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Viscoelastic behavior of PMMA in relation to deformation mode

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Abstract The molecular motions and the behavior in the four characteristic regions of an amorphous poly(methyl methacrylate) (PMMA) were studied using two different attachments of a dynamic mechanical analyzer: tension and bending. Measurements were taken over a wide range of temperatures and frequencies using ramp and step heating programs. A distinct viscoelastic versus temperature behavior was found above and below the glass transition temperature in bending mode. Apparent activation energies for the two relaxations found in PMMA (α and β) using both clamping modes are reported and discussed. Beyond the usual behavior of α- and β-relaxations with increasing frequency, new features are observed: the merging of α- and β-relaxation. Experimental results are explained on the basis of cooperativity concept.

Keywords Relaxation · Dynamic mechanical analysis · Viscoelastic properties · Poly(methyl methacrylate) · Thermomechanical properties

Introduction

Poly(methyl methacrylate), a linear amorphous thermoplastic polymer, has been one of the most widely studied polymers in the last decades due to its outstanding and promising mechanical and physico-chemical properties [1]. It combines stability and chemical resistance with superior optical properties (clarity, transparency from the near UV to the near IR), chemical inertness, good mechanical and electrical properties, thermal stability, weather resistance, formability, moldability and easy shaping. Another major benefit is that PMMA is 100 % recyclable, which makes an essential contribution to saving natural resources [2].

Its chemical structure is responsible for the tough and rigid characteristics. The presence of the pendent methyl (CH_3) groups prevents the polymer chains from packing closely in a crystalline fashion and from rotating freely around the carbon–carbon bonds. The conformational characteristics of the polymer chains play a key role in determining the physical properties of the polymeric materials, particularly the chain stiffness, the glass transition temperature (T_g) or the relaxation behavior.

The investigation into the major relaxations of PMMA and the unveiling of the origin and the nature of the molecular motions underlying these relaxations was the topic of several studies. A combination of many techniques [dynamic mechanical analysis (DMA) [3, 4], dielectric analysis (DEA) [5–7], fluorescence [8], thermally stimulated depolarization currents (TSDC) [9], nuclear magnetic resonance (NMR)] [10–12] was necessary to explain the origin of PMMA relaxations taking into account that the motions in polymer chain are strongly coupled, each of them stressing different aspects and giving distinct details of the relaxation.

The study of molecular motions in PMMA has revealed four types of relaxations with increasing temperature: γ, δ, β and α (Scheme 1) [8].

In PMMA, the lowest temperature relaxations are the δ- and γ-relaxation. These two relaxations were detected by Deus et al. [8], through the technique of fluorescence emission with the variation of temperature, around

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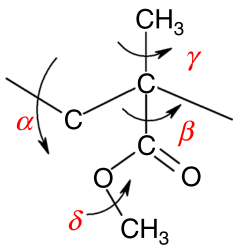


Scheme 1 Relaxations detected in PMMA using different techniques

−193 °C (δ) and −103 °C (γ). The δ-relaxation is attributed to the rotation of the methyl group of the ester, while the γ-relaxation is ascribed to the motion of α-methyl groups covalently bonded to the main chain. The γ-relaxation is also a water-related movement [3, 13, 14] and depends on the tacticity of the polymer as was proved by Williams and Eisenberg study [11], when two separate relaxations labeled γ_1 and γ_2 can be observed.

The molecular nature of β-relaxation (−43 to 33 °C) has been the subject of a great number of studies and also a source of controversy [15–17]. The 180° rotational jump of the side group around the bond linking it to the main chain has been the main explanation for the relaxation peak which usually appears in the temperature range −43 to 20 °C. This assumption was sustained by dielectric study of Tetsutani et al. [18] and NMR investigation of Kuebler et al. [12]. NMR multidimensional studies of Schmidt-Rohr et al. [10] proved that this process is more complicated than expected. In addition to the well-recognized rotation of the side group, there is evidence that also hindered local motions of the backbone contribute to the loss process. The interactions of the adjacent units with the main chain methyl groups and the rotational readjustments are supplemented by motions of the backbone around the local chain axis. The shape of β-relaxation is independent of the main chain conformation [19], while its intensity is determined by the magnitude of the steric hindrances exerted on the ester groups by the neighboring α-methyl groups or by extrinsic molecular species residing in the vicinity of the side group [9].

Rather than modifying the existing β-relaxation, the presence of water gives rise to a new relaxation phenomena (β′) in PMMA. It appears as a shoulder on the low-temperature side of the β-relaxation peak which partially overlaps the β-relaxation [3]. Moreover, it was reported that the β-relaxation process in PMMA was coupled to some extent with the main chain motion (α-relaxation), the coupling mechanism between α- and β-relaxations being studied through several types of experimental techniques [5, 6, 20, 21].

The glass transition temperature of PMMA associated with α-relaxation is ascribed to long-range conformational motions involving between 8 and 20 bonds and ranges from 85 to 165 °C. The range is so wide because of the vast number of commercial compositions. For example, there is a difference of 22° between the T_g of atactic and syndiotactic PMMA [9].

In what concerns dynamic mechanical aspects, PMMA relaxation behavior has been extensively studied. Most of the studies focused on the dependence of the nature and the magnitude of relaxations on the experimental conditions: temperature, frequency, heating rate and moisture. Among these factors, a major aspect regarding the accuracy of the experiment is the precise knowledge of the effect of clamping arrangement [22–28]. Different types of clamping give rise to different deformations mode and types of stresses acting on the sample.

As far as we know, detailed studies on the influence on the low- and high-frequency relaxation behavior of PMMA using tension and bending mode are lacking in the open scientific literature. Keeping all these in mind, we tried by our investigation to provide enlarged data on dynamic mechanical analysis using a range of frequencies and temperatures that far exceed those used by previous investigators.

Experimental

Materials

The PMMA sample with dimensions of 20 × 10 × 1.44 mm^3 was supplied by PerkinElmer company.

Methods

A PerkinElmer Diamond DMA instrument was used to test the same sample in two different measurement modes. The tension tests were performed with a tension clamp, while during the bending tests, a single cantilever clamp was used. So, the sample was denoted as PMMA_t for tension and PMMA_b for bending testing, respectively. Both tests were carried out in similar conditions in order to obtain reliable results.

A ramp temperature scan was performed over the temperature range of −150 to 250 °C with a heating rate of 2 °C min^{-1} and a frequency of 1 Hz, under nitrogen atmosphere. The variation of the storage modulus (E'), loss modulus (E'') and loss factor (tan δ) as a function of temperature was obtained. The drops in E' curves, the peaks in E'' and tan δ curves report on the relaxations in polymers. The shape factor values α [m] were computed by PerkinElmer Diamond DMA software.

The multifrequency experiment was conducted with the heating rate of 2 °C min^{-1}, at five different frequencies (0.5, 1, 2, 5, 10 Hz) on the same temperature range.

The step-scan experiment was run at ten different frequencies (0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, 20 Hz), with a step of 2 °C and a soak time of 300 s.

The apparent activation energies of the relaxations were determined from multifrequency and step-scan experiments.

Results and discussion

Temperature sweep experiments

The aim of the DMA temperature scan is to characterize the viscoelastic behavior of PMMA in terms of storage modulus, loss modulus and tan δ factor. The evolution with temperature of these parameters indicates the macroscopic consequences of the molecular movements, being well known that molecular mobility is function of temperature. The results of the dynamic mechanical analysis of PMMA deformed under tension and under bending are displayed in Fig. 1.

At first sight, some similarities are detected: a glassy region with a storage modulus higher than 10^9 Pa, low loss modulus and very low tan δ; a glass transition region denoted by an abrupt decrease in the storage modulus and peaks on E'' and tan δ curve; a rubbery plateau region. A further consideration accentuates some peculiarities for each sample.

In the glassy region, PMMA sample presents a similar behavior in the two deformation modes. The values of E' modulus at very low temperatures for $\mathrm{PMMA_t}$ and $\mathrm{PMMA_b}$ are higher than 10^9 Pa (Table 1).

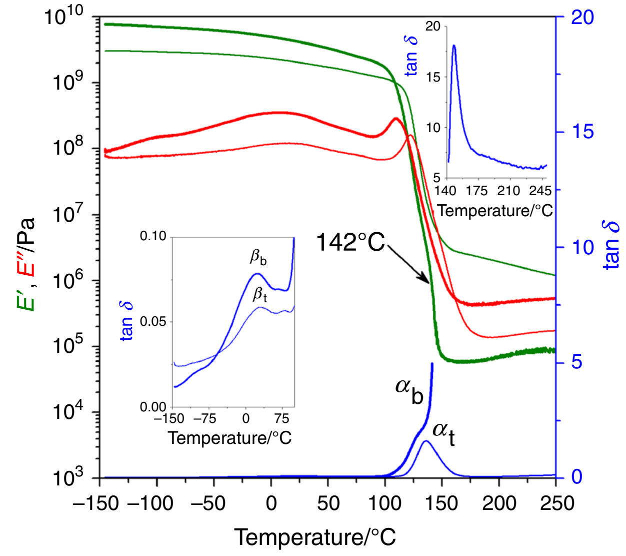


Fig. 1 Temperature dependence of the storage modulus, loss modulus and loss factor of PMMA measured in tension and bending mode at 1 Hz; tan δ–temperature plot in the β-relaxation region of $\mathrm{PMMA_t}$ and $\mathrm{PMMA_b}$ (*left-side inset*); tan δ–temperature plot of $\mathrm{PMMA_b}$ in the temperature range 140–245 °C (*right-side inset*)

The PMMA sample looks to be more rigid under bending deformation ($\mathrm{PMMA_b}$). The storage modulus in the glassy region is more than two times higher for $\mathrm{PMMA_b}$ than $\mathrm{PMMA_t}$. This difference arises from the complexity of the deformation in bending clamping system due to existence of biaxial stresses. This difference can be quantified by the shape factor which depends on the shape of the sample, dimensions and deformation mode [23]. A smaller value of the shape factor was obtained in bending mode (5.8×10^{-5} m) than in tension mode (7.2×10^{-4} m). Maybe, these differences in shape factor can anticipate the dissimilarities observed in the other regions, taking into account that as its value gets smaller, the deformation performing becomes easier, while at larger value, the deformation becomes more difficult to be accomplish.

The first small, monotonous drop on E', in the range from −100 to 100 °C and the extremely large and asymmetric peaks on E'' and tan δ curve report on the β-relaxation. It is assigned to the rotation of the methoxy-carbonyl side group around the bond linking the group to the main chain. The peak temperatures are presented in Table 1. Since tan δ is defined as the ratio of the energy dissipated and the energy stored, it is possible to investigate the energy dissipation because of molecular motions. The loss factor peaks are small because nearly all the energy stored in the deforming the material is quickly recovered when the stress is removed, since in this region, the chain segments are frozen and their mobility restricted. The thermal energy conferred by increasing temperature permits only small relative movements of side groups or short chain segments. Our results indicate that this motion dissipates energy much stronger in bending mode than in tension mode, i.e., an increased freedom of side chains movement increases the strength of the transition (left-side inset of Fig. 1). The origin of the asymmetry of β-relaxation was mentioned by Hirota et al. [29] in an in situ dielectric measurement and was ascribed to the density fluctuation of the amorphous structure, i.e., the presence of low and high density region.

The difference between the tension and bending mode data persists in the glass transition region; moreover, it intensifies as the segments of polymeric chains start to move. In both cases, the storage modulus decreases in one step during the glass transition process, in the temperature range between 115.2 and 154 °C for $\mathrm{PMMA_t}$, and 109.4 and 150 °C for $\mathrm{PMMA_b}$, respectively. The fall of the E' modulus around three orders of magnitude, on a short temperature range (30° to 40°), suggests the amorphous character of both samples.

In tension mode, this decrease in E' occurs along with the presence of an important tan δ peak and a broad

Table 1 Dynamic mechanical characteristics of PMMA relaxation processes

Sample	Glassy region				Glass transition region				Rubbery plateau
	E'/GPa −140 °C	β-relaxation			α-relaxation				E'/MPa 174 °C
		T/°C		$h_{\tan\ \delta}$	T/°C			$h_{\tan\ \delta}$	
		E''_{peak}	tan δ		E'_{onset}	E''_{peak}	tan δ		
Tension	3.04	17.56	23.6	0.058	115.2	124.9	136.8	1.61	2.45
Bending	7.66	7	11.2	0.076	109.4	111.4	128.7	1.88	0.06

$h_{tan\ \delta}$ the maximum value of tan δ peak

shoulder on E'' curve. In the case of bending mode, α-relaxation appears as a shoulder on tan δ curve, followed by a sudden increase, probably as a result of the overlapping with the flowing deformation. A closer look on Fig. 1 shows that the steep increase in tan δ is accompanied by a weak upturn slope change in the E' drop at about 142 °C. The very high flexibility of polymeric chains imparted by the increased temperatures induces motions of very large segments of chains or even coordinated movements of the whole polymeric chain. So, the slipping of the polymeric chain segments past each other takes place. This assumption is confirmed by the behavior of PMMA$_b$ in the rubbery plateau region. When E' modulus reaches the plateau, tan δ begins to decrease (right-side inset of Fig. 1). So, this slippage is stopped at a given moment by the processes that take place even during the slipping. Very likely an alignment of macromolecular chains induces an increase in the rigidity and the appearance of the rubbery plateau region. Actually, E' still has a slightly increasing trend on this plateau. The E' modulus remains on a plateau until the end of the experiment, its value being lower than that corresponding to PMMA$_t$.

The large differences obtained using tension and bending mode can be ascribed to dissimilar relaxation times. The apparent sluggish relaxation in the bending test is the result of a longer relaxation time, the relaxation taking place more slowly than in tension mode.

Multifrequency experiment

Temperature scans experiments performed at multiple frequencies allow the calculation of the activation energy according to Arrhenius equation and can disclose the origin of some events that cannot be explained by the result of the experiment at one frequency. Thus, it provides useful information on how to differentiate between a relaxation and a kinetic effect and whether in the glass transition region, there are overlapped phenomena.

By the examination of the multifrequency DMA experiments (0.5, 1, 2, 5, 10 Hz), some differences between the evolution of α- and β-relaxation with temperature at different frequencies can be observed. In the case of β-relaxation of PMMA, only the tan δ data are recalled in Fig. 2.

With increasing frequency, the tan δ peak shifts to higher temperature and its height increases. More comments on this behavior will be made in the section dedicated to step-scan experiment.

The multifrequency experiment recorded for α-relaxation evidenced a stronger frequency dependence than in the case of β-relaxation (Fig. 3).

For PMMA$_t$, tan δ peak shifts to higher temperatures and becomes broader with increasing frequency, while the peak intensity decreases. A higher frequency is equivalent to a shorter time available for polymer chains to respond to the applied stress. Therefore, the molecular movements related to α-relaxation are activated at higher temperature. This is why the storage modulus is higher as the frequency is increasing, i.e., the polymer looks more rigid than it actually is (Fig. 3a, b). The result of E' modulus increase is the decrease in tan δ. This behavior confirms that during α-relaxation, no other important process takes place (Fig. 3c).

In the case of PMMA$_b$ (Fig. 3d), the glass transition temperature increases with increasing frequency, but tan δ peak height is constant on the frequency range studied.

This relatively constant value (≈ 1.7) can be explained upon the hypothesis that on a small temperature range, the decrease in the storage modulus is compensated by a supplementary increase in loss modulus as a result of extra mobility. The further increasing tendency of tan δ clearly indicates that a flowing phenomenon overlaps α-relaxation. There are not only coordinated movements of segments of polymer chains, but larger segments of polymer chains start to slip one past another. As a consequence, the E' modulus decreased after the glass transition to smaller values in bending ($\sim 10^5$ Pa) than in tension ($\sim 5 \cdot 10^6$ Pa).

Data corresponding to α- and β-relaxation are presented in the Arrhenius diagram, both relaxations showing the typical linearity according to Arrhenius equation (inset in Figs. 2, 3):

$$\ln f = \ln A - (E_a/RT) \qquad (1)$$

where f is the frequency (Hz), A is the pre-exponential factor, T is the absolute peak temperature (K), R is the gas

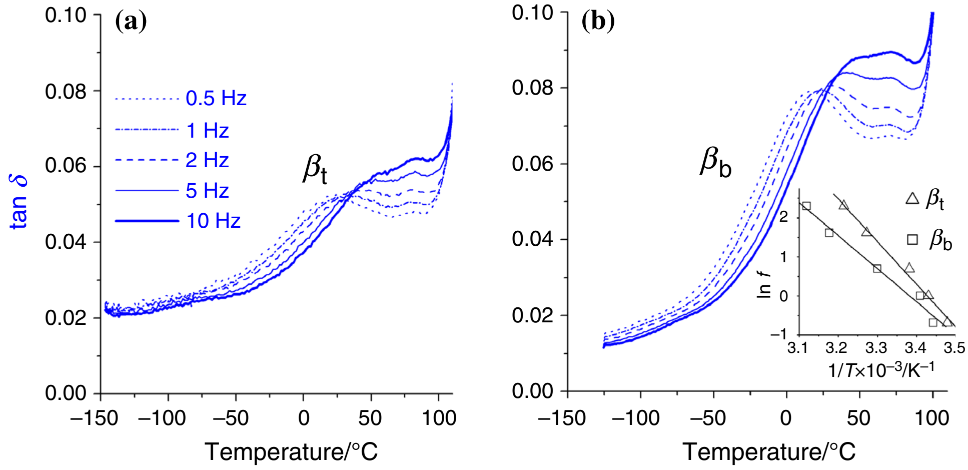


Fig. 2 Multifrequency tan δ plot (0.5, 1, 2, 5, 10 Hz) in the β-relaxation region of PMMA$_t$ and PMMA$_b$ recorded at 2 °C min^{-1}; Arrhenius plot for β-relaxation (*inset figure*)

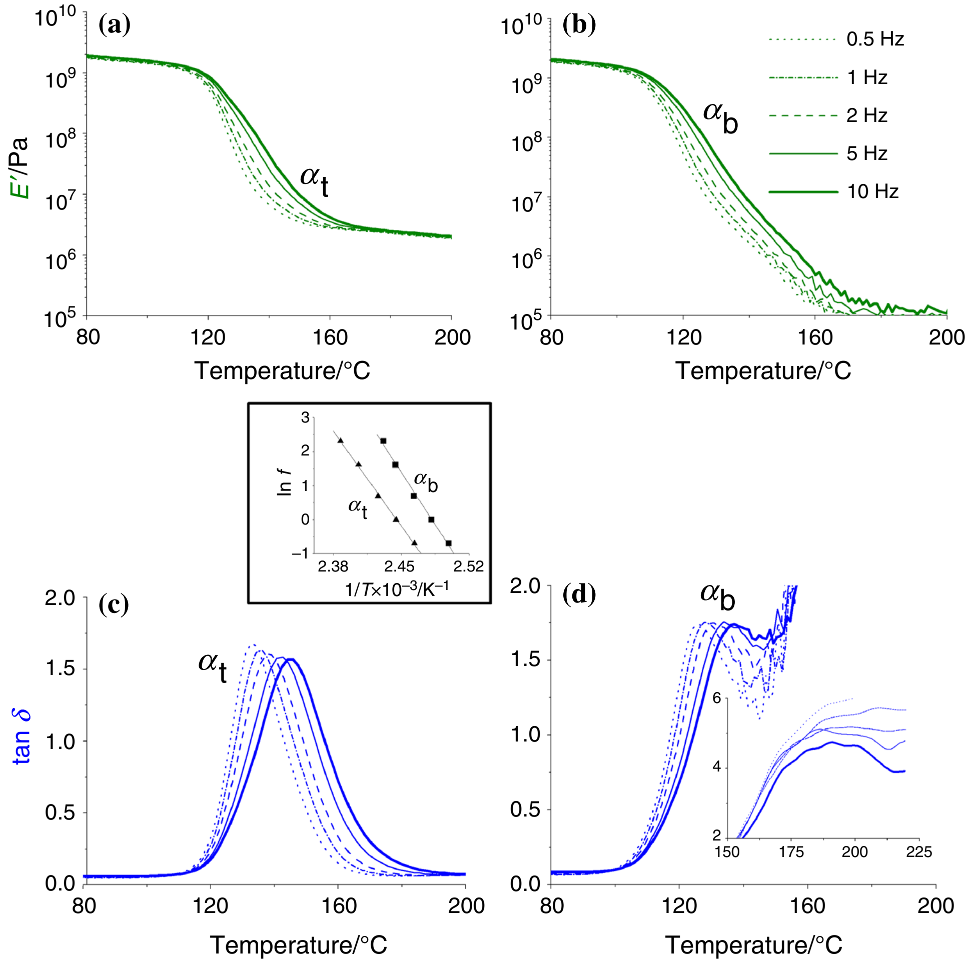


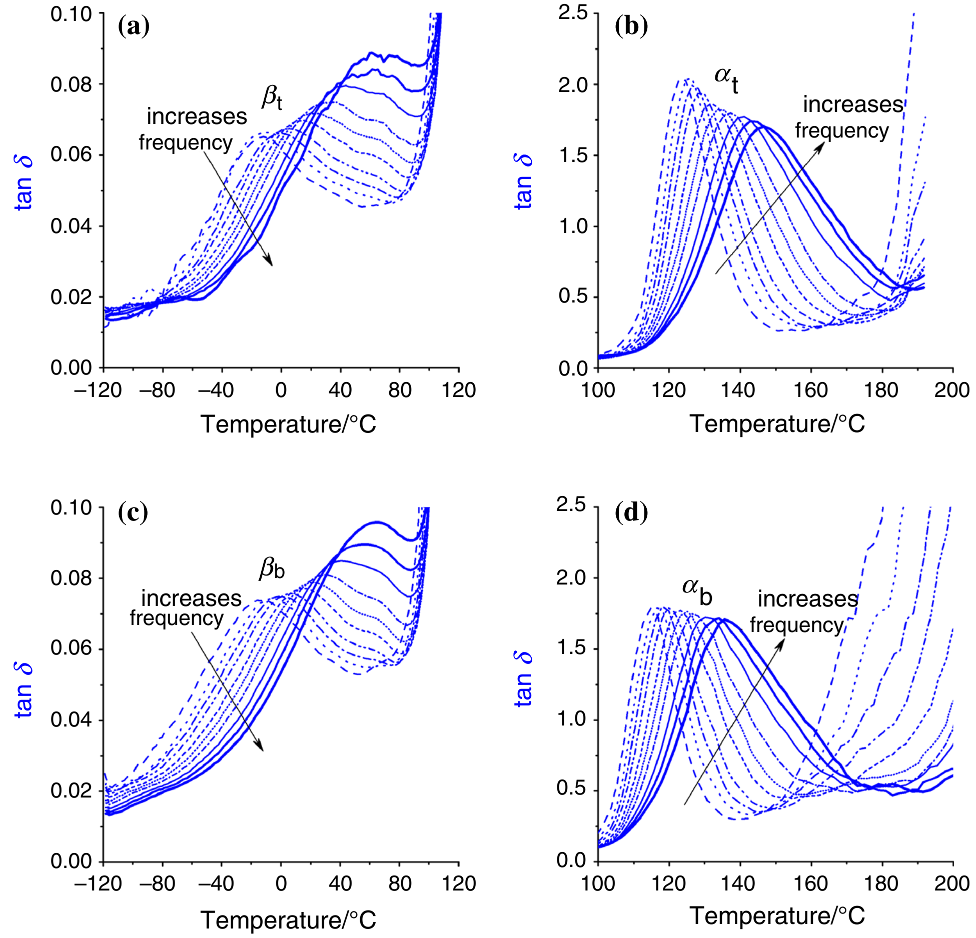
Fig. 3 Multifrequency E' and tan δ plot (0.5, 1, 2, 5, 10 Hz) in the α-relaxation region of PMMA$_t$ and PMMA$_b$ recorded at 2 °C min^{-1}; Arrhenius plot for α-relaxation (*inset figure*)

constant (8.314 J mol^{-1} K^{-1}) and E_a is the activation energy (J mol^{-1}).

The apparent activation energies of the relaxations were determined from the slope of the straight-line plot of ln frequency versus reciprocal temperature of relaxation.

The high values of the activation energy indicate that α-relaxation originates from the coordinated molecular motions, as expected for the glass transition. These values are higher than those reported by Dionisio et al. [7] (120 kJ mol^{-1}) and Li et al. [5] (150 kJ mol^{-1}) using dielectric spectroscopy, but are in agree with those of Deus et al. [8] obtained using dynamic mechanical analysis (353 kJ mol^{-1}). The discrepancies between DMA and DEA activation energy reflect the differences in the

Fig. 4 Variation of tan δ with temperature in the β- and α-relaxation region of $PMMA_t$ and $PMMA_b$ in the step-scan experiment



mechanism involved in the responses provided by each method.

The activation energy of the β-relaxation is typical for local molecular motions [30]. The shift of the tan δ peak temperature that corresponds to a decade change in frequency is smaller than that corresponds to α-relaxation for the same decade of frequency.

Step-scan experiment

It is well known that a low working frequency is more sensitive in detecting and separating relaxations. When performing a DMA experiment with the variation of temperature in ramp mode at low frequency, a drawback is the obtaining of scattered points [31]. Working at low frequency requires longer times to get one DMA point, and inappropriate heating rate can give incomplete DMA results. This fact can be overcome by performing the experiment in step-scan mode. Moreover, this type of experiment diminishes the problem related to the thermal lag, since the sample is equilibrated at the working temperature for some time [32]. The evolution of α- and β-relaxation in the step-scan experiment is displayed in Fig. 4.

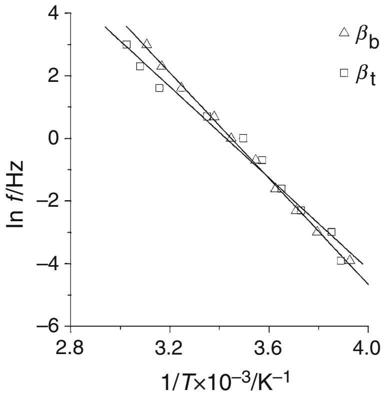


Fig. 5 Arrhenius plot for β-relaxation of $PMMA_t$ and $PMMA_b$ from step-scan experiment

At lower temperatures, β-relaxation was reported to be a localized non-cooperative process [33]. With increasing frequency, β-relaxation is shifted to higher temperatures. But as the temperature is higher, the characteristics of the motion associated with β-relaxation change becoming “locally cooperative” [34]. The side chain movement implies also coordinated motion with neighboring side chains.

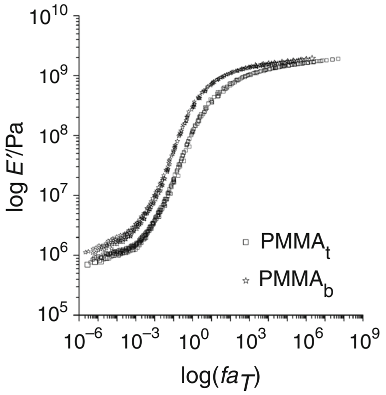


Fig. 6 Storage modulus master curve generated of the PMMA deformed in tension and bending mode with respect to a reference temperature of 124 °C for tension and 114 °C for bending

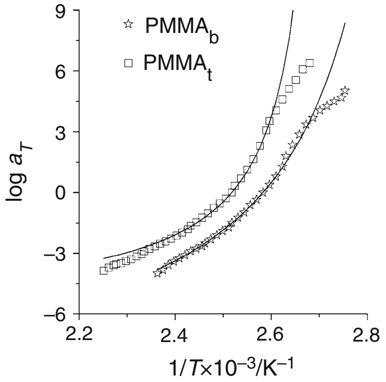


Fig. 7 Temperature dependence of the shift factor for the DMA master curves presented in Fig. 6. The *solid lines* are the WLF fittings of the corresponding results

Table 2 WLF and VFT parameters for the PMMA studied in tension and bending mode from the step-scan experiment

	C_1	C_2/°C	T_0/°C	B/K
$PMMA_t$	5.4	30.7	93.3	380.9
$PMMA_b$	9.1	50.1	63.9	1046.6

In Fig. 4a, c this is reflected in the asymmetry of the peak and a pronounced deviation in the high-temperature side. This is the result of the contribution of α-relaxation at higher temperatures, as the two relaxations tend to approach with increasing frequency. Schönhals et al. [35] and Hensel et al. [36] performed dielectric experiments in polymeric solids. They showed that the low-temperature side is related to short-range molecular motions, while the high-temperature side is related to large-scale molecular motions. The shift to higher temperatures indicates the increase in the cooperative nature of the motion.

Eventually, β- and α-relaxations tend to merge with the increase in frequency. This new relaxation, observed especially in the dielectric studies at frequencies higher than 1000 Hz [5, 21], is referred in the literature to as αβ relaxation [20]. There is a very high probability that this process is not just the result of the overlapping of α- and β-relaxations. This new αβ process has a more complex character; the molecular motions of the side groups interfere with the motion of the main chain and influence each other in a cooperative manner [6]. This change in the intermolecular cooperativity produces also a broadening of the α-relaxation with increasing frequency that will be showed below. However, a single relaxation peak cannot be emphasized in DMA because of the low-frequency range (less than 100 Hz) covered by this method.

It is observed that in the case of α-relaxation the increasing of frequency with two orders of magnitude induces decreasing intensities of the peaks, shift of their position to higher temperatures and broadening at higher frequencies (Fig. 4b, d). Such a broadening of tan δ peak may be the consequence of the coexistence of domains with different molecular mobilities. Mobility is higher in region where molecular rearrangements occur independently of the local environment. The mobility slows down in the glass transition region known to be cooperative, where the rearranging movement of one structural unit is only possible if a certain number of neighboring units is also moved.

The variation ln f versus $1/T$ represented in Fig. 5 indicates that β-relaxation follows a linear Arrhenius type equation in the investigated frequency range.

Table 3 Apparent activation energies (E_a) of α- and β-relaxations estimated from multifrequency and step-scan data

Sample	α-relaxation			β-relaxation			
	Multifrequency experiment		Step-scan experiment	Multifrequency experiment		Step-scan experiment	
	E_a/kJ mol^{-1}	R^2	E_a/kJ mol^{-1}	E_a/kJ mol^{-1}	R^2	E_a/kJ mol^{-1}	R^2
$PMMA_t$	329.65	0.9985	528.62	70.45	0.981	60.61	0.981
$PMMA_b$	365.63	0.994	520.87	90.67	0.989	70.23	0.998

The viscoelastic behavior of the studied PMMA was investigated within the glass transition region by isothermal frequency DMA scans. The master curves for both types of deformations were obtained by simple shifting of the isothermal results along the frequency scale, according to time–temperature superposition.

Representative results for PMMA deformed in tension and bending mode are shown in Fig. 6 with log E' plotted as a function of reduced frequency fa_{T}, for the reference temperature $T_{\mathrm{ref}} = 124$ °C in tension mode and $T_{\mathrm{ref}} = 114$ °C in bending mode. The reference temperature was taken as that of the loss modulus peak at 1 Hz.

The temperature dependence of the shift factor for the DMA master curves presented in Fig. 6 was fitted according to the Williams Landel Ferry (WLF) equation [37–39] (Fig. 7):

$$\log a_{\mathrm{T}} = -C_1(T - T_{\mathrm{ref}})/(C_2 + T - T_{\mathrm{ref}}) \qquad (2)$$

where T_{ref} is the reference temperature and C_1 and C_2 depend on the material and on T_{ref}.

The fitting parameters values for α-relaxation are listed in Table 2. The quality of the fits was good with statistical R^2 values greater than 0.90. Regression of the data was limited to the range between T_{ref} and $T_{\mathrm{ref}} + 50$ due to the validity of the WLF equation in this temperature region.

Another model frequently used for describing the non-Arrhenius behavior is the Vogel–Fulcher–Tammann (VFT) equation [40, 41]:

$$f = f_0 \exp(-B/T - T_0) \qquad (3)$$

where B is a measure of activation energy and T_0 is the Vogel temperature, also known as the ideal glass transition temperature.

The WLF and VFT equations are mathematically equivalent, and their parameters are related through $C_2 = T_{\mathrm{ref}} - T_0$ and $C_1 = B/2.303\ C_2$. The WLF and VFT parameters for the studied PMMA in the two different deformation modes are presented in Table 2.

The tension and bending deformation mode give activation energies for β-relaxation around 60–70 kJ mol^{-1}.

In the WLF equation, the activation energy at the reference temperature can be expressed by the constants C_1 and C_2 as [37]:

$$E_{\mathrm{a}} = 2.303 \cdot R \cdot (T_{\mathrm{ref}})^2 \cdot C_1/C_2 \qquad (4)$$

The activation energy of α-relaxation calculated at T_{g} tends to increase slightly in the step-scan experiment relative to multifrequency test (Table 3).

The much longer step-scan experiment gives time to the molecular motions of the side groups interfere with the motion of main chain and influence each other in a cooperative manner, and consequently a higher activation energy is needed to cause further mobility in the polymer structure.

Conclusions

The combination of temperature and frequency scans revealed several modifications for the α- and β-relaxations investigated in PMMA, using dynamic mechanical analysis. The polymer behaves relatively different above and below T_{g}, in correlation with the deformation mode. Large discrepancies were experienced in measurement of the storage modulus and tan δ using bending mode. Below the glass transition temperature, a more rigid backbone and an extremely large and asymmetric tan δ peak, much stronger in bending than tension mode was observed. Above the glass transition, the three point bending was found to be the most suitable for measuring temperature-dependent tan δ, since it can detect the interference of the final region of α-relaxation and the flowing deformation.

The activation energy of β- and α-relaxation was also found to be susceptible to the type of deformation. Moreover, an increase in frequency with two orders of magnitude changes the non-cooperative β-relaxation of PMMA into a "locally cooperative" process as a result of the interference of the side group motion with the main chain motion. The complexity associated with this relaxation mechanism which involves a high degree of cooperativeness of the moving units is certified by the larger values of the activation energy obtained in the step-scan experiment.

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