2007 International Nuclear Atlantic Conference - INAC 2007
Santos, SP, Brazil, September 30 to October 5, 2007
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: 978-85-99141-02-1

GRAFTING OF STYRENE ONTO POLYPROPYLENE MEMBRANES

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ABSTRACT

The grafting of styrene onto polypropylene (PP) by simultaneous radiation was carried out. The effects of absorbed dose and the pos radiation period on the grafting yield were investigated. The experiment comprised PP films with 40µm thickness exposed to gamma ionizing radiation at room temperature and nitrogen atmosphere. The films were immersed in styrene/toluene and then irradiated at total dose of 40, 80 and 100 kGy. After irradiation the samples were evaluated at periods of 0, 7, 14, 21 and 28 days at room temperature in order to observe the behavior of grafting degree. Structural, chemical changes and surface morphologies of the modified PP films were characterized by infrared spectroscopic analysis (FTIR), differential scanning calorimetry analysis (DSC), thermogravimetric analysis (TGA) and the degree of grafting (DOG) was gravimetrically determined. The simultaneous radiation indicated the dependency of the percent graft on the absorbed dose. The DOG values are higher when the film was submitted at 100 kGy dose. The thermal stability shows a decrease in the degradation temperature of the modified samples in comparison with the pure polymer.

1. INTRODUCTION

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 radiation-induced reactions of crosslinking, degradation and grafting 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 [1].

Many types of grafting polymerization techniques have been developed in recent years by electron beam irradiation [2], proton beams [3], gamma ray irradiation [4], ultraviolet light and plasma polymerization [5].

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. Polypropylene (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.

Owing to the hydrophobic nature of polypropylene and the absence of any reactive functional groups in its molecular structure, its use in certain applications faces some problems.

Modification of PP through a grafting technique with reactive monomers is considered to be one of the main routes to overcome these problems.

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.

In this work, it was studied the effects of irradiation dose of 40, 80 and 100 kGy on simultaneous radiation method, using styrene as monomer. The PP films were irradiated using a cobalt–60 source of gamma rays. The samples were characterized by TGA, DSC, FTIR and degree of grafting (DOG).

2. EXPERIMENTAL

2.1. Materials

Braskem Industry supplied polypropylene films with 40 μm thickness. The styrene monomer (Maxepoxi) was mixed with toluene (Merck) in a proportion of 1:1. The gamma ray radiation was the first chosen to do this experiment, in the future different dose rate and graft polymerization will be studied. 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}. Several samples of the PP films were submitted at 40, 80 and 100 kGy dosis.

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 radiation 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 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.

2.2. Methods

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

$$\%DOG = [(W_f - W_i)/W_i] \times 100 \quad (1)$$

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 thermo balance in nitrogen atmosphere of 50 mL min^{-1}, in the range from 25 up to 700 °C at a heating rate of 10 °C min^{-1}. Samples about 10 mg were placed at alumina pans. This technique is used to obtain the initial degradation temperature (T_{onset}).

Differential Scanning Calorimetry (DSC) was carried out in a 822 Mettler-Toledo under nitrogen atmosphere of 50 mL 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 about 2 - 4 mg were placed in closed aluminum pans.

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

3. RESULTS AND DISCUSSION

The samples were analyzed before and after grafting process.

Table 1. Degree of grafting in the samples for different dosis radiation

Sample	7 (days)	14 (days)	21 (days)	28 (days)
PP Pure	0	0	0	0
PP 40 kGy	8.8 +/- 0.5	11.7 +/- 1.2	15.1 +/- 0.4	9.8 +/- 1.2
PP 80 KGy	10.0 +/- 0.3	11.2 +/- 0.3	13.3 +/- 0.5	10.1 +/- 0.8
PP 100 kGy	12.6 +/- 1.0	14.9 +/- 0.2	15.1 +/- 0.5	13.3 +/- 0.5

Table 1 shows the evaluate DOG for all samples in all periods of pos radiation. The best result was after 21 days of the simultaneous radiation, for 40 kGy DOG was 15.1%, at 80 kGy was 13.3% and at 100 kGy was 15.1%.

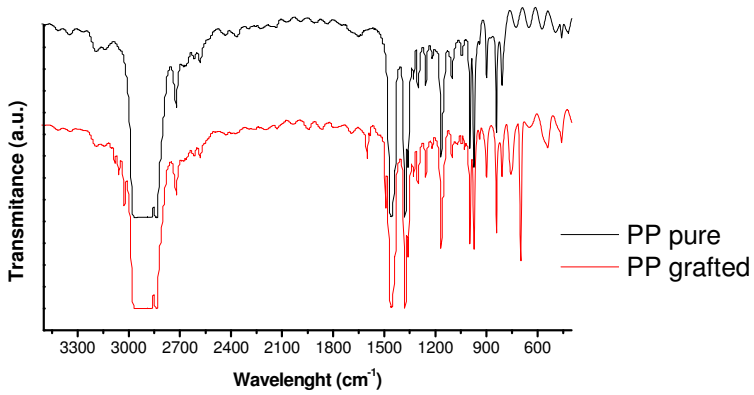

Figure 1. Infrared spectra of PP pure (black line) and PP grafted (red line)

The infrared spectra of the grafted film (Figure 1) shows 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, all of these peaks are absent in the pure PP spectrum [6] .

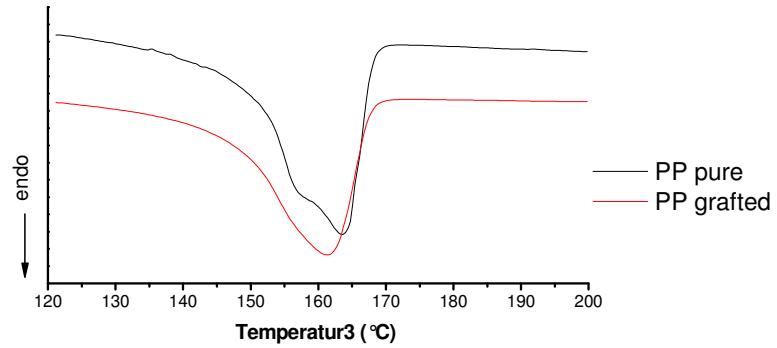

Figure 2. DSC curves of PP pure (black line) and PP grafted (red line)

Figure 2 shows the DSC curves indicating the melting temperature (T_m) for PP films ungrafted and graft. DSC analysis allows the evaluation of the crystallinity, X_c that is given by the equation (2):

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

where $\Delta H_{m100\%}$ correspond the value of enthalpy for a PP 100% crystalline (209 kJ kg^{-1}) [7] and ΔH_m is the experimental value.

Table 2. Thermal analysis of the samples pure and grafted.

Sample	T_{onset} (°C)	T_m (°C)	T_c (°C)	ΔH_m (J g^{-1})	X_c (%)
PP Pure	434.86	163.05	95.02	66.37	31.77
PP 40 kGy	396.78	163.01	90.12	46.74	22.36
PP 80 KGy	397.91	161.14	98.76	46.92	22.45
PP 100 kGy	395.36	160.15	97.33	40.61	19.43

T_{onset}: initial degradation temperature; $T_{m:}$ melting temperature; T_c: crystallization temperature; ΔH_m: melting enthalpy; X_c: degree of crystallinity

The morphology of the semi-crystalline polymers is modified when it was exposed to a radiation degradation process. This fact is attributed to the degradation mechanisms, owing to chains scission of the molecule [8]. In general, because of the chemical degradation the crystallinity increase but due to graft polymerization the degree of crystallinity (X_c) decrease. The experimental T_m is nearly from the reported value of 165 °C, according to the literature [9]. The results are showed in Table 2. The samples grafted show a decrease in the values of T_{onset} (Table 2) when they are compared with the pure polymer.

4. CONCLUSION

The grafting polymerization by radiation-induced process was successfully carried out. The DOG increases with increase the absorbed dose. The graft reaction was confirmed by infrared spectroscopy, where is possible identify the peaks referents to the styrene. The thermal analysis (T_{onset}) indicates that the grafted membranes are less stable than the pure membrane.

ACKNOWLEDGMENTS

This work was supported by CNPq (Conselho Nacional de Pesquisa e Desenvolvimento) processes numbers: 50.7100/2004-2, 50.5205/2004-1 and 133961/2005-2, CAPES, IPEN/CNEN-SP, Eleosmar Gasparin – CQMA–IPEN, Sandra Maria Cunha – CCTM-IPEN and BRASKEM for the PP film.

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