

MECHANICAL BEHAVIOR OF STYRENE GRAFTED PVC FILMS BY ELECTRON BEAM IRRADIATION

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ABSTRACT

The polyvinyl chloride (PVC) is a technological and low cost polymer, however it presents high sensitivity to high energy irradiation because of the weakness of carbon-chloride bond face to carbon-carbon and carbon-hydrogen bonds. Grafting is a type of co-polymerization process that can allow it an increase of mechanical characteristics. The aim of this work is to evaluate the mechanical properties of styrene grafted PVC by electron beam irradiation using mutual and pre-irradiation methods to verify the mechanical resistance changes of obtained product whether grafting process is applied from non-irradiated or from pre-irradiated substrates. The irradiation procedures were performed in atmosphere air or inert atmosphere and the irradiation conditions comprised doses from 10 kGy to 100 kGy and dose rates of 2.2 kGy/s and 22.4 kGy/s. The styrene grafted samples were analyzed by gravimetry to determinate the grafting yield; the final values have been averaged from a series of three measurements. The Mid-A TR-FTIR was the spectrophotometer technique used for qualitative/semi-quantitative analysis of grafted samples. The Young's module and tensile strength of pre-irradiated and grafted PVC samples at both methods were measured at a Lloyd LXR tensile tester at a cross-head speed of 10.00 mm/min. We observed the decrease of Young's module and tensile strength with the increase of absorbed dose at pre-irradiated PVC samples. These mechanical parameters results are discussed.

1. INTRODUCTION

PVC is a low cost polymer for which the synthesizing process and characteristics are well known; these facts make PVC the most widely used commodity throughout the world [1]. Thus, polymer modification processes which can be applied onto PVC substrates have an important appeal because of the requisites to combine special required physical and chemical properties using this simple and cheap material.

The polymer modification by co-polymerization is a traditional process to generate materials with distinct characteristics. The grafting co-polymerization process is known since mid-20th century [2]. The graft co-polymers have chemically different polymer segments combined within the molecule of polymer substrate.

This modification process may happen through many ways. For the chemical process, one of the mechanisms is the nucleophilic substitution, which is considered by a number of authors as an appropriate method for improving the polymer's thermal stability (through the replacement of labile chlorine atoms) and its mechanical properties [3-6]; in this case, the utilization of azides and dithiocarbamates is necessary [7,8]. In a solution of polar aprotic solvents, these nucleophilic anions are strongly reactive to the chlorine of the PVC backbone, thus leading to the formation of macro initiators in the substrate chain [7,9]. These reagents must be carefully handled because of their hazardness [12,13].

On the other hand, irradiation also has become popular as it is faster, simpler and it does not require chemical reagents, which often are hazardous to the human health and to the environment. The grafting process with high energy ionizing radiation accounts for homolytic bond scission of molecules and release of free radicals [10]. Irradiation grafting can occur by the following methods: pre-oxidation, pre-irradiation and mutual irradiation [11].

In pre-oxidation, the polymeric material is first irradiated under atmospheric air or an oxygen flux; the grafting on the irradiated substrate is achieved by its subsequent treatment with the monomer under high temperatures. The peroxides on polymeric substrate thus decompose themselves to generate radicals which initiate the grafting process. Pre-irradiation, like per-oxidation, also occurs in two steps; however, it is carried under vacuum or an inert gas; the hydrogen and chlorine radicals are formed and active radical sites become present in substrate backbone; the grafting then happens in the same way, but now within the vacuum/inert gas system. Some authors do not make distinction between the former and later on the particularities of both methods [14-16]; also, the expression per-irradiation is also applied when per-oxidation is used.

In mutual irradiation technique, the polymer and the monomer are irradiated simultaneously, and free radicals are formed with subsequent generation of monomer-substrate chemical bonds [17]. Differently from the ionizing irradiation methods above, this is a one-step process and it is faster than pre-irradiation methods. It also leads to low chain scission levels, which as an advantage, should the final product requires adequate mechanical properties.

The aim of this work is to evaluate the mechanical properties of styrene grafted PVC by electron beam irradiation using both mutual and pre-irradiation methods to verify the mechanical resistance changes of obtained product when grafting process is applied from non-irradiated and from pre-irradiated substrates. The pre-irradiation method was carried under atmospheric air (per oxidation) and the grafting process in PVC substrate was verified by gravimetry and infrared spectrophotometry.

2. EXPERIMENTAL

The mutual and pre-irradiation grafting was performed with a Job 188 Dynamitron® Electron Beam Accelerator with 1.5 MeV energy. Beam current was 25 mA, beam power was 37.5 kW; the scan range was 50 to 120 cm. Absorbed doses ranged from 10 kGy to 100 kGy and dose rates of 2.2 kGy/s and 22.4 kGy/s, for the given irradiation conditions. The polymer substrate used was a PVC commercial film (Vulcan) with thickness of 210 μ m.

For uni-axial tensile tests, dumbbell shaped ASTM D882-10 polymer samples were cut with dimensions 4 mm(W) x 27 mm(L) with a standard molded razor before irradiation. These samples were washed in analytic grade ethanol, dried at room temperature and weighted. The monomer used for grafting was commercial grade styrene pre-treated by inhibitor removal with molecular sieves. The grafting media for both irradiation methods was 1:1 styrene/butanol-1 mixture. The mutual grafting was performed under atmospheric air. The grafting on pre-irradiated PVC samples was performed at 323 K under thermostatic bath and

nitrogen flux; total time for this grafting process was 4 hours. The treatment of post-irradiation (for mutual grafted samples) and of post-grafting (for pre-irradiated grafting samples) was homo-polymer extraction by toluene immersion, followed by ethanol washing.

Mechanical tests at pre-irradiated (peroxidized only) and at grafted PVC samples by both methods were evaluated at room temperature on a universal Lloyd LXR tensile testing machine, with control of longitudinal strains in the active zones of samples. The tensile force was measured with a standard load cell. The engineering stress was determined as the ratio of the axial force to the cross-sectional area of specimens in the stress-free state. The elongation rate for all essays was 10.00 mm/min.

The styrene grafted samples were analyzed by gravimetry to determinate the grafting yield; final values have been averaged from a series of five measurements. Mid-AT R-FTIR spectrophotometry was used for qualitative/semi-quantitative styrene analysis; the spectra was acquired in a Perkin-Elmer FTIR spectrophotometer model spectrum 100 by transmission method.

3. RESULTS AND DISCUSSION

The prominent feature of radiation-grafted membranes is their low synthesis cost, since it just takes commercial-grade PVC film to be accomplished. The inevitable drawbacks are a lack of precise information about film specification and possible sample deviation. Thus, commercial reference film must be carefully used.

Now, interesting observations can be made from the styrene grafting reaction yield; this is shown in Fig. 1. When mutual grafting method is applied to styrene grafting onto PVC commercial film, the degree of grafting increases proportionally to the absorbed dose. This result is in agreement with the bibliography [14-16]: high values of absorbed dose provide high percentage of monomer grafting onto polymeric substrates. Particularly, these results are related to absorbed doses supplied under low dose rate; at a high dose rate (22.4 kGy/s), weight loss is observed by 70 kGy and low percentages of styrene grafting at 100 kGy. The application of monomer grafting by pre-irradiation method resulted in sample weight loss for all PVC pre-irradiated samples (from 10 kGy to 100 kGy), with the same loss ratio: about 17 % at 22.4 kGy/s and about 12 % at 2.2 kGy/s. This behavior is neither time nor absorbed dose dependent.

These results suggest that grafting by pre-irradiation method often leads to sample degradation when compared to mutual grafting at low dose rates. The dose rate effect is evident: the grafting reaction happens mostly under low reaction time constant; in high reaction time constants, the substrate degradation is outstanding.

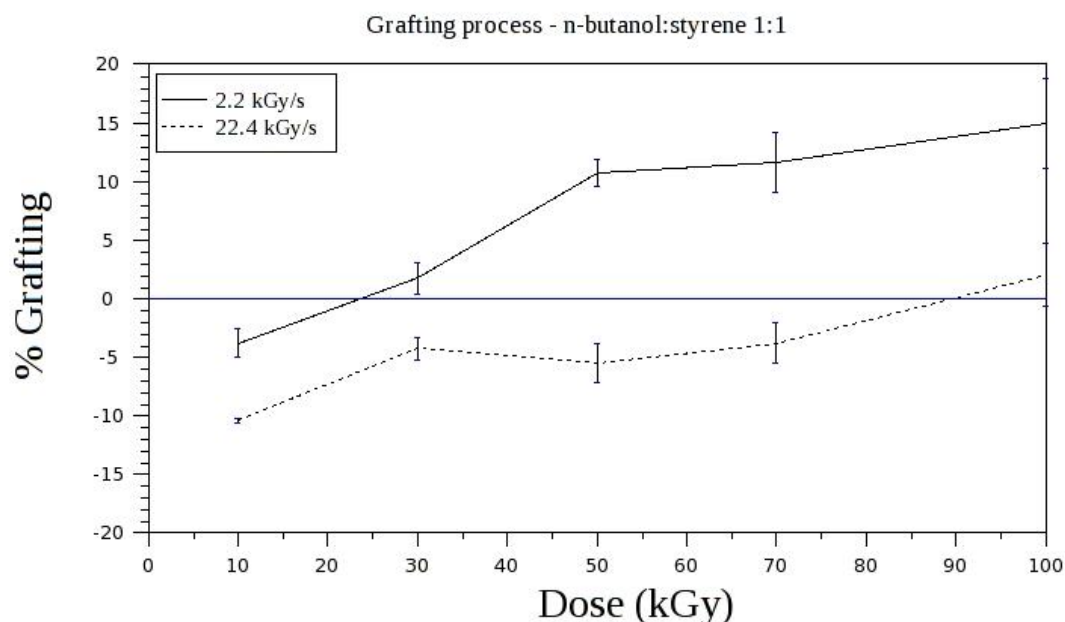


Figure 1. Degree of grafting of styrene grafted onto PVC samples. Results obtained at 2.2 kGy/s and 22.4 kGy/s.

The Mid-FTIR spectrophotometric analysis shows that pre-irradiated PVC samples oxidize under the applied experimental conditions; this is evidenced by the broadening of the 3400-3410 cm^{-1} absorption band (Fig. 2). As a remark of semi-quantitative aspect, the broadening of this mentioned region is wider in the spectra of low dose rate irradiated samples than in the high dose rate ones. This result suggests the oxidation is more effective under low dose rates and this observation is in agreement with the bibliography [17-19].

Mutual styrene grafted samples show typical styrene absorption bands (Fig. 3): the 540 cm^{-1} band regards planar vibrations of C-H bond in aromatic ring; the 750 cm^{-1} band regards the out of plane bending of H-bond in aromatic ring; the 1494 cm^{-1} band regards the plane deformation of C=C bond at styrene backbone; the set of absorption bands at 1800 cm^{-1} , 1870 cm^{-1} and 1940 cm^{-1} regard C-C bond deformation; they indicate the presence of styrene in mono-substituted styrene aromatic ring. The absorption bands at 620 cm^{-1} , 690 cm^{-1} and 1255 cm^{-1} are typical of PVC absorption bands.

Fig. 4 shows the spectra of styrene grafting onto PVC pre-irradiated samples; these spectra show the same absorption bands evidenced at Fig. 3. These results suggest that styrene is grafted onto polymeric substrate; however, the quantitative aspects are compromised and the only evidence is the low intensity of these typical styrene absorption bands.

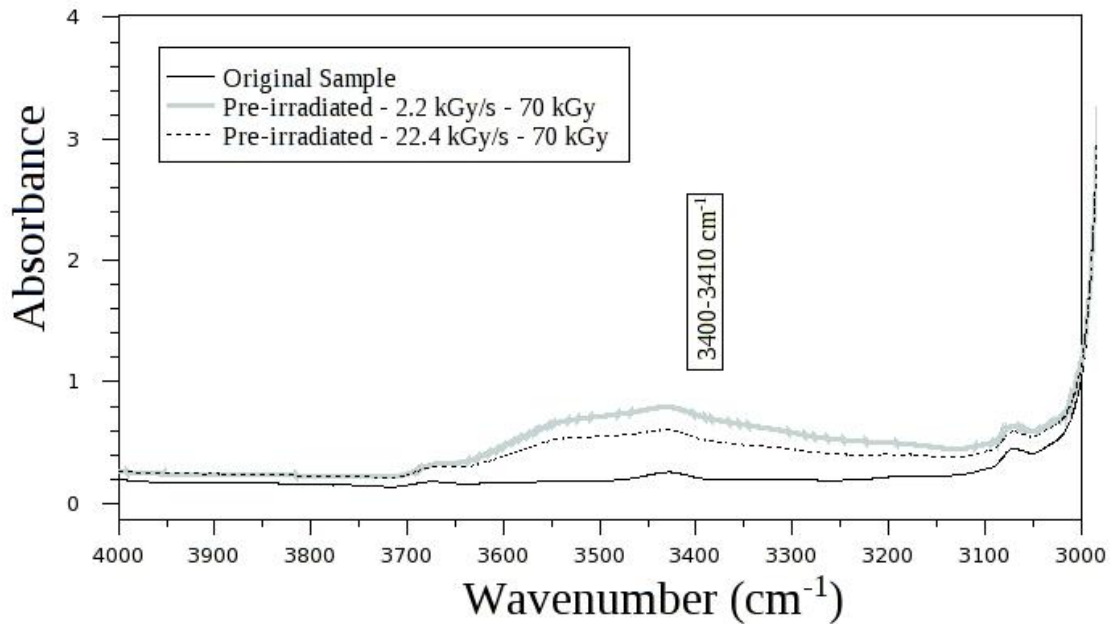


Figure 2. Mid-FTIR spectra of pre-irradiated PVC samples at 2.2 kGy/s and 22.4 kGy/s.

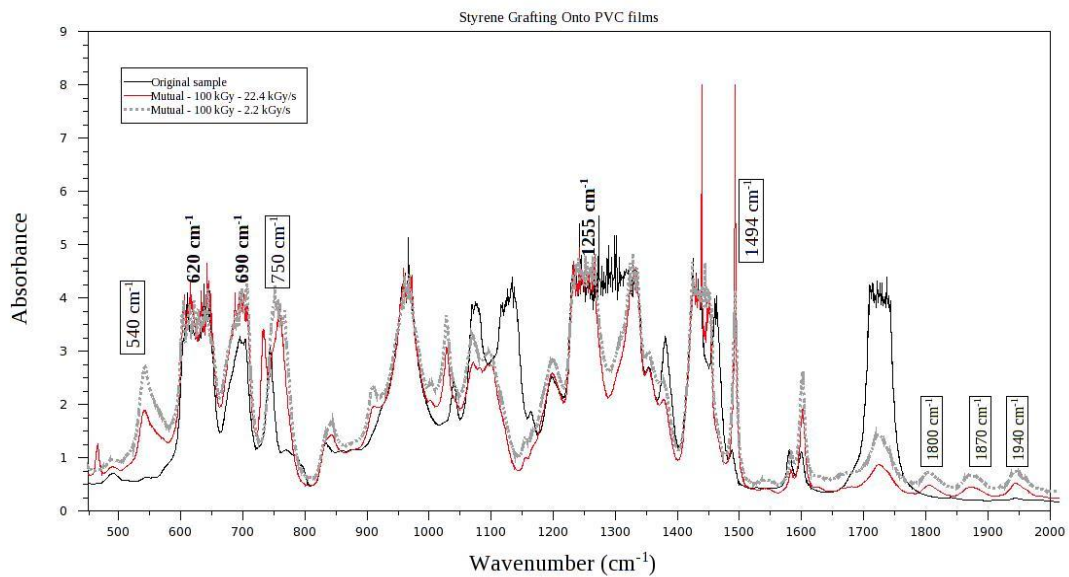


Figure 3. Mid-FTIR spectra of mutual styrene grafting PVC samples at 2.2 kGy/s and 22.4 kGy/s.

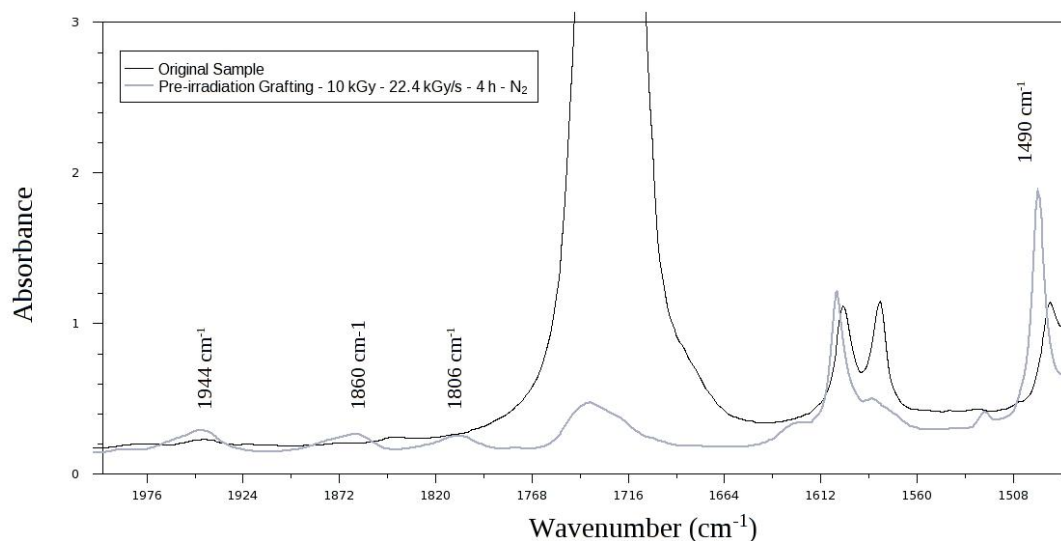


Figure 4. Mid-FTIR spectra of styrene grafting of PVC pre-irradiated samples at 2.2 kGy/s and 22.4 kGy/s.

Finally, the mechanical analysis of these irradiated materials shows that each kind of modified material has specific characteristics.

In Fig. 5, it was observed an increase of Young's module (elasticity module) of pre-irradiated samples with increase of absorbed dose; this is more evident at low dose rates. For grafted samples at 2.2 kGy/s, the pre-irradiated samples always have higher values of this mechanical parameter compared to original samples. However, styrene-mutual grafted samples at dose rates about 22.4 kGy/s present lower module values compared to original sample and the value for this parameter increases again only at 100 kGy. The grafting process applied to pre-irradiated PVC samples shows the highest values of the elasticity module at 10 kGy, but the value of this parameter decreases at 50 kGy and it increases again at 70 kGy.

These results suggest the grafted samples present high stiffness compared to original sample. This behavior is expected in this case once polystyrene has high degree of crystallinity and low T_g . Additional informations between mechanical properties (macroscopical effect) and molecular arrangements at grafted PVC must be investigated by other analytical techniques [20]. At high dose rates, the degradation process concurs to the monomer grafting and it results in low stiffness samples compared to the grafted samples obtained at low dose rates.

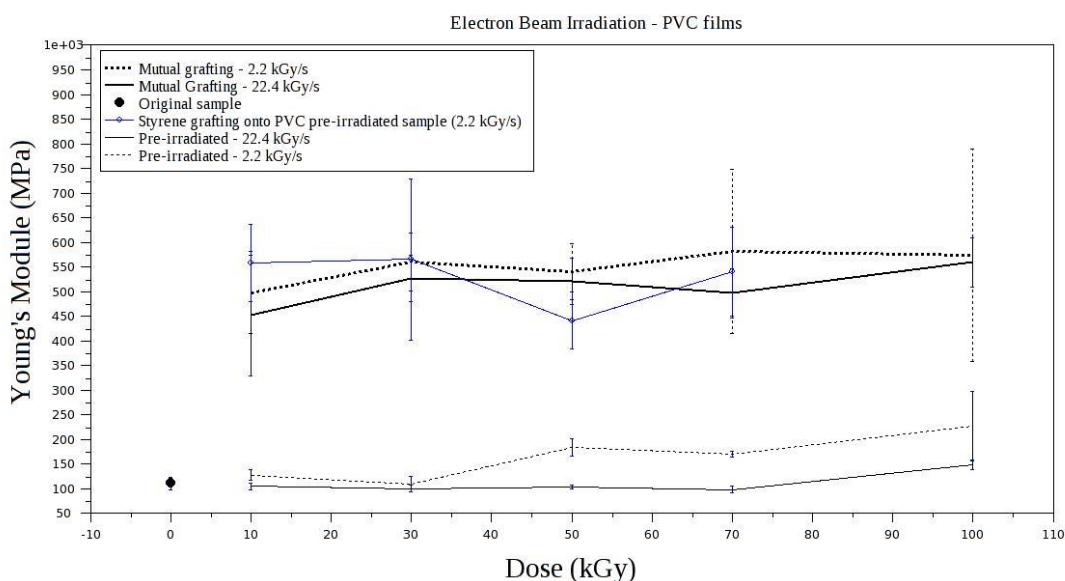


Figure 5. Young's module of pre-irradiated PVC, mutual grafted and pre-irradiated samples at 2.2 kGy/s and 22.4 kGy/s.

The high Young's module presented by pre-irradiated samples at the low dose rate is related to the peroxides and hydro-peroxides formed at substrate. These chemical species can allow some inter-molecular bond formation and the macroscopic effect is the increase of mechanical strength of the sample; at the high dose rate the degradation process - which includes chain scissions - is dominant and the decrease of modulus values are observed.

The tensile strength is higher only at 50 kGy/2.2 kGy/s and at 100 kGy for both dose rates on pre-irradiated samples compared to original sample (Fig. 6). These results show the increase of mechanical strength and this macroscopic effect can be related to a cross-linking process in these conditions.

The styrene mutual grafted samples present high values of tensile strength when grafting process occur at low dose rates and it suggests the modification process under this conditions increase the mechanical strength; however, the value of this parameter decreases at 100 kGy due the degradation process from irradiation condition and from oxygen presence.

At high dose rates, the tensile strength is maximum at 100 kGy and it suggests the low reaction time constant promotes the styrene grafting without damage the final product.

The lower values of tensile strength for styrene grafting onto PVC pre-irradiated samples, compared to those presented for styrene mutual grafted samples may be related to the main process, degradation, which prevents the grafting process.

The Fig. 7 shows the "strain maximum" behavior (as indicated by the Lloyd LXR instrument) of PVC irradiated samples. The grafted samples (mutual grafting at high dose rate and grafting onto pre-irradiated samples) do not present elongation or deformation; the samples just collapse when submitted to a "stress maximum" (again as indicated by Lloyd LXR).

The samples irradiated at 10 kGy and 70 kGy by mutual grafting with low dose rate presented great percentage of strain maximum. This is an interesting result because mainly at 70 kGy the samples presented a good level (about 10 %), these samples have an adequate level of elasticity module and tensile strength and additionally they can be elongated at an adequate value.

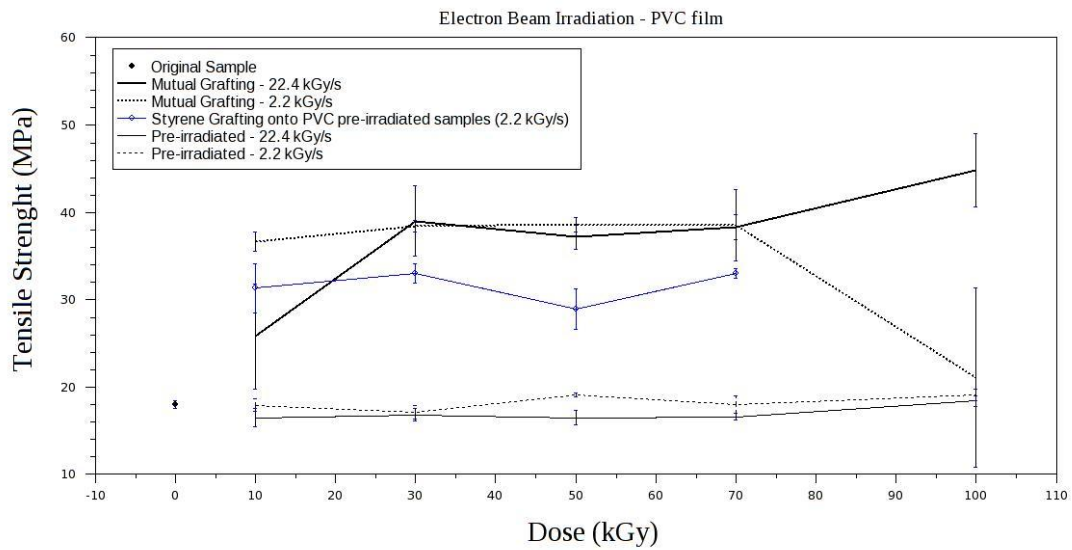


Figure 6. Tensile strength of pre-irradiated PVC, mutual grafted and pre-irradiated samples at 2.2 kGy/s and 22.4 kGy/s.

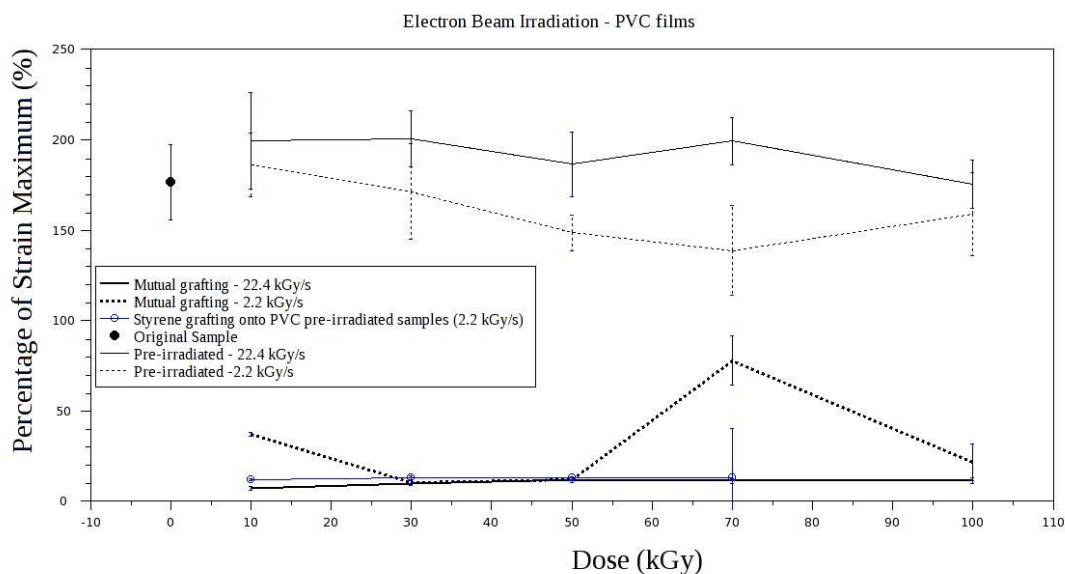


Figure 7. Percentage of strain maximum of pre-irradiated PVC, mutual grafted and pre-irradiated samples at 2.2 kGy/s and 22.4 kGy/s.

Analyzing the pre-irradiated samples, one can observe the effect of cross-linking under low dose rate conditions, where the elongation/deformation decrease with increasing absorbed dose values. At high dose rate conditions, the pre-irradiated films have high percentage of strain maximum compared to the original sample and it can be related to chain scissions process that characterize degradation.

4. CONCLUSIONS

In this work, the PVC samples were grafted with two methodologies: mutual and pre-irradiation grafting. The grafting onto pre-irradiated samples is an inadequate method to be applied to PVC substrates since degradation is the main active process. Mutual grafting at low dose rate is the process where grafting is achieved in adequate levels; moreover, this process does not degrade the mechanical characteristics of the modified material. The presented results encourage to obtain this new material by new tests with other grafting solutions to enhance its mechanical properties.

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