

Thermomechanical Properties of Corn Starch Based Film Reinforced with Coffee Ground Waste as Renewable Resource

Elisa Camarin Gazonato^a, Amanda Alves Domingos Maia^a, Virginia Aparecida da Silva Moris^a,

Jane Maria Faulstich de Paiva^{a,b,*} 

^aDepartamento de Engenharia de Produção, Universidade Federal de São Carlos - UFSCar, Sorocaba, SP, Brasil

^bPrograma de Pós-Graduação em Ciência dos Materiais - PPGCM, Universidade Federal de São Carlos - UFSCar, Rod. João Leme dos Santos, km 110, Bairro do Itinga, 13052-780, Sorocaba, SP, Brasil

Received: June 15, 2018; Revised: October 02, 2018; Accepted: November 23, 2018

Starches polymeric films offer several advantages for the replacement of synthetic polymers due to their biodegradability, non-toxicity, availability and low cost. However, the high biodegradation potential can cause fragility, considering some fundamental mechanical properties. Therefore, starch based polymeric films were reinforced incorporating lignocellulosic waste from coffee grounds post-consume. The effect of incorporation of coffee ground in cornstarch matrix and polymer interaction on morphology, thermal and mechanical properties were investigated. The characterization analyzes were based on Dynamic Mechanical Thermal Analysis (DMTA), Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and Scanning Electronic Microscopy (SEM). The coffee ground behaved as reinforcement agent according tensile values. Thermochemical conversion showed that polymeric films molding did not change his thermal stability. In temperature range was possible to observe the devolatilization, organic and inorganic compounds decomposition. SEM images showed the coffee ground adhesion in the polymer matrix promoting a better mechanical tensile strength.

Keywords: *Coffee ground, reuse of waste, reinforcement agent, cornstarch film.*

1. Introduction

Industrial process produces an enormous amount of waste materials, which may be not deposited safely. The population increasing is responsible for the amount and type of waste generated ^{1,2}, promoting an environmental problems. Furthermore, fossil fuels consumption are related to environmental degradation that threatens human health, through climate changes and greenhouse gas emissions ³. Recycling is an effective process for the reuse of some types of waste, however, in Brazil, recycling of solid urban and industrial wastes is still a problem ^{4,5}. The last IBGE official data reported that only 1.4% of Brazilian urban solid waste is sent to sorting and after, recycling facilities ⁶.

Therefore, nowadays, environmentally alternatives to unsustainable waste disposal techniques are being sought ⁵. The current interest of industries is to use the cleaner technologies, reusing or avoiding the generation of waste and by-products of the productive processes ^{7,8}. Furthermore, there is difficulty in recycling synthetic polymers, which encourages the study and development of biodegradable materials ⁹.

The polymer biodegradation is considered a natural process, caused by the microorganisms action modifying and consuming the product, changing in its properties ^{10,11}.

Most biodegradable plastic films are produced from starch, due to their low cost and abundance in nature, as well as being renewable ¹². However, starch has high sensitivity to water and mechanical fragility, which makes it difficult to expand its applications and justifies the need for constant improvement of its properties ^{12,13}. Based on this information and for improving the characteristics of the starch films, reinforcing agents can be used, giving to the compound better mechanical properties, especially elasticity (tensile and flexural) and mechanical strength ¹⁴.

In addition, Brazil began to produce soluble coffee in 1962, and it has been a major world producer since then ^{15,16} and for each ton of coffee produced, 480 kg of sludge of coffee ground are generated, considered a solid residue, which is normally used to generate energy in the boilers and in the manufacture of animal feed ^{17,18}.

Coffee grounds has a very heterogeneous composition being considered as a lignocellulosic waste, usually rich in cellulose, hemicellulose, polysaccharides, fermentable organic, matter content, caffeine, tannins and polyphenols ¹⁸⁻²⁰, soluble carbohydrates, oligosaccharides sucrose, polymers, non-volatile and volatile aliphatic acids, oils, waxes, proteins and free amino acids ²¹. Nevertheless, in literature, few works related to the coffee ground waste valorization have been reported, and then this is an opportunity because of large amount of waste and its composition.

*e-mail: jane@ufscar.br.

Thus, the aim of this study was to incorporate coffee grounds waste as a reinforcing agent in starch plastic films maintaining the biodegradable potential of this polymer, with the advantages of low cost and high availability in Brazil.

2. Experimental

2.1 Sample preparation

The coffee grounds waste considered was the insoluble residue that remains after coffee beans are dehydrated, milled and brewed, retained in used paper filters and collected at Federal University of São Carlos (UFSCar) - Sorocaba, Brazil, from automatic coffee machine, which process commercial coffee beans. Therefore, the coffee grounds post-consume waste was sieved (NBR 200#/0.074 mm). After some laboratory tests, the particle size the 200-mesh granulometry facilitated the mixing and dispersion of the coffee ground waste during casting molding of the films.

The films preparation involved the total mass was 100g, cornstarch and glycerin amounts were constant (5g each one). The water and coffee grounds values completed the 90g remaining. After mixed up, the samples were brought to the microwave for heating under a power of 40W for 6 minutes with pauses for mixing and checking the temperature. Then, it was deposited into three polyacrylic molds (approximately 25g each one) and left in an oven at 32 °C, no air circulation, for four days. In Table 1 the samples and their respective concentrations of components can be observed.

2.2 Dynamic mechanical thermal analysis

Analysis was carried out at DMTA equipment (DMA Q800 - TA Instruments) considering a force ramp rate of 0.8 N/min was applied until 18 N. For this type of analysis was set isotherm at 25°C, the mode of adjustment was controlled force and the grip was of the strain film type. Because of the analysis mode selected, the films were analyzed through stress x strain curves, in which the values of maximum tensile (MPa) and deformation (%) were found. Ten specimens of each type of film were tested. Each film sample tested had a length of 35 mm and a width of 5 mm.

2.3 Differential scanning calorimetric analysis

The samples were carried out to DSC analysis on DSC-50-Shimadzu equipment, under inert atmosphere, flow rate of 100 mL/min, heating rate of 10 °C/min, in a temperature range of -50 °C to 400 °C. Approximately 5 mg was deposited was placed in aluminum pan.

2.5 Thermogravimetric analysis

The thermal stability of the samples was studied by using thermogravimetric analysis (TGA) and were performed on the Shimadzu TGA-50 equipment under nitrogen atmosphere, flow rate of 50 mL/min, a heating rate of 10 °C/min and temperature range of 20°C to 800 °C. Approximately 5mg was placed on platinum pan.

2.6 Morphological analysis

Scanning Electronic Microscopy (SEM) analyzes were carried out at microscopy TM 3000, Hitachi, using carbon tapes and 50x and 150x magnifications.

3. Results and Discussion

3.1 Dynamic mechanical thermal analysis

Mean values and standard deviation of tensile mechanical properties of the polymeric films were obtained and are shown in Table 2.

According to the Table 2 and Figure 1 it is possible to note that the incorporation of coffee grounds can be responsible for increasing tensile strength for almost all samples.

The type of film number 7 (Table 2), specimens with 0.50% of coffee ground, did not present a satisfactory value, its can mean that coffee ground it was just a filler and not as a reinforcing agent. The coffee ground presence caused a reduction in the deformation capacity (Table 2 and Figure 1) of the films because became more rigid. The sample without coffee ground presented an average deformation of about 43%.

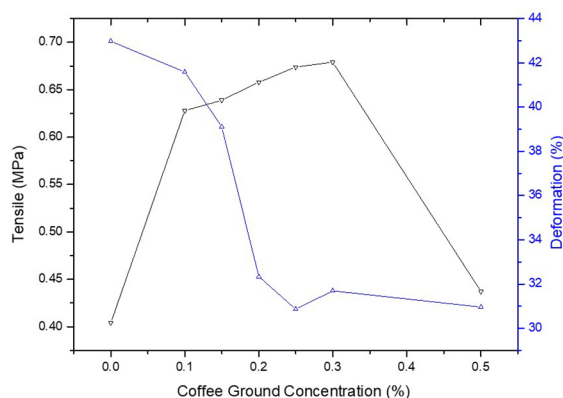
It is possible to observe that increasing coffee ground concentration in the films occurs deformation values variation.

Table 1. Composition of films with different concentrations of coffee grounds.

Samples	Coffee ground concentration (%)	Coffee grounds (g)	Glycerol (g)	Starch (g)	Water (g)
1	0%	0	5.0	5.0	90.00
2	0.10%	0.10	5.0	5.0	89.90
3	0.15%	0.15	5.0	5.0	89.85
4	0.20%	0.20	5.0	5.0	89.80
5	0.25%	0.25	5.0	5.0	89.75
6	0.30%	0.30	5.0	5.0	89.70
7	0.50%	0.50	5.0	5.0	89.50

Table 2. Tensile strength and deformation average, and standard deviation.

Samples	Tensile (MPa)		Deformation (%)	
	Average	Standard deviation	Average	Standard deviation
1	0.404	0.053	42.982	9.761
2	0.628	0.080	41.582	8.491
3	0.639	0.079	39.113	8.602
4	0.658	0.048	32.330	10.521
5	0.674	0.148	30.861	10.879
6	0.679	0.061	31.693	5.716
7	0.437	0.125	30.949	6.096

**Figure 1.** Tensile strength and deformation properties of starch films according to coffee ground addition.

It is can be related to the non-homogeneous dispersion during molding process.

3.2 Differential scanning calorimetry

According DSC analysis it was noted a first endothermic peak between temperature range of 93.34°C and 114.30°C representing residual water evaporation, which was used during the molding process. Thus, higher is coffee ground concentration lower is the amount of water in the process and higher the temperature of the residual water. A similar behavior was observed in literature²² reporting an endothermic peak at approximately 108°C representing residual water evaporation, which was a plasticizer in a cornstarch film. Higher concentration of water during molding process is probably responsible for residual water bound to the polymeric matrix of the material.

The melting temperatures of the crystalline structure can be observed in the range 149.41°C to 155.48°C. The film containing 0.25% of coffee grounds presented a higher melting temperature (155.48°C). However, there was no great variation between the values found. An endothermic peak approximately at 140°C can be associated with the melting of the crystalline structure of the polymer matrix²³. It was probably caused by lignosulfonates addition in cornstarch,

which promoted a higher thermal stability, as both its crystalline melt and thermal decomposition values were higher. The thermal decomposition temperature, as well as the melting temperature of the crystalline structure can be considered as an indicator of the thermal stability of the films. The values indicated that the molding process did not alter the thermal stability of the films, because the degradation temperatures did not show significant differences. Figure 2 shows the DSC curves of the films and the Table 3 presents the temperature of the volatilization, melting and degradation stages.

3.3 Thermogravimetric analysis

The thermal degradation stages of these films can be observed in Figure 3 and for better comparison between these curves. Table 4 shows stage of mass loss, its temperature range (ΔT (°C)), mass loss percentage (Δ Massa (%)), mass loss maximum temperature (max. temp. (°C)) and total mass loss (%).

The determination of thermal stability and the degradation temperature of the films can also be observed. The first stage of mass loss, which occurred in temperature range of 35.14 and 163.71 °C, observed at all samples, can represents plasticizers devolatilization, as well as a residual water and glycerin, used in the process of gelatinization of the films. The highest percentage of mass loss in this stage was observed in the sample with 0.20% of coffee grounds (approximately 16.76%) and, in this case, the maximum mass loss temperature was 70.76 °C. In previous study, also carried out cornstarch films, it was possible to observe a similar thermal behavior.

The mass loss was approximately 10% and it was attributed to residual water devolatilization at temperature range of 51.82 and 149.80 °C²².

In temperature range of 151.78 and 287.80°C can be observed the second stage of mass loss. It was also observed that the highest percentage of mass loss was of the sample with 0.30% of coffee grounds presented a maximum loss temperature of 187.91 °C. This behavior it was probably caused by degradation of the coffee fiber components (cellulose and hemicellulose), temperature range for cellulose was about 240 °C and 360 °C, hemicellulose decomposition temperature range was 200 °C and 260 °C^{24,25}.

The Figure 3A, does not present coffee grounds in its composition, so its decomposition behavior represents cornstarch thermochemical conversion. Figure 3 shows the TG and DTG curves of the analyzed films. In the third stage, the temperature range was about 274.14 and 358.17°C, observing a greater percentage of mass loss (41.73%) in the sample A, without coffee grounds and maximum mass loss temperature of 290.30 °C. This thermal conversion can be associated with amylose and amylopectin decomposition in the starch polymer matrix. After 600 °C, the main products were mainly the inorganic residues, oxides and carbonates.

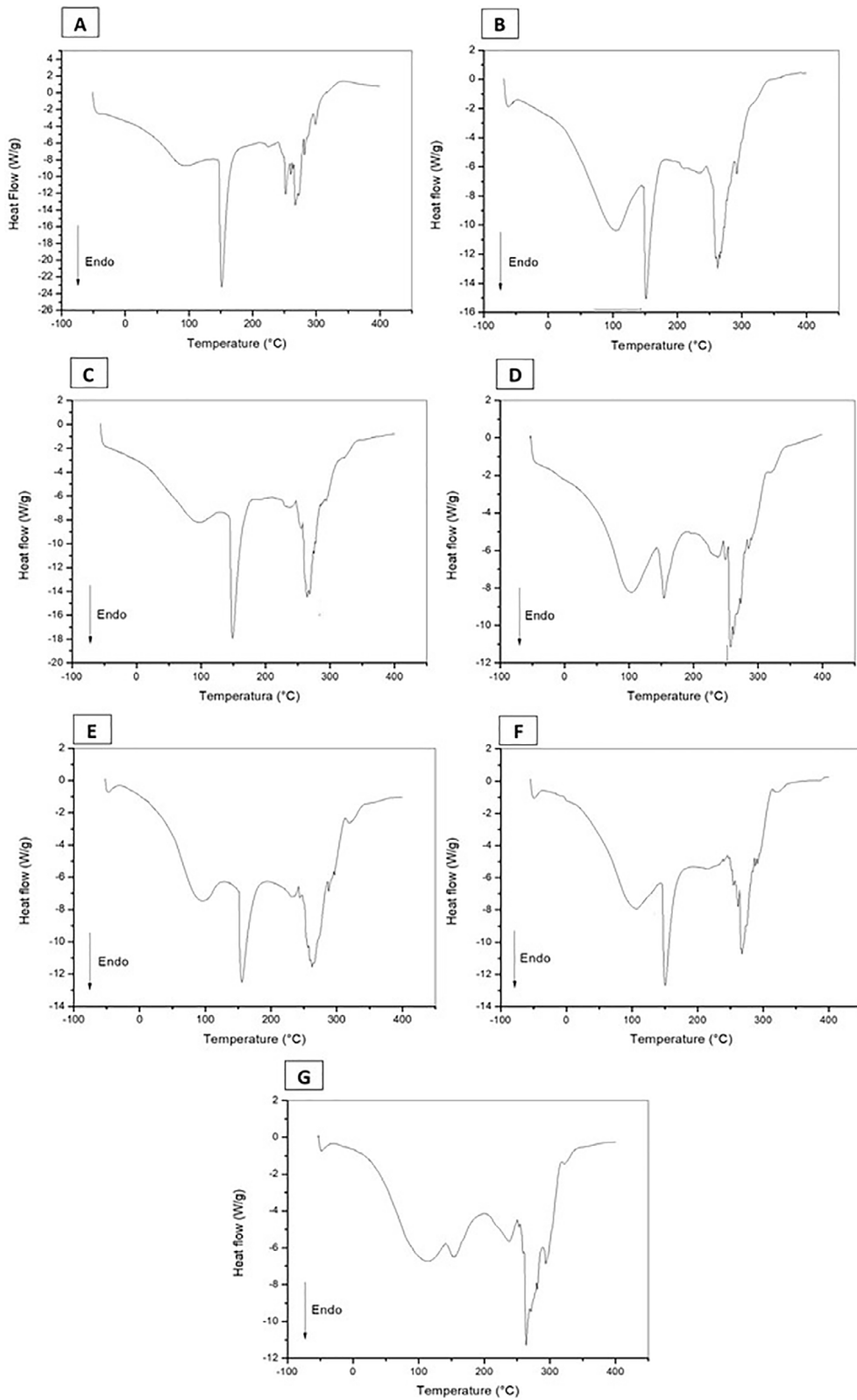


Figure 2. DSC curves under inert atmosphere. Samples containing different concentrations of coffee ground. Samples: (A) - 0% coffee ground; (B) - 0.1% coffee ground; (C) - 0.15% coffee ground; (D) - 0.20% coffee ground; (E) - 0.25% coffee ground; (F) - 0.30% coffee ground and (G) - 0.50% coffee ground.

Table 3. Volatilization, melting and degradation temperatures according DSC curves.

Samples	Tv (°C)	Tm (°C)	Td (°C)
1	93.34	151.27	266.80
2	105.34	151.12	262.23
3	97.24	149.41	264.56
4	103.46	153.84	256.78
5	95.83	155.48	262.49
6	106.82	150.47	267.87
7	114.30	153.83	263.74

Tv: Temperature of volatilization; Tm: Melting temperature; Td: Temperature of degradation.

In literature ²⁶, it was noticed that most of the thermal degradation of the film was caused by starch decomposition, characterizing the hydroxyl groups volatilization and depolymerization of carbon chains, as well as, between temperature range of 314.10 and 358.10 °C thermal decomposition of amylose and amylopectin ²⁷. These thermal behaviors allowed to understand that polymer decomposition is relate to the organic macromolecules inside the polymer matrix as well as low- molecular weight organic molecules are stable only up to a certain temperature range.

3.4 Scanning electron microscopy

The SEM images allowed to observe that the coffee ground it was adhered the polymer matrix, probably due to his low granulometry promoting a better mechanical tensile strength. The micrographs can be observed in the Figure 4.

SEM analyzes indicated that the film without the coffee grounds (Figure 4A, B) did not present granules in the cornstarch matrix. Its can be explained by good interaction between the plasticizer and the starch, promoting an efficient gelatinization of the film during molding process. In addition, no precipitates, voids and cavities were observed and it proves the good bonding between cornstarch and coffee ground. However, it can be observed that there are some spots with cracks or cracks along the fracture of the analyzed film. The Figure 4 (C,D) 0.10% coffee grounds, it is possible to observe small points indicating the reinforcing agent presence (Figure 4D). In addition, a roughness increasing was also noted. Figure 4 (E,F), sample with 0.15% of coffee ground, shows an intense coffee grounds appearance and moderately smooth fractured surface deformation.

In Figure 4 (G,H), 0.20% coffee grounds, a small crack increasing can be noted. Figure 3 (I,J), 0.25% coffee grounds, irregularities and deformations were observed. Figure 4 (K,L), 0.30% coffee ground, revealed a heterogeneous fracture surface and ruptures. Figure 4 (M,N), no cracks and fractures are observed, the presence of several coffee grounds can be noted, as well as small bubbles that are generally responsible for concentrating the tension, causing a decrease in values of mechanical properties.

The bubbles formation can interfere directly in the quality of the film ^{28,29} decreasing its mechanical resistance. Moreover, polymers exposure to ambient conditions, such as air humidity and high temperatures, can promotes the voids appearance, favoring water absorption by matrix, affecting its mechanical and physical properties. At greater percentage of coffee ground, the distance decreases leading to agglomerated within the matrix and more uniform distribution suggests that the coffee ground and matrix were thoroughly mixed.

4. Conclusions

The results of the mechanical characterization indicated an increase in the tensile strength of the samples that had the coffee residue in their composition. All of the films, except for the one with 0.50% of coffee ground waste, had higher values of tension higher than that of the film without coffee grounds, and the best result was that of the film with 0.30% of coffee ground. Thus, it can be considered that the coffee grounds acted as a reinforcing agent, improving the mechanical properties of the polymer films. Scanning Electron Microscopy (SEM) confirmed that during molding process was observed a better incorporation of coffee ground waste into the matrix, reducing the amount of stress concentration points that are harmful to the mechanical properties of the films.

These behaviors occurred because the residues of coffee ground are lignocellulosic and its present a good chemical compatibility with the starch and glycerol matrix. In terms of particle size the 200-mesh granulometry facilitated the mixing and dispersion of the coffee ground waste residues during casting of the films.

The thermal characterization of the films indicated that although there is no standard of improvement of the thermal properties associated to the increase of the concentration of the coffee grounds in the samples, these are better considering films without coffee ground, since they begin their thermal degradation at higher temperature, considering the various stages of mass loss. The DSC analyzes did not reveal a better film in relation to the thermal characteristics, since for both crystalline melting temperature and thermal decomposition of the films, the values did not present great differences.

Therefore, it is possible to consider the use of these films as an alternative to substitute some types of packages, as they offer advantages of low cost and high availability of materials used for molding, as well as better tensile and thermal properties.

5. Acknowledgments

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001, and FAPESP (06/60885-2).

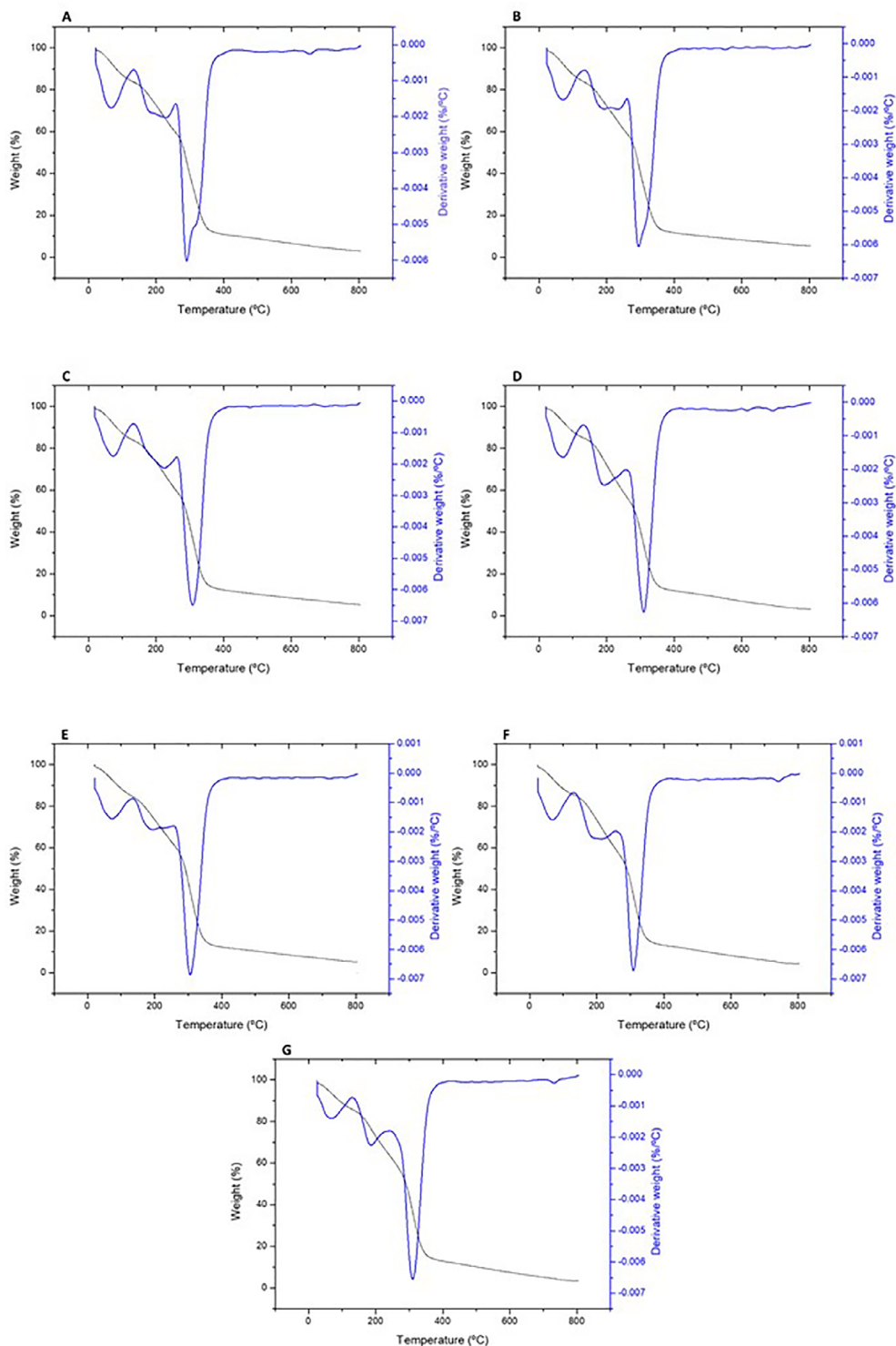


Figure 3. TGA and DTG curves under inert atmosphere. Samples containing different concentrations of coffee ground. Samples of films: (A) - 0% coffee ground; (B) - 0.10% coffee ground; (C) - 0.15% coffee ground; (D) - 0.20% coffee ground; (E) - 0.25% coffee ground; (F) - 0.30% coffee ground and (G) - 0.50% coffee ground.

Table 4. Decomposition stages observed in the TGA and DTG curves.

Samples	Step one			Step two			Step three			Total Mass loss (%)
	$\Delta T(^{\circ}C)$	Δ Mass (%)	T loss max ($^{\circ}C$)	$\Delta T(^{\circ}C)$	Δ Mass (%)	T loss max ($^{\circ}C$)	$\Delta T(^{\circ}C)$	Δ Mass (%)	T loss max ($^{\circ}C$)	
1	35.1–151.7	16.16	66.07	151.7–274.1	26.64	231.94	274.1–352.9	41.73	290.3	96.94
2	42.1–160.6	16.56	71.19	160.6–276.8	25.64	190.83	276.8–358.0	41.31	294.7	94.53
3	36.7–154.6	16.02	72.8	154.6–278.6	26.73	223.68	278.6–352.0	39.82	307.1	94.64
4	36.3–163.7	16.76	70.76	163.7–281.4	30.53	188.39	281.4–355.6	36.71	310.5	96.67
5	42.4–157.1	15.3	72.3	157.1–279.2	26.22	188.14	279.2–358.1	41.39	306.4	94.72
6	41.5–161.6	15.24	67.45	161.6–287.8	31.23	187.91	287.8–356.0	35.46	308.6	95.67
7	40.5–157.4	14.57	67.44	157.4–285.7	30.6	185.29	285.7–353.1	36.56	310.2	96.51

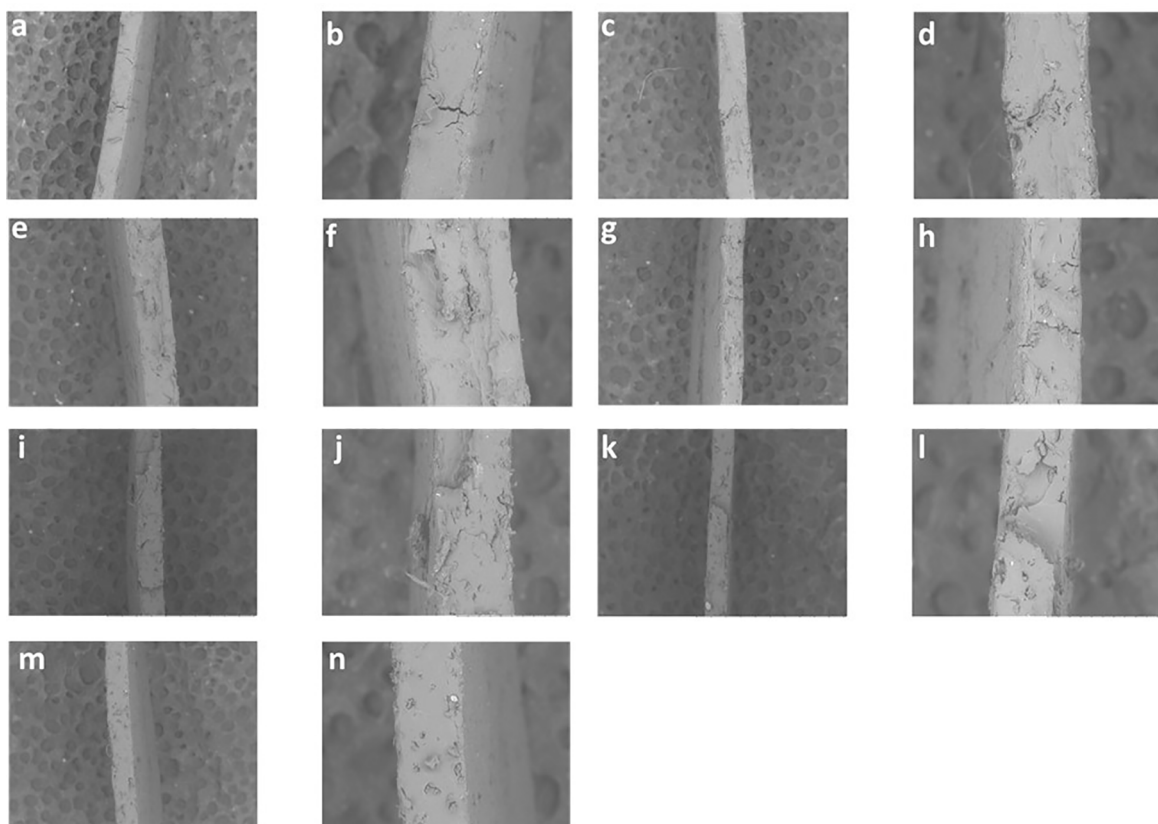


Figure 4. Scanning electron micrographs. Samples containing different concentrations of coffee ground. Samples of films: (A, B) - 0% coffee ground - 50x and 150x; (C, D) - 0.10% coffee ground - 50x and 150x; (E, F) - 0.15% coffee ground - 50x and 150x; (G, H) - 0.20% coffee ground - 50x and 150x; (I, J) - 0.25% coffee ground - 50x and 150x; (K, L) - 0.30% coffee ground - 50x and 150x and (M,N) - 0.50% coffee ground - 50x and 150x.

6. References

1. Anupam AK, Kumar P, Ransinchung RN GD. Use of Various Agricultural and Industrial Waste Materials in Road Construction. *Procedia - Social and Behavioral Sciences*. 2013;104:264-273.
2. Avelar NV, Rezende AAP, Carneiro ACO, Silva CM. Evaluation of briquettes made from textile industry solid waste. *Renewable Energy*. 2016;91:417-424.
3. Vamvuka D. Bio-oil, solid and gaseous biofuels from biomass pyrolysis processes-An overview. *International Journal of Energy Research*. 2011;35(10):835-862.
4. Brazil. Ministério do Planejamento, Desenvolvimento e Gestão. IPEA Instituto de Pesquisa Econômica Aplicada. TD 2268. *A organização Coletiva de Catadores de Material Reciclável no Brasil: dilemas e potencialidades sob a ótica da Economia Solidária*. Brasília: IPEA; 2017.
5. Jacobi PR, Besen GR. Solid Waste Management in São Paulo: The challenges of sustainability. *Estudos Avançados*. 2011;25(71):135-158.
6. Brazil. Ministério do Meio Ambiente. *Plano Nacional de Resíduos Sólidos*. Brasília: Ministério do Meio Ambiente; 2011.
7. Ioppolo G, Cucurachi S, Salomone R, Saija G, Ciraolo L. Industrial Ecology and Environmental Lean Management: Lights and Shadows. *Sustainability*. 2014;6(9):6362-6376.
8. Basu AJ, van Zyl DJA. Industrial ecology framework for achieving cleaner production in the mining and minerals industry. *Journal of Cleaner Production*. 2006;14(3-4):299-304.
9. Miller L, Soulliere K, Sawyer-Beaulieu S, Tseng S, Tam E. Challenges and Alternatives to Plastics Recycling in the Automotive Sector. *Materials (Basel)*. 2014;7(8):5883-5902.
10. Restrepo-Flórez JM, Bassi A, Thompson MR. Microbial degradation and deterioration of polyethylene - A review. *International Biodeterioration & Biodegradation*. 2014;88:83-90.
11. Shah AA, Hasan F, Hameed A, Ahmed S. Biological degradation of plastics: A comprehensive review. *Biotechnology Advances*. 2008;26(3):246-265.
12. Mbey JA, Hoppe S, Thomas F. Cassava starch-kaolinite composite film. Effect of clay content and clay modification on film properties. *Carbohydrate Polymers*. 2012;88(1):213-222.
13. Tang S, Zou P, Xiong H, Tang H. Effect of nano-SiO₂ on the performance of starch/polyvinyl alcohol blend films. *Carbohydrate Polymers*. 2008;72(3):521-526.
14. Mirjalili F, Chuah L, Salahi E. Mechanical and Morphological Properties of Polypropylene/Nano a-Al₂O₃ Composites. *The Scientific World Journal*. 2014;2014:718765.
15. Nugroho A. The Impact of Food Safety Standard on Indonesia's Coffee Exports. *Procedia Environmental Sciences*. 2014;20:425-433.
16. Lamine SM, Ridha C, Mahfoud HM, Mouad C, Lotfi B, Al-Dujaili AH. Chemical Activation of an Activated Carbon Prepared from Coffee Residue. *Energy Procedia*. 2014;50:393-400.
17. Reffas A, Bernadet V, David B, Reinert L, Lehocine MB, Dubois M, et al. Carbons prepared from coffee grounds by H₃PO₄ activation: Characterization and adsorption of methylene blue and Nylosan Red N-2RBL. *Journal of Hazardous Materials*. 2010;175(1-3):779-788.
18. Wobiwo FA, Ercoli Balbuena JL, Nicolay T, Larondelle Y, Gerin PA. Valorization of spent coffee ground with wheat or miscanthus straw: Yield improvement by the combined conversion to mushrooms and biomethane. *Energy for Sustainable Development*. 2018;45:171-179.
19. Campos-Vega R, Loarca-Piña G, Vergara-Castañeda HA, Dave Oomah B. Spent coffee grounds: A review on current research and future prospects. *Trends in Food Science & Technology*. 2015;45(1):24-36.
20. Scully DS, Jaiswal AK, Abu-Ghannam N. An Investigation into Spent Coffee Waste as a Renewable Source of Bioactive Compounds and Industrially Important Sugars. *Bioengineering (Basel)*. 2016;3(4). pii: E33.
21. Esquivel P, Jiménez VM. Functional properties of coffee and coffee by-products. *Food Research International*. 2012;46(2):488-495.
22. Silva-Pereira MC, Teixeira JA, Pereira-Júnior VA, Stefani R. Chitosan/corn starch blend films with extract from Brassica oleraceae (red cabbage) as a visual indicator of fish deterioration. *LWT - Food Science and Technology*. 2015;61(1):258-262.
23. Campagner MR, Moris VAS, Pitombo LM, do Carmo JB, de Paiva JMF. Filmes poliméricos baseados em amido e lignossulfonatos: preparação, propriedades e avaliação da biodegradação. *Polímeros*. 2014;24(6):740-751.
24. Morais LC, Maia AAD, Guandique MEG, Rosa AH. Pyrolysis and combustion of sugarcane bagasse. *Journal of Thermal Analysis and Calorimetry*. 2017;129(3):1813-1822.
25. Maia AAD, de Morais LC. Kinetic parameters of red pepper waste as biomass to solid biofuel. *Bioresource Technology*. 2016;204:157-163.
26. Taghizadeh MT, Abdollahi R. A Kinetic Study on the Thermal Degradation of Starch/Poly (Vinyl Alcohol) Blend. *Chemical and Materials Engineering*. 2015;3(4):73-78.
27. Wang L, Xie B, Xiong G, Du X, Qiao Y, Liao L. Study on the granular characteristics of starches separated from Chinese rice cultivars. *Carbohydrate Polymers*. 2012;87(2):1038-1044.
28. de Moraes JO, Reszka A, Laurindo JB. Espalhamento e secagem de filme de amido-glicerol-fibra preparado por "tape-casting". *Pesquisa Agropecuária Brasileira*. 2014;49(2):136-143.
29. Czaputa K, Brenn G, Meile W. The drying of liquid films on cylindrical and spherical substrates. *International Journal of Heat and Mass Transfer*. 2011;54(9-10):1871-1885.