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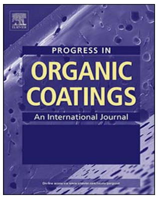

Short communication

Spectroscopic characterization of covalently constrained hybrid coating clusters prepared by Michael Addition and Ring opening mechanism

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ABSTRACT

The influence of the reaction time on hydrolysis and condensation reaction of sol–gel hybrid coatings prepared by Michael Addition and Rings Opening Mechanism was evaluated by Raman spectroscopy, FTIR (Fourier-transform infrared spectroscopy) and electron microscopy. The results of the Raman and TEM (Transmission electron microscopy) analysis revealed that HYBRID I is more beneficial than HYBRID II for the preparation of symmetric and uniform cross-linked sol–gel coatings. Extensive studies reveal fundamental differences during the nucleation phase of hybrid material formation that is directly dependent on the symmetric nature of the coating materials. The higher symmetric structure enables the convenient preparation of hybrid coatings with improved morphological.

1. Introduction

Sol-gel is a well-known process for preparing organic-inorganic hybrid materials [1–4]. It comprises the growth of inorganic networks through the formation of a colloidal suspension (sol). The siloxane network structure is formed by converting of sol phase to a continuous gel phase. Organofunctional alkoxy silane is hydrolyzed to form an interpenetrating and cross-linked network structures with improved properties has been well known [3,4]. Succeeding hydrolysis reaction, a reactive silanol group is formed, which can condense with other silanol groups to form siloxane linkages. Stable condensation products are also formed with other oxides such as those of aluminum, zirconium, tin, titanium, and nickel. The TMSPM, APTMS and GLYMO sol-gel precursors have potential for the preparation of anticorrosion coatings similarity with tretraethoxysilane (TEOS) [5–8], tetramethoxysilane (TMOS) [9] and 1,2-bis(triethoxysilyl)ethane (BTSE) [10] TMSPM, APTES and GLYMO, can form covalent bonds on both sides of the precursor molecule. The hydrolysable trimethoxysilyl and triethoxysilane groups on one side of GLYMO, TMSPM and APTES, after hydrolysis to silanol groups, can react among themselves and in addition with the hydroxylated metal surface for formation of covalent Al—O—Si bonds on aluminum alloys [11]. On the other side of the GLYMO and TMSPM molecule, amine compounds can open and react with the epoxy ring and conjugated double bond under catalysed [12–15] and even in uncatalysed [16–18] conditions. The curing of GLYMO with various amines is well-known and has been studied for various systems [2,5,8,11,14,16]. Atul Tiwari et.al. [19], studied the development of low-temperature hardening silicone ceramer coatings for the corrosion protection of metals. R. Zandi-zand et.al. [20], have developed organic–inorganic hybrid coatings based on sol–gel process for corrosion protection of 1050 aluminum alloys by dip coatings technique. There have been more attempts to use 3-Trimethoxysilylpropyl diethylenetriamine (TEDATE), TMSPM, APTES and GLYMO species in anticorrosion coatings, either as precursors for the preparation of pure hybrid coating or as additives or curing agents. In this work, 3-Trimethoxysilylpropyl diethylenetriamine (TEDATE) was used as an triamine-bearing compound to open and cure the GLYMO ring and also process Michael addition reaction with TMSPM (**Supplementary Information: Scheme S1, S2, S3 and S4**). **Scheme S2** and **Scheme S4** represent the condensation reaction of HYBRID I and HYBRID II. Here, we present the results of an investigation into how the reaction time influences the hydrolysis and condensation reaction of sol–gel coatings based on TMSPM and GLYMO precursors. The conditions of hydrolysis and condensation of HYBRID I and HYBRID II coatings were determined by Raman spectroscopic, FTIR and TEM measurements. As a catalyst, boron trifluoride diethyl etherate ($BF_3 \cdot O(C_2H_5)_2$; $Mw = 141.93\ g\ mol^{-1}$) was used with (0.05 wt%) based on the weight of TMSPM and GPTMS. TEM techniques were also employed for the determination of particle size of the hybrid coatings during the hydrolysis and condensation reaction. Scheme 1 represents the reaction setup, hydrolysis and condensation product of HYBRID I and HYBRID II and hydrolysis and condensation reaction structure of HYBRID I. Scheme 2 shows the reaction mechanism of HYBRID I and HYBRID II coating materials.

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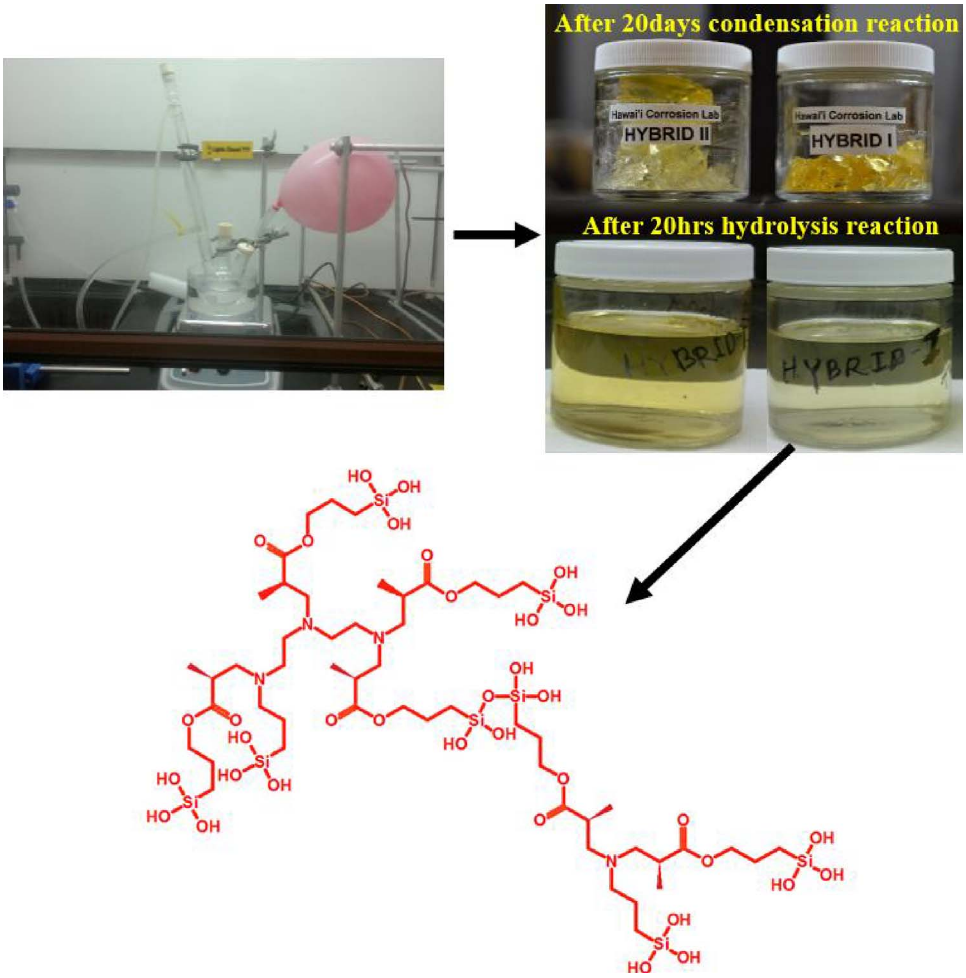

Scheme 1. Systematic designed reaction setup, hydrolysis and condensation product of HYBRID I and HYBRID II and representative hydrolysis and condensation reaction structure of HYBRID I.

2. Results and discussion

2.1. FTIR analysis

The hydrolysis and condensation reaction study of HYBRID 1 and HYBRID II in the spectral range 4000–400 cm^{-1} is shown in Fig. 1**(a)** and **(b)**. The results revealed that the methoxy (—Si—OMe) bands at 838 cm^{-1} disappeared from the spectra after only 10 h in case of HYBRID I, while they were extinguished after 15 h in HYBRID II. However, with the disappearance of the Si—OMe bands, an increase in intensity of the peaks at 935 cm^{-1} (Si—OH) [21,22] and 3625 cm^{-1} (O—H stretching) confirms the hydrolysis reaction was taken place in the HYBRID 1 and HYBRID II. The —Si—OMe remained in the FTIR spectra measured up to 10 h but gradually decreased in intensity with time. In addition, the gradual formation of a band at 1070 cm^{-1} [22] indicated that condensation started exactly after hydrolysis, leading to the formation of a silsesquioxanes (Si—O—Si) sol–gel network.

The more significant peaks are attributed to structural backbone of HYBRID I after 24 h hydrolysis reaction are reported in **Fig. S1(a)**. Major groups such as hydroxyl, ester carbonyl, methyl, methylene, siloxane, silanol are centered at 3400 cm^{-1} (O—H stretching), 1600–1800 cm^{-1} (ester carbonyl stretching), 2800–3000 cm^{-1} (methyl and methylene), 910–940 cm^{-1} (Si—OH), and 1000–1200 cm^{-1} (Si—O—Si stretching), respectively. **Fig. S1(b)** shows the FTIR spectra of HYBRID II after 24 h hydrolysis and condensation reaction. The characteristic bands of the HYBRID II are CH_2 symmetric and anti-symmetric stretching vibrations (2800–3000 cm^{-1}), antisymmetric ν_{as} (CH_3) and symmetric ν_s (CH_3) stretching of methyl groups (2800–3000 cm^{-1}), C—N stretching (1500–1589 cm^{-1}), CH_2 scissoring, CH_3 deformation and CH_2 bending (1450–1461 cm^{-1}), stretching and rocking vibrations of the C—C and CH_2 groups (1000–1030 cm^{-1}), C—O stretch + CH_2 rocking (855 cm^{-1}), and Si—O—Si symmetric and anti-symmetric stretching vibrations (1000–1200 cm^{-1}), respectively [23,24]. The structural backbone of HYBRID I has higher Si—O—Si stretching vibration centered at 1000–1200 cm^{-1} due to the hydrolysis and condensation of the alkoxy silane groups leading to much more Si—O—Si bonds.

2.2. Raman analysis

Raman spectroscopy was used to obtain an insight into the course of hydrolysis and condensation in hybrid coatings (Fig. 2**(a)** and **(b)**). Moreover, it is important to determine their stability and the possibility of preparing anticorrosion coatings with reproducible structural properties. Fig. 2**(a)** and **(b)** shows the Raman spectra of HYBRID I and HYBRID II after different hydrolysis and condensation time in the spectral range 3500–100 cm^{-1}. The spectra exhibited the disappearance of the symmetric ν_s (Si—OMe) and asymmetric ν_{as} (Si—OMe) bands at 644 and 614 cm^{-1} after 15 h. This indicated the beneficial influence of molar ratio of H_2O: $BF_3{\cdot}O(Et)_2$: Si—OMe, in which one water molecule for every methoxy group was present in the sol. The disappearance of the ν(Si—OMe) bands, the symmetric $\nu(CH_3)$ stretching band at 2843 cm^{-1} [17] also decreased in intensity. This indicates the hydrolysis of the methoxy groups of TEDATE, APTMS and TMSPM. A band of methanol that formed after the hydrolysis of methoxy group was noticed at 1032 cm^{-1} [16] and the intensity increased with increasing time. The intensity of methanol band became more pronounced after 15 h. This could be due to the condensation