

Rheological behaviour of polyethylene with peroxide crosslinking agent

Ismaeil Ghasemi¹, Peter Szabo², Henrik Koblitz Rasmussen³

1-Iran Polymer Institute, Tehran, Iran, P.O.BOX 14965/115

2-Danish Polymer Centre, Department of Chemical Engineering

3-Danish Polymer Centre, Department of Production and Management

Technical University of Denmark, Building 423, DK-2800 Kgs. Lyngby, Denmark

ABSTRACT

One of the most important post-reactor modifications of polyethylene is cross-linking. Cross-linking improves some properties of polyethylene such as: environmental stress cracking resistance (ECSR), chemical and abrasion resistance, service temperature etc. In this study the rheological variation due to a peroxide cross-linking reaction of low-density polyethylene (LDPE) was tracked by a combination of creep tests and differential scanning calorimetry (DSC) tests in isothermal conditions. The peroxide was dicumyl peroxide and its concentration was 2 wt%. The experiments were carried out at 150,160 and 170°C. The aim of the present work is to determine the viscosity in terms of the degree of cross-linking of LDPE in isothermal conditions by a combination of DSC and creep tests.

INTRODUCTION:

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 processes where the crosslinking reaction completes during the processing and forming operations⁽¹⁾. As the crosslinking reaction takes place in melt condition the network develops along the production line.

The rheological properties change during network formation and it is important to determine this variation in terms of the chemical conversion. We attempt to do this

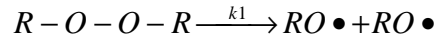
by considering the viscosity as a function of conversion and shear rate⁽²⁾:

$$\mathbf{t}_{yx} = \mathbf{h}_{yx}(\mathbf{a}, \dot{\mathbf{g}}_{yx}) \dot{\mathbf{g}}_{yx} \quad (1)$$

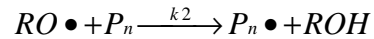
In forming Eq. (1) it is assumed that the time scale for the chemical reaction (cross-linking) can be separated from viscoelastic relaxations. Therefore, it needs to be determined in which conditions the equation applies.

In Fig.1, we show the dominant chemical reactions in the peroxide cross-linking of polyethylene.

Formation of free initiator radicals:



Chain transfer:



Combination of chain radicals:

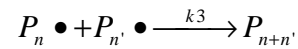


Figure 1: Schematic of the steps in the cross-linking reaction of polyethylene.

Based on the three dominating reactions stated above we can form a set of non-dimensional differential equations that describes the kinetic behaviour:

Consumption of peroxide initiator

$$\frac{dy_1}{dt} = -k_1 y_1 \quad (2)$$

Concentration of free initiator radicals:

$$\frac{dy_2}{dt} = 2k_1y_1 - c_2y_2 \quad (3)$$

Concentration of chain radicals:

$$\frac{dy_3}{dt} = c_2y_2 - 2c_3y_3^2 \quad (4)$$

Formation of chain cross-links:

$$\frac{dy_4}{dt} = c_3y_3^2 \quad (5)$$

Here the non-dimensional concentrations were defined by: $y_1=[\text{ROOR}] / [\text{ROOR}]_0$, $y_2=[\text{RO}\bullet] / [\text{ROOR}]_0$, $y_3=[\text{P}_n\bullet] / [\text{ROOR}]_0$ and $y_4=[\text{P}_{n+n}] / [\text{ROOR}]_0$. The modified rate constants: $c_2=k_2 [\text{P}_n]$ and $c_3=k_3/[\text{ROOR}]_0$, where the polymer concentration, $[\text{P}_n]$, was assumed to be practically constant.

From the reaction enthalpies we may form an expression that expresses the total heat flow during cross-linking:

$$\frac{dQ}{dt} = \Delta H_{r_1} \cdot r_1 + \Delta H_{r_2} \cdot r_2 + \Delta H_{r_3} \cdot r_3 \quad (6)$$

This heat flow function can be determined from DSC measurements.

MATERIALS AND METHODS

The LDPE was a lupolen 3020D from Basell and the peroxide initiator was dicumyl peroxide (DCP) from Akzo Nobel (Perkadox BC-FF, 98 % purity).

The differential scanning calorimeter was a TA Instruments model DSC 1000.

For the creep tests we used a Stresstech controlled stress rheometer from Rheologica Instruments AB with a plate/plate geometry ($D=20$ mm). For easy and safe cleaning a special plate/plate geometry with single-use inserts was applied in each experiment⁽²⁾. LDPE and DCP were mixed for 5 minutes in 60 cm³ Brabender internal mixer with 2 Wt% of DCP at 130 °C (below the safety temperature of DCP, 140°C). The DSC and creep experiments were carried out in isothermal conditions at 150, 160 and 170 °C. The stress levels during the creep tests were 5 kPa, 10 kPa and 15 kPa.

RESULTS AND DISCUSSION

It is clear from Eq. (1) that precise data for the chemical conversion, α , is needed in order to relate kinetic data to rheological measurements. From isothermal DSC experiments we can compute the total heat flow dQ/dt . By accurately fitting the model (3-6) to the data, we can extract the contribution, $H(t)$, from the combination reaction (Fig.1). The conversion, α , is then computed from Eq. (7),

$$a(t) = \frac{H(t)}{H(\infty)} \quad (7)$$

where $H(\infty)$ is the ultimate heat of reaction.

In the Figs. 2-3 we show data obtained from dynamic and isothermal DSC (160°C) scans (for LDPE with 2 Wt% of DCP). In Fig 2. the exothermic peak above the melting point is related to the cross-linking reaction. By increasing the Wt% DCP the peak area increases. We performed a dynamic scan after the isothermal experiment and verified that the cross-linking reaction had completed.

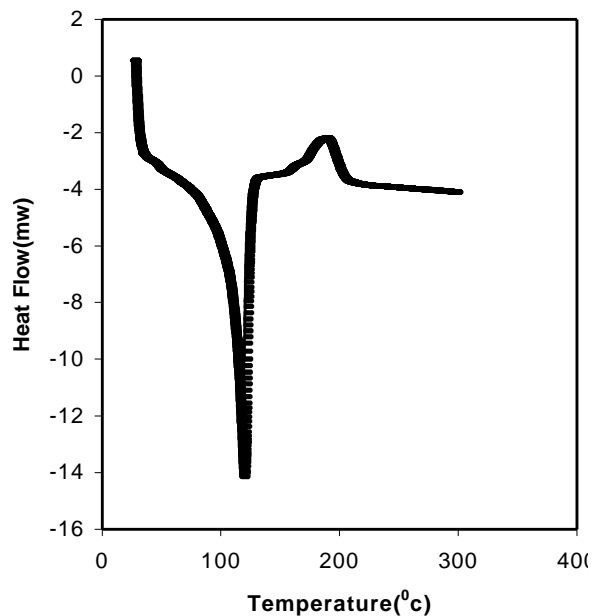


Figure 2 Dynamic DSC scan on a virgin sample of LDPE with 2 Wt % of DCP.

In Fig. 3 we show an example result of the fitting procedure. Afterwards, the model

simulation based on the fit can be used to generate a heat curve for the combination reaction $H(t)$.

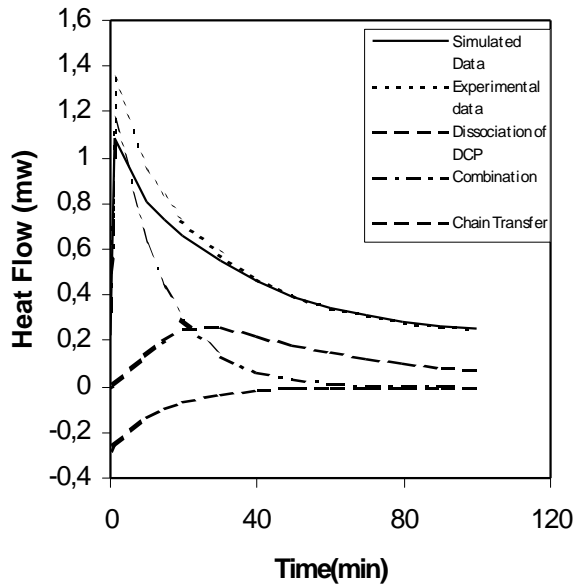


Figure 3 Isothermal DSC scan of LDPE with 2 Wt% of DCP at 160 °C. Also shown are curves from the reaction model (3-6).

The isothermal shear measurements were performed at constant stress values (creep). In such conditions, and assuming validity of Eq. (1), the following equation can be derived⁽²⁾.

$$\left(\frac{\partial \mathbf{h}}{\partial t}\right)_{\dot{\mathbf{g}}_{yx}} = \frac{1}{\dot{\mathbf{g}}_{yx}} \left(\frac{\partial \mathbf{t}_{yx}}{\partial \dot{\mathbf{g}}_{yx}}\right)_t \left(\frac{\partial \dot{\mathbf{g}}_{yx}}{\partial t}\right)_t \quad (8)$$

In this equation the time dependent viscosity function may be replaced by a function of the conversion defined according to Eq. (9),

$$\left(\frac{\partial \mathbf{h}}{\partial \mathbf{a}}\right)_{\dot{\mathbf{g}}_{yx}} = \left(\frac{d\mathbf{a}}{dt}\right)^{-1} \left(\frac{\partial \mathbf{h}}{\partial t}\right)_{\dot{\mathbf{g}}_{yx}} \quad (9)$$

where da/dt is determined from isothermal DSC measurements whereas $(\partial \mathbf{h} / \partial t)_{\dot{\mathbf{g}}_{yx}}$ is determined from creep experiments.

The use of Eq. (8) is based on curves for the creep compliance. In Fig. 4. we show the creep compliance, J_c , versus time at three levels of stress at 160°C. Below 5 kPa the

data were very noisy and beyond the sensitivity of the instrument. As we need to estimate local derivatives of the creep

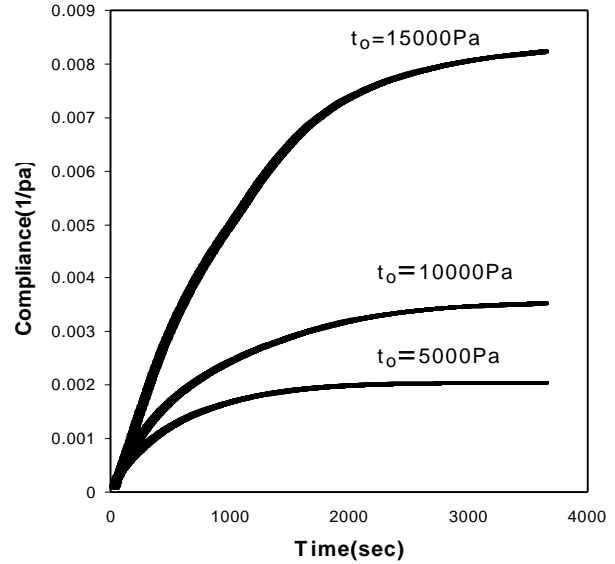


Figure 4 Creep compliance of LDPE with 2 Wt% of DCP at 160 °C and different levels of stress

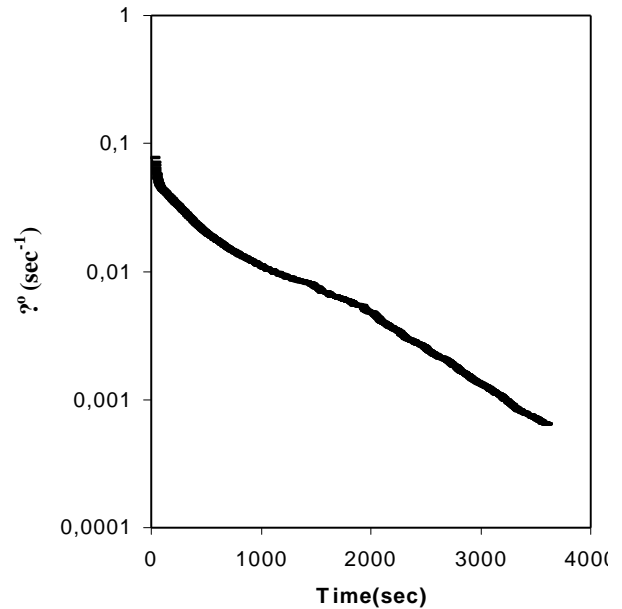


Figure 5 Shear rate at 10 kPa and 160 °C.

compliance data a smoothing technique was used to minimise the influence from small-scale fluctuations in the data. A three-point

difference scheme was used for the data described here. This simple technique could eliminate noise to within an acceptable accuracy. In Fig. 5 we show an approximation to the shear rate at 10 kPa. It is clear that the viscosity increases by a factor of 100 during the sampled time interval.

Furthermore, Fig. 6 shows a preliminary calculation of the function $(\partial h / \partial a)_{g_{yx}}$ versus time at 10 kPa.

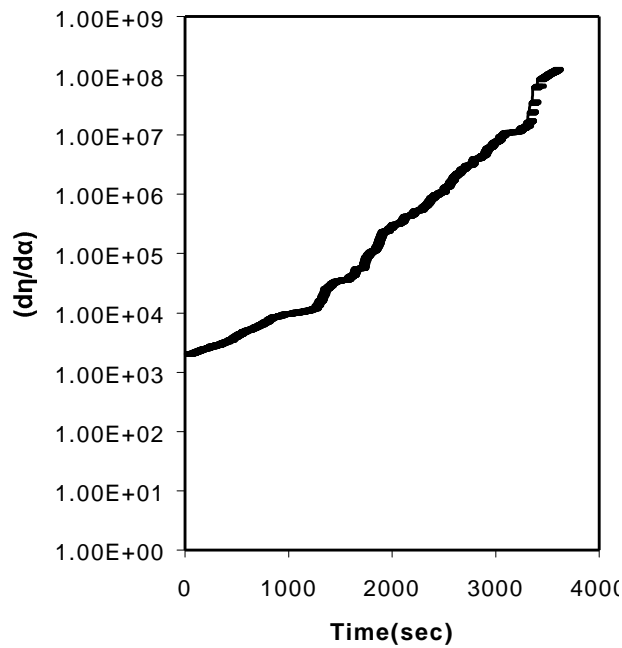


Figure 6 Variation of $(\partial h / \partial a)_{g_{yx}}$ versus time at 10 kPa and 160 °C.

CONCLUSIONS

During peroxide cross-linking of LDPE a combination of DSC measurements and creep data were used to determine the dependency of the viscosity to the degree of cross-linking. The accuracy of the analysis would be more accurate if we had access to creep experiments performed at a wider stress interval. However, it seems that the method described here will be a useful tool provided accurate kinetic modelling and a careful estimation of the initial transient of the DSC experiment.

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