An Investigation on Rheology of Peroxide Cross-linking of Low Density Polyethylene

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A B S T R A C T

One of the most important post-reactor modifications of polyethylene is cross-linking. It improves some properties of polyethylene such as environmental stress cracking resistance, chemical and abrasion resistance, and service temperature. In this study, the effect of peroxide cross-linking on the rheological behaviour of low density polyethylene was investigated by using a combination of creep test and differential scanning calorimeter (DSC) in isotherm condition. The used peroxide was di-cumyl peroxide and its concentration was 2 wt%. The experiments were carried out at 150,160, and 170°C and the change of bulk viscosity due to network developing was determined. For delivering of local derivatives smoothing techniques were applied on creep data. The rate of increment of viscosity increased with increasing the temperature, and the major of this increment took place in the first stages of reaction.

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INTRODUCTION

The rheologically tracking of developing network system (DNS) is very important in the design and optimization of flow process. The DNS includes a wide range of materials such as radiation curable monomers, more viscous two components, and high viscous thermally curable fluids. Many researchers have investigated on rheological behaviour of cross-linking reaction of thermoset resins such as: epoxy, polyester, polyurethane, and phenolics. In these systems, according to the chemistry

of reaction, by increasing the degree of reaction, viscosity increases dramatically up to the gel point .At this point the viscosity tends to infinity and liquid-solid transition occurs. [1-6].

In general, the production of cross-linked polyethylene (by organic peroxides) in form of cables, pipes, heat shrinkable articles, etc. is carried out in continuous operation and cross-linking reaction is completed during the different steps of the processing. Cross-linking reaction takes place in melt condition and network develops along the production line [7-11].The rheological properties change with developing of network and it is often vital to know the trend of these variations and the time for reaching the gel point. [12-13].
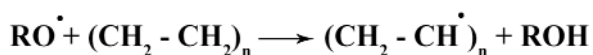
The DNS Viscosity depends on chemical structure, processing condition, and the characteristics of the growth of the network. Thus, the viscosity is expressed as function of temperature, pressure, time (conversion), and shear rate (14).

The dominant chemical reactions in peroxide cross-linking of polyethylene follows three steps namely peroxide decomposition, radical chain transfer ,and combination of radicals. The schematic of these steps is shown in Figure (1). There are two methods for tracking the variation of viscosity in accordance with degree of cross-linking; (1) continuous measuring during cross-linkig reaction and (2) step by step viscosity measurments by sampling of the cross-linked polymer .
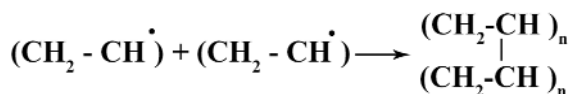
The aim of the our work is to measure the viscosity versus degree of cross-linking reaction (during per-oxide crosslinking reaction) of LDPE at isothermal condition using a combination of DSC and creep test.

EXPERIMENTAL

Materials
Low density polyethylene (LDPE), Lupolen 3020D (MFI = 1.5 g/10 min, d = 0.913 g/cm^3) from Bassel and di-cumyl peroxide (DCP) from Akzo Nobel (perkdox BC-FF trade name) with 98% purity were used.

Instruments
The conversion of reaction was measured by DSC (Advanced Technology model DSC 1000). Stresstech controlled rheometer (Rheological Instruments AB) was used for creep test in plate/plate geometry (D = 20 mm). Special single use plate-plate geometry was used for easy and safe cleaning tests [14] (Figure (2))

Method
Polyethylene and 2 wt% DCP were mixed in 60 cm^3 Brabender internal mixer at 130ºC, under the safety temperature of DCP (140ºC). The DSC and creep experiments carried out in isothermal condition at 150,160, and 170ºC. The levels of stress in creep test were 5000, 10000, and 15000 Pa.
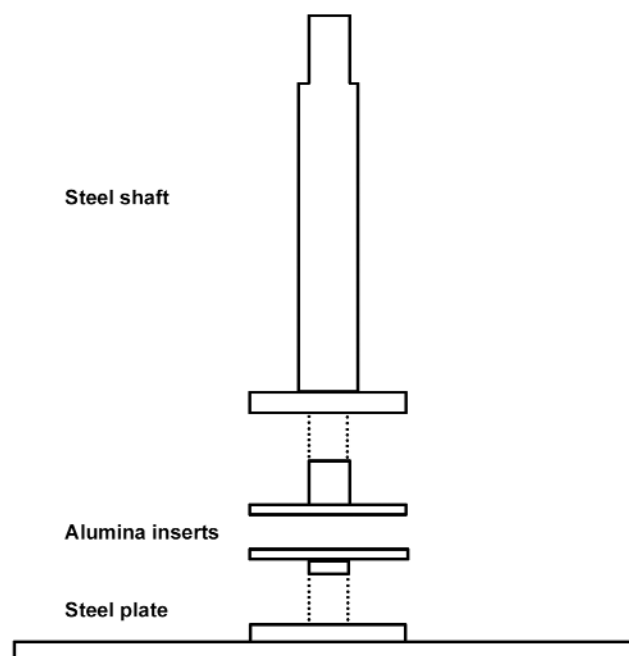
$$R-O-O-R \xrightarrow{\Delta} RO^{\bullet} + RO^{\bullet}$$

Formation of free initiator radical

$$RO^{\bullet} + (CH_2 - CH_2)_n \longrightarrow (CH_2 - CH^{\bullet})_n + ROH$$

Chain transfer

$$(CH_2 - CH^{\bullet}) + (CH_2 - CH^{\bullet}) \longrightarrow \begin{array}{c}(CH_2-CH)_n \\ | \\ (CH_2-CH)_n\end{array}$$

Combination of chain transfer

Figure 1. A schematic of cross-linking reactions of polyethylene

Figure 2. A schematic of the plate/plate geometry [14].

RESULTS AND DISCUSSION

We considered viscosity as function of time (cross-linking reaction) and shear rate, so in isothermal shear deformation, the stress can expressed as :

$$\tau_{yx} = \eta_{yx} (t, \mathring{\gamma}_{yx}) \mathring{\gamma}_{yx} \qquad (1)$$

At constant stress we may show that [14]:

$$\left(\frac{\partial \eta}{\partial t}\right)_{\mathring{\gamma}_{yx}} = -\left[\frac{\eta}{\mathring{\gamma}_{yx}} + \left(\frac{\partial \eta}{\partial \mathring{\gamma}_{yx}}\right)_t\right]\left(\frac{\partial \mathring{\gamma}_{yx}}{\partial t}\right)_{\tau \circ} \qquad (2)$$

Similarly, at constant time, we may drive the expression:

$$\left(\frac{\partial \tau_{yx}}{\partial \mathring{\gamma}_{yx}}\right)_t = -\mathring{\gamma}_{yx}\left[\frac{\eta}{\mathring{\gamma}_{yx}} + \left(\frac{\partial \eta}{\partial \mathring{\gamma}_{yx}}\right)_t\right] \qquad (3)$$

With combining equations 2 and 3, we obtain:

$$\left(\frac{\partial \eta}{\partial t}\right)_{\mathring{\gamma}_{yx}} = \frac{1}{\mathring{\gamma}_{yx}}\left(\frac{\partial \tau_{yx}}{\partial \mathring{\gamma}_{yx}}\right)_t\left(\frac{\partial \tau_{yx}}{\partial t}\right)_{\tau \circ} \qquad (4)$$

In the above equations η, τ, t and $\mathring{\gamma}_{yx}$ are viscosity, shear stress, time and shear rate, respectively. Equation (4) relates the reaction dependence of viscosity to quantities measurable in a creep experiment. The conversion of cross-linking reaction (α) was determined according to eqn (5).

$$\alpha = \frac{H(t)}{H_u} \qquad (5)$$

Where H(t) is heat released by the cross-linking reaction up to time t and H_u is the summation or ultimate heat of reaction. Hence the change in viscosity due to reaction can be expressed as

$$\left(\frac{\partial \eta}{\partial \alpha}\right)_{\mathring{\gamma}_{yx}} = \left(\frac{d\alpha}{dt}\right)^{-1}\left(\frac{\partial \eta}{\partial t}\right)_{\mathring{\gamma}_{yx}} \qquad (6)$$

Where dα/dt is determined from isothermal DSC experiments and $(\partial_\eta/\partial_t)_{\mathring{\gamma}_{yx}}$ is determined from creep experiments.

In eqn (1) it is assumed that the time scale for the chemical reaction (cross-linking) can be separated from
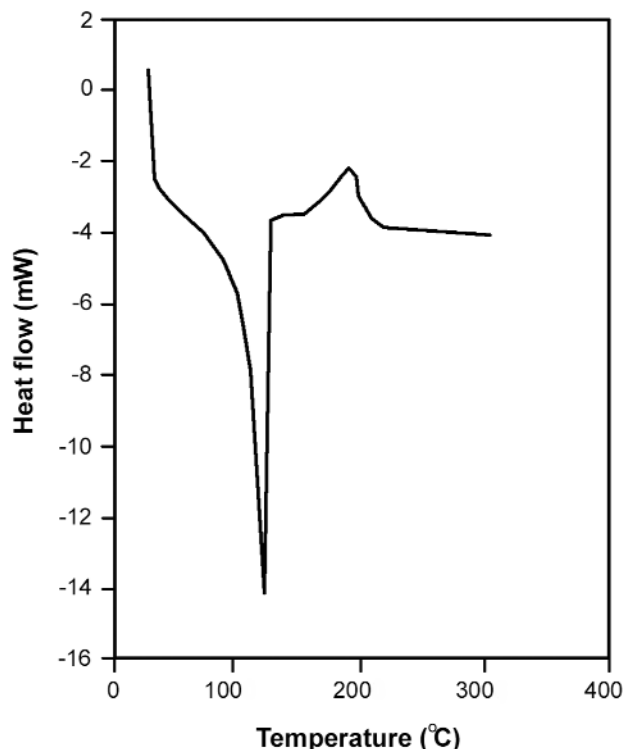

Figure 3. Dynamic DSC scan of LDPE with 2 wt % of DCP.

viscoelastic relaxation. Therefore, it needs to be determined in which condition the equation applies.

Figures 3-5 show the data obtained from dynamic and isothermal (160°C) DSC scans and H(t) for LDPE with 2 wt% of DCP, respectively. In Figure 3 the
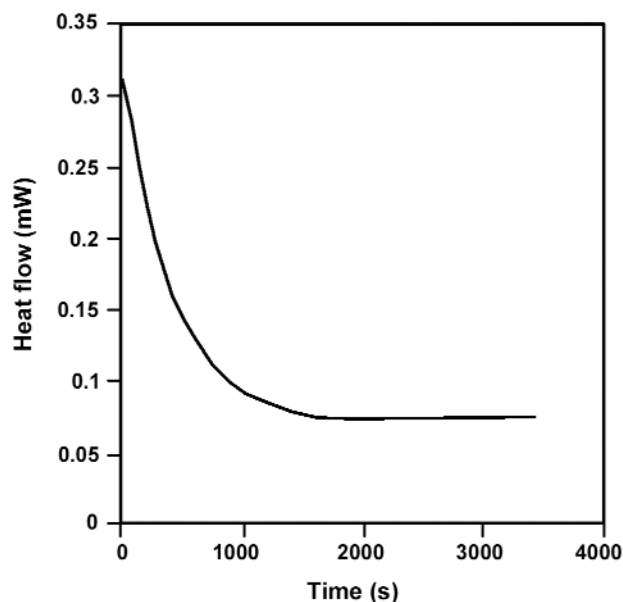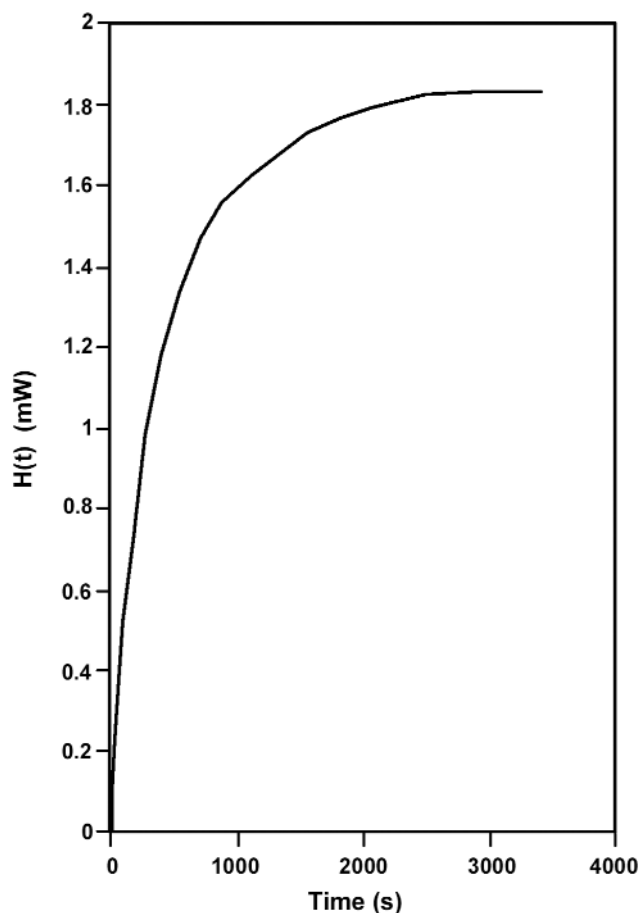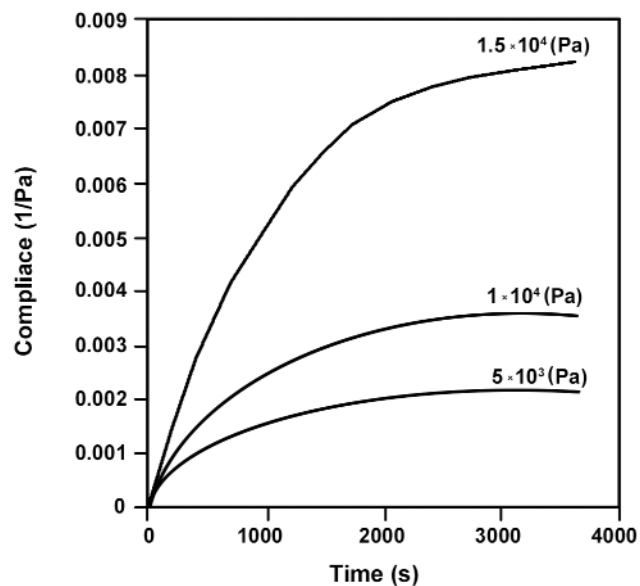

Figure 4. Isothermal DSC scan of LDPE with 2 wt% of DCP at 160 C.

Figure 5. Heat of reaction up to time t for LDPE with 2 wt% of DCP at 160 C.

Figure 6. Creep compliance of LDPE with 2 wt % of DCP at 160 C and different stress levels.

Figures 7 and 8 show an approximation of shear rate value and its time derivative at 160°C and 10^4 Pa, respectively. Figure 9 shows $(\partial_\eta/\partial_t)_{\mathring{\gamma}_{yx}}$ versus time at 160°C and 10^4 Pa. The rate of cross-linking reaction increases via increasing temperature which is revealed
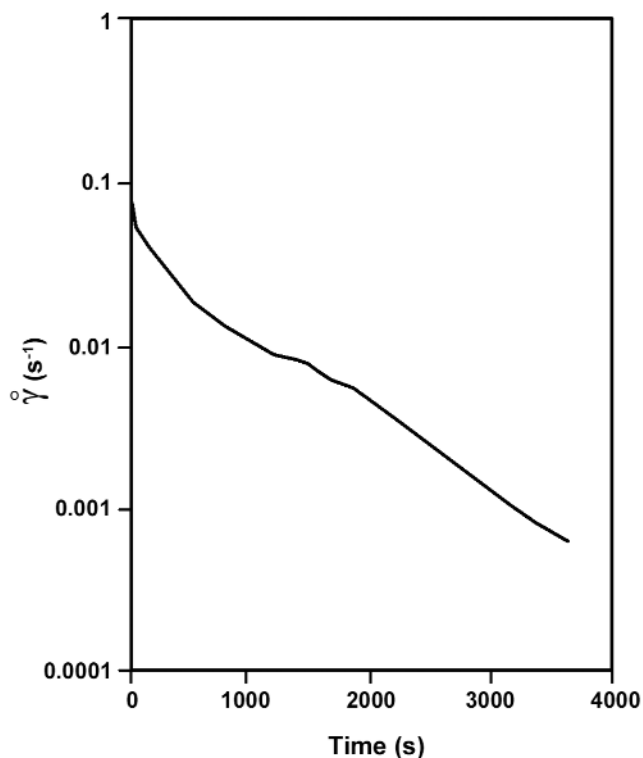
exothermic peak after the melting point is relevant to the cross-linking reaction. By increasing of DCP wt%, the area under the peak and the rate of reaction increase. By doing the dynamic scan after isothermal experiments on the same sample, there was no exothermic peak and it seems that cross-link reaction has been completed.

Figure 6 shows the creep compliance, J_c versus time at three levels of stress at 160°C. Below the 5000 Pa the data were very noisy and beyond the sensitivity of instrument. According to above equations for obtaining of $\mathring{\gamma}$ and $\partial\mathring{\gamma}_{yx}/\partial_t$ for determining the dependency of viscosity to degree of reaction. we should determine derivatives of creep compliance for two times. Because of small-scale fluctuation in these data, we were not able to obtain any derivative by simple difference scheme. For manipulation of data smoothing the average of five point technique was applied. This simple technique can eliminate noises [15].

Figure 7. Shear rate at 10^4 Pa and 160 C.
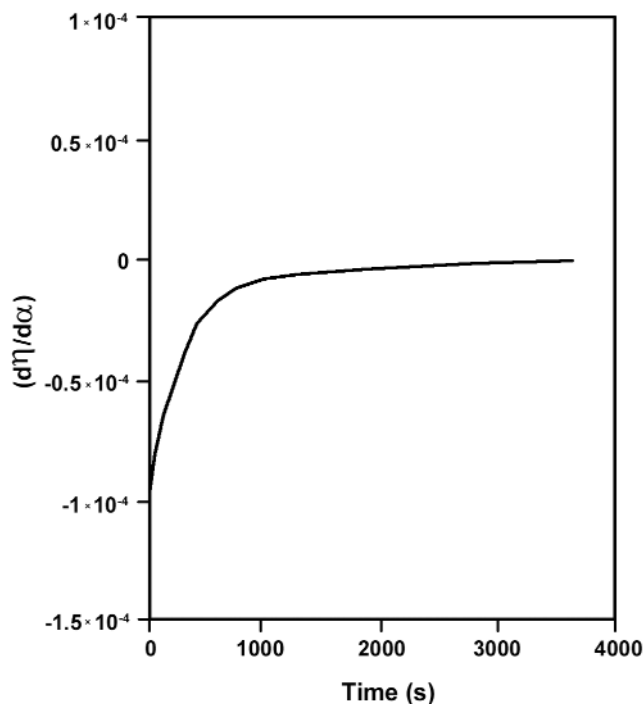
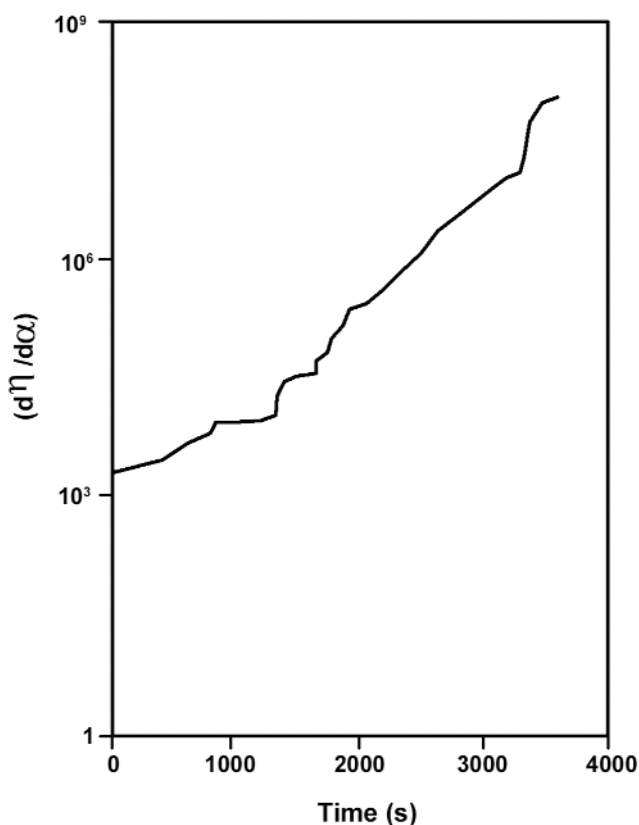**Figure 8.** Time derivative of shear rate at 10^4 Pa and 160 C.

Figure 9. Variation of $(d\eta/d\alpha)_{\dot\gamma_{yx}}$ vs. time at 10^4 Pa and 160 C.

in the slop of the curves. It is obvious that by preceding the cross-linking reaction, viscosity increases and the major increment takes place in the first stage of reaction.

CONCLUSION

During peroxide cross-linking reaction of LDPE, by combining DSC and creep experimental data one can determine the dependency of viscosity on the degree of cross-linking reaction. The analysis would be more accurate if plenty of creep tests could be conducted under variety of stress levels.

Without employing smoothing operation on data, the derivatives cannot be represented by simple difference scheme, it seems that, noise elimination is necessary to continue the analysis by this method.

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