

Investigation of Styrene-Assisted Free-Radical Grafting of Glycidyl Methacrylate onto High-Density Polyethylene Using Response Surface Method

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ABSTRACT: In this study, the free-radical grafting of glycidyl methacrylate (GMA) onto high-density polyethylene (HDPE) in the presence of styrene, as a comonomer, is investigated using a Brabender internal mixer. To optimize grafting level of GMA onto HDPE, response surface method (RSM) was exploited. Using RSM method of experimental design, it was possible to investigate the individual effects of various variables including dicumyl peroxide (DCP) concentration, GMA content, as well as reaction time, and their interactions on grafting efficiency. The fitted quadratic model obtained from statistical analysis is expressed by an approximating function to investigate the final torque as a responding variable over the experimental range of the independent variables. The grafting yield of GMA onto HDPE for the prepared samples was determined using titration/

back-titration technique and Fourier transform infrared spectroscopy (FTIR). According to the torque–time diagrams, increasing the DCP content led to an increase in GMA grafting yield. Also, it was found that the reaction time imparts minor effect on the final processing torque, and there exists an interaction between DCP and GMA content. The results of melt flow index (MFI) test showed that increasing the reaction time at constant DCP and GMA content enhances the MFI values of the samples, due to the more probability of chain scission phenomenon. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1600–1605, 2009

Key words: high-density polyethylene; free-radical grafting; glycidyl methacrylate; grafting yield; response surface method

INTRODUCTION

The free-radical grafting of reactive monomers, such as maleic derivatives, onto polyolefins has been extensively studied during the last decade.^{1–3} These monomers can be grafted onto polymer backbone via radical grafting reaction. The modified polymers are mainly used to achieve compatibilized blends of polyolefins/engineering plastics with a suitable combination of properties. A free-radical grafting system often contains three main reactants: polymer, unsaturated monomers like vinyl monomer, and a free-radical initiator. Some of the most frequently used monomers are unsaturated maleic anhydride (MAH), maleic acid, dibutyl maleic, acrylic acid, and its esters such especially as glycidyl methacrylate (GMA). Study of the effect of MAH and GMA chemical nature on grafting efficiency of polyolefins showed that the double bond of MAH has lower reactivity than that of GMA due to adjacent electron-attractive carbonyl groups of MAH.⁴ In other words, MAH does not react easily with free radicals,

and the efficiency of its radical grafting onto polyolefins is limited.⁴ It is believed that the improvement of morphology and physical/mechanical properties of PET/PP blend would be enhanced via compatibilization with PP-g-GMA compared with those compatibilized with MAH grafted PP.^{5,6} Also, it was observed that grafting yield was improved with increasing the peroxide content.⁷ However, detrimental reactions of crosslinking or chain scission of polyolefins during grafting process decrease the efficiency of initiator and consequently the grafting yield of MAH. These competing reactions occur due to hydrogen abstraction of polymeric chains and the formation of radical sites on polymer backbone. The electron transfer from donor to acceptor, in the presence of a comonomer, creates a charge-transfer complex.⁴ It was proposed that the addition of a vinyl monomer like styrene would alleviate the low efficiency of grafting reaction.^{4,8} In this way, the macroradicals are more consumed by the grafting reaction rather than the undesirable crosslinking and chain scission reactions.

According to the literature, to achieve an efficient free-radical grafting, the [styrene]/[vinyl monomer] molar ratio should be optimized.^{4,5} In the recent years, GMA is used progressively to functionalize

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polyolefins. GMA is a bifunctional monomer containing an unsaturated group suitable for free-radical grafting and an epoxy group capable of interacting with numerous reactive groups such as hydroxyl, carbonyl, and amine.⁹ Several studies have examined the free-radical grafting of GMA onto polyolefins^{5,9–14} and all have shown that usage of styrene as a comonomer improves the yield and rate of GMA grafting.¹⁰ Furthermore, it was found that the most efficient styrene to GMA molar ratio should be as close to unity to achieve the highest level of GMA radical grafting onto polypropylene chains.¹⁴ Although the effect of main independent parameters such as peroxide content, reactive monomer concentration, using a comonomer, on grafting yield is well studied, nevertheless, the interaction effects of these parameters have not been studied yet.

The objective of this study was to evaluate the individual effects and interactions of three independent parameters including dicumyl peroxide (DCP) content, GMA level and reaction time, on the efficiency of grafting reaction onto HDPE. To achieve this goal, experimental design using response surface method (RSM) was utilized successfully, by applying the central composite design (CCD) for fitting a quadratic (second order) model on sequential experimentation.¹⁵ The final processing torque as a responding variable was highlighted for investigating the influence of the independent variables and their interactions on grafting yield.

EXPERIMENTAL

Materials and equipments

High-density polyethylene (HDPE) is provided from Bandar Imam Petrochemical Corp., BIPC, (a local company) with density range of 0.956–0.962 g/cm³ and melt flow index (MFI) range of 0.28–0.43 g/10 min (190°C, 2.16 kg) as reported by the BIPC. The MFI value of the used sample was measured, as 0.3439 ± 0.005 g/10 min, according to ASTM D1238. GMA (97% purity) and styrene (99% purity) monomers with density values of 1.08 g/cm³ and 0.906 g/cm³, respectively, were supplied by Merck Co. and used as received. Other solvents and chemical reagents used for titration were purchased from Merck Co. and used as received.

The free-radical grafting experiments were carried out in a Brabender internal mixer with capacity of 60 mL.

The MFI test was carried out on grafted samples using Ceast apparatus (Italy) MFI recorder. For each sample the MFI test was carried out, according to the ASTM D1238 at 190°C. Because of the high viscosity of the grafted samples, it was decided to mea-

sure the MFI values at the load of 21.6 kg which is in accordance with ASTM D1238.

The Fourier transform infrared spectroscopy (FTIR) spectra were recorded in the transmittance mode on Bomem (Canada) FTIR spectrometer at a resolution of 4 cm⁻¹. For each sample, the spectrum was obtained using at least five scans, in the wave number range of 4000–400 cm⁻¹.

Experimental design by response surface method

Response surface methodology or RSM is a collection of mathematical and statistical techniques useful for the modeling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize the response. When selecting a response surface design, some of the features of a desirable design¹⁵ are listed as providing a reasonable distribution of data points throughout the region of interest; allowing the investigation of model adequacy including lack of fit; designing of higher order model approximation; providing a precise estimate of the model coefficients; obtaining a good profile of the prediction variance throughout the experimental region; no requirements for a large number of runs; requiring not too many levels of the independent variables; and making ensure of simplicity of the model parameters' calculation.

In this way, the RSM results could be represented by contour plots, an array of digits or a function of the changing variables which is modeled by two types of approximating functions, First and second-order (quadratic) models [eqs. (1) and (2)]:

$$y = a_0 + \sum_{i=1}^n a_i X_i \quad (1)$$

$$Y = a_0 + \sum_{i=1}^n a_i X_i + \sum_{i=1}^n a_{ii} X_i^2 + \sum_{i=1}^n \sum_{j=1}^n a_{ij} X_i X_j \quad (2)$$

where Y is the responding variable, X_i is the independent variable, a_0 is the intercept of regression function, a_i is the regression coefficient for independent variable.

In eq. (2), a_{ii} is the curvature term of independent variable and a_{ij} is the interaction coefficient between variables X_i and X_j . When the study of interaction between changing variables is of vital importance, a second-order regression function should be fitted using CCD. The practical deployment of CCD often arises through sequential experimentation. Generally, the CCD consists of a 2^k factorial with n_F runs, $2k$ axial runs and n_C center runs, where k is the number of changing variables. The user should arrive in the vicinity of the optimum level. This is

TABLE I
Experimental Variables and Their Variation Ranges

Changing variable	Unit	Ranges
X_1 , Reaction time	s	180–480
X_2 , DCP content	phr	0.2–0.6
X_3 , GMA content	phr	3–9

usually indicated by lack of fit of a first-order model with 2^k factorials. Under that condition, $2k$ additional axial experiments are conducted to obtain a more precise estimate of optimum. This is the main reason why the CCD method is a very efficient design for fitting the second-order model. More details on CCD could be found elsewhere.¹⁵

In the present investigation, according to our previous study,¹⁴ reaction time, DCP and GMA contents were chosen as changing variables (Table I), whereas final processing torque was considered as the responding variable.

It is important to note that the value ranges of variables has been determined based on the knowledge about the reaction and practical considerations, which is already well studied.¹⁴ For three changing variables, the CCD method is capable of designing the experiments using at least 15 runs, including the center point; however, it is suggested to consider three to five excess centers to adequately minimize the operational errors.¹⁵ Therefore, based on RSM and using the full CCD method, 20 experimental runs were arranged, as summarized in Table II. The centers of the approximation are repeated five times in accordance with the run numbers (1), (5), (13), (14), (15) and (17).

TABLE II
Experimental Runs Designed by CCD Method of RSM

Run no.	Reaction time (s)	DCP (phr)	GMA (phr)
1	330	0.40	6.00
2	240	0.28	4.22
3	240	0.52	7.78
4	330	0.60	6.00
5	330	0.40	6.00
6	330	0.20	6.00
7	330	0.40	9.00
8	420	0.52	4.22
9	180	0.40	6.00
10	240	0.52	4.22
11	240	0.28	7.78
12	330	0.40	3.00
13	330	0.40	6.00
14	330	0.40	6.00
15	330	0.40	6.00
16	420	0.28	7.78
17	330	0.40	6.00
18	480	0.40	6.00
19	420	0.28	4.22
20	420	0.52	7.78

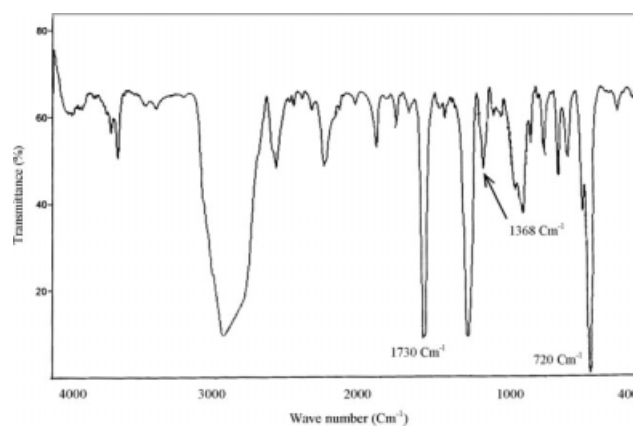


Figure 1 FTIR spectrum of HDPE-g-GMA in the presence of styrene as a comonomer.

Grafting procedure

Grafting reaction was carried out in an internal Brabender mixer. The sequence of ingredients addition to the mixer will influence the efficiency of free-radical grafting. Therefore, polyethylene was initially introduced and then styrene, GMA and DCP ingredients were injected into the system successively during 3 min, according to the conditions presented in Table II. To promote the efficiency of grafting, the amount of styrene was selected so that the molar ratio of styrene to GMA equals to unity as it is recommended by several researches.^{5,9,10,14}

The operating conditions were kept constant at 175°C and 50 rpm.¹² It should be noted that inevitable evaporation of the GMA and styrene during their addition to the mixer was negligible. To prevent the continuation of the reaction and accurate evaluation of reaction time influence, each grafted sample was immersed in 0°C water, immediately after discharging from the mixer. The final processing torque, as the responding variable, was recorded throughout each experimental run.

Grafting yield measurement

To measure grafting level and efficiency, reacted samples were dissolved in hot xylene (100 mL)

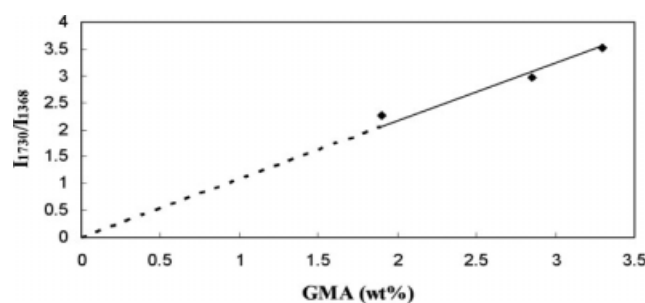


Figure 2 FTIR Calibration curve for the grafting yield of GMA onto HDPE at constant DCP content of 0.4 phr.

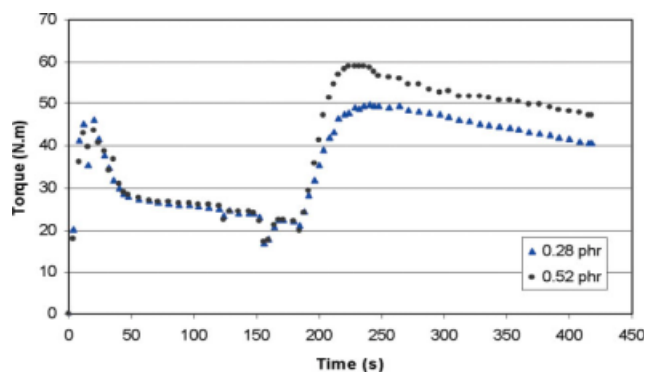


Figure 3 Influence of DCP level on torque at constant GMA content of 7.78 phr, (\blacktriangle): DCP = 0.28 phr; (\bullet): DCP = 0.52 phr. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

while stirring for 2 h and then precipitated with excess amount of acetone (200 mL). Before precipitation, the hot solution of polymer was filtered through a fine grid to verify the possible formation of gel. The precipitated specimen was then filtered, washed three times with acetone and dried under vacuum at 80°C overnight for complete purification⁹ and release of unreacted monomers.

A nonaqueous backtitration was used to determine the amount of grafted GMA onto HDPE.¹⁶ About 1 g of the purified sample was dissolved in 150 mL of hot xylene followed by addition of 1.5 mL of 0.3M xylene solution in trichloro acetic acid (TCA). The mixture was maintained at 100–110°C for 2 h so as to complete the reaction of TCA with grafted GMA. The solution was then precipitated with excess acetone (300 mL), filtered and washed. The filtrate was titrated with 0.1M KOH solution in methanol and then was backtitrated with 0.1M HCl solution in isopropanol using phenolphthalein as an indicator.^{8,16}

On the other hand, to obtain relative amount of GMA grafting, FTIR technique was applied. As shown in Figure 1, the new transmittance peak appeared around 1730 cm^{-1} is assigned to the carbonyl stretching of grafted GMA and the peak at 1368 cm^{-1} corresponds to the HDPE methylene group stretching. In addition, the assigned peak nearby the 720 cm^{-1} is associated to the styrene. To determine the grafting yield of GMA, the intensity ratio of GMA carbonyl FTIR peak to HDPE methyl-

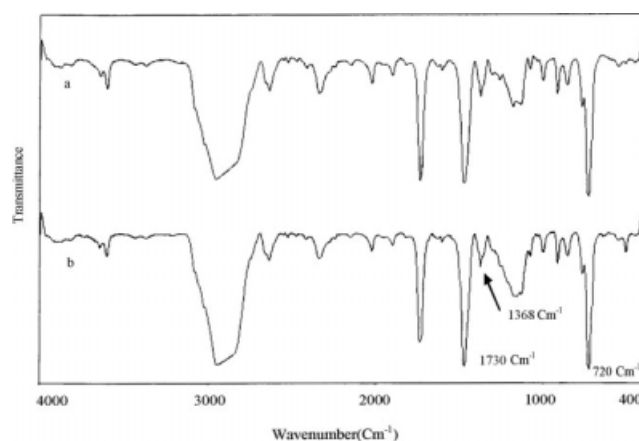


Figure 4 FTIR spectra of the HDPE-g-GMA copolymer with constant GMA content of 7.78 phr at different DCP content: (a) 0.28 phr and (b) 0.52 phr.

ene group peak (I_{1730}/I_{1368}) was calculated, and a calibration curve was generated with the help of absolute values measured by titration method. Chosen samples for this purpose were sample Nos. 7, 12, and 18 that have the same amount of DCP (0.4 phr) and are different in GMA content (3, 6, and 9 phr). The results indicated a linear correlation, as illustrated in Figure 2.

RESULTS AND DISCUSSION

Experimental design by RSM and approximating function

The fitted model obtained from statistical analysis by CCD of RSM experimental design can be expressed as eq. (3) using appropriate statistical Minitab software:

$$Y = 30.24 - 0.069X_1 + 82.7X_2 + 4.59X_3 - 8.92X_2X_3 \quad (3)$$

where Y is the final processing torque. This equation presents a good prediction for the final processing torque as a function of the experimental variables. It is interesting to mention that there is an obvious interaction dependency of responding variable specified in X_2X_3 term that shows the interaction between DCP and GMA contents, whereas there is an insignificant interaction between time and other two variables. More detailed study of the role of each

TABLE III
Experimental and Calculated Torque and Grafted GMA Values as a Function of DCP Content at Constant GMA Level

Run no.	GMA content (phr)	DCP content (phr)	Y_{exp}	Y_{cal}	I_{1730}/I_{1368}	Grafted GMA (wt %)
16	7.78	0.28	40.58	40.69	3.506	3.254
20	7.78	0.52	46.68	43.88	4.088	3.794

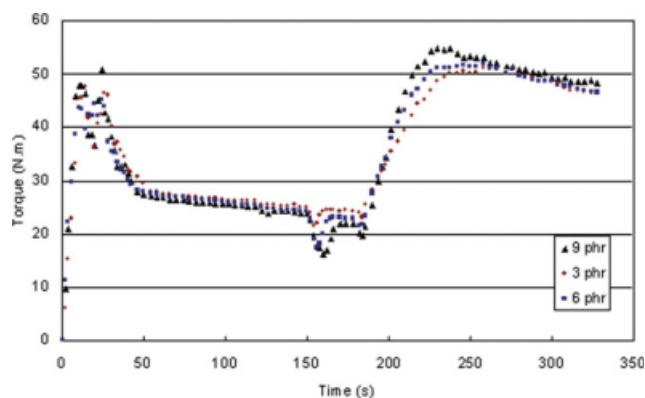


Figure 5 Influence of GMA content on torque at constant DCP level of 0.4 phr, (●): GMA = 3 phr; (■): GMA = 6 phr; (▲): GMA = 9 phr. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

parameter is highlighted in the next sections, individually.

Effect of the peroxide initiator level

As shown in Figure 3, at constant content of GMA (7.78 phr), the processing torque increased significantly with increasing the amount of DCP. It may be a result of more crosslinking reaction. It is believed that increasing the amount of DCP initiator leads to the formation of more activated sites, and therefore, both the grafting and crosslinking reactions are enhanced considerably.

Although the experimental torque results take effect of both gel content and grafted polymer, it is worthwhile to differentiate between them. To resolve this issue, at first the I_{1730}/I_{1368} ratio is calculated from the FTIR spectra of samples (16) and (20) as shown in Figure 4, and consequently, the GMA grafted content of HDPE at two DCP concentrations is calculated using the calibration curve (Fig. 2). As it is represented in Table III, the grafted GMA content, increases by raising the DCP content, showing that GMA grafting contributes to the torque results parallel with unwelcome crosslinking reaction. Furthermore, a comparison of torque values obtained from experimental results (Y_{exp}) and those calculated (Y_{cal}) from RSM [eq. (3)] is represented. The results are fully consistent and demonstrate an

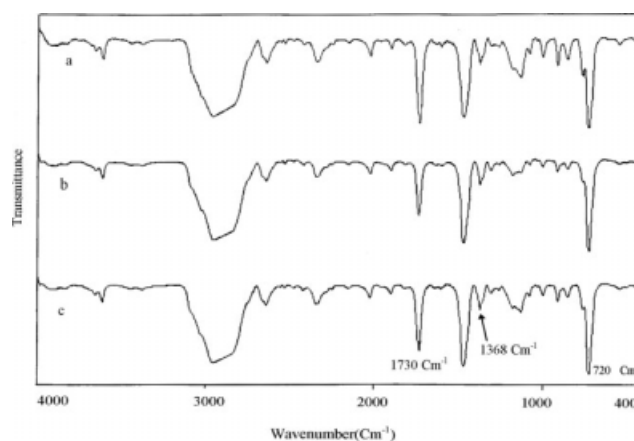


Figure 6 FTIR spectra of the HDPE-g-GMA copolymer with constant DCP content of 0.4 phr at different GMA content: (a) 9 phr, (b) 3 phr, and (c) 6 phr.

increase in torque values by increasing the DCP content in the reactive mixture.

Effect of GMA monomer

By increasing GMA content at fixed level of DCP (0.4 phr), the evolution of torque values versus reaction time showed a simultaneous increment both in slopes and the values of the secondary peak in torque diagram (Fig. 5). This is probably due to recombination of styrene and GMA macroradicals that can lead to branching or crosslinking.

As stated in the case of DCP dependency of results, the grafting level shows an increase with increasing the GMA content at constant DCP concentration. In a similar trend, the ratio of I_{1730}/I_{1368} and GMA wt % were calculated from Figures 6 and 2, respectively, and the results are summarized in Table IV. This is the proof for cooperative effect of GMA grafting and HDPE crosslinking on the torque values. Also, experimental results are in good agreement with calculated torque values using eq. (3).

Effect of reaction time

It was found that reaction time has minor effect on the final processing torque. Prolonged reaction time had caused a tendency to decrease torque level. As half-life of the initiator in the operational temperature and shear rate is less than 1 min, the difference

TABLE IV
Experimental and Calculated Torque and Grafted GMA Values as a Function of GMA Content at Constant DCP Level

Run no.	DCP content (phr)	GMA content (phr)	Y_{exp}	Y_{cal}	I_{1730}/I_{1368}	Grafted GMA (wt %)
12	0.4	3	46.27	43.62	2.262	2.1
18	0.4	6	46.44	46.68	2.972	2.758
7	0.4	9	48.42	49.75	3.519	3.266

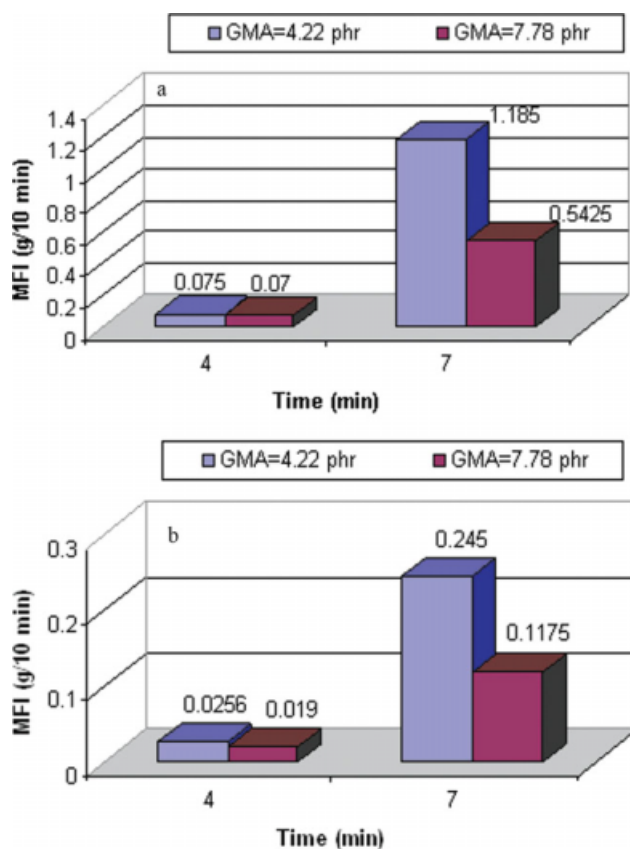


Figure 7 MFI values as a function of time and GMA content at two different DCP content: (a) 0.28 phr and (b) 0.52 phr. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of torque values due to variations of DCP content would not vary in the specified reaction times in this study. Therefore, it is expected that grafting process would be completed during 4–5 min. Existence of great difference between MFI values, supports this hypothesis [Fig. 7(a,b)]. This fact could be due to competitive reactions of grafting and chain scission of the branched copolymer induced by shear stresses. The branching reaction completes after 4–5 min and increasing the reaction time will induce more shear stress on melted copolymer. Therefore, possibility of chain scission of the grafted chains increases. Furthermore, comparison of Figure 7(a,b) shows that at the same reaction time and constant GMA content, increasing the DCP content from 0.28 to 0.52 results into a decrease in MFI values which is expected, due to more crosslinked structure.

CONCLUSIONS

In this research, we performed a detailed study of the free-radical grafting of GMA onto HDPE in the presence of styrene as a comonomer applying RSM of experimental design. Obtained results showed that CCD is a useful method to investigate the interactive effects of the independent variables on grafting yield. According to the CCD method, 20 runs were arranged and a predictive function over the experimental ranges was obtained that was consistent with experimental results. The grafting yield of GMA onto HDPE was determined using FTIR and titration/back-titration methods, and a calibration curve was developed successfully. Furthermore, it is shown that the higher the DCP and GMA content, the higher is the GMA grafting yield and final torque values which is influenced by both GMA grafting and crosslinking comparably. Also, it was found that the reaction time has minor effect on the final processing torque. Moreover, the appreciation of the interactions between variables was successfully achieved through RSM method and an interaction between DCP content and GMA wt % was perceived. The MFI test showed that after 4–5 min, excessive reaction time leads to enhancement of MFI values at constant DCP and GMA levels, due to the higher chain scission phenomenon.

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