

Effect of water on the relaxation spectrum of poly(methylmethacrylate)

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Summary

Dynamic mechanical and dielectric spectroscopies have been used to investigate the relaxation behavior of Polymethylmethacrylate (PMMA) both in the dry and in the wet state. Absorbed water shifts the main glass transition to lower temperature and contributes two loss processes (γ and β') in the glassy state. The location and activation energy of the low temperature water-related relaxation (γ) are typical of local molecular motions. Conversely, the second water-induced absorption (β') is characterized by high values of the activation parameters, suggesting that the dissipation process originates from cooperative relaxation phenomena.

Introduction

It is well recognized that absorbed water has a very pronounced effect on the relaxation behavior of hydrophilic macromolecules [1-4]. When dissolved in the polymer matrix, water molecules increase chain mobility and allow the long-range motions associated with the glass transition to take place at lower temperatures. In this respect water behaves as a plasticizer for the hydrophilic polymer. In the glassy state, secondary relaxations are markedly affected by water in a much more complex way, which results from several different competitive mechanisms. Interactions of water with the polymer segments may hinder the local motions characteristic of the dry macromolecule and give rise to bulkier units that can relax only at higher temperatures [5-8]. Alternatively, addition of water can intensify a pre-existing secondary relaxation [9-10] or induce new low-temperature loss processes in polymers that exhibit no secondary absorptions in the dry state in the range from 80 to 250 K [3, 11]. Among polymers with a hydrophobic main chain, Polymethylmethacrylate is considered an example of the last behavior. Owing to the polar side groups, PMMA can absorb small amounts of water from the environment and in room stored samples a low-temperature water-related loss peak (γ) has been observed [10, 12, 13]. The mechanical and dielectric relaxation spectrum of amorphous Polymethylmethacrylate in the dry state shows two characteristic relaxations, called α and β respectively. The α process undoubtedly involves large-scale conformational rearrangements of the polymer main chain and appears in correspondence with the glass-to-rubber transition. The molecular mechanism of the secondary β relaxation has been a source of

controversy in the literature [14-16] because there is evidence that also hindered local motions of the backbone contribute to the loss process in addition to the well-recognized rotations of the side groups. No significant effect of moisture on the location and intensity of the β relaxation region has been reported in the literature.

In the present paper the dynamic mechanical and dielectric properties of PMMA, both in the 'dry' and 'wet' state, have been carefully re-examined. The results obtained lead to the conclusion that water – besides the low temperature γ absorption – contributes another loss process (β') which partially overlaps the β relaxation.

Experimental

Polymethylmethacrylate (PMMA) was an amorphous product purchased from the Polysciences Company ($M_n = 169000$ and $M_w = 350000$, by GPC). Films (about 0.21 mm thick) for dielectric measurements were obtained by compression molding at 200°C for 2 min, under a pressure of 0.5 tons/m², in a Carver laboratory press. Small bars (30 x 8 x 1.8 mm³) for dynamic mechanical measurements were prepared by injection molding at 220°C using a miniature injection-molding machine.

PMMA was conditioned prior to measurements as follows. 'Dry' samples were obtained by keeping the PMMA bars under vacuum over P₂O₅ up to constant weight or by heating the PMMA films directly in the DETA instrument up to 120°C under vacuum. 'Wet' samples were obtained by storing specimens in a closed vessel saturated with water vapor at room temperature up to constant weight. The amount of absorbed water, gravimetrically quantified with respect to the dry sample, was 1.5 wt %.

Dynamic mechanical measurements were performed from -150 to 150°C with a DMTA (Polymer Laboratories) equipment, using the three-point bending geometry, at a frequency of 3 Hz and a heating rate of 3°C/min. When dry samples were tested, dried nitrogen was used to purge the heating chamber during measurement.

Dielectric measurements were carried out from -120 to 120°C with a DETA (Polymer Laboratories) instrument at five selected frequencies (0.03, 0.1, 0.3, 1 and 3 kHz), at a heating rate of 1°C/min. When dry samples were analyzed, cooling to room temperature in dry nitrogen atmosphere followed vacuum heating to 120°C and purge gas was switched off before measurement.

Results

Dynamic mechanical measurements

The DMTA spectra (loss tangent $\tan \delta$ and storage modulus E') of dry and wet PMMA are shown in Figure 1. In agreement with literature results [4, 14], dry PMMA shows a quite intense α relaxation at about 120°C, in correspondence with the glass transition, and a broad secondary β relaxation centered around 20°C. The wet sample has a more complex DMTA spectrum, with an additional low-temperature relaxation ($\tan \delta$ maximum at -100°C) and a splitted glass transition peak, shifted to lower temperature with respect to the dry sample. The splitted glass transition is caused by two phenomena: 1) the plasticizing effect of absorbed water that decreases the PMMA glass transition temperature (lower peak) and 2) the partial loss of water during heating that induces a subsequent shift of the transition to higher temperature (upper

peak). The β peak is apparently unaffected by the presence of water molecules, whereas the low-temperature relaxation corresponds to the water-induced γ absorption commonly observed in hydrated PMMA [12, 14].

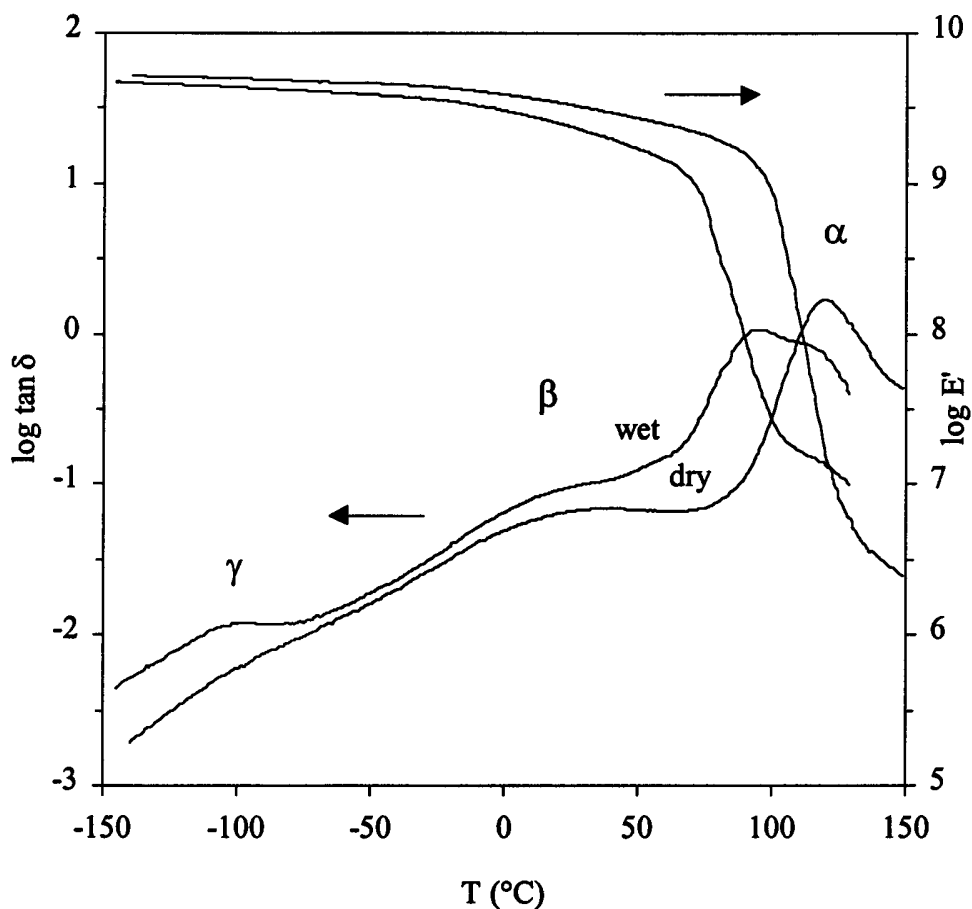


Figure 1 Dynamic mechanical spectrum (3 Hz) of dry and wet PMMA

Dielectric measurements

The DETA spectrum of dry PMMA is shown in Figure 2a) as a function of temperature and frequency. At the lowest frequency (30 Hz) investigated two dielectric loss peaks are observed, the very intense one being the secondary β relaxation associated with the polar side groups, whose mobilization is quite active dielectrically, and the small absorption above 100°C being the glass transition. With increasing frequency both relaxations shift to higher temperature, and eventually they merge into an α/β overlapped loss region. The results obtained from the dielectric analysis of wet PMMA are reported in Figure 2b) as a function of temperature and frequency. At low frequency (30 Hz), besides the glass transition on the high temperature side, the relaxation spectrum displays two secondary loss processes centered at about 25°C and -85°C, the latter being of very small intensity and barely visible in the scale of Figure 2b). The effect of frequency on the lowest temperature relaxation of wet PMMA is as expected (shift to higher temperature with increasing frequency) whereas the changes induced on the dielectric loss above -20°C are quite complex.

In an attempt to isolate the influence of water on the dielectric spectrum, subtraction of the dry PMMA curves (Figure 2a) from the spectra of the wet sample (Figure 2b) was achieved, and the results are shown in Figure 3. The 'difference' curves very clearly indicate that absorbed water induces two new relaxation phenomena in PMMA, namely a small low-temperature (γ) absorption that strongly shifts with frequency and a quite intense loss (called β') that shows a much smaller frequency dependence. The presence of the latter water-induced β' relaxation is easily seen in the loss tangent curve of the wet sample (Figure 2b) at 3 kHz, where it appears as a shoulder on the low-temperature side of the β peak characteristic of dry PMMA. The results of the subtraction procedure also suggest that the β relaxation undergoes only small, if any, changes due to the presence of absorbed water. A close inspection of the $\tan \delta$ curves shown in Figure 3 and 2a) reveals that the dielectric loss associated with the β' absorption starts to increase at temperatures higher than the β relaxation and covers a much narrower temperature range.

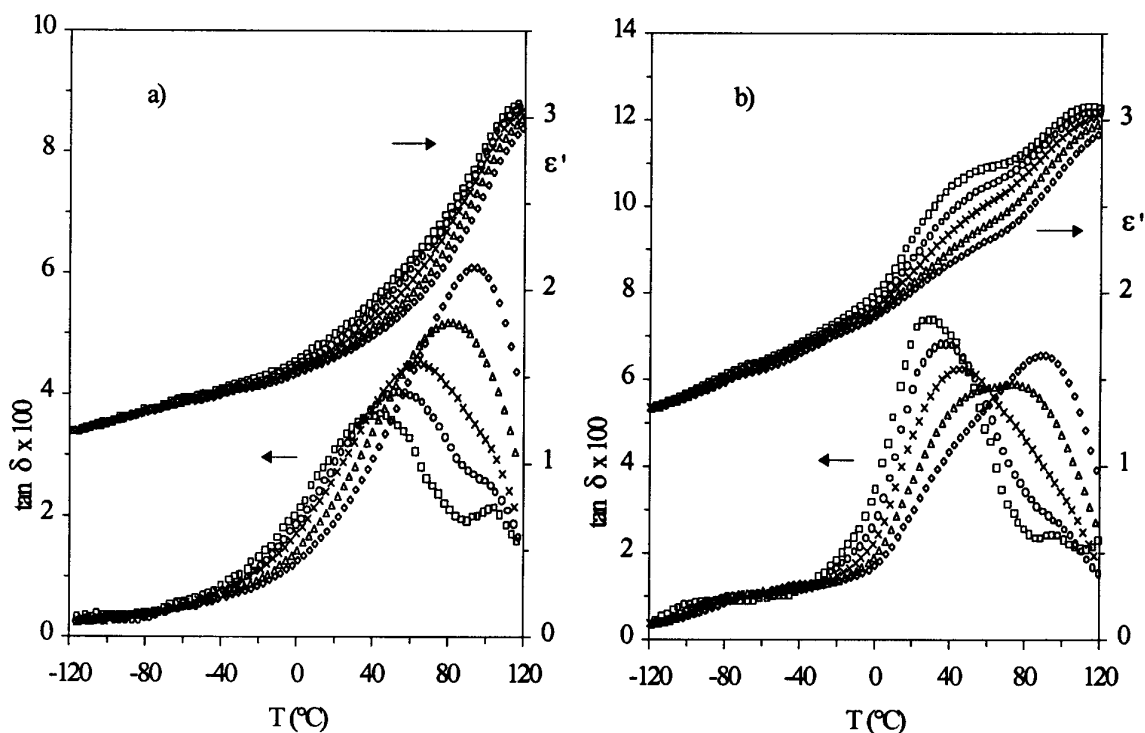


Figure 2 Dielectric spectrum of dry (a) and wet (b) PMMA at 0.03 (squares), 0.1 (circles), 0.3 (crosses), 1 (triangles) and 3 (rhombs) kHz

Figure 4 shows the frequency dependence of the peak temperature of the dielectric loss processes of dry (β) and wet (γ and β') PMMA. The temperatures of the β relaxation were taken from Figure 2a, those of the γ and β' peaks from Figure 3. The very good linear correlation observed indicates that all relaxations follow an Arrhenius-type equation, $\nu = \nu_0 \exp(-E_a/RT)$, in the frequency range investigated. The apparent activation energies (E_a) of the different loss processes, calculated by a linear regression fit to the dielectric data, are as follows: 40 kJ/mol (γ), 78 kJ/mol (β) and

296 kJ/mol (β').

Figure 4 also shows the peak temperatures of the dynamic mechanical γ and β relaxations of Figure 1, obtained at a frequency of 3 Hz. It is seen that the low-temperature DMTA relaxation of wet PMMA nicely falls on the Arrhenius plot of the γ DETA relaxation, the good fit implying that the same type of molecular motion is revealed by the two techniques. As regards the DMTA β process, it appears to be located at the intersection of the lines fitting the DETA results of β and β' absorption peaks. This suggests that, owing to their different activation energies, the two relaxations occur simultaneously at 3 Hz and cannot be resolved in the low frequency (< 100 Hz) range covered by the DMTA measurements.

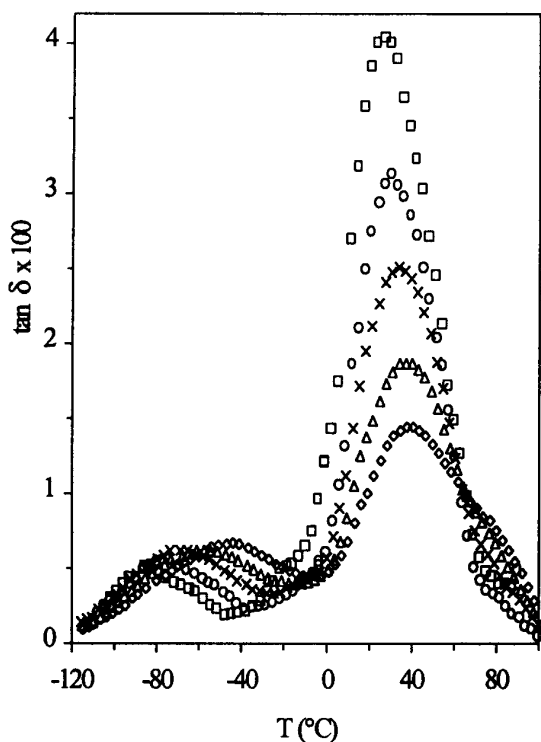


Figure 3 Dielectric 'difference' curves of wet PMMA at different frequencies (symbols as in Figure 2)

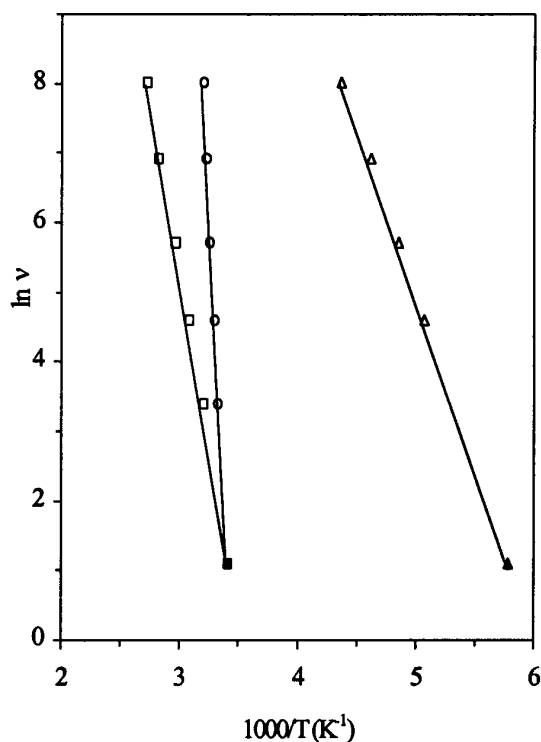


Figure 4 Relaxation map of PMMA loss maxima: γ (triangles), β (squares) and β' (circles). Open and filled symbols: dielectric and dynamic mechanical results respectively

Discussion

The temperature location and activation energy of the secondary β relaxation of dry PMMA are found to be in very good agreement with literature results [4]. In particular, the activation energy presently estimated from multifrequency dielectric data (78 kJ/mol) matches the values (76-74 kJ/mol) obtained by Starkweather [15] from dynamic mechanical measurements and more recently by Garwe et al. [16] from dielectric analysis.

The presence of absorbed water leads to three main modifications in the relaxation

spectrum of PMMA. First of all, the glass transition temperature is lowered owing to the plasticizing effect of water intimately mixed with the PMMA chains. Concomitantly, in the wet sample a low-temperature loss process (γ) appears in a temperature range where dry PMMA shows no absorption phenomena. Early investigations of the effect of water on the relaxation spectrum of several different polymers attributed the appearance of a water-induced loss maximum to the motion either of complex units composed of water molecules interacting with the side chains polar groups [3, 17] or of clustered water molecules [9]. A dielectric absorption was observed in the case of water clusters, with an activation energy of 29 kJ/mol and a temperature of about -150°C at 1 Hz, independent of the host polymer [9]. The water-induced γ relaxation of wet PMMA found in the present work appears at much higher temperature and is characterized by a value of the activation energy (40 kJ/mol) larger than expected for clustered water.

The behavior of secondary loss peaks in glassy amorphous polymers has been early reviewed by Heijboer [14], who suggested a linear correlation between activation energy and peak temperature, given by $E_a = RT \ln v_0$ at 1 Hz, with $v_0 = 10^{13}$ Hz for local motions of side groups. Afterwards, Starkweather [15] used the theory of absolute reaction rates to derive an alternative equation, which contains an activation entropy contribution. In the latter case, the Arrhenius activation energy E_a is related to the peak temperature T at 1 Hz through the relationship:

$$E_a = RT[1 + \ln(kT/2\pi h)] + T\Delta S$$

Loss processes having zero activation entropy are designated by Starkweather 'simple relaxations' and are assumed to involve local motions of small molecular fragments. An activation entropy of zero corresponds to a limiting frequency near 10^{12} Hz in an Arrhenius plot. Taking into account that the temperature and activation energy of the γ relaxation of wet PMMA ($v_0 = 5 \times 10^{12}$ Hz) fall in between the predictions of the two mentioned relationships, it is suggested that the γ loss process is due to restricted motions of small kinetic units resulting from interactions of water molecules with PMMA polar side groups.

The last modification to the relaxation spectrum of PMMA brought about by the presence of water is the loss process that appears as a shoulder on the low-temperature side of the dielectric β peak in wet PMMA. The phenomenon, denoted as β' absorption, has been evidenced in the 'difference' spectrum of Figure 3, obtained by subtraction of the dry PMMA curve from that of the wet sample. The results of Figure 3 suggest that water in PMMA, rather than modifying the existing β relaxation, gives rise to a new peak (β') which partially overlaps the β relaxation. The water-induced β' peak is characterized by a very modest frequency dependence, i.e. by a rather large activation energy (296 kJ/mol). The latter value is much higher than predicted by the mentioned Heijboer correlation for local-mode relaxations [14], suggesting that the molecular units responsible for the β' dielectric dispersion are larger and/or more hindered than expected for a classical glassy-state secondary relaxation located in the observed temperature range. In addition, the loss process has a fairly large activation entropy that - according to Starkweather [15] -- is typical of 'complex relaxations' which involve motions with a high degree of cooperativeness of the moving units. In light of these observations, it is likely that the motional units responsible for the β' peak arise from some association of water-water molecules partially interacting with the polar side groups of PMMA. The onset of mobilization of the side chains, in correspondence with the β relaxation, may activate the concomitant motion of bound

water. The high activation energy of the β' process indicates that the motion of such bound-water/ester units is complex and partially hindered. The proximity of the β' relaxation to the melting point of water alternatively suggests that mobilization of water molecules bound to PMMA is driven by the acquired mobility of water itself. It can be concluded that absorbed water on one hand does not change the nature of the β relaxation characteristic of dry PMMA and on the other contributes two new loss processes, γ and β' , with rather different molecular characteristics. The water-induced γ relaxation at low temperature corresponds to localized motions occurring without cooperativity. In contrast, the relaxation mechanism associated with the β' process shows a high degree of complexity, certified by the large values of both activation entropy and energy.

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