THE INFLUENCE OF THE ATMOSPHERE ON THE PROPERTIES OF RADIATION INDUCED CROSSLINKING AND DEGRADATION BASED ON FLUORINATED POLYMER FILMS

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Abstract

Fluorinated films have toughness, mechanical, thermal and chemical resistance. The chemical inertness is a barrier for its chemical modification by conventional oxidizing agents, so radiation technique is one of the most versatile methods to modify it. This paper explores the modification on mechanical and thermal resistance of PFA and ETFE films when submitted to gamma radiation under crosslinking (acetylene), an inert (nitrogen) and an oxidizing (air) atmospheres. Those films were put into the nylon bag and filled with acetylene, nitrogen or air. Following the procedure, the samples were irradiated at 5 and 10 kGy. The mechanical and chemical properties of the modified and pristine films were evaluated by thermal analyses (TG and DSC), FTIR-ATR and rheological measurement, in order to identify how the reaction conditions affect the properties. The result of analysis indicated that under air the higher is the absorbed dose higher is the degradation effect.

Introduction

Radiation of polymers is a well established process used to modify or improve physical and chemical properties of polymers. Crosslinks or scissions reactions occur when polymers are exposed to high-energy radiation [1].

The atmosphere during irradiation may influence the effects of radiation on the chemical or mechanical properties on polymers and the possibility of minimizing these effects. The effects on the backbone polymer depend on the chemical structure of the polymer.

In the presence of air (oxygen) there is a competition between the crosslinking of the polymer radicals and their reaction with oxygen. Under acetylene not occurs a chain reaction or any other competing processes, so the crosslinking is predominant. In order to suppress the oxidative and croslinked conditions, the irradiation was carried out under nitrogen to evaluate the direct effect of the absorbed doses.

Fluoropolymer is a class of material with excellent thermal, chemical and mechanical properties but is not highly resistant to radiation so, the degradation effect is predominant. However, under special conditions those polymers can be crosslinked by irradiation [2].

PFA (Poly (tetrafluoroethylene-perfluoropropylinylether) and ETFE (Polyethylene-*alt*-tetrafluoroethylene) were the films used to study the effects of atmosphere during irradiation on polymer stability.

Experimental

The commercial films were supplied by Goodfellow Cambridge Lt. The thickness of PFA is 100µm and of ETFE is 125µm. The films were placed inside a nylon bag separately and filled either with acetylene, nitrogen or air. The acetylene and nitrogen gases used in this experiment have about 1000ppm of oxygen content. Following the procedure, the samples were irradiated at 5 and 10 kGy with gamma radiation, using a cobalt-60 source.

Methods

A Thermogravimetric (TG) analysis was carried out from 25 to 700°C at 10 ºC min^{-1} of a heating rate. The differential scanning calorimeter (DSC) curves were obtained under nitrogen atmosphere from 30 to 400 °C, at 10 °C min^{-1} of heating rate. Rheological measurements were performed with parallel plate geometry of 25mm in diameter and 0.200mm gap. The frequency range used 0.1 – 150 (1/s).

Results

By FTIR-ATR analysis no significant difference among the spectra from the crosslinked, oxidized, non-crosslinked and original films were observed.

The thermal stability were determined by TG analysis and showed only one step of degradation for all different films. In all samples of PFA film the initial and final degradation temperatures were found to be almost constant. The values were around 515°C and 580°C, respectively. The ETFE film irradiated under oxygen atmosphere had a decrease in those temperatures when compared to the pure sample for each film, which corroborates the degradation effect in this experiment ambient.

The DSC showed the influence of radiation on the samples. According to those values the melting temperature (T_m) was not altered although the degree of crystallinity (X_m) revealed an increase for PFA film whern the dose increased. This fact can be associated to chain scission reactions and in the alignment of the crystal lamella [3]. In the case of ETFE results the X_m had a decrease in their values indicating the radiation effect over the crystal phase.

The degree of crystallinity was calculated by the Eq (1).

$$X_m = (\Delta H_m / \Delta H_{100\%}) * 100 \qquad (1)$$

where ΔHm is the enthalpy for pristine and modified samples and $\Delta H_{100\%}$ is the enthalpy for 100% crystalline polymer (PFA: $\Delta H_{100\%}$ = 82 J/g and ETFE: $\Delta H_{100\%}$ = 113,4 J/g) [4, 5].

The crosslinking effect was observed by the rheological measurements for the samples irradiated under acetylene when compared to the pristine samples. For both ETFE (Fig. 1) and PFA films (Fig. 2) the curve profile has an increase in the storage modulus at low frequencies which is consequence of the crosslinking reactions and network formation. At high frequencies the oxidation effect due to the air atmosphere is observed by the curve profile of storage modulus, which is very closer to the pristine sample, especially for PFA films that the curve of irradiated sample almost crosses the curve of pure sample. The PFA film irradiated at 10kGy under acetylene do not flow even at temperatures above its melting point due to the viscosity in the molten state was so high.

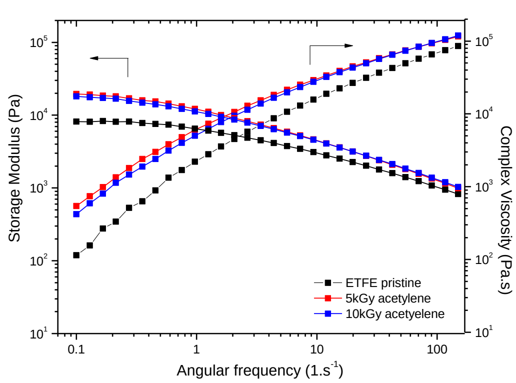

Figure 1: Results of rheological measurements for ETFE

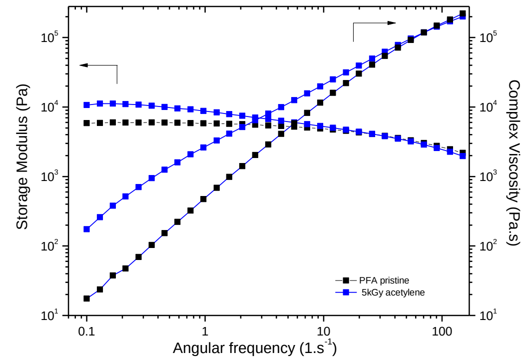

Figure 1: Results of rheological measurements for PFA films

Summary and Conclusions

The irradiation process under acetylene showed the crosslinked effect which was confirmed by the increase in the storage modulus at low frequencies. y the rheological measurements.

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