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ASSESSMENT OF THE EFFECTIVENESS OF SELECTED COATINGS FOR PROTECTION AGAINST UV RADIATION IN GLASS FIBER REINFORCED COMPOSITES (GFRP)

The paper describes the effectiveness of selected protective coatings against ultraviolet radiation in glass fiber reinforced composites. Epoxy resin matrix GFRP composites with 1 mm thick coatings were produced. Four types of coatings were compared: pure epoxy resin, epoxy resin with the addition of a UV stabilizer from the benzophenone group, epoxy resin with an addition of graphite (screening function) and a commercial polyester gelcoat. The composites were irradiated for 1000 h with ultraviolet radiation from three separate radiation ranges: UVA, UVB, UVC. The changes in the surface appearance, flexural strength and chemical structure were described. The results shows that UV radiation caused changes in the surface condition for the reference samples (coating without additives), such as yellowing and matting. Also, a reduction in the flexural strength by over 10% and changes in the chemical structure, mainly caused by oxidation processes and the cracking of chemical bonds were observed. The most beneficial protection was found to be the UV stabilizer from the benzophenone group, the addition of which provides UV protection over the entire radiation range and protects the material against negative changes in the coating's chemical structure. Also, similar results were obtained for the samples with the graphite coating.

Keywords: GFRP, polymer composites, UV degradation, coatings

OCENA SKUTECZNOŚCI WYBRANYCH POWŁOK OCHRONNYCH PRZED PROMIENIOWANIEM UV W KOMPOZYTACH WZMOCNIONYCH WŁÓKNEM SZKLANYM (GFRP)

Opisano skuteczność wybranych powłok ochronnych przed promieniowaniem ultrafioletowym w kompozytach wzmacnianych włóknem szklanym. Wytworzono kompozyty GFRP z żywicą epoksydową i powłokami o grubości 1 mm. Porównano cztery rodzaje powłok: czysta żywica epoksydowa, żywica epoksydowa z dodatkiem stabilizatora UV z grupy benzofenonów, żywica epoksydowa z dodatkiem grafitu (funkcja ekranizowania) oraz komercyjny żelkot poliestrowy. Kompozyty poddawano działaniu promieniowania UV przez trzy różne zakresy promieniowania: UVA, UVB, UVC przez 1000 godzin. Opisano zmiany w wyglądzie powierzchni, wytrzymałości na zginanie i strukturze chemicznej. Wyniki pokazują, że promieniowanie UV spowodowało zmiany w stanie powierzchni dla próbek referencyjnych (powłoka bez dodatków), takie jak żółknięcie i matowienie. Zaobserwowano również redukcję wytrzymałości na zginanie o ponad 10% i zmiany w strukturze chemicznej, głównie spowodowane procesami utleniania i pękaniem wiązań chemicznych. Najkorzystniejszą ochroną okazał się stabilizator UV z grupy benzofenonów, dodatek którego zapewnia ochronę UV w całym zakresie promieniowania i chroni materiał przed negatywnymi zmianami w strukturze chemicznej powłoki. Podobne wyniki uzyskano także dla próbek z powłoką z dodatkiem grafitu.

Keywords: GFRP, kompozyty polimerowe, degradacja UV, powłoki

INTRODUCTION

Glass fiber reinforced composites (GFRP) are currently used in many industrial sectors due to their properties. A particularly important feature of GFRP composites is the combination of high mechanical strength and low density [1]. One of the basic disadvantages of polymer composites is their limited thermal and UV resistance, which are determined by the properties of the polymer matrix [2, 3]. The polymer matrix of the composite may be thermoplastic or thermoset, however, in the case of fiber-reinforced composites, a resin-based thermoset matrix is of paramount importance. The estimated global composites market in 2022 was $93.7B [4], of which 36.7% is the thermoplastic composites market [5], the rest (63.3%) is thermosetting composites. Polyester, epoxy and vinylester resins are most often employed to produce fiber-reinforced composites.

The resins are characterized by good corrosion resistance, water resistance, and in combination with fibrous reinforcement, they often have a synergistic effect of increasing the mechanical strength, stiffness and vibration damping [1, 6-8].

Despite the number of advantages resulting from the use of polymer materials and polymer composites, as well as their favorable economic factors, producers and users are often limited by the degradation of polymers. The degradation of plastics is defined as the partial defragmentation of polymer chains. Depolymerization is a special degradation process during which monomers are formed. Some of the polymer breakdown processes are of practical importance because they enable controlled polymer breakdown in recycling processes. Nevertheless, if polymer decomposition processes are uncontrolled, the nature of the processes changes to undesirable degradation [9-11]. The most common types of degradation of polymer composites include photodegradation, water degradation, chemical degradation, mechanical degradation, thermal degradation and biodegradation [12]. Under natural environmental conditions, several factors usually act on the composite at the same time. The occurrence of several types of degradation often leads to a synergistic effect, as a result of which the material destruction processes are accelerated. Ultimately, degradation processes lead to changes in the properties of the composite as a consequence of structural changes such as oxidation, destruction/depolymerization and cross-linking [11, 13].

The electromagnetic radiation emitted by the sun that reaches the Earth's surface consists of approximately 7% ultraviolet (UV) radiation. Ultraviolet radiation is divided into three basic types based on energy: UVA with a wavelength from 315 to 400 nm, UVB from 290 to 315 nm and UVC from 200 to 290 nm. UVC radiation, which is the most harmful to living organisms and polymeric materials, is almost completely blocked by the Earth's atmosphere and does not reach the surface under normal conditions. The ultraviolet radiation reaching the Earth's surface consists mainly of UVA radiation, and to a lesser extent, UVB radiation (less than 10%). The effects resulting from the impact of UV radiation on polymeric materials are mainly manifested by discoloration, matting and a loss of mechanical properties [14]. The energy of photons in the ultraviolet range is comparable to the dissociation energy of polymer covalent bonds (usually 290-460 kJ/mol). This means that photons absorbed by the polymer initiate photo-oxidation reactions, which leads to structural changes, and ultimately, to a change in the initial properties of the material [15].

The UV degradation of polymer composites leads to concerns about the long-term durability of the material considering the constantly changing environmental conditions. UV radiation affecting the GFRP composite leads to degradation of the polymer matrix, while the glass fibers themselves remain almost unchanged. An increased resistance of polymer materials, including

polymer composite matrices, can be achieved by various methods. The most frequently used methods include screeners, quenchers, absorbers and antioxidants [16].

UV screeners limit the penetration of radiation into deep layers of the material; they can be ZnO, TiO_2, MgO or graphite. Quenchers are responsible for quenching the excited states of chromophore groups in polymers (e.g. nickel chelates). UV absorbers reduce the energy of absorbed radiation quanta; they are mainly chemical compounds from the group of benzotriazoles and benzophenones. Antioxidants delay polymer oxidation reactions [17].

The aim of this paper is to describe the effectiveness of protective coatings against the different ranges of UV radiation exposure. For this purpose, GFRP laminates were prepared by applying resin-based coatings. Three types of coatings were made: with the addition of graphite for a screening effect, with the addition of a UV stabilizer from the benzophenone group for a radiation-absorbing effect, and a commercial polyester gelcoat, in addition to neat resin as the reference material. Tests were carried out for 1000 hours, then the properties of the composites were examined in terms of chemical changes determined by the FTIR method and changes in the mechanical properties based on the three-point bending strength test.

MATERIALS AND METHODS

A set of flat laminates was produced by the hand lay-up process in an open mold. Six layers of cross-weave glass fabric reinforcement with an areal weight of 320 g/m^2 were used. An epoxy resin based on bisphenol A (LH 288, Havel Composites, Czech Republic) and a cross-linking catalyst (H 505, Havel Composites, Czech Republic) were utilized as the composite matrix. The weight ratio of resin to catalyst was 100:27. Four series of coatings were made, and for each series four laminates were prepared for testing, in accordance with the designations in Table 1.

TABLE 1. **Designations of research samples**

Sample series	1	2	3	4
Coating	neat resin	gelcoat	resin + 10 wt.% graphite	2-hydroxy-4-n-octyloxy-benzophenon
Dark	Ref_D	GC_D	Gr_D	Stab_D
UVA	Ref_UVA	GC_UVA	Gr_UVA	Stab_UVA
UVB	Ref_UVB	GC_UVB	Gr_UVB	Stab_UVB
UVC	Ref_UVC	GC_UVC	Gr_UVC	Stab_UVC

All the samples were covered with a 1 mm thick layer of resin (without/with additives). A series of reference samples (Ref) was covered with unfilled epoxy resin, the same as used to make the laminates. A series of samples with commercial gelcoat (GC) was obtained

using a polyester gelcoat compatible with epoxy composites (gelcoat PA 252, Havel Composites, Czech Republic). A series of samples with the screening coating (Gr) was obtained by adding 10% by weight flake graphite (MG 1596, Sinograf, Poland) with a particle size of less than 10 μm to the epoxy resin. The last coating (Stab) was obtained by adding 2% by weight 2-hydroxy-4-n-octyloxybenzophenone (WTH GmbH, Germany) to the epoxy resin, which was in accordance with the manufacturer's recommendations. A diagram showing the method of producing the test samples is presented in Figure 1.
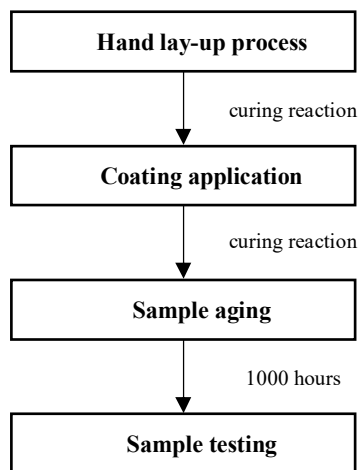

Fig. 1. Scheme of production and testing of GFRP composite samples

GFRP composite samples with dimensions of 100 x 170 mm were subjected to the photoaging process. Narrow ranges of UVA (emission wavelength: 350-400 nm), UVB (emission wavelength: 311 nm) and UVC (emission wavelength: 254 nm) were used separately. Samples without access to UV radiation and solar radiation were also tested (D). The GFRP samples were irradiated for 1000 hours continuously. After aging, all the samples were cut into test pieces with dimensions 20 mm x 70 mm (width x length).

The mechanical strength test was carried out for a three-point bending test in accordance with the PN-EN ISO 14125 standard on a Shimadzu AGX-V testing machine. The bending tests were conduct on a support spacing of 60 mm and deformed at a speed of 10 mm/min. A Fourier-transform infrared spectroscopy (FTIR) test was performed for a series of reference samples and a series of samples that exhibited no changes in mechanical strength after photoaging. The aged GFRP samples were tested using FTIR to describe the chemical changes occurring in the coating. The research was carried out using an FTIR spectrophotometer Thermo Scientific Nicolet 6700/8700 in the range from 390 cm^{-1} to 3890 cm^{-1}.

RESULTS AND DISCUSSION

After aging, the GFRP composite samples were observed to describe visual changes. It was found that the coatings in the reference series, under the influence of ultraviolet radiation, changed color from light green to yellow, lost their transparency and became matte. The greatest changes were observed for the samples irradiated with UVB and UVC. The series of samples with gelcoat, graphite and UV stabilizer coatings did not exhibit any noticeable changes on the surface after photoaging. Example images of the sample surfaces are presented in Figure 2.
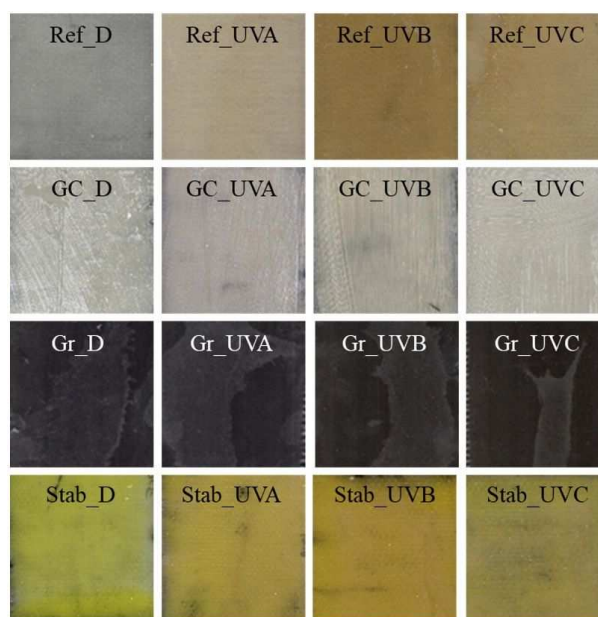

Fig. 2. Change in appearance of selected samples from zone without access to UV radiation and after photoaging in UVB radiation

The flexural strength results for the GFRP composites with the coatings are presented in Figure 3. The flexural strength of the reference sample is approximately 250 MPa (Ref_D). The UV radiation caused a decrease in strength by approximately 10% on average. The use of the commercial gelcoat on the laminate surface did not lead to a change in the flexural strength in the samples without access to UV radiation (GC_D). Ultraviolet radiation acting on the polyester gelcoat caused changes contributing to a rise in flexural strength, which was probably caused by cross-linking reactions initiated by UV radiation. The observed increase in strength was particularly visible in the series treated with UVB (GC_UVB), where the strength increased by approximately 30%. The series of samples with the coating with the addition of graphite exhibited very good resistance to UV radiation. Graphite provides shielding against UV radiation, thanks to which the deep layers of the composite were protected against degradation. The flexural strength in the series of coatings with the addition of UV stabilizer from the benzophenone group was characterized by the smallest devia-

tion in the results from all the series, which is favorable. UV radiation affects the mechanical strength, causing it to decrease by approximately 5-10% compared to the sample in dark (Stab_D). It should be noted, however, that the sample with the addition of the stabilizer and not exposed to UV radiation was characterized by higher strength than the reference sample (Ref_D).
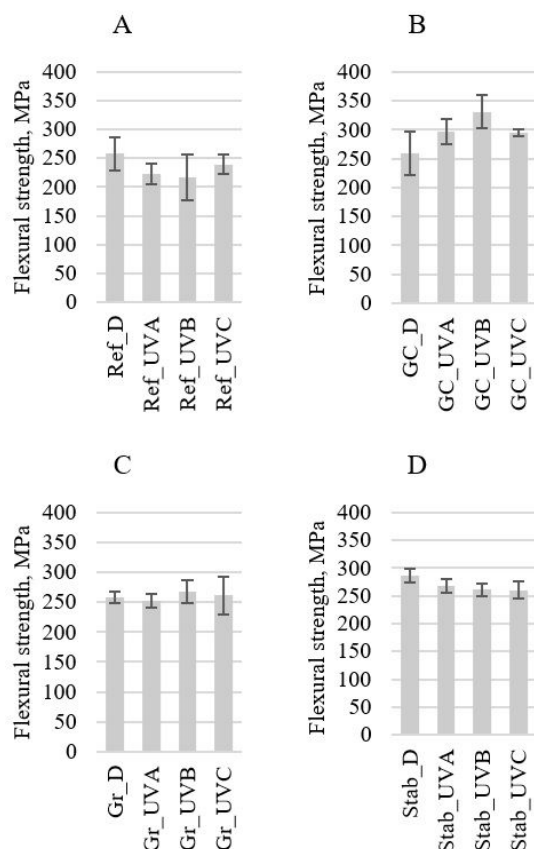

Fig. 3. Flexural strength of GFRP composites with coatings after 1000 h of photoaging (according to PN EN 14125 standard), A) reference samples, B) gelcoat coating, C) coating with addition of graphite, D) coating with addition of UV stabilizer

The obtained results of the mechanical tests were compared with the literature data. Chennareddy et al. in publication [18] described the effect of the addition of carbon nanotubes to epoxy coatings on the surface of a GFRP composite tested for UV resistance. They revealed that the GFRP composite with the coating without the addition of nanotubes (reference sample) was characterized by a decrease in the mechanical strength, determined by tensile strength tests, by approximately 10% following the UV test. Additionally, they demonstrated that coatings with the addition of nanotubes can increase the mechanical strength and provide anti-UV protection by preventing dissociation of the polymer framework and the formation of microcracks in the coating and the composite. In turn, Syamsir et al. in a review article [19], discussed the results on the control of UV radiation durability in GFRP composites, noting that GFRP composites in the first period of UV degradation exhibit signs of plasticization and in the

further period exhibit a significant decrease in mechanical strength. Ghasemi-Kahrizsangi et al. in their research [20, 21] demonstrated the behavior of a modified carbon black (CB) epoxy coating under UV radiation. They compared unfilled epoxy coatings with epoxy coatings with the addition of soot, reporting that after 1000 hours of exposure to UV radiation, the pure resin had numerous microcracks, and the soot-modified coating had no microcracks. FTIR analysis also revealed that the coating with the addition of 2.5% soot was characterized by a significantly lower concentration of carbonyl groups formed as a result of the disruption of polymer chains. Li in publication [22] tested the effectiveness of anti-UV protection using a stabilizer from the benzotriazole group. It was shown that the coatings with the addition of 3 and 5 wt.% stabilizer exhibited significantly higher resistance to photo-oxidation than the coatings without the addition of UV stabilizer.

The literature research and the obtained test results are highly consistent and allow us to conclude that both the addition of screeners, e.g. carbon compounds, and UV stabilizers to polymer coatings ensures extended resistance to ultraviolet radiation.

Figure 4 presents the FTIR spectrum of a sample of pure epoxy resin serving as a reference when analyzing the remaining spectra. Based on literature data [23, 24], characteristic peaks were described, as displayed in Table 2.

TABLE 2. **List of characteristic absorption bands for pure epoxy resin in range 390-4000 cm^{-1} (based on data [23, 24])**

Wavenumber [cm^{-1}]	Type of characteristic vibrations of groups
827 947	Stretching vibrations of C-O-C groups of oxirane ring
1038 1088 1087	Symmetric stretching vibrations of C-O groups of aromatic ring
1182 1245	Asymmetric stretching vibrations of C-O groups of aromatic ring
1299	Deformation vibrations of C-H and -CH$_2$ groups
1363 1384 1458	Bending vibrations of CH$_2$ and CH$_3$ groups
1578 1608	Stretching vibrations of C=C groups of aromatic ring
2878	Symmetrical stretching vibrations of C-H groups –CH$_3$ groups
2932	Asymmetric stretching vibrations of C-H groups –CH$_2$ groups
2957	Asymmetric stretching vibrations of C-H and –CH$_3$ groups

3326	Stretching vibrations of O-H groups (wide band)

Figures 4-7 give the FTIR absorption spectra for the coatings made of pure epoxy resin (Ref) and epoxy resin with the addition of UV stabilizer (Stab).
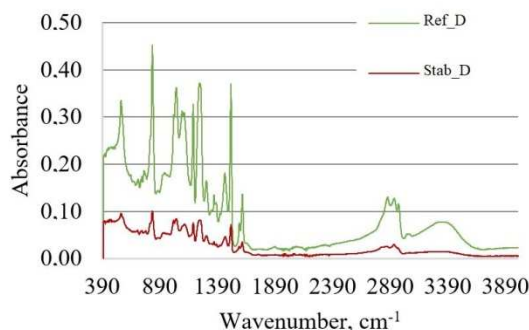

Fig. 4. FTIR spectra of samples without access to UV radiation and sunlight (Ref_D and Stab_D)
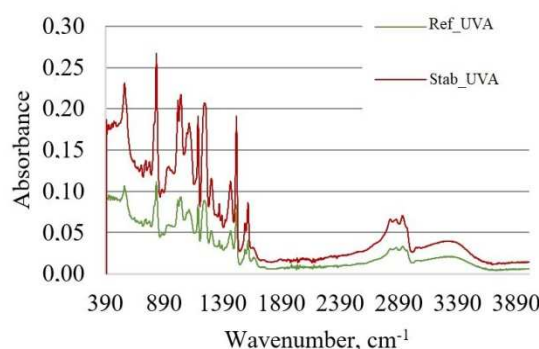

Fig. 5. FTIR absorption spectra of samples from UVA radiation (Ref_UVA and Stab_UVA)
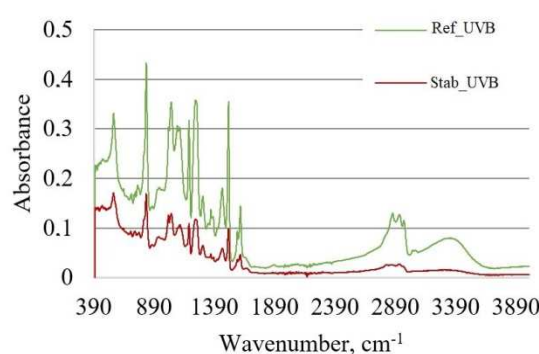

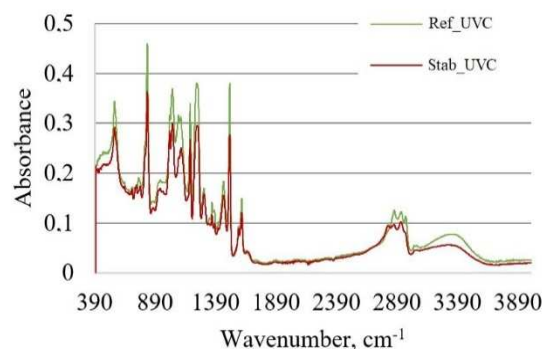Fig. 6. FTIR absorption spectra of samples from UVB radiation (Ref_UVB and Stab_UVB)

Fig. 7. FTIR absorption spectra of samples from UVC radiation (Ref_UVC and Stab_UVC)

In the compared IR characteristics of the unmodified epoxy coatings (Ref) and epoxy coatings with the addition of UV stabilizer from the benzophenone group (Stab), significant differences in the absorption bands were noticed, indicating changes in the chemical structure caused by the aging process with UV radiation. This results in changes in the FTIR characteristics in the wave number range of 390 cm^{-1} - 4000 cm^{-1}. An increase in the intensity of characteristic absorption bands with peaks corresponding to the following wave numbers was observed: 3326, 2957, 2932, 2878, 1606, 1578, 1508, 1458, 1384, 1363, 1299, 1245, 1182, 1088, 1087, 1038, 947, 827 cm^{-1}. An increment in the intensity of bands with wave numbers of 1508 cm^{-1} and 1608 cm^{-1} was observed. This growth was caused by the formation of new C=O carbonyl groups in the material. In turn, the appearance of these groups indicates oxidation processes of the epoxy material taking place in the coatings undergoing the aging process. Also, an increase in absorption bands in the range from 1280 cm^{-1} to 1490 cm^{-1} was noticed. The observed increase indicates a rise in the C-H content, more specifically –CH$_2$ groups. They are located in the vicinity of C=O groups, which in turn confirms the rapid escalation of oxidation processes of the epoxy resin. The photoaging process of the coatings caused the breakage of chemical bonds in the material, which was confirmed by the increased presence of -CH$_3$ groups. Additionally, growth in the intensity of the absorption band with a peak of 3326 cm^{-1} was found. This band corresponds to the stretching vibrations of OH groups. The absorption band with a peak of 827 cm^{-1} also rose in intensity as a result of the photoaging process of the epoxy resin coatings. The reason for this increment was the loss of oxirane rings, most likely caused by the destructive influence of UV radiation. The intensity of the absorption bands responsible for the destructive processes, mainly caused by oxidation processes, decreases after adding a UV stabilizer to the epoxy resin used as a coating material, which is beneficial and proves effective anti-UV protection.

Mailhot et al. in their article [25] described the photodegradation of epoxy/amine resin. In their work, they

concluded that the products resulting from photooxidation come from the oxidation of DGBEA (diglycidyl ether of bisphenol-A). A change in the content of carbonyl groups was observed during photodegradation as a result of the cleavage of the polymer chain. The yellowing of the polymer observed during the examinations resulted from the formation of quinone methide, while the discoloration was caused by thermo-oxidation processes. In their research [26] on the influence of UV on epoxy composites with various types of reinforcement, Awaja and Pigram showed that as a result of photodegradation, complex phenomena occur in the material, where both chain breaking and cross-linking are observed simultaneously. An increase in carbonyl groups during UV degradation processes was observed in the CFRP composite. The publication by Woo et al. [27] confirmed that photodegradation processes of epoxy resin lead to an increase in FTIR bands in the area of carbonyl groups, which results from the disruption of the polymer chain. The researchers noticed the appearance of microcracks on the resin surface after just 300 hours of testing. The color change process reached a plateau after 700 hours of testing.

The literature data compared with the obtained test results allow us to clearly state that the UV degradation processes of epoxy resins are manifested by the growth of carbonyl groups, which results from the disruption of polymer bonds. The applied modifications of coating resins in the form of the addition of graphite and the addition of a stabilizer from the benzophenone group are an effective method in limiting the cracking of bonds and the formation of carbonyl groups.

CONCLUSIONS

The conducted research, focused on assessing changes in the mechanical properties and describing chemical changes, allowed the following conclusions to be drawn:
– Structural changes in the polymer physicochemical transformations results in changes in the initial properties. Signs of changes include: changes in gloss (e.g. surface matting), color (e.g. yellowing), microcracks and an increase in surface roughness. They are caused by the appearance of free radicals, oxidation and the weakening of bonds in the material.
– The addition of a UV stabilizer (2-hydroxy-4-n-octyloxybenzophenone) and graphite with a screening function exhibited the most favorable protection against visual changes caused by UV radiation.
– Ultraviolet radiation leads to a decrease in the mechanical strength by approximately 10% after 1000 h (from 250 MPa to 220 MPa). Chemical changes caused by UV radiation mainly lead to oxidation of the epoxy resin and the cracking of bonds in the material.
– The addition of 2% by weight UV stabilizer from the benzophenone group protects the GFRP com-

posite against UV radiation over the entire range. The introduction of the stabilizer does not lead to negative changes in the chemical structure of the resin.
– The addition of 10% by weight flake graphite to the resin as a coating material is effective and allows effective screening of ultraviolet radiation. The addition of graphite is a simple and economical option to provide increased protection against ultraviolet radiation.
– The use of a commercial polyester gelcoat on a GFRP composite is beneficial and allows the laminate to be protected against the negative effects of ultraviolet radiation. Nonetheless, polyester resin has highly unstable properties and UV radiation leads to changes in them, which are manifested by a decrease in the flexural strength of the composite in the test and a large deviation in the observed results.

Acknowledgments

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