Progress in Organic Coatings 77 (2014) 101–109

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Studying the rheology, optical clarity and surface tension of an acrylic/melamine automotive clearcoat loaded with different additives

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ARTICLE INFO

Article history:
Received 13 April 2013
Received in revised form 17 June 2013
Accepted 29 August 2013
Available online 24 September 2013

Keywords:
Automotive clearcoat
Surface tension
Rheology
RMS
Gonio-spectrophotometer

ABSTRACT

Acrylic/melamine based automotive clearcoats were prepared by inclusion of functional and conventional additives. The conventional additives used were based on polysiloxane chains without any reactive groups. On the other hand, the functional additives were based on polyacrylate and polysiloxane backbones. The additives were added to the clearcoat formulations at different concentrations. Surface tension, optical properties and rheological behaviors of the clearcoats were studied by tensiometer, gonio-spectrophotometer, rheometric mechanical spectrometer (RMS) and Brookfield techniques. Results showed that addition of both conventional and functional additives reduced the surface tension of the clearcoat up to a certain value of the additive concentration. It was seen that functional additives could reduce surface tension much greater than the conventional ones. The coating clarity and transparency were not affected in presence of conventional additives. However, the functional additives, especially the one having higher molecular weight, reduced the coating transparency. The clearcoat viscosity was increased using functional additives. A shear thickening behavior of the clearcoats loaded with functional additives was seen. The conventional additives did not change the clearcoat viscosity. It was concluded that the additive functionality, molecular weight and chemical structure were influential parameters affecting the final properties.

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1. Introduction

Outdoor mechanical factors [1–7], weathering environments (e.g. sunlight, humidity, acid rain) [8–10] and biological substances (e.g. tree gum, bird dropping and insect body) impose different kinds of degradations to automotive clearcoats during their service life [11–18]. As a result, the clearcoat chemical, mechanical and appearance can be significantly influenced. Biological degradation occurs when these natural occurring substances attack the clearcoat. It has been reported that these materials could strongly attach to the clearcoat surface, leading to chemical and physical degradations [3]. Biological substances contain different kinds of enzymes which can hydrolyze ester and ether linkages of the clearcoat resin resulting in formation of cracks and holes on the film surface. One way to enhance the clearcoat resistance against biological degradation is to modify the clearcoat surface morphology. It seems that enhancing the cleanability and increasing mechanical properties of the clearcoat surface are effective to modify the biological resistance. It has been shown that increasing cross-linking density and reducing the surface free energy of the clearcoat surface can improve the surface properties in exposure to biological attack [19]. High cross-linking density strengthens the film and increases uniformity of the chemical and physical structure of the film to restrict the penetration of biological materials while reducing surface energy depreciates adhesion between the biologicals and film [18]. Controlling free surface energy and physical characteristic without changing the bulk properties of the clearcoat have positive roles in this regard. Use of surface active additives is one approach to reach this goal. Various kinds of additives can be used to reduce the surface free energy. Main attention has been focused on the ability of additive to make the clearcoat surface hydrophobic enough to prevent the pollutants adhering to the surface.

There are different kinds of additives to be used in this regard. The conventional polysiloxane additives are the most important ones which contain –$(CH3)_2$–SiO- groups in their structure. These groups of additives, due to their low surface tension, tend to migrate to the clearcoat surface and change the surface characteristics [20]. It has been understood that addition of only low extents of these additives could significantly enhance the coating surface and/or the bulk properties. This depends on the chemical structure, molecular weight and surface tension of additive and resin.

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http://dx.doi.org/10.1016/j.porgcoat.2013.08.009

Table 1
Full information on additives.

	F-5000	F-5001	C-3031	C-3034
Supplier	TEGO	TEGO	EFKA	EFKA
Chemical structure	hydroxy-functional polydimethyl siloxane	hydroxy-functional silicone polyacrylate	Organically modified polysiloxane	Fluorcarbon containing organically modified polysiloxane
Solvent	Esters, ketones and glycol ethers	Butyl acetate	Alkylbenzene	Methoxypropanol
Hydroxyl value	45 mg KOH/g	50 mg KOH/g	0	0
Surface tension (mN/m)	22.1	24.09	23.81	22.08
Molecular mass (g/mol)	1812	355	560	1100
Viscosity (MPa s)	90	90	40	40

Some additives such as polysiloxanes migrate to the surface of the clearcoat whilst others remain in the bulk [22,23]. The chemical structure of the additives can directly influence its migration. Chemical structure, side chains and end groups are some of the factors affecting the surface activity of the additives [20,21,24–26]. For many years, conventional silicone additives have been widely used in formulations of coatings. Although these additives could improve many properties of the coatings, weak interactions produced make them non-effective against outdoor conditions. Attempts have been carried out to use additives with capability to make stronger interactions with the clearcoat matrix. These novel types of additives may react covalently with the binder and act more efficiently compared to the conventional silicone ones which may be easily leached or wiped out from the coating surface due to lack of strong interactions with the coating matrix [12]. New types of silicone additive are functional silicone–acrylates which contain hydroxyl functionality. The chemical interactions it could produce with a polyurethane coating formulation and significant enhancement on the anti-graffiti properties have been studied in our previous work [19]. In another work, it was shown that addition of a functional polysiloxane additive to an acrylic melamine clearcoat could enhance the coating performance against biological materials [25]. It has been found that functional silicone additives could reduce the surface free energy notably, resulting in a weak interaction between natural gum and the film.

The above explanations show that replacing conventional additives with the functional ones may result in better coatings properties. The present work aims to compare the effects of two functional and two conventional polysiloxane additives on the surface tension, rheological and optical properties of an acrylic/melamine base clearcoat in a liquid state. In fact, it has been aimed to find the mechanism by which each additive affects the clearcoat properties.

2. Experimental

2.1. Materials and sample preparation

The clearcoat used in this study was based on acrylic/melamine resins. 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 0.65% and 1.5 mg KOH/g, respectively. The acrylic and melamine resins were mixed at ratio of 3:1 w/w. Additives including C-3031, C-3034, F-5000 and F-5001 were added to the resin mixture at different concentrations. Full information of additives used is given in Table 1.

Table 1 The additives used were all known as surface active additives enabling to reduce the surface tension of the resins in which they are incorporated. This leads to low surface free energy films with enhanced easy-to-clean properties. The effect of these additives in the cured film has been previously reported in reference [27]. These additives were chosen among a list of different additives because they have similar chemical structures but different functionalities and molecular weights. Using these additives, the effects of additives functionality and molecular weight on the properties of the clearcoat can be studied. C-3031 and C-3034 are conventional polysiloxane based additives without functional groups. These additives were added to the clearcoats directly. On the other hand, F-5000 and F-5001 are functional additives with capability of reacting with resin functional groups. To keep the stoichiometric ratio of hydroxyl groups of polyol and melamine cross-linker constant, polyol hydroxyl groups of the resin were replaced by the hydroxyl groups of the additives. 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 means 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. To obtain a homogenous mixture of resin and additive, they were mixed for 15 min under a shear rate of 1000 rpm. The clearcoats formulations are given in Tables 2 and 3.

2.2. Characterization

2.2.1. Appearance analysis

Using a Canon A5000 digital camera, the visual appearance of the clearcoats was studied. The NTU (nephelometric turbidity unit) values were obtained using a HACH 2100 turbidmeter. The UV–Vis test was conducted in order to measure the effects of each additive on the clearcoat transparency both in ultraviolet (UV) and visible regions. The test was carried out by JENWAY 6715 UV–Vis spectrophotometer at the wavelength range of 300 to 700 nm. Also a Macbeth CE-741 GL gonio-spectrophotometer was utilized to investigate the cured films transparency.

2.2.2. Surface properties measurement

The surface tension of the resin mixtures were measured by a KRUESS PROCESSOR TENSIOMETER K14 V3.07 (Wilhelmy Technique). The measurement was done at 25 °C. Elemental composition of the cured films was studied by a scanning electron microscope (SEM) equipped with an Inca Operator energy dispersive spectroscopy (EDS).

2.2.3. Rheological properties characterization

The clearcoats viscosity was studied by rheometric mechanical spectrometer (RMS) and Brookfield viscometer. An Elcometer 2300 RV type Brookfield viscometer was used to measure the clearcoat viscosity at 25 and 60 °C and at different shear rates of 60, 100 and 200 rpm. Using a rheometric mechanical spectrometer (Paar Physica UDS200) with a parallel plate fixture with diameter of 25 mm

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