

DETERMINATION OF POLYMER MELTS FLOW-ACTIVATION ENERGY

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Abstract

In this paper a method is shown to calculate the activation energy of flow of high density polyethylene (HDPE), polystyrene (PS) and polycarbonate (PC). The importance of polymer melt flow properties during processing has required continuous research of polymer melt rheology. In the previous article [1] we described how to measure polycarbonate shear viscosity between 100 to 105 s⁻¹ shear-rate region with standard and non-standard equipment This article represent that shear viscosity and activation energy of flow of the polymers depend on the chemical structure. It was found that more rigid molecular structure results higher values.

1 Introduction

The influence of temperature on the shear viscosity of polymer melts is usually expressed in terms of flow activation energy. In our previous article [1], a method was described to measure and calculate viscosity of polycarbonate melt. Using our raw results, we can calculate activation energy of flow based on known models. An approximation model for kinetic activity in chemistry was developed in the general form by Svante A. Arrhenius who introduced an "activation constant" [2]. The Arrhenius relation in the form of a $\eta(T)$ fitting function describes the change of viscosity for both increasing and decreasing temperatures:

$$\eta(T) = c_1 \cdot \exp(-c_2/T) = c_1 \cdot \exp[(E_A/R_G)/T] \quad (1)$$

with the temperature (T) in [K], and the material constants C1 [Pas] and C2 [K] of the sample (where $C_2=E_A/R_G$), the activation energy of flow E_A [kJ / mol], and the gas constant $R_G=8.314 \cdot 10^{-3}$ kJ/(mol K).

At a certain temperature, the activation energy of flow E_A characterizes the energy needed by the molecules to be set in motion against the frictional forces of the neighboring molecules. This requires exceeding the internal flow resistance, with other words, a material-specific energy barrier, the so-called potential barrier [3].

Our target was compare polyethylene, polystyrene and polycarbonate polymer types flow activation energy considering the macromolecular segment size. In theory this types of polymers looks like linear freely-jointed chains. The freely-jointed chain is the simplest model of a polymer. The Figure 1. shows differences between the polymer types monomer construction. Size of the segment is in non linear contact with the size of the monomer.

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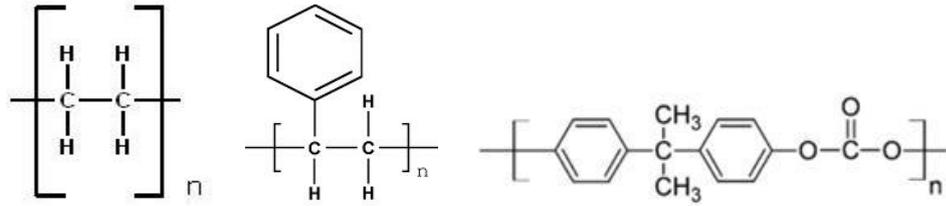


Figure 1. Monomer types of PE, PS, PC

The basic assumption that the flow activation energy based on viscosities at constant shear rate decreases as the segment size increases. Furthermore, based on viscosity decreases the shear rate the flow activation energy will increase.

The samples were PC- sample was Dow Calibre 3030 EP, PS- Eni Edistir N 3380, PE- Mol Tiplen BS-501.

2 Method

Our basic results we got from three shear viscosity investigation methods, which covers a wide range of shear rate and temperature steps near the processing temperature [1]. These were in the low shear rate range of the rotational viscometry (TA Ares G2 range: 0.05 – 30 s⁻¹), in the middle-high range of the capillary viscometry (Göttfert RG25 range: 100 – 10.000 s⁻¹) and in the high range we used a special technique (range: 10.000 – 240.000 s⁻¹) which was based on the capillary viscometry method.

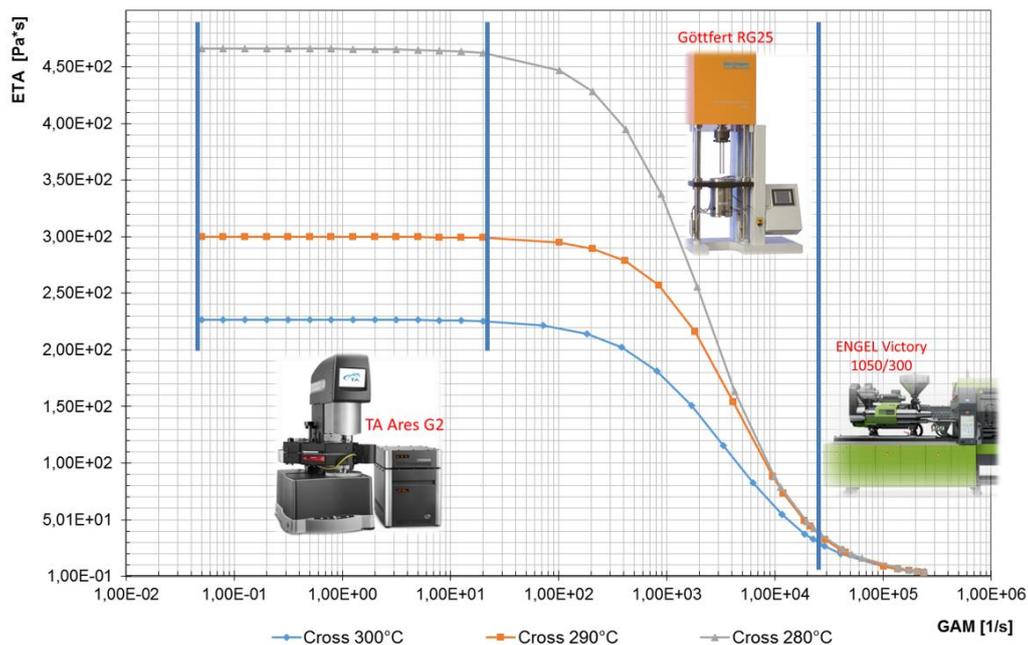


Figure 2. Polycarbonate shear viscosity raw results separated by equipments [1]

From the raw results (Figure 2.) all of the viscosity curves describe by Cross equation [3, 6].

$$\eta = \frac{\eta_0}{1 + \left(\frac{\eta_0 \dot{\gamma}}{\tau^*}\right)^{[1-n]}} \quad (2)$$

Where η is the shear viscosity (Pa*s); $\dot{\gamma}$ deformation rate (s⁻¹); η_0 zero shear viscosity (Pa*s); τ^* stress limit between the Newtonian and non Newtonian region (Pa); $[1 - n]$ slope of the transient region (-).

It was necessary for calculation shear viscosity on constant shear-rate. In this case the constant shear rate mean 100 s^{-1} value. The measured shear viscosity curves compared with the Cross equation curves it shows good correlation (Figure 3).

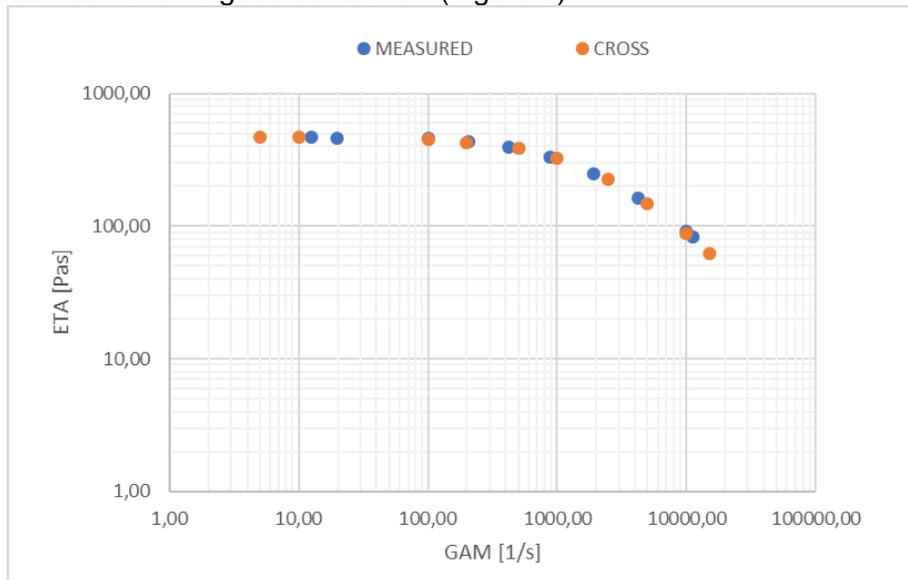


Figure 3. Measured and Cross viscosity curves compare

From the viscosity curves (described with Cross equation) we need just one point per a temperature. To calculate flow activation energy we need to calculate the shear viscosity on constant shear-rate on three temperature in $40\text{-}50^\circ\text{K}$ range $T > T_g + 100\text{K}$ (with the glass-transition temperature T_g).

3 Results

The shear viscosity of polymer melts is temperature dependent. The relationship between the shear viscosity and the temperature of the sample melts can be obtained by plotting $\ln(\eta)^*RG$ against $1/T$ (T is in the absolute temperature scale), as illustrated in Figure 4.



Figure 4. Samples $\ln(\eta)$ and $1/T$ equation

Under same shear rate, the curves of $\ln(\eta)$ versus $1/T$ are closely linear, the linearity suggesting that the dependence of the samples melt shear viscosity on temperature can be described by the Arrhenius equation general format, i.e.:

$$\eta(T) = A \exp\left(\frac{E_A}{R_G}\right) \quad (3)$$

where A is the constant related to the melt viscosity, E_A is the activation energy for viscous flow, and R_G is the universal gas constant. The calculated activation energy values is in Table 1.

Table 1 Samples activation energy

Polymer type	Flow activation energy [J/mol]
PE	5,33E+03
PS	2,75E+04
PC	9,38E+04

The flow of polymer is caused by the movement of the whole molecule, while the molecular movement is caused by the transition of the chain segment. From Figure 5. the melt flow of PC can be seen at wide shear rate range. It is necessary for the thermal motion energy of the molecular chain to be sufficiently high to overcome the internal revolve potential energy since the molecular chain of PC is rigid. As a result, the viscous flow temperature of PC is high. From these results, we can conclude that the activation energy increases with segment size.

As illustrated in Figure 5. the shear rate dependence of samples activation energy shows different behaviors. While the PE and PS samples show near linear dependence PC show nonlinear behavior.

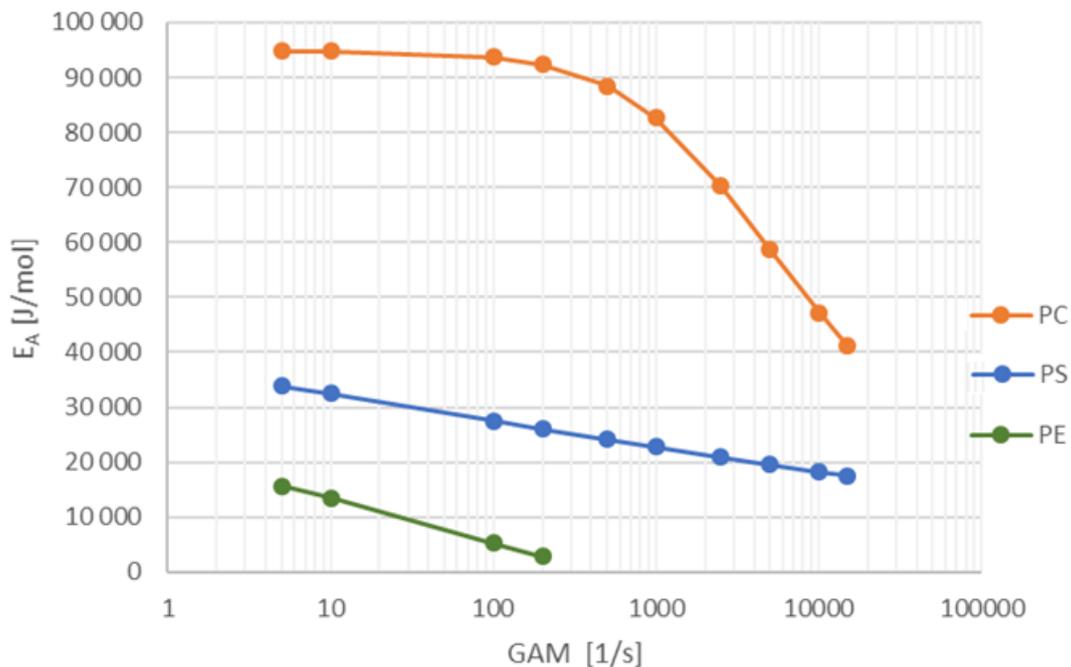


Figure 5. Activation energy shear rate dependence

As illustrated in Figure 5. the shear rate dependence of samples' activation energy shows different behaviors. While the PE and PS samples show near linear (in log scale, but it is exponential) dependence, PC shows nonlinear behavior. It is important that the shear rate dependence is not the same in low and high shear rate range (Figure 5.). Until 10^2 s⁻¹ shear rate, the activation energy is almost constant. Below this value, it decreases like the other two samples. This phenomenon needs further investigation.

It is very important that in Figure 5. the vertical axis shows already the activation energy in linear scale. The horizontal axis shows the shear rate in logarithmic scale. For this plotting mode the experiments should be made at the same temperature steps, but at different shear rate values. So that the determined activation energy for the same temperature ranges (for instance, shown in the

Figure 4.), is measured and calculated in different shear rate steps. This means that the curve in Figure 4. is shown as a point in Figure 5.

4 Conclusion

Under the present experimental conditions, the shear flow of the sample melts obeys the structural shear viscosity theory. The melt shear viscosity depends heavily on the temperature and the relationship between them can be described by the Arrhenius equation. The shear rate dependence of samples' activation energy shows different behaviors. While the PE and PS samples show near linear dependence, PC shows nonlinear behavior. It is important that the shear rate dependence is not the same in low and high shear rate range. Comparing the samples' segment size and the calculated activation energy the linear relationship has been confirmed.

Investigating the samples in constant temperature ranges a linear equation is shown, while the shear rate dependence of the activation energy is an exponential equation. To determine it, we used Arrhenius equation in constant temperature ranges, but at different shear rate values. With this method the shear rate dependence of the activation energy can be calculated using Arrhenius equation.

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