Progress in Organic Coatings 77 (2014) 1200–1207

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Nanoindentation and morphological analysis of novel green quasi-ceramic nanocoating materials

Atul Tiwari*, L.H. Hihara

Department of Mechanical Engineering, University of Hawaii at Manoa, Honolulu 96822, USA

ARTICLE INFO

Article history:
Received 25 September 2013
Received in revised form 20 March 2014
Accepted 24 March 2014
Available online 4 May 2014

Keywords:
Silicone
Titanium
Green coatings
Nanoindentation
Spectroscopy
Microscopy

ABSTRACT

The eco-friendly (green) silicone nanocoating compositions containing titanium nanoparticles were developed and tested for the changes in nanomechanical properties using the nanoindentation technique. Titanium-based nanoparticles were incorporated by two different methods. The nanocoating compositions were studied with the Fourier Transform Infrared spectroscopy (FTIR) and Raman spectroscopy. The surface morphology of the nanocoatings was studied with Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM). The nanomechanical properties of the nanocoatings were studied using the standard nanoindentation test method and the new substrate independent nanoindentation test method. The results obtained from the two test methods confirm the validity of the model used to develop the substrate independent nanoindentation test method. In brief, this study discusses the development of silicone based nanocoating materials and nanomechanical properties of green nanocoatings containing two different types of nanoparticles, evaluated using two different test methods.

Published by Elsevier B.V.

1. Introduction

Thin solid coatings can be developed on the substrate through sol–gel reactions. Such developments often involve the hydrolysis and condensation reactions that occur in metal-alkoxy compounds. When using alkoxysilanes, a product known as ORMOSIL (organically modified silicates) finds wide industrial applications including coatings [1–3]. The thickness and density of the coatings that are applied using sol–gel reaction could be controlled as per the requirement of the application. The use of a large amount of hydrocarbon in the coating formulation results in a semi-porous network, while the use of a large inorganic constituent generates dense network with brittle behavior. Thin and impervious coatings could be effectively developed using the sol–gel technique; however, such coatings lose integrity at the onset of scratches.

The incorporation of nanoparticles to enhance the desired attributes in a material has been well documented in the literature and is a common practice in the industry. The amount of nanoparticles in a continuous matrix influences the properties of the material. The molecular packing arrangement is also affected by the aggregation of foreign moieties in the continuous matrix. In some cases the agglomeration of foreign nanoparticles degenerates the basic properties of the material (e.g., generation of defects, cavities or free volume), while in other cases, the minor agglomeration may contribute to the enhancement of properties (e.g., increase in abrasion resistance).

The mechanical properties of self-supporting films, coatings and polymer matrices can be evaluated using conventional mechanical testing techniques. However, the coatings that are deposited or applied over the metal surface need to be tested using nanoindentation techniques. The modulus (E) and hardness (H) values obtained from nanoindentation techniques are often influenced by the substrate. The H value is dramatically affected because the value is calculated from the fully developed plastic zone that may extend into the substrate [4]. Similarly, elastic deflection both from the film and the substrate contributes to the final E value. Several analytical models have been proposed to determine the properties of materials alone, where the substrate effect has been negated. However, most of these models consist of parameters that need to be determined empirically. Recently Hay and Crawford's [5] model—which requires simple parameters such as approximate thickness of the film, Young's modulus value (E) of the substrate and Poisson's ratio of the film and substrate—has gained significant attention.

1.1. Model studies in nanoindentation analysis

If the film/coating on the substrate is sufficiently thick, it can be treated as a bulk material and typically analyzed using Oliver–Pharr method [6]. To overcome the weakness in previous

* Corresponding author. Tel.: +1 808 956 2365; fax: +1 808 956 2373.
E-mail addresses: tiwari@hawaii.edu (A. Tiwari), hihara@hawaii.edu (L.H. Hihara).

http://dx.doi.org/10.1016/j.porgcoat.2014.03.022
0300-9440/Published by Elsevier B.V.

models, Gao et al. [7] proposed another approximate model without any adjustable parameters. Their model contained two weighing functions I_0 and I_1 necessary to control the transition in elastic properties from film/coating to the substrate. Similarly, Song [8] picked the model proposed by Gao et al. and derived another alternate solution that lead to a better response from the composite material (i.e., combined effect from film and substrate) in case, if the film/coating is more compliant compared to substrate.

1.2. Substrate independent nanoindentation: Hay–Crawford model

The nanomechanical properties derived using Oliver–Pharr model is often influenced by the substrate effect. In order to minimize the substrate effect, the values are often extracted from the 1/10th of the film/coating surface. It is worth noting that for very thin films this 10% rule is not effective. However, these values are not a true representation of the values from the bulk of the material. Recently, Hay and Crawford [5] proposed a model that can accurately predict the intrinsic properties of the bulk material provided that properties of the substrate are known. Their model is based on Song-Pharr and Gao (S-P & G) model that assumes that material under the indenter tip can be treated as a column (Fig. 1a). The film and substrate within the column are treated as two springs connected in series. This S-P & G model resulted into apparent shear modulus (μ_a) related to the shear modulus of the film (μ_f) and that of the substrate (μ_s) by the expression showing in Eq. (1)

$$\frac{1}{\mu_a} = (1 - I_0)\frac{1}{\mu_s} + I_0\frac{1}{\mu_f} \quad (1)$$

where I_0 is weighting function derived by Gao et al. [7] that represents the ratio of the strain energy stored in the film region to the total strain energy stored in the half space. Hay and Crawford improved the S-P & G model by assuming that film can also act as a spring in parallel with the substrate (Fig. 1b). Based on this assumption, they proposed a model shown in Eq. (2).

$$\frac{1}{\mu_a} = (1 - I_0)\frac{1}{\mu_s + FI_0\mu_f} + I_0\frac{1}{\mu_f} \quad (2)$$

where F is a dimensionless empirical constant. The Young's modulus of the film is calculated by solving the Eq. (3) for shear modulus and related with Poisson's ratio as in Eq. (3).

$$E_f = 2\mu_f(1 + \nu_f) \quad (3)$$

In our previous studies, we demonstrated that changing the amount of organic and inorganic components in the material's composition in turn changes the nanomechanical properties of the hybrid materials [9]. In this study, we have investigated how the incorporation of titanium nanoparticles through two different routes affects the nanomechanical properties and morphology of the novel green quasi-ceramic coating materials.

2. Materials and methods

2.1. Materials

The following chemicals were procured for the synthesis of the green quasi-ceramic coatings: methyltriacetoxysilane (purity 95%), methyltrimethoxysilane (purity 98%), and tetramethoxysilane (purity 97%) purchased from Gelest; dibutyltindilaurate catalyst (purity 95%) purchased from Alfa-Aesar; isopropanol (ACS grade); diethylether (ACS grade) purchased from Sigma–Aldrich, USA; and sodium bicarbonate purchased from Merck. Titanium dioxide (anatase) and titanium ethoxide were purchased from Alfa Aesar. All of the chemicals were analytical grade as quoted by the manufacturer. Ultrapure water of 18 MΩ cm resistivity was also used in this study.

2.2. Methods

2.2.1. Development of nanocoating materials

The green quasi-ceramic coating was prepared by following a patented method briefly described here [10]. A mixture of silanes was prepared by reacting calculated quantities of methyltriacetoxysilane, methyltrimethoxysilane, and tetramethoxysilane to a reactor vessel followed by sonication and an addtion of isopropanol. In a second reactor, a calculated quantity of sodium bicarbonate was dissolved in a known volume of water. The water was constantly stirred while sodium salt was added and then stirred every 2 h. The content of the second reactor was added to the content of the first and then sonicated for 30 min. A known quantity of isopropanol, diethylether, and dibutyltindilaurate were mixed separatly in a reaction vessel and added to the solution obatined in the above steps. The entire solution was left for 30 min in ambient conditions before using it as a green coating precursor material (SAnTi).

In order to prepare the nanocoatings, the calculated quantities (i.e., 0.1 wt.% of solid content of SAnTi) of TiO_2 nanoparticles and $Ti(OC_2H_5)_4$ were sonicated in 1 ml isopropanol for 24 h to 7 days. A 10 ml of SAnTi solution was then added to the suspensions of each nanoparticles and sonicated. The composition containing TiO_2 was termed as $SATiO_2$ and other containing $Ti(OC_2H_5)_4$ was termed as SATiOH.

2.2.2. Specimen preparation and coating application

The Al6061-T6 specimens were cut into 1 cm × 1 cm and adhered to circular aluminum stubs using thermoplastic polymer. The specimens were then polished using 0.05 μm aluminum oxide agglomerate solution and dried. The sonicated solutions of coatings were applied to the polished aluminum specimens by spray coating technique and dried in ambient conditions (~25 °C) for 48 h after which they were heated at 37 °C for 48 h. The coated specimens were left in ambient condition for 30 days before their nanomechanical properties were tested. The average thickness of the coating was approximately 2.4 μm as determined by looking into the cross-section of the coated sample under scanning electron microscopy technique.

2.2.3. Fourier transform infrared spectroscopy and Raman spectroscopic analysis of coatings

The Fourier transform infrared spectroscopy (FTIR) spectroscopy on solid coatings applied on aluminum was conducted using a Thermo Electron Nicolet Nexus 760 instrument attached to a continuum microscope. The spectra were continuously recorded for 240 min in a reflectance mode under the microscope to monitor the kinetics of the reaction species formed during various phases of the conversion/curing process. The spectra were analyzed using Thermo Electron's Omnic and Series software. A minimum of 34 scans with a resolution of 4 cm^{-1} of the specimen was employed for each spectrum. A blank background spectrum was collected prior to collecting a spectrum of the sample.

2.2.4. Nanoindentation analysis of coatings

The nanomechanical analysis was conducted on an MTS Nanoindenter XP with a Berkovich diamond tip. The H and E were measured using the continuous stiffness measurement option [11]. Fused silica was used as a standard calibration sample. The experimental data was acquired with the help of TestWork 4 software from MTS instruments. The TestWork software exported the raw data files to the MS Excel software. The Excel data sheets were then imported on Analyst software from the MTS instrument for