

# Comparison of grafting of maleic anhydride onto linear low density polyethylene with hexene-1 and butene-1 comonomers and prediction of optimum ingredients by response surface methodology

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## ABSTRACT

In this work, the grafting of maleic anhydride onto two types of linear low density polyethylene with hexene-1 comonomer (LLDPE-H1) and butene-1 comonomer (LLDPE-B1), in the presence of styrene monomer (St) and dicumyl peroxide initiator (DCP) has been studied. The combined influences of MAH, St and DCP on the grafting efficiency via a melt reactive mixing process have been investigated using response surface methodology and the central cubic design has been employed for experimental design and data analysis. IR spectroscopy, contact angle measurements and adhesion test have been used to evaluate the extent of grafting reaction. The results showed that LLDPE-H1 with a 2.2% maximum grafting content showed more grafting content than the LLDPE-B1 (1.86%). This effect could be attributed to the type of comonomer in LLDPE-H1 which made it more prone to chain scission than LLDPE-B1, and a higher level of grafting was achieved. The gel content measurement showed that lower cross-linked structure was formed during the grafting process in the LLDPE-H1 than that in the LLDPE-B1. The optimum conditions of maximum grafting and minimum gel content were statically investigated. The optimum percentage of grafting for LLDPE-H1 was 1.82% and it was 1.74% for LLDPE-B1, with the minimum gel content of 6.5% and 9%, respectively. It was found that the amount of grafted percentage was sensitive to the concentrations of the MAH, DCP, and St, while the extent of the gel content was more sensitive to the percentage of DCP. **Polyolefins J (2021) 8: 11-19**

**Keywords:** Low density polyethylene; comonomer; maleic anhydride; response surface methodology.

## INTRODUCTION

The grafting process is a technical way to overcome the nonpolar limitation of polyolefins [1, 2]. In recent decades many kinds of researches were conducted to add polarity to polyolefin's structure [3, 4]. From a scientific point of view, monomers have been grafted onto polyolefins by various methods, like melt state and solution, which among these manners melt state is admirable because of simplicity, economic and mass

production. These factors can cause the manufacturer to pay attention to this method [1, 2].

Some reports showed that many parameters including temperature, mixing elements in the extruder, polymer structure and instrument's torque are effective during reactive melt process [5, 6]. Linear low-density polyethylene (LLDPE) is a well-known polyolefin with acceptable properties in many applications especially

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plastic wrap, food packaging, pipes, covers, toys, etc. LLDPE is usually made by copolymerization of ethylene monomers and comonomers. Indeed comonomers are long chain olefins like butene-1, hexene-1, and octene-1 that are usually used for polymerization of polyethylene [7]. It may be necessary to be noted that depending on which type of comonomer is used in the polymerization of ethylene, different properties achieve for final products. Researches have shown that different monomers were grafted onto polyolefins successfully but among them, maleic anhydride (MA) due to a reasonable price, accessibility and desirable product has been more commonly used for grafting. There have been a relatively large number of experiments studied with focusing on successful grafting MA onto polyolefins. Some studies have reported a significant positive effect for styrene (St) toward the enhancing the grafting degree [1, 8].

The impact of initiator type and processing condition on the grafting onto some polymers was the subject of some past research works [5, 9]. Nevertheless, it has been found no study on the influence of comonomer type of linear low density polyethylene on the grafting reactions.

This work is an effort to understand the influence of the length of side chain in the two grades of LLDPE-H1 and LLDPE-B1, one with butene-1 comonomer and the other with hexene-1 comonomer, on the grafting process and to determine the optimum operating conditions by using response surface method (RSM) [10]. Our goal here is to understand how the amounts of peroxide initiator, maleic anhydride and styrene monomer affect the grafting process in competition with gel formation.

The reactive mixing process is carried out in the presence of peroxide initiator, maleic anhydride and styrene monomer as graft assistant agent. The grafting percent for each formulation was calculated and the effect of the comonomer type on the grafting process was also determined.

## EXPERIMENTAL

### Materials

The LLDPE 0209-AA containing butene-1 comono-

mer from Shahzand (Arak-Iran) Petrochemical Co., with a MFI of 0.9 dg/min (190°C, 2.16 kg), and LLDPE SP3010 containing hexene-1 comonomer from Evolve Company (Japan) with a MFI of 0.8 dg/min (190°C, 2.16 kg) were used in this work. Dicumylperoxide (DCP) and maleic anhydride (MAH) were purchased from Merck, and an industrial grade styrene was used.

### Sample preparation

The MAH grafting onto LLDPE-B1 and LLDPE-H1 in the presence of styrene was carried out in the internal mixer (Brabender, Germany) at 170°C and 55 rpm rotor speed for 7 min. Formulations were selected based on experimental design, which are listed in Table 1. It is necessary to note that for each row of this table, two samples were prepared, one with LLDPE-H1 and the other one with LLDPE-B1. It means the total number of samples was 30.

### Sample purification

For quantification of MAH grafted onto LLDPE, the unreacted MAH and its byproducts were removed from samples. In the melt grafting process, the possible byproducts of MAH oligomers and styrene-maleic copolymers (SMA) are soluble in cold xylene and the grafted LLDPE and pure LLDPE are solely soluble in hot xylene. To purify samples out of unreacted materials, 2 g of each sample was dissolved completely in hot xylene at 130°C and then cooled down to room temperature. The precipitated LLDPE and MAH-g-LLDPE were filtered and washed with acetone two times and vacuum dried for one hour at 70°C. The purified samples consequently were converted into film by hot press and used for contact angle measurement and spectroscopic analysis.

### Gel content determination

The gel content (GC) is determined by:

$$GC = \frac{W_b - W_a}{W_s} \times 100 \quad (1)$$

Where,  $W_b$  is the total weight of stainless steel wire mesh and sample after extraction,  $W_a$  is the weight of stainless steel wire mesh and  $W_s$  represent the exact weight of the sample before extraction.

**Table 1.** Samples formulations according to the design of experiment.

Sample	Independent variables			Response
	MA (%)	DCP (%)	St (%)	Polymer (%)
1	3.5	0.05	0.1	96.35
2	3.5	0.075	0.1	96.325
3	5	0.1	2	92.9
4	5	0.1	0.1	94.8
5	2	0.05	2	95.95
6	5	0.05	0.1	94.85
7	5	0.075	1.05	93.875
8	3.5	0.1	1.05	95.35
9	2	0.1	2	95.9
10	2	0.075	0.1	97.825
11	2	0.05	0.1	97.85
12	5	0.05	2	92.95
13	2	0.1	0.1	97.8
14	3.5	0.0625	1.05	95.388
15	3.5	0.05	2	94.45

### Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) of different samples was performed by FTIR spectrum RXI, Perkin Elmer, USA. The carbonyl absorbance was measured at  $1784\text{ cm}^{-1}$  and the carbonyl index (CI) was calculated by:

$$CI_{MA} = \frac{A_{1784}}{A_{720}} \quad (2)$$

Where,  $A_{720}$  is the area under the absorbance band of C-H group of polyethylene at  $720\text{ cm}^{-1}$ .

### Contact angle measurement

To evaluate the surface chemistry of grafted samples and verifying the received results from FTIR, the contact angle was measured. The films made of purified samples were used for contact angle measurement (ISO15989) with placing distilled water on the surface for each of specimens.

### Adhesion test

The adhesion strength of grafted materials to steel is evaluated in two various mode of an applied load: lap shear testing according to ASTM D1002, and peel resistance (T-Peel test) according to ASTM D1062. The steels were properly surface treated and cleaned before test. The samples were applied at  $200^{\circ}\text{C}$  with a thickness of 100 microns.

### Design of experiment planning and analysis

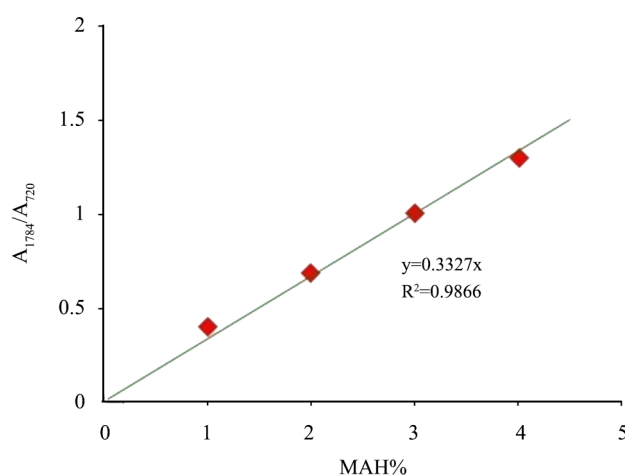
The design of experiment was performed by Design-Expert 10.07. The surface response method (RSM) and analysis of variance (ANOVA) were used to evaluate the results. Three variables of maleic anhydride (MAH), styrene (St) and dicumyl peroxide (DCP) percentage were used in this analysis. The effect of these parameters on the graft percentage and gel content was determined.

## RESULTS AND DISCUSSION

### Graft content and quantification

The extent of grafting is determined by using FTIR test results. The area under the peak at  $1784\text{ cm}^{-1}$  ( $A_{1784}$ ) for maleic anhydride and the peak area of C-H bond for polyethylene A720, with a predetermined amount of maleic anhydride content are calculated and a calibration curve for carbonyl index CI ( $A_{1784}/A_{720}$ ) against MAH wt.% is obtained [11]. The experimental data for the samples with certain amount of maleic anhydride are tabulated in Table 1. The best fit in the experimental data of CI against maleic anhydride content is achieved by the following linear type equation (Figure 1):

The grafting percentage of MAH is estimated by using the calibration curve of Figure 1 and the obtained results are surveyed in Table 2. By comparing the formulations pairwise, it can be seen that the amount of graft onto LLDPE-H1 is higher than that on LLDPE-B1 for all formulations. The peroxide at high pro-

**Figure 1.** The correlation between MA content and  $A_{1784}/A_{720}$  ratio.

cessing temperature can abstract hydrogen more easily from the backbone chains of LLDPE-H1 and it is more prone to participate in the grafting reaction than LLDPE-B1.

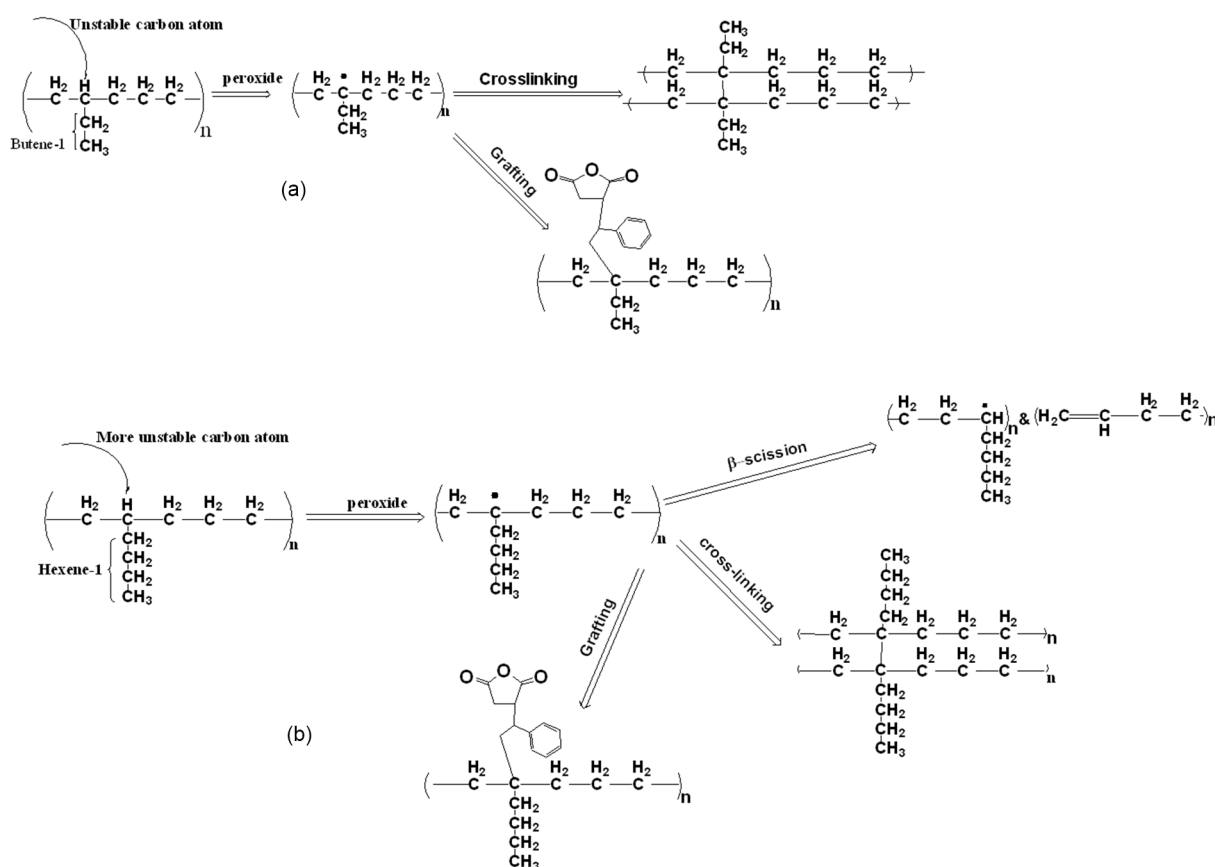
It seems necessary to note that, LLDPE-B1 used in this work is produced by using Ziegler-Natta catalyst and the LLDPE-H1 is produced by metallocene catalyst. The type of catalyst used in the coordination polymerization of LLDPE and the type of comonomer and its percentage have strong effect on the microstructure and consequently on the properties of synthesized polymer [12–14].

The compositional uniformity is a feature of LLDPE synthesized by metallocene catalysts that due to its selectivity leads to evenness in the distribution of alpha olefin along with macromolecules of polymer chains. The overall mechanism for preparing each of the grades is proposed in Figure 2 [15, 16]. It has been proven that the number of comonomer and its distribution along the backbone chains of alpha olefins synthesized by metallocene and Ziegler-Natta catalyst are different [17].

The test method described in ASTM D6635 was used to determine the comonomer content of alpha olefin polymers based on FTIR test results and a calibration curve based on NMR measurements. The number of comonomer (per a thousand atoms of carbon) directly is related to the peak area of  $1378\text{ cm}^{-1}$  over  $2019\text{ cm}^{-1}$  ( $A_{1378}/A_{2019}$ ) in the neat sample of polyolefin. The  $A_{1378}/A_{2019}$  ratio for LLDPE-H1 was 3.13 that was higher than that for LLDPE-B1 ( $A_{1378}/A_{2019}=3.03$ ). In addition to the types of comonomer, the number of comonomers and their distribution along the chains also affect the graft efficiency. It is believed that the higher graft percentage refers to the longer side chain in LLDPE-H1 than LLDPE-B1. Nonetheless the number of comonomer/1000 carbon atoms on the grafting process is also an important factor that needs further study.

### Contact angle measurement

Polyolefins are none polar polymers with low surface energy. By grafting functional monomers such as ma-



**Figure 2.** The mechanism proposed for grafting of MA onto: (a) LLDPE-B1, and (b) LLDPE-H1 in the presence of styrene [21].

leic anhydride onto these polymers, the surface free energy increases. The measurement of contact angle of liquids in contact with polymers is a common method to characterize the surface chemistry of solids. The measurement of contact angle can be carried out by several different methods [18]. The most widely used method is sessile drop technique. It is a convenient method with reasonable accuracy of  $\pm 2^\circ$  with acceptable reproducibility. In this method a droplet of a known liquid such as water, places on the surface of a solid and the contact angle of tangent to the drop curvature measures at the crossing point of the interface of solid substrate, liquid droplet and surrounding air. The contact angles of water on the films prepared by neat LLDPE-B1 and LLDPE-H1, measured here in this work were about  $91 \pm 2^\circ$  for both samples. The surface polarity of LLDPE increased by increasing the grafting percentage and its contact angle with water droplets decreased and diminished at high polarity [19, 20]. The contact angle of water for a number of samples is measured and surveyed in Table 2.

#### Adhesion test

The adhesion test results are collected in Table 3 and Table 4 for lap-shear test and T-peel test, respectively [22]. It is seen that by increasing the graft percentage, higher values for the adhesion force is achieved. This trend for the increase in adhesion forces is observed for both modes of an applied load which return to enhanced polarity of grafted LLDPE. The adhesion test

**Table 2.** Contact angle, gel content and graft percentage of samples.

Parameters	Graft%		Gel content		Contact angle	
	( $\pm 0.1$ )		( $\pm 3\%$ )		( $\pm 2$ degree)	
Sample no	LL-B1	LL-H1	LL-B1	LL-H1	LL-B1	LL-H1
1	1.23	1.38	10	6	82	78
2	1.38	1.46	15	11	76	72
3	1.26	1.55	25	20	80	74
4	1.55	1.67	28	26	72	68
5	1.46	1.58	15	11	73	67
6	1.26	1.49	17	15	80	71
7	1.32	1.44	23	20	79	75
8	1.86	2.18	25	20	66	58
9	1.26	1.44	25	23	79	72
10	0.87	1.20	16	12	85	80
11	0.79	1.00	10	9	89	85
12	1.55	1.80	16	14	72	67
13	1.41	1.70	30	26	73	65
14	1.67	1.70	14	11	66	65
15	1.38	1.55	9	7	78	76

**Table 3.** Lap-shear test results of grafted samples.

Sample no	LLDPE-B1		LLDPE-H1	
	Graft %	Force N	Graft %	Force N
8	1.86	2200	2.18	2400
15	1.38	1400	1.55	1900

result approved the contact angle measurement and the graft percentage calculated by FTIR method.

The quadratic model is used for the statistical evaluation of the grafting reaction. Figure 3 shows the predicted against actual data for LLDPE-H1 and LLDPE-B1. This shows that this model can match well on actual data and can be used for estimating. The coded parameters shown in Table 5 which are allocated between the range of -1 and 1, reveal the influence of MAH (A), DCP (B) and St (C) percentages on the extent of grafting. The higher value for the coefficient of MAH is the evidence of its higher reactivity in LLDPE-H1 than that in LLDPE-B1. The coefficient of DCP is also higher for LLDPE-H1 that leads to the higher grafting percentage for this grade. The results show that DCP initiator and MAH monomer simultaneously have strong effect to increase the graft percentage. The DCP also promote the crosslinking reaction in polyethylene and increase the gel content. This is why determining the optimal amount of DCP is important for the maximum grafting and minimum gel content. Due to the byproducts, each factor is expected to have the optimal value shown in the 3D-plots, at a constant St of 1.05 % for LLDPE-H1 and LLDPE-B1 shown in Figures 4a and 4b.

The quadratic equations with actual parameters for the extent of grafting for LLDPE-H1 and LLDPE-B1 are as bellow:

$$\begin{aligned} \text{Grafted LLDPE-H1 (\%)} &= 1.84 + 0.79A - 65.55B + 1.2C - 1.75AB - 0.007AC - 6.27BC - 0.086A^2 + 544.6B^2 - 0.31C^2 \\ \text{Grafted LLDPE-B1 (\%)} &= 0.064 + 0.97A - 28.9B + 1.22C - 0.44AB - 0.029AC - 8.0BC - 0.125A^2 + 284.1B^2 - 0.21C^2 \end{aligned}$$

A:MAH, B:DCP, C:St

**Table 4.** T-peel test results of grafted samples.

Sample no	LLDPE-B1		LLDPE-H1	
	Graft %	Force N	Graft %	Force N
5	1.46	0.80	1.58	1.00
6	1.26	0.65	1.49	0.81
14	1.67	1.02	1.70	1.05

**Table 5.** Statistical data for maleation of LLDPE-H1 and LLDPE-B1.

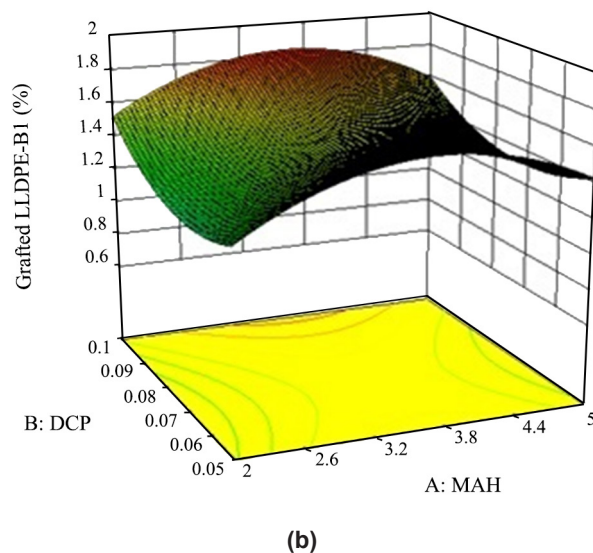
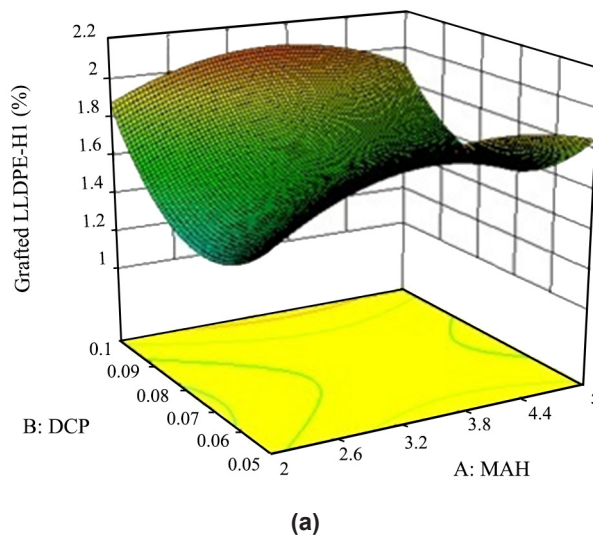
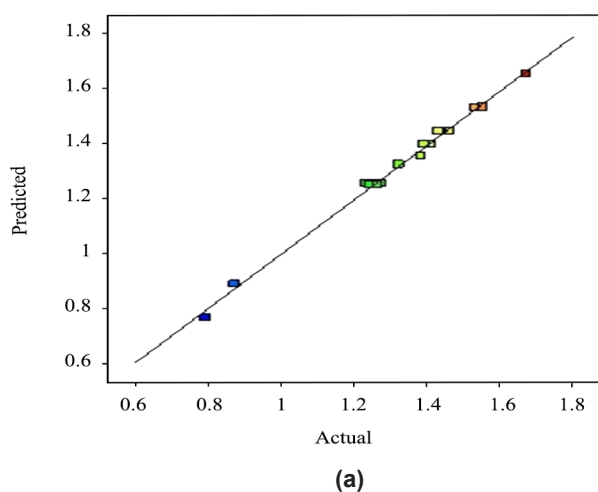
Factor	Coefficient estimate	
	LLDPE-H1	LLDPE-B1
Intercept	1.71	1.66
A-MA	0.062	0.050
B-DCP	0.11	0.089
C-St	0.1	0.09
A*B	-0.036	-0.024
A*C	-0.028	-0.035
B*C	-0.20	-0.21
A <sup>2</sup>	-0.35	-0.38
B <sup>2</sup>	0.29	0.20
C <sup>2</sup>	-0.17	-0.19
Std.Dev.	0.031	0.024
R-squared	0.9912	0.9953
Adj R-squared	0.9799	0.9893
Pre R-squared	0.9130	0.9353

**Gel content**

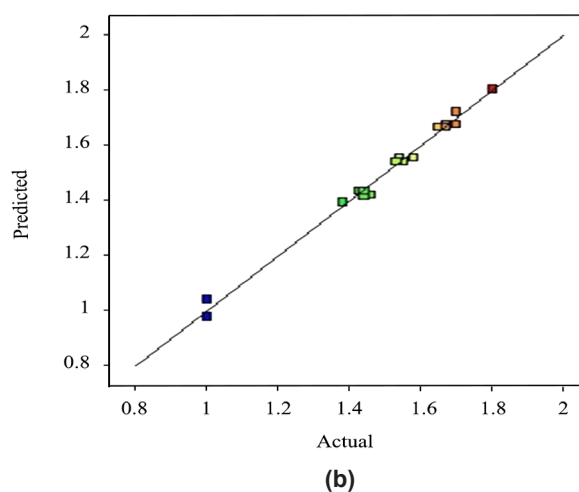
In the grafting process by using peroxide initiator, grafting and crosslinking are two main reactions which may simultaneously happen in the polymer melt. The crosslinking is an undesired reaction that may lead to diverse effect on the process ability. The pendant groups attached to the repeat unit in polymer backbone affect the physical and mechanical properties and also thermal behaviour [23, 24].

It is proved that during reactive extrusion of polypropylene with methyl pendant group, the  $\beta$ -scission reaction is more significant than crosslinking and the gel content decreases [24] while for polyethylene, gel content increases and crosslinking is the dominant reaction.

It is the question that while longer side chain in LL-



**Figure 4.** 3D-plot for grafted percent of (a) LLDPE-H1 and (b) LLDPE-B1.



**Figure 3.** Plot of predicted vs. actual data for two grades (a) LLDPE-B1 (b) LLDPE-H1.

**Table 6.** ANOVA results for analysis of the gel content of LLDPE-B1.

Source	Sum of squares	df	Mean square	F value	p-value
<b>Model</b>	938.82	9	104.31	121.95	< 0.0001*
<b>A-MA</b>	22.44	1	22.44	26.23	0.0009
<b>B-DCP</b>	399.92	1	399.92	467.55	< 0.0001
<b>C-St</b>	16.95	1	16.95	19.82	0.0021
<b>AB</b>	35.20	1	35.20	41.16	0.0002
<b>AC</b>	0.20	1	0.20	0.24	0.6381
<b>BC</b>	7.75	1	7.75	9.06	0.0168
<b>A<sup>2</sup></b>	32.96	1	32.96	38.53	0.0003
<b>B<sup>2</sup></b>	12.91	1	12.91	15.09	0.0046
<b>C<sup>2</sup></b>	17.30	1	17.30	20.23	0.0020
<b>Residual</b>	6.84	8	0.86	4.04	0.0836**
<b>Lack of Fit</b>	4.84	3	1.61		
<b>Pure Error</b>	2.00	5	0.40		

\* Significant, \*\* not Significant

**Table 7.** Statistical coefficients of LLDPE-H1 and LLDPE-B1.

Factor	Coefficient estimate	
	LLDPE-H1	LLDPE-B1
<b>Intercept</b>	12.41	16.59
<b>A-MA</b>	1.52	1.53
<b>B-DCP</b>	5.58	6.53
<b>C-St</b>	-1.31	-1.37
<b>AB</b>	-1.96	-2.07
<b>AC</b>	-0.60	-0.14
<b>BC</b>	-0.83	-0.90
<b>A<sup>2</sup></b>	5.76	4.46
<b>B<sup>2</sup></b>	2.96	2.63
<b>C<sup>2</sup></b>	-3.65	-3.47
<b>Std.Dev.</b>	0.92	1.53
<b>R-squared</b>	0.9928	0.9770
<b>Adj R-squared</b>	0.9846	0.9515
<b>Pre R-squared</b>	0.9317	0.8841

**Table 8.** Optimal values of MAH, DCP and St variables.

Parameter	MAH	DCP	St	LLDPE-B1		LLDPE-H1	
				Graft%	Gel%	Graft%	Gel%
<b>Range (%)</b>	2-5	0.05-0.1	0.1-2	0.79-1.86	9-30	1-2.18	6-26
<b>Optimal Value (%)</b>	3.445	0.05	1.975	1.74	9	1.82	6.5

DPE-H1 structure leads to higher grafting efficiency, how it will be the gel formation during the grafting reaction? It is expected that longer side chain in LLDPE-H1 leads to lower gel content. As is seen, the gel content of the LLDPE-H1 is lower than that of LLDPE-B1 (Table 2). It is found that the gel content is significantly under the influence of peroxide initiator, and a slight increase in DCP content leads to a comprehensive increase in gel content.

Analysis for variance (ANOVA) resulted for the gel content of LLDPE-B1 is carried out by using a quadratic model. The sample analysis results of LLDPE-B1 are summarized in Table 6. A similar table exists for LLDPE-H1 with the same model. The amount of p-value specifies the significance of regression coefficient. When p-value of a variable is less than 0.05, its influence on response model is significant. The ANOVA analysis data of Table 6 validate the desired accuracy of a model used in the analysis of experimental data in this study [25].

The influences of effective coded factors on the gel content are shown in Table 7. It can be seen that the independent variables differently affect the gel content and are not the same. The influence of DCP is most significant on the gel content with a coefficient of 5.58. Meanwhile, the coefficient of St and MAH is -1.31 and 1.52, respectively. The negative sign im-

plies the inverse and negative effect of the styrene on the gel content while the effect of maleic anhydride is positive and additive.

The quadratic equations with actual data for the prediction of gel content are:

$$\text{Gelcontent}(\%)_{\text{LLDPE-B1}} = 19.4 - 8.25A - 115.2B + 10C - 52.7AB - 0.045AC - 41.8BC + 1.9A^2 + 4053B^2 - 3.84C^2$$

$$\text{Gel content}(\%)_{\text{LLDPE-H1}} = 26.4 - 11.4A - 247.1B + 10.6C - 48.7AB - 0.32AC - 44BC + 2.3A^2 + 4615.8B^2 - 3.45C^2$$

### Optimum contents

Grafting and crosslinking, in addition to some other possible reactions, are the main phenomena in the functionalization of polyethylene with MAH. The grafting is the most desired reaction while the minimization of crosslinking also is vital for the sake of process ability. The range of variables of MAH, DCP and the optimal values for LLDPE-H1 and LLDPE-B1 are shown in Table 8. The optimal values and the predicted results were estimated by the model used with the desirability of 0.884.

### CONCLUSION

In this work, two types of LLDPE containing butene-1 and hexene-1 comonomers were used and the influence of alpha-olefin comonomer types on grafting of

maleic anhydride onto these two polymers were investigated.

The results revealed that the percentage of grafting considerably is under the influence of the length of comonomer and it is higher for the LLDPE grade with hexene-1 comonomer.

The grafting of MA onto LLDPE containing longer comonomer hexene-1 led to lower gel content (due to lower crosslinking) than its shorter chain counterpart butene-1 comonomer. LLDPE-H1 with longer chain hexene-1 comonomer is more prone to beta scission than crosslinking in comparison with LLDPE containing butene-1 comonomer.

The measurement of grafting percentage by FTIR analysis and the change of surface chemistry of grafted samples were approved by contact angle measurement and adhesion test. The enhance polarity of grafted samples led to lower contact angle of water droplets on the surface of samples and a higher adhesion strength to metal was achieved.

Response surface methodology was applied to study the effects of MAH, DCP and St, concentration on the grafting efficiency. Predicted models with adequate fitness for grafting percentage of LLDPE-H1 and LLDPE-B1 were proposed and the optimal variable percentages were determined for maximum grafting and minimum gel content.

## REFERENCES

- Moad G (1999) Synthesis of polyolefin graft copolymers by reactive extrusion. *Prog Polym Sci* 24:81-142
- Passaglia E, Coiai S, Augier S (2009) Control of macromolecular architecture during the reactive functionalization in the melt of olefin polymers. *Prog Polym Sci* 34:911-947
- Jahani Y, Valavi A, Ziaee F (2015) Reactive melt modification of polyethylene by ethyl acrylate / acrylic acid copolymers : Rheology , morphology and thermal behavior. *Iran Polym J* 24: 449-458
- Shieh Y, Chuang H, Liu C (2001) Water crosslinking reactions of silane-grafted polyolefin blends. *J Appl Polym Sci* 1799-1807
- Clark DC, Baker WE, Whitney RA (2001) Peroxide-initiated comonomer grafting of styrene and maleic anhydride onto polyethylene: effect of polyethylene microstructure. *J Appl Polym Sci* 79: 96-107
- Liu W, Liu T, Liu T, Liu T, Xin J, Hiscox WC, Liu H, Liu L, Zhang J (2017) Improving grafting efficiency of dicarboxylic anhydride monomer on polylactic acid by manipulating monomer structure and using comonomer and reducing agent. *Ind Eng Chem Res* 56: 3920-3927
- Galland GB, Seferin M, Mauler RS, Dos Santos JHZ (1999) Linear low-density polyethylene synthesis promoted by homogeneous and supported catalysts. *Polym Int* 48: 660-664
- Bettini SHP, Ruvolo Filho AC (2008) Styrene-assisted grafting of maleic anhydride onto polypropylene by reactive processing. *J Appl Polym Sci* 107:1430-1438
- Ramos D, Helson M, Rocha MCG (2006) Study of different peroxide types on the modification of LLDPE . Part 1. Factorial experimental design and thermal properties. *Polym Test* 25:306-312
- Khuri AI, Mukhopadhyay S (2010) Response surface methodology. *Wiley Interdiscip Rev Comput Stat* 2:128-149
- Shi Q, Zhu L, Cai C, Yin JH, Costa G (2005) Kinetics study on melt grafting copolymerization of LLDPE with acid monomers using reactive extrusion method. *J Appl Polym Sci* 101: 4301-4312
- Velthoen MEZ, Muñoz-Murillo A, Bouhmadi A, Cecius M, Diefenbach S, Weckhuysen BM (2018) The multifaceted role of methylaluminumoxane in metallocene-based olefin polymerization catalysis. *Macromolecules* 51:343-355
- Brintzinger HH, Fischer D, Mülhaupt R, Rieger B, Waymouth RM (1995) Stereospecific olefin polymerization with chiral metallocene catalysts. *Angew Chemie Int Ed Eng* 34:1143-1170
- Shamiri A, Chakrabarti MH, Jahan S, Hussain MA, Kaminsky W, Aravind PV, Yehye WA (2014) The influence of Ziegler-Natta and metallocene catalysts on polyolefin structure, properties, and processing ability. *Materials* 7: 5069-5108
- Platzer N (1983) Branched polyethylene : LDPE and LLDPE. *Ind Eng Chem Res* 158-160
- Kaminsky W (1980) Ziegler-Natta Catalysis. *Adv Organomet Chem* 18: 99-149
- Pii P, Marigo A, Zannetti R, Milani F (1997) A small- and wide-angle X-ray scattering study of 1-butene LLDPE obtained by metallocene and Ziegler-Natta catalysis. *Eur Polym J* 33:595-598
- Neumann AW, Good RJ (1979) Techniques of measuring contact angles. In: *Surface and colloid*



- science. Springer, pp 31–91
19. Sa S (2000) Polyethylene grafted maleic anhydride to improve wettability of liquid on polyethylene films. *J Appl Polym Sci* 1802-1808
  20. Sathe SN, Rao GSS, Dev S (1994) Grafting of maleic anhydride onto polypropylene : Synthesis and characterization. *J Appl Polym Sci* 239-245
  21. Ma P, Jiang L, Ye T, Dong W, Chen M (2014) Melt free-radical grafting of maleic anhydride onto biodegradable poly(lactic acid) by using styrene as a comonomer. *Polymers* 6:1528-1543
  22. Schaible S, Meincke O, Schulthess A, Brändli C (2018) Process optimization for improved adhesion in the grafting of triethoxyvinylsilane on VLDPE via reactive extrusion. *Eur Polym J* 107:9-14
  23. Lee BK, Park JH, Park SH, Kim JH, Oh SH, Lee SJ, Lee BY, Kim MS (2017) Preparation of pendant group-functionalized diblock copolymers with adjustable thermogelling behavior. *Polymers* 9: 239
  24. Berda EB, Wagener KB (2008) Inducing pendant group interactions in precision polyolefins: synthesis and thermal behavior. *Macromolecules* 41:5116-5122
  25. Detyothin S, Selke SEM, Narayan R, Rubino M, Auras R (2013) Reactive functionalization of poly (lactic acid), PLA: Effects of the reactive modifier, initiator and processing conditions on the final grafted maleic anhydride content and molecular weight of PLA. *Polym Degrad Stab* 98: 2697-2708