CHAPTER V

RHEOLOGICAL MODIFICATION OF LLDPE THROUGH REACTIVE PROCESSING WITH PEROXIDE

5.1 Abstract

The presence of long-chain branches provides the advantageous properties to a molten polymer in the film production, especially for a fast growing commodity plastic such as polyethylene. Besides the innovation of polymerization, the most attractive method to tailor the molecular structure is peroxide modification via reactive processing which is the post-reactor technique. By this process, it can achieve the enhancement of ability of the melt to be drawn or stretched during the film processing due to branching occurrence. However, to avoid the undesired excess of macroscopic molecular network which may cause the defect in the film product, the small quantity of peroxide initiator was used to modify base resin. The rheological properties as related to molecular characteristic were investigated by capillary rheometer. Rheological analysis of the products modified by different peroxide addition methods was concerned as changing in rheological properties depends markedly on the efficiency of incorporating and mixing the peroxide into the polymer. The process parameters including mixing temperature, peroxide quantity, and mixing speed which appear to be responsible for the molecular characteristic alteration were considered in order to produce materials with preferred rheological properties.

Keywords: Capillary rheometer, Extrudate swell, LLDPE, Reactive processing, Rheology

5.2 Introduction

In addition to the development of polymerization process, the molecular structure of a commodity plastic such as polyolefins can be tailored by post-reactor modification. Main purpose of the post-reactor modification is to optimize the ease in plastic processing, to enhance polarity, and to satisfy specific applications. The economic reason is also in account. One-step reactive processing was introduced as a method for this purpose and it has grown in the attention (Graebling *et al.*, 2002). As it has been named, the reactive processing allows specific reactions to occur during the polymer processing. Many researches have emphasized on adding the coupling agents or reactive components e.g. peroxides to the molten polymers. Polypropylene tends to have chain scission upon reactive processing (Tzoganakis *et al*, 1989; Graebling *et al.*, 1997). On the other hand, the chain extension (not chain degradation) is predominantly found for polyethylene due to the lack of tertiary carbon backbone (Lachtermacher *et al.*, 1995a, 1995b, 1996b; Bremner *et al*, 1992; Kang *et al.*, 2000; Sajkiewicz *et al.*, 1995; Khonakdar *et al*, 2003). The chain extension results from the coupling of macroradicals that are generated on the polymer backbone after peroxide attack. Their combinations lead to more complex chain structure, e.g. branching and longer molecules that obviously influence flow property. However, different applications require different degree of chain combination that finally affects on the end-use product. The level of chain combination, branching or crosslinking; by which the modified-polyethylene product undergoes, depends mainly on the peroxide concentration used (Zhou *et al.*, 1998; Hernandez *et al*, 2000).

Besides the peroxides and other coupling agents, the processing parameters have their influences on the modification of the existing polymers. The reactive processing parameters are mainly process temperatures and mixing speed or the applied shear rate. Many reactive processing works had selected the rheological test to investigate and/or confirm the modification to the chain structure e.g. the increase in viscosity caused by slight cross-linking or grafting structure. It was found that both shear and elongational viscosity increased with the quantity of peroxide initiator. Additionally, shear thinning behaviour became more evident upon reactive processing (Lem *et al.*, 1982; Polance *et al.*, 1995).

In the plastic film manufacturing, long chain branching or slight crosslink structure is more preferable than fully crosslink (Hernandez *et al*, 2000). The characteristics of branching structure significantly affect the flow during the film processing thus rheological properties of resin in the melt state is needed to be examined. Nowadays, there are many types of rheometer adapted to monitor the viscoelastic behavior of molten polymer (Lachtermacher *et al.*, 1996a). One of the best ways to determine the flow behaviour of polymer materials is by capillary rheometer which is capable of reaching the temperatures and shear rates typically used for a wide range of processing equipment (Dealy *et al.*, 1993). The main principle of this instrument is the measurement of the pressure required to extrude materials through a small cylindrical tube at known flow rates. Assuming that no-slip at the wall, fully developed flow with zero radial velocity, incompressible fluid of polymer, and steady isothermal flow, the flow profile is simplified for the analysis of flow testing in capillary rheometer.

In the present work, the Dicumyl peroxide (DCP) which is the most common functional di-tertiary alkyl peroxide was selected as an initiator to modify linear low-density polyethylene via reactive processing because the free radicals generated from dicumyl peroxide decomposition are efficient for modification of polyolefins (Dluzneski *et al.*, 2001). Since the rheological properties may depend on the efficiency of incorporating and mixing the peroxide into the polymer, the different methods of peroxide feeding as well as peroxide content and processing parameters are major concerned in this research. The three different methods of peroxide addition are solution feeding into molten polymer (Mi), direct solid feeding into molten polymer (Mii), and mixed solid blending (Miii). The modified polymer was characterized in term of rheological analysis using capillary rheometer.

5.3 Experimental

5.3.1 Materials

The pellet resin used in this work was commercial film grade of linear low-density polyethylene (LLDPE), DOWLEX 2045. It was supplied by DOW Chemical Company. Melt flow index (MFI) as provided from the manufacturer according to ASTM D1238 is 1.0 g/10 min, the density is 0.920 g/cm^3 and T_m is 124°C. The Bis (α,α-dimethylbenzyl) peroxide or dicumyl peroxide (DCP) as white flake form with 98% peroxide was supplied by Aldrich. The ten hour half life temperature is 114°C. For good dispersion and distribution, it was smash ground before use as initiator. Reagent grade of Isopropanol (IPA) was used as inert carrier to prepare DCP solution before adding into the melt LLDPE according to the first peroxide feeding method (Mi). Xylene with 99% purity was used as solvent for Soxhlet extraction to remove the soluble phase out of the modified products. All chemicals were used without further purification.

5.3.2 Preparation of Peroxide-Modified LLDPE

Melt processing was performed in a 200 cm^3 chamber volume of laboratory internal mixer, Haake Rheomex 90. Since this article emphasized on the method of chemical initiator addition technique, the qualitative variables were then set as low and high levels. The reaction temperatures were varied as 170 and 200°C. The rotor speeds were set as 30 and 70 min^{-1}. DCP quantity was varied as 0.02 and 0.1 phr. In addition, the simple shear of LLDPE (without peroxide) in the internal mixer was also performed as a controlled sample. To investigate the effect of peroxide adding technique, stated in this work as parameter M, three different forms of mixing states were carried out. The first method (Mi) which was the solution form of peroxide added into molten polymer was prepared by dissolving given amounts of DCP in 2 cm^3 of IPA. The small drop of DCP-IPA solution was then added frequently within 1 min into the molten LLDPE. This method was designed since the liquid phase peroxide was believed to simply penetrate into the melts and provided the best mixing efficiency results. Because the solution is volatile at ambient condition, special care was taken to minimize its loss during adding into molten

LLDPE. The second one was the addition of solid peroxide into the molten polymer (Mii) as supported the hypothesis of its readiness to react with the melt. The last one was the solid peroxide added and heated together with solid LLDPE pellets (Miii). This method was set as simulated to the practical feeding into the hopper of continuous melt processing, without side feeder of screw extruder. After peroxide was fed, the reaction had been further continued. When reached 10 min of mixing time, the sample was then removed from the chamber, placed on stainless steel plate and cooled down by atmospheric ambient air. To prepare the sample appropriate for further tested by MFI tester and capillary rheometer, the product was carefully ground into small pieces using the Willey mill laboratory grinder.

5.3.3 Characterizations

5.3.3.1 Melt Flow Index Measurement

Melt flow index (MFI) has been used as a rough estimation of the weight-average molecular weight of a polymer. Normally, the MFI is the only specification of melt consistency that is provided commercially. According to ASTM D1238, a test temperature of 190°C, and a total load of 2.16 kg was used with Kayeness Inc. Galaxy V, model 8052 (MFI test set).

Gel contents were determined by a Soxhlet extraction technique whereby modified LLDPE samples were kept in refluxing xylene for 12 h. The sample holder, thimble, was then dried in a vacuum oven at 110°C. The percentage of the weight remaining, with respect to the initial weight, provided the gel fraction.

5.3.3.2 Rheological Study

Capillary rheometer, Ceast Rheologic 5000, used in this work has a cylinder of 15 mm diameter. All tests were done at 190°C after 2 min of preheating period. A set of capillary dies with the die diameter of 1 mm was selected. The L/D ratios, 0.5/1,5/1, and 20/1, with flat (π/2 angle) entrance were used. To obtain the real rheological data, both Rabinowitch and Bagley corrections were applied. The real shear rate ($\dot{\gamma}_{real}$) is given as in eq.(1) whereas "s" is the slope of log shear stress and log apparent shear rate.

$$\dot{\gamma}_{real} = [(3s + 1) / 4s]\, \dot{\gamma}_{apparent} \qquad (1)$$

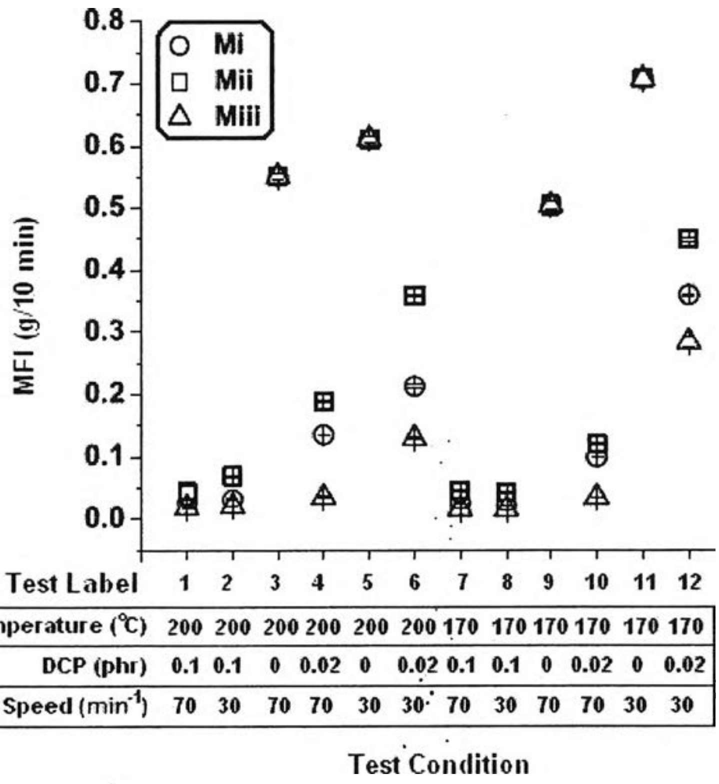
5.3.3.3 Extrudate Swell Measurement

The diameter of each fully swollen extrudate was captured and recorded by the laser equipment consisting of laser ray transmitter and receiver nearby the die exit of the capillary rheometer. The percentage of change in extrudate swell was then measured as percentage of the difference between both extrudate and die diameters divided by die diameter.

5.4 Results and Discussion

Typically, the homolytic cleavage of DCP at elevated temperatures provides free radicals that react to abstract hydrogen from polyethylene chains to form macroradicals. The radicals were then terminated by combination which can result as grafting to make more branches, chain extending to make longer molecules, or crosslinking to make the network or gel.. Increase in branch units or molecular size results in more entanglement and high viscosity. It should be noted, in this work, that no gel fraction was observed from all samples because there is no residue or insoluble phase obtained after Soxhlet extraction. This result was for the extrudate coming out of capillary rheometer after the rheological analysis as well. Therefore, the selected peroxide concentrations and processing conditions were proper to avoid crosslinking or the formation of network structure.

MFI measurement was performed for all samples made from different feeding and mixing conditions. The results are shown in Figure 5.1. It was found that MFI of pure LLDPE was dropped from 0.75 g/10 min which was the value of based LLDPE to the range of 0.5 - 0.7 g/10 min due to shear modified melt structure. When peroxide was incorporated, as expected, the MFI reduced further and got lower as peroxide amount increased. Only DCP of 0.1 phr can reduce MFI to below 0.03 g/10min. Since there was no gel formation, the reduced MFI is due to the highly entanglement caused by increased branching and molecular weight or molecular weight distribution.



Test Label	1	2	3	4	5	6	7	8	9	10	11	12
Temperature (℃)	200	200	200	200	200	200	170	170	170	170	170	170
DCP (phr)	0.1	0.1	0	0.02	0	0.02	0.1	0.1	0	0.02	0	0.02
Rotor Speed (min^{-1})	70	30	70	70	30	30	70	30	70	70	30	30

Figure 5.1 MFI performed at 190°C using 2.16 kg according to ASTM D1238.

Moreover, when compared among peroxide addition methods (parameter M), all samples of Miii provided the highest drop of MFI followed by Mi. The smallest decrease in MFI occurred with Mii. This recommends that, besides the commonly concerned reactive processing parameters, the method of peroxide addition (M) is another key to alter the macromolecular flow behavior as manifestly observed a bit difference in MFI amongst the same test condition.

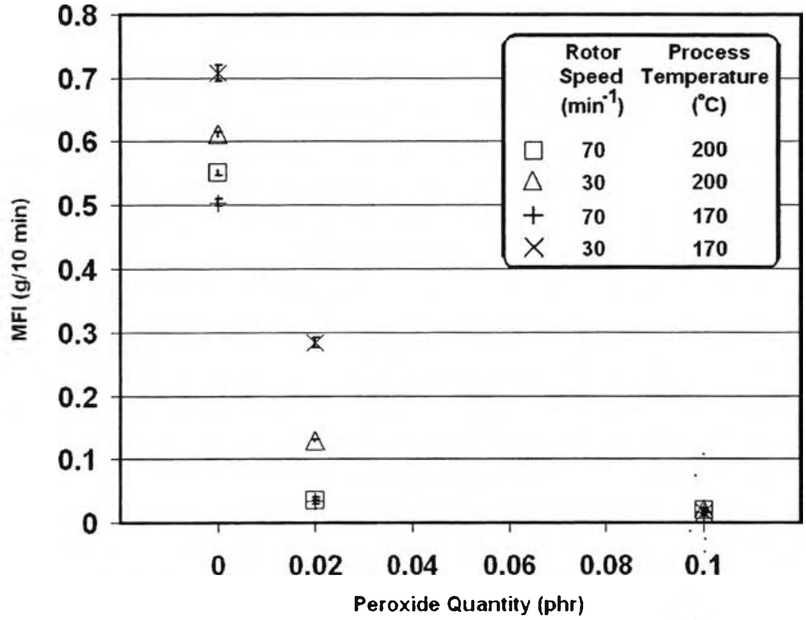


Figure 5.2 Dependence of MFI on peroxide quantity at various process conditions.

In order to examine the influence of considered processing parameters excluding the peroxide addition method on MFI, Figure 5.2 was performed. It shows the dependence of MFI of the LLDPE modified by the third peroxide feeding method (Miii) on peroxide quantity. MFI value which proportionally related to viscosity was depended mainly on peroxide quantity. Increasing mixing temperature and rotor speed also reduced MFI. This implies that the process temperature, amount of peroxide, and mixing rotor speed affected on the flow of the melt. However, at high DCP content, the effect of mixing temperature and rotor speed became insignificant on MFI.

The flow curves of LLDPE modified with 0.1 phr of DCP mixed at 200°C and 70 min^{-1}, Figure 5.3, show the effect of peroxide feeding method. All rheological data plotted in this article were represented via the data given by 20/1 L/D of capillary die using. It should be noted that the melt fracture was observed at shear rate above 500 s^{-1}. Both real shear stress and real shear viscosity of Miii modified LLDPE were the highest following by those of Mi and Mii, respectively. However, a small higher value was observed for Miii and Mi. The results were also relevant to the MFI measurement that the more pressure or stress generated when the melt behaved more resistance to flow.

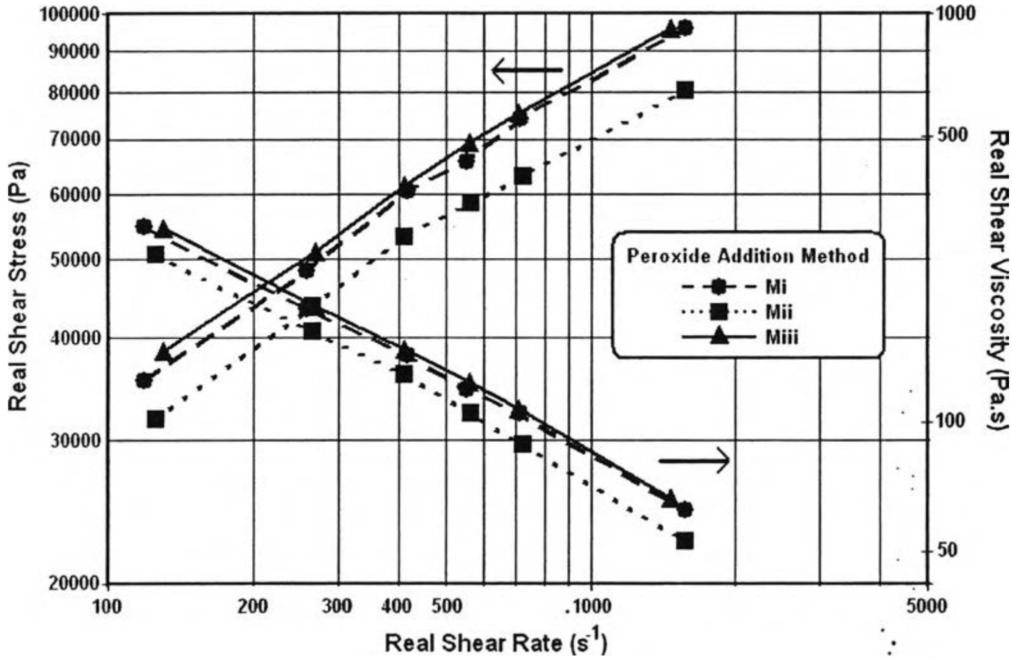


Figure 5.3 Flow curve of LLDPE modified with 0.1 phr DCP processed at 200°C and 70 min^{-1} with various peroxide addition methods.

The process condition that can provide much of the branch or chain combination is preferred as an improvement of the melt strength. This molecular characteristic typically obstructs the flow when it is forced in melt state. Generally, the stress measured from capillary rheometer often records the pressure generated from entrance and exit effects (total pressure drop in the instrument). In addition to real rheological data, the elongational behaviour of the melt is obtained from the data on pressure drop according to Cogswell theory. The elongational viscosity can be used to characterize the molecular feature as it refers to the melt strength property. Figure 5.4 shows the dependence of tensile stress and elongational viscosity on elongational rate of 0.1 phr of DCP modified LLDPE processed at 200°C with 70 min^{-1} of rotor speed. To focus on the method of peroxide incorporation, the plot was presented with different peroxide addition method. Both tensile stress and elongational viscosity for the sample type of the third peroxide adding method (Miii) still lay above those of LLDPE modified by Mi and Mii which ranked the second and the last, respectively. The higher in elongational viscosity can imply to the greater in the ability of polymer melt to be stretched or higher melt strength which strongly related to the more decreasing in MFI. Moreover, the higher melt strength was expected to cause by wider MWD and/or high level of long chain branches. This similar tendency as observed for shear behavior, in Figure 5.3, confirmed that Miii performed the greatest efficiency of peroxide incorporation during the reactive processing in the study range.

The method of peroxide addition that provides most chain combination is Miii which is the method of mixing solid peroxide together with LLDPE pellets that was then melted simultaneously. Since both solids were heated, melted, and mixed together, the well dispersed solid peroxide can decompose in the vicinity of molten LLDPE allowing their reaction to occur readily and most efficiently. The diffusion of the ground peroxide into the molten polymer (Mii) was not easy due to the high viscosity of this grade LLDPE.

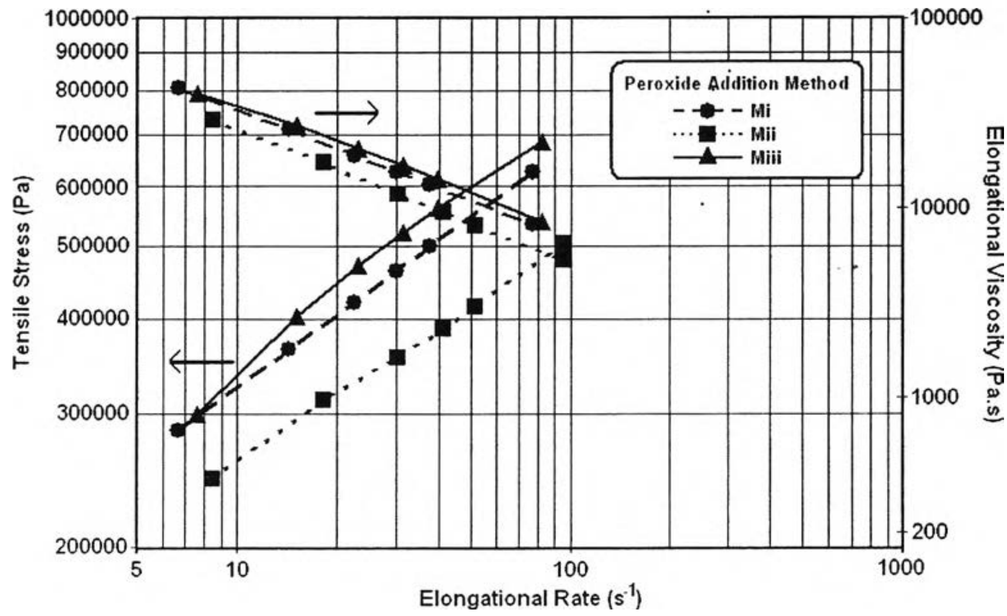


Figure 5.4 Elongational behaviour of LLDPE modified with 0.1 phr DCP processed at 200°C and 70 min^{-1} with various peroxide addition methods.

Lachtermacher and Rudin reported that the peroxide solution performed the best job (Lachtermacher *et al.*, 1996b) which was not similar as our conditions. This may be caused by the volatile loss of peroxide before enter into the melt even special care was taken. Nevertheless, the much finer DCP particles given out after solvent evaporation (for Mi) could be better incorporated and distributed in the molten LLDPE than the ground DCP (Mii). In conclusion, the efficiency of peroxide incorporation according to initiator addition method can be as followed : Miii > Mi > Mii.

In addition to the key parameter of the mixing efficiency which is the method of peroxide addition, the investigation of other parameters is a must as the factors to manipulate the peroxide incorporation in reactive processing. The curve of real shear viscosity and real shear rate performed with the capillary die L/D 20/1 of the Miii samples which were plotted to simplify the analysis of mixing rotor speed effect and of process temperature effect were shown in Figure 5.5 and Figure 5.6, respectively. It was found that the LLDPE modified at 200°C can provide higher shear viscosity than that of one modified at 170°C as observed the higher trend in Figure 5.6.

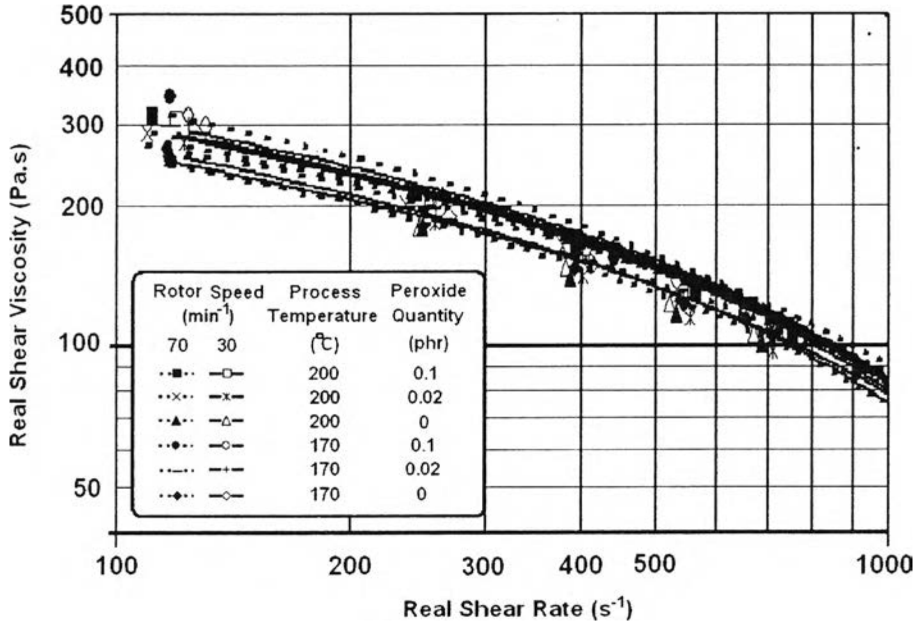


Figure 5.5 Dependence of real shear viscosity on real shear rate: comparison of mixing rotor speed.

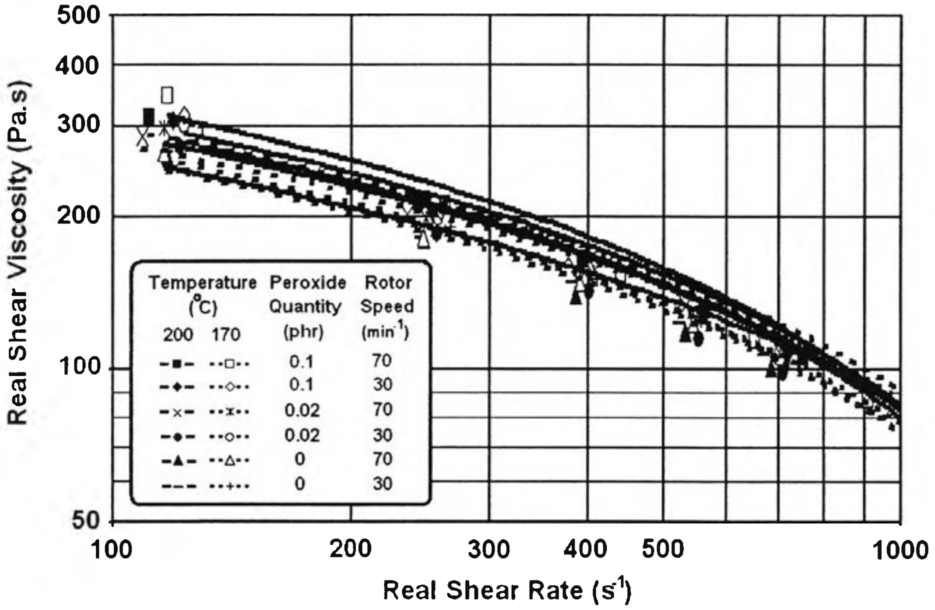


Figure 5.6 Dependence of real shear viscosity on real shear rate: comparison of process temperature.

Another indication of polymer molecular characteristic is extrudate swell. The extrudate coming out of the capillary die exit rapidly increases in cross-sectional area since stress generating *(i)* during the transfer of the melt from the barrel or melt reservoir into the capillary die and *(ii)* shear gradient in capillary. These stresses affect the polymer chain orientations. This phenomenon was normally used for evaluating the elasticity of polymer melt during extrusion and was of great importance in the plastic manufacturing which often desired a resin having prescribed swelling characteristics.

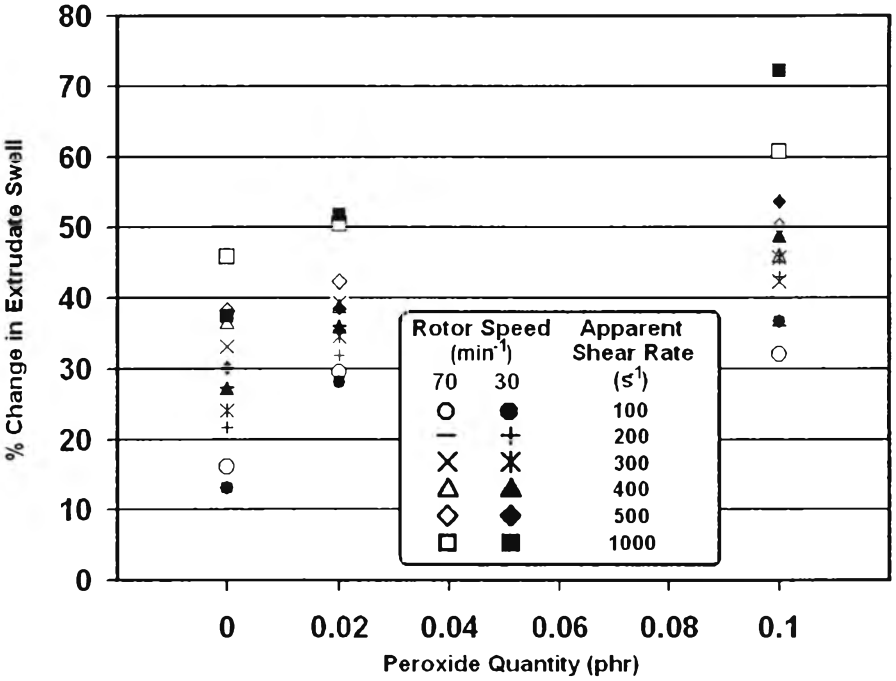


Figure 5.7 Percentage change in extrudate swell vs. apparent shear rate.

Figure 5.7 shows the dependence of percentage change in extrudate swell on peroxide content of all runs processed at 200°C with peroxide addition method Miii. Not surprisingly, increase in peroxide quantity and shear rate for capillary extrusion can generate larger stress and consequently increasing extrudate swell. The lower speed of mixing causes less extrudate swell; however, when using high amount of DCP (0.1 phr), the effect of rotor speed on extrudate swell becomes inversed. It could be referred that the effect of mixing speed indirectly indicating shear rate applied during the melt processing becomes predominant for shear modification. At high peroxide content incorporated with high shear rate applied during mixing, the attack of peroxide which decomposed at processed temperature on LLDPE chain to produce macroradicals occurred quickly and then provided more of shorter chain branches than that of low mixing speed. On the other hand, low shear rate of mixing provided more of longer chain branches in the high-content initiator system which seemed responsible for elasticity property as the high of percentage changes in extrudate swell was observed.

Nevertheless, the use of these rheological data to obtain all information about long chain branching is not feasible, it is necessary to separate the effect of molecular weight distribution from that of long chain branching. This is difficult because both structural features perform similar effects such as, both broadening the MWD and increasing the level of long chain branching have similar effects on the viscosity curve.

5.5 Conclusions

Results of reduced MFI and increasing viscosity with peroxide content indicate the flow difficulty and hence the increase in branching structure or chain extensions to LLDPE molecules as a result of reactive mixing with an initiator, DCP at low content. The all peroxide modified LLDPEs still exhibited pseudoplasticity or shear thinning. Among three methods of initiator addition, Miii is the most appropriate mode of peroxide addition due to the highest real shear stress, viscosity and the lowest MFI. Miii provides the well distributive mixing of the solid peroxide and LLDPE pellets in the dry state prior to heating and thus once they are molten, the peroxide was decomposed inside and readily reacted with molten LLDPE. This allows the most efficient reactive mixing. Processing temperature and mixing rotor speed become more influence on peroxide feeding methods at low amount of peroxide but at high DCP content they show less important effects on extent of reaction in terms of viscosity and elasticity of the reacted LLDPE. Since changing in rheological properties depended markedly on the efficiency of incorporating and mixing the peroxide into the polymer, the method of peroxide addition and the processing conditions were important factors of the reactive process of selected LLDPE.

5.6 Acknowledgements

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