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Studying the role of polysiloxane additives and nano-SiO_2 on the mechanical properties of a typical acrylic/melamine clearcoat

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ABSTRACT

Effects of conventional polysiloxane additives and nano-SiO_2 on the mechanical properties of an automotive acrylic/melamine clearcoat (CC) are studied. Clearcoats formulations were prepared by addition of different concentrations of polysioloxane additives (with different modifications) and hydrophobic nano-SiO_2 particles. Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) and atomic force microscope (AFM) were utilized to evaluate the effects of nano-SiO_2 and polysiloxane additives on the surface properties of the CCs. The mechanical properties of the surface and the bulk of the CCs were studied by nano-indentation and tensile tests, respectively. Results showed that polysiloxane additives can mostly affect the mechanical properties of the surface of the CC. Additives with shorter side chains and therefore higher surface activity caused higher changes on the surface properties the CC. Unlike conventional polysiloxane additives, the nano-SiO_2 particles mainly influenced the mechanical properties of the bulk of the CC.

1. Introduction

Automotive clearcoats are used to produce automobile glossy. However, the appearance of the coating will be spoiled in exposure to environmental condition at long exposure times [1–4]. Mar and scratch are two most important kinds of physical damages which can significantly influence the appearance of the topcoats [5–8]. It has been become increasing customers concerns in recent years. These kinds of mechanical damages occur within a few micrometer of the surface of the clearcoat. Carwashing, keys, fingernails and branches are the most important causes of mar and scratch [8–16]. The morphology and dimension of mar and/or scratch are the most important parameters affecting the appearance of CC. Many parameters can affect the size and morphology of the scratch and/or mar [11–17]. Because of this, they seem complex in their behaviors. The mechanical properties of the CCs can significantly influence the morphology and size of damages. When an automotive clearcoat is exposed to an external force, there would be three different responses: elastic deformation, plastic deformation and fracture deformation. It has been found that the fracture type scratch can influence the visual performance of the CC more than other kinds of deformations. Moreover, the plastic type scratch is a self-healable kind of damage [16–19].

Attempts have been carried out to improve the scratch and/or mar resistance of the CCs by improving their mechanical properties. Both the mechanical properties of the bulk and/or the surface of the CCs are important parameters affecting the coating performance in exposure to the mechanical stresses. Therefore, the mechanical properties of the bulk and/or surface of CC will control the final performance of the coating. Changing the chemical structures of CC may guarantee the modification of the mechanical properties of the coating [19]. However, it may incur unwanted adverse effects on other properties of the clearcoat.

There have been progressive demands for producing automotive coatings with higher outdoor durability. The mechanical properties of the CC can be improved using surface active additives with the lowest creation of unwilled defects in the CC matrix. Polysiloxane additives are the most important kinds of additives with capability of improving the viscoelastic properties of the surface of the CC. Polysiloxane additives contains $-(CH_3)_2-SiO-$ groups in their structure. Because of this, these additives are surface active additive (with low surface energy) with high capability of migration to the surface of the clearcoat [20]. However, depending on the chemical structure of the additives, they may improve the bulk and/or the surface properties of the CC. Some additives migrate to the surface of clearcoat whilst others remain in its bulk [21,22,16,23]. Mechanistically, additives may increase the hardness and the surface slippage of the CC. It is well known that polysiloxane additives are

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capable of decreasing the surface energy of the CC. They also can considerably influence the mechanical properties of the surface of CC. The chemical structure of the additives can directly influence the additives properties. Different parameters including the side chains length and the chemistry of end groups of the additives may influence the surface activity of the additives [20,16].

In recent years nanomaterials have been widely used to improve the mechanical properties of the CC. Nano-SiO_2, nano-Al_2O_3, nano-ZnO and nano-TiO_2 are some of the most important kinds of the nanomaterials [19,23–26]. These nanomaterials, due to their low particle size and high surface area, are capable of improving the mechanical properties of the CC. They can produce less negative effects on the appearance of the CC compared to the micro sized materials. Different parameters including the size, chemistry and surface modification of the particles may influence the interactions among nanoparticles and CC matrix. It seems that nanoparticles and conventional polysiloxane additives can affect the mechanical properties of the CCs by different mechanisms [23–26].

This study deals with studying the effects of conventional polysiloxane additives and nano-SiO_2 on the mechanical properties of an automotive CC. It has been aimed to investigate the mechanism which each polysiloxane additive or nanoparticles may influence the mechanical properties of the coating. Two techniques including nano-indentation and tensile tests were utilized to evaluate the effects of polysiloxane additives and nano-SiO_2 on the mechanical properties of the surface and bulk of the CC.

2. Experimental

2.1. Sample preparation

Acrylic/melamine (with acrylic to melamine ratio of 75:25) based automotive clearcoats were purchased from Rangafarin Co. (Iran). Attempts have been carried out to investigate the effects of conventional polysiloxane additives and nano-SiO_2 on the mechanical properties of the clearcoats. The chemical composition and specific information devoted on each additive are represented in Table 1.

Different concentrations of Si-1 (polydimethylsiloxane (polyether modified), Efka-3288), Si-2 (polydimethylsiloxane (Fluorocarbon modified), Efka-3034), and Si-3 (polydimethylsiloxane (polyether modified), Byk-333) were separately added to the clearcoats. Mechanical mixing was performed the clearcoats at 2000 rpm for 20 min. Pre-dispersed nano-SiO_2 (dispersed in methoxypropylacetate and methoxypropanol 6/1) (Byk-3650) with solid content and average size of 40% and 40 nm was purchased from BYK Co. High shear mixer (at 2000 rpm for 30 min) was performed the CCs containing different loadings of the nanoparticles. The particles dispersion and also stability in the clearcoat matrix have been previously studied by turbidimetry studies [19]. It was found that using nanoparticles up to 5 wt% cannot influence the clarity of the clearcoat indicating appropriate particles dispersion and good stability in the clearcoat matrix at these concentrations. However, using nanoparticles at 6 wt% caused decrease in coating clarity indicating particles aggregation.

Table 1
Sample coding and additives concentrations.

Additive type	Additive content (wt%)				
	No additive	*a*	*b*	*c*	*d*
Si-1	0.0	0.10	0.20	0.25	0.40
Si-2	0.0	0.18	0.26	0.34	0.50
Si-3	0.0	0.10	0.20	0.25	0.40
Nano	0.0	1.25	2.5	3.75	6.0

2.2. Coatings application

It has been aimed to evaluate the clearcoats properties on a fully coated automotive system. The steel sheets of D7-21.2 type, 1.2 mm thick (with dimensions of 0.2 cm × 10 cm × 20 cm), were purchased from Foolad Mobarake Co. Steel substrates were pre-treated in a bath containing three-cationic phosphating conversion coating (supplied by Irankhodro Co.). The phosphated steel substrates were coated by a cationic water-borne electrodeposition coating (ED) containing an amine-modified epoxy resin supplied by PPG. The ED coated samples were then finished by a primer surfacer, followed by curing at 140 °C for 20 min. The surfacer layer was based on a mixture of a saturated polyester resin and melamine cross-linking agent at 70:30 (wt/wt) ratio, on top of which a black basecoat layer was applied, followed by application of a clearcoat layer through a wet-on-wet method. Samples then were cured at 140 °C for 20 min.

The clearcoats were also applied over the surface of the cleaned glass sheets using a film applicator (with a DFT (dry film thickness) of 45–50 μm). Samples then were cured at 140 °C for 20 min. The free films of each clearcoat were prepared from the glass sheets after the curing. This was done by immersing coated glass sheets in water at 40 °C for 30 min.

2.3. Characterization

2.3.1. Study of clearcoats surface characterization

ATR-FTIR analysis was performed the CCs to evaluate the surface composition of the clearcoats. The test was carried out by a CANADA BOMEN ATR-FTIR. The effects of additives and nanoparticles on the morphology of the surface of the clearcoats were studied by Nanoscope III, equipped by atomic force microscope (AFM).

2.3.2. Mechanical properties measurements

The mechanical properties of the clearcoats were studied by elasto-plastic analyses including nano-indentation and tensile tests. The test was performed the CCs using Hysitron Triboscope nano-indenter. The indenter was equipped by a cube corner diamond tip. The indentation was carried out at a progressive force between 0 and 250 μN for 20 s. The measurement was done at three different points of the surface of each sample to evaluate the standard deviation of the measurement. The tensile strengths and Young's modulus of the cleracoats were measured at different strain rates of 0.03, 0.13, 0.26 and 0.53 mm/s (at 25 ± 2 °C) using Instron 5556.

3. Results and discussion

3.1. Evaluation of the surface composition of the clearcoats

The mechanical properties of the bulk and the surface of the clearcoats is expected to be affected in the presence of polysiloxane additives. It is well known that polysiloxane additives can migrate to the surface of the clearcoat, causing decrease in surface energy [20,16]. The general chemical structure of the polyether and fluorocarbon modified polysiloxane additives are shown in Fig. 1.

Additives migration to the surface of the clearcoat is studied by ATR-FTIR. The effects of polysiloxane additives as well as nano-SiO_2 particles on the surface chemistry and morphology of the clearcoats are shown in Table 2.

Based on the experimental results presented in Table 2, the transmittance intensities of –Si–O–Si– and –Si–O–CH_3 peaks are studied at wavelength region 1415–1490 cm^{-1}. In addition, the peaks intensities at 1720–1780 cm^{-1} are attributed to –Si–CH_2 and–Si–CH_3 groups. Table 2 shows that addition of additives can cause decrease in peaks intensities (transmission) at