

MICROENCAPSULATION OF ORGANIC DYES INTO THE HYBRID LAYERS PREPARED BY SOL-GEL METHOD

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Abstract: Inorganic-organic hybrid polymers of the type Ormocer (ORganically MODified CERamics) belong to new hi-tech material. Inorganic-organic hybrid layers on base 3-(trimethoxysilyl) propylmethacrylate were experimentally prepared by modified sol-gel method. Layers were prepared for various substrates (polyester, polyamide, polypropylene, glass, corundum ceramics) and have had good chemical resistance from inorganic acids, hydroxides and organic solvents. Beside pure hybrid layers, there were also prepared nanocomposite layers with encapsulated textile organic dyes. The textile samples were carried out tests - the durability of the washing, sublimation and xenotest (light stability).

Key words: sol-gel method, hybrid coating, Ormocer, nanocomposite, microencapsulation, organic dye

1 INTRODUCTION

Modern history of the method sol-gel 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. At the beginning of 1990's, specialists from Fraunhofer-Institut für Silicatiforschung (ISC) in Würzburg 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. Organic-inorganic hybrid materials may achieve features that the pure inorganic or organic material cannot provide. Generally, organic polymeric components have good elasticity, tenacity, figurability and low density, while inorganic components are hard, stiff and thermally stationary [1,3]. 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].

The next enlargement of possibilities of materials type ORMOCER is preparation of classical composites. Beside common macro-composites, largely nanocomposites on molecular or

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nanoparticle level are of great interest. Method of sol-gel allows to encapsulate big organic molecules (for example organic cationic dyes) or nanoparticles (for example titanium dioxide) to the resulting nets of hybrid material. As these elements in bar of hybrid polymer pent only sterically or by van-der-Waals forces, these are really nanocomposites.

2 METHOD

Organic-inorganic polymers (sols) on base TMSPM (3-(trimethoxysilyl) propylmethacrylate) were experimentally prepared by radical polymerization using initiator dibenzoylperoxide. Methylmethacrylate group can be polymerized by radical mechanism or by thermal mechanism. Structural formula of TMSPM is in figure 1. Precursor of TMSPM is well-soluble in isopropanole and after adding of calculated amount of water and hydrochloric acid like acid catalyst happens to hydrolysis Si-O-C bindings and resulting in polycondensation hydrolytic performances behind rise inorganic nets with Si-O-Si bindings. Subsequent boiling of sol under the reflux condenser resulted in prepolymerization. The prepolymerization of sol is associated with improvement of properties for coating of hybrid layers on the substrates. For experiments there were used cationic organic dyes very well soluble in isopropanole. Then calculated amounts of organic dyes (Astrazone yellow 5GL, red F3BL and violet F3L) were separately added into the sols. Textile samples were prepared from 100% polypropylene textile, type 140 GA690200, made in Hedva, a.s. Moravská Třebová, Czech Republic. Half of textile samples was put into the plasma reactor (model DSCBD A4-LIN) for 1 minute from both sides. Different types of coloured sols were fixed on the substrate (polypropylene textile) by method of dip-coating. Hybrid layers with encapsulated organic dyes on textile were heated at the temperature 80 °C for 3 hours. Low temperature of heating was eliminated decomposition of polypropylene textile.

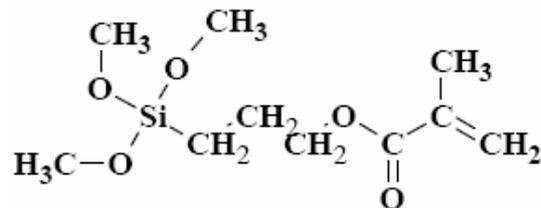


Figure 1: Structural formula of precursor TMSPM (3-(trimethoxysilyl) propylmethacrylate).

Stability of hybrid layers with encapsulated organic dyes on textile samples was tested [5] by the following methods: the durability of the washing ([6], washing at constant temperature 40 °C for 30 minutes, ratio of bath 1 : 50, commercial washing powder about concentration 5 g/l), sublimation ([7], M247A SCORCH TESTER by company SDL ATLAS, temperature 100 °C for 1 hour between two layers of cotton) and xenotest (light stability [8], Xenotest 1200 by company SDL ATLAS for 24 hours).

3 RESULTS

Hybrid layers prepared by radical polymerization were 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. 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). Graph shows polymerization of sol and heating of hybrid layer.

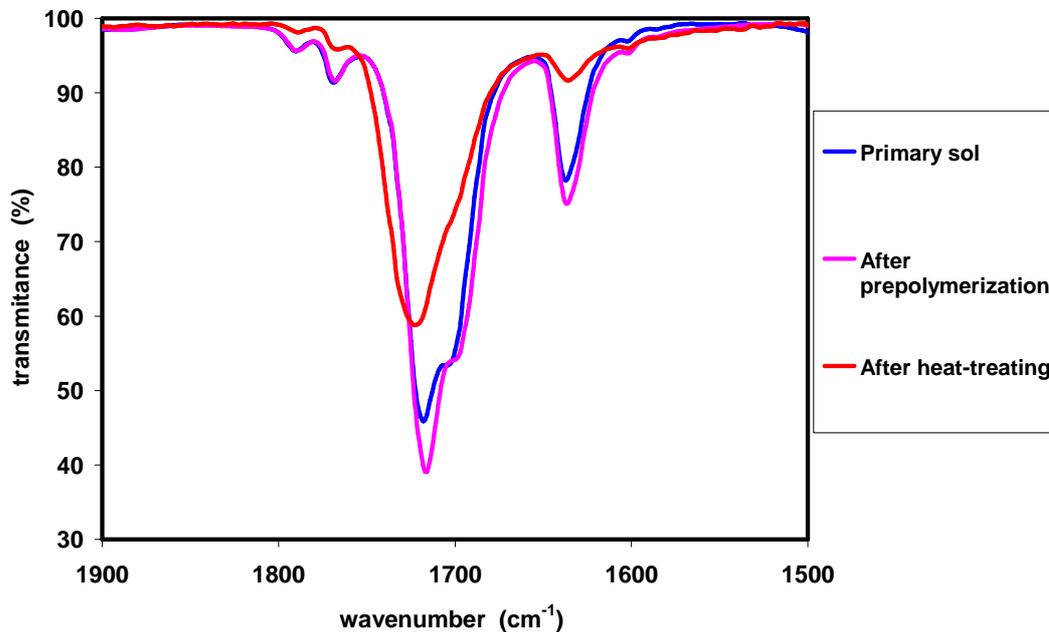
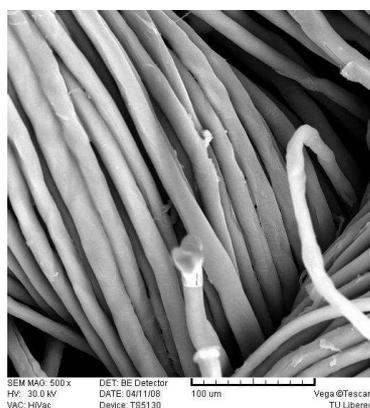
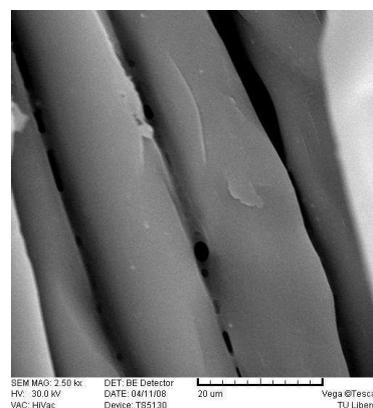


Figure 2: Part of IR spectra of polymerization of sol TMSPM, detail in part from 1500 to 1900 cm^{-1} . 1635 cm^{-1} – valence vibration of C=C binding in methylmethacrylate group, 1700 and 1715 cm^{-1} valence vibration of C=O binding in MMA (non-polymerized part of sol), 1730 cm^{-1} valence vibration of C=O binding in PMMA (polymerized part – hybrid layer).

Nanocomposite layers with textile organic dyes were prepared successfully. Polypropylene samples, which were in plasma reactor, didn't have higher stability of hybrid layers with encapsulated organic dyes than non-plasma samples. Hybrid layer is of high quality according to pictures from SEM (figure 3a). A few parts of the hybrid layer create bridge between the fibres of polypropylene (figure 3b).



3a



3b

Figure 3: SEM pictures of samples of polypropylene with hybrid layer (TMSPM). SEM VEGA, back-scattered electrons.

All of the three organic dyes had good resistance against leaching from hybrid layer in cold water but low in washing test. Electrophilic centres of organic dyes didn't have sufficient interaction with nucleophilic centres of hybrid layer and molecules of organic dyes were kept in hybrid layer only sterically and by weak van-der-Waals forces. To increase the stability of fixation of the dyes, it would be appropriate to fix the dyes into the hybrid layer with covalent bond. Stability of organic dyes was also very low in xenotest, especially the one of the dye Astrazone violet F3L. The hybrid layer doesn't absorb UV light and discoloration of the layers was caused by degradation of dyes exposed to UV light. Changes in colouring of the samples of polypropylene fabric with coloured hybrid layer after tests performed are documented in figures 4 to 6.

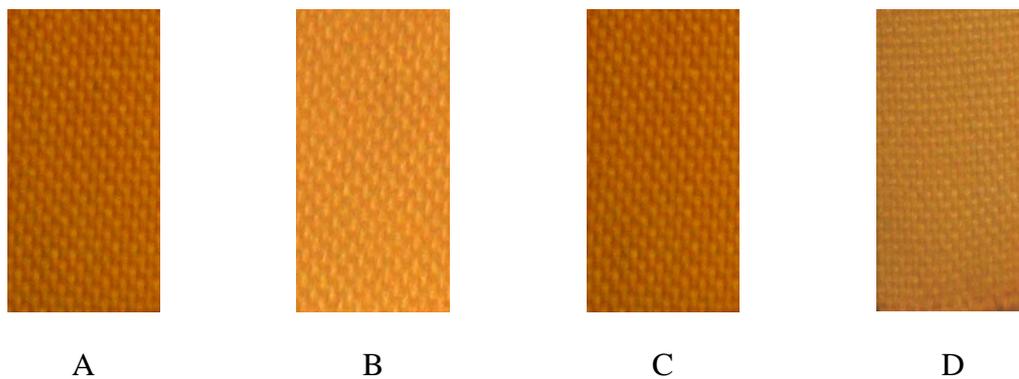


Figure 4: Appearance of hybrid layer with organic dye Astrazone yellow 5GL after preparing (A), after washing at temperature 40 °C (B), after sublimation (C) and after xenotest (D).

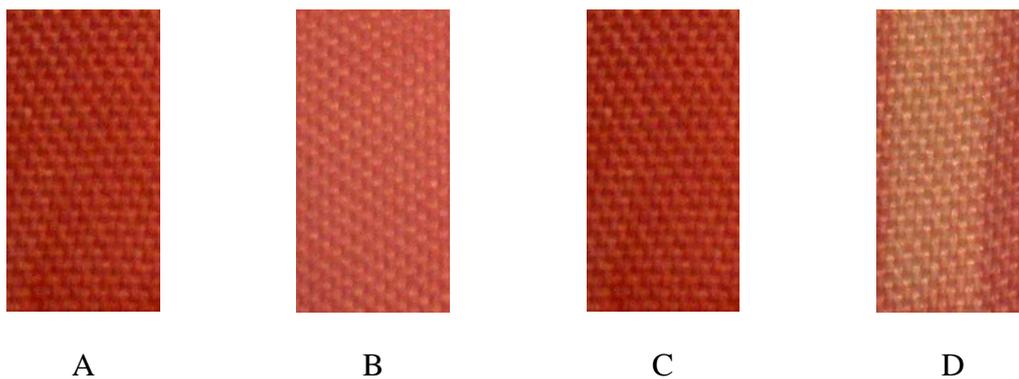


Figure 5: Appearance of hybrid layer with organic dye Astrazone red F3BL after preparing (A), after washing at temperature 40 °C (B), after sublimation (C) and after xenotest (D).

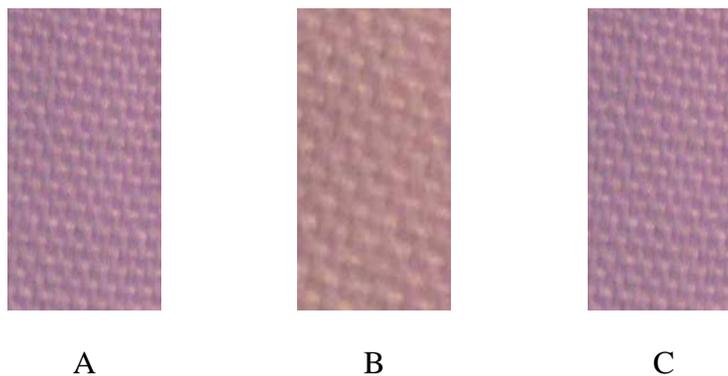


Figure 6: Appearance of hybrid layer with organic dye Astrazone violet F3L after preparing (A), after washing at temperature 40 °C (B) and after sublimation (C). After xenotest was sample completely discoloured.

4 CONCLUSION

Hybrid organic-inorganic layers with three types of microencapsulated organic dyes were prepared successfully. All tested samples with these organic dyes (Astrazone yellow 5GL, Astrazone red F3BL and Astrazone violet F3L) have good stability in cold water and sublimation. On the contrary, all samples have the worst stability in the durability of the washing and in xenotest. To increase the stability of fixation of the dyes, it would be appropriate to fix the dyes into the hybrid layer with covalent bond. For the higher light stability of hybrid layers with organic dyes, it is necessary to add UV filters into them.

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Acknowledgement

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