



Influence of silane structure on curing behavior and surface properties of sol–gel based UV-curable organic–inorganic hybrid coatings



Majid Mohseni^a, Saeed Bastani^{a,b,*}, Ali Jannesari^c

^a Surface Coatings and Corrosion Department, Institute for Color Science and Technology, Hosein Abad Square, Tehran 16765-654, Iran

^b Center of Excellence for Color Science and Technology, Hosein Abad Square, Tehran 16765-654, Iran

^c Resins and Additives Department, Institute for Color Science and Technology, Hosein Abad Square, Tehran 16765-654, Iran

ARTICLE INFO

Article history:

Received 2 February 2014

Received in revised form 29 March 2014

Accepted 5 April 2014

Available online 4 May 2014

Keywords:

Sol–gel

Silane precursor

UV-curing

Hybrid coatings

Photo-DSC

Surface properties

ABSTRACT

In this study, three usual silane precursors, tetraethoxysilane (TEOS), vinyltrimethoxysilane (VTMS), and 3-methacryloxypropyltrimethoxysilane (MPS), and different binary and triplet blends of them were polymerized via a sol–gel method under acidic conditions. ²⁹Si NMR spectroscopy was used to characterize and quantify the degree of condensation of oligomers. The organic phase was based on a three-acrylate monomer trimethylolpropane triacrylate (TMPTA). The effect of prepared oligomers on the curing behavior of hybrid materials and the interaction between organic and inorganic phases were monitored via photo differential scanning calorimetry (Photo-DSC). Atomic force microscopy (AFM) was used to investigate the surface properties of UV-cured hybrid materials. Photo-DSC results showed that the addition of functionalized oligomers can increase both the photopolymerization rate and the final degree of conversion. They also indicated that oligomers containing MPS are more compatible with the organic phase than other oligomers. Topography and phase trace images of AFM showed that oligomers containing VTMS migrate to the surface of films and affect the water contact angle. In contrast to VTMS, the presence of MPS in oligomers causes the formation of covalent bonds between the organic and inorganic phases in the bulk of the film, and so the surface properties of the film remain unchanged.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

In the last few decades, so-called hybrid materials have been the subject of many studies as new materials because of their peculiar properties. These materials combine the high ductility and low-temperature processing conditions of polymers with the outstanding properties of ceramics, such as hardness, high modulus, and thermal stability as well as low coefficient of thermal expansion [1–9]. Photoinduced polymerization is a rapidly expanding technology resulting from its main advantages: the process is solvent free, energy efficient and generally economical. As a subdivision of hybrids, UV-curable hybrid materials show the synergistic advantages of both UV-curing process and nanotechnology and therefore impart some unique properties to these materials, finally finding potential uses in fields such as printing, inks, adhesives, and especially clear coats [1,10–12].

The sol–gel process is a proper method for the preparation of organic–inorganic hybrid materials, and it overcomes the thermodynamically low affinity of organic and inorganic phases [3,5,13]. It provides a convenient way to strictly interconnect the polymeric media to the inorganic dispersed phase at a nanometric level through covalent bonds. Moreover, the problems associated with the dispersion of the inorganic phase into the organic phase are almost completely resolved [1]. The sol–gel process is usually defined as the hydrolytic process organometallic alkoxides, for example silicon, zirconium or aluminum alkoxide. In the case of silicone alkoxides, upon the addition of water, the silane precursor in the co-solvent hydrolyzes and polymerizes to build a silicate network. In time, the system arrives at the sol–gel transition where a gel exists [14,15]. The sol–gel process occurs under mild conditions, and polymers that are destroyed at ceramic-process temperatures can be incorporated. Thus, this process is the impetus for the formation of many hybrid materials [14,15]. The sol–gel process is greatly affected by certain factors, including temperature, pH, and the molar ratio of water to alkoxide catalyst as well as type of precursor [16]. Many studies have investigated the sol–gel process to successfully generate some added value hybrids. Li et al. [17] used TEOS to prepare colloidal silica microspheres with MPS as the

* Corresponding author at: Surface Coatings and Corrosion Department, Institute for Color Science and Technology, Hosein Abad Square, Tehran 16765-654, Iran. Tel.: +98 21 229 76848.

E-mail address: bastani@icrc.ac.ir (S. Bastani).

modifier and studied the effect of silica particle size on the surface roughness of films. Their results showed that increasing the particle size of silica caused a decrease in surface roughness. Photo-curing behavior and mechanical properties of hybrid UV-cured films based on vinyltrimethoxysilane (VTMS) as an inorganic precursor were reported by He et al. [16,18]. Their results showed that the addition of VTMS colloids accelerated the overall UV-curing reaction, and as the concentration of VTMS increased, the rate of polymerization of hybrid film also increased. Choi et al. [9] also successfully used VTMS to chemically modify clay for waterborne polyurethane/clay nanocomposites *via* sol-gel reaction. Yahyaei et al. [10] polymerized TEOS and MPS as a network former and network modifier, respectively, and studied the effect of the sol-gel precursor ratio on the morphology of hybrid materials using small angle X-ray scattering (SAXS). Their results showed that an organic-substituted precursor can change sol-gel reactions, and the morphology of hybrid materials is governed by this.

Although there are a lot of reports on the use of different silane precursors and different double blends of them, few studies have focused on a triple blend and the surface properties of precursors themselves. Thus, the main aims of this work were to prepare a UV-curable hybrid coating using TEOS, MPS, and VTMS and different double and triple blends of them and to study the effect of organic chain type substituted in the silane precursor on UV-curing behavior and surface properties of a UV-curable hybrid coating.

2. Materials and methods

2.1. Materials

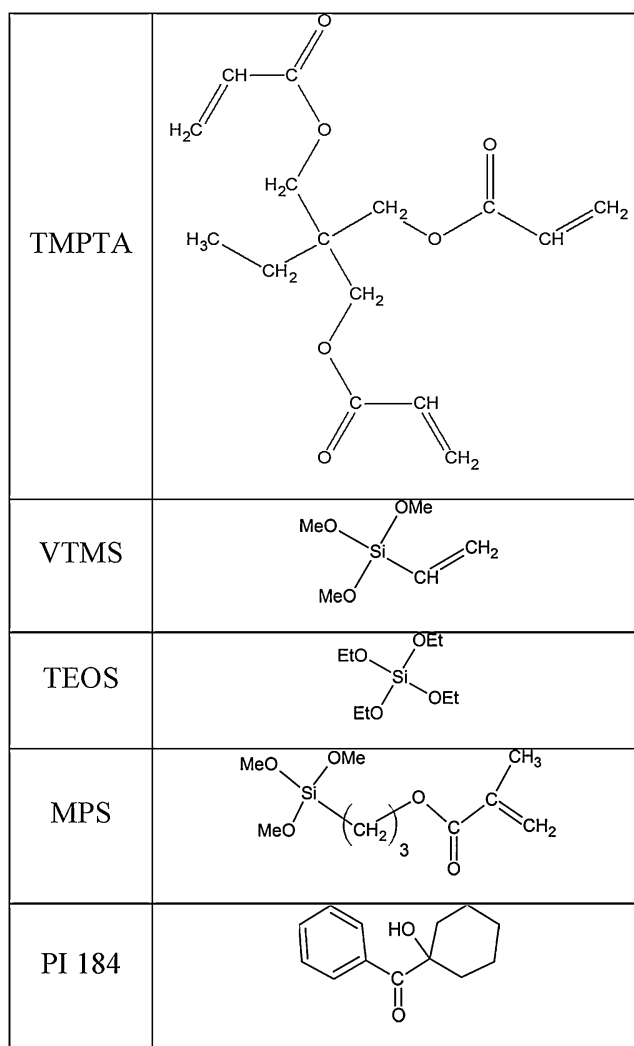
Vinyltrimethoxysilane (VTMS) was purchased from Aldrich; tetraethoxysilane (TEOS), 3-methacryloxypropyltrimethoxysilane (MPS), hydrochloric acid (37%), and ethanol (98%) were supplied by Merck; the photo-initiator (1-hydroxy-cyclohexyl phenyl ketone), PI 184, and acrylate monomer (trimethylolpropane triacrylate, TMPTA), EM231 were obtained from Eternal Chemical Corporation. All chemicals were used as received.

The structure and abbreviations of all components are shown in Scheme 1.

2.2. Instruments

^{29}Si NMR spectra were recorded on an Avance-300 spectrometer (Bruker) in CD_3OD solvent with tetramethylsilane (TMS) as a reference. The acquisition parameters are: frequency of 59.62 MHz, 7.5 recycle delay, $\pi/3$ (16.8 μs) pulse, spectral width of 500 ppm and 512 scans. All of NMR-spectroscopies were carried out at 2 °C. Photo-polymerization was observed on a DSC 1 differential scanning calorimeter (DSC) (Mettler Toledo) equipped with a LC8 Lightingcure UV source accessory (Hamamatsu). The UV light intensity at the sample was 20 mW/cm^2 over a maximum wavelength of 360 nm. Samples weighing 2.0 ± 0.1 (mean \pm SD) mg were placed in uncovered aluminum pans. Isothermal photo curing experiments were performed at ambient temperature (25 °C). The data were analyzed using the MATLAB® software. AFM images of the hybrid films in tapping mode were recorded by a DualScope® C-26 (DME) with a silicon probe in air and at 24 ± 1 °C and 30% relative humidity. The scan size varied between 1 and 5 μm ; roughness analysis was performed on $5 \times 5 \mu\text{m}^2$ images. The roughness of the surface is reported as the average roughness (S_a). S_a is the average of the Z values in the vertical direction from the mean line (Z_{ave}) to each point, as calculated by Eq. (1).

$$S_a = \frac{\sum_{i=1}^n |Z_i - Z_{\text{ave}}|}{n} \quad (1)$$



Scheme 1. Chemical structure of TMPTA, TEOS, VTMS, MPS and PI 184.

The sessile drop method was used to measure water contact angles (WCAs). A laboratory-made contact angle goniometer was utilized to determine WCAs (Fig. 1). WCAs were measured at fifteen different points on the surface of each sample with deionized water. For these tests, the specimens were prepared by applying the composite materials to degreased aluminum plates

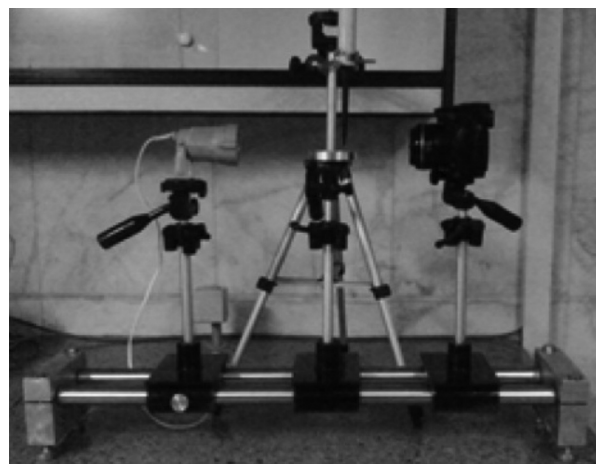


Fig. 1. Laboratory-made system to measure WCAs.

Download English Version:

<https://daneshyari.com/en/article/692716>

Download Persian Version:

<https://daneshyari.com/article/692716>

[Daneshyari.com](https://daneshyari.com)