Mechanical Characterization of two Amorphous Polymers in Traction-Compression Test using A Viscoelasticimeter

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***Abstract*—** *Using the viscoelasticimetric tests in traction and compression mode, the viscoelastic sizes E', E" and tanδ were characterized according to the temperature and this, for amorphous polymer samples differentiated by their fluidity index. It is noted that the stiffness is intermediate size making it possible to characterize the conservative components E' easily and the dissipative one E" of the module complexes E* like its temperature of glass (vitreous) transition from polymer trough the factor of loss tanδ. These sizes in comparison with the abundant data by the manufacturers make it possible to consolidate the mode of request retained:*

- *The temperature of vitreous transition Tg obtained on the two samples from methylpolymethacrylate (PMMA) in modetraction compression is integrated in the interval of temperatures (110 to 135°C) advised by the manufacturers of this material.*
- *The ranks of polycarbonate (PC) tested in the two modes had a constancy of behaviour with Tg quasi equivalent to150°C with a variation of 5°C.*

Keywords*— *amorphous polymer, viscoelacticimetry, temperature, vitreous transition.

I. INTRODUCTION

The behavior of polymeric materials, by taking temperature as a descriptive variable of their hierarchization, makes it possible to specify in particular the domain of their specific properties which concern:

- The solid-state viscoelastic materials associated with the notion of rigid-rubber transition,
- The more intuitively characteristic flows of a viscous liquid state.

These two aspects define the rheological behavior of these materials and we simply recall that rheology is, as a first approach, the science that studies the evolution of the deformation and flow of condensed phases under imposed stress. In practice, the dependent parameter may be in addition to the temperature, the deformation or the rate of deformation.

In addition, pasty solid-solid, solid-solid, viscous solid, viscous-liquid solid, solid-liquid, liquid-liquid solid passages are sometimes difficult to apprehend. This is explained by the fact that these different state phases are sometimes a function of the temperature of the test, the mode of loading and the time of application.

The range of reference temperatures that make it possible to qualify the evolutions of polymer materials via thermal experimental references mainly comprises [1-16], [26]:

- The glass transition temperature;
- The Vicat softening temperature;
- The Martens temperature;
- The embrittlement temperature;
- The temperature of deflection under load;
- The liquid-liquid transition temperature;
- The freezing temperature;

- The melting temperature in the case of semi-crystalline polymers.

On this basis, it was envisaged to carry out a structured study concerning a contribution to the qualification of the rheology of different amorphous polymeric materials: polymethylmethacrylate (PMMA), polycarbonate (PC), polyetherimide (PEI), materials selected for their practical applications.

General laws of rheological behavior can in fact be released without involving molecular approaches complementary to these descriptive approaches.

To qualify the linear viscoelastic behavior of polymeric materials [2, 4, 6, 17-19], recalling classically that these materials have an intermediate behavior between that of an elastic solid obeying the Hooke's law (or in shear to the relation) and that of a viscous liquid described by Newton's law (that is to say the relation $\tau = \eta (\gamma)^{\cdot}$ [3, 6, 10, 12, 20, 21].) We opted to conduct experiments in dynamic mode at using tensile-compression type tests using a viscoelasticimeter, in order to determine the dynamic quantities in terms of complex modulus, of loss factor, with the aim of achieving a hierarchy of observed behaviors.

The resulting representations are of the type: Modules (dissipative or conservative) function of the temperature f (T).

The apparatus, which in principle can be considered as a "capillary rheometer", has been used by imposing different loads on the material so as to obtain experimental data which can be presented in the form of rheograms:

$$\tau = f(\dot{\gamma}) \tag{1}$$

It is on this basis that the work carried out has been implemented paying particular attention to:

a) In the first place to the experimental determination of the characteristic temperatures and following different complementary approaches.

The variability or the conservatively of these data being associated with the different selected materials ranked in first approach according to the value of their melt index.

b) In the second place to the rheological evolutions of the polymers taken as model of behavior, and this according to an apparatus currently or not used for these determinations.

The originality of the chosen approach concerns the different geometrical configurations that are sometimes non-standard and their extrapolation makes it possible to obtain descriptive rheograms of the properties of use.

II. MATERIAL AND METHOD

2.1 Material

The device used at the Laboratory of Surface Microanalysis (LMS) was a visco-analyzer brand Metravib. (Fig. 2) schematizes the various functional components of the apparatus which are:

- A frequency exciter operating in the range 7.8 - 1000 Hz,
- A displacement sensor which directly measures the displacement for the frequency selected for the tests,
- A force sensor,
- A phasemeter calculating and displaying the phase difference between the signals supplied by the displacement sensor and those originating from the force sensor,
- An amplifier which filters, amplifies and converts the displacement and force signals into proportional DC voltages so as to allow direct display of the stiffness,
- A temperature regulator of the enclosure in which the sample is positioned.

Practically one imposes for a frequency of stress, an initial deformation, as well as the amplitude of deformation on both sides of the imposed value.

The experimental variable is the temperature selected in the range [20; 200 ° C] for the amorphous materials retained in this work.

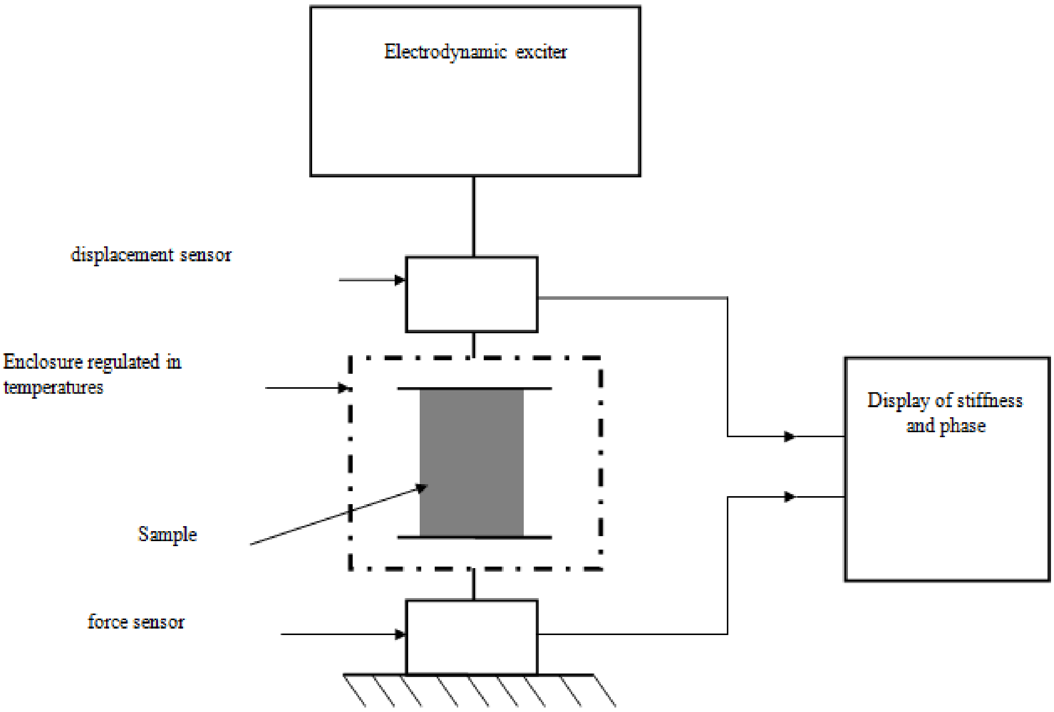

FIGURE 1: Schematic representation of the visco-analyzer metavib principle [7, 22]

The massive sample of defined geometry (parallelepiped or cylinder) is positioned by gluing between two trays of the sample holder (see Figure 1).

2.2. Method

The materials selected for this work, PMMA amorphous polymers and PC, were selected from the polymers that we studied in our PhD work [26].

Samples of tested materials are shaped by cutting into polymer sheets.

We deduce the values associated with the notions of:

- excited surface (Se = π R2 case of the cylinder, Se = L x l case of the parallelepiped, R being the radius, L and l being respectively the length and the width),
- free surface (Sl = 2π R H case of the cylinder, Sl = 2 H (L + l) case of the parallelepiped), if H is the height of the cylinder or the parallelepiped,

Which make it possible to apprehend the value of the form factor [18, 20].

$$f_c = \frac{1}{1 + 2\left[\frac{S_e}{S_l}\right]^2} \tag{1}$$

To overcome the correction, we seek a corrective factor equal to unity. Most often one selects L = 20 mm, l = 10 mm, H = 20 mm, R = 5 mm,

Which gives:

Se = 40 mm^2 and Sl = 600 mm^2, ie fc = 0.996 for the parallelepiped, and

Se = 78.5 mm^2, Sl = 314 mm^2, ie fc = 0.89 for the cylinder.

Several works [1, 4, 5, 10-13] have shown that from the stiffness k, a non-conservative size of a material, one can model its elastic and viscoelastic properties.

Generally, the quantification of k is determined by making the ratio of the applied force (ΔF) to the associated displacement (Δx):

$k = \frac{\Delta F}{\Delta x}$,k expressed in g.μm^{-1} or in N.m^{-1}

Stiffness metrology, which is a Young's modulus-related quantity E for a constant sample geometry $k = \frac{ES}{L}$ where S and L are characteristics of the geometry of the sample), is often carried out via the following mechanical test methods: compression, tension, shear, bending, buckling or torsion [14] [15].

A corrective factor fc is associated with k to take into account the so-called lateral deformation in the sample [3]:

$$k = f_c \cdot E \frac{S}{L} \tag{3}$$

Since, with the chosen test apparatus, we work in dynamic mode, the notion of dynamic stiffness k* is introduced by expressing:

$$\left|k^*\right| = \left|\frac{F(t)}{x(t)}\right| = f_c E^* . \frac{S}{L} = k' + i\, k'' \tag{4}$$

The final expression of k*, just like that of the dynamic complex module E* = E'+ i E', is dependent on the rheological model selected to describe the behavior of the material.

It is recalled that k ', E' respectively correspond to the stiffness and the conservative module, and k ", E " are associated with the dissipative quantities of the stiffness and the complex modulus.

III. RESULTS AND DISCUSSION

Different rheological models combining springs and dampers make it possible to describe the viscoelastic behavior of materials [1, 5, 10, 12, 17] and we will not recall for the record that the results are associated with the Kelvin-Voigt model.

This conventional model consists of a spring and a damper of characteristic η in parallel circuit, both subjected to a force F (t) generating a deformation ε (t) resulting from the displacement x (t) caused. The descriptive constraint of the Kelvin-Voigt model is written:

$$\sigma(t) = E\, \varepsilon\,(t) + \eta \frac{d\varepsilon(t)}{dt} \tag{5}$$

The complex quantities F * and x * associated with the values of F (t) and x (t) are such that [5, 7, 13, 18-20]

$$F^* = k \cdot x^* + \eta \frac{S}{L} \frac{dx^*}{dt} \tag{6}$$

The complex quantities F * and x * associated with the values of F (t) and x (t) are such that [5, 7, 13, 18-20]

$$k^* = k\left[1 + \eta \frac{S}{L} \frac{i\omega}{k}\right]$$

$$k_{dyn} = \left|k^*\right| = k\sqrt{1 + \frac{\omega^2}{k^2}\left(\eta \frac{S}{L}\right)^2} \tag{7}$$

Expression that one writes fluently according to the loss factor tanδ :

$$k_{dyn} = k\sqrt{1 + \tan^2 \delta} > k_{stat}$$

From the expression of k * we can go back to the dynamic module E *.

$$\begin{cases} E' = k'\dfrac{L}{S} = k\dfrac{L}{S}\cos\delta \\ E'' = k''\dfrac{L}{S} = k\dfrac{L}{S}\sin\delta \\ \tan\delta = \dfrac{E''}{E'} = \dfrac{k''}{k'} \end{cases} \tag{8}$$

These expressions do not take into account the form factor fc.

From a practical point of view, it is recalled that the equipment used gives for a given geometry of samples (S and L), values of k and δ.

3.1 Fractional Derivative Models [3, 19, 21] [7]

The mathematical tool associated with the fractional derivation is based on the introduction of an operator, the derivative of order a with respect to the time t($D_t^\alpha = \dfrac{d^\alpha}{dt^\alpha}$ with $0 < \alpha < 1$), in writing the equations governing the associated rheological models.

In the case of the Kelvin-Voigt model, the classical expression of σ (t) written in the form

$$\sigma(t) = E\,\varepsilon(t) + \eta\frac{d\varepsilon(t)}{dt} \text{ becomes : } \sigma(t) = ED_t^\alpha\varepsilon(t) + \eta D_t^\alpha\varepsilon(t) \tag{9}$$

D_t^α is called fractional derivative with $0 \le \alpha \le 1$

For a viscoelastic material described by the fractional model of Kelvin-Voigt we have:

$$T\,F\left[D_t^\alpha\sigma(t)\right] = [E + \eta(i\omega)^\alpha]TF[\varepsilon(t)] = E^*\ TF[\varepsilon(t)] \tag{10}$$

Since it is shows that the Fourier transform of D_t^α f(t) is written:

$$TF\left[D_t^\alpha f(t)\right] = (i\omega)^\alpha TF[f(t)] \tag{11}$$

This method used in the thesis of MARTIN C. [7] allows in particular to easily apprehend the value of δ.

3.2 Results and discussion

The work yielded numerical data which led to the representative curves of the modules E '(T), E "(T) and the loss factor tanδ (T). They describe the dynamic behavior of the different classes of polymeric materials, selected according to their differentiated melt index are shown in Figures 3 to 5 and in Table 1.

The following comments may be associated with them:

a) For polymethyl methacrylate (PMMA) material, it is noted (see Figures 2 to 4):

A decrease in the conservative (E ') and dissipative (E ") modules as a function of the increase in the melt index, which results in a decrease in the dynamic modulus as a function of the increase in the value of this index (see Table 1),

A measurable variation of the glass transition temperature determined in dynamic mode for the two melt flow indices selected.

b) These modifications observed on the amplitudes of the modules and the descriptive temperatures of the viscoelastic behavior are found on the material polycarbonate (PC) by noting that (see figures 5 to 7) and table 1:

The variation calculated directly on the complex module remains of the order of 10%; the variation of the glass transition temperature noted is 5°C.

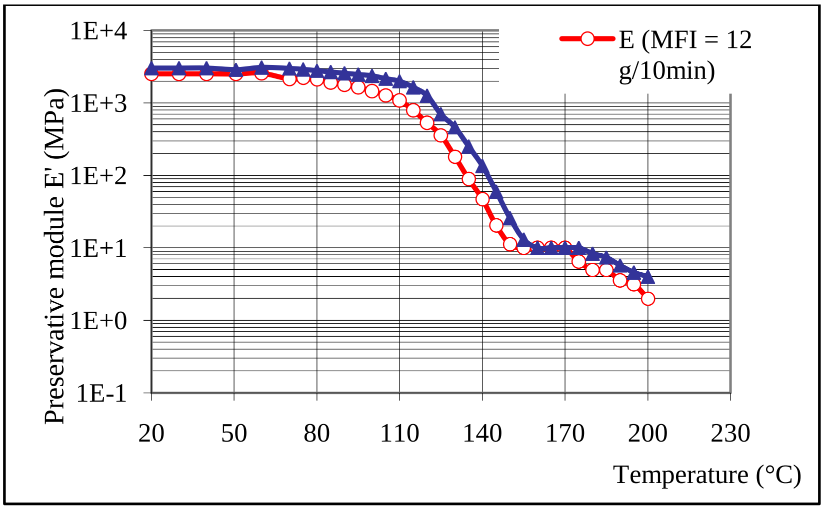

FIGURE 2: Conservative module E 'of polymethyl methacrylate (PMMA) characterized by differentiated fluidity indices, tested in dynamic traction-compression mode.

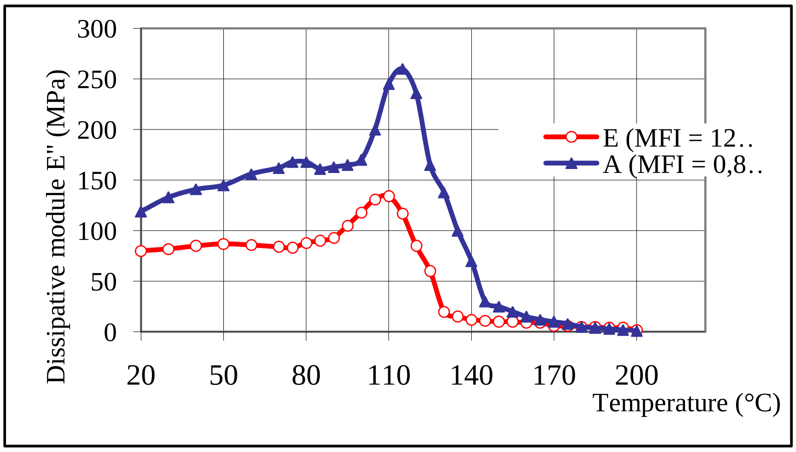

FIGURE 3: Dissipative module E "of polymethylmethacrylate characterized by differentiated melt indexes, tested in dynamic traction-compression mode

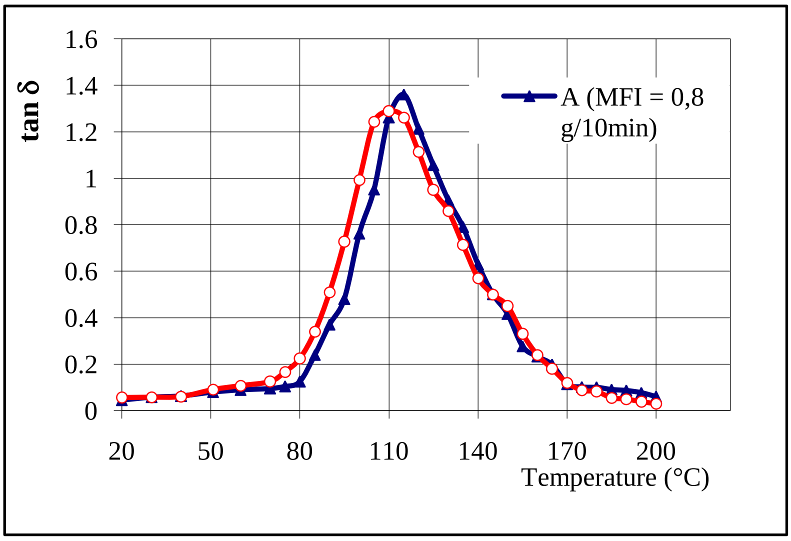

FIGURE 4: Polymethyl methacrylate tanδ loss factor characterized by differential fluidity indices, tested in dynamic traction-compression mode

TABLE 1
VALUES OF THE COMPLEX DYNAMIC MODULUS E * AND OF THE GLASS TRANSITION TEMPERATURE IN TRACTION-COMPRESSION TYPE DYNAMIC MODE.

Materials	Melt Flow Index MFI (g/10min)	dynamic module E* (MPa) (20°C)	Vitreous (Glass) transition Temperature measured T_g (°C)
PMMA	0,8	3020	115
	12	2510	110
PC	10	2250	150
	17,5	2000	145

From the experimental results, we can observe the following graphics of the preservative module E'.

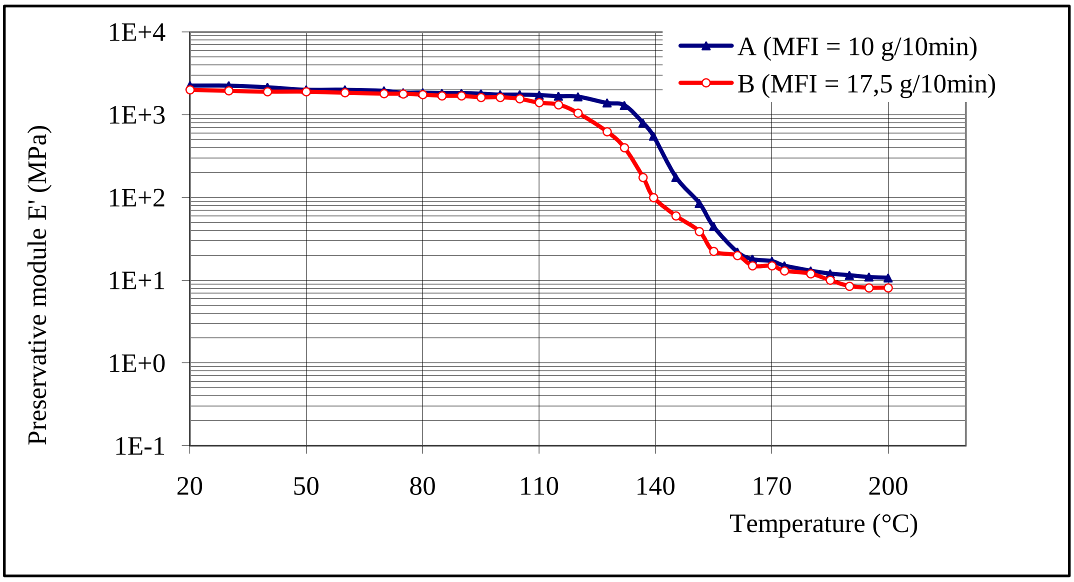

FIGURE 5: Preservative module E 'of polycarbonate characterized by differentiated fluidity indices and tested in dynamic traction-compression mode.

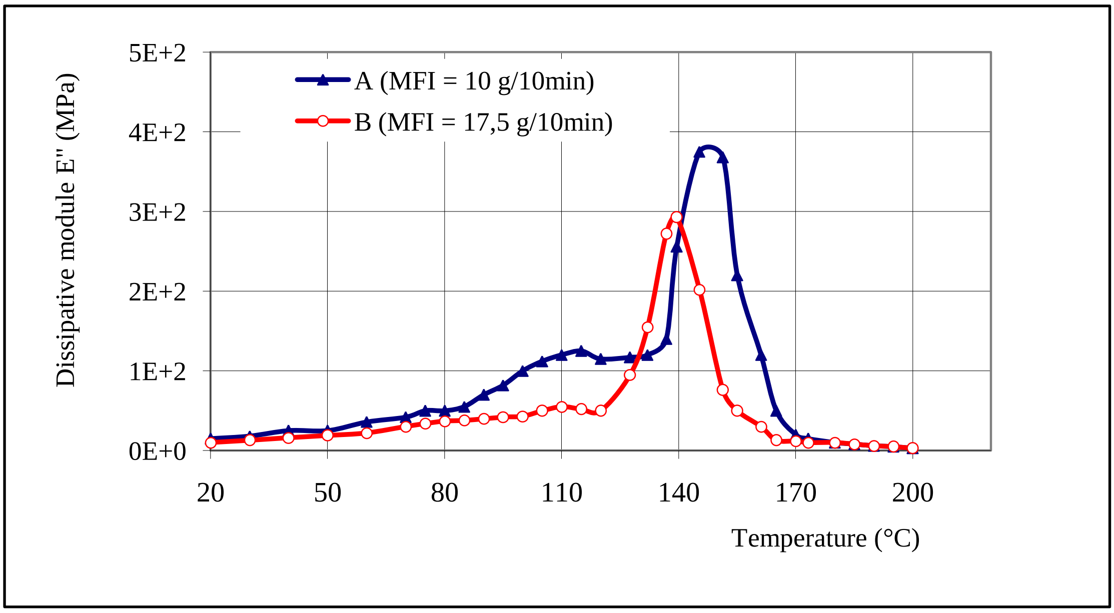

FIGURE 6: Dissipative module E" of Polycarbonate characterized by differentiated fluidity indices and tested in dynamic traction-compression mode

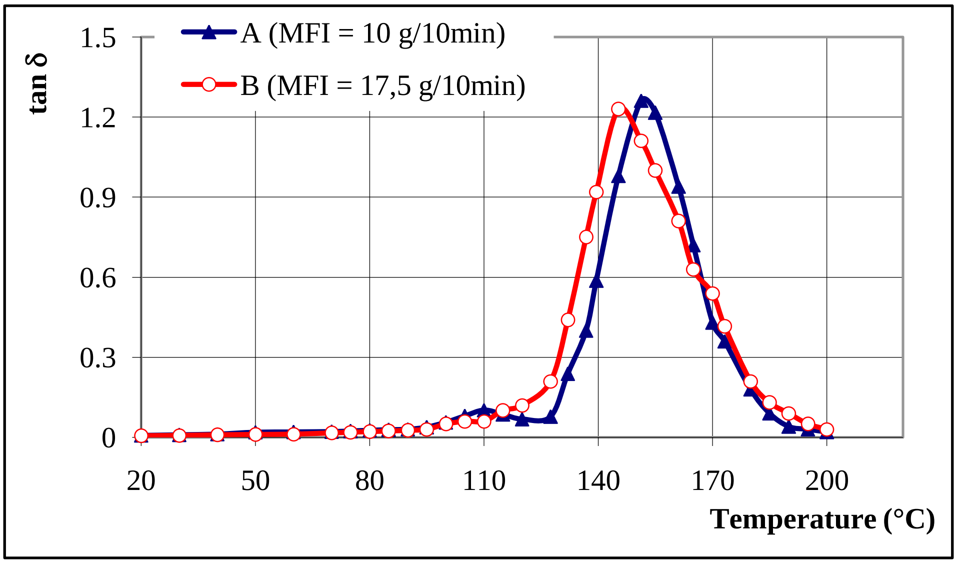

FIGURE 7: Loss factor tanδ of polycarbonate characterized by differentiated fluidity indices and tested in dynamic traction – compression mode.

However, the change in the melt index even in a factor of 4 does not have any effect on the value of the glass transition temperature.

IV. CONCLUSION

The representation of the different viscoelastic quantities (E ', E ", tanδ) of each material as a function of temperature (see Fig. 3 to 8) made it possible to differentiate the behavior of the polymers of distinct melt index.

For all the results obtained by the tensile-compression mode tests on the different amorphous polymers (PMMA, PC), it was found that the evolution of the loss factor tanδ qualifying the glass transition temperature (Tg) by a maximum peak has been used to record Tg supporting the theoretical data provided in the technical brochures and in the literature [1, 4, 10, 21, 23].

The values recorded could be associated with the Vicat softening temperatures of the material.

In a global way, the variation of the conservative modulus E '= f (T) allowed, whatever the material tested in traction - compression mode, to identify three domains of behavior:

- elastic-vitreous where the rigidity of the polymer is observed,
- viscoelastic in which the amplitude of E "and the Tg are recorded,
- elastic - rubbery.

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