

LAYERS OF INORGANIC-ORGANIC MATERIALS PREPARED BY SOL-GEL METHOD

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Abstract

Mezi nové hi-tech materiály patří anorganicko-organické hybridní polymery typu Ormocer (ORganically MOdified CERamics). Experimentálně byly připraveny anorganicko-organické hybridní vrstvy na bázi 3-(trimethoxysilyl) propylmethakrylátu modifikovanou metodou sol-gel. Vrstvy byly připraveny na různé substráty (sklo, korundová keramika, hliník, polyester, polyamid, polypropylen) a měly vynikající chemickou odolnost vůči koncentrovaným anorganickým kyselinám, hydroxidům (30 % NaOH) i organickým rozpouštědlům.

Vedle čistých hybridních vrstev byly připraveny i nanokompozitní vrstvy s enkapsulovanými textilními barvivými nebo nanočásticemi oxidu titaničitého. Přidané složky byly v hybridní vrstvě pevně fixovány.

Key words: *sol-gel method, hybrid coating, Ormocer, nanocomposite*

Introduction

Modern history of the sol-gel method isn't older than forty years. In the first phase, the preparation of clean inorganic layers, above all silica and titanium dioxide, was accomplished. The main use of these materials was in the form of layers in optics, electronics and optoelectronic. In the second phase, it was broadened how chemical variety materials (combination materials with aluminium, zirconium, boric oxides etc.), the form as well (beside layers and fibres, powders and aerogels) for all sorts of technical applications.

At the beginning of the ninetieth years last century started the next phase use of sol-gel method. Specialists from Fraunhofer–Institut für Silicatforschung (ISC) in Wurtzburg prepared the first inorganic-organic hybrid polymers named Ormocer (ORganically MOdified CERamics) [1,2]. In the following years these problems started to be developed and in other workplaces there were prepared inorganic-organic materials analogous types named Ceramer [2], Ormosil [3] and others.

Inorganic-organic hybrid materials may achieve features that the pure inorganic or organic material cannot give to. Generally, organic polymeric materials have good elasticity, tenacity, figurability and low density, while inorganic materials are hard, stiff and thermally stable [1,4]. The materials of the type Ormocer can combine these characteristics. On principle, it is not primarily composites, because resulting product is polymer with three-dimensional inorganic and three-dimensional organic net interconnected with covalent bindings C-Si.

ORMOCERs can be usually prepared by polymerization at increased temperature (from 80 to 200 °C), UV/VIS radiation or radical polymerization. These conditions allow the preparation layers of type ORMOCER also for substrates with low thermal resistance, as are plastics [4]. Uniqueness of these hybrid materials is in possibilities to compile optimum features directly for given application and it makes materials fit for different uses and hi-technologies from them. The biggest enlargement was attained by ORMOCERs like special functional layers resist from scratching or misting-up and with antistatic, water-receptive or water-repellent, conductive or, on the contrary, non-conducting features and so on [1,4].

Even though we know about it, layers of type ORMOCER can be seen for example in the form of layers named Abrasil on plastic spectacle lenses or during preservation of the reliques from glass, ceramics and brass. Layers named Decosil are used for dyeing household glass on arbitrary and at the same time reproducible shade, which is difficult during glass - staining in melt [1].

The principle of preparation of these materials is in use of alkylalkoxysilane in classical progress sol-gel method. The basis is hydrolyse bindings C-O-Si and stability bindings C-Si in conditions of preparation material in solution of alcohol. As for reactive alkyl – groups acrylate, methacrylate or epoxydes is possible to use. During the sol-gel process of preparation ORMOCERs there is first inorganic net formed and organic cross-linking is final hardened step [4].

Precursors used for preparation inorganic-organic materials can be divided subsequently [4]:

- I. Type: formation inorganic silicate nets, based on Si-O-Si bindings (organic unmodified Si alkyloxides, for example tetraethoxysilane)
- II. Type: formation inorganic oxidic nets, other than those only structures Si-O-Si (for example alkyloxides of aluminum, titanium, zirconium, tin etc.)
- III. Type: modification of inorganic nets by organic (nonreactive) functional units (alkylalkoxysilanes with nonreactive organic groups, e.g . methyl, phenyl etc.)
- IV. Type: formation of secondary organic nets (alkylalkoxysilanes with reactive groups, for example methacryl, vinyl or epoxy groups).

The first step of preparation ORMOCERs is forming of inorganic nets controlled by hydrolysis and polycondensation in progress at the same time, which is identical with classical inorganic sol-gel processes. The second step of synthesis is organic cross - linking during final hardening. Depending on character of reactive organic groups present at ORMOCER precursors, can be used various ways of polymerization (thermal, UV/VIS radiation or radical mechanism) to creation 3D polymeric textures connected by covalent bindings C-Si basic inorganic oxidic net [4].

The next enlargement of possibilities materials type ORMOCER is preparation of classical composites. Beside common macro-composites are of grade interest largely nanocomposites on molecular or nanoparticle level. Sol-gel method allows encapsulate big organic molecules (for example textile dyes) or nanoparticles (for example titanium dioxide) to the resulting net of hybrid material. As these particles in net of hybrid polymer kept only steric or by van der Waals forces, these are really nanocomposites.

Experimental part

The basic experiments came from commercially accessible TMSPM (3-trimethoxysilyl) propylmethacrylate, in which it is possible organic methylmethacrylate group polymerize by radical mechanism or by thermal mechanism. Structural formula of TMSPM is in figure1.

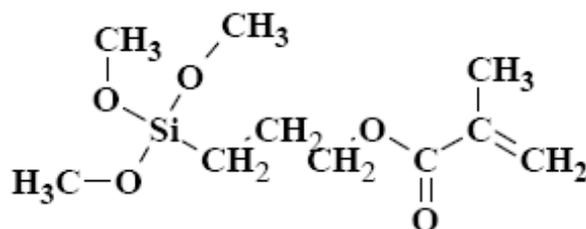


Fig. 1 Structural formula of TMSPM (3-(trimethoxysilyl) propylmethacrylate).

Initial TMSPM is well-soluble in isopropyl alcohol and after adding of calculated amount of water and hydrochloric acid like acid catalyst happens to hydrolysis Si-O-C bindings and resulting polycondensation hydrolytic performances behind rise inorganic nets with Si-O-Si bindings. Either in those phase, or after partial polymerization of methylmethacrylate groups warming at increased temperature with radical mechanism catalysts dibenzoyl peroxide, is the final sol deposited on substrate (glass, ceramics, metal, plastic, textile) by dipping or using of analogous procedures (dip-coating, spin-coating). After evaporation of the rest solvent, is polymerization of organic parts completed at increased temperature.

Results and discussion

The products prepared radical mechanism of polymerization (dibenzoyl peroxide at 80 °C), heat polymerization at 150 °C or UV radiati on (UV A, UV B or UV C from fluorescent tube Philips, catalysts dibenzoyl peroxide) were compared. Polymerization degree and presence of residual dibenzoyl peroxide were controlled using IR spectroscopy. In figure 2 there is a typical example of the part of IR spectra manifesting entire polymerization (fading away zone of C=C bindings and change in zone corresponding to valence vibration bindings C=O from methylmethacrylate group MMA or from polymethylmethacrylate group PMMA) product after heat polymerization.

Layers prepared by radical polymerization and heat polymerization were after enough long time (2 to 3 hours) completely polymerized, however in the case of radical polymerization it was necessary to keep experimental conditions, otherwise the polymerization didn't have to be finished. According to skeletal parts of IR spectra, these productions were slightly different. Significant differences were displayed during following testing features of layers. Experiments with polymerization of dibenzoyl peroxide with help of UV radiation were unsuccessful. Radiation in the area UV A wasn't sufficient for initiation of dibenzoyl peroxide. Even though radiation of UV B and UV C initiated decomposition of dibenzoyl peroxide but polymerization of methylmethacrylate group didn't arise.

Perfectly polymerized hybrid layers showed high chemical resistivity against concentrated inorganic acids (H_2SO_4 , HNO_3 , HF), alkali hydroxide (30 % NaOH) and organic solvents e.g. hot toluene. If polymerization wasn't entire, products were slowly dissolved in 30 % NaOH .

Initial sol had very good wetting features on all examinational surfaces (glass, corundum ceramics, aluminium, polyester, polyamide, polypropylene). In case of polypropylene, for improvement of adhesion resulting layers, surface plasmatic adjustment was also successfully tested.

Beside pure hybrid layers, there were also prepared nanocomposite layers with textile dyes or nanoparticles of titanium dioxide. From series of examinational textile dyes, was the best get right cationic dye Astrazonyellow 5GL and dispersion dye Disperse Red 50, which have significant electrophilic centre suitable for interaction with nucleophilic centres of hybrid layer. Coloured hybrid layers were built-up also on textile (polyester, polypropylene). From present results follow on, the resulting layers are resistant to incidence waters and isopropyl alcohol. They also kept up washing process. Hybrid layers, which were prepared by radical mechanism of polymerization with dibenzoyl peroxide at $80\text{ }^\circ\text{C}$, perfectly encapsulate textile dyes, but to the solutions liberate small amount of layer substance (probably crumbling by movement of textile). On the other hand, the hybrid layers prepared by thermal polymerization released a little bit of textile dyes, but they were mechanically more resistant than the layers, which were prepared by radical polymerization.

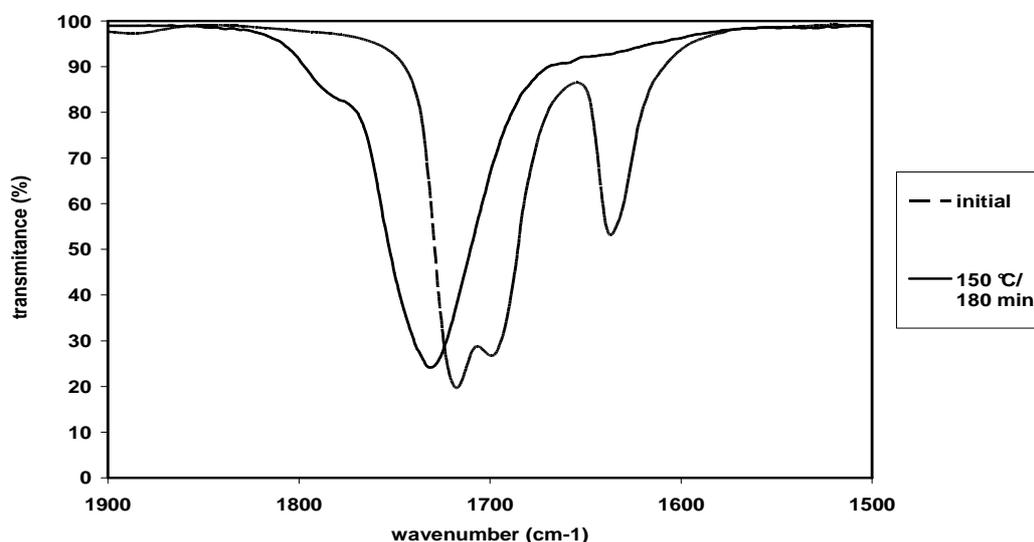


Fig. 2 Part of IR spectra of layer without dibenzoyl peroxide before and after thermal processing by $150\text{ }^\circ\text{C}$. 1635 cm^{-1} – valence vibration of $\text{C}=\text{C}$ binding in methylmethacrylate group, 1700 and 1715 cm^{-1} valence vibration of $\text{C}=\text{O}$ binding in MMA, 1730 cm^{-1} valence vibration of $\text{C}=\text{O}$ binding in PMMA.

For preparation of nanocomposite hybrid layer from TMSPM and nanoparticles titanium dioxide it was used photo-active material P-25 of firm Degussa. Nanoparticles were dispersed in prepared sol by the help of ultrasonic apparatus and were built-up on various

substrates. Nanoparticles were regularly dispersed in layer and they didn't relieve from the prepared layer. Comparative analysis confirmed, that the photocatalytic effectivity of nanoparticles of titanium dioxide, after their encapsulating to the hybrid layer, was very markedly retrenched. This result is logical, because the whole surface of nanoparticles of titanium dioxide has been coated with inorganic-organic layer. The hybrid layer blocks access of responsive chemicals to surface of nanoparticles.

Conclusion

Inorganic-organic hybrid layers on the basis of 3-(trimethoxysilyl) propyl methacrylate were successfully prepared by sol-gel method. Polymerization of methacrylate group was achieved by radical mechanism of polymerization (dibenzoyl peroxide at 80 °C) or thermal polymerization at 150 °C. Polymerization with UV radiation was unsuccessful. Layers were prepared on various substrates (glass, corundum ceramics, aluminum, polyester, polyamide, polypropylene) and adhesion of layers was very good in all cases. From chemical aspects polymerized layers kept up excellent chemical resistivity against concentrated inorganic acids (H₂SO₄, HNO₃, HF), alkali hydroxide (30 % NaOH) and organic solvents e.g. hot toluene. Resulting characteristics of layers were gently distinguished after way of preparation.

Beside pure hybrid layers, there were also prepared nanocomposite layers with encapsulated textile dyes or nanoparticles of titanium dioxide. Added components in hybrid layer were fast fixated.

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