CHEMICAL ENGINEERING TRANSACTIONS

VOL. 87, 2021

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Laura Piazza, Mauro Moresi, Francesco Donsì

ISBN 978-88-95608-85-3; **ISSN** 2283-9216

DOI: 10.3303/CET2187098

Spent Coffee Grounds Extract for Active Packaging Production

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The interest in searching an alternative to the condition of "waste" for spent coffee is continuously growing in the scientific community. Indeed, the high content of polyphenols, caffeine, and tannins in this residue can potentially lead to pollution for water and soil, since they show toxicity for various plants, microorganisms, and aquatic organisms. Nevertheless, these same antioxidants find wide applications in the food, cosmetic and pharmaceutical industries, especially caffeine and chlorogenic acid, thanks to their ability to prevent or slow down the oxidation of the substrate.
In the context of active packaging, the use of compounds recovered from spent coffee grounds is promising, since they allow extending the shelf-life of food while maintaining its sensory and nutritional properties.
In this work, High Pressure and Temperature Extraction process was used to extract antioxidants from spent coffee grounds. The obtained extract was used for the fabrication of zein-based films intended for active packaging applications. Biopolymer films loaded with spent coffee grounds extract were prepared using two different techniques: solvent casting and electrospinning. Films were characterized in terms of morphology and antiradical power of the released active components.
Considering the large amount of exhausted coffee produced annually and the global extension of the coffee industry, the proposed application could represent a profitable alternative to conventional waste disposal, as well as an advantage for the environment and the food industry.

1. Introduction

Food deterioration can occur during storage, processing, transport, or production, which is the reason for the loss of quality and safety of fresh food products. In recent years, the development of advanced packaging solutions has gained increasing attention to extend the food shelf life, preserving its quality and safety (Barden and Decker, 2016). One of the most interesting strategies to face this problem has turned out to be active packaging, which involves the antioxidant or antimicrobial agents controlled release (Domínguez et al., 2018, Drago et al., 2020). Many plants, herbs, and spices are considered as potential antioxidant sources due to the content of phenolic acids, carotenoids, and polyphenols in their extracts, which can be added to packaging materials, resulting in an extension of the food shelf-life (Valdés et al., 2015). Some studies highlighted the increase in antioxidant and antimicrobial activity of natural compounds when present in mixtures or extracts compared to the same amounts of a single compound. For this reason, studies on active packaging dealing with the incorporation of natural extract rather than single compounds in polymers for food applications are increasingly attracting the scientific community's attention. Moreover, some residues coming from the agri-food industry are still rich in antioxidant compounds, which can be recovered for waste valorization (Pettinato et al., 2019). Taking into consideration the large extension of coffee industry and the increasing trend of coffee market (Seninde and Chambers, 2020), a more environmentally-friendly management of coffee waste deserves more attention (Iriondo-DeHond et al., 2020). Coffee waste includes pulp, husk, coffee beans, and spent coffee grounds (SCG). SCG are among the most abundant waste, considering that 650 kg of SCG are generated by 1000 kg of green coffee beans processed (Ramón-Gonçalves et al., 2019). These residues contain substantial amounts of high added-value bioactive compounds with antioxidant activity, like melanoidins, caffeine, chlorogenic acid, and polyphenols. Thus, some attempts at extracting these compounds

Paper Received: 20 September 2020; Revised: 2 March 2021; Accepted: 5 April 2021
Please cite this article as: Pettinato M., Drago E., Campardelli R., Perego P., 2021, Spent Coffee Grounds Extract for Active Packaging Production, Chemical Engineering Transactions, 87, 583-588 DOI:10.3303/CET2187098

from SCG have been performed using organic solvent extraction. However, one of the natural antioxidants' main problems is related to their sensitivity to oxygen, heat, and light, which can induce a loss of their activity (Pettinato et al., 2017). Thanks to non-conventional processes such as High Pressure and Temperature Extraction (HPTE), whose efficiency and greener approach in the recovery of the aforementioned compounds from natural sources was reported (Medina-Jaramillo et al., 2017), active ingredients can be extracted without degradation and loss of function. Attention must be paid in the food packaging manufacturing process when natural compounds are added as active components.

Active packaging can be prepared by different traditional techniques, such as extrusion or molding. One of the main drawbacks of these techniques is the deterioration of the bioactive compounds due to high process temperatures (Wu et al., 2014). This limitation can be overcome by producing active packaging through electrospinning, a promising technique in which an electrostatic force draws polymer solutions into nanofibrous films (Li et al., 2021). Electrospinning is a suitable method for food packaging fabrication due to the production of mats with high surface-to-volume ratio, high porosity, and small pore size distribution (Liu et al., 2018). Alternatively, the solvent casting of thin biopolymer films can be carried out. This versatile manufacturing procedure involves solubilisation, casting, and drying steps. The advantages of this technology include film uniform thickness distribution, maximum optical purity, and extremely low haze. The optical orientation is virtually isotropic and the films have excellent flatness and dimensional stability (Siemann, 2005, Drago et al., 2020). In this context, this work aimed to produce an active packaging based on zein, a completely biodegradable polymer extracted from corn, loading it with active compounds recovered from spent coffee grounds by HPTE. Electrospinning and solvent casting were employed for the fabrication of the active films, which were characterized in terms of morphology, total polyphenols, antioxidant activity and release kinetics into food simulant.

2. Experimental section

2.1 Materials

Ethanol (>99.8 %, liquid), glycerol (≥99.5%, liquid), Folin-Ciocalteu's reagent, and all the reference standards were purchased from Sigma Aldrich (Milan, Italy). Purified zein was purchased from Acros Organics (Morris Plains, NJ). SCG of *Coffea canephora* variety were collected by the coffee vending machine at the Department of Civil, Chemical and Environmental Engineering of the University of Genoa, Italy.

2.2 High Pressure and Temperature Extraction

SCG were dried in a laboratory oven at 45 °C up to constant weight and stored in the dark at room temperature. Extraction of antioxidants from SCG was carried out in a stainless-steel stirred extractor (Parr Instruments Company, model 350 M – 4650 Series, Illinois, USA). Detailed description of the apparatus is reported elsewhere (Pettinato et al., 2020a). Operating conditions were fixed at a liquid-to-solid ratio of 10 mL/g at 150 °C and 7.2 bar, using ethanol 54% v/v aqueous solution as solvent and an extraction time of 1 hour. At the end of the extraction, total polyphenols content was evaluated according to the modified version of the Folin-Ciocalteu's assay (Swain and Hillis, 1959) reported by (Pettinato et al., 2020). Total polyphenols in the extract were expressed as mg of caffeic acid equivalents (mg_{CAE}/mL) evaluated via UV–Vis spectrophotometer (model Lambda 25, Perkin Elmer, Wellesley, MA), from the absorbance of the samples at 725 nm ($ABS_{725\ nm}$) by the calibration curve, obtained from standard solutions of caffeic acid. Extract antioxidant activity was determined by the $ABTS^{\bullet+}$(2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)) assay, following the protocol reported by (Re et al., 1999). Antioxidant activity was expressed as micrograms of trolox equivalents (TE) per L of extract ($\mu g_{TE}/L$), according to the calibration curve of trolox, reported by (Pettinato et al., 2020).

2.3 Zein and Zein Loaded with SCG Extract Film Production

The electrospinning technique was used to produce zein and zein loaded with SCG extract films. The electrospinning apparatus (Basic Lab Unit, Spinbow, Bologna, Italy), is mainly composed of a syringe pump (KDS-100, KD Scientific, Holliston, MA, USA), a high voltage power supplier (PCM series, Spellman, NY, USA), an 18-gauge needle, corresponding to 1.27 mm of outer diameter and a metal plate collector.

Zein solutions were prepared dissolving a fixed amount of zein (35% w/w with respect to the solvent content) in ethanol 80% v/v aqueous solution. The solution was heated up to 70 °C under stirring, then cooled up to 40 °C. Once this temperature was reached, loaded films were produced by adding amounts of SCG extract to obtain a theoretical SCG loading from 15 to 35% w/w, concerning the zein content. The obtained solution was maintained at 40 °C under stirring for 8 min. 10 mL of prepared solution were electrospun with a flow rate of 1.20 mL/h, a voltage of 17.0 kV, and 16.5 cm between the tip of the needle and the collector. The scheme of the electrospinning film preparation method is shown in Figure 1a.

Solvent casting technique was also used to produce zein and zein loaded with SCG extract films. The solution was prepared similarly to what described for electrospinning, but in this case, zein concentration in ethanol 80% v/v aqueous solution was fixed at 20% w/w. SCG extract load was in the range from 15 to 35% w/w with respect to the zein content. For the preparation of the solvent casting solution, 0.24 mL of glycerol was also added as plasticizer together with SCG extract. Finally, the prepared solutions were stirred for about 30 min at 40 °C after which 2.5 mL of each solution were poured onto Petri's dishes placed at 50 °C in an oven for 2 h before being analyzed. Experimental conditions for the tests performed for the production of zein and zein loaded with SCG extract film are reported in Table 1.

Table 1: Experimental conditions to produce zein active film by solvent casting (C#) and electrospinning (E#) with different percentages of SCG extract.

Sample	Zein [%w/w]	SCG [%w/w]
C0	20	0
C1	20	15
C2	20	20
C3	20	25
C4	20	35
E0	35	0
E1	35	15
E2	35	20
E3	35	25
E4	35	35

The scheme of the solvent casting technique is shown in Figure 1b.

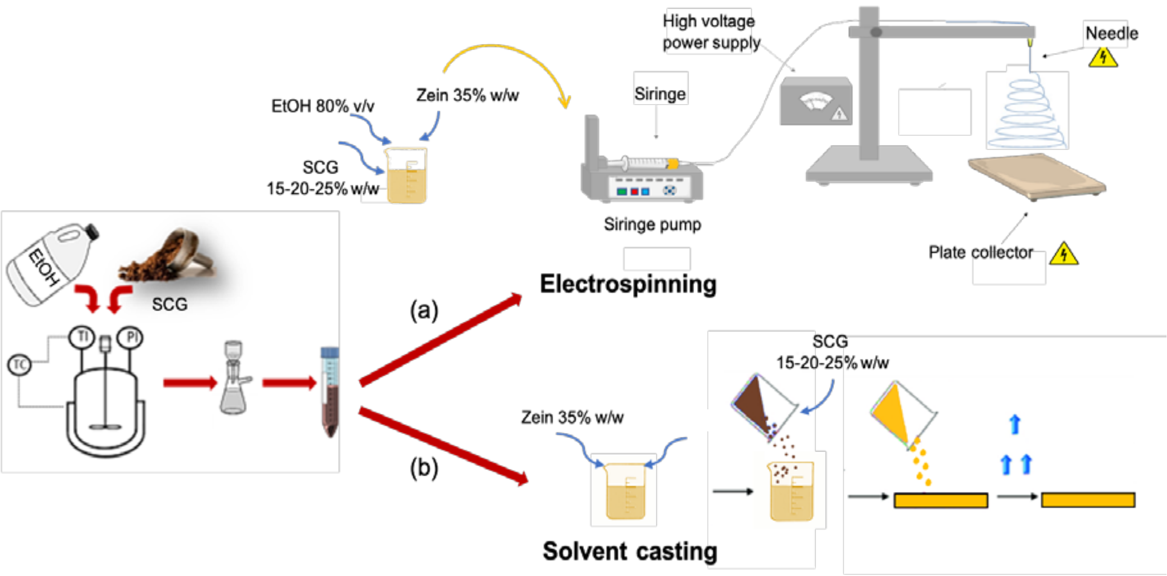


Figure 1. Schematic representation of zein loaded with SCG extract film production from extraction step to electrospinning (a) and solvent casting (b) procedures.

2.4 Film Characterizations

2.4.1 Scanning Electron Microscopy (SEM) Analyses

Field emission scanning electron microscopy (FE-SEM, mod. LEO 1525, Carl Zeiss SMT AG, Oberkochen, Germany) was employed for film morphology study. Samples were mounted on aluminum stubs using carbon tape. All specimens were sputter-coated with gold. Film thickness was measured by SEM image at five random locations along with the film (magnification 1.00 kX, 10 kV applied voltage).

2.4.2 Release Tests

The films produced (approximatively 0.50 g) were placed in contact with 20 mL of 10% (v/v) ethanol solution (food simulant) under mild agitation and light exposure at room temperature. This food simulant was selected in accordance with the Commission Regulation (EU) 2016/1416 of 24 August 2016 amending and correcting regulation (EU) no. 10/2011 concerning plastic materials and objects intended to come into contact with food products. Aliquots of the food simulant were taken over-time for 48 h and the antiradical power of the bioactive compounds released into the simulant was measured using the $ABTS^{\bullet +}$ assay. Tests were performed in triplicate.

3. Results and Discussion

In HPTE, temperature and pressure are strictly related since the second one corresponded to the vapor pressure of the solvent at the set point temperature. The main significant advantage of the HPTE extraction process is the possibility to work at a higher temperature than the solvent boiling point at atmospheric pressure. Dried SCG were used as solid raw material for the extraction study. Table 2 shows the total polyphenol content and antioxidant activity of the extract obtained by processing SCG with 54 % v/v ethanol aqueous solution as solvent at 150 °C for 60 min as extraction time. Extraction conditions were selected considering previous extraction studies (Casazza et al., 2015, Pettinato et al., 2020b). The selected HPTE operating conditions showed an extract with high content of polyphenols (4.96 ± 0.25 mg $_{CAE}$/mL) and high antioxidant activity (59.0 ± 3.1 mg$_{TE}$/L) (Table 2), however after two months of storage at 20 °C the bioactive compounds presented partial degradation that resulted in a slight decrease in the content of polyphenols (3.90 ± 0.11 mg $_{CAE}$/mL) and antioxidant activity (46.2 ± 5.2 mg$_{TE}$/L) (Table 2).

Table 2: Total polyphenol and antioxidant activity of extract obtained by HPTE from SCG at 150 °C and 7.2 bar, for 60 min.

	After extraction	After 2 months of storage at 20 °C
Total polyphenol content (mg $_{CAE}$/mL)	4.96 ± 0.25	3.90 ± 0.11
Antioxidant activity (µg$_{TE}$/L)	59.0 ± 3.1	46.2 ± 5.2

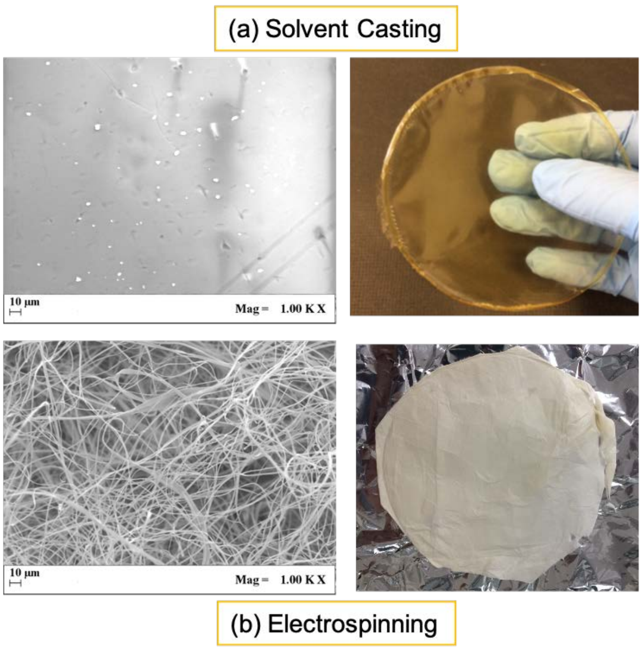


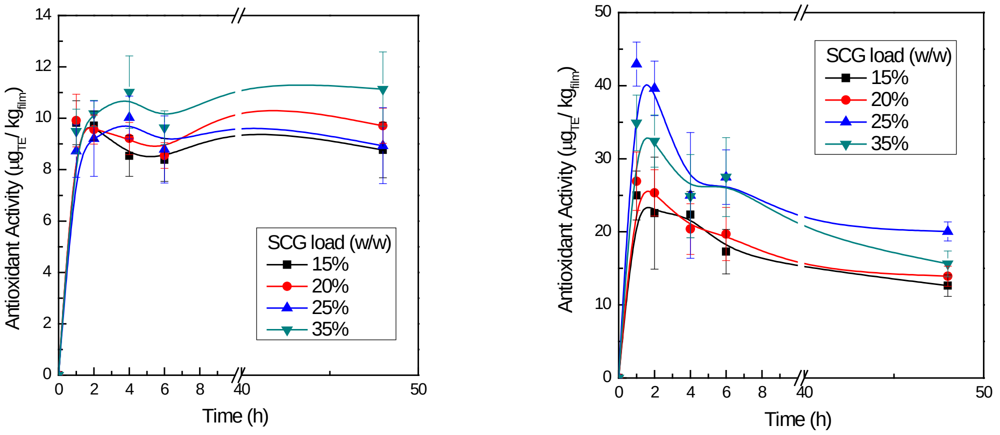
Figure 2. FE-SEM images of zein films produced by solvent casting (sample C2) (a) and electrospinning (sample E2) (b).

For this reason, to prevent their aging deterioration, active compound mixtures obtained by SCG extraction have been stabilized into the zein polymeric support. Two different film production methods have been adopted and compared: electrospinning and solvent casting. Zein was dissolved in ethanol 80% v/v aqueous solution and processed according to the procedures described in section 2. Solvent casting provided a thin and transparent film with a yellowish color due to the brown extract (Figure 2a). This process has been optimized to obtain a film as homogeneous as possible and with compatible characteristics for the proposed application. Preliminary tests were conducted with zein alone (not loaded with the extract, blank) to evaluate appropriate process parameters. The second experimental step evaluated the effect of the extract loaded into the film on its properties. For this reason, different concentrations of SCG extract were tested (Table 1). The thickness of the solvent casting films varied between 20-30 μm whereas the specific weight was in the range from 70 to 100 g/m^2, being proportional to SCG extract load.

Electrospinning led to the production of electrospun mats with a homogeneous appearance and a pale-yellow colour (Figure 2b). These films, unlike the films produced by solvent casting, are opaque due to their fibrous structure. However, the electrospun films had a specific weight of about 20 g/m^2 whereas their thickness was about 60 μm, which indicates its higher void degree, compared to the samples obtained by solvent casting. For both elctrospun mats and films by solvent casting the increase in SCG extract concentration provided a more intense brownish color.

Besides, release tests of the active component from the obtained films in a food simulant were carried out.

From the antioxidant release tests reported in Figure 3, it can be observed that films obtained using the solvent casting method showed a slower release kinetic if compared to films obtained by the electrospinning process. Indeed, for the electrospinning process, in the first 10 hours of contact, the antioxidant activity ranged between 17.28 ± 3.03 and 42.96 ± 3.01 $\mu g_{TE}/kg_{film}$, whereas the solvent casting films had a smaller release (between 8.37 ± 0.83 and 11.012 ± 1.41 $\mu g_{TE}/kg_{film}$) at the same contact period. These results indicate that the higher exposed surface of the electrospun matrix allows a faster release of the active compounds. It can also be noted that the electrospun samples had a faster degradation kinetic, after a first important release of the active compounds (Figura 3).



(a) (b)

Figure 3. Release tests in aqueous solution of ethanol at 10% by volume (food simulant) for solvent casting film (a) and electrospinning (b).

4. Conclusions

Zein films loaded with spent coffee ground extract were successfully obtained. Extracts from coffee grounds demonstrated to be a good biosource of antioxidants, able to provide antioxidant activity to the produced films. Electrospinning and solvent casting proved to be efficient production methods, able of modulating the antioxidant migration kinetic. These properties are tunable according to the different manufacturing methods adopted. Solvent casting provided 20-30 μm thick transparent films, whose loading release was slower compared to electrospun mats. Indeed, these last mats exhibited a fibrous structure, leading to an opaque appearance, higher thickness and a high void degree, and the larger surface exposed to food simulant provided a faster release, but also a faster degradation kinetic, of the antioxidant power of the active agent. Furthermore, the addition of antioxidants from spent coffee grounds is expected to be able to provide an increase of barrier properties, acting as oxygen scavengers. For this reason, future development of this study will regard the study of oxygen permeability of obtained bio-packaging components. Considering the promising results, both of the loaded films are particularly suitable for the storage of food products that may undergo to lipid oxidation and characterized by low water activity.

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