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Glass fibres reinforced polyester composites degradation monitoring by surface analysis

Catalin Croitoru [a], Silvia Patachia [b,*], Adina Papancea [b], Liana Baltes [a], Mircea Tierean [a]

[a] "Transilvania" University of Brasov, Materials Engineering and Welding Department, Eroilor 29 Str., 500036 Brasov, Romania
[b] "Transilvania" University of Brasov, Product Design Environment and Mechatronics Department, Eroilor 29 Str., 500036 Brasov, Romania

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ABSTRACT

The paper presents a novel method for quantification of the modifications that occur on the surface of different types of gel-coated glass fibre-reinforced polyester composites under artificial UV-ageing at 254 nm. The method implies the adsorption of an ionic dye, namely methylene blue, on the UV-aged composite, and computing the CIELab colour space parameters from the photographic image of the coloured composite's surface. The method significantly enhances the colour differences between the irradiated composites and the reference, in contrast with the non-coloured ones. The colour modifications that occur represent a good indicative of the surface degradation, alteration of surface hydrophily and roughness of the composite and are in good correlation with the ATR-FTIR spectroscopy and optical microscopy results. The proposed method is easier, faster and cheaper than the traditional ones.

1. Introduction

Glass fibre reinforced polyester composites (GFPCs) are currently used in a plethora of applications such as construction structures, automotive covers, boat hulls, blades for wind turbines and so forth. Thus, studies regarding the influence of UV radiation on the GFPCs structure and properties under prolonged exposure are of outmost importance. Usually, these studies could be assessed by complex structural analysis, such as scanning probe microscopy, FTIR spectroscopy, correlated with colorimetric or mechanical analysis, which are expensive and time consuming [1–4].

The aim of this study is to present a simple and time efficient method for assessing the chemical modifications that occur on the surface of different types of GFPCs exposed to artificial ageing under 254 nm UV radiation, namely photographic image analysis of the surface of the composite material. The image analysis method has been successfully applied in our previous studies in order to assess the roughness profile of wood materials, UV or electron beam degradation of wood veneers [5,6] as well as the adsorption kinetic and equilibrium of different types of dyes on poly(vinyl alcohol) cryogels [7,8]. Also, degradation of synthetic polymers or composites has been studied by CIELab method, based on chromophoric group formation during the degrading process that leads to materials yellowing or browning [9a].

Even though the CIELab method has been already used for GFRPCs materials to study their degradation [9b], the novelty of this work consists in the following two aspects: (1) characterization of the sample's colour by analysing the photographic image of the sample, using a suitable software and avoiding expansive spectrophotometers use and (2) increase the sensitivity of the coloristic method by enhancing the modifications in the CIELab colour space parameters of the surface by using an ionic or polar dye adsorption on the composite surface.

The novelty of this work consists in enhancing the modifications in the CIELab colour space parameters of the surface of different types of composites when submitted to UV-irradiation, through an ionic or polar dye adsorption on the composite surface. The method relies on the principle that UV irradiation could promote degradation on the surface of the composites, which leads to the formation of polar groups. The polar groups are responsible for a higher methylene blue adsorbed amount, which leads to an intensification of the stain colour, thus providing information about the performance of the material (testing of UV-protective coatings, correlation with the water adsorption values). Methylene blue adsorption from aqueous solutions has been widely used in determinations regarding the oxidation degree for cellulosic materials or for surface area determinations of different oxide materials, calcium carbonate [10], graphite, activated carbons, yeast [11,12],

* Corresponding author. Tel.: +40 741649792.
E-mail address: st.patachia@unitbv.ro (S. Patachia).

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etc. Also, staining with this dye is frequently used in medicine and microbiology in order to enhance the visibility of the cellular components or to highlight possible dysfunctionalities (such as abnormal growth) [13].

Up to this date, there are no studies in the reference literature regarding the possibility of monitoring the degradation of GFPCs exposed to UV radiation, by quantifying the amount of methylene blue adsorbed on the material's surface, through CIELab method.

Studies regarding the influence of radiation with a wavelength smaller than 300 nm on the structure and properties of polyester composites have not been extensively reported up to date. Most of the studies from the reference literature report the use of prolonged UV-A and UV-B irradiation on several unsaturated and/or aromatic polyester matrices [14,15]. Our approach, in using a low wavelength UV radiation (254 nm) decreases the necessary time in evaluation of the surface changes and offers permanent information regarding the efficiency of the protective coating.

2. Materials and methods

2.1. Materials

In this study, two different types of commercial GFPCs with red and white acryl coatings of 0.2 mm thickness have been used.

The polymer matrix of the composites is composed of an ortophtalic-based resin (ENDYNE H 68372TA) and the reinforcing agent consists in a glass-fibre mat roving (E-type, Owens-Corning Composites LLC, U.S.A.). The average fibre weight fraction of the composites has been 32%.

The red-coated composite consists in a layer of glass-fibre roving embedded between two layers of ortophtalic resin and the white-coated composite contains uniformly distributed glass fibres into the resin.

For the image analysis, water adsorption, methylene blue staining and FTIR spectroscopy the composites have been cut into circular specimens of 30 mm diameter (the white coated samples) and 20 mm diameter (the red samples) respectively. The composite material average thickness was 2.50 mm for the white samples and 3.30 mm for the red samples.

All of the specimens were washed with ethanol in order to remove the contaminants from the surface, dried at 105 °C for 4 h and then conditioned for a week at 24 °C and 54% relative humidity prior to analysis. The average humidity at equilibrium for the two types of conditioned composites was 0.150% for the white samples and 0.206% for the red samples.

2.2. Methods

2.2.1. Accelerated ageing of GFPCs

The conditioned GFPCs have been introduced in an UV-irradiator (Bio-Link 254, Viber-Lourimat) and exposed for a total time of 10 h to a UV radiation of 254 nm, having the irradiance value set at 120 mJ/cm^2. During the irradiation experiments the relative humidity in the chamber was 55 ± 5% and the temperature 24 ± 5 °C. Two sets of samples from each types of obtained composite have been exposed to UV on the coated and respectively non-coated side.

The notation of the samples in the tests performed is the following:

I: initial non-irradiated sample;
R: sample with red coating;
W: sample with white coating;
F: coated side of the sample;
B: uncoated side of the sample;
UVF: UV-irradiated on the coating;
UVB: UV-irradiated on the back (not protected by coating);
MB at the end of the codification: samples immersed in methylene blue solution.

2.2.2. Water adsorption tests

The conditioned GFPCs were immersed into closed recipients containing 10 mL of distilled water, and their mass has been determined at precise time intervals during a 24 h interval.

The relative mass gain at equilibrium (Δm_{eq}) of the samples during water storage was calculated using Eq. (1) [16]:

$$\Delta m_{eq} = \frac{(m_{eq} - m_{t=0})}{m_{t=0}} \times 100 \quad (1)$$

where m_{eq} is the mass of the composite (initial and irradiated on various sides) at equilibrium of water sorption and $m_{t=0}$ is the mass of the composite before water immersion (at $t = 0$).

2.2.3. Methylene blue adsorption on the composite's surface

In order to determine the possible structural modifications that occur on the surface of the samples during UV irradiation (polar groups formation) the GFPCs samples have been introduced in 10 mL of 200 mg/L aqueous methylene blue solution for 1 h, removed from the liquid and dried for 24 h at room temperature. Then, the pictures of coloured dried samples have been taken and used for the image analysis interpretation, according to Section 2.2.4.

2.2.4. Image analysis

Colour changes on GFPCs surfaces due to UV-irradiation were analysed using an alternative technique to those extensively used up to this date. The novelty is the using of photographic image analysis, instead of a photocolorimeter. In our previous papers we have demonstrated that this technique offers good relative results on UV-irradiated wood, in agreement with experimental data obtained by other analysis methods, such as FTIR spectroscopy [5,6].

Initial photographic images of the irradiated samples and reference, as well as of the samples after MB sorption have been taken with the help of a Sony DSC110 digital camera (3072 × 2034 pixels resolution), under the same lighting conditions.

The individual images of the samples have been loaded in Adobe Photoshop and the L^*, a^*, b^* parameters using the CIELAB (8 bit) channel were determined in twenty points for each specimen, and the average value was used in further interpretations.

L^* represents the lightness and varies from 100 (white) to 0 (black) while a^* and b^* represent chromaticity indexes: $+a^*$ red, $-a^*$ green, $+b^*$ yellow, $-b^*$ blue.

The colour differences have been calculated using Eqs. (2)–(4) and the total colour difference parameter ΔE^* has been calculated from Eq. (5) for each irradiated sample before and after MB sorption [17]:

$$\Delta L^* = L_2^* - L_1^* \quad (2)$$

$$\Delta a^* = a_2^* - a_1^* \quad (3)$$

$$\Delta b^* = b_2^* - b_1^* \quad (4)$$

$$\Delta E^* = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}} \quad (5)$$

where subscript 1 denotes the values obtained for the reference and subscript 2 denotes the values after UV irradiation on the coated and uncoated side respectively.

Positive values of Δa^* describe a red shift, negative values of Δa^* a green shift, while positive values of Δb^* represent a yellow shift and negative values of Δb^* a blue shift for the colour of the irradiated samples, in comparison to the reference.

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