Journal of Colloid and Interface Science 513 (2018) 617–628

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

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

Regular Article

Structure and properties of epoxy-siloxane-silica nanocomposite coatings for corrosion protection

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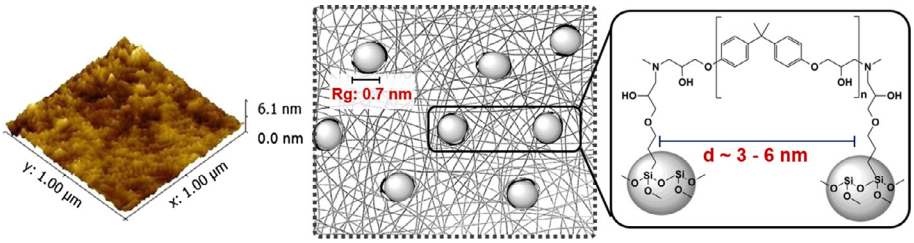
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 August 2017
Revised 22 November 2017
Accepted 23 November 2017
Available online 24 November 2017

Keywords:
Sol-gel process
Organic-inorganic hybrid
Structural properties
Multifunctional coatings
Corrosion protection

ABSTRACT

Hypothesis: The fraction of the silica/siloxane phase is a crucial parameter, which determines the structure and thus the properties of epoxy-siloxane-silica hybrid coatings. A careful adjustment of the colloidal precursor formulation allows tuning the nanostructure towards a highly condensed and cross-linked hybrid nanocomposite, suitable as an efficient anticorrosive coating.

Experiments: Novel epoxy-siloxane-silica hybrids have been prepared through the curing reaction of poly (bisphenol A-co-epichlorohydrin) (DGEBA) with diethyltriamine (DETA) and (3-glycidoxypropyl)methyl triethoxysilane (GPTMS), followed by hydrolytic condensation of tetraethoxysilane (TEOS) and GPTMS. At a constant proportion of the organic phase, the effects of the varying molar proportions of siloxane (GPTMS) and silica (TEOS) on the film properties have been investigated.

Findings: A detailed structural analysis suggests for intermediate TEOS to GPTMS ratios a structure of highly condensed silica-siloxane domains covalently bonded to the embedding epoxy phase. The homogeneous distribution of the quasi-spherical sub-nonmetric silica-siloxane nodes is in agreement with low surface roughness (<5 nm), observed by atomic force microscopy. This dense nanostructure results in high thermal stability (>300 °C), strong adhesion to steel substrate and excellent barrier property in saline solution, with corrosion resistance in the GΩ cm^2 range.

1. Introduction

Organic-inorganic hybrids belong to the class of nanocomposite materials, which combine two or more phases with at least one component on the nanometric length scale. Consequently, the properties of the hybrid material are not simply the sum of the contributions of each phase, but depending on the nature and type of interphase bonding, result in new materials with unique

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https://doi.org/10.1016/j.jcis.2017.11.069
0021-9797/

characteristics. The nature of interphase interactions determines the type of the hybrid material. In the presence of weak interaction between the organic and the inorganic phases, such as van der Walls, ionic or hydrogen bond, the hybrid material is classified as type I, while in the case of covalent bonding the hybrid is known as type II [1]. Among the different methods to synthesize organic-inorganic hybrids, such as solution and melt blending or high-energy ball milling [2], the sol-gel process has several advantages. This is due to the mild conditions of the synthesis, homogeneous dispersion of constituents forming the colloidal solution and the possibility of combining a large number of precursors reagents at different proportions. The possibility to create a variety of new synthetic materials opens a large space for deepening the knowledge of the phenomena and mechanisms involved in the formation of hybrid networks from colloidal solutions, and this in turn allows designing and optimizing the structural properties for specific applications. Consequently, the conjugation of ceramic and polymeric phases results in multifunctional materials with interesting optical, thermal, mechanical and barrier properties, allowing a wealth of applications such as drug delivery systems, optoelectronic devices, catalysts, photochromic devices, transparent insulating films, anticorrosive coating systems, among others [1]. Concerning the latter appliance, one of the main industrial challenges is the reduction of reposition costs resulting from the corrosion of metallic components by development of economical, efficient and environmentally compliant corrosion protection methods.

The degradation of metallic materials can be either caused by mechanical wear and fatigue or by chemical processes such as dissolution, leaching and corrosion. Among these mechanisms, the corrosion process is the most common cause of failure and deterioration of metallic components. Some of the traditionally applied methods that prevent or at least delay this natural aging process involve hazardous substances as those present in the hexavalent chromium-conversion process, which forms a protective layer of insoluble trivalent chromium species. However, recent legislations impose increasing limitation on the use of toxic hexavalent chromium, still widely applied in the aeronautic industry [3,4]. Hence, the development of new efficient, low-cost methodologies to replace the use of hexavalent chromium-conversion for corrosion protection is the goal of many present research activities.

One methodology that complies with these standards is the sol-gel synthesis of organic-inorganic hybrid coatings [5]. The first attempts to synthetize this kind of material have been reported by Messadeq et al. [6] and others, such as the work of Guglielmi et al. [5]. Using a class I hybrid based on ZrO_2–PMMA (polymethyl methacrylate) they were able to increase the corrosion resistance of stainless steel by a factor of 30 [6]. Nonetheless, the weak interaction between the organic and inorganic parts caused delamination and subsequent film failure. Although there are numerous studies applying type II hybrids as anticorrosive coating [7], only few research groups succeeded to develop high performance hybrid barrier layers, which combine elevated corrosion resistance with long-term protection in aggressive environments. In these terms, very promising results were achieved for silica based hybrid coatings [8–11] and those containing corrosions inhibitors, such as cerium species [12,13]. The excellent barrier performance of these coatings have been associated with a nanostructure formed by a dense network of ramified silica-siloxane cross-link nodes covalently linked by short PMMA chains segments [10]. Despite of this progress, PMMA-siloxane-silica coatings suffer from their relatively poor thermal and mechanical properties, due to their relatively higher proportion of the PMMA phase of 70–80%.

It is known that cured epoxy polymers possess enhanced thermal and mechanical stability due to their cross-linked polymer structure provided by curing agents (hardeners). Hence the use of thermoset polymers for the synthesis of organic-inorganic nanocomposites is a promising alternative for the development of multifunctional hybrid materials, including applications such as protective coatings. In view of the innovative potential of epoxy-siloxane-silica hybrids the research activities have been considerably intensified. Matejka et al. have underlined the importance of synthesis conditions on the final structure of epoxy-siloxane-silica hybrid network [14], and a later study has demonstrated the importance of using functionalized inorganic precursor to achieve dense networks [15]. Furthermore, Nazir et al. have demonstrated that the addition of silica precursor in form of tetraethoxysilane (TEOS) and the coupling agent aminopropyltriethyoxysilane (APTES) into the epoxy matrix resulted in an increase of its thermal and mechanical stability, however anticorrosive properties of the material were not evaluated [16]. Brusciotti et al. synthetized epoxy-siloxane-silica hybrid coatings on the AZ31 Mg alloy based on different functionalized silanes linking to the epoxy phase, which has been cured using an amine hardener (diethyltriamine - DETA). The coatings with a thickness of 8–14 μm yielded a corrosion resistance of several $G\Omega\ cm^2$ and durability of up to one month in pH-neutral 0.3% NaCl solution [17]. More recently, Zahed et al. achieved active corrosion inhibition for their epoxy-siloxane coatings prepared using APTES as coupling agent and a reversible tetrasulfide reagent. The 50–350 μm thick coatings, deposited on AA2024-T3 Al alloy, presented an impedance modulus in the $G\Omega\ cm^2$ range during several months of immersion in 3.5% NaCl solution [18]. The cited studies [17,18] are based on the hybridization of the epoxy matrix using organosilanes, however the presence of silica, provided from an inorganic precursor, might play a crucial role for the hybrid structure and consequently its properties.

In the present study we report on a detailed structural characterization of epoxy-siloxane-silica hybrids prepared by a systematic variation the precursors proportion of silica (TEOS) and organosilane (3-glycidoxypropyl)methyltriethoxysilane (GPTMS) as coupling agent, keeping the proportion of cured epoxy to silica or organosilane constant. The fine-tuning of the proportion of colloidal precursors allows to obtain a nanocomposites structure that provides coatings with excellent thermal, mechanical anticorrosive performance, thus making them a promising alternative to conventional protective systems.

2. Materials and methods

2.1. Synthesis

All reagents were purchased from Sigma-Aldrich and used without further purification, including poly(bisphenol A-coepichlorohydrin), glycidyl end-capped (DGEBA) with an equivalent weight of 377 g/mol, diethyltriamine (DETA), (3-glycidoxypro pyl)methyltriethoxysilane (GPTMS), tetraethoxysilane (TEOS), tetrahydrofuran (THF). A1020 carbon steel (dimensions of 25 m m × 25 mm × 4 mm) was used as metallic substrate, having a nominal composition (wt%) of C = 0.08–0.13%, Mn = 0.3–0.6%, P_{max} = 0.04% and S_{max} = 0.05%, with the balance consisting of Fe.

The epoxy-siloxane-silica nanocomposites were synthetized in two stages using the sol-gel route. In the first reaction step the organic component was prepared by reacting DGEBA, GPTMS and DETA in THF under stirring and reflux for 4 h at 70 °C and additional 25 min at 25 °C. The epoxy groups of DGEBA and GPTMS react with the amine groups of DETA to form a highly cross-liked network. Thereafter, TEOS, ethanol and acidified water (pH 1, using nitric acid) were added into the reflux system and the solution was stirred for an additional 1 h at 25 °C to allow the hydrolysis and condensation reactions of TEOS and GPTMS. The sol-gel reactions