Thermoplastic Starch and Graphite Biocomposite Electrode for Electrochemical Catechol Sensor

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There is interest in obtaining alternative materials for application in electrochemical sensing. Thermoplastic starch (TPS) was used because it is a polymer with high availability and biodegradability, which can be incorporated into graphite (Gr) forming a conductive material. This work describes the characterization of the material produced by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), contact angle, X-ray diffraction (XRD) and Raman spectroscopy. The techniques used allowed to show a good interaction between graphite and TPS and confirmed the predicted conductive properties, showing the potential of application as a substrate, in the development of electrochemical sensors. Electrochemical characterization by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) was also carried out, which allowed defining the best proportion of graphite:TPS as the composite of 60:40 w/w. The technique of differential pulse voltammetry (DPV) was used to determine the catechol molecule over a range of 0.1 to 2.0 mgol L−1, showing a linear regression (R²) of 0.9996 and limit of detection (LOD) and limit of quantitation (LOQ) values equal to 1.85 × 10⁻⁶ mol l⁻¹ and 6.18 × 10⁻⁷ mol l⁻¹, respectively. The results showed good precision, selectivity, and stability, proving the application as an electrochemical sensor to detect catechol (CC) in contaminated waters.

Manuscript submitted July 2, 2022; revised manuscript received September 7, 2022. Published September 29, 2022.

Supplementary material for this article is available online.
characterized by the techniques of scanning electron microscopy, Fourier transform infrared spectroscopy, contact angle, X-ray diffraction and Raman spectroscopy. The electrochemical characterization of the material was performed by electrochemical impedance spectroscopy and cyclic voltammetry, aiming at a possible application in electrochemical sensing substrate. The electrochemical analysis of tap water contaminated with catechol proved the sensor detection potential, with stability, reproducibility, and selectivity. In addition, the material developed is biodegradable, disposable, and low cost.

Experimental

Materials.— All reagents used were analytical grade. The starch used was AMIDEX 3001, supplied by DAXIA (Characteristics - Maximum humidity: 14%; pH: 4.5 – 5.5). Glycerin P.A. (Glycerol) and dimethyl sulfoxide were purchased from Dinámica. Synthetic graphite powder (<20 μm, assay 99%). All reagents used were analytical grade. The starch used was AMIDEX 3001, supplied by DAXIA (Characteristics - Maximum humidity: 14%; pH: 4.5 – 5.5). Glycerin P.A. (Glycerol) and dimethyl sulfoxide were purchased from Dinámica. Synthetic graphite powder (<20 μm, assay 99%).

Preparation of thermoplastic starch (TPS).—A mixture of 110 g ultrapure water, 30 g starch and 10 g glycerol were heated under stirring until it reached ±80 °C and maintained for 5 min at this temperature. The solution obtained was divided into Falcon tubes with one-third of their total volume capacity filled (±15 ml), and the tubes were capped and taken to the freezer for 24 h at −18 °C. After freezing the samples were taken to a freeze-dryer in FreezeZone 2.5 Plus, Labcon, for 24 h with a vacuum of 0.220 mBar and a temperature of −83 °C. After removal from the freeze-dryer the dried samples were fragmented and sieved.

Fabrication of the electrode TPS-Gr based on the solvent-assisted technique.—Four different compositions of the test materials were prepared for the evaluation of the electrochemical properties, varying the mass in the proportion % (w/w) graphite: TPS, A) 80:20, B) 70:30, C) 60:40 and D) 50:50. Such substrates were obtained using TPS, graphite and DMSO (Fig. 1A). The component masses were weighed in a beaker for each substrate composition. They were placed on a heating plate under stirring until they reached a temperature of approximately 80 °C and kept at this temperature for 5 min (Fig. 1B). After this period, the mixture presented a viscous aspect, being poured into a Petri dish with a diameter of 7 cm (Fig. 1C), and dried in an oven at 80 °C for 24 h (Fig. 1D) for substrate formation (Fig. 1E), and then pressed for substrate compression at 2.0 ton for 5 min (Fig. 1F).

Characterization of the TPS-Gr substrate.—The structural characterization of the substrate was carried out using Fourier transform infrared spectroscopy in a Nicolet summit IR 200 FTIR, in absorbance mode, using 126 scans, nominal resolution of 4.0 cm\(^{-1}\), in the range of 4000 to 400 cm\(^{-1}\). The spectra were obtained in the Ominic Paradigm (Thermo Scientific, USA). Raman spectroscopy was performed on a Horiba T64000 confocal with 532 nm laser, 30 mW power, 100x objective, 200 μm aperture, 100 μm slit, 15 s of exposure and 5 scans. X-ray diffraction was performed in a diffractometer XRD-6100 SHIMADZU, with Cu Kα radiation, with a step of 0.1 s\(^{-1}\) and a speed of 5° min\(^{-1}\) using a generator voltage and current of 40 kV and 30 mA, respectively. The morphology characterization was done by scanning electron microscope, model TM3000, with an applied acceleration voltage of 15 kV. The wettability of the substrate was measured by the sessile drop technique in a Ramé Hart goniometer (model 100-00) with deionized water. For each sample, three droplets of water were deposited on different points on the surface, each with 10 contact angle measurements. The results correspond to the average of 30 measurements.

Electrochemical measurements.—Electrochemical measurements were performed in a potentiostat/galvanostat from AutoLab, model PGSTAT30 (Eco Chemie, Utrecht, Netherlands), using a three-electrode electrochemical cell, reference Ag/AgCl (3.0 mol l\(^{-1}\) KCl), platinum auxiliary 1.0 cm\(^2\) and TPS-Gr as the working electrode. A schematic of the experimental apparatus and detection phenomena has been added to the supplementary information, Fig. S11 (available online at stacks.iop.org/ECSA/1/036504/mmedia). The electrochemical characterization of the TPS-Gr sensor was performed in the presence of 5 × 10\(^{-4}\) M Fe(CN)\(_6\)\(^{3-}\) containing 0.1 M KCl, using the cyclic voltammetry - technique with potential range of −0.2 V to +0.6 V, with a scan rate of 50 mVs\(^{-1}\). The electrochemical impedance spectroscopy technique with 10 mV amplitude and 10\(^{-1}\) to 10\(^5\) Hz frequency was also used for the sensor characterization measurement using the same solution. The electrochemical technique DPV (Differential Pulse Voltammetry) was used to detect the analyte, as well as in pH studies in a potential range of 0.0 V to 0.4 V, with a scan rate of 50 mVs\(^{-1}\), with an amplitude of 5 mV and a modulation time of 1 s. Same conditions were used to perform raw sample analysis tap water. The supporting electrode solution consisted of 0.1 mol l\(^{-1}\) phosphate-buffered-saline (PBS) solution prepared at pH 8. Furthermore, selectivity tests were performed, by DPV in the in the same conditions used to the analytical curve with the individual addition of paracetamol, sodium chloride, ascorbic acid, calcium carbonate, hydroquinone, uric acid and 2-chlorophenol (0.75 m mol l\(^{-1}\) in PBS solution) as potentially interfering species. These species were chosen because they are common interferents in pharmaceutical and/or environmental samples.

Figure 1. Schematic representation of the preparation of the TPS-Gr material. (A) Weighing of the components used, TPS, glycerol and DMSO. (B) Homogenization of components. (C) Division of the solution into Petri dishes for drying. (D) Oven drying of the substrate. (E) Removal of the formed substrate from the plate. (F) Substrate hot pressing.
Results and Discussion

Fabrication of the electrode TPS-Gr based on the solvent-assisted technique.—Initially, a study based on graphite and TPS mass proportions of 50:50, 60:40, 70:30 and 80:20 (w/w; graphite: TPS) was carried out to optimize the best electrochemical response. Figure 2A shows the voltametric behavior of the redox probe for each biocomposite sensor, which showed current density (J) values equal to 0.14 ± 0.02, 0.36 ± 0.03, 0.25 ± 0.03 and 0.46 ± 0.04 (mA cm⁻²) for the 50:50, 60:40, 70:30 and 80:20 graphite and TPS proportions, respectively. In that same order, Fig. 2B presents the Nyquist plots, where we obtained the Rct values equal to 1.88 ± 0.16, 0.21 ± 0.03, 0.68 ± 0.08, and 0.12 ± 0.02 (kΩ cm²), respectively.

The effect of the scan rate was performed from 0.01 to 0.2 V s⁻¹, using 5 × 10⁻³ mol l⁻¹ Fe(CN)₆³⁻/⁴⁻ in 0.10 mol l⁻¹ KCl (see Fig. S2) to determine some parameters, such as electroactive area (A), and heterogeneous electron transfer rate constant (k⁰). Using the Randles-Sevčik equation for a reversible electrochemical process (Eq. 1), the electroactive area of the electrodes fabricated in different ratios were determined. Where Ip is the peak current, n is the number of transferred electrons, A is the electroactive area (cm²), D is the diffusion coefficient of Fe(CN)₆³⁻/⁴⁻ in 0.10 mol l⁻¹ KCl solution (7.6 × 10⁻⁶ cm² s⁻¹); C is the concentration of Fe(CN)₆³⁻/⁴⁻ (mol cm⁻³), and v is the scan rate (V s⁻¹). Subsequently, the electron transfer rate constant (k⁰) was determined from Eq. 2, where R is the gas constant (8.314 J mol⁻¹ K⁻¹), T is the thermodynamic temperature (298 K), F is Faraday’s constant (96485 C mol⁻¹), A is the electrode area, and C is the concentration of electroactive species (5 × 10⁻⁶ mol cm⁻³).

The corresponding electroactive areas can be seen in Table I for the TPS-Gr electrodes at different ratios. From these results, it could be concluded that the electrochemically active areas of the TPS-Gr sensors showed an increase with respect to their geometric areas, which were around 0.20 cm². Therefore, as expected, the k⁰ value obtained for the 80:20 TPS-Gr unit is significantly higher compared to the other ratios, however, the 60:40 TPS-Gr was the second one that showed the highest k⁰, indicating that the electrochemical activity is higher for the sensor that has a higher k⁰ value.

\[
I_p = \frac{\pm (2.69 \times 10^5) n^2 A \ D^2 C \ v^1}{RT} \quad [1]
\]

\[
k^0 = \frac{RT}{F^2 A C \ R_{CT}} \quad [2]
\]

The study allowed selecting the best ratio to be used in the sensing substrate. Based on the results presented in Fig. 2 and Table I, the 60:40 ratio stood out as the best composition. Since it presented higher values of current density, electroactive area, and k⁰, as well as lower Rct than the 50:50 and 70:30 ratios. However, the 80:20 ratio showed the parameters mentioned better than the 60:40 ratio, but its capacitive current was relatively higher than the 60:40 ratio, from these results the TPS-Gr 60:40 sensor was chosen as the best ratio condition for further studies.

Characterization

Fourier transform infrared spectroscopy (FTIR).—Figure 3A shows the FTIR spectra for the pure TPS and for the biocomposite, TPS-Gr. For the TPS spectrum it is possible to observe some characteristic bands of starch and glycerol, which are the TPS components. The band around 3300 cm⁻¹ is typically attributed to hydroxyl bonds, characteristic of the formation of hydrogen bonds in the starch D-glucose molecule, and it is possible to observe a band at 3282 cm⁻¹, characteristic of axial deformation of OH. The presence of this band indicates the contribution of the elongation of OH, common in glycerol, which generates changes in the intensity of intermolecular hydrogen bonds in the starch/glycerol system.28 The band at 2925 cm⁻¹ is attributed to the axial deformation of C–H.29 The band centered at 1645 cm⁻¹ is characteristic of the angular deformation of OH in water. The region of 1400–1500 cm⁻¹ presents characteristic absorptions of glycerol, such as the band at 1477 cm⁻¹ referring to the COH groups.30 The absorptions observed between 1080 and 960 cm⁻¹ are characteristic of C–O deformation, due to the interactions of the plasticizer glycerol and starch.31 For the TPS-Gr spectrum, it is possible to observe bands in the same regions observed for the TPS sample; however, the intensity of the bands is attenuated. This phenomenon can be attributed to the presence of graphite, which despite not having absorptions in the infrared spectrum, acts masking the TPS absorptions. Thus, it was possible to observe that there were no chemical interactions between TPS and graphite, which would appear through the formation of new bands attributed to these interactions. However, the phenomenon of attenuation of the TPS bands suggests a good dispersion of graphite in the polymer matrix.

X-Ray diffraction (XRD).—Figure 3B show the diffractograms of TPS which has the characteristic of a semicrystalline material.32 The diffractogram revealed crystalline peaks at 15°, 17°, 19° and 22°, values similar to those reported in the literature for starch.33,34 In the TPS-Gr diffractogram, it is possible to observe that the addition of graphite generated two peaks that stand out over the polymer peaks, confirming the crystallinity of the graphite inserted in the polymeric material. The peaks with diffraction angle 2θ more evident appear near 26° and 54°. The first one has a very strong

![Figure 2](image-url)

Figure 2. Optimization of the main fabrication parameters of the TPS-Gr biocomposite by CV (A) and EIS (B) mass proportion studies carried out for 50:50, 60:40, 70:30, and 80:20 (w/w; graphite:TPS). Conditions: CV was used in a potential range from −0.2 V to +0.60 V, scan rate of 50 mV s⁻¹; EIS was employed in a frequency range from 0.1 Hz to 1.0x10⁵ Hz. All measurements were carried out in 0.1 mol l⁻¹ KCl and 5.0 × 10⁻³ mol l⁻¹ [Fe (CN)₆³⁻/⁴⁻].
signal, corresponding to the graphite planes 002, and the second one has a low intensity, referring to the 004 plane, both planes are characteristic of graphite and have already been reported previously in literature.\textsuperscript{18} Thus, the plans found for the composite produced prove that the addition of graphite to the TPS polymer matrix increased the crystallinity of the material in its entirety, expressed by the sharpness of the Bragg reflections, justifying the conductive properties.\textsuperscript{35}

**Scanning electron microscope (SEM).—**Surface morphology of TPS, Fig. 3C, and the TPS-Gr, Fig. 3D was analyzed by scanning electron microscopy. For pure TPS, a compact morphology was observed. The surface of the TPS-Gr has a supposedly ordered morphology of the graphite particles incorporated into the TPS. The compact orientation of the graphite particles and the porosity of the film are responsible for producing a large conductive area on the surface of the film. In the literature it is possible to find this behavior of graphite in other polymeric materials.\textsuperscript{18,36,37}

**Wettability.**—To verify the change in wettability of the TPS with the addition of graphite, measurements of the contact angle with water were performed. Figure 3E shows the image of TPS and, Fig. 3F, to TPS-Gr with their respective contact angle values. The study of wettability allowed us to verify that the insertion of graphite in the TPS caused a decrease in the angle of the material. The substrate with TPS alone has an angle of 59.53° ± 0.38°, and the TPS-Gr biocomposite has an angle of 88.64° ± 0.27°. This behavior allows us to understand that there was an increase in the cohesion force, which seeks to contract the droplet scattering to a minimal geometric surface. Consequently, the material showed a more hydrophobic character after the incorporation of graphite.\textsuperscript{38}

**Raman spectroscopy.**—Figure 3G shows the Raman spectrum for the TPS-Gr sensor material, in which it is possible to verify three characteristic bands of graphite. D band represents the defective part of the graphite, and the intensity of the G band represents the crystalline part of the graphite. The presence of graphitic carbon was proven by the formation of its characteristic bands D and G. The G band represents the defective part of the graphite, and the intensity of the G band represents the crystalline part of the graphite. \textsuperscript{18}

The peak intensity ratio, \( I_D/I_G \), was used to measure the amount of disorder in a graphite sample, for pure graphite, a value of 0.76 was reported.\textsuperscript{40} The average value found for the material developed was equal to 0.114, which is within an approximate range of values found in the literature.\textsuperscript{36}

**Electrochemical Measures**

**pH study.**—The influence of pH was investigated by the DPV technique using catechol at different concentrations. This molecule was chosen because CC is highly toxic to human health and is widely used for the production of preservatives, dyes, stabilizers, antioxidants and cosmetics.\textsuperscript{18,40,41} First, a pH study in the range of 5.0–9.0 was performed from the DPV technique, as shown in Fig. S13. With increasing pH, the molecule shows an oxidation peak at more negative potentials, and specifically at pH 8.0, the CC showed a higher current density (3.39 × 10^-4 mA cm^-2). This behavior can be directly linked to its pKa, with a value equal to 9.5, where below this value, the molecule is in its deprotonated form and above it is in its protonated form.\textsuperscript{32,43} Thus, a pH equal to 8.0 was chosen as the ideal analytical condition because it provided selectivity (low potential) and high detectability.

**Electrochemical detection of CC.**—The electrochemical technique DPV was used to obtain the analytical curve of CC, in triplicate (n = 3), with concentrations ranging from 0.1 mmol l^-1 to 2.0 mmol l^-1, as presented in Fig. 4A. Figure 4B shows a linear increase in the analytical curve, which showed a sensitivity value and linear regression equal to 2.53 × 10^-4 (mA cm^-2)(mmol l^-1)^-1 and 0.9996, respectively. The electrochemical reaction mechanism of the CC molecule is proposed in Fig. 4C; thus, we can suggest that this molecule was converted to quinone by the release of two protons that were involved in the redox reaction.\textsuperscript{31,42} The Miller and Miller statistical method\textsuperscript{44,45} was used to calculate the LOD and the LOQ, which showed values equals to 1.85 × 10^-6 mol l^-1 and 6.18 × 10^-7 mol l^-1, respectively.

**Selectivity study and real sample analysis.**—For the study of selectivity, some molecules that may interfere in the CC molecule were investigated by DPV in a 0.1 mol l^-1 PBS solution (pH 8.0). The concentrations of potentially interfering species, such as paraquat, sodium chloride, ascorbic acid, calcium carbonate, hydroquinone, and uric acid, were fixed at 0.75 mmol l^-1. These molecules were selected because they are commonly used in pharmaceuticals and/or environmental samples. As shown in Fig. S14, only hydroquinone showed potential to interfere with CC detection, as it presented a peak potential equal to 0.07 V, close to CC, which presented a peak potential equal to 0.18 V. However, this result is expected due to the similarity between their chemical structures.

The standard addition method was used to justify sensor effectiveness on real samples and determine CC in tap water samples. Table II shows the actual concentration values, measured concentrations and recovery values obtained for actual samples. The recoveries vary from 97.16 to 106.49% in real samples. These results indicated that the proposed sensor demonstrated good sensitivity for application in electrochemical detection in potentially toxic molecules. On the basis of the carcinogenicity of CC, for which there may be a probability of harm at any level of exposure.\textsuperscript{46}

**Conclusions**

The methodology used for the manufacture of thermoplastic starch and graphite biocomposites, with different proportions, proved to be viable. The device presents easy execution and good reproducibility of the results. Among the tested compositions, the one that delivered the best results in the electrochemical analysis was TPS-Gr 80:20.

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**Table I.** Electrochemical parameters obtained by CV and EIS measurements for electrodes fabricated with starch and graphite. The geometric area for these electrodes was approximately 0.20 cm^2.

| Sensor unit | Parameters | Parameters | Parameters | Parameters |
|-------------|------------|------------|------------|------------|
| TPS-Gr 50:50 | J (mA cm^-2) | 0.14 ± 0.02 | Rct (kΩ cm^2) | 1.88 |
| TPS-Gr 60:40 | 0.36 ± 0.03 | 1.05 | 2.70 × 10^-5 |
| TPS-Gr 70:30 | 0.25 ± 0.03 | 0.21 | 1.65 |
| TPS-Gr 80:20 | 0.46 ± 0.04 | 0.21 | 1.54 |

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\( R_k (\text{cm} \cdot \text{s}^{−1}) = \frac{1}{\text{Rct} \cdot A} \)
Figure 3. (A) FTIR spectra of TPS and TPS-Gr. (B) X-ray diffractograms of TPS and TPS-Gr. Surface micrographs of the films (C) pure TPS and (D) composite TPS-Gr. Contact angle measurements for: (E) TPS and (F) TPS-Gr substrates. (G) Raman spectrum of TPS-Gr.
measurements was the composite prepared with 60% graphite and 40% TPS. Thus, this composition was physiochemically characterized by several techniques. FTIR analysis showed that there was a good interaction and a homogeneous dispersion of graphite in the polymer matrix. The diffractograms also confirmed the good dispersion through the characteristic graphite planes found for the composite and the increase in crystallinity of TPS-Gr about TPS. The sharpness of the Bragg reflections justifies the conductive properties, which were also evidenced in the morphological analyses, where the graphite particles and the substrate porosity observed are responsible for producing a large conductive area to the material. Based on the results of Raman spectroscopy, it was possible to calculate the peak intensity ratio, \( \frac{I_D}{I_G} \), and the average value found for the material developed was equal to 0.114, which is characteristic of crystalline graphite and in an approximate range of values found in the literature. As a proof of concept, a fabricated electrode was used for CC determination using the DPV electrochemical technique. The electrode showed a detection limit equal to \( 1.85 \times 10^{-6} \text{M} \) and a sensitivity of \( 2.53 \times 10^{-2} \text{ (mA cm}^{-2} \text{)} \text{ (mM)}^{-1} \); thus, TPS-Gr exhibited good accuracy, selectivity, and stability in electrochemical applications to detect pollutant molecules such as catechol.

| Sample | Added (m mol \( \text{l}^{-1} \)) | Found (m mol \( \text{l}^{-1} \)) | Recovery (%) |
|--------|-------------------------------|-----------------|--------------|
| CC     | 0.10                          | 0.11            | 106.49       |
|        | 0.45                          | 0.44            | 98.73        |
|        | 1.00                          | 0.97            | 97.16        |

Acknowledgments

This work was supported by CAPES grants 88882.430936/2019-01 (ASMF) and 88887.497915/2020-00 (CCM); FAPESP projects 2019/15976-0 (APL) and 2020/12659-0 and 2014/50869-6 (MF); CNPq grants 313989/2018-4 (APL) and 301955/2019-0 (MF). The authors would like to thank the Servier Medical Art image bank.

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