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Preparation of surface energy controlled automotive clearcoats loaded with functional silicon additives: Studying the resistance against tree gum attack

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ABSTRACT

The aim of this study is enhancing an automotive clearcoat easy-to-clean property against simulated tree gum (Arabic gum) using hydroxyl-functional silicone polyacrylate additives having different hydroxyl contents. The clearcoat surface, mechanical and chemical properties were studied using a contact angle measuring device, dynamic mechanical thermal analysis (DMTA) and Fourier Transform Infrared spectroscopy (FT-IR) respectively. It was found that additive with lower hydroxyl content gave rise to better easy-to-clean properties of the clearcoat against Arabic gum. This additive also resulted in lower contact angles and higher cross-linking density, tensile stress and work of break of the clearcoat.

1. Introduction

Photo-degradation, hydrolytic degradation and scratch/mar are the three common phenomena causing most automotive coatings to fail during their exposure to outdoor conditions [1–4]. These include mainly hot–cold shocks, humidity, UV radiation and sharp objects [5–8]. It has been found that various pollutants originated from different natural sources can cause coating degradation severely [9,10]. This phenomenon which is named biological degradation is one of the rarely reported kinds of degradations produced by different biological compounds [11–13]. Various types of biological materials are responsible for this degradation; the most important of which are insect's gums, tree gums, and bird droppings. Beside the visual alterations of clearcoat brought about by these materials, dramatic changes in mechanical and chemical properties may also occur [14–16]. The degrading mechanism of these materials has not been clearly proved yet. Biological materials having various chemical compositions can affect coatings degradation differently [17–20].

For bird droppings, it has been demonstrated that the presence of enzymes catalyzes the hydrolytic cleavage of the coating resin in a hot–humid atmosphere. Amylase, lipase, and protease are among the enzymes available in these natural compounds. Bird droppings can highly degrade the clearcoat chemically [18,20]. Another type of biological material, to which automotive coatings are commonly exposed, is tree gums. It is a general belief, that cars should be kept in the shadow of a tree in order to prevent them from a direct sunlight exposure. However, in this case the effects of gums extracted from the tree may be simply neglected. Results have shown that, the pronounced effect of Arabic gum and natural tree gum is a severe crack formation and shrinkage on fully coated systems and free film samples, respectively [12,20]. It was also shown that, gum strongly attach to clear coat surface before the drying process commences. During gum drying, significant stress can be applied on the coating layers, especially the clear coat. Based on the coating properties, i.e. viscoelasticity and toughness, different behaviors of coatings against applied stress, such as stress relaxation and/or coating failure were observed. The surface cracks observed on the samples exposed to Arabic gum and tree gum revealed that the stress intensity performed by such a drying process was greater than that of the coating relaxation. Attempts have been carried out to enhance clearcoat resistance against biological degradation. To this end, two main approaches are followed to improve the clearcoat resistance against biological attack. Reducing surface free energy and consequently depreciation of adhesion to the film is one way to reduce biological materials influence [20].

Increasing clearcoat cross-linking density may result in lower gum diffusion into the coating matrix. Reducing gum adhesion to the surface can result in lower stress creation during gum drying

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process. Improving the clearcoat physical and mechanical properties can result in stress dissipation during gum drying. In fact, increased clearcoat toughness can result in better capability of stress damping, leading to lower crack formation. It seems that reduced surface free energy and surface mechanical properties simultaneously, may significantly improve its resistance against biological substances [18–20].

One common way to reduce surface free energy of clearcoat is using low surface tension additives. Functional surface active additives might be an alternative approach for reducing the surface energy and enhancing surface mechanical properties of the clearcoat without disturbing its appearance. These additives due to their low surface energy can migrate to the clearcoat surface and reduce surface free energy. Moreover, they produce covalent bonds with clearcoat matrix resulting in physical and mechanical properties changes [21–27].

The aim of this study is formulating an acrylic/melamine clearcoat with hydroxyl-functional silicone polyacrylate additives having similar chemical structures but different hydroxyl contents. The surface free energy, mechanical properties and biological resistance of the clearcoat against Arabic gum are studied.

2. Experimental

2.1. Materials and sample preparation

An acrylic resin (polyol) and a partially butylated melamine resin (curing agent) were utilized in order to prepare the clearcoat. The acrylic resin (Takril 765 ZA), purchased from Taak Resin Co. (Iran), contains 2.7% hydroxyl content and 60 ± 1 wt% solid content. The viscosity, density and acid value of the resin are 1300–2300 cp (AFNOR4), 1 g/ml^3 and 5–10 mg KOH/g, respectively. The melamine resin, also supplied by Taak Resin Co. (Iran), is a partially butylated melamine resin having solid content and acid value of 65% and 1.5 mg KOH/g, respectively. The leveling agent (BYK-306) (0.1 wt%) and defoamer (Efka-2025) (0.1 wt%) were added to the clearcoats formulation in order to control their application properties. A ratio of 3:1 wt/wt of acrylic and melamine resins were mixed in order to prepare the clearcoat. Hydroxyl-functional silicone polyacrylate additives (T-5001 and B-3700) having similar chemical structures but different hydroxyl contents were used to prepare the easy-to-clean clearcoats. The additives used were purchased from Evonik Tego Chemie GmbH (T-5001) and BYK Co. (B-3700). The additives full details are given in Table 1.

Additives were partially substituted by hydroxyl functional groups of the acrylic resin at different concentrations. To this end, B-3700 was used at 0, 2, 4, 6 and 8 mol%. T-5001 was used at 0, 0.5, 1, 1.5 and 2 mol%. The reason to replace some parts of the polyol is because the additives are OH functional compounds enabling them to take part in the reaction with the melamine resin. This ensures that the same ratio between reactive groups is experienced in the curing process either in presence or absence of the additive. Accordingly, the additives could participate in curing reaction with melamine cross-linker and influence the clearcoat mechanical properties. The mixtures was then mixed by a mixer at 500 rpm for 20 min.

Table 1
Full information on additives.

	B-3700	T-5001
Supplier	BYK Co	Evonik Tego Chemie GmbH
Chemical structure	Hydroxy-functional silicone polyacrylate	Hydroxy-functional silicone polyacrylate
Solvent	Esters, ketones and glycol ethers	Butyl acetate
Hydroxyl value	30 mg KOH/g	50 mg KOH/g
Surface tension (mN/m)	22.1	24.09
Molecular mass (g/mol)	255	355

The clearcoats were applied on glass sheets using a film applicator at wet thickness of 120 μm. Samples were then left at temperature and humidity of 25 ± 2 °C and 30 ± 5%, respectively for flash off. They were then kept in an oven at 140 °C for 20 min for curing. The baked films were 50 ± 5 μm thick. The free films of clearcoats were prepared by immersing the glass-coated samples (after curing) in water at ambient temperature for 30 min, followed by drying at 40 °C for 24 h.

2.2. Instrumentations

2.2.1. Surface characterization

A Kruss G40 type contact angle measuring system was utilized in order to measure the static contact angle and surface free energy of the clearcoats using distilled water at temperature and humidity of 25 ± 2 °C and 30 ± 5%, respectively. To this end, a small drop of distilled water (2–3 μl) was deposited on the surface of the clearcoat using a micro-liter syringe. The shape of droplet was recorded by a Canon type digital camera after 10 s. The images were transmitted to a personal computer for evaluation. The test was done three times and the average of the measurement was reported. The surface morphology of the clearcoats exposed to Arabic gum was also studied by a Leica DMR optical microscope (×500).

2.2.2. Mechanical and structural studies

The viscoelastic properties of the clearcoats (cured at 140 °C) were studied by a Tritec 2000 dynamic mechanical thermal analysis (DMTA). The test was performed on free film of each clearcoat (with thickness of 50 ± 5 μm) at frequency, temperature and heating rate of 1 Hz, −30 to 120 °C and 5 °C min^{-1}, respectively. Various parameters including cross-linking density and glass transition temperature were deduced from DMTA diagrams. Tensile test was also carried out to better investigate the mechanical properties changes of the clearcoats. The test was done at strain rate of 2 mm/min (at room temperature) on films with 50 ± 5 μm thickness using an Instron 5556. The test was carried out on three replicates in order to evaluate the measurement repeatability. The clearcoat chemistry changes, after addition of additives, were studied by a BOMEN type FT-IR on free films. To prepare free films, the clearcoats were applied on the glass slides followed by curing. They were then immersed in water for 30 min. The free films were then kept in desiccator for one week to dry.

2.2.3. Biological test procedure

It has been attempted to simulate the tree gum attack on the clearcoats. To this end, Arabic gum (prepared from Merck Co.) was used as simulated tree gum. The biological test was done according to the testing procedure developed in our lab based on PSA D27 1389 standard [19]. A mixture of water and gum powder (5:1) was left at ambient temperature for 72 h. The Arabic gum solution was then exposed to 3 cm^2 of the clearcoats. Samples were then kept in an oven at 60 °C for 72 h. Water was sprayed on samples every three hours periodically. This was done to simulate the outdoor wet and dry conditions.

3. Results and discussion

3.1. Surface properties

Reducing surface energy of the clearcoat has shown to be an effective strategy to improve the clearcoat resistance against tree gum. This ensures reduction of gum adhesion to the clearcoat