## - 2 -

# HOW TO INVESTIGATE THE INFLUENCE OF TEMPERATURE WITH A MFI-TYPE DEVICE?

## A. CALCUATIONS

### 1) *WLF equation*

The empirical relationship of Williams-Landel-Ferry (or WLF law) was described for the first time in 1955, in their article entitled "The Temperature Dependence of Relaxation Mechanisms in Amorphous Polymers and Other Glass-forming Liquids". It helps to know the evolution of the viscosity of polymers according to the temperature.

Nevertheless, this law is only valid for temperatures near the glass transition temperature $T_g$ (i.e. in the interval [$T_g$ ; $T_g$ + 50°C]).

The WFL is:

$$\ln \mu = \ln \mu_0 - \frac{C_1(T - T_0)}{C_2 + T - T_0}$$

The constants $C_1$ (without unit) and $C_2$ (°C) depend on the polymer and $T_0$, a suitably selected reference temperature. For many polymers, orders of magnitude of $C_1$ and $C_2$ are respectively 15 and 50 ° C.

When $C_1$ and $C_2$ are unknown, it is necessary to measure the viscosity at different temperatures and plot the curve:

$$\frac{1}{\ln\left(\frac{\mu}{\mu_0}\right)} = f\left(\frac{1}{T - T_0}\right)$$

If the resulting curve is a straight line of equation y = ax + b, so:

- $C_1 = 1 / b$;
- $C_2 = a / b$.

If the resulting curve is not a straight line, the WLF law does not adequately describe the variation of the viscosity as a function of temperature. The Arrhenius law is then used.

### 2) *Arrhenius law*

It is conventional to use an Arrhenius law for describing the variation of the viscosity with the temperature above $T_g$ + 100 ° C. The equation governing this variation is as follows:

$$\mu = \mu_0\, e^{\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)}$$

Where $E_a$ is the activation energy of viscous flow, varies from one polymer to another (for PE, the value can vary from 10 to 90kJ/mol depending on the type of PE, molar mass and branching[1]), R is the gas constant (= 8.3145 $J.mol^{-1}.K^{-1}$) and $\mu_0$ is the viscosity at the reference temperature $_{T0}$.

In this case, the activation energy is unknown. To know it, simply plot the curve ln μ = f(1/T), the slope K is equal to $E_a/R$.

## B. METHOD

The method used is identical to that used in the first article.

Temperatures studied were 150°C, 170°C, 190°C, 210°C and 230°C.

## C. RESULTS

The curves of the natural logarithm of the true viscosity as a function of the natural logarithm of the shear rate as a function of temperature are shown in the graph below (*Figure 1*).

Le traitement complet des paramètres rhéologiques tel qu'effectué au cours du premier article est résumé dans le *Tableau 1*.

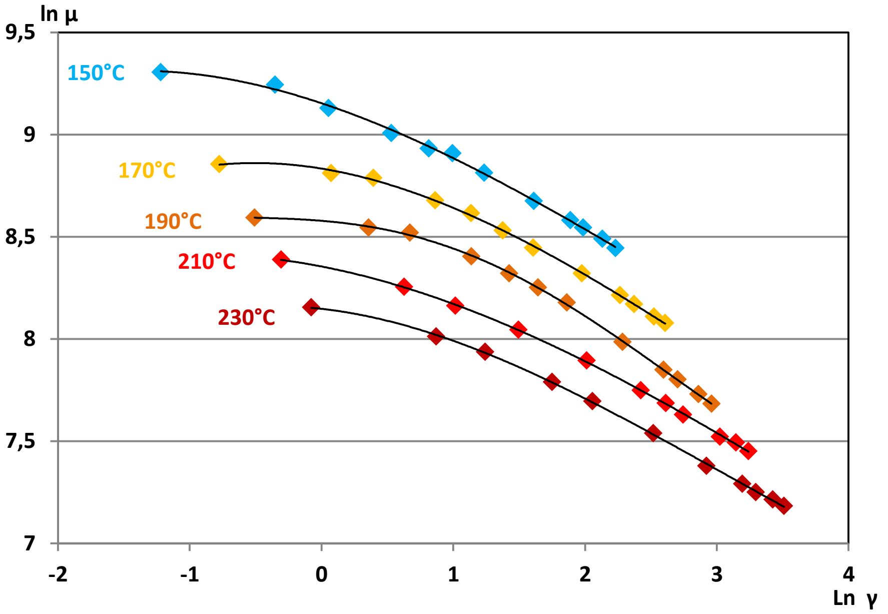

**Figure 1:** ln μ = f (ln γ) curve at different temperature.

| Temperature (°C) | Newtonian viscosity $\mu_N$ (Pa.s) | Critical shear rate $\gamma_{cr}$ ($s^{-1}$) | Rheological equation (above de $\gamma_{cr}$) |
|---|---|---|---|
| **150°C** | 11000 | 0,86 | $\mu = 10605.\gamma^{-0,37}$ |
| **170°C** | 7015 | 1,49 | $\mu = 8824.\gamma^{-0,39}$ |
| **190°C** | 5700 | 2,23 | $\mu = 8310.\gamma^{-0,45}$ |
| **210°C** | 4400 | 2,34 | $\mu = 5673.\gamma^{-0,37}$ |
| **230°C** | 3750 | 2,39 | $\mu = 4212.\gamma^{-0,33}$ |

Tableau 1: **Rheological data at different temperatures.**

First, the WLF law is applied. Nevertheless, we see (*Figure 2*) that the resulting curve is not a straight line. This method of treatment is therefore not suitable to determine the change in viscosity as a function of temperature in this case. Since the material used is polyethylene ($T_g \approx 100$ ° C) and that one is outside of the range of temperature [$T_g$; $T_g + 50$ ° C], this result makes sense.

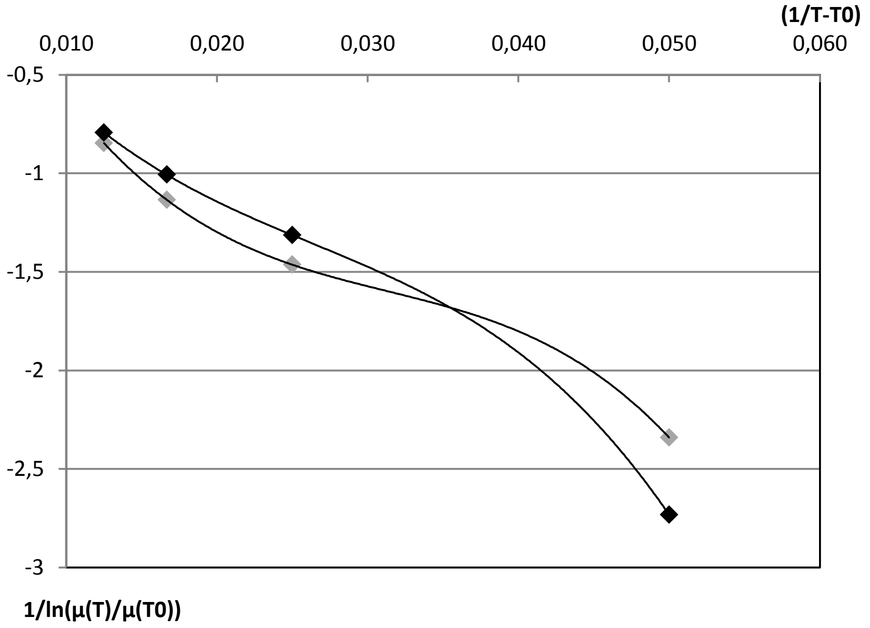

**Figure 2:** Determination of the WLF equation constants.

Subsequently, a mathematical treatment Arrhenius law-type was used. The curves obtained for different stresses are straight (*Figure 5*). All have the same slope.

So **$E_a$ = 27,5 ± 0,8 kJ/mol**. This value is in agreement with values found in the literature for LDPE[2-5].

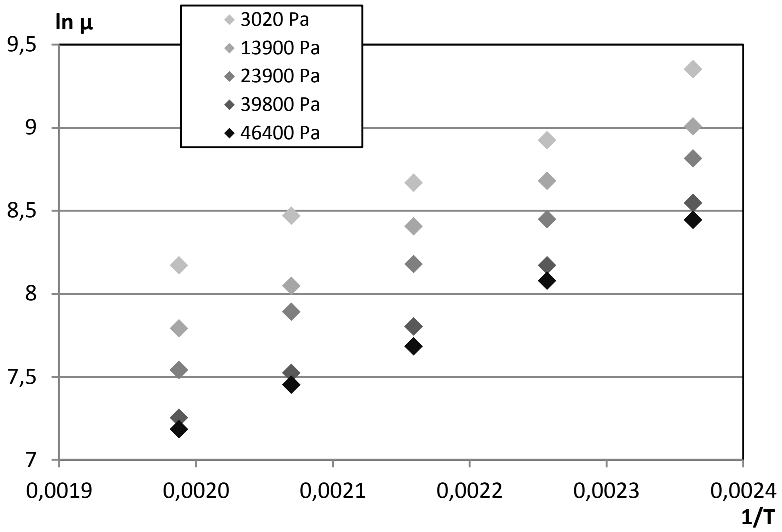

**Figure 3:** Determination of the Arrhenius law parameters.

| **Stress (MPa)** | 3,0 | 7,0 | 9,5 | 13,9 | 17,4 | 20,4 | 23,9 | 30,8 | 37,3 | 39,9 | 43,8 | 46,4 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Slope** | 3007 | 3227 | 3206 | 3264 | 3226 | 3391 | 3301 | 3435 | 3371 | 3452 | 3382 | 3362 | **3302** ± **97** |

## *D. CONCLUSION*

In the second part on the study of the rheological behavior of thermoplastics with a MFI, we measured the effect of temperature on viscosity. Different models were used: WLF and Arrhenius. The latter gave satisfactory results and a value of activation energy was calculated. This value can be used to optimize the processing temperature:

- Hence by increasing the temperature to increase fluidity and thus, reduce cycle/dwell time (and being careful not to degrade the material);
- Hence by lowering the temperature to reduce the carbon footprint of its production.

In the third and final article, we will discuss the phenomena of swelling at the die exit.

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### *Suggested bibliographic reference*

**[1]** C.VASILE, M. PASCU; *Practical Guide to Polyethylene,* Rapra Technologies Limited (2005).

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**[3]** Xiaohua QIU, M. D. EDIGER, *Branching Effects on the Segmental Dynamics of Polyethylene Melts*, Journal of Polymer Science: Part B: Polymer Physics 38 (2000) 2634–2643.

**[4]** Junting XU, Xurong XU, Qiang ZHENG, Linxian FENG, Wai CHEN, *Dynamic rheological behavior of metallocene-based ethylene-butene copolymers and their blends with low density polyethylene*, Eur. Polym. J.l 38 (2002) 365-375.

**[5]** Claudio J. PEREZ, Guillermo A. CASSANO, Enrique M. VALLES, Marcelo D. FAILLA, Lidia M. QUINZANI, *Rheological study of linear high density polyethylenes modified with organic peroxide*, Polymer 43 (2002), 2711-2720.