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Evaluation of degradability of two polyurethane refinish coatings against biological materials: A case study

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ABSTRACT

In this study the effect of bird droppings and tree gums on two different polyurethane refinish coatings has been investigated. To this end, Arabic gum and pancreatin were used as simulated tree gum and bird dropping, respectively. These substances were applied on coatings exposed to UV radiation and moisture for different exposure times. Various techniques were used to study the appearance of the degraded coatings. Structural analysis of samples was done by FTIR spectroscopy. Surface free energy and thermo mechanical characteristics of refinish coatings were studied by contact angle measurement and DMTA respectively. All experiments were carried out before and after degradation process. In general, it was revealed that while pancreatin degraded the coatings chemically, Arabic gum affected it mechanically and chemically, leading to wrinkle-like deformations on the coating surface. It was also concluded that the cross-linking density and surface free energy have vital roles in the degradation of automotive refinish coatings. It was demonstrated that low cross-linking density and Tg of polyurethane system created a dynamic system which can be post-cured during experiment, leading to enhanced biological resistance. According to this finding, it was also revealed that coating history before bio attack is an important factor in the biological performance of polyurethane systems.

1. Introduction

Automotive coatings and their appearance retention have great importance for customers due to their major role in esthetic of a car body. The overall performance of an automotive coating system depends on the efficiency of each layer, including phosphate layer, electrodeposition (ED), primer, basecoat and clearcoat. The clearcoat is the top layer which should withstand the environmental factors such as mechanical (scratch, stone chipping, etc.) and chemical ones (i.e. sunlight, water, humidity, acid rain, etc.) [1–9]. In recent years the effect of environmental factors on physico-chemical and mechanical properties of automotive coatings has been extensively investigated [10–14]. The influence of biological substances such as tree gums, bird droppings and insect gums has also been studied in details [15–23]. It was found out that in spite of short-time contact with automotive coatings, these substances threaten both short-term and long-term properties of coating system [23]. It was proved that pancreatin and Arabic gum as synthetic materials could be utilized to successfully simulate the action of bird droppings and tree gum in experiments respectively. These studies had mainly focused on acrylic melamine clearcoats as OEM. Severe degradation occurs to coatings exposed to biologicals causing significant appearance changes. It was illustrated that both bird droppings and tree gums degrade the coating system via chemical and physical mechanisms. While the chemical degradation mechanism is more involved in bird droppings, the physical one is more dominating in Arabic gum damages. In fact various enzymes such as lipase, amylase and protease which exist in bird droppings play a catalytic role in hydrolysis reaction of clearcoats [23,24]. Tree gums mainly degrade the clearcoat mechanically as it is sticky in liquid state and apply stress on surface during drying. It was also demonstrated that owing to its acidic nature, tree gum could catalyze the hydrolytic degradation of acrylic melamine to some extent [18–21].

Apart from the clearcoat which is applied as the final layer of automotive coating system, attention should be paid to refinish coatings as well. In production line of car companies, the coating may experience scratch or impact during assembling. The damaged areas are repaired by refinish coatings which are usually cured at low temperatures. Equal quality of OEM and the refinish coatings is required and it is necessary to have the same resistance against weathering and biological degradation [25]. Thus, the refinish coatings performance is as important as OEM coatings. While OEM resistance against biological substances has been extensively studied, there is no report for evaluation of biological degradation

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of refinish coatings. This study aims to evaluate the biological resistance of refinish coatings based on a two-pack polyurethane resin. It is noticeable that polyurethane is a commonly used topcoat which has been widely utilized in diverse applications such as general industrial, oil and gas, architecture, traffic and automotive coatings. To this end, different analytical techniques were employed to assess the behavior of polyurethane coatings. The experiments not only investigate the inherent properties of intact samples but also evaluate them after being aged in order to find out all possible changes during aging process.

2. Experimental

2.1. Sample preparation

The experiments were conducted on a complete automotive system in order to simulate the real conditions. A multi-layer automotive coating system composed of an epoxy-amine electro deposited (ED) layer, a polyester melamine primer, and a black polyurethane basecoat was applied on phosphated steel panels. Two clearcoats based on acrylic polyol/hexamethylenediisocyanate (HDI) trimer (coded as CL1 and CL2) were separately applied as final layer on basecoat using a wet-on-wet procedure. Clearcoats were commercial samples provided by Khosh Resin & Paint Company, Iran. The molecular weight and solid content of both acrylic polyols used for CL1 and CL2 formulations were about 13,000 gr/mol and 75%, respectively. The viscosity for both polyols at 25 °C was adjusted to 60 poise. The differences between the clearcoats were the OH contents and acid value of their acrylic polyols. The hydroxyl content for acrylic polyol incorporated in CL1 and CL2 were respectively 4.1 and 3%. Acid value (in solid state) of acrylic polyols used for CL1 and CL2 formulations was approximately 8–13 mg/g. The curing process of basecoat/clearcoat was done simultaneously at 80 °C for 20 min.

Dynamic mechanical thermal analysis (DMTA) was conducted on free films. For this purpose, the clearcoat solutions were applied on pre-cleaned glass substrates. After curing, coated glass was immersed for a few minutes in water and then the free films were easily detached from the substrates. Drying was performed in a vacuum oven overnight.

2.2. Biological evaluation

As stated before, pancreatin and Arabic gum could successfully simulate the degradation caused by bird droppings and tree gums respectively. Both pancreatin and Arabic gum were purchased from Merck Company. According to the PSA Peugeot-Citroen D27 5415 standard, a known amount of pancreatin powder was dissolved in water with the ratio of 1:10, pancreatin: water. The solution was remained intact for 72 h to attain a stable paste. The Arabic gum was also mixed with water with the ratio of 1:5. The accelerated testing approach was taken in this study, i.e. the biological materials were deposited on each coating then the plates underwent the condition of accelerated QUV chamber. This reproduces the damage caused by sunlight, rain and dew. In this study the QUV/basic model from Q-LAB company was employed in which the samples were exposed to alternating cycle of UV radiation for 8 h at 60 °C and then moisture for 4 h at 50 °C. In QUV/basic chamber, the UV light is provided by a fluorescent lamp (UVA-340 nm) with radiation in wavelength range of 295–365 nm and maximum radiation at 340 nm. The samples were removed after pre-determined exposure time (100 and 300 h). G100 and G300 represent samples exposed to Arabic gum for 100 h and 300 h. P100 and P300 also refer to pancreatin-exposed samples. It has to be noted that half of each sample surface was remained unexposed to biological and was only influenced by QUV.

2.3. Characterization

Surface free energy of different clearcoats was calculated by Owens–Wendt method (Eq. (1)) [26]. In this method the dispersive and polar components of surface tension as well as contact angle of liquid probes were used to calculate the surface free energy of the solid. The test was carried out by means of an OCA 15 contact angle measurement instrument (Dataphysics Co.) on a fully coated system. The instrument was equipped with a CCD camera to record the contact angle images. In this study, three different liquid probes were used and for each probe the test was repeated for 5 times. Since pancreatin and Arabic gum are aqueous solutions, water was considered as one of the liquid probes. The other two liquid probes were formamide and n-hexadecane. In Eq. (1), θ is contact angle, σ_L^D and σ_L^P are dispersive and polar components of liquid probe surface tension respectively, σ_S^D and σ_S^P are for clearcoats surface free energy as well.

$$\frac{\sigma_L(\cos\theta+1)}{2(\sigma_L^D)^{0.5}} = (\sigma_S^P)^{0.5}\frac{(\sigma_L^P)^{0.5}}{(\sigma_L^D)^{0.5}} + (\sigma_S^D)^{0.5} \quad (1)$$

This equation has the linear form of $y = ax + b$, wherein:

$$y = \frac{\sigma_L(\cos\theta+1)}{2(\sigma_L^D)^{0.5}}, \quad a = (\sigma_S^P)^{0.5}, \quad x = \frac{(\sigma_L^P)^{0.5}}{(\sigma_L^D)^{0.5}}, \quad b = (\sigma_S^D)^{0.5}$$

By using the surface tension and contact angle of the three liquid probes and applying linear regression, the surface free energy of each sample before and after aging process was obtained.

The fundamental characteristics of intact clearcoats such as Tg and cross-linking density were determined by the aid of a Tritec 200 DMTA instrument. Two different approaches were employed to carry out the DMTA experiments on intact and aged clearcoats. For intact clearcoats, DMTA experiments were conducted on free-standing films of CL1 and CL2. The frequency, temperature range and heating rate were 1 Hz, −40 °C to 120 °C and 5 °C/min, respectively. It is essential to carry out the DMTA test for aged samples with various exposure time in order to determine the level of changes in thermo-mechanical properties of clearcoats during aging. Since it was not possible to prepare free films of aged samples, DMTA experiments for these samples were performed on the powders obtained from degraded areas. For this purpose, a surgery knife was utilized to prepare powder samples from degraded areas of CL2 P300, CL1 G300 and CL2 G300. The employed instrument for these samples was same as the one used for intact samples, but with the temperature range of −60 °C to 200 °C, 1 Hz frequency and 5 °C/min temperature rate.

2.4. Appearance and visual analysis

Appearance attributes including gloss and color characteristics were measured during biological attacks to investigate how degradation affects the refinish coatings. The gloss was measured by a BYK-GARDNER MICRO-Tri Gloss meter. The measurement angle was 20°. The color of automotive coatings might be influenced under the aging condition. For calculating the ΔE of each coating, values of $L^*{\cdot}a^*{\cdot}b$ were recorded by a MacBeth CE-741 GL goniospectrophotometer at angle of 110° with D65 illuminant. $L^*{\cdot}a^*{\cdot}b$ are three parameters of a CIE color space which form a coordinate system to describe a color. The a^* axis represents the red/green opponent colors, with green at negative a^* values and red at positive a^* values. The b^* axis stands for yellow/blue opponent colors, with blue at negative b^* values and yellow at positive b^* values. The degree of lightness is determined by L^*, $L^* = 0$ and $L^* = 100$ are defined as the darkest black and brightest white, respectively. The images of samples were taken by a Canon