

Study of Coffee Grounds Oil Action in PVC Matrix Exposed to Gamma Radiation: Comparison of Systems in Film and Specimen Forms

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The poly (vinyl chloride), PVC, undergoes changes in its physicochemical properties when it is exposed to gamma radiation. Thus, the radiolytic stabilization of PVC is one way for obtain a material with radiation resistance. In this work, we studied the coffee grounds oil as PVC radiolytic protection in two systems forms: PVC film and PVC specimen. The systems were irradiated at sterilization dose of medical devices and viscosity measurements were performed. According to viscosity assays of PVC films, there was a 67% protection in polymer matrix promoted by the oil. On the other hand, the mean viscosity molar mass (Mv) of PVC specimens increased about 13%, indicating predominance of crosslinking effect, however samples containing the oil showed no Mv significant changes. Therefore, the oil can be considered a PVC radio stabilizing substance and open a way for use of sustainable additive in PVC industry.

Keywords: *sustainability, additive, stabilization, polymer.*

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 reaction².

On the other hand, poly (vinyl chloride), PVC, is a polymer widely used for food packaging and medical devices both 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 effects³. 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}. Furthermore, HCl molecules are also released in the radiolytic process. There are some studies about radiolytic stabilization of PVC^{7,8,9}. For example, Vinhas et al. (2004)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 not manufactured to radiation resistance action, but the successful of it use is believed to interrupt oxidative propagation reaction by scavenging of chlorine radical formed in PVC radiolysis. However, no studies that reported the use of vegetable oil as radiolytic protectors of polymers are known. In this way, preparation of PVC films and PVC specimens containing oil extracted from coffee grounds (OCG), which is a discard, has of a great interest and not found data about this proposed system. Films and specimens 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, FT-IR spectrum, and mechanical properties of PVC with OCG, for both forms, 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

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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 and PVC specimens

The studied polymer material was commercial PVC (BRASKEM, Brazil). The films ($\approx 60 \mu\text{m}$ thickness) of PVC and PVC with addition of OCG (PVC/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.

On the other hand, the PVC and PVC/OCG specimen samples were produced by BRASKEM, Brazil. The Norvic SP 1300FA resin ($K = 71$) was used for the production of PVC specimens. The resin was mixed (Mecanoplast mixer, 9 liter ML9, 1200 rpm) with solid additives as the thermal stabilizers, at room temperature ($\approx 27^\circ\text{C}$). Then the mixture was heated and at 80°C the liquid additives as plasticizer Dioctyl Phthalate and OCG were added. The blend was processed on a two roll calender at a temperature of 150 °C for 3 minutes (20 rpm). Then, the specimens were pressed in Luxor press with a pressure of 100Kgf/cm² for 2 min and a pressure of 200Kgf/cm² for 1 minute, consecutively. Afterwards, the PVC specimens were cooled to 40°C and they were cut in tie-type IV dimensions of standard ASTM-D 638 ($\approx 3\text{mm}$ thickness). According the manufacturer, the specimens were produced for medical applications (catheter). They were processed with additives as plasticizers, lubricants, and thermal protectors. For both systems the concentrations of OCG used was 0.50 wt%. This concentration was obtained in ours previous study¹⁰.

2.3 Viscosity measurements

The viscosity measurements of PVC and PVC/OCG samples 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^{8,11}. The viscosity average molar mass, M_v , was then calculated from the corresponding $[\eta]$

values trough the Mark-Houwink equation ($[\eta] = K M_v^a$)¹². For Mark-Houwink equation, K and a are $1.5 \times 10^{-4} \text{ dL/g}$ and 0.766, respectively for the THF-PVC system at 25°C¹³.

Radio stabilizing action of OCG on PVC matrix can be assessed by comparison of degradation index (DI) parameter, $\text{DI} = (M_{v0}/M_v) - 1$, 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

The samples were exposed to gamma radiation from a ⁶⁰Co 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 coffee grounds oil

The efficiency of OCG to scavenge the 2,2-diphenyl-1-(2,4,6-trinitrophenyl)-hydrazyl radical (DPPH) was determined in this study. The standard reaction consists in the mixture 0.0024g of the DPPH in the 100 mL of ethanol. Appropriate amount of oil was mix with the DPPH solution and the system must be vigorously agitated. The reaction was carried out at ambient temperature ($\approx 27^\circ\text{C}$) 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 OCG (equation 1).

$$\%SC = \frac{A_s - A_{sn}}{A_s} \times 100 \quad (1)$$

Where A_s = DPPH solution absorbance and A_{sn} = DPPH solution absorbance for system with OCG. BHT (2,6-bis(1,1-dimethylethyl)-4-methylphenol) was used as positive control. All tests were conducted in triplicate.

2.6 FT-IR characterization

Infrared spectra of PVC and PVC/OCG samples were obtained by Fourier Transform Infrared Spectroscopy (Bruker-IFS66), equipped with an attenuated total reflection accessory (FTIR-ATR), in the 4000-400 cm⁻¹ wavenumber region, 75 scans per spectrum, with 4 cm⁻¹ resolution.

2.7 Mechanical properties

The tensile properties of the PVC film samples were determined according to ASTM D-882 using an Instron machine IMIC, DL-500 N. The crosshead speed was 3 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 with sample dimension of 2.5 x 7.5 cm x 0.11 mm. On the other hand, the tensile properties of PVC

specimen samples were determined according ASTM D-638, four samples and using similar machine used for PVC film samples. Assays were performed under the following conditions: load cell of 500 N, crosshead speed of 2 mm/min, and at room temperature ($\approx 27^\circ\text{C}$).

3. Results and Discussions

3.1 Radiolytic action of coffee grounds oil in PVC matrix

The oil content of the coffee (*Coffea arabica L*) grounds was calculated to 10% and are comparable to the ones for commercial vegetable oils like soybean (11-25%)¹⁴. The oil was incorporated in the PVC matrix and were formed a homogeneous material for both PVC film and PVC specimens. After irradiation a yellow color was observed for all systems.

Radio stabilizing results are shown in Table 1 that shows M_v for the PVC systems before and after irradiation. The results revealed that M_v decreased for irradiated PVC films and increased for PVC specimens. In radiolysis process may occurs the scission and the crosslinking effects of polymeric materials. The formation of unsaturated linking, formation of gasses, and low molecular weight products also are generated by radiolysis^{4,5}.

Ours results for PVC film showed the predominance of main chain scission, in agreement with the literature that reports about gamma radiation effects on the PVC matrix^{4,5,7}. However, the analysis of Table 1 revealed less chain scissions occur in PVC/OCG films at 0.50wt% concentration. At sterilization dose (25 kGy) we calculated $DI=0.126$ for PVC and $DI=0.041$ for PVC/OCG films. These data represent a decrease 67% in scissions per original molecule of PVC.

On the other hand, according Table 1, the PVC specimens undergoes an increase of 13% on M_v and it represents the crosslinking as main effect in the PVC chain. The PVC specimens have larger thickness than PVC film then it is probable that larger section interacting with radiation which can contribute to increased formation of radiation products. In next step, these products seem to suffer predominantly radiation crosslinking effect, which leads to increased M_v . In addition, the antioxidant additives phenolic and phosphate

usually presents in PVC plasticized, undergo preferably degradation in the processes of irradiation because of the partial radiolysis^{15,16}. Thus, PVC specimens are more sensitive to the conditions of irradiation and more susceptible to oxidative degradation than the own resins which not contain additives like the PVC film. However, no significant event (scission or crosslinking effects) was found for PVC/OCG specimens systems. This result, open an important way for radiolytic stabilization of PVC by use of sustainable additive.

In addition, the M_v of PVC specimen are lower than M_v of PVC film. These results imply decreases in intrinsic viscosity, which are results of the contraction of PVC molecule coil in solution. The molecules of some additives can cause the contraction of the PVC molecules due to lack of chemical affinity, for example. Thus, the contracted PVC coil (in PVC specimens) yields a lower hydrodynamic volume, which facilitated the passage of the polymer solution through the viscometer capillary tube and decrease its viscosity.

On the other hand, further evidences on intermolecular interactions between PVC and OCG also could be assessed by viscosity analysis. The Table 1 shows an increase in M_v for PVC/OCG for both film and specimen systems. These increases in M_v means expansion of PVC molecule coil in solution, most probably due to interactions of some OCG group and chlorine of PVC molecule by dipole-dipole interaction and cause expansion of molecule with increasing viscosity. Nevertheless, further discussions about molecular interactions between the OCG and PVC will be presented by FT-IR analyses.

To the best of our knowledge, 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 occur when the polymer system is exposed to gamma irradiation. The gamma rays can break covalent bonds in PVC molecule to directly produce the free radicals^{17,18}. The efficiency of certain composts in the stabilization of polymer molecules against radiation may be evaluated by measuring theirs effect 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.

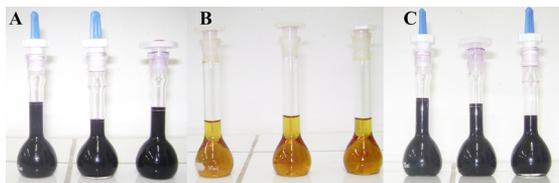
Table 1. Viscosity results obtained for PVC/OCG

Systems	Dose (kGy)	M_v (g/mol)	Main event	ID (%)
PVC (film)	0	63,874 \pm 1,399	scission	0.126
	25	56,732 \pm 1,767		
PVC/OCG (film)	0	68,666 \pm 1,121	scission	0.041
	25	65,960 \pm 1,420		
PVC (specimen)	0	41,310 \pm 385	crosslinking	-
	25	46,898 \pm 244		
PVC/OCG (specimen)	0	43,047 \pm 420	no event	-
	25	42,814 \pm 350		

Table 2. Radical DPPH scavenging capacity (SC) results

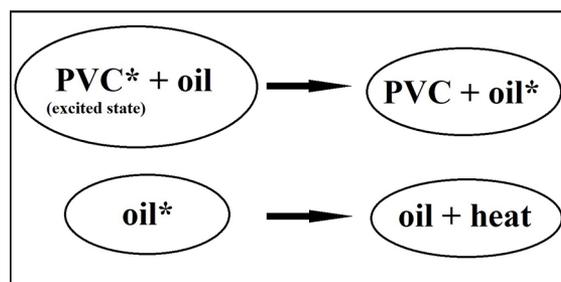
Systems	Absorbance (515 nm)	SC (%)
DPPH puro	1.24 ± 0.02	-
DPPH + OGC	1.23 ± 0.02	-
DPPH + BHT	0.34 ± 0.06	72.58 ± 0.7

DPPH is a stable free radical, non-natural, and it can react with another free radical. The DPPH solution 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 (Fig. 1a). 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^{19,20}. The degree of discoloration is directly correlated with the free radical scavenger activity of the evaluated substance^{21,22}.

**Figure 1.** Results obtained for: a) DPPH solution; b) DPPH+BHT and c) DPPH +OCG

Ours results reveal that OCG in the amount of 0.0090g (equivalent to concentration of 0.5 wt% in PVC matrix) not have scavenger free radical action because the DPPH+OCG solution showed no discoloration (Fig. 1c). On the other hand, the positive control of BHT exhibited radical scavenging capacity by solution discoloration (see Fig. 1b).

Thus, the mechanism proposed to action of OCG in the PVC matrix is by Quencher action. Quencher stabilizer acts dissipating the excess energy by fluorescence, phosphorescence, or conversion to heat, instead of letting it break chemical bonds. Then the OCG molecule causes a decrease in the formation of free radicals, which are responsible for scission degradation or crosslinking reaction. The possible mechanism is represented on the scheme 1.

**Scheme 1.** Proposed mechanism of OCG action in PVC molecule exposed to gamma irradiation

We assumed the quencher stabilizer is the principal function of the OCG on the PVC films and PVC specimens, but further work is required to providing a better understanding of all processes involved in the radiolytic action of the oil on PVC matrix.

3.2 Characterization of the PVC film and PVC specimen

FT-IR spectroscopy was used to detect and identify the presence of intermolecular interactions between PVC and OCG molecules. The existence of specific C-Cl oil interactions in the PVC/OCG system could be inferred from a shift in C-Cl stretching vibrations with the presence of OCG or other changes such as broadening of the C-Cl stretching peak or its intensity change, and even a new peak formation^{23,24}.

Figure 2 shows FT-IR spectra of PVC and PVC/OCG for non-irradiated and irradiated films in the 4000-500 cm⁻¹ wavenumber for PVC film (2a) and PVC specimens (2b). The band assignments for all systems (irradiated and non-irradiated) of PVC and PVC/OCG are listed in Table 3.

It can be observed in the spectra of PVC specimen (Figure 2a) and spectra of PVC film (Figure 2b) that OCG addition is not easily visually detected, because the positions of absorbance peaks are similar. However, according Table 2, the vibrational peaks assignment to C-Cl stretching of PVC are shifted in PVC/OCG for both PVC specimen and PVC film systems. Moreover, the peak of PVC specimens at 1423 cm⁻¹ has changed from two sharp peaks at 1423 and 1460 cm⁻¹ in PVC/OCG specimen for non-irradiated system, for example. Similar behavior was observed for 1354 cm⁻¹ absorption in PVC specimen (non-irradiated). This peak has from two sharp peaks at 1356 and 1381 cm⁻¹ in PVC/OCG specimen. The assignments of additional peaks are showed in Table 2. The change in shape and position of the peaks confirms that interactions occurred between PVC and OCG molecules²⁵. On the other hand, the spectra obtained for irradiated samples do not showed significant changes.

In addition, the C=O vibration was observed in the systems, except the irradiated PVC/OCG film. In case of films, the vibration may be attributed to residual solvent (methyl-ethyl-ketone) used in the casting production of samples. However, for PVC specimens, the additives, like plasticizers, are incorporate in the polymer matrix and C=O vibration may be assignment to these molecules. The confirmation is the presence of peak assignment to C-O-C axial vibration only in the PVC/OCG specimen spectrum (see Table 3).

3.3 Mechanical properties

The results of mechanical measurements for PVC and PVC/OCG are summarized in Table 4. The properties studied were elongation at break (Eb) and Young's modulus (Ym). The mean values of the mechanical properties were

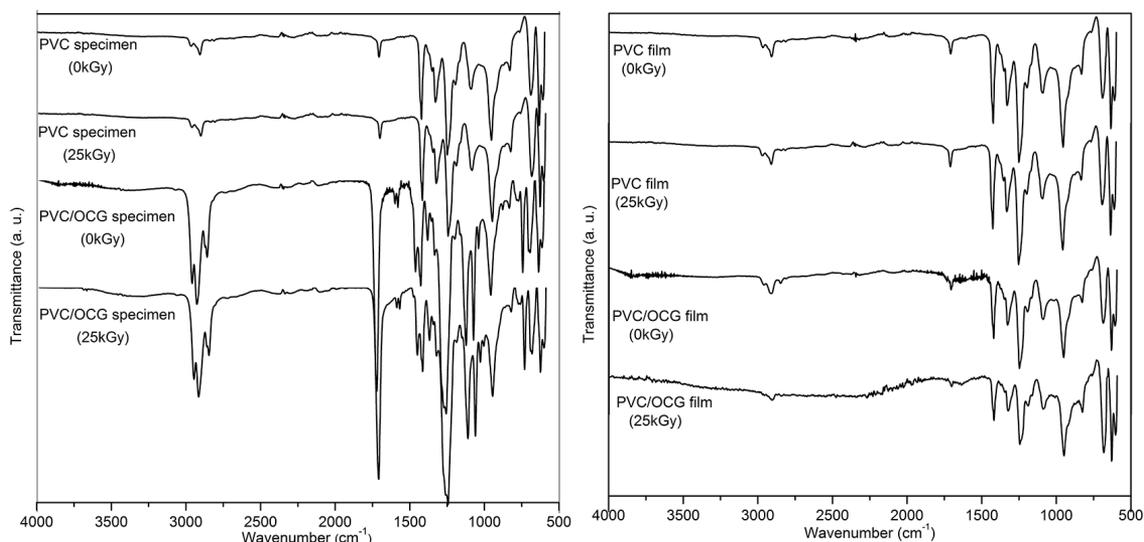


Figure 2. FT-IR spectra obtained for a) PVC specimen and b) PVC film

Table 3. Peak assignments for FT-IR spectra of PVC and PVC/OCG systems

Specimens		Absorption peak (cm ⁻¹)						Peak assignment
PVC (0kGy)	PVC (25kGy)	PVC/OGC (0kGy)	PVC/OGC (25kGy)	Films PVC (0 kGy)	PVC (25 kGy)	PVC/OGC (0 kGy)	PVC/OGC (25 kGy)	
2971	2970	2959	2961	2967	2971	2964	2965	CH stretch, out of phase, on neighboring CHCl groups
2910	2912	2925 2850	2927 2852	2912	2909	2915	2912	CH ₂ stretch, asymmetrical, in phase
1718	1719	1722	1720	1712	1710	1709	-	C=O axial, carbonyl group
-	-	1460	1462	-	-	-	-	CH ₂ bend
1423	1423	1423	1424	1428	1427	1426	1426	CH ₂ bend, in phase
-	-	1381	1383	-	-	-	-	C-H bend, CH ₃ bond
1354	1354	1356	1356	1354	1354	1354	1354	CH ₂ wag, in phase
1337	1331	1334	1333	1333	1332	1331	1329	C-H bend of CHCl, out of phase
1258	1253	1267	1266	1252	1252	1254	1250	C-H bend of CHCl, in phase
1196	1192	1191	1198	-	-	-	-	C-O-C axial, asymmetrical
1120	1121	1121	1123	1120	1120	1122	1122	CH wag, out of phase
1094	1093	1094	1092	1096	1094	1096	1093	C-C stretch, perpendicular
956	956	957	957	957	957	957	955	CH ₂ rocking
831	832	840	841	832	832	832	832	C-C stretch
690	689	700	704	696	692	687	688	C-Cl stretch
638, 611	634, 610	647, 615	638, 612	638, 615	636, 612	632, 609	631, 608	

compared statistically by *Student's t-test*, with a significance level of 5% ($p < 0.05$).

Analyzing first the PVC films non-irradiated it was found that the value of Y_m for PVC/OCG decreases 3% when compared with the Y_m value of PVC. This result means a decrease in rigidity of the PVC film and consequently explains the increase of 9% on E_a value of PVC/OCG. Generally, 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). Intermolecular interactions between PVC and OCG were discussed by FT-IR analyses. These interactions could be weakened by special action of OCG, which promote decrease in the density of entanglements points of the polymer molecules. In addition, it was found a decrease of 26% in Y_m value with consequent increase

Table 4. Effects of OCG (0.5 wt%) and gamma irradiation in the mechanical properties of PVC

System	Dose (kGy)	Ym (MPa)	Eb (%)
PVC film	0	913.33±82.24 ^a	7.43±0.83 ^a
	25	674.23±61.08 ^b	8.89±0.43 ^b
PVC/OCG film	0	883.05±73.98 ^c	9.17±0.43 ^c
	25	746.30±54.78 ^c	9.73±0.25 ^c
PVC specimen	0	0.106±0.022 ^d	295.59±18.41 ^d
	25	0.107±0.011 ^d	293.42±5.53 ^d
PVC/OCG specimen	0	0.103±0.011 ^e	336.85±21.94 ^e
	25	0.126±0.048 ^f	261.75±11.28 ^f

Means with the same letter in the same column do not differ with $p < 0.05$ for the Student's t-test.

of 16% in Eb value for PVC films irradiated at 25 kGy. The chain scission effect obtained by gamma irradiation (Table 1) 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^{12,17}. On the other hand, decrease of 15% in Ym value and less influence in Eb were found for irradiated PVC/OCG. These results are explained by stabilizer action of OCG in the PVC matrix and agree with the viscosity measurements.

Similar results were found for non-irradiated PVC specimens, i. e., the OCG provoke decrease in rigidity of polymer with decrease of Ym value and consequent increase of percentage of elongation. The results also showed a good radiation resistance of PVC specimens, unlike PVC in film form systems, since the radiation does not influence significantly their mechanical properties. On the other hand, increase of Ym and decrease of Ea values were found in PVC/OCG specimens as effect of radiation. It should be noted that the results shown in Table 4 reveal a fairly plasticized material due to the low Ym value and consequent high Eb value. The large amount of plasticizer and other additives in the polymer matrix must have influenced the non-significant action of OCG on the mechanical properties of PVC specimens.

4. Conclusions

The oil content in the coffee (*Coffea arabica* L) grounds was calculated to 10%. This oil was added in PVC matrix to form two systems: the PVC/oil films and PVC/oil specimens. The viscosity analyses suggest that oil (0.5 wt%) protected PVC for both forms against radiolysis by Quencher mechanism. The FT-IR analyses showed specific molecular interactions between PVC and oil molecules. The incorporation of coffee ground oil in PVC film influenced directly its mechanical properties. The material in film form has become more plasticized and the gamma irradiation

undergoes less damage in its mechanical properties. On the other hand, great mechanical resistance of PVC specimens was found and no-significant action of oil was found for these systems.

Our results confirmed, which the polymer industry can produce materials with sustainable additives and applications that require resistance to gamma radiation. The pioneering nature of our study opens a fruitful path for new studies that use discards to generate a positive impact on the environment and on polymer science.

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