

Synthesis and Characterization of Functionalized Polypropylene with Maleic Anhydride

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(Received 13th May, 2006, revise 15th November, 2006)

Summary: Grafting of maleic anhydride onto polypropylene in xylene medium initiated by benzoyl peroxide under nitrogen atmosphere has been studied. The effects of reaction time, reaction temperature, maleic anhydride concentration, benzoyl peroxide and material to monomer ratio have been studied in terms of % GE and % Add-on. The optimum conditions obtained for the grafting of maleic anhydride on 5.0 g of polypropylene were [BPO] = 8.25×10^{-2} mol/L, [MAH] = 2.04×10^{-3} mol/L, temperature = 120 °C, time = 300 min and polypropylene to solvent ratio = 1:2.0. The graft copolymer was characterized by FTIR spectrum.

Introduction

Graft copolymerization is a well-established technique used to modify properties of natural [1-9] and synthetic polymer [10-11]. Graft copolymerization of maleic anhydride with natural and synthetic polymer has been widely studied in recent years. The introduction of polar group onto the main chain has been widely performed in order to modify the properties of polyolefin's.

Unmodified polyolefin's present incompatibility with almost all other polymers due to the polarity of the aliphatic back bone and therefore, functionalization has been considered as a good way to obtain compatible blends polar polymers.

Modification with functional monomer particularly with maleic anhydride, [MAH] has been carried out by using free radical initiators. The reaction with several kinds of polyolefin's (LLDPE, LDPE, HDPE, ethylene propylene rubber) has been performed. The functionalization leads to systems with different properties and it is possible to receive a new kind of polymer, which has created a new properties.

The grafting of polypropylene with maleic anhydride represents on the oldest attempts to bind polar groups to the polypropylene chain to improve the compatibility of polypropylene with polar polymers or its adhesion to polar surfaces such as glass and inorganic materials.

Various mono-functional and bi-functional monomers can be used for the grafting of polypropylene through different routes, by solution state, [12-15] melt state [16-18] and by photo grafting process.

In the solution process, the polymer is dissolved in suitable solvent at an elevated temperature, and a monomer is added with initiator. The purified PP-g-MAH can be obtained by precipitation with large quantity to another solvent mainly acetone.

In this study maleated [PP] was prepared by solution state graft polymerization, using p-xylene as a solvent under free radical condition. The experiments were carried out to study the effect of different parameters such as reaction time, reaction temperature, [MAH] Concentration, [BPO] concentration and PP to solvent ratio on the percentage of grafting efficiency [% GE] and percentage add-on [% Add-on].

Results and Discussion

Grafting Evidence

Gravimetric Estimation: The grafting polymerization process was followed gravimetrically. The increase of weight of grafted PP over the weight of PP indicated the grafting of MAH onto PP.

FT-IR Spectroscopy: The FTIR spectra of the original PP and PP-g-MAH are shown in Figure 1a

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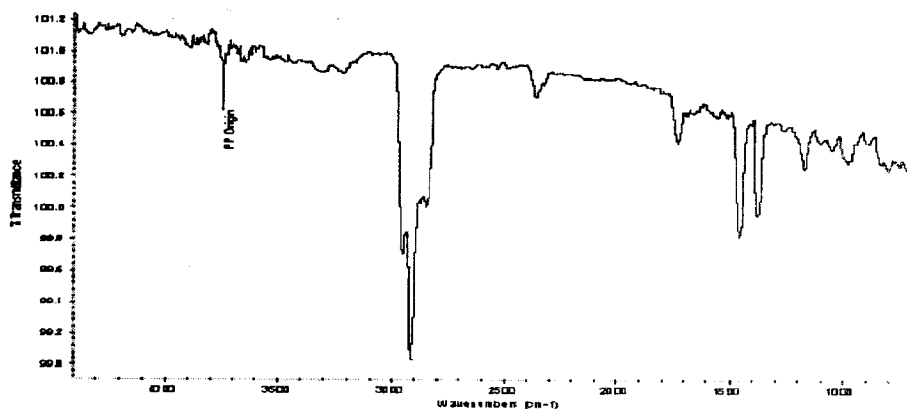


Fig. 1a: The FTIR spectra of PP original.

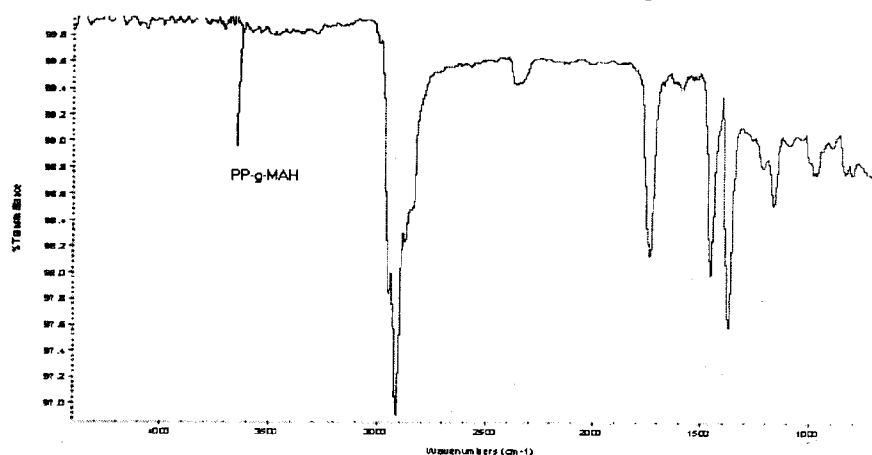


Fig. 1b: The FTIR spectra of PP-g-MAH.

and 1b It can be seen that a characteristic peak of carbonyl group ($>C=O$) at 1738 cm^{-1} is observed in the grafted polypropylene spectrum, which is not present in original PP (figure 1a). The carbonyl group providing evidence of grafting of MAH onto PP.

At first, the formation of free radicals was due to the thermal decomposition of the BPO and the radicals abstracted hydrogen atoms from the macromolecules, generating macro radicals which mostly participate in combination reactions. The grafting reaction mechanism of MAH onto PP was set out in the scheme

Effect of polymerization time

Table-1 Illustrates the effect of polymerization time from 60 min up to 360 min. It appears that grafting is increasing rapidly in between the intervals of 60 min to 300 min. Then it stays approximately

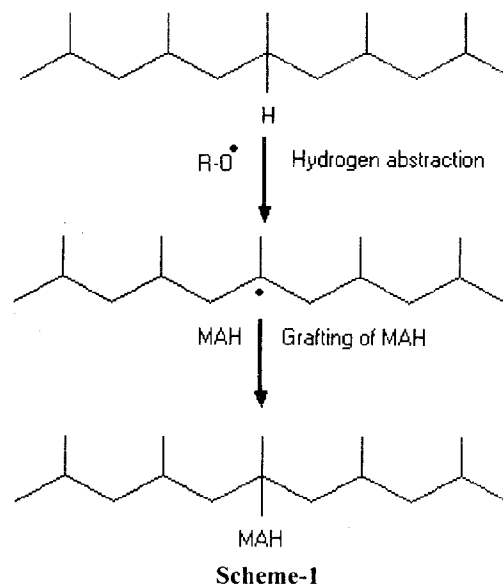


Table-1: Effect of reaction time on grafting of MAH onto PP (Reaction condition: [PP] = 5.00 g, [MAH] = 2.04×10^{-3} mol/ L [BPO] = 8.25×10^{-5} mol/ L, reaction temperature = 120 °C in 100 ml xylene)

Reaction Time (min)	% GE	% Add-on
60	10	0.40
120	18	0.72
180	25	1.00
240	48	1.90
300	64.5	2.30
360	64.5	2.50

Table-2: Effect of reaction Temperature on grafting of MAH onto PP (Reaction condition: [PP] = 5.00 gm, [MAH] = 2.04×10^{-3} mol/ L, [BPO] = 8.25×10^{-5} mol/ L, reaction time = 240 min, and reaction Temperature = 120 °C in 100 ml xylene)

Reaction Temp.(°C)	% GE	% Add-on
90	13	0.5
100	22	0.9
110	36.5	1.5
120	48.0	1.9
130	62.5	2.45
140	64.0	2.5

constant at 300 min probably due to an increase in rate of initiation and propagation, and this consistency in grafting at about 300 min. is clearly remark the optimum graft copolymerization time for grafting of MAH onto PP.

Effect of polymerization temperature

Table-2 shows the % GE and % Add-on at different temperature ranging from 90 – 140 °C. It is seen that effect of temperature on the % GE and % Add-on increased with increasing of temperature for whole range of polymerization temperatures used. This can be due to increase in numbers of radicals formed, which was favorable for the grafting polymerization.

Effect of [MAH] concentration

The effect of [MAH] concentration is shown in Table-3. The result shows that the % GE and % Add-on increases to a maximum with the increasing of initial [MAH] concentration up to 2.04×10^{-3} moles / liter of [MAH] concentration and than decrease after the further addition of a [MAH] concentration. The higher initial [MAH] concentration caused the formation of homopolymers. These homopolymers hindered the rate of penetration of [MAH] to [PP] macro-radicals, resulting with formation of relatively low molecular weight chain of

PMAH and decrease in % GE. As the [MAH] concentration increased, the rate of homopolymerization increased, leading to low % GE.

Effect of [BPO] concentration

The initiator [BPO] effect on the grafting of MAH onto PP is illustrated in Table-4. Initially both % GE and % Add-on increases with the increasing [BPO]. This is expected to be due to increasing number of macro-radicals on PP, which is the reflected on the increasing of [MAH] grafted onto [PP]. Thus at [BPO] = 0.826×10^{-4} moles/ liters and above both of % GE and % Add-on starts declining. This can be attributed to the formation of homopolymers & termination of growing grafted chains by excess primary radicals generated. These factors responsible lower the % GE and % Add-on.

Table-3: Effect of [MAH] concentration on grafting of MAH on PP (Reaction condition: PP = 5.00 gm, [BPO] = 8.25×10^{-5} mol/L, reaction time = 240 min and reaction Temperature = 120 °C in 100 ml xylene)

[MAH] (mol/ L) x 10^{-3}	% GE	% Add-on
0.509	40	0.4
1.02	42	0.8
1.53	43	1.27
2.04	48	1.9
2.55	36	1.76
3.06	30	1.76

Table-4: Effect of initiator concentration on grafting of MAH on, PP (Reaction condition: PP = 5.00 gm, [MAH] = 2.04×10^{-3} mol/ L, reaction time = 240 min and reaction Temperature = 120 °C in 100 ml xylene)

[BPO] (mol/L) x 10^{-4}	% GE	% Add-on
0.206	5	0.5
0.412	16	0.65
0.826	48	1.9
1.24	43	1.7
1.65	37	1.45
2.06	35	1.40

Effect of PP to solvent ratio

Table-5, shows the effect of PP to solvent (Xylene) ratio. The PP to solvent ratio was changed by reducing the volume of solvent in reaction mixture. It can be seem that % GE and % Add-on increasing as the PP to solvent ratio increases. This is due to increase in probability of collisions, than at [PP] to solvent ratio of 1:10 grafting is reduced due to restricted moment of [MAH] molecules, leading to lower % GE and % Add-on values. Thus it is concluded that the best PP to solvent ratio is 1:20.

Table-5: Effect of PP to solvent (xylene) ratio on grafting of MAH onto PP (Reaction condition: PP = 5.00 gm, [MAH] = 2.04×10^{-3} mol/ L, [BPO] = 8.25×10^{-5} mol/ L, reaction time = 240 min, reaction Temperature=120 °C in 100 ml solution).

PP to solvent ratio	Solvent (ml)	% GE	% Add-on
1:30	150	31	1.23
1:25	125	36	1.42
1:20	100	48	1.9
1:10	50	26	1.03
1:5	25	13	0.52

Experiments

Materials

Polypropylene [PP] with a density of 0.916 g/cm³ and MFI 5.07 g/ 10 min. , 190 °C, 2.16 Kg by Haake Melt Flow HT, Thermo electron, Karlsruhe GmbH. Maleic anhydride [MAH] from Merck was recrystallized from benzene, benzyl peroxide [BPO] from BDH and xylene used as a solvent was refined by distillation.

Grafting process

The grafting reactions were carried out in three necked round bottom flask, equipped with thermometer, reflux condenser, nitrogen inlet. First certain amount of PP dissolved in hot xylene. When dissolution was completed, desired amount of [MAH] and [BPO] were added to the PP mixture. After reaching the desired time, the reaction was stopped and grafted PP was precipitated in acetone, washed with acetone. Traces of excess homo-polymer completely removed by Soxhlet for six hours. The grafted products were dried in oven at 60 °C to obtain constant weight.

The percentage grafting efficiency (% GE) and add on (% Add-on) can be calculated from the relations.

$$\% \text{ GE} = 100 (W_2 - W_1) / W_3 \quad \text{--} \quad 1$$

$$\% \text{ Add-on} = 100 (W_2 - W_1) / W_2 \quad \text{--} \quad 2$$

Where W_1 , W_2 and W_3 are the weights of PP, graft copolymerization and MAH respectively.

FT-IR analysis

An IR spectrum of final product was recorded from AVATAR 320 FT-IR (Thermo Nicolet) in the range of 4000 – 400 cm⁻¹ used to record the IR spectra grafted and un-grafted Polypropylene.

Conclusions

The result proved that the insertion maleic anhydride onto polypropylene backbone in presence of benzyl peroxide as a free radical initiator can be easily achieved. Percentage of grafting efficiency and percentage Add-on increases with increasing of maleic anhydride and initiator concentration. It passes to maximum and then decreases with further increasing of maleic anhydride and benzyl peroxide concentration. The percentage of grafting efficiency and percentage Add-on also increase with increasing polymerization time and polymerization temperature.

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