

Thermal evaluation of the calcium stearate influence on polystyrene by in-line colorimetry

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Abstract

This paper investigates evidence regarding the influence of a CaSt₂ residual additive in the optical properties of a commercial polystyrene. This work proposes an in-line optical detector operating by illuminating the polymer with a red monochromatic light in order to evaluate its thermal behavior during a heat cycling. The detection system was bench validated by measuring the light absorption of aqueous solutions of organic acid dyes. The system showed great sensitivity in detecting the contamination's effect on the polymer, as a great impact on the polymer's behavior was observed due to the presence of the additive during different thermal cycles. The detector system showed that the salt's presence elevates absorbance by five times when the temperature is higher than its fusion temperature. The in-line optical detector has proved to be suitable to quantify the presence of additives that affects the polymer's optical properties.

Keywords: absorbance, calcium stearate, heat cycling, in-line optical detector, thermal characterization.

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1. Introduction

The color of a material is the result of the human visual perception of the combination of wavelengths not absorbed by a substance on which a beam of white light is impinged^[1]. Thus, color is not a specific property, depending how it interacts with the electromagnetic radiation. For instance, pure red color has its complementary color green and vice-versa, as shown in Ostwald's cycle^[2]. In other words, a red object is red by our perception because the material absorbs mainly in the green's wavelength letting pass light in the red's wavelength color region.

The addition of chromophore species, i.e., conjugate systems that absorb light at a specific frequency^[3], may enhances the attenuation of the light beam by absorption^[4,5]. This reduction in the intensity of the transmitted light beam (*I*) in relation to the initial intensity (*I*₀) supplied to the sample is given as a ratio between them, known as absorbance (*A*), given by Equation 1.

$$A = -\log\left(\frac{I}{I_0}\right) \quad (1)$$

Beer-Lambert's Law, Equation 2, establishes a relation between absorbance and the concentration of chromophore species^[6]. This law is only valid for monochromatic light beams and only if the absorbent substance doesn't change

its physical state or chemical composition with the variation of concentration^[7].

$$A = \varepsilon \cdot d \cdot c \quad (2)$$

being ε the molar extinction coefficient (or molar absorptivity), *d*, the optical path length and *c*, the concentration of the attenuating species, respectively.

Colorimetry is an established characterization tool in polymer science which has the light's attenuation by absorption as object of study, being used by many scholars^[8-15]. Ordinarily, researchers focus on the influence of distinct chromophore species on polymeric systems, such as dyes^[8-12], pigments^[13] and others additives^[14,15], although few works take into account the effects of temperature variation, which is a frequent feature in polymer processing and may change the optical contribution of, for instance, existing additive in terms of absorbance. Phillips et al.^[16] evaluated the thermal behavior of metal stearate lubricant mixtures for polymer compounding applications. It was observed rheological changes for all samples through cooling cycles. Zhang et al.^[17] investigated the structural evolution of zinc stearate (ZnSt₂) and calcium stearate (CaSt₂) in a polypropylene random copolymer (PPR) upon heating and cooling. The CaSt₂ in PPR exhibited vitreous agglomerates with lamella ordered structure at low temperatures and transformed to diverse colloidal liquid crystal aggregates

during heating, showing the temperature dependence of its structure. Antunes et al.^[18] investigated the effect of manganese stearate (MnSt) concentrations on the thermo-oxidative degradation of high density polyethylene. Temperatures from 60 °C to 80 °C were performed. It was shown that the additives were able to accelerate the oxidative abiotic degradation of the polymer and promote the biodegradation of the material. Bensaad et al.^[19] studied the effects of CaSt₂ as pro-oxidant agent on the degradation of polypropylene (PP) under natural exposure. The results showed that the concentration of 5% wt calcium stearate was sufficient to initiate the process of degradation. Despite these and other contributions, there is lack of studies focusing how temperature affect the impact of the polymer's additives in its optical properties. The applied temperatures are still far from those found in real polymer processing conditions. In this context, the aim of this work was to evaluate the influence of temperature in the polymer processing range in the absorbance of a polystyrene (PS) additivated with calcium stearate by quantifying in-line the transmitted light attenuation by absorption during a thermal cycle process with temperatures ranging in the typical processing conditions.

2. Materials and Methods

2.1 Polymer

A commercial grade of polystyrene (PS) provided by Innova (Brazil), code N2560, with the presence of a single residual additive: Calcium stearate (CaSt₂), was used in this work. Polystyrene is commonly additivated with low quantities of CaSt₂, which acts as lubricant and releasing agent during molding^[20]. In addition, it modifies the filler surface reducing water absorption, preventing agglomeration of the filler particles, and reduces the surface energy helping its dispersion^[21]. Also the calcium stearate has a wide melting temperature range of $T_m = 130$ °C up to 180 °C^[22].

2.2 Acid dyes

Water soluble organic acid dyes with the colors: Red (N-2R 200), Green (N-3G 200) and Blue (N-2R 200) provided by Quimanil Produtos Químicos Ltda (Brazil) were used in the previous stages of this work to evaluate the efficiency of the proposed detection system. The dyes chemical structures are presented in Figure 1.

2.3 Thermal stage system

An optical microscope Leica DMRXP (Figure 2a) with a hot stage system CSS450 from Linkam Scientific

Instruments (Figure 2b) was used for thermo-optical characterization. This system constitutes of a hot chamber with two parallel quartz windows between which the specimen is positioned (Figure 2c), allowing efficient temperature control (-50 °C to 450 °C) at defined different heating rates.

2.4 In-line optical detector system

The in-line optical detector is placed over the two parallel quartz windows in the hot stage system. For this system, in one side is positioned the light emitting diode LED of red (630 nm) monochromatic wavelength and at the other side there is a single phototransistor in order to collect the transmitted light's intensity. The light exiting the LED passes through the first transparent window, through the molten polymer stream, in which is attenuated by light absorption, exit through the second transparent window and, lastly, reaches the phototransistor which quantifies the transmitted light intensity. Changes in it are collected by software, developed in LabVIEW 8.6 (National Instruments™) platform for data collection, real-time calculation, screen presentation and data archiving. The adopted optical configuration is in agreement with previous set-ups^[15,23].

2.5 Experimental procedure

2.5.1 Bench validation of the optical detector with aqueous solutions

The in-line optical detector was tested and its response validated quantitatively by using aqueous solutions of the reference dyes. To avoid metal oxidation a slit-die made of Teflon was constructed and used for the bench validation. A schematic representation of the complete validation system is presented in Figure 3.

The validation set-up consists of a water circulating closed-loop, fed by a large beaker containing 1.0 Liter of filtered water, pumped by a submersed aquarium plastic pump, circulating through the Teflon slit-die, having it being fitted with the in-line optical detector. A concentrated mother water solution was prepared and stepwise added to the circulating system in known volumes via a syringe, increasing their content progressively. The concentrated solution is produced with 1.0 g of dye placed in 250 mL of water. After each addition of the concentrated solution, a 3 min minimum period is waited for complete mixing, and then the detector signal is recorded, measuring the transmitted light intensity and averaging during a 3 min time interval.

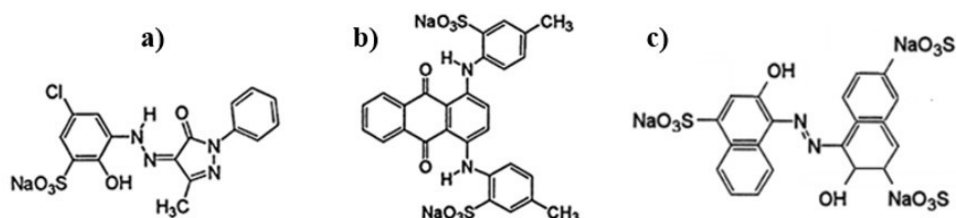


Figure 1. Chemical structure of the organic acid dyes: (a) red, (b) green and (c) blue.

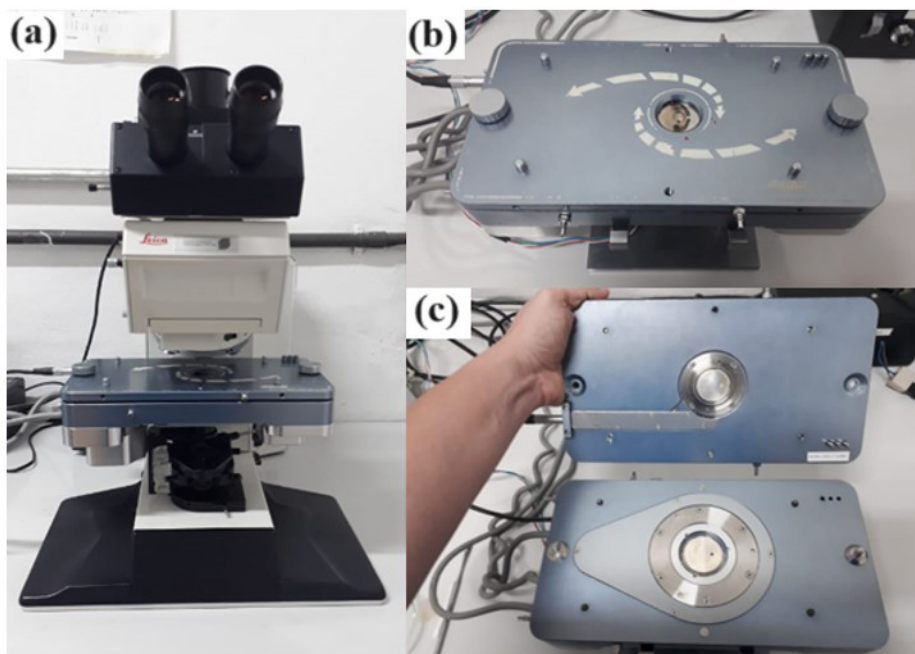


Figure 2. (a) The optical microscope (Leica DMRXP) fitted with the hot stage system (CSS450 from Linkam Scientific Instruments); (b) Hot stage front closed view; and (c) Front opened view.

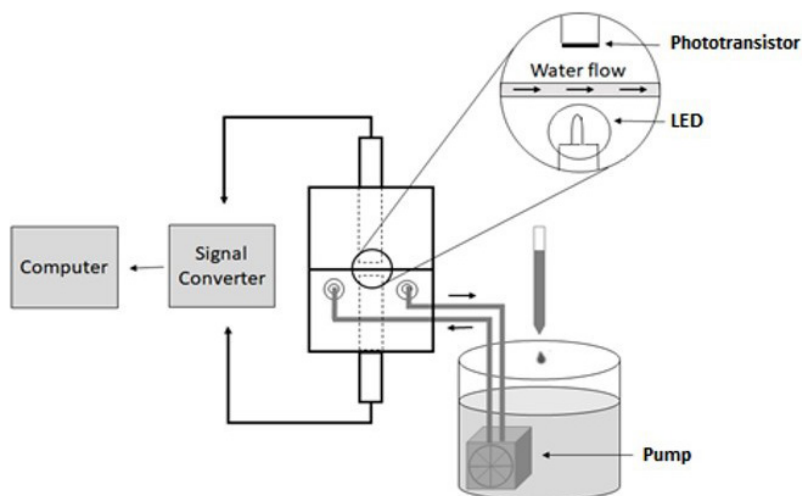


Figure 3. Sketch of the bench validation system of the in-line optical detector using a closed water flowing loop, pumped through a Teflon slit-die.

2.5.2 Optical evolution during the thermal cycling of the PS/CaSt₂

The in-line optical detector was allocated in the Linkam thermal stage, and a complete thermal cyclic process was applied at a constant rate of 10 °C min⁻¹, cooling from 210 °C down to 80 °C and heating back again to 210 °C. Each optical characterization analysis was repeated in triplicates for better accuracy of the results. Pellets of the polystyrene as received and pellets of the polystyrene after an extraction process were added between the two parallel quartz windows of the Linkam system, with a constant gap

of 1.5 mm. The extraction process was done solubilizing it with chloroform and then precipitating the solubilized polymer with ethanol. A period of one week was waited for the completed evaporation of residual solvents. Samples of PS after the additive extraction were obtained and the extracted residue was collected. During each thermal cycle, absorbance intensity measurements were collected as a function of the analysis temperature. By comparing the absorbance variations, information regarding the influence of the additive on the optical response of the polystyrene is quantified.

3. Results and Discussions

3.1 Bench validation of the optical detector with aqueous solutions

The response of the optical detector was tested for each colored organic acid dye dissolved in an aqueous solution. For that, the absorption of each dye with red illumination color was measured using pure filtered water as reference medium. Increasing stepwise the dye concentration one can obtain curves of absorbance (as normalized transmitted light intensity) as a function of dye concentration in the aqueous solution. Figure 4 shows the curves and, as expected^[7], the results are linear crescent curves.

The aqueous solution with the red dye absorbs weakly the red light illumination, which is in agreement with literature^[1], since absorption of a specific color wavelength by a sample of the same color is minimal. On the other hand, as observed from the performance of the solution with the green dye, showing a significant absorption under red illumination, the absorption of a specific color wavelength by a sample of the complementary color is maximal. The blue dye, whose complementary color is yellow, has a significant absorption under red illumination, which lead us to conclude that the blue acid dye used here is not a pure color (referring to the Ostwald's cycle), but an intermediate color instead.

The optical detector operating as an in-line colorimeter has shown: i) linear response to the increase dye concentration, obeying Beer-Lambert's law^[6], and ii) correct response under the respective color illumination. This performance has indicated to us the proper function of the in-line colorimeter under light absorption, validating it.

3.2 Optical evolution during the thermal cycling of the PS/CaSt₂

The optical characterization of the polystyrene, measured as absorbance curves as a function of temperature is shown in Figure 5.

A molten pure polymer, particularly polystyrene, is expected to does not absorb visible light, i.e., be transparent. During its heating thermo-oxidative degradation can occur, which produces chromophores groups, contributing to color

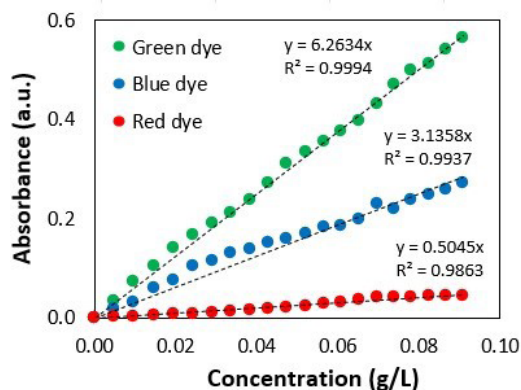


Figure 4. Absorbance as normalized transmitted light intensity as a function of the dyes' color and concentration, in aqueous solutions, using monochromatic red light illumination.

changes due to the light absorbance of these degradation products. The presence of the strong hysteresis in Figure 5, set between 80 °C and 170 °C, let clear that another effect beyond the contribution of these chromophores groups is contributing for this optical behavior and, the presence of the calcium stearate, CaSt₂, may be this factor. Calcium stearate has a wide melting temperature range of $T_m = 130$ °C up to 180 °C^[22], which coincides to the sigmoidal change in the absorbance curves' during heating, shown in Figure 6a.

In order to further investigate the optical influence of the CaSt₂ observed in this commercial polystyrene sample, another experiment was performed. Initially, a polystyrene sample as received was thermally cycled from 210 °C down to 80 °C at a constant cooling/heating rate of 10 °C min⁻¹ for five consecutive cycles. The resultant changes in the transmitted light intensity curves are presented in Figure 6, separated into two groups, that due to the heating (Figure 6a) and cooling (Figure 6b) portions.

The results observed in Figure 6 show that the additive strongly affects the light absorbance of the polymer, in which, for each additional cycle, the additive's contribution is stronger, featuring a possible transformation of this additive^[17,24] which leads to higher passage of light through the sample, implying bigger negative values of absorbance. The normalized absorbance was arbitrarily set zero at 210 °C.

The next step was to evaluate the influence of the additive in the absorbance in isotherms under and above its melting temperature. Isotherms at fixed temperatures, seen in Figure 7, were done in the Linkam System CSS450 for pure polystyrene.

The results presented in Figure 7 show the optical polymer's response for each temperature. The absorbance is negative above the additive's fusion temperature and positive below it, namely, the additive absorbs less light when molten.

To show this influence of the additive, it was necessary to repeat the same hot stage measures, but with the PS without it, i.e., after the extraction process previously prepared. First, the extracted residue was submitted to FTIR analysis to ratify its identity as stearic acid calcium salt. The results are presented in Figure 8.

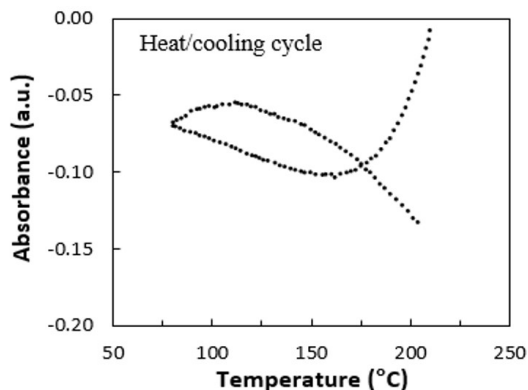


Figure 5. Absorbance as a function of temperature for the PS, heat cycled between 210 °C and 80 °C, at 10 °C min⁻¹.

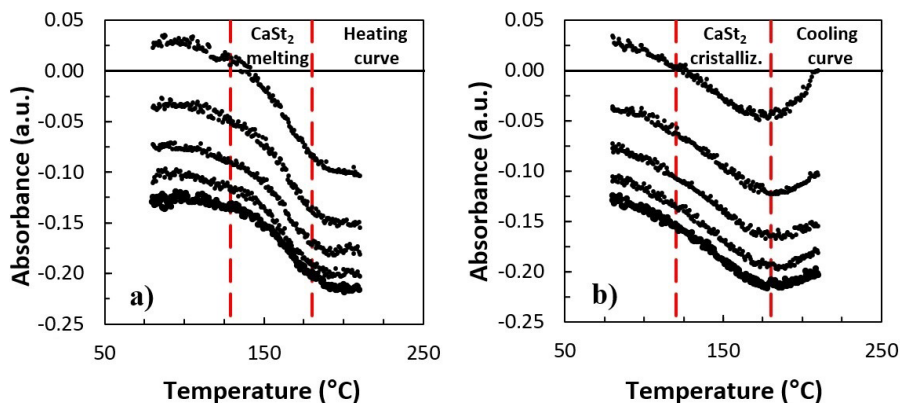


Figure 6. Light absorbance during five heat/cooling cycles of the polystyrene sample as received, ranging from 80 °C to 210 °C. In (a) the heating curves and in (b) the cooling curves. Dashed lines correspond the melting/crystallization temperature ranges of the CaSt_2 , 129 - 180 °C and 180 - 120 °C, respectively.

In the spectra, it's observed two main groups of bands around 1500 and 2900 cm^{-1} . The peak values lead us to conclude, according to previous works available on literature^[25], that the obtained residue is, in fact, calcium stearate, since, such additive presents characteristic bands at 1542 and 1575 cm^{-1} due to antisymmetric stretching bands for unidentate and bidentate association with calcium ions and at 1472 cm^{-1} due to methylene scissoring band and 2850, and 2914 cm^{-1} symmetric and antisymmetric methylene stretching band respectively.

The PS after the extraction was submitted to thermal cycling from 210 °C down to 80 °C at a constant heating rate of 10 °C min^{-1} for five consecutive cycles. The results are presented in Figure 9.

The results presented in Figure 9 display the polymer's response for continuous thermal cycles. The absorbance is now increasing after each cycle, contrasting with the previous results obtained before the additive extraction. It's intuitive to conclude that the additive was impacting the optical properties of the polymer and pushing the collected absorbance values to a negative range.

The next step was to repeat the isothermal measurements with the PS samples after the extraction process. Figure 10 shows the differences of maximum absorbance intensity achieved in each isotherm for the commercial PS before and after the additive extraction process.

The results showed in Figure 10 corroborate the data presented in Figure 9 in which the influence of the stearic acid calcium salt is confirmed as the cause of the negative absorbance values. The salt's presence elevates the collected light intensity by the phototransistor when the temperatures are higher than its fusion temperature. On the other hand, in its absence, the light intensity doesn't change considerably, being five times less intense as before. The weak deviation from the zero-line in Figure 10 are due to thermal degradation.

Investigating the values in Figure 10, it's verified a remarkable reduction in the absorbance intensity after the thermal cycles. This fact can be explained by the removal of not only the residual additive previously existent in the polymer system, but also the removal of possible degrading

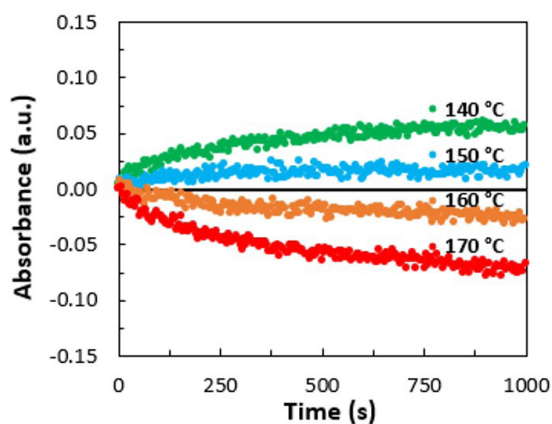


Figure 7. Absorbance as a function of time (s) for polystyrene as received. Isotherms of 140 °C, 150 °C, 160 °C and 170 °C were evaluated.

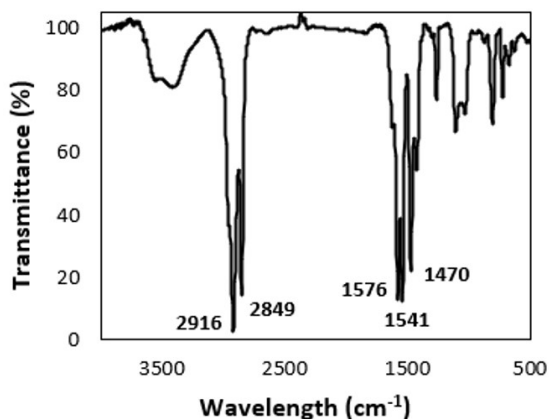


Figure 8. Transmittance (%) versus wavelength (cm^{-1}) for the extracted additive.

agents such as free radicals and residual catalyst, which suggests a PS more resistant to degradation over time after the extraction process.

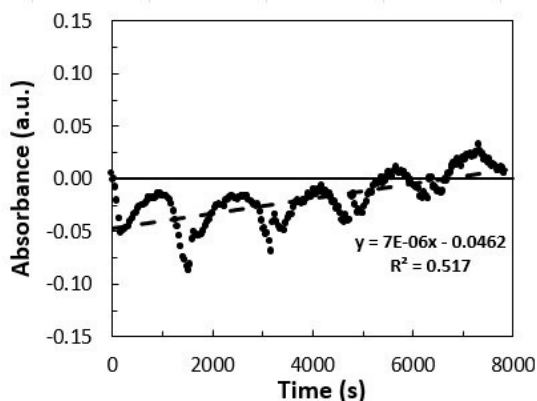


Figure 9. Absorbance as a function of time (s) for polystyrene after the additive extraction. Five heat cycles were evaluated from 210 °C to 80 °C.

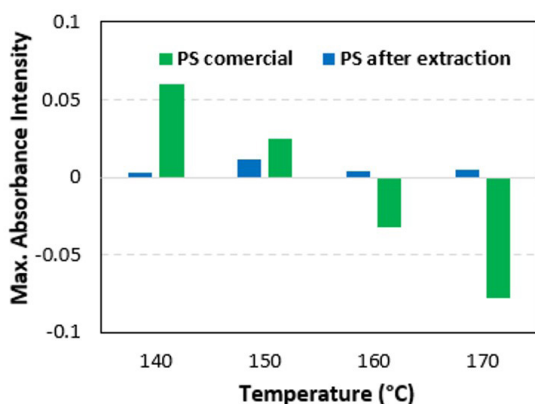


Figure 10. Maximum absorbance intensity for polystyrene as received and after the additive extraction process. Isotherms of 140 °C, 150 °C, 160 °C and 170 °C were evaluated.

4. Conclusions

A thermal cycling method has been proposed for quantify changes in the absorbance of a polymer matrix with residual additives in high temperatures. This work showed that the resulting absorbance is a function of the pair polymer and wavelength illumination and, its behavior changes with the presence of a contaminant additive, leading even to negative values. The additive's extraction process lead to a more resistant polymer to degradation, showing that besides additives are important in the polymer manufacturing, sometimes, depending on the type of analysis, they can have negative effects. Optical properties, such as absorbance analyzed in this paper, as they are more sensitive to internal changes in the polymeric system, are affected by the presence of an additive and, consequently, its structural changes with temperature.

5. Author's Contribution

- **Conceptualization** – Felipe Bernardo; Sebastião Vicente Canevarolo Junior.

- **Data curation** – Felipe Bernardo; Sebastião Vicente Canevarolo Junior.
- **Formal analysis** – Felipe Bernardo; Sebastião Vicente Canevarolo Junior.
- **Funding acquisition** – Sebastião Vicente Canevarolo Junior.
- **Investigation** – Felipe Bernardo; Sebastião Vicente Canevarolo Junior.
- **Methodology** – Felipe Bernardo; Sebastião Vicente Canevarolo Junior.
- **Project administration** – Felipe Bernardo; Sebastião Vicente Canevarolo Junior.
- **Resources** – Sebastião Vicente Canevarolo Junior.
- **Software** – Felipe Bernardo.
- **Supervision** – Sebastião Vicente Canevarolo Junior.
- **Validation** – Felipe Bernardo; Sebastião Vicente Canevarolo Junior.
- **Visualization** – Felipe Bernardo; Sebastião Vicente Canevarolo Junior.
- **Writing – original draft** – Felipe Bernardo; Sebastião Vicente Canevarolo Junior.
- **Writing – review & editing** – Felipe Bernardo; Sebastião Vicente Canevarolo Junior.

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