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Synthesis, Characterization of Guar-Containing Polyurethane Films and their Non-enzymatic Caffeic Acid Sensor Applications

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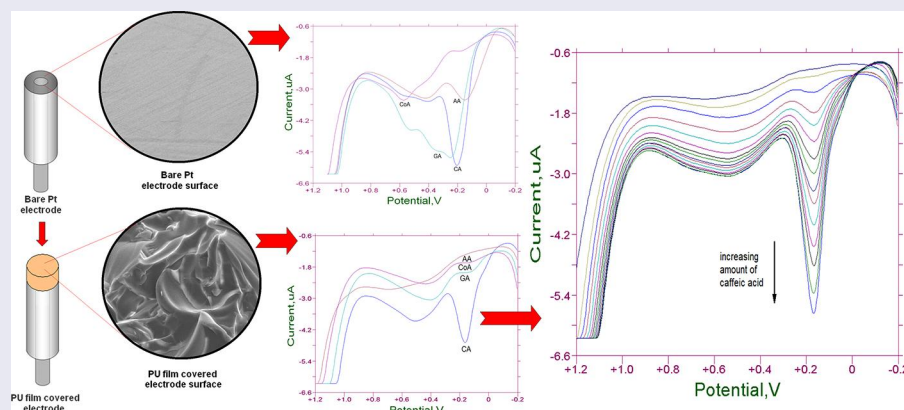
ABSTRACT

Stable voltammetric sensors were fabricated by dropping the guar-containing polyurethane films on a platinum electrode for the non-enzymatic determination of caffeic acid. The voltammetric responses of PU-G-1% toward caffeic acid have a linear concentration range from 1 to 15 mM with a correlation coefficient of 0.9938. The detection limit of PU-G-1% electrode was approximately 0.25 mM. PU-G-1% sensor showed the good sensitivity, selectivity, high R -value, low detection limit, and high reproducibility toward caffeic acid. Therefore, it is claimed that the polyurethane film containing 1% guar can be used as an excellent selective membrane for caffeic acid detection in the presence of interferent molecules.

KEYWORDS

Caffeic acid; polyurethane films; sensors; voltammetric sensor

GRAPHICAL ABSTRACT



Introduction

Phenolic compounds have antioxidant properties that prevent auto-oxidation via the inhibition of radical formation. Thus, a diet rich in vegetables and fruits that contain these compounds plays an important protective role in human health against chronic degenerative diseases associated with oxidative stress in the body^[1–4]. Caffeic acid (3,4-dihydroxycinnamic acid) (CA) is a phenolic compound which is found in coffee, tea, olive oil, fruits, vegetables, and wine^[5,6]. CA is known to display a wide variety of biological functions, including antioxidant, anticarcinogenic activities, antidepressive, anti-inflammatory, antimutagenic, antianxiety, and inhibition of human immunodeficiency virus (HIV) replication^[7–10]. The CA is one of the most researched derivatives not only because of its protective antioxidant

feature, but also due to its effectiveness against cancers, cardiovascular disease, neurological diseases, immunoregulation diseases, asthma, and allergic reactions^[11]. Additionally, recent studies have displayed that CA derivatives exhibited potential activity against HIV integrase and can inhibit HIV replication with moderate anti-HIV activity in cell culture^[12,13].

In recent years, many methods have been used for determination of CA. Among these methods, it has been demonstrated that enzymatic sensors^[14,15], high pressure liquid chromatography^[16,17] and gas chromatography^[18,19], UV-vis spectrophotometry^[20], capillary electrophoresis, and electroanalytic techniques^[21] have the facility for determination of CA concentration. However, it is claimed that these methods have relatively expensive, require

pretreatment, and have poor sensitivity and selectivity. Electrochemical methods have attracted much attention because of low detection limit, fast response time, easy to use, high sensitivity, and less expensive^[22,23].

However, there has been little reported in the literature on determination of CA in the presence of various interferent molecules using the electrochemical method^[24]. Especially, polymers have been successfully used to eliminate the interferent species for determination of biochemical molecule because of their unique properties, flexibility in design, and low cost^[25]. Among these polymers, polyurethanes (PUs) have important structural, morphological, and chemical properties for sensor applications. Thus, PUs have been widely employed for the construction of pressure sensors^[26,27], glucose sensors^[28,29], gas sensors^[30–32], humidity sensors^[33,34], piezoelectric tactile sensors^[35,36], and hormone sensor^[37,38] due to their simple preparation method, mechanical and thermal stability, and high biocompatibility.

In this article, novel guar-containing PU films as CA selective membrane were synthesized from 4,4'-methylene diphenyl diisocyanate (MDI), guar (G), and ethylene glycol (EG) with different monomer ratios. The structure, morphology, and thermal behavior of PU films were characterized by Fourier transform infrared (FTIR) spectroscopy, scanning electron micrograph (SEM), and thermal analysis [differential thermal analysis (DTA)/thermogravimetric analysis (TGA)/differential scanning calorimetry (DSC)] techniques. Furthermore, guar-containing PU films were also examined whether this PU film can be used as a membrane for accurate determination of CA. The PU films were formed on bare Pt electrode using a simple drop-casting method. Electrochemical measurement results illustrated that the PU electrode completely eliminated the unwanted responses from guar (G), gallic acid (GA), *p*-coumaric acid (CoA), ascorbic acid (AA), lactose (LAC), sucrose (SUC), fructose (FRU), maltose (MAL), and glucose (GLU). As a result, it has been claimed that these guar-based PUs could be used as selective polymeric membrane for the rapid and accurate determination of CA.

Materials and methods

Materials

4,4'-Methylene diphenyl diisocyanate, CA, guar (G), GA, CoA, AA, LAC, SUC, FRU, MAL, GLU, and other reagents were purchased from either Sigma-Aldrich Chemical Company or Merck and used without purification. Solutions of AA solution were prepared

freshly for each experiment. 0.1 M phosphate buffer solution (pH 7) was used as the supporting electrolyte solution. The buffer solutions were made from Na₃PO₄, NaH₂PO₄, and Na₂HPO₄ and the pH was adjusted with 1.0 mol L⁻¹ NaOH solution. All aqueous solutions were prepared with deionized and doubly distilled water.

Instrumentation

Infrared spectra were recorded in the range 4,000–400 cm⁻¹ on Perkin Elmer 283 model Fourier transform spectrometer. Surface analysis and elemental mapping were performed via a Leo EV0 40xVP model scanning electron microscope. Incident electron beam energies from 3 to 13 keV had been used. In all cases, the beam was at normal incidence to the sample surface and the measurement time was 100 s. DTA and thermogravimetry (TG) were performed with Shimadzu DTA-50 and TGA-50 thermal analyzers, respectively. All of the thermal analysis studies were performed at a heating rate of 10°C min⁻¹ in an air atmosphere from 20 to 800°C using 10 mg for DTA and TGA. DSC analysis was performed with Shimadzu DSC-60. DSC is at 5°C min⁻¹ heating rate and under 25 mL min⁻¹ dynamic nitrogen atmosphere. Analyses were carried between 300°C and room temperature. The amount of sample was taken 5 mg for DSC.

All voltammetric measurements were performed in a conventional three-electrode cell at room temperature. The working electrode was one platinum disk electrode (CHI, 2 mm diameter) modified with guar-based polyurethane films. The auxiliary electrode was a Pt wire coil, and an Ag/AgCl electrode saturated with KCl was used as reference. All pH measurements were performed using a Jenway 3010 pH meter. Differential pulse voltammetry (DPV) experiments were performed by a BAS 100 W (Bioanalytical Systems, Inc.) electrochemical analyzer. The voltammograms were recorded by scanning potential using differential pulse voltammetry.

Synthesis of guar-based polyurethanes

The guar-based polymers were produced with MDI, guar, and ethylene glycol (EG) by polyaddition reaction using THF:DMF (9:1) as a solvent and triethylamine as a catalyst, where total solvent volume was fixed at 30.0 mL. The molar ratios based on functional groups of MDI:guar:EG units in the PUs were 1:0.01:0.99, 1:0.03:0.97, 1:0.05:0.95, and 1:0.10:0.90, respectively. Polymerization procedure was explained as follows. First, MDI was dissolved in THF:DMF mixture in a Schlenk tube equipped with a magnetic stirrer. Then, different ratios EG and guar were added to the

isocyanate solution at the previous rates. After 30 min of stirring, the Schlenk tube was placed in oil bath at 90°C and refluxed for 3 h. Thereafter, the tube was removed from the bath and it was cooled to room temperature. The guar-based polymers were obtained by removing the solvent under vacuum, washed several times with distilled water. Finally, the products were dried in a vacuum oven at 30°C and were weighed. The same procedure was also carried out for other monomer ratio. The prepared products were characterized for understanding their structural and thermal properties.

Preparation of PU electrodes

Prior to starting chemically modification of electrodes, the surface of working electrode was carefully cleaned and polished with successively finer grades of diamond polishing compounds and aqueous alumina slurry down to 0.5 mm and finally thoroughly washed with double-distilled water^[39]. The PU solution was prepared by dissolving 20 mg of guar-based polyurethanes in 2 mL N-Methyl-2-Pyrrolidone (NMP). Platinum working electrodes were modified by dropping 6 μ L of polyimide solution on bare Pt electrodes.

Results and discussion

Characterization of guar-based polyurethane films

Chemical and molecular structures of synthesized guar-based polyurethanes were confirmed by FTIR spectroscopy. The FTIR spectrum of these polyurethane films with different guar ratios is shown in Figure 1. In the FTIR spectra of the guar-based PUs, there is no free isocyanate peak at 2,265 cm^{-1} and this indicates that there is no residual MDI in the polyurethane structures.

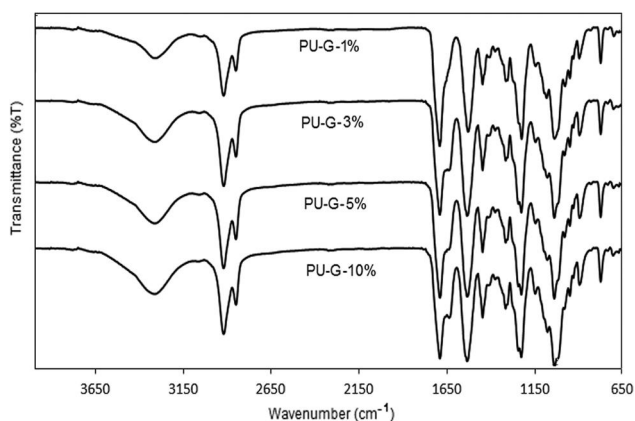


Figure 1. FTIR spectrum of the guar-based polyurethane films. Note: FTIR, Fourier transform infrared.

For guar-based polyurethanes, the characteristic peaks of both urethane bond and polyol groups were appeared at 1,733 cm^{-1} (C=O ester groups), 1,367 cm^{-1} (C–N), 1,614 cm^{-1} (C=O), 1,533 cm^{-1} (C=O), 2,937 cm^{-1} (C–H stretching frequencies for the aliphatic $-\text{CH}_2-$ groups), and 3,300 cm^{-1} and the N–H stretching disappearance also proved us that the desired structure is obtained. Moreover, the peaks at 1,522 cm^{-1} were belong to $-\text{NH}$ and $-\text{CH}$ stretching vibrations. Increasing guar ratio in the PUs increases aliphatic $-\text{CH}$ and C–O–C stretching vibration.

To investigate the thermal properties and the effect of guar over thermal stability of PUs, TGA, DSC, and DTA techniques were performed. Figure 2 shows the TGA thermograms depending on guar ratios of PUs. In the TGA thermograms of all guar-based polyurethane films, three thermal degradation patterns were observed. These three weight loss patterns stem from the degradation of the methylene groups, the polyethylene glycol (PEG) units, and guar units which are cross-linkers in the polyurethane film structure. First, thermal degradation of the PUs was initiated due to the guar units at 110–180°C and second thermal decomposition was observed at 180–360°C corresponding to the degradation of the soft segment of PEG and $-\text{CH}_2$ groups of isocyanate units. The last thermal degradation pattern resulting from the hard segment of cyclic $-\text{CH}_2$ groups of isocyanate units was observed at 400–620°C as the last thermal decomposition. With increasing guar unit amount, the flexibility of PU chains is decreased due to the excessive branching and cross-linking. But, thermal stability of guar-based polyurethane films was increased.

Figure 3 shows the DTA thermograms of PU-G-1%, PU-G-3%, PU-G-5%, and PU-G-10%. DTA analysis results were matched with TG analysis. All thermograms of the synthesized guar-based polyurethanes include three thermal decomposition peak (first peak at 150–300°C belongs to degradation of the cross-linking groups and bounds, second peak at 300–460°C belongs to aliphatic $-\text{CH}_2$ groups of soft segment of polyurethane structure, and third peak at 475–650°C belongs to degradation of hard segment and polymer structure). The thermal stability of the polymers was increased by being increased in guar amount due to the cross-linking of guar-based polyurethane chains.

In the preliminary study, the effect of the guar groups in the cross-linking and glass transition of the polyurethane films was determined by DSC analysis. Figure 4 shows the DSC thermograms of guar-based polyurethanes. Glass transition (T_g) of the PUs was observed at around -18.21°C . Classical and commercial polyurethanes have linear polymer chain structure.

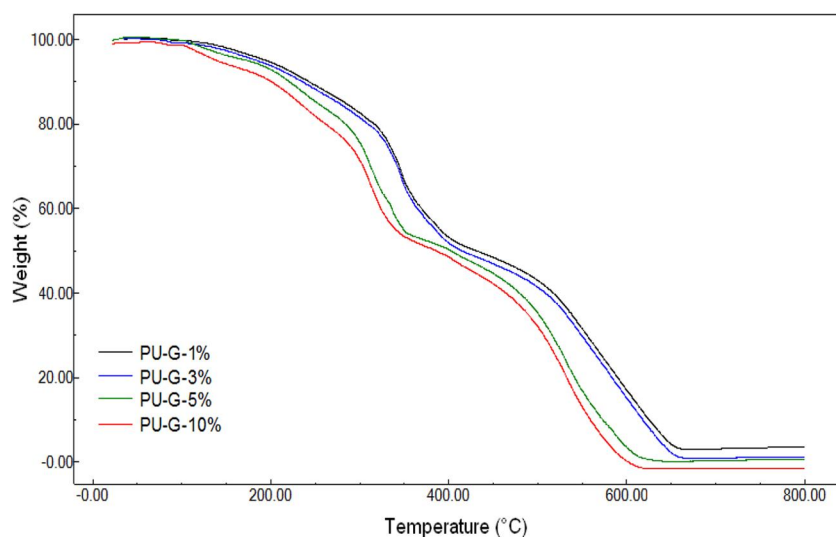


Figure 2. TGA thermograms of the guar-based polyurethane films.

Thus, they formed a stacked polymer chain structure more compact and intermolecular forces are stronger when the polymer chains pack together in a regular way as in these linear polyurethanes. Therefore, T_g of this stacked structure increases and these types of polyurethanes are not suitable for selective membrane application because of low permeability. On the other hand, T_g values, free volume, and permeability increased with the guar amount of the polyurethane. T_g values of PU-G-1%, PU-G-3%, PU-G-5%, and PU-G-10% were observed as 49.35, 57.65, 60.58, and 62.89°C, respectively. T_g increased steadily with the guar content for synthesized polyurethanes. The high cross-link density restricted main chain motion and caused an increase

in T_g . Other important factor of the selectivity of polymeric film based amperometric sensors is hydrophilicity of polymeric membrane on the surface of electrode. The ability of transportation of the analyzed species on the electrode surface and wettability affect the detection parameters and detection time. Therefore, the synthesized polyurethane film contact angle of the films was measured and the results are given in Figure 5. Contact angle values of PU-G-1%, PU-G-3%, PU-G-5%, and PU-G-10% were observed as 67.80°, 73.72°, 74.88°, and 76.42°, respectively. Contact angles results increased with the guar amount in polyurethane structure.

For the detection of CA in analysis of multi-component mixtures such as wine and fruit juices,

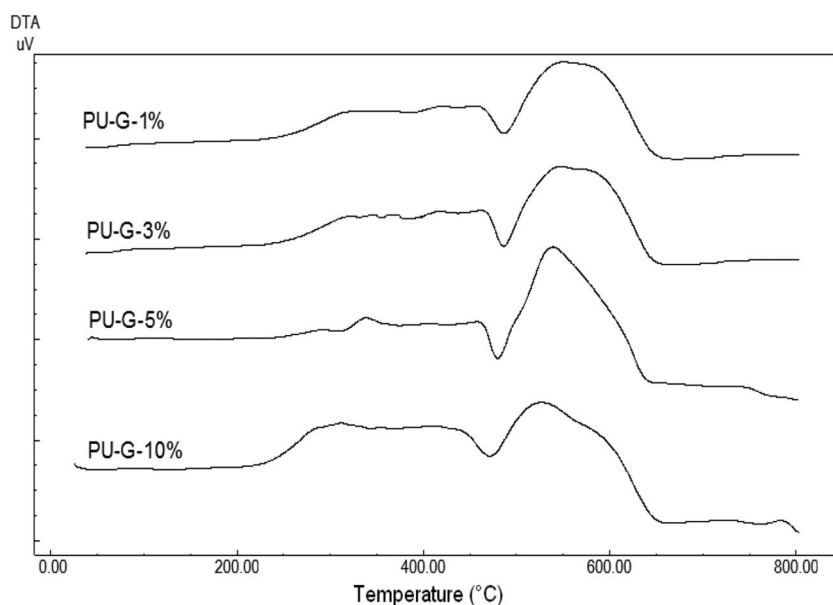


Figure 3. DTA thermograms of the guar-based polyurethane films. Note: DTA, differential thermal analysis.

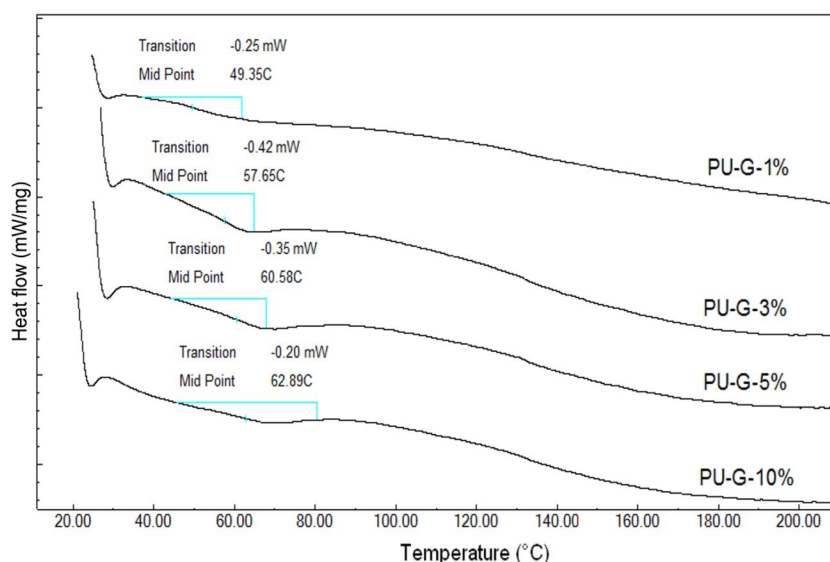


Figure 4. DSC thermograms and T_g values of the guar-based polyurethane films. Note: DSC, differential scanning calorimetry.

electroactive interference is a major problem. Guar-based polyurethane membranes were used in the elimination of these electroactive interferent species and modification of the electrode surface. Polyurethanes have been preferred because of their ease of application, stability at the electrode surface, high adhesive properties, and the formation of an anionic surface. This polyurethane membrane structures enable the removal of anionic interferent species from the surface. Figure 6 shows the surface images of bare Pt electrode and modified electrodes. Before and after modification

of the surface of the electrode with guar-based polyurethanes, the obtained SEM images were indicated in Figure 6. It can be seen from these images that the polymeric film on the electrode surface had a uniform, homogeneous, and porous surface. These porous structures are suitable for selectivity. From these surfaces, the surface of the PU-G-1% structure is more porous and rougher than PU-G-3%, PU-G-5%, and PU-G-10%. For this reason, PU-G-1% has a higher electrode surface area. Thus, response of this electrode is higher than other prepared electrodes.

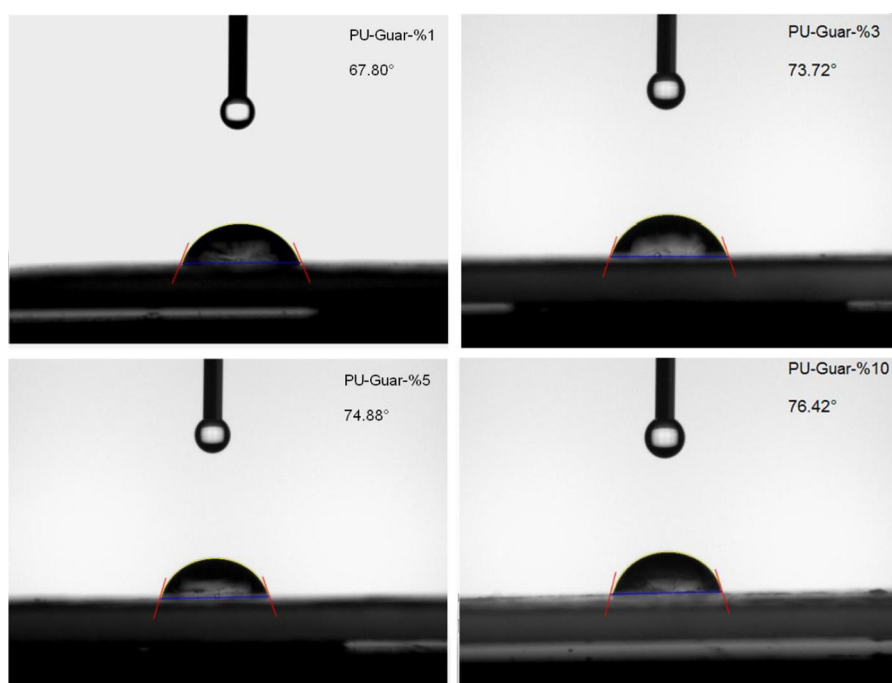


Figure 5. Contact angle values and contact angle measurement images of the guar-based PU films.

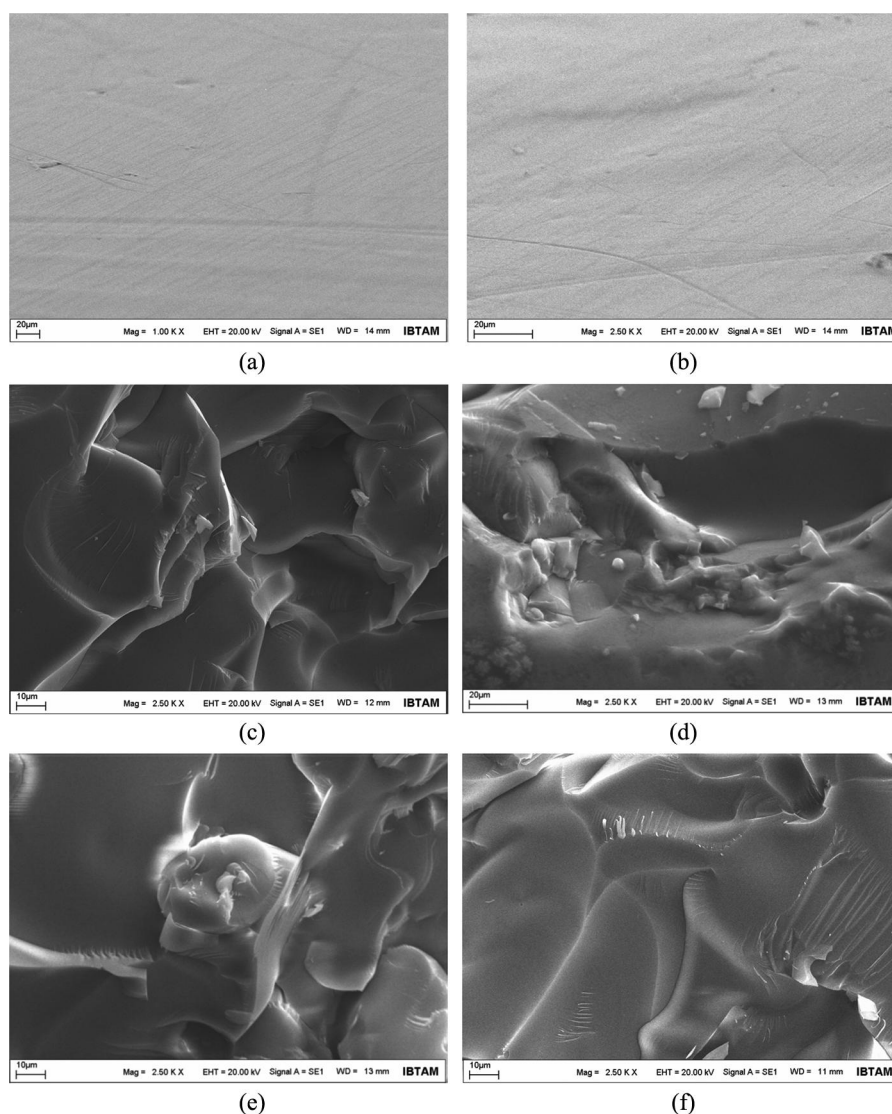


Figure 6. SEM images of the bare electrode (a, low; b, high magnification) and guar-based PU modified electrodes with different guar ratios (c, PU-G-1%; d, PU-G-3%; e, PU-G-5%; f, PU-G-10%). Note: SEM, scanning electron micrograph.

Amperometric measurements of the polyurethane modified electrodes

Amperometric CA measurements with the guar-based PUs were performed with DPV technique using BAS 100W (Bioanalytical Systems, Inc.) electrochemical analyzer. DPV measurement is more selective and sensitive than cyclic voltammetry. Therefore, differential pulse voltammetry (DPV) technique was selected to investigate the electrochemical behavior and determination of the CA at modified electrode. To confirm the selectivity of bare and the guar-containing polyurethane electrode, differential pulse voltammetry (DPV) technique was used to investigate the electrochemical behavior of the CA. Figure 7 depicts the DPV behaviors of CA, CoA, GA, and AA in pH 7.0 phosphate buffer solution at a bare Pt and modified electrode. From the

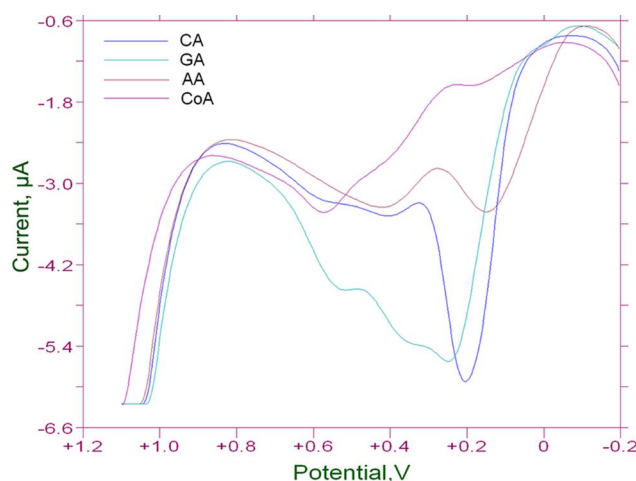


Figure 7. DPV behaviors of CA, CoA, GA, and AA in pH 7.0 PBS at the bare electrodes. Note: DPV, differential pulse voltammetry; CoA, *p*-coumaric acid; PBS, phosphate buffer solution.

DPV studies, it is easily seen that guar-containing polyurethane electrode permitted penetration of CA while blocking CoA, GA, and AA interferent. This voltammetric behavior reflects that the oxidation peaks of interferences were completely suppressed with the guar-containing polyurethane electrode. The results showed in Figure 7 suggest that the proposed sensor is highly selective for CA, once the potential interferences did not affect the peak current of CA, at concentrations tested. The high selectivity of sensor can be explained by the size and functional group arrangement of specific cavities matched with CA in the all PU film (PU-G-1%, PU-G-3%, PU-G-5%, and PU-G-10%). On the other hand, Figure 8a–d showed that the all polyurethane electrodes had good electro-oxidation for CA. This voltammetric behavior reflects that responses of AA, CoA, and GA were completely eliminated with these polyurethane membranes. However, as shown in Figure 8a–d, the amperometric responses of PU-G-1% in Figure 8a are higher. Therefore, we have focused on the other PU-G-1% film for the preparation of CA electrode.

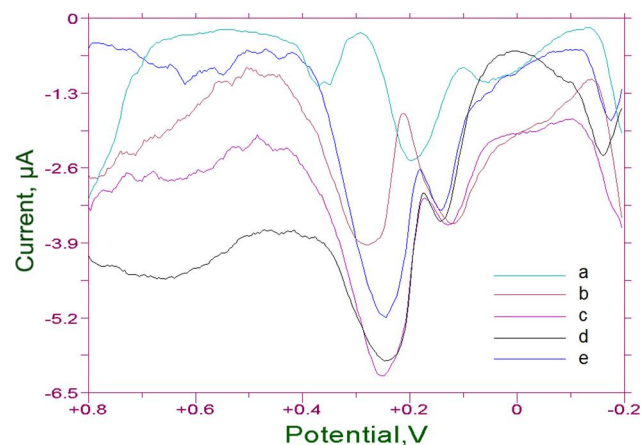


Figure 9. The effect of the film thickness of PU-G-1% on the CA response (a, 2 μL ; b, 4 μL ; c, 6 μL ; d, 8 μL ; and e, 10 μL PU solution covered Pt electrode).

The selectivity and response time of guar-based PU electrodes depend on the film thickness. To evaluate the effect of the film thickness to performance of the PU-G-1% electrode, we adjusted the amount of polyurethane solution on the Pt electrode. The amperometric

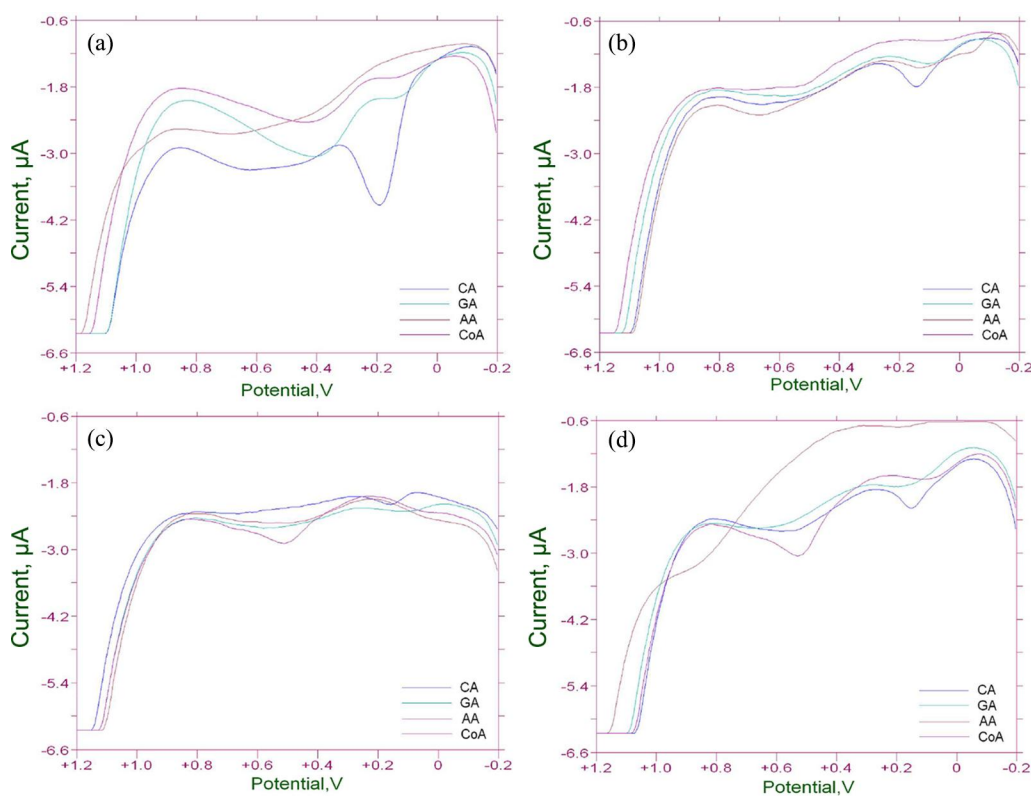


Figure 8. DPV behaviors of 1 mM AA, 1 mM CoA, 1 mM GA and AA, and 1 mM CA in pH 7.0 PBS at the PU electrodes. (a, PU-G-1%; b, PU-G-3%; c, PU-G-5%; and d, PU-G-10%). *Note:* DPV, differential pulse voltammogram; CoA, *p*-coumaric acid; PBS, phosphate buffer solution.

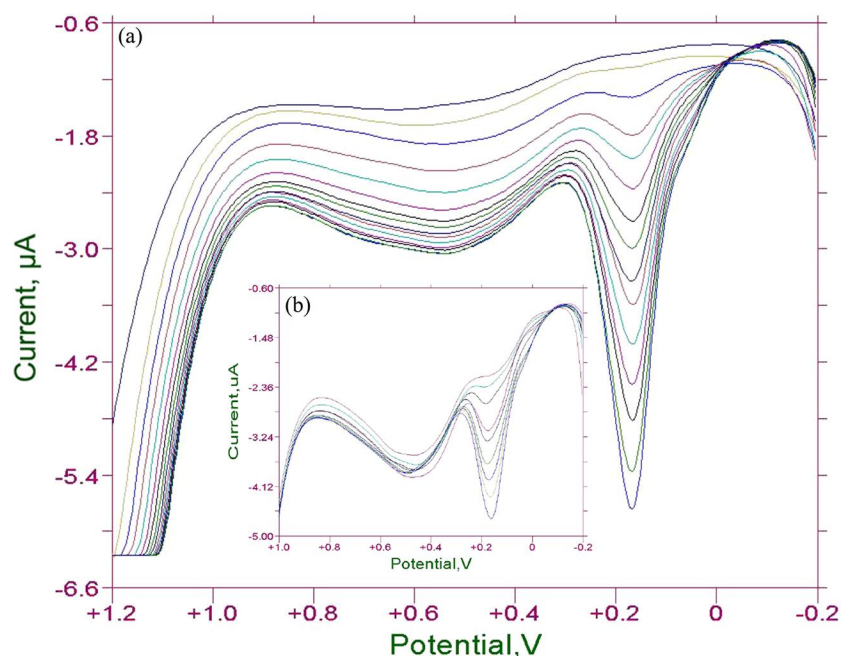


Figure 10. DPVs of the PU electrode to increasing concentration of CA in the presence of interferences (a—concentration of CA: 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 $\times 10^{-3}$ M; b—low concentration of CA: 0.25, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 $\times 10^{-3}$ M) (interferents: CoA, AA, GA, LAC, SUC, FRU, MAL, and GLU = 2 mM). *Note:* DPV, differential pulse voltammogram; CoA, *p*-coumaric acid; LAC, lactose; SUC, sucrose; FRU, fructose; MAL, maltose; GLU, glucose.

responses toward CA of PU-G-1% electrodes prepared with 2, 4, 6, 8, and 10 μ L polyurethane solution are shown in Figure 9, respectively. From Figure 9, it is clearly seen that the amperometric response toward CA of the PU-G-1% electrode prepared with 6 μ L polyurethane solution was higher than the others. Therefore, optimal film thickness of polyurethane electrode was selected as 6 μ L for advanced CA sensor applications.

To obtain an analytical curve for the constructed amperometric sensor, DPV for CA oxidation was carried out at different CA concentrations in the presence of the electroactive (CoA, AA, and GA) and non-electroactive interferences (LAC, SUC, FRU, MAL, and GLU). As a result, it found that the oxidation peak current increased linearly with increasing CA concentration at guar-containing polyurethane electrode, even in interferences. From the amperometric responses

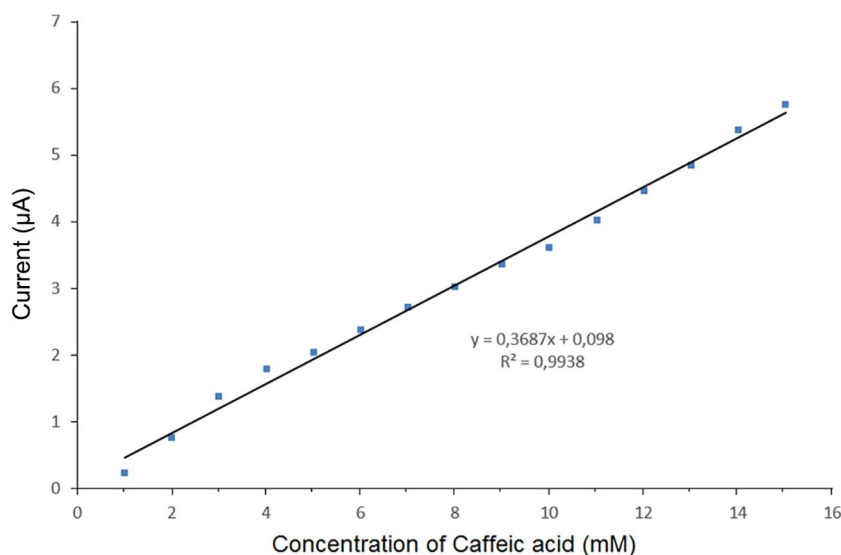


Figure 11. Calibration curves of PU-G-1% electrode for CA response.

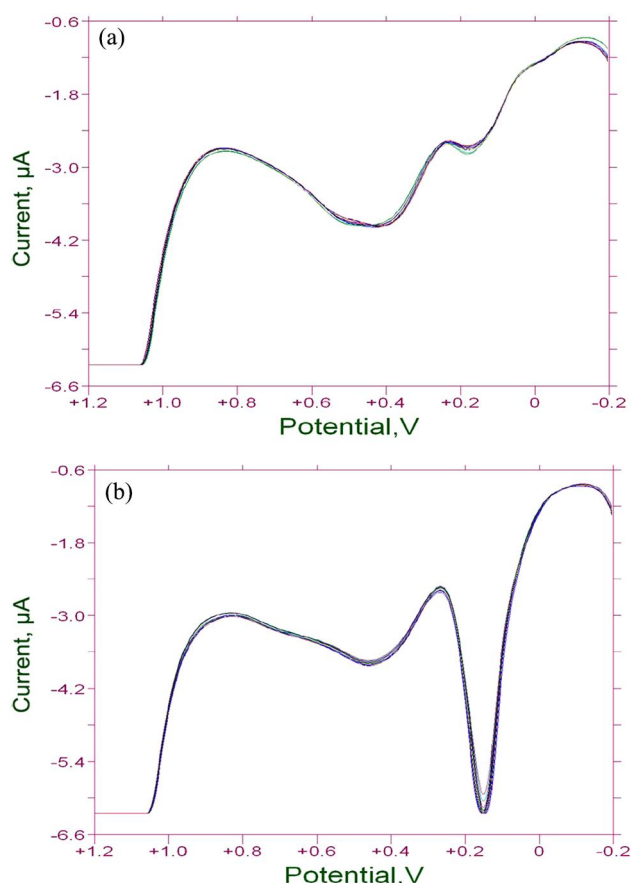


Figure 12. The reversibility of electrochemical measurements for the guar-based PU modified electrode for 2 mM CA in the presence of the above-mentioned interfering compounds. (a, concentration of CA: 0.5 mM; b, concentration of CA: 4 mM) (interferents: CoA, AA, GA, LAC, SUC, FRU, MAL, and GLU = 2 mM). Note: CoA, *p*-coumaric acid; LAC, lactose; SUC, sucrose; FRU, fructose; MAL, maltose; GLU, glucose.

observed in Figure 10, the analytical calibration curve for different CA concentrations was obtained (Figure 11). As could be easily seen from the DPVs of

guar-containing polyurethane electrode, the sensor showed a linear response range from 1 to 15 mM with a correlation coefficient value (R^2) of 0.9938. The developed sensor showed a linear current response to the CA concentration in the range from 0.25 to 15 mM, with a detection limit of 0.25 mM.

The reversibility of electrochemical measurements for CA response was also checked for both 0.5 and 4 mM CA in the presence of the above-mentioned interfering compounds (Figure 12). The amperometric results obtained from 10 successive experiments demonstrated that the developed sensor gave good reproducible responses for the repeated curves.

To determine storage stability of the guar-based PU electrode, the voltammetric 4 mM CA responses of the prepared PU-G-1% electrode were monitored every 3 days (Figure 13). The PU-G-1% electrode was kept stored at 4°C when not in use. The CA responses were average values of three repeated measurements. During 3 months of storage, the prepared guar-based electrode has presented a well-defined response; 91.66% of its initial peak current has been retained in 3 months of its continuous use, revealing the acceptable storage stability of the sensor.

Conclusion

In this paper, guar-containing polyurethane films as CA selective membrane were synthesized and fully characterized. The structure, morphology, and thermal behavior of guar-containing polyurethane films were characterized by FTIR spectroscopy, SEM, X-ray diffraction, and thermal analysis (DTA/TGA/DSC) techniques. Furthermore, it was also examined whether these guar-containing polyurethane films can be used as a membrane for non-enzymatic determination of CA in

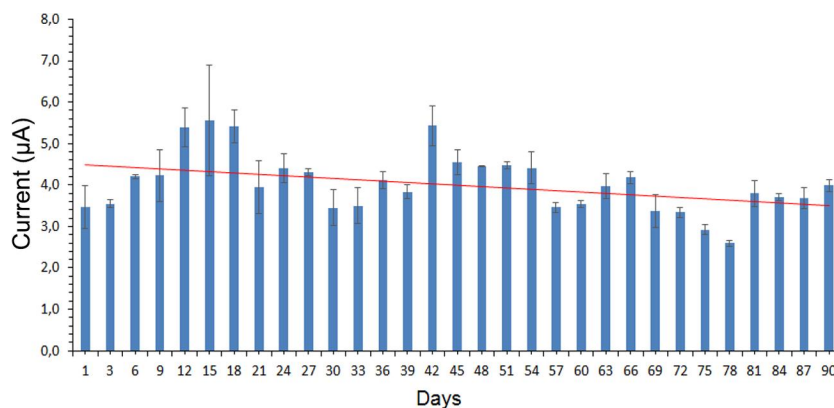


Figure 13. Storage stability of the guar-based PU electrode (concentration of CA: 4 mM) (interferents: CoA, AA, GA, LAC, SUC, FRU, MAL, and GLU = 2 mM). Each value is the average of triplicate experiments with error bars indicating STDEVs(σ_{n-1}). Note: CoA, *p*-coumaric acid; LAC, lactose; SUC, sucrose; FRU, fructose; MAL, maltose; GLU, glucose.

the presence of electroactive and non-electroactive species. The guar-containing PU films were formed on bare Pt electrode using a simple drop-casting method. The interferents of AA, CoA, and GA were eliminated effectively. The PU-G-1% film exhibited excellent selectivity, very high *R* value (0.9938), and low detection limit (0.25 mM) toward CA, as well as good reversibility for CA determinations and for sensor preparation. As a result, it has been claimed that PU film containing 1% guar could be used as selective polyurethane membrane for non-enzymatic determination of CA in the presence of various interferent compounds.

Funding

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