nanoscratch tester (Open Platform CSM Instruments, Switzerland) and Amtec-Kistler car-wash tester (Amtec, Germany).^{32,33} The nanoscratch testing method is a reproducible quantitative technique in which critical loads at which failures appear are used to compare the cohesive and adhesive properties of coatings. During the test, scratches are made on the sample with a sphero-conical stylus (tip radius 2 μ m) 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. Sphero-conical stylus is available with different radii which describes the “sharpness” of the stylus. Common radii are from 1 to 20 μ m for nanoscratch tests. 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⁻¹ for the comparison of relative scratch damages occurring in clearcoats. To acquire the real surface topology of clearcoat samples, a prescan method using the same probe, prior to the regular scratch test was conducted. A prescan with a scanning load of 1 mN ensures the real penetration depth (Pd) of the surface by subtracting the initial surface profile from the loaded scratch scan profile. A postscan with a scanning load of 1 mN observes the topographical pattern of the residual depth (Rd) in the damaged surface after the scratch test. Two samples, the conventional acryl-melamine clearcoat and 5 wt % of NSB- γ -MPS-PMMA-loaded acryl-melamine clearcoat (Sample A), are compared by the terms of the scratch test, gloss differences, pencil hardness of the surfaces, and penetration depth. The nanoindenter probe of sphero-conical 90° with an indenter radius of 2 μ m was used. The formulation of the conventional acryl-melamine clearcoat was described as: Butyl acetate (5%): Xylene (5%): Tinuvin-400/Tinuvin-200 (1.5%, BASF SE): Setalux 1756W-65 (45%, Nuplex): Setulux 91772SS-60 (20%, Nuplex): Setamine US 138 BB-70 (15%, Nuplex): Batsilon OL-10 (0.5%, Bayer AG): Solvesso #100 (9%).

RESULTS AND DISCUSSION

Synthesis of NSB- γ -MPS-PMMA Hybrid Complex

Nanosilica ball (NSB) was first synthesized by sol-gel process.²⁷ The procedure to prepare hybrid inorganic–organic compounds from the colloidal NSB is schematically shown in Figure 1. The polymerization of NSB- γ -MPS-MMA was performed in two

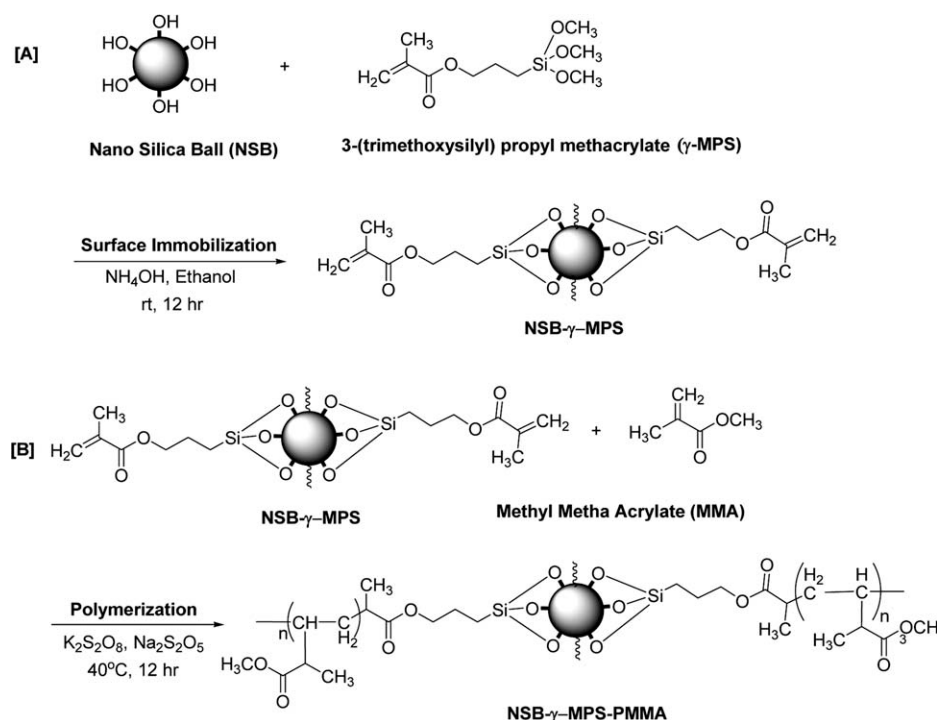


Figure 1. Schematic procedure for preparing the NSB- γ -MPS-PMMA hybrid complexes.

steps. The colloidal NSB particles with large number of exposed hydroxyl group reacted with γ -MPS via hydrolysis, association, and condensation process by Stober method.³⁴ The exposed hydroxyl groups on NSB can react with methoxy groups of γ -MPS to produce NSB- γ -MPS particles during modification (Step A in Figure 1). The surface Si—OH groups in NSB are multifunctionalized by introduction of vinyl groups in the Step A. The copolymerization of the γ -MPS on NSB and MMA yields the hybrid composite (Step B in Figure 1). Figure 2 shows the SEM images of NSB- γ -MPS for various weight ratios of its constituents. The average size of NSB was tunable in the range 10–50 nm by the control of sol–gel process.²⁷ The size of the spherical NSB could increase from of 30 nm up to 38 nm after the reaction with γ -MPS [Figure 2(c)]. When γ -MPS was overloaded (NSB : γ -MPS = 1 : 2), NSB was completely covered with γ -MPS, forming aggregates [Figure 2(d)]. The amount of incorporated γ -MPS corresponded to an average γ -MPS shell thickness (2–10 nm on the parent silica sphere of 30 nm in diameter). Because the density of silica (2.05 g cm^{-3}) is much bigger than that of γ -MPS (1.12 g cm^{-3}),²⁴ the shell thickness is somewhat thicker than that obtained by calculation. Figure 3 illustrates the SEM images of NSB- γ -MPS-PMMA obtained by the reaction of MMA (17.12 mL) with NSB- γ -MPS of various weight ratios (NSB : γ -MPS = 1 : 0.5, 1 : 1, 1 : 2, and 1 : 4). The average diameter of NSB- γ -MPS-PMMA increased to 391.5 nm for the case of NSB : γ -MPS = 1 : 1 [Figure 3(b)]. Huang and Qui suggested that the transparent phase of NSB- γ -MPS-PMMA can be prepared by *in situ* sol–gel process.²⁵ The SEM images of NSB- γ -MPS-PMMA, shown in Figure 3, suggest that two different phases, a spherical phase and an aggregate phase, can exist. Therefore we suggest that spherical NSB- γ -MPS can

be encapsulated with PMMA to form NSB- γ -MPS core PMMA shell structured hybrid complex having a single spherical phase at the specific reaction condition even though the interior

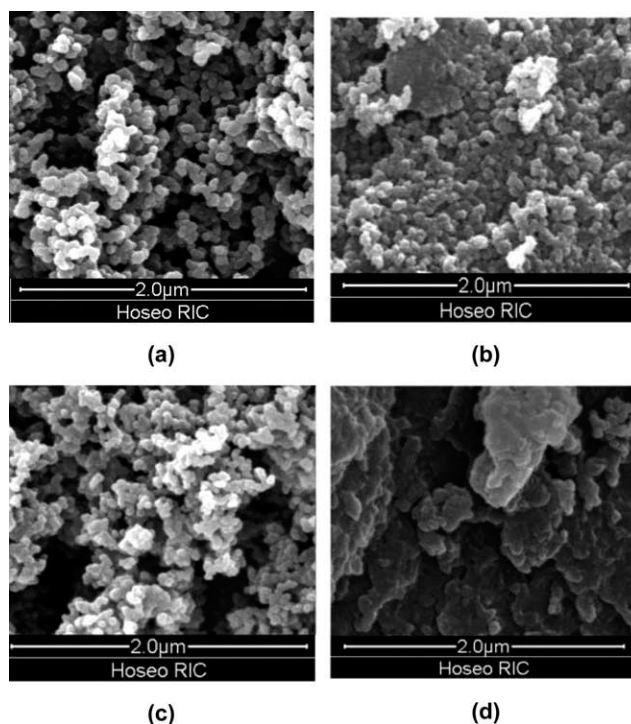


Figure 2. Scanning electron microscopy images of NSB : γ -MPS wt % ratio as (a) 1 : 0, (b) 1 : 0.5, (c) 1 : 1, and (d) 1 : 2.

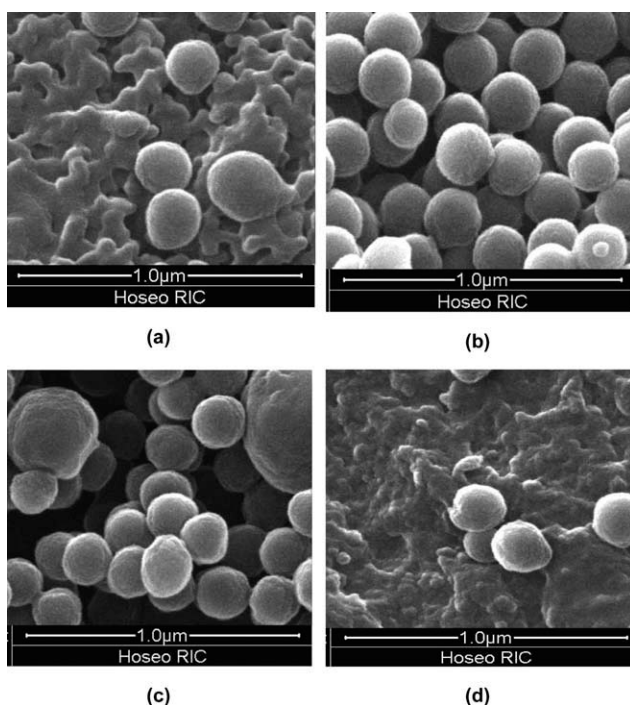


Figure 3. Scanning electron microscopy images of NSB : γ -MPS-PMMA formed by the reaction of MMA with (a) NSB : γ -MPS = 1 : 0.5, (b) NSB : γ -MPS = 1 : 1, (c) NSB : γ -MPS = 1 : 2, and (d) NSB : γ -MPS = 1 : 4.

structure of the composites has not been fully characterized. The yields of the obtained NSB- γ -MPS and NSB- γ -MPS-PMMA were about 96.5 and 66.8%, respectively. To understand the morphology of the hybrid samples, particle size analysis was conducted (Figure 4). The average diameter of colloidal silica synthesized by sol-gel process was 15.9 nm (width 9.6 nm). When γ -MPS was anchored on NSB, the diameter increased to 32.2 nm (width 14.6 nm), indicating the formation of the organic-inorganic hybrid complex. After the polymerization of NSB- γ -MPS and MMA, a single sphere phase of diameter 391.5 nm (width 49.3 nm) was observed. Both SEM and particle size analyses confirm that the core-shell structured NSB- γ -MPS-PMMA of a single spherical phase can be synthesized. Because our research focuses on the synthesis of core-shell hybrid materials, the development of rapid and sensitive methods to synthesize them with one single phase is of great significance.

Characterization of NSB- γ -MPS-PMMA Hybrid Complex

The FTIR spectra of NSB, NSB- γ -MPS, and NSB- γ -MPS-PMMA were compared in Figure 5 to confirm the chemical modifications of the nanosilica ball (NSB) surface. The adsorption band around 2960 cm^{-1} corresponds to the stretching vibrations of the C-H bond in the alkyl group of γ -MPS and methyl methacrylate.³⁴⁻³⁶ The bands at 1720 and 1638 cm^{-1} are attributed to the stretching vibrations of the C=O and C=C bonds, respectively, both in MPS and in methyl methacrylate.³⁶ The bands at 1458 and 1130 cm^{-1} are associated with the deformation vibrations of the C-H bond in CH_2 and CH_3 groups. The three shoulders between 1130 and 1458 cm^{-1} are associated

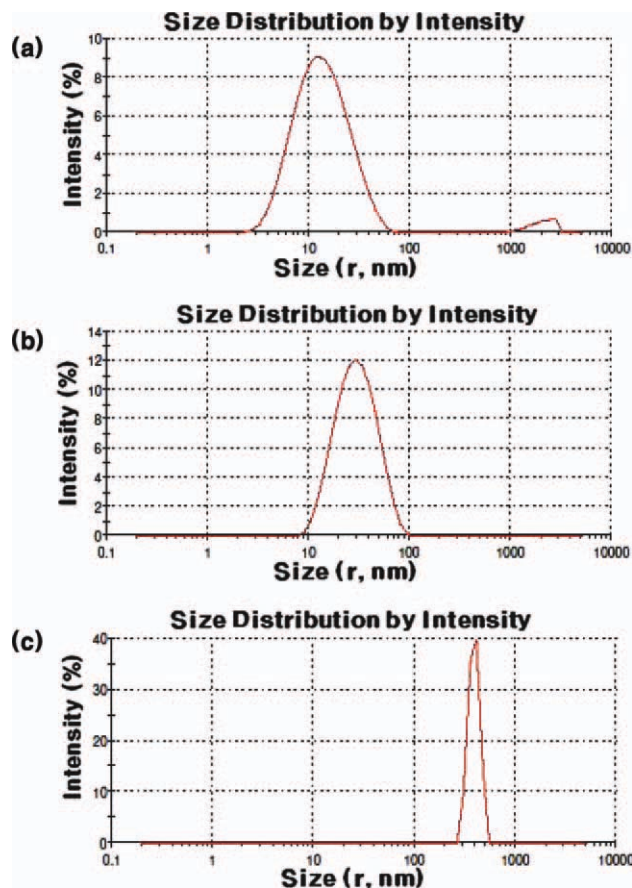


Figure 4. Particle size distribution of (a) nanosilica ball (NSB) (15.6 nm), (b) NSB- γ -MPS (32.2 nm), and (c) NSB- γ -MPS-PMMA (391.5 nm). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to the asymmetric and symmetric vibrations of the C—O and C—O—C bonds.³⁶ During the synthesis of NSB- γ -MPS-PMMA, the enhanced intensity of the C=O peak at 1720 cm^{-1} and the

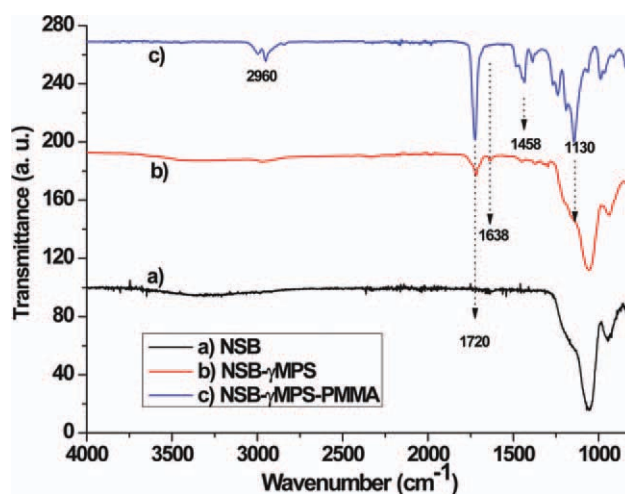


Figure 5. FTIR spectrum of (a) nanosilica ball (NSB), (b) NSB- γ -MPS, and (c) NSB- γ -MPS-PMMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reduced intensity of C=C peak at 1638 cm^{-1} indicate the copolymerization between MPS and MMA. Thermo gravimetric analysis was performed to clarify the thermal degradation behaviors of the chemically modified silica balls. As the temperature of NSB sample was increased by 5°C min^{-1} from room temperature to 900°C , weight loss of 15% was observed [Figure 6(a)]. The 5% weight loss from room temperature to 200°C is probably due to water or ethanol. The other 10% weight loss is associated with unknown organics, probably unreacted organic components in NSB. Ford et al. suggested the parent colloidal silica has ethoxy groups isolated in the matrix and OH groups on the surface.^{16,24} They explained, based on the analysis of magic angle spinning (MAS) NMR spectroscopy and elementary analysis, that hydrolysis of the tetraethyl orthosilicate was incomplete and produced colloidal silica particles contains ethoxy group ($-\text{OC}_2\text{H}_5$).²⁴ NMR spectroscopy and elementary analysis.²⁴ Ni and coworkers explained that 180°C heat treatment causes further condensation on the basis of observation of infrared spectra and thermo gravimetric analysis.⁹ After the modification of NSB by γ -MPS, about 30% weight loss associated with the dissociation of γ -MPS was observed between 380 and 500°C [Figure 6(b)]. Figure 6(c) shows the TG graph of NSB- γ -MPS-PMMA. The weight loss of $>90\%$ was observed at below 400°C and the weight loss was from the dissociation of PMMA.^{16,24}

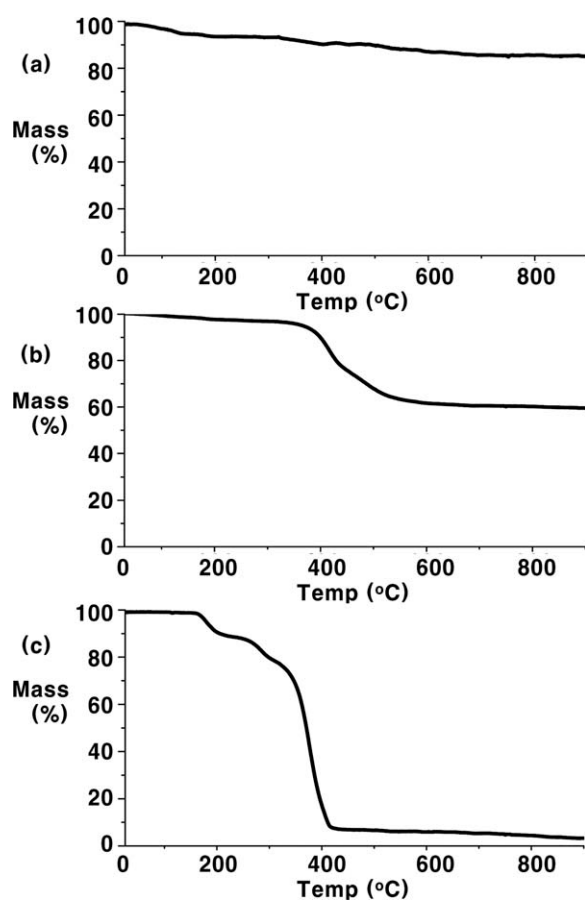
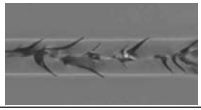


Figure 6. TGA thermograms of (a) nanosilica ball (NSB), (b) NSB- γ -MPS, and (c) NSB- γ -MPS-PMMA.

Table I. Nanoscratch Test After Application of NSB- γ -MPS-PMMA (5 wt %) into Conventional Acryl-Melamine Clearcoat System

	Conventional clearcoat	Sample A
Content of NSB(%)	0	5
Initial gloss	90.8	90.6
Gloss retention after nanoscratch test(%)	74	79
Pencil hardness	B	HB
Penetration depth (μm)	9.15	5.20
Surface topology		

Application of NSB- γ -MPS-PMMA Hybrid Complex

The NSB- γ -MPS-PMMA hybrid materials have been extensively applied for specific optical fields. The composite films prepared from monodispersed colloidal silica and PMMA have been applied to narrow bandwidth optical filters.^{20–24} For the application of silica-PMMA particle to optical field, colloidal silica size larger than 150 nm is required to diffract the light. Hse et al. synthesized transparent silica-PMMA nanocomposite films, by the copolymerization of MMA and alkylglycidyl ether functionalized silica particles on a glass plate, in a spin-coating process.²⁶ The film having silica contents higher than 70% increased the surface hardness up to 9H grade. Meng et al. reported that unmodified silica nanoparticles had poor dispersibility and cause harmful coating defects, whereas surface modified silica nanoparticles by γ -MPS enhanced dispersibility and improved the antiscratching properties. Table I shows the results of nanoscratch test after application of NSB- γ -MPS-PMMA (5 wt%) into the conventional acryl-melamine clearcoat system. Pencil hardness test is a standard industrial method which can roughly evaluate the short term scratch resistance of the nano-coating. The pencil hardness increased from B to HB after adding 5 wt % of NSB- γ -MPS-PMMA to the conventional acryl-melamine clearcoat system. The addition of NSB- γ -MPS-PMMA causes a decrease of penetration depth from 9.15 to $5.20\ \mu\text{m}$, which also indicates the increase of surface hardness. Although the surface topology captured by the conventional microscope equipped with nanoscratch tester were not distinctly discerned due to similar fracture patterns, from the combined measurements of pencil hardness and penetration depth, it turned out to be enhanced the scratch resistance of the Sample A. Therefore, it is suggested that increasing surface hardness inhibit the penetration of scratching objects into clearcoats and hence prevent scratches.

CONCLUSIONS

NSB core-PMMA shell composites, NSB- γ -MPS-PMMA, have been synthesized by continuous sequential reactions of sol-gel process to form NSB; hydrolysis, association, and condensation process to form NSB- γ -MPS; and copolymerization of NSB- γ -MPS and MMA to form the core-shell hybrid compounds. Based on the SEM images and TG analyses of NSB- γ -MPS-PMMA, it is

suggested that NSB- γ -MPS core PMMA shell structured hybrid complex with a single spherical phase can be synthesized at the specific reaction condition. The addition of the core-shell hybrid materials to the conventional acryl-melamine clearcoat system enhances the surface hardness and inhibits the penetration of scratching objects into clearcoats and hence prevents scratches.

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