

TEMPERATURE AND STRAIN RATE EFFECT ON MECHANICAL PROPERTIES OF ETHYLENE-PROPYLENE BLOCK COPOLYMERS

T. Gómez-del Río, A. Salazar, A. Cea, R. Hernández, J. Rodríguez

Departamento de Ciencia e Ingeniería de Materiales,
Escuela Superior de Ciencias Experimentales y Tecnología,
Universidad Rey Juan Carlos, C/ Tulipán s/n, Móstoles, 28933 Madrid, España.
E-mail: jesus.rodriquez.perez@urjc.es

ABSTRACT

The effect of temperature and strain rate on elastic modulus, Poisson's ratio and yield stress of several ethylene-propylene block copolymers with different ethylene content is analyzed. To determine the elastic properties, a video-extensometer is used. The experimental results are interpreted in terms of the well known principle of temperature-time equivalence. Several models have been considered to explain the significant increase in the yield stress at lower temperatures or higher strain rates.

KEYWORDS: yield stress, strain rate, temperature, ethylene-propylene block copolymers.

1. INTRODUCTION

Polypropylene is one of the most used thermoplastics due to its balanced properties, cost and recyclability [1]. There is a severe disadvantage for the application of isotactic polypropylene as engineering plastic: its low fracture toughness, in particular at low temperatures and/or under impact conditions. The improvement of the mechanical properties under impact conditions can be achieved by the incorporation of a dispersed rubbery phase in PP matrix which induces the appearance of toughening mechanisms. The rubber modification of PP can be performed by physical blending with various types and amounts of modifiers or by copolymerization with other polyolefins with lower glass transition temperatures, T_g , than PP, such as the polyethylene. The resulting block copolymers are heterophasic materials with a two phase structure where an elastomeric phase in form of spherical domains, usually ethylene-propylene copolymer rubber (EPR), is dispersed uniformly within the PP homopolymer matrix [2, 3]. The increased application of polypropylene for load-bearing structures has led to renewed interest in the study of its mechanical behaviour at different loading rates and temperatures.

Many molecular theories have been proposed for the prediction of the yield stress of amorphous polymers. These models consider the yield behaviour as a thermally activated process affected by strain rate and temperature. The first model known is the Eyring theory [4], initially developed for shear induced in viscous fluid, but successfully used to describe the yielding process of solid polymers. Macroscopic yielding is assumed to be the result of basic processes consisting of jumps of macromolecular segments from one equilibrium position to another through a potential

energy barrier. The yield stress is given by the following expression:

$$\frac{\sigma_y}{T} = \frac{k}{V} \sinh^{-1} \left(\frac{\dot{\epsilon}}{\dot{\epsilon}_0 \exp\left(-\frac{\Delta H}{kT}\right)} \right) \quad (1)$$

where σ_y is the yield stress, T the absolute temperature, k the Boltzmann's constant, V an activation volume, ΔH an activation energy, $\dot{\epsilon}$ the strain rate and $\dot{\epsilon}_0$ a constant.

In many systems, yielding has to be described at least by two processes simultaneously active. In those cases, two activation volumes, V_1 and V_2 , and two activation energies, ΔH_1 and ΔH_2 , have to be used. The resulting equation can be written as:

$$\frac{\sigma_y}{T} = \frac{k}{V_1} \left[\ln \left(\frac{2\dot{\epsilon}}{\dot{\epsilon}_{01}} \right) + \left(\frac{\Delta H_1}{kT} \right) \right] + \frac{k}{V_2} \sinh^{-1} \left(\frac{\dot{\epsilon}}{\dot{\epsilon}_{02} \exp\left(-\frac{\Delta H_2}{kT}\right)} \right) \quad (2)$$

where $\dot{\epsilon}_{01}$ and $\dot{\epsilon}_{02}$ are constants that can be obtained by fitting of experimental data. Bauwens-Crowet et al. [5, 6] used successfully this equation in several amorphous thermoplastics.

Fotheringham and Cherry [7] introduced the idea that yielding needs the cooperative motion of multiple chain segments. They modified the original Eyring equation raising the hyperbolic sine function to the n th power (n segments participating in the process) and introducing an internal stress as a new structural parameter. Richeton et al. [8] in a recent development extended the

cooperative model to a wide range of strain rates and temperatures, below and above the glass transition temperature. The expressions provided by the cooperative model so extended are given by:

$$\frac{\sigma_y}{T} = \frac{\sigma_i(0) - mT}{T} + \frac{2k}{V} \sinh^{-1} \left[\frac{\dot{\epsilon}}{\dot{\epsilon}_0 \exp\left(-\frac{\Delta H_\beta}{kT}\right)} \right]^{1/n} \quad \text{for } T \leq T_g \quad (3)$$

$$\frac{\sigma_y}{T} = \frac{2k}{V} \sinh^{-1} \left[\frac{\dot{\epsilon}}{\dot{\epsilon}_0 \exp\left(-\frac{\Delta H_\beta}{kT_g}\right) \exp\left(\frac{\ln 10 \times c_1^g (T - T_g)}{c_2^g + T - T_g}\right)} \right]^{1/n} \quad \text{for } T > T_g \quad (4)$$

where ΔH_β is the β activation energy; c_1^g and c_2^g are the Williams-Landel-Ferry (WLF) parameters at the glass transition temperature, T_g , $\sigma_i(0)$ is the internal stress at 0 K and m is a material parameter roughly equal to $\sigma_i(0)/T_g$ in the case of amorphous polymers [9].

Most of the previous models are not focused on semicrystalline materials. Gueguen et al. [10] considered that semicrystalline polymers, unlike amorphous ones, are less sensitive to variations of stiffness above the glass transition and below the melt temperature. As a consequence, they used the classical form of the cooperative model with the Arrhenius law, rather than the modified form according to WLF theory, for temperatures above the glass transition. They also maintain the linear dependence of the internal stress for temperatures above T_g .

$$\frac{\sigma_y}{T} = \frac{\sigma_i(0) - mT}{T} + \frac{2k}{V_{eff}} \sinh^{-1} \left[\frac{\dot{\epsilon}}{\dot{\epsilon}_0 \exp\left(-\frac{\Delta H_{eff}}{kT}\right)} \right]^{1/n} \quad (5)$$

where ΔH_{eff} and V_{eff} are the effective activation energy and activation volume, respectively. These parameters were obtained from the activation parameters of the amorphous phase, ΔH_a and V_a , and of the crystalline phase, ΔH_c and V_c .

In this work, the tensile behavior of three semicrystalline ethylene-propylene block copolymers is analyzed at different strain rates in a wide range of temperatures (from -120 to 23 °C). The applicability of the previously described models will be evaluated on the base of a general acceptance of the time-temperature superposition principle.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

The materials studied were three commercial grade ethylene-propylene block copolymers: EPBC1, EPBC5 and EPBC7, supplied by Repsol in form of pellets. The specimens were prepared by injection molding. The basic characteristics such as the ethylene content, the

molecular weight, M_w , and the glass transition temperatures are collected in Table 1.

Table 1. Basic properties of the copolymers under study

	Ethylene content (%)	M_w (kg/mol)	T_g PP (°C)	T_g EPR (°C)	Cryst. Index (%)
EPBC1	7.0	816	19.5	-44.4	41.6
EPBC5	8.5	353	18.1	-48.0	44.6
EPBC7	8.5	302	19.0	-45.1	45.3

Tensile tests were carried out in an electromechanical testing machine (MTS RF/100) with load cells between ± 2.5 kN and ± 30 kN, following the ISO-527 guidelines and changing the cross-head speed (from 1 mm/min to 100 mm/min) and the temperature (from -120 °C to 20 °C). Strains in the specimens were measured by a contact extensometer (MTS 634-12F-54) and also using a LIMESS video-extensometer. Raw data of longitudinal and transversal displacements were simultaneously recorded to extract Young's modulus and Poisson's ratio. From the loading history, the yield stress could be derived. The low temperature tests were conducted placing the load train (hinges, grips or bending fixture and sample) inside an environmental chamber (MTS 651.06E-03), which was connected to a Dewar flask containing liquid nitrogen. The cooling process consisted of adding liquid nitrogen continuously until the load frame ceased to move to balance the thermal contractions and maintains a constant load of 15 N on the specimen. Once the target temperature was reached and before starting the test, conditioning was held 20 minutes more to guarantee that the specimen was in thermal equilibrium.

3. RESULTS AND DISCUSSION

Figure 1 shows an example of the characteristic stress-strain curves of the copolymers tested. The effects of temperature and strain rate are presented in Figures 1a and 1b, respectively. Independently of the material and the testing conditions, the same tendency is observed: the yield stress decreases as the strain rate is reduced and the temperature is increased. It should be taken into account that at the lower temperatures of -80 °C and -120 °C no yielding but brittle fracture was detected.

The effect of temperature on the values of Young's modulus, Poisson's ratio and yield stress are summarized in Figure 2. The strain rate during the tests included in these graphs corresponds to $\sim 2.6 \cdot 10^{-4} \text{ s}^{-1}$. Young's modulus increases its value from 1.5 GPa at 20 °C to ~ 5 GPa at -120 °C. The most notable variation is observed after passing the glass transition temperature, T_g , of the polypropylene matrix. The material stiffness is mainly controlled by crystallinity. Thus, due to the very similar values of crystallinity index, no significant differences are expected between materials at room temperature. At temperatures lower than T_g , the role played by the different ethylene content or molecular weight becomes greater. The values of the

Poisson's ratio are very similar in the three materials under study, ranging from 0.4 at room temperature to 0.3 at -120 °C.

The yield stress is around 20 MPa at room temperature for the three copolymers tested. A huge increase is observed, especially at temperatures lower than the T_g of the elastomeric phase, T_g EPR, up to values close to 100 MPa. Its lower ethylene content and its higher molecular weight justify the higher values of yield stress measured in the material EPBC1.

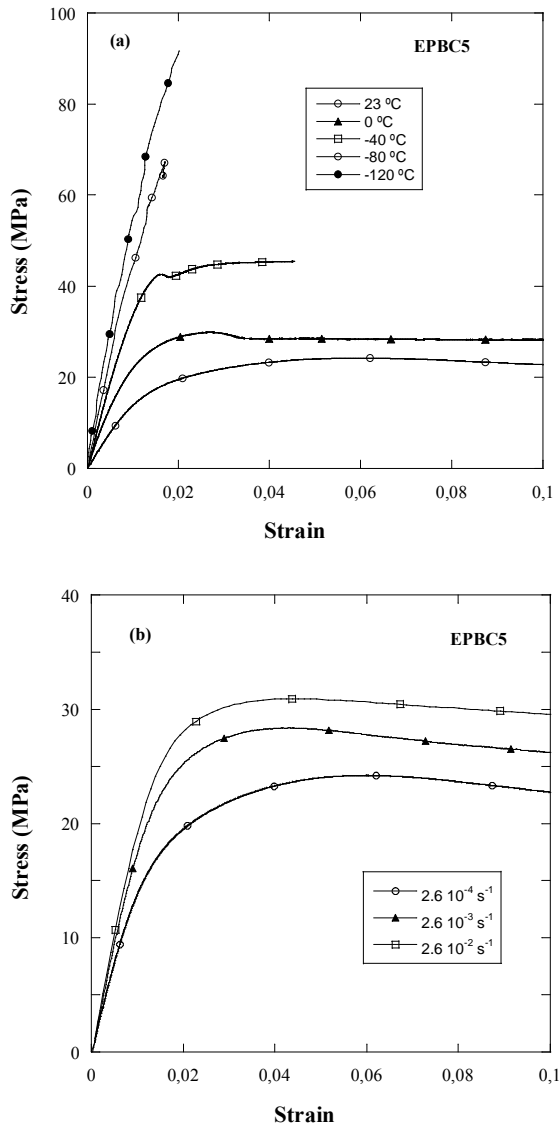


Figure 1. Stress – strain curves of EPBC5 at (a) different temperatures and 0.00026 s^{-1} and (b) different strain rates and 23 °C.

Figure 3 shows the effect of strain rate on the yield stress at several temperatures. In the limited range analyzed, from 10^{-4} to 10^{-2} s^{-1} approximately, yield stress exhibits moderate augment with the strain rate.

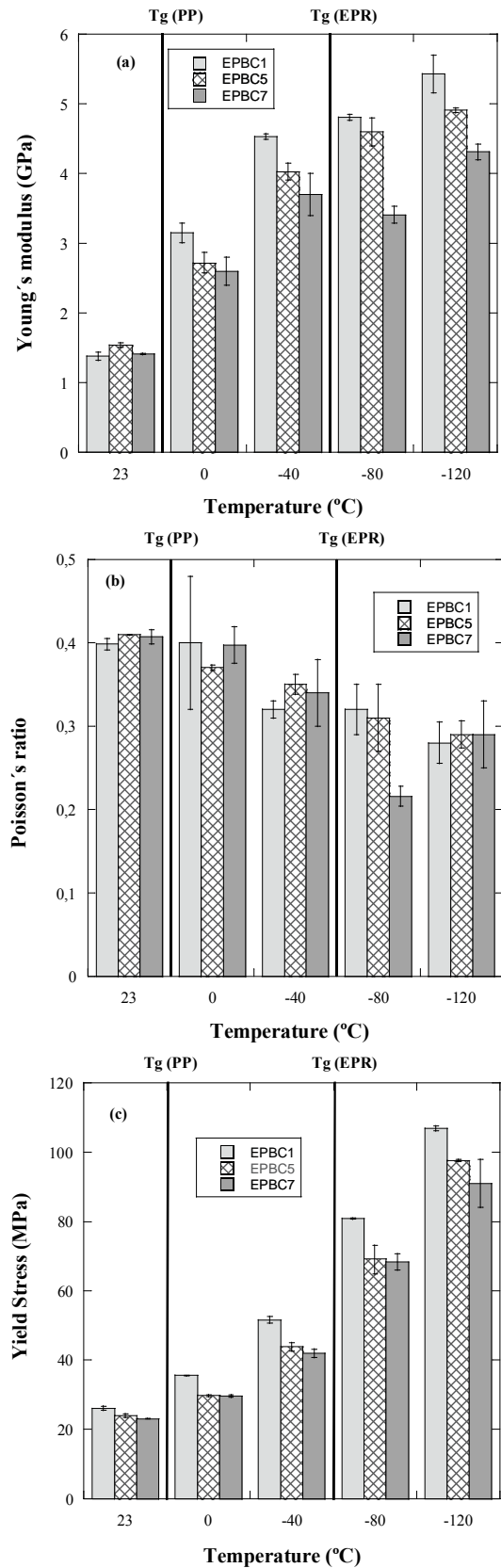


Figure 2. Influence of temperature on Young's modulus, Poisson's ratio and yield stress.

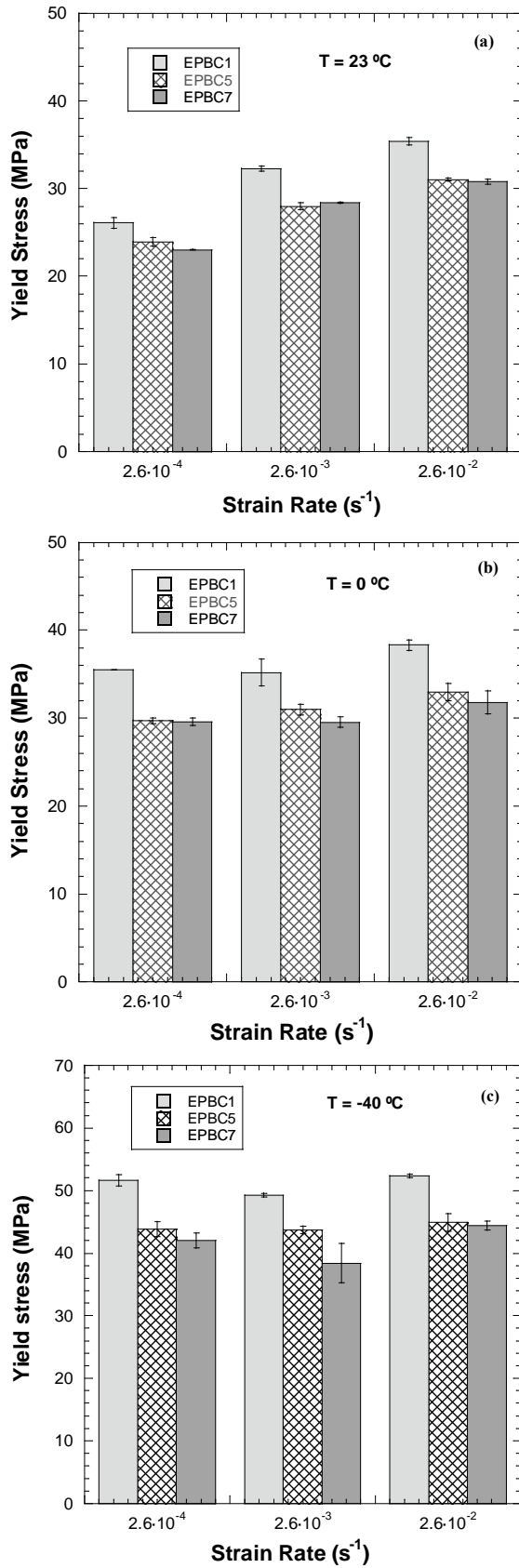


Figure 3. Influence of strain rate on the yield stress at different temperatures.

Considering the semicrystalline nature of the materials analyzed and assuming that they verify the

well known strain rate-temperature superposition principle, i. e., a decrease in temperature will have the same effect on the yield stress as an increase in strain rate, the reduced yield stresses σ_y/T versus $\log \dot{\epsilon}$ can be combined to generate a master curve at a reference temperature, T_{ref} . Original data must be shifted horizontally and vertically according to the following expressions [8]:

$$\Delta(\log \dot{\epsilon}) = \frac{\Delta H_{eff}}{k \ln 10} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \quad (6)$$

$$\Delta \left(\frac{\sigma_y}{T} \right) = -\sigma_i(0) \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \quad (7)$$

Once the T_{ref} of $23 \text{ }^{\circ}\text{C}$ has been chosen, the parameters ΔH_{eff} and $\sigma_i(0)$ can be derived until a unique master curve is generated. The values of ΔH_{eff} and $\sigma_i(0)$ finally selected are those providing the best fit of the experiments. The remaining parameters, m , V_{eff} , n and $\dot{\epsilon}_0$, can be calculated fitting the data of the master curve to equation 5, as it is shown in Figure 4. An acceptable agreement between experiments and model is achieved, taken into account that data from tests performed at different temperatures and strain rates are considered.

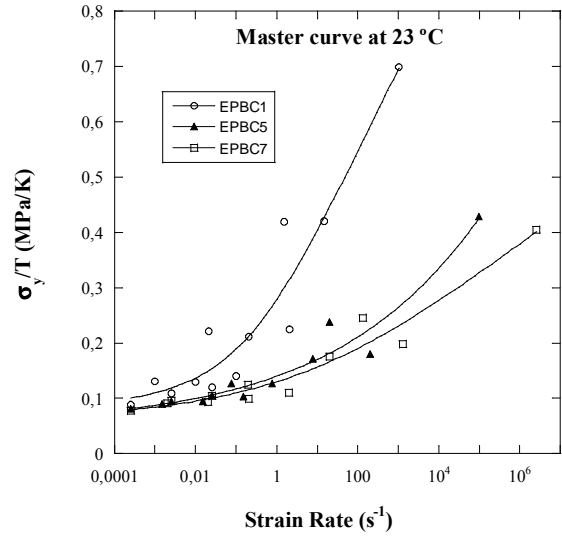


Figure 4. Master curve at $23 \text{ }^{\circ}\text{C}$ showing the reduced yield stress versus strain rate for the three different copolymers under study.

Table 2 shows the model parameters obtained for materials under study. They are in the same order of magnitude than those found in bibliography for other thermoplastics, such as PET and polyethylene [10]. Apart from this, the values of the parameters m and $\sigma_i(0)$ are consistent with the relationship predicted by Rault [9].

Table 2. Parameters of the tensile yielding model.

PARAMETERS	EPBC1	EPBC5	EPBC7
n	3,23	5,47	6,78
$V_{\text{eff}}(\text{m}^3)$	$1,38 \cdot 10^{-28}$	$2,76 \cdot 10^{-28}$	$1,70 \cdot 10^{-28}$
$\sigma_i(0)$ (MPa)	74,4	66,2	60,3
m (MPa K ⁻¹)	0,17	0,16	0,15
$\dot{\epsilon}_0$ (s ⁻¹)	$1,14 \cdot 10^7$	$6,5 \cdot 10^{11}$	$1,18 \cdot 10^{13}$
$\Delta H_{\text{eff}}(\text{kJ mol}^{-1})$	40	52	60,6

4. CONCLUSIONS

Tensile tests at different temperatures (-120°C - 23 °C) and strain rates (10^{-4} - 10^{-2} s⁻¹) have been carried out in three ethylene-propylene block copolymers. From the experimental results the following conclusions can be ascertained:

- Polypropylenes under study show a significant increase of their tensile yield stress stress as temperature is decreased. This increase is accentuated with the strain rate, in agreement with the time – temperature superposition principle.
- Under the testing conditions, the material with the highest molecular weight exhibits more sensibility to strain rate and temperature.
- The extension of the cooperative model to semicrystalline polymers seems to provide reasonable results in ethylene-propylene block copolymers at cryogenic temperatures and moderate strain rates.

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