



## Thermal stability and thermokinetics studies on silicone ceramer coatings: Part 1-inert atmosphere parameters

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### ARTICLE INFO

#### Article history:

Received 12 October 2008

Received in revised form

11 June 2009

Accepted 12 June 2009

Available online 21 June 2009

#### Keywords:

Silicone coatings

FTIR spectroscopy

Thermokinetics

Thermogravimetry

Differential thermal analysis

### ABSTRACT

Two silicone ceramer coatings were synthesized and studied according to their thermal stability, using Fourier Transformation Infra-red (FTIR) spectroscopy. Differential thermal analysis was conducted on a liquid precursor to the coatings to study the phase transformations occurring in the material as the temperature was altered. The kinetics of the thermal degradation of coatings was analyzed; and the corresponding thermokinetics parameters were determined using Friedman's method, the Flynn-Wall-Ozawa method and the American standard test method E698. A thermogravimetric analysis was conducted on the liquid precursors as well as on the solidified coatings at various heating rates. The gaseous products that were obtained as a result of pyrolysis were analyzed employing an attached FTIR spectrometer.

Published by Elsevier Ltd.

## 1. Introduction

### 1.1. Scope of the work

The hazardous nature of hexavalent chromium has restricted its use in under coatings as a corrosion inhibitor due to regulations imposed by the Environmental Protection Agency (EPA) [1]. Therefore, alternative under coatings are needed to replace the hexavalent chromium systems. Organic polymer-based coatings would generally not be reliable for long-term corrosion protection due to the disordered packing arrangement in the macromolecular architecture, which provides paths for the ingress of water and corrosive ions. The hybridization of inorganic constituents with organic polymer coatings, however, could reduce the extent of the disordered packing structure in the coating network, and improve barrier properties. These hybrid inorganic-organic materials are known as ceramers, and their properties are dependent on the type of structure present in the ceramer backbone. For silicate-based materials, the ceramers are also referred to as ormosils.

The stability of ceramer coatings can be assessed by studying the breakdown properties during elevated-temperature excursions. As temperatures are increased, degradation occurs by the breakup of chemical linkages or bonds. Coatings that resist degradation at higher temperatures have greater stability. In this study, two

promising ceramer coatings [2] for the use as corrosion barriers were investigated. In the literature, few attempts have been made to monitor the cure profile of precursors as well as the degradation mechanism of the cured coatings. This article reports thermal studies conducted on the liquid precursor and as well as cured coatings using simultaneous TGA-FTIR analysis. The thermokinetics for the degradation of the ceramer coatings was analyzed.

### 1.2. Background

Multiple researchers have demonstrated the importance of studying the thermal stability of polymers, ceramics and ceramers. Wang et al. [3] studied thermal degradation and fire resistance of nanocomposite coating. They found that a uniform distribution of nano-SiO<sub>2</sub> enhances the thermal stability of the acrylic nanocomposite coating, while an agglomeration of these nanoparticles in the polymer can deteriorate the properties of these coatings. They also discovered that the formation of the Si–O–Si network by evenly distributed nano-SiO<sub>2</sub> tends to contribute to the anti-oxidation process, char-accumulation and stable char architecture.

Zaharescu et al. [4] reported on the thermal stability of methyltriethoxysilane and tetraethoxysilane-based hybrid material. Using derivative thermogravimetry (DTG) and mass spectroscopy, they found that as the amount of tetraethoxysilane in the composition increases the decomposition temperature of Si–CH<sub>3</sub> increases. This finding suggests that a dense inorganic network hinders the out-diffusion of decomposed products and thereby increases the overall thermal stability of the material.

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Chiang et al. [5] prepared an organic-inorganic hybrid containing nitrogen, phosphorous and silicon in epoxy resin. They compared their hybrid system with pure epoxy resin and found that the residue obtained after the complete decomposition was higher in hybrid materials due to the synergistic effect from the nitrogen, phosphorous and silicon in the system. Also, the activation energy from the decomposition of the hybrid material was higher than that of the pure epoxy, proving the higher thermal stability of the hybrid material as compared to the pure organic polymer.

Dobkowski et al. [6] investigated the thermal properties of a polysiloxane-poly(tetrafluoroethylene) semi-interpenetrating coating system using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) techniques. They found that thermal stability of the coating system increases with the increase in the poly(tetrafluoroethylene) content. They also found a single glass transition temperature ( $T_g$ ) for their compositions, suggesting that their blends were in single phase. Also, they observed transitions corresponding to semi-IPN network. Stefanescu et al. [7] studied the interaction between tetraethoxysilane and polyols using thermal analysis, Fourier transformation infra-red (FTIR) spectroscopy and solid-state nuclear magnetic resonance (NMR) spectroscopy. Their thermal analysis demonstrated that the polyols were bound to the silica matrix through chemical as well as hydrogen bonding.

Parra et al. [8] reported the thermal behavior of epoxy-polyester powder coating containing  $YiO_2$  and  $SiO_2$  particles. Using the TG/DTA-GC/MS technique, they found benzene and phenol as a result of thermal decomposition. Also, the thermal stability of the cured coating was higher than that of the individual resin. They suggested that the reticulation of resin chains was responsible for the higher thermal stability of coatings than that of their parent compounds.

Wu et al. [9] reported on the thermal stability and corrosion resistance of hybrid coating prepared by reacting 3-glycidoxypropyltrimethoxysilane and amino-terminated siloxane with tetraethoxysilane. They used FTIR and  $^{29}Si$  solid-state NMR to characterize the different forms of silicone in the coating structure. Deconvolution of the DTG curve showed four step decomposition pattern under a nitrogen atmosphere. The thermal stability and energy of the activation required for the decomposition of 3-glycidoxypropyltrimethoxysilane-tetraethoxysilane hybrid was higher than that required for polydimethylsiloxane-tetraethoxysilane hybrid. This finding suggests that the degradation of aliphatic *n*-propyl segment was enhanced by the higher thermal conductivity of silica.

Zhang et al. [10] conducted TGA on an organic/inorganic hybrid of a  $SiO_2$ -matrix composite prepared through a sol-gel process utilizing tetramethoxysilane and tetraethoxysilane as a precursor. They found that the thermal stability of the hybrid material is enhanced by the presence of tetramethoxysilane. A pure silica network was detected due to the thermal degradation and evaporation of the incorporated organic groups above 500 °C.

Sun et al. [11] have studied the thermal degradation kinetics of the methacryloyl group containing poly(methylphenylsiloxane) using TGA. Friedman, Flynn-Wall-Ozawa, Coats-Redfern and Phadnis-Deshpande methods were used to study the kinetics of degradation. They found that the first stage of poly(methylphenylsiloxane) material followed a three-dimensional diffusion mechanism, while the second degradation stage followed a nucleation and growth mechanism.

## 2. Experimental

### 2.1. Materials

Tetraethoxysilane (Sigma Aldrich); 1, 6-hexanediamine (Across Organics);  $\gamma$ -glycidoxypropyltrimethoxysilane (Alfa Aesar); 3-aminopropyltrimethoxysilane (Avocado Research Chemicals Ltd); phenyltrimethoxysilane ( $C_6H_5-Si(OCH_3)_3$ ) marketed as Z-6124 silane

(Dow Corning); 2-(3,4-epoxycyclohexyl)ethyl-trimethoxysilane (Sigma Aldrich); dibutyltindilurate (Sigma Aldrich); zincacetate (Merck); 90% denaturated ethanol with 5% methanol and 5% isopropanol (Alfa Aesar) were used in the synthesis of the ceramer coatings. All of the chemicals were analytical grade as quoted by the manufacturers; hence, they did not undergo further purification. Ultrapure water with a resistivity of 18 M $\Omega$  cm was used in this study.

### 2.2. Sol preparation

Various compositions of coating formulation were prepared and named as Coat3 and Coat5 (see Ref. [2]).

Formulation of Coat3 was obtained following the reaction route shown in Fig. 1. In this case, 2.21 ml of  $\gamma$ -glycidoxypropyltrimethoxysilane and 0.55 ml of tetraethoxysilane were added to 5 ml ethanol. This chemical mixture was termed as Product-A. Solution obtained was sonicated for approximately 30 min. In another reaction vessel, 0.05 g of hexamethylenediamine and 0.43 ml of 3-aminopropyltrimethoxysilane were added to 5 ml ethanol. Solution was sonicated for approximately 30 min. This chemical mixture was termed as Product-B. Solutions of Product-A and Product-B were mixed together and sonicated for approximately 30 min. The Product-C so obtained was charged with 60  $\mu$ l of dibutyltindilurate and 1 ml of ultrapure water. Finally, the solution was sonicated for additional 1 h and left overnight. Expected mechanism at different stages of the reaction (similar to that proposed elsewhere [12–15]) is shown as Scheme 1 while FTIR spectra are shown in Fig. 2.

Formulation of Coat5 was achieved by following the synthetic route shown in Fig. 1. In this case 2.31 ml of 2-(3,4-epoxycyclohexyl)trimethoxysilane, 1 ml of phenyltrimethoxysilane (Z-silane) and 2.23 ml of tetramethoxysilane were added to 5 ml ethanol. Solution obtained was sonicated for 30 min and termed as Product-A. In another reaction vessel, 1.16 g of solid hexamethylenediamine was added to 5 ml of ethanol and sonicated for 15 min to ensure proper dissolution. This chemical mixture was then added to the Product-A and sonicated for 30 min to get Product-B. In a separate reaction vessel, 0.05 g of zincacetate, 1 ml of 1 wt.% carbon nanotube suspension in ethanol and 1 ml of 5 wt.% Nanosil<sup>®</sup> silica nanoparticle suspension in ethanol and 1 ml of ultrapure water were mixed together. This solution mixture was then added to the Product-B and sonicated for 30 min to result into Product-C. The Product-C so obtained was charged with 60  $\mu$ l of dibutyltindilurate catalyst. Finally, the solution was sonicated for additional 1 h and left overnight. Expected mechanism at different stages of the reaction (similar to that proposed elsewhere [12–15]) is shown as Scheme 2 while FTIR spectra are shown in Fig. 2.

The coating liquid precursors were hardened at an ambient temperature for the determination of their thermal properties. Two coatings are synthesized for different applications. Coat3 acts as a topcoat material for another coating while Coat5 consists of nano-fillers for the better scratch resistance properties. Both the coatings have similar chemical components, but Coat5 has less amine and higher hydrocarbon portion to hold the nano-fillers. Although the chemical entities in the coatings are similar, the different quantities of organic portion as well as inorganic fillers change the final chemistry and therefore the degradation pattern of the materials. Since it was difficult to study the final chemical structure of the coating, monitoring the thermal degradation pattern was expected to better elucidate the inherent structural features in the solidified coatings.

### 2.3. Thermogravimetric analysis

TGA was performed on two different instruments. The coating liquid precursors were analyzed with a TA instrument model

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