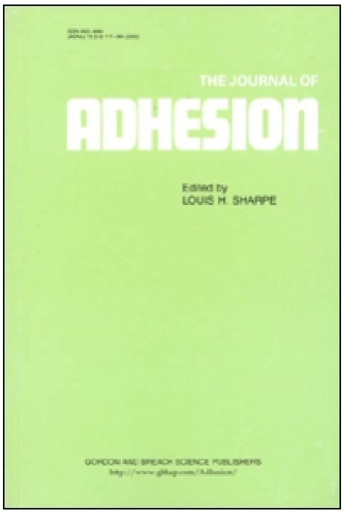
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Adhesion of Injection Molded PVC to Steel Substrates

F. J. Boerio[a]; P. Shah[a]
[a] Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, Ohio, USA

To cite this Article Boerio, F. J. and Shah, P.(2005) 'Adhesion of Injection Molded PVC to Steel Substrates', The Journal of Adhesion, 81: 6, 645 — 675

To link to this Article: DOI: 10.1080/00218460590954656

URL: http://dx.doi.org/10.1080/00218460590954656

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The Journal of Adhesion, 81:645–675, 2005
Copyright © Taylor & Francis Inc.
ISSN: 0021-8464 print/1545-5823 online
DOI: 10.1080/00218460590954656

Adhesion of Injection Molded PVC to Steel Substrates

F. J. Boerio
P. Shah
Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, Ohio, USA

Interactions occurring at the interface between injection-molded poly (vinyl chloride) (PVC) and steel substrates that were coated with thin films of aminosilanes were investigated by X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FTIR). The silane films were formed by adsorption of γ-aminopropyltriethoxysilane (γ-APS) or N-(2-aminoethyl-3-aminopropyl)trimethoxysilane (γ-AEAPS) from 2% aqueous solutions onto polished steel substrates. PVC was injection molded onto the silane-primed steel substrates and annealed at temperatures up to 170°C for times as long as 30 min. PVC was peeled off of the primed steel substrates using a 90° peel test and the substrate failure surfaces were thoroughly rinsed with tetrahydrofuran (THF) and distilled water to remove PVC and other compounds that were not strongly bonded to the substrates. The PVC failure surfaces were characterized by attenuated total reflection infrared spectroscopy (ATR) and PVC rinsed off of the substrate failure surfaces was characterized by transmission infrared spectroscopy. The resulting transmission and ATR spectra showed an absorption band near 1650 cm^{-1} that was attributed to unsaturation in PVC. The substrate failure surfaces were characterized by XPS; curve-fitting of N(1s) and Cl(2p) high-resolution spectra showed the formation of amine hydrochloride complexes by protonation of amino groups of the silanes with HCl that was liberated from PVC during the onset of thermal dehydrochlorination. Furthermore, quaternization or nucleophilic substitution of labile pendent allylic chloride groups by amino groups on the silanes took place, thus grafting PVC onto the aminosilanes. It was determined that PVC that had β-chloroallyl groupings along its chains showed better adhesion with steel primed with aminosilanes and that generation of allylic chloride groups in PVC chains was the rate-limiting step in the reaction between PVC and aminosilane. Moreover, the effect of crosslinking of silane films on adhesion between PVC and aminosilane primed steel was investigated and it was concluded that interdiffusion of the polymer phase and the silane phase was also critical in obtaining good adhesion.

Received 16 August 2004; in final form 15 March 2005.

Address correspondence to F. J. Boerio, Department of Chemical and Materials Engineering, University of Cincinnati, Cincinnati, OH 45221-0012, USA. E-mail: f.james.boerio@uc.edu

Keywords: Polyvinylchloride; Silanes; γ-Aminopropyltriethoxysilane; N-(2-aminoethyl-3-aminopropyl)trimethoxysilane; X-ray photoelectron spectroscopy; Fourier-transform infrared spectroscopy; Peel tests; Dehydrochlorination

INTRODUCTION

Organosilanes are widely used in industrial applications [1]. Most of these applications involve the use of organosilanes as coupling agents to promote adhesion between polymers and inorganic materials. Silane primers used as coupling agents have the general structure

$$R-Si-R'_3$$

In this expression, R is an organofunctional group that is compatible with a particular polymer and R′ is a functional group that can be hydrolyzed. Several models have been proposed to explain the mechanisms by which silanes function as coupling agents [2]. According to one of the most widely discussed models, silanes bind an adhesive or matrix resin to a substrate by forming covalent bonds across the interface [2].

Aminosilane coupling agents have been used to bind poly(vinyl chloride) matrix materials to mineral surfaces [3–6]. Rahrig [3] demonstrated the use of aminosilanes as sizing agents in glass fiber–reinforced vinyl chloride polymer products to improve bonding between glass fibers and the vinyl chloride resin. They found that vinyl chloride resins, particularly poly(vinyl chloride) and chlorinated poly(vinyl chloride) reinforced with glass fibers sized with a particular aminosilane coupling agent and an alkylene oxide containing film former, failed only cohesively in the vinyl chloride resin [3]. Matuana et al. [4] used aminosilane coupling agents to improve interfacial interactions between cellulosic fibers and plasticized PVC in PVC/cellulose fiber composites. Aminosilanes have also been used as crosslinking agents for plasticized PVC. Gilbert and Rodriguez-Fernandez [5, 6] demonstrated reaction of plasticized PVC with aminosilanes during processing on a two-roll mill, yielding silane-grafted PVC that was cross-linked by a hydrolytic mechanism.

The molecular structure of thin films formed by aminosilanes deposited onto inorganic substrates from aqueous solutions has been extensively studied [7–13]. Ondrus and Boerio [7, 9] suggested that films formed by γ-aminopropyltriethoxysilane (γ-APS) adsorbed onto iron, 1100 aluminum, 2024 aluminum, and copper substrates from aqueous solutions at the natural pH of 10.4 absorbed carbon dioxide and water vapor to form amine bicarbonate salts. These bicarbonates dissociated when γ-APS films were heated at temperatures above 90°C. Horner, Boerio and Clearfield [11] used X-ray photoelectron spectroscopy (XPS) to investigate the adsorption of aminosilanes onto different metal substrates. They found that γ-APS was partially adsorbed onto the oxidized surfaces of certain metals through the amino group. Fowkes *et al.* [12] also obtained spectroscopic evidence showing that γ-APS could also adsorb onto acidic glass surfaces through the amino groups.

Although the molecular structure at the interface between aminosilanes and mineral surfaces is reasonably well established, the exact nature of interactions taking place at the interface between aminosilanes and PVC has not been extensively discussed. The purpose of this paper is to report results that we have obtained using XPS and Fourier-transform infrared spectroscopy (FTIR) to determine the chemical interactions that take place at the interface between aminosilane films and PVC.

EXPERIMENTAL

γ-Aminopropyltriethoxysilane (γ-APS) and N-(2-aminoethyl-3-aminopropyl) trimethoxy-silane (γ-AEAPS) were obtained from Aldrich Chemical Co., Milwaukee, WI, USA. 1018 cold-rolled steel was obtained from Central Steel and Wire Company (Cincinnati, OH, USA). PVC (VNC-80) was obtained from Vichem Corporation (Grand Rapids, MI, USA).

1018 cold-rolled steel was obtained from Central Steel and Wire Company. Steel substrates (60 mm × 25 mm) were ground successively using silicon carbide papers (Pace Technologies, Tucson, AZ, USA) of grit 60, 180, 400, 600, 800, and 1200. Between grinding steps, the substrates were rinsed with distilled water and blown dry in a stream of nitrogen gas. The substrates were then polished using 1-μm aluminum oxide powder on nylon cloth (Buehler, Lake Bluff, IL, USA).

2% (v/v) aqueous solutions of γ-APS and γ-AEAPS in distilled water were prepared. The silanes were hydrolyzed for 1 h before the ground steel substrates were immersed into the solutions. After 2 min, the substrates were removed from the solutions and excess solution was gently blown off the surface using a stream of nitrogen gas. The primed substrates were then dried in air at a temperature of 60°C, 79°C, 93°C, or 107°C for 1 h. To determine the effect of bicarbonate formation on adhesion of PVC to primed steel substrates, some steel substrates were primed with γ-AEAPS in a nitrogen environment in a glove box. The aqueous γ-AEAPS solutions were also purged by

TABLE 1 Basic Parameters Used on a Battenfeld BSK 22-M Injection Molding Machine to Injection Mold PVC (VNC 80) onto Steel Substrates that were Primed with an Aminosilane

Parameter	Value
Barrel zone 1	176°C
Barrel zone 2	176°C
Nozzle	171°C
Screw speed	80 rpm
Mold temperature	Room temperature
Injection pressure, time	1034 kPa–1724 kPa; 6 s
Holding pressure, time	<345 kPa; 40 s

Note: The steel substrates were placed in the cavity half of the mold.

bubbling nitrogen through the solution by means of a glass tube inserted into the solution. The silane films were dried at room temperature or at 90°C under nitrogen in the glove box.

Peel-test specimens were prepared by injection molding PVC onto primed steel substrates using a Battenfeld BSK 22-M injection-molding machine (Gloucester Engg. Co., Gloucester, MA, USA) and a specially constructed mold. The relevant parameters used during injection molding are shown in Table 1. After injection molding, the peel-test specimens were annealed in an oven at 170°C for 10 min, 20 min, or 30 min. The specimens were then cooled to room temperature and the PVC was peeled off of the steel substrates in a 90° peel test (ASTM D429-99, method B) using a Instron (Model 4465), Canton, MA, USA, and a crosshead speed of 2.54 mm/min. The substrate failure surface was thoroughly rinsed with THF (Fisher Scientific, Pittsburgh, PA, USA, 99.0%) and distilled water to remove any unreacted PVC and other compounds.

X-ray photoelectron spectroscopy (XPS) was used to characterize as-molded PVC and the substrate failure surfaces of peel-test specimens. As-molded PVC was examined without any additional sample preparation. The substrate failure surfaces were thoroughly rinsed with tetrahydrofuran (THF) (Fisher Sci., 99.0%) and distilled water prior to XPS analysis to remove unreacted PVC and other compounds. All XPS investigations were carried out using a Perkin-Elmer model 5300 spectrometer (Physical Electronics Corp., Eden Prairie, MN, USA) that was equipped with a nonmonochromatic, dual-anode (Mg/Al) X-ray source operated at 300 W and 15 kV DC. Mg Kα X-rays having energy of 1253.6 eV were used to excite the spectra. High-resolution scans were obtained at a pass energy of 35.75 eV and were corrected for charging by assigning a value of 284.6 eV to the C(1*s*) peak for saturated hydrocarbons. Because nonmonochromatic X-rays were used, this method for charge compensation was sufficient and other methods, such as the use of an electron flood gun, were not required [14]. Curve fitting of the high-resolution spectra was accomplished using 90% Gaussian peaks. Atomic concentrations were obtained from the high-resolution spectra using the sensitivity factors provided with the software (RBD Enterprises, Bend, OR, USA). All spectra were collected using a take-off angle of 45°.

As indicated, the substrate failure surfaces of some peel-test specimens were rinsed with tetrahydrofuran (THF) to remove PVC that was not strongly adhered to the substrate. A few drops of these solutions were placed onto KBr discs and the solvent was allowed to evaporate; transmission infrared spectroscopy was used to characterize the PVC extracted from the substrate failure surfaces. Reflection–absorption infrared spectroscopy (RAIR) was used to characterize silane films that were deposited onto polished steel substrates from aqueous solutions. Attenuated total reflection infrared spectroscopy (ATR) was used to characterize as-molded PVC and the PVC failure surfaces of peel-test specimens. All infrared spectra were obtained using a Nicolet Magna 760 FTIR spectrometer (Thermo Electron Corp., Madison, WI, USA). ATR spectra were acquired using a Spectra-Tech HATR accessory equipped with a Ge crystal and RAIR spectra were acquired using a Spectra-Tech FTS-85 external reflection (Thermo Electron Corp., Madison, WI, USA) accessory that provided one reflection at an angle of 85°. Most FTIR spectra were obtained by averaging 512 scans at a resolution of 4 cm^{-1}.

Several experiments were carried out to determine the effect that dehydrochlorination of PVC had on adhesion of PVC to primed steel substrates. Dehydrochlorination of PVC (referred to as DHPVC) was carried out in pyridine solution at a concentration of 41.7 g/L for 30 h at room temperature and at times between 20 and 30 h at 65°C. Steel coupons were primed with γ-AEAPS and the films were dried in air at 90°C for 1 h. PVC was cast from solution in pyridine onto steel substrates that were primed with silane and the solvent was allowed to evaporate overnight. In some cases, these substrates were then heated at 100°C under a nitrogen environment for 20 min, rinsed thoroughly with THF and HPLC grade water to remove any unreacted PVC or other compounds, and then characterized by XPS. In other cases, injection-molded PVC was clamped against the substrates and annealed at 170°C for 15 min. The samples were cooled down to room temperature and PVC was peeled off of the substrates using the Instron. Similar experiments were carried out using THF as the solvent. In those cases, PVC was dissolved in THF at a concentration of 41.7 g/L and the solution was held at a temperature of 65°C for 30 h. Steel coupons were primed with γ-AEAPS and the films were dried at 90°C for 1 h. PVC was cast from the solution in THF onto the primed steel and the solvent was allowed to evaporate overnight. Injection-molded PVC was clamped against these samples and annealed at 170°C for 15 min. These samples were also cooled to room temperature and peel tests were conducted using the Instron.

RESULTS AND DISCUSSION

XPS of Injection-Molded PVC

The XPS survey spectrum of injection-molded PVC is shown in Figure 1. Peaks resulting from barium, oxygen, calcium, carbon, chlorine, and silicon were observed. High-resolution spectra and atomic concentrations were obtained for all elements that were detected in

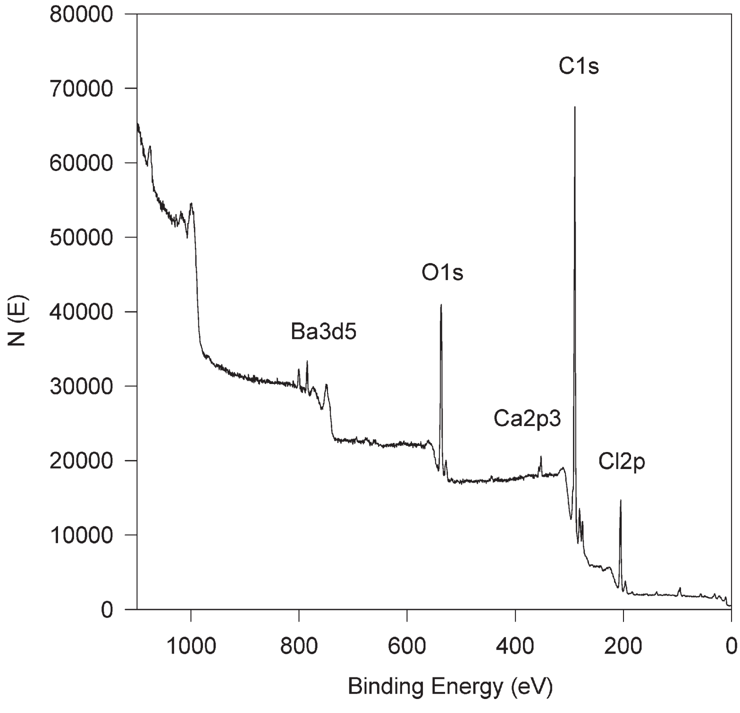


FIGURE 1 XPS survey spectrum obtained from injection-molded PVC. The parameters shown in Table 1 were used during injection molding of the PVC.

TABLE 2 Atomic Concentration of Elements Detected in Injection Molded PVC Specimens that were Prepared Using the Injection Molding Parameters Indicated in Table 1

Element	C	O	Cl	Ca	Ba
Atomic concentration	76.2	15.2	7.7	0.7	0.2

Note: The XPS take-off angle was 45°.

the survey spectrum (see Table 2). Curve-fitting showed that the high-resolution C(1s) spectrum (see Figure 2 and Table 3) consisted of three components at 284.6, 286.1, and 288.7 eV. The component at 284.6 eV was attributed to C–C and C–H bonds whereas the component at 286.1 eV was related to overlapping peaks resulting from C–Cl bonds in PVC and C–O bonds in a phthalate ester plasticizer. The

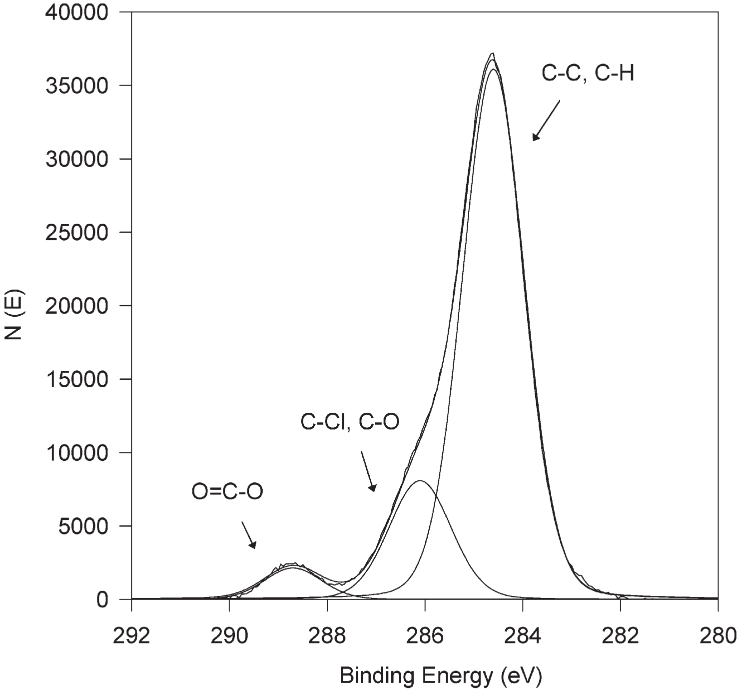


FIGURE 2 C(1s) high-resolution XPS spectrum obtained from injection-molded PVC. The parameters shown in Table 1 were used during injection molding of the PVC.

TABLE 3 Binding Energies and Assignments of the Peaks that were Used to Curve-Fit the C(1s) and Cl(2p) High-Resolution XPS Spectra Obtained for PVC that was Injection Molded Using the Parameters Indicated in Table 1

Binding energy (±0.1 eV)	Bond assignment(s)	Bond percentage
C(1 s)		
284.6	C−C, C−H	77.9
286.1	C−Cl, C−O	17.4
288.7	O=C−O	4.6
Cl(2p)		
199.8	$2p_{3/2}$ electron C−Cl	66.3
201.4	$2p_{1/2}$ electron C−Cl	33.7

Note: The take-off angle used to obtain the XPS spectra was 45°.

component at 288.7 eV was attributed to the O−C=O bonds associated with the plasticizer. Curve fitting also showed that the Cl(2p) high-resolution spectrum consisted of a doublet at 199.8 eV [Cl($2p_{3/2}$)] and at 201.4 eV [Cl($2p_{1/2}$)] (see Figure 3). These binding energies were consistent with covalent C−Cl bonds in PVC. Barium and calcium were attributed to stabilizers in the PVC, which has a strong tendency toward dehydrochlorination. Weak peaks were observed near 100 and 150 eV and attributed to silicon in silica, which was a component of the highly formulated PVC.

XPS of the Substrate Failure Surfaces of Peel-Test Specimens

PVC was injection molded onto steel substrates primed with aminosilane films, annealed at 170°C for various times, and then peeled off of the steel substrates using the Instron. The failure surfaces of the steel substrates were rinsed thoroughly with THF and distilled water to remove soluble compounds and then characterized by XPS. Although high-resolution spectra were obtained for all elements detected, this discussion will mostly concern the Cl(2p) and N(1s) spectra, because they are most important in understanding the chemical interactions across the interface between PVC and aminosilanes.

The atomic concentrations of all elements detected on the substrate failure surfaces of the peel-test specimens are summarized in Table 4. It is interesting to note that the atomic concentration of Cl on the failure surfaces of substrates primed with γ-APS increased from 0.5% to 2.5% to 3.8% as the annealing time increased from 10 to 20 to 30 min. This indicated that the amount of PVC that was bound to the

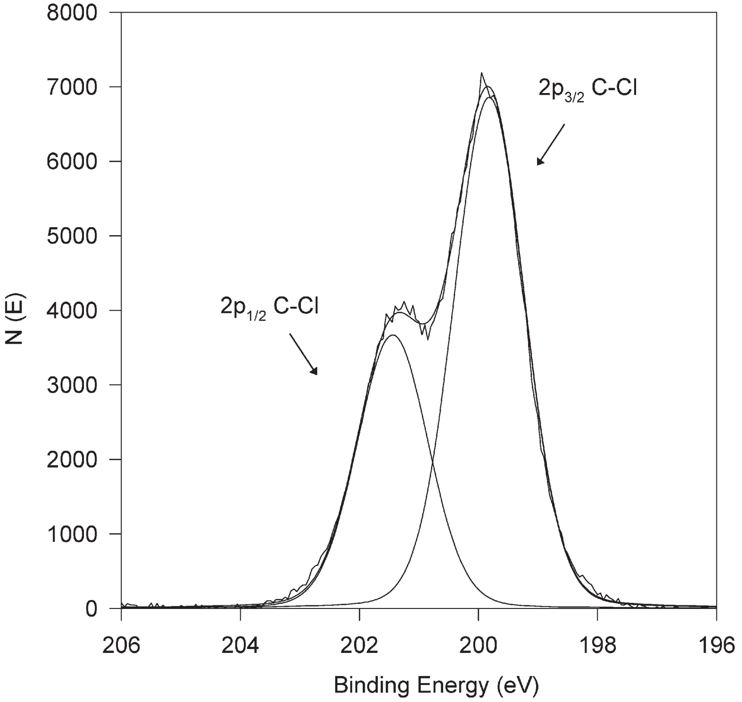


FIGURE 3 Cl(2p) high-resolution XPS spectrum obtained from injection-molded PVC. The parameters shown in Table 1 were used during injection molding of the PVC.

TABLE 4 XPS Atomic Concentration at Take-Off Angle 45° of Elements on Failure Surface of Steel Substrates Primed with γ-APS and AEAPS Films onto which PVC was Injection Molded and Annealed

	C (%)	O (%)	N (%)	Si (%)	Cl (%)
γ-APS primed substrate					
170°C for 10 min	62.9	31.6	1.3	3.7	0.5
170°C for 20 min	67	26.1	1.5	2.9	2.5
170°C for 30 min	64	27.1	2.0	3.1	3.8
γ-AEAPS primed substrate					
170°C for 10 min	72.9	19.8	4.5	3.0	0.8
170°C for 20 min	75.7	14.7	3.8	2.3	3.5
170°C for 30 min	78.8	12.0	2.2	1.4	5.7

Note: Annealed at 170°C for 10 min, 20 min, and 30 min; PVC was peeled off the steel substrate. The failure surface of steel substrate was thoroughly rinsed with THF and distilled water.

substrate, and was thus insoluble, increased with annealing time. The atomic concentration of chlorine was greater on the failure surfaces of substrates primed with γ-AEAPS than on those primed with γ-APS and increased from 0.8% to 3.5% to 5.7% as the annealing time increased from 10 to 20 to 30 min. More PVC was bound to the substrate surface after annealing when the substrates were primed with γ-AEAPS than when the substrates were primed with γ-APS.

N(1s) high-resolution spectra obtained from the substrate failure surfaces of peel-test specimens that were prepared from substrates primed with γ-APS and annealed at 170°C for 10, 20, or 30 min are shown in Figure 4. The N(1s) spectra clearly consisted of two components near 399.3 and 401.2 eV that were attributed to free and protonated amino groups, respectively. The protonated amino groups were

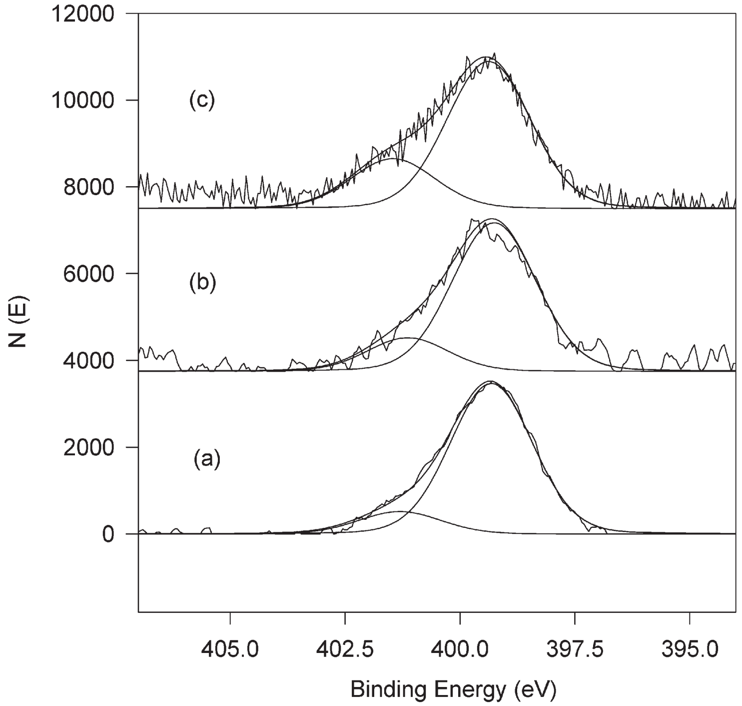


FIGURE 4 N(1s) high-resolution XPS spectra obtained from the substrate failure surfaces of peel-test specimens prepared from substrates that were primed with γ-APS and annealed for (a) 10 min, (b) 20 min, and (c) 30 min. The substrate failure surfaces were thoroughly rinsed with THF and water before XPS analysis.

TABLE 5 Peak Assignments and Percentage Obtained from N(1s) High-Resolution Spectra at Take-Off Angle 45°

Binding energy (±0.1 eV)	Peak assignment(s)	γ-APS primed substrate % 170°C 10 min	γ-APS primed substrate % 170°C 20 min	γ-APS primed substrate % 170°C 30 min	γ-AEAPS primed substrate % 170°C 10 min	γ-AEAPS primed substrate % 170°C 20 min	γ-AEAPS primed substrate % 170°C 30 min
399.3	Free amino groups	87.0	82.3	74.7	84.6	80.5	77.4
401.2	Protonated amino groups	13.0	17.7	25.3	15.4	19.5	22.6

Note: For failure surface of steel substrates primed with γ-APS and AEAPS films onto which PVC was injection molded and annealed at 170°C for 10 min, 20 min, and 30 min; PVC was peeled off the steel substrate. The failure surface of steel substrate was thoroughly rinsed with THF and distilled water.

in the form R-NH_3^+. Based on the relative intensities of the two components in the N(1s) high-resolution spectra of the substrate failure surfaces of peel test specimens, it was determined that the percentage of amino groups that were protonated increased as the annealing time increased. Thus, the extent of protonation increased from 13% to 17% to 25% as the annealing time increased from 10 to 20 to 30 min. A summary of the N(1s) curve fits for these specimens is presented in Table 5.

Cl(2p) high-resolution spectra obtained from the substrate failure surfaces of peel-test specimens prepared from substrates that were primed with γ-APS and annealed for 10, 20, or 30 min are shown in Figure 5. Curve-fitting indicated that when the annealing time was 10 min, the Cl(2p) spectra consisted of a spin-orbit-split doublet with the binding energy for the Cl($2p_{3/2}$) peak at ~197.9 eV and that of the Cl($2p_{1/2}$) peak at ~199.5 eV. This doublet was at a lower binding energy than the doublet observed for injection-molded PVC (see Figure 3) and was attributed to anionic chlorine species associated with protonated amino groups and with metal chlorides formed by metal ions from the stabilizers and chlorine released from PVC. These results suggested that when injection-molded PVC was annealed against primed steel substrates at 170°C, a loss of HCl took place in a single step *via* a four-center transition state with a large amount of charge separation in breaking the C−Cl bond. This generated sites of unsaturation and β-chloroallyl groupings in the PVC chains. The β-chloroallyl groupings had a destabilizing influence on the C−Cl bonds and made them thermally unstable [15]. Amino groups of the aminosilane were protonated by HCl that was liberated, forming amine

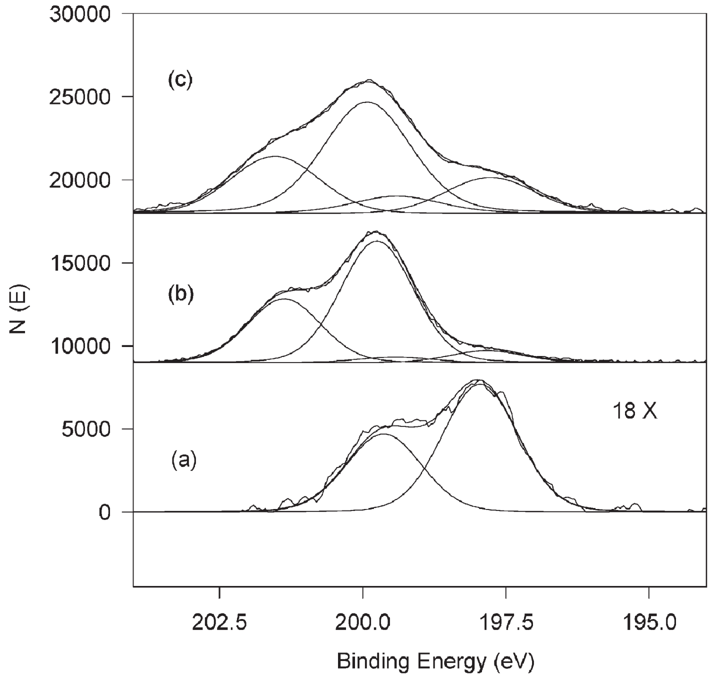


FIGURE 5 Cl(2p) high-resolution XPS spectra obtained from the substrate failure surfaces of peel-test specimens prepared from substrates that were primed with γ-APS and annealed for (a) 10 min, (b) 20 min, and (c) 30 min. The substrate failure surfaces were thoroughly rinsed with THF and water before XPS analysis.

hydrochlorides. Some metal chlorides may also have formed by reaction of chlorine with metal ions from stabilizers.

When the annealing time was increased to 20 or 30 min, curve-fitting indicated the presence of two spin-orbit-split doublets in the Cl(2p) spectra (see Figure 5). One doublet was located at 197.9 and 199.5 eV and the second was at 199.8 and 201.4 eV. These two doublets were attributed to anionic and covalent chlorine species, respectively. Covalent chlorine species were clearly related to C–Cl bonds in PVC and anionic chlorine species were attributed to formation of amine hydrochlorides and of metal chlorides as described. A summary of the Cl(2p) curve fits for these specimens is presented in Table 6.

Very similar results were obtained when injection-molded PVC was annealed against steel substrates primed with thin films of γ-AEAPS. High-resolution N(1s) spectra of the substrate failure surfaces of peel-test specimens prepared from substrates primed with γ-AEAPS

TABLE 6 Peak Assignment and Percentage Obtained from Cl(2p) High-Resolution Spectra at Take-Off Angle 45°

Binding energy (±0.1 eV)	Peak assignment(s)	γ-APS primed substrate % 170°C 10 min	γ-APS primed substrate % 170°C 20 min	γ-APS primed substrate % 170°C 30 min	γ-AEAPS primed substrate % 170°C 10 min	γ-AEAPS primed substrate % 170°C 20 min	γ-AEAPS primed substrate % 170°C 30 min
197.9	$2p_{3/2}$ electron of anionic Cl	62.1	5.9	15.0	65.6	9.8	22.8
199.5	$2p_{1/2}$ electron of anionic Cl	37.9	2.9	7.6	34.4	4.9	11.5
199.8	$2p_{3/2}$ electron of covalent Cl	—	60.9	51.4	—	55.8	43.3
201.4	$2p_{1/2}$ electron of covalent Cl	—	31.3	25	—	29.6	22.4

Note: For failure surface of steel substrates primed with γ-APS and AEAPS films onto which PVC was injection molded and annealed at 170°C for 10 min, 20 min, and 30 min; PVC was peeled off of the steel substrate. The failure surface of steel substrate was thoroughly rinsed with THF and distilled water.

consisted of two components near 399.3 and 401.2 eV that were attributed to free and protonated amino groups, respectively (see Figure 6). Protonated amino groups were in the form of $R{-}NH_3^+$ and $R{-}NH_2^+$ in the case of γ-AEAPS films. The fraction of protonated amino groups increased from 15.4% to 19% to 23% on the substrate failure surfaces of peel specimens prepared from substrates primed with γ-AEAPS as the annealing time increased from 10 to 20 to 30 min. A summary of the N(1s) curve fits for these specimens is also presented in Table 5.

Cl(2p) high-resolution spectra obtained from the substrate failure surfaces of peel-test specimens that were prepared from substrates primed with γ-AEAPS and annealed at 170°C for 10, 20, or 30 min are shown in Figure 7. Curve-fitting again indicated the presence of two spin-orbit-split doublets in the Cl(2p) spectra, one located at 197.9 and 199.5 eV and another at 199.8 and 201.4 eV. The two doublets were again attributed to anionic and covalent chlorine species, respectively. Covalent chlorine species were clearly related to C−Cl bonds in PVC and anionic chlorine species were attributed to amine hydrochloride complexes and to formation of metal chlorides. It was observed that the atomic concentration of chlorine on the substrate failure surfaces of peel specimens prepared from substrates that were primed with γ-AEAPS was greater than for peel specimens prepared from substrates primed with γ-APS. This indicated that the interaction between PVC and γ-AEAPS films was greater than that between PVC and γ-APS films. A summary of the Cl(2p) curve fits for these specimens is also presented in Table 6.

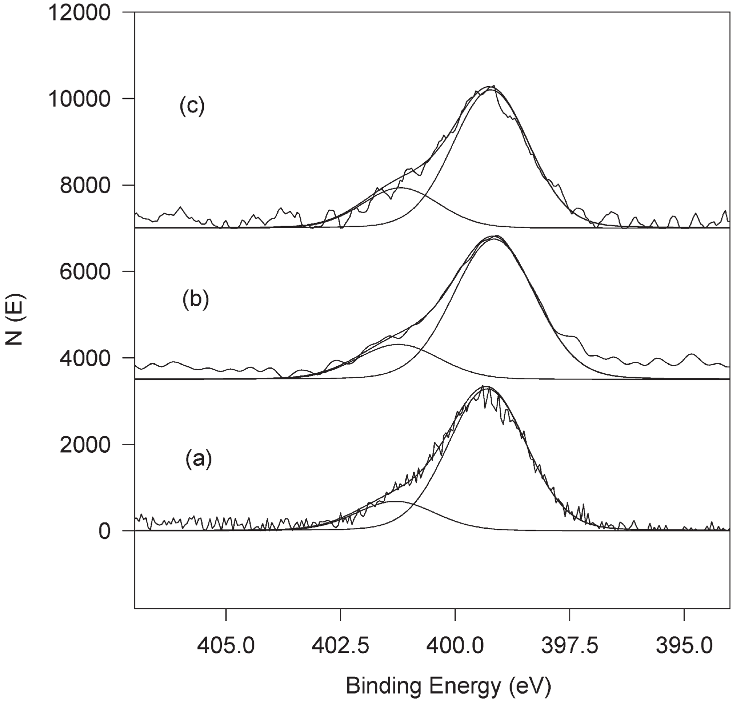


FIGURE 6 N(1s) high-resolution XPS spectra obtained from the substrate failure surfaces of peel-test specimens prepared from substrates that were primed with γ-AEAPS and annealed for (a) 10 min, (b) 20 min, and (c) 30 min. The substrate failure surfaces were thoroughly rinsed with THF and water before XPS analysis.

The PVC used in this investigation (VNC 80) contained mainly mixed metal stabilizers that react with allylic chlorides, the intermediates in the degradation reaction [16–18]. This process should be faster than the chain propagation itself and, thus, requires a very active nucleophile. However, the reactivity of the nucleophile should not be so great that it reacts with the secondary chlorine of the PVC chain, because this process would rapidly exhaust the stabilizer. To be effective, the stabilizer should form complexes with polymer chlorine atoms, which means the stabilizer should have a Lewis acid character. Stabilizers also act by scavenging hydrogen chloride generated by dehydrochlorination to stop the degradation process because HCl is a catalyst for the chain-propagation reaction and the initiation step [16–18]. Ba stearates with little or no Lewis acidity are mostly HCl scavengers. Zn stearates, which are stronger Lewis acids and which form covalent carboxylates, not only

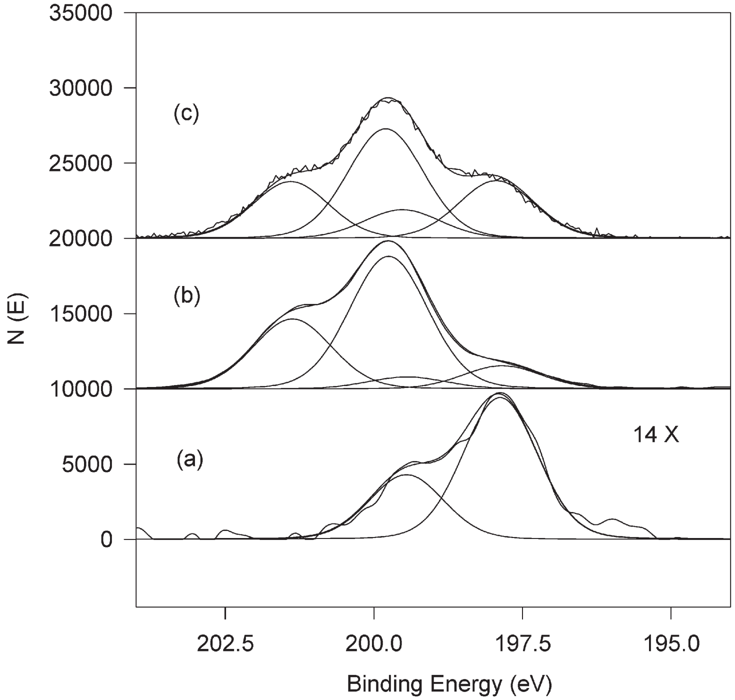


FIGURE 7 Cl(2p) high-resolution spectra obtained from the substrate failure surfaces of peel-test specimens prepared from substrates that were primed with γ-AEAPS and annealed for (a) 10 min, (b) 20 min, and (c) 30 min. The substrate failure surfaces were thoroughly rinsed with THF and water before XPS analysis.

scavenge HCl but also substitute carboxylate for the allylic chlorine atoms. Costabilizers react with active Lewis acids formed (*i.e.*, Zn chlorides) and form metal complexes with them. This explains the increase in the relative intensity of peaks corresponding to anionic chlorine in Cl(2p) high-resolution spectra with increasing annealing time. Furthermore, the primary amino and secondary amino groups of aminosilanes are strong nucleophiles. This means that HCl liberated may have been scavenged not only by secondary stabilizers but also primary and secondary amino groups of aminosilane. This explains the increase in the relative intensity of peaks corresponding to protonated amino groups in N(1s) high-resolution spectra with increase in annealing time. Also, amino groups, being strong nucleophiles, react with allylic chloride groups generated during dehydrochlorination either through quaternization or nucleophilic substitution reaction.

These results suggested that adhesion between PVC and aminosilane films took place through quaternizing or nucleophilic substitution reactions between pendant allylic chloride groups of PVC and amino groups of aminosilanes.

Infrared Spectroscopy of Injection-Molded PVC

The ATR infrared spectrum obtained from injection-molded PVC is shown in Figure 8. Most of the bands observed in this spectrum were attributed to vibrations of PVC molecules. However, a few bands were assigned to vibrational modes of the plasticizer. The peaks at 2956, 2925, and 2873 cm^{-1} were attributed to symmetric and asymmetric stretching vibrations of CH_2 and the peak at 1726 cm^{-1} was due to the ester groups of phthalate plasticizers in PVC. The spectrum also showed a typical doublet between 1575 and 1600 cm^{-1} resulting from phthalates [19, 20]. The bands corresponding to carbonyl and ester groups as well those corresponding to aromatic and aliphatic C–H bonds were observed. The peaks at 1427 and 1435 cm^{-1} were due to

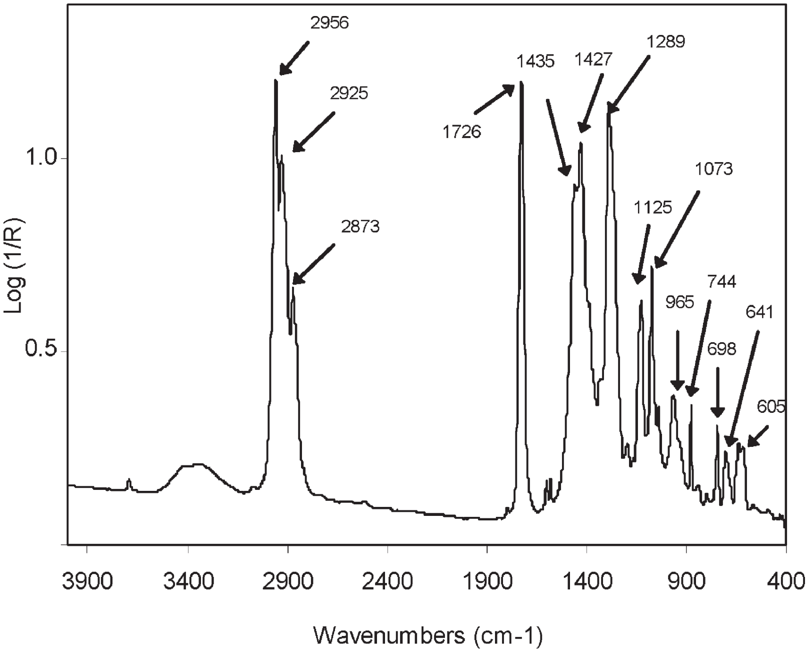


FIGURE 8 ATR infrared spectrum of injection-molded PVC.

TABLE 7 Band Assignments for Different Absorbance Bands Observed in the ATR Spectrum of as Molded PVC

Band frequency (cm^{-1})	Band assignment
2956, 2925, 2873	Symmetric and asymmetric stretching vibration of $C-H_2$
1726	ν (C=O) from DOP[a] plasticizers
1598, 1572	Doublet due to in-plane ring from DOP plasticizer
1435	Methylene groups associated with syndiotactic sequences in PVC
1427	Methylene groups associated with isotactic sequences in PVC
1289	γ (C−O) from DOP plasticizer
1125, 1073, 1037	ν (C−O) from DOP plasticizer
965	ν (CH_2) from PVC
744	CH out of plane ring
605 and 641	C−Cl bond in a syndiotactic configuration and ttt conformation in PVC
698	C−Cl bond in a isotactic configuration in PVC

[a] DOP (di-2-ethylhexylphtalate).

methylene groups. The methylene groups with an absorbance band at $1427\,cm^{-1}$ were associated with isotactic sequences in the polymer, thus contributing to the crystalline nature of the polymer. However, the methylene groups with an absorbance band at $1435\,cm^{-1}$ were associated with syndiotactic sequences in the polymer, thus contributing to the amorphous nature of PVC. Different vibrational modes of C−Cl bond were observed in the region of $600–700\,cm^{-1}$. The bands at 605 and $641\,cm^{-1}$ were associated with C−Cl bond in a syndiotactic configuration and ttt conformation. Isotactic configurations were associated with absorption at $698\,cm^{-1}$ [19, 20]. A summary of the band assignments for some of the most prominent bands in the infrared spectrum of PVC is presented in Table 7.

Infrared spectroscopy was also used to probe the failure surfaces of peel-test specimens. In these experiments, peel-test specimens were prepared by injection molding PVC onto steel substrates that were primed with γ-AEAPS and then annealing the specimens at 170°C for 30 min. After annealing, PVC was peeled off of the steel substrates using the Instron. Visually, it was observed that failure occurred cohesively in the bulk of the PVC. The PVC failure surfaces were characterized by attenuated total reflection infrared spectroscopy (ATR). The ATR spectrum obtained from one such specimen is shown in Figure 9. When the ATR spectrum of the PVC failure surface was compared with that of neat injection molded PVC (see Figure 8), it was observed that the spectra were very similar. However, a new,

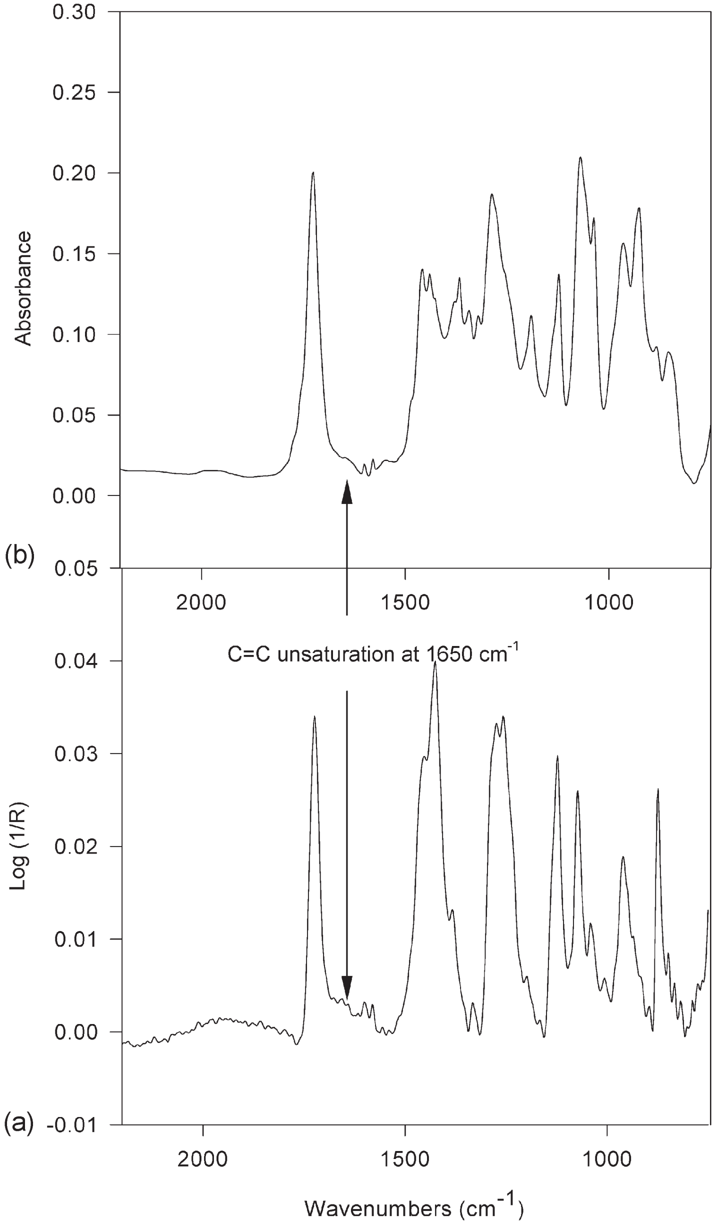


FIGURE 9 (a) Transmission infrared spectrum of the solute that was rinsed off of the substrate failure surface of a peel-test specimen prepared by injection molding PVC onto a steel substrate that was primed with γ-AEAPS from a 2% aqueous solution and then annealing the specimen at 170°C for 30 min; (b) ATR infrared spectrum of the PVC failure surface of the same peel-test specimen.

weak peak was observed at about 1650 cm^{-1} in the spectrum of the PVC failure surface. This new peak was attributed to >C=C< bonds that were generated in PVC resulting from a dehydrochlorination process.

The substrate failure surface of the same specimen was rinsed with THF. A few drops of the resulting solution were placed onto a KBr pellet and the solvent was allowed to evaporate. The residue on the KBr pellet was then characterized by transmission infrared spectroscopy; the spectrum obtained was similar to the ATR spectrum of the PVC failure surface and also showed a peak at 1650 cm^{-1} [see Figure 9]. These results confirmed that failure of peel-test specimens took place cohesively in the bulk of the PVC and supported the suggestion that unsaturation occurred in the PVC during annealing and was related to the adhesion mechanism.

Effect of Drying Temperature on Structure of γ-AEAPS Primer Films

To further explore the adhesion mechanism, we investigated the effect of drying time and temperature on the structure of the silane films and on their properties as primers for adhering PVC to steel. Thin films of γ-AEAPS were adsorbed onto steel substrates from 2% aqueous solutions and then dried at different temperatures. The films were then examined by RAIR to determine the effect of drying temperature on the structure of the silane. RAIR spectra that were obtained from the γ-AEAPS films are shown in Figure 10. Generally speaking, the extent of condensation was inversely proportional to the intensity of the band at 940 cm^{-1} because the silanol groups condensed to form siloxane networks. Thus, the RAIR spectrum of a γ-AEAPS film that was adsorbed onto a steel substrate from a 2% aqueous solution and dried in air at room temperature showed a broad peak at 3285 cm^{-1} resulting from the hydroxyl groups (see Figure 10a). Bands resulting from stretching vibrations of the amino groups were not visible because they overlapped with the band resulting from hydroxyl groups. The intensity of the band resulting form Si–OH at 940 cm^{-1} was relatively large, indicating a high percentage of silanol groups in the structure and, hence, a relatively low extent of condensation. When the drying temperature increased, several changes were observed in the spectra. Thus, when the drying temperature was increased to 60°C, the RAIR spectrum showed that the relative intensity of the Si–OH band dropped significantly, indicating conversion of silanol groups to Si–O–Si groups resulting from condensation reactions (see Figure 10b). A sharp new peak appeared at 1037 cm^{-1}

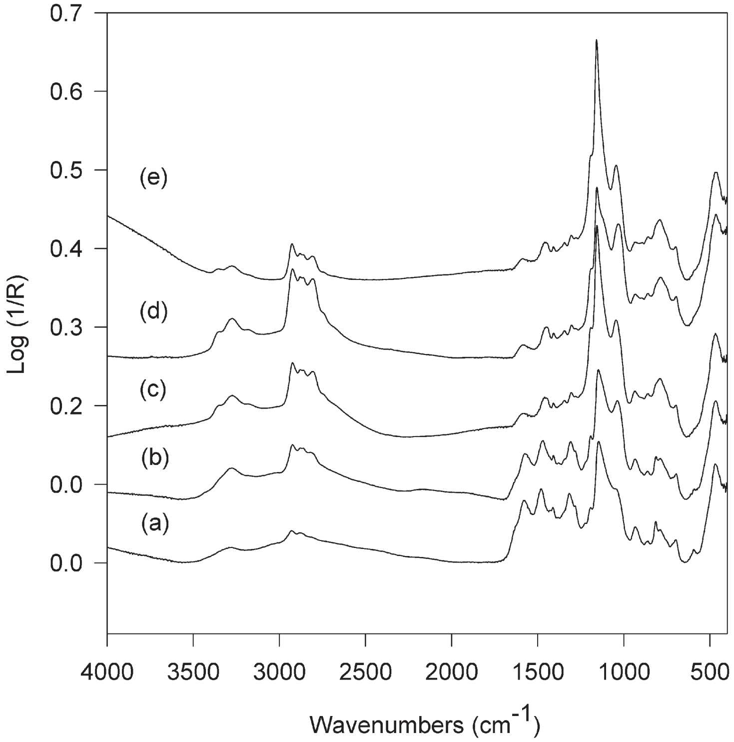


FIGURE 10 RAIR spectra of γ-AEAPS films deposited onto steel substrates from 2% aqueous solutions and dried in air for 1 h at (a) 23, (b) 60, (c) 79, (d) 93, and (e) 107°C.

resulting from the siloxane network. When the drying temperature was increased to 79°C, further decreases in the intensity of the Si–OH band near 940 cm^{-1} were seen, indicating that additional condensation reactions had taken place (see Figure 10c). In addition, the peaks from asymmetric and symmetric stretching vibrations of N–H groups of primary and secondary amine groups in the silane were visible at 3346, 3274, and 3172 cm^{-1}. Moreover, drying the films at a temperature of 79°C resulted in a significant loss of intensity for bands near 1330, 1470, and 1570 cm^{-1} that were related to amine bicarbonates. The RAIR spectra obtained from films that were dried at temperatures of 93°C or 107°C were mostly similar to those obtained from films dried at 79°C (see Figures 10d and 10e) except that the bands from Si–OH and bicarbonates continued to decrease in intensity.

Effect of Drying Temperature of γ-AEAPS Primer Films on Strength of PVC/Steel Peel-Test Specimens

The effect that drying of γ-AEAPS primer films had on the strength of PVC/steel peel-test specimens was determined. Peel specimens were prepared by injection molding PVC onto steel substrates primed with γ-AEAPS films and then annealing the specimens at 170°C for 20 min. The γ-AEAPS films were dried in air at room temperature, 60°C, 79°C, 93°C, or 107°C for 1 h before injection molding. These specimens were tested for peel strength using the Instron; the results are shown in Table 8. It was found that all of the peel-test samples showed cohesive failure in the bulk of the PVC. The maximum peel strength was obtained when the γ-AEAPS films were dried at 79°C for 1 h. When mean peel strength was plotted against drying temperature as shown in Figure 11, it was observed that the peel strength increased as the drying temperature of the γ-AEAPS films increased up to 79°C; thereafter, peel strength decreased for higher drying temperatures. It was concluded that the maximum that occurred in peel strength when the γ-AEAPS films were dried at 79°C was related to the structure of the primer films. When the films were dried at temperatures of 79°C or higher, the silanol groups condensed to form siloxanes and the amine bicarbonates were driven off. These two effects allowed PVC molecules to interpenetrate with the siloxanes and allowed allylic chloride groups to react with the amino groups. When the primers were dried at higher temperatures, cross-linking of the films became excessive. In that case, PVC molecules could not interpenetrate with the silane films and adhesion decreased.

TABLE 8 Peel Strength Results for Adhesion between Injection-Molded PVC and Steel

Drying condition	Set 1 (N/m)	Set 2 (N/m)	Set 3 (N/m)	Mean (N/m)
Air dried	2790	2938	3309	3012
60°C for 1 hr	3502	3462	3802	3588
79°C for 1 hr	4394	4169	4069	4209
93°C for 1 hr	2798	3528	3610	3311
107°C for 1 hr	2469	3393	3512	3126

Note: Steel substrates were primed with γ-AEAPS and the γ-AEAPS film was dried under different conditions. The samples were annealed at 170°C for 20 min and peel strength of the samples was tested by Instron Tensile Tester, using 90° peel configuration and speed of 2.54 mm/min.

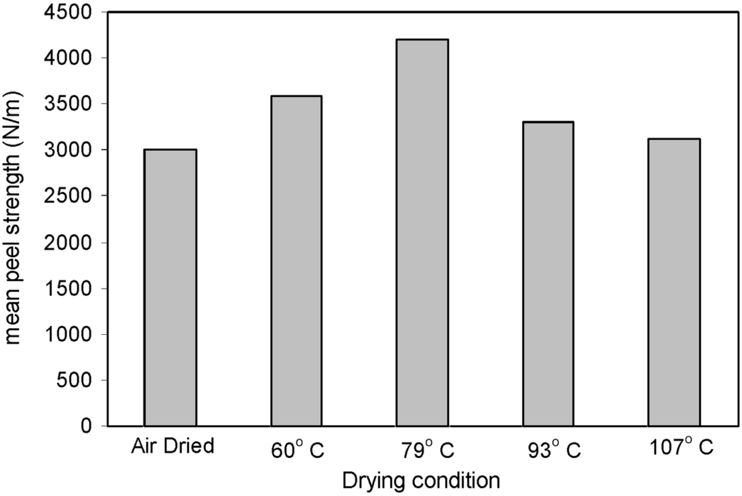


FIGURE 11 Mean strength of PVC/steel peel-test specimens *versus* drying conditions of γ-AEAPS primer films that were applied to the steel substrates and then dried for 1 h at various temperatures before PVC was injection molded onto the substrates. The peel-test specimens were annealed at 170°C for 15 min; the peel strengths of the specimens were determined using an Instron, a 90° peel test, and a crosshead speed of 2.54 mm/min.

Effect of Drying Environment and Temperature on Structure of γ-AEAPS Films

To further explore the importance of amine bicarbonates on adhesion of PVC to γ-AEAPS films, we investigated the structure and properties of γ-AEAPS films that were formed in air or nitrogen environments and dried in air or nitrogen at room temperature or at 90°C. The RAIR spectrum of a γ-AEAPS film that was adsorbed onto steel from a 2% aqueous solution in air and dried in air at room temperature is shown in Figure 12a. As indicated previously, the bands near 1575, 1475, and 1325 cm^{-1} were related to amine bicarbonate complexes [7]. The large broad peak located near 1100 cm^{-1} was characteristic of an asymmetric Si–O–Si stretching vibration, indicating that some polymerization of the silane took place during drying but the presence of the band near 940 cm^{-1} indicated that there were still silanol groups in the films. Figure 12b shows the infrared spectrum of a γ-AEAPS film that was adsorbed onto steel from a 2% aqueous solution in air and dried in air at 90°C. When the spectra in Figures 12a and b were compared, it was evident that the peaks associated with amine bicarbonate complexes decreased in intensity relative to the

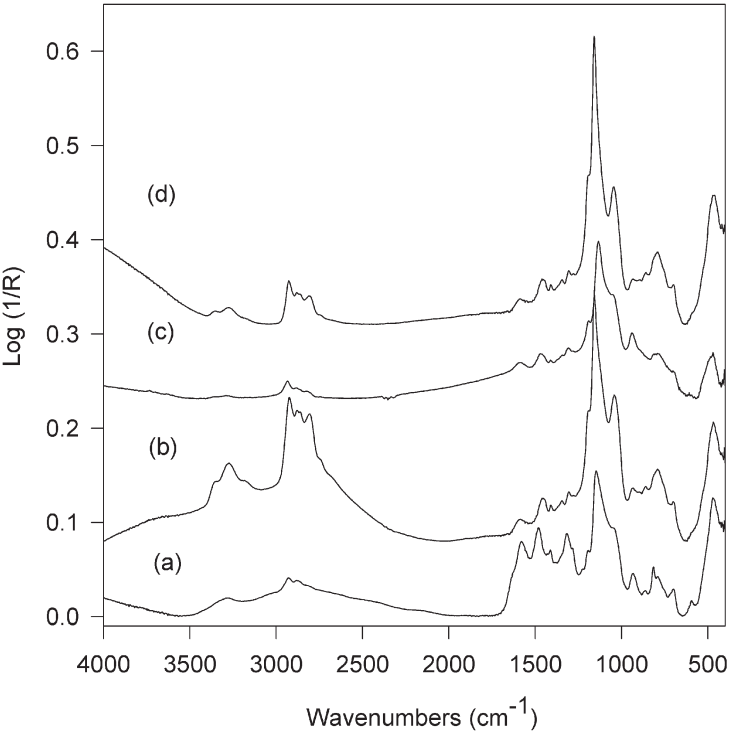


FIGURE 12 RAIR spectra of γ-AEAPS films deposited onto steel substrates from 2% aqueous solutions in air or nitrogen and then dried for 1 h at room temperature or at 90°C: (a) deposition and drying were carried out in air at room temperature; (b) deposition was in air and drying was at 90°C in air; (c) deposition and drying were at room temperature in nitrogen; (d) deposition was in nitrogen and drying was at 90°C in nitrogen.

siloxane peak, indicating that CO_2 was driven off during heating at 90°C, leaving free amino groups. Moreover, the band around 1100 cm^{-1} split into two discrete bands, a strong band around 1150 cm^{-1} and a smaller band around 1050 cm^{-1}, and the peak near 940 cm^{-1} almost disappeared, indicating extensive cross-linking of the silane film after drying at 90°C. When the γ-AEAPS film was adsorbed onto steel from a 2% aqueous solution in a nitrogen environment and dried under nitrogen at room temperature, the bands near 1575, 1475, and 1325 cm^{-1} were relatively weak, indicating that formation of amine bicarbonates was restricted under these circumstances (see Figure 12c). However, the band near 940 cm^{-1} was relatively strong, indicating that cross-linking of the films was limited and that considerable numbers of silanol groups remained in the films. Figure 12d shows the infrared spectrum of a γ-AEAPS film that was adsorbed onto steel in a nitrogen environment and dried at 90°C for 1 h in nitrogen. In this case, the peaks associated with amine bicarbonate complexes were very weak. Moreover, the peak that was assigned to SiOH groups at 940 cm^{-1} was very weak. It was concluded that when γ-AEAPS films were formed and dried at 90°C under nitrogen, there were few residual amine bicarbonate and silanol groups and that polymerization in the films was extensive.

Peel-test specimens were prepared from steel substrates that were primed with γ-AEAPS films that were adsorbed from 2% aqueous solutions in air or nitrogen environments and dried in air or nitrogen at room temperature or at 90°C. A thin film of dehydrochlorinated PVC (DHPVC) was cast from a solution in pyridine onto the primed steel substrates and PVC was injection molded against the substrates. The pyridine solution was held at 65°C for 30 h before the film was cast. The resulting specimens were annealed at 170°C for 15 min and then their peel strengths were determined using the Instron (see Table 9 and Figure 13). Poor adhesion was observed between PVC and γ-AEAPS primed steel when the γ-AEAPS films were formed in air and dried in air at room temperature and the peel strength was negligible. This was undoubtedly related to the formation of amine bicarbonate complexes by reaction of amino groups from the silane film with H_2O and CO_2 from the air [7]. However, when the γ-AEAPS

TABLE 9 Peel Strength Results for Adhesion between DHPVC and Steel

Coating, drying condition of γ-AEAPS	Sample 1, peel strength (N/m)	Sample 2, peel strength (N/m)	Sample 3, peel strength (N/m)	Sample 4, peel strength (N/m)	Mean peel strength (N/m)	Std deviation (N/m)
In air, at rt for 1 h (A)	No adhesion	No adhesion	No adhesion	No adhesion	—	—
In air, at 90°C for 1 h (A 90)	2938	3309	3047	3071	3091	156
In N_2 at rt, in N_2 for 1 h (N)	2790	2798	2469	2660	2679	154
In N_2 at 90°C, in N_2 for 1 h (N 90)	4169	4069	4394	4450	4271	181

Note: Steel substrates were primed with γ-AEAPS and dried under different conditions. The samples were annealed at 170°C for 15 min and the peel strength of the samples was determined using the Instron, a 90° peel configuration, and crosshead speed of 2.54 mm/min.

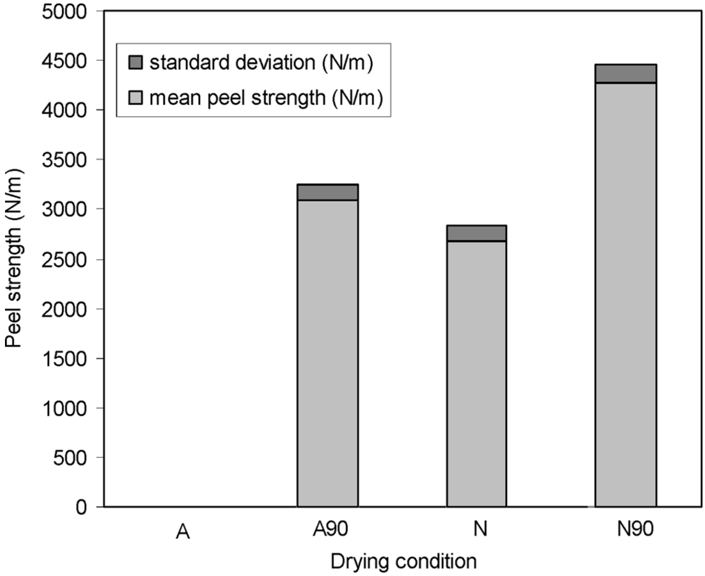


FIGURE 13 Mean strength of peel-test specimens prepared by injection molding PVC onto steel substrates primed with γ-AEAPS films that were dried in air or nitrogen at room temperature or 90°C. A thin film of DHPVC was then cast onto the steel substrate from a pyridine solution that was held at 65°C for 30 h before injection molding. The peel test specimens were annealed at 170°C for 15 min; the peel strengths of the specimens were determined using an Instron, a 90° peel test, and a crosshead speed of 2.54 mm/min.

films were adsorbed onto steel from a 2% aqueous solution in air and were dried in air at 90°C, good adhesion was observed. In this case, there were few amine bicarbonates to hinder the reaction between amino groups in γ-AEAPS and allylic chloride groups in DHPVC and the peel strength was about 3091 N/m. When γ-AEAPS films were adsorbed onto steel from a 2% aqueous solution in a nitrogen environment and dried under nitrogen at room temperature, excellent adhesion was also observed. In this case, the peel strength was about 2679 N/m. Once again, adhesion was excellent when there were few amine bicarbonates to hinder the reaction between amino groups in γ-AEAPS and allylic chloride groups in DHPVC. Finally, the peel strength was greatest when the γ-AEAPS primer films were adsorbed onto steel in a nitrogen environment and dried at 90°C for 1 h in nitrogen. In that case, the peel strength was about 4271 N/m. These results demonstrated that the greatest peel strengths were observed when the γ-AEAPS primers were

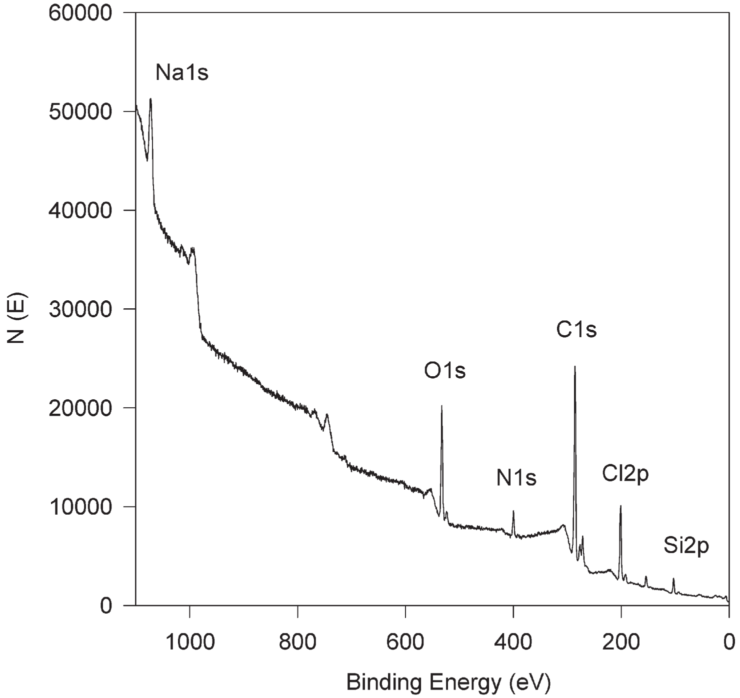


FIGURE 14 XPS survey spectrum of a steel substrate that was coated with a thin film of γ-AEAPS that was dried in air at 90°C for 1 h. A thin film of PVC film was then cast onto the γ-AEAPS film from a solution in pyridine at room temperature. The solvent was allowed to evaporate overnight before the substrate was heated at 100°C for 20 min in nitrogen and then rinsed thoroughly with THF and water to remove unreacted PVC and other compounds.

extensively cross-linked and contained few amine bicarbonate groups and when a thin film of DHPVC that contained allylic chlorides was cast onto the γ-AEAPS films before injection molding of the PVC.

Adhesion between PVC that was Dehydrochlorinated in Pyridine and Steel Primed with γ-AEAPS

The importance of allylic chlorides on adhesion of PVC to steel primed with amino silanes was investigated further. Several drops of a PVC solution in pyridine were placed onto a substrate that had been previously primed with γ-AEAPS and dried at 90°C for 1 h and the solvent was allowed to evaporate. Injection-molded PVC was then clamped against the steel substrate and annealed at 170°C for 15 min. When

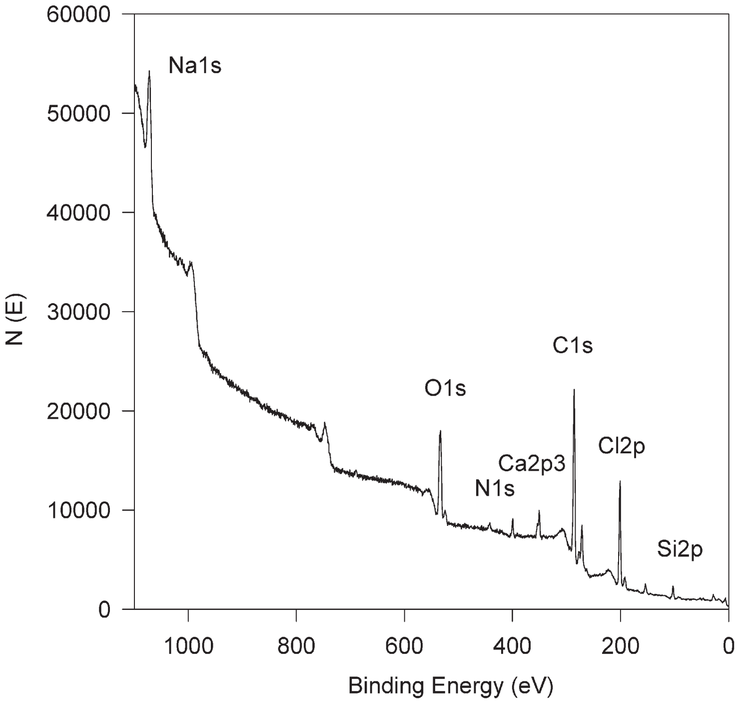


FIGURE 15 XPS survey spectrum of a steel substrate that was coated with a thin film of γ-AEAPS that was dried in air at 90°C for 1 h. A thin film of PVC film was then cast onto the γ-AEAPS film from a pyridine solution that was held at 65°C for 20 h. The solvent was allowed to evaporate overnight before the substrate was heated at 100°C for 20 min in nitrogen and then rinsed thoroughly with THF and water to remove unreacted PVC and other compounds.

the PVC was peeled off of the steel, cohesive failure in the PVC took place. This result indicated strong bonding between PVC films that were cast from solution in pyridine and the γ-AEAPS film. According to Mukherjee and Gupta, PVC was dehydrochlorinated thermally in pyridine solution [21]. During dehydrochlorination there was no HCl evolution because a pyridine hydrochloride complex that is supposed to act as a catalyst for dehydrochlorination was formed. Thus, allylic chloride groups were presumably formed when PVC was dissolved in pyridine and the solution was heated to 65°C. When the solution was cast onto a substrate that was primed with aminosilane, strong bonds formed between allylic chlorides in the PVC and amino groups in the silane.

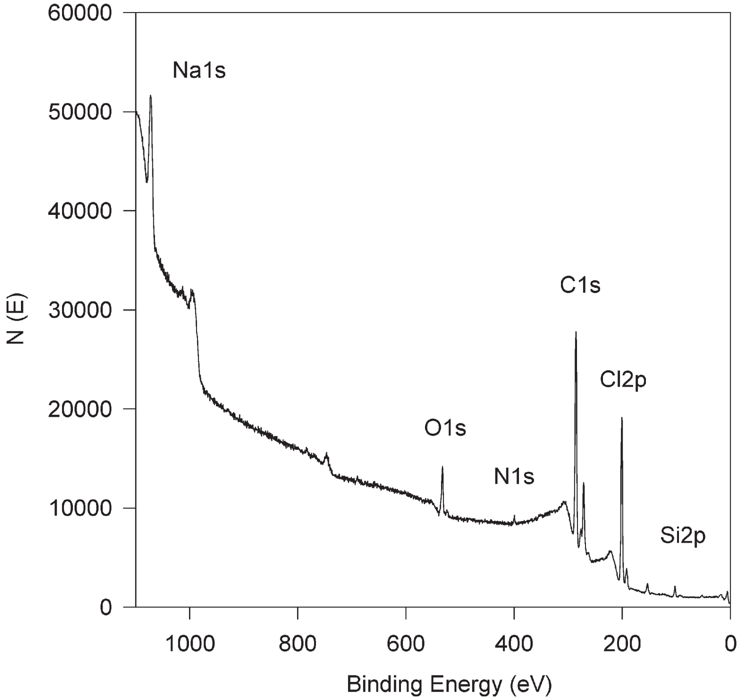


FIGURE 16 XPS survey spectrum of a steel substrate that was coated with a thin film of γ-AEAPS that was dried in air at 90°C for 1 h. A thin film of PVC film was then cast onto the γ-AEAPS film from a pyridine solution that was held at 65°C for 30 h. The solvent was allowed to evaporate overnight before the substrate was heated at 100°C for 20 min in nitrogen and then rinsed thoroughly with THF and water to remove unreacted PVC and other compounds.

In a related experiment, several drops of a PVC solution in THF were placed onto a substrate that had been previously primed with γ-AEAPS and dried at 90°C for 1 h. The solvent was allowed to evaporate and injection-molded PVC was then clamped against the steel substrate and annealed at 170°C for 15 min. When the PVC was peeled off the steel, failure took place at the interface between the cast PVC film and the γ-AEAPS primer film. This result indicated that there was little adhesion between γ-AEAPS films and PVC films that were cast from solution in THF, whereas there was excellent adhesion between γ-AEAPS films and PVC films cast from solution in pyridine. This experiment confirmed that allylic chlorides were responsible for adhesion of PVC to steel substrates primed with aminosilane films.

Determination of Rate-Limiting Step in the Chemical Reaction between PVC and γ-AEAPS

The chemical interaction between PVC and aminosilanes consists of two steps, generation of allylic chlorides in PVC and reaction of allylic chlorides with amino groups of the silane. Hence, it was important to determine the rate-limiting step in the reaction. An experiment was conducted in which γ-AEAPS films were adsorbed onto steel substrates from 2% aqueous solutions and dried in air at 90°C for 1 h. A PVC film was then cast onto the substrates from solution in pyridine at room temperature. The solvent was allowed to evaporate overnight and the sample was then heated at 100°C for 20 min in an N_2 environment. The substrate was cooled to room temperature and then rinsed thoroughly with THF and HPLC-grade water to remove unreacted PVC and other impurities. The XPS survey spectrum obtained from the specimen indicated the presence of chlorine, suggesting that a reaction between the cast PVC films and the aminosilane films had taken place (see Figure 14). Similar experiments were carried out using PVC films that were cast from pyridine solutions that had been held at a temperature of 65°C for 20 or 30 h. The XPS survey spectra obtained from those samples are shown in Figures 15 and 16. Comparing the spectra in Figures 15 and 16, it was observed that the atomic concentration of chlorine on the substrate was greater when PVC was cast from solution in pyridine at 65°C than when PVC was cast from solution in pyridine at room temperature (see Table 10). This suggested that the interaction between PVC and aminosilane increased as the extent of dehydrochlorination in PVC increased. Also, the high resolution XPS spectra of chlorine showed the presence of the spin-orbit-split doublet with the binding energy

TABLE 10 XPS Percentage Atomic Concentration at Take-Off Angle 45° of Elements Present on the Steel Substrate

Solution of PVC in pyridine prepared under different conditions	Atomic concentration (%)						
	C	Ca	Cl	N	Na	O	Si
At rt for 30 h	63.8	—	7.2	5.3	5.9	13.3	4.5
At 65°C for 20 h	57	2.0	9.9	3.7	7.8	16.5	3.3
At 65°C for 30 h	67.2	—	17.3	1.2	6.6	5.4	2.3

Note: Steel substrate was primed with γ-AEAPS; PVC was cast from solution in pyridine at different times and temperatures onto it; the substrates were later heated at 100°C for 20 min in a nitrogen environment and rinsed thoroughly with THF and HPLC grade water.

of Cl($2p_{3/2}$) lying at 199.8 eV, suggesting that chlorine was from PVC. This result showed that generation of allylic chloride in PVC was the rate-limiting step in the reaction.

CONCLUSIONS

Amine hydrochloride complexes were formed at the interface between injection-molded PVC and steel that was primed with an aminosilane. The amine hydrochlorides were formed by protonation of amino groups of aminosilane with HCl liberated from PVC chains during thermal dehydrochlorination of PVC. Elimination of HCl from PVC chains generated allylic chlorides in the PVC chains. Quaternization or nucleophilic substitution of labile allylic chloride groups by amino groups of aminosilane occurred during adhesion between PVC and steel primed with an aminosilane. Allylic chlorides were essential for adhesion of PVC to steel primed with aminosilanes. Generation of allylic chlorides in PVC was the rate-limiting step in the chemical interaction between PVC and aminosilane.

ACKNOWLEDGMENTS

The work described here was supported in part by Pilkington North America. Thanks to Bryan Kazmer (Vichem) for providing the PVC samples and for useful suggestions regarding processing of PVC.

REFERENCES

[1] Plueddemann, E. P., *Silane Coupling Agents*, 2nd ed. (Plenum Press, New York, 1990).

[2] Erickson, P. W. and Plueddemann, E. P., *Composite Materials*, Vol. 6, (Academic Press, New York, 1974), Chap. 1.

[3] Rahrig, D., US Patent No. 4,536,360 (August 20, 1985).

[4] Matuana, L. M., Woodhams, R. T., Balatinecz, J. J., and Park, C. B., *Polym. Comp.* **19**, 446–455 (1998).

[5] Gilbert, M. and Rodriguez-Fernandez, O., *J. Appl. Polym. Sci.* **66**, 2111–2119 (1997).

[6] Gilbert, M. and Rodriguez-Fernandez, O., *J. Appl. Polym. Sci.* **66**, 2121–2128 (1997).

[7] Ondrus, D. J. and Boerio, F. J., *J. Colloid Interface Sci.* **124**, 349–357 (1988).

[8] Theidman, W., Tolan, F. C., Pearce, P. J., and Morris, C. E. M., *J. Adhes.* **22**, 197–210 (1987).

[9] Boerio, F. J. and Ondrus, D. J., in *Surface and Colloid Science in Computer Technology*, K. L. Mittal (Ed.) (Plenum Press, New York, 1987), pp. 155–170.

[10] Moses, P. R., Weir, L. M., Lennox, J. C., Finklea, H. O., Lenhard, J. R., and Murray, R. W., *Anal. Chem.* **50**, 576–585 (1978).

[11] Horner, M. R., Boerio, F. J., and Clearfield, H. M., *J. Adhes. Sci. Technol.* **6**, 1–22 (1992).

[12] Fowkes, F. M., Dwight, D. W., Cole, D. A., and Huang, T. C., *J. Non-Cryst. Solids* **120**, 47–60 (1990).

[13] Naviroj, S., Koenig, J. L., and Ishida, H., *J. Adhes.* **18**, 93–110 (1985).

[14] Beamson, G. and Briggs, D., *High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database*, (John Wiley & Sons, Chichester, England, 1992), p. 6.

[15] Starnes, W. H., Jr., *Prog. Polym. Sci.* **27**, 2133–2170 (2002).

[16] Titow, W. V., *PVC Plastics: Properties, Processing and Applications* (Elsevier Applied Science, London and New York, 1990).

[17] Jiminez, A. and Zaikov, G. E., *Polymer Analysis and Degradation* (Nova Science Publishers, New York, 2000).

[18] Ivan, B., in *Polymer Durability: Degradation, Stabilization, and Lifetime Prediction*, R. L. Clough, N. C. Billingham, and K. T. Gillen (Eds.) (American Chemical Society, Washington, DC, 1996).

[19] Marcilla, A., Beltran, M., and Garcia, J. C., *Eur. Polym. J.* **33**, 453–462 (1997).

[20] Kuptsov, A. H. and Zhizhin, G. N., *Handbook of Fourier Transform Raman and Infrared Spectra of Polymers* (Elsevier, Amsterdam, 1998).

[21] Mukherjee, A. and Gupta, A., *J. Macromol. Sci. Chem.* **A16**, 783–792 (1981).