Grafting of styrene onto polypropylene using chemistry radiation

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The grafting of styrene onto polypropylene (PP) by the simultaneous radiation method was studied in this work. PP films with 40µm thickness were exposed to gamma ionizing radiation at room temperature and nitrogen atmosphere. The structural changes and surface morphologies of the modified PP films were characterized by a Fourier transform infrared spectroscopy (FTIR), DSC, and TGA. The degree of grafting was investigated after material radiation showing the higher values at 21 days of pos-radiation.

Introduction

Polypropylene (PP) is a semi-crystalline thermoplastic and 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.

Grafting polymerization is an effective method for chemical and physical modification of properties of polymeric surfaces.

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.

This work presents the preliminary data of PP films grafted with styrene by chemistry radiation.

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

In this experiment the radiation grafting of styrene onto PP was initiated by simultaneous irradiation method under cobalt–60 gamma rays source, under nitrogen atmosphere at room temperature.

The material was submitted to 40 kGy and 100 kGy doses with a dose rate of 10 kGy h^{-1}.

After irradiation, the samples were evaluated at room temperature for 14, 21 and 28 days to observe the degree of grafting behavior.

The styrene monomer was mixed with toluene in a proportion of 1:1.

Thermal treatment were made after irradiation and then extracted by hot acetone in Sohxlet to remove the remaining homopolymer. After that the films were dried in vacuum oven to eliminate residual solvents and impurities.

Materials and Methods

It was used a 40µm thick film of polypropylene supplied by Braskem and styrene monomer by Rudnick.

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

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

Where Wi and Wf are the masses of the PP samples before and after grafting, respectively.

Thermogravimetric Analysis (TGA) were recorded with a Mettler-Toledo TGA / SDTA 851 thermobalance in static and dynamic atmosphere from 25 up to 700 °C at a heating rate of 10 °C min^{-1} under inert atmosphere.

Differential Scanning Calorimeter (DSC) measurement was carried out in a 822 Mettler-Toledo under nitrogen atmosphere at a heating rate of 10 °C min^{-1} and temperature range of -50 to 280 °C, keeping in 280 °C for 5 minutes and from 280 to -50 °C at a colling rate of 50 °C min^{-1} and finally from -50 up to 280 °C at heating rate of 10 °C min^{-1}.

The films were cut into pieces and analyzed at Nexus 670 FTIR of Thermo Nicolet spectrometer was used to record the spectra of samples ungrafted and grafted.

Results and Discussion

The samples were analyzed before and after grafting process.

Figure 1 shows that both doses 40 kGy and 100 kGy had the best result after 21 days of the simultaneous radiation and grafting process. For 40 kGy DOG was 9.55% and at 100 kGy was 8.3%.

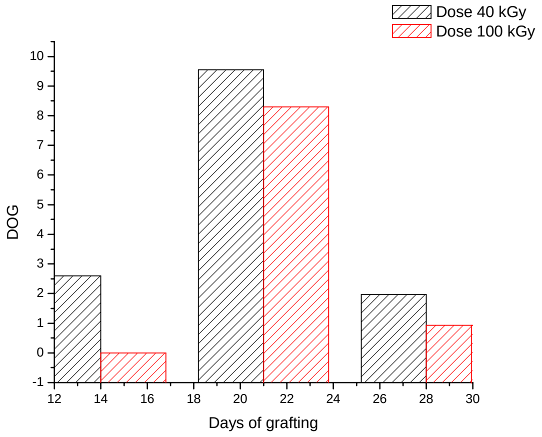

Figure 1 – Relation between degree of grafting and the days of grafting after the radiation.

For the films with the higher degree of grafting the spectra show the characteristic IR absorption peaks of benzene ring at 698 cm^{-1}, of styrene 3080 - 3010 cm^{-1} and 1601 – 1500 cm^{-1} attributed to the deformation C=C of the aromatic rings, all of these peaks are absent in the pure PP spectrum [5].

Table 1 – Crystallization and Melting Temperature.

Sample	Tc (°C)	Tm (°C)
Pure	95.02	164.06
40 kGy	105.8	162.93
100 kGy	105.2	160.62

Tc = Crystallization temperature
Tm – Melt temperature

All the samples presented increasing of Tc temperature and a decreasing in the melting point with grafting time in relation to the pure polymer. The results are showed in Table 1.

The morphology of the semi-crystalline polymers are modified when it were exposed to a chemical degradation process. This fact is attributed to probable the degradation process, which have caused scission of molecular chains [6].

The experimental Tm is nearly from the reported value of 165 °C, according to the literature [7].

The Tonset (initial degradation temperature) for pure PP was 435.05 °C while 411.25 °C at 40 kGy and 407.97 °C at 100 kGy.

Table 2 – Experimental temperatures by TGA.

Sample	Tonset(Ti)	Tendset(Tf)	Tf -Ti
Pure	435.05	467.8	32.72
40 kGy	411.25	462.4	51.15
100 kGy	407.97	459.81	51.84

Ti = Initial degradation temperature
Tf = Final degradation temperature

The difference Tf – Ti, as shown in Table 2, is called reaction interval. How smaller this interval is more stable is the material under thermal degradation; however this was not observed in these films. Which means that the graft films are less stable to thermal degradation than the ungrafted films.

Conclusion

Through the IR absorption technique was possible to confirm the graft.

Although the graft had occurred at both doses when the films are submit at 100 kGy they become fragile. In the continuity it will study variations of dose to evaluate the influence in the graft polymer behavior in order to obtain thermal stable films.

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References

1. J. Chen; L. Yang; L. Chen; M. Wu; Y. C. Nho; I. Kaetsua *Rad. Phys. and Chem.* 2004, *69,*149.
2. R. Mazzei. D. Tadey; E. Smolko; C. Rocco *Nuc. Inst. and Meth. B* 2003, *208,* 411.
3. Y. Izumi; H. Nagaike; S. Tabuse; Y. Yoshida; S. Tagawa *Rad. Phys. and Chem.* 2001, *62,* 83.
4. C. Y. Huang; C. L. Chen *Surf. and Coat. Tech.* 2002, *153,* 194.
5. D. Lin-Vien; et. al in *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, Academic Pr, New York, 1991; 469.
6. H. Otaguro; B. W. H. Artel; D. F. Parra; E. C. L. Cardoso; L. F. C. P. Lima; A. B. Lugão *Pol. Ciência e Tecn.* 2004, *14,* 99.
7. C. G. Mothé; A. D. Azevedo, *Análise Térmica de Materiais,* Ieditora, São Paulo, 2002; 195.