

The Effect of UV Exposure on the Service-life of Thermochromic Microcapsules Integrated into the Epoxy Matrix

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The effect of ultraviolet (UV) exposure on the service-life of thermochromic microcapsules integrated into the epoxy matrix was investigated. The microcapsules of the formaldehyde shell contain the core of thermochromic leuco dye. Seven sets of epoxy resin samples filled with concentrations from 0 to 10 wt.% of microcapsules were investigated. The composite samples were exposed to UV for approximately 1000 h. For the quantitative evaluation of colour change under UV, a fast and simple original procedure based on samples' image treatment was developed. With the exposure time intervals of 50 h, samples were taken out from the UV light chamber to evaluate the exposure effect on their reversible thermochromic ability and mechanical properties. Periodical evaluation of the UV light effect on mechanical properties during the exposure was performed by microhardness tests. Tensile tests of the samples till the fracture were performed every 200 h. The critical time under the exposure of the UV lamp that destroys the reversible thermochromic reaction of the microcapsules was defined as 200 h. At the same time, it has been found that the mechanical properties of the epoxy resin under the same UV source were not strongly affected after 1000 h of irradiance and changed in the frame of ~ 10 %.
Keywords: thermochromic materials, microcapsules, ultraviolet degradation, epoxy resin.

1. INTRODUCTION

Application possibilities of a composite structure could be extended by incorporating stimuli-responsive microcapsules in the structure [1]. Thanks to relatively simple manufacturing conditions, the use of microcapsule-filled polymers is advantageous compared to other methods, such as the embedding of sensors or other complicated methods. The reaction on various triggers, like applied force [3, 4], elevated temperatures [5], or ultraviolet (UV) light [6] could be integrated into polymers. By this simple approach, smart structures with extended applications could be developed.

In the present work, triggers reacting on elevated temperatures were studied – namely, microcapsules containing thermochromic dyes. Thermochromic dyes reversibly change colour when heated and return to the original colour on cooling [7]. Thermochromic dyes can be used as a temperature indicator for various applications (toys, souvenirs, paints, clothes, packaging). Studies devoted to the energy storage and efficiency of buildings, e.g., smart windows, where solar heat flow can be dynamically controlled [8], are of particular interest. Construction materials [9, 10] or roof coatings [11] with thermochromic dyes can affect optical properties, thus controlling the surface temperature, and as a result, indoor temperature.

The thermochromic dye is encapsulated to protect it from the effects of environmental factors, but even encapsulated, it remains sensitive to UV. Thermochromic microcapsule colours are visible to the naked eye due to transparent capsule shells, exposing the thermochromic core and letting light interact with chromophores through

absorption and emission. This naturally raises the question of whether these microcapsules are viable for use in constructions under direct sunlight as UV radiation is a part of the total terrestrial insolation spectrum. Thus, the aim of the study was to evaluate the effect of UV exposure on the service-life of thermochromic microcapsules integrated into the polymer matrix and on the mechanical properties of such composite. To achieve the aim, several tasks were outlined:

1. Develop a procedure for the quantitative evaluation of samples' colour change.
2. Applying the procedure, experimentally evaluate the change of thermochromic ability and estimate the service-life of microcapsules in the composite under UV exposure.
3. Evaluate an effect of UV exposure time on mechanical properties of epoxy resin matrix loaded with thermochromic microcapsules.

2. EXPERIMENTAL DETAILS

2.1. Materials and samples

Epoxy resins are widely used as bases for paints and finishing coatings and have good adhesion to different surfaces. Epoxy resin Biresin® CR122 (A) with hardener (B) Biresin® CH122-5 (both from Sika) in a ratio of 100:30 by weight were used as a polymer matrix for sample manufacturing.

The reverse thermochromic microcapsules (Insilico) with shell material containing formaldehyde and thermochromic leuco dyes as a core, were used as a filler. The “reverse” means that colour appeared after applied heat over ~ 60 °C (coloured phase) and disappeared after the

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cooling down (colourless phase). Microcapsules were provided in powder form. Microcapsules were added into the epoxy resin and hand-mixed for 5 min.

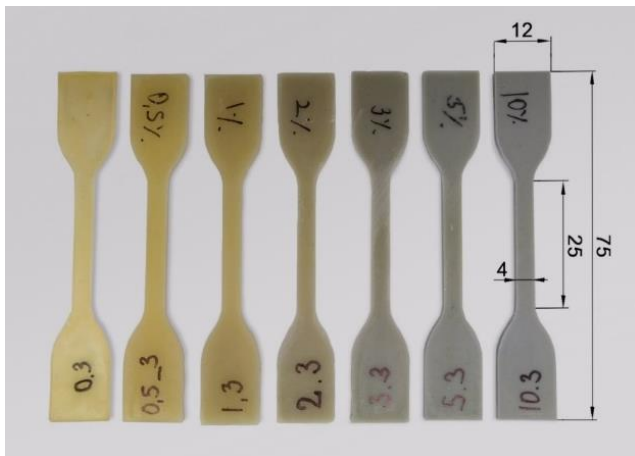


Fig. 1. Dog-bone shape samples with different concentrations of microcapsules

Next, the hardener was added and mixed for around 2 min. The final mixture was vacuumed for 5 min and cast in the silicone moulds. Series of samples with a concentration of microcapsules 0, 0.5, 1, 2, 3, 5, and 10 wt.% were prepared. Representative samples are presented in Fig. 1. Dog-bone shape samples were produced for mechanical testing and rectangular ones for the evaluation of colour change.

After the curing at room temperature for 24 h, samples were post-cured at 50 °C for 8 h. The microcapsules colour activation temperature was not to exceed for the long time periods. It was defined that storing samples at 70 °C for 24 h did not influence the ability of the sample to change colour after cooling down and heating again. While after storing at 110 °C, the sample changed its colour irrevocably, and after the cooling down and heating, the difference in colour was notable slightly, see Fig. 2.

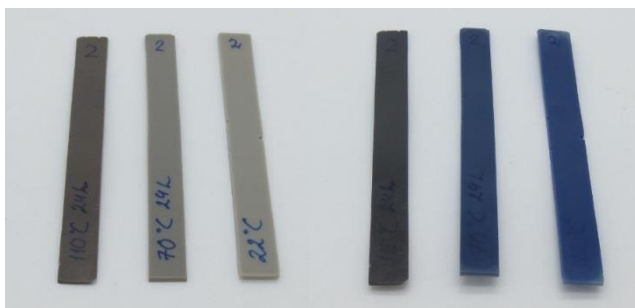


Fig. 2. Samples on the colourless form stored at 110, 70, and 22 °C for 24 h (left), same samples in the coloured form (right)

2.2. The procedure for the quantitative evaluation of samples' colour change

A procedure for the quantitative evaluation of samples' colour change includes two steps: photographing and image treatment.

At first, before UV, three images were taken: a neat epoxy sample, sample with thermochromic microcapsules in the colour phase and in colourless phase. During UV treatment, after certain time intervals, images of the same

samples were repeated. To exclude the influence of the surrounding light, samples were photographed in the lightbox and the parameters of the camera were not changed.

The image treatment procedure for quantitative evaluation of samples' colour change was performed in the graphic editor Adobe® Photoshop® software and included the following actions. A grayscale mask as a filter was put on the image to adjust the luminosity. For the control of the luminosity on each photo, we had a red silicone rectangle next to the samples, and exactly it was used for photo calibration. It was matte, and no reflections were formed on it. The area from the silicone rectangle was "cut and placed" on other images. A grayscale mask as a filter was put on the image, and the luminosity was adjusted. Schematically, the image treatment procedures' steps are presented in Fig. 3. In this case, the luminosity does not influence the data of the image and data could be compared for different images. For comparison of samples with different UV exposure-times in coloured and colourless phases, data of the image was collected from the Histogram panel. A Histogram panel illustrates how pixels in an image are distributed by graphing the number of pixels at each colour intensity level. The Histogram panel offers many options for viewing tonal and colour information about an image, but in the present work, only options Mean, and channels R, G, and B were used to obtain information about the image. Here Mean represents the average intensity value, and R, G, B – every colour intensity value, respectively [12].



Fig. 3. The reference sample (left) and sample under treatment (middle), treated sample with a grayscale mask and adjusted luminosity (right). The selected area for the adjustment of luminosity is shown in all images

2.3. Selection of samples for testing

Samples for testing were selected by two criteria: 1) Samples should be enough colour contrast between coloured and colourless phases; 2) The mechanical properties of the filled samples should not be significantly degraded by the added microcapsules, so a threshold of 10 % was chosen. Applying the image treatment procedure described before, the visual reactions of samples depending on concentrations of microcapsules were compared. The intensive visual reaction was observed for samples in the coloured phase at 65 °C filled with 3 wt.% and more, see Fig. 4.

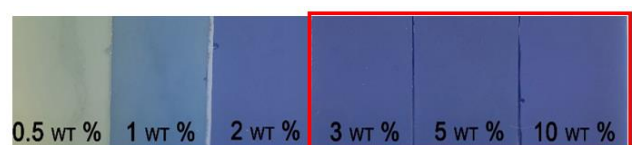


Fig. 4. Samples in coloured phase filled with different concentrations of microcapsules

Colour intensity values R, G, B, and Mean are presented in Fig. 5 (top) and the ratio of each colour to Mean value (bottom). Each colour channel was normalized to the Mean value of the same image to exclude the difference between images obtained by non-controlled factors.

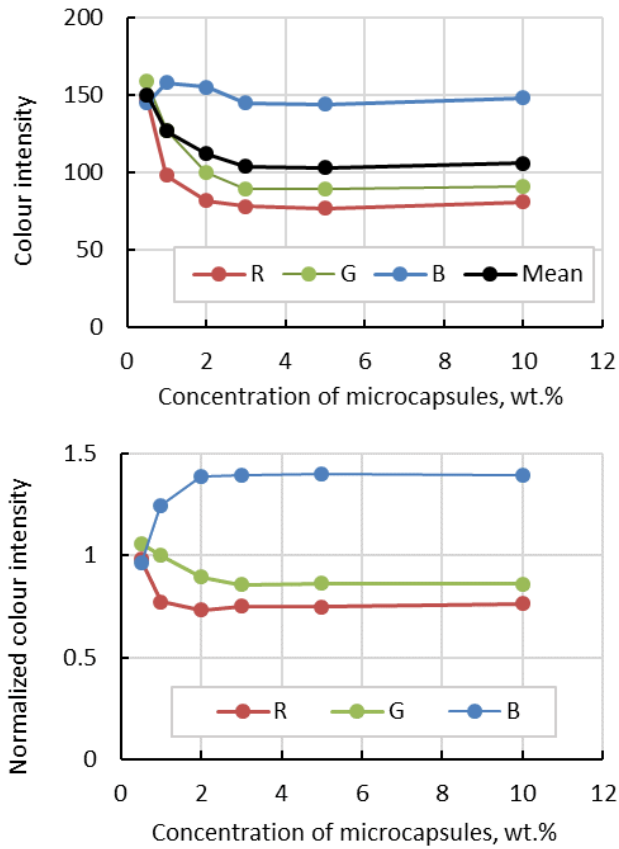


Fig. 5. Colour intensity values of separate channels R, G, B, and Mean dependence on the concentration of microcapsules (top). The dependence of each colour channel R, G, B, normalized to the Mean value on the concentration of microcapsules (bottom) [13]

For samples with all made concentrations, the strength and elastic modulus were determined by quasi-static tensile tests performed on a Zwick 2.5 universal testing machine with a rate of 1 mm/min at a temperature of 22 ± 2 °C. Comparing elastic modulus values of samples with different concentrations of microcapsules, it was defined that filling with microcapsules till 2 wt.% did not affect the value of elastic modulus. Similar results were obtained for the ultimate tensile strength, see Fig. 6. Elastic modulus of samples filled with 3 wt.% of microcapsules $E_{3\%} = 1.67 \pm 0.03$ GPa decreased in 5 % comparing to the reference one $E_0 = 1.75 \pm 0.05$ GPa.

Based on mechanical testing and results of visual response testing, samples with 3 wt.% were selected for further work, and neat samples were used as a reference.

2.4. Colour change under UV

Before UV exposure, three images were taken as references: neat epoxy sample and sample with microcapsules 3 wt.% in coloured and colourless forms. After, these samples were placed under the UV lamp and

stored for 1000 h at 40 °C. During the exposition under the UV lamp, the samples were not in the coloured phase.

As a UV source, a high-pressure mercury-vapour discharge lamp was used with the following parameters: the strongest peak at a wavelength of ~ 365 nm, current 3.8 A, voltage 170 V, power 230 W, and irradiation intensity 40 W/m^2 . Selected irradiance level strongly overcome the typical maximum irradiance of summer sunlight at noon of 0.68 W/m^2 [14].

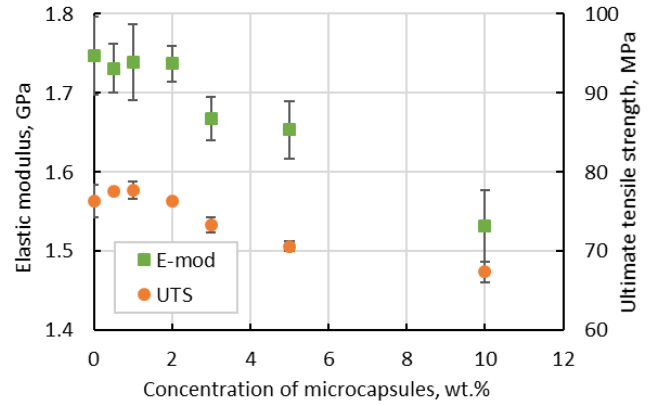


Fig. 6. Elastic modulus (■) and ultimate tensile strength (●) dependence on the concentration of microcapsules in the sample

Photos of samples in colour and colourless phases were taken with a time interval of 24 h from the beginning of the experiment and after the 500 h of UV exposure with the interval of 50 h. In the result of images treatment, data about colour change were collected for the neat sample and samples with 3 wt.% in colour and colourless phases on the dependence of UV exposure time.

2.5. Mechanical properties change under UV

For periodical evaluation of the UV exposure effect on mechanical properties during the irradiation, a microhardness by Vickers was used as a non-destructive method of control. The microhardness was measured with the load $F = 0.1$ kgf and loading time 10 s according to ASTM E384-17. By micro photos, see Fig. 7, diagonal length d was defined. Microhardness by Vickers was calculated by

$$H_v \approx \frac{1.8544 \cdot F}{d^2} \frac{\text{kgf}}{\text{mm}^2}. \quad (1)$$

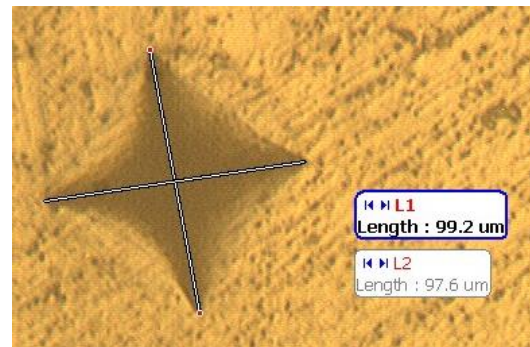


Fig. 7. Elastic image of a neat epoxy sample, the measurement of the diagonal left by the indenter

The measurements were done with the same frequency as a photo control of colour changeability, every 24 h at the beginning of the experiment, and after the 500 h of exposure with the interval of 50 h. Tensile tests till the fracture were performed on universal testing machine Zwick 2.5 every 200 h of exposure with a test speed of 1 mm/min.

3. RESULTS

3.1. Colour change and service-life of microcapsules in the composite under UV

For neat epoxy samples, it was defined that under the action of UV exposure, samples became more yellow. By treatment of images of the neat epoxy samples during UV, was defined that the R colour channel value was sharp growing by the exposure time till 200 h and later remained particularly unchanged, see Fig. 8 top. This result correlates well with the upper line of Fig. 9 for the epoxy sample.

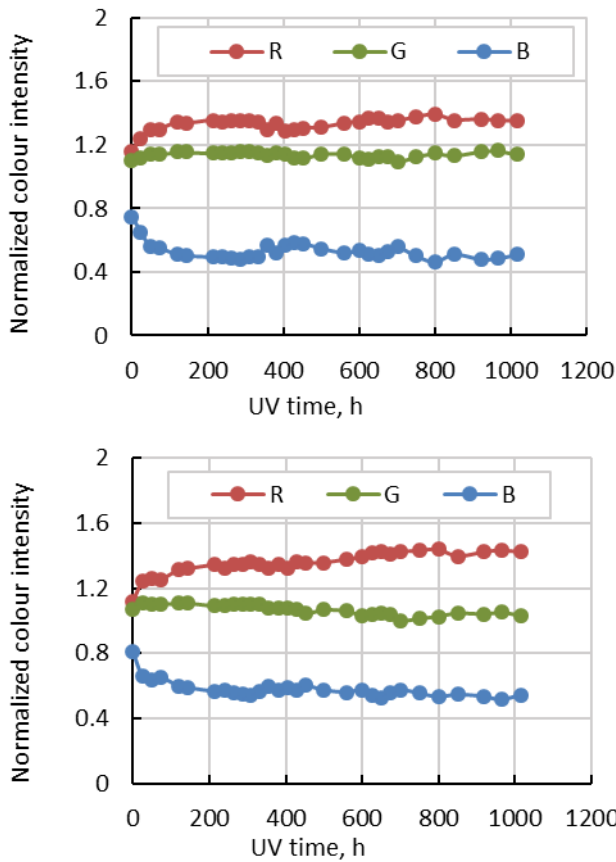


Fig. 8. R, G, B channels values normalized to Mean value for neat epoxy samples (top) and filled samples in colourless phase (bottom) during UV exposure

For filled samples in the colourless phase, a similar tendency was observed for the first 200 h. In the next hours, the value of the R channel continues to grow slower under UV exposure, see Fig. 8 top and the middle line of Fig. 9. It could be concluded that the colour change of samples was influenced both by the colour change of epoxy resin and the degradation of the filler under UV. But the samples in the colour phase are of most interest.

The dependence of R, G, B colour intensity value normalized to Mean on exposure time for samples in coloured phase is presented in Fig. 10.

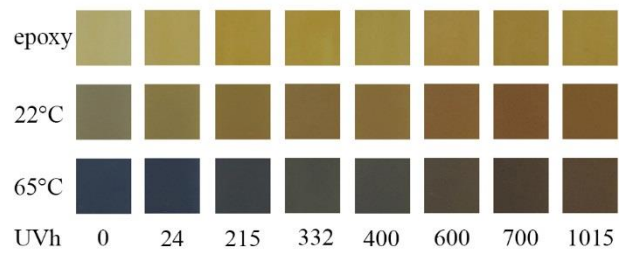


Fig. 9. Samples during UV exposure: neat epoxy (upper line), in colourless (middle line) and colour (lower line) phases

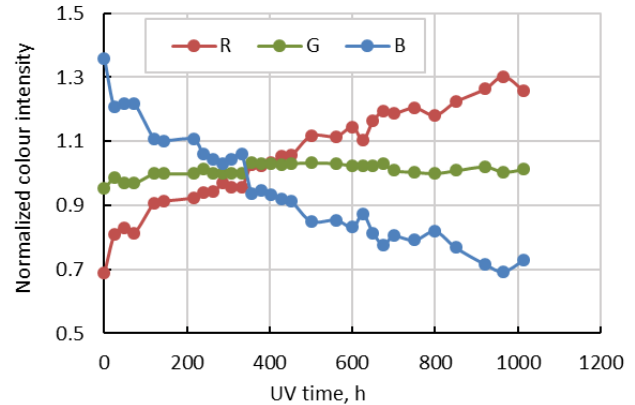


Fig.10. R, G, B channels values normalized to Mean value for filled samples in colour phase during UV exposure [13]

The first intensive drop of B colour value is observed after 24 h, then a plateau is observed till the next drop, and plateau again. This tendency could be observed several times till the cross with the R colour channel and after. Starting from the cross point with the R, approximately at 300 h, the B is not dominating one in samples. So, we can expect that this UV exposure time was enough to destroy the core of thermochromic microcapsules. Further, the R channel became dominating and after the elevating temperatures, samples become more brown than blue, see the lower line of Fig. 9. By growing the red colour value, it was difficult to catch even the difference between samples in colourless and coloured phases.

Verification of the obtained results was performed on samples prepared before (5 and 10 wt.%) and not used for testing. In addition, samples with the same concentration (3 wt.%) were selected. The effect of UV exposure on colour change could be detected after a short period, thus for the testing, only 30 h were selected. As well, this time interval includes 2 points (0 and 24 h) from the previous experiment (Fig. 10). Here, a similar data treatment procedure was applied. In the result, the B value normalized to the Mean value for every observed UV exposure time was obtained, and a similar for each concentration was done. For the comparison of results, the first points of the experiment $B_{UVt=0} / Mean_{UVt=0}$ were defined as 100 % and other points $B_{UVt=i} / Mean_{UVt=i}$ were recalculated in percentage.

Obtained results are summarized in Fig. 11. Data obtained for 3 and 10 wt.% samples showed similar results, while for the concentration of 5 wt.% some deviation was observed. By this deviation, the data measurement method's error was defined as $\pm 4\%$. Two points selected from Fig. 10 matched the error interval; thus, the data obtained in

the long period of UV exposure can be considered as reliable.

For estimation of the time, when the B value is not changing anymore, and consequently, it maximally changed compared to the reference, not UV exposed sample, the fractional conversion α was used. At first, the difference between the reference value B_0 and a value B_t at a certain time t was calculated as

$$\Delta B(t) = B_0 - B_t. \quad (2)$$

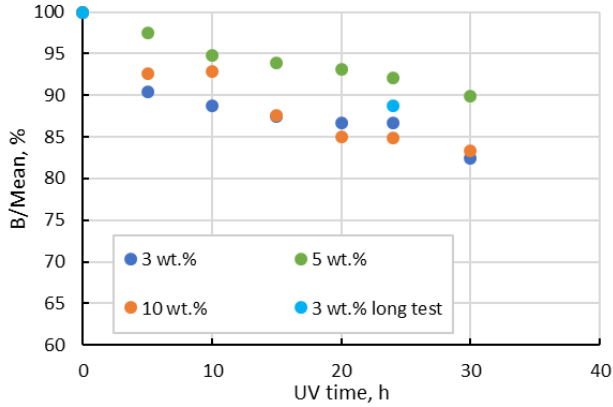


Fig. 11. The change of B/Mean value on UV exposure time for different concentrations of thermochromic microcapsules in the polymer matrix

Then, the experimental value of fractional conversion α_{ex} for blue colour was defined as

$$B\alpha_{ex} = \frac{\Delta B(t)}{B_{max}}. \quad (3)$$

Likewise, for the red colour $R\alpha_{ex}$ was obtained. The average intensity value B_{max} corresponding to the end of the thermochromic ability of microcapsules was calculated at $\alpha = 1$. The kinetics of colour change can be described with the equation

$$\alpha = 1 - e^{-kt}, \quad (4)$$

where k is a reaction rate constant [1]. Eq. 4 allows to predict the reaction run and finish. The same procedure was repeated for the R channel values. To obtain values in one scale, values were calculated as absolute. As a result, the kinetics of change for channels values R and B could be described with the same reaction rate constant $k = 0.0028$, see Fig. 12. In the tested sample, the B value is decreasing with the same speed as R is increasing.

3.2. Verification of the procedure

For the verification of the procedure for the quantitative evaluation of samples' colour change, another type of thermochromic microcapsules (Insilico) were used. The difference was that they were in colour phase at the room temperature and colourless after the activation temperature. Red and blue colour microcapsules with activation over 40 and 50 °C, respectively, were selected. Microcapsules were provided in slurry form. For making a coating for the testing, the suspension was mixed with the acrylic water-dispersed paint (Nuovamat, Rilak).

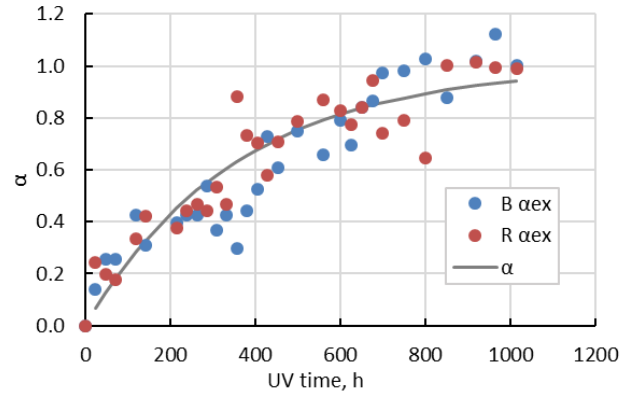


Fig. 12. The kinetics of B (blue dots) and R (red dots) values change in sample vs UV exposure time. Dots for experiment and solid line for calculation [13]

Coatings with thermochromic microcapsules were prepared on plastic panels and placed under UV lamp with the same parameters. Samples were taken out and photographed in the lightbox at certain time intervals, see Fig. 13 (top).

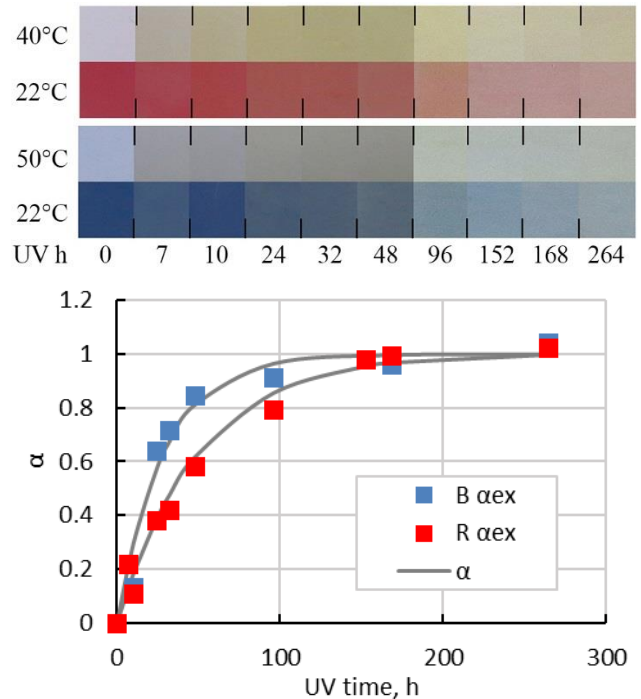


Fig. 13. Samples during UV exposure in colourless and colour phases (top). The kinetics of B and R values change of blue and red colour samples vs UV exposure time, dots are experimental values, solid lines are calculations (bottom). The colour of the experimental dots corresponds to the measured colour

Obtained results show that the developed procedure can be used for both types of samples filled with thermochromic and reverse thermochromic microcapsules.

3.3. Mechanical properties change under UV

In the result of mechanical tests, microhardness measurements (Fig. 14) and tensile tests (Fig. 15), it was defined that UV exposure time till 1000 h with and without the presence of filler does not influence the mechanical

properties of the polymer matrix significantly. The microhardness of both samples increased by ~ 11 %.

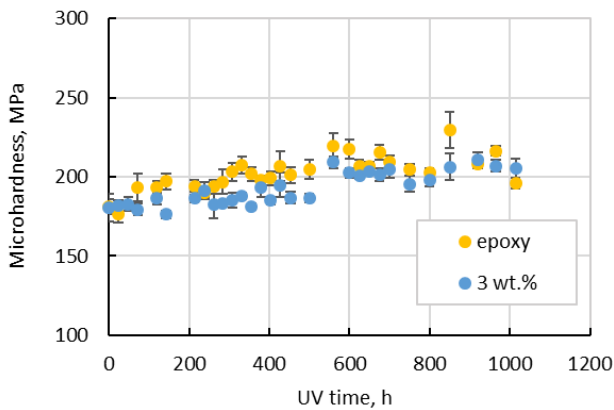


Fig. 14. The microhardness of neat and 3 wt.% filled epoxy samples on UV time

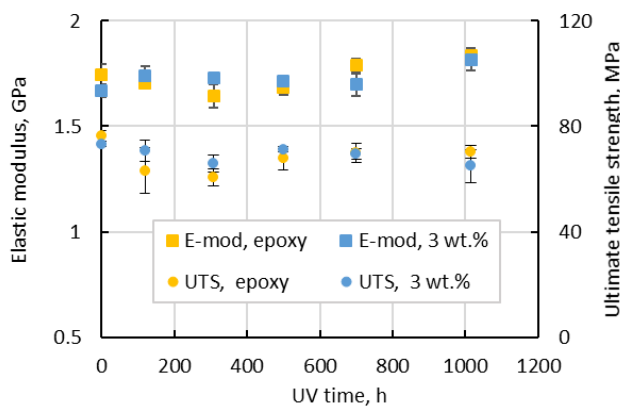


Fig. 15. Elastic modulus (■) and ultimate tensile strength (●) dependence on UV exposure time for neat epoxy (yellow) and filled with 3 wt.% (blue) samples

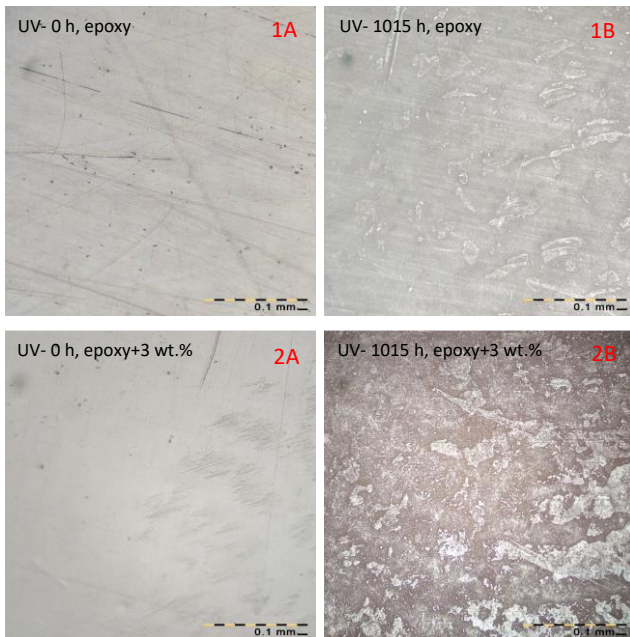


Fig. 16. Neat epoxy sample before (1A) and after UV (1B). Epoxy sample filled with 3 wt.% of thermochromic microcapsules before (2A) and after UV (2B). All under 200× magnification

Results of microhardness testing were verified by the relationship between the ultimate tensile strength σ^* and microhardness H_V in MPa by Eq. 5 [15]:

$$H_V \approx 3 \cdot \sigma^* \quad (5)$$

Obtained results correspond well to the mentioned relationship. Starting from the 500 h of UV exposure, microhardness and ultimate tensile strength stayed particularly unchanged. Comparing the reference, not UV exposed samples, ultimate tensile strength decreased by 8 and 12 %, and elastic modulus increased by 5 and 9 %, respectively, for the neat and filled samples.

Samples' surface before and after UV treatment was examined by optical microscope Olympus BX51 under 200× magnification. After the UV exposure, some changes of the surface can be observed for the neat epoxy sample and sample with thermochromic microcapsules, see Fig. 16, while no cracks were detected. Upon exposure to UV, the epoxy turned yellow as expected [16], either neat or filled with microcapsules.

A more significant change in mechanical properties of epoxy resin samples could be obtained under the combination of aggressive factors, like water or elevated temperature [17]. But relatively to thermochromic microcapsules water is not aggressive and the effect of elevated temperatures on thermochromic microcapsules was defined at the start of the testing.

4. CONCLUSIONS

As the result of the work, the original image treatment procedure for the quantitative evaluation of samples' colour change was developed. The procedure includes samples' photographing and image treatment. For the precise results, samples should be photographed in similar conditions, for example in the lightbox. Also, the parameters of the camera should not be changed during the experiment. Image treatment was performed in the graphic editor Adobe® Photoshop® software and was based on image data collected from the Histogram panel, and a comparison of these data between images. Considering the colour as three separate channels R, G, B, it is possible with a high probability to determine the beginning of the change in each channel. By this procedure, it is possible to detect the difference of colour change, and for thermochromic microcapsules which are not stable under UV exposure, define the service-life under the effect of this factor. The presented procedure allows precise quantitative evaluation of the colour change comparing to the qualitative visual inspection.

For the thermochromic microcapsules in the composite under UV the following time intervals could be outlined:

1. Till 200 h under UV, a stable colour change is observed at elevated temperatures of 65 °C. The thermochromic function of microcapsules is implemented well.
2. From 200 to 500 h under UV, the colour change at elevated temperatures still could be noticed but is not sharp comparing to the sample at room temperature.
3. Starting from 500 h under UV, the colour change of the sample at 22 and 65 °C is not notable – microcapsules fully lose thermochromic function.

For the tested microcapsules containing thermochromic material, the kinetic of colour change under UV exposure was investigated and modelled. By the proposed model based on the first order equation, it is possible to predict samples' kinetics of colour change, colour change rate and define the service life of the thermochromic microcapsules.

Exposure to UV for 1015 h did not affect the mechanical properties of the epoxy resin strictly. Elastic modulus increased by 5 and 9 %, respectively, for the neat and filled sample. At the same time, ultimate tensile strength decreased by 8 and 12 % for the same samples. Both parameters were compared with not irradiated reference samples.

In general, it could be concluded that the presented image treatment procedure of quantitative estimation of colour change allows numerically defining colour change and service-life of the thermochromic ability of microcapsules. The system of microcapsules containing thermochromic dyes can be used as a temperature indicator or regulator of surface optical properties. For the successful application of such a system under outdoor UV exposure, additional protective coating is advisable, but more studies of coating parameters are necessary.

Acknowledgments

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