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Raman characterization of LDPE-g-polyVBC membranes obtained by gamma irradiation simultaneous method

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1. Introduction

The LDPE (Low Density Polyethylene) have been studied because of its importance in industry and other applications [1], such as alkaline membranes in fuel cells [1,2]. Preparation of functional and ionic exchange membranes by grafting copolymerization induced by ionizing radiation (RIG) can be performed using functionalized or not monomers by simultaneous (direct or mutual) and pre irradiation methods. Mutual method besides being more effective, has serious limitation due to high level of homopolymer formation [3]. For both direct or indirect RIG copolymerization of functional monomer into polymers electron beam and gamma radiation have been used [4-8]. According to Nassef [3] degree of grafting (DoG) can be improved to attain specific characteristics. Radiation induced methods can be classified in 6 types based on reaction media: without solvent; with solvent action; emulsion; radical polymerization by atom transfer (ATRP); radical addition fragmentation transfer (RAFT); and by nitroxide. Barsbay et al. [9,10] studied RIG of GMA onto cellulose using RAFT polymerization and Kodama et al. [11] studied RIG of HEMA onto PE/PP nonwoven by RAFT polymerization in order to control DoG and to obtain thin polymer molar weight distribution, so polimeric surface onto base film would be like “brush”.

In order to obtain the best performances in the fuel cells, the process of radiation grafted anion exchange have been studied, tested, and characterized by the RAMAN spectroscopy. It’s importance is because it can develop reliable calibration models, predicting the sample’s physical and chemical properties such as PE and density [12]. With this method, it can be compared multiple different samples of VBC (vinyl benzyl chloride) with different parameters and then see what changed and which one has the best performance. The result of the spectroscopy shows that there’s an increase in then signs of the bands in comparison with the initial sample (VBC). Wang et al. [13] have focused on the study and development of radiation-grafted AEMs (RG-AEMs), which now demonstrate either high performances or high stabilities. They have shown that using low- density polyethylene (LDPE), rather than ETFE, leads to RG-AEMs that are more mechanically robust, such that they can be routinely applied to AEMFCs that are operated at 80 C. In this study, even though samples were prepared using RAFT agents, we will focus in using Raman for characterization of synthesized samples with different DoG.

2. Methodology

LDPE films (Goodfellow, 25 µm) were weighted in analytical balance OHAUSS, Pioneer model. placed inside 4 mL quartz vials with caps in a solution prepared according to modified method used by

Espiritu et al. [14]. Raft agents used were Aldrich Cyanomethyl dodecyl trithiocarbonate and 2-phenyl´2´propyl benzoate. The solution consisted of a mixture (v/v) of toluene (Sigma), 4-VBC (90%, Sigma-Aldrich, without removal of inhibitors) and methanol or ethanol (Exodo), in the proportion of 28:27:45, respectively. Vials containing the solution mixture and LDPE (3 cm X 13 cm) films were irradiated using a Gammacell 220 type irradiator from Atomic Energy of Canada Ltda, Fig. 1. The absorbed doses were 20 and 30 kGy at dose rate of 0.5 kGy h^{-1}.

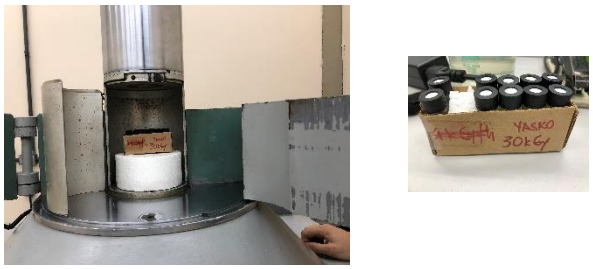

Figure 1: Gammacell 220 irradiation chamber with set of samples inside quartz vials in a cartoon box.

After irradiation, synthesized grafted films were cleaned to remove homopolymers using xylol (PA grade) and acetone (Casa Americana), dried at room temperature. Weight of grafted samples was measured in order to calculate Degree of grafting (DoG) using the Eq. 1:

$$\text{DoG}\ (\%) = \frac{m_G - m_i}{m_i} \times 100 \qquad (1)$$

Raman spectra was obtained using a Raman Horiba XploRA Plus model, 10 s, 5 acquisitions, len 100X, 1800-300cm^{-1}, laser 50 % 785 nm at IPEN.

3. Results and Discussion

Results of measured DoG of prepared samples are presented in Table I .It can be observed that DoG values increased with radiaotn absorbed dose increase. RAFT agent presence in the system affected DoG leading to lower values.

Table I: Degree of grafting of prepared samples using methanol, and ethanol, radiation absorbed doses of 20 kGy and 30 kGy.

Alcohol	**RAFT agent**	**Dose (kGy)**	**DoG (%)**
Methanol	CDB	30	18
Ethanol	CMDTC	20	47
Methanol	-	20	94
Methanol	-	30	181

Raman spectrum of (A) non-grafted LDPE film, and spectra of RIG LDPE-g-poly VBC: (B) Dog 18%, (C) 47%, (D) 94%, (E) 181% and (F) all spectra can be observed in Fig. 2.

According to Sato et al. (2001) [13], absorption at 1460 cm^{-1} and 1439 cm^{-1} can be attributed to anisotropic LDPE CH_2 bending, 1417 cm^{-1} to crystalline CH_2 bending, 1295 cm^{-1} to CH_2 twisting, 1170 cm^{-1} to CH_2 rocking, 1128 cm^{-1} to C-C stretching, 1063 cm^{-1} to C-C stretching and 884 cm^{-1} to C-C stretching of branches. After grafting with VBC, 1612 cm^{-1}, 1266 cm^{-1}, was attributed to VBC by Meek et al. (2020) [1] 837 cm^{-1}, 744 cm^{-1}, 676 cm^{-1}, 638 cm^{-1}. It is possible to observe that 1612 cm^{-1} intensity, attributed to VBC, increases with increasing DoG, Fig. 3.

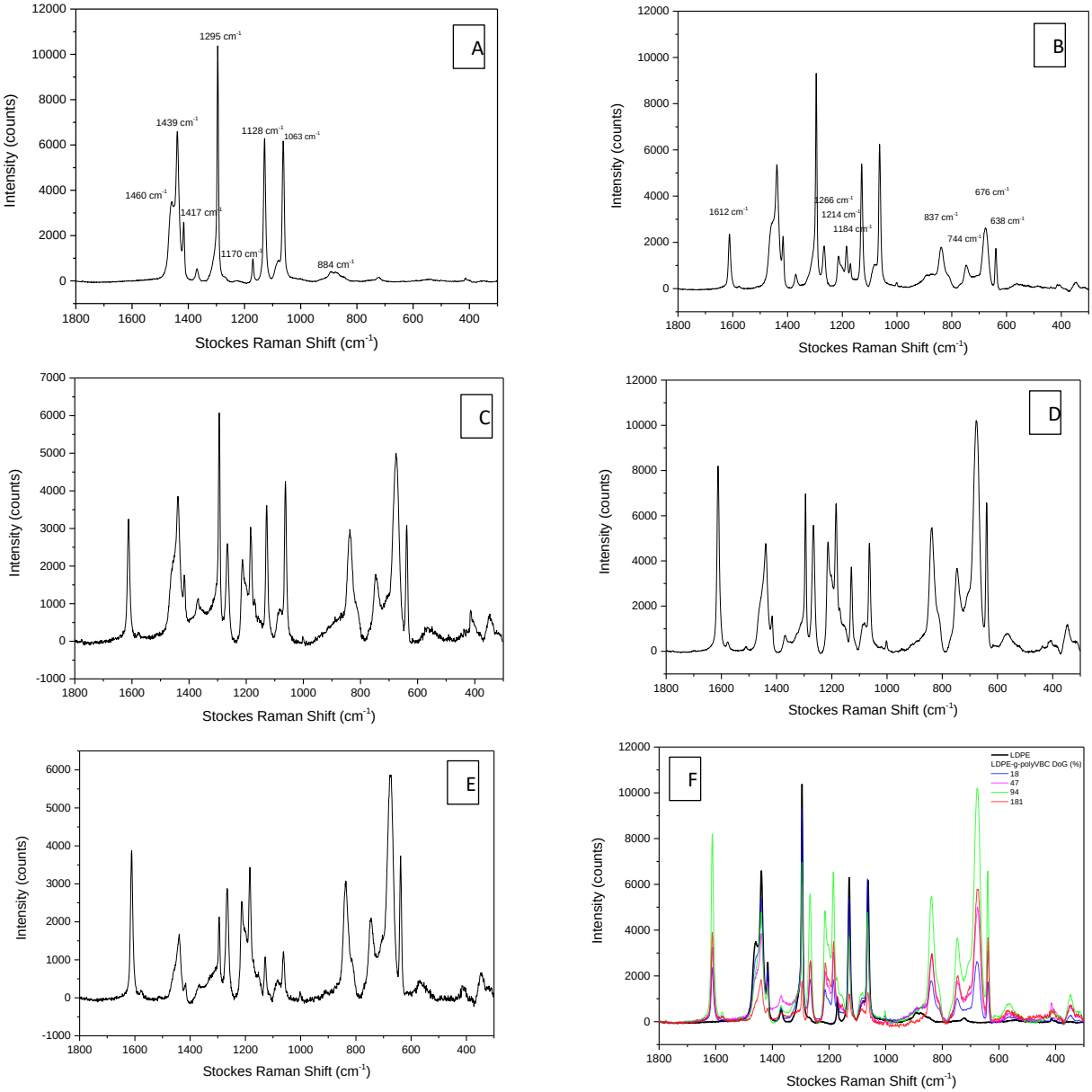

Figure 2: Raman spectrum of non grafted LDPE film, RIG LDPE-g-poly VBC: DoG 18%, 47%, 94%, 181% and all spectra.

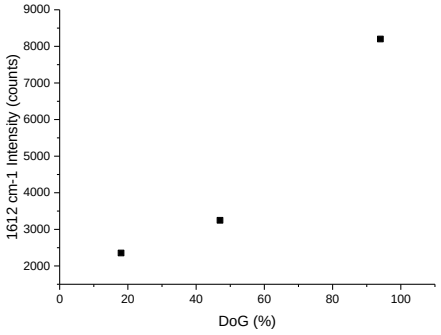

Figure 3: Variation of Normalized intensity (counts) 1612 cm^{-1} Raman shift DoG (%).

4. Conclusions

Mutual method for radiation induced grafting promoted poly VBC copolymerization onto LDPE. Raman microscopy can be used for grafting characterization.

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