



Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

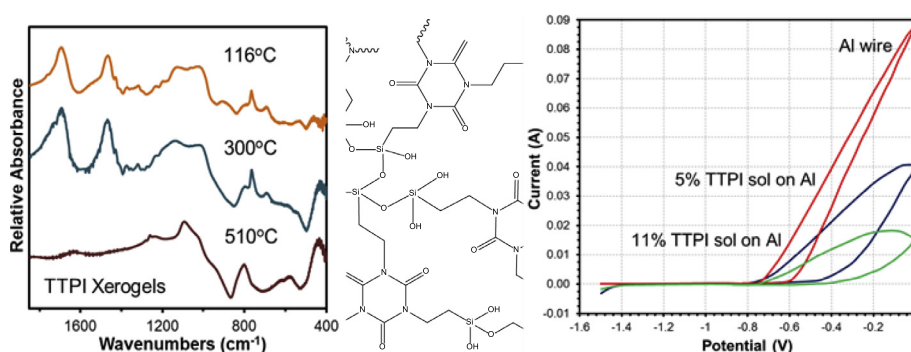
Infrared and Raman spectroscopic studies of tris-[3-(trimethoxysilyl)propyl] isocyanurate, its sol–gel process, and coating on aluminum and copper

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HIGHLIGHTS

- Sol–gels were prepared from tris-[3-(trimethoxysilyl)propyl] isocyanurate.
- Infrared and Raman spectral assignments suggest C₁ point group symmetry.
- At 450 °C the xerogels were found to decompose to silica.
- Coatings at high concentrations were found to protect Al and Cu from corrosion.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 18 February 2014

Received in revised form 17 April 2014

Accepted 23 April 2014

Available online 9 May 2014

Keywords:

Tris-[3-(trimethoxysilyl)propyl]

isocyanurate

Sol–gels

Xerogels

Vibrational spectra

Corrosion protection

Thermal decomposition

ABSTRACT

Tris-[3-(trimethoxysilyl)propyl] isocyanurate (TTPI) has been used as a precursor to prepare a sol using ethanol as the solvent under acidic conditions. The sol–gel was applied for the surface treatment of aluminum and copper. Infrared and Raman spectra have been recorded for pure TTPI and the TTPI sol, xerogel and TTPI sol–gel coated metals. From the vibrational spectra, TTPI is likely to have the C₁ point group. Vibrational assignments are suggested based on group frequencies, the expected reactions in the sol–gel process and the vibrational studies of some related molecules. From the experimental infrared spectra of xerogels annealed at different temperatures and from the thermal-gravimetric analysis, it is found that the TTPI xerogel decomposes at around 450 °C with silica being the major decomposition product. A cyclic voltammeter study of the metal electrodes coated with different concentrations of TTPI ranging from 5% to 42% (v/v) has shown that the films with high concentrations of sol would provide better corrosion protection for aluminum and copper.

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Introduction

Tris-[3-(trimethoxysilyl)propyl] isocyanurate (TTPI), a derivative of cyanuric acid, is an adhesion promoter and cross-linking agent because of its numerous methoxy groups which may easily

undergo hydrolysis in the presence of moisture or water to produce hydroxyl groups. Further reaction by condensation is expected to generate a polymer through the formation and linkage of Si–O–Si bonds. TTPI has been used for the direct conjugation of Pd nano-particles to single walled carbon nanotubes. There are many potential applications for this hybrid structure in the areas of catalysis, electronics and sensors [1].

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In the application of sol–gel coating for metal corrosion prevention [2–8], it is possible under favorable conditions for strong bonding to occur between the coating film and the metal surface. The presence of nine methoxy groups makes possible the production of numerous silica hydroxyl groups (SiOH) after hydrolysis. In coating the TTPI sol onto a metal surface, it is expected to have not only intra-condensation between the silanol groups but also inter-condensation between the silanol and any metal hydroxyl groups present. The former method of condensation is expected to improve the network of the coating film and provide better protection against metal corrosion. The formation of such a coating film helps prevent the metal from coming into direct contact with the corrosive medium. Inter-condensation will strengthen the adhesion of the silyl film on the metal surface. In the present study, we have prepared a TTPI sol under acidic condition. This sol was applied to aluminum and copper surfaces as a treatment for corrosion prevention. Using infrared (IR) and Raman spectroscopic methods, we have characterized the sol–gel process of TTPI and the sol–gel coating on aluminum and copper. Electrochemical methods have been applied to evaluate the anti-corrosion efficiency of the silyl film.

Experimental

Sample preparation

The sample of TTPI (technical grade) was obtained from Aldrich (Milwaukee, WI, USA) and used as received. The TTPI sol was prepared by mixing 0.5–10.0 mL of the silane coupling agent (SCA) with 10.0 mL absolute ethanol (Aaper, Shelbyville, KY, USA). 0.2–3.1 mL of 1 mM HCl solution was added drop-by-drop to the mixture while agitating with a magnetic stirrer. In the reaction mixture, alcohol was used as a homogenizer for the dispersion of TTPI, a viscous liquid with light-brown color. Hydrochloric acid was applied as a catalyst for the sol–gel process. The reaction was conducted at ambient temperature (24 °C). After the complete addition of the acid, the mixture was continuously stirred for 1 h in order to obtain a homogeneous solution.

Copper wire (99.9%), aluminum wire (99.999%), copper tile (99.9%) and aluminum tile (99.9%) were obtained from Alfa Sesar (Ward Hill, MA, USA). For the pre-treatment of metal wires (6 cm length and 1.5 mm diameter) and tiles (8 mm × 16 mm, 0.6 mm thick), the metal substrate was sanded with 3M (St. Paul, MN, USA) 600 grit sandpaper, rinsed generously with water, and ultra-sonicated for 15 min in an Alcojet (Fisher Scientific, Waltham, MA, USA) saturated detergent solution. The cleaned sample was rinsed with deionized water and ultra-sonicated in ethanol.

Sol–gel coating of the metal substrates was carried out by two methods, dip-coating and drop-coating. Dip-coating was carried out by immersing the pre-treated substrate in the sol for 2 min and then withdrawing the substrate from the sol at 2 cm/min. For drop-coatings, two drops of sol were applied onto the metal tile surface, and the tile was slightly tilted to make the sol evenly distribute on the surface. After the coated substrates were dried in ambient condition for 30 min, they were annealed in an oven for 3 h at different temperatures. For abbreviation, we designate the TTPI sol coated aluminum and copper by TTPI/Al and TTPI/Cu, respectively.

Spectroscopy

IR spectra were recorded using a Matson (Madison, WI, USA) Polaris FTIR spectrophotometer equipped with room temperature deuterated triglycine sulfate (DTGS) detector and WinFirst Spectroscopy software. IR spectra of liquid samples were collected in

transmission mode by using KBr (McCarthy, Fallbrook, CA, USA) as window material. In the IR spectral collections, a resolution of 2 cm⁻¹ and a total of 96 scans were applied for transmission. A 3M Type 61 disposable IR card (St. Paul, MN, USA) was also used for a time series and a temperature series study of the sol, in which a sol film was applied uniformly onto the card and transmission IR spectrum was collected. For collecting reflection absorption IR (RAIR) spectra of the coated metal tiles, a Harrick (Pleasantville, NY, USA) Seagull attachment was used. The total number of scans was set at 320 and the resolution was 4 cm⁻¹.

The far IR spectrum (650–100 cm⁻¹) of TTPI was obtained at a resolution of 4 cm⁻¹ using a liquid nitrogen boil-off purged, Perkin Elmer (Bucks, UK) System 2000 fitted with a wire grid beamsplitter and a DTGS detector fitted with a polyethylene window. A film of the sample was formed between two polyethylene windows and 2048 scans were co-averaged. The polyethylene windows were used as a reference.

Raman spectra were obtained from pure TTPI, sol, xerogels and sol–gel coated aluminum tiles at a resolution of 4 cm⁻¹ using a Bruker (Karlsruhe, Germany) RFS-100 FT-Raman spectrometer equipped with an Atlas Nd:YAG laser operating at 1064 nm and a liquid nitrogen cooled Germanium diode detector. The liquids and xerogels were held in glass capillaries. All liquid and solid samples were analyzed in 180° backscatter geometry. Data acquisition was carried out using Bruker OPUS software (version 3.1) by co-averaging 512 scans collected using a laser power of 300 mW. A Blackman–Harris 3-term apodization function was used.

Polarization measurements were carried out using the FT-Raman with the long axis of the capillary at 90° to the incident laser beam and the scattered radiation collected orthogonal to these. The polarization of the laser was rotated using a ½ wave plate and an analyzer was positioned after the collection optics for the scattered radiation. Spectra were obtained using the two unique optical arrangements by co-averaging 512 scans collected using a laser power of 300 mW.

Spectra could not be obtained from the sol–gel coated copper tiles using 1064 nm excitation. For these samples Raman spectra were obtained using a Renishaw (Gloucestershire, UK) inVia confocal microscope system with 514 nm excitation from a Modulaser Stellar Pro ML/150 argon ion laser through a 50× (0.75 na) objective. Incident laser power was 0.78 mW and coaxial backscatter geometry was employed. Spectra were collected over the range 3200–100 cm⁻¹ and averaged over at least 5 scans, each with an accumulation time of 10 s. The Raman shifts were calibrated using the 520 cm⁻¹ line of a silicon wafer. The spectral resolution was ~1 cm⁻¹.

Laser powers were measured at the samples using a Ophir Optronics (Israel) NOVA laser power meter fitted with a PD300-3W head. All data manipulation was carried out using Grams AI software.

Electrochemical measurements

All electrochemical measurements were conducted with a CH Instrument (Austin, TX, USA) Model 660A Electrochemical Workstation using 3% (w/w) NaCl as the electrolyte and a three-electrode configuration. In setting up the electrochemical experiments, Ag/AgCl with 3 M KCl was used as a reference electrode, a platinum wire as a counter electrode and either the metal (Al or Cu) wire or the sol–gel coated metal wire as a working electrode. All of the cyclic voltammogram (CV) measurements were carried out at room temperature in a Faraday cage. The CV curves for the Al wires were collected with an initial potential of -1.5 V and a highest potential of 0.0 V. For Cu wires, potential ranges of -1.3 to 0.2 or 0.6 V were used. The scan rate was 10 mV/s.

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