Characterization of Wastes and Coproducts from the Coffee Industry for Composite Material Production

Nima Zarrinbakhsh,[a] Tao Wang,[a] Arturo Rodriguez-Uribe,[a] Manjusri Misra,[a,b,*] and Amar K. Mohanty [a,b,*]

This study characterizes and compares coffee chaff (CC) and spent coffee grounds (SCG), the two most useful coffee waste products, and evaluates their performance as fillers and/or reinforcing agents in polymer composites. The morphologies of the CC and the SCG were studied using a scanning electron microscope (SEM). Detailed compositional and elemental analyses of the samples were carried out using several techniques. The thermal stabilities of the two types of biomass were evaluated using thermogravimetric analysis (TGA). Infrared spectroscopy was performed to investigate the functional groups available on the surface of the biomass. It was found that the CC had higher thermal stability, lower fat content, and a denser fibrous structure than the SCG, making it potentially a more suitable material than the SCG for use as a reinforcing filler in polymer composites. To verify this potential, CC and SCG filled polypropylene composites were produced and evaluated.

*Contact information: a: Bioproducts Discovery and Development Centre, Department of Plant Agriculture, Crop Science Building, University of Guelph, 50 Stone Road East, Guelph, Ontario, N1G 2W1, Canada, b: School of Engineering, Thornbrough Building, University of Guelph, 50 Stone Road East, Guelph, Ontario, N1G 2W1, Canada; *Corresponding authors: mohanty@uoguelph.ca; mmisra@uoguelph.ca*

INTRODUCTION

Coffee is currently one of the most essential agricultural commodities. According to statistics published by the International Trade Centre (ITC), coffee, with a worldwide export value of almost $31.8 billion in 2014, was the 4th most traded commodity crop, after wheat, corn, and soy bean. Notably, the value of coffee trade exceeds that of rice, barley, and oat (International Trade Center 2015). Compared with tea, the second most popular caffeinated hot drink in the world, coffee was traded more than four times in quantity in 2014 (International Trade Center 2015). Global coffee production in 2013, as reported by the Statistics Division of the Food and Agriculture Organization (FAO) of the United Nations, was as high as 8.9 million tonnes, a more than 30% increase from 1999 (FAOSTAT 2015).

Figure 1 illustrates the anatomy of a coffee cherry. The process of obtaining the coffee bean from the innermost part of the coffee cherry comprises several steps. During the process, the husk, pulp, parchment, and mucilage are removed, and they account for 12%, 29%, 12%, and 5%, respectively, of the dry weight of the cherry (Murthy and Madhava Naidu 2012; Didanna 2014). Once separated and dried, green coffee beans are roasted, ground, and brewed to make coffee. During the roasting process, the innermost skin of the coffee beans, the silverskin, floats free (Ballesteros *et al.* 2014). The collected silverskin is often referred to as coffee chaff (CC) by the coffee industry and is one of the

major by-products of coffee production. The roasted coffee beans are either sold directly or are ground and then sold to consumers, restaurants, and coffee shops for brewing with hot water. The residue of the brewing process, known as spent coffee grounds (SCG), is another major coffee waste product and is available in large quantities in our everyday lives. Approximately 650 kg of SCG is generated from one ton of green coffee (Mussatto *et al.* 2011).
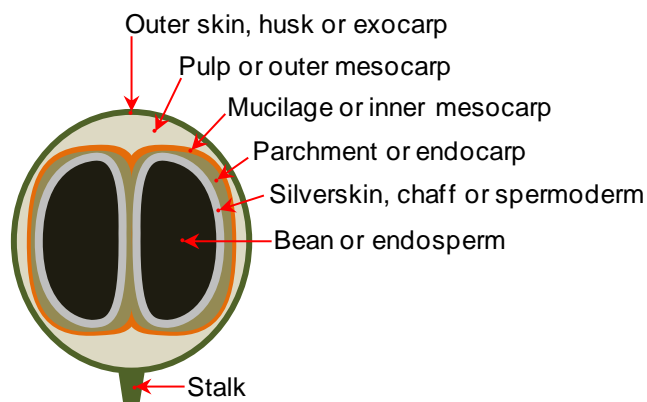
Outer skin, husk or exocarp
Pulp or outer mesocarp
Mucilage or inner mesocarp
Parchment or endocarp
Silverskin, chaff or spermoderm
Bean or endosperm
Stalk

Fig. 1. Schematic of the anatomy of a coffee cherry, drawn based on the information from Avallone *et al.* (2000); Bhushan *et al.* (2003); and Murthy and Madhava Naidu (2012)

Coffee by-products are major contributors of organic waste disposed of in landfills (Murthy and Madhava Naidu 2012; Arulrajah *et al.* 2014). Given the scale of coffee consumption across the globe, it is expected that the generation of coffee wastes poses a major threat to the health of our environment and to the sustainability of the coffee industry if these wastes are not managed properly (Murthy and Madhava Naidu 2012). The utilization of coffee wastes in value-added applications gives new life to these materials, exhibiting their potential as coproducts instead of under-valued wastes from the coffee industry. Several studies have been conducted on the use of coffee wastes in various applications; these range from the production of mushrooms, particleboard, compost, fuel, biogas, and animal feed and are reviewed in Murthy and Madhava Naidu (2012). Although these studies open up new possibilities, other opportunities still exist that have yet to be investigated.

This study explores a new approach to add value to coffee coproducts and wastes, particularly CC and SCG. As inexpensive lignocellulosic biomass, both CC and SCG are potentially good candidates for implementation as fillers and/or reinforcing agents in polymer composites, which may find applications in packaging and consumer products. In recent years, there have only been a handful of published studies in this area. These have mostly focused on SCG biocomposites with polymers including poly(lactic acid) (Baek *et al.* 2013; Lee *et al.* 2015a; Wu 2015), polypropylene (Jaya Chitra *et al.* 2014; García-García *et al.* 2015), recycled high-density polyethylene (Cestari *et al.* 2013), and poly(vinyl alcohol) (Lee *et al.* 2015b). After extensive research, only one publication on CC composites, with feather keratin polymer, was found (Barone 2009). The exploration of these opportunities for utilizing the coffee by-products in biocomposite applications requires a comprehensive understanding of the basic characteristics of the materials. The lack of available information in the open literature, especially in the case of CC, motivates

this study, where the properties of CC and SCG are evaluated for their merits and demerits when used in composite applications.

EXPERIMENTAL

Materials

The coffee chaff (CC) sample was produced by Club Coffee, a coffee company based in Rexdale, Ontario, Canada and was supplied by Competitive Green Technologies (CGTech), Leamington, Ontario, Canada. The sample was provided in the form of fine flakes, which were obtained by grinding the coffee chaff and passing it through a screen with a mesh size of 0.4 mm. The spent coffee grounds (SCG) sample was also supplied by CGTech, but was originally collected from local chain restaurants. This sample was in the form of particulate powders and endured no additional treatment after brewing. The appearance of the as-received materials is shown in Fig. 2. Polypropylene (PP) homopolymer, grade 1120H, was produced by Pinnacle Polymers™ LLC in Garyville, Louisiana, USA, and was purchased from Entec Polymers in Orlando, Florida, USA.

Fig. 2. Digital photographs of (a) as-received CC and (b) as-received SCG samples

Scanning Electron Microscopy

Scanning electron microscopy (SEM) images of CC and SCG were taken using a Phenom ProX (Phenom-World BV, Eindhoven, The Netherlands) at an accelerating voltage of 10 kV. The charge-reduction fixture of the microscope enabled the samples to be observed without coating.

Compositional Analysis

Compositional analysis of the CC and SCG was conducted by Agri-Food Laboratories, Guelph, Canada, for crude protein (Association of Analytical Communities (AOAC) Official Method 990.03 (2005)), fat (ANKOM Technology Method - American Oil Chemists' Society (AOCS) Official Procedure Am 5-04 (2014)), acid detergent fibre and acid detergent lignin (AOAC Official Method 973.18 (2005)), neutral detergent fiber (ANKOM Technology Method 13 (2015)), ash (AOAC Official Method 942.05 (2005)), and starch (American Association of Cereal Chemists (AACC) Method 76-13.01 (1999)). The allergen gluten content of the CC and SCG was evaluated by the Agriculture and Food Laboratory at the Laboratory Services of the University of Guelph, Guelph, Canada. The limit of quantitation (LOQ) for the assay was reported as 5.0 ppm of gluten.

bioresources.com

Elemental Analysis

The elemental analysis of the CC and SCG was performed with three different techniques. The surface elemental analysis of both materials was conducted using energy dispersive spectroscopy (EDS) incorporated with the aforementioned SEM system. Secondly, the carbon, hydrogen, nitrogen, sulfur, and oxygen (CHNS/O) contents of the two materials were measured using a FLASH 2000 CHNS/O organic elemental analyzer from Thermo Scientific (Waltham, Massachusetts, USA). With this equipment, the determination of carbon, hydrogen, nitrogen, and sulfur is achieved by oxidation in a combustion reactor, then subsequent analysis of the eluted gases, while oxygen determination is done in a pyrolysis reactor. The 2,5-bis(5-tert-butyl-2-benzoxazol-2-yl)thiophene (BBOT) standard provided by the company was used as the calibration material for CHNS content determination, and cystine was used for calibration in oxygen content determination. Finally, CC and SCG samples were analyzed to determine their heavy metal contents. The test was performed by Laboratory Services, University of Guelph, using inductively coupled plasma mass spectrometry (ICP-MS).

Thermal Stability

The thermal stability of CC and SCG was investigated by thermogravimetric analysis (TGA) using a Q500 analyzer from TA Instruments (New Castle, Delaware, USA). Approximately 8 and 20 mg of CC and SCG samples, respectively, were heated from room temperature to 800 °C with a ramp rate of 20 °C/min in a nitrogen atmosphere. Both thermogravimetric (TG) and derivative thermogravimetric (DTG) results were reported. The data were analyzed using TA Instrument software, Universal Analysis 2000, version 4.5A.

Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FTIR) spectra of the CC and SCG were obtained in attenuated total reflectance (ATR) mode *via* a Nicolet 6700 instrument from ThermoFisher Scientific (Waltham, Massachusetts, USA). The absorbance was measured with 32 scans per sample from 4000 to 500 cm^{-1} and a resolution of 4 cm^{-1}. The spectra were corrected for the surrounding air as the background spectrum. The results were analyzed using Thermo Scientific OMNIC™ Specta™ software, version 1.0.0.1591.

Production of Polymer Composites

Polymer composites containing 75 wt.% polypropylene (PP) and 25 wt.% of either CC or SCG were produced in a vertical 15-cm^3 micro twin-screw extruder and injected *via* a micro injection molding machine into test bars for tensile, flexural, and impact testing. Both the extruder and the injection unit were manufactured by DSM Xplore (Geleen, The Netherlands). For each test bar, 10 g of a mixture of PP and biomass was fed through the top of the vertical barrel of the extruder set at 180 °C with screws co-rotating at 100 rpm. The mixture was melted and circulated inside the barrel for 2 min before a melt transfer device, composed of a cylinder and a piston and preheated to 180 °C, was connected to the die at the bottom of the barrel. The die was then opened to collect the polymer composite melt into the melt transfer device. The melt was subsequently injected to one test bar at the end of each extrusion and injection cycle. The injection pressure and time were fixed at 6 bars and 18 s, respectively, and the mold temperature was set at 30 °C for all samples. A filler content of 25 wt.% was chosen in this study because the properties at this filler

loading are representative of the effect of filler on processing aspects and mechanical and physical properties of the resulting biocomposites.

Evaluation of Polymer Composites

Tensile and flexural tests were performed according to ASTM D638-14 (2014) and D790-15e2 (2015), respectively, using an Instron (Norwood, Massachusetts, USA) universal testing machine, model 3382, with a 5-kN load cell. For the tensile test, five ASTM Type IV samples were tested at a deflection rate of 5 mm/min; for the flexural test, five rectangular bars of $125 \times 3.25 \times 12.6$ mm^3 were bent in three-point bending mode at a rate of 14 mm/min. Notched Izod impact strength was measured with six replicates in the form of rectangular bars of $65 \times 3.25 \times 12.6$ mm^3, according to ASTM D256-10e1 (2010), using an impact tester from Testing Machines, Inc. (New Castle, Delaware, USA). The samples were notched right after injection, by a motorized notching machine from the same company. The melt flow index (MFI) testing was conducted according to ASTM D1238-13 (2013) with a load of 2.16 kg and the temperature adjusted to 190 °C, to avoid biomass degradation during the 7-min preheating of the composite in the melt flow indexer, model MFI-2000A, manufactured by Qualitest International Inc. (Lauderdale, Florida, USA). Heat deflection temperature (HDT) measurement was done in the three-point bending mode with a dynamic mechanical analyzer (DMA) from TA Instruments (New Castle, Delaware, USA), mimicking the ASTM D648-16 (2016) test method in a heated air environment with rectangular bars of $65 \times 3.25 \times 12.6$ mm^3. The HDT is reported as the temperature at which a sample, loaded with a constant stress of 0.455 MPa, reaches a bending strain of 0.1889%. The average of two measurements is reported for HDT values. The density measurements were performed based on Archimedes' principle on rectangular bars with the dimensions mentioned for impact test bars using an electronic densimeter manufactured by Alfa Mirage Co., Ltd. (Osaka, Japan). The average of three measurements is reported for density values.

Statistical Analysis

Statistical analysis was done through one-way analysis of variance (ANOVA), Tukey method, using Minitab® software, version 17.3.1, to identify mean values that are significantly different with a significance level (α) of 0.05.

RESULTS AND DISCUSSION

Scanning Electron Microscopy (SEM)

The morphologies of the CC and the SCG were observed with SEM. Figures 3a and b show lower-magnification (×300 on the microscope) images of CC and SCG samples, respectively. The CC consisted primarily of flakes, along with some particulates. On the other hand, SCG was mostly in the form of particles of irregular shape. This observation is expected because CC is originally the thin skin on the outside of the coffee bean, while SCG is the hot-water-brewed solid residues.

Figure 3c is a higher-magnification (×2000 on the microscope) image taken on the surface of an individual CC flake. This reveals its longitudinal fibrous structure, with a relatively dense and smooth surface. In contrast, a single SCG particle (Fig. 3d, magnification at ×2000) shows a highly porous granular structure. The porous structure of the SCG could be attributed to the dissolution of some components of coffee grounds

during hot-water brewing. Some of the large chunks appear to have resulted from the agglomeration of smaller particles. The denser and more fibrous structure of the CC, as compared with that of the SCG, is expected to give the CC an advantage over the SCG when being used as a reinforcing component in polymer composites.
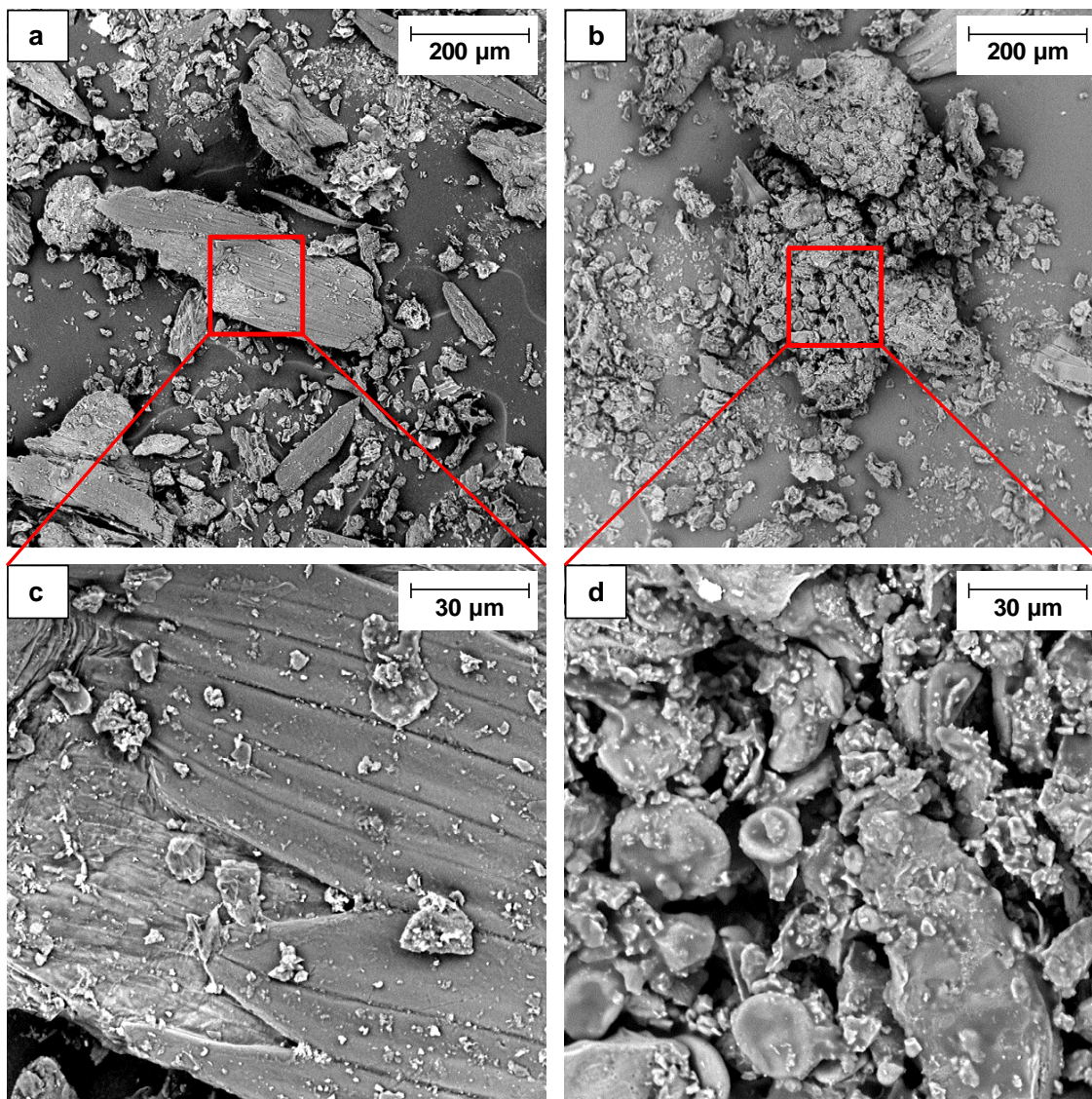

Fig. 3. SEM images of (a and c) CC and (b and d) SCG samples at two different magnifications: (a and b) ×300 and (c and d) ×2000 on the microscope

Compositional Analysis

The results of the compositional analysis of the CC and SCG are provided in Table 1. As observed, both samples comprised more than 70 wt.% carbohydrates on a dry basis, mostly in the form of lignocellulosic matter. The cellulose and hemicellulose contents were calculated from the measured fractions of neutral detergent fibre (NDF), acid detergent fibre (ADF), and lignin. Cellulose content is the difference between ADF and lignin fractions, and hemicellulose content is that between NDF and ADF (Xavier *et al.* 2015). The calculation shows that both samples contained similar cellulose content, of approximately 23 wt.%, dry basis, while the SCG contained more hemicellulose than the

CC. In addition, both samples showed the same lignin content, of approximately 18 wt.%. The protein content, calculated from the total nitrogen content of the samples, was 15.5 wt.% for CC and 13.3 wt.% for SCG. The most noticeable difference is in the fat content of the two samples, with the SCG having almost twice as much fat as the CC. The starch content of both samples was negligible. Because the two materials contained almost the same amount of cellulose, it is expected that the CC, which contained much less fat, would perform better as a reinforcing component in polymer composites in comparison with SCG, as the fat may introduce a lubricating effect in the composite material system.

Table 1. Composition of the CC and SCG Samples (wt.%, dry basis)

Component	Coffee chaff (CC)	Spent coffee grounds (SCG)
Neutral Detergent Fibre (NDF)	53.5	60.6
Acid Detergent Fibre (ADF)	41.4	41.3
Crude Protein	15.5	13.3
Fat	5.8	10.3
Lignin	17.8	18.3
Ash	6.9	2.2
Starch	1.0	0.7
Carbohydrates*	71.9	74.2
Cellulose**	23.6	23.0
Hemicellulose***	12.1	19.4
*Calculated as (100 - protein - ash - fat), **Calculated as (ADF - Lignin), *** Calculated as (NDF - ADF)		

Both samples were also tested to determine their gluten content, which resulted in the detection of no gluten for the CC and 250 ppm gluten for the SCG. This information is important when utilizing the CC and SCG in polymer composites used to produce packaging that may come into contact with foodstuff.

Elemental Analysis

X-ray energy dispersive spectroscopy (EDS) was used to obtain the elemental spectrum from various spots on the surface of CC and SCG particles (Fig. 4). The CC showed the presence of carbon, oxygen, potassium, calcium, phosphorus, and trace amounts of magnesium and sulfur, while the SCG showed carbon, oxygen, potassium, and trace amounts of phosphorus. It is worth noting that the presence of small amounts of potassium, calcium, and magnesium in CC and potassium, magnesium, and phosphorus in SCG has been reported in previous studies (Ballesteros *et al.* 2014).

With respect to the EDS results, it was found that the spectrum obtained was dependent on the spot investigated for elemental analysis and that the compositional make-up changed slightly from point to point on the sample. This can be attributed to the inhomogeneity of both the CC and SCG and to the fact that the EDS signal is collected only from the surface of a particular specimen, even though this surface could represent different parts of a sample. For the same reason, EDS was not used as a quantitative technique for elemental analysis in this study.
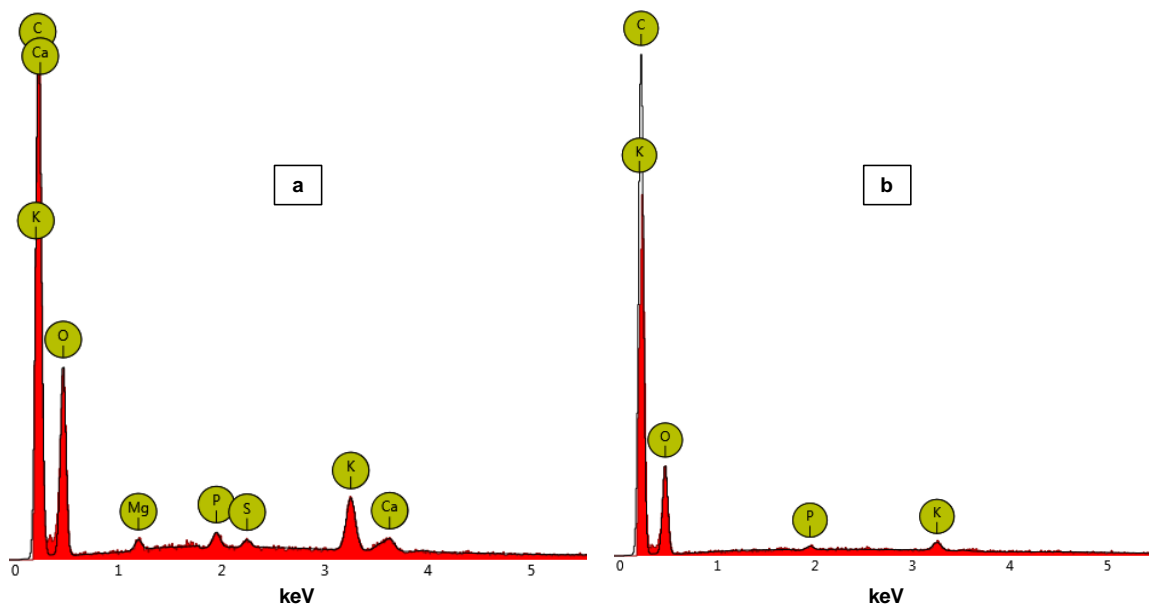
Fig. 4. EDS spectra of (a) CC and (b) SCG samples

An organic elemental analyzer was used to quantitatively determine the contents of C, H, N, S, and O in the two materials. As opposed to the EDS technique, this analyzer combusts or pyrolyzes a few milligrams of a specimen, then measures generated gases in gas chromatographic columns to back calculate the contents of the respective elements. The analysis (Table 2) showed that both the CC and SCG were rich in carbon. The high concentrations of hydrogen and oxygen reflect the high contents of carbohydrates found in the compositional analysis. The nitrogen content was used to calculate the protein content with a conversion factor of 6.25. The CC and SCG contained 11.3% and 9.4 wt% protein, respectively. Finally, both CC and SCG samples showed negligible sulfur content.

Table 2. The Elemental Analysis Results (wt.%, dry basis) Obtained from Combustion and Pyrolysis Methods for C, H, N, S, and O*

Sample	Carbon	Oxygen	Nitrogen	Hydrogen	Sulfur
Coffee chaff	50.3[a] ± 0.2	35.9[a] ± 0.8	1.8[a] ± 0.0	5.7[a] ± 0.1	0.1[a] ± 0.0
Spent coffee grounds	54.2[b] ± 0.3	34.8[a] ± 0.3	1.5[b] ± 0.0	6.7[b] ± 0.1	0.1[a] ± 0.0

* In each column, the mean values that are marked with different superscript letters are significantly different.

The analysis of CC and SCG samples for heavy metal elements is provided in Table 3. This information is important to obtain if the biomass is going to be utilized in materials that will come in contact with food. Table 3 shows that both samples contained the highest concentration of magnesium among all other metals investigated with this technique, followed by iron and aluminium. The concentrations of other heavy metals were very low. In particular, such heavy metals as lead, cadmium, mercury, and arsenic, which are of high potential risk to human health (Järup 2003), were all found to be less than 0.3 mg/kg in the studied CC and SCG samples.

Table 3. Concentrations (mg/kg) of Heavy Metal Elements in the Studied CC and SCG Samples

Element	Coffee chaff	Spent coffee grounds
Aluminium	160	38
Antimony	0.037	0.0095
Arsenic	0.12	0.029
Beryllium	0.019	0.0016
Boron	22	5.3
Cadmium	0.083	0.012
Chromium	1.8	0.47
Cobalt	0.28	0.15
Copper	30	20
Iron	660	230
Lead	0.28	0.087
Magnesium	3000	1300
Manganese	61	38
Mercury	0.0082	0.0016
Molybdenum	0.66	0.2
Nickel	2	0.55
Selenium	0.092	0.042
Tin	0.14	0.03
Titanium	6.4	2.4
Zinc	27	13

It should be noted that the values provided in Table 3 are the concentrations of the listed elements in the biomass in mg element per kg biomass. If the biomass is used as a component of a food packaging material, the most relevant factor to study would be the migration level of these elements from a specific packaging to the food. The allowable migration limit of a specific substance from the packaging to the food is typically expressed in mg substance per kg food and can be obtained from legislation authorities such as the World Health Organization, European Union, Food and Drug Administration of The United States, *etc*. As an example, Welle and Franz (2011) studied the migration of antimony from PET beverage bottles. Using mathematical migration modelling, the research showed that in the worst cases, the level of antimony migration is well below the allowable maximum limit of 0.040 mg antimony per kg beverage set by the European packaging legislation. This is despite the fact that the antimony concentration in the original PET bottles in the study was, on average, 224 mg antimony per kg PET bottle.

Thermal Degradation

With respect to the utilization of biomass in polymer composites, the thermal stability of the biomass is an important aspect to investigate because the processing of the

bioresources.com

composites is carried out at elevated temperatures, above the melting point of the polymer. Depending on the polymer matrix, the processing temperatures typically range from 160 to 250 °C, from commodity plastics to engineering plastics. In the present study, thermogravimetric analysis was implemented to explore the thermal stability of the CC and SCG; the results are shown in Fig. 5, with both the thermogravimetric (TG) and derivative thermogravimetric (DTG) graphs reported. The TG curve tracks the mass loss of the biomass as the temperature increases, and the DTG curve shows the rate at which the mass loss occurs.

The CC and SCG exhibit different thermal degradation behavior. In the TG graphs (mass fraction %) in Fig. 5a and b, both samples showed an initial mass loss, up to approximately 140 °C. This can be attributed to the evaporation of moisture, which usually extends to more than 100 °C because of bound water, which cannot be easily removed at the boiling temperature of water. Given this fact, the CC and SCG samples were found to have moisture contents of 6.8% and 6.6%, respectively. The temperature of 2% mass loss, after moisture evaporation up to 140 °C, is marked for both samples to compare the thermal stability in that temperature range. After moisture evaporation, the 2% mass loss occurred at 214 and 179 °C for the CC and SCG samples, respectively. Overall, the CC exhibited higher thermal stability than the SCG in the temperature range of melt processing discussed above.

From the DTG curves (derivative mass fraction %) in Fig. 5a and b, the CC sample was found to have a large peak with a maximum at 330 °C. This was mostly due to the degradation of lignocellulosic content, more specifically cellulose. Similar behavior has also been reported for other lignocellulosic biomasses, including miscanthus, switchgrass, corn stalk, soy stalk, and wheat straw (Nagarajan *et al.* 2013). On the other hand, the SCG sample exhibited three distinct DTG peaks.

The two peaks with maximum values of 307 and 399 °C, respectively, can be attributed to the degradation of the hemicellulose and lignin in the SCG (Plaza *et al.* 2012; Li *et al.* 2014). In addition, another degradation peak was observed for SCG at a relatively low temperature of 213 °C, which has not been reported by other researchers (Plaza *et al.* 2012; Li *et al.* 2014). However, Grace *et al.* (2015) studied the thermal degradation of coffee oil, extracted from SCG, with a thermogravimetric analyzer at a heating rate of 10 °C/min in nitrogen environment and found that the degradation of the oil occurs in two steps.

The first step began at approximately 150 °C. This observation agrees with the increase in the SCG thermal degradation rate starting from 150 °C, as can be seen in Fig. 5b, which suggests that this degradation stage is due to the volatilization of the oil contained in the SCG.

To further confirm this, another experiment was carried out where a sample of the SCG was placed in a paper bag and dried in a hot-air circulating oven at 80 °C for approximately 24 h. It was observed that the paper bag was stained with the oil that had migrated from the SCG and the DTG peak at 213 °C disappeared in a TGA test of the material (Fig. 6).

Furthermore, the 2% mass loss of this sample occurred at 196 °C, which was 17 °C higher than that of the as-received SCG. Above this temperature, the thermal behavior of this sample did not change markedly from that of the as-received sample.
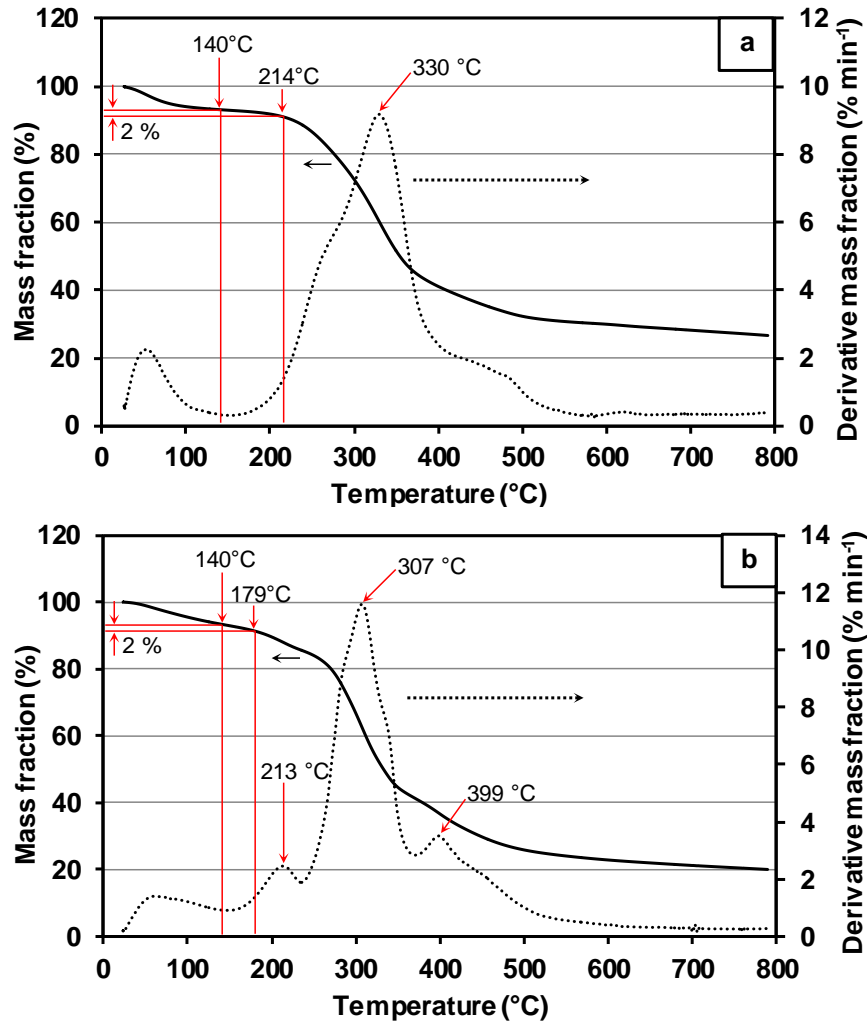
Fig. 5. The TG (mass fraction) and DTG (derivative mass fraction) graphs of (a) as-received CC and (b) as-received SCG
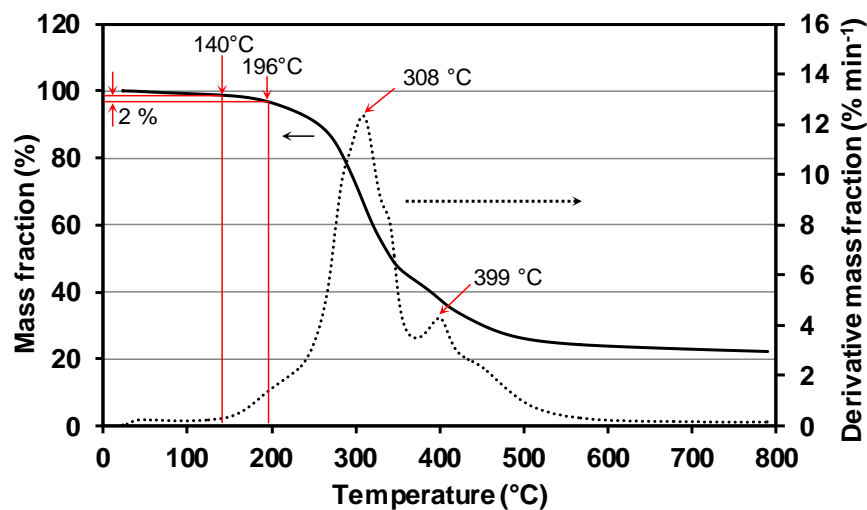

Fig. 6. The TG (mass fraction) and DTG (derivative mass fraction) graphs of SCG dried at 80 °C for more than 24 h prior to TGA

bioresources.com

FTIR Spectroscopy

The FTIR spectra of the CC and SCG are presented in Fig. 7. The spectra of both samples exhibited a broad peak from 3000 to 3600 cm^{-1}, which corresponds to the stretching of O–H and N–H bonds abundantly present in the lignocellulosic components and the protein of the two materials (Li *et al.* 2014). This suggests that the performance of the CC and SCG in a polymeric composite material system can be enhanced by using compatibilizers such as maleic anhydride to improve the interfacial adhesion between the biomass and the polymer matrix (Mohanty *et al.* 2002).

The peaks near 2850 and 2920 cm^{-1} observed in both samples can be attributed to the symmetric and asymmetric stretching of C–H bonds. These two peaks, in conjunction with the stretching absorption of carbonyl (C=O) bond at approximately 1740 cm^{-1}, are associated with the ester group of triglyceride in lipid (fat) (Craig *et al.* 2012), which is present in both samples. A similar observation of the lipid FTIR peaks has been reported for corn-based distillers' grains containing corn oil (Zarrinbakhsh *et al.* 2013). The spectra of both samples have also a similar peak at approximately 1025 cm^{-1} which may correspond to the C–O (C-6 skeletal vibrations) of the cellulosic component (Mosiewicki *et al.* 2011).

The absorption bands between 1500 and 1700 cm^{-1} can be attributed to C=O stretching, C–N stretching, and N–H bending of protein molecules (Kong and Yu 2007). Moreover, the occurrence of two absorption peaks at 1647 and 1705 cm^{-1} in the SCG spectrum is associated with the residue of caffeine in the material. It has previously been reported that caffeine, dissolved in chloroform, exhibits characteristic bands at 1700 and 1655 cm^{-1} (Singh *et al.* 1998). Because the various components of the CC and SCG, *e.g.*, cellulose, hemicellulose, lignin, lipids, protein, and minerals, all have absorption in the fingerprint region (500 to 1500 cm^{-1}) with bands overlapping each other, it is difficult to assign each absorption peak to a specific component.
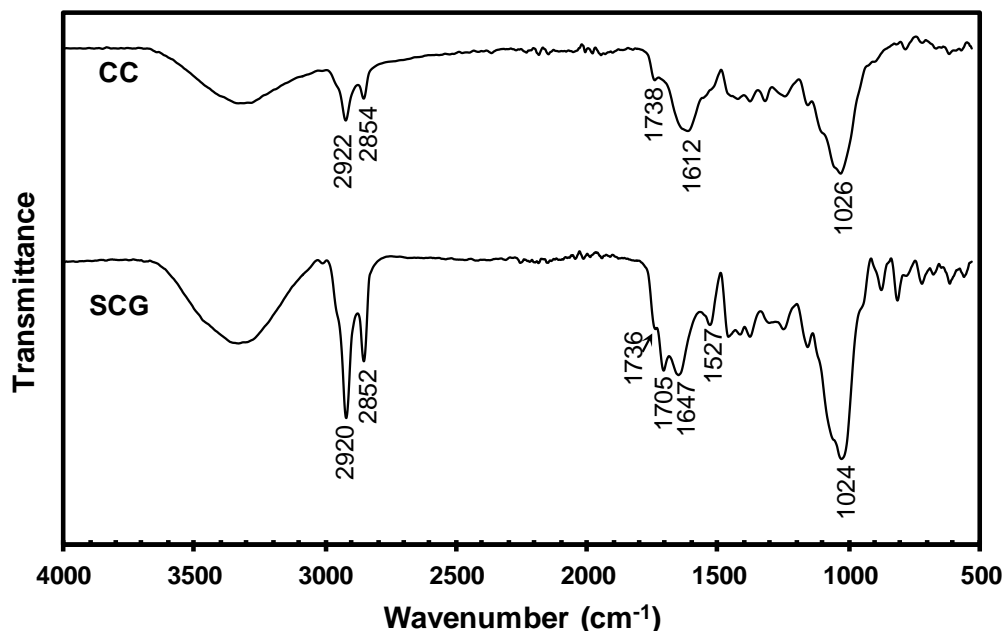

Fig. 7. ATR-FTIR spectra of CC and SCG samples

Evaluation of CC and SCG Polymer Composites

The mechanical and physical properties of the CC and SCG composites based on PP are provided in Table 4. The respective baseline data of the neat PP is also reported for comparison. Compared with the neat PP, both CC and SCG polymer composites showed a lower tensile strength. This observation suggests poor interfacial adhesion and inefficient load transfer between the polymer matrix and the filler because of the hydrophobic nature of PP and the hydrophilic nature of the biomass. Indeed, the CC and SCG particles acted as stress concentration points during the tensile test, resulting in a much lower elongation-at-break in polymer composites than the neat PP. Similar observations have also been reported for distillers' grains polymer composites (Zarrinbakhsh *et al.* 2013). With the abundance of hydroxyl groups observed in the FTIR spectra of CC and SCG in the previous section, it may be possible to improve the compatibility between PP and the CC or SCG using maleic anhydride-grafted PP or other traditional compatibilizers for natural fiber polymer composites.

Table 4. Mechanical and Physical Properties of the CC and SCG Composites Based on PP*

Formulation (wt.%)	Neat PP	PP/CC 75/25	PP/SCG 75/25
Tensile Yield Strength (MPa)	34.8[a] ± 0.1	28.2[b] ± 0.2	24.2[c] ± 0.4
Tensile Modulus (MPa)	1650[a] ± 10	2200[b] ± 10	1530[c] ± 20
Elongation at Yield (%)	7.5[a] ± 0.1	3.3[b] ± 0.1	4.8[c] ± 0.1
Elongation at break (%)	> 700[a]	5.1[b] ± 0.3	7.9[b] ± 0.9
Maximum Flexural Stress (MPa)	55.0[a] ± 0.1	52.5[b] ± 0.7	43.3[c] ± 0.5
Flexural Modulus (MPa)	1930[a] ± 10	2510[b] ± 50	1650[c] ± 30
HDT (°C)	110.9[a] ± 0.4	126.9[b] ± 1.4	102.6[c] ± 3.1
Izod Impact Strength (J/m)	22.4[a] ± 0.2	24.8[b] ± 1.0	24.0[a, b] ± 2.1
MFI (g.10.min^{-1})	10.1[a] ± 0.1	7.6[b] ± 0.1	9.9[a] ± 0.1
Density (kg/m^3)	0.910[a] ± 0.004	0.995[b] ± 0.004	0.985[c] ± 0.007

* In each row, the mean values that are marked with different superscript letters are significantly different.

Comparing the two composites, the lower tensile strength and the higher elongation observed for the SCG polymer composite could be a result of higher fat content of the SCG, causing a plasticizing effect in the polymer composite system. At the same, the difference observed in the morphology of the two biomass samples under SEM could be a source of difference in the strength and rigidity of the studied polymer composites. In this respect, the SCG polymer composite showed a tensile modulus lower than that of the neat PP, while the CC polymer composite had higher modulus, or rigidity, by more than 30%

bioresources.com

compared with the neat PP. Flexural strength and modulus showed a similar behavior to tensile properties.

The HDT data of the neat PP and the polymer composites followed a trend exactly similar to the flexural modulus data. This is explained by the fact that both tests were performed in a three-point bending mode and represent the rigidity of the material. The HDT data confirmed the reinforcing effect of CC as a filler in the polymer composite at elevated temperatures, similar to what was observed from the flexural modulus data at room temperature.

No major difference in the impact strength was observed. The MFI value of the CC polymer composite, in comparison with that of the neat PP, suggests a hindrance imposed by the CC to the flow of the polymer's melt. Finally, it is concluded from the density measurements that both CC and SCG exhibit higher density than the neat PP, leading to higher density values for the polymer composites.

CONCLUSIONS

1. In the present study, coffee chaff (CC) and spent coffee grounds (SCG), two waste materials from coffee production and consumption, were characterized to determine their morphological, compositional, elemental, thermal, and surface properties.

2. The observation of the biomass under SEM revealed a relatively dense fibrous structure for the CC and a granular porous form for the SCG.

3. TGA showed that the temperature of 2% mass loss after the moisture loss was 214 and 179 °C for the CC and SCG, respectively, indicating that the CC is more suitable for high-temperature processing.

4. FTIR study showed the abundance of hydroxyl groups in both samples, suggesting that common surface modification techniques used in biofiber composites can be adapted to enhance the adhesion between the CC or SCG and a polymer matrix.

5. Overall, CC is potentially a better candidate than SCG as a reinforcing agent in polymer composite applications because of its denser fibrous structure, lower fat content, and higher thermal stability compared with SCG. This was confirmed by the production and evaluation of CC and SCG polymer composites using polypropylene as the matrix.

ACKNOWLEDGMENTS

REFERENCES CITED

AACC Method 76-13.01 (1999). "Total starch assay procedure (megazyme amyloglucosidase/α-amylase method)," AACC International, DOI: 10.1094/AACCIntMethod-76-13.01.

ANKOM Technology Method - AOCS Official Procedure Am 5-04 (2014). "Rapid determination of oil/fat utilizing high temperature solvent extraction," https://www.ankom.com/sites/default/files/document-files/XT15_XT10_Analytical_Procedure_121014.pdf [accessed May 9, 2016].

ANKOM Technology Method 13 (2015). "Neutral detergent fibre in feeds-filter bag technique method 13," https://www.ankom.com/sites/default/files/document-files/Method_13_NDF_Method_A2000_RevE_4_10_15.pdf [accessed May 9, 2016].

AOAC Official Method 942.05 (2005). "Ash of animal feed," AOAC International, Gaithersburg, MD.

AOAC Official Method 973.18 (2005). "Fiber (acid detergent) and lignin in animal feed," AOAC International, Gaithersburg, MD.

AOAC Official Method 990.03 (2005). "Protein (crude) in animal feed, combustion method," AOAC International, Gaithersburg, MD.

Arulrajah, A., Maghoolpilehrood, F., Disfani, M. M., and Horpibulsuk, S. (2014). "Spent coffee grounds as a non-structural embankment fill material: Engineering and environmental considerations," *J. Clean. Prod.* 72, 181-186. DOI: 10.1016/j.jclepro.2014.03.010

ASTM D1238-13 (2013). "Standard test method for melt flow rates of thermoplastics by extrusion plastometer," ASTM International, West Conshohocken, PA. DOI: 10.1520/D1238

ASTM D256-10e1 (2010). "Standard test methods for determining the izod pendulum impact resistance of plastics," ASTM International, West Conshohocken, PA. DOI: 10.1520/D0256-10E01

ASTM D638-14 (2014). "Standard test method for tensile properties of plastics," ASTM International, West Conshohocken, PA. DOI: 10.1520/D0638-14

ASTM D648-16 (2016). "Standard test method for deflection temperature of plastics under flexural load in the edgewise position," ASTM International, West Conshohocken, PA. DOI: 10.1520/D0648-16

ASTM D790-15e2 (2015). "Standard test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials," ASTM International, West Conshohocken, PA. DOI: 10.1520/D0790-15E02

Avallone, S., Guiraud, J.-P., Guyot, B., Olguin, E., and Brillouet, J.-M. (2000). "Polysaccharide constituents of coffee-bean mucilage," *J. Food Sci.* 65(8), 1308-1311. DOI: 10.1111/j.1365-2621.2000.tb10602.x

Baek, B.-S., Park, J.-W., Lee, B.-H., and Kim, H.-J. (2013). "Development and application of green composites: using coffee ground and bamboo flour," *J. Polym. Environ.* 21(3), 702-709. DOI: 10.1007/s10924-013-0581-3

Ballesteros, L. F., Teixeira, J. A., and Mussatto, S. I. (2014). "Chemical, functional, and structural properties of spent coffee grounds and coffee silverskin," *Food Bioprocess Tech.* 7(12), 3493-3503. DOI: 10.1007/s11947-014-1349-z

Barone, J. R. (2009). "Lignocellulosic fiber-reinforced keratin polymer composites," *J. Polym. Environ.* 17(2), 143-151. DOI: 10.1007/s10924-009-0131-1

Bhushan, B., Bhat, R., Rao, B. Y. K., Ahmad, R., and Bongirwar, D. R. (2003). "Electron spin resonance studies on gamma-irradiated coffee bean parts," *Int. J. Food Sci. Tech.* 38(1), 11-16. DOI: 10.1046/j.1365-2621.2003.00634.x

Cestari, S. P., Mendes, L. C., da Silva, D. F., Chimanowsky Jr., J. P., Altstädt, V., Demchuk, V., Lang, A., Leonhardt, R. G., and Keller, J.-H. (2013). "Properties of recycled high density polyethylene and coffee dregs composites," *Polímeros* 23(6), 733-737. DOI: 10.4322/polimeros.2014.011

Craig, A. P., Franca, A. S., and Oliveira, L. S. (2012). "Discrimination between defective and non-defective roasted coffees by diffuse reflectance infrared Fourier transform spectroscopy," *LWT - Food Sci. Technol.* 47(2), 505-511. DOI: 10.1016/j.lwt.2012.02.016

Didanna, H. L. (2014). "A critical review on feed value of coffee waste for livestock feeding," *World J. Biol. Biol. Sci.* 2(5), 72-86.

FAOSTAT (2015). "Food and Agriculture Organization of The United Nations - Statistics Division," http://faostat3.fao.org/download/Q/QC/E, accessed 11 Nov 2015.

García-García, D., Carbonell, A., Samper, M. D., García-Sanoguera, D., and Balart, R. (2015). "Green composites based on polypropylene matrix and hydrophobized spend coffee ground (SCG) powder," *Compos. Part B-Eng.* 78, 256-265. DOI: 10.1016/j.compositesb.2015.03.080

Grace, J., Vysochanska, S., Lodge, J., and Iglesias, P. (2015). "Ionic liquids as additives of coffee bean oil in steel-steel contacts," *Lubr.* 3(4), 637-649. DOI: 10.3390/lubricants3040637

International Trade Center (2015). "Trade Map - Trade statistics for international business development," http://www.trademap.org/tradestat/Index.aspx, accessed 11 Nov 2015.

Järup, L. (2003). "Hazards of heavy metal contamination," *Br. Med. Bull.* 68(1), 167-182. DOI: 10.1093/bmb/ldg032

Jaya Chitra, N., Vasanthakumari, R., and Syed Amanulla (2014). "Preliminary studies of the effect of coupling agent on the properties of spent coffee grounds polypropylene bio-composites," *Int. J. Eng. Res. Technol.* 7(1), 9-16.

Kong, J., and Yu, S. (2007). "Fourier transform infrared spectroscopic analysis of protein secondary structures," *Acta Bioch. Bioph. Sin. (Shanghai).* 39(8), 549-559. DOI: 10.1111/j.1745-7270.2007.00320.x

Lee, H. J., Lee, H. K., Lim, E., and Song, Y. S. (2015a). "Synergistic effect of lignin/polypropylene as a compatibilizer in multiphase eco-composites," *Compos. Sci. Technol.* 118, 193-197. DOI: 10.1016/j.compscitech.2015.08.018

Lee, H. K., Park, Y. G., Jeong, T., and Song, Y. S. (2015b). "Green nanocomposites filled with spent coffee grounds," *J. Appl. Polym. Sci.* 132(23), 42043. DOI: 10.1002/app.42043

Li, X., Strezov, V., and Kan, T. (2014). "Energy recovery potential analysis of spent coffee grounds pyrolysis products," *J. Anal. Appl. Pyrol.* 110, 79-87. DOI: 10.1016/j.jaap.2014.08.012

Mohanty, A. K., Drzal, L. T., and Misra, M. (2002). "Engineered natural fiber reinforced polypropylene composites: Influence of surface modifications and novel powder impregnation processing," *J. Adhes. Sci. Technol.* 16(8), 999-1015. DOI: 10.1163/156856102760146129

Mosiewicki, M. A., Marcovich, N. E., and Aranguren, M. I. (2011). "Characterization of fiber surface treatments in natural fiber composites by infrared and Raman

spectroscopy," in: *Interface Engineering of Natural Fibre Composites For Maximum Performance*, N. E. Zafeiropoulos (ed.), Woodhead Publishing, Cambridge, UK, 117-145.

Murthy, P. S., and Madhava Naidu, M. (2012). "Sustainable management of coffee industry by-products and value addition—A review," *Resour. Conserv. Recy.* 66, 45-58. DOI: 10.1016/j.resconrec.2012.06.005

Mussatto, S. I., Machado, E. M. S., Martins, S., and Teixeira, J. A. (2011). "Production, composition, and application of coffee and its industrial residues," *Food Bioprocess Tech.* 4(5), 661-672. DOI: 10.1007/s11947-011-0565-z

Nagarajan, V., Mohanty, A. K., and Misra, M. (2013). "Sustainable green composites: Value addition to agricultural residues and perennial grasses," *ACS Sust. Chem. Eng.* 1(3), 325-333. DOI: 10.1021/sc300084z

Plaza, M. G., González, A. S., Pevida, C., Pis, J. J., and Rubiera, F. (2012). "Valorisation of spent coffee grounds as CO_2 adsorbents for postcombustion capture applications," *Appl. Energ.* 99, 272-279. DOI: 10.1016/j.apenergy.2012.05.028

Singh, B. R., Wechter, M. A., Hu, Y., and Lafontaine, C. (1998). "Determination of caffeine content in coffee using Fourier transform infra-red spectroscopy in combination with attenuated total reflectance technique: A bioanalytical chemistry experiment for biochemists," *Biochem. Educ.* 26(3), 243-247. DOI: 10.1016/S0307-4412(98)00078-8

Welle, F., and Franz, R. (2011). "Migration of antimony from PET bottles into beverages: Determination of the activation energy of diffusion and migration modelling compared with literature data," *Food Addit. Contam. Part A* 28(1), 115-126. DOI: 10.1080/19440049.2010.530296

Wu, C.-S. (2015). "Renewable resource-based green composites of surface-treated spent coffee grounds and polylactide: Characterisation and biodegradability," *Polym. Degrad. Stabil.* 121, 51-59. DOI: 10.1016/j.polymdegradstab.2015.08.011

Xavier, C. A. N., Moset, V., Wahid, R., and Møller, H. B. (2015). "The efficiency of shredded and briquetted wheat straw in anaerobic co-digestion with dairy cattle manure," *Biosyst. Eng.* 139, 16-24. DOI: 10.1016/j.biosystemseng.2015.07.008

Zarrinbakhsh, N., Mohanty, A. K., and Misra, M. (2013). "Fundamental studies on water-washing of the corn ethanol coproduct (DDGS) and its characterization for biocomposite applications," *Biomass Bioenerg.* 55, 251-259. DOI: 10.1016/j.biombioe.2013.02.016