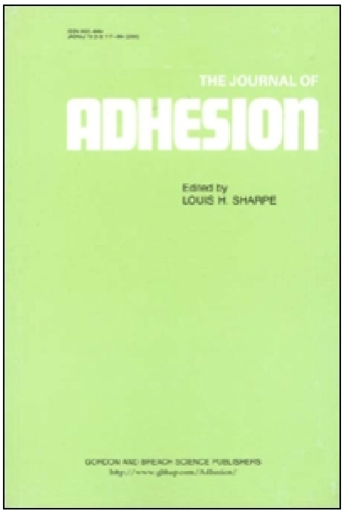

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Adhesion and Scratch Resistance of Polycarbonate Films on Ferroplate Substrates: Effect of γ-APS Primers

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Adhesion and Scratch Resistance of Polycarbonate Films on Ferroplate Substrates: Effect of γ-APS Primers

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The influence of γ-aminopropyltriethoxysilane (γ-APS) primers on the adhesion and scratch resistance of polycarbonate (PC) films on ferroplate substrates was determined from the critical normal loads at which debonding of the films from the substrates occurred during scratch testing. The critical load was a strong function of the concentration of the aqueous solutions from which the γ-APS primers were adsorbed and of the thickness of the primer films. Thus, the critical normal load increased from 0.09 ± 0.02 N to 0.31 ± 0.07 N as the concentration of the γ-APS solutions increased from 0.05% to 0.2%, respectively. However, the critical load increased only slightly as the solution concentration increased beyond 0.2%. The increase in critical load as concentration of γ-APS solutions increased was related to the formation of an interphase involving chemical reaction and physical entanglement of PC and γ-APS molecules. The critical load for debonding of PC films from the substrates also depended strongly on the temperature at which the γ-APS films were dried before application of the PC films. Thus, the critical normal loads for debonding were 0.31 ± 0.07, 0.20 ± 0.02, and 0.05 ± 0.01 N for γ-APS films that were dried for 15 min at room temperature, 60°C, or 110°C, respectively. The decrease in critical load with increasing drying temperature was attributed to the greater cross-link density in γ-APS films that were dried at elevated temperatures, which limited interdiffusion and physical entanglement of PC and γ-APS molecules. High reaction temperature of γ-APS and PC induced a fragmentation of amine. However, it also increased the probability of amines to react with carbonate because of increasing mobility of PC chains. Optimization of these two factors was required to obtain the greatest adhesion and scratch resistance. Chemical reactions occurring between PC films and γ-APS primers were investigated by reflection–absorption infrared spectroscopy (RAIR) and X-ray photoelectron spectroscopy (XPS) using diphenyl carbonate (DPC) as a model compound. The carbonyl absorption band of neat DPC was observed at 1780 cm^{-1}. However, two carbonyl bands were observed at 1738 and 1652 cm^{-1} in RAIR spectra of γ-APS films that were reacted with DPC and were assigned to urethane and

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urea groups, respectively. XPS results revealed that urethane was the main reaction product between DPC and γ-APS. It was concluded that urethane groups formed by the reaction of PC with γ-APS were responsible for adhesion and scratch resistance of PC to ferroplate substrates that were primed with γ-APS.

Keywords: Adhesion; γ-Aminopropyltriethoxysilane; Diphenylcarbonate; Interphase; Polycarbonate; Reflection–absorption infrared spectroscopy; Scratch resistance; X-ray photoelectron spectroscopy

I. INTRODUCTION

We have previously shown that the scratch resistance of polycarbonate (PC) films depends strongly on the hardness of the substrates on which the films are deposited [1]. In particular, it was found that substrates having relatively low hardness, such as Al-1100, were severely deformed during scratching of PC films. However, substrates having intermediate hardness, including Al-6022, Al-6111, and ferroplate (chromium-plated steel), were more resistant to the stresses that were generated during scratching of PC films on those substrates; hence, the deformation of substrates was less severe. Substrates that have high hardness, such as glass, resisted the loads applied during scratching of PC films, resulting in higher stress concentrations in the films and at the film/substrate interface. Consequently, little or no deformation of these substrates was observed during scratching of PC films on glass substrates.

Our previous research also showed that thin films of γ-aminopropyltriethoxysilane (γ-APS) were excellent primers for adhering PC films to substrates such as aluminum, ferroplate, and glass. Several other investigators have also reported that thin films of amino-functional silanes are good adhesion promoters for PC [2–4], although there have been relatively few investigations concerned with the mechanisms responsible for adhesion between PC and aminosilane films. Wen *et al.* used molecular dynamics simulations to determine the nature of the interaction between γ-APS and PC [3]. Their results showed the presence of hydrogen bonds between the amino groups of γ-APS and the carbonate groups in PC. Li and Wilkes [4] used infrared spectroscopy and X-ray photoelectron spectroscopy (XPS) to investigate the reactions occurring between PC and γ-APS. Samples were prepared using three different methods. In one approach, PC substrates were boiled in 0.5% solutions of γ-APS in isopropyl alcohol (IPA) until the solvent evaporated, and then they were heated in an oven at 150°C for 30 min. In another approach, PC substrates were soaked in 0.5%

γ-APS in IPA for 2 h and then washed with fresh IPA. In the third approach, PC substrates were immersed in 5% solutions of γ-APS in IPA at 75°C for 4 h, resulting in significant swelling of the PC. Li and Wilkes observed the carbonyl absorption at 1775 cm^{-1} in infrared spectra of neat PC. However, a new absorption band was observed at 1725 cm^{-1} in infrared spectra of samples prepared by swelling PC in solutions of γ-APS in IPA at 75°C (the third method described by Li and Wilkes) and was attributed to carbonyl groups in urethane linkages. Li and Wilkes did not observe the band at 1725 cm^{-1} in infrared spectra of samples prepared by their first and second methods.

Li and Wilkes used curve fitting of the high-resolution N(1s) XPS spectra to identify the chemical species on the surfaces of PC treated with γ-APS. Two components were observed at 400 and 402 eV in the N(1s) spectra. The component at 400 eV was assigned to nitrogen atoms in urethane groups, whereas the component at 402 eV was related to an unidentified oxidation product that was formed when PC was heated in air.

Several authors have reported that the concentration of γ-APS solutions affects the thickness of primer films deposited from the solutions, the chemical structure of the primer films, and adhesion between polymers and the primed surfaces. Sung and co-workers reported that the thickness of γ-APS primer films deposited from aqueous solutions having concentrations ranging from 0 to 9.0% at the natural pH of 10.4 had a significant effect on adhesion of polyethylene (PE) to aluminum substrates in dry and wet environments [5,6]. They found that the dry peel strength of PE/aluminum joints reached a maximum when the primer film was deposited from 2.0% γ-APS solutions, which corresponded to a film thickness of about 1000 Å. However, under wet environments (immersion in water or exposure to 100% RH), they found that samples prepared from substrates having primer films deposited from 0.3 to 1.0% γ-APS solutions retained higher peel strength than samples prepared from substrates with primer films deposited from 2.0% γ-APS solution. Lund *et al.* investigated the effect of γ-APS concentrations on adhesion of thin polyimide films to silica substrates. γ-APS was hydrolyzed in aqueous solutions having concentrations ranging from 0.00001 to 0.1% [7]. Freshly prepared solutions then were spin-coated onto silicon wafers and heated at 90°C for 30 min. They found that samples having primer films deposited from 0.01% silane solutions gave peel strengths (*i.e.*, $\sim$90 g/mm) similar to those having primer films deposited from 0.1% solutions. The peel strength dropped to 50 and 45 g/mm for samples having primer films deposited from 0.0001 and 0.00001% solutions, respectively. It was found that an optimum thickness of silane films was required to enhance the bond strength between mineral fillers and polymer matrix materials [2,5]. Films that were thicker or thinner than the optimum resulted in lower interfacial bond strengths [5].

Adhesion plays a major role in film/substrate performance and reliability. In scratch tests, film delamination/debonding reflects the adhesion between a film and the substrate on which it is formed. Greater adhesion (*i.e.*, higher scratch resistance) results in a higher critical load for debonding a film from a substrate [1,8,9].

The purpose of this article is to describe results that we have obtained using γ-APS primers to enhance the adhesion and the scratch resistance of PC films on ferroplate substrates. We also describe the chemical structure of the interphase formed by PC and γ-APS and the mechanisms responsible for adhesion of PC films to ferroplate substrates that are primed with γ-APS films.

II. EXPERIMENTAL

A. Materials

Polycarbonate (PC) sheets were purchased from McMaster Carr Co. (Cleveland, OH). γ-APS and diphenyl carbonate (DPC) were purchased from Aldrich Chemical Co. (St. Louis, MO) and were used without further purification. Chloroform was obtained from Tedia Co., Inc. (Fairfield, OH). Commercial photographic ferroplate was purchased from Doran Enterprises, Inc. (Milwaukee, WI).

B. Sample Preparation

In all cases, ferroplate substrates were rinsed in acetone, exposed to the flame of a Bunsen burner for a few seconds, and then etched in air plasmas for 15 min. Fresh solutions of PC were prepared by dissolving 1.5 g of the polymer in 30 ml of chloroform.

1. Vary γ-APS Concentrations

Aqueous solutions of γ-APS having concentrations of 0.05, 0.1, 0.2, 1, 2, and 5% by volume were used to deposit primer films onto ferroplate substrates. γ-APS was first hydrolyzed in high pressure liquid chromatography (HPLC)-grade water at the natural pH of 10.4 for 20 min. Ferroplate substrates were immersed into the silane solutions for 15 min, withdrawn, and blown dry using a strong stream of N_2. PC films were then spin-coated from solution onto the primed substrates using a fixed spin-coating speed and time. Finally, the specimens were heated in an oven at 60°C for 30 min.

2. Vary Heat Treatment of 0.2% γ-APS

The effect of drying temperature on the structure and properties of γ-APS films deposited onto ferroplate substrates from 0.2% aqueous solutions was investigated. Thus, γ-APS films were adsorbed onto clean ferroplate substrates from 0.2% aqueous solutions as described and subsequently dried at either 60 or 110°C for 15 min. PC films were then spin-coated onto the primed substrates as described previously.

3. Vary Reaction Temperature Between PC and 0.2 % γ-APS

The effect of temperature on adhesion of PC to ferroplate substrates that were primed with γ-APS films was also investigated. γ-APS films were adsorbed onto clean ferroplate substrates from 0.2% aqueous solutions of γ-APS as described and dried at room temperature. PC films were then spin-coated onto the primed substrates, and the specimens were heated in the oven at 60, 150, or 225°C for 30 min.

4. Reaction of γ-APS with DPC Model Compound

Diphenyl carbonate (DPC) was used as a model compound to investigate the chemical reactions occurring at the γ-APS/PC interface. Thin films of DPC were spin-coated from 5% solutions in chloroform onto ferroplate substrates that were primed with γ-APS films. These samples were heated in the oven using various combinations of time and temperature and then rinsed with fresh chloroform several times to remove unreacted DPC. The samples were then examined using reflection–absorption infrared spectroscopy (RAIR) or X-ray photoelectron spectroscopy (XPS).

C. Test Methods

1. Thickness Measurement

The thickness of γ-APS primer films was determined using a variable angle spectroscopic ellipsometer (J. A. Woollam Co., Inc., Lincoln, NE). Three different angles of incidence were used (60, 65, and 70°), and a Cauchy model was used to fit the data.

2. Scratch Test

Scratch tests were performed using a custom-built, progressive load scratch tester with a spherical indenter with a tip radius of 89 μm, scratching speed of 33 μm/s, and a maximum load of 0.90 N. 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. Horizontal loads were recorded during scratching. At least two specimens were used at each condition. The minimum load (*i.e.*, critical load) at which debonding of the film from the substrate was regularly observed was used as a measure of scratch resistance.

D. Characterization Techniques

Scratches were observed under an optical microscope at a magnification of 100× to identify the critical normal loads and nature of the debonds upon scratching. Correlations between the optical micrographs and horizontal load profiles were obtained.

RAIR and XPS were used to determine the primer film structure and the interaction between ferroplate/γ-APS and γ-APS/PC films. RAIR spectra were obtained using a Nicolet (Thermo Electron Co., Madison, WI) Magna 760 FTIR spectrometer at the resolution of $4\,\mathrm{cm}^{-1}$. In most cases, spectra were obtained by averaging 2048 scans. However, in some cases, 4096 scans were averaged. The RAIR spectrum of a clean but uncoated ferroplate substrate was used as a background.

XPS spectra were acquired using a Perkin-Elmer model 5300 spectrometer (Perkin-Elmer Corp., Eden Prairie, MN). All spectra were excited using MgK_α radiation and a take-off angle of 45°. Survey and high-resolution XPS spectra were obtained at pass energies of 89.45 eV and 35.75 eV, respectively. Charge correction was performed by referencing the C(1s) binding energy of principal carbon to a binding energy of 284.6 eV. Curve fitting of high-resolution XPS spectra was preceded by linear background subtraction. A combination of Gaussian and Lorenzian lineshapes (90% Gaussian, 10% Lorenzian) was used for curve fitting. The full width at half maximum (FWHM) was kept constant for all peaks during curve fitting. Atomic concentrations were obtained from the high-resolution spectra based on peak areas and sensitivity factors provided with the software.

III. RESULTS AND DISCUSSION

A. Effect of γ-APS Concentrations on Adhesion of PC Films to Ferroplate Substrates

Figure 1 shows the primer film thickness and the critical normal load for delamination of PC films as a function of the concentration of the solutions from which the γ-APS primer films were deposited. The

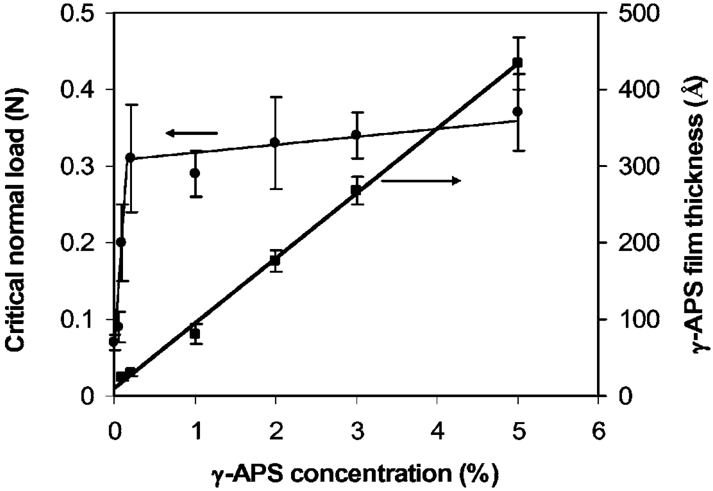


FIGURE 1 Primer film thickness and critical normal load for film delamination obtained for PC films on ferroplate substrates as a function of the concentration of the solution from which the γ-APS primer films were adsorbed. Ferroplate substrates were immersed into aqueous solutions of γ-APS of various concentrations for 15 min, withdrawn, and blown dry using a strong stream of N_2. PC solutions were then spin-coated onto the primed substrates, and the specimens were heated in the oven at 60°C for 30 min. Scratch tests were performed using a spherical indenter with a tip radius of 89 µm, scratching speed of 33 µm/s, and a maximum load of 0.90 N.

thickness of the primer films increased linearly as a function of γ-APS solution concentration over the range of concentrations that was considered. However, the critical normal loads occupied two different regimes. At concentrations of γ-APS that were less than 0.2%, the critical normal loads increased sharply as γ-APS concentration increased. Thus, the critical normal load increased from 0.09 ± 0.02 N to 0.20 ± 0.05 N and then 0.31 ± 0.07 N as the concentration of the γ-APS solutions increased from 0.05% to 0.1% and then 0.2%, respectively. For solution concentrations greater than 0.2% (corresponding to a primer thickness of about 30 ± 3 Å), the critical normal loads increased much more slowly as γ-APS concentration increased. Thus, the critical normal load increased from 0.31 ± 0.07 N to 0.37 ± 0.05 N as the concentration of the γ-APS solutions increased from 0.2% to 5%.

The increase in critical load that was observed when the concentration of the γ-APS solutions was increased was probably related to

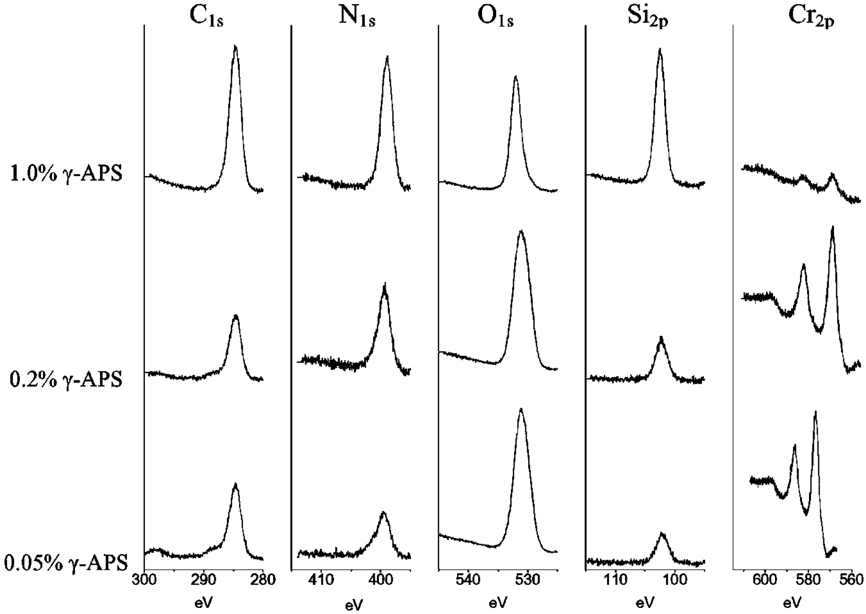


FIGURE 2 High-resolution XPS spectra of γ-APS primer films on ferroplate substrates as a function of the concentration of the solutions from which the γ-APS primer films were adsorbed. Ferroplate substrates were immersed into aqueous solutions of γ-APS for 15 min, withdrawn, and blown dry using a strong stream of N_2.

the formation of an interphase that involved physical entanglement as well as chemical reaction of PC and γ-APS molecules. Primer films obtained from γ-APS solutions with concentrations lower than 0.2% did not completely cover the substrate or were very thin because a relatively large amount of Cr, which was characteristic of the ferroplate substrate, was detected in XPS spectra as shown in Figure 2. Hence, poor adhesion and lower critical loads for film debonding were obtained. Cr was also detected on primer films prepared from 0.2% and 1.0% γ-APS solutions. However, the ratio of the areas under the Si(2p) and Cr(2p) peaks (0.4 and 13.1 for primer films prepared from 0.2 and 1.0% solutions, respectively) and primer film thickness were higher than those of the primer film obtained from 0.05% solution. (The ratio of the areas under the Si(2p) and Cr(2p) peaks was 0.2.) Additionally, adhesion between silane coupling agents and polymers could be enhanced by an interdiffusion mechanism. Interdiffusion between PC and primer films could be limited in the case of primer films prepared from γ-APS solutions with concentrations lower than 0.2% because primer films were too thin (thickness less than 30 ± 3 Å). As primer film thickness increased to 30 ± 3 Å (corresponding to γ-APS solution concentration of 0.2%), the width of the interdiffusion interphase probably reached the minimum value for obtaining good adhesion. Hence, critical loads in scratch tests increased only slightly beyond this point. A similar correlation between interfacial width and adhesion was reported by Schnell *et al.* [10]. They investigated the effect of interfacial width on adhesion between polystyrene (PS) and poly(p-methylstyrene) (PpMS) in the case of a PS/PpMS interface. The interfacial width was measured by neutron reflectivity, and adhesion was evaluated in terms of fracture toughness of the interfaces using double cantilever beam tests. They found that fracture toughness increased rapidly initially up to an interfacial width of about 9–12 nm. Beyond this point, the fracture toughness stayed constant with further interdiffusion or larger interfacial widths. They concluded that the constant fracture toughness beyond an interfacial width of 12 nm was due to sufficient entanglement between polymer molecules.

Horizontal loads were recorded during scratching of PC films on ferroplate substrates that were coated with γ-APS primer films of varying thickness. The results showed that samples prepared from substrates that were primed with γ-APS films that were adsorbed from solutions with concentrations of 0.2% or higher had similar lateral load profiles (see Figure 3). The onset of film debonding observed by optical microscopy corresponded to an abrupt change of the horizontal loads as shown by films deposited from 0.2% and 1.0% solutions. In some cases, the onset of film debonding corresponded to the high variation of the horizontal loads first, and then the abrupt change of the load was observed (as represented by 5.0% γ-APS). The shift of the lateral load to a higher level after film debonding corresponded to the fracture nature of the PC film, in which the film was cohesively failed in the middle of the film.

Below 0.2%, stick–slip debonding of the film/substrate was observed under the optical microscope. This behavior could be related to the pattern found in the lateral load curve as shown in Figure 4 (*i.e.*, increasing of the lateral force followed by an abrupt drop of the load). Lin *et al.* observed similar behavior when the fracture of automotive coatings occurred during scratching [11]. Based on these results, it was concluded that the sudden change in the lateral loads at the onset of film delamination was a better indicator of adhesion between the film and the substrate than large fluctuations of the lateral loads.

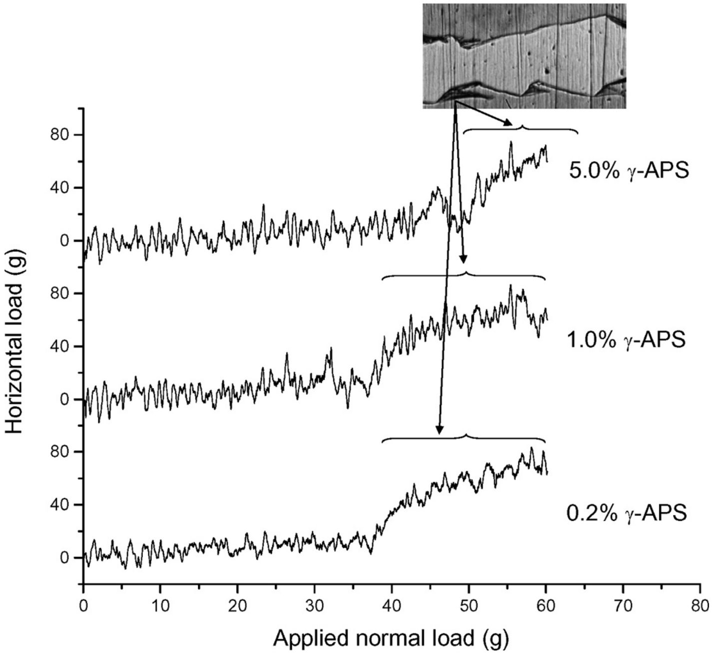


FIGURE 3 Horizontal loads as a function of applied normal loads during scratch testing of PC films on ferroplate substrates that were coated with γ-APS primer films of various thicknesses. The ferroplate substrates were immersed into aqueous solutions of γ-APS having concentrations of 0.2, 1.0, or 5.0% for 15 min, withdrawn, and blown dry using a strong stream of N_2. PC solutions were then spin-coated onto the primed substrates, and the specimens were heated in an oven at 60°C for 30 min. Scratch tests were performed using a spherical indenter with a tip radius of 89 μm, scratching speed of 33 μm/s, and a maximum load of 0.90 N. The optical micrograph image shows the fracture of the PC film after the critical load was reached.

Figure 5 shows RAIR spectra of primer films deposited on ferroplate substrates from 0.2% γ-APS solutions and then heated for various times and temperatures. Ferroplate substrates were immersed into the γ-APS solutions, withdrawn, and blown dry under a strong stream of N_2. After that, they were heated at 60°C and 110°C for 15 min. A broad band between 3500 and 3000 cm^{-1} in the spectra of samples that were not heated could be attributed to stretching vibrations of hydrogen-bonded SiOH and NH groups [12,13]. The bands near 2930 cm^{-1} and the shoulder around 2875 cm^{-1} corresponded to methylene stretching vibrations in propylamine groups. The strong bands near 1120 and 1050 cm^{-1} were assigned to Si–O–Si stretching modes,

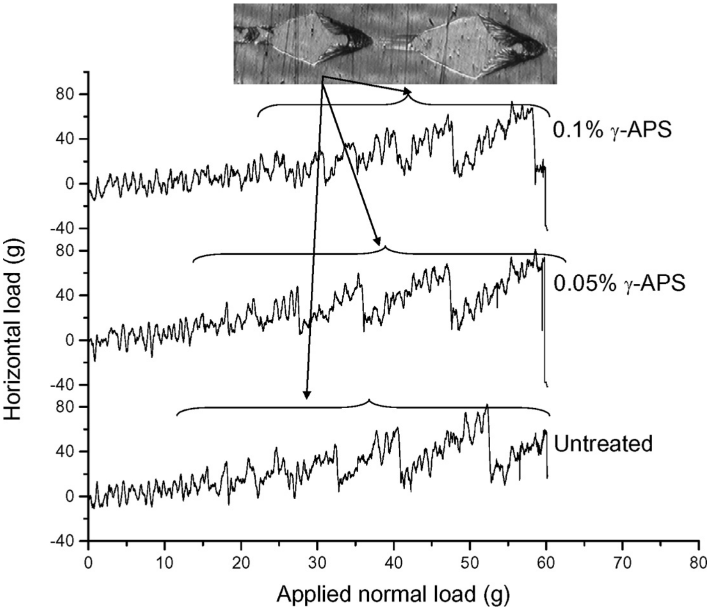


FIGURE 4 Horizontal loads recorded during scratch testing of PC films on untreated ferroplate substrates and substrates that were primed with γ-APS as a function of applied normal loads. The ferroplate substrates were immersed into aqueous solutions of γ-APS having concentrations of 0.05 and 0.1% for 15 min, withdrawn, and blown dry using a strong stream of N_2. PC solutions were then spin-coated onto the primed substrates, and the specimens were heated in an oven at 60°C for 30 min. Scratch tests were performed using a spherical indenter with a tip radius of 89 μm, scratching speed of 33 μm/s, and a maximum load of 0.90 N. The optical micrograph image shows the fracture of the PC film after the critical load was reached.

whereas the band near 935 cm^{-1} was related to Si–O bonds of SiOH groups [12,14]. After the primer films were heated at 60°C or 110°C for 15 min, the relative intensities of the broad band in the 3500–3000 cm^{-1} region and the band at 935 cm^{-1} decreased because of further condensation of the siloxane network. This result confirmed the assignments of the band at 935 cm^{-1} to SiOH groups, which was used in the following section. The peak in a range of 3500–3200 cm^{-1} was not used because of the overlapping of NH stretching in this region. The bands near 1640 cm^{-1} and 1330 cm^{-1} corresponded to antisymmetric and symmetric stretching modes of bicarbonate salts, which formed in the presence of H_2O and CO_2, whereas the bands near

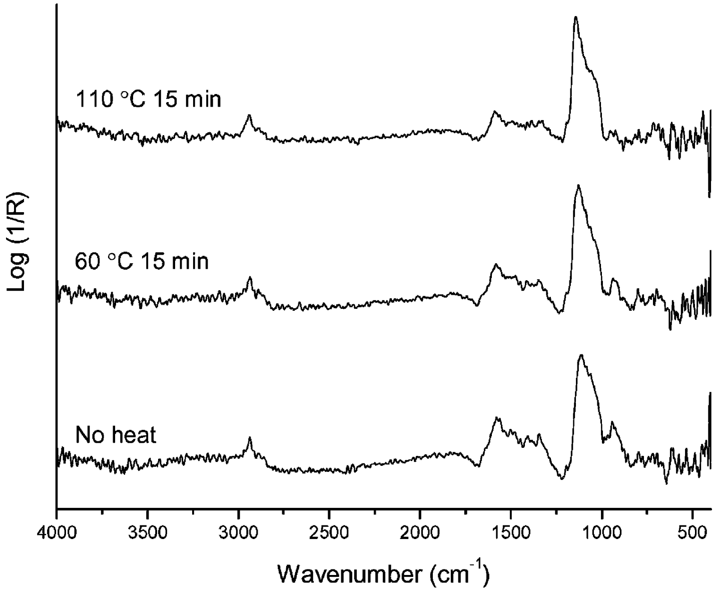


FIGURE 5 RAIR spectra of primer films deposited on ferroplate substrates from 0.2% aqueous solutions of γ-APS. The ferroplate substrates were immersed into the γ-APS solutions for 15 min, withdrawn, blown dry using a strong stream of N_2, and then heated at 60°C or 110°C for 15 min.

1580 cm^{-1} and 1480 cm^{-1} were due to antisymmetric and symmetric stretching modes of $-NH_3^+$, respectively [12,14].

As the thickness of the primer films increased, the condensation of silanol groups in the films also increased. This was evident from the increase in the ratio of the intensities of the bands at 1120 and 935 cm^{-1} that were assigned to Si–O bonds in Si–O–Si and Si–OH OH groups, respectively (see Table 1). Based on the scratch results, it was concluded that a certain degree of silanol condensation was needed in the primer films to obtain adhesion of PC films to ferroplate substrates.

In an attempt to identify the nature of the chemical interaction between γ-APS and PC, PC solutions were spin-coated onto ferroplate substrates that had γ-APS primer films of various thicknesses. After deposition of the PC films onto the primed substrates, the specimens were heated at 60°C for 30 min and then cooled to room temperature. The specimens were then rinsed several times with fresh chloroform to remove any unreacted PC. Figure 6 shows the RAIR spectra obtained from these specimens; the RAIR spectrum of a PC film

TABLE 1 Intensity Ratio of the Bands at 1120 and 935 cm^{-1} in the RAIR Spectra of γ-APS Films Adsorbed onto Ferroplate Substrates as a Function of Solution Concentration

γ-APS concentration (%)	Peak intensity ratios (I_{1120}/I_{935})
0.05	3.5
0.2	4.6
1.0	4.8
5.0	8.7

Note. The ferroplate substrates were immersed into aqueous solutions of γ-APS having various concentrations for 15 min, withdrawn, and blown dry using a strong stream of N_2.

is included in Figure 6 for comparison. The band at 1781 cm^{-1} corresponded to C=O bonds in carbonate groups, whereas the band at 1508 cm^{-1} was related to the p-disubstituted benzene rings of PC. Bands near 1252, 1200, and 1168 cm^{-1} were characteristic of the

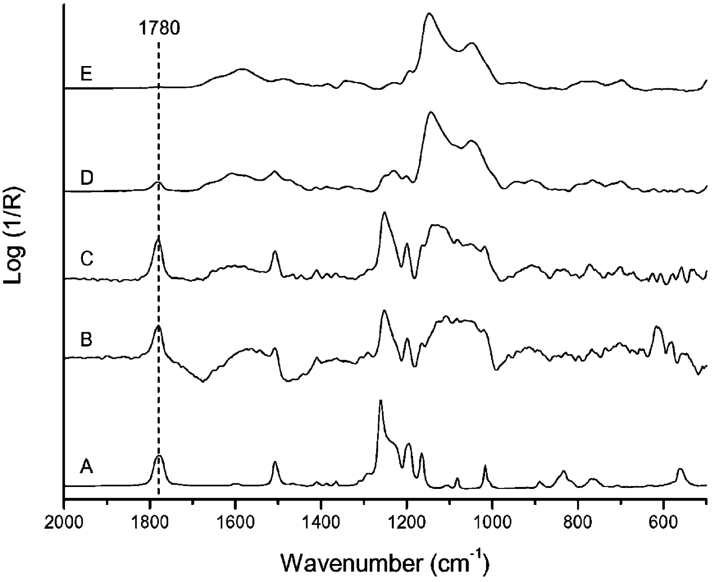


FIGURE 6 RAIR spectra of PC films on ferroplate substrates that were primed with γ-APS. The γ-APS films were adsorbed onto the ferroplate substrates from (b) 0.05, (c) 0.2, (d) 1.0, and (e) 5.0% aqueous solutions and then blown dry in N_2. PC films were then spin-coated onto the primed substrates, and the specimens were heated in an oven at 60°C for 30 min. Unreacted PC was then removed by chloroform. The RAIR spectrum of neat PC is shown for comparison in (a).

O–C–O bonds of PC. As the primer film thickness decreased, bands characteristic of PC became more prominent. The presence of bands characteristic of PC on all primed substrates after unreacted PC was rinsed off by fresh chloroform suggested that a reaction occurred between γ-APS and PC. However, no bands that could be attributed to functional groups produced by the reaction of PC with γ-APS were observed. The reason for this was probably related to the molecular weight of the PC, which was about 44,600 g/mol as measured using a Cannon-Fenske viscometer. Each PC molecule that was retained on the surface of the substrate after washing with chloroform contained many more unreacted carbonate groups than functional groups of the reaction products; therefore, it was very difficult to observe bands because of the reaction products of PC and γ-APS in the RAIR spectra. Hydrogen bonding and covalent bonds between γ-APS and PC were possible because they are sufficiently strong to prevent the removal of PC by organic solvents [15,16].

Further investigation to identify the chemical reaction at γ-APS/PC interfaces was done using the model compound DPC. Figure 7 shows detail of the 1850–1500 cm^{-1} region of RAIR spectra that were obtained from samples prepared by spin-coating DPC onto ferroplate substrates. The spectrum shown in Figure 7a was obtained from a sample that was prepared by spin-coating DPC onto a clean ferroplate substrate. The band attributed to the C=O stretching mode of the carbonate groups was clearly observed at 1780 cm^{-1}. Figures 7b and 7c show the RAIR spectra obtained from samples that were prepared by spin-coating DPC onto clean ferroplate substrates, heating the substrates at 60°C for 5 or 15 min, respectively, and then rinsing the substrates in chloroform to remove unreacted DPC. The carbonyl absorption band in these spectra was observed at about 1756 cm^{-1}; the shift of this band toward lower frequencies after heating at 60°C was probably the result of oxidation of the carbonate groups. Jang and Wilkie reported that the thermal oxidation products of bisphenol-A-based PC in air included alcohols, ether, and aldehyde/ketone [17]. They detected the carbonyl peak shift from 1780 to 1750 cm^{-1} and attributed the carbonyl peak at 1750 cm^{-1} to hydrogen bonds between carbonyl groups and alcohols, which were the main oxidation products of bisphenol-A-based PC. Figures 7d and 7e show RAIR spectra that were obtained from samples that were prepared by spin-coating DPC from chloroform solutions onto ferroplate substrates that were primed with thin films of γ-APS deposited from 0.2% aqueous solutions and then heated at 60°C for 5 or 15 min, respectively. These samples were also rinsed several times in fresh chloroform to remove unreacted DPC

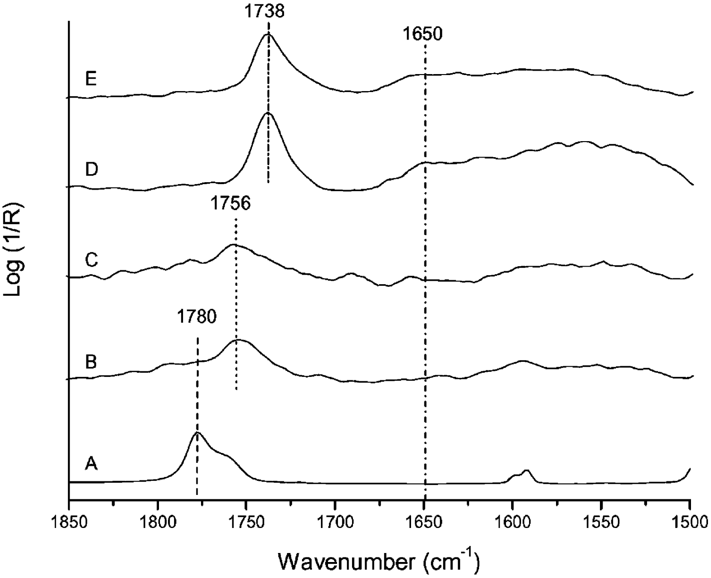


FIGURE 7 RAIR spectra of DPC films on ferroplate substrates. The RAIR spectrum of a neat DPC film is shown in (a). Spectra of DPC films on *unprimed* ferroplate substrates after heating at 60°C for 5 min and 15 min are shown in (b) and (c), respectively. Spectra of DPC films on *primed* ferroplate substrates after heating at 60°C for 5 and 15 min are shown in (d) and (e), respectively. Primer films were deposited by immersing ferroplate substrates into 0.2% γ-APS solutions, withdrawing the substrates, and blowing the substrates dry in a strong stream of N_2. DPC that did not react with the primer films was removed by rinsing the substrates with chloroform after heating was completed.

before the RAIR spectra were obtained. The carbonyl absorption band was observed at 1738 cm^{-1} in these spectra, indicating that the carbonate groups of DPC had reacted with the amine groups of γ-APS to form urethane structures. The assignment of the band near 1738 cm^{-1} in the RAIR spectra shown in Figures 7d and 7e to urethane groups was supported by the observations of Li *et al.* who reported that the carbonyl absorption of N-aliphatic aromatic urethanes (aliphatic–NH–CO–O–aromatic) appeared near 1740 cm^{-1}, whereas the carbonyl peak of N-aliphatic aliphatic urethanes (aliphatic–NH–CO–O–aliphatic) appeared near 1725 cm^{-1} [18]. A broad, weak band that was observed near 1650 cm^{-1} in the spectra shown in Figures 7d and 7e was attributed to the carbonyl absorption of urea groups. The band near 1650 cm^{-1} was not observed in the RAIR spectra of DPC films on unprimed ferroplate.

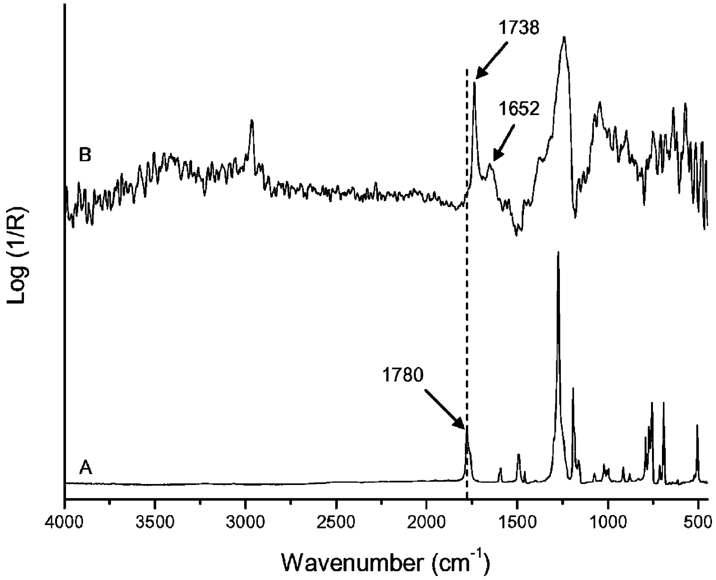


FIGURE 8 (a) RAIR spectrum obtained from a thin film of neat DPC that was spin-coated onto a clean ferroplate substrate; (b) RAIR spectrum of a sample that was prepared by adsorbing γ-APS onto a clean ferroplate substrate from a 0.2% aqueous solution, blowing the substrate dry in a stream of N_2, spin-coating DPC onto the substrate, heating the substrate at 60°C for 15 min, and then rinsing the substrate with chloroform to remove unreacted DPC. The background spectrum used in (b) consisted of the RAIR spectrum of a ferroplate substrate that was coated with a γ-APS film that was adsorbed from a 0.2% aqueous solution, blown dry with N_2, and then heated at 60°C for 15 min.

Figure 8 shows the RAIR spectrum that was obtained from a sample that was prepared by adsorbing γ-APS onto a clean ferroplate substrate from a 0.2% aqueous solution, blowing the substrate dry in a stream of N_2, spin-coating DPC onto the substrate, heating the substrate at 60°C for 15 min, and then rinsing the substrate with chloroform to remove unreacted DPC. A ferroplate substrate that was coated with a γ-APS film that was adsorbed from a 0.2% aqueous solution, blown dry with N_2, and then heated at 60°C for 15 min was used to obtain the background spectrum. Figure 8 also shows the RAIR spectrum of DPC spin-coated onto a clean ferroplate substrate for comparison. The band due to the carbonyl stretching mode was clearly observed at 1780 cm^{-1} in the spectrum of the neat DPC film. However, bands were observed at 1738 and 1652 cm^{-1} in the carbonyl region of the sample prepared with a γ-APS primer,

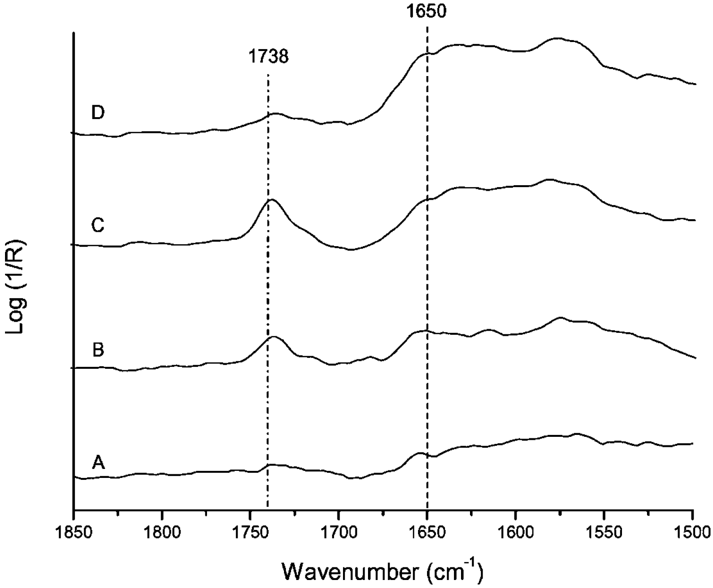


FIGURE 9 RAIR spectra obtained from γ-APS films on ferroplate substrates after reaction with DPC. The γ-APS films were adsorbed onto the substrates from aqueous solutions having concentrations of (a) 0.2, (b) 0.3, (c) 0.4, and (d) 0.5% for 15 min and then blown dry using a strong stream of N_2. DPC solutions were then spin-coated onto the primed substrates, and the specimens were heated in an oven at 50°C for 15 min. Unreacted DPC was removed by rinsing in chloroform before the RAIR spectra were obtained.

indicating that urethane and urea groups were formed by reaction of DPC with γ-APS.

We carried out additional investigations by depositing γ-APS films onto ferroplate substrates by adsorption from aqueous solutions with concentrations between 0.2% and 0.5% and then blowing the substrates dry in a stream of N_2. The substrates were then spin-coated with DPC, heated at 50°C for 5 min, and rinsed with chloroform. RAIR spectra obtained from these samples are shown in Figure 9. As the concentration of the γ-APS solutions increased from 0.2% to 0.4%, the intensity of the urethane peak at 1738 cm^{-1} also increased, but when the concentration of the γ-APS solution was 0.5%, the intensity of the band near 1738 cm^{-1} decreased. However, the shoulder attributed to urea groups near 1650 cm^{-1} increased in intensity as the concentration of the γ-APS solutions and, thus, the thickness of the γ-APS films on the substrates increased. This result

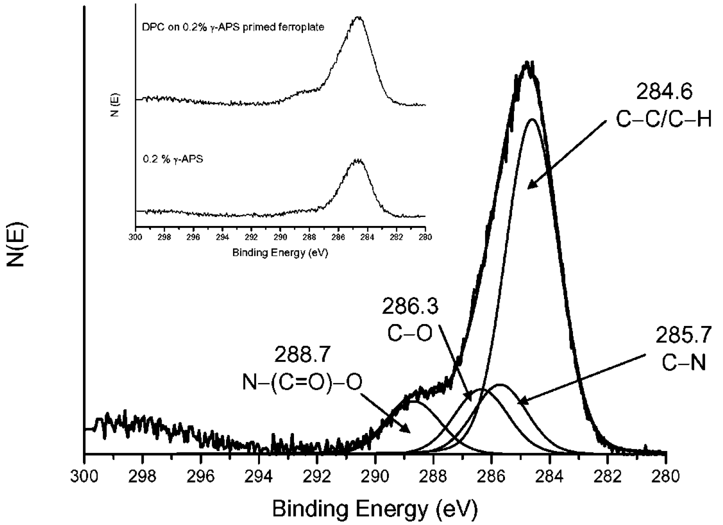
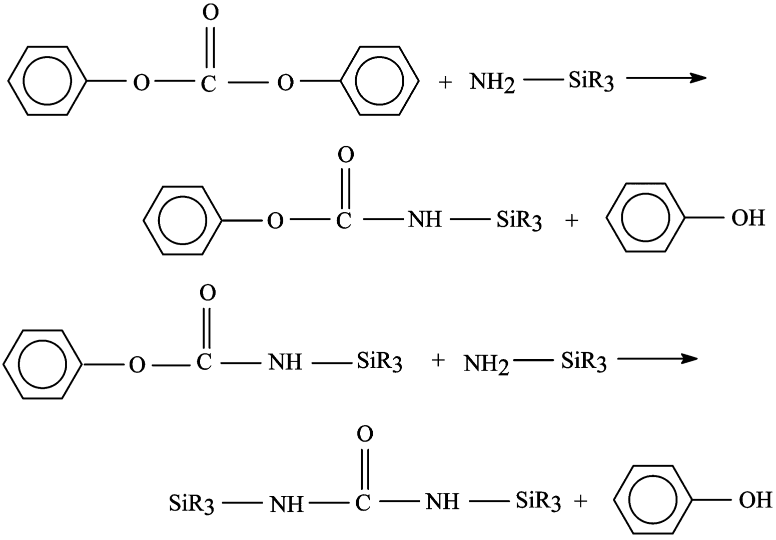


FIGURE 10 High-resolution C(1s) XPS spectra of samples prepared by adsorbing γ-APS onto ferroplate substrates from 0.2% aqueous solutions, spin-coating DPC onto the substrates, heating the substrates at 60°C for 5 min, and then rinsing the substrates with fresh chloroform several times. The C(1s) spectrum of primer films adsorbed from 0.2% aqueous solutions of γ-APS is shown for comparison. Charge correction was performed by referencing the C(1s) binding energy of saturated alkanes to a binding energy of 284.6 eV.

was consistent with those obtained by Li *et al.* who found that as carbonate/amine equivalent ratio decreased, the intensity of the peak due to urea increased, whereas the intensity of the peak due to urethane decreased [18].

Additional investigations of the reaction between DPC and γ-APS were carried out using XPS. Figure 10 shows high-resolution C(1s) XPS spectra of samples prepared by depositing γ-APS onto ferroplate from 0.2% aqueous solutions, spin-coating DPC onto the substrates, heating the substrates at 60°C for 5 min, and then rinsing the substrates with fresh chloroform several times. The C(1s) spectrum of primer films adsorbed from 0.2% aqueous solutions of γ-APS is shown for comparison. The C(1s) spectra of DPC on primed substrate consisted of four components at 284.6, 285.7, 286.3, and 288.7 eV, which were attributed to C–C/C–H, C–N, C–O [19], and N–(C=O)–O [20] bonds, respectively. The area percentage based on curve-fitting results of each component were 64, 13, 13, and 10% for C–C/C–H, C–N, C–O, and N–(C=O)–O, –O, respectively. Urea that was detected by RAIR was difficult to distinguish from urethane because the binding energies of carbon atoms in urea and urethane groups are very similar. However, based on the presence of the component at 286.3 eV, which was related to C–O bonds (found in urethane but not in urea) and the area ratio of C–N:C–O:N–(C=O)–O, which was 1:1:0.8 (compared with the theoretical value of 1:1:1), it was determined that the main reaction product between DPC and γ-APS heated at 60°C for 5 min was urethane. The chemical reaction between γ-APS and DPC based on RAIR and XPS results is presented next.



It was clearly shown by the chemical reaction between γ-APS and DPC that good adhesion would be achieved by the formation of urethane rather than urea groups because urea formation involved chain scission of the carbonate compounds. The chemical reactions of the model compound DPC also showed that there was an optimum γ-APS concentration for urethane formation, whereas urea formation steadily increased as γ-APS concentration increased.

B. Effect of Heat Treatment of 0.2% γ-APS Primer

The effect of drying time and temperature on the structure and properties of the γ-APS films was also determined. Higher drying temperatures resulted in lower scratch resistance because of delamination at the PC/γ-APS interface (as shown in Table 2). The normal load at the onset of film debonding (i.e., the critical normal load) of samples

TABLE 2 Critical Normal Loads for Delamination of PC Films from Ferroplate Substrates as a Function of the Drying Time and Temperature Applied to γ-APS Primer Films

Heat treatment of primer films adsorbed from 0.2% solutions of γ-APS and blown dry with N_2	Critical normal load for debonding (N)
None	0.31 ± 0.07
60°C for 15 min	0.20 ± 0.02
110°C for 5 min	0.12 ± 0.03
110°C for 15 min	0.05 ± 0.01

Note. Scratch tests were performed using a spherical indenter with a tip radius of 89 μm, scratching speed of 33 μm/s, and a maximum load of 0.90 N. Ferroplate substrates were immersed into aqueous solutions of 0.2% γ-APS for 15 min, withdrawn, and blown dry using a strong stream of N_2. The primer films were subsequently dried at either 60 or 110°C for 5 or 15 min. PC films were then spin-coated onto the primed substrates from chloroform solutions, and the substrates were finally heated in an oven at 60°C for 30 min.

prepared from substrates that were primed with γ-APS films that were simply blown dry with N_2 was 0.31 ± 0.07 N. However, when the γ-APS primers were dried at 60°C for 15 min, 110°C for 5 min, or 110°C for 15 min, the critical normal loads were 0.20 ± 0.02, 0.12 ± 0.03, and 0.05 ± 0.01 N, respectively.

Figure 11 and Table 3 summarize the effect that drying the γ-APS primer films at elevated temperatures had on the RAIR spectra of samples prepared by spin-coating PC films onto primed ferroplate substrates, heating the substrates at 60°C for 30 min, and then rinsing the substrates in chloroform to remove unreacted PC. As the temperature at which the γ-APS films were dried increased, the ratio of the intensities of the bands at 1780 cm^{-1} and 1128 cm^{-1} decreased. This result suggested that as the drying temperature of the γ-APS films increased, the amount of PC that interacted with γ-APS decreased. Increasing the temperature at which the γ-APS films were dried also resulted in greater cross-linking in the primer films and decreased diffusion of PC molecules into the primer films. Therefore, a lower critical normal load for debonding of PC films from the substrates was observed when γ-APS films were dried at 60°C and 110°C for 15 min.

C. Effect of Reaction Temperature Between PC and 0.2% γ-APS

The effect of reaction temperature on the structure and properties of scratch test specimens was also determined (see Table 4). It was found

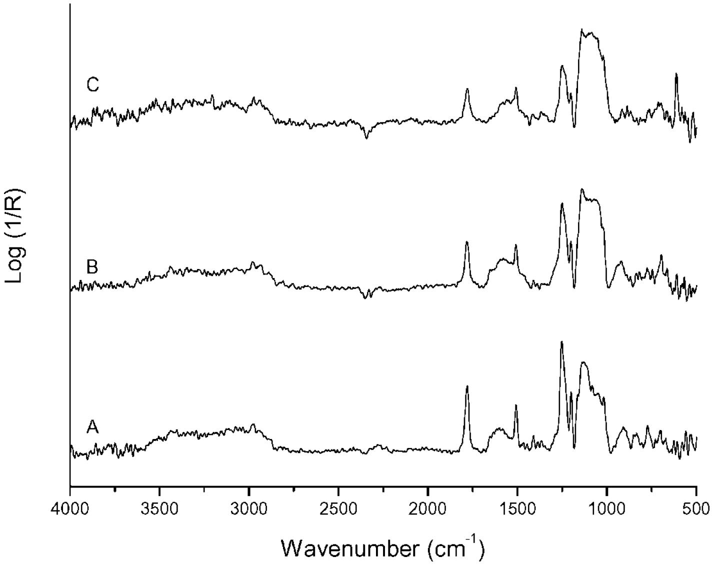


FIGURE 11 RAIR spectra obtained from substrates that were prepared by spin-coating PC films onto ferroplate substrates that were coated with γ-APS films. The γ-APS films were adsorbed onto the ferroplate substrates from 0.2% aqueous solutions and dried at (a) room temperature, (b) 60°C, and (c) 110°C for 15 min. The substrates were then spin-coated with PC films, heated at 60°C for 30 min, and rinsed in chloroform to remove unreacted PC before the RAIR spectra were obtained.

TABLE 3 Intensity Ratio of the Bands at 1780 and 1128 cm^{-1} in the RAIR Spectra of PC Films on Ferroplate Substrates as a Function of the Drying Conditions Applied to γ-APS Primers

Heat treatment of primer films adsorbed from 0.2% solutions of γ-APS and blown dry with N_2	Peak intensity ratio (I_{1780}/I_{1128})
None	0.8
60°C for 15 min.	0.5
110°C for 15 min.	0.3

Note. Ferroplate substrates were immersed into aqueous solutions of 0.2% γ-APS for 15 min, withdrawn, and blown dry using a strong stream of N_2. The primer films were subsequently dried at either 60 or 110°C for 15 min. PC films were then spin-coated onto the primed substrates from chloroform solutions, and the substrates were heated in an oven at 60°C for 30 min. Unreacted PC was then removed by washing with chloroform.

TABLE 4 Critical Normal Loads for Delamination of PC Films from Ferroplate Substrates as a Function of the Temperature at which the PC Films were Reacted with γ-APS Primers

Reaction temperature (°C)	Critical normal load for delamination (N)
60	0.31 ± 0.07
150	0.41 ± 0.06
225	0.37 ± 0.08

Note. Scratch tests were performed using a spherical indenter with a tip radius of 89 μm, scratching speed of 33 μm/s, and a maximum load of 0.90 N. Ferroplate substrates were immersed into aqueous solutions of 0.2% γ-APS for 15 min, withdrawn, and blown dry using a strong stream of N_2. PC films were then spin-coated onto the primed substrates from chloroform solutions, and the specimens were heated in an oven at 60, 150, or 225°C for 30 min.

that the scratch resistance of samples that were heated at 150 and 225°C for 30 min was greater than that of samples that were heated at 60°C. Horizontal load profiles for this set of samples showed a sudden change at the onset of film debonding.

RAIR spectra obtained from PC films on ferroplate substrates that were primed with thin films of γ-APS are shown in Figure 12. The ferroplate substrates were immersed into 0.2% aqueous solutions of γ-APS for 15 min, withdrawn, and blown dry using a strong stream of N_2. PC films were then spin-coated onto the substrates, and the substrates were heated in an oven at 60, 150, or 225°C for 30 min. As the reaction temperature increased from 60 to 150 or 225°C, the ratio of the intensities of the bands at 1780 cm^{-1} (characteristic of PC) and 1128 cm^{-1} (characteristic of γ-APS) increased, indicating that the amount of PC retained on primed ferroplate substrates also increased after the substrates were washed with chloroform (see Table 5). As the reaction temperature increased from 60 to 150°C, a band near 1580 cm^{-1} decreased in intensity, and two overlapping bands appeared near 1650 and 1665 cm^{-1}. When the reaction temperature increased to 225°C, the band at 1665 cm^{-1} shifted to higher frequencies and was centered near 1675 cm^{-1}; the band near 1650 cm^{-1} became a shoulder on this band. The band near 1650 cm^{-1} was attributed to urea formation based on the RAIR spectra of the reaction products of DPC and γ-APS. Some researchers attributed the band near 1665 cm^{-1} to imine [12]; others assigned this band to vinyl end groups [21]. However, both assignments suggested that propylamine groups in γ-APS had undergone degradation reactions.

The increase in the scratch resistance of samples that were heated at 150°C (*i.e.*, at about the T_g of PC) was due to greater mobility of

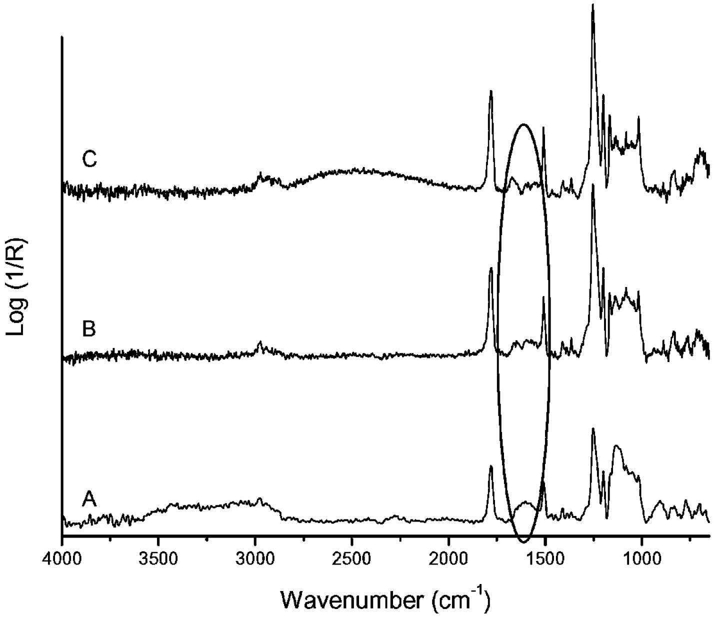


FIGURE 12 RAIR spectra obtained from PC films on ferroplate substrates that were coated with thin films of γ-APS. The ferroplate substrates were immersed into 0.2% aqueous solutions of γ-APS for 15 min, withdrawn, and blown dry using a strong stream of N_2. PC films were then spin-coated onto the substrates, and the substrates were heated in an oven at (a) 60, (b) 150, or (c) 225°C for 30 min. Unreacted PC was then removed by rinsing the substrates in chloroform before the RAIR spectra were obtained. The circle shows the spectral region of interest.

TABLE 5 Intensity Ratio of the Bands at 1780 and 1128 cm^{-1} in the RAIR Spectra of PC Films on Ferroplate Substrates as a Function of the Temperature at which the PC Films were Reacted with γ-APS Primers

Reaction temperature (°C)	Peak intensity ratio (I_{1780}/I_{1128})
60	0.8
150	1.4
225	2.0

Note. Ferroplate substrates were immersed into aqueous solutions of 0.2% γ-APS for 15 min, withdrawn, and blown dry using a strong stream of N_2. PC films were then spin-coated onto the primed substrates from chloroform solutions, and the specimens were heated in an oven at 60, 150, or 225°C for 30 min. Unreacted PC was then removed by washing the substrates with chloroform.

the PC backbone chains and the greater possibility of PC reacting with γ-APS. The degradation of amine was not so great at this condition as compared with 225°C. Increasing the reaction temperature between γ-APS and PC to 225°C resulted in competitive reactions between urethane formation and degradation of amine. However, as the reaction temperature increased from 60 to 225°C, the intensity ratio of the band at 1780 cm^{-1} to the band at 1128 cm^{-1} still increased.

IV. CONCLUSIONS

The molecular structure of γ-APS interfacial layers had a significant influence on adhesion of PC films to ferroplate substrates. The critical load for delamination/debonding of PC films increased rapidly as the concentration of the solutions used to deposit the γ-APS films increased from 0.0 to 0.2%; thereafter, the critical load increased only slightly as the concentration of the γ-APS solutions increased from 0.2 to 5%. Chemical reaction between amine groups of γ-APS and carbonate groups forming urethane and urea structures was revealed using the model compound DPC. The carbonate band of DPC shifted from 1780 cm^{-1} to 1738 cm^{-1} as urethane groups were formed. A band near 1650 cm^{-1} was due to urea formation. Results from curve fitting of C(1s) XPS spectra showed that the main reaction products between DPC and 0.2% γ-APS were urethanes, which corresponded well with the RAIR results. The amount of urethane or urea formed depended strongly on the concentration of the solutions used to deposit γ-APS films on the substrates and the reaction conditions, including temperature and time.

Drying of γ-APS films at elevated temperatures resulted in greater cross-linking and decreased the ability of PC to diffuse into the γ-APS primer films. Therefore, the adhesion between the PC films and the ferroplate substrate also decreased (*i.e.*, lower critical loads as heat-treatment temperature increased).

As the reaction temperature between γ-APS and PC increased, the critical load reached a maximum at 150°C and then decreased slightly at 225°C. Increasing the reaction temperature to 150°C (close to T_g of PC) also increased the mobility of PC chains, resulting in higher chemical reaction between amine groups and carbonate groups. As temperature increased to 225°C, RAIR spectra clearly showed degradation of propylamine groups as new bands appeared near 1665 and 1675 cm^{-1}.

Abrupt changes in the lateral load were observed when the critical normal loads were more than 0.30 N. Below a critical load of 0.30 N, significant fluctuations in the lateral loads were observed.

Horizontal load profiles could be used to access the onset of critical normal loads for delamination as well as to predict the rupture pattern of the PC films. However, the lower the critical loads, the more difficult it was to identify the onset of delamination using the horizontal load profile.

V. ACKNOWLEDGMENTS

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