Chemical Modification of Polypropylene by Maleic Anhydride: Melt Grafting, Characterization and Mechanism

Oromiehie A., Ebadi-Dehaghani H., and Mirbagheri S.

Abstract—Polypropylene (PP) was functionalized with maleic anhydride (MAH) in the presence of dicumyl peroxide (DCP) via melt grafting in a batch mixer, where the maleic anhydride and peroxide concentrations were varied. The effect of concentration of monomer and initiator on the degree of functionalization and properties of the products was FT-IR spectroscopy, investigated bv contact angle measurement, thermal analysis and titration. It was found that the degree of functionalization depends on the initial concentration of monomer and initiator that used in reaction. Finally a mechanism of melt grafting MAH onto PP proposed on the basis of our experimental results and other experimental finding published in the literature.

Index Terms—Characterization, modification, PP.

I. INTRODUCTION

Isotactic polypropylene (PP) is one of the most important thermoplastics in the world today. PP has gained an important position among other polymers due to its versatile and broad range of applications [1]. It is extensively used in a wide range of applications including carpet backing, face yarn and construction fabrics, self-hinging packages, appliance parts, medical equipment, automobile parts, films, bottles, containers, and so forth. The functionalization possibilities of PP by polar monomers as an effective way of increase the polarity of polypropylene and so its affinity with other polar materials is interesting. In fact, these kinds of grafted polymers have been widely used to improve interfacial adhesion between the components in polymer blends [2]-[7]. Maleic anhydride has been used recently for the functionalization of polyolefins due to the higher reactivity of the anhydride group toward successive reactions [8]-[10].

The succinic anhydride groups of malice anhydride graft polymers are highly reactive and can form covalent bonds to polar polymer backbones and end groups. Since chemical reactions in polypropylene melts are attractive routes to new polymers, reactive processing technology has been studied extensively [11], [12].

Grafting reaction of maleic anhydride onto PP by reactive processing involves reaction between the polymer melt with maleic anhydride, in the presence of organic peroxides. The organic peroxides are thermally unstable and undergo hemolytic scission at the oxygen-oxygen bonds to form primary radicals at the processing conditions used. The radicals with draw hydrogen atoms from the polypropylene chains forming macro radicals on the polymer backbone can initiate the grafting process. However, such reactions are accompanied by chain scission, which alters the rheologic characteristics of PP [13]. Finding the optimum conditions of the grafting process is a very complicated investigation, in virtue of the great number of variables involved, among which are: type and concentration of peroxide, maleic anhydride concentration, reaction time, reaction temperature, rotor speed, addition sequence of the reagents, and presence or not of stabilizers. In a number of studies a graft copolymer is used as a compatibilizing agent, where the polymer consists of a polyolefin backbone grafted with functional groups such as butyl acrylate or maleic anhydride [14]-[16].

In our work, the functionalizing reactions were carried out in an internal mixer, at optimum conditions. The amount of reacted maleic anhydride and the extent of degradation in the PP were determined by means of FT-IR, DSC and MFI respectively. The current article will evaluate the effect of the concentrations of maleic anhydride on the dependent variables presented above.

II. EXPERIMENTAL

A. Materials

Isotactic PP (commercial code V30S) with MFI=7.9 g/10 min (ASTM D1238) from Arak Petrochemical Co. Iran, maleic anhydride (MA), DCP from Merck and Irganox B225 from Ciba Co. were used.

B. Processing

First Step: Grafted PP with overall contents of 0,1,2,3 and 4 phr of maleic anhydride and 0.1 phr of DCP and 0.01phr Irganox B225 were performed by melt mixing in an optimum condition for processing in Haake Rheometer 90 were selected from published studies [7], [14] at 180 °C, 60 rpm and 10 min.

Second Step: In this process PP was grafted with constant concentration 3 phr of maleic anhydride, but various portions of DCP (0.1, 0.2, 0.4&0.6 phr of DCP) and 0.01 phr Irganox B225 were performed as in the first step.

C. Characterization

All crude graft PP samples were dissolved in xylene in

Manuscript received September 18, 2013; revised November 30, 2013.

A. R. Oromiehie and S. Mirbagheri are with the Iran Polymer and Petrochemical Institute of Tehran, Iran (e-mail: a.oromiehie@ippi.ac.ir, a.oromiehie@ippi.ac.ir).

H. Ebadi-Dehaghani is with the Shahrza Branch, Islamic Azad University (e-mail: ebadi@iaush.ac.ir).

order to remove the non-reacted monomers and oligomers if formed during process (reaction 8 in the Fig. 1) and initiator by refluxing in xylene for 4 hours and precipitated in acetone. Finally, they were dried in a vacuum oven at 105 $^{\circ}$ C for 3 hours to constant weights.

Decomposition of the initiator





Fig. 1. Proposed Mechanism using our experiments and literature review.

D. Titration of Anhydride Content

The anhydride concentrations of all samples were determined by titration of 0.5 gram of PP-g-MA in 50 milliliters xylene at boiling temperature that repeated 3 times for each sample. Some drop of distilled water was added in order to hydrolysis anhydride into carboxylic acid. The carboxylic acid concentration was determined directly by alcoholic potassium hydroxide 0.1N. The indicator used was bromo thymol blue 1% in DMF solvent. The PP-g-MA was completely soluble at the boiling temperature and did not precipitate during titration. The grafting percent (*G*) was determined by using the following relation:

$$A.N = (mlKOH \times N \times 56.1)/gr polymer$$
 (1)

$$G = (A.N \times M_m) / (2 \times 561) \tag{2}$$

where

A.N= Acid Number

 M_m = Molecular weight of grafted monomer

FT.IR Spectroscopy

The evidence of functionalizing as well as its extent was determined by *FT.IR* spectroscopy. Thin films of PP and functionalized PP were obtained by compression molding between steel plates covered with thin aluminum sheets at 180 °C . *IR* spectra were recorded on a Bruker *FT.IR* spectrophotometer model Exonix 55 from 500cm⁻¹ to 4000cm⁻¹.

E. Contact Angle Measurement

The contact angles of distilled water on the thin films of PP and functionalize PP were measured by the sessile drop method that were performed at the room temperature using KRUSS G2/G40 contact angle measuring system equipped with software for drop-shape analysis. The grafted PP samples were placed on the sample holder and distilled water (0.05 ml) was then placed on the specimen using a microsyringe. The angle between the baseline of the drop and the tangent at the drop boundary was measured, using a direct reading goniometry telescope, with a magnified image of the droplet displayed on a screen. The measurement was completed after about 60s. In order to prevent test liquid evaporation, measurements were performed under closed chamber. The drop shape was solved numerically and fitted by means of mathematical functions. Each contact angle is the average of value of 6 measurements. The contact angle was obtained according to the following equation [10]:

$$\theta = 2 \tan^{-1} \left(\frac{2h}{w} \right) \tag{3}$$

where, θ is the contact angle, *h* is height and *w* is the wide of the droplet that were measured from the photograph and from the geometric considerations.

F. Thermal Analysis (DSC)

Thermal properties melting temperature (T_m) and crystallization temperature (T_c) of PP and functionalized PP were recorded in a Perkin-Elmer model Pyris1, differential scanning calorimeter (DSC) by heating ~5mg of samples at 10°c/min under nitrogen atmosphere from ambient to 200°C. The sample was kept at 200°C for 5min and then cooled to room temperature at rate of 10°C/min.

The values obtained for heat of fusion, from DSC measurement, for PP and functionalized PP samples were used to estimate the percentage of crystallinity (%*x*). This was done by using the value for enthalpy of fusion $\Delta H_f *$ of 100% crystalline PP as 198J/g. The crystallinity of various samples was obtained according to the following equation [17]:

%Crystallinity (
$$X_c$$
) = ($\Delta H_f / \Delta H_f^*$) ×100 (4)

where ΔH_f is the heat of fusion of functionalized PP and ΔH_f^* is heat of fusion of 100% crystalline PP.

III. RESULTS AND DISCUSSION

A. Titration Results of Purified Grafted Pp (PP-g-MA) with Various Content of Monomer

Titrations were preformed onto washed and dried PP-g-MA to determine the amount of grafted anhydride. Results are summarized in Table I which shows that an increase in the monomer content from 1 to 3 phr lead to increase in graft percentage but it decreased by more adding of MA (>3phr). This is due to the MA homopolymerization.

TABLE I: TITRATION RESULTS OF PP-G-MA SAMPLES WITH 1, 2, 3 AND 4 PHR OF MALEIC ANHYDRIDE AND 0.1 PHR OF DCP

MA Conc. (PHR)	Mean Value V(ml)	Acidic Number	% Grafting
1	0.34	3.03	0.27
2	0.42	3.75	0.33
3	0.49	4.37	0.38
4	0.44	3.93	0.34

B. Titration Results of Purified Pp-G-Ma with Various Content of DCP

The peroxide concentration is the independent variable that has the greatest effect on amount of grafted maleic anhydride. This effect is shown in Table II where the peroxide concentrations are varied.

TABLE II: TITRATION RESULTS OF PP-G-MA SAMPLES WITH CONSTANT CONCENTRATION 3 PHR OF MALEIC ANHYDRIDE, BUT VARIOUS PORTIONS OF DCP (0.1, 0.2, 0.4, 0.6 AND 0.8 PHR OF DCP)

DCP Content (PHR)	Mean value V(ml)	Acidic Number	% Grafting
0.1	0.34	3.03	0.27
0.2	0.42	3.75	0.33
0.4	0.49	4.37	0.38
0.6	0.44	3.93	0.34
0.8	0.44	3.93	0.34

This Table shows that the grafting percentage increased with peroxide concentration and increase in the percent grafting is caused by an increase in concentration of radicals formed through the decomposition of initiator. Thus the higher the concentration of radicals, the higher the chain transfers to polymer backbone and the higher the grafting percentage [7].

C. FT-IR Spectroscopy

The FT-IR results of purified PP-g-MA shown in Fig. 1. In the IR spectra of PP-g-MA absorption peak at (1680cm⁻¹) is due to the anhydride groups. It can be seen that the intensity of peaks increased by increasing the MA monomer content from 1 to 3 phr that lead to increase the graft percentage, but it decreased by more adding of MA (>3phr). It seems that is due to the MA homopolymerization.

Fig. 2 shows the FT-IR spectra of grafted PP with 3 phr of maleic anhydride and 0.1, 0.2, 0.4, 0.6 and 0.8 phr DCP. As seen in this figure the FT-IR spectrum of PP-g-MA shows the absorption band at (1700-1740cm⁻¹) that is due to the presence of DCP and absorption bands at (1760-1800cm⁻¹) and around 1850cm⁻¹ can be assigned to grafted anhydride because an intense absorption band near 1785cm⁻¹ and a weak absorption band near 1850cm⁻¹ is due to symmetric and asymmetric C=O stretching respectively.[8], [14], [15]. It has been shown that the intensity of peaks increased by

increasing the DCP content from 1 to 4 phr that lead to increase the graft percentage but it decreased by more adding of DCP (6phr) that may be due to decomposition effect of initiator.



Fig. 1. IR spectra of PP-g-MA samples with 0,1,2,3 and 4 phr of maleic anhydride and 0.1 phr of DCP.



Fig. 2. Magnified part of spectra of samples with constant concentration 3 phr of maleic anhydride, but various contents of DCP (0.1, 0.2, 0.4 and 0.6 phr) from 1900 to 1650 cm-1.



Fig. 3. Contact angle results of PP-g-MA samples with 0,1,2,3 and 4 phr of maleic anhydride and 0.1 phr of DCP comparing of origin PP.

D. Contact Angle Measurement

The polarity of the functionalized PP was measured by contact angle of distilled water on the sample films.

The angle for a pure PP film without any functionalized monomer was measured and it was 97 . The contact angle of the purified PP-g-MA with various content of monomr and

PP with 3phr MA and various content of DCP were shown in Fig. 3 and Fig. 4 respectively.

IV. CONCLUSION

In the case of first and second process, as the monomer content increase to 3 phr, contact angle decrease, but it increased by more content of monomer. It seems that it is due to the MA homopolymerization. As seen in the case of PP-g-MA with various content of DCP, an increase in monomer content lead to decrease in the contact angle to 4phr DCP but it increased with 6phr (DCP), that it may due to decomposition effect of initiator.



Fig. 4. Contact angle results of PP-g-MA samples with constant concentration 3 phr of maleic anhydride, but various contents of DCP (0.1, 0.2, 0.4, 0.6 and 0.8 phr).

E. Thermal Analysis (DSC)

The DSC results of samples and the change of crystalline temperature of copolymer are given in Table III and Table IV.

The values obtained for heat of fusion from DSC measurement, for PP and functionalized PP samples were used to estimate the percentage of crystallinity. It was observed a higher crystalline temperature for PP-g-MA than that for PP. The increasing in crystalline temperature could be attributed to MA acting as nucleating in PP and also because of the connection of the carbonyl group to PP.

The crystalline percent of PP-g-MA copolymers were shown that increasing the percent of monomer to 3phr as well decreased the crystalline percentage but it slightly increased by more addition, that it may due to MA homopolymerization (reaction 8 in the mechanism).

TABLE III: THERMAL PROPERTIES OF SAMPLES WITH 0, 1, 2, 3 AND 4 PHR OF MALEIC ANHYDRIDE AND 0.1 PHR OF DCP.

MA Conc.(phr)	$T_m(\mathcal{C})$	ΔH_f (Cal/g)	% Crystallinity
0	168	23	46.00
1	169.34	22.8	45.60
2	171.47	22.57	45.14
3	169.6	21.69	43.38
4	169.7	22.61	45.22

TABLE IV: THERMAL PROPERTIES OF SAMPLES WITH CONSTANT CONCENTRATION 3 PHR OF MALEIC ANHYDRIDE, BUT VARIOUS CONTENTS OF DCP

of Der .						
DCP Content (phr)	$T_m(\mathcal{C})$	ΔH_f (Cal/g)	% Crystallinity			
0	168	22.8	45.6			
0.1	169.0	22.5	45.1			
0.2	171.2	21.7	43.4			
0.4	171.8	21.3	43.0			
0.6	170	22.6	45.2			
0.8	170.5	23	46.0			

Polypropylene was functionalized with different ratios of MA and DCP in optimum processing conditions by melt mixing. The properties of functionalized PP were characterized by titration, FT-IR spectroscopy, Contact angle measurement and thermal analysis. It was concluded that the degree of functionalized PP depends on the concentration of both monomer and initiator. It was found that the increase in peroxide concentration to 4phr resulted in the elevation in the percent reacted MA, and the elevation in the initial maleic anhydride concentration in the reaction mixture led to an increase in percent MA, passing through a maximum value, with posterior decline, The initial increase in the percent grafting is caused by an increase in concentration of radicals formed through the decomposition of initiator, and also it was found that the monomer content from 1 to 3 phr of monomer has satisfied results, but in higher amount of monomer the functionality was decreased, this due to homopolymerization of monomer during processing.

According to our findings and review of other experimental findings our proposed mechanism is as in the Fig. 1. MA monomer (reaction 2 and 3). One of the possible reactions for polypropylene radicals is chain scission (reaction 4) [9].

The mechanism includes three stages; Initiation, Grafting and termination. As seen in the proposed mechanism radical formation could carry out both in polypropylene chain and Gel formation was observed in purification of samples that a yellow bulk gel wasn't dissolved in xylene. Grafting of maleic anhydride onto PP was shown in 6 and 7 reactions. As seen in titration and IR results homopolymerization of maleic anhydride (reaction 8) happened at high content of MA. Chain transfer reaction was shown in reaction 9 and different kind of termination reactions included combinations and disproportions were shown in 10 to 21 reactions.

ACKNOWLEDGMENT

The work described in this paper was supported by a grant from the Iran Polymer and Petrochemical Institute (IPPI). The authors gratefully acknowledge the Research Vice Chancellor of IPPI and his co-workers.

REFERENCES

- I. K. Mehta, S. Kumar, G. S. Chauhan, and B. N. Mishra, "Grafting onto isotactic polypropylene. III. Gamma rays induced graft copolymerization of water soluble vinyl monomers", *J. Appl. Polym. Sci.*, vol. 41, pp. 1171-1175, March 2003.
- [2] D. R. Paul, Polymer Blends, Academic, N.Y, 1978, pp. 200-235.
- [3] N. G. Gaylord, "Compatibilizing Agents: Structure and Function in Polyblends", *J. Macromol. Sci. Chem.*, *Part A*, vol. 26, pp. 1211-1218, Dec. 1989.
- [4] M. Xanthos, Interfacial agents for multiphase polymer systems: Recent advances, *Polym. Eng. Sci.*, vol. 28, pp. 1392-1398, November 1988.
- [5] K. Cho, F. Li, J. Choi, Crystallization and melting behavior of polypropylene and maleated polypropylene blends, *Polymer*, vol. 40 1719–1729, May 1998.
- [6] J. M. Garcia-Martinez, O. Laguna and E.P. Collar, "Chemical modification of polypropylenes by maleic anhydride: Influence of stereospecificity and process conditions", *J. Appl. Polym. Sci.*, vol. 68, pp. 483-492, December 1998.
- [7] A. R. Oromiehie, S. A. Hashemi, D. N. Waters, I. G. Meldrum, "Functionalisation of Polypropylene with Maleic Anhydride and Acrylic Acid for Compatibilising Blends of Polypropylene with

Poly(ethylene terephthalate)", *Polym. Int.*, vol. 42, pp. 117-125, March 1999.

- [8] De Roover, B. Selavons, M. Carlier, V. Devaux, J. R. legras and A. Momtaz, "Molecular characterization of maleic anhydride-functionalized polypropylene", *J. Polym. Sci., Part A, Polym. Chem*, vol. 33, pp. 829-834, March 1995.
- [9] S. M. Mirabedini, H. Rahimi, Sh. Hamedifar and S. M. Mohseni, "Microwave irradiation of polypropylene surface: a study on wettability and adhesion", *International Journal of Adhesion and Adhesives*, vol. 24, pp. 163-170, May 2004.
- [10] D. Shi and J. Yang, "Functionalization of isotactic polypropylene with maleic anhydride by reactive extrusion: mechanism of melt grafting," *Polymer*, vol. 42, pp. 5549-5556, May 2001.
- [11] Z. M. Wang, H. Hong, and T. C. Chung, "Synthesis of Maleic Anhydride Grafted Polypropylene with High Molecular Weight Using Borane/O₂ Radical Initiator and Commercial PP Polymers," *Macromolecules*, vol. 38, pp 8966-8970, October 2005.
- [12] S. H. P. Bettini and J. A. M. Agnelli, "Grafting of maleic anhydride onto polypropylene by reactive processing. I. Effect of maleic anhydride and peroxide concentrations on the reaction," *J. Appl. Polym. Sci.*, 74, pp. 247-251, October 1999.
- [13] P. A. Callais and R.T. Kazmierezak, ANTEC, DALLAS, TX, (1990), May 7-11.
- [14] N. G. Gaylord, US Patent, No. 4506056 (1985).
- [15] B. De Roover, M. Sclavons, V. Carlier, J. Devaux, R. Legras and A. Momtaz, "Molecular characterization of maleic anhydride-functionalized polypropylene," *J. of Polym. Sci. Part A: Polym. Chem.*, vol. 33, pp 829-842, April 1995.

- [16] M. Yazdani-Pedram, H. Vega and R. Quijada, "Modification of poly(propylene) through grafting with dimethyl itaconate in solution", *Macromol. Chem. Phys.*, vol. 199, pp. 2495-2506, Dec. 1998.
- [17] L. J. Bellamy, *The infrared spectra of complex Molecules*, John Wiley & Sons, New York, 1964.
- [18] H. Ebadi, A. A. Yousefi and A. R. Oromiehie, "Preparation and Barrier Properties of PP/PET Blends," *Iran. Polym. J.*, vol. 16, pp. 659-669, March 2007.



A. R. Oromiehie was born in Najaf, Iraq, Iranian on Jan. 13, 1950. He received a bachelor of B.Sc: Chemistry, University of Sulymania, Iraq, 1968-1972 and M.Sc: Instrumental Methods of Analysis, University of Southampton, Southampton, UK, 1978-79. Who was dubbed the Ph.D. of Polymer Chemistry, Brunel University (West London), London, UK, 1993-1997.



H. Ebadi-Dehaghani was born on June 17, 1978, he is an Iranian. He was dubbed the Ph.D. student in polymer Engineering Iran Polymer and Petrochemical Institute (IPPI), 2011, M. Sc. in polymer Engineering Iran Polymer and Petrochemical Institute (IPPI), 2001-2003, B.Sc. in Applied Chemistry Esfahan university, Esfahan, Iran, 1996-2000.