

Reactive Processing of Polyolefins with MAH and GMA in the Presence of Various Additives

PRAVITRA CHANDRANUPAP, SATI N. BHATTACHARYA

Rheology and Materials Processing Centre, Department of Chemical and Metallurgical Engineering, Royal Melbourne Institute of Technology (RMIT University), Melbourne, Victoria, Australia

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ABSTRACT: This paper describes the initial results obtained on the study of the reactive processing of polyolefins (LLDPE, PP) with maleic anhydride (MAH) and glycidyl methacrylate (GMA) in the presence of styrene, dimethyl sulfoxide (DMSO), and dimethylacetamide (DMAC). The investigation of the processing torque obtained from the grafting reaction showed that the torque could be used as an indicator for some product properties such as gel content and percentage of grafting. Addition of a monomer such as styrene and electron donor compounds such as DMSO and DMAC showed significant improvement in processing properties in comparison with additive-free systems. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2405–2415, 2000

Key words: reactive processing; polyolefins grafting; experimental design

INTRODUCTION

Polyolefins are the principal commodity thermoplastics. Major types of polyolefins are polyethylene (PE) and polypropylene (PP). Almost 75% of polyethylene (i.e., low density polyethylene (LDPE) and linear low density polyethylene (LLDPE)) are used in film and sheet applications.¹ A large portion of PP is used as extrusion products, especially as flat film products because of its good properties such as high surface quality, excellent chemical resistance, and high application temperature.² However, these polyolefins have limited use in applications that require good surface/interface properties, such as printing, painting, and polymer blend compatibility, because of their lack of reactive functional group for interfacial adhesion and bonding.³

In order to improve such properties, reactive processing is employed. It is the modification of a polymer by chemical reaction while the polymer is

being processed.⁴ Reactive processing by grafting reaction is originally a grafting process that attaches polar groups onto polymer backbones. Such reaction was proved to overcome property limitations such as poor adhesion of ink in the printing process of base polymer.^{4,5} Moreover, this processing method may easily be carried out in the polymer production plant by standard processing machines.

Among the most frequently used monomers are the unsaturated carboxylic derivatives such as maleic anhydride (MAH), acrylic acid, or acrylate ester, or analogs such as glycidyl methacrylate (GMA).⁶ These monomers can graft onto polymer backbone via radical reaction as shown in Figure 1.

Between MAH and GMA, the double bond position of MAH has lower reactivity than that of GMA due to two adjacent electron-attracted carbonyl groups of MAH. However, the reactivity of GMA is also limited by its bulky size. The electron density of the two monomers was developed by Hyperchem molecular modelling program developed by Hypercube, Inc., Waterloo, Canada. The effect of the adjacent carbonyl groups is seen in

Correspondence to: S. N. Bhattacharya.

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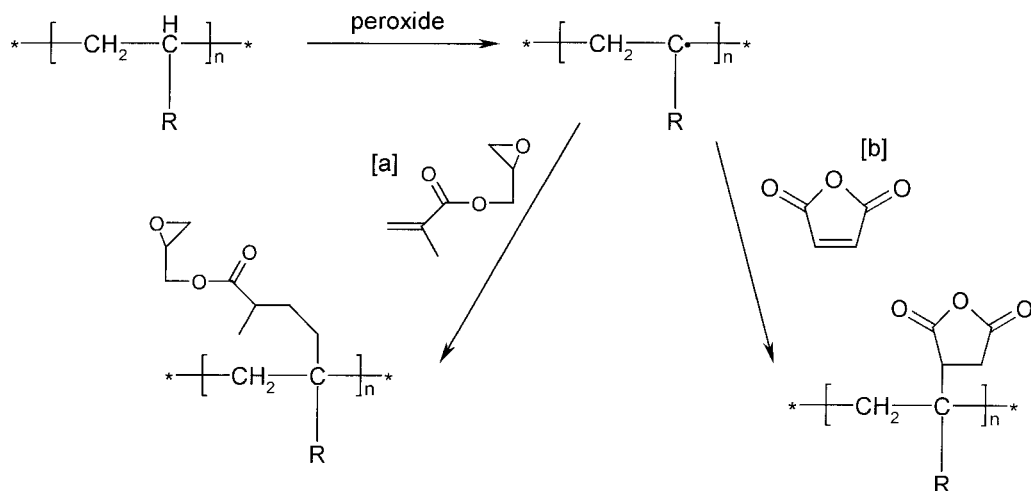


Figure 1 Peroxide-initiated graft reaction of polyolefin backbone with (a) glycidyl methacrylate and (b) maleic anhydride.

the low electron density of the double bond shown in Figure 2.

However, other competitive reactions such as cross-linking and/or chain scission of polymer backbones also occur from hydrogen abstraction that forms radical sites on polymer backbones. The macroradicals usually undergo cross-linking through coupling in PE or chain scission as a result of disproportionation in PP^{7,8} as shown in Figure 3.

Reduction of cross-linking/chain scission can be done by the addition of vinyl monomer such as styrene or electron donor compounds (compounds that contain nitrogen, phosphorus, or sulfur atoms).⁹ These compounds can inhibit cross-linking/chain scission in many ways.^{6,9,10}

The aim of this paper is to examine the processing results (processing torque value) obtained by reactive processing of LLDPE and PP with

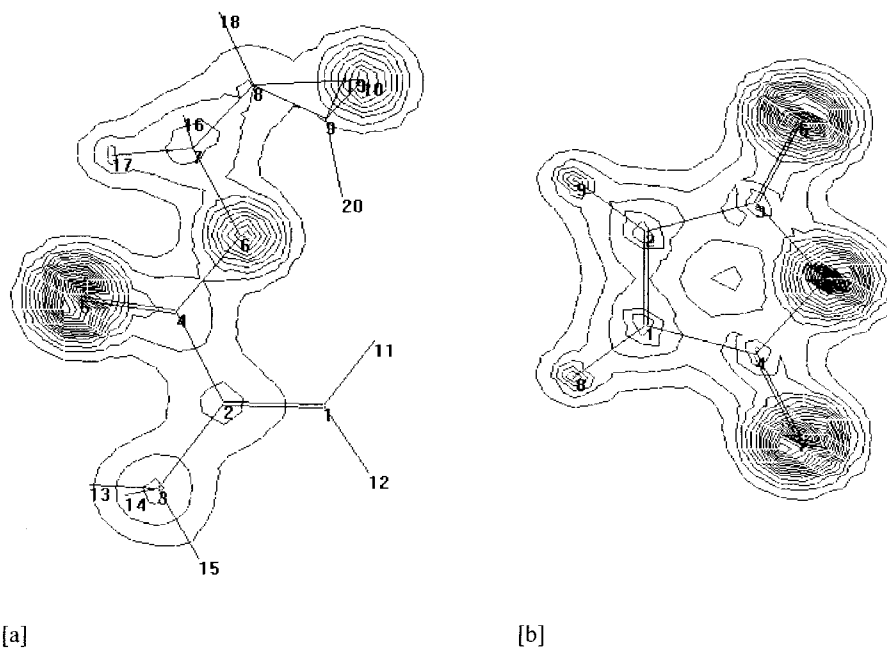


Figure 2 Electron density plot of (a) GMA and (b) MAH. Macroradicals normally attack position 1 of GMA and position 1 or 2 of MAH because of their electron deficiency.

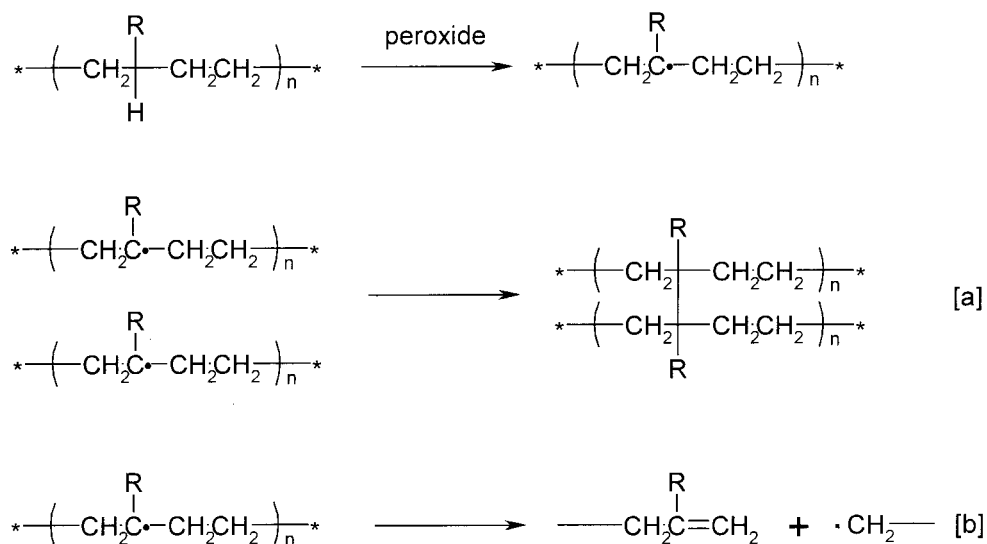


Figure 3 (a) Cross-linking reaction in PE backbone; (b) chain scission in PP backbone.

MAH and GMA in the presence of various additives via batch mixing process. A further aim is to discuss the mechanism leading to the reduction of cross-linking/chain scission in this reactive processing.

EXPERIMENTAL

Materials

Materials used in this work are summarized in Table I.

Experimental Design

A number of experimental runs were conducted by using the full central composite design.¹³ Sixteen sets of experiment were done as described in Table II. Table III summarizes the independent

variables that were also chosen as the experimental ranges selected for these variables.

Polyolefins Grafting Procedure

Each sample was divided into two parts. The first part, consisting of polymer powder, grafting compound, and comonomer (or additive), was added in an Haake Rheomix 600 internal mixer coupled with Haake Rheocord 90. After melting and torque stabilization (about 4 min after charging of material), the second part of polymer powder, consisting of 2 g of polymer and peroxide, was added into the reactor. This was taken as the zero time of reaction. Reaction time was varied between 1 to 15 min. Torque and mixing temperature were recorded throughout each run. Final torque was used as statistical response to investigate its relation among components in the system.

Table I Materials Used in the Present Work

Material	Function	Supplier	Remarks
LLDPE	Based polymer	ICI (Australia), Melbourne, Australia	Powder form
PP	Based polymer	Hoechst (Australia), Melbourne, Australia	PPU-180 (powder)
Maleic anhydride	Graft monomer	Sigma, Melbourne, Australia	Granular
Glycidyl methacrylate	Graft monomer	Fluka, Sydney, Australia	
Lupersol-101	Peroxide initiator	Elf Atochem (Australia)	
Styrene monomer	Additive	Sigma, Melbourne, Australia	
Dimethyl sulfoxide	Additive	Fluka, Sydney, Australia	
Dimethylacetamide	Additive	Fluka, Sydney, Australia	

Table II Summary of all Experimental Sets Done in this Experiment

Set Number	System	Set Number	System
1	LLDPE-MAH-L101	9	PP-MAH-L101
2	LLDPE-MAH-Styrene-L101	10	PP-MAH-Styrene-L101
3	LLDPE-MAH-DMSO-L101	11	PP-MAH-DMSO-L101
4	LLDPE-MAH-DMAC-L101	12	PP-MAH-DMAC-L101
5	LLDPE-GMA-L101	13	PP-GMA-L101
6	LLDPE-GMA-Styrene-L101	14	PP-GMA-Styrene-L101
7	LLDPE-GMA-DMSO-L101	15	PP-GMA-DMSO-L101
8	LLDPE-GMA-DMAC-L101	16	PP-GMA-DMAC-L101

Gel Content of Grafted LLDPE

The method described by Gaylord et al.⁹ was used to determine the gel content of the polymer. About 5 g of crude polymer from the batch mixer was cut into small pieces and put in the container made from wire gauze. The container was submerged in 250 mL of hot xylene and refluxed for 5 hours. The remaining xylene-insoluble part in the container, gel polymer, was dried in an hot air oven at 90°C overnight and, after subtracting the weight of the container, yielded the gel content of the polymer.

Grafting Determination of Grafted LLDPE

Fourier Transform Infrared Analysis of LLDPE Samples

LLDPE thin sheet samples that were prepared by compression press were used as a sample to in-

vestigate surface functional group by Fourier transform infrared (FTIR) spectrometer. The instrument used is Perkin-Elmer FTIR spectrum 2000 spectrometer supplied by TA Instruments, Melbourne. Samples were tested in attenuated total reflection (ATR) mode that detected polymer surface chemically. Each sample was investigated in the range between 4000 to 600 cm^{-1} .

Grafting Efficiency Determination of GMA

In order to quantitatively measure the grafting efficiency, Igetabond grade E was used to develop a calibration curve. Igetabond grade E is a copolymer of ethylene and 12 wt % of GMA. Mixtures of Igetabond grade E and LLDPE with different compositions (2, 4, 6, and 8 wt % GMA) were prepared. The mixture was dissolved in refluxing toluene at a concentration of about 4% wt/vol. The solution was precipitated into 7 vol of methanol,

Table III Independent Variables and Experimental Ranges in the Present Work

Process	Independent Variable	Unit	Experimental Range	
			Min	Max
LLDPE-based processing	Peroxide (L101) concentration	phr	0.10	0.25
	MAH	phr	4.00	9.00
	GMA	phr	4.00	9.00
	Styrene	mol St: mol monomer	0.50	1.50
	DMSO	phr	0.40	0.90
	DMAC	phr	0.40	0.90
	Reaction time	s	60.00	780.00
	PP-based processing	Peroxide (L101) concentration	phr	0.03
MAH		phr	4.00	9.00
GMA		phr	4.00	9.00
Styrene		mol St: mol monomer	0.50	1.50
DMSO		phr	0.40	0.90
DMAC		phr	0.40	0.90
Reaction time		s	60.00	780.00

Table IV Model Fitting Results from Design Expert

System	Model Fit by Design Expert	Model's R-Square
LLDPE-MAH	Quadratic	0.9153
LLDPE-MAH-St	Linear	0.9162
LLDPE-MAH-DMSO	Quadratic	0.9577
LLDPE-MAH-DMAC	Linear	0.8489
LLDPE-GMA	Linear	0.9013
LLDPE-GMA-St	Linear	0.9135
LLDPE-GMA-DMSO	Linear	0.8298
LLDPE-GMA-DMAC	Linear	0.8194

filtered, washed, and dried overnight. The ratio of carbonyl stretch (νCO , 1725 cm^{-1}) from the GMA to the methyl bending (δCH_3) was used to determine grafting efficiency of GMA onto LLDPE.

Grafting Efficiency Determination of MAH

The amount of MAH grafting was done by titration method as described by Gaylord.¹⁴ A sample of 0.5 g was put in refluxing 150 mL water-saturated xylene for 1.5 hours. The hot solution was then titrated with 0.05 N ethanolic KOH using thymol blue indicator. A 0.5–1.0 mL excess of KOH solution was added and the deep blue color was back-titrated to a yellow end point by the addition of 0.05 N isopropanolic HCl to the hot solution. The KOH solution was standardized against a solution of potassium hydrogen phthalate. The ratios of carbonyl stretch (νCO , 1780 cm^{-1}) from the MAH to the methyl bending (δCH_3) versus grafting efficiency were plot to determined grafting efficiency of MAH onto LLDPE.

RESULTS AND DISCUSSION

Statistical Model

In this work, final processing torque at various reaction times is used for investigating the result because it is a good indicator of the preferred reaction in each run. The central composite design (CCD) was used in order to model the process. In general, a CCD is one kind of response surface method (RSM) design that is well described elsewhere.¹³ The fitted models from statistical analysis are presented in Tables IV and V. Linear model means response (torque) can be expressed by a linear combination of factors

(amounts of additive, time, etc.) in the experiment. In case of a quadratic model, the interaction terms and the square terms are added in order to express the response that the linear model cannot fit properly.

General form of linear model:

$$\text{Response} = a_0 + \sum_{i=1}^n a_i x_i$$

x_i = independent variables in system, a_0 , a_i

= constant.

General form of quadratic model:

$$\text{Response} = a_0 + \sum_{i=1}^n a_i x_i + \sum_{i=1}^n \sum_{j=1}^n \sum_{j=1}^n a_{ij} x_i x_j; a_0, a_{ij}$$

= constant.

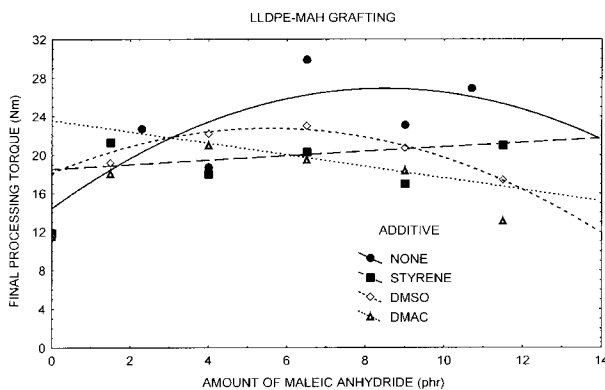
The value for r^2 , correlation coefficient, indicates the mathematical accuracy of the model. The more the value of r^2 approaches 1, the better representative the model becomes for the experimental set. The r^2 values from the analysis showed that most of the fitted models are good representatives for each system in the experimental range. However, a few models that have low value of r^2 (0.8–0.9) still present good prediction for the relation of the processing torque with the experimental variables.

Effect of Peroxide Initiator

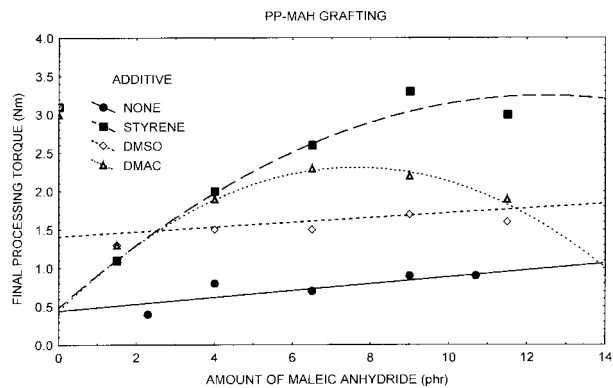
The effect of peroxide on reactive processing is well known. The processing torque increased with

Table V Model Fitting Results from Design Expert

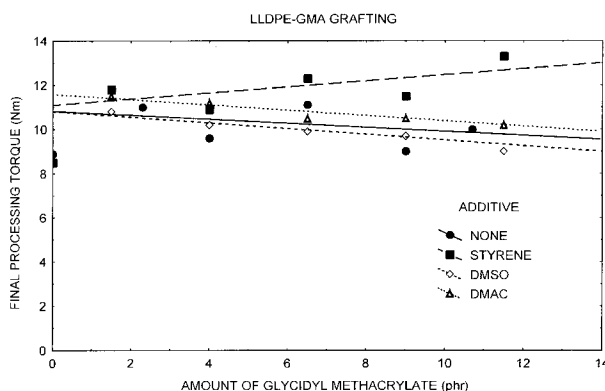
System	Model Fit by Design Expert	Model's R-Square
PP-MAH	Linear	0.9068
PP-MAH-St	Quadratic	0.9670
PP-MAH-DMSO	Linear	0.9342
PP-MAH-DMAC	Quadratic	0.9538
PP-GMA	Linear	0.8485
PP-GMA-St	Linear	0.9485
PP-GMA-DMSO	Linear	0.9240
PP-GMA-DMAC	Linear	0.8361



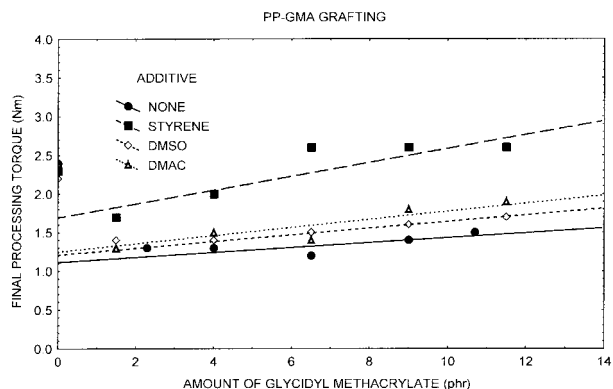
[a]



[c]



[b]



[d]

Figure 4 (a–d) Plots of monomer concentration vs. processing torque. Other variables were fixed at [peroxide in LLDPE] = 0.175 phr; [peroxide in PP] = 0.055 phr; [styrene] = 1 mole styrene/mole monomer; [DMSO/DMAC] = 0.65 phr; reaction time = 420 s. (a) LLDPE-MAH grafting; (b) LLDPE-GMA grafting; (c) PP-MAH grafting; (d) PP-GMA grafting.

increasing amounts of peroxide due to more cross-linking. In contrast, PP-based polymer showed more chain scission via torque decreasing.

Effect of Monomers on Polyolefins Processing

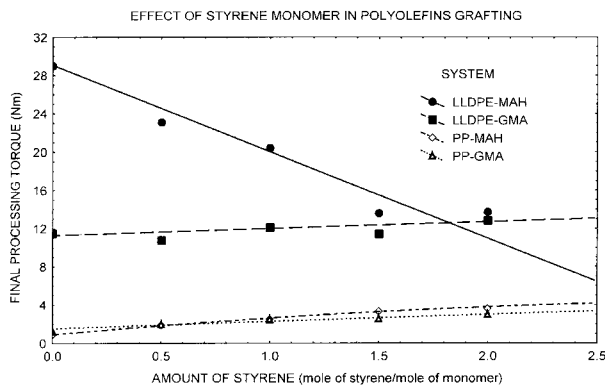
Figures 4a–d present the plots between final processing torque versus the amount of monomer used in this experiment. In case of maleic anhydride with LLDPE (Fig. 4a), processing torque increases whereas the amount of monomer increases through a maximum and then drops at high concentration of MAH for the additive-free as well as the dimethyl sulfoxide (DMSO)-added system. In the system with styrene, final processing torque didn't change much due to the reason that the increase in the MAH concentration was followed by the equivalent increase in styrene concentration as well. In the PP-based polymer,

the addition of the monomer tends to increase the processing torque due to a lower degree of chain scission.

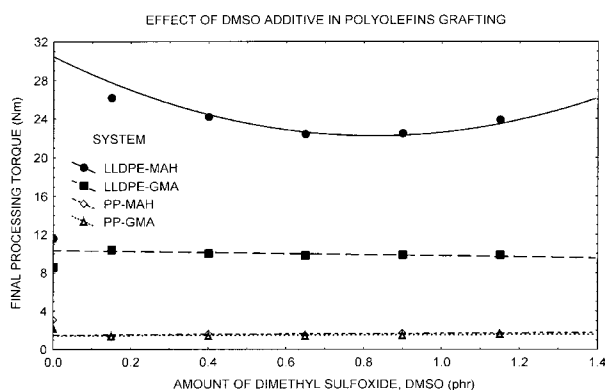
GMA is more reactive than MAH as discussed previously and its bulky structure could inhibit cross-linking/chain scission in polymer backbone. This is shown by low processing torque of the LLDPE-GMA system. However, the processing torque of PP-MAH and PP-GMA system is of the same order of magnitude (Figures 4b, d). The factor that could explain the reduction of GMAs reactivity is its bulky size, which inhibited PP macroradicals in attacking the monomer.

Effect of Additive

The effect of comonomer (styrene) and electron donor additive (DMSO/dimethylacetamide [DMAC]) has been represented in Figures 5a–c. The



[a]



[b]

Figure 5 Plots of additive concentration vs. processing torque. (a) Styrene monomer additive; (b) DMSO additive; (c) DMAC additive. Other variables were fixed at [peroxide in LLDPE] = 0.175 phr; [peroxide in PP] = 0.055 phr; [MAH/GMA] = 6.5 phr; reaction time = 420 s.

amount of monomer (MAH/GMA) in all the plots was fixed at 6.5 phr, the reaction time set at 420 s. From Figure 5a, it is seen that styrene has a great influence in the LLDPE-MAH process. It also showed significant influence in other systems. Several papers⁹⁻¹¹ suggested the reaction mech-

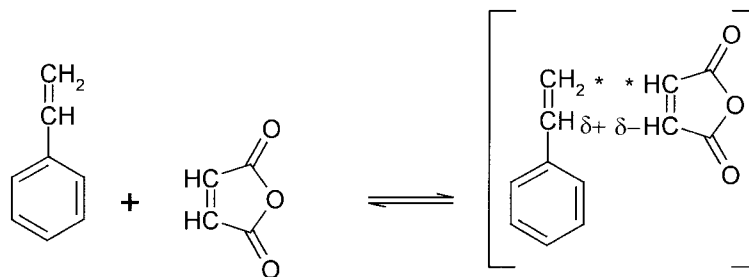


Figure 6 Charge transfer complex mechanism between styrene and MAH.

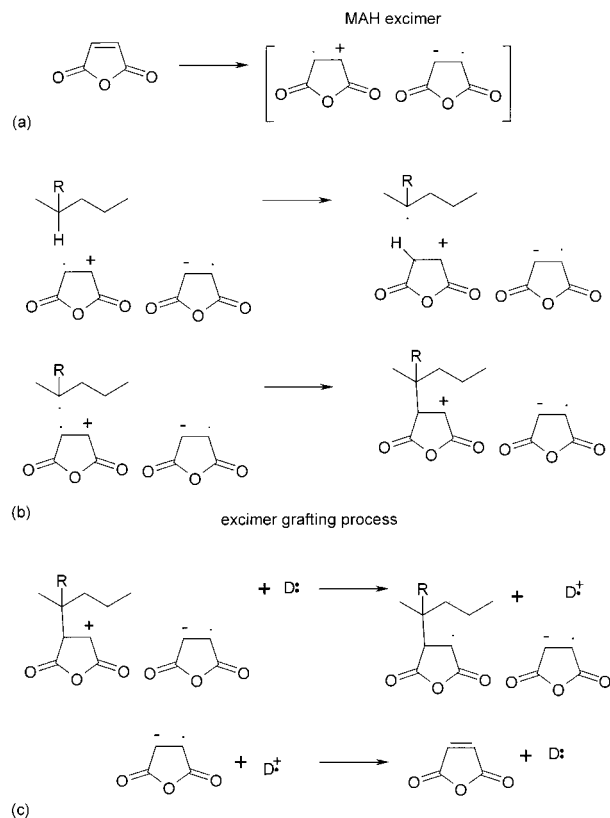


Figure 7 Proposed mechanism in PE-MAH system with electron donor additives.

anism, when styrene monomer was present in the reaction process. When both MAH and styrene monomers are present, styrene reacts with MAH to form charge transfer complex (CTC), which highly activates the weakly reactive double bond of MAH towards free radical.¹¹ The CTC mechanism is presented in Figure 6.

The reaction mechanism of styrene in GMA is different from that of the MAH. The mechanism⁶ suggests that when styrene is present, the dominating grafting mechanism is that styrene reacts with polyolefin macroradicals to form more stable

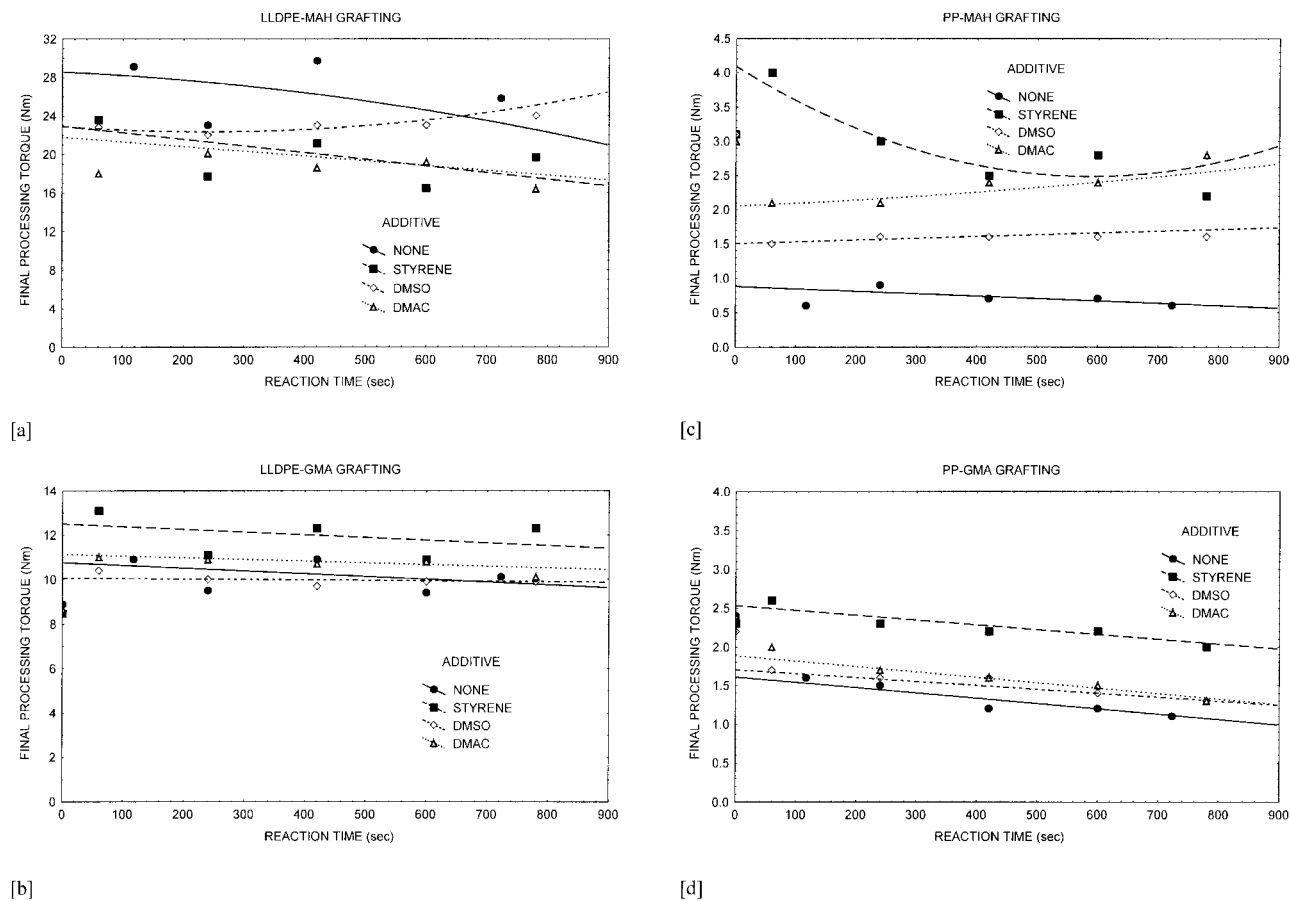


Figure 8 Plots of reaction time vs. processing torque. (a) LLDPE-MAH grafting; (b) LLDPE-GMA grafting; (c) PP-MAH grafting; (d) PP-GMA grafting. Other variables were fixed at [peroxide in LLDPE] = 0.175 phr; [peroxide in PP] = 0.055 phr; [MAH/GMA] = 6.5 phr; [styrene] = 1 mole styrene/mole monomer; [DMSO/DMAC] = 0.65 phr.

styryl macroradicals that react with GMA to form GMA-grafted PE (or PP).

The contribution of the electron donor molecules such as DMSO and DMAC is mainly to decrease the extent of cross-linking and/or chain scission. In case of MAH monomer, the presence of peroxide not only generates macroradicals, but also induces MAH excimer (Fig. 7a)¹² that interacts with the macroradical species to form grafting. Electron donor species donate an electron to the MAH cation resulting from excimer addition to polymer radical (Fig. 7b). The donor cation radical accepts an electron from the MAH anion radical to regenerate the donor compound and MAH (Fig. 7c). Thus, due to the conversion of terminal cation to the terminal radical, the generation of active monomer and excimer is prevented and cross-linking/scission is minimized. In the case of GMA monomer, DMSO and DMAC additives have little effect on the processing

torque. The reason is that the bulky size of the GMA makes it improbable to generate excimer like MAH molecule.

Effect of Reaction Time

The effect of reaction time on final processing torque is presented in Figures 8a–d. It has been found that the reaction time has little effect on the final processing torque. Prolonged reaction time has a tendency to decrease torque in both LLDPE-based and PP-based systems. However, the difference of torque values between minimum and maximum reaction time is very close because half lifetime of peroxide initiator is normally short (no more than 1 min at processing temperature) and grafting process is expected to be completed in around 4–5 min. So, it can be seen that a reaction time of around 4 min is enough for the grafting reaction.

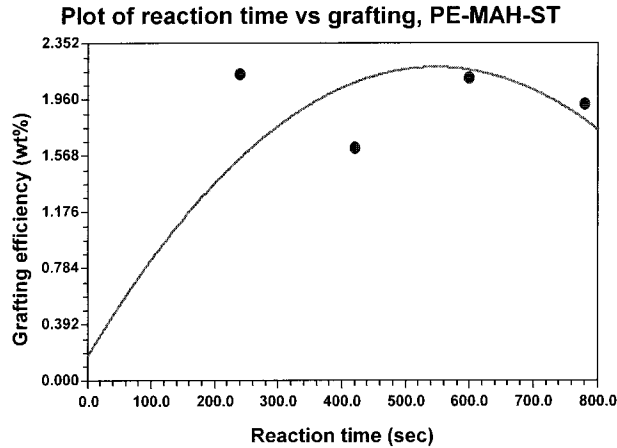


Figure 9 Plot of grafting efficiency (wt %) vs. reaction time. Other variables were fixed at [peroxide] = 0.175 phr; [MAH] = 6.5 phr; [styrene] = 1 mole styrene/mole monomer.

Grafting Kinetics of Grafted LLDPE

LLDPE-MAH-Styrene (ST) Grafting

In order to study the time-dependent behavior of LLDPE grafting, plots between maleic anhydride grafting (wt %) versus reaction time of LLDPE polymer are shown in Figure 9. The amount of peroxide, monomer, and styrene additive were fixed at certain values.

From Figure 9, grafting rate ($d[\text{grafting}]/dt$) can be calculated by statistical analysis. A plot between grafting rate at various reaction times is shown in Figure 10.

The result from Figure 10 is reasonable. Grafting rate is reached to maximum and then drops to

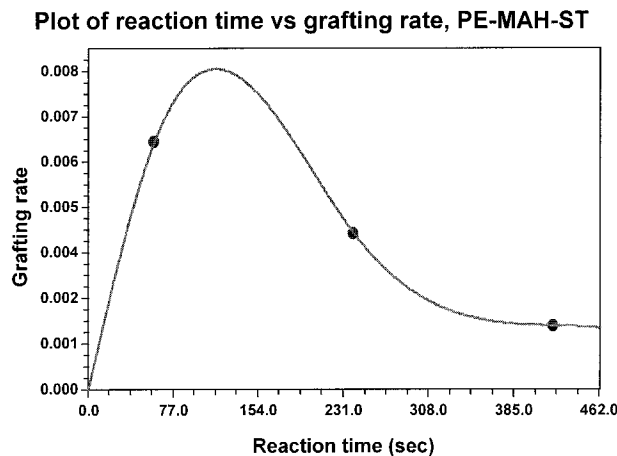


Figure 10 Plot of reaction time vs. grafting rate of LLDPE-MAH-ST grafting.

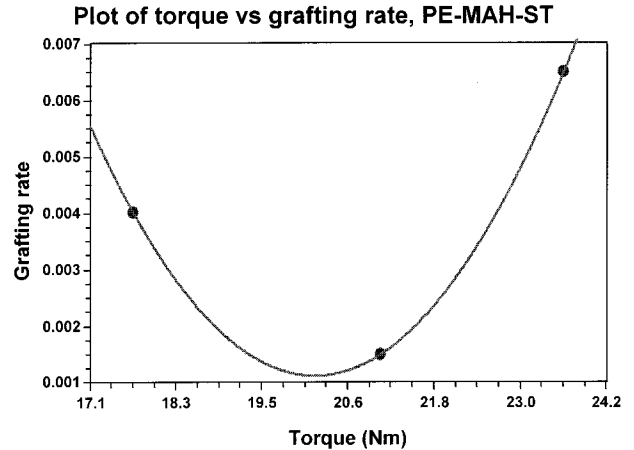


Figure 11 Plot of processing torque vs. grafting rate of LLDPE-MAH-ST grafting.

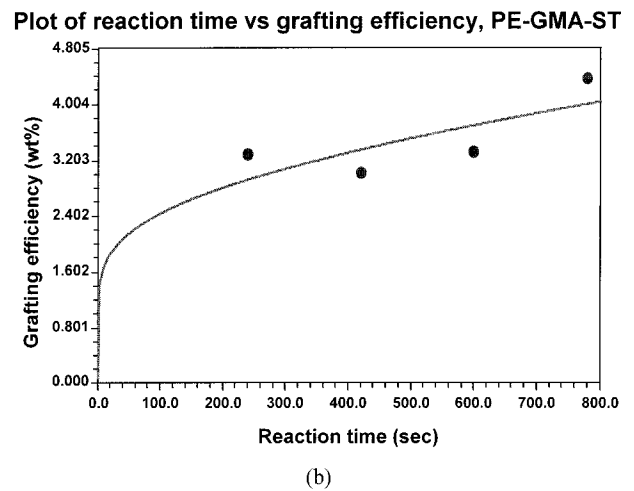
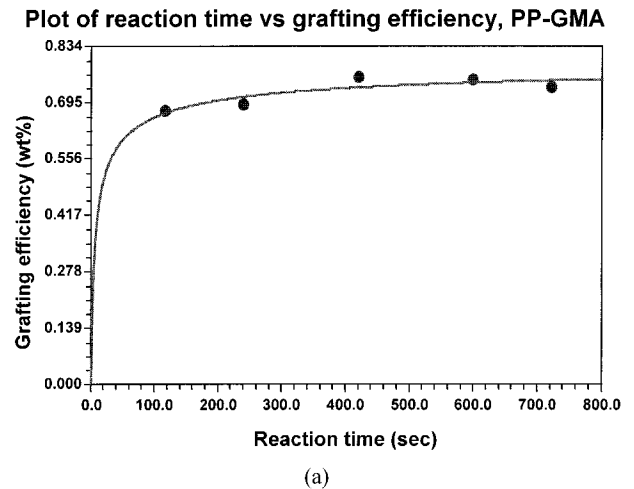


Figure 12 Plot of reaction time vs. grafting percentage. (a) PP-GMA; (b) PE-GMA-ST. Other variables were fixed at [GMA] = 6.5 phr; [peroxide] = 0.175 phr; [styrene] = 1 mole styrene/mole monomer.

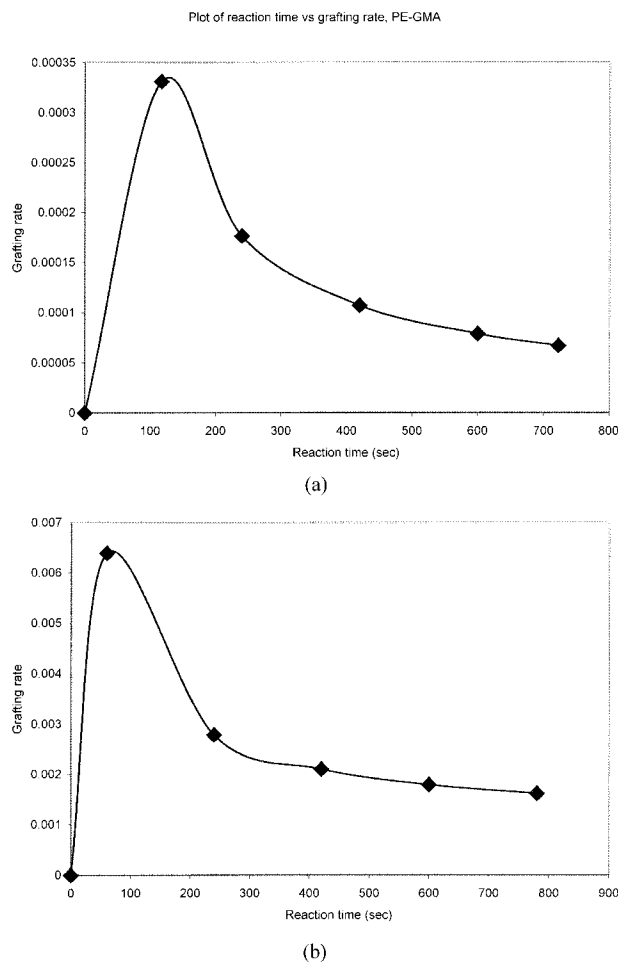


Figure 13 Plot of reaction time vs. grafting rate. (a) PE-GMA; (b) PE-GMA-ST.

lower values when reaction time is increased. This is due to the decrease of free monomer during grafting process.

Figure 11 was plotted to investigate the effect of various processing torque on grafting rate. Grafting rate decreased to the certain torque and increased again. This is due to the reduction of competitive reaction (cross-linking) and more grafting can be introduced in the reaction chamber.

LLDPE-GMA Grafting System

In order to study the time-dependent behavior of LLDPE-GMA grafting, plots between GMA grafting (wt %) versus reaction time of LLDPE polymer is shown in Figures 12a and b. The amount of peroxide, monomer, and styrene additive were fixed at certain values.

It is clearly seen that the formulation with added styrene monomer has higher percentage of

grafting than GMA alone. This is due to the forming of styryl macroradicals that can stabilize long enough to react with steric GMA.

The grafting rate of GMA was calculated the same way of MAH grafting. The plot between reaction time and grafting rate are shown in Figures 13a and b.

Figure 13 shows the same result. We can notice that grafting rate of both styrene-free system and styrene-added system reach to maximum at around 120 s of reaction time. It can be noticed that grafting rate of the styrene-added system is higher than that of the styrene-free system.

Figures 14a and b showed the effect of various processing torque on grafting rate. The grafting rate has a trend to increase when increasing processing torque. This is due to good diffusion that

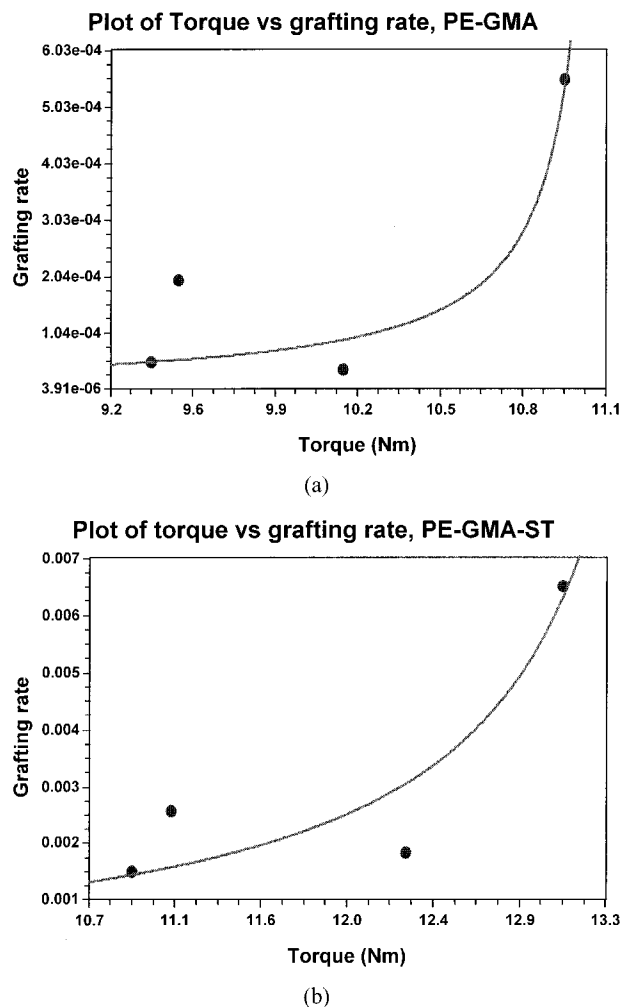


Figure 14 Plot of torque vs. grafting rate. (a) PE-GMA; (b) PE-GMA-ST.

is produced by high mixing that can accelerate grafting reaction.

CONCLUSION

Experimental design is a very useful tool in the construction of an experimental set that can be analyzed effectively by statistical method. In reactive processing of polyolefins, it can be seen that the properties of the grafted products were affected by injecting additives to the formulations. LLDPE-grafted systems with additives offer lower mixing torque close to the value of the pure polymers due to a reduction in cross-linking. PP-grafted systems with additives also improve processing torque due to reduction in chain scission. Among additives used, vinyl monomer such as styrene is the best among the three compounds used to improve the processing torque of the grafted products. Grafting efficiency of LLDPE-based polymer showed fast grafting rate at the first 200 s of reaction time and it has a trend to increase when processing torque increased. Finally, reaction time has little effect on the processing torque due to fast grafting process.

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