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Rhodamine-loaded TiO2 particles for detection of polymer coating UV degradation.

Rhodamine-loaded TiO$_2$ particles for detection of polymer coating UV degradation

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Abstract

Epoxy based composites filled with RhB-loaded TiO$_2$ containers were prepared. SEM, EDX mapping, and Raman spectroscopy showed a uniform distribution of the TiO$_2$ particles in the polymeric matrix. The sensitivity of the composites to UV irradiation was studied. Efficiency of the composite decolorization was found to depend on the amount of RhB-loaded TiO$_2$ containers incorporated into the coating. Accelerated decomposition of Rhodamine B in the composite under UV irradiation takes place due to photocatalytic activity of the TiO$_2$ particles. The prepared composites can be used as UV-sensor material.

Keywords: Epoxy coating ; UV detection ; Titanium dioxide ; Rhodamine B

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1. Introduction

Polymer nanocomposites have attracted considerable interest due to synergistic properties of polymer matrix and nanoscale materials [1]. The small size of nanoparticles (NPs), their high surface-to-volume ratio and strong interaction between the polymer and NPs are crucial factors which significantly improves the properties of polymeric coatings even at low NPs content [2]. Among diversity of polymer matrixes, epoxy resins have special place owing to their good performances such as electrical and corrosion resistance, excellent chemical, moisture and solvent resistance, good dimensional stability, good adhesion to many substrates, easy of cure and processing [3]. Moreover, the proper selection of resin, modifiers and cross-linking agent allows controlling the final properties of the cured epoxy resin whereby epoxy resins have found large-scale application in different field of science and industry [4]. However, epoxy resins are brittle materials due to crosslinked structure [2]. The fabrication of epoxy resin based composites by intercalation of different nanofillers can significantly improve performance characteristics of the cured epoxy coatings. Among different nanoparticles used as additives for epoxy resins, TiO_2 is the most perspective owing to unique properties, relative low cost and wide-spread application. Different authors reported that presence of TiO_2 nanoparticles in epoxy resins can improve mechanical [5], viscoelastic [6] and thermal properties [6], increase corrosion resistance [7] and provide excellent optical characteristics [8] of the epoxy based coatings.

During the service of the epoxy resin and other polymer coatings, variation of environments such as sunlight, temperature, humidity, etc. can lead to deterioration of the coating properties [9]. In particular, UV radiation comprised approximately 8–9% of the total solar radiation is harmful to polymers, a phenomenon known as photodegradation, which affects the physico-chemical, optical and mechanical properties of polymers [10]. The detection of the external UV radiation dose affecting the polymeric materials is an actual task. The aim of the present work is the preparation of Rhodamine B (RhB)-loaded TiO_2/epoxy composites and their study as UV-sensor material.

2. Experimental

2.1. Synthesis of RhB-loaded TiO_2 containers

Mesoporous TiO_2 powder was synthesized from TiC according to the method described in [11]. The as-prepared powder was annealed for 1 h at 200 °C and then used as a container for RhB. To adsorb RhB onto the TiO_2 surface, 1 g of the TiO_2 powder was placed in a glass with 40 mL of 0.5 mM RhB solution. After agitation the obtained suspension was kept under vacuum ($\approx 5 \times 10^3$ Pa) for 30 min. The evacuation was needed for removing air from mesopores in the TiO_2 particles. The suspension was then shacked for 1 h in the dark to achieve equilibrium in the system. The RhB-loaded TiO_2 containers were separated from the solution by centrifugation at 5000 rpm.

2.2. Preparation of the epoxy based coatings

CHS-EPOXY 200 V 55 epoxy emulsion and Telalit 180 amine hardener (SPOLCHEMIE) were used for preparation of the epoxy coatings with a recommended mixing ratio of epoxy emulsion to hardener as 4 to 1 by mass. RhB-loaded TiO_2/epoxy composite coatings with 0.5, 1.0, and 2.0 wt.% of TiO_2(RhB) and RhB/epoxy coatings with 0.025 wt.% of RhB were prepared by introducing an appropriate amount of RhB-loaded TiO_2 containers or RhB into the epoxy resin followed by mechanical dispersing and then addition of curing agent. The casting blade method (200-µm applicator) was used for coating preparation. The distribution of the TiO_2 particles in the cured epoxy matrix was studied by SEM and EDX mapping (TESCAN Vega3 SB microscope combined with an energy dispersive spectrometer system from EumeX), and Raman spectroscopy (Bruker Senterra Raman microscope).

2.3. Measurement of Rhodamine B photodegradation in the epoxy based coatings

Mercury lamp (Narva UVK-125-2) with maximum intensity at 365 nm was used as the UV light source. The RhB-loaded TiO_2/epoxy and RhB/epoxy coatings were irradiated by UV light for 60 min. The content of RhB in the coatings was analyzed every 5 min from the intensity of RhB characteristic peak at 553 nm. UV-Vis spectra of the coatings were recorded by a Shimadzu UV-2550 spectrophotometer.

3. Results and discussion

3.1. Characterization of the RhB-loaded TiO_2 containers

Structural characterization of the TiO_2 powder synthesized from TiC was presented in detail in [11]. The obtained titania annealed at 200 °C consists of anatase phase with a crystallite size of 3.9 nm, has mesoporous structure and a surface area of 353 m^2 g^{-1}. FTIR spectroscopy data showed the presence of a high amount of nitrate groups on the surface of as-synthesized and annealed at 200 °C TiO_2 powder. The surface nitrate groups determine negative charge of the oxide surface and superior sorption capacity to the positively charged dyes. Adsorption isotherm of RhB onto the TiO_2 powder is presented in Fig. 1. The sorption capacity of the powder annealed at 200 °C to RhB is about 35 mg/g. Intensive red coloration of the RhB-loaded powder gives an evidence of the superior dye adsorption on the titania surface (Fig. 2).
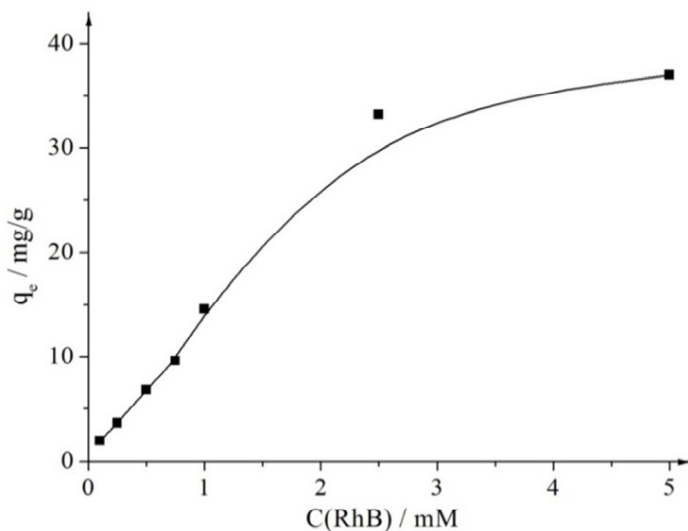

Fig. 1. Adsorption isotherm of RhB onto the synthesized TiO_2 powder annealed at 200 °C
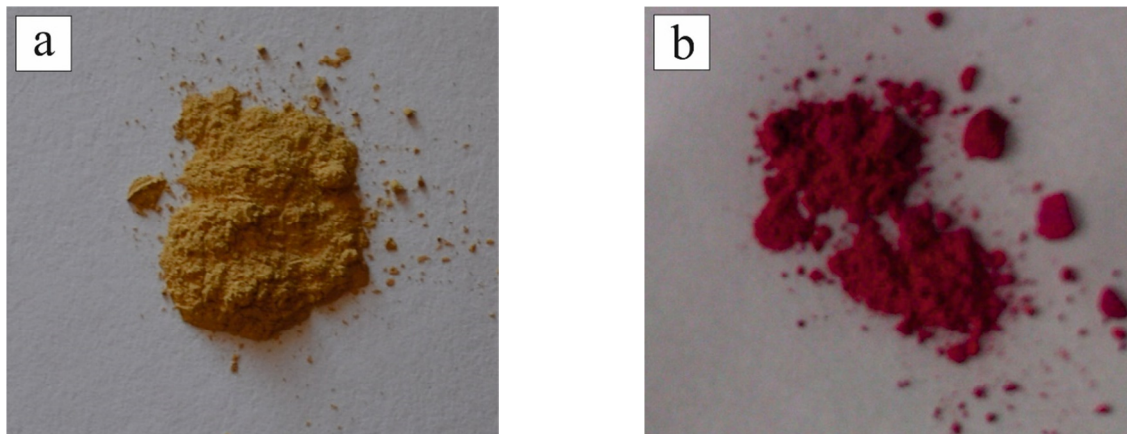
Fig. 2. Images of the TiO$_2$ powder: (a) unmodified; (b) loaded with RhB

It is well known that titanium dioxide possesses high activity in photodecomposition of the organic molecules under UV-irradiation. Upon absorption of photons with energy larger than the band gap of TiO$_2$ (3.0 – 3.2 eV [12]), electrons are excited from the valence band to the conduction band, creating electron-hole pairs. These charge carriers migrate to the surface and react with the adsorbed chemicals, decomposing them. This photodecomposition process usually involves one or more radicals or intermediate species such as ·OH, O^{2-}, H$_2$O$_2$, or O$_2$, which play important role in the photocatalytic reaction mechanism [13].

It was previously shown [11] that the mesoporous TiO$_2$ powder synthesized from TiC is photocatalytically active in the photodegradation of Rhodamine B in aqueous solutions under UV irradiation. Based on the data of high sorption capacity and photocatalytic activity under UV irradiation, we assumed that such TiO$_2$ containers loaded with RhB can be used as fillers of polymer coatings for determination of UV irradiation impact on the coating.

3.2. Characterization of the epoxy based coatings

The prepared epoxy films have a thickness of ~60 µm and non-porous structure (Fig. 3). UV–Vis spectroscopy demonstrates that the TiO$_2$-free epoxy coatings are transparent at $\lambda > 300$ nm (Fig. 4a). Thus, the epoxy coatings are characterized by transparent window, which allows photons with energy from the region of intrinsic absorption of TiO$_2$ to penetrate to the oxide particles and generate electron-hole pairs in TiO$_2$.
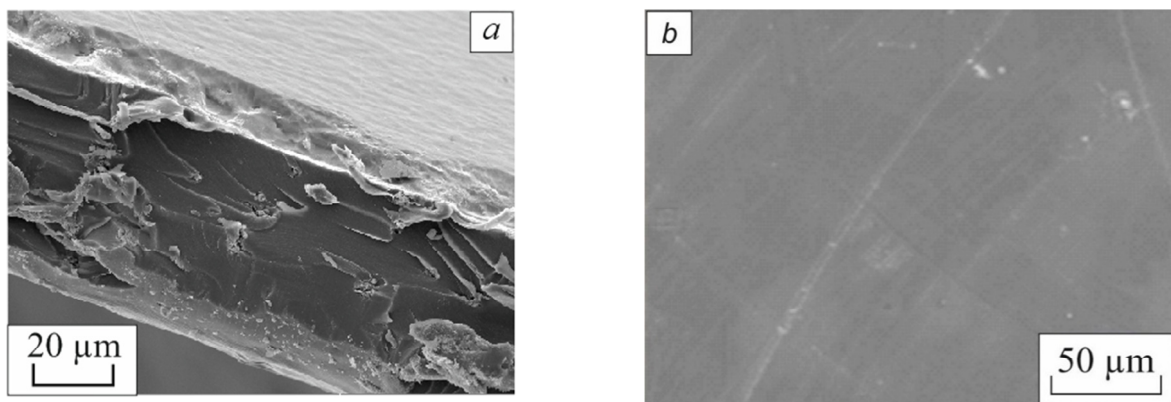
Fig. 3. SEM images of the TiO$_2$-free epoxy coating: (a) cross-section; (b) top view
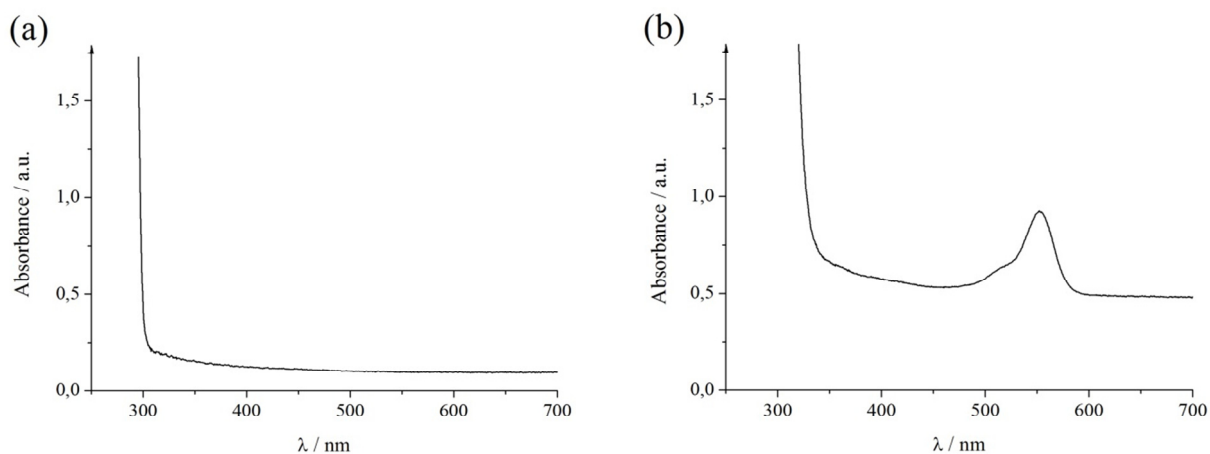

Fig. 4. UV-Vis spectra of TiO$_2$-free epoxy coating (a) and epoxy coating filled with 1 wt.% of RhB loaded-TiO$_2$ containers (b)

Filling the epoxy coating by RhB loaded-TiO$_2$ containers results in a partial reduction of the transparency of the coating due to light scattering by oxide particles and RhB absorption peaked at 553 nm (Fig. 4b).

The micron size of the TiO$_2$ containers [11] allows dispersing them mechanically in the polymer matrix. The epoxy based coatings with 0.5, 1.0, and 2.0 wt.% of RhB loaded-TiO$_2$ containers are characterized by an uniform distribution of the containers. Fig. 5 shows SEM image and corresponding EDX mapping of the epoxy based coating filled with 1 wt.% of the containers. Raman spectroscopy data confirm the uniform distribution of the titania particles in the polymeric matrix (Fig. 6). The most intensive Raman band of anatase phase at 154 cm^{-1} was used for identification of the TiO$_2$ particles [14].
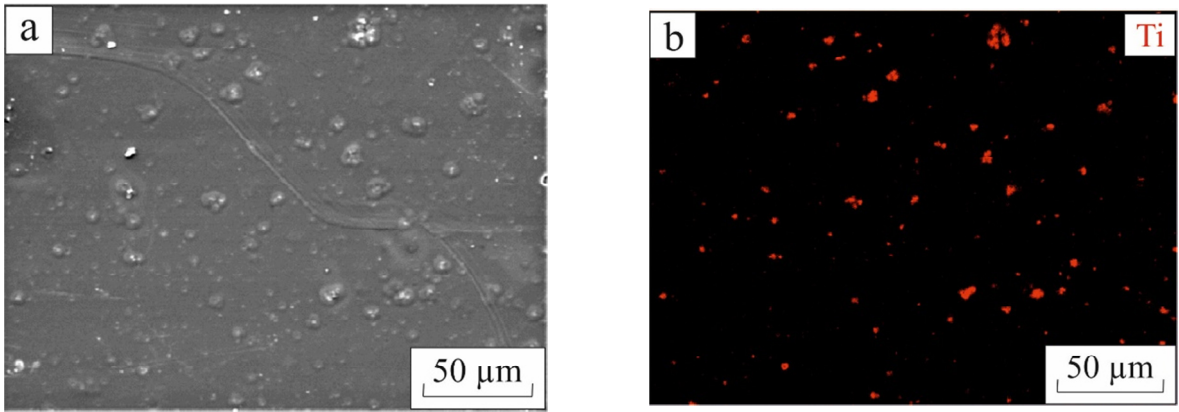
Fig. 5. SEM image (a) and corresponding EDX mapping for Ti element (b) of the epoxy based coating filled
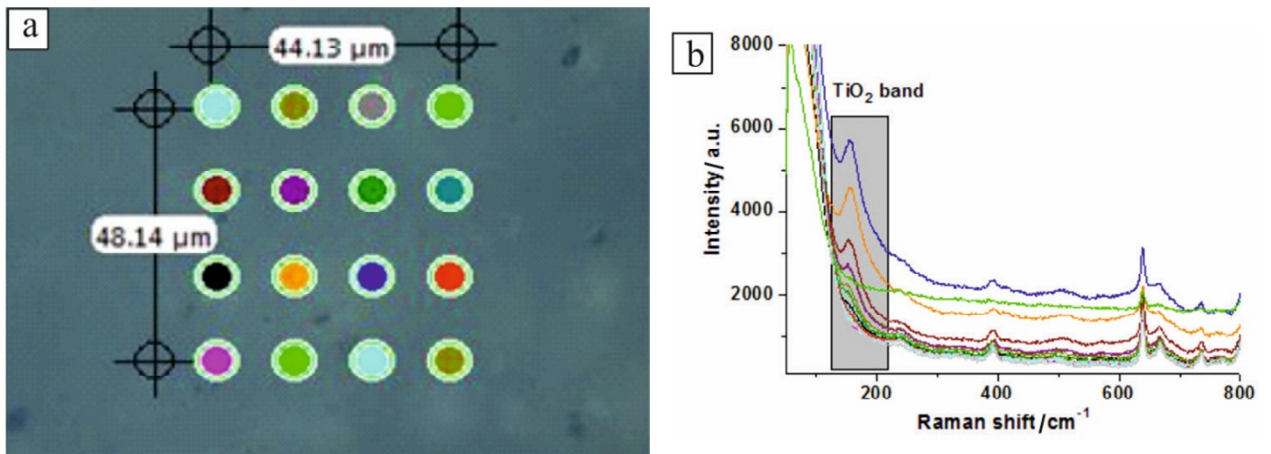with 1 wt.% of RhB loaded-TiO_2 containers

Fig. 6. Optical image (a) and corresponding Raman spectra (b) of the epoxy based coating filled with 1 wt.% of RhB loaded-TiO_2 containers

3.3. Discoloration of the TiO$_2$(RhB)/epoxy coatings under UV irradiation

The prepared epoxy based composites filled with RhB loaded-TiO$_2$ containers were found to be sensitive to UV radiation. Fig. 7 shows evolution of the RhB absorption peak for the composites as a result of their exposure to UV light for different periods of time. This evolution occurs due to dye degradation in contact with titania. Changing the RhB content in the TiO$_2$-free composite after 60 min of UV irradiation was significantly weaker than in the case of the composites filled with RhB loaded-TiO$_2$ containers, evidencing that TiO$_2$ plays a key role in the RhB decomposition under UV illumination of the coatings.
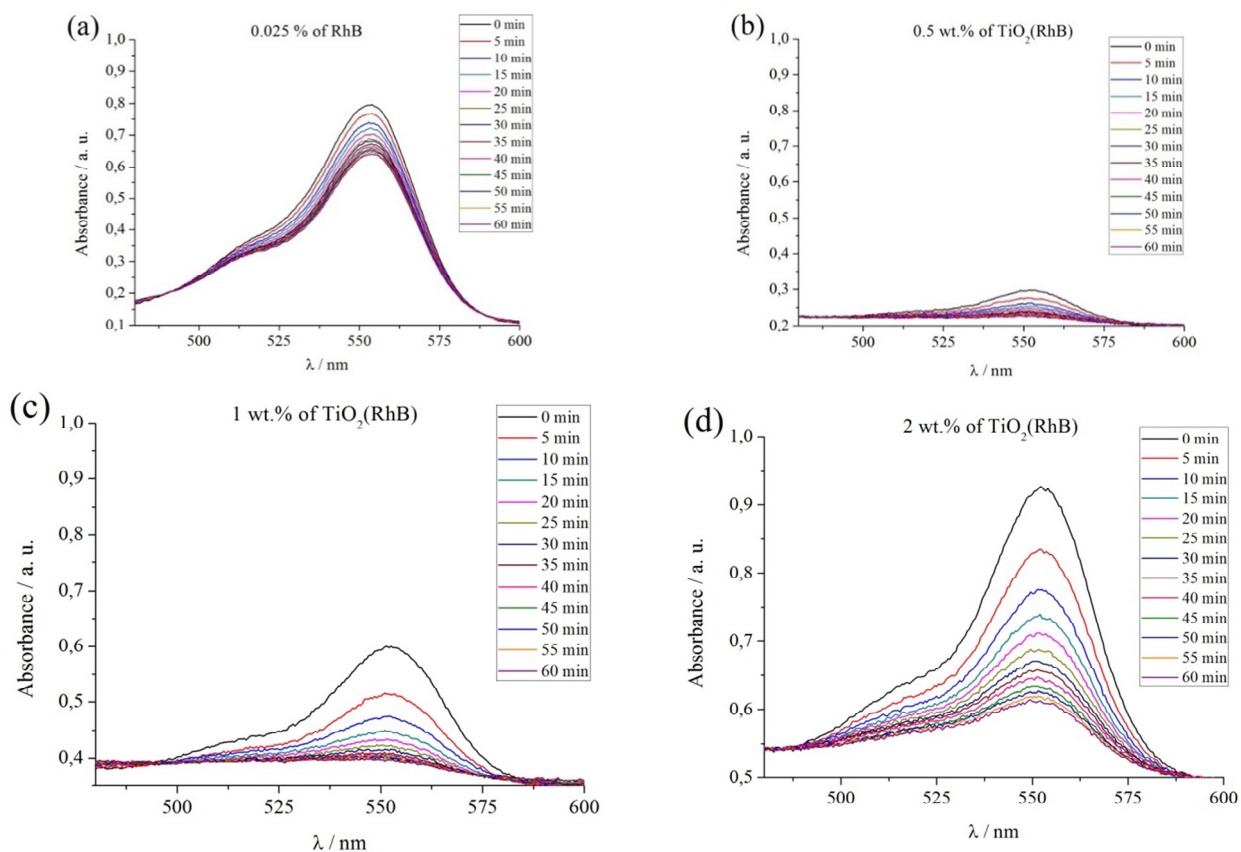

Fig. 7. UV-Vis spectra of the epoxy coatings filled with 0.025 wt.% of RhB (a) and
0.5 (b), 1.0 (c), 2.0 (d) wt. % of RhB loaded-TiO$_2$ containers after exposure to UV light for different periods of time

The kinetics of RhB photodecomposition on the oxide surface can be described by the second-order equation:

$$\frac{c_0}{c} = 1 + kt, \tag{1}$$

where k is the rate constant (min^{-1}), C_0 the initial concentration of the dye, and C the actual concentration of the dye at irradiation time t. Fig. 8b presents the linear relationship between C_0/C and irradiation time. The rate constant k is determined from the slope of the linear C_0/C vs t plots. The value of k gives an indication of the efficiency of discoloration of the coating under UV irradiation. The rate constant for the composite filled with 1.0 wt.% of RhB loaded-TiO$_2$ containers is 0.1499 min^{-1}. Increase or decrease of the amount of the additive leads to lowering the efficiency of coating discoloration. Rate constant for the composite filled with 0.0025 wt. % of RhB without TiO$_2$ has a very low value (0.0048 min^{-1}).
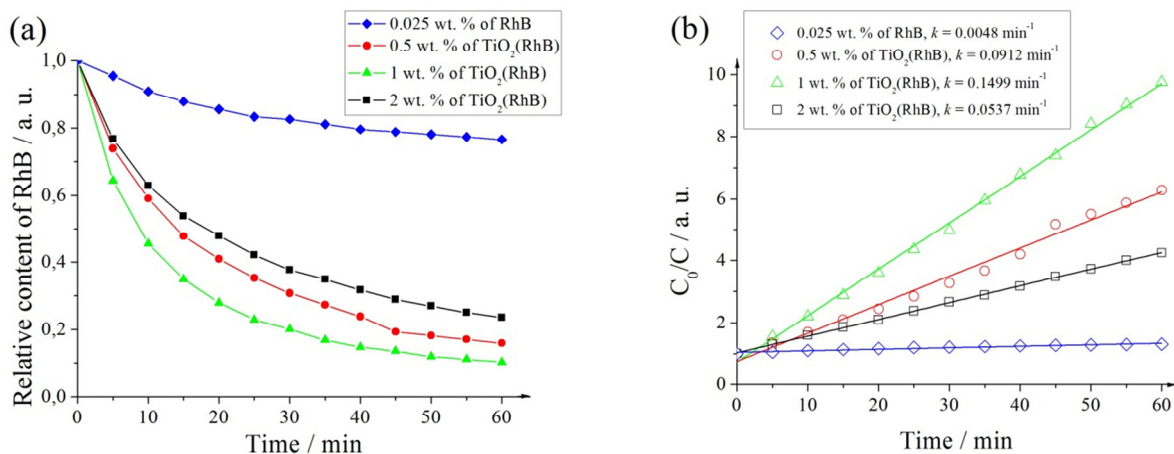

Fig. 8. Variation of the relative RhB content in TiO$_2$(RhB)/epoxy coatings as a function of irradiation time (a) and fitting of the experimental data using second-order kinetic model (b)

Fig. 9 shows images of the as-prepared epoxy based coatings filled with RhB loaded-TiO$_2$ containers and UV irradiated during 60 min. Thus, UV irradiation of the coatings can be detected not only by special equipment (for example, densitometer), but also visually. Variation of the introduced amount of the additive allows getting materials, which will possess sensor response to different intensity of UV radiation affecting the coating.

Fig. 9. Images of the as-prepared epoxy based coating filled with RhB loaded-TiO$_2$ containers (a) and UV irradiated during 60 min (b)

4. Conclusion

RhB-loaded TiO_2/epoxy composite coatings with a uniform distribution of the titania particles have been prepared. It has been shown that these composites effectively decolorize under UV illumination. Efficiency of the decolorization depends of the amount of RhB-loaded TiO_2 additive introduced into the coating. The epoxy coating with 1 wt.% of RhB loaded-TiO_2 containers is characterized by the highest rate of decolorization. Decomposition of Rhodamine B in the epoxy coatings under UV irradiation has been found to occur mainly due to photocatalytic activity of the TiO_2 powder. The prepared composites can be used as UV-sensor materials.

Acknowledgements

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