



Microwave Cross-linking of LDPE: Experimental Modelling of Gel Content by Taguchi Method and Optimum Processing Conditions

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ABSTRACT

Low density polyethylene (LDPE) properties could be modified by cross-linking. In this research, crosslinking of LDPE was studied under microwave irradiation. Moreover, carbon and chlorinated paraffin were added to LDPE as UHF-active aids. Carbon, chlorinated paraffin, and peroxide contents, as well as irradiation time were determined as the most important and effective parameters based on some initial experiments. LDPE compound was prepared in an internal mixer. Torque-time curve, during the mixing process was measured as the indication of the suitable compounding with no partial cross-linking. The gel content of cross-linked LDPE (XLPE) was studied as a measure of cross-linking degree. In theoretical section, L_9 orthogonal array method (Taguchi design) was applied as the design of experiments (DOE). Results were analyzed using Minitab and Qualitek4 softwares. Various statistical criteria were applied on the results showing the same conclusion on the parameters behaviour. It was found that an experimental relationship (by regression) may be offered between the gel content and the main parameters. Consequently, optimum cross-linking condition was determined. The result may be used as a quantitative relationship in product design applications.

Key Words:

polyethylene;
cross-linking;
microwave;
DOE;
peroxide.

INTRODUCTION

Over the last twenty years, microwave application has been enjoying a lot of considerations due to fast heat transfer and energy saving. Cooking with microwave is a well established concept [1]. Today, there are more than sixty million microwave ovens around the

world. However, material processing by microwave is a novel idea due to properties improvements as well as economic aspects [2-4]. The important advantages of microwave processing are physical properties improvements, ease of processing, less environmental im-

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pacts, energy saving, and ability to possess certain microstructures [4,5].

In traditional heat transfer methods (conduction, convection, and radiation) heat is transferred to the material by means of temperature gradient via its surface. Therefore, there is a heat flow from surface to the bulk. However, by microwave the whole material is heated simultaneously, because electromagnetic field directly produces energy inside the material. The produced energy is interchanged into molecular kinetics and potential energies. In other words, the bulk as well as the surface absorb energy [1,3]. In traditional heating, there is a limit in heat transfer rate which is determined by temperature gradient. Polymer conductivity is normally as low as 0.1 w/m.K and therefore, processing time increases. In this way, there is a trade off between processing time and product quality.

Energy generation has direct relationship with dielectric properties of a material. For higher dielectric loss factor, higher energy is generated. In multiple phase systems, it is possible to have selective heating rate because of different dielectric loss factors of different phases, which would lead to new structure products. Electromagnetic field properties, chemical composition of materials, structural changes, material geometry, interaction between field and material, and etc. make microwave processing a complex one [1-3]. The most studied microwave processing in polymer science and technology are synthesis and polymerization [6-10].

Polymer cross-linking [11-13] increases organic material diffusion in polymers [14], resin transfer moulding[15], and adhesive curing [16] are some examples of polymer science applications. Cross-linked polyethylene (XLPE) is enjoying increasing consumption in cable insulation industry, hot water pipe, foam, etc. This is due to improvement in heat distortion behaviour and mechanical properties of XLPE [17-19]. There are three main methods in cross-linking of polyethylene namely electron beam irradiation, peroxide, and silane [13, 17, 19-22]. Rado et al. [13] have described technological processes for cross-linking of polyethylene including continuous and discontinuous processes by various methods for different applications and introduced the main processing parameters. They have also focused on the applications of XLPE as the insulation of cables [22].

Rafizadeh et al [23] have applied the Taguchi orthogonal array to determine the significance level of various factors which affect the impact strength of PC/ABS parts. They have presented an experimental model that can predict the impact strength. Based on the analysis of variance (ANOVA) blend composition, the mixing time, temperature, and mould and injection temperatures had more effect on impact strength of the blend, respectively.

In this research, the four most effective parameters on cross-linking of polyethylene were recognized. They are irradiation time and peroxide, chlorinated paraffin, and carbon contents. The gel content relationship with the above given factors was studied by an experimental design (DOE). The DOE is a powerful tool in research and industrial studies. It gives more detailed results within shorter time length and expenses [24,25]. L_9 (3^4) orthogonal array (Taguchi approach) was applied which includes nine experiments with three levels of four factors. A regressive relationship was presented. Finally, this relationship was applied to determine the optimum point via constrained optimization method. In this work, it was found that cross-linking can be performed within shorter time length and at lower temperature. Finally, an experimental relationship is given for the first time.

THEORETICAL ASPECTS

In cross-linking of polyethylene by peroxide, this initiator decomposes at suitable temperature to produce radical(s) [19]:



In the next step, radicals attack polymer chains producing polyethylene macroradical:



Finally, macroradicals could undergo reactions to produce three-dimensional cross-linked structures:



From practical point of view, there are two distinct

steps in cross-linking by a peroxide system: -preparing cross-linkable compound including peroxide in a compounding equipment such as internal mixer and -shaping and heating of compound which leads to cross-linked polyethylene. The type and the amount of peroxide are the key parameters. Normally, cross-linking temperature is higher than heat distortion temperature. However, temperature gradient is a limiting factor. Microwave, as a heating medium, is a good alternative in order to overcome this problem. However, various parameters could affect the process.

In some preliminary experiments, the mixture of polyethylene and peroxide only went under irradiation at different time lengths (2-8 min). There was no sign of gel formation, indicating that it is vital to add some microwave absorbant materials such as carbon and chlorinated paraffin. It is necessary to say that elongation of irradiation time may warm up the magnetron and harm the microwave oven itself. However, it is possible to start irradiation with warm and hot materials to start cross-linking without any need for an absorbant material [12]. In this study, carbon, chlorinated paraffin, peroxide contents, and irradiation time were selected as main factors. Adding microwave absorbant materials makes it possible to perform process with low microwave power (1000 w) and avoid high powers such as 2100 w [12,26].

Taguchi method $L_9 (3^4)$ was selected to design experiment strategy. $L_9 (3^4)$ array has various aspects such as low number of experiments (9 runs), high number of factors and levels (up to 4 factors and 3 levels), ability to catch curvature and the second order relationship [25,27]. The following second order surface response was fitted in this research:

$$y = a_0 + \sum_{i=1}^4 a_i x_i + \sum_{i=1}^4 a_{ii} x_{ii}^2 \quad (1)$$

EXPERIMENTAL

In this study, low density polyethylene (Poliran LF0200), supplied by Bander Imam Petrochemical Complex (BIPC), Iran was used. Carbon, N550 grade, was supplied by Ahwaz Carbon Co., Iran. *tert*-Butyl peroxy benzoate (TBPB) with trade name Trigonox C, supplied by Akzo Nobel was used as an initiator [28]. Chlorinated paraffin, with trade name CP-152 sup-

plied by Geohall Co. was added. The gel content of cross-linked polyethylene was measured based on the ASTM-2765 D. Para-xylene was used as solvent of the uncross-linked part. BHT antioxidant was added to the extraction medium. Table 1 gives some properties of these materials.

All compounds were prepared in a laboratory size Brabender internal mixer with 60 mL capacity. Banbury type rotor was used in order to have maximum extent of distribution and dispersion. Cross-linking was performed in a microwave oven which could provide ten different levels of irradiation up to 1000 w. All tests were performed under 1000 w irradiation. Sample sheets were prepared in a 20 tons compression moulding machine with 1 mm thickness.

A series of preliminary experiments were conducted in order to determine the suitable mixing, cross-linking, and the levels of factors. Table 2 shows the design of experiments based on the $L_9 (3^4)$ array. This table contains nine experiments including peroxide (Pr), carbon (C), chlorinated paraffin (Pa), and irradiation time (T) factors at three different levels. Each composition was mixed in an internal mixer and sheets were obtained by compression moulding and consequently underwent cross-linking and the gel content was determined.

In the first step, polyethylene was entered to the internal mixer at 30°C with 35 rpm rotor rotation speed. After melting was completed, carbon was added to the mixer and then TBPB was added and rotor speed decreased to 10 rpm after complete mixing of polyethylene and carbon. Torque-time curve

Table 1. Materials properties.

Material	Property
Polyethylene	$\rho=0.9190-0.9225$ g/mL
	MFI=1.8 - 2.2 g/10 min
<i>tert</i> -Butylperoxy benzoate	Active oxygen= 8.16 w/w%
	PERCENTAGE = 99%
	Density at 20°C = 1.04 g/cm ³
Chlorinated paraffin	Chlorine Content by WT Pct=50-52
	Specific Gravity (25°C) =1.23-1.27
	Viscosity 25°C (Poise) = 11-16

Table 2a. Coded experiments in DOE based on the $L_9 (3^4)$.

Run	Factors	Peroxide	Chlorinated paraffin	Carbon	Irradiation time
1		1	1	1	1
2		1	2	2	2
3		1	3	3	3
4		2	1	2	3
5		2	2	3	1
6		2	3	1	2
7		3	1	3	2
8		3	2	1	3
9		3	3	2	1

Table 2b. Experimental table including runs, levels, usage parameters, and uncoded value of factors in DOE based on the $L_9 (3^4)$.

Run	Factors	Peroxide (g)	Chlorinated paraffin (g)	Carbon (g)	Irradiation time (min)
1		0.78	0	0	2.5
2		0.78	0.96	1.93	5
3		0.78	1.93	3.86	7.5
4		1.16	0	1.93	7.5
5		1.16	0.96	3.86	2.5
6		1.16	1.93	0	5
7		1.55	0	3.86	5
8		1.55	0.96	0	7.5
9		1.55	1.93	1.93	2.5

was used in order to recognize the suitable mixing of compound and avoid the over heating because of shear viscous heating. Figure 1 shows two typical torque-time curves during the mixing process. In the mixer which contained chlorinated paraffin, the solution of peroxide in chlorinated paraffin was added to the internal mixer. Peroxide was mixed with the mixture for at least 3 min. During this period, there was not any increase in torque which meant that there was no sign of peroxide decomposition and cross-linking. Peroxide half time in mixing temperature was around 7 h. Therefore, there was no chance for early cross-linking of polyethylene. For the mixture without carbon, polyethylene was introduced into the mixer in 130°C and peroxide was added after torque curve was reached a plateau.

A specific amount of polyethylene was weighed for producing 1 mm sheet and compression moulded at 130°C for 3 min. There was not any risk of cross-linking in this temperature. Then, temperature was

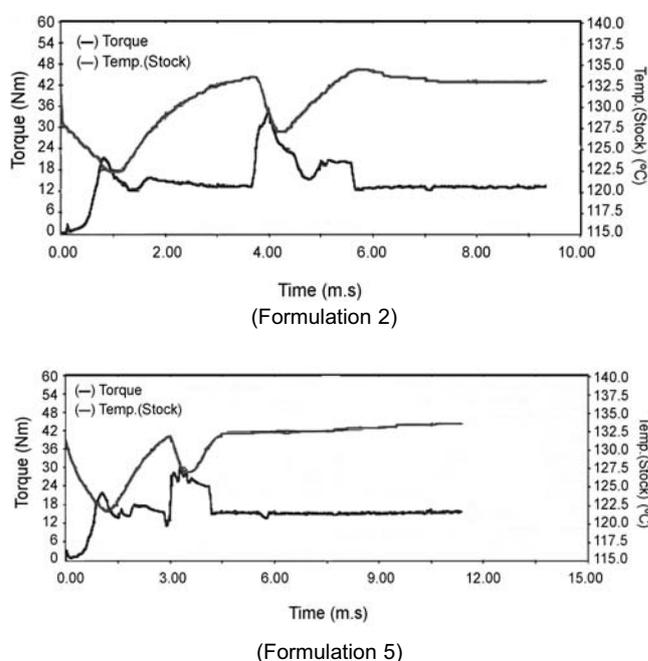
**Figure 1.** Torque-time and temperature-time curves during the mixing.

Table 3. The gel content of each run.

Run	1	2	3	4	5	6	7	8	9
Gel content after curing in microwave	0	40	70	27	55	40	80	25	77

reduced to 70°C and sheets were stored in a refrigerator in a controlled atmosphere. Sheet samples, in $4 \times 4 \text{ cm}^2$ were irradiated in a microwave oven under inert atmosphere (nitrogen). Sample temperature was measured by infrared temperature sensor right after completion of irradiation time. Four distinct samples of each sheet were measured for their gel content.

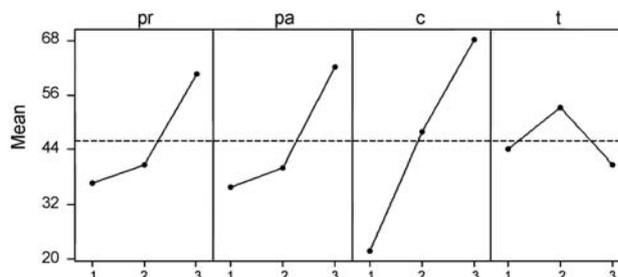
RESULTS AND DISCUSSION

Table 3 gives the results of gel content measurements. Each result is the mean of at least two measurements. Results were analyzed by Minitab and Qualitek 4 softwares. Minitab had been used to study the main effects for means, response for means, analysis of variance, and signal to noise (S/N) ratios. Qualitek 4 has been used to find the optimum point for maximum gel.

Response table mean was produced to have preliminary studies of the results. Table 4 shows the response table mean in each level of various factors. Delta in this table is defined as the difference between maximum and minimum means of each factor. Higher value of delta indicates a higher effect on response. Therefore, carbon has the highest effect on gel content and subsequently the chlorinated paraffin, peroxide, and time have less effects, respectively. Figure 2 shows means versus the level of each factor. It is observed that gel content is directly proportional to carbon, chlorinated paraffin, and peroxide contents. Energy generation increases by carbon and chlorinat-

Table 4. Response on the basis of mean.

Level	Pr	Pa	C	t
1	36.67	35.67	21.67	44.00
2	40.68	40.00	48.00	53.33
3	60.68	62.33	68.33	40.67
Delta	24.00	26.66	46.66	12.67
Rank	3	2	1	4

**Figure 2.** Main effects plot for means.

ed paraffin, then, there will be more gel content, due to further decomposition of peroxide. There is a decrease in gel content with increasing irradiation time from level 2 to level 3. It is believed to be the result of degradation of the compound because carbon microwave absorbance is high. There is, however, an increase in gel content with chlorinated paraffin from level 2 to level 3. Increasing the dipolar polarization of compound, by increasing chlorinated paraffin, could be an explanation for more absorbance and gel content. The increase in peroxide content had dual role in more energy absorbance because of dipolar nature of peroxide itself and the presence of more initiator in cross-linking.

Table 4 shows the sorting levels of each factor. Table 5 shows level of each factor corresponding to maximum level of gel content. Experiments with these levels results in the gel content of 91.11 which is higher than the tested values. Based on the understanding of the process this value is logical and expectable.

Taguchi suggested a criterion named signal to

Table 5. Optimum levels on the basis of mean response.

Importance	Factor	Optimum level	Gel content
1	C	3	68.33
2	Pa	3	62.33
3	Pr	3	60.67
4	t	2	53.33

Table 6. Response for signal to noise ratios.

Level	Pr	Pa	C	t
1	9.65	8.90	6.67	10.85
2	31.82	31.60	32.80	34.05
3	34.58	35.56	36.59	31.16
Delta	24.93	26.66	29.92	23.20
Rank	3	2	1	4

noise (S/N) to study the effectiveness of each factor. Merits of this criterion are when considering the variance, mean, and closeness to target at the same time. In the cross-linking of polyethylene, one of the main objectives is maximum gel content. Hence, "larger is better" case was selected:

$$\text{Large-the-better } S/N = -10 \log \left[\frac{1}{n} \sum_{i=1}^n \frac{1}{y_i^2} \right] \quad (2)$$

Table 6 gives signal to noise ratio for various levels and Figure 3 shows the main effects versus the S/N ration. Results of Figure 2 and Table 4 are in agreement with those of Figure 3 and Table 6. Table 7 shows the sorting of "signal to noise" parameters. It is seen that the main effect of parameters result and the "signal to noise" result are the same.

Analysis of variance (ANOVA) was performed to study the meaning of parameters. Table 8 gives the result of ANOVA using ($\alpha = 0.05$). P-value column in Table 8 proves that all parameters are significant. Comparison of F-value with Adj MS reveals that carbon has the highest effect, followed by chlorinated paraffin, peroxide, and irradiation time having more effects, respectively.

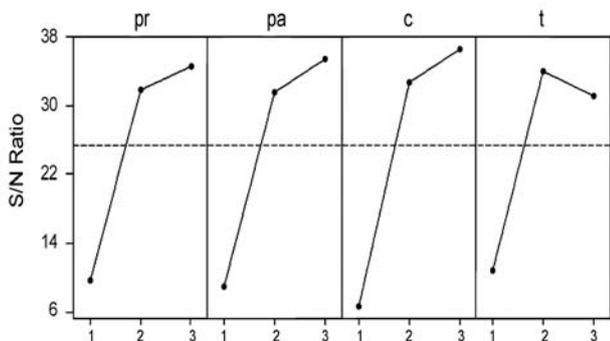


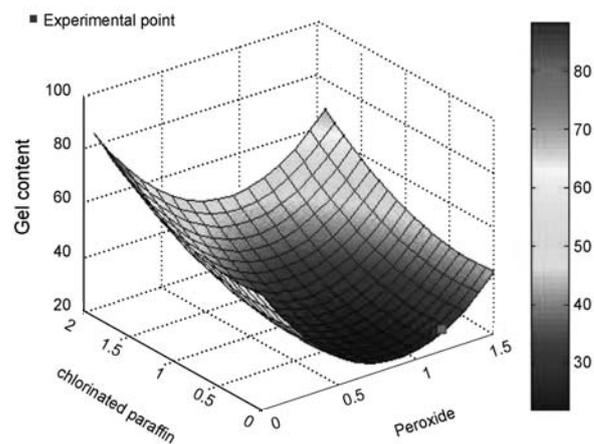
Figure 3. Main effects plot for S/N ratio.

Table 7. Optimum levels for signal to noise response.

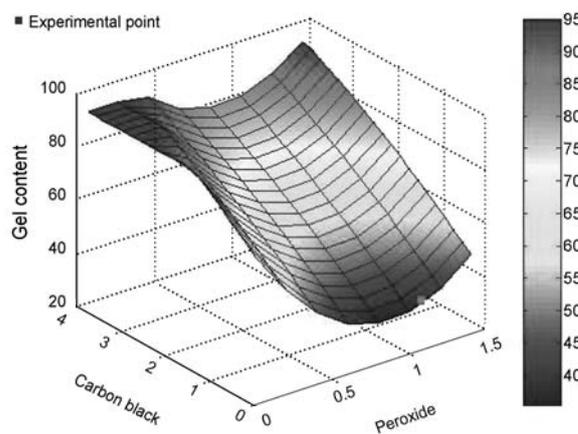
Importance	Factor	Suggested level based on the S/N	S/N value
1	C	3	36.59
2	Pa	3	35.56
3	Pr	3	34.58
4	t	2	31.16

A second order relationship was fitted on the data. The following equation presents this model:

$$\begin{aligned} (\%)Gel = & 8.3468 - 92.1570 Pr - 4.6932 Pa \\ & + 15.1986C + 16.9333t + 52.9295 Pr^2 \\ & + 9.5908Pa^2 - 0.8054C^2 - 1.7600t^2 \end{aligned} \quad (3)$$



(Response surface for $t=7.5$ and $C=1.93$)



(Response surface for $t=5$ and $Pa=1.92$)

Figure 4. The effects of factors on the gel content on the basis of second order relationship.

Table 8. Analysis of variance for gel content using adjusted SS for Tests.

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Pr	2	1569.0	1569.0	784.5	142.64	0.000
Pa	2	2396.3	2396.3	1198.2	217.85	0.000
C	2	6337.3	6337.3	3168.7	576.12	0.000
T	2	624.3	624.3	312.2	56.76	0.000
Error	9	49.5	49.5	5.5	-	-
Total	17	10976.5	-	-	-	-

The regression coefficient is $R^2 = 0.99998$ and the error is 2.147×10^{-22} . Figure 4 shows plot of modeled gel content versus two factors in three-dimensional space in order to give better understanding. When the model was converted to the coded factors, by defining suitable variable variation, each factor is changing in $[-1, 0, 1]$ range. The coded model is:

$$\begin{aligned} (\%)Gel = & 46.0751 + 12.0340Pr + 13.3488Pa \\ & + 23.3333C - 1.6667t \end{aligned} \quad (4)$$

the bigger the coefficient of each factor, the larger effect has on the gel content. Hence, the effect of factors can be sorted as follows:

$$C > Pa > Pr > t \quad (5)$$

By partial fractioning with respect to each factor, unconstrained minimization procedure of eqn (3) would give maximum gel content of 80.1. However, the higher gel content has been tested. In this regard, the constrained minimization method, using Levenberg-Marquardt procedure gives gel content equals to 94.5. This gel content value corresponds to carbon, chlorinated paraffin, and peroxide level 3 and time level 2.

CONCLUSION

The cross-linking of polyethylene by microwave radiation was studied. It is vital to use microwave absorbant materials such as carbon and chlorinated paraffin. Carbon, chlorinated paraffin, and peroxide

contents as well as irradiation time were used as the main factors which affect cross-linking parameters. The gel content was measured as the response variable. L_9 Orthogonal array method was used to design the consequence of experiments. Up to the point of experiment completion, main factors were sorted as carbon, chlorinated paraffin, peroxide, and time based on their effect on response variable. A second order model was fitted on the data with good fitness. This model was used to determine the optimum processing point by using the constrained Levenberg-Marquardt procedure.

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APPENDIX

Levenberg-Marquardt Method

In optimization problems it is normally desired to find vector x in such a way that minimizes function $f(x)$ [29]:

$$\text{Find: } x^* = [x_1^* \ x_2^* \ \dots \ x_n^*]$$

that minimize $f(x_1 \ x_2 \ \dots \ x_n) \equiv f(x)$

To do so, the function is approximated by Taylor series expansion:

$$f(x) = f(x^*) + \nabla^T f(x^*) \Delta x + 1/2 (\Delta x^T) \nabla^2 f(x^*) \Delta x + O_3(\Delta x) + \dots, \quad (A-2)$$

$$\text{where } \Delta x = x - x^* \quad (A-1)$$

Newton used Hessian matrix, $H(x^*)$ of $f(x)$, instead of $\nabla^2 f(x^*)$ is interpreted as being orthogonal to a linear approximation of the objective function. Hence, general form of recursive formula is:

$$x^{k+1} - x^k = -\alpha^k [H(x^k)]^{-1} \nabla f(x^k) \quad (A-3)$$

The Levenberg-Marquardt method is the one way for the correction of the negative-definite Hessian matrix. They have suggested to use the following modified $\tilde{H}(x^*)$:

$$\tilde{H}(x) = H(x) + \beta I \quad (A-4)$$

where β is a positive constant large enough to make $H(x)$ positive-definite.

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