Grafting of styrene onto poly(vinylidenefluoride) and poly(tetrafluoroethylene) films via gamma radiation

Adriana Napoleão Geraldes [1*], Heloísa Augusto Zen [1], Duclerc Fernandes Parra [1], Ademar Benévolo Lugão [1], Marcelo Linardi [1]

[1]*Instituto de Pesquisas Energéticas e Nucleares –IPEN - Centro de Química e Meio Ambiente, Av Lineu Prestes, 2242, 05508-900 Butantã, São Paulo, SP -* angeral@ipen.br

In this work were prepared poly(vinylidenefluoride), PVDF and poly(tetrafluoroethylene), PTFE films followed by styrene graft polymerization using a Co^{60} source. The films were irradiated at 40 and 100 kGy doses. The chemical changes in the PVDF and PTFE films after styrene grafting were monitored by infrared spectroscopic analysis (FTIR), differential scanning calorimeter analysis (DSC) and thermogravimetric analysis(TGA). The degree of grafting (DOG) was also determined.

Introduction

The irradiation of polymers creates active radical centers which initiates the polymerization of monomers leading to the formation of graft polymers. This method has been used to prepare polymer electrolyte films suitable for many applications. Fluoropolymers are a class of polymers with excellent chemical and thermal stability. Almost all fluoropolymer available materials, such as, PTFE, FEP and PVDF are used as the base of styrene grafting of films or membranes under simultaneous irradiation method or pre-irradiation method[1].

In this study, we have used PVDF and PTFE films followed by styrene graft polymerization using a Co^{60} source (simultaneous irradiation method). Films irradiated were prepared with 40 or 100 kGy doses with a dose rate of 10 kGy h^{-1}. The chemical changes in the PVDF and PTFE films after styrene grafting on irradiation were monitored by IR spectroscopic analysis, differential scanning calorimeter analysis (DSC), and TGA analysis. The degree of grafting (DOG) was also determined.

Experimental

Prepared films

PTFE was used in the form of film of 0,2 mm thickness. The PVDF was supplied in the form of pellets. The PVDF pellets had been pressed between two finely polishing inox steel plates. By this process, films of PVDF of 0,12mm had been made. The films of PTFE and PVDF had been immersed in styrene / toluene 1:1 (Merck) and irradiated. After the irradiation the films had been washed with toluene (Merck) in soxhlet extractor and dried in vacuum until constant weight. Irradiations were accomplished via Co^{60} source at 40 or 100 kGy doses at room temperature and oxygen free atmosphere .

After irradiation the samples were evaluated at room temperature for 7, 14, 21 and 28 days to observe the degree of grafting behavior.

Instrumental analysis

The FTIR analyses were performed on Nexus 670 FT-IR Thermo Nicolet.

TGA and DSC techniques were accomplished, at first in a Mettler - Toledo TGA / SDTA 851 thermobalance, by using variable heating rates under static and dynamic atmosphere, from 25 to 750° C temperature program, at a 10° C / minutes rate.

DSC curves, in a Mettler-Toledo DSC 822, under nitrogen atmosphere, for PTFE, from 0 to 400 °C, at 20° C/minute heating rate; keeping at 400 °C per 3 minutes; 400 to 0 °C at -50° C/minute heating rate; keeping at 0 °C per 3 minutes and reheating from 0 to 400 °C, at 10° C/minute heating rate.

For PVDF, from -25 to 240 °C, at 10° C/minute heating rate; 240 to -25 °C at 5 °C/minute heating rate; keeping at -25 °C per 5 minutes and reheating from -25 to 300 °C, at heating rate of 10° C/minute.

The degrees of grafting (DOG) were determined as the mass increase of the samples according to the equation (1).

$$DOG\ (\%) = [(wg-wo)/wo)]x100 \quad (1)$$

where wg and wo are the masses of the samples after and before grafting, respectively.

Results and Discussion

The films were analyzed before and after grafting process. The DOG (calculated from equation 1) in the grafting films has varied from 1.7% to 7.9% and 2.5% to 6.3% for PVDF films at 40 and 100 kGy respectively (figure 1). For the PTFE grafting films the DOG varied from 3.1% to 9.3% and 9.3% to 16% at 40 and 100 kGy respectively (figure 2).

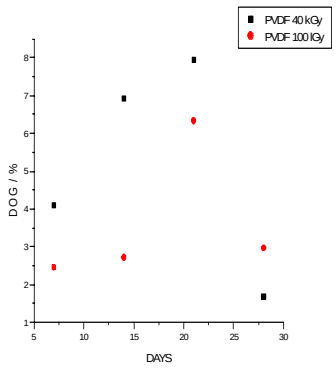
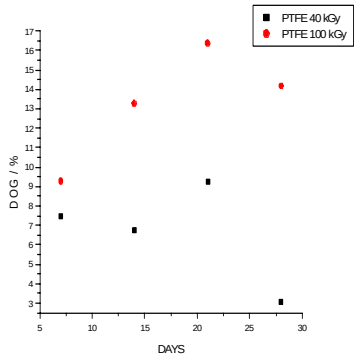


Figure 1– Relation between degree of grafting (DOG), % and the days after irradiation for PVDF films at 40 and 100 kGy doses.



I**Figure 2**– Relation between degree of grafting (DOG), % and the days after irradiation for PTFE films at 40 and 100 kGy doses.

According to figures 1 and 2, the higher results were achieved after 21 days of simultaneous radiation and grafting process.

To confirm the grafting of styrene in the grafted PVDF and PTFE films, FTIR spectra was conducted. The characteristics peaks in the PVDF base polymer are those near to 3000 cm^{-1} representing C-H stretching vibration. In infrared spectra of the graft PVDF films new peaks appeared in the region 3080 - 3010 cm^{-1}, due to aromatic C-H stretching vibrations; 2975 - 2840 cm^{-1}, due to aliphatic C-H stretching vibration and 1601-1500 cm^{-1}, attributed to aromatic C=C stretching vibrations[2]. In the FTIR spectra of the graft PTFE films, new peaks appeared in the region 3100 to 3000 cm^{-1}, due =C-H stretching vibration of the styrene groups. The band at 2920 cm^{-1} (is the asymmetric stretching) and 2850 cm^{-1} (symmetric stretching) were attributed to the aliphatic CH_2 group of the styrene graft. The band at 1600 cm^{-1} is the skeletal C=C stretching vibration and 1490 e 1460 cm^{-1} are the skeletal C=C in plane deformation of styrene graft[3].

For TGA results, the initial degradation temperature (Tonset) for the non grafted PVDF film, was 436.9 °C. After grafting the values were displaced to Tonset was 461.7 °C and 456.6 °C, at 40 and 100 kGy respectively, therefore the films are more stable thermally. The melting temperature (Tm) of original PVDF was 172.3 °C. The incorporation of styrene side chain graft into PVDF films caused decrease in Tm, 161.1 for 40 kGy and 159.6 for 100kGy, in agreement with the literature[4]. In the PTFE films, the Tonset for the non grafted PTFE film, was 555,4 °C. For the grafted films, there are mainly two separated steps degradation pattern in the TGA. The first degradation step presents the Tonset of 403.9 °C and 403.2 °C; and the second degradation step of 562.7 °C and 558.6 °C at 40 and 100 kGy respectively. The first degradation step should be attributed to the degradation of styrene graft and the second degradation step should be attributed to the degradation of the film matrix[3]. The Tm of original PTFE was 322.9 °C. The incorporation of styrene side chain graft into PTFE film have caused no significant change in Tm (323.0 °C for 40kGy and 321.0 °C for 100 kGy)[5].

Conclusion

The radiation induced grafting of styrene onto PVDF and PTFE films were promoted considerable strutural changes. The changes in the melting temperature (Tm) was found to be insignificant regarding to original films. These results are in a complete agreement with the results presented in the literature.

Acknowledgement

This work was supported by CNPq (Conselho Nacional de Pesquisa e Desenvolvimento) and IPEN (Instituto de Pesquisas Energéticas e Nucleares). We thanks to Fábio Paganini, ARKEMA GROUP for the PVDF and ULTRAHI PLASTICOS for the PTFE films.

References

1. J. Li; S. Ichizuri; S. Asano; F. Mutou; S. Ikeda; M. Iida; T. Miura; A. Oshima; Y. Tabata; M. Washio *Applied Surface Science*, 2005, *245*, 260.
2. S. D. Flint; R. C. T. Slade *Solid State Ionic*, 1997, *97*, 299.
3. J. Li; K. Sato; S. Ichizuri; S. Asano; S. Ikeda; M. Iida; A. Oshima; Y. Tabata; M. Washio *Eropean Polymer Journal*, 2005, *41*, 547.
4. M. M. Nasef; R. R. Suppiah; K. Z. M. Dahlan *Solid State Ionics*, 2004, 171, 243.
5. M. M. Nasef *Eropean Polymer Journal*, 2002, *38*, 87.