CHARACTERIZATION OF POLYPROPYLENE FILMS MODIFIED FOR USING AS ION EXCHANGE MEMBRANE
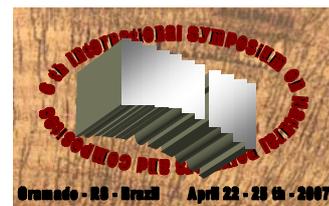
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Grafting of styrene onto PP films was investigated using the simultaneous radiation process under inert atmosphere. The influence the concentration of monomer / solvent was investigated at 40 kGy dose in the period of 0 to 28 days after radiation. The best result of degree of gel content (DOG) was reached after 21 days. FTIR, TGA, DSC techniques were used to characterize the samples. Structurals and chemicals changes were observed. The presence of the styrene monomer has difficulted the crystallinity increasing by chain scission mechanism.

Introduction

The proton exchange membrane (PEM) is the most important component in a proton exchange membrane fuel cell (PEMFC). This membrane is used as an electrolyte for transporting protons from the anode to cathode in a PEMFC. The most used membrane is the Nafion® (made by Dupont) because of its chemical stability. However, Nafion® is very expensive, so many studies have been made to development new types of proton exchange membranes.

Many alternatives membranes have been studied by radiation graft polymerization of styrene monomer onto polymer matrix, such as poly(tetrafluoroethylene) (PTFE),(tetrafluoroethylene-co-hexafluoropropylene) (FEP), polyvinylidene fluoride (PVDF), polyethylene (PE) and others. After radiation graft process is carry out the sulfonation modification. The sulfonation process allows the introduction of ionic groups into the modified polymer.

Radiation processing has been demonstrated on a large commercial scale to be 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 formed polymer components. The reactions of cross-linking, degradation and grafting on polymers initiated by radiation have found many useful applications in plastic and rubber materials. Important properties of polymer materials, such as mechanical properties, thermal stability, chemical resistance, melt flow, process ability and surface properties can be significantly improved by radiation processing.

Many types of grafting polymerization techniques have been developed in recent years by electron beam irradiation [1], proton beams [2], gamma ray irradiation [3], ultraviolet light and plasma polymerization[4].

Among these techniques, the radiation process of grafting permits the uniform and rapid creation of active radical sites without contamination in the resultant grafted samples.

A several studies have been performed in order to improve the membrane performance, mainly to obtain a new polymer material with the same or better chemical stability than Nafion®.

Thermal stability of polystyrene grafted films prepared by radiation grafting onto poly(tetrafluoroethylene), PTFE[5–7],(tetrafluoroethylene -co-hexafluoropropylene), FEP [8], and polyvinylidene fluoride, PVDF [9 - 11], and poly(tetrafluoroethylene-co-perfluorovinyl ether) was studied using thermal gravimetric analysis (TGA) and differential scanning calorimetry analysis (DSC) under nitrogen atmosphere.

Peterson et al [12] worked to obtain reliable values of the activation energy for the thermal and thermoxidative degradation of PS, PE, and PP. They obtained data were compared with numerous previously reported values and interpreted in terms of reaction mechanisms.

Polymeric materials are one of the largest application areas of thermal analysis methods[13]. Thermal analysis is used to study the physical processes of melting, crystallization and glass transition as well as chemical processes of polymerization and degradation.

The usefulness of polymeric materials is largely determined by their thermal, oxidative, and fire resistance. Crucial information in this area is obtained from kinetic and mechanistic studies of thermal degradation that presents a wide application area for thermal analysis methods.

Polypropylene (PP) is a semi-crystalline thermoplastic. It has a two-phase system consisting of amorphous and crystalline domains. During irradiation, energy is deposited uniformly and radicals are formed throughout the polymer in both domains. Different chemistry can result from energy deposition in the two

regions since oxygen, stabilizers and specific active radical species are excluded from the crystalline phase. PP is known for its balance of strength, modulus, chemical resistance to solvents and low cost. It has many potential applications such as packaging, automobile industry, fibers, non-durable goods, in building construction and new developments for use in fuel cells membranes.

In this work is used the simultaneous method, which means that the polymer is immersed in the monomer then exposed to ionizing radiation. Both the polymer and the monomer are exposed to radiation at the same time.

The graft and ungraft samples were characterized by TGA, DSC, FTIR and degree of grafting (DOG).

Experimental

Materials

Braskem Industry supplied polypropylene films with 40 µm thickness. The styrene monomer (Maxepoxi) was mixed with toluene (Merck) in a proportion of 1:4, 1:1 and 4:1.

PP was grafted by simultaneous radiation process, under nitrogen atmosphere at room temperature using a cobalt–60 source of gamma rays operating at dose rate of 10 kGy h⁻¹.

PP films were submitted at 40 kGy dose.

After irradiation, the samples remaining at room temperature and were evaluated in the period of 0, 7, 14, 21 and 28 days. The films were kept in inert atmosphere during those periods of time after irradiation in order to avoid reactions of free radicals with oxygen. Free radicals produce peroxy-radicals that increase the polymer degradation mechanisms.

In the sequence thermal treatment of the irradiated samples were made in vacuum oven for 8h, at 70 °C.

Extraction procedure of the samples was carried out after the thermal treatment in Soxhlet system using acetone as solvent. The extraction to remove the remaining homopolymer was effective in 8h. The films were dried in vacuum oven at the temperature of 70 °C to eliminate residual solvents and impurities, until constant mass.

The degree of grafting (DOG) has been evaluated in all samples.

Methods

The degree of grafting was determined as the following equation (1):

$$\% DOG = [(W_f - W_i)/W_i] \times 100 \qquad \text{eq. (1)}$$

where W_i and W_f are the masses of the PP samples before and after grafting, respectively.

Thermogravimetric Analysis (TGA) was recorded with a Mettler-Toledo TGA / SDTA 851 thermobalance in nitrogen atmosphere of 50mL.min⁻¹, in the range from 25 up to 700 °C at a heating rate of 10 °C min⁻¹. Samples at about 10 mg were placed at alumina pans.

Differential Scanning Calorimetry (DSC) was carried out in a 822 Mettler-Toledo under nitrogen atmosphere of 50mL.min⁻¹ at a heating rate of 10 °C min⁻¹, in the temperature range of -50 to 280 °C, keeping in 280 °C for 5 minutes and from 280 to -50 °C at a cooling rate of 50 °C min⁻¹ and from -50 up to 280 °C at heating rate of 10 °C min⁻¹. The polymer samples at about 2-4 mg were placed in closed aluminum pans.

Infrared spectroscopy was performed at Nexus 670 FTIR of Thermo Nicolet. S.A with samples of the films cut into pieces and analyzed them.

Results and Discussion

Free radicals were generated on PP membrane surface by gamma radiation. These radicals initiated grafting of styrene monomer, and the polymerization reaction was proceeded. It is known that free radicals created by radiation process may be immobilized and remain trapped for a considerable length of time.

In this work will be discussed samples in different proportions of monomer/solvent kept in inert atmosphere for 21 days after irradiation. These samples presented the highest degree of grafting in this period and

The DOG values increase with increase of styrene concentration (Table 1). The samples are identified according to: 20 % st. is the sample with 1:4 proportion of styrene / toluene; 50 % st. is the sample with 1:1 proportion; 80 % st. is the sample with 4:1 proportion.

Table 1: DOG values for different solutions

Sample	DOG (%)
20 % st.	0.00
50 % st.	15.1
80 % st.	16.3

DOG: Degree of grafting; 20 % st., 50 % st. and 80% st. are the concentration of styrene present in the solution.

FTIR spectra show chemical structures of PP membrane before and after the grafting reaction (Figure 1). The characteristic absorption peak of the benzene ring at 698 cm⁻¹, of styrene 3080 - 3010 cm⁻¹ and 1601 – 1500 cm⁻¹ attributed to the C=C deformation of the aromatic rings are presented in spectra of grafted samples except in sample with 20 % of styrene. All of these peaks are absent in the pure PP spectrum[14].
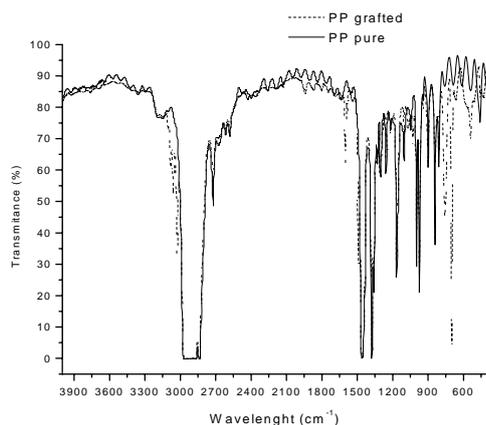
Figure 1: Infrared spectra of PP pure (solid line) and grafted (dashed line) films.

The effect of ionizing radiation on polymeric materials can propitiate molecular weight increasing by crosslinking and the other molecular decreasing by degradation.

DSC analysis permits to evaluate the crystallinity, X_c that is given by the equation (2):

$$X_c = [\Delta H_m / H_{m100\%}] \times 100 \qquad eq. (2)$$

where $H_{m100\%}$ corresponds to the value of enthalpy for a PP 100% crystalline (209 kJ.kg^{-1}) [15] and H_m is the experimental value. As the results indicated the grafted samples present decreasing of crystallization temperature (T_c) and the degree of cristallynity, with grafting time in relation to the pure polymer. The results are showed in Table 2.

Table 2: Cristallyzation and melting temperature.

Sample	ΔH_m (J.g^{-1})	X_c (%)	T_c (°C)	T_m(°C)
PP pure	418.14	31.76	95.02	163.05
20 % st.	189.68	21.61	90.61	162.33
50 % st.	275.77	22.36	90.12	163.01
80 % st.	231.98	28.46	94.19	162.76

ΔH_m: melting entalpy; X_c: degree of crystallinity; T_c: crystallinity temperature; T_m: melting temperature.

The morphology of the semy-cristalline polymers is modified when exposed to a radiation process. This fact is attributed to the degradation mechanisms, owing to chains scission of the molecules[16]. The degree of crystallinity (X_c) of pure PP is higher than 50 % st. and 80 % st samples.

According to Rabello et. all [19] when PP sample is exposed to radiation reaction occurs chain scissions. This reaction occurs preferentially in the amorphous phase of the higher permeability to oxygen and the degree of crystallinity increases with the chain scission process. The entangled sections of the molecule can be released to the crystalline phase and further crystallization occurs. However, the crystallinity of

polypropylene is reduced if the regularity decreases, as occurs when a co-monomer is present.

In this work the radiation process in the PP membranes was carried out in inert atmosphere with styrene monomer. Therefore occurring the graft the regularity decreases and consequently the degree of crystallinity decreases as a result.

Figure 2: DSC analysis indicating melting temperature in the samples of PP pure, 20
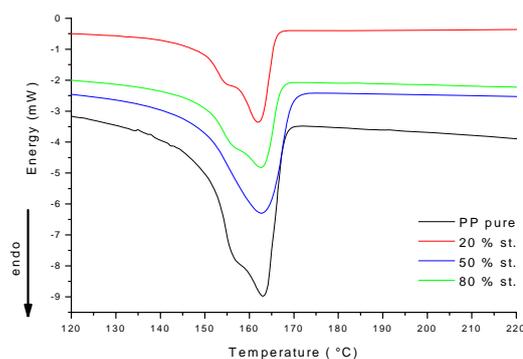
% st., 50 % st. and 80 % st.

The experimental T_m is nearly from the reported value of 165 °C, according to the literature[18] and keeps stable in modified samples in relation to the pure polymer (Table 2).

Figure 2 shows the DSC analysis curves of PP graft and ungraft. It is observed doubled peaks in the most of the samples, characteristic feature of the polymers where the exothermic recrystallization was superimposed on the endothermic melting process[19].
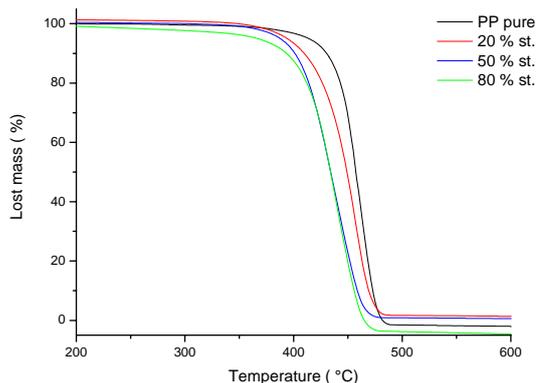
Figure 3: TG curves for thermal decomposition of PP pure and grafted.

The effect variation of the degree of grafting on the thermal stability was investigated. All the samples show only one step degradation pattern (Figure 3). This fact confirms the success in the extraction procedure to eliminate homopolymer, unreacted styrene and impurities.

The Tonset around 400 °C (Table 3) indicates that the decomposition temperature of the PP grafting with styrene is also independent of the degree of grafting.

Table 3: Intial and final degradation temperature

Sample	T_{onset} (°C)	T_{endset} (°C)
PP pure	434.86	467,79
20 % st.	417.35	462.23
50 % st.	396.78	453.77
80 % st.	401.29	451.63

T_{onset}: Initial degradation temperature; T_{endset}: Final degradation temperature

Conclusions

Polypropylene was grafted by gamma ionizing radiation. The higher content of styrene grafting onto polypropylene was obtained after 21 days of radiation process, under inert atmosphere.
The thermal stability of the membrane showed no drastic changes. The presence of monomer and graft condition implies in the reduction of crystallinity degree in consequence of the regularity decrease.

Acknowledgements

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