

INFLUENCE OF THE DOSE RATE IN THE PVDF DEGRADATION PROCESSES

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ABSTRACT

Modification in polymeric structure of plastic material can be brought either by conventional chemical means or by exposure to ionization radiation from gamma radioactive sources or highly accelerated electrons. The prominent drawbacks of chemical cross-linking typically involve the generation by products such as peroxide degradation. Radiation cross-linking technologies include: application in cable and wire, application in rubber tyres, radiation vulcanization of rubber latex, polymer recycling, hydrogels etc. The degradation of PVDF polymer exposed to gamma irradiation in oxygen atmosphere in high dose rate has been studied and compared to obtained under smaller dose rates. The samples were irradiated with a Co-60 source at constant dose rate (12 kGy/h and 2,592 kGy/h), with doses ranging from 100 kGy to 3,000 kGy. Different dose rate determine the prevalence of the processes being evaluated in this work by thermal measurements and infrared spectroscopy. It is shown that the degradation processes involve chain scissions and crosslink formation. The formation of oxidation products was shown at the surface of the irradiated film. The FTIR data revealed absorption bands at 1730 and 1853 cm^{-1} which were attributed to the stretch of C=O bonds, at 1715 and 1754 cm^{-1} which were attributed to the C=C stretching and at 3518, 3585 and 3673 cm^{-1} which were associated with NH stretch of NH_2 and OH. Thermogravimetric studies reveal that the irradiation induced the increasing residues and decrease of the temperature of the decomposition start.

1. INTRODUCTION

Poly(Vinylidene Fluoride) (PVDF) is a specialty thermoplastic material in the fluoropolymer family; it is used generally in applications requiring the highest purity, strength, and resistance to solvents, acids and bases¹. When heat is applied to such a material, the chains are free to slip and flow under relatively small outside force. Such a material is called a thermoplastic. If we are able to introduce cross-linking bonds between adjacent molecular chains, this adds form stability at higher temperatures. There will still be some loss of

strength at elevated temperatures, but the crosslinked molecular chains are much more resistant to flow when stress is applied. Crosslinking can be accomplished chemically or by irradiation. Chemical crosslinking with rubber material is called Vulcanization. For wire and cable insulations, chemical crosslinking is performed by passing the wire through a long pressurized steam tube, called a continuous vulcanizing (C.V.) machine. Other methods of crosslinking include: Moisture cure, salt cure, and hot air vulcanization (HAV)². A discussion of the effect of radiation on mechanical strength as a consequence of the balance between crosslinking and oxidative degradation is presented in many publications. In general the literature shows a clear relationship between the absorbed dose and the parameters of mechanical resistance of polymers. However, the tendency of this relationship cannot be easily determined. The formation of crosslinking and oxidative degradation seem to occur simultaneously and in a nonhomogeneous way across the sample, while the mechanical resistance parameters show the results of integration of these phenomena across the sample³. This work presents experimental results of the irradiation in air with a Cobalt-60 gamma source of PVDF samples to address the radiation effect evaluated for two dose rates and absorbed dose between 100 to 3,000 kGy. The influence of dose rate on degradation processes in this work shows a greater predominance of oxidation in air irradiation, which is accentuated by a reduction in dose rate. The formation of oxidation products was shown at the surface of the irradiated film. The FTIR data revealed absorption bands at 1730 and 1853 cm^{-1} which were attributed to the stretch of C=O bonds, at 1715 and 1754 cm^{-1} which were attributed to the C=C stretching and at 3518, 3585 and 3673 cm^{-1} which were associated with NH stretch of NH_2 and OH. Thermogravimetric studies reveal that the irradiation induced the increasing residues and decrease of the temperature of the decomposition start. The decrease in the onset decomposition temperature could be due to the scission of polymer-chains and, the increase of the residual amount, could be associated with the formation of crosslinking between the polymeric chains.

2. EXPERIMENTAL, RESULTS AND DISCUSSION

2.1. Experimental

PVDF homopolymer resins were supplied by ATOCHEM (France). The film samples were produced by melting at 200°C under 300 bar, and subsequent air-cooling to room temperature. This process produced transparent films of about 170 μm . The samples were irradiated with a Co-60 source at constant dose rate (12 kGy/h and 2,592 kGy/h), with doses ranging from 100 kGy to 3,000 kGy. TG curves were obtained using a Netzsch model STA 429. Samples of 10 mg were degraded in a dynamic nitrogen atmosphere at a heating rate of 10 °C/min. The FTIR spectra, collected with 32 scans each, were measured at a BOMEM 100 spectrometer for wavenumbers ranging from 300 to 4000 cm^{-1} .

2.1.1. Results and Discussion

In Fig. 1, shows the TG results with percent the residues in the samples irradiation with dose rate the 12 kGy/h and 2,592 kGy/h. Shows too temperature of the decomposition start and the relationship between the increasing radiation doses with the increasing residues, and the correspondent decomposition temperature.

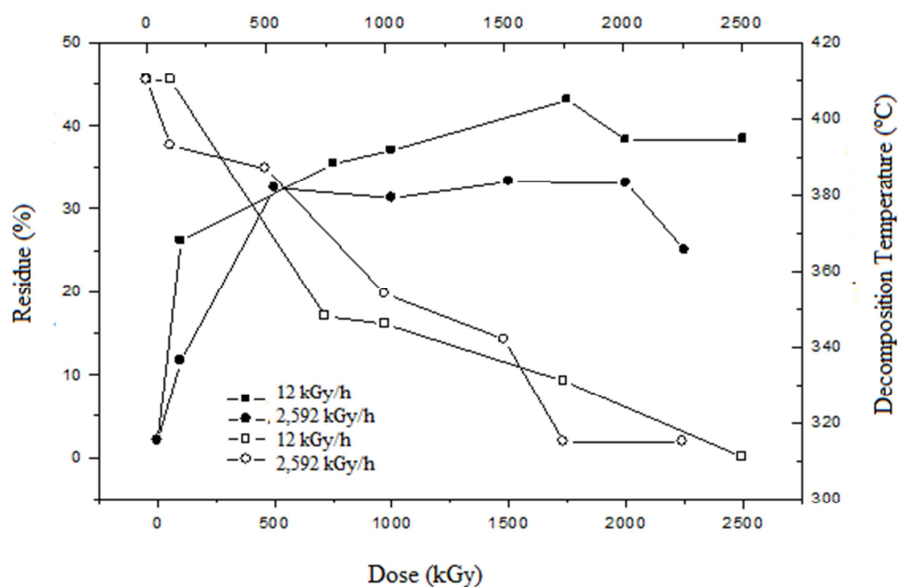
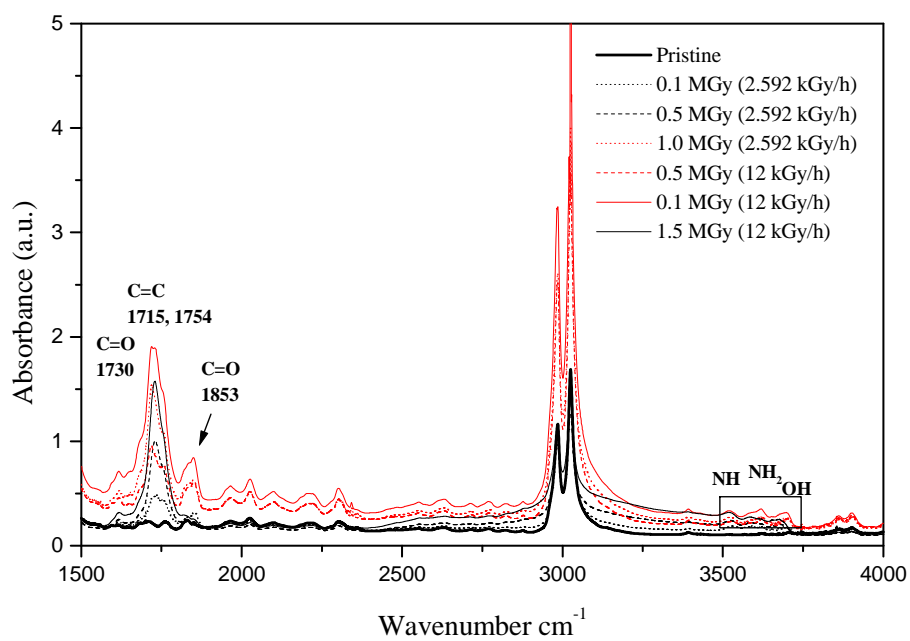
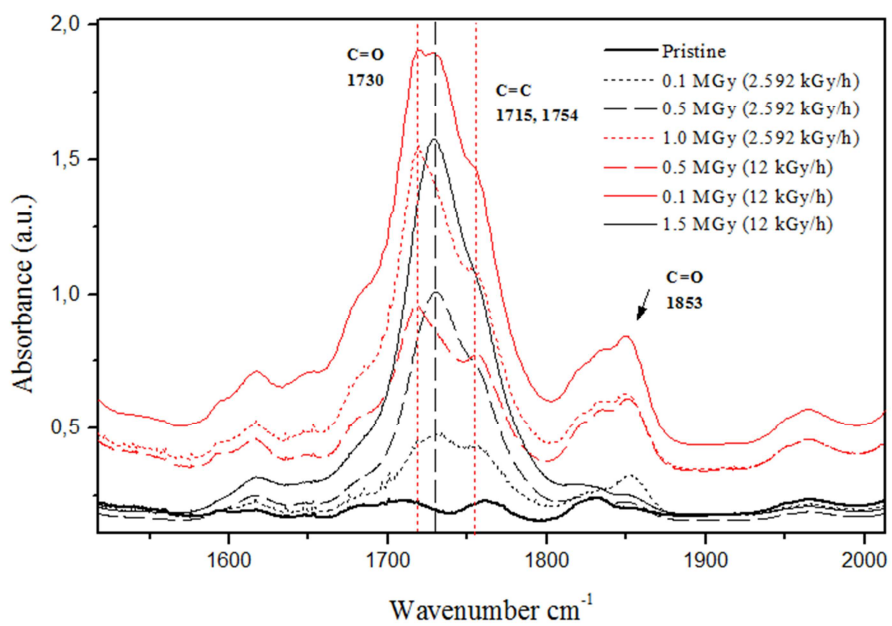


Figure 1: Comparison between the variation of residue percentage formation and the initial temperature value of the first ramp degradation of virgin PVDF and irradiated with doses ranging from 100 to 2500 kGy close to the source (dose rate of 12 kGy/h) and it 30cm to the source (2,592 kGy/h).

In Fig. 1 the observed decrease in the onset decomposition temperature could be due to the scission of polymer-chains and, the increase of the residual amount, could be associated with the formation of crosslinking between the polymeric chains⁴. In fact, ionizing radiation-induced chain crosslinking has been reported to start to occur for doses as low as 50 kGy⁵. We can see that the residue formation is greater in the irradiated near the source, so steepest decline in initial temperature of degradation, reflecting increased damage sample when irradiated with higher dose rates. The Fig. 2a shows the FTIR spectra for unirradiated and irradiated PVDF samples for gamma doses ranging from 0.1 MGy to 1.5 MGy, with dose rate of the 12 kGy/h and 2,592 kGy/h. The FTIR data revealed absorption bands at 1730 and 1853 cm^{-1} which were attributed to the stretch of C=O bonds, at 1715 and 1754 cm^{-1} which were attributed to the C=C stretching and at 3518, 3585 and 3673 cm^{-1} which were associated with NH stretch of NH₂ and OH. The detail shown in Figure 2b we see the growth of peaks at 1730 and 1854, referring to the C = O bonds, the more pronounced in the samples irradiated with a dose rate of 12 kGy / h (curves in black). In contrast we observe the evolution peak in 1730 as the major peak in growth at the samples irradiated with 2 kGy / h (curves in red), with peaks in 1715 cm^{-1} and 1754 cm^{-1} , concerning the formation of C = C, less prominent than in the samples irradiated with higher dose rates, which can establish a prevalence oxidation process in this samples in relation to the samples irradiated with higher dose rates, where we see a combination of the appearance of C = C and C=O bonds.



a)



b)

Figure 2: a) FTIR spectra for pristine sample and samples irradiated with 0.1, 0.5, 1.0 and 1.5 MGy with dose rate of 12 kGy and 2,592 kGy, for wavelengths ranging from 1500 to 4000 cm^{-1} and b) details of wavelengths ranging from 1500 to 1860 cm^{-1} .

3. CONCLUSIONS

The FTIR data revealed absorption bands at 1730 and 1853 cm^{-1} which were attributed to the stretch of C=O bonds, at 1715 and 1754 cm^{-1} which were attributed to the C=C stretching and at 3518, 3585 and 3673 cm^{-1} which were associated with NH stretch of NH_2 and OH. The influence of dose rates on degradation processes shows a greater predominance of oxidation in air irradiation, which is accentuated by a reduction in dose rate. Thermogravimetric studies reveal that the irradiation induced the increasing residues and decrease of the temperature of the decomposition start. The decrease in the onset decomposition temperature could be due to the scission of polymer-chains and, the increase of the residual amount, could be associated with the formation of crosslinking between the polymeric chains.

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