J Therm Anal Calorim (2010) 102:13–21
DOI 10.1007/s10973-009-0442-4

A study of thermal–mechanical properties of an automotive coating exposed to natural and simulated bird droppings

B. Ramezanzadeh · M. Mohseni · H. Yari · S. Sabbaghian

Received: 28 April 2009 / Accepted: 18 August 2009 / Published online: 19 September 2009

Abstract Biological resistance of coatings can be regarded as one of the main properties in automotive industries. This study aims to investigate the effects of biological materials on the mechanical performance of an automotive clear coat. To this end, two acrylic melamine clear coats containing different melamine cross-linker contents were used. In addition, biological resistance of these clear coats were studied at two different ageing processes including pre-ageing and post-ageing which involve various hot-cold, humid shockings and UV radiation of sunlight. By the aid of optical microscopy, micro Vickers and DMTA analyses, different optical and mechanical properties such as micro hardness, T_g, cross-linking density and storage modulus were studied. Results revealed an inverse impact of both biological materials to decrease the clear coats mechanical attributes. In addition, a complicated effect of ageing conditions was observed for both clear coats exposed to these materials. It was shown that the coating having a higher mechanical properties and T_g even resulted in a lower biological resistance.

Keywords Bird droppings · Pancreatin · Biological degradation

Introduction

In recent years, there have been a vast number of studies to investigate the effects of environmental factors on the automotive coating degradation phenomena and their influence on film properties including appearance and mechanical performance [1–5]. Different parameters such as T_g and cross-linking density of a coating can be responsible for the mechanical properties in its service life when it is exposed to outdoor degrading conditions i.e., hot-cold and internal stresses due to the presence of humidity and UV radiation [1, 5–8]. Accordingly, dissociation processes involving hydrolytic cleavage and photo degradation of the polymeric coating may occur, resulting in changes to the pristine mechanical attributes of the coating [1, 8]. On the other hand, biologically induced degradation can also take place. This type of degradation, commonly known as biological degradation, has not been studied in details. In this regard, an automotive coating may be attacked by various biological compounds, mainly being bird droppings, tree resins dragonflies and insect gums [9–11]. The chemical composition of the most biological materials such as bird droppings is not clearly known, as they contain different enzymes, the presence of which may vary depending on a bird type and nutrition behaviour. The common degradation mechanism introduced for the biological attack may be an enzymatically induced hydrolytic reaction catalyzed in the presence of these enzymes [12–14]. Hydrolytic degradation process during biological attack can be regarded as severe as any other type of hydrolytic degradation processes reported so far [6, 7]. This effect is more pronounced as the coatings experience ageing conditions in a real atmospheric environment such as UV radiation. In this study, the effects of two different ageing processes consisting of a pre-ageing (to simulate the hot-cold, humid shockings and UV radiation from the sunlight) and a post-ageing (to simulate the outdoor ageing condition after the exposure of biological materials) on the performance of an automotive clear coat have been investigated.

B. Ramezanzadeh · M. Mohseni (✉) · H. Yari
Department of Polymer Engineering, Amirkabir University of Technology, P.O. Box 15875-4413, Tehran, Iran
e-mail: mmohseni@aut.ac.ir

S. Sabbaghian
Paint Shop 1, Irankhodro Co., P.O. Box 11365-1313, Tehran, Iran

Experimental

Sample preparation

Two types of acrylic–melamine resins containing different ratios of acrylic/melamine cross-linkers being 80/20 and 70/30 were utilized as the clear coat. In addition, a polyester–melamine resin was also used as the metallic basecoat layer in a multilayered automotive coating system. This multilayer system involves a thin layer of a phosphating conversion coating with 2–3 μm in thickness applied on carefully acid washed metal plates, followed by an electrophoretically deposited primer in 10–15 μm in thickness. In addition, a polyester–melamine layer having 30–45 μm in thickness was applied on the electrophoretically deposited layer followed by curing at 413 K for 20 min. The basecoat consists of a black pigmented layer being 10–15 μm thick, on top of which different clear coat formulations in 30–45 μm in thickness were applied, in a process known as wet-on-wet application. The curing was conducted at 413 K for 20 min. All these coating systems were supplied by Irankhodro Company production line. Sample codings used in this study are shown in Table 1.

The reason to use a complete coating system is because there is no other way logical to study the top layer alone as the resistance against any influential outdoor conditions mainly depends on the whole layers. This is so in all studies concerning the automotive coatings, either for weathering resistance or biological resistance. This means that the testing conditions are as near as the real conditions a car body experiences. This work, too, has tried to study the biological attacks of bird droppings on a complete coated car body which is attacked by biological materials during its service life. In the traditional automotive coating systems, a solid coating is used. Clear coat as a top coat layer of a complete automotive coating system is responsible for the appearance, while the basecoat protects the coating system against various outdoor conditions. On the other hand, in our previous studies [15–17], it was demonstrated that basecoat pigmentation can significantly affect the chemical and mechanical properties of the clear coat layer during weathering test and biological attack. Therefore, the role of basecoat layer on biological degradation of clear coat layer can justify the employed multi layer coating used. The use of top layer alone may simply neglect the role of other layers especially the base coat.

Table 1 Samples coding

Coding	Specification
Bl (Cl-1)	Blank clear coat with the ratio of acrylic/melamine of 80/20
Bl (Cl-2)	Blank clear coat with the ratio of acrylic/melamine of 70/30
Pre-aged sample (Cl-1)	Cl-1 Clear coat has exposed to four pre-ageing processes
Pre-aged sample (Cl-2)	Cl-2 Clear coat has exposed to four pre-ageing processes
Pre-aged panc (Cl-1)	Pre-aged Cl-1 exposed to pancreatin
Pre-aged panc (Cl-2)	Pre-aged Cl-2 exposed to pancreatin
Pre-aged bird (Cl-1)	Pre-aged Cl-1 exposed to bird droppings
Pre-aged bird (Cl-2)	Pre-aged Cl-2 exposed to bird droppings
Post-aged panc (Cl-1)	Cl-1 clear coat has exposed to pancreatin and post-ageing process consecutively
Post-aged panc (Cl-2)	Cl-2 clear coat has exposed to pancreatin and post-ageing process consecutively
Post-aged bird (Cl-1)	Cl-1 clear coat has exposed to bird droppings and post-ageing process consecutively
Post-aged bird (Cl-2)	Cl-2 clear coat has exposed to bird droppings and post-ageing process consecutively

Bird droppings and pancreatin were utilized as the natural and simulated biological materials according to the literature [9]. The natural bird droppings were obtained from a sparrow bird. In addition, due to its impurities this was purified before use. To maintain the natural state of bird droppings, a simple purification on natural bird droppings have been done. To this end, a simple purification on natural bird droppings has been done. The bird droppings obtained by a bird in outdoor environment contains various excessive bird food particulates causing the biological test difficult to perform. Therefore, bird droppings were firstly dissolved in DI water and then the solution was filtered. Finally, the solution was kept in room temperature for vaporization of water. The maintained bird droppings powder were gathered and used as a purified bird dropping.

The pancreatin was supplied from Merck Company. pHs of natural bird droppings and pancreatin slurries were 6.3 and 6.25, respectively. In addition, the appearance and physical state of final purified bird droppings and pancreatin were grey and white powders, respectively.

Biological experiments

According to PSA Peugeot-Citroen D27 5415 standard, a known amount of pancreatin and bird droppings powder was dissolved in water with the ratio of 10:1. The solution was remained for 72 h to obtain a stable paste. Two different ageing processes were utilized to simulate the effects of outdoor ageing conditions as follows:

Ageing process

The automotive clear coat' properties can be affected as it is exposed to different outdoor conditions such as hot-cold, humid environment and UV radiation from the sunlight before and after the biological attack. Therefore outdoor ageing conditions may affect the coating differently. To this end, two different pre-ageing (ageing before exposure to biological materials) and post-ageing (ageing after exposure to biological materials) were conducted to simulate the effects of real outdoor conditions.

Pre-ageing process

First stage (climatic test) In the first stage of pre-ageing process, effects of hot-cold and humid shockings exposed to clear coats during its service life were simulated by a climatic test. In this test, different hot-humid shocking cycles are experienced by the coatings. According to Fig. 1, one completed cycle of this experiment takes 400 min. This procedure was performed in five consecutive cycles according to PSA Peugeot-Citroen D27 5415 standard.

Second stage (xenon test) After the five consecutive climatic hot-humid shockings, the samples were exposed to UV radiation of a xenon test for 100 h. In this experiment, the ageing effects of UV radiation are simulated using a xenon cabinet test (Radiance: 0.4 W m^{-2}, wavelength: 340 nm, internal and external filters: quartz, temperature: 353 ± 3 K).

Third stage (climatic test) After the second ageing stage, for the second time, the samples were again exposed to the five consecutive climatic test cycles (as shown in Fig. 1).

Forth stage (humidity test) In the final ageing stage, all samples which have been exposed to the three previous pre-ageing stages were examined by a humidity test cabinet. To this end, samples were covered by a strip of an absorbent cotton-wool soaked by 10 times of fresh water as its weight. After that, all samples were kept in a polyethylene bag at 333 K for 48 h ± 30 min in an oven.

After these four pre-ageing stages, biological test was carried out in which a 0.5 mL of bird droppings and pancreatin solution were placed to 1 cm^2 of the sample surface followed by a heat treatment at 333 K for 24 h. Regarding the bird droppings and pancreatin degradation mechanisms, the enzymatic structure of these biological materials are believed to be responsible for the severe hydrolytic degradation of clear coat. The catalyzed induced hydrolytic degradation of clear coat produced by the enzymes presented in bird droppings or pancreatins depends on various parameters including temperature and pH. Before biological test, these substances were exposed to clear coat surface and kept in various temperatures being 293, 313, 333 and 353 K. By comparing the visual performance of the samples exposed to the temperatures used, it has been revealed that no effects on the samples exposed to biological materials can be seen except for the one tested at 333 K. Therefore, biological materials maximum activity can be observed in the temperature of 333 K. The same temperature of 333 K is suggested in Peugeot-Citroen D27 5415 standard for other biological materials. The second reason for choosing this temperature can be related to the car body temperature during the summer sun light. In the spring and summer, the direct light of sun causes a temperature to rise to 333–353 K. In addition, the temperature range of T_g of the used clear coats in this study was near 333–343 K causing greater effects of biological materials on clear coat hydrolytic degradation.

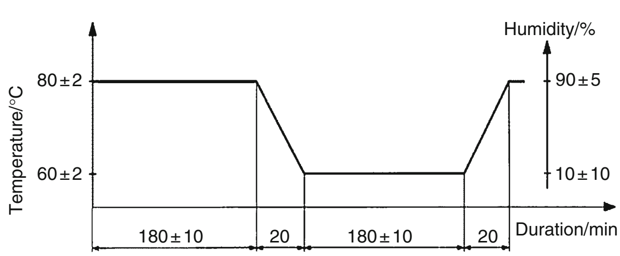

Fig. 1 Climatic test cycle for simulation of hot-humid ageing conditions

Post-ageing process

Biological materials may influence an automotive clear coat before it is exposed to any outdoor ageing conditions. By this method, effects of ageing conditions were studied after the biological attack. Therefore a xenon test was utilized to simulate the effects of UV radiations from the sunlight on clear coats previously exposed to bird droppings or pancreatin. All samples, which have been covered by a 0.5 mL of bird droppings and pancreatin, were exposed to 300 h xenon exposure (with the xenon condition being: 353 ± 3 K, with spraying of fresh water after each 100 h).

Both pre- and post-ageing processes are schematically shown in Figs. 2 and 3.

Instrumentation

An Atlas Xenotest Beta LM weather-o-meter, utilizing a Xenon arc light source, with inner and outer quartz/quartz

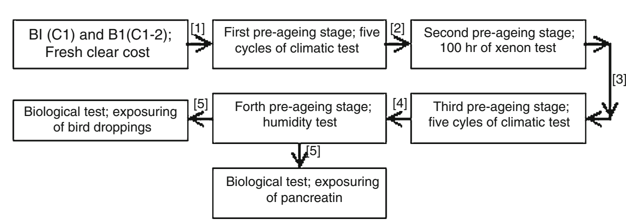

Fig. 2 Schematic illustration of different pre-ageing stages and biological test

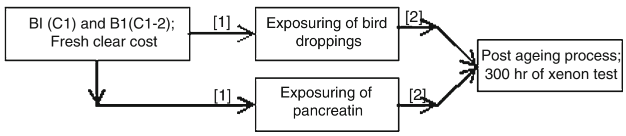

Fig. 3 Schematic illustration of different biological test in a post-ageing process

filters was utilized to simulate the outdoor ageing condition of clear coat under xenon radiation in accordance to the Peugeot D27 1389-95 standard. In addition, a climatic enclosure was used to apply different thermal and humidity ageing conditions according to PSA Peugeot-Citroen D27 5415.

A Leica DMR Optical Microscope was used to capture the visual effects of biological materials on clear coats morphology. Mechanical properties of clear coats exposed to biological materials at different ageing processes were studied by a DMTA and micro hardness measurements. A Leica VMHTMOT micro hardness instrument, at a load and loading times of 19.6 N and 20 s, and a Tritec2000 DMTA, at the frequency, temperature and heating rate of 1 HZ, 223 to 553 K and 258 K min^{-1}, were used. DMTA test was applied on crushed and grinded powders collected from the surface of the films. To evaluate the thickness of degraded layer of coating, a SEM was used but, due to a non-uniform etched surface of degraded clear coat at different areas, use of this technique could not help to detect the exact degradation depth. Therefore, according to the hole depth and width of degraded parts of clear coat obtained by AFM and optical microscope micrographs, it was demonstrated that hole widths and depths range were 300–500 nm and 2,000–7,000 nm, respectively [14]. Regarding this observation, a cutter was used to prepare degraded clear coat samples almost at a top layer having thicknesses lower than 300 nm. It should be noted that using other methods was not applicable.

Results and discussion

Chemical composition of natural and simulated bird droppings were studied by the use of FTIR spectroscopy as shown in Fig. 4.

According to this figure, similar vibration peaks for pancreatin and bird droppings can be observed. Therefore, it can be claimed, that the overall chemical structure of these materials are more or less the same. However, different intensity of those vibration frequency bands for these materials can reveal the slight difference between them. Based on the proposed enzymatic structure of these materials cited in the literatures and different vibrations peaks observed at 500–2,000 cm^{-1} in Fig. 4, chemical

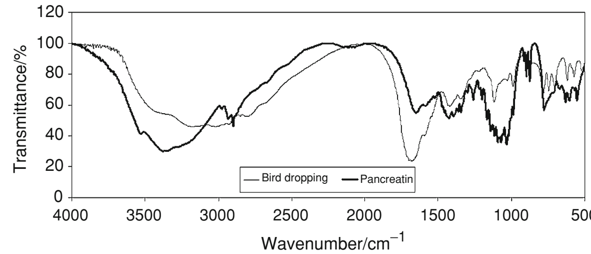

Fig. 4 FTIR analysis of biological materials

compositions of these materials seems complicated. The effects of biological materials at different ageing conditions on visual performance of two different clear coats were obtained from optical micrographs shown in Figs. 5 and 6.

According to the observations made in Figs. 5 and 6, ageing conditions and types of biological materials, significantly affect the surface morphology of clear coats

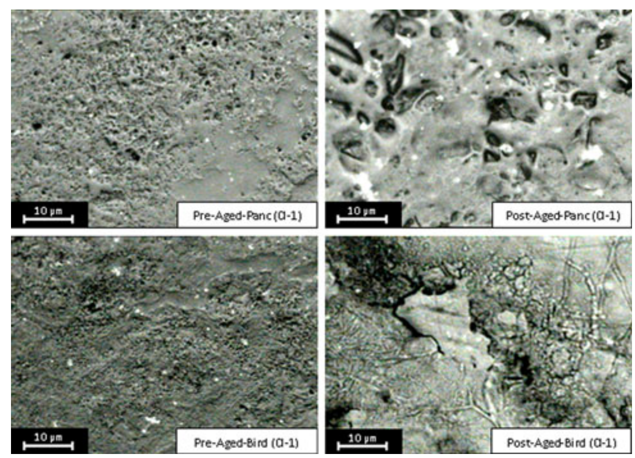

Fig. 5 Optical microscope images of biologically degraded Cl-1 samples

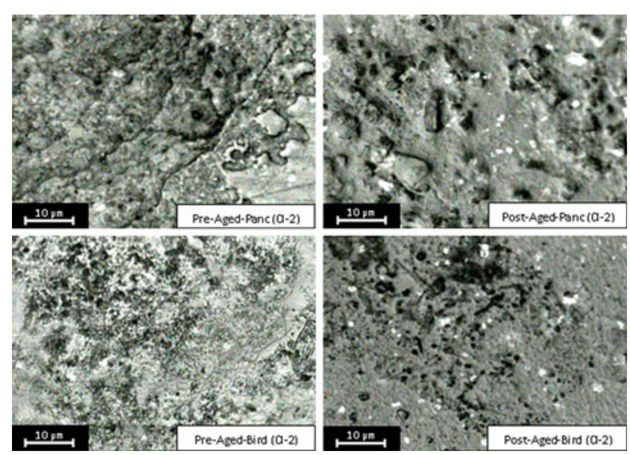

Fig. 6 Optical microscope images of biologically degraded Cl-2 samples

samples. Moreover, sever surface holes and cracks observed for the samples exposed to biological materials in both pre-aged and post-aged conditions can indicate the degradation process of Cl-1 and Cl-2 samples. The bigger holes and cracks observed for the post-aged-panc and post-aged-bird samples may be attributed to the more irretrievable degradation process of clear coat under post-ageing conditions. Results show that bird droppings have affected the clear coat surface with greater intensity compared to pancreatin. These observations clearly suggest that both biological material type and ageing conditions have a detrimental effect on clear coat visual properties. Therefore, it may be expected that biological degradation affect the mechanical and chemical properties of clear coats significantly. Therefore, the mechanical properties of different clear coats were studied to correlate the effect of biological materials to mechanical attributes of the films.

In Figs. 7, 8 and 9 variations of Tan δ (loss peak) and storage modulus versus temperature from the DMTA studies for different clear coats (Cl-1 and Cl-2) exposed to biological materials at different ageing conditions are shown.

According to these Figures greater melamine content of clear coat (Cl-2) has a significant impact on the Tan δ peak width and height. The decreased loss peak (Tan δ) height and width as the melamine crosslinker content is decreased

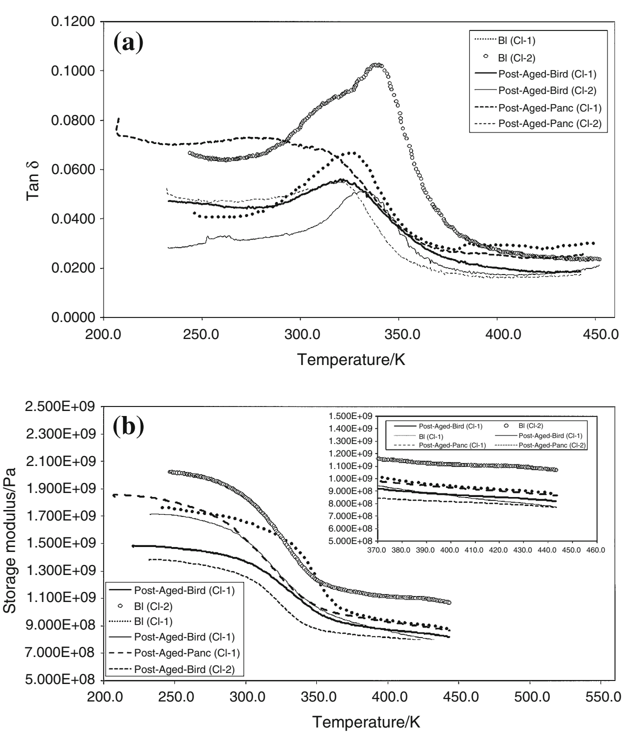

Fig. 7 Variation of **a** Tan δ and **b** storage modulus versus temperature for two types of clear coats exposed to bird droppings and pancreatin under post-ageing condition

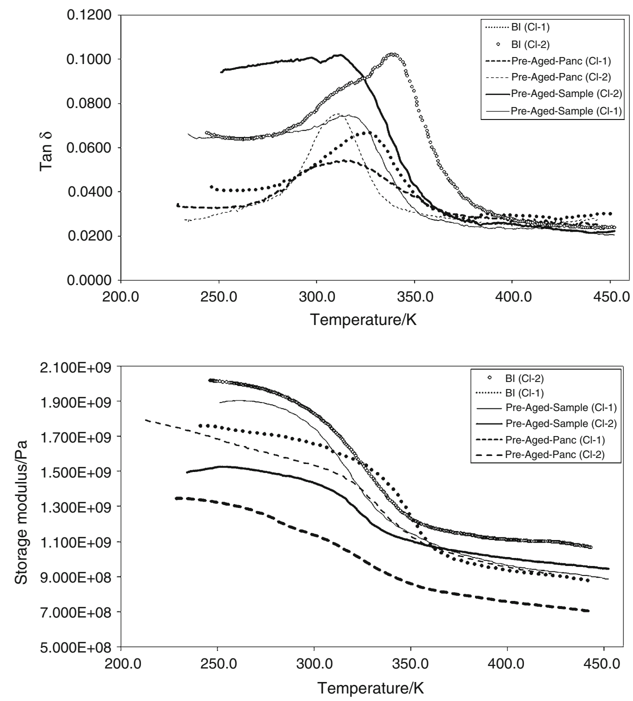

Fig. 8 Variation of Tan δ versus temperature for two types of clear coats exposed to pancreatin under pre-ageing condition

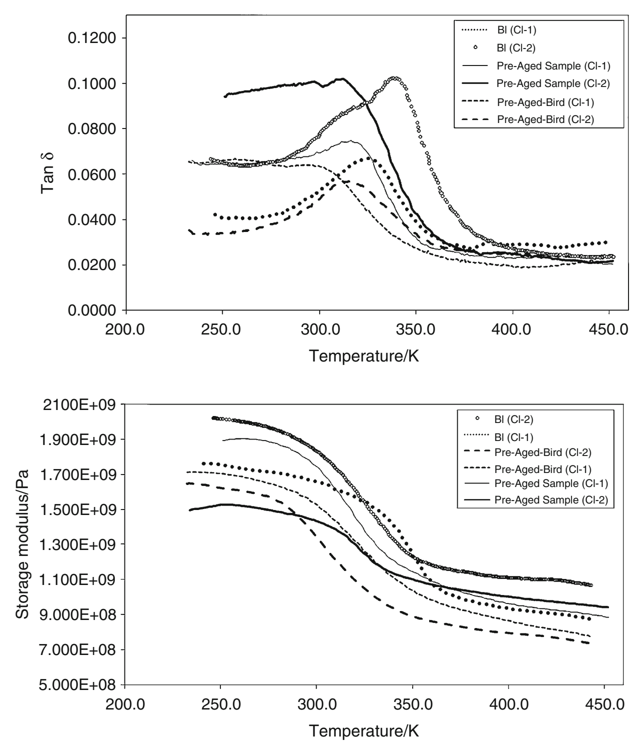

Fig. 9 Variation of Tan δ versus temperature for two types of clear coats exposed to bird droppings under pre-ageing condition

may be attributed to an incomplete curing process of Cl-1 compared to that of Cl-2. In addition, the higher storage modulus of Cl-2 in rubbery platue zone can be attributed to the cross-linking density and therefore a more complete curing reaction of the clear coat containing the greater melamine crosslinker (Cl-2). Regarding these results, the proper ratio of melamine cross-linker to acrylic polyol is 30:70. However, although Cl-1 showed an incomplete degree of cure, the reason for using this system was to investigate the effects of curing degree of clear coat on its biological performance.

Results observed in Fig. 9 clearly show the significant effects of biological materials on Cl-1 and Cl-2 mechanical properties. According to these results, a pronounced decrease of Tan δ is observed for both clear coats. However, although Cl-2 has a higher initial Tan δ and storage modulus compared to Cl-1, the greater decrease of these parameters for Cl-2 can reveal that, a better curing process may not necessarily lead to a more biological resistance. In addition, the lower Tan δ and storage modulus of clear coats exposed to bird droppings can elucidate the more sever effects of natural biological material on clear coat degradation and its decrease of mechanical properties. In Fig. 8, effects of pancreatin on clear coats samples exposed to pre-ageing conditions are shown. Similar to what observed for the clear coat exposed to biological materials in the post-ageing condition (Fig. 7), the higher initial Tan δ and storage modulus of Cl-2 will not result in a better biological resistance in the pre-ageing condition in comparison to Cl-1. According to the variations of Tan δ and storage modulus of the clear coats exposed to pre-ageing conditions (Pre-Aged sample (Cl-1) and (Cl-2)), the hot-humid stages exposed to clear coat (before the biological attack) negatively affect the storage modulus and Tan δ of the clear coats, but the effects of this ageing process in comparison to the effects of biological materials on clear coats properties do not seem significant. The *sever* effects of pancreatin on clear coat properties in a pre-ageing condition can be observed by a significant decrease in Tan δ peak height and width (as shown in Table 2) for pre-aged-panc (Cl-1) and (Cl-2) samples. In addition, the same trend was observed for the variations of storage modulus of clear coats exposed to pancreatin. Both clear coat storage moduli were decreased negatively after the biological test. Although pre-ageing stages have a negative effect on storage modulus, the effects of biological attack on clear coats storage modulus (especially Cl-1) is greater. The same results are observed for the clear coats exposed to bird droppings (Fig. 9). According to the observations made in this figure, a significant decrease of Tan δ and storage modulus of the Cl-1 and Cl-2 samples can be observed. The higher effects of bird droppings on Tan δ peak height and width decrease of Cl-2 sample (although this clear coat had a higher initial peak height and width in Tan δ curve and had greater storage modulus) in comparison to Cl-1, may suggest that the effects of bird droppings

Table 2 Cross-linking density and loss peak (Tan δ) height of clear coats exposed to biological materials

Sample	Cross-linking density/mol cm^{-3} (100×)	Peak height of tan δ
Bl (Cl-1)	10.42	0.04
Bl (Cl-2)	9.18	0.07
Pre-aged-panc (Cl-1)	6.63	0.03
Pre-aged-panc (Cl-2)	8.64	0.05
Pre-aged-bird (Cl-1)	7.44	0.05
Pre-aged-bird (Cl-2)	7.27	0.03
Post-aged-panc (Cl-1)	8.36	0.04
Post-aged-panc (Cl-2)	7.43	0.044
Post-aged-bird (Cl-1)	8.01	0.04
Post-aged-bird (Cl-2)	6.48	0.04

on clear coat mechanical properties could not be completely attributed to the curing history of clear coat. Generally, results observed in Figs. 7–9 can easily demonstrate the irretrievably effects of biological degradation on the clear coat mechanical properties more considerably than any hot-humid ageing processes.

More information from Figs. 7 to 9 can be obtained by measurement of clear coats' glass transition temperature (T_g), cross-linking density and loss peak width and height. The variations of clear coats T_g before and after biological test are shown in Figs. 10–12.

Results shown in Fig. 10 clearly reveal the significant effects of biological materials on clear coats mechanical properties. Comparing the T_g of clear coats before exposure to biological materials (Bl (Cl-1) and Bl (Cl-2)) can show the higher T_g of the clear coat containing the greater ratio of melamine crosslinker to acrylic resin (340.1 K for Bl (Cl-2) in comparison to 327.2 K for Bl (Cl-1)). This significant difference may be attributed to a more complete curing process and therefore a higher cross-linking density of Cl-2 sample. Results show a considerable effect of

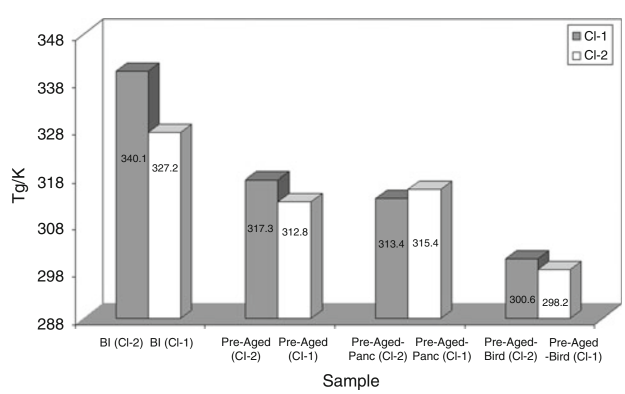

Fig. 10 Variation of the T_g of clear coats (Cl-1 and Cl-2) exposed to biological materials in a pre-ageing condition

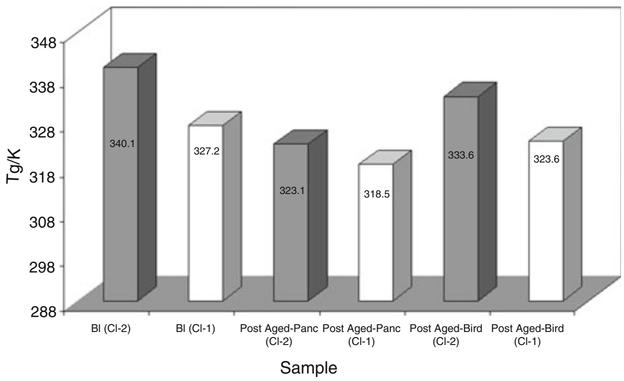

Fig. 11 Variation of T_g of clear coats exposed to biological materials in a post-ageing condition

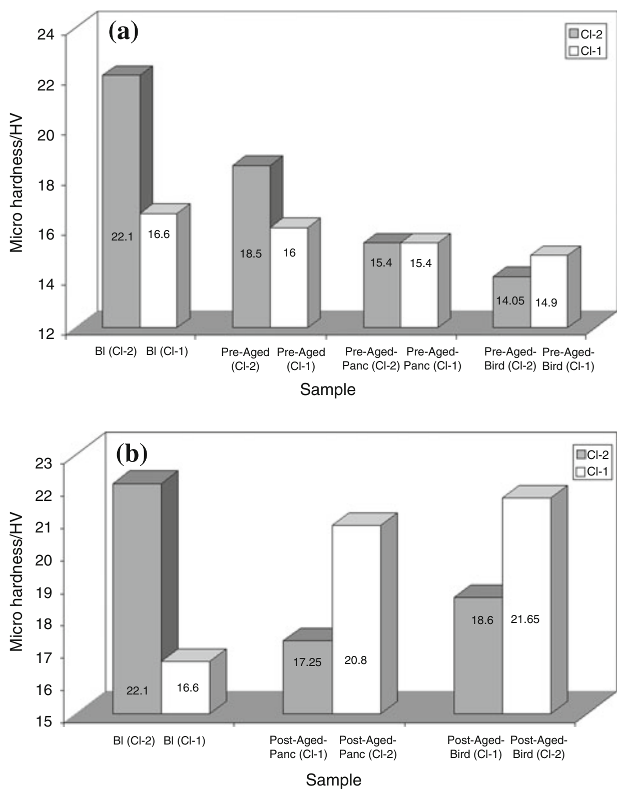

Fig. 12 Micro Vickers hardness of clear coats (Cl-1 and Cl-2) exposed to biological materials in **a** pre-ageing and **b** post-ageing condition

biological materials on the decrease of both clear coats T_g after the exposure to pre-ageing condition (295.7 and 297.4 K for Cl-2 and Cl-1 samples, respectively). These results can show that ageing condition highly affects the clear coats mechanical properties prior to being exposed to biological materials. In addition, although Cl-2 has a higher initial T_g and, therefore a greater cross-linking density, the effects of ageing conditions on the decrease of clear coat T_g is noticeable. The effects of biological materials on clear coats T_g (after the pre-ageing condition) are different for pancreatin and bird droppings. Results obviously show a little effect for pancreatin exposed samples. On the other hand, bird droppings caused a significant decrease in T_g. These results can show the effects of biological materials, especially bird droppings on clear coats mechanical performance. Results do not differ obviously in T_g for Cl-1 and Cl-2 samples exposed to pancreatin and bird droppings. The hydrolytic degradation of clear coat can be catalyzed during exposure to humidity and biological materials at 333 K. Therefore, etching phenomena during biological degradation can be attributed to the etheric bond (N–H) cleavage or the increase in OH bonds as shown previously in our study [14]. According to the results shown in the literature, cross-linking density can directly affect the hydrolytic degradation of a coating in which the lower cross-linking density cause greater diffusion of humidity into clear coat [18]. In addition, it was shown that the areas of coating surface having lower cross-linking density show greater degradation rate causing hole growth on the coating surface or etching process [2]. Results shown here revealed that greater cross-linking density has not caused the greater biological resistance of clear coat having more complete curing process. The most parameter affecting catalyzing efficiency of a biological material on hydrolytic degradation can be attributed to the counter effects of clear coat surface and biological materials. Most of biological materials especially natural bird droppings and pancreatin are including various types of enzymes having low compatibility to water. An enzyme has two different parts of hydrophobic protein chain and hydrophilic end groups (which can cause greater compatibility of enzyme and water). Adhesion of an enzyme is one of the main factors affecting the enzymes effects on biological degradation process [19]. The greater melamine hardener content causes greater condensation reaction between melamine and polyol functional groups as well as self condensation of melamine functional groups. It seems that clear coat surface having greater melamine is more hydrophobic and therefore the greater adhesion of enzymes and clear coat surface can be obtained. Therefore, two different controversial processes can affect the clear coat biological degradation: greater cross-linking density can cause higher humidity diffusion, whilst the greater cross-linking causes the lower interaction of enzyme on clear coat surface. Therefore, the interaction of enzyme for biological degradation process plays a key role, indicating the complex effects of cross-linking density on clear coat biological performance. Hence it can be concluded that, a greater cross-linking density of clear coat could not cause a better biological performance.

Effects of biological materials on clear coat T_g, was studied in the post-ageing condition are shown in Fig. 11.

Observations made in Fig. 11 clearly show a complicated phenomenon of biological attack in the post-ageing condition. In this method, as for pre-ageing method, bird droppings and pancreatin have caused a decrease of clear coats T_g. The higher T_g of clear coats exposed to bird droppings, however, in comparison to pancreatin exposed samples, and the lower decrease of clear coat T_g after being exposed to these materials, may be attributed to the synergistic effect of UV radiation in post-ageing condition. The effect of pancreatin in the post-ageing condition shows a decrease in T_g of 290 and 281.7 K for post-aged-panc (Cl-2) and post-aged-panc (Cl-1), respectively. The same results can be observed for the samples exposed to bird droppings. These results may be attributed to the controversial effects of UV radiation during the post-ageing test in a xenon condition. Clear coats exposed to UV radiation in xenon test may show simultaneous phenomena being occurred, i.e., photo degradation, post-curing (the reaction of unreacted functional groups of clear coat) and radical reactions of degraded products. As expected, these reactions can differently affect the clear coat properties. Photo degradation leads to lower mechanical properties, while the post-ageing process may positively affect the clear coat mechanical properties. Therefore, the same phenomena can be occurred for the samples exposed to biological materials in the post-ageing condition. In this method, biological materials can negatively decrease the clear coats T_g, but the post-ageing and residual radical reactions (which can be occurred during the biological test) may positively increase the T_g. Therefore, the lower decrease of clear coats T_g in post-ageing condition (in comparison to pre-ageing) may be attributed to both simultaneous phenomena, but the decrease of clear coat T_g seems to be in favour of inferior biological resistance of the samples. On the other hands, the lower T_g of Cl-1 (in comparison to Cl-2) may be attributed to the greater post-curing reaction of Cl-1(because of UV radiation). These results revealed that T_g alone could not be a usable parameter for the evaluating the effects of biological materials on clear coat mechanical properties.

Therefore, mechanical properties of different samples were investigated by the aid of micro Vickers hardness as shown in Fig. 12.

Results observed in Fig. 12 show a higher hardness of Bl (Cl-2) in comparison to Bl (Cl-1). This can be attributed to the higher T_g of Cl-2 in comparison to Cl-1 sample. In addition, the clear coats exposed to pre-ageing hot-humid stage show a decrease of micro hardness with a more pronounced effect in Cl-2. This is in agreement with the results observed in Figs. 7–9, in which the higher T_g of Bl (Cl-2) (in comparison to (Cl-1)) did not result in a better performance in ageing stages. For both clear coats, significant decrease of micro hardness is observed for the samples exposed to biological materials. The lower hardness of pre-aged-bird (Cl-1) and (Cl-2) in comparison to the samples exposed to pancreatin can be attributed to the more sever effects of natural bird droppings on clear coats degradation process and, therefore, its effect on the decrease in T_g in comparison to pancreatin. Again, the greater decrease of micro hardness of Cl-2 samples exposed to biological materials compared to Cl-1 can demonstrate that the higher T_g or cross-linking density of the clear coat may not be an effective parameter for the better biological resistance. Therefore, according to these results, it seems that biological degradation process is a complex phenomenon depending on different parameters such as clear coat chemical composition.

According to the results observed for the samples exposed to biological materials to a post-ageing process, two different phenomena observed for two clear coats. For Cl-1 samples, exposure of biological materials in a post-ageing condition has caused a lower micro hardness, which can be attributed to the biological degradation. On the other hand, an increase in Cl-2 samples exposed to biological materials in the post-ageing condition can be attributed to the controversial effects of UV radiation on clear coat properties. Both degradations and post-curing reactions of unreacted groups of clear coat can affect the mechanical properties during the post-ageing test. For the Cl-1 samples, due to an incomplete curing process (because of lower content of crosslinking agent) further reaction can be occurred during the post-ageing process, whilst the degradation process affects the clear coat simultaneously. After the biological test, degraded parts of clear coat were removed from the surface and the residue (non-degraded) was exposed to UV radiation. It was observed that the micro hardness increased. In addition, Cl-2, due to a more incomplete initial curing process did not show any post-curing during the exposure to biological materials.

Conclusions

Mechanical properties of two acrylic melamine clear coats (containing different melamine crosslinker) exposed to biological materials at two different ageing processes were studied. Results clearly revealed that bird droppings and pancreatin considerably affect the clear coat mechanical properties. According to these results, T_g and storage modulus (specially in rubbery plateau zone) of both biological materials were negatively decreased. In addition, the decreased micro harnesses of clear coats exposed to these biological materials was the another observation indicating the severe effects of biological materials on the mechanical properties of clear coats. It was shown that, the natural bird droppings had a more inverse effect on the clear coat properties than pancreatin. Both pre-ageing and post-ageing processes had shown the similar effects on clear coat properties but the effects of biological materials was more pronounced than post-ageing process. In addition, it was demonstrated that the better initial mechanical properties of the clear coat could not necessarily cause a better biological performance.

References

1. Osterhold M, Patrick G. Influence of weathering on physical properties of clear coats. Prog Org Coat. 2001;41:177–82.
2. Nguyen T, Martin J, Byrd E, Embree N. Relating laboratory and outdoor exposure of coatings: II Effects of relative humidity on photodegradation and the apparent quantum yield of acrylic melamine coatings. J Coat Technol. 2002;74:65–80.
3. Bartolomeo P, Irigoyen M, Aragon E, Frizzi MA, Perrin FX. Dynamic mechanical analysis and Vickers micro hardness correlation for polymer coating UV ageing characterization. Polym Degrad Stab. 2001;72:63–8.
4. Schmitz PP, Holubka JW, Xu LF. Mechanism for environmental etch of acrylic melamine based automotive clear coats: indentation of degradation products. J Coat Technol. 2008;72:39–45.
5. Skaja A, Fernando D, Croll S. Mechanical property changes and degradation during accelerated weathering of polyester urethane coating. J Coat Technol Res. 2006;3:41–51.
6. Nguyen T, Martin JW, Byrd E. Relating laboratory and outdoor exposures of acrylic melamine Coatings IV Mode and mechanism for hydrolytic degradation of acrylic-melamine coatings exposed to water vapor in the absence of light. J Coat Technol. 2003;75:37–50.
7. Nguyen T, Martin JW, Byrd E, Embree N. Relating laboratory and outdoor exposure of coatings III Effect of relative humidity on moisture-enhanced photolysis of acrylic-melamine coatings. Polym Degrad Stab. 2002;77:1–16.
8. Nichols ME, Gerlock JL, Smith CA, Darr CA. The effects of weathering on the mechanical performance of automotive paint systems. Prog Org Coat. 1999;35:153–9.
9. Gaszner K, Neher-Schmitz H, Kuntz T. The effects of bird droppings, insects and tree resins on automotive coatings. Glob Automot Manuf Technol. 2003.
10. Stevani CSV, de Faria DLA, Porto JS, Trindade DJ, Bechara EJH. Mechanism of automotive clear coat damage by dragonfly eggs investigation by surface enhanced Raman scattering. Polym Degrad Stab. 2000;68:61–6.
11. Stevani CV, Porto JS, Trindade DJ, Bechara EJH. Automotive clearcoat damage due to oviposition of dragonflies. J Appl Polym Sci. 2000;75:1632–9.
12. Nagata M, Machida T, Sakai W, Tsutsumi N. Synthesis, characterization, and enzymatic degradation of network aliphatic copolyesters. J Polym Sci A. 1999;37:2005–11.
13. Matheson LA, Santerre JP, Labow RS. Changes in macrophage function and morphology due to biomedical polyurethane surfaces undergoing biodegradation. J Cell Physiol. 2004;199:8–19.
14. Ramezanzadeh B, Mohseni M, Yari H, Sabbaghian S. An evaluation of an automotive clear coat performance exposed to bird droppings under different testing approaches. Prog Org Coat. 2009;66:149–60.
15. Yari H, Moradian S, Ramazanzade B, Kashani A, Tahmasebi N. The effect of basecoat pigmentation on mechanical properties of an automotive basecoat/clearcoat system during weathering. Polym Degrad Stab. 2009;94:1281–9.
16. Ramazanzade B, Moradian S, Yari H, Kashani H, Niknahad M, Chadle H et al (2008) The effects of basecoat pigmentation on weathering performance of an acrylic-melamine basecoat clearcoat automotive finish. In: Proceeding of automotive adhesive, sealants and coatings, Stuttgart, Germany.
17. Ramezanzadeh B, Mohseni M, Yari H. A study of the effects of basecoat pigmentations on biological performance of an automotive acrylic/melamine clear coat. J Appl Polym Sci. (under review).
18. Nivedita S, Malshe VC. Permeability of polymers in protective organic coatings. Prog Org Coat. 2004;50:28.
19. Astrid S, Fritz P. The role of Na^{+} and Ca^{2+} ions on the action of pancreatic lipase studied with the help of immobilisation techniques. Eur J Biochem. 1984;140:547–51.