

The Effect of Co-agent on the Peroxide Cross-linking of LDPE

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ABSTRACT

Peroxide cross-linking of polyethylene is one of the most important methods for the production of cross-linked polyethylene (PEX). The kinetic study of the cross-linking reaction of low density polyethylene (LDPE) in the presence of 2,4-diphenyl-4-methyl-1-pentene (MSD), pentaerythritol triacrylate (PETA) and divinylbenzene (DVB) as the co-agent and dicumyl peroxide (DCP) as the cross-linking agent was carried out by differential scanning calorimeter (DSC, non-isothermal condition), rheometer and internal mixer (isothermal condition). The reaction was first order and independent of DCP and the co-agent concentration. The activation energy and $\ln k_0$ ($\ln k_0$ defined as the intercept of ΔH vs. $1/T$) did not change with DCP concentration but energy of activation decreased with co-agent and the highest decrement was observed with respect to MSD. The overall reaction rate constant (with constant value of DCP) increased with temperature due to the faster decomposition rate of peroxide at higher temperatures. By comparison of the three methods used, it was found that the different results obtained were in good agreement with each other. However, because of the higher shear rate and mechanical stress experienced in the internal mixer, the measured overall reaction rate constants were of higher values with respect to those obtained from other methods.

Key Words:

LDPE;
co-agent;
DCP;
kinetics;
rheometer;
internal mixer; cross-linking.

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INTRODUCTION

One of the most important post-reaction modifications on polyethylene is cross-linking. Cross-linking improves some of the properties of polyethylene such as: environmental stress cracking (ESCR), abrasion and chemical resistance, low tem-

perature properties, service temperature and mechanical properties (impact and tensile strength) [1-7].

Due to the above properties, cross-linked polyethylene (PEX) can be used in the production of heat shrinkable articles, central heating

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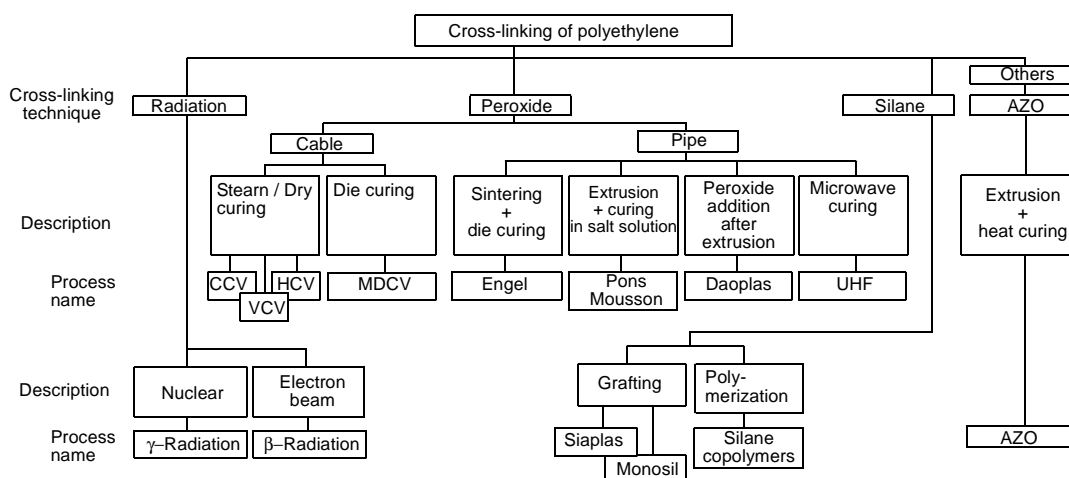


Figure 1. Diagram of different methods of cross-linking for PE.

tubes, cables (medium and high voltage), films, foam [8-11].

There are three principal technologies in producing the PEX:

- peroxide,
- silane,
- irradiation [12].

The details of these methods are illustrated in Figure 1 [13].

In the peroxide method, free radicals are generated by using a heat activated peroxide to abstract a hydrogen atom from one of the carbon atoms in the polyethylene chain which leaves localized PE radicals.

Cross-linking bonds are formed by the combination of PE radical bonds. The chemistry of PE cross-linking has been investigated and many different reactions have been realized among free radicals, macroradicals and PE in the peroxide method [14-18].

It has been reported that in the presence of unsaturated structures in PE, especially vinyl group, cross-linking efficiency increases [19-21]. Vinyl groups in PE can be formed in the polymerization process by chain transfer agent and its amount is in the range of 0.1 to 0.4 per 1000 carbons. If unsaturated groups are 0.7 per 1000 carbons, the required amount of peroxide (e.g., DCP) decreases from 2.1 to 1.3 percent [13].

The co-agent can increase the unsaturated bonds and it is commonly added to peroxide/cross-linkable compounds such as PE and rubber. These materials are usually polyfunctional monomers or oligomers such as methacrylates and allyl compounds [22].

Using 2,4-diphenyl-4-methyl-1-pentene (MSD), ethylene glycol dimethacrylate, trimethylpropane trimethylacrylate (TMPTA), 1,2-polybutadiene, divinylbenzene and triallyl cyanurate, etc., as the co-agents in polyethylene have been reported [23-28].

During the cross-linking reaction co-agents are grafted to PE chains (by reaction with macroradicals), which increase the number of vinyl groups, thus creating more active sites for cross-linking reactions [29].

In this study a kinetic approach to cross-linking of PE by DCP and effect of various co-agents on cross-linking has been investigated by differential scanning calorimeter (DSC), internal mixer and rheometer.

EXPERIMENTAL

Materials

In this study the following materials were used: low density polyethylene (LDPE) from Iran Petrochemical Co., grade Lf0200 with $d=0.920$ g/mL and MFI = 2 g/10 min, DCP from Hercules Co., as the cross-linking agent, grade Di-cup 90 with 98% purity.

2,4-Diphenyl-4-methyl-1-pentene (MSD) from NOF Co. pentaerythritol triacrylate (PETA) from Merck and divinylbenzene (DVB) from Merck as the co-agents.

Instruments

Differential scanning calorimeter (DSC) from polymer laboratory, model STA 625. The experiments were carried out in N_2 atmosphere with heating rate of 10 C/min from 25 C temperature to 250 C.

Internal mixer was from Haake Co. model Sys 9000 and rheometer from Zwick Co. Model 4301 was used for sample preparation and evaluation.

Sample Preparation

The samples were prepared by internal mixer using cam-type mixing head at 115 C and 60 rpm. The com-

Table 1. Composition of samples.

No	LDPE	DCP	MSD	PETA	DVB
1	99.5	0.5	—	—	—
2	99.5	0.5	0.1, 0.3	—	—
3	99.5	0.5	—	0.1, 0.3	—
4	99.5	0.5	—	—	0.1,0.3
5	99	1	—	—	—
6	99	1	0.1,0.3	—	—
7	99	1	—	0.1,0.3	—
8	99	1	—	—	0.1,0.3
9	98	—	—	—	—
10	98	2	0.1,0.3	—	—
11	98	2	—	0.1,0.3	—
12	98	2	—	—	0.1,0.3
13	97	3	—	—	—
14	97	3	0.1,0.3	—	—
15	97	3	—	0.1,0.3	—
16	97	3	—	—	0.1,0.3
17	95	5	—	—	—
18	95	5	0.1,0.3	—	—
19	95	5	—	0.1,0.3	—
20	95	5	—	—	0.1,0.3

position of the samples are depicted in Table 1. Different formulations were made with five different amounts of peroxide and two different amounts of each co-agent. The LDPE was added to the mixer at 115 C and once the melting completed, DCP and co-agent were added. Mixing continued for 3 min. Samples were kept at 0 C before carrying out the experiments.

Method

Isothermal experiments were carried out in both

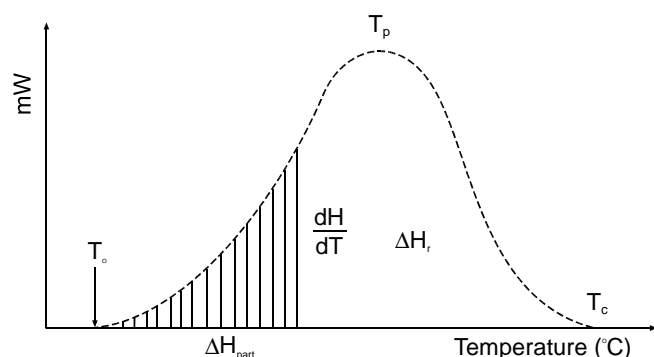


Figure 2. Typical exothermic peak of LDPE cross-linking in DSC [18].

rheometer and internal mixer. DSC Was performed on non-isothermal samples.

For non-isothermal tests, the general mathematical model for the kinetics of the chemical reaction was as follows [28].

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \quad (1)$$

where, $\frac{d\alpha}{dt}$ = rate of reaction, k = reaction rate constant, α = fraction of radicals reacted ($0 \rightarrow 1$), and n = order reaction

In general, cross-linking of LDPE is an exothermic reaction and an exothermic peak appears after the melting point of LDPE in DSC thermogram, (Figure 2). Any fraction of LDPE when cross-linked produces a certain change in the observed enthalpy, which can be expressed as:

$$d\alpha = \frac{dH}{\Delta H_{Total}} \quad (2)$$

where, ΔH_{Total} is the whole area of exothermic peak and dH is the fraction of the enthalpy measured.

Differentiating the above equation with respect to time gives:

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_{Total}} \quad \text{or} \quad \dot{\alpha} = \frac{\dot{H}}{\Delta H_{Total}} \quad (3)$$

$$\text{By substituting } \alpha = \frac{\Delta H_{part}}{\Delta H_{Total}} \text{ and } (1-\alpha) = \frac{\Delta H_r}{\Delta H_{Total}}$$

in eqn (1) and using the Arrhenius equation (temperature dependency of reaction constant).

where :

$$K = k_0 e^{-\frac{EA}{RT}} \quad (4)$$

k_0 is the pre-exponential factor, EA the activation energy, and R the gas constant. The equation in logarithmic form results in:

$$\ln \frac{\dot{H}}{\Delta H_{Total}} = \ln k_0 + EA \left(-\frac{1}{RT}\right) + n \ln \frac{\Delta H_r}{\Delta H_{Total}} \quad (5)$$

H , ΔH_{Total} and ΔH_r can be measured from DSC thermogram directly. By linear regression of eqn (5), one can estimate the parameters n , E_A , and $\ln k_0$.

In isothermal experiments, when cross-linking starts at constant temperature, torque increases in the rheometer and internal mixer after scorch time (t_i).

The fraction of polymer unreacted is equal to:

$$1 - \alpha = \frac{R_{\max} - R_t}{R_{\max} - R_{\min}} \quad (6)$$

where:

R_{\max} = maximum torque, R_{\min} = minimum torque and R_t : torque at time t.

If the order of reaction (n) is 1, by substituting in eqn (1) the following equation is obtained

$$\ln(1 - \alpha) = -k(t - t_i) \quad (7)$$

If this assumption is correct, then $\ln(1 - \alpha)$ versus time in eqn(7) will give a straight line. R_{\max} , R_{\min} and R_t from the rheograph would give linear regression, which allows us to estimate the overall reaction rate constant (k) and the activation energy.

RESULTS AND DISCUSSION

Non- isothermal Condition

Figure 3 shows DSC thermograms for samples without co-agent. In all the thermograms, two peaks are observed; one endothermic which is related to melting point and the other exothermic peak which is related to the cross-linking reaction of LDPE.

In these thermograms, it is observed that the area under the exothermic peak increases with increasing of DCP content. Furthermore, the maximum rate of curing occurs at 180 ± 3 C. Table 2 shows the exothermic heat of the cross-linking reaction and the temperature at maximum rate of curing.

By using eqn (5) and plotting $(\ln \frac{\dot{H}}{\Delta H_{\text{Total}}} - n \ln \frac{\Delta H_r}{\Delta H_{\text{Total}}})$ versus $\frac{1}{T}$, the activation energy and $\ln k_0$ were calculated.

Table 2. Exothermic heat of cross-linking reaction and temperature of maximum rate of curing.

DCP (%)	Exothermic ΔH (J/g) cross-linking reaction	Temperature of maximum cure rate
0.5	5.52	184
1	5.59	183.1
2	6.98	183
3	8.23	182
5	10.23	181

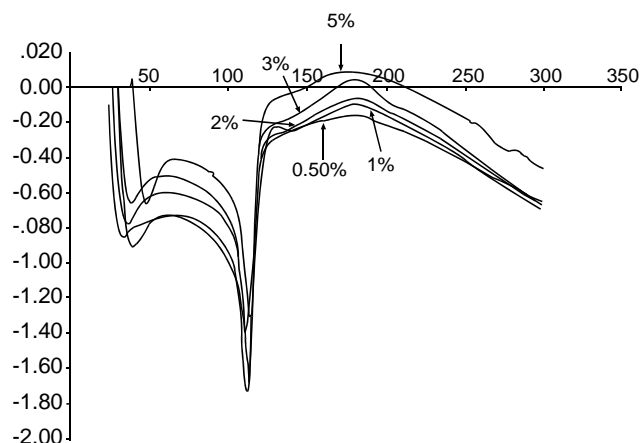


Figure 3. DSC Thermograms of samples without any co-agent. ed from the slope and the intercept of fitted straight line.

At first it was assumed that $n = 1$ and if the best straight line had high regression coefficient, the accuracy of the assumption would have been confirmed. For example, Figure 4 shows the straight line obtained for the sample containing 2% DCP with high regression coefficient while other samples without co-agent showed similar behaviour, justifying the unit order of cross-linking reaction.

Therefore, all samples without any co-agent showed first order reactions and were found to be independent of the cross-linking agent (DCP) concentration.

Table 3 shows the value of $\ln k_0$ and E_A . These parameters have not changed dramatically with alteration of DCP concentration.

By the same calculations on the samples containing the various co-agents, it was found that the order of cross-linking reaction was first order. Furthermore, the type and amount of co-agents had no effect on the order.

Table 4 shows exothermic cross-linking reactions, the activation energy and $\ln k_0$ for samples containing 2% DCP and different co-agents.

Results showed that the activation energy decreased in the presence of co-agent and the amount of decrement was different depending on the type and amount of the co-agent used. These differences are due

Table 3. The values of $\ln k_0$ and E_A for samples without co-agent.

DCP (%)	5	3	2	1	0.5
E (kcal /mol)	52.109	57.33	53.85	47.76	49
$\ln k_0$	53.58	59.218	58.44	52.14	52.232

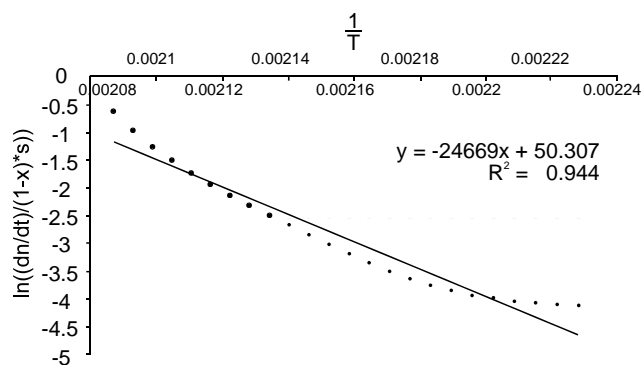


Figure 4. Linear regression of DSC data for samples containing 2% DCP.

to the various mechanisms that the co-agent enters in the cross-linking reaction [23-25].

The highest amount of decrement was observed for the sample containing MSD as co-agent.

Because of the higher efficiency of cross-linking reaction the area of exothermic peak increased in samples containing co-agents. However, $\ln k_0$ was found to be constant and independent of the type and amount of the co-agents.

Isothermal Condition

In carrying out the experiments isothermally in the rheometer and internal mixer due to the cross-linking reaction, the torque was increased after the scorch time. Figure 5 shows a rheograph for samples containing 3% DCP, PETA from the rheometer. By reading R_t , R_{min} , R_{max} from the rheograph and plotting $\ln(1-\alpha)$ from eqn (7) versus time a straight line is obtained. It was revealed that the reaction was first order and independent of DCP and co-agent concentration.

Increasing the temperature from 160 to 200 C, did not affect the order of the reaction, but the overall reaction rate constant (K) varied. Table 5 shows the overall rate constant at different temperatures. These

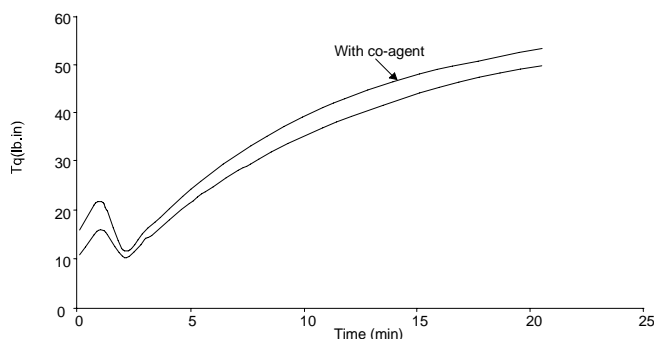


Figure 5. Rheograph for samples containing 3% DCP, 3% DCP, and 0.3% PETA .

Table 4. Exothermic cross-linking reaction, activation energy and $\ln k_0$ for samples containing 2% DCP and different co-agents (0.3 %).

Co-agent	Order of reaction	Exothermic cross-linking reaction (J/g)	$\ln k_0$	Activation energy (kcal/mol)
-	1	6.98	58.44	53.85
MSD	1	10.2	57.22	41.27
PETA	1	8.7	54.3	48.9
DVB	1	7.5	58.5	49.24

values are obtained from the slope of $\ln(1-\alpha)$ versus time based on eqn(7). The overall reaction rate constant (with constant value of DCP) increased with temperature due to the faster decomposition rate of peroxide at higher temperatures.

At the same temperature, the samples containing co-agents have higher overall reaction rate constants. These higher values are consistent with the higher efficiency in cross-linking reaction and are due to the inclusion of the co-agents. The highest amount of increase for the overall reaction rate constant temperature was demonstrated by the samples containing MSD.

The same trend in the order of reaction and the overall reaction rate constant was obtained for experiments conducted in the internal mixer. However, because of higher shear rate and mechanical stress experienced in the internal mixer, the measured overall reaction rate constants were of higher values with

Table 5. Overall reaction rate constants at different temperatures and co-agents with 2% DCP.

Temperature (°C)	DCP	MSD	PETA	DVB	k(1/min)
160	1	—	—	—	1.96
	1	0.3	—	—	2.83
	1	—	0.3	—	2.007
	1	—	—	0.3	2.3218
180	1	—	—	—	1.6713
	1	0.3	—	—	3.9232
	1	—	0.3	—	3.2243
	1	—	—	0.3	3.0256
200	1	—	—	—	2.9928
	1	0.3	—	—	6.7844
	1	—	0.3	—	5.3456
	1	—	—	0.3	5.0032

respect to those obtained from the rheometer .

CONCLUSION

The aim of this study was to investigate the effect of co-agent on peroxide cross-linking reaction of LDPE. The kinetics of reactions were studied by DSC, rheometer and internal mixer in the presence of various co-agents. It was found that the reaction was first order and independent of the cross-linking agent and co-agent concentrations. Energy of activation and $\ln k_0$ did not change with DCP concentration, but the energy of activation decreased with co-agent concentration and the highest decrement was observed with respect to MSD. By comparison of the three methods used, it was found that the different results were in good agreement with each other.

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