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Effect of Gamma Irradiation on the Crystalline Structure of Poly(Vinylidene Fluoride)

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***Abstract*—**The irradiation of polymeric materials has received much attention because it can produce diverse changes in chemical structure and physical properties. Thus, studying the chemical and structural changes of polymers is important in practice to achieve optimal conditions for the modification of polymers. The effect of gamma irradiation on the crystalline structure of poly(vinylidene fluoride) (PVDF) has been investigated using differential scanning calorimetry (DSC) and X-ray diffraction techniques (XRD). Gamma irradiation was carried out in atmosphere air with doses between 100 kGy at 3,000 kGy with a Co-60 source. In the melting thermogram of the samples irradiated can be seen a bimodal melting endotherm is detected with two melting temperature. The lower melting temperature is attributed to melting of crystals originally present and the higher melting peak due to melting of crystals reorganized upon heat treatment. These results are consistent with those obtained by XRD technique showing increasing crystallinity with increasing irradiation dose, although the melting latent heat is decreasing.

***Keywords*—**Differential scanning calorimetry, gamma irradiation, PVDF, X-ray diffraction technique.

I. Introduction

FLUOROPOLYMERS have become important commercial materials for industry because of their physicochemical properties, which enable them to meet a variety of severe requirements present by modern engineering [1]. Among them, poly(vinylidene fluoride) (PVDF) $–(CF_2–CH_2)_n–$ has attracted considerable attention in many areas of research and industrial use. This is due to its electrical properties, resistance to weathering, durability, biocompatility, and processibility [2]. PVDF exist in at least four different crystalline phases: phase I (β form), phase II (α form), phase III (γ form) and phase IV (δ form). Two of these stable crystalline forms have been well characterized. Phase I has a planar zigzag chain conformation, producing a polar crystal, and is the most important of the PVDF polymorphs. Phase II is the most common polymorph of PVDF, with TGTG' chain conformation, producing a nonpolar crystal [3]. Fig. 1 shows PVDF different crystalline phases.

Irradiation by ionizing radiation has been found to induce changes in the chemical structure and physical properties of polymers. Such changes may be in the form of crosslinking, main chain session, or evolution of hydrogen depending upon the radiation [2].

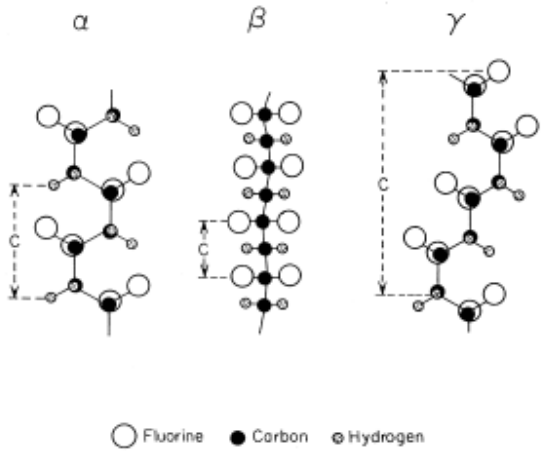


Fig. 1 Atomic arrangements of PVDF α-, β - and γ-phases [4]

The present word differential scanning calorimetry (DSC) and X-ray diffraction techniques (XRD) were used to investigate multiple melting behavior of PVDF after gamma irradiation. This behavior is generally referred to as dual endothermic melting behavior, and since it has been reported for other semicrystalline polymers [5].

Five different models have been put forward to explain the annealing peak: (1) different crystal morphologies; (2) different populations of crystalline sizes (primary crystallization forms larger crystalline lamellae compared to the lamellae formed during secondary crystallization); (3) more or less perfect crystals (a second, less perfect "pseudo-crystalline" phase is induced on annealing); (4) crystal perfecting by melting and recrystallization (to morphological changes in the microstructure of the semicrystalline samples during the DSC scan) and (5) three – phase model (the crystalline/amorphous interface is considered to be a "rigid amorphous" phase) [6]. The model more fit with the experimental results considers that the formation of "pseudo – crystalline" phase explains our result best.

II. Experimental

PVDF homopolymers were supplied by ATOCHEM (France). The film samples were produced by melting at 200°C under 300 bar, with subsequent air-cooling to room temperature. This process produced transparent films of about 160 μm. The samples were irradiated with a Co-60 source in

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the Gamma Beam-127 irradiator at Centro de Desenvolvimento da Tecnologia Nuclear (CDTN) at constant dose rate (12.0 kGy/h), with doses ranging from 0.1 to 3000.0 kGy. Thermal behavior studies were made using a DSC TA Q10, with heating and cooling rates of 10ºC/min, in the second run, from 25 to 180ºC. The equipment was calibrated using an Indium sample (T_M = 156.6ºC) and the measurements were taken with samples weighting around 10 mg, using an aluminum crucible.

Structural characterization was made using X – ray diffractometry Shimadzu XRD – 7000 Maxima –X. All measurements were taken immediately after the irradiation process.

III. Results and Discussion

DSC was used to examine the change in the melting transitions of PVDF films and also variation in the heat of fusion before and after γ-irradiation. Fig. 1 shows DSC scans of the melting transitions of unirradiated and irradiated (250, 1000 and 3000 kGy) PVDF films. It can be shown that melting temperature (T_M) of PVDF film decreases from 160ºC to 110ºC with increasing irradiation dose.

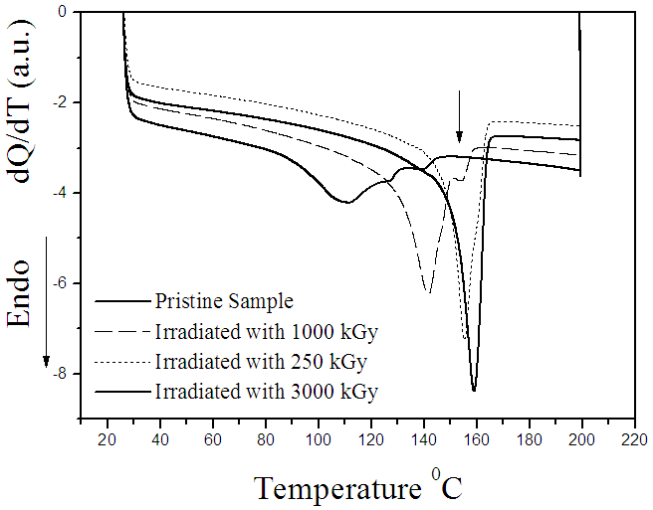


Fig. 2 2nd heating cycle thermograms for pristine PVDF and samples exposed of gamma radiation

This decrease shows that the damage caused by radiation in the polymer chain facilitate the crystalline melt, which melts at lower temperatures. An interesting anomaly is observed in these curves, where we see the appearing of additional smaller endothermic peaks in the higher temperature side of the main melting peak which can been see in Table I. Also, there is a remarkable decrease in the melting latent heat ranging from 46 J/kg (pristine sample) to 26 J/kg (3,000 kGy), which is proportional to the area under the peak, confirming the decrease in the crystalline fraction. In Fig. 3 observed decrease of the heat latent of crystalline phase with the radiation dose increased. This decrease is shown in Fig. 3 loss of crystalline order caused by the interaction of radiation with the polymer chain.

TABLE I
The Crystallinity of Annealed Poly(Vinylidene Fluoride) for Different Annealing Temperatures

Irradiation Dose (kGy)	Melting temperatures (ºC) Higher peak	Lower peak
Pristine	160	-
250	155	160
500	149	157
750	144	155
1000	141	154
3000	110	126

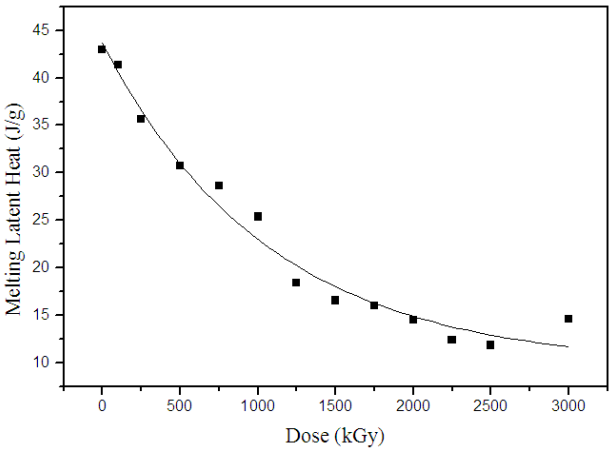


Fig. 3 Plot of the Melting Latent Heat (obtained from the DSC curves) as a function of the delivered gamma dose, for the homopolymer PVDF

Other authors irradiated PVDF samples with different types of radiation also reported the appearance a bimodal melting endotherm with two melting temperatures [2], [3], [7], [8]. However, that when used corpuscular radiation, such as electrons and protons; the second peak appears at temperatures below the main peak [2], [7]. In the other hand, researches with electromagnetic radiation (X-rays and gamma radiation) resulted in the appearance of crystalline melting peaks at temperatures higher than the main peak [3], [8]. This seems to indicate that different types of radiation induce different radio-degradation processes in the polymer structure. In the fact, models have been put forward to explain the annealing peak, which considers the different populations of crystallites sizes (2) refers the formation of the secondary crystallization, wherein the secondary formed lamellae melt first at lower temperatures and give rise to the extra melting endothermic in the DSC scans [6]. In the other hand, in the model considering the presence of the more and less perfect crystals (3), the phase melts just above the annealing temperature at which it was formed.

Primary crystallization results in the formation of spherulites comprised of primary lamellar stacks. Secondary crystallization which comprises thinner lamellae than the primary lamellar stacks (Fig. 4).

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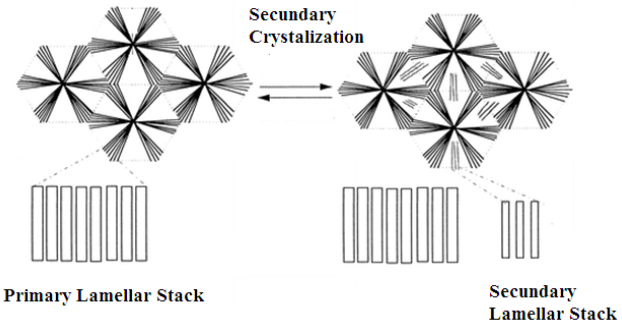


Fig. 4 Model for the morphological changes that occurs during crystallization and subsequent melting [5]

We remark that PVDF homopolymer is basically constructed sandwiching several alternated lamellas of amorphous and crystalline regions. Particularly, when the radiation damages are located in the crystalline lamellae, they are considered as crystalline defects, which in turn are removed to the amorphous phase by the increase of the chain fold [1]. This phenomenon results in a decrease of the original crystalline volume and in the appearing of a second crystalline region full of defects, between the original one and the amorphous phase. We think that the additional peaks observed in Fig. 2 may be related to this phenomenon and is represented in Fig. 5 on what the "annealing peak" results from the relaxation of the "pseudo-crystalline" phase.

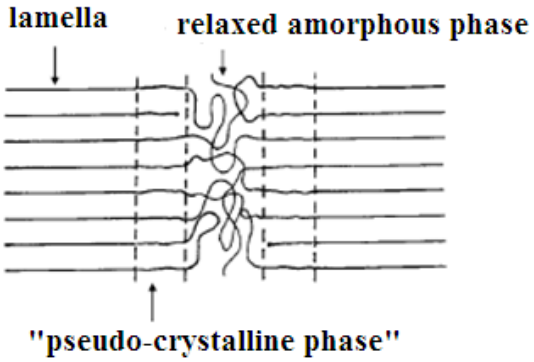
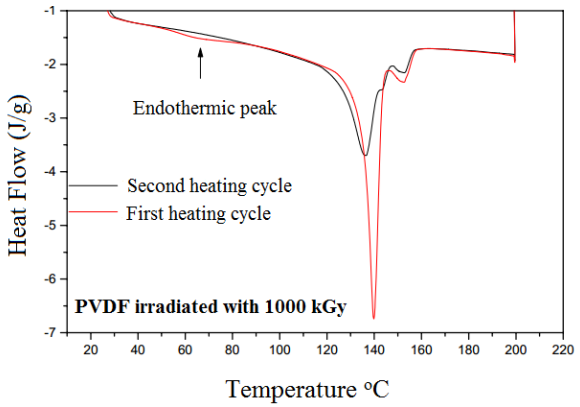


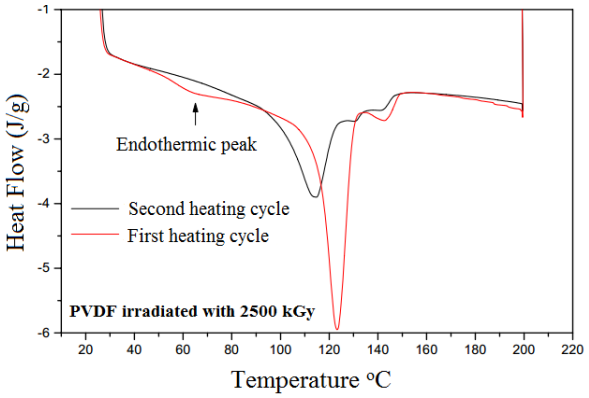
Fig. 5 The crystal / amorphous interphase [6]

Most of the papers that explain the annealing peak by melting and recrystallization processes, do not accept DSC as a suitable method to give direct information on the nature of the morphological changes involved. They argue that melting and immediate recrystallization cannot be detected by DSC.

For a simultaneous melting and recrystallization process, an endothermic peak in the reversing heat flow and an exothermic peak in the nonreversing heat flow is expect. Instead, we observe an endothermic peak in the nonreversing heat flow and a transition step in the reversing heat flow [6]. Also the softening of the annealed materials in the "annealing peak" investigated by DSC it was recorded in the second run of thermo measurements. Figs. 6 (a), (b) show endothermic peaks in temperature below the melting latent heat in thermograms recorded in the first run of thermo measurements.



(a)



(b)

Fig. 6 2nd and 1st heating cycle thermograms for pristine PVDF samples exposed of 1000.0 and 2500.0 kGy of the gamma radiation

The X-ray diffractograms are show in Fig. 7. In the XRD patterns, it is clear the gradual shift of the reflection plane 110, α-phase 2Θ = 20.14 °, the sample irradiated with 1000.0 kGy to 2Θ = 21.32 ° in the sample irradiated with 2000.0 kGy, corresponding to the same reflection in γ-phase. This shift corresponds to an increase in parameters ***a*** and *b* of the elementary crystalline lattice, indicating that it swells in these directions to accommodate the radiation-induced defects within it. There is also a large decrease in peak α-phase 2Θ = 17.88° sample irradiated with 1000.0 kGy, related to the reflection plane 100, leading to a very similar configuration to the γ-phase by other authors [8]. Thus, compared with DSC measurements of the increase in volume of the elementary mesh (V = abc) is compatible with the decrease of the melting temperature and decrease of Latent Heat of Melting. With regard to the crystalline phases of the PVDF, which can be concluded is that initially, before irradiating the polymer was in α-phase gradually moving into a γ-phase increment for increasing doses.

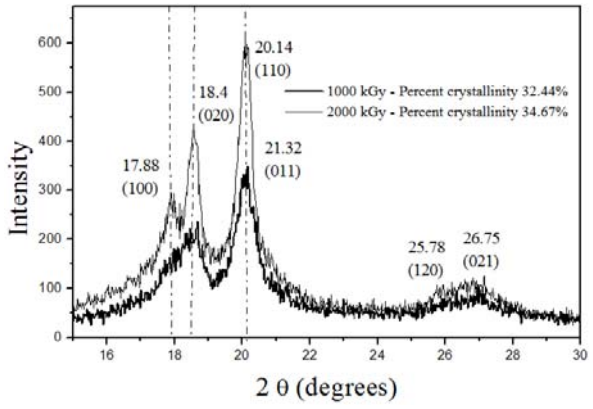


Fig. 7 X –rays diffractograms for the irradiated samples of PVDF with 1000.0 and 2000.0 kGy

IV. Conclusions

PVDF irradiated with gamma radiation exhibits changes in its crystalline phase with formation the "pseudo – crystalline" phase responsible for the appearance of the second crystalline melting peak at temperatures higher than the main peak. The X-ray diffractograms show that PVDF samples before irradiating was in α phase gradually moving into a γ phase for increasing doses.

Acknowledgment

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