Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thin Solid Films 513 (2006) 84 – 89
www.elsevier.com/locate/tsf

Dynamics and corrosion resistance of amine-cured organically modified silicate coatings on aluminum alloys

K.H. Wu [a],*, T.C. Chang [a], C.C. Yang [b], G.P. Wang [b]

[a] *Department of Applied Chemistry, Chung Cheng Institute of Technology, NDU Tahsi, Taoyuan 335, Taiwan*
[b] *Chemical Systems Research Division, Chung Shan Institute of Science and Technology, Taoyuan 325, Taiwan*

Received 16 May 2005; received in revised form 5 December 2005; accepted 13 January 2006
Available online 21 February 2006

Abstract

Hybrid coatings based on amine-cured organically modified silicate were synthesized through a sol–gel technique. 3-glycidoxypropyltrimethoxysilane tetraethylenepentamine, and tetraethoxysilane were used as precursors for the hybrid coatings. These Ormosil films were deposited via spin coating onto an aluminum alloy to improve the corrosion protection. The effects induced by the curing agent content of tetraethylenepentamine (TEPA) on the chain dynamics and corrosion performance of the coated samples were investigated. The Si–H polarization transfer relaxation times and the rotating-frame spin-lattice relaxation times indicated that the configuration of the Ormosil films was highly crosslinked and dense and adhered to the aluminum alloy substrates. Potentiodynamic evaluation revealed that the Ormosil films provided exceptional barrier and corrosion protection in comparison with untreated AA substrates.

Keywords: Alloys; Coatings; Corrosion; Electrochemistry; Nuclear magnetic resonance (NMR); Amines

1. Introduction

Organically modified silicates (Ormosils) are hybrid organic–inorganic materials formed through the hydrolysis and condensation of organically modified silanes with traditional alkoxide precursors. Ormosil materials have been investigated for the corrosion protection of aluminum alloy (AA) substrates [1–8]. Ormosil coatings exhibit increased flexibility and thickness in comparison with their inorganic counterparts. In general, these sol–gel derived coatings have been found to provide good corrosion resistance for metal substrates because of their barrier properties, tenacious adhesion to metal substrates, chemical inertness, versatility in coating formulations, and ease of application under ambient-temperature conditions. 3-Glycidoxypropyltrimethoxysilane (GPTMS) is one of the most important precursors [9–11] used for the preparation of organic–inorganic hybrids after sol–gel processing. This precursor is a combination of two different components, namely, glycidoxy (organic) and silicon alkoxy (inorganic) groups. Therefore, GPTMS has the ability to form simultaneously an organic network through the polymerization of glycidoxy groups and an inorganic SiO_2 network through the hydrolysis and subsequent condensation reactions of alkoxy groups.

Nuclear magnetic resonance (NMR) relaxation time measurements are sensitive to short-range interactions and can be used to estimate the scale of miscibility of an organic–inorganic hybrid. ^{29}Si and ^{13}C NMR can be expected to provide information on the motional dynamics and internuclear distances of a polymer. The relaxation properties and domain size of a polymer can be estimated from measurements of the Si–H polarization transfer relaxation time (T_{SiH}) and the rotating frame spin-lattice relaxation times ($T_{1\rho}^{H}$) [12–14]. In the literature a systematic spectroscopic (^{29}Si and ^{13}C NMR) investigation for the chain dynamics of the amine-cured GPTMS–tetraethoxysilane (TEOS) Ormosil coatings is lacking. The chain dynamics of the Ormosils provide important additional information for its use and applications as an anticorrosion coating. To understand the effect of the curing agent tetraethylenepentamine (TEPA) on the chain dynamics of the GPTMS–TEOS Ormosils, we have measured T_{SiH} and $T_{1\rho}^{H}$,

---

* Corresponding author. Tel.: +886 33891716; fax: +886 33808906.
E-mail address: khwu@ccit.edu.tw (K.H. Wu).

0040-6090/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2006.01.022

respectively. Additionally, electrochemical analysis has been used to investigate the relation between the relaxation behavior and corrosion resistance of the amine-cured GPTMS–TEOS Ormosils.

2. Experimental

2.1. Amine-cured GPTMS–TEOS Ormosil preparations

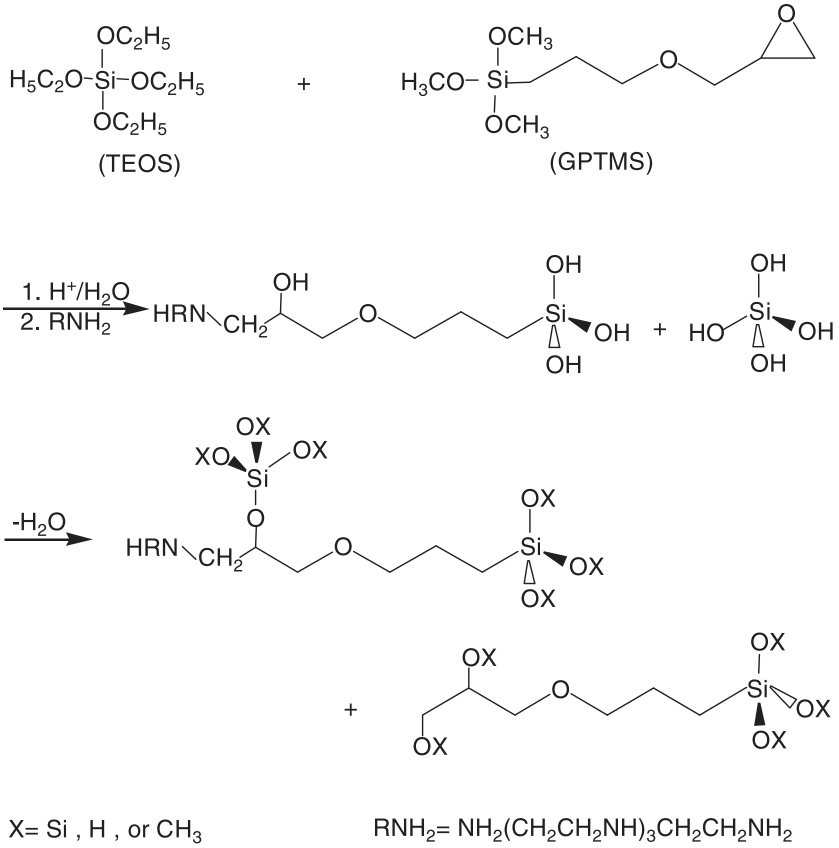
The amine-cured Ormosil hybrids were prepared as described in Scheme 1. An acid-catalyzed process with TEPA, GPTMS and TEOS as precursors prepared the Ormosil solution. The reagents were purchased from Aldrich chemicals and used as received. GPTMS and TEOS were placed in a beaker with 0.05 M HNO_3. The resultant two-phase solution was vigorously stirred to induce mixing and initiate hydrolysis. Ormosils were prepared containing 0.02 mol of TEOS to 0.09 mol of GPTMS. The total amount of hydrolysis water added was 6 mol (4 mol of TEOS + 3 mol of GPTMS). The sol was allowed to stir for 3 days before the addition of the curing agent. Five milliliters of 0.5 M TEPA was added per 10 mL of GPTMS–TEOS sol. After an additional 3 h of stirring, it was prepared for spin coating onto to precleaned 2024-T3 and 6061-T6 aluminum to form a film. Each single layer of the sol–gel film was spun onto the substrate at 1000 rpm for 30 s and this was repeated for three layers. Then, the coated films were allowed to dry under the ambient conditions for 24 h and dried under a furnace at 60 °C for 2 h, at 100 °C for 2 h and at 150 °C for 2 h.

2.2. Characterization of the hybrids

Amine-cured Ormosil hybrids were confirmed by Fourier transform infrared (FTIR) spectra (DA 3.002, Bomem) of samples prepared with the KBr pellet technique. The ^{13}C and ^{29}Si NMR spectra of the solid-state hybrids were determined (MSL-400, Bruker) with the cross-polarization/magic-angle spinning (CP/MAS) technique. The $^{1}H-^{29}Si$ spin contact time with the Hartmann−Hahn condition fulfilled in the rotating frame was typically about 5 ms, but was optimized in a range of 0.5−20 ms. The $T_{1\rho}^{H}$ values were measured with a ^{1}H spin-lock τ-pulse sequence followed by cross-polarization. The ^{1}H 90° pulse width was 4.5 μs, and the cross-polarization contact time was 2 ms. The delay time (τ) ranged from 0.2 to 20 ms for $T_{1\rho}^{H}$. The nomenclature of T^i and Q^i is taken from Glaser et al. [15]. T^i and Q^i denote, respectively, species that have one and no organic side group, where i refers to the number of −O–Si groups bounded to the silicon atom of interest.

2.3. Polarization measurements

Electrochemical measurements were performed with an EG&G 263A unit and a three-electrode cell equipped with a platinum electrode, a Ag/AgCl/Cl− reference electrode, and a



Scheme 1.