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## Effect of radiation induced crosslinking and degradation of ETFE films

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## ABSTRACT

In this study the ETFE film with 125  $\mu\text{m}$  of thickness was placed inside a nylon bag and filled with either acetylene, nitrogen or oxygen. Following the procedure, the samples were irradiated at 5, 10 and 20 kGy. The physical and chemical properties of the modified and pristine films were evaluated by rheological and thermal analyses (TG and DSC), X-ray diffraction (XRD) and infrared spectroscopy (IR-ATR). In rheological analysis the storage modulus ( $G'$ ) indicates opposite profiles when the atmospheres (acetylene and oxygen) are evaluated according to the absorbed dose. For the samples submitted to radiation under oxygen atmosphere it is possible to observe the degradation process with the low levels of the storage modulus. The changes in the degree of crystallinity were verified in all modified samples when compared to the pristine polymer and this behavior was confirmed by DSC analysis. A decrease in the intensity of crystalline peak by X-ray diffraction was observed.

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## 1. Introduction

ETFE is a semi-crystalline, melt processable thermoplastic that is essentially a 1:1 alternating copolymer of ethylene and tetrafluoroethylene. Poly(ethylene-*alt*-tetrafluoroethylene) (ETFE) has better radiation stability than its perfluorinated counterparts, and it is non-reactive with acids or alkalis and has relatively high mechanical, thermal and electrical resistances. Therefore, due to its physical and chemical stability, it is an interesting material to be used as a support for ion exchange membranes. However, the same chemical inertness is a barrier to its chemical modification by conventional oxidizing agents. Ionizing radiation is known to be a powerful tool to create reactive species in the bulk and surface of fluorinated polymers.

Radiation processing has been shown to be, on a large commercial scale, a very effective means of improving end-use properties of various polymers. It is a well-established and economical method of precisely modifying the properties of bulk polymer resins and also polymer components are formed. The effect produced by ionizing radiation is habitually a function of the irradiated dose, which is absorbed by the material; thus reactive species are generated to initiate chemical reactions (Silverman, 1977). The reactions of crosslinking, degradation and grafting on polymers initiated by radiation have many useful applications in plastic and rubber materials. Important properties of polymer materials (Chappas et al., 1982) such as surface properties, thermal stability, chemical resistance, melt flow, processability and mechanical properties can be significantly improved by radiation processing.

However, the exposure of ETFE to radiation promotes degradation of its molecular structure, compromising some of its desirable properties for ion exchange membrane applications. Charlesby (1960) described a list of covalent bond energies: for the H-F bond, 5.82 eV; for the C-F bond, 4.42 eV; for the C-H bond, 4.28 eV; and for the C-C bond, 3.44 eV. ETFE contains tetrafluoroethylene and for this fluoropolymer the initial bond breaking occurs in the side chain (C-F) rather than in the main chain (C-C); the scission of the C-F bond yields a highly reactive fluorine atom which immediately attacks a C-C bond in the main chain to produce two chain fragments (Lyons, 1995). Because of that the degradation effect in this polymer is predominant.

In order to minimize the degradation effect in ETFE the use of crosslinking promoters is necessary. Several functional monomers have been suggested to be used to improve thermal stability and mechanical properties and to enhance the crosslinking yield during the irradiation process, such as divinylbenzene (DVB), 1, 2-bis(*p,p*-vinylphenyl)ethane (BVPE) (Chen et al., 2006), trimethylolpropane-trimethacrylate (TMPTM), triallylcyanurate (TAC), triallylisocyanurate (TAIC) and acetylene. The G.G. Scherer group in Paul Scherrer Institute has studied divinylbenzene (DVB) that is used for fluoropolymers as a crosslinker in radiation-grafted membranes due to the significant influence on the properties of water uptake, proton conductivity, mechanical strength and thermal/chemical stability (Gubler et al., 2005, 2008; Ben youcef et al., 2008; Schmidt et al., 2005).

Another important monomer is acetylene which is a multi-functional monomer used as a crosslinking agent. Bol'bit et al. (2008) reported that the use of gaseous acetylene as a crosslinking agent is an elegant means for facilitating the achievement of a radiation-chemical yield at room temperature to form a network in

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PTFE (poly(tetrafluoroethylene)). For fluoropolymers the acetylene enables the enhancement in mechanical and chemical properties. Yoshiga et al. (2009) studied the role of radiation and acetylene on the long chain branching formation of iPP (polypropylene isotactic) with distinct molar masses, using gamma radiation.

One of the most common techniques to measure the cross-linking in polymers is the sol–gel fraction, and for this analysis it is necessary that the polymer should be soluble in a solvent, but ETFE is insoluble in common solvents; consequently its use is unviable. So, the purpose of this work is to characterize the effect of radiation in crosslinking (acetylene), inert (nitrogen) and oxidizing (oxygen) atmospheres by rheological measurements. This analysis is a powerful technique which is able to evaluate molar mass, cross-linking density, graft branches and scission chains.

## 2. Experimental

### 2.1. Processing films

The commercial poly(ethylene-*alt*-tetrafluoroethylene) (ETFE) film with 125  $\mu\text{m}$  of thickness was supplied by Goodfellow Cambridge, Ltd. The film was placed inside a nylon bag and filled with either acetylene, nitrogen or oxygen. The acetylene and nitrogen gases used in this experiment have about 1000 ppm of oxygen content.

Following the procedure, the samples were irradiated at 5, 10 and 20 kGy with gamma radiation, using a cobalt-60 source.

### 2.2. Methods

The rheological measurements were taken at 300 °C using a rotational Physica rheometer (MCR300) with parallel plate geometry of 25 mm diameter and 0.200 mm gap. The frequency range used was 0.1–150 (1/s) with a strain of 3%.

The infrared spectroscopy was performed on Nexus 670 Thermo Nicolet equipment using transmittance mode, positioning the film directly inside the equipment.

Thermogravimetric (TG) analyses were accomplished in a Mettler-Toledo TGA/SDTA 851 thermobalance, using an inert atmosphere of  $\text{N}_2$  from 25 to 700 °C temperature program at a heating rate of 10 °C  $\text{min}^{-1}$ .

The differential scanning calorimeter (DSC) curves were obtained in a Mettler-Toledo DSC 822, under nitrogen atmosphere from 30 to 400 °C, at a heating rate of 10 °C  $\text{min}^{-1}$ ; isotherm at 400 °C per 5 min; in a sequence from 400 to –50 °C at a cooling rate of –10 °C  $\text{min}^{-1}$  and reheated to 400 °C, at 10 °C  $\text{min}^{-1}$ .

The degree of crystallinity was calculated by

$$X_c = (\Delta H_m / \Delta H_{100\%}) \times 100$$

where  $\Delta H_m$  is the heat of melting for pristine and modified samples and  $\Delta H_{100\%}$  is the heat of melting for 100% crystalline ETFE ( $\Delta H_{100\%} = 113.4 \text{ J/g}$ ) (Gursel et al., 2008).

The X-ray diffraction (XRD) analyses were conducted at an ambient temperature using a Rigaku MiniflexII X-ray diffractometer ( $\lambda(\text{CuK}\alpha) = 1.54 \text{ \AA}$ ) in configuration theta/theta on slabs of samples. XRD spectra were recorded in the 0.5–80°  $2\theta$  range with a step of 0.05°, and a step time of 1 s.

## 3. Results and discussion

The FTIR was not an appropriate technique to identify the presence of double bonds referring to the acetylene on the polymer matrix, although it was expected to be. It was not possible to verify changes in the polymer structure. In all atmospheres the spectra were identical to the pristine sample.

The effects of atmosphere during radiation could be observed by rheological measurements. The samples irradiated at different doses in nitrogen have similar curve profiles of storage modulus and complex viscosity (Fig. 1). At low shear rates the melts in the complex viscosity of samples pristine, 5 kGy and 10 kGy, present a Newtonian behavior, going to a plateau. The viscosity in this case (plateau) gives information about the molar mass, which means that all these samples have much closer values of molar mass. This fact indicates the absence of degradation reaction. The curves of samples pure and irradiated at 5 kGy have exactly the same profile about the complex viscosity and this behavior is also observed for the storage modulus analysis for samples pristine and irradiated at 10 kGy, where the curves are overlapping.

The sample irradiated at 20 kGy has a change in the slope of both curves of complex viscosity and the storage modulus at low shear rates. The increase in the storage modulus, when compared to samples at 20 kGy and pure, reveals an increase in polymer entanglement and indicates the beginning of crosslinking and/or a long chain branching (Yoshiga et al., 2009).

The effect of oxidizing in the ETFE polymer is verified when the irradiation is done in the presence of oxygen (Fig. 2). The irradiation of the polymer by gamma rays occurs via oxidative mechanism, through chain scission. The higher the dose irradiation, the higher the degradation in the polymer, due to an increase in the active sites

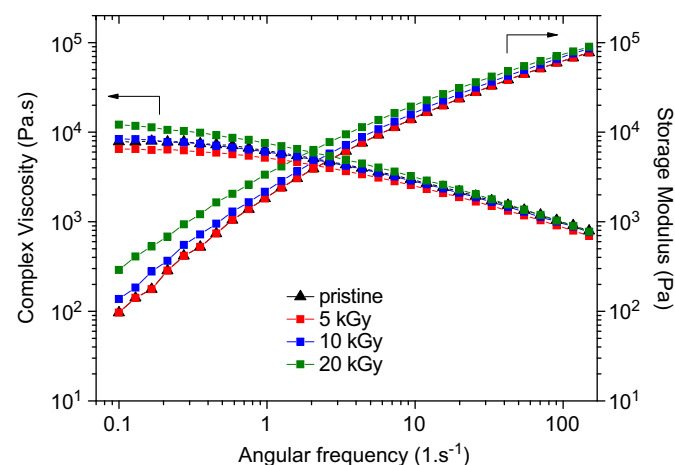


Fig. 1. Rheological measurements for samples irradiated under nitrogen atmosphere.

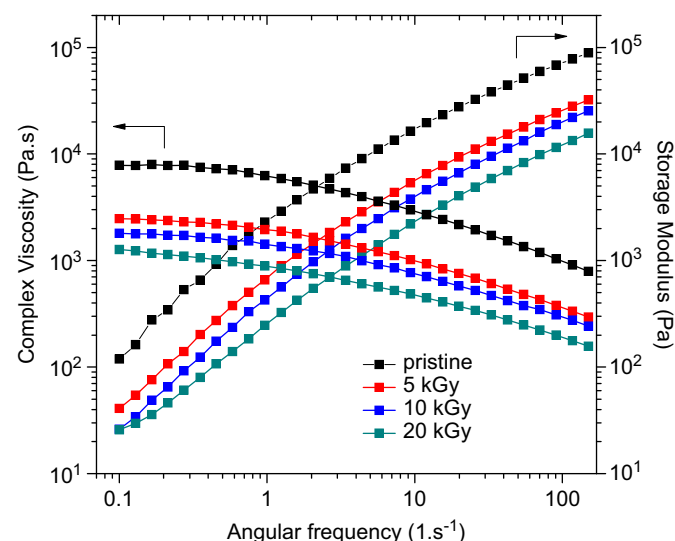


Fig. 2. Rheological measurements for samples irradiated under oxygen atmosphere.

created in the polymer that combine with the peroxy radicals. This fact is confirmed by the rheological analysis, which proves that the degradation is lower at 5 kGy and higher at 20 kGy.

Although the degradation reaction is predominant in an oxidizing atmosphere, the slope of the curve at low frequencies, for complex viscosity and for the sample processed at 20 kGy, shows a tendency to become a plateau, which can indicate the presence of a crosslinking reaction occurring at the same time with the oxidation, but at a low rate.

To form a crosslinked polymer it is necessary to form a three-dimensional network, and to achieve this goal generally is used a multifunctional monomer that is compatible with the polymer matrix. According to Bol'bit et al. (2008), gaseous acetylene is capable of penetrating into the bulk of the polymer and has the capability to bridge chains, consuming one macroradical and leaving another in the living state.

In this work the network formation was observed by the rheological measurements for the samples irradiated under acetylene when compared to the pristine samples. The change of the curve profiles of the storage modulus and complex viscosity shows the crosslinking effect in the samples irradiated at 5 and 10 kGy. The increase in the storage modulus at these doses is due to the formation of a network in the ETFE film. For these samples the slope of both curves approaches the pristine curve, which indicates a small decrease in the molar mass of these samples. This fact, associated with the values of storage modulus at low frequency, is evidence that the degradation reaction was not intense. The extent of the radiation-induced C–C bond scission reaction leads to chain scission and a decrease in molecular weight and is more likely to be broken by the lowering bond strength (Gubler et al., 2005).

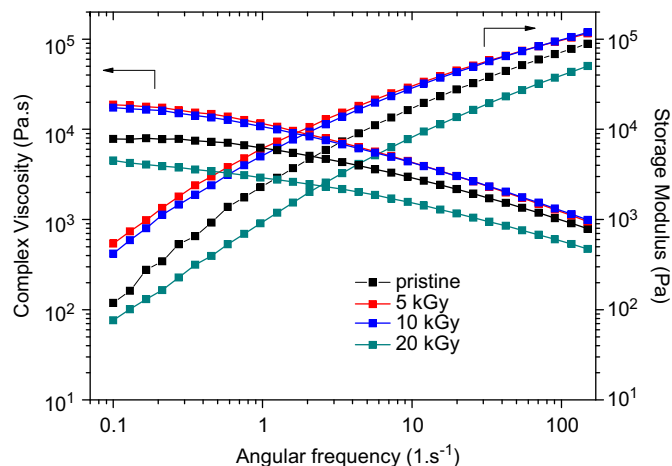
The sample irradiated at 20 kGy under this atmosphere is an exception, where a degradation behavior is observed at the high dose absorbed. As the acetylene contains 1000 ppm of oxygen, this content induced the degradation reaction associated with the high dose. This fact is confirmed by DSC results (Table 1) that show a decrease in the melting temperature for this sample Fig. 3.

The differential scanning calorimeter (DSC) results shown in Table 1 refer to the first ( $T_{m1}$ ) and second ( $T_{m2}$ ) scanning measurements and corroborated the three effects shown in the rheological measurements. During the first heating all temperatures are practically equal.

The melting temperature represents the crystallite size and an increase in  $T_m$  is related to a high level of perfection of crystal phase. Under oxygen atmosphere, the values of the temperature during second scanning ( $T_{m2}$ ) decreased, which indicates the degradation caused by the main chain scission and formation of defects in the crystalline phase.

**Table 1**  
DSC results for all samples.

Atmosphere	Dose (kGy)	$T_{m1}$ (°C)	$X_{m1}$ (%)	$T_{m2}$ (°C)	$X_{m2}$ (%)	$T_c$ (°C)
Pristine sample	–	263	49	262	57.1	246
Nitrogen	5	263	34.8	263	53.4	250
	10	264	34.6	263	55.5	250
	20	264	33.5	263	57.2	250
Acetylene	5	267	36.1	262	60.7	250
	10	264	35.3	262	54.9	250
	20	262	34.9	254	57	250
Oxygen	5	265	35.6	250	51.7	250
	10	265	45.2	250	45.2	250
	20	264	37.7	250	61	250



**Fig. 3.** Rheological measurements for samples irradiated under acetylene atmosphere.

**Table 2**  
XRD results refers to pristine and irradiated at 5 kGy samples.

Sample	$2\theta$ /crystallite size (nm)			
Pristine	–	–	19.33/4.15	38.35/1.11
Nitrogen	–	–	19.20/4.07	38.71/1.08
Acetylene	–	–	19.39/4.04	38.68/1.14
Oxygen	14.19/6.62	17.09/6.34	19.81/3.94	39.17/1.34

For the samples irradiated under nitrogen and acetylene the melting temperature is very close and the exception is the sample irradiated at 20 kGy under acetylene. The DSC result for this sample confirms the degradation effect that was indicated in the previous analysis.

As was expected, the degree of crystallinity ( $X_{m1}$ ) for modified films, at first melting temperature, had a decrease in value, indicating the radiation effect over the crystal phase.

The increase in the radiation dose causes an increase in the chain scission accompanied by a reduction in the lengths of chains suitable for recrystallization. This effect followed by the degradation reaction resulted in a decrease in the degree of crystallinity ( $X_{m1}$ ), which is observed for the samples irradiated under oxygen. In the second scanning the radiation effect was excluded and the  $X_{m2}$  at 20 kGy increased, meaning that it is possible that the peroxide species interacted between chain segments and the deformation in crystalline structure was reduced (Nasef and Dahlan, 2003; Nasef et al., 2003).

The melting temperature remained practically unaltered in all modified samples and it means that there are no significant changes in the crystallite size. This fact is in agreement with X-ray diffraction (Table 2). It is possible to observe one intense peak at about  $2\theta = 19^\circ$  and one low intense peak at about  $2\theta = 38^\circ$ . These peaks can be attributed to the polymer matrix (poly(tetrafluoroethylene)) of the ETFE (Tanigami et al., 1986a,b).

However, for the samples irradiated under oxygen, there was an appearance of two different spots which were not present in the other samples. Both peaks (Fig. 4) have low intensities at about  $2\theta = 14^\circ$  and  $2\theta = 17^\circ$ , which can be attributed to a reorganization of chain polymers with the oxygen present in the atmosphere. The atmosphere exerts a dilution effect on the crystallinity of ETFE film without causing any disruption to the inherent crystallites.

For all samples the thermogravimetric analyses show only one degradation step. Table 3 shows the results of initial degradation temperature ( $T_{on}$ ). The samples irradiated in the oxygen atmosphere show a decrease in this temperature when compared to

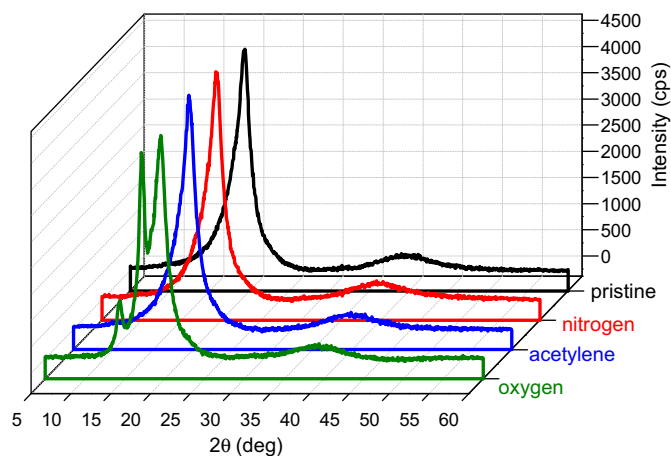


Fig. 4. XRD curves for samples pure and irradiated at 5 kGy.

the others. In fact these films presented the highest residues after the complete analysis resulting from the crosslinking and degradation effects that occurred at the same time but in different levels at high doses. The thermogravimetric curves for samples irradiated under oxygen presented exactly the same profile and all curves were overlapping.

#### 4. Conclusion

This paper shows the importance of a controlled atmosphere during an irradiation test. Depending on the objective of the study, the priority is to guarantee a free oxygen atmosphere to avoid the degradation effect.

Irradiation under acetylene was carried out and the goal of a crosslinked film in this condition was obtained. In this case the rheological technique was an appropriate tool to verify this effect. Analyzing the results, the optimum crosslinking is achieved at the lower dose under acetylene atmosphere.

As expected, the films irradiated under nitrogen demonstrated no drastic changes in their structure, being similar to a pristine sample.

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Table 3  
Thermogravimetric results for samples.

Atmosphere		$T_{on}$ (°C)	$T_{max}$ (°C)
Pristine sample	–	488	508
Nitrogen	5	481	504
	10	479	498
	20	464	487
Acetylene	5	482	503
	10	482	506
	20	474	491
Oxygen	5	478	503
	10	478	501
	20	478	503

$T_{on}$ : initial degradation temperature;  $T_{max}$ : maximum rate degradation temperature.

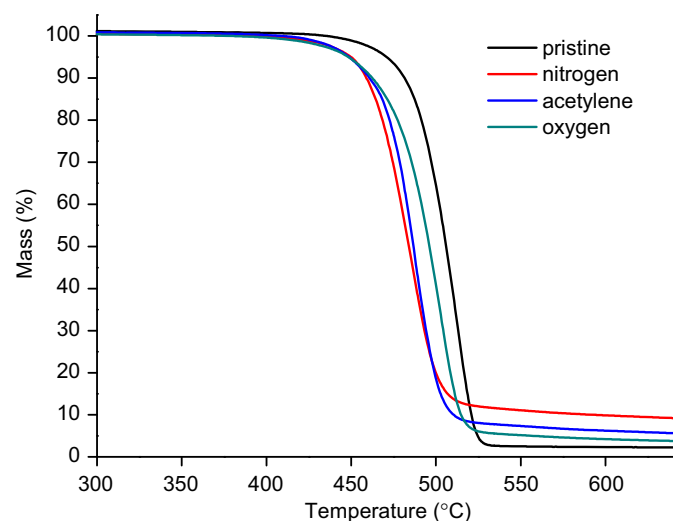


Fig. 5. TG curves for samples pristine and irradiated at 20 kGy.

the pure sample, which corroborates the degradation effect in this experiment ambient.

The slope of the curve is steeper (Fig. 5) for the samples irradiated at 20 kGy under acetylene and nitrogen, which means that the thermal stability of these samples is lower than that of