



Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis



Influence of coating bath chemistry on the deposition of 3-mercaptopropyl trimethoxysilane films deposited on magnesium alloy

A.F. Scott, J.E. Gray-Munro*, J.L. Shepherd

Dept. of Chemistry and Biochemistry, Laurentian University, Sudbury, Ontario, Canada P3E 2C6

ARTICLE INFO

Article history:

Received 29 October 2009

Accepted 27 November 2009

Available online 4 December 2009

Keywords:

Organosilane

Magnesium

Coatings

Hydrolysis

Condensation

ATR–FTIR

ABSTRACT

Magnesium alloys have a low specific density and a high strength to weight ratio. This makes them sought after light weight construction materials for automotive and aerospace applications. These materials have also recently become of interest for biomedical applications. Unfortunately, the use of magnesium alloys in many applications has been limited due to its high susceptibility to corrosion. One way to improve the corrosion resistance of magnesium alloys is through the deposition of protective coatings. Many of the current pretreatments/coatings available use toxic chemicals such as chromates and hydrofluoric acid. One possible environmentally friendly alternative is organosilane coatings which have been shown to offer significant corrosion protection to both aluminum alloys and steels. Organosilanes are ambifunctional molecules that are capable of covalent bonding to metal hydroxide surfaces. In order for covalent bonding to occur, the organosilane must undergo hydrolysis in the coating bath followed by a condensation reaction with the surface. There are a number of factors that influence the rates of these reactions such as pH and concentration of reactants. These factors can also influence competing reactions in solution such as oligomerization. The rates of hydrolysis and condensation of 3-mercaptopropyltrimethoxy silane in methanol have been analyzed with ^1H NMR and ATR–FTIR. The results indicate that organosilane oligomers begin to form in solution before the molecules are fully hydrolyzed. The organosilane films deposited on magnesium alloy AZ91 at a variety of concentrations and pre-hydrolysis times were characterized with a combination of ATR–FTIR, ellipsometry and SEM/EDS. The results show that both organosilane film thickness and uniformity are affected by the chemistry occurring in the coating bath prior to deposition.

Crown Copyright © 2009 Published by Elsevier Inc. All rights reserved.

1. Introduction

Rising fuel costs and global warming have initiated a push towards light weight construction materials to improve vehicle fuel economy. Magnesium alloys are of particular interest for this purpose because they have a specific density 1/4 that of steel and 2/3 that of aluminum [1–5]. Magnesium alloys also have a high strength to weight ratio which makes them an ideal light weight construction material [1–5]. Unfortunately, their widespread use in industry has been limited since they are highly susceptible to corrosion. However, their corrosion resistance can be improved by applying protective coatings that do not affect the bulk mechanical properties of the material.

The high reactivity of magnesium surfaces and the fast formation of a relatively thick native oxide layer pose major challenges in producing coatings with sufficient adhesion for optimum corrosion resistance on these materials [1]. Upon exposure to the atmosphere, an oxide/hydroxide/carbonate layer forms readily over the

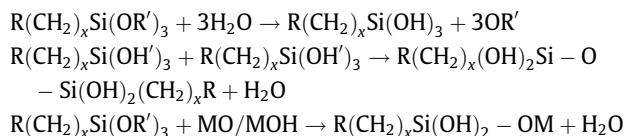
surface due to reaction with atmospheric oxygen, water and carbon dioxide [4]. In solution, an oxide/hydroxide/carbonate layer is also formed over the surface [4,5]. While these oxide layers do offer some corrosion protection to the magnesium alloy, in the presence of aggressive environments the films tend to break down [2–5]. For most coating processes, oxide layers are undesirable because they can ultimately affect the adhesion of protective films [1,6]. Most current coating processes for magnesium alloys involve an initial step to remove the oxide layer [1,7–10]. This is typically done by replacing the oxide layer with a chromate or fluoride layer through a chemical reaction with either chromic acid or acid fluoride treatments [1,3,4,7–10]. These chemicals are toxic to both human health and the environment. Alternatives to these harsh treatments are currently under investigation and the use of organosilanes, also known as silanes, have become of interest for magnesium as well as other materials such as aluminum and ferrous alloys [11–20].

Organosilanes have generally been used as adhesion promoters between inorganic substrates and organic coatings [21,22]. However, they have recently been shown to act as corrosion resistant protective coatings for aluminum and ferrous alloys [17–20].

* Corresponding author.

E-mail address: jgray@laurentian.ca (J.E. Gray-Munro).

Organosilanes are ambifunctional molecules with the general structure $(R'O)_3Si-R-X$. Where R is an alkyl chain, R' can be Cl, F, CH_3 or C_2H_5 and X is a functional group such as a thiol, amine, carboxylic acid, alcohol or alkyl group. The alkoxy silane portion of the molecule is capable of bonding with a variety of mineral or metal surfaces through complex hydrolysis/condensation reactions where Si–O–Metal bonds are ultimately formed [11,20,23]. The deposition of organosilane molecules onto solid surfaces requires two reactions. Both hydrolysis and condensation of the molecules must occur as shown in the reactions below [11,18,21–27]:



The hydrolyzed organosilane molecules can undergo condensation with the surface or they can react with other organosilane molecules to form oligomers in solution. The rates and extent of these reactions depend on a number of factors such as the organosilane of interest, the solvent, water availability, solution pH, silane concentration and the surface to be coated [11,18,21–27]. These factors can also affect the quality of the deposited silane film.

The silane of interest can affect the rates of reaction and the corrosion protection to the underlying substrate. Chemisorbed amino silanes have been shown to undergo self-catalyzed hydrolysis of the Si–O–Metal bond resulting in poor stability of the films in aqueous environments [15,21,22]. This does not occur with thiolated organosilanes [21,22]. Organosilanes with short alkyl chains tend to form disorganized films with random orientation while organosilanes with long alkyl chains form well ordered films due to increased intermolecular interactions between the adsorbed molecules [11,28,29]. There have also been several reported studies where the functional group, X, attached to the alkyl chain interacts with the substrate via an acid–base interaction [16,30]. This orientation is undesirable because the physisorbed molecules do not have sufficient stability to provide long term corrosion protection.

The availability of water, solution pH and silane concentration also affect the rates of hydrolysis and condensation [11,18,21–27]. The rate of hydrolysis is faster than condensation when water is in excess and the pH of the solution is low [21,22,27,31]. The observed kinetics suggest that the hydrolysis of silanes may be a stepwise pseudo first order reaction [27]. The rate of condensation is faster than hydrolysis when small amounts of water are present and the solution pH is high [21,22,27,31]. The rate of condensation has also been shown to increase with increasing organosilane concentration. The possibility that organosilane hydrolysis and condensation occur simultaneously in solution has also been postulated [22,27].

Organosilanes bond to inorganic substrates through Si–O–Metal bonds. This means that the presence of an oxide layer on the surface is essential for adhesion of the molecules. Basic oxide layers, such as those found on Mg alloy surfaces, should promote silane film deposition [11,28,30,32,33] eliminating the need to remove the oxide layer prior to coating.

There are only a few published studies on the interactions of organosilanes with magnesium alloy substrates [11–16]. Zucchi et al. have compared the protective properties of organosilanes with short alkyl chains to their long chain counterparts at different pH values on Mg alloys WE43 and AZ31 [11,12]. There was an optimum pH for hydrolysis associated with each silane studied. The films formed from those solutions provided the best corrosion protection. Zucchi et al. also found that long chained silanes provided better corrosion protection than their short chain counterparts. Montemor et al. have studied the corrosion protection properties of silane films with incorporated rare-earth salts and carbon nano-

tubes [13,14]. The incorporated rare-earth salts and carbon nanotubes improved the corrosion protection of the silane films on the Mg alloy. Our research group has recently published a paper on the interactions of 3-mercaptopropyltrimethoxysilane (MPTS) and Magnesium alloy AZ91 [16]. In these studies it was determined that MPTS did not preferentially deposit on the primary α phase or β phase of the alloy. The solution concentration and pH were shown to influence both coating thickness and uniformity. X-ray photoelectron spectroscopy studies revealed that the organosilane molecules interacted with the surface in several orientations. Some of the MPTS molecules bonded to the surface through Si–O–Mg bonds while others interacted with the surface through an acid–base interaction between the organosilane thiol group and the magnesium hydroxide layer.

The purpose of the present study was to determine the influence of coating bath chemistry on the deposition of MPTS onto magnesium alloy AZ91. It was our hypothesis that allowing the coating bath to pre-hydrolyze prior to immersion of the magnesium alloy substrate would have a significant impact on the nature of the deposited organosilane films. The solution chemistry as a function of time was evaluated through a combination of in situ proton nuclear magnetic resonance (1H NMR) and attenuated total reflection fourier transform infrared (ATR–FTIR) studies. The impact of the changes in coating bath chemistry due to pre-hydrolysis time on the deposited organosilane films was evaluated by ATR–FTIR, scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) and ellipsometry.

2. Experimental details

2.1. Substrate preparation

Diecast magnesium alloy AZ91 sheets were obtained from Lunt Technologies. The sheets were cut into coupons with dimensions of 1" by 1/2". The coupons were polished to a 1 μ m mirror finish with polishing pads and diamond suspension oils purchased from Buehler Canada. They were rinsed with water between polishing steps to remove excess polishing oil. After polishing, they were sonicated successively in acetone and methanol for 15 min to remove residual polishing oils followed by a final rinse in deionized water for 30 s. They were then alkaline aged in 0.5 M NaOH for 1 h at 50 °C, rinsed in deionized water for 30 s and blown dry. Alkaline ageing has been previously shown to increase the hydroxide surface concentration on Mg alloy AZ91 [16]. The basic oxide layer produced is expected to promote surface condensation of MPTS.

2.2. In situ determination of coating bath chemistry

The hydrolysis and condensation reactions of the organosilane molecules in the coating bath as a function of time were evaluated using a combination of 1H NMR and in situ ATR–FTIR analysis.

2.2.1. 1H NMR studies

MPTS was purchased from Sigma–Aldrich Canada and was used as received. The influence of pH on the rate of hydrolysis was determined with 1H NMR. The reaction mixture consisted of 2% v/v MPTS in CD_3OD and 3% v/v D_2O in an 800 μ L, 300 MHz NMR tube. Predetermined volumes of D_2SO_4 and NaOD were added to the solutions to obtain pH values of 4, 7 and 10. The experiments were carried out on a 200 MHz NMR and peak integrations were determined with the computer software. The production of methanol and loss of methoxy groups were monitored over a period of time. Time zero began when MPTS was added to the solution. From the information collected, the rates of hydrolysis and the optimum coating bath pH were determined.

2.2.2. ATR–FTIR studies

The hydrolysis and condensation reactions in solution were also monitored with ATR–FTIR spectroscopy. These experiments were carried out at pH 4 with 2% v/v MPTS and 3% v/v H₂O in methanol. MPTS was added to the reaction mixture at time zero and was pumped through a flow cell with a ZnSe crystal (Pike Technologies). The background spectrum was the coating bath at time zero. Difference spectra were then collected as a function of time to eliminate solvent interference and enable the observation of small changes in peak intensity and/or frequency. The reported spectra are an average of 100 scans with a resolution of 4 cm⁻¹. The spectra were collected every 30 min over a 6 h period. These experiments were carried out on a Bruker Optics Tensor 27 infrared spectrometer equipped with a liquid nitrogen cooled mercury–cadmium–telluride (MCT) detector and a horizontal ATR (Pike Technologies). Atmospheric compensation and baseline correction, were performed with the OPUS computer software. This software was also used for peak picking and peak integration.

2.3. Ex situ characterization of organosilane coatings as a function of pre-hydrolysis time

The effects of coating bath pre-hydrolysis on the properties of the MPTS films deposited on magnesium alloy AZ91 were studied by characterization of the coatings with a combination of ATR–FTIR, ellipsometry and SEM/EDS. The coating baths consisted of 2–3 (v/v%) ratios of MPTS to H₂O adjusted to pH 4 in methanol. The solutions were hydrolyzed for various specified periods of time before coating. The samples were then immersed into the coating bath for 5 min. The excess solvent was removed by drying the samples in a stream of air. The samples were then cured in an oven at 100 °C for 1 h. It has been shown by some authors that initially organosilanes adhere to substrate surfaces through hydrogen bonding between the silanol groups and the metal oxide. Film curing has been shown to be required to ensure cross-linking of the silane molecules and adhesion to the surface [17,23,24].

2.3.1. ATR–FTIR analysis

ATR–FTIR spectra were collected using a Bruker Optics infrared microscope with an ATR objective and a Ge crystal. The resolution

of the spectrometer was 4 cm⁻¹. Each spectrum is the result of 500 scans. The spectrometer was equipped with a MCT detector that was liquid nitrogen cooled. The spectra were corrected for CO₂ and H₂O with the atmospheric compensation function of the software. The OPUS software was also used to integrate the area under the peaks of interest.

2.3.2. SEM/EDS analysis

Samples to be analyzed were sputter coated with a thin film of carbon to render the sample conductive. All samples were analyzed with a Zeiss EVO50 SEM, EDS spectrometer. The vacuum in the chamber was 1.14 × 10⁻⁶ mbar. The beam current of the electron gun was set at 1.0 nA. A spot size of 520 nm was used with a working distance of 8.5–9 mm. The collection time for the EDS was set for 45 s.

2.3.3. Ellipsometry

Ellipsometry was performed with a MM-16 Horiba Jobin Yvon spectrometer. The circularly polarized light was in the visible range with an incident angle of 70°. The Delta Psi 2 computer software was used for determining film thicknesses.

3. Results and discussion

3.1. In situ ¹H NMR studies on the hydrolysis of MPTS at pH 4, 7 and 10

Although, the rate of hydrolysis of a variety of organosilanes as a function of pH has been reported [21–24,27,31], the rate of hydrolysis of MPTS in methanol has not been studied. The rates of hydrolysis for MPTS at pH 4, 7 and 10 were examined with ¹H NMR. It is generally accepted that at low pH, hydrolysis will be complete before condensation occurs while at high pH, the condensation process begins with incomplete hydrolysis [11,18, 21–27,31]. Under acidic conditions, the rate of hydrolysis has previously been reported to be faster than condensation. However, the reaction is often oversimplified by assuming that the hydrolysis reaction has gone to completion prior to condensation while in fact it is likely that once a significant fraction of hydrolyzed molecules are formed; condensation begins to occur simultaneously in solu-

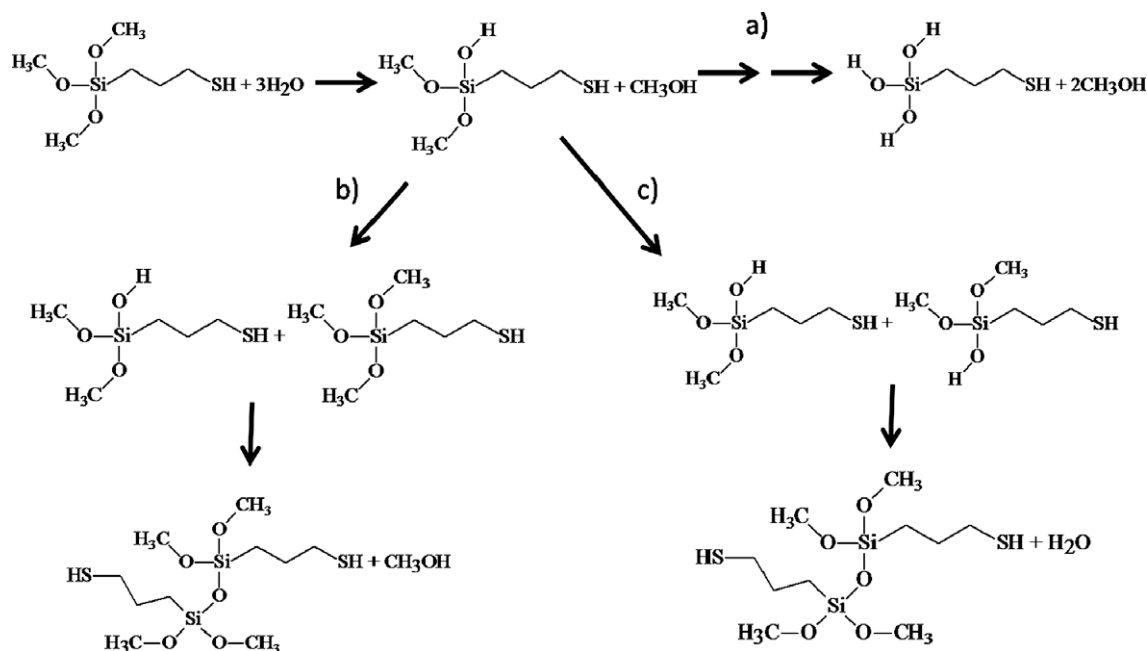


Fig. 1. Schematic representation of the hydrolysis and condensation reactions that occur in the coating bath.

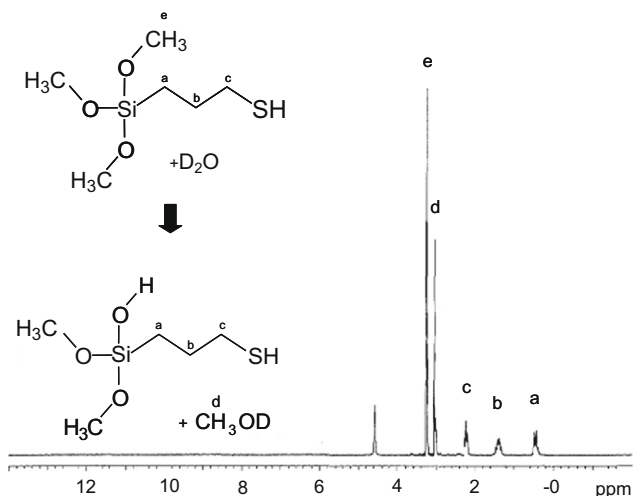


Fig. 2. Schematic representation of the hydrolysis reaction and a representative ^1H NMR spectrum with relevant peak assignments.

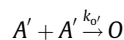
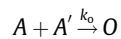
tion. A schematic diagram representing the possible reactions is shown in Fig. 1.

In these ^1H NMR studies, the loss of the alkoxy groups was monitored simultaneously with the production of deuterated methanol. A representative ^1H NMR spectrum with peak assignments is shown in Fig. 2. The thiol shift was not observed in the spectrum because of rapid exchange with the CD_3OD and D_2O . (see Fig. 2) The peaks labelled a, b and c are unaffected by hydrolysis and act as internal references. Fig. 3 shows the change in the normalized peak integrations for the hydrolysis of the alkoxy group of the MPTS molecule (peak e, 3.25 ppm) and the production of deuterated methanol (peak d, 3.05 ppm) at pH 4, 7 and 10 as a function of time.

Regardless of pH, a near exponential decay of the NMR signal for peak e due to a decrease in the number of alkoxy groups was observed as a function of time. This decrease was attributed to the hydrolysis of the organosilane methoxy groups. A concomitant near exponential increase of the NMR signal for peak d was also observed at pH 4, 7 and 10. Peak d has been assigned to the protons in CH_3OD . The growth in this peak confirms that hydrolysis occurs at all pH values. However, the rate of hydrolysis changes significantly as a function of pH. At pH 4, complete hydrolysis, within the detection limit of the instrument, was observed after 6 h. At pH 7, complete hydrolysis was observed only after 46 days of reaction time. However, some precipitation of condensation products was observed prior to complete hydrolysis. At pH 10, complete hydrolysis was observed after only 3.5 h. As observed at pH 7, precipitation of condensation products was observed in solution prior to completion of the hydrolysis reaction.

The hydrolysis of organosilanes has previously been reported to be a pseudo first order reaction when the concentration of water is in excess [27]. At first glance, all of the kinetic data appears to be exponential. However, plots of \ln peak integration vs. time (not shown) showed significant deviations from linearity. This indicates that disappearance of alkoxy groups from the silane molecules is not a simple pseudo first order reaction. There are in fact two possible reactions that would result in a decrease in the number of alkoxy groups. The first is hydrolysis of MPTS (Fig. 1, path a). In the presence of excess water, this reaction can be modeled as a pseudo first order reaction. The second is a condensation reaction between a hydrolyzed MPTS molecule and an unhydrolyzed MPTS molecule (Fig. 1, path b) [21–23]. Both of these pathways also produce methanol as a reaction product. Finally a third reaction involving the condensation of two silanols as shown in Fig. 1, path c, also occurs.

This reaction cannot be directly observed by ^1H NMR. Using the three reactions below, differential rate equations were determined.



A represents unhydrolyzed MPTS, A' partially hydrolyzed MPTS and O the product of condensation to form an oligomer in solution. The rate equation below was developed by treating the hydrolyzed silane molecules (A') as an intermediate; the steady state approximation was used to set $d[A']/dt = 0$. With these assumptions $d[A]/dt$ has the form of a first order ordinary differential equation (ODE) which was solved using an integration factor. This gave the equation shown below where k_h and k_o' are the rate constants for hydrolysis and condensation respectively and A_i is the initial concentration of MPTS in solution. The term $k_o'[A']^2$ is a constant and was assigned the symbol r . The rate constant k_h is actually a pseudo first order rate constant because the concentration of water is in excess.

$$A(t) = \frac{r}{2k_h} [1 - e^{-2k_h t}] + A_0 e^{-2k_h t}$$

All fits were done using the Excel Solver tool with k_h and r as fit parameters. A_0 was fixed as the value of your data at time zero. The initial guess values in every fit were $k_h = 0.001$ and $r = 0.001$. The constraints were $k_h = 1 \times 10^{-8}$ and $r = 1 \times 10^{-8}$.

This equation was used to determine the rate of hydrolysis and condensation of MPTS at pH 4, 7 and 10.

The rate constants obtained at each pH value are tabulated in Table 1.

The model was a good fit for the data at all three pH values as evidenced by the sums of the squares of the errors reported (Table 1). The rate constant for the condensation of two silanols (k_o') was essentially zero at pH 4 and increased as a function of increasing pH. This is consistent with previous reports [22,23] that have shown that the rate of condensation is low under acidic conditions and higher in basic solution. The observed rate constant for hydrolysis (k_h) was highest at pH 4, dropped two orders of magnitude at pH 7 and was highest at pH 10 (by a small amount). The results indicate that hydrolysis dominates at low pH. At neutral pH, the rates of hydrolysis and condensation are the same order of magnitude (10^{-5} min^{-1}). At pH 10, the rate of hydrolysis is slightly higher than the rate of condensation. However, in comparison to pH 4 and pH 7, the rate of the condensation reaction is the highest under basic conditions. In summary, the rate constants show that hydrolysis is faster than condensation at acidic and basic pH values. The solution chemistry was also studied by in situ ATR-FTIR and will be further discussed in the next section.

An optimum organosilane coating bath must be a stable solution in order to allow hydrolyzed organosilane molecules to condense with the surface. Despite having the fastest hydrolysis rate, pH 10 was not chosen as the optimum coating bath pH. This is due to the high degree of oligomerization observed in solution. The physisorption of large oligomers can result in poor adhesion and non-uniform film formation which negatively impacts corrosion resistance. The optimum pH of the coating bath was chosen to be pH 4. This is due to the fact that a significant number of hydrolyzed organosilanes were observed in solution within a reasonable time frame (a few hours) without any visible precipitation of condensation products. Neutral pH was not chosen due to the extremely long hydrolysis time (days), this would be inconvenient for industrial applications. At pH 4 a balance is struck between the availability of silanol ($\text{Si}-\text{OH}$) groups for surface bonding and minimal interference from solution phase oligomers. All further experiments were carried out at pH 4.

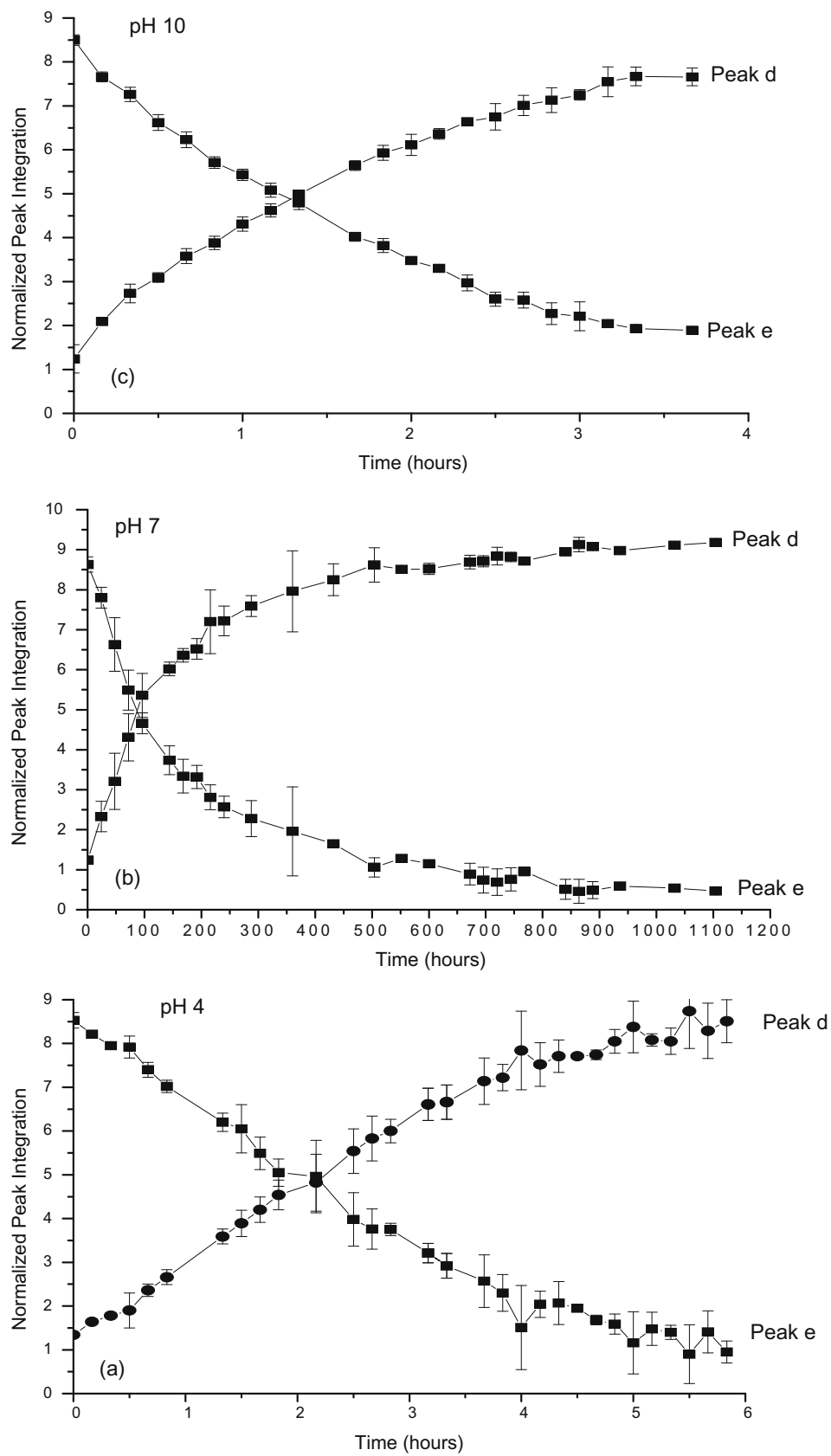


Fig. 3. Monitoring the disappearance of alkoxy groups and appearance of CH_3OD : graphs of normalized peak integration vs. time: (a) pH 4, (b) pH 7, and (c) pH 10.

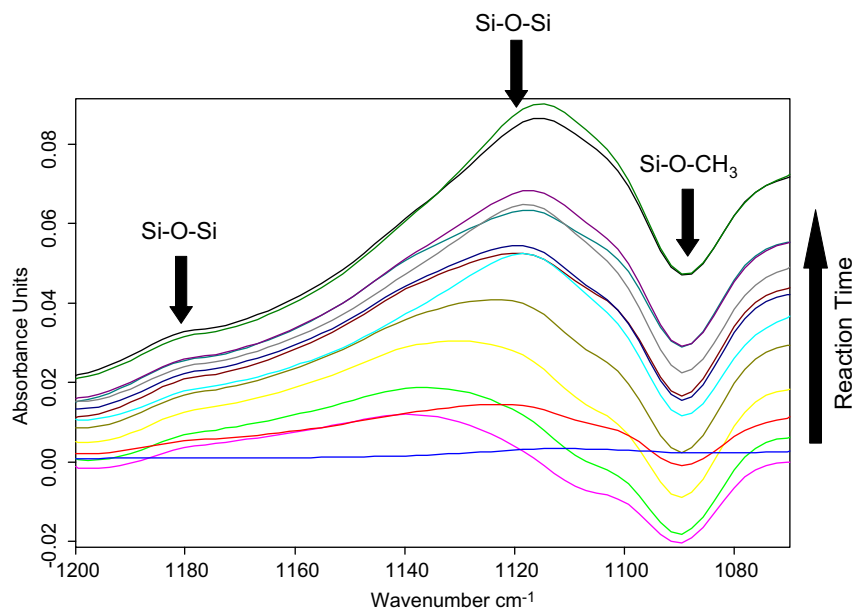


Fig. 4. In situ ATR-FTIR difference spectra for MPTS in CH₃OH and H₂O from 1200 to 1070 cm⁻¹.

Table 1

Kinetic rate constants for hydrolysis and condensation of MPTS in methanol.

	pH 4	pH 7	pH 10
Rate constant hydrolysis (k_h)	$2.74 \times 10^{-3} \text{ min}^{-1}$	$4.93 \times 10^{-5} \text{ min}^{-1}$	$3.98 \times 10^{-3} \text{ min}^{-1}$
Rate constant oligomerization (k_o)	$1 \times 10^{-8} \text{ min}^{-1}$	$6.27 \times 10^{-5} \text{ min}^{-1}$	$2.04 \times 10^{-3} \text{ min}^{-1}$
Sum of squares of the error	7.72	0.059	0.25

3.2. In situ ATR-FTIR studies on the hydrolysis and condensation of MPTS

The hydrolysis and condensation reactions of MPTS in methanol were studied in an in situ ATR-FTIR experiment. In the difference spectra collected, there are two main regions of interest associated with silane hydrolysis and condensation. Fig. 4 shows the difference spectra collected as a function of time in the region from 1200 cm⁻¹ to 1070 cm⁻¹. Fig. 5 shows the difference spectra in the region from 960 cm⁻¹ to 830 cm⁻¹. In the difference spectra, the flat line spectrum was taken immediately after the background was collected. New spectra were collected every 30 min after this point. Significant changes were observed in the infrared spectra as the reaction progressed. Fig. 4 shows that there is a decrease in peak intensity for the band at 1089 cm⁻¹ which can be attributed to the Si-O-CH₃ band of MPTS. This functional group is converted to Si-OH as hydrolysis proceeds. As observed from the NMR experiment, this functional group is also consumed in a condensation reaction between Si-O-CH₃ and Si-OH groups. Two increasing peaks are also observed in this region of the spectra. These peaks are both due to Si-O-Si symmetric and asymmetric stretching. The absorption at 1120 cm⁻¹ is due to poorly cross-linked, linear oligomer chains forming in solution. The absorption at the higher wavenumber of 1185 cm⁻¹ is due to highly cross-linked, cyclical oligomers. The spectra in the second region of interest (Fig. 5) show two main peaks of interest. These peaks can be attributed to Si-O stretching and deformation, with some small contributions from Si-OH. These peaks increase slightly with time due to the formation of silanols (Si-OH) in solution.

This experiment was repeated with D₂O instead of H₂O. Similar spectra were observed; likely due to rapid H/D exchange between

methanol and D₂O. The change in peak intensity as a function of time for the Si-O-Si at 1120 cm⁻¹ and for the Si-OH peak at 910 cm⁻¹ for both the H₂O and D₂O experiments are compared in Fig. 6. In Fig. 6a, the peak intensities for the two systems is identical confirming our hypothesis that this peak is due to condensation of the silane molecules in solution. If this peak was due to one of the new species formed during hydrolysis (Si-OH/Si-OD or CH₃OH/CH₃OD) we would expect significant changes in the frequency of the deuterated species and consequently a decrease in intensity for the non-deuterated band. In Fig. 6b there is a decrease in the peak intensities of the peak at 910 cm⁻¹ in the presence of D₂O. This confirms that this peak is due to the formation of Si-OH groups during hydrolysis of the organosilane. Despite rapid H/D exchange in the system, the deuterated solution contains some hydrolyzed silane with Si-OD groups. The deuterated silanols would absorb at a markedly different frequency than Si-OH leading to an overall decrease in intensity for the Si-OH absorption band. This confirms that the peak at 910 cm⁻¹ can be assigned to Si-OH.

Upon comparison of Fig. 6a and b it is also apparent that the peak intensities at 910 cm⁻¹ were larger than those at 1120 cm⁻¹. Si-O-Si has strong infrared absorption peaks while Si-OH has medium absorption bands. The fact that the infrared bands at 910 cm⁻¹ are more intense indicates that the rate of hydrolysis is faster than the rate of condensation [22]. The results from this study indicate that both hydrolysis and condensation occur simultaneously in solution even at low pH. However, although some oligomers do form in solution at this pH, there are still a significant number of Si-OH groups available for grafting to the magnesium alloy surface.

3.3. Characterization of the influence of solution chemistry on the nature of MPTS coatings on magnesium alloy AZ91

The influence of hydrolysis and condensation on MPTS films deposited on Mg alloy AZ91 was monitored with ATR-FTIR, ellipsometry and SEM/EDS. The effects of coating bath ageing (pre-hydrolysis time) and MPTS concentration were studied. The pre-hydrolysis times of interest ranged from no pre-hydrolysis (0 h) to 24 h of pre-hydrolysis prior to coating. The solution concentrations studied were 1%, 2% and 4% (v/v) MPTS at pH 4.

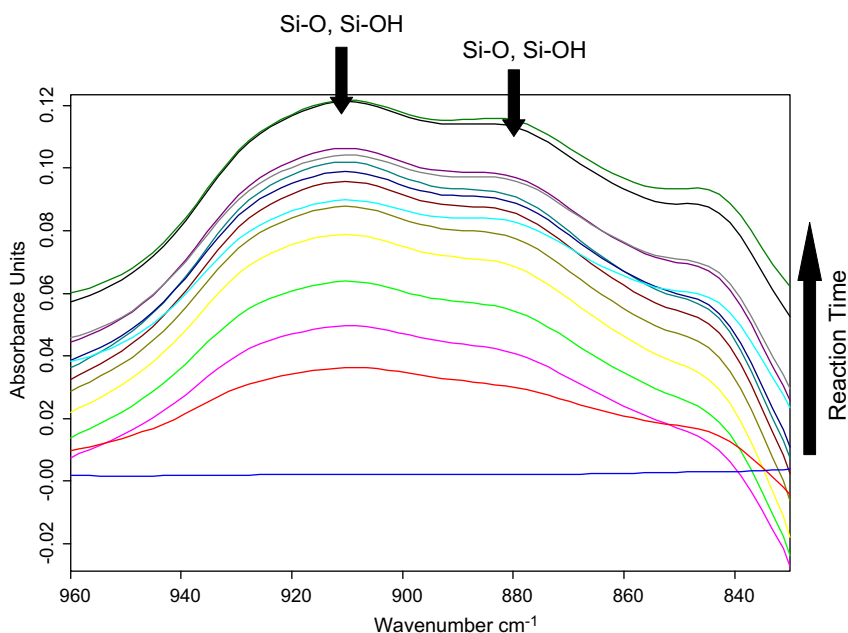


Fig. 5. In situ ATR-FTIR difference spectra for MPTS in CH_3OH and H_2O from 960 to 830 cm^{-1} .

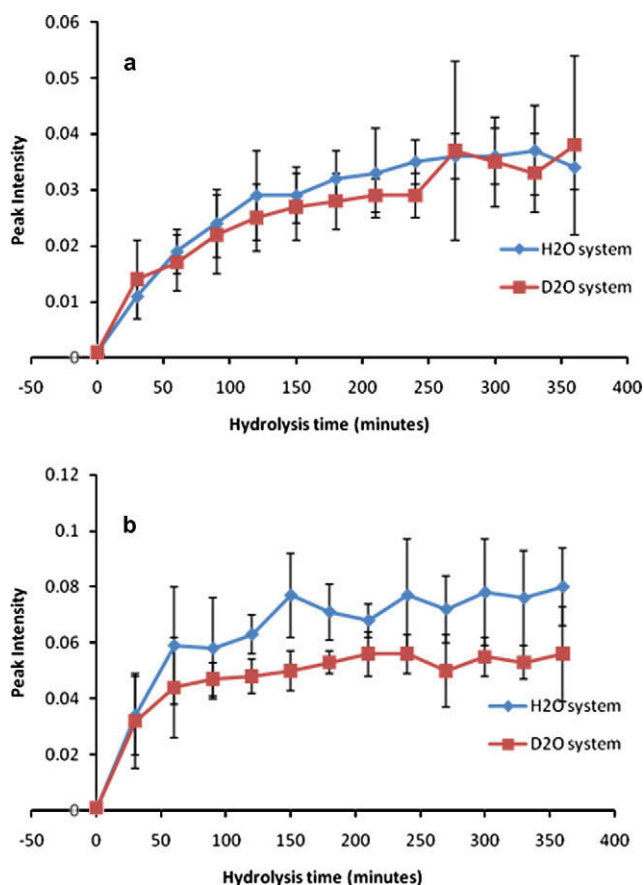


Fig. 6. Intensities of in situ ATR-FTIR absorption bands for H_2O and D_2O systems: (a) Si-O-Si absorption peak at 1120 cm^{-1} and (b) Si-O/Si-OH absorption peak at 910 cm^{-1} .

3.3.1. Ex situ ATR-FTIR analysis

Infrared spectra were collected on each of the coated magnesium alloy coupons. A representative infrared spectrum is shown

in Fig. 7 and the band assignments are given in Table 2. All of the spectra obtained showed absorption peaks from both the magnesium alloy substrate and the MPTS film. This indicates that even at high concentrations and/or long pre-hydrolysis times the coating thickness is less than the sampling depth of the instrument ($\sim 1 \mu\text{m}$).

For a given absorption band, the intensity is dependent on the degree of coverage and thickness of the MPTS film. Less MPTS on the surface results in large substrate peaks and small MPTS peaks while the opposite is observed for thicker MPTS layers. In order to qualitatively determine the influence of pre-hydrolysis time and solution concentration on film thickness the change in intensity of the MPTS band at 1250 cm^{-1} was monitored. This band was chosen because there is no interference from the substrate in this region of the spectrum. Furthermore, this peak is insensitive to degree of hydrolysis and/or condensation since it represents the Si-C stretch of the MPTS molecule which is unaffected by either reaction. The intensity of this peak should accurately represent all of the surface bound organosilane. The change in intensity of this peak as a function of increasing pre-hydrolysis time at differ-

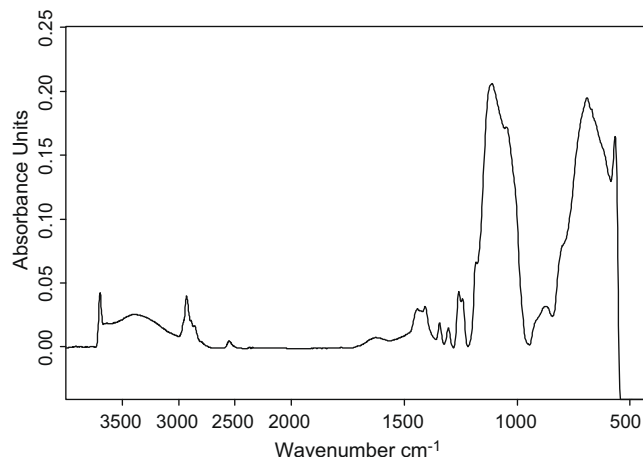


Fig. 7. IR spectrum of an MPTS film on Mg alloy AZ91.

Table 2
Infrared peak assignments for MPTS on magnesium alloy AZ91.

Magnesium alloys substrate peaks		3-Mercaptopropyltrimethoxysilane peaks	
Wavenumber (cm ⁻¹)	Assignment	Wavenumber (cm ⁻¹)	Assignment
3700	OH stretch	2550	S–H stretch
2930	CH _{sp3} stretch	1408	CH ₂ alkyl chain bend
2850		1343	
		1305	
1500	MgCO ₃	1250	Si–C stretch
1089	Al(OH) ₃	1120	Si–O–Si, Si–O–Mg, MgSO ₄

ent concentrations is shown in Fig. 8. Each data point is an average of nine measurements (three samples, three spots each).

3.3.1.1. Influence of coating bath concentration on film thickness. Fig. 8 shows that regardless of pre-hydrolysis time, there is an increase in peak intensity as a function of MPTS concentration in solution. This indicates that as would be expected, the degree of surface condensation increases when there are more MPTS molecules available for surface bonding. Interestingly, the size of the error bars for each data point also increases at higher concentrations. These error bars largely represent variations in film thickness from sample to sample and from spot to spot. The fact that the error bars are larger for the films deposited from 2% to 4% solutions compared to the 1% solution indicates that film uniformity is better at lower concentration. This may be due to increased solution condensation of MPTS at higher concentration resulting in increased physisorption of oligomers at the surface.

3.3.1.2. Influence of pre-hydrolysis time on film thickness. At all concentrations studied, the level of organosilane deposition was low

until a minimum pre-hydrolysis time was reached. After this point, the thickness of the deposited MPTS films increased significantly.

For the 1% MPTS solutions, very little organosilane adsorption was observed for pre-hydrolysis times of 0–2 h. After a 4 h solution pre-hydrolysis, the intensity of the infrared band increases dramatically indicating an increase in film thickness. Beyond this hydrolysis time, the thickness of the MPTS films decreased slightly and remained constant within error. At the low hydrolysis times, there are fewer hydrolyzed molecules available in solution for surface bonding. As the solution hydrolysis time increased, the number of both hydrolyzed molecules and oligomers increases. The large increase observed for 4 h of pre-hydrolysis may be due to the presence of oligomers in solution that contain a significant number of Si–OH groups (they have not cross-linked to a high degree). In order to covalently bond with the surface Si–OH groups must condense with Mg–OH groups to form Si–O–Mg bonds. Partially cross-linked oligomers would have Si–OH groups available for interaction with the surface and with each other promoting surface adsorption. A slight decrease in film thickness for pre-hydrolysis times greater than 4 h was observed. At higher reaction times, the solution phase oligomers would be more highly cross-linked and contain fewer Si–OH groups for interaction with the surface leading to a decrease in surface adsorption.

The results obtained for the 2% v/v MPTS solutions were similar to those observed for the 1% solutions. Low pre-hydrolysis times led to little deposition of MPTS onto the surface. In this case a minimum pre-hydrolysis time of 2 h was required to obtain thicker MPTS films. This is lower than the minimum time observed for 1% solutions because at higher concentrations, the rate of formation of oligomers is faster. After a minimum pre-hydrolysis time, the thickness of the MPTS films remained constant within error.

For the MPTS films deposited from a 4% solution, much thicker films were observed even at low pre-hydrolysis times. Given that the results for the 1% and 2% solutions demonstrated that hydrolysis of the molecules is important for surface adsorption, it is unli-

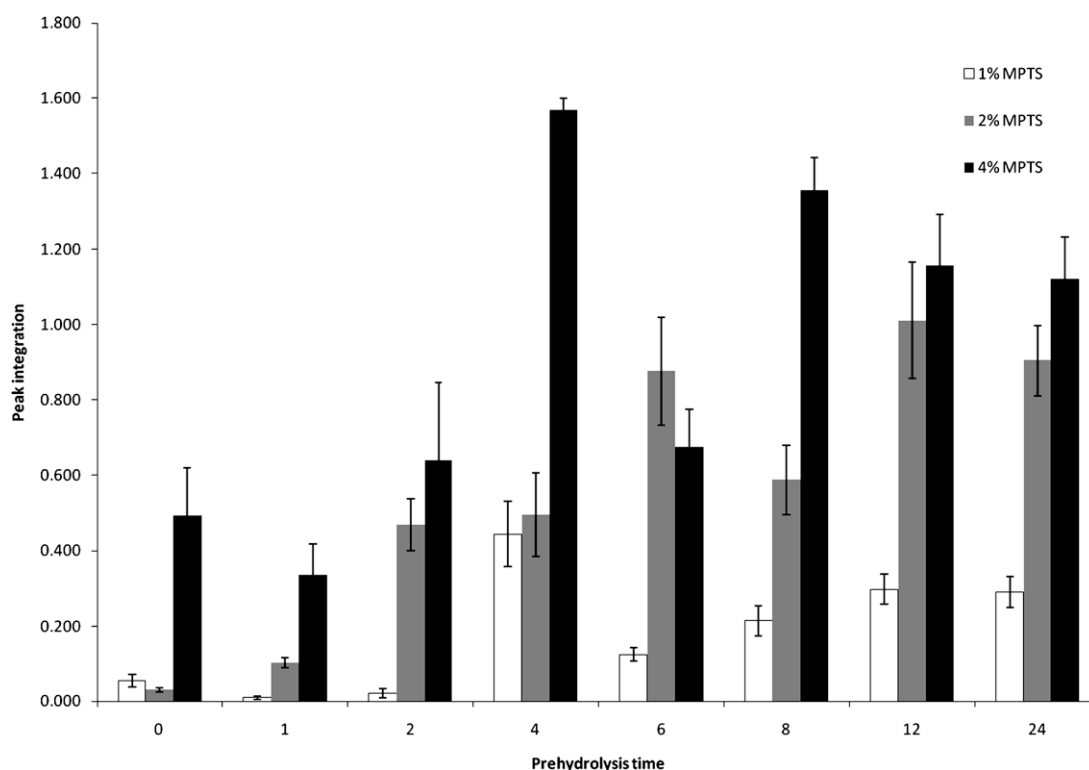


Fig. 8. IR peak intensity at 1250 cm⁻¹ for MPTS films on Mg alloy AZ91 at various solution pre-hydrolysis times and concentrations.

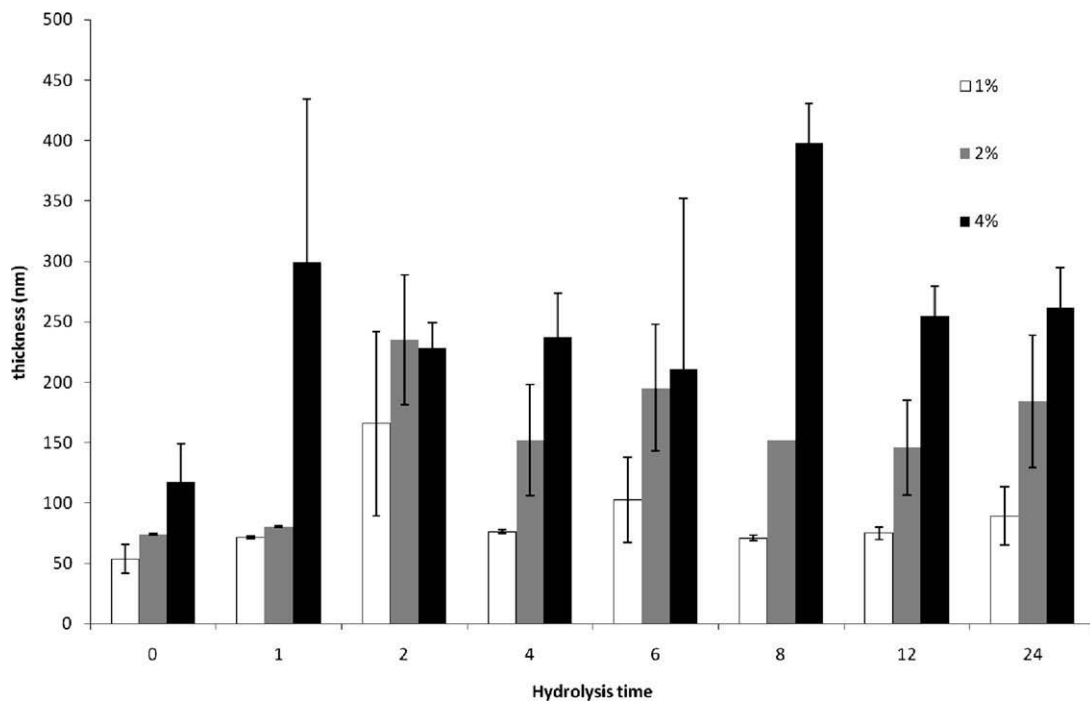


Fig. 9. Approximate film thicknesses for 1%, 2% and 4% MPTS solutions deposited on Mg alloy AZ91 at various pre-hydrolysis times.

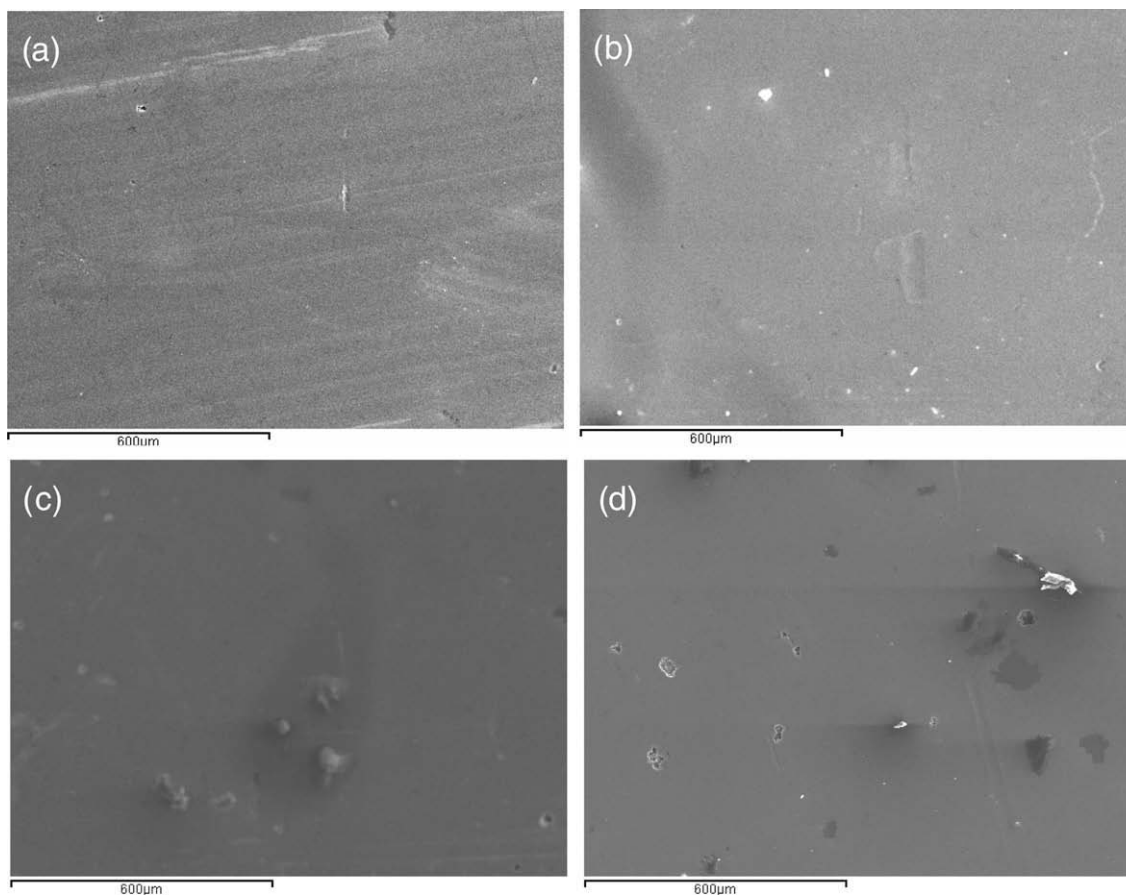


Fig. 10. SEM images of MPTS films: (a) 1% MPTS, 2 h pre-hydrolysis, (b) 4% MPTS, 2 h pre-hydrolysis, (c) 1% MPTS, 24 h pre-hydrolysis, and (d) 4% MPTS, 24 h pre-hydrolysis.

kely that unhydrolyzed molecules readily bond to the surface. Therefore, it is likely that the increased adsorption at the lower pre-hydrolysis times is due to increased physisorption at the high-

er concentration. As the pre-hydrolysis time increased beyond 2 h, an increase in adsorption was observed. This is similar to what was observed for the 1% and 2% solutions and has been previously

Table 3
Average atomic % silicon on MPTS coated magnesium alloy coupons.

Sample	Average atomic % silicon
1% MPTS, 2 h pre-hydrolysis	0.22 ± 0.28
4% MPTS, 2 h pre-hydrolysis	5.33 ± 7.50
1% MPTS, 24 h pre-hydrolysis	4.40 ± 8.65
4% MPTS, 24 h pre-hydrolysis	6.33 ± 2.35

attributed to an increase in both the availability of Si–OH groups for surface bonding and the formation of solution phase oligomers that deposit on the surface.

3.3.2. Determination of film thickness by ellipsometry

The thickness of the oxide/hydroxide layer on Mg alloy AZ91 was determined to be approximately 55 ± 5 nm by ellipsometry measurements. The approximate thicknesses of the MPTS films on Mg alloy AZ91 were also determined using ellipsometry. The results obtained are shown in Fig. 9 and are similar to those observed by ATR–FTIR. Shorter hydrolysis times resulted in thinner films that increased in thickness after a minimum hydrolysis time was reached. After this time, there was no statistically significant increase in film thickness. The overall thicknesses of the MPTS films also increased as the MPTS solution concentration increased. The error bars associated with this analysis are very large. This is due to variations in film thickness from sample to sample and from spot to spot indicating that the MPTS films produced via dip coating tend to be non-uniform.

3.3.3. SEM/EDS analysis

Fig. 10 shows SEM images for MPTS coated samples as a function of both solution concentration and pre-hydrolysis time. These images show that all of the films are relatively smooth. However, the films produced from solutions that had pre-hydrolyzed for 24 h in Fig. 10c and d had a few small bumps and dark regions. EDS analysis confirmed that there was significantly more silicon in the darker regions than on the rest of the sample. The average atomic % silicon for each sample is tabulated in Table 3. The average values were calculated from approximately 10 spots within the image field of view. The coating produced from the low concentration, low pre-hydrolysis time had very low levels of silicon indicating that the coating is very thin. The measured atomic % silicon for the rest of the samples is the same within error. In every case the error is very large. This is due to non-uniformity of the coatings. While silicon was consistently observed on these samples, the dark areas contained significantly more silicon than the lighter regions. This is mostly likely due to the presence of a few relatively large oligomers on the surface of the samples. The observed non-uniform film thickness is consistent with both the infrared and ellipsometry results obtained.

4. Conclusions

The purpose of this paper was to explore the influence of coating bath chemistry on the properties of 3-mercaptopropyltrimeth-

oxysilane films deposited on magnesium alloy surfaces. The main conclusions can be summarized as follows:

1. The most uniform MPTS coatings are obtained from a pH 4 coating bath. At this pH, a balance is struck between the availability of silanol (Si–OH) groups for surface bonding with minimal interference from solution phase oligomers.
2. Pre-hydrolysis of the coating bath is essential to promote condensation of MPTS with the magnesium alloy surface. This is important for producing MPTS films on magnesium alloys with optimum adhesion and corrosion resistance.

Acknowledgments

The authors gratefully acknowledge the financial support of the National Science and Engineering Research Council of Canada, the Canadian Foundation for Innovation and the Ontario Research Fund. We would also like to thank Dr. William Zhe for his assistance with the carbon coating of specimens for SEM/EDS analysis.

References

- [1] J.E. Gray, B. Luan, *Alloys Compd.* 336 (2003) 88.
- [2] R. Ambat, N.N. Aung, W. Zhou, *Corros. Sci.* 42 (2000) 1433.
- [3] G.L. Makar, J. Kruger, *Int. Mater. Rev.* 38 (1993) 138.
- [4] E. Ghali, W. Dietzel, K.U. Kainer, *J. Mater. Eng. Perform.* 13 (2004) 7.
- [5] G.L. Song, A. Atrens, *Adv. Eng. Mater.* 1 (1999) 11.
- [6] E. Ghali, W. Dietzel, K.U. Kainer, *J. Mater. Eng. Perform.* 13 (2004) 517.
- [7] Y. Song, D. Shan, E. Han, *Can. Metall. Quart.* 45 (2006) 215.
- [8] Y. Xiang, W. Hu, X. Liu, C. Zhou, W. Ding, *Trans. Inst. Met. Finish.* 79 (2001) 27.
- [9] Y. Xiang, W. Hu, X. Liu, C. Zhou, W. Ding, *Trans. Inst. Met. Finish.* 79 (2001) 30.
- [10] J.E. Gray, B. Luan, L. Huntington, *Appl. Surf. Sci.* 254 (2008) 2871.
- [11] F. Zucchi, V. Grassi, A. Frignani, C. Monticelli, G. Trabaneli, *Surf. Coat. Technol.* 200 (2006) 4136.
- [12] F. Zucchi, A. Frignani, V. Grassi, A. Balbo, G. Trabaneli, *Mater. Chem. Phys.* 110 (2008) 263.
- [13] M.F. Montemor, M.G.S. Ferreira, *Electrochim. Acta* 54 (2007) 7486.
- [14] M.F. Montemor, A.M. Simoes, M.J. Carmezim, *Appl. Surf. Sci.* 253 (2007) 6922.
- [15] J. Kim, K.C. Wong, P.C. Wong, S.A. Kulich, J.B. Metson, K.A.R. Mitchell, *Appl. Surf. Sci.* 253 (2007) 4197.
- [16] A. Scott, J.E. Gray-Munro, *Thin Solid Films* 517 (2009) 6809.
- [17] A. Franquet, H. Terryn, J. Vereecken, *Appl. Surf. Sci.* 211 (2003) 250.
- [18] D. Susac, X. Sun, K.A.R. Mitchell, *Appl. Surf. Sci.* 207 (2003) 40.
- [19] M. Yamaura, R.L. Camilo, L.C. Sampaio, M.A. Macedo, M. Nakamura, H.E. Toma, *J. Magn. Magn. Mater.* 279 (2004) 210.
- [20] P.E. Hinze, L.M. Calle, *Electrochim. Acta* 51 (2006) 1761.
- [21] P. Eaton, P. Holmes, J. Yarwood, *J. Appl. Polym. Sci.* 82 (2001) 2016.
- [22] R. Pena-Alonso, F. Rubio, J. Rubio, J.L. Oteo, *J. Mater. Sci.* 42 (2007) 595.
- [23] S.A. Torry, A. Campbell, A.V. Cunliffe, D.A. Tod, *Int. J. Adhes. Adhes.* 26 (2006) 40.
- [24] L. Guoli, X. Wang, A. Li, W. Wang, L. Zheng, *Surf. Coat. Technol.* 201 (2007) 9571.
- [25] M.L. Abel, R.D. Allington, R.P. Digby, N. Porritt, S.J. Shaw, J.F. Watts, *Int. J. Adhes. Adhes.* 26 (2006) 2.
- [26] M. Tsai, Y.D. Lee, K.N. Chen, *J. Appl. Polym. Sci.* 86 (2002) 468.
- [27] H. Jiang, Z. Zheng, X. Wang, *Vib. Spectr.* 46 (2008) 1.
- [28] J. Kim, P. Seidler, L.S. Wan, C. Fill, *J. Colloid Interf. Sci.* 329 (2009) 114.
- [29] B. Wu, G. Mao, K.Y. Ng, *Colloid Surf. A* 162 (1999) 203.
- [30] J. Song, W.J. Van Ooij, *J. Adhes. Sci. Technol.* 17 (2003) 2191.
- [31] M.C. Brochier Salon, P.A. Bayle, M. Abdelmouleh, S. Boufi, M.N. Belgacem, *Colloid Surf. A* 312 (2008) 83.
- [32] J. Zhang, J. Hoogboom, P.H.J. Kouwer, A.E. Rowan, T. Rasing, *J. Phys. Chem. C* 112 (2008) 20105.
- [33] A. Wang, H. Tang, T. Cao, S.O. Salley, K.Y. Simon, *J. Colloid Interf. Sci.* 291 (2005) 438.