Application of SiO₂ a TiO₂ layers on polymer surfaces by sol-gel method

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Annotation
SiO₂ and TiO₂ layers from two sols of different concentration were deposited on polyester and polyamide fabrics and foils by sol-gel method. According to investigation in scanning electron microscopy prepared layers were first-rate and they were almost without cracks in a case of lower concentration of sols. Adhesion of layers was relatively good, only at thicker layers of TiO₂ on polyester fabric there was locally established disengaging of layer from the basis. Prepared layers were highly porous because temperature of heat treatment was very low with regard to used polymers. That presented by high excluding of Astrazonrotviolet FRR dye, which was added into part of prepared sols before preparing of layers. The aim is ensuring of perfect adhesion of layers on polymers and fixation of dyes by covalent bond. Therefore it would be suitable to use inorganic-organic materials with functional groups able to chemical bonding with polymer and dye instead of clear inorganic layers, which are fixed only by physical power on the surface of polymers.

Key words: sol-gel method, polymers, fibers, scanning electron microscopy

Introduction
Possibility of finishing surface properties of materials is deposition functional or inorganic top-coat by sol-gel method. One of advantages of this method is possibility of preparation thin layers on various materials. Up to now mainly inorganic substrates (glass, ceramic, metals etc.) were used, however thin layers can be deposited also on organic materials, especially on polymers.

Principle of sol-gel method is preparation of homogeneous solution of starting components, which is transferred into sol by controlled hydrolysis and polycondensation [1]. This sol is deposited on surface of materials, transferred into gel and finally on layer of oxide by heat treatment. Layer of oxide is nonporous and glassy or crystalline at higher temperatures of heat treatment. However at lower temperatures of heat treatment it stays amorphous and porous. In a production and for research purposes SiO₂ and TiO₂ layers are deposited most often, also layers of many other constituions containing Al₂O₃, B₂O₃, ZrO₂, PbO and another oxides are usually prepared. Next to clearly inorganic layers also hybrid inorganic-organic layers are developed (production terms ORMOCER, ORMOSIL and NANOMER) which contain also chemical bonding of organic substances and functional groups next to silicon, titanium, zirconium and oxygen [2]. Preparing of very thin layers (10 up to 500 nm thick) of composite nanomaterials is further possibility of this method [3].

Layers prepared by sol-gel method are industrially used like reflex and antireflex layers in optics, protective, catalytic, modified and functional layers in material engineering and functional layers in microelectronics and biotechnology [1,2].

Experimental part
Sols for layer depositing were prepared by controlled hydrolysis and polycondensation tetraethylsilicate (TEOS) or tetraisopropylorthotitanate (IPTi) in isopropanol by catalysis HCl (in case of IPTi with addition acetylacetone as complexing agent) always in two concentrations 0,8 and 4 g oxide for 100 ml solution [4]. Practical tests of deposition of SiO₂ and TiO₂ layers were realized with samples of polyester fabric (PL) and nylon (PA), polyester (PL) and polyamide (PA) foils and also glass for comparison. Finally layer was heat treated
by temperature of 200 °C during 5 minutes after deposition of layer by dip coating and extraction of samples by speed of 6 cm/min and after completion of hydrolysis of humidity from the surroundings.

Thickness and index of refraction of layers (on the even surface of comparative glass) were counted according to the published formulas [5] from the dependence of light permeability on wave length in range from 380 to 1000 nm measured by spectrophotometer GBS. Quality of resulting layers was watched by scanning electron microscopy on the apparatus Vega (TESCAN Brno).

Parallel with depositing sols on polymers tests with addition of colorant Astrazonrotviolett FRR (Bayer) into deposited sols (0,33 g dye into 80 g solution) was done and these sols were deposited on slides. In this series of tests amount of dye was observed by spectrophotometer GBS commensurate with temperature of heat treatment of layers (in range from 100 to 400 °C) and extraction of colorant from the layer executed by temperature of 200 ºC for 5 minutes in water, 9,6% solution of CH$_3$COOH and isopropanol.

**Results and discussions**

Thickness and refractive indexes of layers were determined on slides from optical measurements. That was 17 and 84 nm at SiO$_2$ layers (at refractive index n$_D$ = 1,464) and 9 and 44 nm at TiO$_2$ layers (at refractive index n$_D$ = 2,09). Values of determined refractive index accorded well with values, which are given for amorphous SiO$_2$ and TiO$_2$. Determined thickness of layers accorded with an even surface, which redundant sol flowed down from. It is a condition, which should be the same also for polyester and polyamide foil next to glass. However in the case of fabrics conditions are conspicuously different because sol is held in interfibre space and resulting thickness will be regularly thicker. According to a watching by scanning electron microscopy prepared layers of SiO$_2$ and TiO$_2$ on polymers are first-rate. On the picture 1 there is documented the duality of SiO$_2$ layer from the lower concentration of sol on nylon. Sporadic cracks occur only in the point of crossing of fibers of fabrics. The similar situation is also on polyester fabric (picture 2). TiO$_2$ layer from the lower concentration of sol on nylon has similar appearance and duality like SiO$_2$ layer (picture 3), however higher concentration of sols formed meaningfully stronger layers on some points of fabrics and mainly in place of crossing of fibers and these layers were shaky (picture 3). The similar situation with TiO$_2$ layer from the higher concentration of sol was also on polyester fabric, where considerable amount of cracks in the layer in space among touching fibers of fabric was observed (picture 4). Seldom there was found also disengaging of TiO$_2$ layer from the substrate (picture 4). Layers on foils were watched just in points of their damaging by scanning electron microscopy. All layers on polyamide foil were first-rate and also TiO$_2$ layer from the higher concentration of sol had only exceptionally perceptible cracks (picture 5). SiO$_2$ and TiO$_2$ layers from the lower concentration of sol on polyester foil were without cracks and they copied the relief of foil surface (picture 5). TiO$_2$ layer from the higher concentration of sol on polyester foil had only small amount of cracks (picture 6). There is perceptible only from the detail of chance crossing of cracks (picture 6) that layers really on the foil. Colorant Astrazonrotviolett FRR tinted surface layers the both of oxides with high quality but it was permanent only to temperature of 150 °C. Above this temperature there was surly degradation of this colorant. Example of the dependence of stabilization of dye on temperature of heat treatment is on the picture 7. The dye excluded easily in all three used mediums inclusive distilled water by test of excluding of dye from the TiO$_2$ layers which were heat treated by 200 °C for 5 minutes. The dye from analogously prepared SiO$_2$ layers did not practically exclude in distilled water. The dye was considerably excluded in 9,6% solution of CH$_3$COOH and totally in isopropanol.
Fig. 1: Nylon modified by sol-gel method with SiO$_2$ layer, the lower concentration of sol, detail of crack in the layer in the point of crossing of fibers of fabric is on the right side

Fig. 2: Polyester fabric modified by sol-gel method with SiO$_2$ layer, the lower concentration of sol, detail on the right side

Fig. 3: Nylon modified by sol-gel method with TiO$_2$ layer, the higher concentration of sol on the left side, the lower concentration of sol on the right side
Fig. 4: Polyester fabric modified by sol-gel method with TiO$_2$ layer, the higher concentration of sol, detail of cracks on the touch of fibers on the left side, disengaging layer on the right side.

Fig. 5: Polyamide foil modified by sol-gel method with TiO$_2$ layer, the higher concentration of sol (left) and polyester foil modified by sol-gel method with SiO$_2$ layer, the lower concentration of sol (right).

Fig. 6: Polyester foil modified by sol-gel method with TiO$_2$ layer, the higher concentration of sol, detail of the crossing of cracks on the left side.
Fig. 7: Graphic dependence of absorbance of TiO$_2$ layer from the lower concentration of sol on glass by wave length 560 nm on temperature of heat treatment

**Conclusion**

There was experimentally confirmed that layers of inorganic oxide can be deposited by sol-gel method not just on polyester and polyamide foils but also on fabrics. However it is necessary to reduced concentration of deposited sols for fabrics. Prepared layers were first-rate and they were almost without cracks for the lower concentration of sols. Adhesion of layers was relatively good, only by the thicker TiO$_2$ layers on polyester fabric there was locally found disengaging of layer from the substrate.

Prepared layers were highly porous because temperature of heat treatment was very low with regard to use polymers. The high porosity and only physical adsorption of dye in the layer produced its high excluding.

The aim is ensuring of perfect adhesion of layers on polymers and fixation of dyes by covalent bond. Therefore it would be suitable to use inorganic-organic materials with functional groups able to chemical bonding with polymer and dye instead of clear inorganic layers which are fixed only by physical power on the surface of polymers.

**Literature**
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