Anti-scratch Properties of Clearcoat after Application of Polymer Coated Silica Ball†

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Organic/inorganic hybrid materials such as core-shell hybrid nanocomposites have attracted great interest in automotive industry since they can be adjustable through the control of functionality of the components and exhibit markedly improved durability on outdoor weather and scratch. We have synthesized nano silica ball, γ-methacryloxy propyl trimethoxy silane modified nano silica ball (NSB-γ-MPS), nano silica ball core-polymethylmethacrylate shell hybrid complex (NSB-PMMA) and nano silica ball core-poly (MMA-AN-styrene) shell structured materials (NSB-MAS) and applied to conventional clearcoat and compared the anti-scratch properties by nano scratch tester.

Key Words: Nano silica ball, Nano scratch, Clearcoat, Polymer coating, Core-shell composite.

INTRODUCTION

The vehicle industry uses a multilayer coating system that is one of the most technologically complex coating processes composed of electrical deposition coating, basecoat and clearcoat[1-3]. The most important requirements of car coatings are colour, gloss, mar and scratch resistance. The clearcoat is the coating layer that forms the last interface to the environment[3]. Even though many progresses regarding on gloss and scratch resistance in automotive painting field have been accumulated, anti-scratching of clearcoating layer in various coating layer is still remaining to be studied[3-7]. An excellent scratch resistance and environmental etch resistance of silane based clearcoat led to their acceptance as topcoats for eight of the 10 top selling vehicles since 2000, including Ford Taurus, Toyota Camry and Honda Civic[2]. Recently, addition of organic-inorganic hybrid materials to clearcoat have been spotlighted since the organic component is related to flexibility and compatibility with clearcoat and inorganic component improves the anti-scratch properties[8-11]. We have synthesized nano silica ball, γ-methacryloxy propyl trimethoxy silane modified nano silica ball (NSB-γ-MPS), nano silica ball core-polymethyl-methacrylate shell hybrid complex (NSB-PMMA) and nano silica ball core-poly (MMA-AN- styrene) shell structured materials (NSB-MAS) and applied to conventional clearcoat and compared the anti-scratch properties by nano scratch tester[12-15].

EXPERIMENTAL

Nano silica ball (NSB) was synthesized by the hydrolysis and condensation of tetraethylorthosilicate (TEOS)[12]. The colloidal nano silica ball particles with large number of exposed hydroxyl group reacted with γ-methacryloxypropyltrimethoxy silane (γ-MPS) *via* hydrolysis, association and condensation process by Stober method[13] to form NSB-γ-MPS. Polymerization of methyl methacrylate in water solution was conducted by the polymerization of γ-MPS at the surface of NSB-γ-MPS with MMA to form NSB-PMMA[14]. Copolymerization of the γ-MPS on nano silica ball with acrylonitrile, styrene and methyl methacrylate monomer was performed at water solvent environment to form NSB-MAS[15].

Application of core-shell compounds to acrylic/melamine automotive clearcoat: The substrate used throughout experiments was steel panels containing zinc phosphate pretreated layer, electrical deposition coating layer, basecoated layer and clearcoated layer. After application of core-shell compounds to conventional acryl-melamine clearcoat nano scratch test was conducted. Table-1 shows the clearcoat composition used for the experiment. The formulation of the crosslinking network inside the clear coat samples was induced by the polycondensation reaction between the hydroxyl functional groups in the acrylic resin and the amino crosslinking agents in the melamine resin under curing temperature between 140 and 150 ºC.

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TABLE-1
COMPOSITION OF CLEARCOAT WITHOUT
SILANE MODIFIED COMPOUNDS

Components	Maker	Content (%)
Butyl acetate	Aldrich	5.0
Xylene	Aldrich	4.0
Tinuvin-400/Tinuvin-200	BASF SE	1.5
Setalux 1756W-65	Nuplex Co. Ltd.	45.0
Setalux 91772SS-60	Nuplex Co. Ltd.	20.0
Setamine US 138 BB-70	Nuplex Co. Ltd.	15.0
Baysilon OL-100	Bayer AG	0.5
Solvesso #100	Exxon Mobil	9.0

Transmittance of clearcoat before and after application of additives: In the beginning, 1 g of four samples (NSB, NSB-γ-MPS, NSB-PMMA and NSB-MAS) was dissolved to 200 mL of ethyl acetate with 1 g of HS-dispersant (amine functionalized carboxylic acid typed dispersant, Shinheung Advanced Materials, Korea) for 3 h. The samples were loaded into the clearcoat by 5 wt %. Therefore, the actual loading of samples to the clearcoat was 0.025 wt %. For the observation of transmittance by UV-VIS spectrophotometer (Perkin Elmer Lamda-950), the samples and reference clearcoat were loaded to glass plate. Transmittance of the clearcoating layer of the samples on the glass plate was observed and compared.

Nano scratch test: The scratch resistance of clearcoats was evaluated by a nano-scratch tester (Open Platform CSM Instruments Co. Ltd., Switzerland). The test method is known to be 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 nano scratch test, scratches can be observed 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 was gradually increased from an initial load of 1.0 mN to the end load of 30 mN. The scanning load was 1mN and the scan speed was 2 mm/min. As the increase of the normal force acting on clearcoat, the point of first fracture was observed. The first scratch occurring on the surface is called to be the point of first fracture (L_c, mN).

RESULTS AND DISCUSSION

Fig. 1 shows the SEM images of nano silica ball, NSB-γ-MPS, NSB-PMMA and NSB-MAS synthesized. The average diameter of the samples gradually increases as the polymer anchor to the surface of spherical nano silica ball (Table-2). Based on the SEM images, nano silica ball core-polymer shell hybrid compounds synthesized have a single spherical phase and have quite narrow particle size distribution. The size of the spherical nano silica ball could increase from 54 nm up to 60 nm after the reaction with γ-MPS (Fig. 1b). The amount of incorporated γ-MPS corresponded to an average γ-MPS shell thickness (6 nm on the parent silica sphere of 54 nm in diameter). Since the density of silica (2.05 g/cm^3) is much bigger than that of γ-MPS (1.12 g/cm^3), the shell thickness is somewhat thicker than that obtained by calculation. After the polymerization of NSB-γ-MPS and MMA, a single sphere phase of diameter 168 nm (width 43 nm) was observed. Both

SEM and particle size analyses confirm that the core-shell structured NSB-PMMA of a single spherical phase can be synthesized. After the copolymerization of NSB-γ-MPS and styrene, acrylonitrile and methyl methacrylate, one single sphere phase with mean diameter 198 nm (width 53 nm) was observed. Since 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. After loading of samples to the clearcoat by 5 wt % (actual solid content 0.025 wt %), the transmittance by UV-VIS spectrophotometer of all samples were 100 %. Therefore, reduction of transparency after loading of core-shell hybrid compounds was not observed even though the nano particles were added to clearcoat.
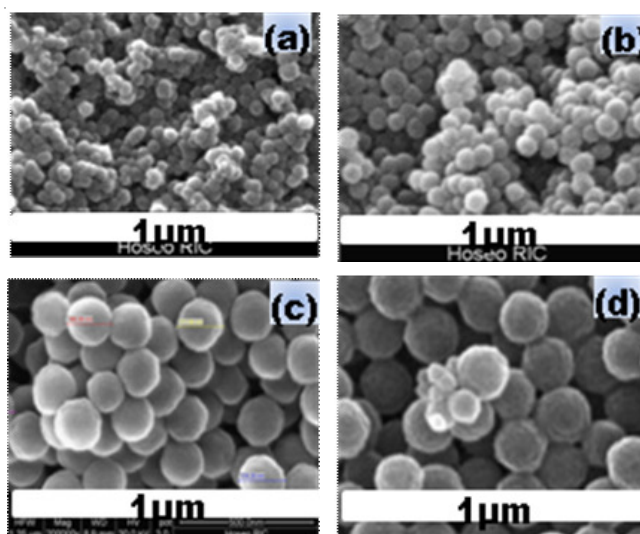

Fig. 1. SEM images of (a) NSB, (b) NSB-γ-MPS, (c) NSB-PMMA and (d) NSB-MAS

TABLE-2
PARTICLE SIZE DISTRIBUTION OF SAMPLES

Sample	(a) NSB	(b) NSB-γ-MPS	(c) NSB-PMMA	(d) NSB-MAS
Average diameter (nm)	54	60	168	198
Width (nm)	21	28	43	53

Fig. 2 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) of clearcoat without silane modified compounds was 7.96 mN. The L_c increases 12 % from 7.96 to 8.92 mN after formation of NSB-γ-MPS. When NSB-γ-MPS is applied to clearcoat, the first fracture point, L_c increases 12.7 % from 7.96 to 8.97 mN. The first fracture point increases by 16.2 % from 7.96 to 9.25 mN after application of NSB-MAS by 0.025 wt % addition, which indicates the increase of surface hardness and anti-scratch property.

Conclusion

Nano silica ball, NSB-γ-MPS, NSB-PMMA and NSB-MAS are synthesized. The average diameter of the samples gradually increases as the polymer anchor to the surface of spherical nano silica ball. Based on the SEM images, nano silica ball core-polymer shell hybrid compounds synthesized
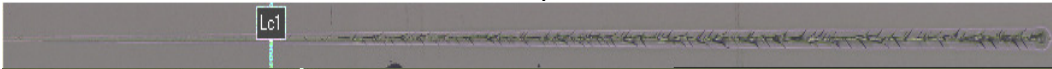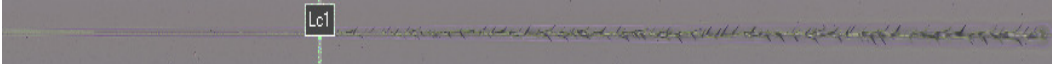
Sample	Panorama pictures	L_c [mN]
(a)		7.96
(b)		8.92
(c)		8.97
(d)		9.25

Fig. 2. After nano scratch test, panorama pictures and the point of first fracture (L_c, mN) of (a) clearcoat control and after addition of (b) NSB-γ-MPS, (c) NSB-PMMA and (d) NSB-MAS to clearcoat control by 0.025 wt %, respectively

have a single spherical phase and have quite narrow particle size distribution. When the samples are loaded to conventional clearcoat by 0.025 wt %, no reduction of transparency is observed. Based on the nano scratch test results, we suggest that the scratch resistance can be increased by application of NSB-PMMA or NSB-MAS to clearcoat.

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