Progress in Organic Coatings 70 (2011) 358–364

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Relation between the scratch resistance and the chemical structure of organic–inorganic hybrid coatings

Y. Bautista*, M.P. Gómez, C. Ribes, V. Sanz

Instituto de Tecnología Cerámica, Asociación de Investigación de las Industrias Cerámicas, Universitat Jaume I, Campus Universitario Riu Sec, 12006 Castellón, Spain

ARTICLE INFO

Article history:
Received 2 June 2010
Received in revised form 1 September 2010
Accepted 3 September 2010

Keywords:
Organic–inorganic coating
Silsesquioxanes
Sol–gel
Scratch resistance

ABSTRACT

Organic–inorganic hybrid materials can be defined as materials combining organic and inorganic domains in a nanometric scale. The development of these organic–inorganic hybrids has achieved properties from both organic and inorganic materials.

In this research we have studied the scratch behaviour of coatings of organic–inorganic hybrid materials prepared by sol–gel processing, using as precursors, trialkoxysilanes with organic functionalities that react via free radical polymerization. We have also evaluated the influence of pure inorganic precursor as tetralkoxysilanes or pure organic precursors on the scratch behaviour. The main goal of this research was to evaluate how the chemical structure of the organic–inorganic hybrid influences the scratch behaviour of the coatings.

1. Introduction

Organic–inorganic hybrid materials can be defined as materials combining organic and inorganic domains in a nanometric scale [1]. The development of these organic–inorganic hybrids has achieved properties from both organic and inorganic materials. Organic polymers are often flexible, deformable and therefore hold out well impacts. Ceramic materials have excellent mechanical properties, as surface hardness, but generally do not support impacts without breaking. The control of the synthesis conditions can lead to the improvement of materials performance with tailored properties.

Sanchez and Ribot [2] categorized the organic–inorganic hybrid materials into two different classes. In class I, hybrid with weak interactions (hydrogen, van der Waals or ionic bonds) between the organic and inorganic components, are considered. In class II, the organic and inorganic components are linked by strong bonds (covalent and iono-covalent bonds). The chemical structure of the hybrid (class I or class II) determines the mechanical and tribological properties of these materials.

The development of organic–inorganic hybrid materials was made possible by the sol–gel science [3]. Sol–gel processing allows formation of M–O–M chemical bonding at ambient conditions, in the presence of organic monomers, as opposed to high temperature traditional ceramic processing.

Different combinations of organic and inorganic functionalities lead to a great number of possible hybrid materials [4], with very different properties. Some of these hybrid materials have been prepared by sol–gel processing as coatings with high abrasion resistance. Numerous papers have been published on the mechanical properties of organic–inorganic hybrid materials [5,6], however only some of them are focused on their scratch behaviour [7], which is one of the most important mechanism of degradation. The scratch behaviour is influenced by a combination of hardness, viscoelasticity, and toughness. Then, to understand wear of materials we need to evaluate all these properties.

In this research we have studied the scratch behaviour of coatings, which were prepared by sol–gel processing. Trialkoxysilanes with organic functionalities which react via free radical polymerization were used as precursors. Inorganic precursors, as tetralkoxysilanes, and organic monomers were evaluated on the scratch behaviour. The main goal of this research is to evaluate how the chemical structure of the organic–inorganic hybrid influences the scratch behaviour of the coatings.

2. Materials and methods

2.1. Materials

Tetraethyl orthosilicate (TEOS) and methacryloxypropyltrimethoxysilane (MAPTMS) were both purchased from Sigma–Aldrich. 1,6-Hexanedioldiacrylate (HDDA) was provided by Cytec Industries Inc. (Belgium), and Irgacure 651 by Ciba (Switzerland). MA0735 a Methacryl POSS Cage was purchased from Hybrid Plastics. All these products were used without further purification.

---

* Corresponding author. Tel.: +34 964342424; fax: +34 964342425.
E-mail address: yolanda.bautista@itc.uji.es (Y. Bautista).

0300-9440/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.porgcoat.2010.09.033

Table 1
Compositions prepared.

Compositions	MAPTMS (%)	TEOS (%)	HDDA (%)
100S	100	–	–
90S-10T	90	10	–
80S-20T	80	20	–
90S-10H	90	–	10
80S-20H	80	–	20

2.2. Coatings processing

Organic–inorganic hybrid materials were prepared by two consecutive reactions. The first one was a sol–gel reaction. The alkoxy groups of the silane were hydrolysed and condensed in acidic conditions, obtaining a high viscosity liquid that can be applied as a coating. The second reaction was a free radical polymerization started by UV radiation based on acrylate groups.

Different compositions were prepared to evaluate the influence of inorganic and organic precursors on the scratch resistance. In Table 1 the different compositions studied in this work are displayed. Compositions prepared with TEOS increases the fraction of inorganic components, while compositions prepared with HDDA increases the fraction of organic components.

The hydrolysis and condensation were performed in a solution of 0.01 M of HCl in water, using 1.5 equivalents of water per each hydrolysable group (3 in MAPTMS and 4 in TEOS). In any case, the photoinitiator Irgacure 651 was used in a 3% (wt.) respect to the trialkosysilane and in a 6% (wt.) respect to the HDDA resin.

The compositions were applied at 60 μm thickness, on a glass sample. The UV irradiation source was a Superfici source (160 W/cm) equipped with an H-bulb lamp. The samples were passed successively 3 times under the lamp at a speed of 5 m/min.

2.3. Characterization

2.3.1. Viscoelastic behaviour

The viscoelastic behaviour of sols was determined in a CVO-HR 120 Bholin rheometer. The dynamic storage and loss moduli (G' and G'') were determined in the linear viscoelastic regime, using a cone-plate measuring system. The samples were thermostated at 25 °C.

2.3.2. Liquid ^{29}Si NMR spectroscopy

The kinetic of hydrolysis and condensation of alkoxysilanes was followed by liquid ^{29}Si NMR spectroscopy. The measurements were performed on a Varian 500 MHz spectrometer. NMR spectra were recorded on a solution in $CDCl_3$, with trimethylsilane (TMS) as internal chemical shift reference. The chemical shifts were given in ppm relative to the internal reference.

The silicon sites are labelled with the conventional T_n or Q_n notation [8]. T_n represents a silicon atom with three potential reactive groups (silicon coming from the MAPTMS). Q_n represents a silicon atom with four potential reactive groups (silicon coming from the TEOS). The 'n' index represents the number of other silicon atoms bonded to the first silicon by an oxygen bridging atom.

2.3.3. Mass spectrometry

The mass spectrometer was a hybrid equipment QTOF I (quadrupole–hexapole-TOF) with an orthogonal interface Z-spray-electrospray (Micromass).

2.3.4. FT-IR

Fourier transform infrared spectrometer (FT-IR) was carried out using the attenuated total reflectance (ATR) mode on a THERMO model NICOLET 6700 spectrophotometer, with a 64-scan per sample cycle and a resolution of 4 cm^{-1}. The samples were scanned between the following wavelengths of 4000–600 cm^{-1}.

2.3.5. Scratch tester

The scratch test was performed in a Nano-Indenter. A diamond indenter with conical geometry (Rockwell) and spherical tip radius of 25 μm was used. The scratch test was carried out with progressive loading, which involves applying a charge on the surface at a constant rate of increase as the sample moves a certain distance laterally, progressively increasing the applied load along from 0 to 2000 mN. This test allows the knowledge of the behaviour of the material in the range of load, studying both elastic and plastic deformation, recovery and analysing the degradation mechanism.

To avoid errors caused by point defects on the surface to be tested, which might influence the tests results, three stripes have been performed on each sample, each of 2 mm in length.

Before and after scratching the surface, the indenter traverses the area to try, applying a minimum load, recording the contours of the surface. Comparing the first and the last profiles obtained changes in depth on the scratched surface can be detected. In all tests, load and length of the line were increased simultaneously at a speed of 10 mN/s and 10 μm/s, respectively. The three surface profiles measured for each strip can be defined as follows:

- Original profile: profile of the surface of the coating before damage.
- Scratching profile: profile followed by the indenter during the scratch test.
- Final profile: profile of the surface of the coating after damage.

After the scratch test, with an optical profilometer, topographic maps of the damaged surface were obtained, evaluating the changes in the mechanism of scratch and the critical loads.

Adhesion of the coating to the substrate, generation of cracks, change in the scratch mechanism and both elastic and plastic deformations were evaluated with this test. From the results, the resistance of the coating against scratching can be estimated.

2.3.6. Microhardness and elastic modulus

The microhardness and the elastic modulus were calculated from the indentation test with a tip with Berkovich geometry. A Nanotest purchased from Micromaterials Company, was used to do these assays. This device records, throughout the process of indentation, the depth values obtained by the indenter as a function of the load on him. The microhardness value was calculated with Eq. (1), applying a maximum load of 1000 mN during 10 s with a speed of 100 mN/s.

$$H = \frac{F}{A_c} = \frac{F}{24.5 \cdot u_r} \tag{1}$$

The elastic modulus was calculated from the slope of the obtained line formed by the first points recorded at the beginning of the discharge cycle, when the elastic recovery occurs, according to Eq. (2).

$$E_r = \frac{S}{2}\sqrt{\frac{\pi}{24.5 \cdot u_r^2}} \tag{2}$$

E_r, elastic modulus; S, inverse of the slope of the line drawn; u_r, crossover with the axis of the ordinates of the straight line.

The value of the elastic modulus was calculated as the average of twenty indentation trials done in different parts of the coating.