Cation exchange membrane by radiation-induced grafting of styrene onto polpypropylene : Effect of grafting conditions

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Abstract

In a first step towards preparation of cation exchange membrane, styrene monomer was grafted onto polypropylene (PP) film using simultaneous radiation-induced grafting technique. The effect of monomer concentration and irradiation dose on the degree of grafting was investigated. The grafting yield was found to increase until 40 % monomer concentration and beyond which tends to level off. The degree of grafting was found to increase gradually to the irradiation dose. The obtained grafted PP films (PP-g-PS) were characterized by FTIR-ATR to confirm the presence of polystyrene grafts in the PP films.

Keywords : Polypropylene, Styrene, Radiation-induced grafting.

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1. Introduction

Various types of techniques have been developed in recent years to prepare ion exchange membranes for various applications such as electrodialysis, waste water treatment, fuel cell and batteries [1-6]. Among all, radiation-induced grafting is an attractive method to prepare cation exchange membrane with high quality and low cost. This unique method can combine two incompatible polymers with high degree of control. The irradiation of polymers creates active radical sites on the polymer backbone which can be used to initiate the polymerization in the presence of monomers leading to the formation of side chain grafts [1,7].

Styrene is often used as a grafting monomer to produce copolymer that can host sulfonic acid group. [2, 8-10]. Therefore cation exchange membrane (strongly acidic) preparation involves two steps procedure: grafting of styrene onto polymer film and functionalizing the grafted film by sulfonation reaction. The objective of this work is to investigate the effect of monomer concentration and irradiation dose on degree of grafting of styrene onto PP film.

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2.1. Materials

Polypropylene (PP) film of 50 μm thickness was obtained from commercial source. Styrene (99% purity) was used without any further purification. Acetone, methanol and other chemicals were reagent grades and used as received.

2.2. Preparation of grafted film

Polypropylene (PP) films of thickness 50 μm were washed in acetone, dried at 60^oC in a vacuum oven, weighed and immersed in glass ampoules which contain styrene and methanol with different monomer concentration. The grafting solutions are purged with nitrogen to provide an inert atmosphere. The ampoule is then subjected to Co^{60} gamma rays at a certain period of time. The grafted films were removed and ultrasonically cleaned in toluene for 30 min and soaked overnight to remove the residual of ungrafted monomer and homopolymer that formed during the grafting reaction. The films were dried in vacuum oven at 70^oC until a constant weight is obtained. The degree of grafting was determined by percentage increase in weight:

$$\text{Degree of grafting (\%)} = \left(\frac{W_g - W_i}{W_i} \right) x\, 100\%$$

where W_g and W_i are the weights of grafted and original films, respectively.

2.3. Characterization of the grafted films

Fourier Transform Infra-red Spectroscopy (FTIR) measurement is to be carried out using a Perkin Elmer Spectrum 2000 equipped with ATR. The spectra are to be measured in transmittance mode at a wave number range of 3600-600cm^{-1}.

3. Results and discussions

Figure 1 shows the relationship between degree of grafting and monomer concentration for grafting of styrene onto PP films at different irradiation dose. The obtained degree of grafting increases until 40% monomer concentration and tends to level off after this point. The weight of the grafted film decreases until 100%. This phenomenon is due to

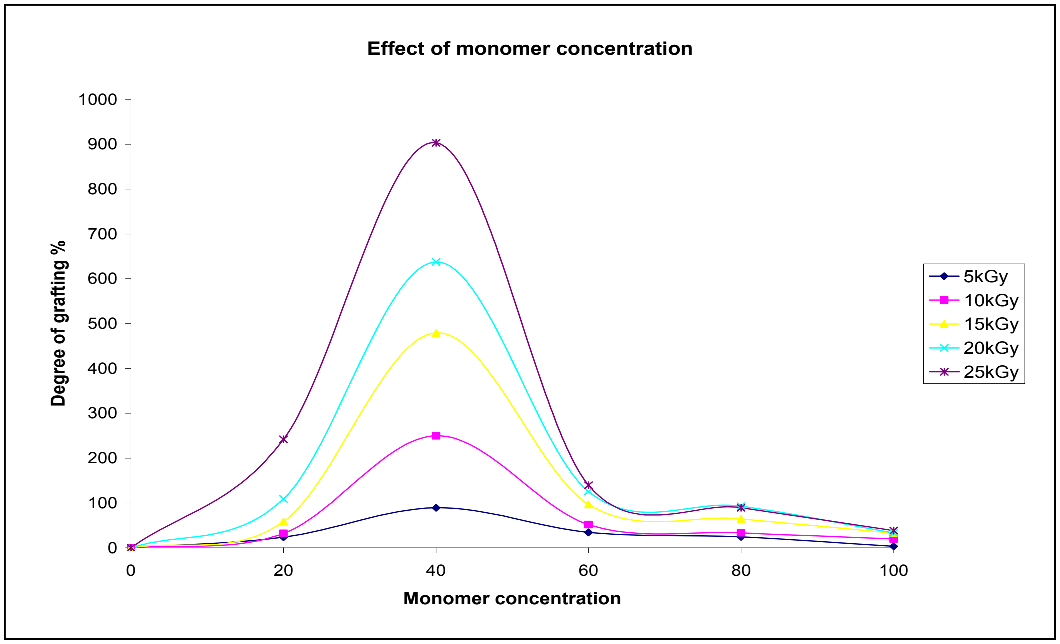
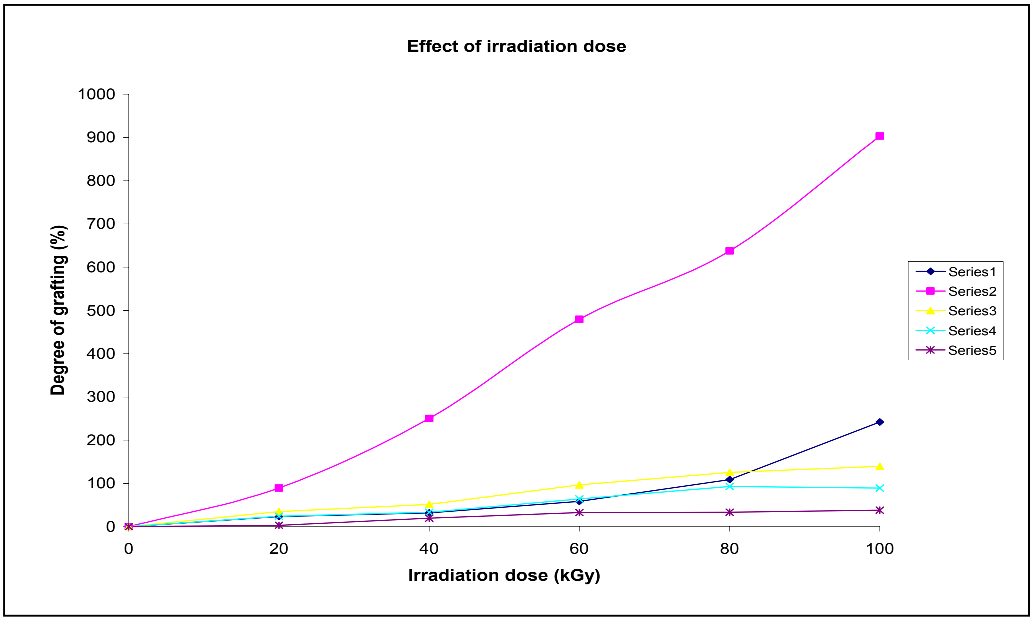


Fig.1: Degree of grafting (%) vs monomer concentration (%)

Trommsdorff effect [11]. Similar result has demonstrated by Nho when styrene is grafted onto polypropylene fabric and this plot is splitted into two regions [12].

The increase is due to styrene diffusion through the polymer matrix and it is suggested that the grafting occurs at the surface first. Then styrene swells and diffuses into the grafted layer and grafting occurs until the middle part of the film. Methanol as the solvent helps to swell the film. The higher viscosity of polystyrene impedes styrene diffusion until equilibrium swelling is reached at 40 % monomer concentration. The original PP surface looks smooth and the surface become rougher after being exposed to gamma radiation.

Figure 2 shows the relationship between the degree of grafting and irradiation dose in different monomer concentration. This result shows that the degree of grafting increases gradually with the increase in irradiation dose. This behavior is due to the more free radicals are formed and the opportunity of grafting reaction to occur is high. The degree of grafting with 40% monomer concentration reach the highest degree of grafting compared to other composition as the diffusion of styrene into the polymer at this level is enhanced.



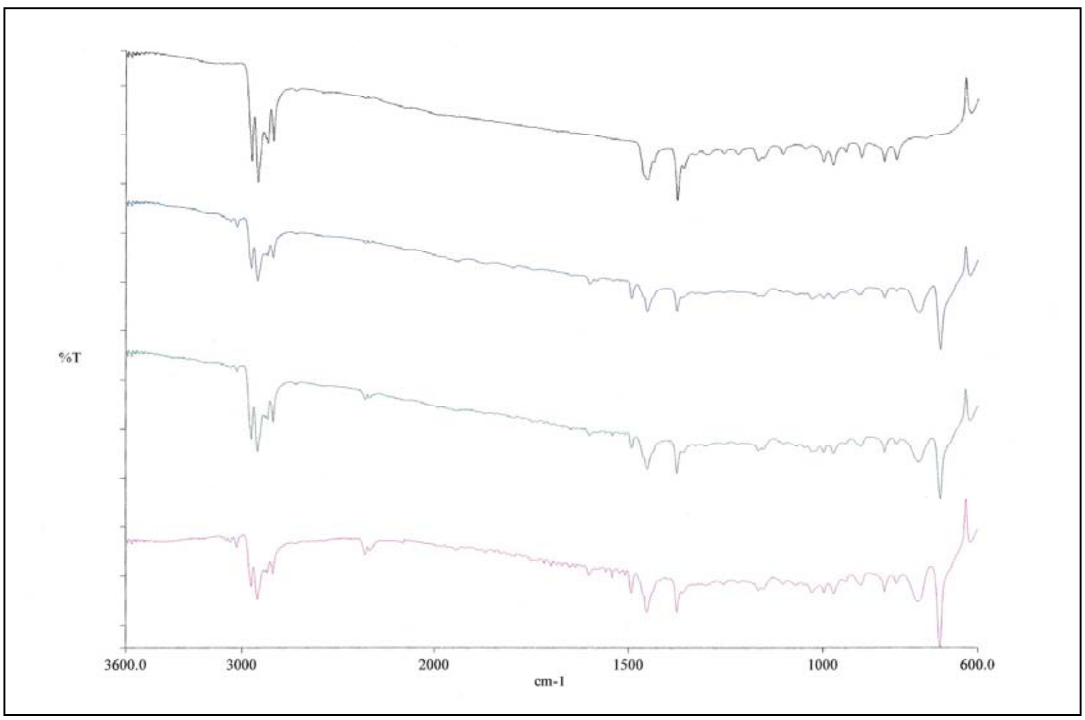


Fig.3: FTIR spectra of (a) original PP film (a) and PP-g-PS films with degrees of grafting (b) 139% (c) 89% (d) 33%

Characteristic transmittance peaks of functional groups of PP-g-PS were detected by a Fourier Transform Infra-red Spectroscopy (FTIR-ATR). The FTIR peaks of original PP and PP-g-PS (139.39% DOG) are shown in figure 3. New peaks appeared in the grafted film at 3050, 1500 and 1600 are resulting of benzene ring structure. The absorption bands appeared at 2800-2900 and 2900-3000 cm^{-1} are attributed to symmetric and asymmetric stretching of CH_2 group respectively.

4. Conclusion

PP-g-PS films capable of hosting sulfonic acid groups were successfully prepared by radiation-induced grafting. The degree of grafting was found to be strongly dependent on the monomer concentration and the irradiation dose. The FTIR measurement has confirmed the presence of polystyrene chain grafts onto polypropylene films. In future work, grafted films will be sulfonated and membrane properties are to be determined.

Acknowledgement

Authors would like to thank to Ministry of Science, Technology and Environment for funding this work.

References

[1] B. Gupta and G. G. Scherer, Proton Exchange Membranes by Radiation-Induced Graft Copolymerization of Monomers into Teflon-FEP Films, *Chimia* 48; 1994 : 127-137.

[2] E. A. Hegazy, H. Kamal, N. Maziad, A. M. Dessouki, Membranes Prepared by Radiation Grafting of Binary Monomers for Adsorption of Heavy Metals from Industrial Wastes, *Nucl. Instr. Meth. B* 1999; 151: 386-392.

[3] M. M. Nasef, H. Saidi, H. M. Nor, K. Z. M. Dahlan, K. Hashim , Cation Exchange Membranes by Radiation-Induced Graft Copolymerization of Styrene onto PFA Copolymer Film. I. Preparation and Characterization of the Graft Copolymer, *J. Appl. Polym. Sci.* 1999; 73 : 2095-2102.

[4] M. M. Nasef, H. Saidi and H. M. Nor, Proton Exchange Membranes Prepared By Simultaneous Radiation Grafting of Styrene onto FEP Films. I Effect of Grafting Conditions, *J. Appl. Polym. Sci.* 2000; 76: 220-227.

[5] M. M. Nasef, H. Saidi, H. M. Nor, M. F. Ooi, Proton Exchange Membranes Prepared By Simultaneous Radiation Grafting of Styrene onto FEP Films. II Properties of the Sulfonated Membranes, *J. Appl. Polym. Sci.* 2000; 78; 2443-2453.

[6] M. M. Nasef, H. Saidi, Preparation of Crosslinked Cation Exchange Membranes by Radiation Grafting of Styrene/Divinylbenzene Mixtures onto PFA Films, *J. Mem. Sci.* 2003; 5572: 1-12

[7] A. Chapiro, Radiation chemistry of Polymeric Systems, Eds.H.Mark, C.S.Maxell and H.W.Melville, *High Polymers Vol.XV* 1962, Interscience, London.

[8] Y. H. Chi, L. C. Chen, The Effect of Plasma Surface Modification From a Rotary Plasma Reactor on The Styrene Grafting onto Polypropylene Surface, *Surf. Coat. Tech*. 2002; 153 : 194-202.

[9] K. M. El-Samawi, A. M. El-Naggar, H. M. Said, A. H. Zahran, Graft Copolymers of Polypropylene Films. 1. Radiation-induced Grafting of Mixed Monomers, *Poly. Int.* 1997; 42 : 225-234.

[10] E. A. Hegazy, H. A. El-Rehim, N. A. Khalifa, A. E. Ali, Preparation and Characterization of Supported Hydrogels Obtained by Radiation Grafting of Binary Monomers, *Rad. Phys. Chem*. 1999; 55 : 219-229.

[11] Y. C. Nho, J. Chen, J. H. Jin, Grafting Polymerization of Styrene onto Preirradiated Polypropylene Fabric, *Rad. Phys. Chem.* 1999; 54 : 317-322.

[12] P. A. Dworjanyn, J. L. Garnett, M. A. Long, Y. C. Nho, M. A. Khan. Eds. E. Reichmanis, C. W. Frank, J. O'Donnell, Role of Homopolymer Suppressors in UV and Radiation Grafting in the Presence of Novel Additives, ACS Symposium Series 1993; 527: 103-117.