

CHAPTER VI
THE EFFECTS OF PROCESSING PARAMETERS ON RHEOLOGICAL
PROPERTIES OF LOW-DOSE PEROXIDE MODIFIED LLDPE

6.1 Abstract

Peroxides are typically known as a chemical initiating source applied to the reactive processing system. It performed well to alter the molecular characteristics consequently affected to the product properties including rheological one. Other basic processing parameters which were mixing rate and process temperature, however, had to be in account as regarded to the acting on peroxide cooperating efficiency. On the other hands, those showed the combination effect on the mixing results. In this research, the statistical analysis was applied to verify this hypothesis. It was found that the MFI values as a response variable was affected by both qualitative parameter i.e. peroxide addition method and quantitative parameters which were the amount of peroxide, rotor speed, and the combination among them. Moreover, small amplitude dynamic shear rheometer was employed. Complex viscosity, consistency index, and shear thinning characteristics were enhanced with peroxide content. The crossover modulus was shifted to the lower frequency and lower modulus value as an evidence of long-chain branches occurrence.

Keywords: Oscillatory shear rheometer, Reactive Processing, Response surface method, Viscoelastic property

6.2 Introduction

By the industrial and economic reasons, the modification of LLDPE in a single step during the processing, called reactive processing, is in need with further results of structure modification. In general, the reactive processing of PE can be described by the radical modification. Their reactions involve chain scission but turn to dominate cross-linking or grafting for most PE system due to no existence of tertiary backbone radicals and steric hindrance effect (Debbaut *et al.*, 1998; Smedberg *et al.*, 2003). However, to avoid the undesired excess of crosslinking which may cause the defect in the film product, the quantity of peroxide initiator used was kept below the concentration that produces a macroscopic molecular network (Suwanda *et al.*, 1993).

In addition to the type of peroxide, the other processing parameters such as amount of initiator used, process temperature, mixing screw speed affected on the modified product properties as well as its molecular characteristic. In this case, it is possible to correlate linear viscoelastic behavior with molecular characteristic by small amplitude oscillatory shear (Turcsanyi *et al.*, 1993; Ghosh *et al.*, 1997; Liao *et al.*, 2003).

As a screening experiment for continuous reactive process, the process parameters have to be taken into consideration in order to produce the DCP-modified LLDPE with preferred rheological properties (Ramos *et al.*, 2004) Therefore, an experimental design was carried out to evaluate the effect of processing parameters which play an important role to the microstructure modification. Peroxide addition methods (M), amount of initiator used (P), process temperature (C) as well as mixing rotor speed (R) were investigated in this work. Nevertheless, the mentioned processing parameters may have a co-occurrence effect on the microstructure of resulting product; hence two-level factorial designs was introduced to estimate the effect of each parameter or combination of processing parameters on the selected variable, in this case was MFI. In a factorial experiment, effects of a number of different parameters are investigated simultaneously. The runs consist of all possible combinations of the levels from the different parameters or factors. Factorial design is highly efficient because every observation provides information about all the

factors in this experiment. When interactions among the factors exist, a factorial design is necessary to avoid confusing conclusions. When no interactions exist, a factorial design gives the maximum efficiency in the estimation of the main effects of the factors (Box *et al.*, 1978). Therefore, two-level factorial design was applied and response surface method was selected to analyze such design.

6.3 Experimental

6.3.1 Materials

Linear low density polyethylene (LLDPE) used in this work is the commercial available film grade DOWLEX 2045 supported as the pellet form by DOW Chemical Company. Melt flow index (MFI) according to ASTM D1238 shows 1.0 g/10 min with density of 0.920 g/cm^3 and melting Temperature (T_m) as reported by supplier is 122°C .

The Dicumyl peroxide (DCP), obtained from Aldrich, in white flake form with 98% peroxide was used as chemical initiators. It was ground to reduce agglomeration before use. Isopropanol reagent grade was used as solvent and inert carrier for the addition of peroxide into the melt. Xylene with 99% purity was used as solvent to extract the soluble grafting modified products. All chemicals were used without further purification.

6.3.2 Procedure

6.3.2.1 *Statistical Experimental Design*

The effects of temperature (C), peroxide concentration (P), and rotor speed (R) on the MFI value, as a response variable, were analyzed using a 2^3 factorial design with four central points (O). The values of inferior (-1) and superior (+1) levels of codified inputs are presented in Table 6.1. The experiments were randomized and run to a total of twelve runs as shown in Table 6.2. Six observations taken at each particular treatment combination for melt flow index (MFI) evaluation. After the evaluation of the main and the interaction effects, a surface response was built using the significant factors. The peroxide addition method is a qualitative factor; therefore this variable was analyzed separately in term of

modification efficiency according to relatively low melt flow index. Moreover, the response surface method was applied to illustrate other two variables of flow behavior which were consistency and power law index as well.

2³ Factorial Experimental Design

Table 6.1 Two level parameters for 2³ factorial experimental design

Factors			
Level	Process Temperature (°C)	Peroxide Quantity (phr)	Rotor Speed (min⁻¹)
+ 1	200	0.1	70
0	185	0.06	50
- 1	170	0.02	30

Table 6.2 2³ factorial experimental level (variables in coded unit level) with 4 center points

Test	C	P	R	Combination
1	+ 1	+ 1	+ 1	CPR
2	+ 1	+ 1	- 1	CP
3	+ 1	- 1	+ 1	CR
4	+ 1	- 1	- 1	C
5	- 1	+ 1	+ 1	PR
6	- 1	+ 1	- 1	P
7	- 1	- 1	+ 1	R
8	- 1	- 1	- 1	-
O1 – O4	0	0	0	O

6.3.2.2 Preparation of Peroxide-Modified LLDPE

A certain amount of LLDPE pellets were allowed to melt for 2 min, otherwise stated, in a laboratory internal mixer, Haake Rheomex 90, before the initiator was added. Various process temperature and rotor speed was set as shown in Table 6.1. The peroxide quantity was varied as 0.02, 0.06, and 0.1 phr. Moreover, the absence of peroxide was observed as shear modification. To investigate the effect of peroxide adding technique (M), three different form of mixing states were carried out. The first method (Mi) which was the solution form of peroxide addition into molten polymer was prepared by dissolving given amounts of DCP in 2 cm³ of isopropanol (IPA), consequently changed in concentration or ratio of peroxide and solvent. Since the DCP solution is volatile at room temperature and pressure, special care was taken to minimize its loss during adding into molten LLDPE. The second one is the addition of solid peroxide into the molten polymer (Mii) and the last one is the solid peroxide added together with solid polyethylene pellets (Miii). After peroxide adding, the mixing in batch mixer had been further to reach the desired processing time which was 10 min. The sample then was removed from the chamber, placed on stainless steel plate and cooled down by atmospheric ambient air. Grinding into small pieces was the last step for batch reactive processing.

6.3.2.3 Torque Measurement

The viscosity of the materials can be compared relatively via torque measurement throughout the melt processing. Using internal batch mixer programmed with Rheomix 90, the mixing torque was recorded during processing.

6.3.2.4 Characterizations

The modified LLDPEs to be characterized in this chapter were the same materials obtained in chapter V and their melt flow index (MFI) values were used for statistical analysis in this chapter.

Moreover, frequency dependence of small amplitude oscillatory shear moduli in the molten state was done using a plate-plate rheometer, TA Instruments model AR2000. The measurements were performed at 190°C. The diameter and the distance between these two parallel plates were 25 mm and 0.8 mm, respectively. Linear viscoelastic properties such as the complex shear viscosity (η^*),

the storage (G') modulus as well as the loss modulus (G'') were obtained for each sample.

6.4 Results and discussion

Response Surface of MFI

Measured MFI of shear modified LLDPE with various processing conditions were shown in Table 6.3. The higher DCP content incorporated into the single-phase LLDPE reactive processing, the lower MFI values of the modified LLDPE were. The peroxide addition method was the key parameter affecting on the MFI value as concluded in the previous work (Tasanatanachai *et al.*, 2008). The capillary rheometer was employed in order to observe the steady shear flow and to differentiate the effect of other processing parameters within the sample group of same peroxide addition method. However, it was interesting to verify these experimental data and to picture the overall effects.

Table 6.3 Average melt flow index (MFI) of peroxide modified LLDPE

Test	Level Conditions			Averaged MFI (g/10 min)		
	C	P	R	Mi	Mii	Miii
1	+1	+1	+1	0.0261	0.0433	0.0192
2	+1	+1	-1	0.0312	0.0692	0.0204
3	+1	-1	+1	0.1352	0.1885	0.0349
4	+1	-1	-1	0.2126	0.3585	0.1296
5	-1	+1	+1	0.0258	0.0448	0.0208
6	-1	+1	-1	0.0212	0.0418	0.0152
7	-1	-1	+1	0.0989	0.1190	0.0338
8	-1	-1	-1	0.3590	0.4488	0.2840
9	0	0	0	0.0475	0.059	0.0278
10	0	0	0	0.0529	0.0586	0.0287
11	0	0	0	0.0477	0.0600	0.0274
12	0	0	0	0.0503	0.0594	0.0293

The estimated effects of those parameters on the response variable, MFI, were determined statistically and the results were shown in the Table 6.4. In this case, the peroxide addition method was designed as a qualitative variable which use

as the blocks to estimate the effect of quantitative factors. The most significant parameter obtained statistically was amount of peroxide added to the reactive processing system. Mixing rotor speed and the combination effect of peroxide quantity and rotor speed were the second and third significant parameters, respectively. However, the analysis of variance, Table 6.5, implied that the peroxide addition method (parameter M) play a significant role on the MFI value as well.

Table 6.4 Estimated effect percentage of variables on the MFI values

Variable	Regression Coefficient	Averaged Effect	Contrast	Sum of Square (SS)	%
C	-0.0103	-0.0204	-0.2444	0.0025	0.79
P	-0.0843	-0.1687	-2.0238	0.1707	54.20
R	-0.0501	-0.1001	-1.2012	0.0601	19.09
CP	0.0135	0.0270	0.324	0.0044	1.39
CR	0.0189	0.0377	0.4526	0.0085	2.71
PR	0.0485	0.0969	1.1632	0.0564	17.91
CPR	-0.0226	-0.0453	-0.5434	0.0123	3.91

Table 6.5 Analysis of variance for MFI prediction

Source of Variation	Averaged Effect	SS	DF	MS	F ₀	P-Value
M		0.0790	2	0.0394	24.03	0.0000
C	-0.0204	0.0008	1	0.0008	0.47	0.5044
P	-0.1687	0.3683	1	0.3683	224.71	0.0000
R	-0.1001	0.0841	1	0.0841	51.33	0.0000
CP	0.0270	0.0048	1	0.0048	2.90	0.1108
CR	0.0377	0.0070	1	0.0070	4.27	0.0577
PR	0.0969	0.0769	1	0.0769	46.93	0.0000
CPR	-0.0453	0.0173	1	0.0173	10.58	0.0058
Error		0.0230	14	0.0016		
Total		0.6610	23			

The response surface method was then applied to picture the response of these important quantitative processing factors. Linear regression analysis was done, according to analysis of variance, in order to obtain the model shown below:

$$\text{MFI} = \beta_0 + \beta_1\text{P} + \beta_2\text{R} + \beta_3\text{PR}$$

where: β = the regression coefficients

The regression coefficients for the MFI response surface models of the modified LLDPE with various peroxide addition method was shown in Table 6.6. This model performed the best fit to the measured data of all methods although R^2 for Miii was much deviated from “one” meaning that there was divergence between predicted MFI value and the measured ones.

Table 6.6 Regression coefficients for the response surface models of the MFI

Variable	Experimental Set					
	Method i		Method ii		Method iii	
	Parameter	95% Confidence Interval	Parameter	99% Confidence Interval	Parameter	95% Confidence Interval
Mean (β_0)	0.5017	± 0.0575	0.7112	± 0.0603	0.4116	± 0.0541
P	-4.8247	± 0.7987	-6.5873	± 0.8388	-3.9998	± 0.7525
R	-0.0053	± 0.0011	-0.0077	± 0.0011	-0.0054	± 0.0010
PR	0.0527	± 0.0148	0.0745	± 0.0156	0.0546	± 0.0140
SSE	0.0151		0.0166		0.0134	
R²	0.8564		0.9096		0.7902	

As insignificant coefficient, the regression model for the MFI shows that mixing temperature has less effect on MFI than amount of peroxide and mixing speed. The response surface of predicted MFI of LLDPE modified with the third method of DCP addition was shown in Figure 6.1. This plot pictured that high shear rate applied to the system of high peroxide content resulted in getting lower of MFI value corresponding to the molecular structure that greatly resisted to flow; i.e. branching or side chain entanglements.

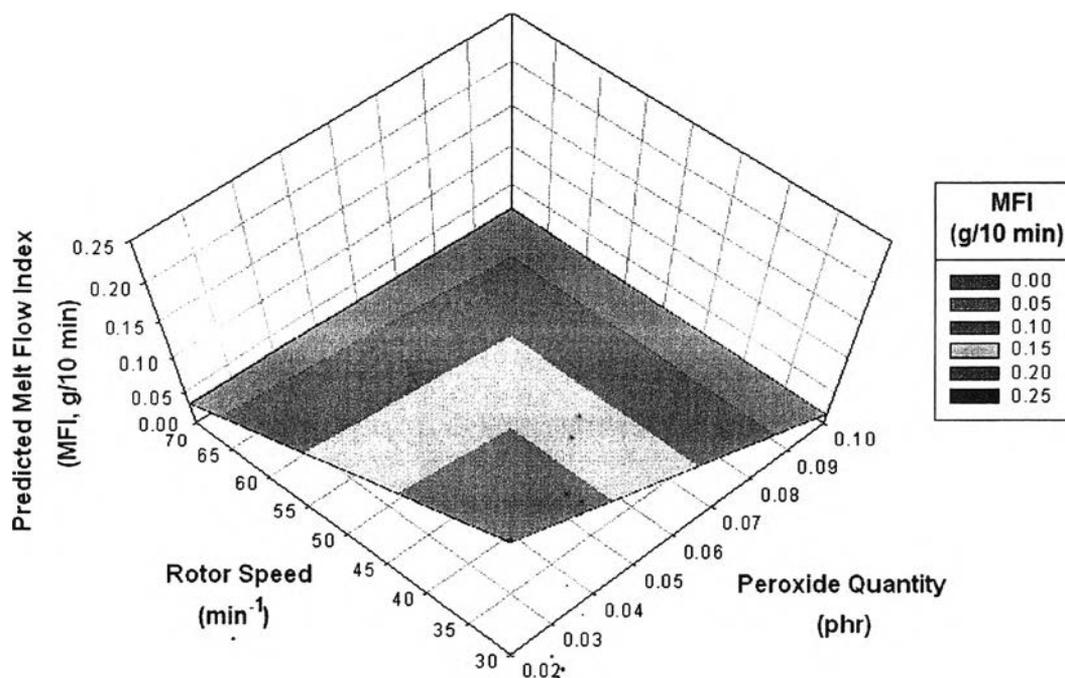


Figure 6.1. Response surface for the melt flow index (MFI): for Miii.

Response Surface of K and n

The characteristic flow of melts was estimated according to the relationship between the shear stress and shear rate. The dependence of shear stress as a function of shear rate could be described by the empirical power equation as $\tau = K\dot{\gamma}^n$ where n and K were constants. By substituting $\eta = \tau/\dot{\gamma}$ then another equation was derived as $\eta = K\dot{\gamma}^{n-1}$. Thus, the constant K was a measure of consistency and n was the flow behavior index or power law index (Dealy *et al.*, 1990). K and n values of peroxide modified LLDPE using Miii of peroxide addition method were shown in Table 6.7.

Table 6.7 Consistency index (K) and power law index (n) Values for Miii

Test	Level Conditions			Characteristics	
	C	P	R	K	n
1	+1	+1	+1	49767	0.28
2	+1	+1	-1	43185	0.30
3	+1	-1	+1	33089	0.34
4	+1	-1	-1	24389	0.38
5	-1	+1	+1	46984	0.29
6	-1	+1	-1	41396	0.33
7	-1	-1	+1	31059	0.35
8	-1	-1	-1	19006	0.44
9	0	0	0	41261	0.32
10	0	0	0	41880	0.32
11	0	0	0	41613	0.32
12	0	0	0	41227	0.32

The models for response surface fitting of variable K and variable n were shown below.

$$K = \beta_0 + \beta_1 P + \beta_2 R + \beta_3 PR + \beta_4 CPR$$

$$n = \beta_0 + \beta_1 C + \beta_2 P + \beta_3 R$$

where: β = the regression coefficients

The regression coefficients for the K response surface model of the modified LLDPE with the third method of peroxide addition (Miii) was shown in Table 6.8 and the response surface of predicted K of LLDPE modified at 200°C was shown in Figure 6.2. It was found that all processing parameters including peroxide content (P), rotor speed (R), and processing temperature (C) affected on the consistency index. However, the most significant factor was the concentration of peroxide added into the system. The combination effects of peroxide content and rotor speed ranked the second while that of processing temperature, peroxide content, and rotor speed was less significant parameter. Numerically, the consistency index was equal to the viscosity under normalized condition where $\dot{\gamma} = 1 \text{ s}^{-1}$. Hence, the incorporation of

high DCP content under high shear rate would provide the molecular structure with high resistance to flow as shown and discussed in previous chapter.

Table 6.8 Regression coefficients for the response surface models of the consistency index (K)

Variable	Experimental Set	
	Method iii	
	Parameter	95% Confidence Interval
Mean (β_0)	8616	+ 3504
P	297645	+ 48714
R	286	+ 65
PR	-4502	+ 2470
CPR	17	+ 12

SSE	4.49E + 07
R ²	0.9489

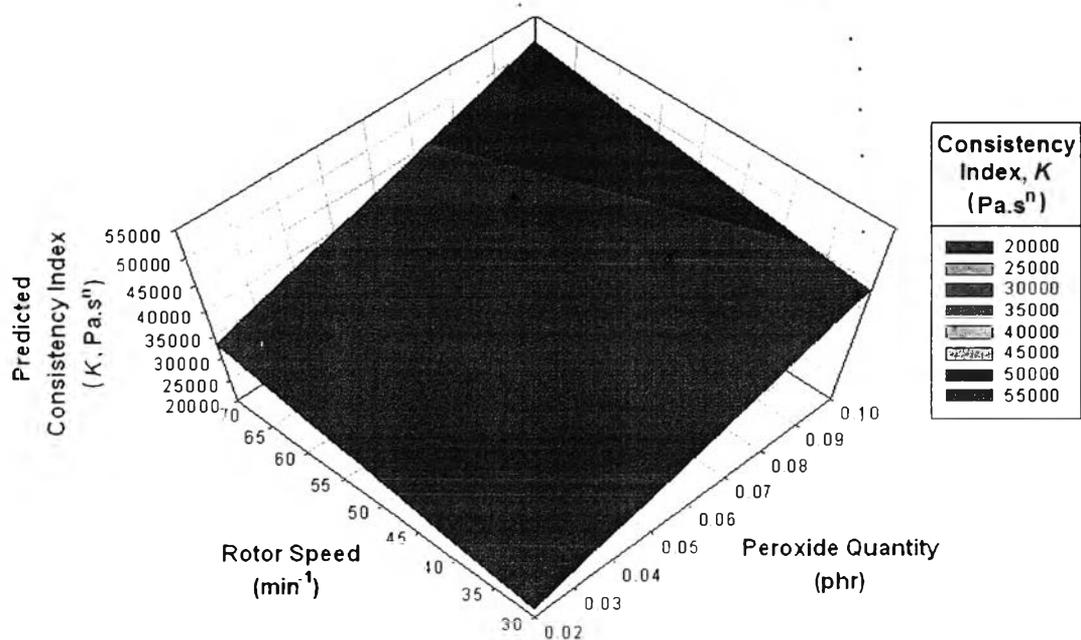


Figure 6.2 Response surface for the consistency index (K) at processing temperature of 200°C.

For power law index (n) response surface model, the regression coefficients, shown in Table 6.9, would predict the surface response of n of LLDPE modified with Miii at 200°C as shown in Figure 6.3. As expected, peroxide content

played the most important role on shear thinning behavior as reflected by decrease in power law index (Bocok *et al.*, 2005). Both processing temperature and rotor speed were not inconsiderable as well. Using a high amount of peroxide with high rotor speed, the molecular structure was altered much since the n value was dramatically deviated from Newtonian fluid ($n = 1$).

Table 6.9 Regression coefficients for the response surface models of the power law index (n)

Variable	Experimental Set	
	Method iii	
	Parameter	95% Confidence Interval
Mean (β_0)	0.5886	± 0.0519
C	-0.0008	± 0.0003
P	-0.9338	± 0.1021
R	-0.0011	± 0.0002
SSE	0.0018	
R ²	0.8988	

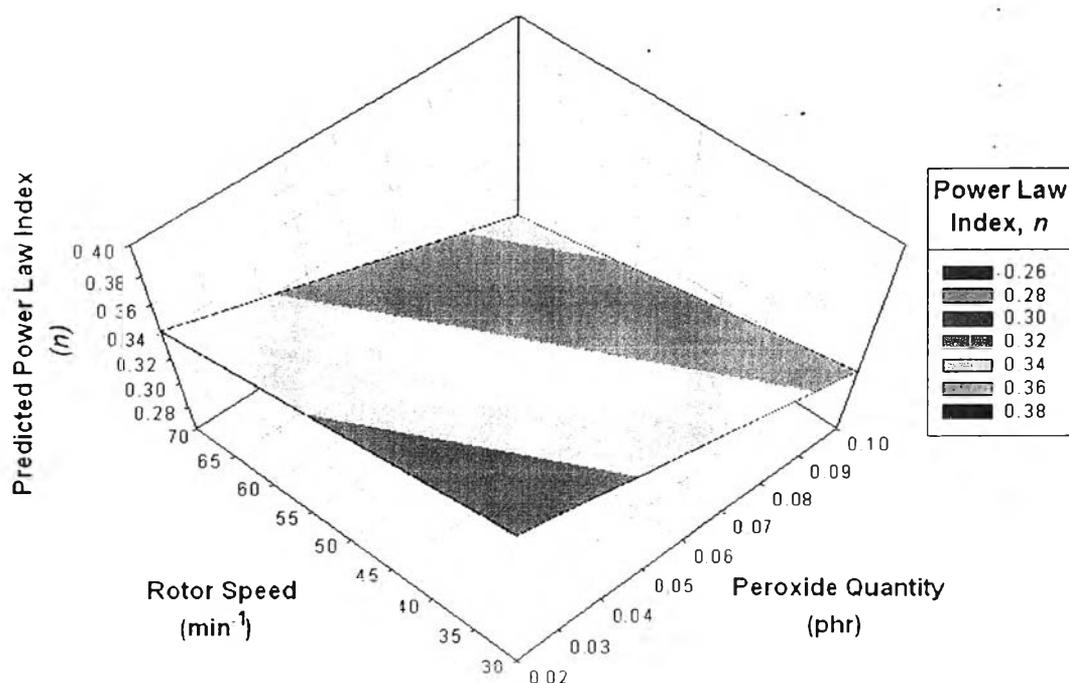


Figure 6.3 Response surface for the power law index (n) at processing temperature of 200°C.

The resistance to flow or viscosity of the melt during mixing was indirectly implied by the mixing torque. The final torque of the melt was shown in Figure 6.4. It was observed that the final torque of LLDPE modified with Miii were more resist to flow than that of LLDPE modified with Mi and Mii. This result confirmed the MFI measurement. The predicted final mixing torque can be applied and the response surface can be obtained using the linear regression analysis as well, however, being different in the regression coefficients.

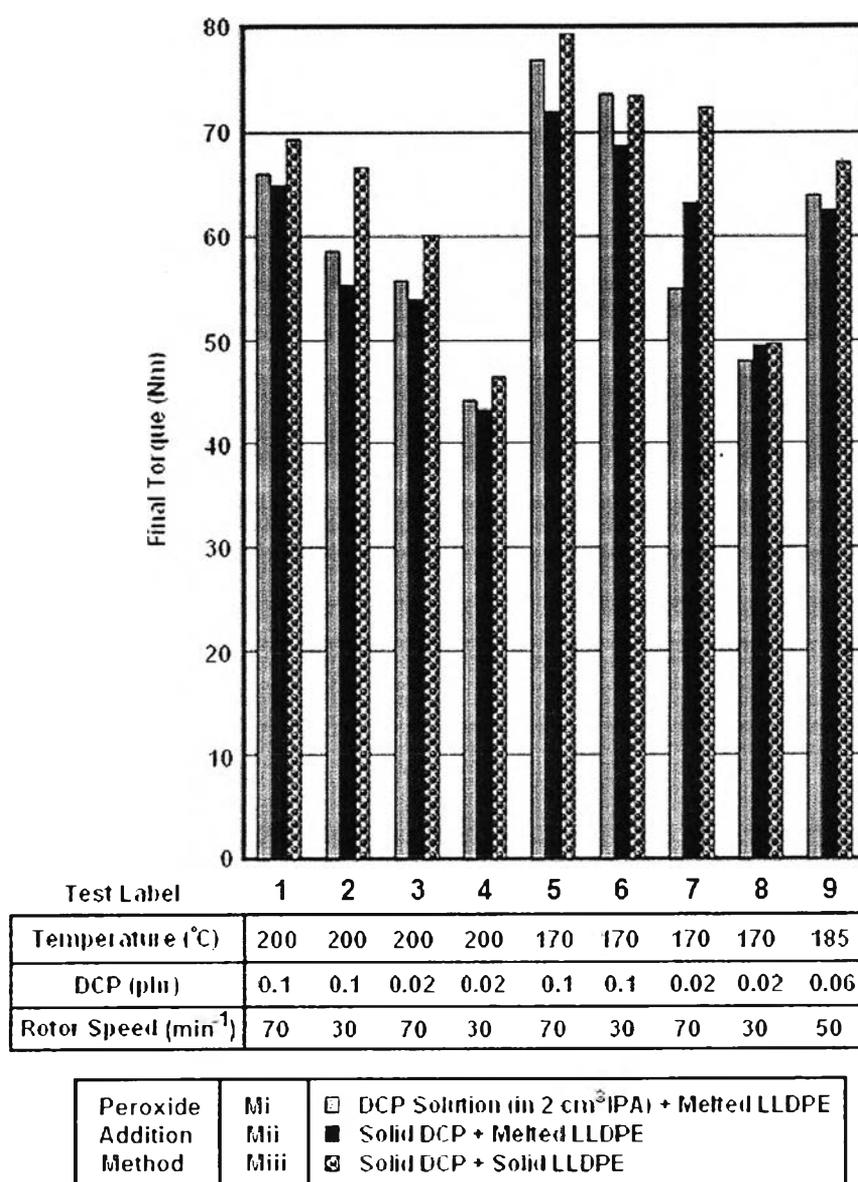


Figure 6.4 Final torque of batch mixing of DCP modified LLDPE: comparison in the addition method of peroxide.

Since there was no gel content in all modified samples, the rheological properties relating to the molecular build-up characteristic was then investigated. According to the viscoelastic property of polymer, a parallel plate oscillatory rheometer was employed in order to investigate the effect of branch resulting from the reactive processing.

According to the Cox-Mez rule, the curve of shear viscosity as a function of shear rate is often identical to the curves of complex viscosity versus frequency (Rohn, 1995). Dependence of complex shear viscosity on frequency of LLDPE modified with low/high amount of peroxide and/or with low/high mixing shear rate was shown in Figure 6.5.

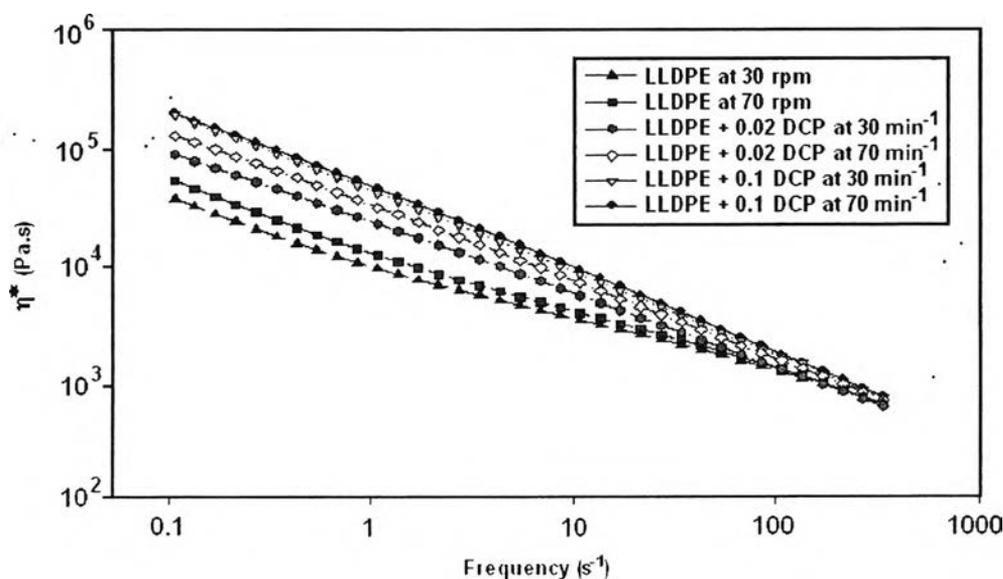


Figure 6.5 Complex shear viscosity of LLDPE modified by shearing force with and without DCP loaded.

At low frequency, the complex shear viscosity among them was obviously noticed. Low shear modification (without peroxide addition) provided the lowest viscosity, and the value increased when using high mixing rate. When the DCP was incorporated with high shear, the viscosity was greater than with the low one. It implied to the branching occurrence since the more presence of LCB, the higher complex viscosity. However, at high DCP content, the effect of mixing shear rate

was insignificant. The same manner was also found for storage modulus, as shown in Figure 6.6.

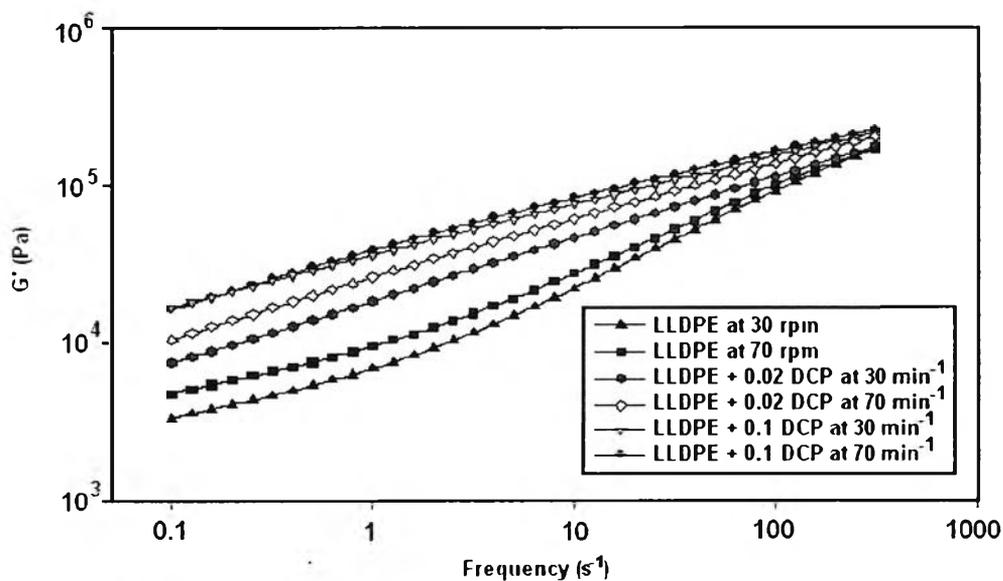


Figure 6.6 Storage modulus of LLDPE modified by shearing force with and without DCP loaded.

Figure 6.7 are the plots of G' , G'' of a raw resin, LLDPE, used in this research and those of 0.1 phr of DCP modified LLDPE at 70°C with 70 min^{-1} rotor speed. It was obviously seen that G'' of raw resin was higher than its G' at low frequency which was the characteristic of linear chain polymer, Figure 6.7 (A). When the long chain branches were present the crossover modulus was then shifted to lower frequency and lower modulus value as observed in Figure 6.7 (B).

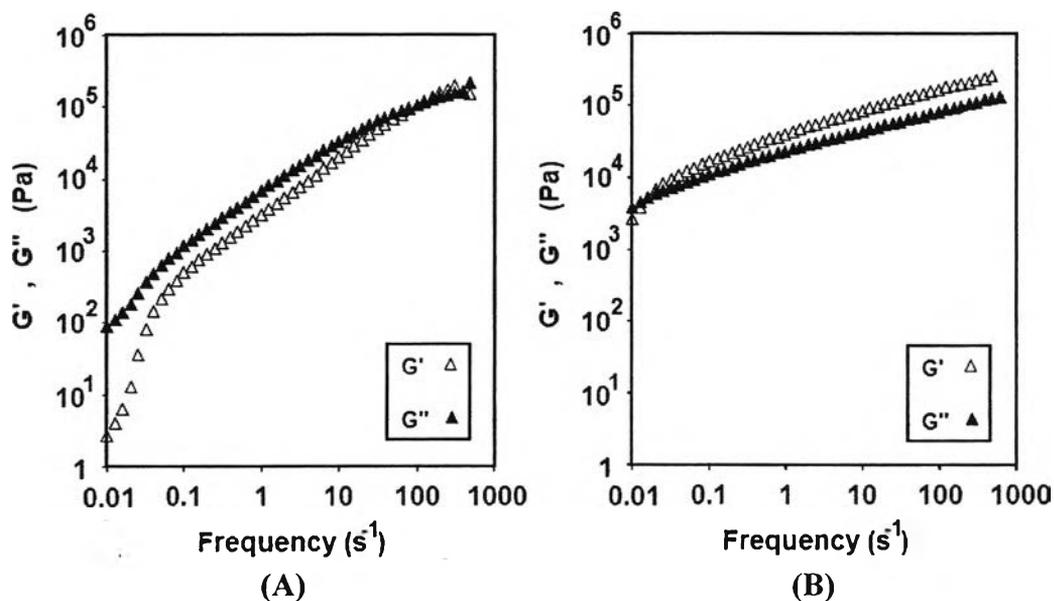


Figure 6.7 Crossover modulus of (A) based LLDPE without modification and (B) LLDPE modified with 0.1 phr DCP using 70 min⁻¹ at 70°C

Although it was quite difficult to separate the effects of molar mass, molar mass distribution, and LCB, these results implied that the reactive processing via lose-dose DCP could provide some side chain and/or broaden MWD as well.

6.5 Conclusions

As shear thinning behavior, getting higher shear viscosity as well as lower crossover modulus were influenced either by the presence of long-chain branches or by molecular mass distribution, it could directly imply that those was affected by reactive processing. The peroxide concentration (P) as well as peroxide addition method (M) were significantly factors as referred to the efficiency of peroxide cooperation in the reaction. The fitted model of measured MFI, K , and n values also supported this speculation as it showed that mixing rotor speed significantly influenced the MFI values as well as their combinations.

6.6 Acknowledgements

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6.7 References

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