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Effects of Environmental Conditions on Degradation of Automotive Coatings

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1. Introduction

Two main goals are expected when coatings are applied to substrates. The main one is protection of substrate from various aggressive environments such as sunlight and humidity. The second is to impart color and aesthetic to the substrate to be coated. In some applications such as automotive coatings, these two are highly important. Exposure for a long time to different permanent (sunlight, rain & humidity) and occasional (acid rains and various biological substances) parameters during the service life of these coatings results in loss of performance. Such phenomena not only render the coating to degrade also lead to depreciation of appearance attributes of the finished car. Automotive coatings are usually multi-layered systems in which each layer has its predefined function. These make the whole system resist to various environmental factors. Figure 1 shows a typical automotive coating system.

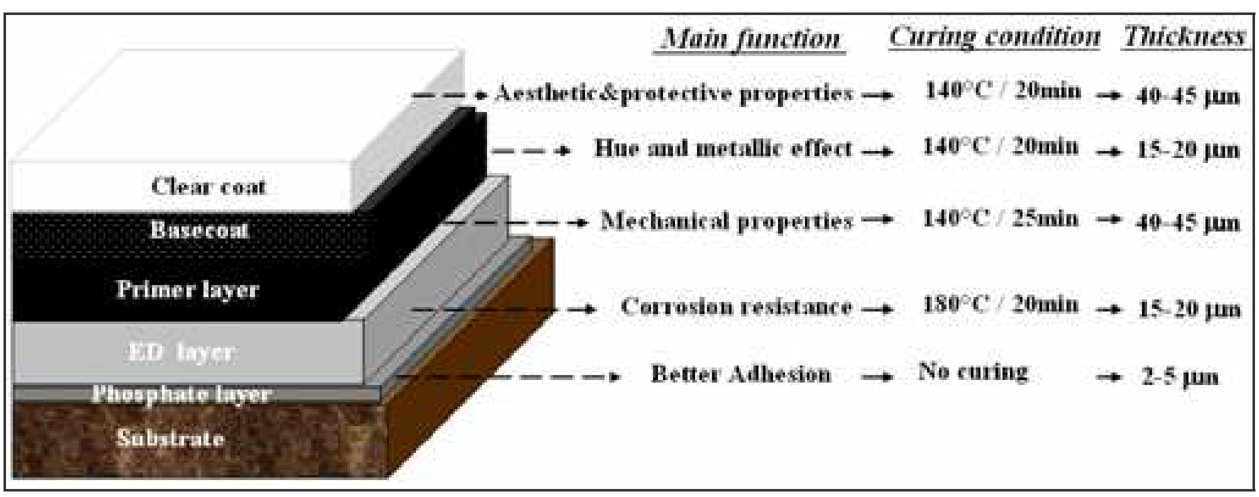


Fig. 1. Specifications of a multilayer automotive system

As figure 1 describes, the substrate is initially coated by a conversion layer such as phosphate or chromate to enhance the adhesion and corrosion protection of the metallic substrate. Then, an electro deposition (ED) coating, usually based on epoxy-amine containing anticorrosive pigments and zinc powders, is applied to protect the coating from corrosion. The primer surfacer which is a polyester melamine coating is then applied. The main function of this layer is to make the coating system resist against mechanical deformations such as stone chipping. The color and special effects, such as metallic luster are obtained using a basecoat layer which is typically an acrylic melamine resin pigmented with metallic and pearlescent pigments. To protect the basecoat, a non-pigmented acrylic melamine clear coat is applied over this layer. This latter layer is responsible for the gloss and smoothness of the coating system. On the other hand, the clear coat, apart from creating a highly glossy surface, is intended to protect the underneath layers, even the substrate, against various aggressive weathering (i.e. humidity and sunlight) and mechanical (i.e. mar and scratch) factors during service life.

It should be noted that all layers are applied when the previous layer has dried, except for the clear coat that it is applied through a wet-on-wet method in which it is applied on the wet basecoat layer after a short time for flashing off the solvents. The curing processes of all layers are presented in figure1.

In order to fulfill the required properties, automotive coating systems are required to remain intact during their service life, because they are extremely vulnerable to deteriorate (Nguyen et al., 2002 a; b; 2003; Yari et al., 2009a). There are various environmental factors which can potentially be fatal for these coatings and may cause loss of appearance and protective aspects of the system. The consequences of these factors are discoloration, gloss loss, delamination, crack propagation, corrosion, and gradually building up coating degradation. Acid rain, hot-cold shocks, UV radiation, stone chips, car washing, fingernail and aggressive chemical materials are among those parameters rendering the coatings to fail in short and/or long exposure times to environment. These would lead to dissatisfaction of customers. Therefore, it is vital to enhance the resistance of the coating against environmental factors.

In the following part of this chapter, different environmental conditions and their effects on various aspects of coating have been presented. Preventive methods will be given where necessary. Among the environmental factors, the influence of biological materials will be explained with more details because their effects have not been discussed elsewhere.

2. Environmental factors

Environmental factors are those substances or conditions imposed by the environment to which the automotive coatings are exposed. As such, different chemical and/or mechanical alterations (degradation) may result. Here, they have been divided to three main subcategories, i.e.; mechanical, weathering, and biological factors.

2.1 Mechanical damages

Automotive coatings can be encountered different outdoor conditions during their service life. Mechanical objects can put severe effects on these coatings. Depending on the type of imposed stress to these coatings various kinds of degradation can be observed (Shen et al., 2004). The most important of these can be seen in Figure 2.

2.1.1 Chipping resistance

The ability of multi-layer automotive coatings to withstand against foreign particles without being damaged is named stone-chip resistance. It is found that, when stone particles attack a coating they have velocity near to 40-140 km/h. This can cause coating delimitation from the

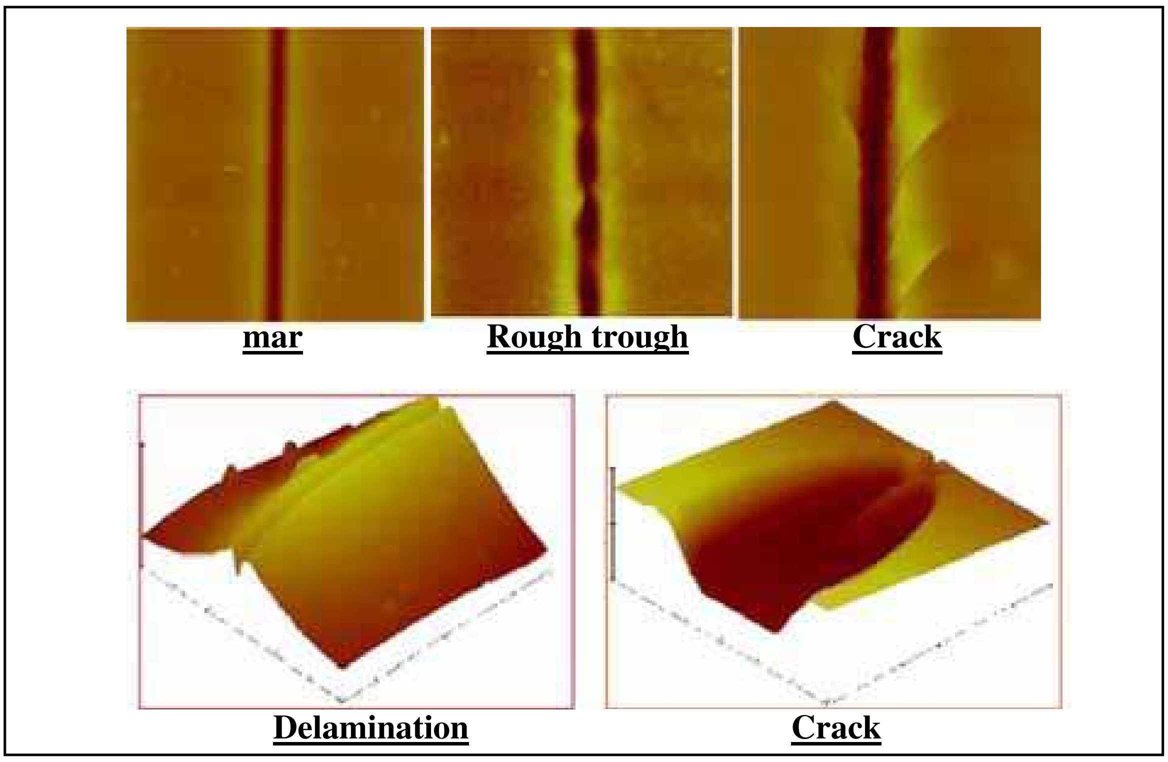


Fig. 2. Different type of mechanical damage occurring on automotive coatings (Shen et al., 2004).

paint-substrate interface (Lonyuk et al., 2007; Buter & Wemmenhove, 1993). For multi-layer system, coating layers interadhesion, coatings mechanical properties and coating interaction to substrate are the most important factors affecting chip-stone resistance. These can make the chipping resistance of these systems very complicated. It has been demonstrated that, the mechanical properties of each layer can affect their chip resistance. In this regard, it has been found that glass transition temperature of the primer layer is the main factor controlling coating chipping resistance. The greater glass transition temperature may cause adverse performance. The temperature at which this measurement is conducted is also very influential. The failure appeared during chipping in a multi-layer coating system can be both adhesive and/or cohesive failure. It was found that when the strength between two layers exceeded, the defect was mainly adhesive failure. As a result of this, delaminating, flaking or peeling will occur. On the other hand, crack initiation and propagation within a coating layer across the other layers can cause cohesive failure (Lonyuk et al., 2008) (Figure 3).

2.1.2 Abrasion resistance

Basecoat/clear coat systems create an outstandingly high glossy appearance in comparison to other automotive paint systems. However, such a high gloss makes mechanical damages more visible when they appear. Scratch and mar are the most important of these failures. They are micrometer deep surface damages that may ruin the initial appearance of automotive finishes. The difference between mar and scratch is mainly in their different sizes and morphologies. Scratch is a consequence of tribological events encountered by automotive clear coats. The size for this type of damages is 1-5 µm (Courter, 1997; Tahmassebi et al., 2010). To show how these types of damages influence coating appearance, the visual performance of coating before and after scratching are shown in Figure 4.

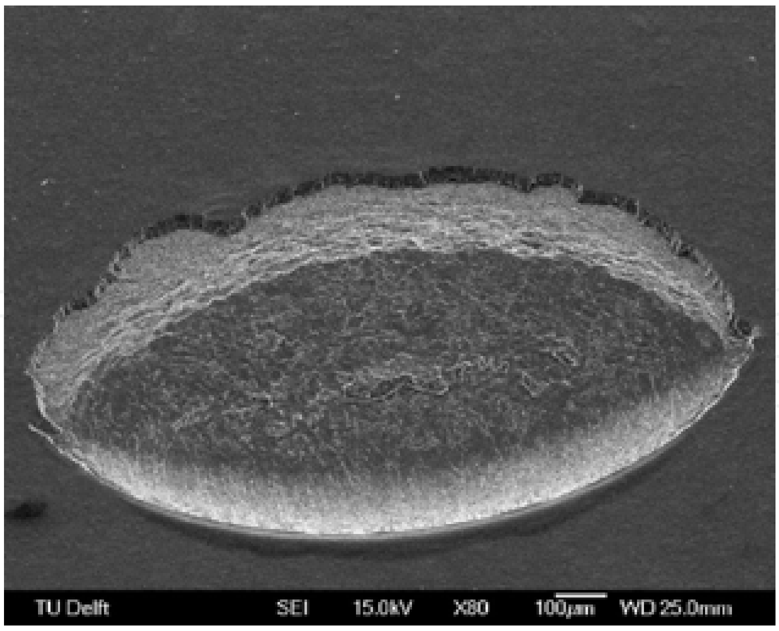


Fig. 3. The SEM micrograph of the chipped surface of coating (Lonyuk et al., 2008).

Fig. 4. Visual differences of automotive coating before and after scratching.

Mechanical damages of these types may be caused by polishing equipments, carwash bristles, tree branches and sharp objects such as keys (Tahmassebi et al., 2010).

2.1.3 Scratch type

The performance of automotive coatings is further complicated by nature of the created scratches, which in turn is influenced by the viscoelastic properties of the clear coat itself, and the conditions under which they are created. In this regard, when an external stress is applied to coating, there would be three different kinds of coating responses: elastic deformation, plastic deformation and fracture deformation (Tahmassebi et al., 2010; Lin et al., 2000; Hara et al., 2000). Elastic deformation has limited effect on the appearance of a coating, therefore determination of plastic and fracture deformation seem more important. Some scratches are irregular and of a fractured nature (Figure 5-a) and may involve material loss, while others are smooth (Figure 5-b), regular and involve plastic deformation of clear coats (Lin et al., 2000; Ramezanzadeh et al., 2010; Jardret & Morel, 2003; Jardret & Ryntz, 2005; Jardret et al., 1998).

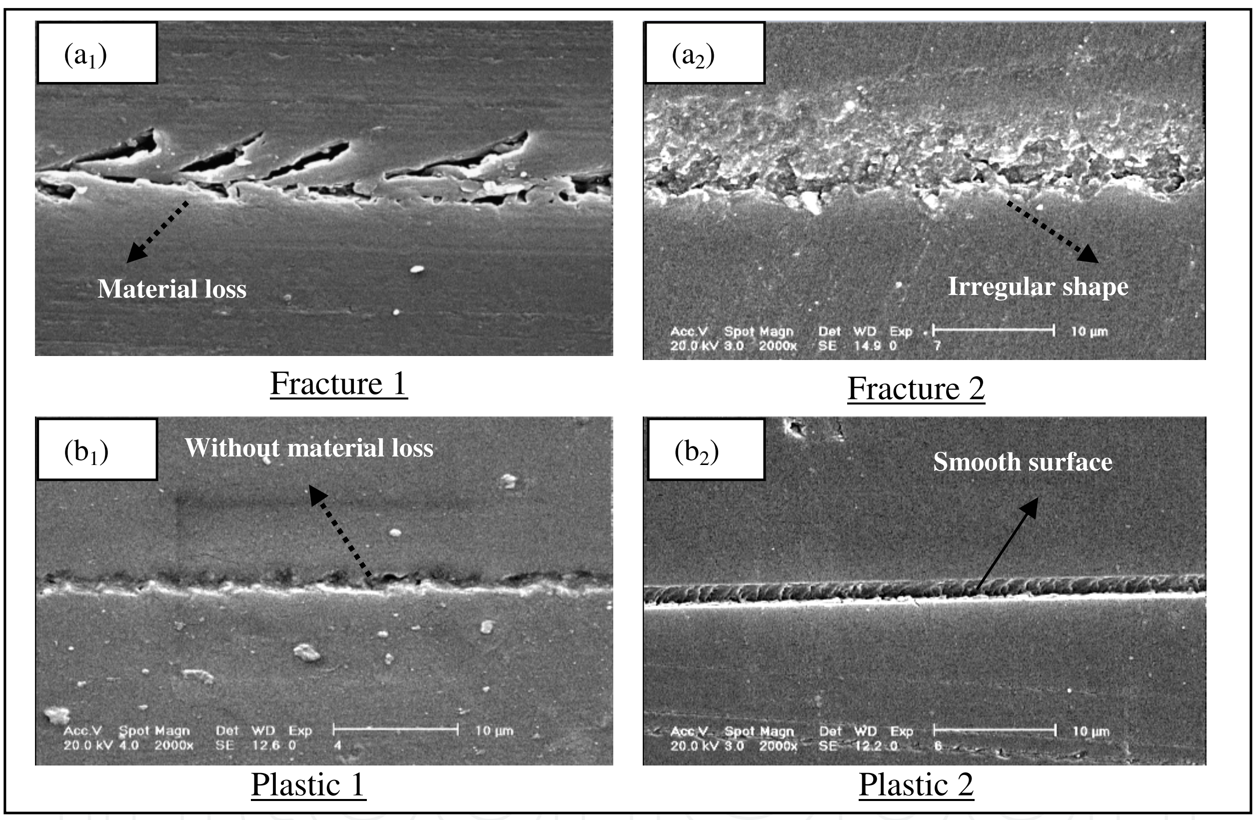


Fig. 5. SEM micrographs of two types of (a) fracture and (b) plastic scratches (Tahmassebi et al., 2010; Ramezanzadeh et al., 2010).

Various parameters such as scratch force, scratch velocity and environmental temperature would influence the type and form of scratch produced.

There are many differences between these two types of scratches. First, fracture types are irregular and may involve material loss (Figure 5-a), while others are smooth, regular with no material loss (Figure 5-b). The visibility of fracture-type scratches is independent on the direction of incident light and illumination. Conversely, plastic-type scratches are not visible if the longitudinal direction of the scratch coincides with the direction of the lighting. These differences are schematically shown in Figure 6-a and b (Lin et al., 2000).

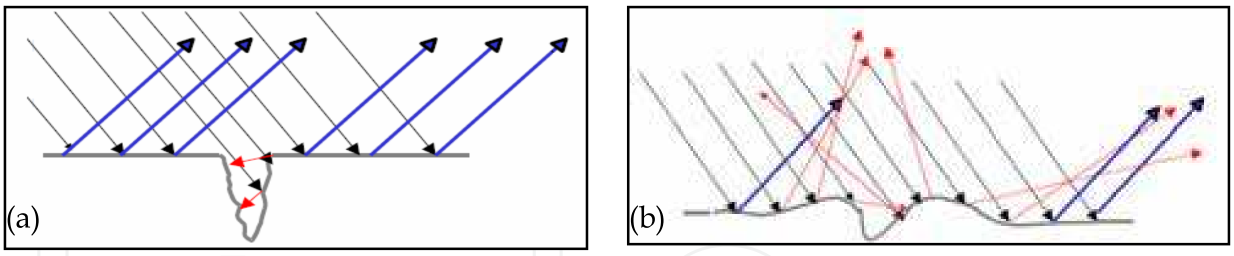


Fig. 6. Schematic illustration of (a) fracture and (b) plastic type's scratches

Elastic or plastic behaviors of a clear coat result in spontaneous or retarded recovery of the created scratches, respectively. This is usually named as healing ability of clear coat. Fracture behavior, on the other hand, arises from tearing apart of polymer chains contained within the clear coat, therefore recovery or healing of the created scratches would not be possible. The mechanism by which scratch can be formed by a scratch indenter are shown in Figure 7 (Hara et al., 2000).
According to figure 6, different parameters like indenter tip morphology (tip radiance and stiffness), tip velocity and coating viscoelastic properties affect the coating response against applied stress. As shown in this figure, applied force can be divided into tangential and vertical vectors. Tangential forces cause compression and stretching in the clear coat in front and behind of such particles, respectively. Tensile stresses produced behind such particles can cause cracks in the clear coat and/or aid in scratch formation. Consequently, the tensile stress/strain behavior of clear coats can be used to predict scratch behavior. This phenomenon has been shown by Jardret and Morel in detail (Jardret et al., 2000; Jardret & Morel, 2003).

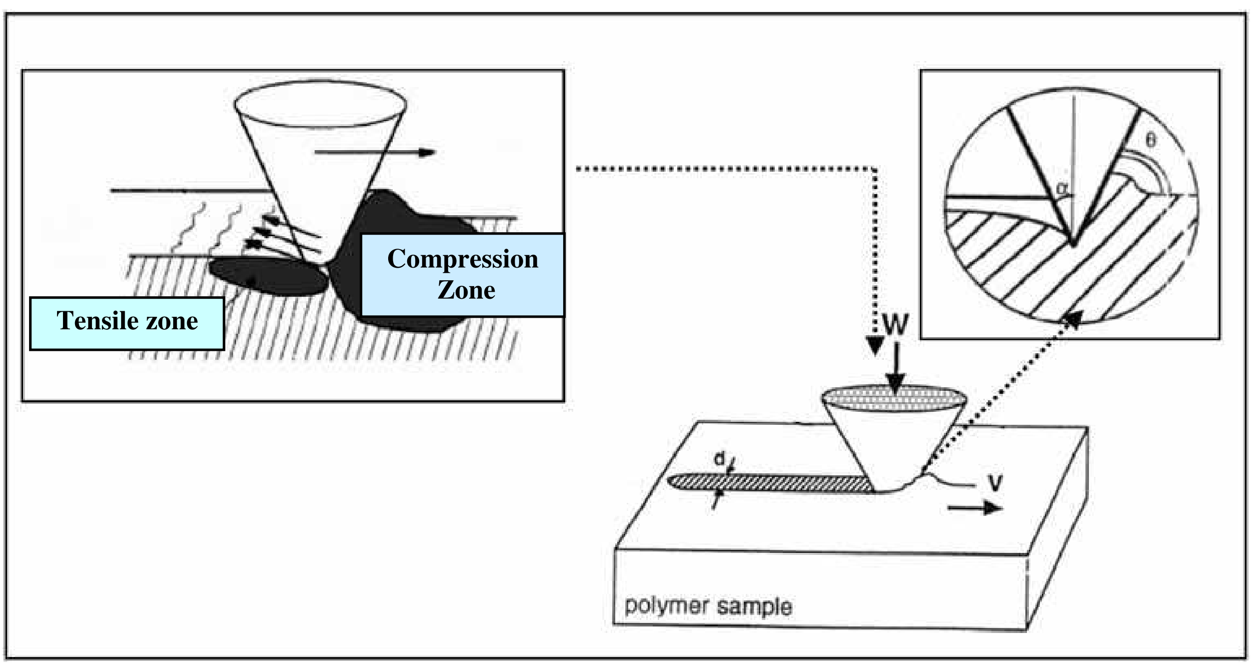


Fig. 7. Schematic illustration of how scratch indenters affect coating deformation type (Hara et al., 2000).

2.1.4 Methods to improve coating scratch resistance

Based on the above explanations, improving scratch resistance and variations in scratch morphology are of utmost importance in the research and development departments of the automotive finishing industry. Accordingly, researchers have proposed various methods for improving the scratch resistance of automotive clear coats. The proposed methods include procedures to increase surface slippage and hardness, as well as enhancing cohesive forces within clear coats that modify the viscoelastic properties of clear coats as a whole. Increasing surface slippage and hardness inhibit the penetration of scratching objects into clear coats, thereby increase the force necessary to create scratches. If forces generated by scratching objects exceed that of the cohesive forces within a clear coat, then polymer chains of the clear coat tear apart and show a fracture-type (Hara et al., 2000). There are many methods to improve coating viscoelastic properties including changing clear coat chemistry and using different pigments (in both nano and micro size) and additives (like polysiloxane additives). However, changing the chemical structure of a clear coat would not guarantee modification of its viscoelastic properties. Furthermore, changing the chemical structure of a clear coat may incur unwanted adverse effects on other properties of the resultant clear coat and will in most cases, increase its price. Consequently, attempts have been made in many research programs to modify viscoelastic properties by physical incorporation of various additives into a clear coat of known chemical structure. Controlled use of these additives could ensure minimization of unwanted variations in other properties of the resultant clear coat as well as being an attractive and economically viable alternative (Tahmassebi et al., 2010; Ramezanzadeh et al., 2010; Zhou et al., 2002; Ramezanzadeh et al., 2007; Ramezanzadeh et al., 2007; Jalili et al., 2007).

2.1.5 Methods to evaluate coating scratch resistance

Several methods have been used to evaluate the scratch and mar resistance of clear coats. Scratch-tabber is one of the most traditional used methods for analyzing coating scratch resistance. This method can predict coating scratch resistance based on the weight loss of coating during scratch test (Lin et al., 2000). Laboratory car wash simulator is another method which has been used in recent years. This is a useful method based on an appropriate simulation from a real scratching process in an outdoor condition (Tahmassebi et al., 2010). Nano and micro-indentation are powerful methods to evaluate both scratch resistance and morphology of coating. In addition, use of these methods could be favorable for analyzing clear coat scratch resistance, deformation type of the clear coat (plastic or fracture) and viscoelastic properties (Tahmassebi et al., 2010). Gloss-meter and goniospectrophotometer have been used to evaluate the effects of scratches produced on the appearance of clear coat (Tahmassebi et al., 2010). Microscopic techniques including optical, electron and atomic microscopes have been used to investigate scratch morphology.

2.2 Weathering factors

Weathering factors are those that are applied to the coating by weathering (or climate), and cause alteration in chemical structure (Nguyen et al., 2002 a; b; 2003, Bauer, 1982), affecting various aspects of the coating properties such as physical (Osterhold & Patrick, 2001), mechanical (Tahmassebi & Moradian,2004; Nichols et al., 1999; Gregorovich et al., 2001; Nichols & Darr, 1998; Nichols,2002; Skaja, 2006) and electromechanical (Tahmassebi et al., 2005) properties. The severity of degradation caused by weathering factors depends strongly on climatic condition. Sunlight and humidity are the most important weathering factors. It is almost impossible to prevent automotive coatings being exposed to sunlight.

2.2.1 Sunlight

Sunlight reaching the earth contains a wide range of wavelengths from 280 to 1400nm (Valet, 1997). The most harmful part is the uv range (less than 380 nm). Most polymers are sensitive to this part of the sunlight. For example polyesters and alkyds have absorption peaks around 315 and 280-310 nm, respectively (Valet, 1997). The absorbed energy can cause a kind of degradation called "photodegradation", the mechanism of which is known and has been extensively discussed in litreatures (Pospısil & Nespurek, 2000; Valet, 1997). A brief description of photodegradation is given here. The absorbed energy by some chromophoric groups (ch) of the polymer turns it to an excited state (ch*). This excited state is able to induce formation of various free radicals. The following equations present different free radicals produced during photodegradation.

A) Initiation

$$\text{Polymer (p)} \xrightarrow{\text{Sunlight}} \text{Free radicals } (P\bullet, PO\bullet, HO\bullet, HOO\bullet, \ldots)$$

B) Propagation

$$P\bullet + O2 \longrightarrow POO\bullet$$

$$POO\bullet + PH \longrightarrow POOH + P\bullet$$

$$PO\bullet + HO\bullet \longrightarrow POOH$$

$$2\ POOH \longrightarrow PO\bullet + POO\bullet + H_2O$$

$$PO\bullet + PH \longrightarrow POH + P\bullet$$

$$PH + HO\bullet \longrightarrow P\bullet + H_2O$$

C) Termination

$$P\bullet + P\bullet \longrightarrow P\text{-}P$$

$$POO\bullet + P\bullet \longrightarrow POOP$$

$$P\bullet + PO\bullet \longrightarrow POP$$

$$PO\bullet + PO\bullet \longrightarrow POOP$$

As a consequence, chain scission and formation of various stable and unstable spices such as peroxide, hydroperoxide, hydroxyl and carbonyl groups are the most important reactions involved in photodegradation. Formation of different polar species leads to an increase in surface energy of the coating (Tahmassebi & Moradian, 2004). These produce hydrophilic groups in the coating and increase the susceptibility for water diffusion. Finally, this leads to greater potential of underneath layer to be corroded.

2.2.2 The effect of basecoat pigmentation

Due to significant role of the clear coat on weathering and mechanical properties of automotive coatings, most of the previous studies have focused on an isolated clear coat layer. But there are reasons to believe that the basecoat greatly affects the weathering performance of its attached clear coat. In order to illustrate how a basecoat could vary the weathering performance of a clear coat, it is necessary to clarify how a basecoat reacts to incident light. As stated before, common basecoat contains colored pigments and/or metallic flakes. Colored pigments absorb and/or scatter incident visible light reaching the bulk of a basecoat, according to their color, size and refractive index. Metallic flakes, based on their level of orientation, reflect and/or scatter incident light only at the surface of the clear coat. In this manner, fractions of returned incident light passing through the clear coat are decisive in causing chemical changes in the clear coat structure, leading to alterations in the clear coat properties.

In order to elucidate the influence of basecoat pigmentation on degradation of a typical automotive clear coat during accelerated weathering tests, using two different basecoats (i.e. silver and black) can be useful. Amongst common commercial basecoats, silver and black seem to be two extreme basecoats. In other words, a silver basecoat is characterized by the presence of high loads of aluminum flakes (acting as a reflective source of visible light), and a lack of colored pigments, in which the chance of reflecting incident light is high and the chance of absorbing incident light is minimal. While the black basecoat, is characterized by the presence of high loads of a black pigment (acting as an absorbent of visible light), and a lower load of aluminum flakes; this means that the reflection or scattering chances of incident light are low and its absorption is high. Figure 8 schematically shows how two different basecoat pigmentations react to incident light.

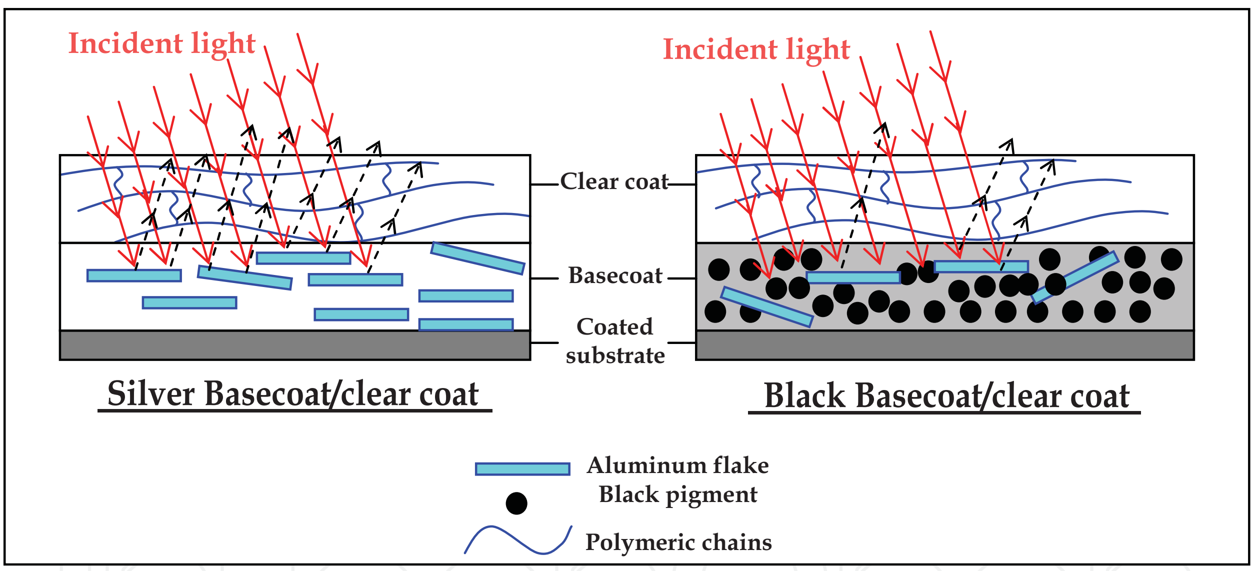


Fig. 8. The reaction of two different basecoat pigmentations to incident light.

Therefore, these two basecoats seems to be two extreme examples in their reaction to incident light. Other basecoats, depending on their ability to reflect or absorb light could be ranked to be somewhere between the black and silver.

The rate of variations in carbonyl groups of a coating during weathering can in fact be considered as the photodegradation rate of that coating (Mielewski et al., 1991). Figure 9 shows normalized absorbances of carbonyl bands of clear coats attached to silver or black basecoats.

It is clearly obvious that the photodegradation rate of the clear coat having a silver basecoat is greater than that of the black one during weathering. Such results indicate the higher ability of silver basecoat to induce photodegradation reactions in the clear coat during weathering exposure (Yari et al., 2009a).

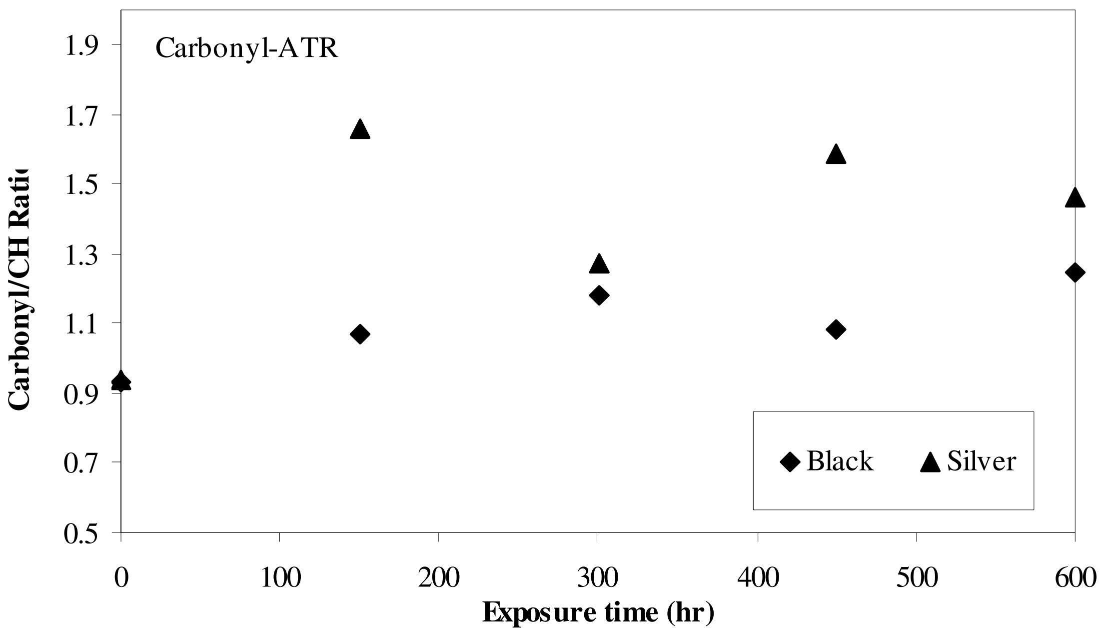


Fig. 9. Normalized absorbances of carbonyl bands of clear coats attached to silver or black basecoats.

Various approaches are available for lower photodegradation mechanisms given above. The first method is to prevent the UV rays from being reached the coating chromophores by adding substances which are able to strongly absorb and filter the UV wavelengths (Valet, 1997; Bauer, 1994). These materials are called Ultra Violet Absorber (UVA). The conventional UVAs are benzotriazoles, triazines and bezophenones. Nowadays, by advances obtained in nanotechnology, new generation of materials have been achieved that not only are capable to absorb UV rays, but also can improve the mechanical, thermal and electrochemical performance of the coating (Peng et al, 2008; Dhoke et al., 2009; Xu & Xie, 2003) . The best choices for this purpose are titanium dioxide, zinc oxide, cerium oxide, iron oxide or even silica nanoparticles. Because of the high surface area of these nanoparticles the absorption efficiency of these materials has been promoted considerably. Figure10 shows AFM topographic images of two acrylic melamine clear coats containing 0 and 3.75% nanosilica after 1000 hours exposure times (Yari, 2008).

Figure 10 also clearly reveals that the most variations is assigned to neat polymer while nanocomposite tolerates less variation in surface topology, meaning less weathering degradation. This indicates that incorporation of nano silica into acrylic melamine not only has not any effect on weathering durability, it enhances its resistance during weathering. The better weathering performance of clear coats containing nanosilica is assigned to the ability of nano silica particles to absorb the ultra violet and visible light, resulting in less degradation in nano silica-containing clear coats (Jalili, 2007; Zhou, 2002).

Another preventive strategy for improving the resistance of coatings against photodegradation is the use of quenchers and radical scavengers. Quenchers are materials that can transfer the excited state of ch* to themselves. They then become excited. Their excited state is not able to produce free radicals. Radical scavengers convert the active free radicals to inactive ones and are unable to participate in photodegradation reactions. Hindered amine light stabilizers (HALS) are the most typical kinds of additives for this purpose(Bauer et al., 1992; Seubert, 2003; Mielewski et al., 1993). Synergestic effect of HALS and UVA have made a significant improvement in photostability of the coatings.

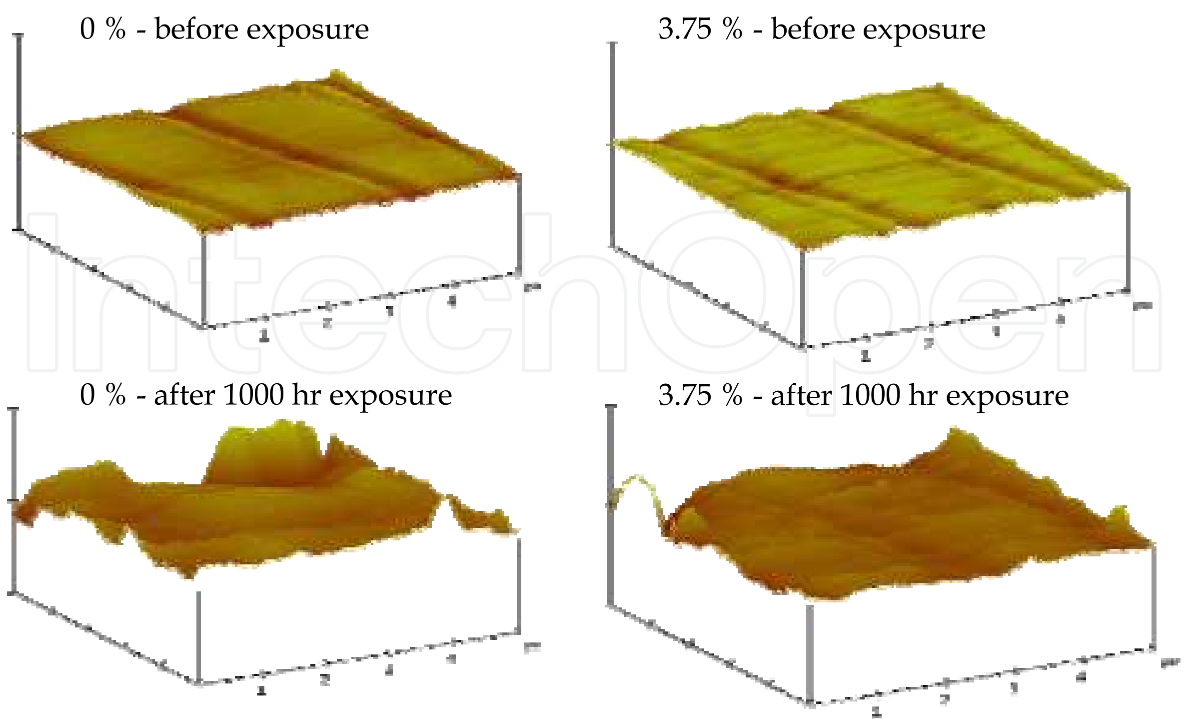


Fig. 10. AFM topographic images of different clear coats after various exposure times.

2.2.3 Water and humidity

Raining, car-washing, and dew formation are conditions by which water is in contact with automotive coatings during its service life. While, most polymers are hydrophobic and are not affected by water and humidity, some polymers that have water-sensitive linkages in their structure can be hydrolyzed by water or humidity. Acrylic/melamine as the most typical structure used in automotive clear coats, is vulnerable to water and well susceptible to hydrolytically degrade.

Figure 11 depicts different reactions happening in hydrolytic degradation of a typical acrylic melamine.

In these hydrolytic degradations, various etheric, esteric and methylene bridges are broken, creating various OH&NH-containing products, i.e. methylol melamine and primary or secondary amines (Nguyen et al., 2002 a; b; 2003). Meanwhile, other reactions called self-condensation reactions occur between methylol melamine groups present either in initial structure of clear coats or formed during early times of reactions. As a result of self-condensation reactions, different melamine-melamine linkages i.e. new methylene or etheric bridges (reactions c and d in figure 11) are formed. These new formed linkages have less flexibility than the initial linkages. This results in a higher glass transition temperature.

It has been demonstrated that chemical structure (like the ratio of acrylic/melamine or polyol/isocyanate) and cross-linking density of the clear coat have a significant impact on the intensity of the hydrolytic degradation (Yari et al., 2009b). The lower the cross-linking density, the greater is water permeation and blister formation. The assessment of the resistance of the coating against humidity is carried out by saturated humidity test. The results of blister formation and the visual appearance of two different coatings (with high and low cross-linking densities) are shown in Figure 12.

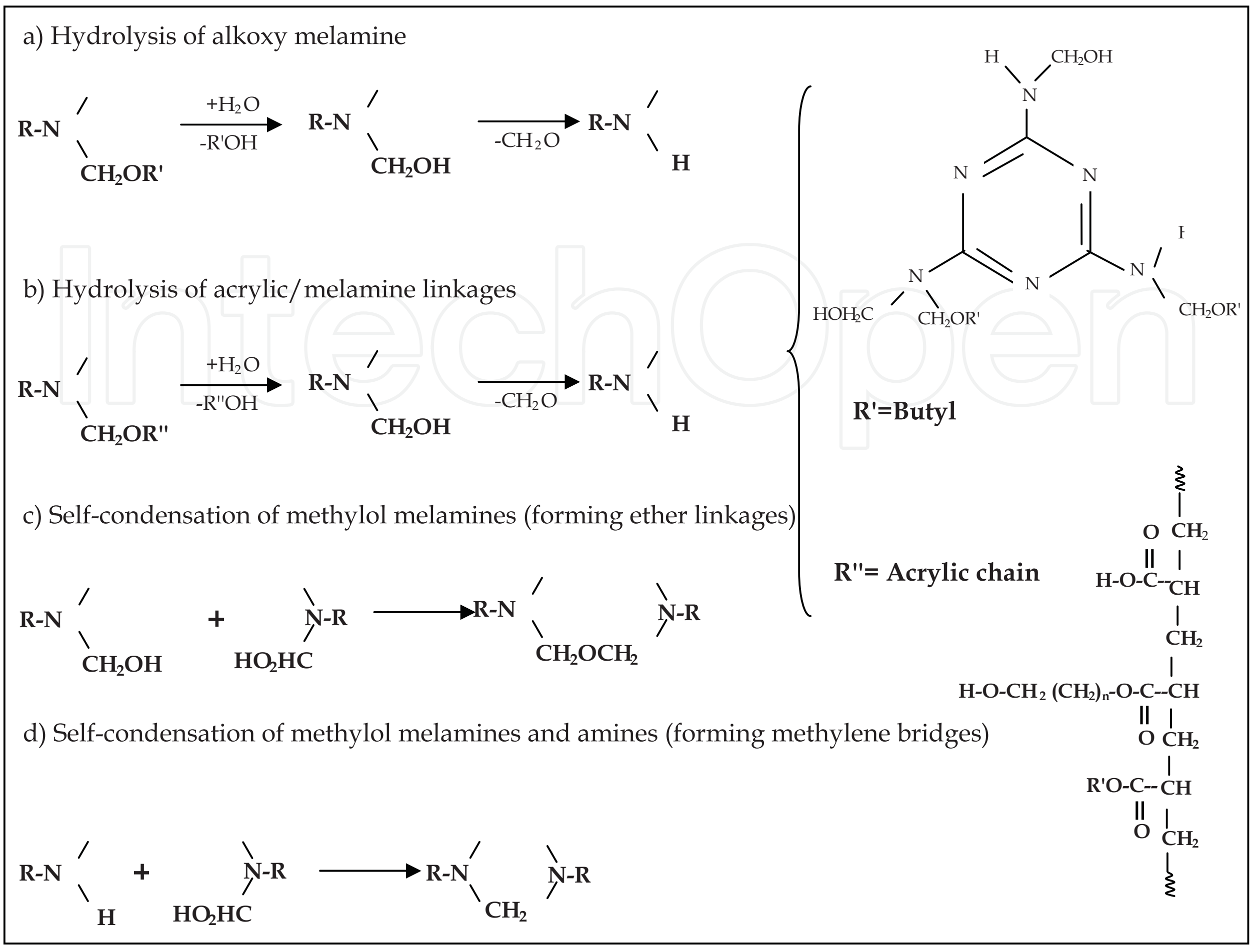


Fig. 11. Degradation and self-condensation reactions for a typical acrylic melamine.

Fig. 12. Results of humidity test for different types of coating.

Coating 1 is an automotive type with high cross-linking density (v_e= 0.002673 mol/cm^3) and coating 2 is the same one with lower cross-linking density(v_e= 0.000486 mol/cm^3). In contrary to coating1, which shows no blistering, severe blisters are seen on the surface of coating2. Blistering is a result of diffusion of water and other soluble materials into coating.

2.2.4 Acid rain

Acid rain which is a very common phenomenon in urban and industrial areas is a catalyzed type of hydrolytic degradation. Acidic environment catalyzes the hydrolysis reactions. Various gases like SO_2 produced in the polluted areas are converted into sulfuric acids which makes the precipitates acidic. These acidic rains when fall on the coatings catalyze the hydrolysis reaction of acrylic melamine clear coat. The acid catalyzed hydrolysis has been investigated in several works (Mori et al., 1999; Schulz, et al, 2000; Palm& Carlsson, 2002). It has been found that the acid rain and the acid catalyzed hydrolysis are most likely to occur at moderate to strong acidic environments. For example, the results reported by Schulz and co-workers (Schulz, et al, 2000) showed that, the pHs of a real acid rain even at the aggressive environments (Jacksonville, Florida) lied in the range of 3.5-4.5. Acid rain etches the acrylic melamine and strongly decreases the coating surface.
Different strategies can be adopted to increase the hydrolytic resistance of an acrylic melamine coating; decreasing the ratio of melamine, use of hydrophobic chains, decreasing melamine solubility, decreasing the basic strength of melamine and partially replacing of melamine with other amino resins.

2.3 Biological materials

Biological materials are those substances produced from bio sources. These are the most important environmental factors which affect the chemical, mechanical and visual performance of automotive coatings. These mainly include insect bodies, tree gums and bird droppings. Whilst, the influence of sunlight, humidity and acid rain on automotive coatings, especially on clear coat has been studied thoroughly, the effect of biological materials has not been dealt with in more details. In this regard, an automotive coating is repeatedly exposed to different biological materials such as bird-droppings, tree gums and insect bodies. Therefore, the investigation of the influence of such materials and the coating degradation mechanism seems inevitable. Stevani and co workers (Stevani et al., 2000) studied the influence of dragonfly eggs, a native insect of north and south America, on an acrylic melamine automotive clear coat. They found that hydrogen peroxide released during hardening of eggs, oxidizes the cysteine and cystine residues present in the egg protein, leading to the formation of sulfinic and sulfonic acids. The acids produced catalyze the hydrolytic degradation.

2.3.1 Bird droppings

In different papers, the effects of bird droppings on appearance and thermal-mechanical properties of coating have been investigated (Ramezanzadeh et al., 2009; Ramezanzadeh et al., 2010 a). Typical defects observed on the clear coats influenced by bird droppings were investigated by different techniques as shown in figure13 (Ramezanzadeh et al., 2010 a; Yari et al., 2010).
The optical microscope images of clear coats show that even at a relatively short exposure time to bird droppings and pancreatin, the clear coat surfaces have been etched severely.

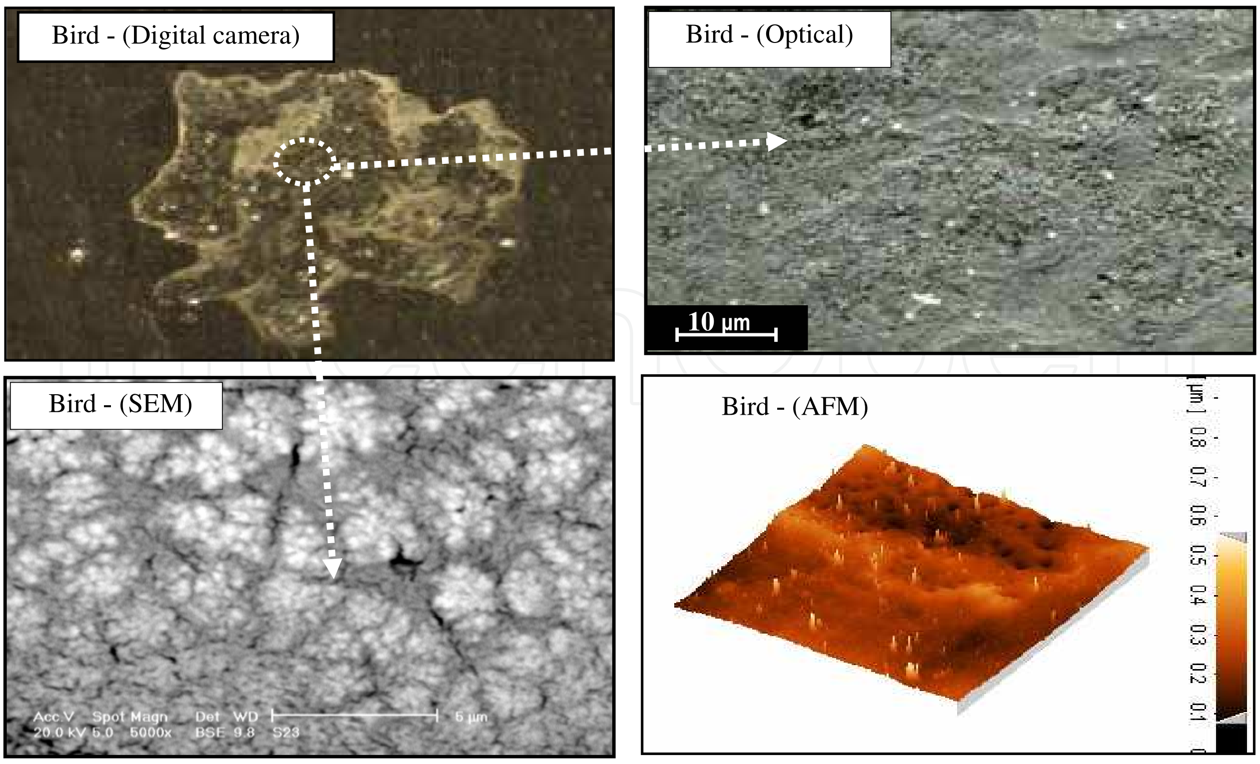
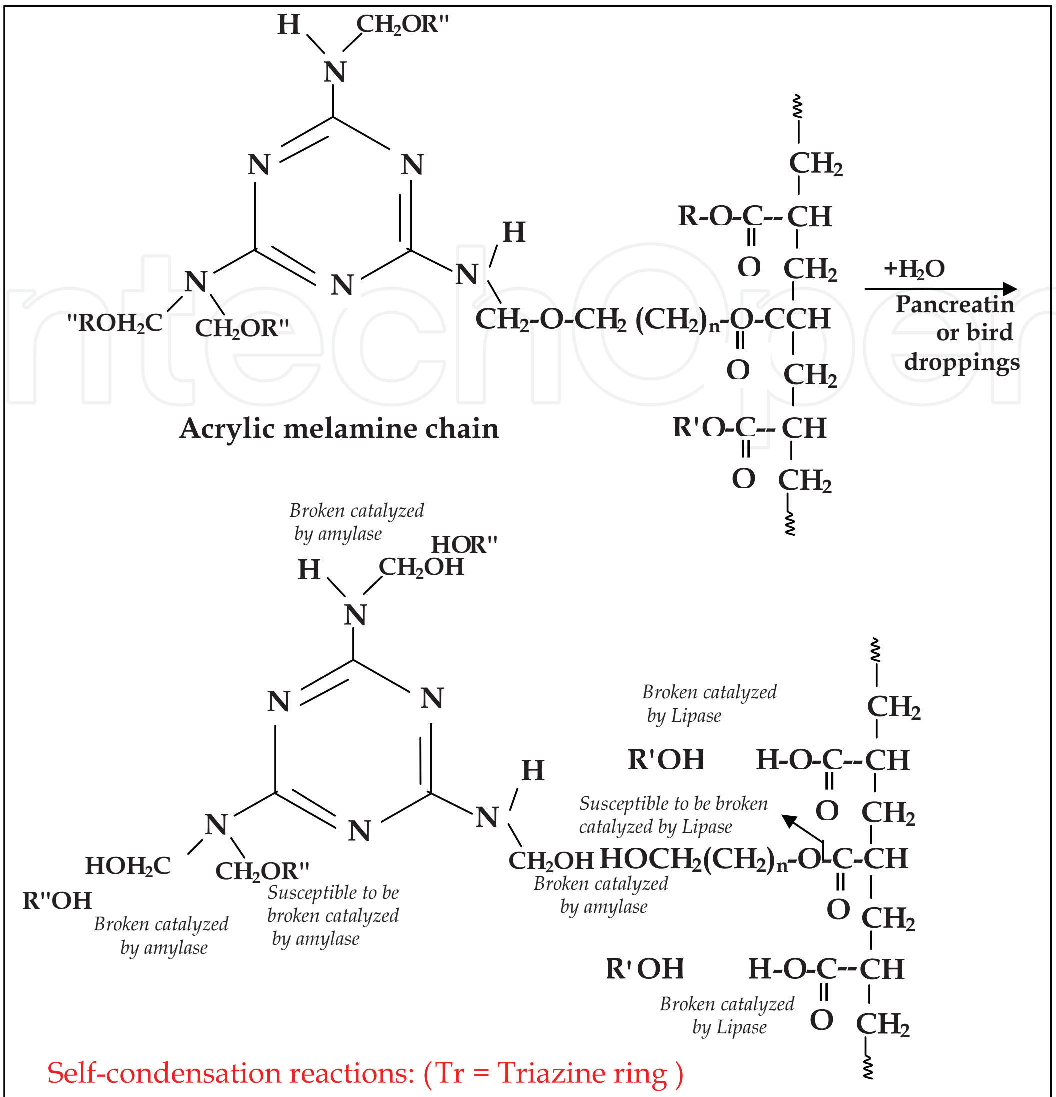


Fig. 13. Appearance of defects created after being exposed to bird droppings.

These images may confirm that chemical reactions have occurred at the surface, leading to dissolved and etched areas. It was found that bird droppings decreased the appearance parameters of clear coat, i.e. gloss, distinctness of image (DOI) and color values, therefore affecting the aesthetic properties of the coating system (Ramezanzadeh et al., 2009). Thermal-mechanical studies also showed that hardness, glass transition temperature and cross-linking density of degraded clear coats decreased in the presence of bird droppings (Ramezanzadeh et al., 2010 a). Also, the influence of aging method (pre-aging or post-aging) and chemical structure of clear coats against such bio attacks, were reported (Ramezanzadeh et al., 2009; Yari et al., 2009 c) [11,12]. It was observed that post-aging process, which simultaneously exposes bird droppings and UV radiation to coatings, degraded the clear coat much more intensively than the pre-aging one, in which only bird droppings on pre-weathered clear coats was exposed (Ramezanzadeh et al., 2009). The investigation of clear coat chemistry revealed, that incorporating higher ratios of melamine cross-linker, in spite of resulting a higher cross-linking density, led to an inferior biological resistance (Yari et al., 2009 c).

Although the main process was a hydrolytic cleavage, it was also a catalyzed hydrolytic degradation. The mechanism of this bio-attack is shown in figure14.

It has been reported that bird droppings consists of amylase, lipase and protease which are all hydrolase enzymes and are responsible for cleavage of C-O-C (for example in starches), COO esteric linkage (for example in glycerin) and CO-NH peptide amide linkages (for example in proteins), respectively. Enzymes are amino-acid molecules that their function is to catalyze various chemical reactions in biological environments, e.g. in the human body or animals. The rate of most enzyme-catalyzed reactions is millions of times faster than those of comparable un-catalyzed reactions.



Self-condensation reactions: (Tr = Triazine ring)

A) $2\ Tr\text{-}NH\text{-}CH_2\text{-}OH \longrightarrow Tr\text{-}NH\text{-}CH_2\text{-}O\text{-}CH_2\text{-}NH\text{-}Tr$ (formation new etheric linkages)

Or

B)

B-1) $Tr\text{-}NH\text{-}CH_2\text{-}OH \xrightarrow{Fast} Tr\text{-}NH_2 + CH_2O$

B-2) $Tr\text{-}NH\text{-}CH_2\text{-}OH + Tr\text{-}NH_2 \rightarrow Tr\text{-}NH\text{-}CH_2\text{-}NH\text{-}Tr$ (formation new methylene bridges)

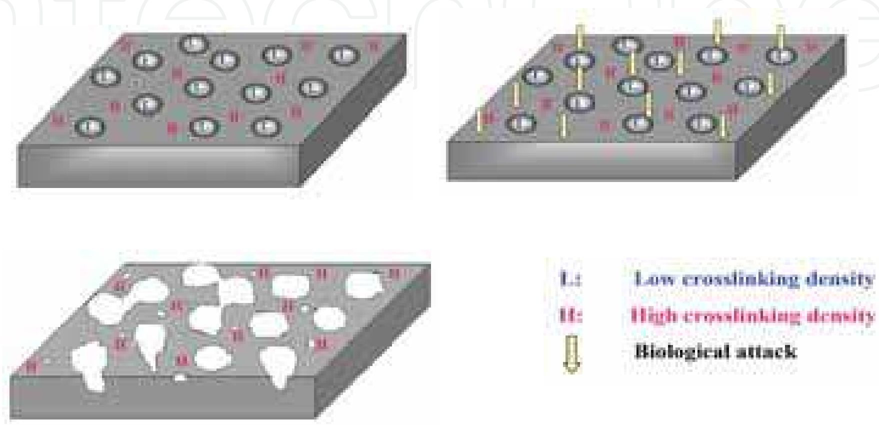


Fig. 14. Degradation Mechanism of a typical acrylic melamine caused by bird droppings.

After pancreatin or bird-droppings deposition on clear coat surface, the hydrolysis reaction can take place. The enzymes present in these materials catalyze the hydrolysis reaction. Among these enzymes, protease due to the absence of amide linkages (-CONH-) is relatively inactive on acrylic melamine. However, amylase and lipase enzymes act on etheric and esteric linkages respectively, accelerating the cleavage of these bonds. Due to the presence of high active sites (etheric and esteric linkages) in acrylic melamine, the cross-linked network is cleaved. This leads to formation of soluble products and releasing from the coating, leaving etched area on the surface. The clear coat consists of high cross-linking and low cross-linking regions. The latter are more vulnerable against hydrolytic degradations (Sangaj & Malshe, 2004) and are more affected.

As seen in SEM images of figure13, there are some micro cracks at degraded areas. This may be attributed to an ion-induced oxidation due to the presence of metal ions (Ratner et al., 1997).

Moreover, extensive studies on the similarity of bird droppings and pancreatin using X-ray fluorescence and Fourier Transform Infrared Analyses (Yari et al., 2010) showed that the chemical structures are generally similar. So same effects are created on coating after being exposed to bird droppings and pancreatin. Therefore, the use of pancreatin instead of natural bird dropping seems an alternative.

2.3.1.1 The effect of clear coat chemistry

The monomer types of acrylic resin, the functional groups of melamine cross-linker and the acrylic/melamine ratio, are the main factors which affect the curing (and inevitably its performance) in the resultant coating. However, due to the presence of esteric and etheric linkages in the structure of these resins, the occurrence of hydrolytic reaction seems probable, leading to inferior chemical and weathering resistance. It has been found that the chemistry of clear coat affects the coating performance against bird-dropping. It was shown that two acrylic melamine clear coats differing in melamine ratio had different resistance against bird dropping. Figure 15 shows the optical Images of two different partially methylated acrylic/melamine clear coat (Cl-1 and Cl-2) which only differ in acrylic:melamine ratios. Cl-1 has more melamine portion in its formulation.

The comparison of optical images of both clear coats shows that the Cl-1 undergoes more catastrophic etching compared to Cl-2. It may be attributed to higher portion of melamine component of Cl-1 which is more susceptible to hydrolysis reaction and therefore, a higher etching. whereas Cl-2 sample, with less amount of melamine, experiences lower etching (Yari et al., 2009 c).

2.3.1.2 The effect of basecoat pigmentation.

It has been demonstrated that basecoat pigmentation via affecting the efficiency of curing process of its attached clear coat influences the biological resistance of automotive coating system. In seeking the reason why the degrees of cure are different, the effect of pigmentation on heat transfer should be considered. In Figure 16 various mechanisms of heat transfer during the curing process are schematically shown (Ramezanzadeh et al., 2010 b).

The typical ovens used for curing of the coatings utilize hot air conditioning as well as IR lamps. It may also be expected that convection and radiation heat transfer are more important during such curing processes. The difference in curing behavior of clear coats attached to black and silver basecoats (two extreme basecoats) can be explained by emissivity factor of these basecoats. Emissivity factor of a material is the relative ability of its surface to emit energy by radiation. It is defined by the ratio of energy radiated by a

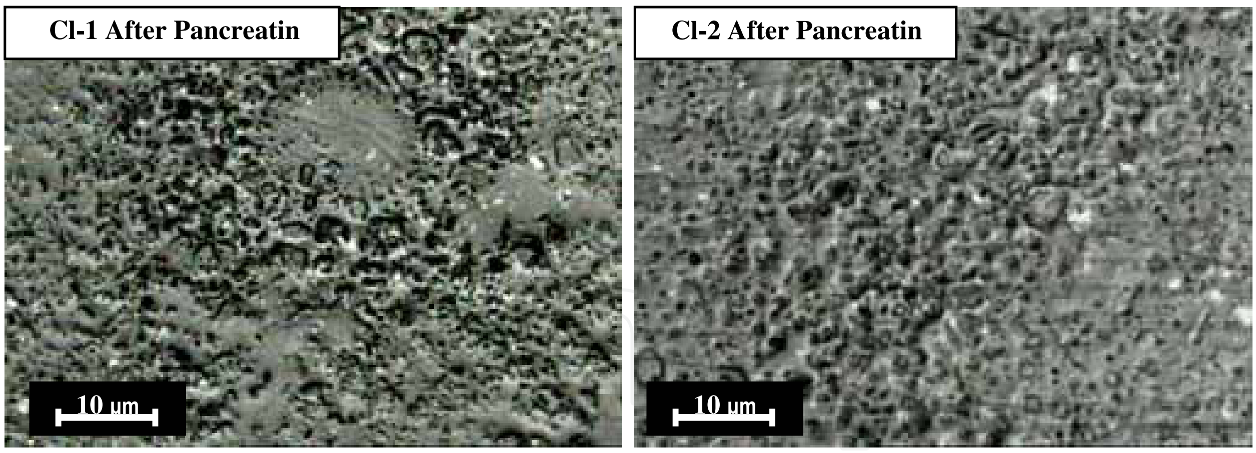


Fig. 15. Optical microscope micrographs of different samples differing in melamine ratio (Cl-1 has more melamine portion) degraded by pancreatin (or bird droppings) .

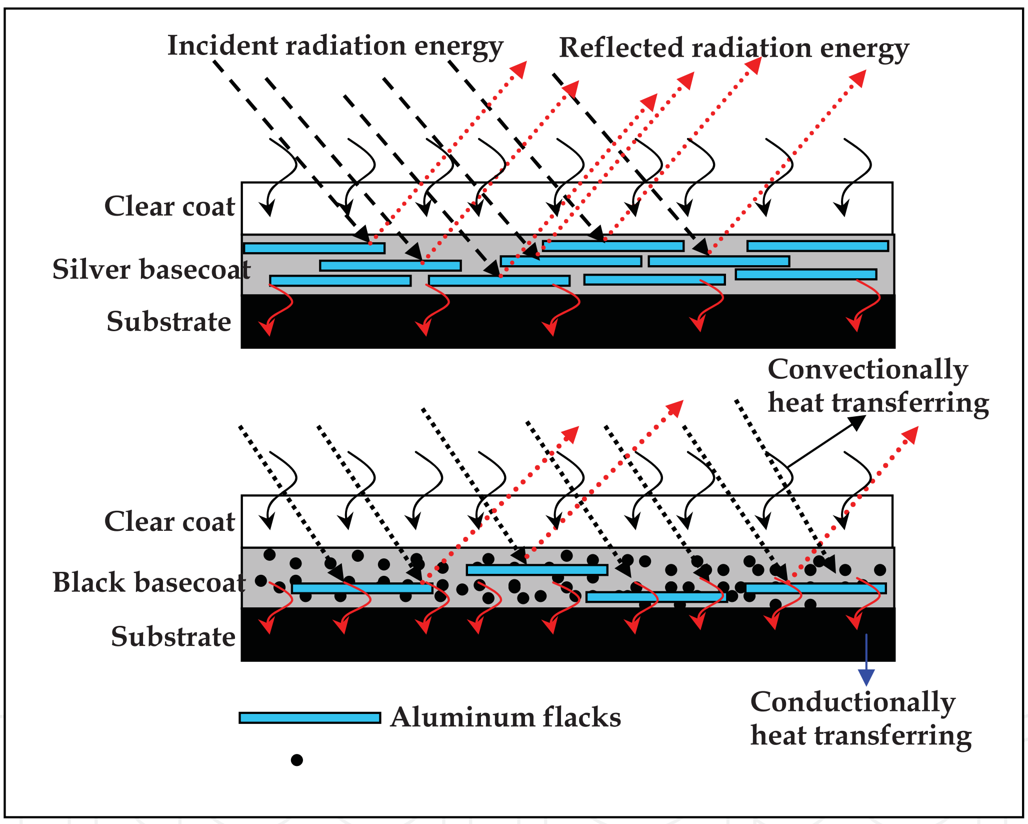


Fig. 16. Schematic representation of heat transfer during the curing process

particular material to energy radiated by a black body. According to Thomas (Thomas, 2005) the infrared emissivity factor of basecoats containing a typical carbon black pigment or a typical non-leafing aluminum pigment are 0.88-0.9 and 0.29-0.33, respectively. The greater the emissivity factor of a coating the lower is its infrared reflection. Additionally, it is highly likely that a silver basecoat would contain larger loads of an aluminum pigment compared to a black basecoat. Therefore, it is probable that the clear coat attached to a silver basecoat would be exposed to extra infrared radiation than that attached to a black basecoat. This extra energy may in turn induce a more complete degree of cure in the clear coat attached to a silver basecoat than that attached to a black basecoat.

Effects of basecoat pigmentation on visual performance of clear coats experiencing bird dropping attack can clearly be observed in Figure17.

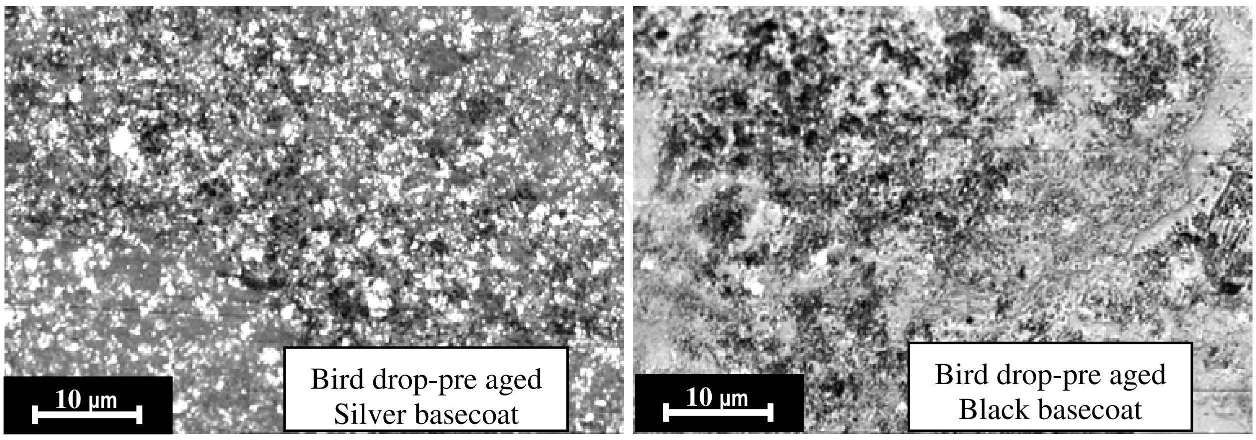


Fig. 17. Optical micrographs of the clear coat samples on silver and black basecoats exposed to biological materials

It is seen that the more efficient curing on clear coat having silver basecoat results in better performance compared to that of having a black basecoat.

2.3.1.3 The effect of aging process

As the biological materials affect the coating both in aged samples (exposed to environment) and its freshly prepared form, the aging conditions used to study the effect of these materials included a pre-aging and post-aging. Pre-aging means that before the exposure of clear coat to biological attack a four-stage aging process is performed. This multi-stage aging is conducted according to PSA D27 5415 standard. The details of stages have been explained elsewhere (Ramezanzadeh et al., 2009). In summary, these stages are schematically presented in figure 18. In post-aging method, the coating is subjected to both aging and biological attacks simultaneously.

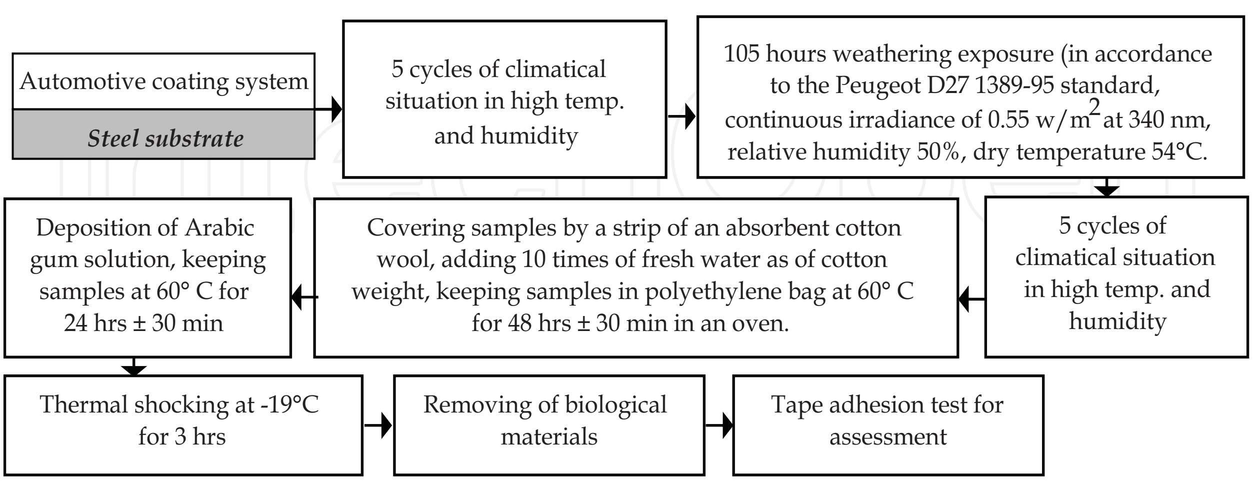


Fig. 18. A brief description of test method PSA Peugeot – Citroen D27 5415**.**

It was found that clear coats which have experienced simultaneous weathering and biological materials(post-aging) was more degraded than those being initially experienced

weathering condition followed by exposure to biological materials. It is due to the intensifying effect of UV radiation as well as sunlight.
Different methods can be pursued to prevent from degradation caused by bird droppings. Making the surface more hydrophobic, using clear coat with fewer esteric or etheric reactions can also be useful.

2.3.2 Natural tree gum

It is a general belief, that cars should be better kept under the shadow of trees 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. This can be seen from Figure 19.

Fig. 19. Effect of Arabic gum on car body.

The visual effect which is produced under tree gum attack can be shown in Figure 20.
According to Figure 20, the clear coats exposed to natural tree gums show considerable surface cracks indicating a severe physical effect. In addition, etching behavior of both materials, shown itself as numerous holes on the surface, can be also observed in the case of this kind of degradation. According to the above explanation, the general effects of gums can be appeared in both physical and chemical on the surface of coating. In addition, SEM micrographs of this kind of degradation can reveal sub-cracks inside of macro cracks shown in optical images. It can be also found that, the affected area (inside the crack) is lighter than the unaffected parts of coating. This can illustrate different elemental composition inside and outside the cracks. This can, similar to bird droppings, reveal the presence of metal compounds in gums structure. This phenomenon will be discussed later. The increased roughness in nano-scale of degraded parts of coatings (exposed to Arabic gum) can be obtained from the AFM micrograph (Ramezanzadeh et al., 2010b).

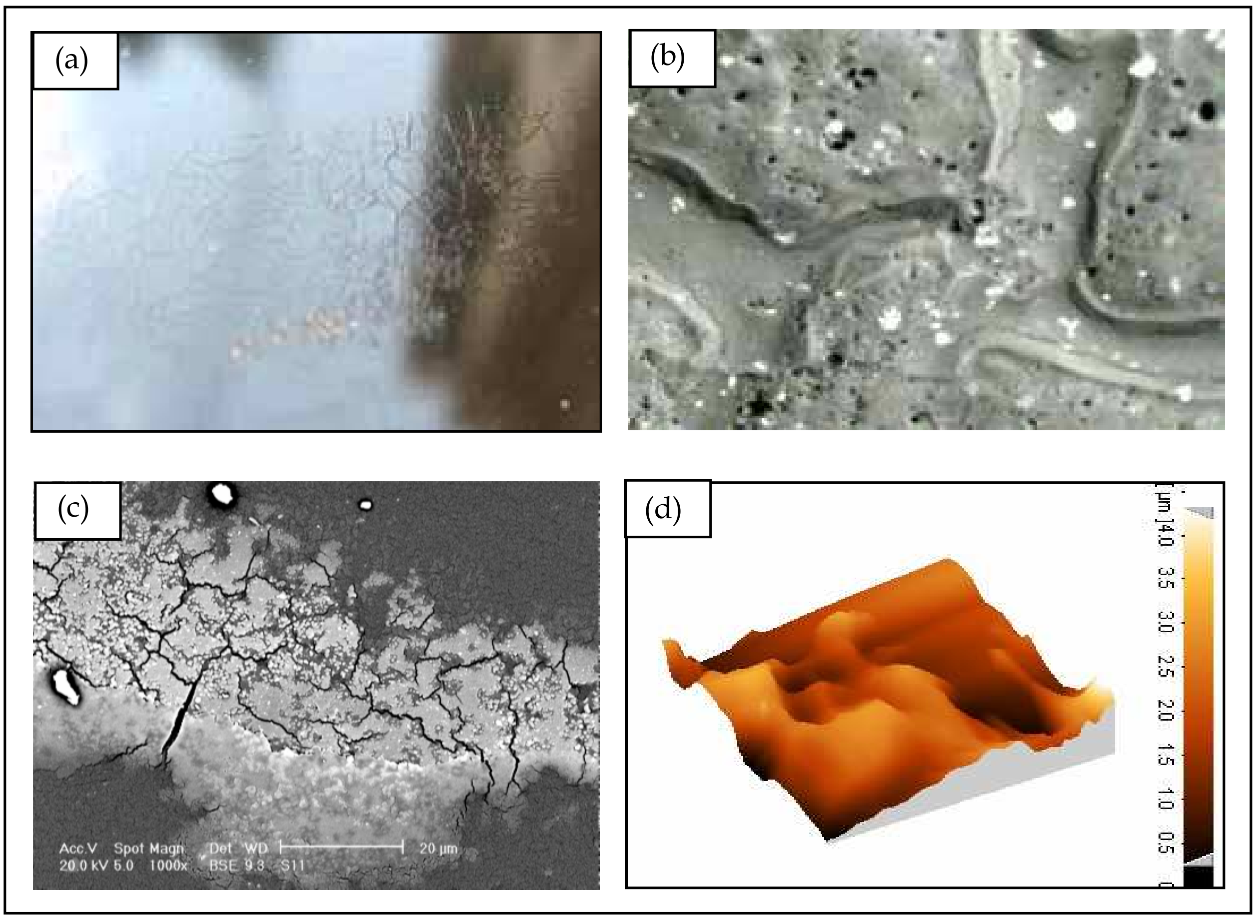


Fig. 20. Visual performance of coating after the tree gum attack, (a) visual performance, (b) optical image, (c) SEM micrograph and (d) AFM micrograph (Ramezanzadeh et al., 2010c).

2.3.2.1 Tree gum characteristics

Tree gums are completely soluble in water and have a sticky behavior in this state. The pH of this material is about 4.5 in a slurry state. Arabic gum has been used as a synthetic equivalent for tree gums. This was due to the similar acidic nature, physical state in water and their similar chemical structures (shown in Figure 21). However, many parameters i.e. soil nature, climatic condition (which trees grow there) and the type of tree can influence these characteristics (Ramezanzadeh et al., 2010b; Ramezanzadeh et al., 2010c).

The solubility of these gums can be explained by the presence of high amount of –OH groups (as shown in Figure 21) making them soluble in water. Due to these OH groups, Arabic gum has a sticky behavior in the slurry state. Therefore, when gum is exposed to the clear coat surface, based on the surface chemistry (hydrophobicity or hydrophilicity) a good adhesion can be obtained between the polar groups of coating and gum. When this system is exposed to higher temperatures, water is gradually vaporized. During the gum drying process, a significant stress can be imposed by the gum to the surface. To have a more understanding on how these applied stresses act, the visual performance of gum exposed clear coats are given in Figure 22 (Ramezanzadeh et al., 2010c).

According to the observations made in Figure 22, two different phenomena can be observed on the free films and the full system on metal plates. In the latter, a severe crack formation can be seen for the dried gum exposed samples, causing similar cracks on the clear coat layer. On the other hand, gum applied on free films has made the films to shrink. For the

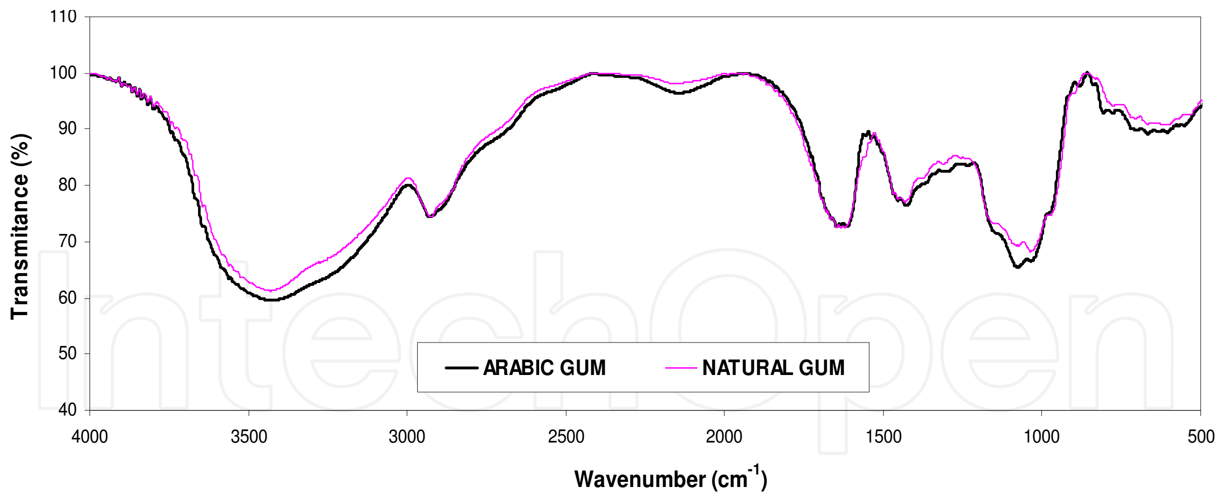


Fig. 21. FTIR spectra for natural and synthetic (Arabic) tree gum (Ramezanzadeh et al., 2010c).

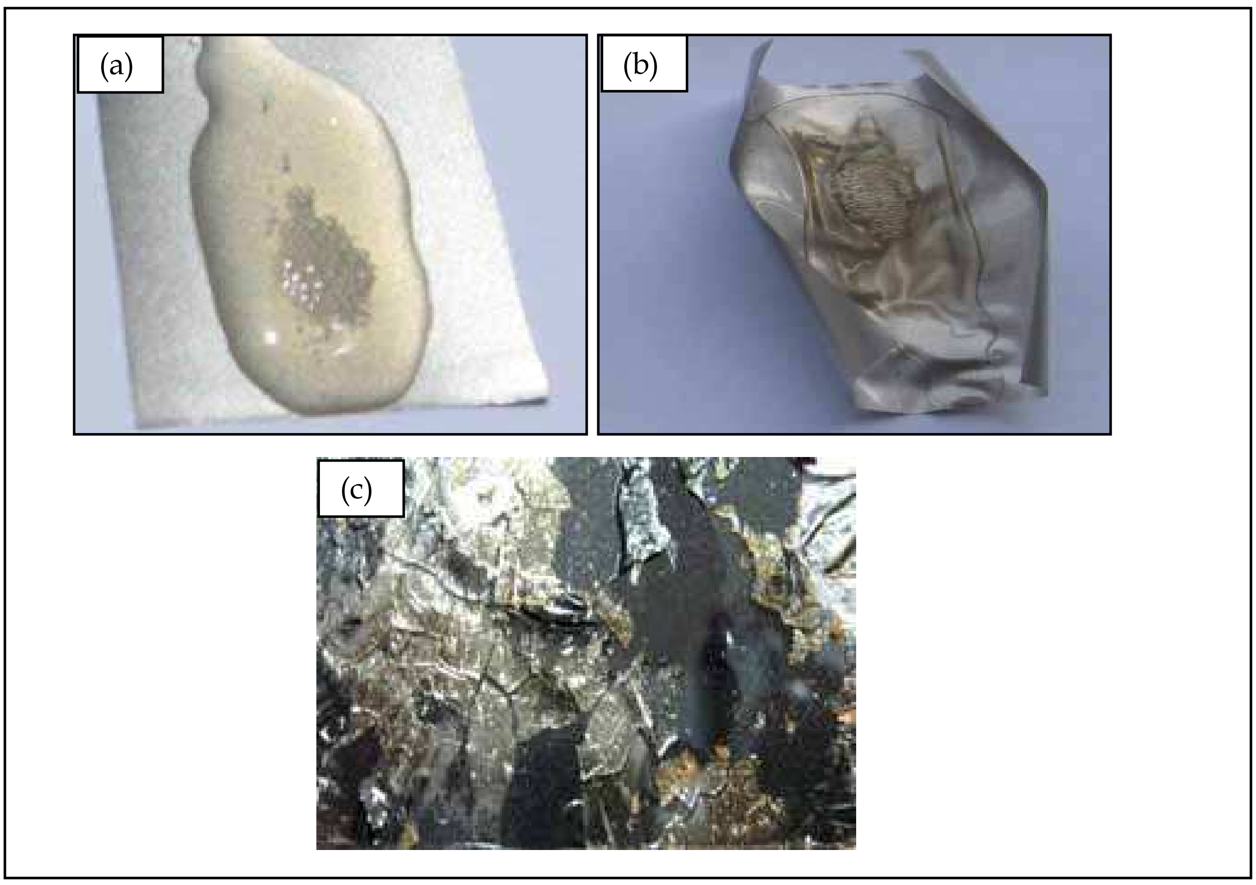


Fig. 22. The visual effect of gum attacked to (a) fully coated system on metal substrate and (b) free film of basecoat/clear coat (Ramezanzadeh et al., 2010c).

clear coat applied on the full automotive system, due to the great adhesion of clear coat to basecoat layer, and basecoat layer to other layers which are in contact with metal substrate, the stress cannot overcome the adhesion force and therefore, it causes surface cracks to propagate. However, for the free films, due to the lack of adhesion to the substrate, the greater cohesion force, in comparison to its adhesion, would turn the film to shrink. Different factors including aging condition, clear coat surface chemistry and basecoat pigmentation can influence this kind of degradation which will be briefly discussed later. Regarding the above explanations, the main source of producing this kind of degradation is the stress formation during gum drying. The stress can overcome adhesion force (between coating and substrate or clear coat and the other coating layers in a multi layer system) and/or cohesion of the clear coat and/or basecoat layers. The ability to store such stress and dissipate it can be depended on many factors, mainly coating viscoelastic properties and temperature. These will be explained later.

2.3.2.2 Physical attack by tree gum

2.3.2.2.1 Effect of aging condition on gum attack

In a real outdoor condition, coatings properties are continually affected by aging conditions. These effects could irretrievably change the chemical and mechanical properties of coatings. Aging process has been shown as an important factor which significantly influences the clear coat properties before and after the biological attack by bird droppings (Yari et al., 2010c; Ramezanzadeh et al., 2010). As previously discussed, two different ideas of the effect of aging on gums attack can be available. Aging condition can influence the degradation occurring during gum attack by affecting coating properties before the test. The second idea is the effect of weathering condition imposed to clear coat in contact with gum. The mechanisms by which these two aging conditions affect gum attack severity are completely different. To show how aging, before or after gum attack, can influence coatings properties, the visual performances of samples experienced these are given in Figure 23.

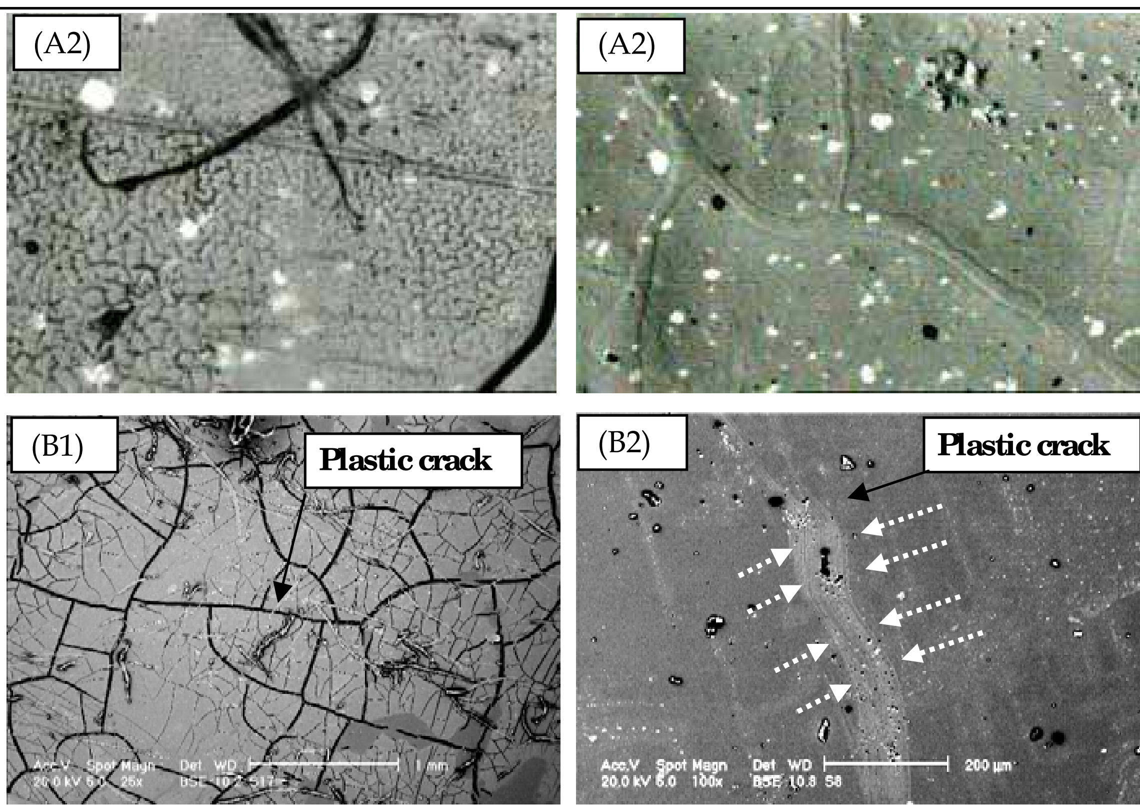


Fig. 23. Samples attacked by gum in A1 (optical micrograph) and B1 (SEM micrograph) post-aging and A2 (optical micrograph) and B2 (SEM micrograph) pre-aging processes (Ramezanzadeh et al., 2010c).

According to Figure 23, a greater surface crack has been produced on the samples exposed to gum at the post-aging process, in comparison to the pre-aging one. These results can reveal that, aging is an important parameter influencing the clear coat biological behavior. This explains that the effects of gum to give rise in surface attack may not only show the crack density or size differences but also reveals that the cracks produced on the samples experienced pre-aging condition have a plastic morphology, whilst cracks created under post-aging show a fracture nature. Highly fractured cracks observed on the clear coats exposed to gum under post-aging process, in comparison to the plastically deformed ones shown in the samples exposed to pre-aging, clearly reveal the importance of aging process on the crack morphology evolution (Ramezanzadeh et al., 2010c).

A significant increase of $\Delta[NH/NH_2$ and $OH]/[CH]$ after pre-aging process (before biological test) has occurred. This indicates that aging may significantly affect the clear coat by a chemical degradation mechanism. The increase in surface OH groups in the pre-aging condition, leads to significant increase of clear coat hydrophilicity (Ramezanzadeh et al., 2010c), and therefore, stronger interaction with gum. In addition, decreased Tg and crosslinking density of clear coat were obtained at this condition. These changes can negatively influence coating properties against the stress performed by gum. On the other hand, during the biological test in the post-aging, using water sprayed to the clear coat surface (during 300 h of xenon test), a greater interaction of gum and clear coat surface can be created. This can cause a more severe crack on the samples experienced post-aging. A decrease in drying process of gum can result in a greater interaction to clear coat, and therefore enhanced surface attack (Ramezanzadeh et al., 2010c).

2.3.2.2.2 Effect of coating chemistry on gum attack

As it was previously shown (Ramezanzadeh et al., 2010b; Ramezanzadeh et al., 2010c), due to the sticky behavior of gums in the slurry state, it makes a good adhesion to clear coat surface. Many researchers have tried to distinguish the main source of this adhesion. In fact, the tendency of Arabic or natural tree gum to adhere to the surface, results from the polar groups existed in this material. Therefore, the adhesion of Arabic gum to coating can directly depend on the clear coat surface energy (balance of hydrophilicity and hydrophobicity). According to the above explanations, the effect of gums on the clear coat can be directly corresponded to the strong adhesion before the experiment, as well as to the weak attachment after the drying. This behavior causes a great stress to the clear coat, which in turn is responsible for the physical degradation of coating, as shown in Figures 22 and 23. The failure which this stress can perform to clear coats can depend on both clear coats compositions and the undercoat layers mechanical and viscoelastic properties. In addition, the effects of this stress on coating performance can be discussed by two different phenomena as (i) stress restoring and (ii) crack propagation. Based on coating viscoelastic properties, different behaviors of the coating against the inserted stress is predictable. The greater toughness and elastic properties of a coating, the higher the ability is for stress restoring, leading to relaxation during a period of time. In this case, stress can not affect the coating properties. However, most coatings have a viscoelastic properties rather than elastic. The viscose part of the coating does not have restoring and relaxing behavior against applied stress. So, the stress causes a failure on the coating. When the applied stress is not able to overcome the adhesion forces between coating layers, it can affect the cohesion. Different factors may affect the coating cohesion properties, especially the cross-linking density. A lower cross-linking density can cause a lower cohesion. In a real condition, coating surface contains different areas having different cross-linking densities. Theses parts of coatings have a lower elastic behavior and, therefore are able to restore the stress. In addition, the lower cross-linking density of some parts of clear coat may be attributed to a lower curing degree. Therefore, it may be expected that, these parts of coating have a more polarity than other parts due to the presence of unreacted functional groups. This may cause a stronger interaction of gums polar groups to clear coat surface at these areas. Based upon the above explanations, the stress inserted to the clear coat can affect some parts of the coating more intensively than the other parts. Therefore, stress can be propagated from the weak points. In this way, the applied stress may be dissipated by the crack formation (Ramezanzadeh et al., 2010c).

2.3.2.2.3 Effect of basecoat pigmentation on gum attack

It was previously demonstrated that (Ramezanzadeh et al., 2010c; Yari et al., 2009a), basecoat pigmentation can considerably influence the mechanical properties of an automotive clear coat. This behavior was attributed to the curing degree and post reactions occurred. Therefore, according to these results, outdoor weathering conditions may well affect the clear coat properties based on the type of basecoat. Biological resistance of an automotive clear coat can also be expected to show different behavior depending on the basecoat pigmentation type. To show how basecoat pigmentation affect coating behavior against gum attack, the effect of gum on fully coated and free films of the clear coats applied over silver and black basecoat are shown in Figure 24 (Ramezanzadeh et al., 2010c).

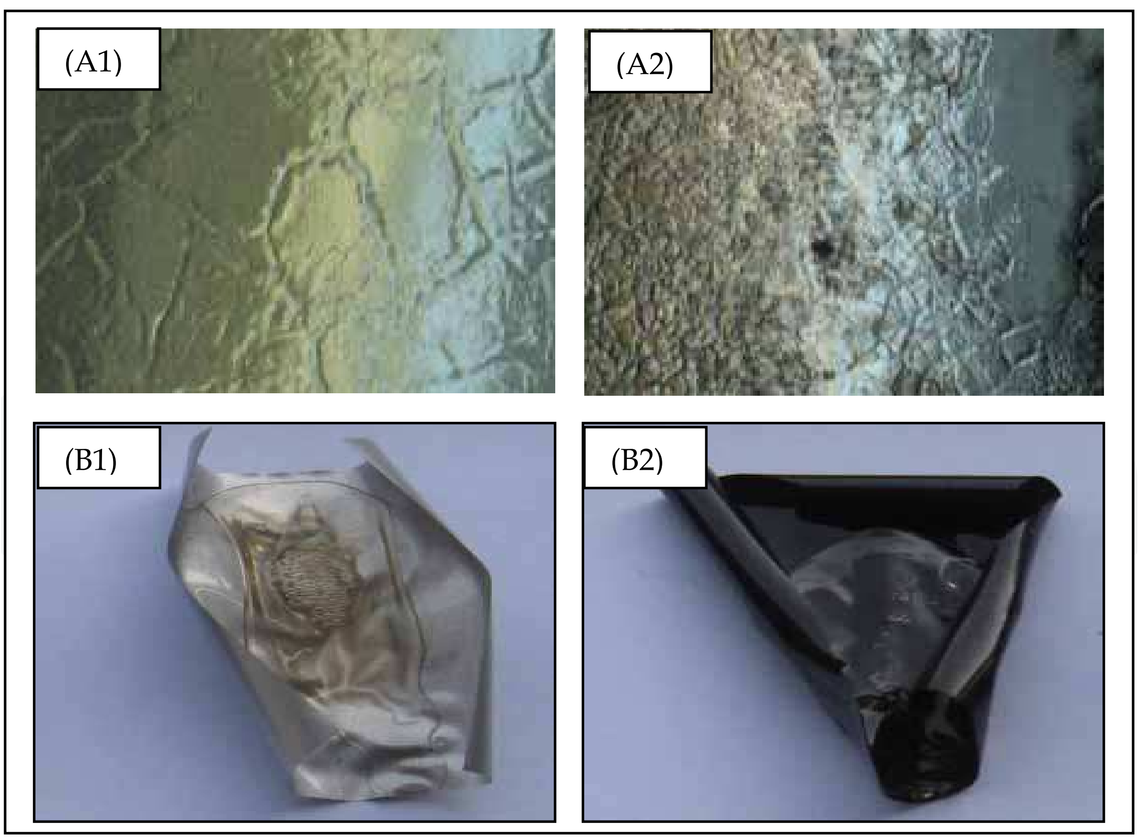


Fig. 24. Effect of basecoat pigmentation on their biological performance in the case of gum attack on (A1) and (A2) full coated and (B1) and (B2) free films (Ramezanzadeh et al., 2010c).

It can be seen that the surface cracks produced by gums over the clear/black system are smaller in size. However, fewer cracks being greater in size for the clear coat on the silver basecoat can be observed. Smaller cracks appeared in the black coating system revealed the greater ability to restore and relax the stress. To show how gum can differently affect clear coats applied over different basecoats, the drying process of gum on these two different samples are shown in Figure 25 (Ramezanzadeh et al., 2010c).

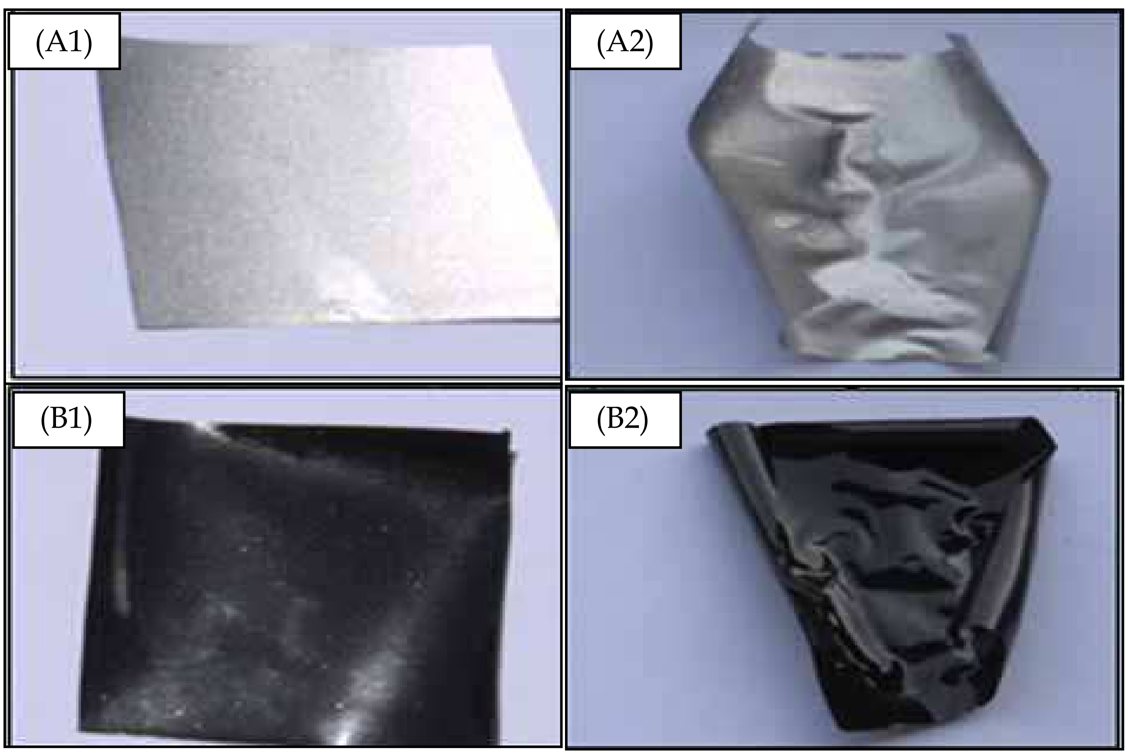


Fig. 25. Effect of gum on (A1) silver and (B1) black (before exposure) samples, and (A2) silver and (B2) black samples after exposure (Ramezanzadeh et al., 2010c).

According to Figure 25, greater shrinkage of black sample can be obtained. These differences can be resulted from the many different factors mainly the difference between the chemical structures of the clear coats applied over these basecoats and the mechanical properties of basecoat layer. In a silver system, due to the lower emissivity factor of basecoat, a greater curing can be obtained resulting in a higher cross-linking density and toughness. In addition, as a result of this better curing, less hydrophilicity and therefore adhesion of gum to clear coat surface can be obtained. The higher Tg of the clear coat on the silver system, as well as its greater cross-linking density, would result in different mechanical properties (Ramezanzadeh et al., 2010c). Moreover, a greater clear coat storage modulus of the silver system (at the temperature of biological test), can reveal different mechanical properties of this clear coat, which can effectively influence the biological attack to tackle the stress. The result is a higher capability of this coating to restore and further dissipate the stress performed by Arabic gum. This means that the greater cross-linking density of this sample (silver one) causes a higher cohesion. Therefore, the ability of the clear coat to distribute the stress on the entire film and other layers is prevention of the stress concentration and formation of cracks, the consequence of which is that the mechanical properties of basecoat layer are affected. Hence, as the mechanical properties of basecoat layers are different, the higher vulnerability of the black system in biological attack is probable. The greater aluminum flakes presented in the silver basecoat, due to the formation of a stronger physical network, causes a higher toughness, in comparison to the black basecoat, causing greater resistance of coating against the applied stress for this system. In addition, the presence of aluminum flakes in the basecoat can cause a greater damping behavior of this layer by preventing the stress concentration on coating (Ramezanzadeh et al., 2010c).

2.3.2.3 Chemical attack by tree gum

As shown in Figure 20, several etched areas can be observed on the clear coats which only experienced 300 h exposure to simultaneous weathering and gums. The presence of these etched areas in a relatively short exposure time indicates that, gums can accelerate the hydrolytic degradation of acrylic melamine, leading to extensive formation of soluble products which are easily released from the coating, leaving spotted etched areas. As stated before, the pHs of Arabic and natural gums are acidic (4.7 and 4.28, respectively). The acidic environment created by gums may also account for the occurrence of such accelerated etching phenomenon. It has been found that, acidic solutions can affect and catalyze the hydrolysis reactions in the same way (Zhou et al., 2002; Schulz et al., 2000). Several researchers have studied this condition for acrylic melamine, in terms of degradation caused by ''acid rain'', which is also a very common phenomenon. The pH of acid rain is around 3.5–4.5. A stronger acidic environment causes more catastrophic degradations. Therefore, the grater variations in FTIR spectra of clear coats exposed to natural gum, compared to that of samples in contact with gum, can be explained by the more acidic nature of this material. These observations can illustrate that, gums can influence coating properties both in chemical and physical ways but mainly in physical direction (Ramezanzadeh et al., 2010c).

3. Concluding remarks

The properties and characteristics of automotive coatings have been discussed. The complicated conditions imposed to these systems need to be well understood in order to enhance their resistance against environment. Photo and hydrolytic degradations are the two common phenomena occurring under external conditions. In addition, the viscoelastic behavior of coatings is also detrimental for a proper mechanical performance. Above all, biological degradation is as important as the other types of failures.

To highlight this kind of degradation the effects of bird droppings and tree gums on an automotive clear coat have been studied. Results showed an irretrievable effect of these biologicals on the visual performance, mechanical and chemical properties of clear coat. Effect of clear coat chemistry on its biological performance, exposed to natural and synthetic biological materials, has been studied. The effects of basecoat pigmentation and aging condition on the biological performance of the clear coat have been also investigated. The general conclusions obtained are shown below:

1. It has been found that the catalytic hydrolysis of etheric and esteric bonds are the reasons for coating degradation when exposed to bird droppings. It was found that natural bird droppings, due to containing some digestive hydrolyse enzymes such as amylase and lipase, are able to catalyze the hydrolytic cleavage of etheric and esteric linkages of acrylic melamine clear coat. The consequence of these cleavages is the release of water soluble products from the coating, leaving etched areas and local

defects as well as decreased appearance on clear coat surface. Results clearly revealed that bird droppings considerably affect the clear coat mechanical properties. According to these results, Tg and elastic modulus were negatively decreased. In addition, the decreased micro hardnesses of clear coats exposed to these biological materials was a further observation indicating the severe effects of biological materials on the mechanical properties of clear coats.

2. The pronounced effect of natural tree gum was a severe crack formation and shrinkage on fully coated systems and free film samples, respectively. It was also shown that, gum could strongly attach to clear coat surface before a drying process commenced. During gum drying, significant stress can be applied on the coating layers, especially the clear coat. Based on the coating properties, i.e. viscoelastic and toughness, different behaviors of coatings against applied stress, such as stress relaxation and/or coating failure were observed.
3. It has been demonstrated that many parameters mainly surface chemistry and viscoelastic properties of clear coat (the balance of surface hydrophobicity/ hydrophilicity), aging condition (post or pre aging) and basecoat pigmentation (metallic or non-metallic) can influence coatings biological performance.

4. Future trends

It would be interesting to further study the effects of surface chemistry (hydrophilicity/hydrophobicity balance) on the biological resistance of automotive coatings. Also investigating the influences of viscoelastic properties of coating systems need more attention. Use of nano-based materials such as additives and pigments seem to be effective.

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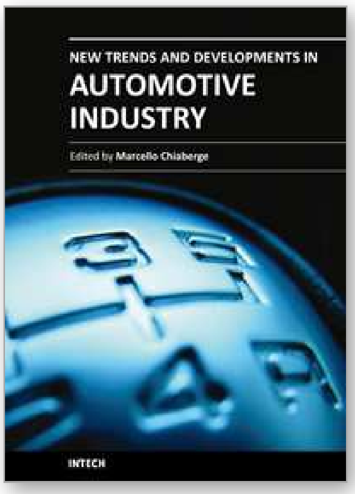

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This book is divided in five main parts (production technology, system production, machinery, design and materials) and tries to show emerging solutions in automotive industry fields related to OEMs and no-OEMs sectors in order to show the vitality of this leading industry for worldwide economies and related important impacts on other industrial sectors and their environmental sub-products.