

Effect of oil extracted from coffee grounds in the radiolytic stabilization of PVC

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ABSTRACT

Commercial Poly(vinyl chloride) (PVC) containing oil extracted from coffee grounds (OCG) at concentrations of 0.50; 1.00 and 1.50 wt% were investigated. The samples were irradiated with gamma radiation (^{60}Co) at room temperature and air atmosphere. The viscosity-average molar mass (M_v) was measured for PVC systems without and with oil. Decreases in molar mass observed when the systems were gamma irradiated reflect the random scission effects that take place in the main chain. Degradation index (DI) value was also obtained by viscosity analysis. DI results showed that the addition of OCG at 0.5 wt% into PVC matrix irradiated at dose of 25 kGy decreased the number of main chain scissions and was calculated a protection index of 67% in PVC matrix. Results about the free radical scavenger action of the OCG were obtained by use of 2,2-diphenyl-1-(2,4,6-trinitrophenyl)-hydrazyl radical (DPPH) and are discussed in this study. Decrease of 7% of Young's modulus value and a decrease of 31.5% on the elongation at break value were recorded for PVC films exposed to gamma irradiation. However, no significant changes were recorded in mechanical properties of PVC with OCG.

1. INTRODUCTION

Recent decades have seen a significant rise in coffee consumption and consequently an increase in the coffee waste generation. Thus, alternative routes are needed for coffee grounds management, developing new treatment or valorization strategies that should be viable both technically and economically. The composition of coffee grounds is very complex as a wide variety of chemical compounds are present, suggesting that this residue can be used for various applications. Kondamudi et al (2008) [1] recorded a possible valorization of coffee waste route is the production of sugars to be fermented for bioethanol that can be used as fuel or for any other purpose due to its high lignocellulosic content. Caetano et al (2012) [2] found that coffee grounds have oil content in the order of 10-20 wt% which can be used for biodiesel. In addition, bioethanol can be used in conjunction with the lipid fraction extracted from coffee to produce biodiesel via a transesterification reaction [2].

PVC is a polymer widely used for food packaging and medical devices sterilized by gamma irradiation. However when the polymer systems are submitted to sterilization by gamma radiation (25 kGy dose) their molecular structures undergo modification mainly as a result of main chain scission and crosslinking effects [3]. Both processes coexist for PVC molecules and either one may be predominant depending not only upon the chemical structure of the polymer, but also upon the conditions (temperature, environment, dose rate, etc.) under which irradiation is performed. The crosslinking and main scissions that take place during irradiation may lead to sharp changes in physical properties of the PVC [4, 5, 6]. Vinhas et al.

[7] reported radio-protective action of a common photo-oxidative stabilizer like HALS (Hindered Amine Light Stabilizer) in PVC films plasticized with DEHP (di-2-ethylhexyl phthalate). The HALS additive is believed to interrupt oxidative propagation reaction by scavenging of chlorine radical formed in PVC radiolysis.

The preparation of polymer films containing oil extracted from coffee grounds (OCG) has of a great interest and not found data about this proposed system. Films of PVC with OCG were exposed to gamma irradiation and the effects of the oil on the viscosity average molar mass (M_v) of gamma irradiated PVC were studied. In addition the free radical scavenger action of OCG and mechanical properties of PVC with OCG films were discussed in this study.

2. EXPERIMENTAL

2.1 Coffee Grounds Samples and Oil Extraction

Coffee grounds samples were obtained from residencies located in Recife/PE, Brazil. The samples were dehydrated at 60°C during 24h. Once dried, they were manually crushed and ground and stored at 18°C temperature until use.

Oil extraction from dried coffee grounds was performed in a soxhlet apparatus utilizing n-hexane as solvent. The 8h extraction was carried out for total removal of oil. Solvent was removed from the resulting product using a simple distillation at 60°C. The oil was kept away from light and air at 18°C until processing and analysis took place.

2.2 Preparation of PVC Films

The studied polymer material was commercial PVC (BRASKEM, Brazil). The films of PVC and PVC with addition of OCG were prepared by solvent-casting from methyl-ethyl-ketone (MEK) solvent by slow evaporation in air at room temperature ($\approx 27^\circ\text{C}$) upon 48h of magnetic stir of the polymer solution (1,8g of the PVC/40 mL of the MEK). MEK was dried with Na_2SO_4 and purified by distillation. In this study the PVC films are named PVC/oil for PVC+ OCG systems. The concentrations of OCG used in this study were 0.50; 1.00 and 1.50 wt%.

2.3 Viscosity Measurements

The viscosity measurements of PVC and PVC/oil films were carried out in THF solution at $25.0 \pm 0.1^\circ\text{C}$ using an Ostwald viscometer in a thermostatic bath. The intrinsic viscosity of the samples was calculated from the relative viscosity, $\eta_{\text{rel}} \approx v/v_0 \approx t/t_0$, within range of 1.1 – 1.9, where v and v_0 are the cinematic viscosities on the polymer solution and the solvent, respectively. The t and t_0 are flow times of solution and solvent, respectively. Therefore, η_{rel} was calculated from t/t_0 ratio. The specific viscosity ($\eta_{\text{sp}} = \eta_{\text{rel}} - 1$) and the reduced viscosity ($\eta_{\text{red}} = \eta_{\text{sp}}/C$), where C is the concentration of the solution (0.6 g/dL), were calculated as well. The intrinsic viscosity $[\eta]$ was determined by the Solomon-Ciuta equation [8]:

$$[\eta] = \left(\frac{1}{C}\right) \sqrt[4]{(\eta_{sp} - \ln \eta_{rel})} \quad (1)$$

Then the viscosity average molar mass, M_v , was calculated from the corresponding $[\eta]$ values through the Mark-Houwink equation [9]:

$$[\eta] = K M_v^a \quad (2)$$

Where K and a are 1.5×10^{-4} dL/g and 0.766, respectively for the THF-PVC system at 25°C [10].

Radiostabilizing action of OCG on PVC matrix can be assessed by comparison of degradation index (DI) parameter, $DI = (M_{v0}/M_v) - 1$, for a determined irradiation dose. The M_{v0} and M_v are the viscosity average molar mass before and after the gamma irradiation, respectively. DI is obtained from viscosity analysis and reflects the number of main chain scissions per original molecule after irradiation.

2.4 Irradiation of Samples

PVC and PVC/oil films were exposed to gamma radiation from a ^{60}Co source (dose rate of 6.13 kGy/h) at dose of 25 kGy (sterilization dose) in presence of atmosphere air and at room temperature ($\approx 27^\circ\text{C}$).

2.5 Free Radical Scavenger Action of the Nanoparticles

2,2-diphenyl-1-(2,4,6-trinitrophenyl)-hydrazyl radical (DPPH) solution was prepared using ethanol as solvent. Was dissolved 0.0024g of the DPPH in the 100 mL ethanol. Appropriate amount of oil were mix with the DPPH solution and the mixture must be vigorously agitated. The reaction was carried out at ambient temperature for 30 min. The absorbance at 515 nm was measured against a blank of pure ethanol after the reaction in a UV-vis spectrophotometer Spectro 22, 108-D and 60 Hz. Radical DPPH scavenging capacity (%SC) was estimated from the difference in absorbance with or without nanoparticles (equation 3).

$$\%SC = (A_s - A_{sn}) \times 100 \quad (3)$$

Where A_s =DPPH solution absorbance and A_{sn} =DPPH solution absorbance for system with sulfide nanoparticles. All tests were conducted in triplicate.

2.6 Mechanical Properties

The tensile properties of the films were determined according to ASTM D-882 using an Instron machine IMIC, DL-500 N. The crosshead speed was 10 mm/min. The tests were carried out at room temperature ($\approx 27^\circ\text{C}$) and the results shown in this study are an average of four samples.

Table 1 shows M_v for the PVC/oil before and after irradiation. Note that M_v also decreases in irradiated samples of films. However the analysis of Tables 1 revealed less chain scissions occur in PVC/oil films at 0.50wt% concentration. At sterilization dose (25 kGy) we calculated $DI = 0.126$ for PVC and $DI = 0.041$ for PVC/oil films. These data represent a decrease 67% in scissions per original molecule of PVC. In addition, with the increase of concentration of the OCG in the PVC matrix was observed a decrease of the stabilizing action of oil on the systems until the total loss of stabilizer action at 1.5 wt% concentration. More investigations are necessary for explains the OCG behavior.

No information about use of OCG in the radiolytic stabilization of polymers has been published and consequently the mechanism of radiolytic stabilization effect of this oil is not clear. However, some probable reactions may be going on under gamma irradiation. The gamma rays can break covalent bonds in PVC molecule to directly produce the free radicals as was shown in Scheme 1 (I and II). The gamma rays can also produce excited states in PVC which undergo further reactions to produce the A radical (Scheme 1) indirectly. The efficiency of certain composts in the stabilization of polymer molecules against radiation may be evaluated by measuring the effect of these composts on the free radical population after irradiation, as well as on its rate of decay. The Table 2 shows the results obtained by use of OCG as a scavenger free radical on the DPPH solution.

Table 1: Viscosity results obtained for PVC/oil.

Concentration of OCG (wt%)	Dose (kGy)	M_v (g/mol)	DI	Protection (%)
0.0	0	63874±1399	0.126	-
	25	56732±1767		
0.5	0	68666±1121	0.041	67
	25	65960±1420		
1.0	0	69201±1819	0.086	32
	25	63741±1283		
1.5	0	70663±1355	0.205	-
	25	58626±1301		

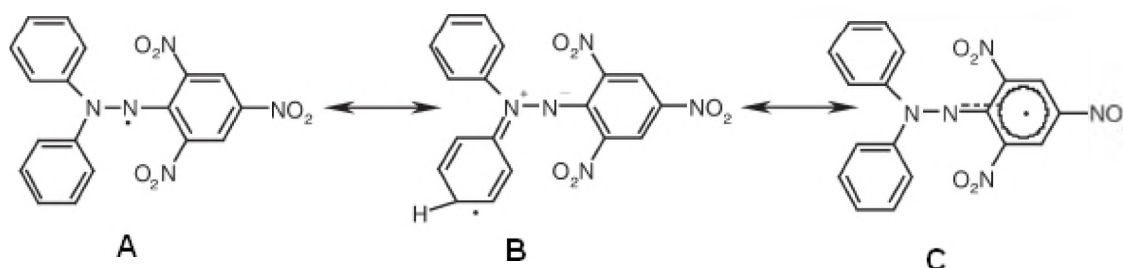
DPPH is a stable free radical, non-natural, whose properties differ from the highly reactive oxygen radicals such as the hydroxyl, alkoxy and superoxide. Looking at this structure (Scheme 2) it is expected that DPPH can react with another free radical in several different ways: i) by coupling to the nitrogen-centered radical (structure A); ii) by coupling in the para-position on the phenyl ring (structure B), and iii) coupling somewhere on the picryl moiety (structure C). Thus, the DPPH free radical scavenging assay presents itself as a test of prediction of the antioxidant potential activity. The assay is grounded on the DPPH property of presenting a strong absorption at visible spectrum in wavelength of 515 nm, characterized by an intense violet coloration, due to the presence of free electrons. When the DPPH is in the presence of substances able to scavenge free radicals, the absorption is inhibited, leading to a stoichiometric discoloration in relation to the number of reduced molecules of DPPH.

The degree of discoloration is directly correlated with the free radical scavenger activity of the evaluated substance [15, 16, 17, 18].

Table 2: Radical DPPH scavenging capacity (SC) results.

System	Absorbance	SC (%)
DPPH	0.83 ±0.02	-
OCG	0.81±0.07	2.40

Ours results reveal that oil in the amount of 0.0090g (equivalent to concentration of 0.5 wt% in PVC matrix) not have scavenger free radical action because the system with oil showed a discrete discoloration and only 2.40% of free radical capture was found. Thus the mechanism proposed to action of OCG in the PVC matrix is by Quencher way. Quencher stabilizer acts dissipating the radiation energy as heat instead of letting it break chemical bonds. This in turn causes a decrease in the formation of free radicals, which are responsible for scission degradation reaction. The possible mechanism is represented on the scheme 3.



Scheme 2: Capture mechanism of DPPH free radical [15].

The chain property species in autoxidation caused by oxygen action on PVC radical formed by gamma irradiation are peroxy radicals (scheme 1) and an effective inhibitor must interrupt these chains. We assumed the quencher stabilizer is the principal function of the OCG on the films of PVC, but further work to require to providing a better understanding of all processes involved in the radiolytic action of the oil on PVC matrix.



Scheme 3: Proposed action mechanism for OCG in PVC matrix.

3.4 Mechanical

The results of mechanical measurements for PVC and PVC/oil are summarized in Table 3. The properties studied were elongation at break (Eb) and Young's modulus (Ym).

Analyzing the unirradiated systems was found that the value of Ym for PVC/oil decreases 3% when compared with the Ym value of PVC. This result means a decrease in rigidity of the PVC and consequently explains the increase of 9% on Ea value of PVC/oil. Thus, the oil act also as a plasticizer in the PVC molecule. The possible explication is that PVC shows dipole-dipole attraction as a result of the electrostatic interactions between the chlorine atom of one polymer chain (negative pole) and the hydrogen atom of another polymer molecule (positive pole). These interactions could be weakened by intermolecular interactions between PVC and OCG, which promote decrease in the density of entanglements points of the polymer molecules. This effect increasing the polymer flexibility, decreasing the Ym value and consequently increase the Eb values.

For the films of PVC irradiated at 25 kGy was found a decrease of 26% in Ym value with consequent increase of 16% in Eb value. The chain scission effect obtained by gamma irradiation (Figure 3) provokes the decrease of average length of PVC molecule. The density of entanglements points decreases leading to a decrease of the Ym value as consequence of PVC radiolytic degradation. The lower molecular weight also makes fibrils less stable and therefore favors brittle fracture [9]. On the other hand, the changes of Ym and Eb values were found for irradiated PVC/oil, but the decrease of 15% in Ym value and less influence in Eb were found. These results are explained by stabilizer action of OCG in the PVC matrix and agree with the viscosity measurements.

Table 3: Effects of OCG (0.5 wt%) and gamma irradiation in the mechanical properties of PVC.

	Dose (kGy)	Ym (MPa)	Eb (%)
PVC	0	913.33 ±82.24	7.43±0.83
	25	674.23±61.08	8.89±0.43
PVC/oil	0	883.05±73.98	9.17±0.43
	25	746.30±54.78	9.73±0.25

4. CONCLUSIONS

The oil content of the coffee (*Coffea arabica L*) grounds was calculated to 10%. The oil was added in PVC matrix to form PVC/oil films. The viscosity analyses suggest that oil (0.5 wt%) protected PVC against radiolysis by quencher mechanism. However, the incorporation of nanoparticles in PVC matrix influenced directly its Young's modulus, which showed reduction in these values in unirradiated films. On the other hand, the changes of Y_m and E_b values were found for irradiated PVC/oil, but the gamma irradiation undergoes less influence in mechanical properties of PVC/oil films.

ACKNOWLEDGMENTS

We would like to thanks for BRASKEM-Brazil for PVC samples.

REFERENCES

1. N. Kondamudi, S. K. Mohapatra, M. Misra, Spent coffee grounds as a versatile source of green energy, *J Agri Food Chem*, **56** (24), p.p.11757-11760 (2008).
2. N. S. Caetano, V. F. M. Silva, T. M. Mata, Valorization of Coffee Grounds for Biodiesel Production, *Chem Engin Transac*; **26**, pp. 267-272 (2012).
3. A. Charlesby, *Atomic radiation and polymers*, Pergamon Press, New York USA (1960).
4. G. M. Vinha, R. M. Souto-Maio, Y. M. B. Almeida, B. B. Neto. Radiolytic degradation of poly(vinyl chloride) systems, *Polym Degrad Stab*, **86**, pp. 431-436 (2004).
5. E. Mendizabal, L. Cruz, C. F. Jass, T. Burillo, V. T. Davin, Radiation Crosslinking of highly plasticized PVC, *Radiat Phys Chem*, **47**, pp. 305-309 (1996).
6. M. Dole, *The Radiation Chemistry of macromolecules*, v 2, Academic Press, New York USA (1973).
7. G. M. Vinha, R. M. Souto-Maio, Y. M. B. Almeida. Radiolytic degradation and stabilization of poly(vinyl choride), *Polym Degrad Stab*, **83**, pp.429-433 (2004).
8. L. H. Cragg, C. C. Bigelow, The viscosity slope constant K-ternary systems: Polymer-polymer-solvent, *J Polym Sci*, **16**, pp. 177-191 (1955).
9. J. Guillet, *Polymer photophysics and photochemistry*, Cambridge University Press, New York USA (1985).
10. J. Brandrup, E. H. Immergut, *Polymer Handbook*, John Wiley Sons, New York USA (1989).
11. V. L. E Ajiwe, S. C. Umerie, C. A. Okeke, V. N. Oburota, Extration and utilization of cassava seed oil. *Bioresource Technol*, **47**, pp. 85-86 (1994).
12. Baccaro S, Brunella V, Cecília A, Costa L. γ irradiation of poly(vinyl choride) for medical applications, *Nucl Inst and Meth Phys Res*, **208**: 195-198 (2003).
13. T. L. Cottrel, *The strengths of chemical bonds*, Butterworths, London England (1954).
14. C. Walling, *Free radicals in solution*, Jon Wiley and Sons Inc, New York USA (1957).
15. M. Leopoldini, T. Marino, N. Russo. M. Toscano, Antioxidant properties of phenolic compounds. H-atom versus electron transfer mechanism, *J Phys Chem B*, **108**, pp. 4916-4922 (2004).
16. L. Mathiesen, K. E. Malterud, R. B. Sund, Hydrogen Bond Formation as Basis For Radical Scavenging Activity: A Structure-Activity Study of C-Methylated

- Dihydrochalcones from *Myrica gale* and Structurally Related Acetophenones, *Free radical Biol Med*, **22**, pp. 307-315 (1997).
17. P. Ionita, T. Constantinescu, H. Caldararu, C. Luca, M. T. Caproiu, F. Dumitrascu, I. Silberg, A. T. Balaban, Reaction between the DPPH free radical and potassium cyanide in the presence of crown ether 18-C-6: a correction, *Rev Roum Chim*, **44**, pp. 393-396 (1999).
 18. P. Ionita, F. Spafiu, T. Constantinescu, H. Caldararu, The reaction of 2,2-diphenyl-1-picrylhydrazyl stable free radical with sodium tetra-phenylborate in the presence of 18-C-6 crown ether, *Rev Roum Chim*, **44**, pp. 497-500 (1999).