Progress in Organic Coatings 88 (2015) 172–180

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Weatherability of hybrid organic–inorganic silica protective coatings on glass

Barbora Holubová [a,*], Zuzana Zlámalová Cílová [a], Irena Kučerová [b], Martin Zlámal [c]

[a] Department of Glass and Ceramics, Technická 5, Prague, Czech Republic
[b] Department of Chemical Technology of Monument Conservation, Technická 5, Prague, Czech Republic
[c] Department of Inorganic Technology, University of Chemistry and Technology, Technická 5, Prague, Czech Republic

ARTICLE INFO

Article history:
Received 5 March 2015
Received in revised form 4 June 2015
Accepted 1 July 2015
Available online 23 July 2015

Keywords:
Sol–gel
Hybrid organic–inorganic silica coatings
Glass protection
Weatherability

ABSTRACT

Currently, there is a growing interest in the application of silicon-based technologies for the development of advanced hybrid organic–inorganic coatings with strong weatherability. In this study, the sol–gel process is used to prepare such coatings on glass and their resistance to weathering effects is assessed afterwards. Various sols were prepared by mixing a silica-based inorganic matrix (tetraethyl orthosilicate) with different quantities of silica alkoxides functionalised with various organic groups. Subsequently, the sols were dip-coated onto glass samples at low temperatures without any heat treatment. The coatings prepared were analysed before and after three model ageing tests simulating various weathering parameters. After ageing, the best performing coatings showed good overall homogeneity and transparency (optical microscopy, SEM), improved water repellency and adhesion to the glass substrate (static contact angle measurements, cross-cut tape tests) and no colour or chemical composition changes (UV–VIS, FTIR). Compared with commercial hybrid silica products, the alkyl- and methacryloxy-functionalised silica coatings particularly displayed improved homogeneity, elasticity and barrier properties. Thus, these low temperature coatings, easily applicable to thin films, appear to fulfil the main requirements for the protection of the glass exposed to weathering phenomena.

1. Introduction

Protective coatings on exterior glass exposed to weathering phenomena have been used in restoration–conservation and building maintenance practice with mixed success since the beginning of the last century [1,2]. Current research primarily focuses on hybrid organic–inorganic silica based compounds as it is believed that their proper use can enhance water, chemical, abrasion and UV resistance [3–11]. In general, these coatings with low toxicity do not alter optical characteristics of substrate and display improved flow properties when applied [12,13]. In addition, there is a possibility to apply them without any further heat treatment, which is particularly suitable for the application on cultural heritage objects and in building maintenance [5,14,15]. One of the most important assets is then their design variability as there is a wide range of organo-reactive or non-reactive moieties attached to the silicon atom allowing formulas to be designed in accordance with specific application performance requirements [12,13,16]. Nevertheless, the influence of silica matrix functionalisation with various organic moieties on the protective efficiency and weatherability of silica-based coatings was studied more extensively in relation to the corrosion protection of metals [17,18].

Hybrid organic–inorganic silica materials are characterised by dual behaviour which comes from their structure consisting of an inorganic part (heteropolysiloxane backbone) capable of strong, covalent siloxane bonding to glass surfaces, and an organic part (containing different organic functionalities) providing coatings with added properties (Table 1). Moreover, it is also capable of covalent bonding with other organic network topcoats. This enables to create materials with hybrid properties between organic polymers and silicates, so that they are often called organically modified or organo-functional silica materials [12,13,16].

Generally, the functionalisation (modification) of silica based material means the formation of a covalent bond between silicon of a substrate surface or coating matrix and silicon of a modifier (organo-functional alkoxysilanes). Commonly, it occurs via oxygen bridges so that siloxane bonding forms. There are two major ways how to obtain a functionalised material:

(a) *Grafting method*: consists in the subsequent functionalisation of a pre-treated surface by derivatization. This method is rather disadvantageous because of an uneven distribution of

* Corresponding author.
E-mail address: Barbora1.Holubova@vscht.cz (B. Holubová).

http://dx.doi.org/10.1016/j.porgcoat.2015.07.001
0300-9440/

Table 1
Abbreviations, chemical names, functional groups and added properties to silica based coatings of several commonly applied organo-functional alkoxysilane precursors [3–22].

Abbreviation	Chemical name	Functional group	Added properties to silica based coating
MTES MTMS	Methyltriethoxysilane Methyltrimethoxysilane	Methyl-	- crosslinking agent, organic compatibility
OTES	Octyltriethoxysilane	Octyl-	- organic compatibility; paintability, substantivity and occlusivity; improved gloss, water repellency and self-cleaning properties
HDTMS	Hexadecyltrimethoxysilane	Hexadecyl-	
VTMS	Vinyltrimethoxysilane	Vinyl-	- adhesion promoter; crosslinking agent; water scavenger
PTMS	Phenyltrimethoxysilane	Phenyl-	- greater oxidation resistance; higher refractive index; improved thermo plasticity and toughness; superior thermal stability; organic and pigment compatibility
AMEO AEAPS	3-Aminopropyltriethoxysilane 3-(2-Aminoethyl) aminopropyltrimethoxysilane	Amino-	- improved substantivity to metals and coatings; crosslinking agent; adhesion promoter; corrosion resistance
GLYMO GLYEO	3-Glycidoxypropyltrimethoxysilane 3-Glycidyloxypropylmethyldiethoxysilane	Glycido- (Epoxy-)	- high reactivity due to easily opened ring (with amines, hydroxy and carboxy groups); crosslinking, adhesion promoter; improved durability, gloss, spread, elasticity; strengthening
MEMO	γ-Methacryloxypropyltrimethoxysilane	Methacryloxy-	- adhesion promoter; co-binder and crosslinking agent; strengthening
MTMO	γ-Mercaptopropyltrimethoxysilane	Mercapto-	- reacts with isocyanates, acrylates, unsaturated polymers; crosslinking agent; adhesion promoter
TTS	(Tridecafluoro-1,1,2,2-tetrahydrooctyl) triethoxysilane	Fluoroalkyl-	- greater chemical resistance; oil, fuel and solvent resistance; stain-resistance; easy-to-clean properties

functionalities on the surface of a substrate and the necessary pre-treatment of materials, which makes this method longer and more complicated [12,16,19,20].

(b) *Condensation method*: consists in the introduction of an organo-functional co-precursor with desired properties already during the synthesis of a silica based material (often tetraethyl orthosilicate (TEOS) or tetramethyl orthosilicate (TMOS) matrix). It represents a one-step route method enabling better fixation and distribution of organic functionalities on a surface (see in Fig. 1). However, a certain disadvantage could lie in the formation of less ordered structures and hence, the functionalisation may often be irreproducible. Nevertheless, this route is the simplest and thus, very popular in the creation of a wide range of organically modified materials as it can simultaneously construct a solid surface with appropriate surface roughness and low surface energy. This method is commonly called the sol–gel method (process) [12,16,17,19].

In detail, organo-functional primers (modifiers) for such a material are of the general molecular form R—Si—$(Y)_3$ [13,16], where the —Y group is commonly a hydrolysable alkoxy or acetoxy group ensuring the linkage to the inorganic substrate and the —R group is a non-hydrolysable organic group that could be reactive (e.g. amino-, epoxy-, vinyl- etc.) or non-reactive (e.g. alkyl-) towards another chemical. This organic group on the silane is compatible with the silica matrix and can bring particular properties depending on its nature (Table 1 [3–23]). The —R group can also consist of a spacer located between an organic functionality and a silicon atom (typically a short aryl or alkyl chain). The potential impact of a spacer on the reactivity of silicon atom reactivity depends on the distance between them [13].

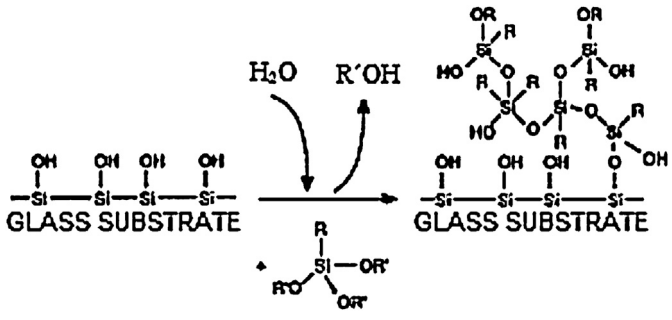

Fig. 1. Schematic visualisation of organo-functional silane hydrolysis, condensation and covalent bonding to inorganic substrate (drawn in accordance with [12]).

In this work, the choice of the organo-functional co-precursors (modifiers) and their relative ratios to silica matrix was based on the recent studies concerning the surface treatment of glass [3–21]. For example de Ferri et al. [3], Carmona et al. [4,14], De Bardi et al. [5] and Dal Bianco et al. [6,15] used sol–gel silica coatings based on TEOS non-modified or modified with various organo-functional silane modifiers to test their protection efficiency for historical glass. Likewise, there is a vast literature particularly on enhancement of strengthening and self-cleaning properties of coated glass surfaces for different applications [7–11]. For example, Briard et al. [8] used an aqueous silane solution with addition of epoxy- and amino-silane precursors to strengthen the coated glass surface. In order to obtain the best results in term of hydrophobicity, for example, Eshrad-Lagroudi et al. [7], Ganbavle et al. [9], Wang et al. [10], Rao et al. [11] and Ramezani et al. [20] proposed to use the glass surfaces treated with TEOS or TMOS based coatings mixed with various fluoalkyl-, phenyl- or short/long alkyl-silane precursors. An actual example of practical use of organo-functional silica materials can be found in design of protective multilayer system on the Last Judgement Mosaic in St. Vitus Cathedral in Prague, Czech Republic [24], although its maintenance is about to be rethought [25]. In addition, as previously mentioned, a broader insight could be found in works related to the use of organo-functional silica materials on metal substrates [17,18].

As described in the following sections, several tests were performed to examine the effect of different organically functionalised Si-alkoxide co-precursors (alkyl-, amino-, epoxy- and methacryloxy-silane modifiers) on the final performance of protective sol–gel based silica coatings on glass when exposed to simulated weathering tests. The present work uses tetraethyl orthosilicate (TEOS) as the main precursor (silica matrix) functionalised with different ratios of organo-functional silane modifier. Moreover, the optimisation of the sol–gel process was studied using different quantities of functionalised Si-alkoxides with the main TEOS matrix and different time periods of sol-polycondensation. The coated samples have been dried at laboratory conditions without any further heat treatment. This procedure was chosen on