

1 Proceedings

2 The addition of charcoal fines can increase the photodegrada- 3 tion resistance of polymeric biocomposites

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13 **Abstract:** This study aims to analyze the addition of widely available, cheap, and biologically-based
14 residues, such as charcoal fines, in the production of polymeric biocomposites reinforced with nat-
15 ural fibers subjected to UV-c radiation. The addition of charcoal fines was 0, 10, 20, 30% in the pol-
16 ymeric matrix of the biocomposites. Mechanical and chemical properties of the biocomposites were
17 evaluated. The flexural strength was more resistant when subjected to UV-c radiation with 20%
18 filling. These results attested that biocomposites with the addition of vegetative charcoal fines were
19 less susceptible to photodegradation.

20 **Keywords:** natural fibers; biomass residues; charcoal fine filling; UV-c radiation

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22 1. Introduction

23 Currently, polymer composites reinforced with natural fibers are gaining attention
24 worldwide due to environmental concerns and the advantages of natural fibers over tra-
25 ditional synthetic fibers used in composites. In this conception, many studies have been
26 based on the use of industrial waste that has the potential to obtain new materials. Often
used in the steel industry, charcoal is one of the oldest and most well-known materials in
the world. However, as it is a highly fragile material, it generates significant amounts of
fines that, in most cases, do not have an adequate destination and constitute a problem to
be solved. In this sense, we believe that these residues can be used as raw materials for
the new products development, as a reinforcement agent in the production of polymeric
biocomposites, and used in various industrial applications. Carbon filler is an important
component of polymer composites due to its favorable properties and the possibility of
modification which, when combined with suitable polymer matrices, have a positive ef-
fect on improving electrical properties, polymer resistance to environmental factors, and
resistance UV-c dilation [1,2]. Epoxy resin, for example, performs several other functions
in biocomposites, such as protecting against abrasion and the environment [3–5].

37 In the action of solar radiation, polymeric materials undergo oxidative chemical re-
38 actions that result in material degradation, causing loss of brightness, color change, loss
39 of transparency, formation of cracks, mechanical and physical fragility [1,6,7]. Although
40 the photodegradation mechanism of most polymers is well established, the behavior of
41 polymer composites against UV-c radiation is still a field to be explored. This study aimed
42 to investigate the mechanical and chemical properties of the effect of UV-c radiation on

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1 polymeric biocomposites with and without charcoal fines. Thus, we investigated the res-
2 idues of charcoal fines as reinforcement, aiming its use as a raw material for the produc-
3 tion of carbonaceous biocomposites.

4 2. Materials and Methods

5 For the production of charcoal, wood from a ten-year-old *Eucalyptus saligna* planta-
6 tion was used. For this purpose, wood samples were fragmented in a Wiley knife mill and
7 previously dried in an oven at $105 \pm 2^\circ\text{C}$. The pyrolysis was carried out in a metallic reactor
8 inside a muffle furnace, at an initial temperature of 30°C and a final temperature of 400°C ,
9 the heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$, until reaching the final temperature, where they remained
10 for 120 min. The production of charcoal fines on a laboratory scale passed in the MA-500
11 model ball mill for three hours. For homogenization of the samples, the charcoal fines
12 were sieved obtaining a final granulometry of 100 mesh (0.154 mm). A polymer com-
13 pound was made with an epoxy resin matrix in addition to charcoal fines with percentage
14 participation of 10%, 20%, 30% of the composition. A sample containing 100% epoxy resin
15 was produced. The effect of degradation under UV-c radiation on chemical and mechan-
16 ical properties was evaluated using a photodegradation chamber apparatus, where the
17 biocomposites were exposed for 360 hours. To determine the mechanical property of flex-
18 ural strength was determined from ASTM D 7264M-21 standard [8]. Fourier transform
19 infrared spectroscopy (FTIR) analysis) were recorded in a Bruker spectrometer, model
20 Tensor 27, by the attenuated total reflectance (ATR) technique. The samples were scanned
21 in the range of $4000\text{--}600\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} . In this analysis, 32 scans were
22 collected for each FTIR spectrum.

23 2.1. Data analysis

24 Data were submitted to normality (Shapiro-Wilk) and homoscedasticity (Bartlett)
25 tests. The analysis of variance was performed following a completely randomized design,
26 with four response variables related to the proportion of charcoal added (0, 10, 20 and
27 30%). Identifying significant differences in relation to some dependent variables, the re-
28 gression model adjustment that best predicted the behavior of the data was performed.
29 Tests were performed at 95% probability. Standard deviation measures of dispersion were
30 provided to better understand the confidence interval obtained for each variable studied.

31 3. Results

32 The effect of adding coal fines on the flexural strength (specifically the modulus of
33 rupture and elasticity) and FTIR spectra of polymeric biocomposites were evaluated. The
34 mechanical properties of biocomposites after being subjected to UV-c radiation are shown
35 in Figure 1. Figure 1 shows the modulus of rupture (MOR) values, corresponding to
36 $7.82 \cdot 10^4\%$, $1.66 \cdot 10^4\%$, $1.66 \cdot 10^4\%$, $4.92 \cdot 10^4\%$ (0%, 10%, 20% and 30% addition, respectively),
37 and modulus of rupture (MOE) 6.67, 2.27%, 1.30%, 3.0% (0%, 10%, 20% and 30% addition,
38 respectively).

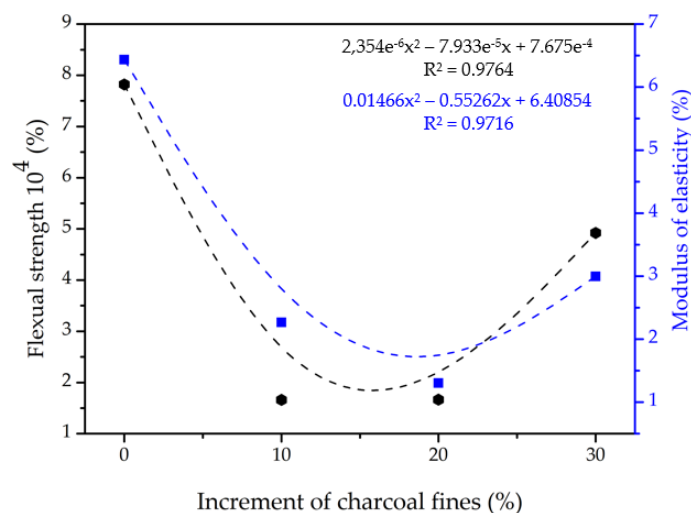


Figure 1. Flexural strength analyzing the modulus of rupture and elasticity of biocomposites in the respective study proportions.

FTIR spectroscopy is a powerful tool for analyzing the photodegradation effect caused by UV light on the polymeric matrices. In Figure 2, we compared both FTIR spectra of the epoxy resin before and after 360 hours of UV irradiation, and we observed the chemical changes in the epoxy resin structure. The characteristic bands of epoxy resin are present in the spectra, such as the peaks at 3045 cm^{-1} (symmetrical and asymmetrical C-H stretch in aromatic), in the range of $1600\text{--}1460\text{ cm}^{-1}$ (C-C stretching vibration in aromatic), 1295 cm^{-1} (asymmetrical -CH_2 deformation), 1237 cm^{-1} (asymmetrical aromatic C-O stretch), 1181 cm^{-1} (asymmetrical aliphatic C-O stretch), 1030 cm^{-1} (symmetrical aromatic C-O stretch), 916 cm^{-1} (epoxide ring vibrations), and 827 cm^{-1} (-CH out of plane deformation in aromatic) [9]. Moreover, bands assigned to hydroxyl and carbonyl groups were also observed in the $3100\text{--}3700\text{ cm}^{-1}$ and $1800\text{--}1600\text{ cm}^{-1}$ spectral regions, respectively. In particular, the absorption peaks located in the last-mentioned wavenumber regions were enhanced in the FTIR spectrum of irradiated epoxy resin, indicating the photodegradation process. In addition, the effect of UV irradiation on the epoxy resin can be considered due to the appearance of the absorption bands in the range of $3400\text{--}2400\text{ cm}^{-1}$, which correspond to carboxylic acids [10].

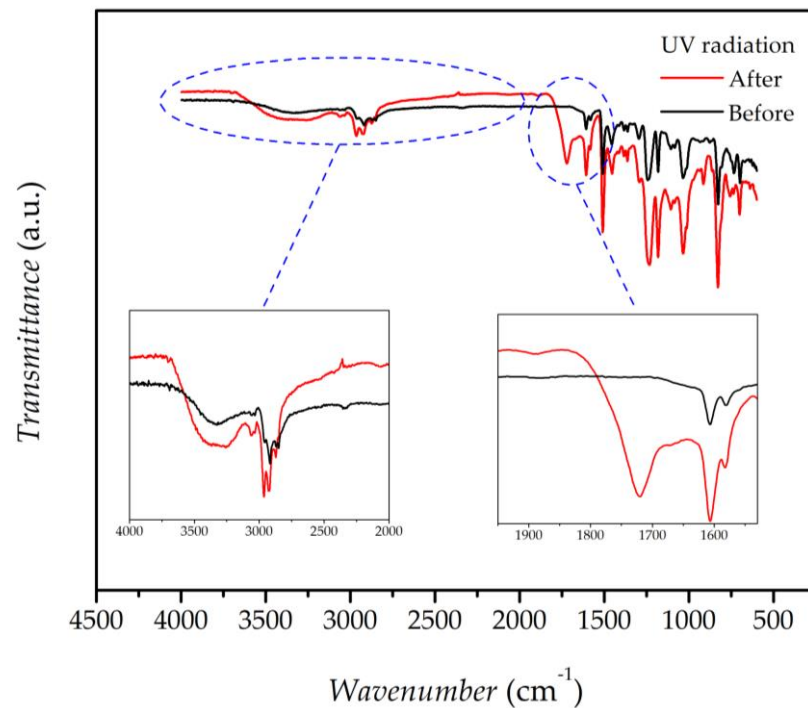


Figure 2. FTIR spectra of epoxy resin before and after the UV irradiation.

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3 The FTIR spectra of 10, 20 and 30% of the charcoal fines and epoxy resin biocomposites before and after UV irradiation are shown in Figure 3. The FTIR spectrum profiles of the unordered composites are very similar to those obtained for epoxy resin fresh and no noticeable differences were caused by the addition of charcoal fines fill. However, the greatest changes are observed when the FTIR spectra of the irradiated composites were compared to the FTIR spectrum of UV-irradiated epoxy resin, mainly as to the intensity of signals attributed to the carbonyl and hydroxyl peaks. It is evident that smaller amounts of carbonyl (1800–1600 cm⁻¹) and hydroxyl (3100–3700 cm⁻¹) groups were generated during the UV degradation of the composites than of the epoxy resin, since less pronounced peaks were recorded in the composite spectra. No evidence of the formation of carboxylic acids was detected in the FTIR spectra of composites, suggesting a preservation effect provided by the biocarbon additive.

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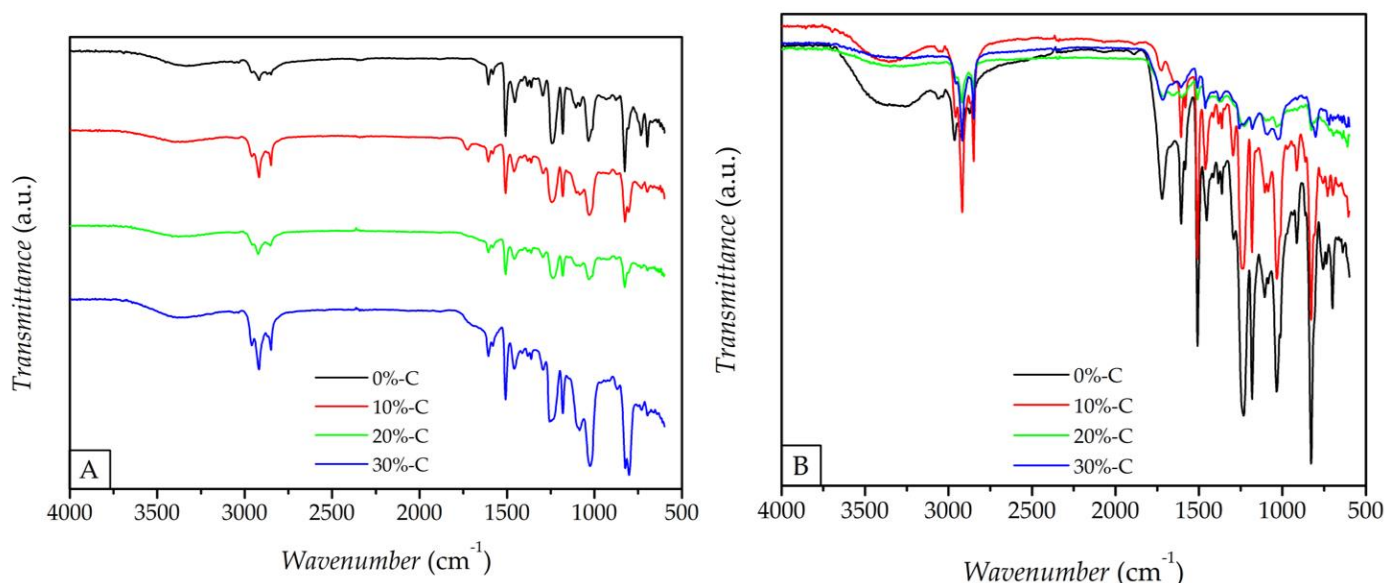


Figure 3. FTIR spectrum of epoxy resin and 10, 20 and 30% of epoxy-charcoal fines biocomposites. (A) before and (B) after UV irradiation.

4. Discussion

The polymer composite without the addition of carbon fines showed a higher loss of strength after exposure to UV-c radiation when compared to treatments with 10 and 20% addition of charcoal fines. Note that the increase in certain quantities of charcoal fines will minimize the loss of resistance of the material when subjected to photodegradation radiation, corroborating trends found in the literature. Flexural properties showed greater strength in 20% of charcoal fines. Filler particles obstruct the sliding of polymer matrix chains and this leads to increased flexural properties of biocomposites [6]. However, with the addition of more filler, such as 30%, the properties decreased, similar to that found by [6]. Such an event can be attributed to the weak polymer-fiber interaction, voids, and weak dispersion of fibers in the matrix [6]. However, it also depends on other factors such as size, shape, and type of fill material [11–13]. Carbon filling is an important component of polymer biocomposites, due to its favorable properties and the possibility of modification, which, in combination with suitable polymer matrices, has a positive effect on the mechanical property and improvement in the resistance of polymers to actors environmental and UV-c radiation [1]. Related studies obtained good results obtained with carbon filling, which significantly increased the mechanical strength of the material [1,7,14].

The FTIR analysis allowed us to evaluate the chemical changes caused by the photodegradation of epoxy resin as well as the beneficial effect of biocarbon addition on the material. As observed in the FTIR spectrum of the UV irradiated epoxy resin (Figure 2), the intensities of the carbonyl group (1800-1600 cm^{-1}) increased, which reveals a relative degree of photodegradation. The carbonyl species are generated as a result of β -scission from the alkoxy radicals produced by recombination of alkyl radicals in the first steps of UV radiation exposition [15]. Another evidence of epoxy resin degradation is the presence of bands assigned to carboxylic acids (3400-2400 cm^{-1}). These species can be formed as a result of C-C dissociation bonds in the presence of oxygen and UV light [16]. The FTIR spectra of the composites after the UV irradiation showed a decrease in the signal intensities of degradation bands, probably due to the low contents of carbonyl, hydroxyl, and carboxylic acids in the polymeric chain. These results attested that the composites were less susceptible to photodegradation. The protection effect of biocarbon may be summarized in terms of an antioxidant effect, probably via an efficient catalytic decomposition free radical scavenger. Although the FTIR analysis has shown that the addition of carbon

avoided the degradation of the polymer chain, it was not possible to obtain information about the suitable carbon/resin ratio.

5. Conclusions

It was found that the analyzed charcoal fines can be used as reinforcement for polymer matrices, due to their stability against UV-c radiation, resulting in improved mechanical properties. Further studies on chemical, elemental and microstructural properties are recommended, in addition to the use of charcoal fines at different pyrolysis temperatures and particle sizes.

Declarations

Author Contributions: The F.M.D. performed the laboratory experiments, analyzed the data and prepared the manuscript. A.K.S.P., A.M.S., E.C.S., M.P.O., D.P., L.P.R.P., A.F.D.J. provided critical feedback, review and editing of the manuscript. D.P and L.P.R., strongly assisted in the execution and review of chemical analyses. A.F.D.J. and F.M.D. designed the study and administered the project. All authors read and agreed with the published version of the manuscript.

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Conflicts of Interest: The authors declare that they do not have a financial conflict of interest, however, the product developed in this manuscript is under patent process with government agencies in Brazil.

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