Dose Rate Effect on Grafting by Gamma Radiation of DMAEMA onto Flexible PVC

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ABSTRACT

Intravenous tubing, blood bags and catheters stays in contact with blood and body fluids. They are normally made by flexible PVC. The contact of PVC with this fluid is not possible for long periods and there is the necessity of addition of non-thrombogenic substances into blood. This work shows the radiation grafting process to produce copolymer PVC-g-DMAEMA, a new material that allows a future grafting of Heparin on it, and will have the perspective of avoiding undesirable substances additions to blood or body fluid contact. In this preliminary work, only radiation dose rate effect on grafting was studied.

Key words: *grafting, PVC, DMAEMA, gamma radiation*

INTRODUCTION

Flexible Polyvinyl Chloride, PVC, is an important polymer used by medical suppliers as intravenous tubing and bags, catheters, nasogastric tubes, dialysis bags and tubing, blood bags, transfusion tubing and air tubes [1,2]. Some PVC graft copolymers are new materials with inert properties in contact with blood, corporal fluids and food [3]. Dimethyl aminoethyl methacrylic acid, DMAEMA, is a hidrophylic monomer used to change properties of polymeric hydrofobic materials by grafting process [4]. This monomer is easily linked to heparin sodium salt to promote non-trombogenic surfaces, which is desirable for blood contact. The graft copolymer PVC-g-DMAEMA-g-Heparin has been developed last years, in the Institute of Energetic and Nuclear Research (IPEN) [5]. After having interesting conclusions in a doctorate work of such scope, this work will present some of those results and new ones, where dose rate is changed, in order to optimize the process. Grafting degree and infrared spectroscopy were used for characterization of the samples until now.

MATERIALS AND METHODS

More details of the materials and methods are in [5]. Here is shown important aspects of preparation and for preliminary results interpretation, when dose rate was changed (not discussed in [5]).

Preparation of PVC films

The flexible PVC, kindly given by Dacarto Benvic-Solvay, is a compound that contains many additives, most of them not informed by the producer.

Due to the presence of these additives, the solubility of pellets on tetrahydrofuran (THF) and in ciclohexanone was affected. So, it was prepared solutions at many different polymer concentrations in both solvents, in order to determine parameters like solvent evaporation time, film thickness and transparency.

The chosen concentrations were 3% and 5% w/w in tetrahidrofuran and ciclohexanone, respectively. Films of PVC compound (PVC-C) were prepared by slow solvent evaporation, at chosen solutions, in order to obtain homogeneous films and to keep them free from effects like pressure or heat. To the polymer dissolution, PVC-C was weighed and THF was added slowly to prepare the 3 and 5% solutions, respectively. The system was maintained in reflux and constant agitation for 4 hours at 65^{o}C (THF) and 95ºC (ciclo-hexanone). After complete dissolution of the polymer, it was maintained at rest by 15 minutes to eliminate bubbles. Following, the solution was spilled into petri dishes (60 mL), and maintained inside a previously leveled dry chamber, see Figure 1.

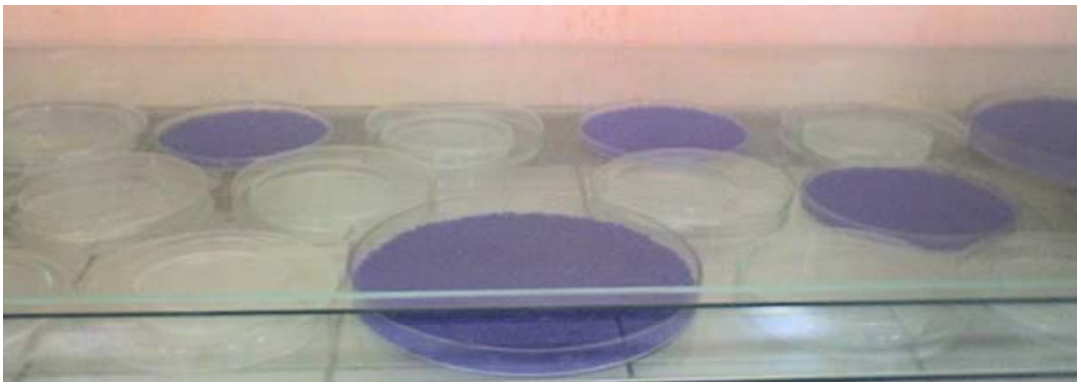

Figure 1 - Dry chamber used to prepare PVC-C films by slow solvent evaporation. In blue it is seen the silica-gel dishes.

This dry chamber is a closed glass chamber that was maintained leveled and with an excess of silica-gel inside it. Nitrogen was used to create an inert atmosphere in contact with the films surface.

The complete drying process occurred after 10 to 15 days. After that, films were washed by neutral soap and rinsed into current water. After, a new rinsing process was made with ethanol and dried in a vacuum stove at 60^{o}C until mass constant, to guaranty that it was removed any solvent residues inside polymer matrix. So, the films are cut in pieces of 20x20mm and selected by thickness homogeneity (from 0,17 to 0,23mm), using a micrometer for measurements at four points in each film.

Gamma Irradiation / Grafting

It was used a ^{60}Co gamma irradiator “Gammacell” model 220, always at 5 kGy and variable dose rates of 2,5; 1,25; 0,75 and 0,25 kGy/h. Film samples (20x20mm) were immersed in a glass vessels containing 7mL of DMAEMA (dimethilaminoethil metacrilate)

watery solution (30% w/w). Nitrogen gas bubbles during 5 minutes before the sealing, to purge Oxygen. The sealed vessels waited 24 hours before radiation session, to promote film swelling.

After irradiation, PVC-g-DMAEMA films were washed in current water to remove homopolymer and solution residues. Following, films were identified and maintained at 37^{o}C in a stirred bath for 12 hours. Following, films were maintained at rest by 12 h. After this, the samples were washed with neutral soap and current water, following a rinsing process with distilled water and a new rinsing process with methanol. Methanol excess was removed with an absorbent paper and a session of 4h and 37^{o}C on a vacuum stove.

Degree of grafting (%G)

Degree of grafting was determined by gravimetry. Films were weighed before (Wo) and after the grafting process (W) and applied the following equation [6]:

$$\%G = \frac{W - W_0}{W_0} \qquad (2)$$

Every essay happened in duplicate, and the mean value was used.

RESULTS AND DISCUSSION

It was determined some new experimental parameters to the film production, different from [5], due to different PVC and other reagents and products suppliers. Infrared spectroscopy (FTIR) and gravimetry before and after grafting process were done until now, but other characterization processes will be added to.

Beside other parameters, the grafting of PVC is affected by film thickness, concentration and kind of monomer, dose and dose rate of gamma radiation. The optimized parameter achieved by Panzarini at [5] were dose at 5 kGy and, for monomer DMAEMA, concentration at 30%, so these values were not questioned and they were used in every assay. It was evaluated the effect of dose rate, always on simultaneous radiation grafting process, that was proved by [1] that do not affect the monomer molecule.

By results observed in Figure 2, it is possible to see that dose rate affects considerably the grafting degree (%G). The dose rate of 1,25 kGy/h promotes the mainly increasing of grafting, achieving 28,9% ±0,7%. Higher dose rates cause a decreasing in the degree of grafting.

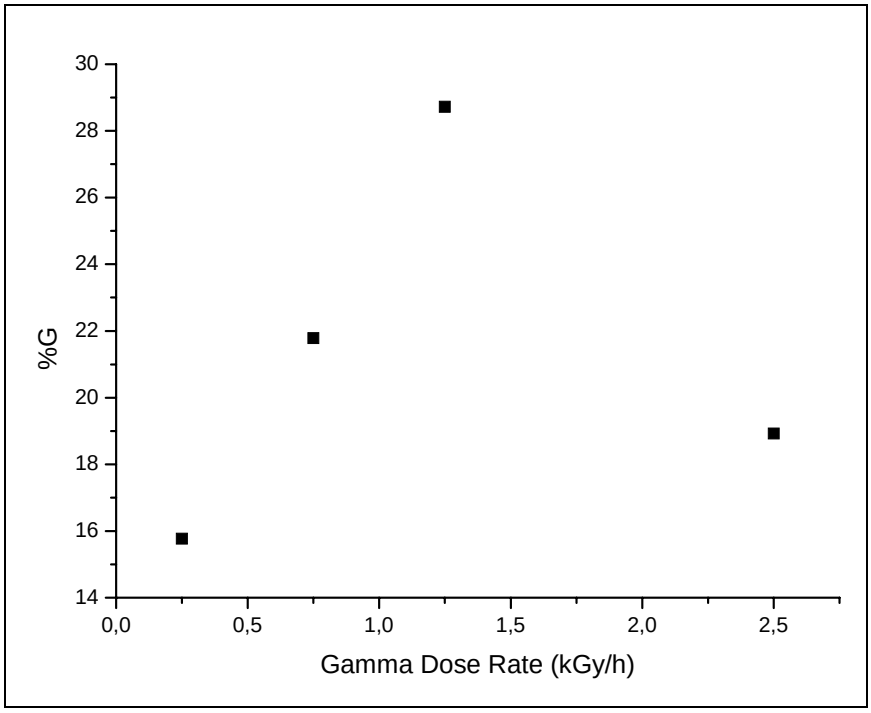

Figure 2 – Dose rate effects in the grafting degree, %G, of the PVC-g-DMAEMA films.

It should be noticed that higher degree of grafting do not means that the material will be more suitable to heparin grafting or the final product will have the desire anti-thrombogenic properties.

To identify the presence or not of the chemical functional groups, due to polymer changes promoted by gamma irradiation, PVC and copolymeric films was analysed by FTIR spectroscopy.

The residue of the PVC films extracted with ether was analysed by FTIR, as can be seen in Figure 3, and the absorption bands are compatible with that ones observed for DEHP, as described in the literature [7]. The most prominent peak is at 1722 cm^{-1}.

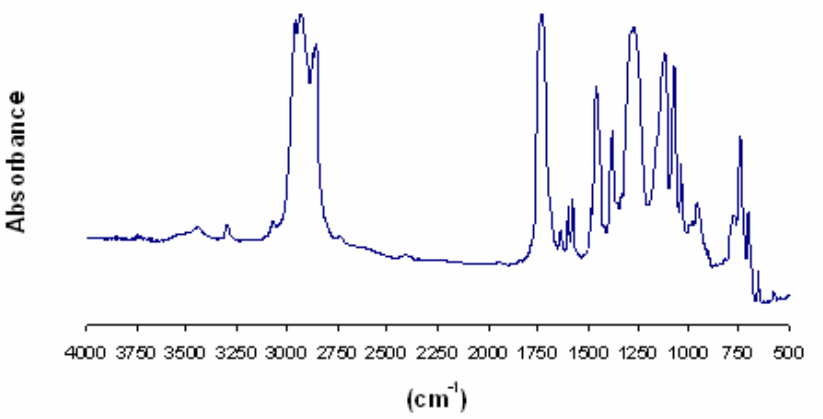

Figure 3 - Absorbance FTIR spectrum of residue of PVC after ether extraction.

The transmittance FTIR spectrum of the PVC and those of the grafted copolymeric films are presented in Figure 4.

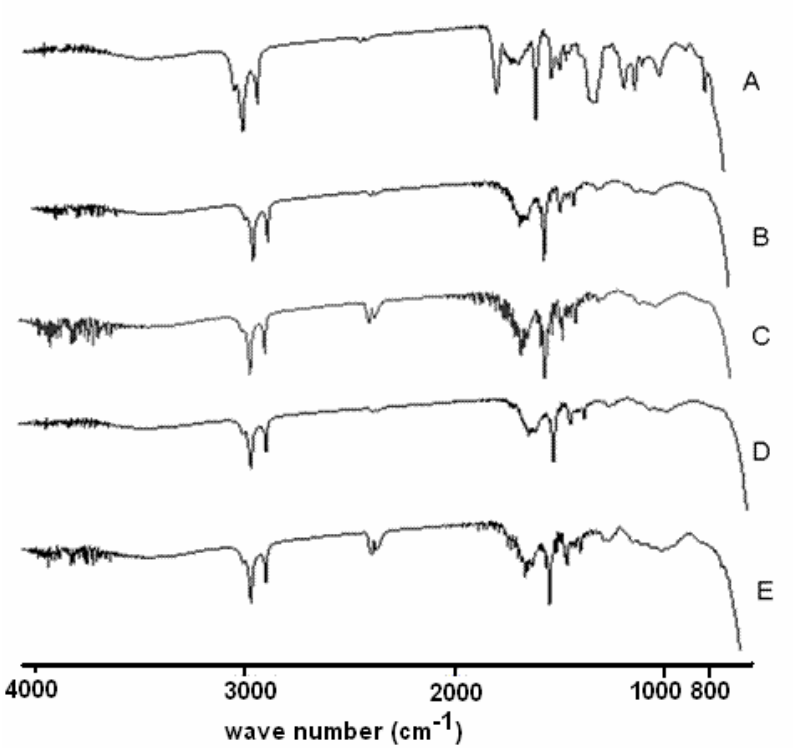

Figure 4 - Preliminary Spectra of FTIR-ATR: (A) Commercial PVC film gamma irradiated; (B) PVC-g-DMAEMA (Dose rate of 0,25 kGy/h); (C) PVC-g-DMAEMA (0,75 kGy/h); (D) PVC-g-DMAEMA (1,25 kGy/h); (E) PVC-g-DMAEMA (2,50 kGy/h).

It is strange that carbonyl absorption bands in 1722cm^{-1} was not observed in the grafted copolymeric films. This fact is been investigated, but there is suspicion that changes in thickness of the films cause this absence. It could be necessary special preparation for future FTIR analysis.

In Figure 5 is shown the thickness variation due to dose rate changes.

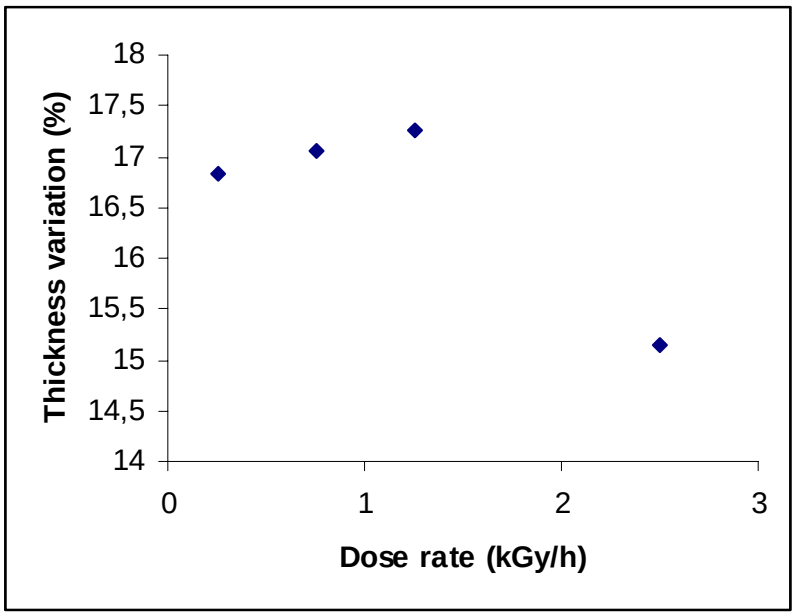

Figure 5 – Changes in the film thickness as a function of irradiation dose rate.

It seems that small radiation dose rates (more slow radiation session) permits a kind of increase on swelling of the samples and more internal (bulk) grafting. Morphological analysis, like MEV, will help us in this evaluation.

When FTIR spectrum of the copolymeric films obtained at different dose rates were superposed, see Figure 6, no difference were observed in the characteristic absorption bands.

It could be an indication that no changes in chemical functional groups were promoted when dose rate is changed. More essays are going on to confirm or not this assertion. The FTIR analysis could be useful for quantifications, not only identifications, of the grafted samples, and this possibility is been studied.

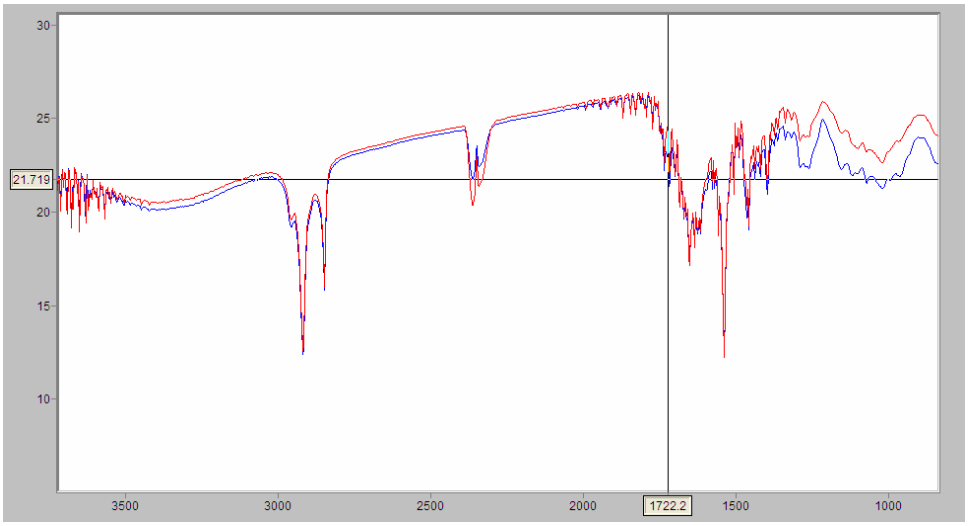

Figure 6 - Superposition of two preliminary FTIR spectra of PVC-g-DMAEMA samples, gamma irradiated at 0,25kGy/h (—)and 0,75kGy/h (—).

CONCLUSIONS

It was shown many aspects on the preparation of PVC films and theirs radiation grafting process with DMAEMA monomer.

The grafting degree of DMAEMA in PVC thin films is affected by dose rates, when it was simultaneously gamma irradiated at 5kGy.

The thickness of the films was changed by the dose rate, although no changes in the characteristic FTIR spectra were observed. Dose rate variation could promote some superficial or bulk changes in the copolymeric films, which will be following characterized by scanning electron microscopy.

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