

Adhesion Failure of Antiscratch Coatings on Polycarbonate Under UV Irradiation

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ABSTRACT: The adhesion failure of antiscratch (AS) coatings on unmodified and plasma-modified polycarbonate (PC) substrate was studied using both chemical and physical methods while considering the surface and interface changes between coatings and PC under ultraviolet (UV) irradiation. The differences in the wettability and surface elemental compositions of the PC surface (PCs) and AS coatings after UV ageing were evaluated by contact angle and Fourier transform infrared (FTIR) measurements. The nanoindentation technique was employed for the quantitative assessment of the changes in the nanomechanical properties of both PCs and AS coatings under UV irradiation. The adhesion of coating on plasma-modified PC was found to be significantly better than that of unmodified substrates. The hydrophilicity and polarity of PCs covered by AS coatings were significantly increased because of the photodegradation of PCs, whereas silicon coatings remained invariant. Nanoindentation tests revealed an obvious enhancement in stiffness of the coating and exposed PC after ageing. Based on these experiments, we proposed that adhesion failure under UV irradiation may be caused by two reasons: first, the photodegradation that occurred at the PCs covered by AS coatings; and second, the stress induced by the changes in stiffness of both AS and PCs under UV ageing. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40507.

KEYWORDS: ageing; coatings; mechanical properties; polycarbonates; surfaces and interfaces

Received 17 November 2013; accepted 23 January 2014

DOI: 10.1002/app.40507

INTRODUCTION

Given its properties, such as low weight, transparency, easy processability, thermal stability, and high impact strength, polycarbonate (PC) has been used in numerous fields, such as the automotive industry, optic implementation, and aeronautics.^{1–3} However, the relatively low abrasion resistance and environment degradation of PC cause the deterioration of its optical quality and physical properties, thus hindering its further application. Antiscratch organic coatings are the predominant topcoat used on PCs to enhance their mechanical properties and antiscratch performance.^{4–6}

Protective coatings used in the aeronautical industry, to some extent, can deteriorate because of poor flying environments, which include ultraviolet (UV) irradiation, hygrothermal effects, and salt spray. The evaluation of ageing properties to explain the failure mechanism for the coating system is critical to its safe usage. Traditional methods used to evaluate the failure of coatings mainly focus on chemical ageing caused by UV radiation, temperature, and moisture, and the general mechanism to understand why and how coating degradation occurs is relatively well known.^{7,8} For example, Fourier transform infra-red

(FTIR) spectroscopy^{9,10} and X-ray photoelectron spectroscopy (XPS)¹¹ have been widely used to investigate the chemical degradation of coatings, as the ageing process can change the chemical composition of coatings, resulting in the deterioration of their chemical stability. Despite the introduction of various methods and techniques to evaluate the weathering performance of coating systems, analyses of physical properties can provide additional information, as polymer degradation is a result of a combination of both chemical and physical processes.^{12,13} Coatings can detach and/or crack from the substrate because of these combined processes. However, compared with chemical process analysis, the physical process has not received considerable attention because of the complexity of the process during coating degradation. Understanding the weathering-induced degradation processes of the coating system both by chemical and physical methods is thus important.

Failure analysis of coating–substrate adhesion is fundamental to study coating failure mechanism and guarantee the safety of the coating when used. This work systematically studies the adhesion failure of silicon coatings [antiscratch (AS)] deposited on unmodified PCs and plasma-modified PCs under UV

irradiation, both by chemical and physical detection methods. No ultraviolet absorbent is present in the transparent silicon coatings used in our experiments. Thus, PCs covered by AS coatings can be influenced by UV irradiation, causing changes in the interface between coatings and PC substrate. Therefore, the ageing process of both coatings and PC substrates should be evaluated to investigate the interface changes and analyze adhesion failure. The thickness of transparent AS in our experiment is very thin ($\sim 4 \mu\text{m}$). Thus, we employ the nanoindentation technique, using depth-sensing method to provide information on hardness and modulus properties, for the quantitative assessment of the changes in nanomechanical properties of both PCs and AS coatings under UV irradiation.

EXPERIMENTAL

Materials

Commercially available 3 mm thick PC sheets were supplied by GE plastics (General Electric, USA). The PC sheets were washed with neutral detergent, ethanol, and distilled water, then dried at 70°C for 1 h prior to surface pretreatment.

The scratch-resistant coating material was prepared using sol-gel methods. An initial solution was prepared by mixing acid-silica, methyltriethoxysilane (MTES), and tetraethoxysilane (TEOS) using HCOOH as catalyst. Further processing of the sol required additional polycarbonate diol (PCD) (MW = 1 000). 2,3-epoxypropoxy propyltrimethoxysilane (KH550), curing agent, and flow control agent were then added to the sol. The sol contained MTES: TEOS: silica: PCD: KH550 = 21 : 2 : 2 : 1 : 2 by weight. Prior to coating deposition, the PC sheets were pretreated with plasma. The AS coatings were curtain-coated on the untreated and fresh plasma-treated PC sheets. After drying at 75°C for 15 min, the coated sheets were cured at 120°C for 2 h.

UV irradiation was conducted using a 400 W low-pressure mercury lamp in the 313 nm wavelength without optical filter. The UV lamp was positioned at a distance of 75 cm from the sample. Irradiations were performed at 25°C under “dry” conditions (i.e., room relative humidity). After UV irradiation for different intervals of time (0, 8, 20, 30, 50, 80, and 120 h), adhesion, contact angle, UV-vis, and nanomechanical properties were used to evaluate the ageing behavior of AS coatings and PCs respectively.

The cleaned PC plates were premodified using the Ar/oxygen ion beam generated by a gridless ion beam source with low energy. For Ar-oxygen containing plasma, two competing processes occurred, namely, etching of the polymer surface and chemical modification. Before deposition, the reactor was vacuumed to a base pressure below 3×10^{-3} Pa. Plasma was created with Ar/oxygen mixed gas (Ar : O₂ = 4 : 1 by volume) at a working pressure of 0.3 Pa and an overall flow rate of 30.0 cm³/min. Plasma power was fixed at 200 W, and gas distance from plasma outlet to sample PC was fixed at 20 cm. The treatment time was fixed at 4 min. The working diameter was ~ 120 mm according to our ion beam source.

Characterization

Contact angle measurements have been extensively used to evaluate surface chemical properties, which are related to surface

wettability. To assess the effect of UV ageing on PCs and AS coatings, contact angle was measured using deionized water (DI-H₂O) as reference solvent. An OCA 20 surface analysis system (DataPhysica, German) was used to measure contact angle. Results were the average of eight determinations.

The characterization of adhesion behavior of AS coatings on PC substrate was performed using cross-cut and tape peel test (ASTM D 3359-08). UV/visible spectra were obtained using a Cary 5000 spectrophotometer (Varian, Inc. Australia) from a wavelength of 3300 nm to 175 nm. Yellowing index measurements of PCs, AS/PCs, and AS/plasma-PCs were performed in transmission mode, followed by the calculation of the data from 400 to 700 nm.

IR spectra were recorded using a Perkin Elmer Spectrum GX spectrometer (USA) in attenuated total reflectance mode for PC substrate ageing. The chemical natures of the coatings deposited on KBr plates were characterized by FTIR spectroscopy (Magna-IRTM spectrometer 750) in the transmittance mode.

The thickness of the transparent silicon coating used in our experiment was $\sim 4 \mu\text{m}$, according to cross-section images of the coating-substrate interfaces obtained by scanning electron microscopy (SEM). Nanoindentation methods,^{14–17} which provide more accurate information of thin films and avoid the influence of substrates, are helpful in the quantitative evaluation of the nanomechanical properties (hardness and elastic modulus) of thin films. In this research, the nanomechanical changes in coatings and PCs during UV irradiation were determined using the commercially available TriboIndenter system (TI 950, Hysitron, USA) at room temperature and ambient atmosphere with a maximum loading force of 10 mN. The load resolution is 1 nN and displacement resolution is 0.04 nm, which provides the indentation tests with high resolution at the nanoscale. The hardness and elastic modulus were conducted using the indentation mode with a Berkovich, three-sided pyramid diamond indenter. The curvature radius of the indenter tip was 1 μm , and the cone angle was 143.2° .

RESULTS AND DISCUSSIONS

Adhesion Behavior of AS to PC Substrate During Irradiation

Before UV irradiation, no evident difference in terms of enhancing adhesion behavior was observed for unmodified and plasma pretreatment, both ranking as 5B. UV ageing was conducted to study the adhesion behavior of coating-substrate and the effects of using the two-surface modification. The adhesion behavior of the silicon coatings relative to the unmodified and plasma-modified PC substrates under UV irradiation was compared using cross-cut and tape peel tests. Table I presents the adhesion properties of coatings on unmodified and plasma-modified PC (plasma-PC) substrate. UV ageing tests revealed that the adhesion of coating on plasma-PC substrates was superior to that of unmodified substrates. As expected, the adhesion on unmodified PCs remained in good condition until 20 h after UV irradiation, ranking as 2B. Thereafter, the AS coating on the unmodified PCs was totally pulled off by tape, and a fresh, clean PC surface, which can be considered as the interface between the coating and PC substrate, was exposed. Although

Table I. Adhesion Behavior of AS to PC During UV Irradiation

Time (h)	0	8	20	30	50	80	120
AS/PC	5B	5B	2B	0B	0B	0B	0B
AS/plasma-PC	5B	5B	5B	4B	2B	1-2B	0-1B

the level of adhesion was 5B before irradiation, the interface between coating and PC was not infiltrative, such that clean PCs can be obtained. For plasma-PCs, the adhesion remained satisfactory until 30 h irradiation, ranking as 4B. Thereafter, the AS coating can be partly pulled off by tape, but the new surface was not clean and showed minimal remnants even after 120 h of exposure. Results of UV ageing tests revealed that the adhesion of the coating on plasma-modified substrates was superior to that on unmodified substrates, which can prolong the lifetime of coatings under UV irradiation. To evaluate the wettability of the plasma-modified PCs, contact angles after plasma treatment were determined through contact angle measurements. Results showed that the DI-H₂O contact angle of the PC substrate decreased from 81° to less than 9° and the total surface free energy increased from 24.66 mN/m to 87.86 mN/m after plasma treatments, mainly caused by the introduction of polar groups such as carboxylic acids (-COOH) and hydroxyl groups to the surface of the PC after plasma treatment.¹⁸ So the enhanced capability for adhesion can be attributed to the higher wettability of PCs and cross-linking of C—O—Si bonds at the interface between coatings and substrate after plasma activation.^{19,20}

UV-Visible Spectra Analyses

The prolonged exposure of PC and AS/PC to UV irradiation resulted in an increase in absorbance in both the tail of the UV (380–400 nm) and the visible range, as shown in Figure 1. The existence of AS coatings can increase the transmission of light in the visible range. Furthermore, both PC and AS/PC systems can totally absorb light lower than 380 nm, as no ultraviolet absorbent was present in the coatings in our experiment.

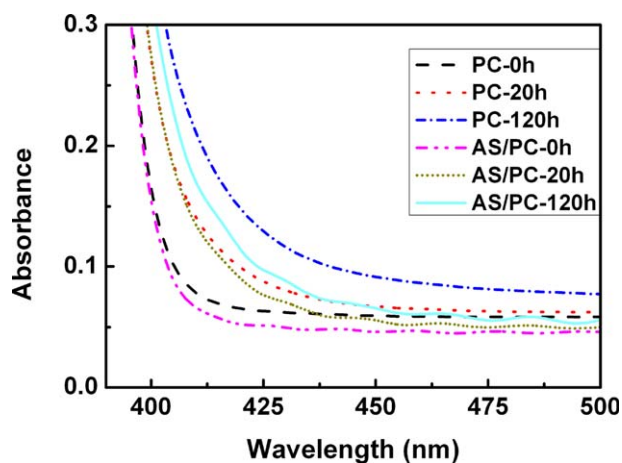


Figure 1. UV/visible absorption spectra of PC and AS/PC systems exposed to UV at various exposure times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The yellowing index (YI) was measured after exposure to UV for different durations, as shown in Figure 2. PC, AS/PC, and AS/plasma-PC samples show a visible increase in YI as UV irradiation progressed. The YI of AS/PC was only slightly smaller than that of PC, which indicated that the AS coatings cannot prevent the photodegradation of PC substrates and that photodegradation can occur at the surface of a PC substrate covered by AS coatings, actually at the interface between coating and PC substrate. For plasma-PC, the YI before UV ageing, as shown in Figure 2 (AS/plasma-PC-1), was larger than that of PC and AS/PC because of the UV radiation of the plasma. The UV component of the plasma with high energies may give rise to cross-linking by activated species of inert gases and scission by O₂ etching, which may be responsible for the increase in the YI of PC after plasma-pretreatment. If the YI of AS/plasma-PC was reduced to the same level as PC and AS/PC, as shown in Figure 2 (AS/plasma-PC-2), it was significant to find that the increasing slope of plasma-PC under UV ageing was lower than that of PC and AS/PC. The yellowing of PC is attributed to the photodegradation of PCs, such that the effect of photodegradation on plasma-PC covered by AS coating is the least.

Surface Wettability Analyses

Contact angle measurements, using the DI-H₂O as reference solvent, were performed after UV irradiation. AS coatings can be peeled off by tape, and a clean PC surface was exposed after UV irradiation. Thus, the fresh PC surface can be considered as the interface between PC and AS coatings. As shown in Figure 3, four kinds of surfaces, namely, uncoated PC (PC₁), AS coatings, PC after AS peeling (PC₂), and plasma-PC after removing

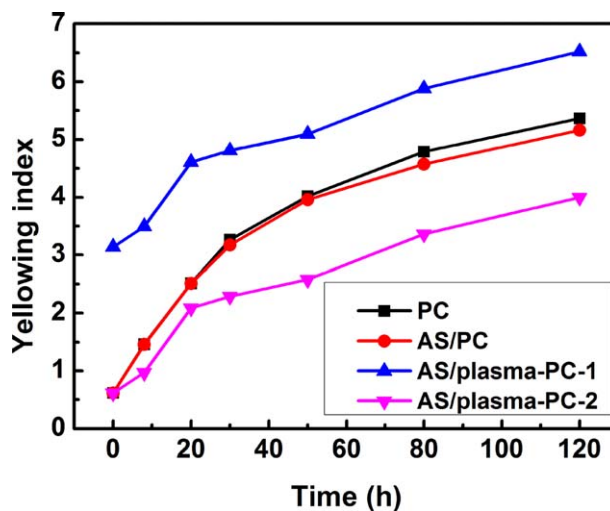


Figure 2. Variation in the YI of PC, AS/PC, and AS/plasma-PC systems exposed to UV at various exposure times. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

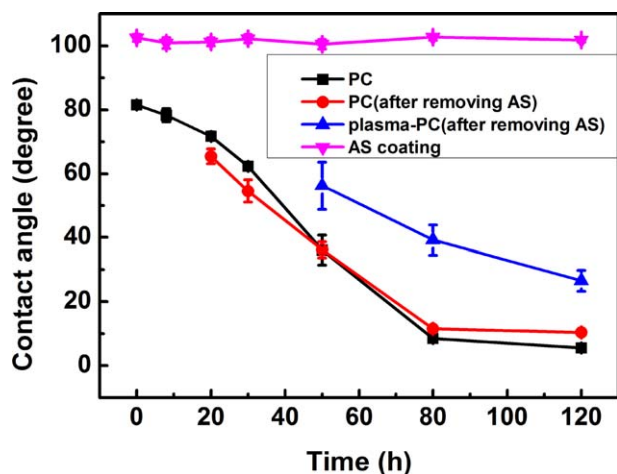


Figure 3. Variation of contact angle versus the UV irradiation time for uncoated PC, AS coatings, and coated PC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

AS (PC₃), were measured. The DI-H₂O contact angle of PC₁ sharply decreased from 81° to 10° after 80 h of UV exposure, and the surface becomes super-hydrophilic (less than 10°) thereafter. The decrease in contact angles shows that the surface free energy evidently increased. For coated PC, PC₂ notably exhibited similar wettability as PC₁, which suggests that the same degradation process can occur at the surface of PCs covered by AS coating. The contact angles of PC₃ decreased under UV ageing, but the contact angles were evidently larger than those of PC₁ and PC₂, which indicates that weaker photodegradation occurred in the plasma-PCs. Following the ageing process by UV irradiation, functional polar groups, such as carboxylic acid (-COOH) and hydroxyl groups (-OH), can be introduced to the surface of PC by photodegradation and thus increase surface polarity, as proven by FTIR and XPS characterization.^{21,22}

Changes in AS coatings under UV irradiation significantly differed. No significant variation in contact angle was observed, with the remaining at ~100° for DI-water, as shown in Figure 3. Results of surface wettability show that photodegradation occurs at the surface of a coated PC substrate, which causes the rupture of chemical bond and unmatched surface energy at the interface between coatings and PC substrate. This condition results in the adhesion failure of AS coatings on PC substrate.

FTIR Characterization

The effect of weathering, particularly UV, on PC is well known. For PC, the chemistry underlying photodegradation has been attributed to two reactions: photo-Fries and photo-oxidation, where the latter requires the presence of oxygen to occur. As the wavelength used in this research was 310 nm, both photo-Fries rearrangement and photo-oxidation reactions occurred under exposure. In this study, the mechanism of photodegradation is not discussed in detail, as it has been widely studied and can be found in the literature.^{23,24}

FTIR was employed to investigate the surface elemental compositions of the PCs and AS coatings after UV ageing. Figure 4 shows the FTIR spectra of PC in the 400 cm⁻¹ to 4500 cm⁻¹ region after exposure to UV radiation for different durations.

The evident change is the increase in the broad hydroxyl peak (3100 cm⁻¹ to 3500 cm⁻¹), which can explain the increase in the surface energy of PC. Meanwhile, the adsorption in the carbonyl region (1600 cm⁻¹ to 1770 cm⁻¹) became broader, thus proving the formation of various photo-oxidation products, including carboxylic acid, aliphatic esters, and aromatic esters. The formation of carboxylic acid can also increase the polarity of PC surface. The FTIR spectra of coated PC after AS coating removal were measured simultaneously, and the result was similar to that of uncoated PC, which corresponds with the aforementioned observations. The products formed by PC photo-oxidation can be found in the surface of PC covered by AS coatings, which indicated that oxygen in the air can penetrate through the AS coatings and facilitate the interfacial reaction.²⁵ The main bond (Si—O—Si) in silicon coatings is known to have a large band angle and band length, making the free volume sufficiently large to enable oxygen to penetrate freely through the coatings, thus causing photo-oxidation. The lower oxidation rates of plasma-PC are attributed to the good adhesion between AS and PCs, which is essential to enhance the oxygen barrier property of PC substrate.

The FTIR spectra of AS coatings before and after UV irradiation are presented in Figure 5. The main contribution of AS coatings appears between 1000 and 1200 cm⁻¹, which can be attributed to Si—O—Si stretching vibration. The broad adsorption band appearing at ~3420 cm⁻¹ indicates the presence of an -OH group. The peak at 770 cm⁻¹ is assigned to the Si—C stretching vibration. The FTIR spectra of PC substrate have been obviously altered, but no evident change in the AS coatings under UV irradiation is found.

Nanoindentation Characterization

Based on the above experiments, we propose that the adhesion failure under UV irradiation may be caused by the photodegradation that occurred in the PCs covered by AS coatings, whereas no evident changes were observed for AS coatings. However, the adhesion failure of coating-substrate can be a combination of

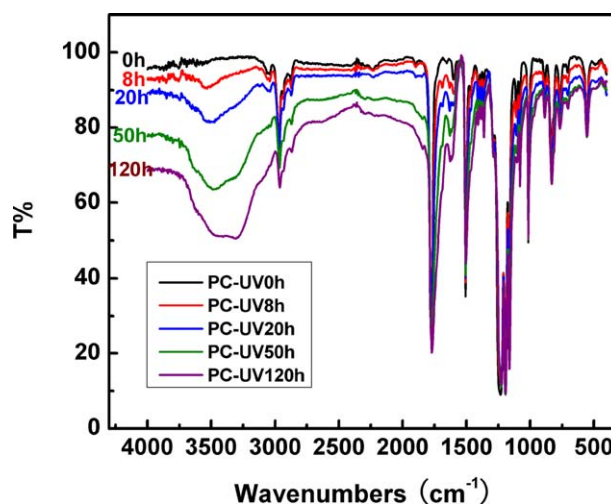


Figure 4. FTIR spectra of PC exposed to UV at different duration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

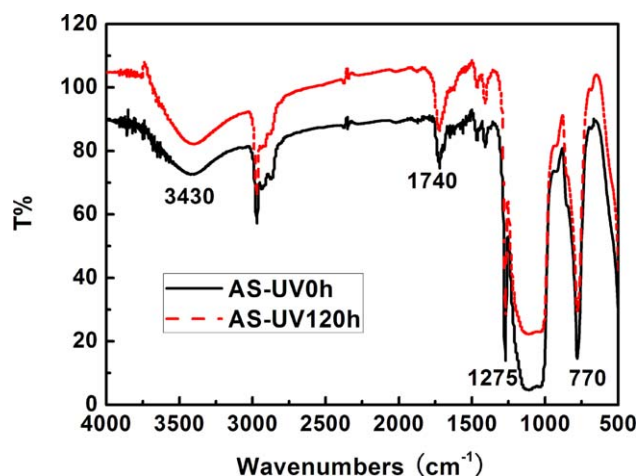


Figure 5. FTIR spectra of AS coatings under UV irradiation at different durations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

both AS coating and PC substrate. The transparent thin coatings in our experiments exhibited no evident changes through conventional characterization, such as SEM, IR, and surface polarity. Nanoindentation tests using depth-sensing method can provide nanomechanical information on the thin-film coating. Thus, we ran the tests to evaluate the performance of the coatings and track the ageing process under UV irradiation quantitatively. PC degradation is a surface phenomenon that only extends $\sim 25 \mu\text{m}$ into the exposed surface.²³ Thus, using nanoindentation technology to analyze the mechanical changes of PC after UV irradiation is also meaningful.

Indentation tests were performed in a load–displacement controlled testing mode to obtain accurate and precise forces or displacements. For the loading function of indentation in this study, we chose to adjust peak load with a constant segment duration, which consisted of 10 s linear loading and 10 s unloading segments, along with dwelling time of 10 s at the peak load to reduce the influence of creeping effect. Each curve in Figure 6(a,b) shows the variation in elastic modulus with

contact depth under increasing loads for the AS coatings and PCs, respectively. In order to avoid the substrate's influence, the contact depth must be not larger than 1/5 of coating thickness. As the thickness of coating is about $4 \mu\text{m}$, the contact depth should be smaller than 800 nm. The loads for coatings on PC were from $500 \mu\text{N}$ to $2000 \mu\text{N}$, whereas the loads on AS coatings were from $2000 \mu\text{N}$ to $8000 \mu\text{N}$ in geometric proportion mode for the uncoated PC plates. The elastic modulus of both AS coatings and PC increased with the extension of UV irradiation, which indicates a stiffness enhancement of the silicon coating and PCs.

To compare the changing rates of mechanical properties under UV irradiation, further indentations were performed on AS coatings with $2000 \mu\text{N}$ indentation load, whereas the loads were $4000 \mu\text{N}$ for PCs. The final values of hardness and modulus were taken as the average of five indentations conducted in different spots on the same material. The variation of elastic modulus and hardness of AS and PCs under different irradiation times is shown in Figure 7(a,b). During irradiation, the values of elastic modulus of both AS and PC, shown in Figure 7(a), sharply increased before 20 h of UV ageing. Furthermore, the rates of increase were gradual and remained almost unchanged after 80 h of ageing. However, the result was different for the hardness properties. The values of hardness for PCs under UV ageing remained unchanged, whereas a significant increase was observed for AS coatings before 30 h of irradiation, as shown in Figure 7(b). Although IR and SEM detection found no evident changes, the stiffness of silicon coating was enhanced after UV irradiation. The observed increase in the elastic modulus and hardness may be linked to the densification of polymer²⁶ and the decrease in free volume attributed to changes in orientation of polymeric chains under UV irradiation.

The stresses produced in coating systems, including mechanical, internal, and ageing stresses, are known to be the main reasons for adhesion failure on the coatings. Directly evaluating the stress of thin organic coatings is difficult. Thus, the changes in mechanical properties with the ageing process, as detected by nanoindentation technology, can be helpful in proving the formation of

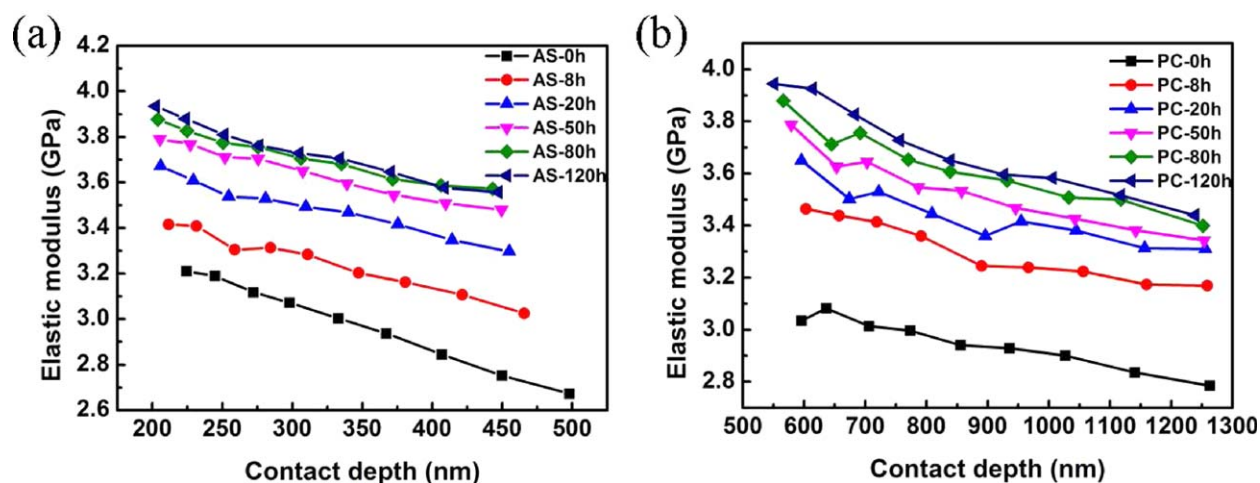


Figure 6. Elastic modulus measurements of the AS coatings (a) and PC (b) versus exposure UV time at different indentation depths under increasing load. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

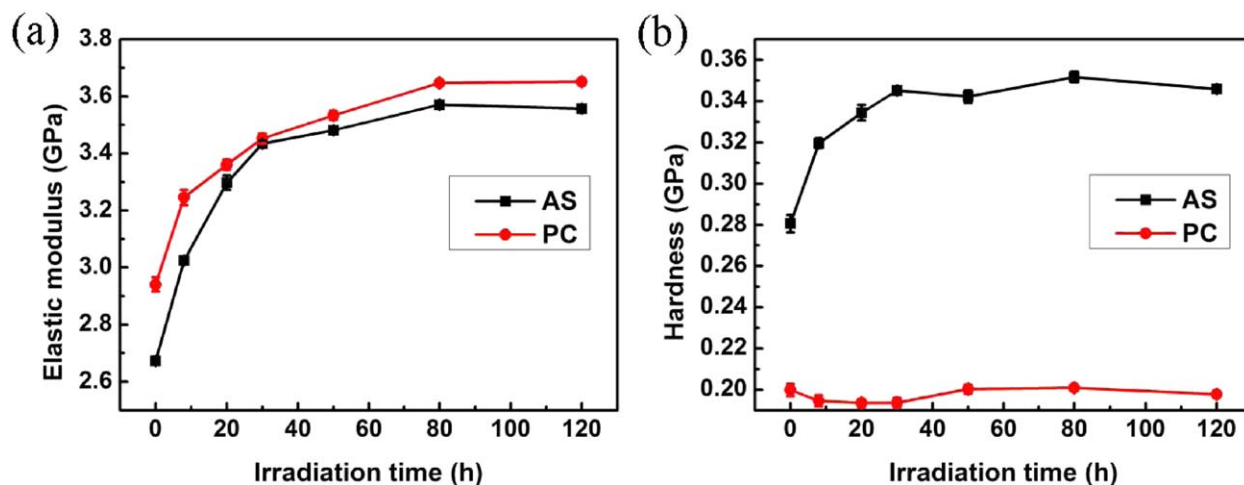


Figure 7. Elastic modulus (a) and hardness (b) for different irradiation times with an indentation load of 2000 and 4000 μN for AS and PC, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

stress. Following the evident increase in hardness and elastic modulus of coatings during UV irradiation, increasing stress is generated. Furthermore, contrary to the unchanged hardness of PCs, the enlargement of coatings is responsible for the stress because of the insufficient extensibility of the coating in response to dimensional changes in the substrate during UV ageing. This condition may result in adhesion failure. When the stress is lower than the coating adhesion, the coatings adhere well to the substrate; conversely, detachment occurs when the stress is larger than adhesion.²⁷ Under UV irradiation, following the decrease in adhesion because of photodegradation at the PCs and the increase in stress, the coatings can be detached from the PCs when the stress is larger than adhesion. Contrary to the results from unmodified PCs, the plasma-PCs showed better ageing properties because of stronger interfacial bonding between the plasma-PC and the coating and weaker photodegradation at the PCs.

CONCLUSIONS

The adhesion failures of AS coatings deposited on unmodified PC and plasma-PC substrates under UV irradiation were investigated by both chemical and physical detection methods based on the surface and interface changes between coatings and PC substrate. UV-visible spectra and surface energy analyses proved that the AS coatings cannot prevent PC photodegradation at the interface of coating on the PC substrate. Nanoindentation technique was employed for the quantitative assessment of the nanomechanical changes in coatings and PCs under UV irradiation ageing. Evident changes in the elastic modulus and hardness of coatings and PC were observed, which indicated the mechanical changes caused by UV irradiation.

The changes in the physical and chemical properties of coatings and PC substrates can explain the adhesion properties of coatings on PC substrates. Results showed that the adhesion failure after UV irradiation may be caused by two reasons: first, the photodegradation that occurred at the surface of PC substrate covered by AS coatings, which caused the rupture of chemicals at the interface between coatings and PC substrate; and second, the stress formed by UV ageing, followed by the changes in the

stiffness of both AS coatings and PC substrates. Results of UV ageing tests revealed that the adhesion of the coating on plasma-modified substrates was superior to that on unmodified substrates because of stronger interfacial bonding between plasma-PC and the coating.

ACKNOWLEDGMENTS

Financial support by Aviation Industry Corporation of China is gratefully acknowledged.

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