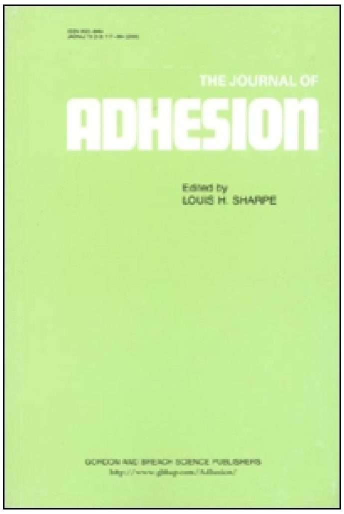

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Effect of Adhesion, Film Thickness, and Substrate Hardness on the Scratch Behavior of Poly(carbonate) Films

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Effect of Adhesion, Film Thickness, and Substrate Hardness on the Scratch Behavior of Poly(carbonate) Films

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The effect of adhesion, film thickness, and substrate hardness on the scratch behavior of poly(carbonate) (PC) films was investigated. Films of various thickness were prepared by spin-coating solutions of PC in chloroform onto glass, ferroplate, Al 1100, Al 6022, and Al 6111 substrates. Adhesion between the films and the substrates was controlled by pretreatment of the substrates and the thickness of the films was controlled by the concentration of the PC solutions. Adhesion of the films to the glass substrates was measured by a blister test. Scratch tests were performed using a custom-built, progressive-load scratch tester with interchangeable diamond indenters; the resulting scratches were observed by optical microscopy, atomic force microscopy (AFM), and environmental scanning electron microscopy (ESEM). The critical normal load (i.e., the smallest applied normal load for which delamination of the film from the substrate was observed) was used as a criterion to determine the scratch resistance of the films. It was found that better film/substrate adhesion resulted in a higher critical load for delamination. As film thickness increased, the critical load and, thus, scratch resistance also increased. Substrate hardness had a strong influence on the scratch behavior of the PC films. For a low-hardness substrate (i.e., Al 1100), the work from scratching was mainly consumed by deforming the substrate. In the case of substrates with intermediate hardness (i.e., Al 6022, Al 6111, and ferroplate), the substrates were more resistant to the stresses that were generated in the films; hence, the deformation of the substrates was less severe. A high-hardness substrate (i.e., glass) resisted the applied load and resulted in higher stress concentrations in the films and at the interface. Consequently, a rougher surface inside the scratch track was observed.

Keywords: Adhesion; Blister test; Scratch behavior; Substrate hardness; Plastic deformation; Poly(carbonate)

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INTRODUCTION

Scratch resistance is one of the most important properties required for many applications of polymers and coatings, such as automotive topcoats, floor coatings, and optical components, because most polymer products encounter a wide range of mechanical stresses during their working lifetime. There are three main deformation features of a scratch on bulk materials [1]. *Elastic deformation* results in no scratch after the load is released because the surface recovers to its original dimensions almost instantaneously. *Plastic deformation* does not result in fracture or loss of material, and the deformation can be recovered upon heating the specimen above its glass transition temperature. Piling up of the material may be observed at both edges of the scratch track. For *fracture deformation*, cracks are observed. In the case of coating systems, *delamination* is an additional important deformation feature that influences the surface aesthetics, durability, and functionality of the coatings.

Pile formation resulting from plastic deformation, brittle fracture, and delamination of the coating play a crucial role in making deformation of a coating visible [2, 3]. However, plastic deformation can be recovered by a heating process, whereas the other two types of deformation cannot be recovered. Small amounts of brittle fracture and delamination have significant effects on both functional reliability and aesthetics of the coatings. Delamination can cause catastrophic failure of the coatings.

Scratch resistance of coatings is a complex phenomenon because there are many factors involved, including coating parameters (*i.e.*, molecular weight, degree of cross-linking, glass transition temperature, and mechanical properties of the coating), scratching conditions (*i.e.*, shape of an indenter, applied load, and scratching speed), and substrate properties (*i.e.*, modulus and hardness). The effects of scratching conditions as well as material parameters of polymers and coatings have been widely studied in the past [4–7].

The properties and performance of a film during scratching are strongly dependent on adhesion of the film to the substrate. Scratch tests have been extensively employed to access the adhesion of thin, hard coatings [*i.e.*, TiN, SiC, and diamond-like carbon (DLC)] to the substrates [8–13]. Poor adhesion leads to early delamination of the films. Burnett and Rickerby showed that TiN coatings that have poor adhesion to the substrate had larger plastic zones under indentation than those that have stronger adhesion [8]. Similar results were reported on DLC and SiC coatings under scratching. Films with good adhesion showed narrower scratch widths than those with poor adhesion [9].

Numerous methods have been used to determine the adhesion of thin films to the substrates on which they are formed. These methods include tape tests, peel tests, and blister tests. However, tape tests only provide qualitative adhesion results, whereas peel tests and blister tests provide quantitative adhesion strength and are suitable for flexible adhering films. The peel test is simple in terms of the experiment; however, the specimens usually experience severe plastic deformation during the test. As a result, the adhesion strength obtained by a peel test frequently contains both fracture energy and the energy consumed by plastic deformation of the sample.

Blister tests are a promising alternative method for adhesion measurement of a flexible adhering film because there is no direct mechanical contact and energy dissipation during the test can be minimized by keeping the detachment angle small (*i.e.*, by minimizing bending of the material) and by keeping the debonding rate low. Furthermore, the fracture surface is axisymmetric, which minimizes the effect of sample nonuniformity, and the applied forces are uniform [14].

Dannenberg introduced the blister test in 1961. It was first used with elastomers and rigid bulk adhesives. Subsequently, it was applied to polymer films such as polystyrene and polymethyl methacrylate (PMMA) and pressure-sensitive adhesive tapes on rigid substrates [15, 16]. Recently, it was used to determine the fracture energy of polyimide to aluminum substrates [17].

In the blister test, a gas or a liquid is used to pressurize the interface between a substrate and a coating so that the coating delaminates from the substrate, forming a blister. Hence, adhesion between a deformable adhering layer and a rigid substrate can be determined based on the pressure and the blister height during the detachment of the film from the substrate [16, 18]. Gent and Lewandowski modified a method developed by Hinckley to calculate the fracture energy based on membrane analysis. They showed that the fracture energy (G_a) could be obtained in two ways based on the applied pressure (P) and the blister geometry [*i.e.*, blister height (y) and blister radius (a)] [16]. First, the fracture energy is proportional to the product of the pressure after debonding starts and the blister height as shown in Equation 1:

$$G_a = 0.649\,Py \tag{1}$$

At the same time, the fracture energy can be obtained from the critical pressure and the radius of the blister as shown in Equation 2:

$$G_a = \left[\frac{(Pa)^4}{(17.4\,Et)}\right]^{1/3} \tag{2}$$

where E and t are the Young's modulus and the thickness of the adhering layer. Equation 2 is only applicable when the blister diameter is much larger than the thickness of the adhering film. Note that P in Equations 1 and 2 is not the same; P in Equation 1 is the pressure after debonding begins, whereas P in Equation 2 is the pressure at which debonding starts (*i.e.*, the critical pressure).

Most investigations that were concerned with the effect of substrate hardness on the scratch resistance considered inorganic hard coatings [10, 19–22]. Knight, Page, and Hutching systematically investigated the influence of substrate hardness on the scratch response of TiN coated on a series of steel substrates (thickness of the coating was in a range of 1–2 μm) [19]. They found that the penetration depth of the indenter was a strong function of substrate hardness. As substrate hardness increased, the penetration depth decreased drastically. As hardness of the substrate increased, less plastic deformation of the substrate was observed, while microcracking in the substrate increased; however, the critical load for delamination of the coatings decreased as substrate hardness increased. Shen *et al.* [20] reported similar results for inorganic–organic hybrid coatings produced by plasma-enhanced chemical vapor deposition with coating thickness ranging from 1.70 to 3.50 μm. They found that when the substrates were soft, the coatings cracked as normal load increased, whereas in the case of glass substrates (*i.e.*, hard substrates), the coatings were delaminated from the substrate at the same applied load.

Despite the results from Knight *et al.* and Shen *et al.*, Ronkainen *et al.* [21] found that increasing substrate hardness resulted in higher critical load at the onset of crack formation of DLC coatings (film thickness was 0.5 μm and 3 μm). Hainsworth and Soh found no correlation between the substrate hardness and critical load of delamination of TiN coatings [22].

So far, there are very few papers that have investigated the influence of substrate properties on the scratch behavior of polymer coatings. However, Roche *et al.* found that the nature and mechanical characteristics of the substrate had great influence on the scratch behavior of UV-cured coatings [23]. For thin coatings (*i.e.*, less than 10 μm) on hard substrates (e.g., glass and aluminum), either cracks or delamination were observed as the applied normal load increased. In the case of soft substrates (e.g., PC), they found that the deformation upon scratching involved both the coating and the substrate underneath. However, no specific mechanical properties of the substrates were measured and related to the scratch behavior of the coatings.

As indicated previously, the effects of adhesion and substrate hardness on scratch resistance have mainly been examined for inorganic coatings that were normally coated on softer substrates. On the other hand, organic coatings are frequently applied to harder substrates. The purpose of this paper was to determine the effect of adhesion on scratch behavior of PC films on glass substrates. Substrate hardness was related to the scratch behavior of PC film/substrate systems. Along with the effect of adhesion and substrate hardness on the scratch behavior, the effect of film thickness was investigated as well.

EXPERIMENTAL

Materials

Poly(carbonate) (PC) sheet was purchased from McMaster Carr Co., Cleveland, OH, USA. The glass transition temperature of the PC was 148°C (determined by differential scanning calorimeter model 2010, TA Instruments, New Castle, DE, USA) and the viscosity average molecular weight was about 44,600 (using a Cannon-Fenske routine viscometer, Fisher Scientific, Pittsburgh, PA, USA). Solutions were prepared by dissolving PC in chloroform at concentrations of 0.1%, 5%, 10%, and 15% weight by volume.

Five different substrates were used, including Al 1100, Al 6022, Al 6111, ferroplate, and glass. Al substrates were ground with SiC paper and polished to a mirror surface with 2 μm of MgO. Polished Al alloy substrates were subsequently cleaned by air plasma treatment for 15 min using a small RF reactor (PDC-3XG, Harrick Scientific, Ossining, NY, USA). Ferroplate was rinsed in acetone and then exposed to the flame of a Bunsen burner. Glass substrates were rinsed in acetone and then cleaned in the air plasma for 15 min.

γ-aminopropyltriethoxysilane (γ-APS) was purchased from Aldrich Chemical Co. (St. Louis, MO, USA) 0.1 or 0.2% solutions of γ-APS in deionized water were hydrolyzed for 20 min at their natural pH of 10.4.

Sample Preparation

The spin-coating technique was used to prepare PC films on the substrates. Film thickness was controlled by the concentration of the PC solutions (with fixed spin-coating speed and spin-coating time). The influence of adhesion and film thickness on the scratch behavior was determined for PC film/glass substrate systems.

Adhesion of the PC films was controlled by pretreatment of the substrate. For good adhesion, glass substrates were treated with 0.1 % γ-APS for 15 min and then they were blown dry with N_2 before spin-coating of the PC solutions. In the case of intermediate-adhesion samples, 0.1% PC solution was spin-coated onto cleaned glass substrates. After that, the sample was exposed to an air plasma for 30 s. Then, a concentrated PC solution (5%, 10%, or 15% PC solution) was spin-coated onto the sample. The spin-coat time for all PC solutions was 30 s. Films with poor adhesion were prepared by spin-coating a 0.1% PC solution onto the substrate followed by spin-coating the concentrated PC solution without any pretreatment.

Effect of substrate hardness on scratch behavior was determined using silane-treated substrates with a film thickness of $3.2 \pm 0.4\,\mu m$. Substrates were treated with 0.2% γ-APS before spin-coating of PC solution was done.

Test Methods

PC Film Thickness Measurements

Film thickness was determined by weighing substrates before and after coating and assuming that the density of PC was $1.2\,g/cm^3$. At least three samples were measured per concentration.

Adhesion Measurements

Preliminary adhesion tests were done using simple tape tests. Films were applied to substrates by spin-coating as described. The films were cut into squares of 1.6 mm × 1.6 mm (8 × 8 squares) with a fresh razor blade. An adhesive tape was pressed against the 8 × 8 squares and the tape was peeled off in a 90° direction. The number of squares left on the substrate and the number removed were observed to determine qualitatively the degree of adhesion of the films to the substrates.

Blister tests were used to further determine the adhesion of the PC films to the glass substrates. A glass substrate with a diameter of 76.2 mm and thickness of 6.4 mm with a 7.5 mm hole at the center and Al substrate with a similar centerline hole that was threaded to facilitate connection to the pressure system were used for the tests. Glass and Al substrates were rinsed in acetone and then cleaned in an air plasma for 15 min. The cleaned substrates were then treated with 1% γ-glycidoxypropyltrimethoxysilane (γ-GPS, Aldrich Chemical Co.), which was hydrolyzed in deionized water for 60 min at its natural pH of 6.5. The silane solution was applied onto glass and Al substrates using a brush and left for 10 min. After that, the substrates were blown dry with N_2 and heated at 93°C for 30 min. Then, they were bonded together using a two-part epoxy. The specimen was left overnight under laboratory environment and was postcured at 100°C for

60 min. A KBr disk was made *in situ* to plug the hole and to provide a smooth surface for film application. Samples with various degrees of adhesion (*i.e.*, poor adhesion, intermediate adhesion, and good adhesion) were prepared as described previously, except that the thickness of the PC films was about 94 ± 13 μm. After the PC film was spin-coated onto the glass substrate, the KBr disk was dissolved in water and blister tests were done. De-ionized water was used to pressurize the blister at a constant flow rate of 0.2 ml/min using a syringe pump (Harvard Apparatus 22, Holliston, MA, USA).

During the blister test, the blister height initially increased as pressure increased until it reached the critical pressure (*i.e.*, the pressure at which debonding started); then, as debonding proceeded, the pressure dropped as the blister grew in radius. During the experiment, the pressure was recorded as a function of time using a pressure transducer (PX602, Omega Engineering, Inc., Stamford, CT, USA), which was connected to a Universal Serial Bus (USB) data acquisition system (OMB-DAQ-55, Omega Engineering, Inc.) with pDaq View software. Pictures of the PC "blister" were taken using a video camera and Image-Pro Plus 4.1 software (Media Cybernetics, Silver Spring, MD, USA). Numerous frames of the blister were taken before and during the debonding process and the height and the radius of the blisters were then measured using the same software. The fracture energies were calculated based on Equations 1 and 2.

Hardness Measurements of the Substrates

Microhardness of the substrates and PC was measured using a Vickers microhardness tester (Leco M-400-H1, Akashi Corporation, Zama, Japan). A load of 100 g was used. Five measurements were done per sample.

Scratch Tests

Scratch tests were performed using a custom-built, progressive-load scratch tester with interchangeable diamond indenters. In the progressive-load scratch tests, the applied normal force increased linearly as a function of scratching time and distance. Thus, the normal load at the onset of important failure events (*i.e.*, delaminating of the films) was detected. A spherical indenter with a tip radius of 89 μm was used for scratching experiments with a full-scale load of 0.90 N and a scratching speed of 0.033 mm/s. The samples were scratched under loads ranging from 0 to 0.45 N and from 0.45 to 0.90 N on each sample because of a limitation of the sample size. The samples were scratched until continuous delamination was observed or until the full-scale load was reached. Seven to ten scratches were done per sample on at least two specimens.

Characterization of Scratches on PC Films

The residual scratch width and depth were measured using an atomic force microscope (AFM, Dimension 3100, Digital Instruments, Santa Barbara, CA, USA). The resulting scratches were also observed under an optical microscope with a magnification of 100×. In some cases, the samples were examined using an environmental scanning electron microscope (ESEM, XL30 ESEM-FEG, Philips, FEI Co., Hillsboro, OR, USA).

RESULTS AND DISCUSSION

The effect of adhesion and film thickness on scratch behavior was investigated for PC film/glass substrate systems. Table 1 shows the tape adhesion test results. It was found that samples without any pretreatment of the substrate showed poor adhesion. All of the squares peeled off and no film deformation was observed. When a film was spin-coated onto a glass substrate from a 0.1% solution of PC and treated with an air plasma for 30 s before the concentrated PC solution was spin-coated onto the substrate, all of the squares were peeled off. However, considerable film deformation was noticed. This result indicated that samples in the second group had better adhesion than samples prepared from substrates that were not pretreated. It has been

TABLE 1 Tape Adhesion Test Results of PC Film/Glass Substrate Samples

Sample details	Tape adhesion test results	Remark
Glass substrates were treated with 0.1% γ-APS	None of the squares peeled off	Good adhesion
A thin film of 0.1% PC solution spin-coated onto glass substrate was treated with air plasma for 30 s before a concentrated PC solution was spin-coated on it	All squares peeled off but there was deformation of peeled films	Intermediate adhesion
No pretreatment on either the film or the substrate	All squares peeled off easily without any film deformation	Poor adhesion

Note: Different pretreatment was used to obtain different degrees of adhesion between the film and the glass substrate.

reported that modification of PC in an air plasma improved the adhesion of PC to both metal [24] and polymer [25] substrates because of an increase in surface energy of PC and the availability of new surface functional groups for bonding to other materials. When glass substrates were treated with 0.1% γ-APS, none of the squares, or, in some cases, very few squares (2–3 squares) were peeled off.

Further investigation on adhesion strength of the samples was done using the blister test. Figures 1 to 3 show typical plots of blister height *versus* pressure during debonding of the PC film/glass substrate samples with poor adhesion, intermediate adhesion, and good adhesion, respectively. During debonding, the pressure dropped while the blister height still increased. Deviations of the experimental data from the predicted curve (*i.e.*, $P \propto y^{-1}$, by Gent and Lewandowski based on Equation 1) were due to the experimental setup, which initially provided a higher debonding rate than at a later stage of debonding. At the beginning of the debonding stage, the blister size was smaller than that of the later debonding stage; as a result, the debonding rate was higher at the beginning because the pressure flow rate was kept constant throughout the experiment. Chu and Durning [14] and Gent and Lewandowski [16] reported similar observations. Table 2 shows the average fracture energies of the PC film/glass samples with various degrees of adhesion based on both criteria presented by Gent and Lewandowski (*i.e.*, Equations 1 and 2). Both methods gave similar

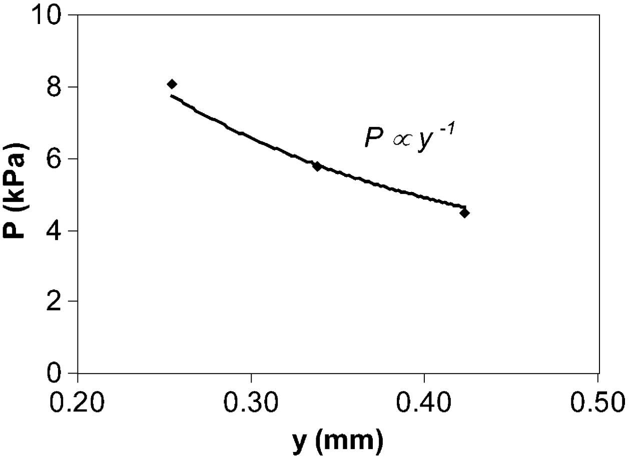


FIGURE 1 Typical plot of blister height (y) versus pressure (P) during debonding of PC film/glass substrate samples with poor adhesion. Solid line shows the relationship between P and y based on equation 1 ($P \propto y^{-1}$).

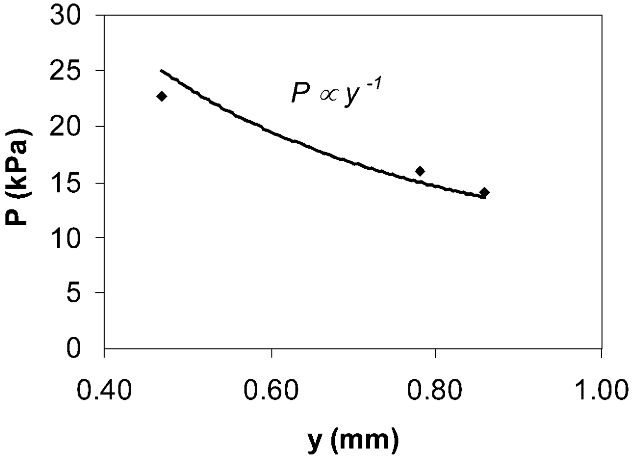


FIGURE 2 Typical plot of blister height (y) versus pressure (P) during debonding of PC film/glass substrate samples with intermediate adhesion. Solid line shows the relationship between P and y based on equation 1 ($P \propto y^{-1}$).

results. PC film/glass samples with poor adhesion had very low fracture energy (*i.e.*, in the range of 2–3 J/m^2 based on Equations 1 and 2), whereas the PC film/glass samples with intermediate adhesion had a fracture energy in the range from 6 to 8 J/m^2. PC film/glass samples with good adhesion had the highest fracture energy, in the

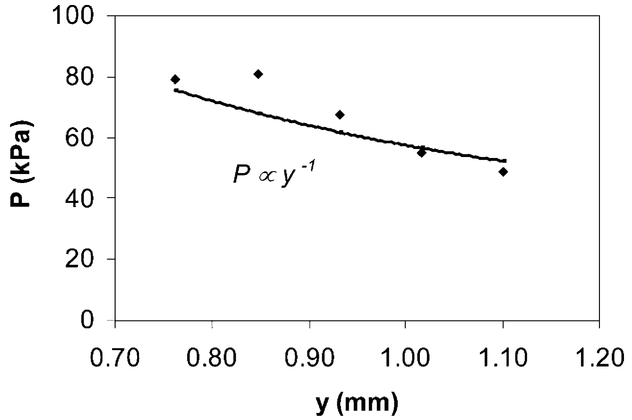


FIGURE 3 Typical plot of blister height (y) versus pressure (P) during debonding of PC film/glass substrate samples with good adhesion. Solid line shows the relationship between P and y based on equation 1 ($P \propto y^{-1}$).

TABLE 2 Fracture Energies of PC Film/Glass Substrate Samples with Various Degrees of Adhesion, Calculated from Equations 1 and 2

Sample	Fracture energy (G_a) (calculated from Eq. 1) (J/m^2)	Fracture energy (G_a) (calculated from Eq. 2) (J/m^2)
Poor adhesion	2.0 ± 0.8	2.6 ± 1.1
Intermediate adhesion	6.4 ± 1.1	8.0 ± 0.3
Good adhesion	38.6 ± 5.1	42.8 ± 3.7

Note: A water flow rate of 0.2 ml/min was used for the blister tests.

range from 38 to 43 J/m^2. From these results, it was determined that film/substrate adhesion could be controlled by applying different surface pretreatment methods to the substrates and that the blister test could be used to quantitatively determine the adhesion of the PC films to the glass substrates.

Considering the four deformation features (*i.e.*, elastic deformation, plastic deformation, fracture, and delamination) caused by scratching of organic coatings, only delamination is related to the adhesion between the film and the substrate. Figure 4 shows the normal loads

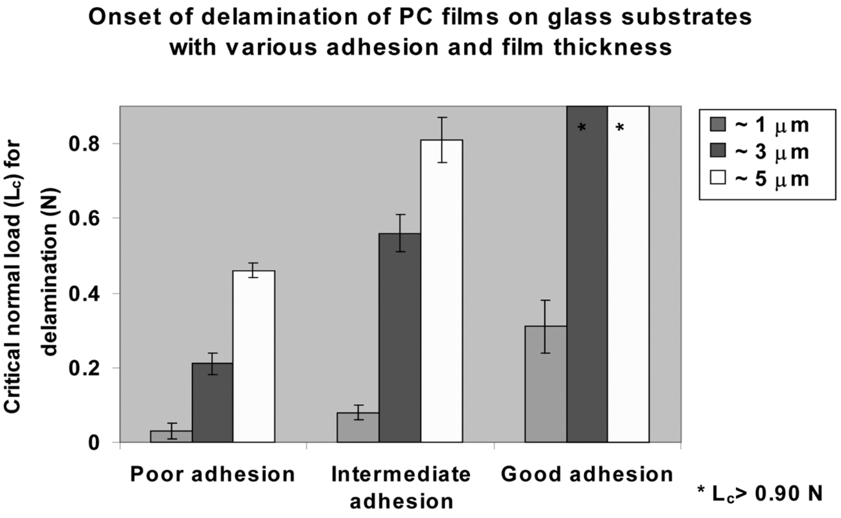


FIGURE 4 Critical normal load (L_c) for PC film/glass samples with various degrees of adhesion and film thickness (*i.e.*, as a function of PC concentrations). For samples with good adhesion, which were prepared from 10% and 15% PC solutions (*i.e.*, film thickness of ~3 and ~5 μm), the critical normal loads were higher than the full-scale load (0.90 N) used in this experiment.

at the onset of delamination (*i.e.*, at the critical normal load) as a function of adhesion strength. It was found that for each PC concentration (*i.e.*, constant film thickness), the better the adhesion, the higher the critical load of delamination. In this study, the substrate was harder and stronger than the film. As a result, the substrate could help to carry the contact load upon scratching. However, adhesion between the film and the substrate played an important role for load transfer to the substrate. Better adhesion resulted in more efficient load transfer from the film to the substrate.

It was also observed that samples with poor adhesion showed only smooth scratched surfaces before delamination was observed, whereas samples with intermediate adhesion showed a rougher surface before delamination (*i.e.*, for the film thickness of 2.8 ± 0.3 μm). This was due to delamination of samples with poor adhesion at a much lower load than samples with intermediate adhesion. The stress generated between the indenter and the film surface at the delamination point was still smaller than the cohesive strength of the film in the case of samples having poor adhesion. However, the stress at the interface was high enough to result in delamination of the film. In the case of samples with intermediate adhesion, the stress generated during scratching was greater than the cohesive strength of the film. Therefore, the scratch had a rougher surface before delamination. It was also noticed that for samples with poor adhesion, the delamination had a stick-slip pattern up to the full-scale load. Stick-slip delamination resulted in a larger exposed substrate area beside the scratch track. The larger exposed substrate area would result in more severe corrosion of the substrate if the substrate were a metal or more deterioration of the aesthetics of the products. As adhesion improved, the size of the exposed substrate area reduced. In the case of samples with good adhesion (*i.e.*, the film thickness of 1.1 ± 0.4 μm), films were delaminated within the vicinity of the scratch track. The influence of

TABLE 3 Film Thickness of Spin-Coated PC Films on Glass Substrates as a Function of Solution Concentration

PC concentation (%)	Film thickness (μm)
5	1.1 ± 0.4
10	2.8 ± 0.3
15	4.8 ± 0.5

Note: The film thickness was determined by weighing the substrate before and after spin-coating and assuming that the density of PC was 1.2 g/cm^3. At least three samples for each concentration were measured.

adhesion on the scratch behavior of PC films clearly showed that good adhesion was necessary for the film/substrate systems to function properly.

Table 3 shows the film thickness as a function of PC solution concentration. As PC concentration increased, the film thickness increased. The film thickness was 1.1 ± 0.4 μm, 2.8 ± 0.3 μm, and 4.8 ± 0.5 μm at PC concentrations of 5%, 10%, and 15% weight by volume, respectively. Thus, the film thickness could be controlled by the concentration of the PC solutions.

Figure 4 also shows the effect of film thickness on the critical normal load (L_c). Thicker films showed higher L_c for delamination for all samples (*i.e.*, those with poor adhesion, intermediate adhesion, and good adhesion). As the thickness of the film increased, the film carried more of the load and there was lower stress concentration at the film/substrate interface. Hence, film delamination was not observed for samples with good adhesion when the film thickness was about 3 μm or higher. Furthermore, as the film was thicker, the indenter had to penetrate deeper into the film to overcome the

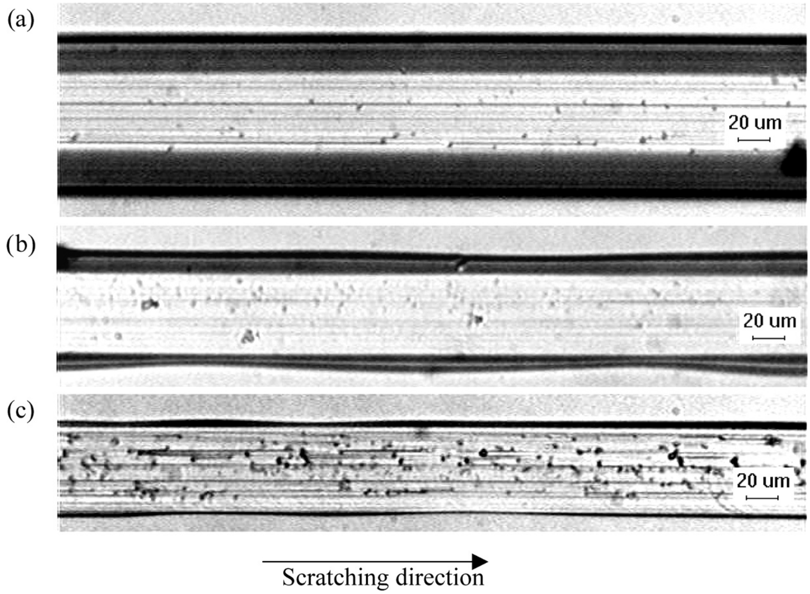


FIGURE 5 Optical micrographs (100×) of the scratches produced in (a) bulk PC and in PC films on glass substrates with a film thickness of (b) 4.8 ± 0.5 μm and (c) 2.8 ± 0.3 μm. The radius of the spherical indenter was 89 μm, the full-scale load was 0.90 N, and the scratching speed was 0.033 mm/sec.

adhesion strength. Higher normal loads were required for the indenter to penetrate deeper. Therefore, higher critical loads were obtained as film thickness increased. Nie *et al.* obtained similar results on oxide-coated aluminum alloys (hard coatings) [26]. They found that the critical loads for delamination increased as coating thickness increased. The coatings supported higher loads as the thickness increased because Nie *et al.* found that there was no penetration of the indenter under the load of 100 N on the coating with the thickness of about 180 μm. Muzeau, Von Stebut, and Magny investigated the effect of thickness (*i.e.*, the thickness ranging from 24 to 200 μm) on the scratch resistance of UV-cured coatings. They found that the thicker the coating, the better the scratch resistance [27]. As the film thickness increased, the scratch behavior of film/glass substrate systems became more like that of bulk PC. PC is prone to plastic deformation under a blunt indenter [6, 28]. However, when the optical images of scratches on PC films on glass substrates were compared with those of scratches on bulk PC (see Figure 5), it was observed that films on glass substrates showed rougher scratch tracks than bulk PC. Also, the width of the scratch tracks at the load of 0.90 N on the films with the thickness of 2.8 ± 0.3 μm and 4.8 ± 0.5 μm was less than those of the bulk PC. Scratch tracks on films with thickness of 2.8 ± 0.3 μm and 4.8 ± 0.5 μm were 64% and 79% of the width of scratch tracks on bulk PC, respectively. The rigidity of the substrate maintained a smaller scratch depth, which resulted in a narrower scratch width. On the other hand, high rigidity of the substrate induced a higher

TABLE 4 Modulus of Elasticity and Vickers Microhardness (H_{v100}) of PC and Substrates Used in this Experiment

Materials	Modulus of elasticitya (GPa)[a]	E_1/E_2[b]	H_{v100}[c]
PC	2.3	—	14 ± 0.1
Al 1100	69	0.033	44 ± 2
Al 6022	69	0.033	89 ± 2
Al 6111	69	0.033	102 ± 3
Ferroplate	205[d]	0.011	120 ± 6
Glass	68	0.034	407 ± 6

Note: A load of 100 g was used for measuring the microhardness. At least five measurements were done per sample.

[a] Values from www.matweb.com.

[b] E_1 is the modulus of elasticity of the coating, which is PC in this case, and E_2 is the modulus of substrates.

[c] Measured hardness values.

[d] Value for steel [modulus of elasticity of Cr (recrystallized) is 248 GPa].

stress concentration at the interface. As a result, the film/glass substrate samples showed a rougher scratch surface than bulk PC. As the film thickness increased, the influence from the substrate was less.

The effect of substrate properties on the scratch behavior of PC films was determined for five different substrates, including Al 1100, Al 6022, Al 6111, ferroplate, and glass. In these investigation, the film

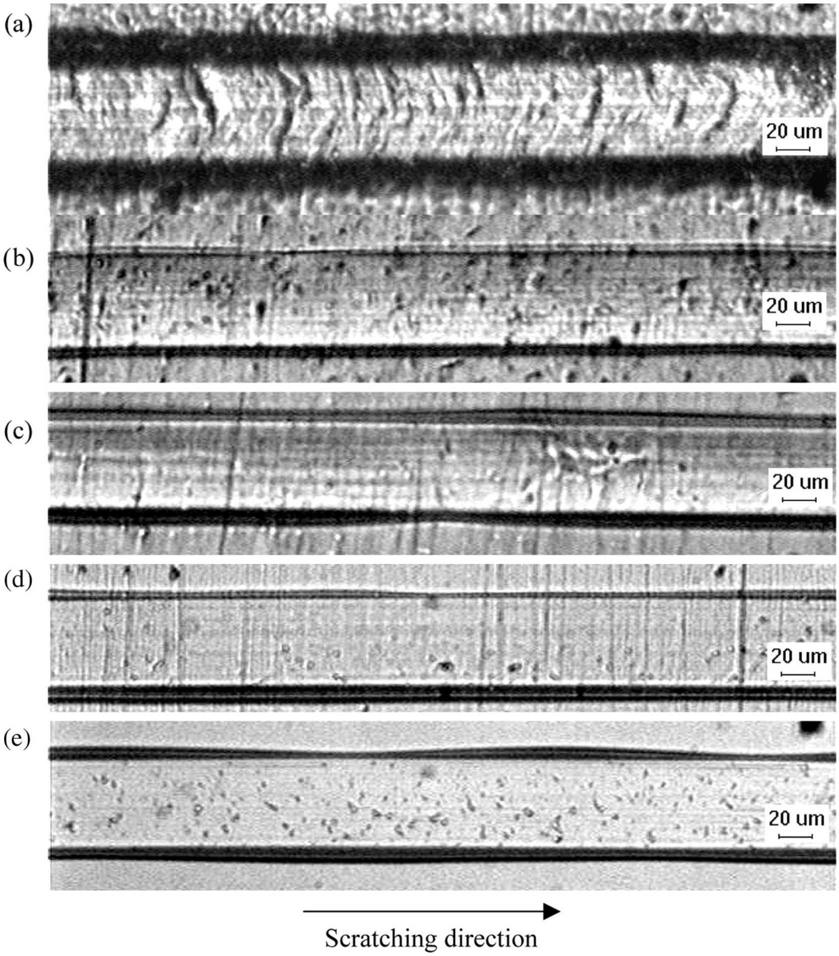


FIGURE 6 Optical micrograph images (100×) of the scratches produced at the applied load of 0.90 N: (a) PC film/Al 1100, (b) PC film/Al 6022, (c) PC film/Al 6111, (d) PC film/ferroplate, and (e) PC film/glass samples. The film thickness was about $3.2 \pm 0.4\,\mu\text{m}$.

TABLE 5 Residual Scratch Depth and Width of the Scratches on PC Film/Substrate Samples as Measured by AFM

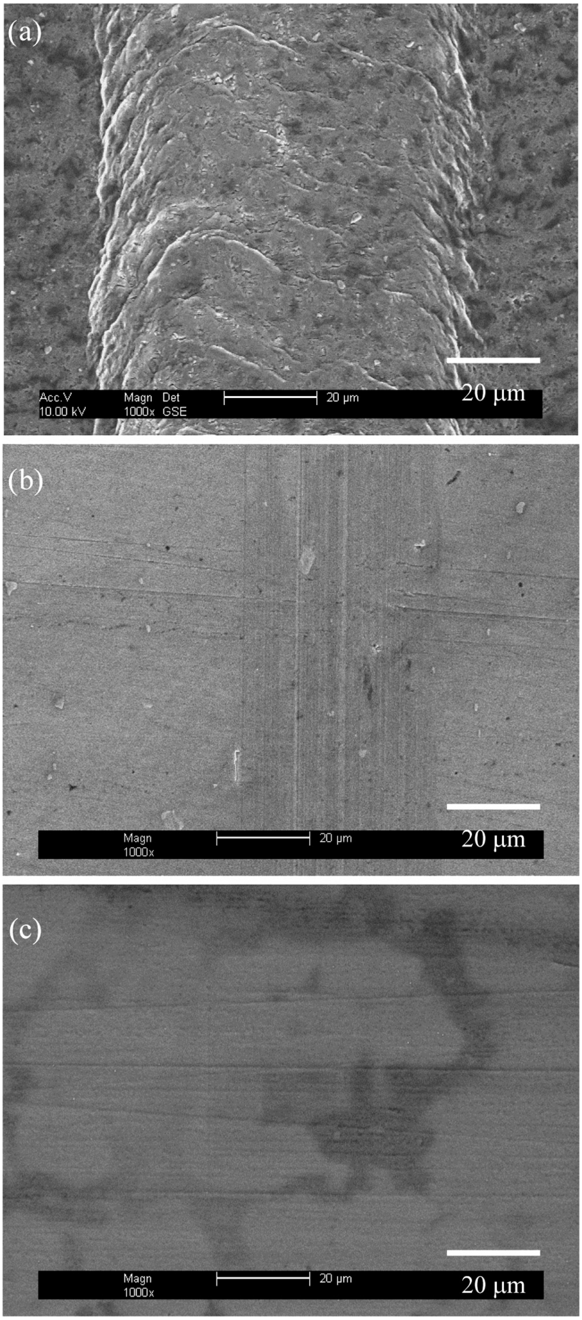
Samples	Scratch depth (μm)	Scratch width (μm)
PC film/Al 1100	4.6 ± 0.2	79.0 ± 1.4
PC film/Al 6111	1.0 ± 0.1	61.6 ± 0.1
PC film/glass	1.1 ± 0.2	62.2 ± 0.6

Note: The applied load was 0.90 N and the film thickness was 3.2 ± 0.4 μm. Scratch tests were done using a spherical indenter with tip radius of 89 μm, a full-scale load of 0.90 N, and a scratching speed of 0.033 mm/s.

thickness was 3.2 ± 0.4 μm. Table 4 shows the modulus and hardness of the substrates. The modulus of PC was much lower than those of the substrates. However, the ratio of the film modulus to the substrate modulus was not much different for the various substrates. As a result, the effect of substrate modulus on the scratch behavior of PC films was not great in these experiments. However, the substrate hardness covered a large range, from 44 to 407.

There are three main stress fields (*i.e.*, normal stress, tensile stress, and shear stress) induced by scratching using a spherical indenter. O'Sullivan and King found that the normal stress for soft coatings on hard substrates was low but distributed over a large area [29]. Also, the normal stress was concentrated at the surface of the coatings. The scratches on PC film/Al 1100 showed deformation bands that were convex with respect to the sliding direction (see Figure 6a). AFM results of the residual scratch depths are shown in Table 5. It was found that the residual depth of the scratches on PC films on Al 1100 substrates was 4.6 ± 0.2 μm, whereas the film thickness was 3.2 ± 0.4 μm. This result suggested that the Al 1100 substrate was deformed under these scratching conditions. Further investigation was performed by dissolving the PC film on the Al 1100 substrate in chloroform and then examining the Al 1100 by ESEM. Figure 7a shows an ESEM image of the Al 1100 substrate after removing the film. Clear evidence of substrate deformation was observed. The deformation bands inside the scratch tracks on Al 1100 substrate were similar to the deformation bands on the film/Al 1100 samples. This ductile

FIGURE 7 ESEM images (1000×) of the scratches left on the substrates after a PC film was scratched at the applied load of 0.90 N and then dissolved in chloroform. Scratching direction was from bottom to the top. (a) Al 1100 substrate, (b) Al 6111 substrate, and (c) ferroplate substrate.


(a)
Acc.V
10.00 kV
Magn
1000x
Det
GSE
20 µm
20 µm
(b)
Magn
1000x
20 µm
20 µm
(c)
Magn
1000x
20 µm
20 µm

damage showed that film material was pushed aside by the moving indenter and that the film became thinner as the load increased [19]. As a result, as the load increased, the substrate experienced more imposed load. For soft substrates (*i.e.*, lower hardness, such as Al 1100), a high imposed load or high stress, which was generated in the film, penetrated through the interface to the substrate; hence, it deformed the substrate.

Substrates with intermediate hardness, such as Al 6022, Al 6111, and ferroplate, were more resistant to the imposed load. No deformation bands were observed inside the scratch tracks, as shown in Figures 6b–d. ESEM images of Al 6111 and ferroplate substrates after film removal (see Figure 7) showed that the severity of substrate deformation decreased as the hardness of the substrates increased. Only smooth deformation features were observed on the Al 6111 substrate and no substrate deformation was observed on the ferroplate substrate. As the hardness of the substrate increased (*i.e.*, glass substrate), the substrate resisted the applied load, resulting in higher stress concentration at the interface. Hence, the PC film experienced higher stress, which resulted in a rougher surface inside the scratch tracks as shown in Figure 6e. Table 5 shows the residual scratch depth and width of film/substrate samples. It was found that the scratch depth and width for films on Al 6111 and glass substrates were similar, approximately 1 μm deep and 62 μm wide. Compared with the scratches on the film on Al 1100, the scratches on films on Al 6111 and glass substrate were much shallower and narrower. Harder substrates had more resistance to the stress to penetrate through the interface than soft substrates (*i.e.*, Al 1100). Therefore, stress was mainly concentrated in the films and at the interface, as a result of a rougher surface inside the scratch tracks and less substrate deformation in the films on high hardness substrates. These results showed that the substrate hardness had a strong influence on the scratch behavior of PC film/substrate systems.

When the coefficient of friction was zero, the in-plane stresses were all compressive [29]. However, when friction was present, compressive stresses were generated ahead of the indenter whereas tensile stresses were generated in the wake of the indenter. This tensile stress was believed to responsible for crack formation during scratching [27, 30]. However, PC is prone to plastic deformation under these scratching conditions. Therefore, the contribution from tensile stress might not play a crucial role in the scratch behavior of PC films.

Using a mathematical model, O'Sullivan and King found that the maximum shear stress was beneath the contact surface for low modulus coatings on harder substrates [29]. Youn and Su used finite element analysis and obtained similar results [31]. In addition, Youn and Su also found that the maximum strain occurred at the surface. This implied that deformation would occur at the surface rather than at the maximum shear stress region beneath the contact area. Also, when there was friction present between the indenter and the film surface, the maximum shear stress increased and moved toward the surface of the coatings [29]. This increased the potential for surface yielding of the films. As a result, the deformation of PC film/substrate systems was mostly observed in the PC films.

CONCLUSIONS

Films with better adhesion (*i.e.*, having higher interfacial fracture energy) to the substrate had higher critical normal loads for delamination and, hence, had better scratch resistance. Better adhesion between the film and the substrate resulted in more efficient stress transfer from the film to the substrate. As film thickness increased, scratch resistance to delamination increased because of lower stress concentration at the interface and more load support by the film. Also, thicker films required higher loads for the indenter to penetrate deep enough into the films to cause enough stress to overcome adhesion of the film to the substrate. As the film thickness increased, the scratch behavior of film/glass systems was more like that of bulk PC. The hardness of the substrates played a major role on the scratch behavior of the PC film/substrate systems. For low hardness substrates (*i.e.*, Al 1100), it was easier for the imposed load or stresses generated in the film to penetrate through the substrate, thus damaging the substrate. Substrates with intermediate hardness (*i.e.*, Al 6022, Al 6111, and ferroplate) and high hardness (*i.e.*, glass) were more resistant to the penetration of the stresses to the substrates. Hence, the deformation of the substrates was less severe. However, this led to higher stress concentration in the film and at the interface. As a result, a rougher surface inside the scratch track was observed. Optimization of the film thickness and substrate hardness had to be considered to obtain the best performance of the film/substrate systems on the scratch resistance. Good adhesion between the film and the substrate was necessary to prevent catastrophic failure resulting from delamination of the films.

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