CHAPTER V

CONCLUSION

The kinetics of peroxide crosslinking reaction of LDPE and LLDPE in the absence and in the presence of an inhibitor were studied in details. The peroxide compound and the inhibitor employed in these studies were respectively dicumyl peroxide (DCP) and tetrakis[methylene 3-(3′,5′-di-t-butyl-4′-hydroxyl)propanoate] or Irganox 1010. The amount of DCP and Irganox 1010 were varied from 0 to 2%w/w and from 0.1 to 0.6%w/w, respectively. The reaction temperature was in the ranges of 293 to 423 K and 446 to 473 K depending upon the techniques used for the studies which were rheometry and differential scanning calorimetry. Specifically the former used Brabender Plasti-Corder with a mixing chamber as the reaction reactor with twin contra-rotors at the fixed speed of 50 rpm. To be claimed here, the latter was employed for the first time to study such the kinetics, and it was found that the technique is very useful and various vital kinetic parameters could be obtained. Significant findings of this study are summarized here. Since there was a limited time as well as a limited equipments available during the study, therefore, a number of interest topics have remained to purpose further studies, which are mentioned subsequently in suggestion for further work section.

1. Thermal properties, including T_m, T_c and crystallinity, and configuration in term of degree of branching of LDPE and LLDPE used in this study were characterized. The significant properties are summarized in Table 5.1

2 The rate of crosslinking reaction in the absence of Irganox 1010 followed the first order kinetic which was proportional to [DCP]. In other words, the rate determining step is the rate of dissociation of DCP, i.e., $R_x = k_x[DCP]$. The kinetics values evaluated in this study are summarized in Table 5.2.

Table 5.1 Characteristics of LDPE J4324 (TPI) and LLDPE L2020 F (TPE).

Item	J4324	L2020 F
Branching , per 1000 atoms of carbon	1.61	1.42
T_m, °C	101.1	119.9
T_c, °C	95.2	112.2
Crystallinity, %	31.1	34.9
$MFI_{2.16,190\,°C}$, g/10 min	2.01	1.89
Mw, g/mol	228,127	232,405
Polydispersity index	9.2	8.7

Table 5.2 The kinetic values of crosslinking reaction of LDPE and LLDPE with DCP in the absence of Irganox 1010 as evaluated by the rheometric and DSC techniques.

Parameter	LDPE		LLDPE	
	DSC	RHE	DSC	RHE
DCP order	1.24	1.03	1.27	1.06
k'_x (at 413 K), $(sec)^{-1}$	6.15×10^{-5}	-	5.83×10^{-5}	-
k'_x (at 446 K), $(sec)^{-1}$	-	5.74×10^{-3}	-	6.22×10^{-3}
Activation energy, (kJ/mol)	184	118	176	112
Preexponential factor,(sec^{-1})	3.56×10^{19}	3.23×10^{11}	3.64×10^{18}	0.82×10^{11}

Whilst, in the presence of Irganox 1010, the rate of crosslinking reaction depended not only on [DCP] but also on [Irganox 1010], which it can be expressed as

	Rheometry	DSC
LDPE	$Rx = k_{xz}[DCP]/[Irganox1010]^{0.21}$	$Rx = k_{xz}[DCP]/[Irganox1010]^{0.23}$
LLDPE	$Rx = k_{xz}[DCP]/[Irganox1010]^{0.27}$	$Rx = k_{xz}[DCP]/[Irganox1010]^{0.31}$

The order of the crosslinking reaction in the presence of LDPE and LLDPE was 0.77-0.79 for LDPE and 0.69-0.73 for LLDPE, which implied that in the presence of the inhibitor the rate of crosslinking reaction was suppressed. In addition, DCP was partially consumed due to the reaction of DCP radicals with the inhibitor so that the higher DCP amount was required to obtain similarly degree of crosslinking to that prepared from the reaction in the absence of the inhibitor. The values of k'_{xz} of LDPE and LLDPE evaluated in this study by the techniques of rheometry and DSC were

Technique	LDPE	LLDPE
Rheometry (at 446 K)	2.11×10^{-3}	2.33×10^{-3}
DSC (at 413 K)	4.22×10^{-5}	3.74×10^{-5}

3 Approximately 65% of polymer radicals combined via the bimolecular combination mechanism. At the same degree of crosslinking of the crosslinked LDPE and LLDPE, the degradation of the latter as observed by rheometry showed slower than the former which was due to the higher long chain branching in LDPE.

4 The amount of crystallinity of the crosslinked LDPE or LLDPE decreased with the increase of degree of crosslink since the three dimensional network structure destroyed the original crystal structure of the virgin polymers.

5 Gel content of the crosslinked polymer increased with the increase of DCP amount and could achieve a constant at more than 80% when using DCP higher than 1.6% w/w. When 0.1-0.2%w/w Irganox 1010 was used in compounded LDPE and LLDPE containing about 2%w/w of DCP, the gel of crosslinked polymer remained constant. After that it decreased with the increase of Irganox 1010 concentration.

Suggestion for Further Work

1. The higher amount of DCP more than 1.6%w/w should affect on the frequency of crosslinking or crosslink density on the resulting polymer, which has not yet been proved in this study. It is interesting to determine the optimum DCP amount that results in the maximum crosslinking density because it is one of the factors effect

to the final properties of crosslinked polymers, such as tensile strength , elongation, flexibility.

2. Since the main application of LDPE and LLDPE is in power cable area. Therefore, the prevention of degradation of crosslinked polymer by metal especially copper should be investigated. Not only the selection of the existing type of antioxidant but also the synthesis of the new antioxidant is interesting.

3. A method to improve the efficiency of the combination reaction of the polymer radicals is also interesting by consideration of the suitable cure conditions or addition of the other compounds which can promote such the reaction.