Ageing effects on dynamic shear moduli at the onset of the dynamic glass transition in two poly(alkyl methacrylate)s

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(Received 21 December 1993)

Time dependent-measurements of the dynamic shear modulus in the splitting region $a \leftrightarrow \alpha + \beta$ of poly(n-butyl methacrylate) (PnBMA) and poly(ethyl methacrylate) (PEMA) are reported. Non-equilibrium effects in the frequency–temperature region around the onset of the α transition are discussed. Physical ageing effects on the intensity, shape and position of the α and β peaks of the shear loss modulus are reported. For the α relaxation a shift of the mean relaxation frequency to lower values, a peak sharpening, and an increase in intensity during ageing are observed, whereas the β intensity decreases significantly. Long times are necessary to reach the equilibrium state a few kelvins below the onset temperature ($\approx$glass transition temperature for PnBMA). A small amplitude fine structure was found in the frequency sweeps at temperatures below the onset temperature, which is discussed in terms of McCrum's sequential ageing.

(Keywords: shear modulus; poly(n-butyl methacrylate); poly(ethyl methacrylate))

INTRODUCTION

Experiments in the splitting region $a \leftrightarrow \alpha + \beta$, where the high-temperature relaxation (a) splits off into the main (α) and the ordinary secondary (β) relaxation, are assumed to offer interesting information about the onset of the glass transition[1–3]. This region can be investigated by standard dynamic mechanical measurements in the hertz range in several poly(alkyl methacrylate)s (see *Figure 1*)[4]. Interesting topics for consideration are the behaviour of a characteristic length ξ_a for the dynamic glass transition[5,6] and the thermokinetic heterogeneity[7–9].

The idea of molecular co-operativity is generally accepted for glass transition phenomena below the α onset[10,11]. The co-operative motions forming the α relaxation onset in the splitting region should involve only a minimal number of particles corresponding to a small correlation length. Below a minimal number of particles, co-operative motion does not seem to be a realistic picture. The co-operative motions are assumed to stop and the intensity of the α glass transition is assumed to disappear (concept of minimal co-operativity)[12,13]. The aim of our dynamic mechanical investigations is to look for the location (in a log frequency–inverse temperature diagram) and the details of the assumed intensity disappearance of the α relaxation.

In an earlier paper[6], measurements of the shear loss modulus G'' in the splitting region of poly(n-butyl methacrylate) (PnBMA) were reported. We observed a separated onset of the dynamic glass transition α in this polymer near $T = 20°\mathrm{C}$ and $\omega = 1\ \mathrm{rad\,s^{-1}}$, well below the β frequency at this temperature ($\omega \approx 70\ \mathrm{rad\,s^{-1}}$). This result was taken from isothermal measurements after pre-ageing for 20 min at the measuring temperature. At temperatures below 10°C we found strong deviations from the equilibrium behaviour, e.g. the mean relaxation frequencies of the α relaxation were shifted to higher values than expected from equilibrium extrapolation.

Ageing is well known from dynamic mechanical measurements near and below the glass transition temperature (T_g) of polymers[14–16]. The time dependence of G'' between the α and β relaxation for poly(methyl methacrylate) (PMMA; an example of a polymer with the splitting region above 100 kHz) is shown in *Figure 2*. A shift of the α relaxation to lower frequencies and a decrease of G'' between the α and β relaxation is observed during the ageing process.

There are also considerable ageing effects for other physical properties at temperatures below the T_g. The accepted understanding of these phenomena is that, during sample cooling at a constant rate, in the glass transition zone the time is too short for the relaxation processes to occur. They become 'frozen-in' which is the reason for the non-equilibrium of the glass state. At lower temperatures, such frozen-in relaxations are present over long times. Their 'thawing' is called structural relaxation and is accompanied by a densification of the system e.g. a loss of free volume. After logarithmic time-scales physical ageing leads to the equilibrium state. The details of ageing, such as the shape and intensity variation of the α and β relaxation, can be described by different models[17–23]. A generally accepted treatment for the quantitative description does not exist as yet.

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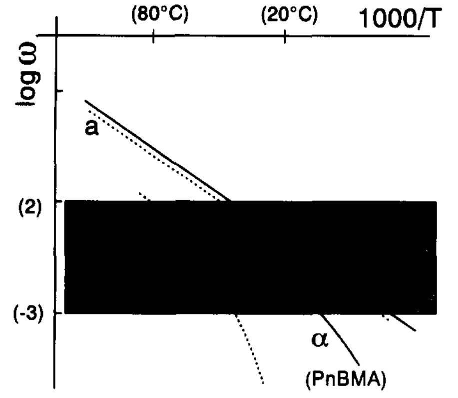

Figure 1 Frequency windows of the dynamic shear measurements in an Arrhenius diagram for (—) PnBMA and (······) PEMA: (α) dynamic glass transition (α relaxation); (β) local mode; (a) high temperature process. The traces in the regions outside the shaded area are extrapolated or assumed. The onset of the α relaxation in PnBMA was detected at $\log[\omega(\mathrm{rad\,s^{-1}})]\approx 0$ and $T\approx 20°\mathrm{C}$[6]. The estimated PEMA onset region is obtained by an extrapolation based on a comparison with PnBMA. Dielectric loss measurements (connected with the $\rho\rho$-correlation function) show another behaviour (splitting instead of an α onset). Both are compared in reference 6

The aim of this paper is to investigate in detail the influence of physical ageing on the dynamic shear modulus near the onset of the dynamic α glass transition in the splitting region of PnBMA and poly(ethyl methacrylate) (PEMA).

EXPERIMENTAL

Materials

PnBMA and PEMA were purchased from Polyscience Inc. Average molecular weights ($\bar{M}_w$) and polydispersity ($\bar{M}_w/\bar{M}_n$) were determined by g.p.c. T_gs were calculated by an equal area construction from heat capacity (C_p) measurements. The C_p data were taken from d.s.c. using a Perkin-Elmer DSC-2 ($\dot{T}=+10\,\mathrm{K\,min^{-1}}$). The values obtained for PnBMA are $\bar{M}_w=330\pm 8\,\mathrm{kg\,mol^{-1}}$, $\bar{M}_w/\bar{M}_n=2.35\pm 0.1$ and $T_g=22°\mathrm{C}$, and for PEMA are $\bar{M}_w=72\pm 3\,\mathrm{kg\,mol^{-1}}$, $\bar{M}_w/\bar{M}_n=1.9\pm 0.1$ and $T_g=74°\mathrm{C}$. N.m.r. experiments showed that both samples are atactic (PnBMA contains 78±4% *syn* sequences, corresponding to ~60% *syn* triads, and PEMA contains 78±3% *syn* sequences, corresponding to ~60% *syn* triads).

Mechanical experiments

The dynamic shear modulus $G^*(\omega)=G'+iG''$ was measured in the frequency range from 500 to 0.001 rad s^{-1} using Rheometrics RDA II analysers. To investigate the influence of non-equilibrium effects a special time–temperature program was used. All isothermal measurements were carried out identically. The sample was equilibrated at a temperature T_i above T_g for 10 min (PnBMA: $T_i=50°\mathrm{C}$; PEMA: $T_i=105°\mathrm{C}$). The sample reached equilibrium after a few minutes, and the 'memory' of the glass transition was deleted. Then, the sample was cooled down ($\dot{T}\approx -0.9\pm 0.2\,\mathrm{K\,s^{-1}}$) to the measuring temperature T_e and isothermally aged for $t_e=5$ min prior to the shear measurements. Two isothermal frequency sweeps in the range from 500 to 0.001 rad s^{-1} were continuously performed, beginning at high ω values. The first was carried out immediately ($t_e=5$ min), and the second was carried out after an additional ($t_e=600$ min) isothermal ageing at T_e.

RESULTS

The G'' values of PnBMA in the range from −10 to 30°C are presented in *Figure 3*. The first set of frequency sweeps, started after isothermal ageing for 5 min ($t_e=5$ min), are shown in *Figure 3a*. The development of the α process is only detectable as a change in the slope in the low frequency wing of the β relaxation, or a broadening of this process below 20°C. There is no indication of two separated processes, i.e. α and β processes. The situation

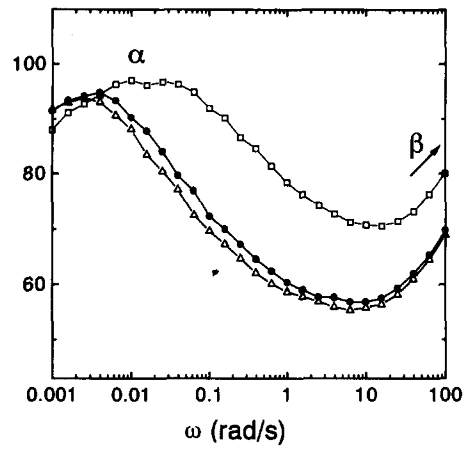

Figure 2 Shear loss modulus G'' of PMMA as a function of frequency ω for different ageing times (□, $t_e=5$ min; ●, $t_e=600$ min; △, $t_e=1195$ min) at a temperature $T_e=T_g-8\mathrm{K}=93°\mathrm{C}$. For details of the time–temperature program, see text

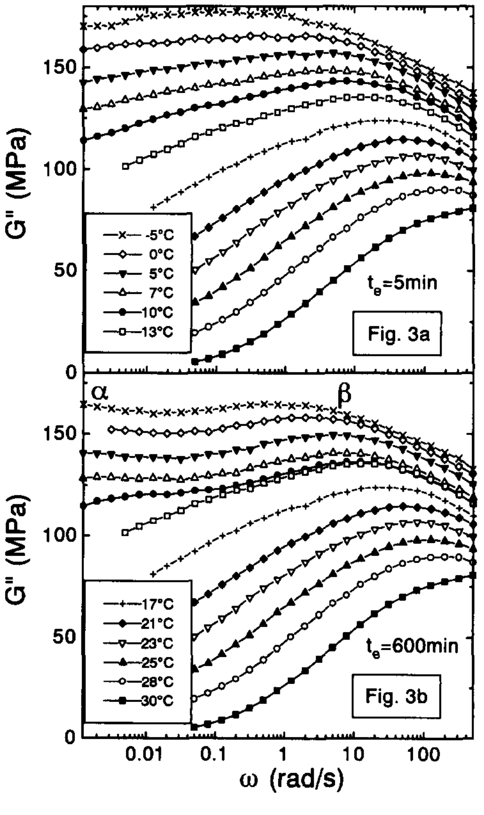

Figure 3 Isothermal measurements of the shear loss modulus G'' in the onset region of PnBMA (a) before ($t_e=5$ min) and (b) after isothermal ageing ($t_e=600$ min). The details of the time–temperature program are described in the text. The curves are vertically shifted by 9.85 MPa per isothermal data set; the modulus scale is for $T_e=30°\mathrm{C}$. The development of the α relaxation during the ageing process on the low frequency wing of the local β mode is clearly visible

after $t_e = 600$ min is presented in *Figure 3b*. The frequency sweeps at higher temperatures ($T_e > 12°C$) are virtually unchanged by physical ageing while the other sweeps are dramatically modified. At $T_e < 12°C$ the development of the α process is now clearly visible as a shoulder or, at lower temperatures, as an independent relaxation peak. From additional measurements at longer times (not shown here) we conclude that below $T_e = -3°C$ equilibrium is not reached after $t_e = 600$ min. This is also evident from an upward bending of the α trace in the Arrhenius representation of our data at $T_e \approx 21°C$ ($1000\,K/T = 3.4$) for $t_e = 5$ min and at $T_e \approx 4°C$ ($1000\,K/T = 3.6$) for $t_e = 600$ min (*Figure 4*).

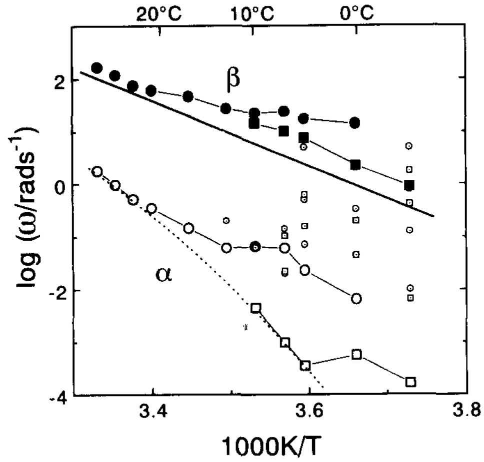

Figure 4 Arrhenius diagram for the maxima of the shear loss modulus of PnBMA. The large symbols are the values taken from a fit with two logarithmic Gauss functions [●, β ($t_e = 5$ min); ■, β ($t_e = 600$ min); ○, α ($t_e = 5$ min); □, α ($t_e = 600$ min)]: (——) β fit from dielectric, photon correlation spectroscopy and shear measurements over a wide frequency–temperature range[6]; (····) interpolated equilibrium curve for the α relaxation. The small symbols represent the rippling maxima (*Figure 6*) for different ageing times (⊙, $t_e = 5$ min; ⊡, $t_e = 600$ min). Above $T_e = 13°C$ no rippling was detected

The values for the mean relaxation frequencies shown in the Arrhenius diagram (*Figure 4*) were taken from a fit of the $G'' - \log \omega$ sweeps by a superposition of two logarithmic Gauss functions. These fits of the shear loss α and β maxima in the onset region agree well with the experimental data (*Figure 5*).

Two ageing effects seem to be significant for the G'' curves in PnBMA. First, there is a shift of the developing α relaxation to lower frequencies with increasing ageing time. This shift is, of course, connected with an increasing separation of the α and β processes (the formation of two maxima in G''). Second, there is a decrease of the maximum value of the β relaxation, $G''_{\beta\max}$, which seems to be accompanied by a decrease of the β intensity (especially in the low frequency part). This effect is related to an increase of the α intensity and a sharpening of the α relaxation.

Analysing the measurements at $T_e < 15°C$ (e.g. at $T_e = 5°C$ in *Figure 6*) we see some 'rippling' (small maxima of G'') in all frequency sweeps below 13°C. To our knowledge, this effect has not been previously reported. (Small peaks in the network plateau zone of different polymers and a multiplicity of the local mode of PMMA were described by Bartenev and Sanditov[24].) Under identical conditions, rippling is reproducible within 0.3 decades in PnBMA. The rippling structure of the frequency sweeps is somewhat smoothed by the ageing process, but the rippling effect survives even after very long ageing times. The ripples seem to shift to lower ω values (small symbols in *Figure 4*), in accordance with

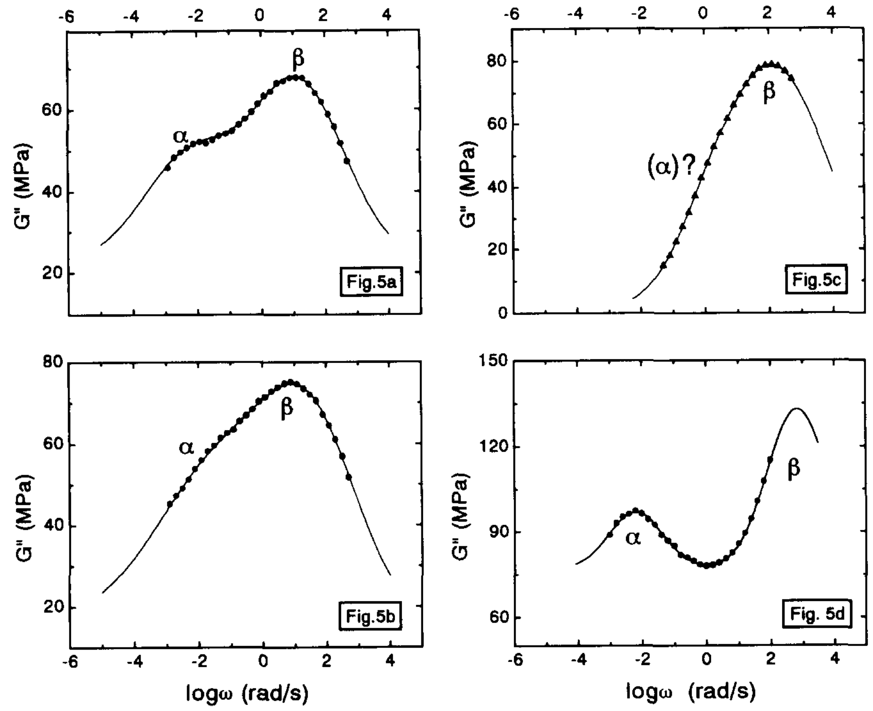

Figure 5 Examples for the fitting of the G'' data near the α and β loss maxima by two logarithmic Gauss functions. The maxima frequencies are: (a) PnBMA, $t_e = 600$ min, $T_e = 10°C$, $(\log \omega)_\alpha = -2.27 \pm 0.17$, $(\log \omega)_\beta = 1.16 \pm 0.05$; (b) PnBMA, $t_e = 5$ min, $T_e = 10°C$, $(\log \omega)_\alpha = -1.14 \pm 0.25$, $(\log \omega)_\beta = 1.42 \pm 0.11$; (c) PnBMA, $t_e = 600$ min, $T_e = 25°C$, $(\log \omega)_\alpha = -0.01 \pm 0.05$, $(\log \omega)_\beta = 2.08 \pm 0.02$, $A_\alpha = 7.97$, $A_\beta = 335$; (d) PEMA, $t_e = 600$ min, $T_e = 63°C$, $(\log \omega)_\alpha = -2.20 \pm 0.01$, $(\log \omega)_\beta = 2.85 \pm 0.20$

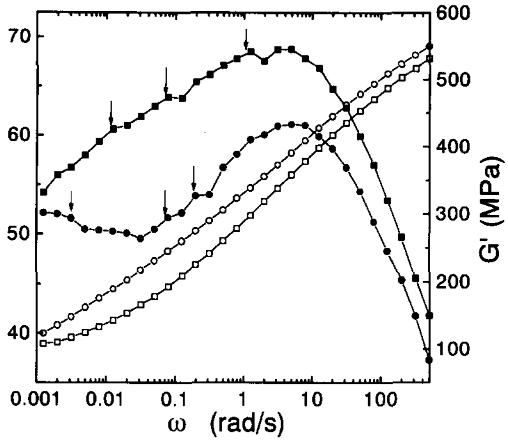

Figure 6 Rippling in the frequency sweeps of PnBMA at $T_e = 5°C$ (solid symbols, G''; open symbols, G'; squares, $t_e = 5$ min; circles, $t_e = 600$ min). The arrows label the positions of the rippling maxima

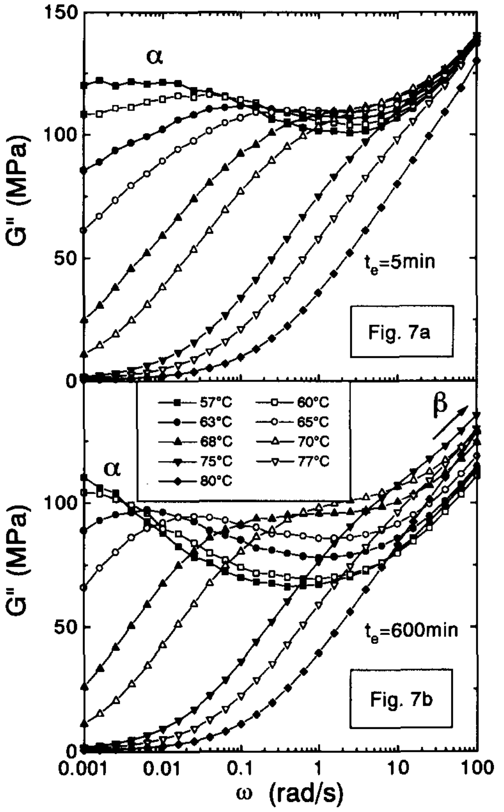

Figure 7 Shear loss modulus as a function of frequency in the frequency window below the assumed α onset region of PEMA. Frequency sweeps after (a) $t_e = 5$ min and (b) $t_e = 600$ min isothermal ageing. For details of the time–temperature program, see text. The curves are not vertically shifted

the general trend during the ageing process. Possible explanations of rippling are discussed below.

Ageing in PEMA at different temperatures T_e between 57°C and 80°C is presented in *Figure 7*. The experiments were performed in the same manner as for PnBMA. The general situation in PEMA is somewhat changed in comparison to PnBMA because the onset of the α transition is at higher frequencies than in PnBMA (*Figure 1*). Hence, the measurements can only detect the α relaxation after splitting, on the low frequency wing of β. Considerable non-equilibrium effects also exist in this region ($T_g = 74°C$). In the first frequency sweeps (corresponding to $t_e = 5$ min) the α relaxation is merely a significant shoulder (*Figure 7a*); clearly visible α maxima far away from the local β mode are observed again after $t_e = 600$ min (*Figure 7b*).

Some significant rippling near the loss maximum of the α relaxation is also observed in PEMA (*Figure 8*). This fine structure is, similar to the PnBMA ripples, reproducible and is also detectable in slight modification for the long ageing times.

An overview of the dynamic shear measurements in PEMA is given in the Arrhenius representation in *Figure 9* (similar to *Figure 4* for PnBMA). The large symbols represent the mean relaxation frequencies taken from a fit of the G'' data with the two logarithmic Gauss functions. Influenced by non-equilibrium, both α traces ($t_e = 5$ and 600 min) deviate from the assumed (dotted) equilibrium trace at low temperatures. The bending temperatures are $T_e = 73°C$ ($1000\,K/T = 2.88$) at $t_e = 5$ min, and $T_e = 66°C$ ($1000\,K/T = 2.95$) at $t_e = 600$ min.

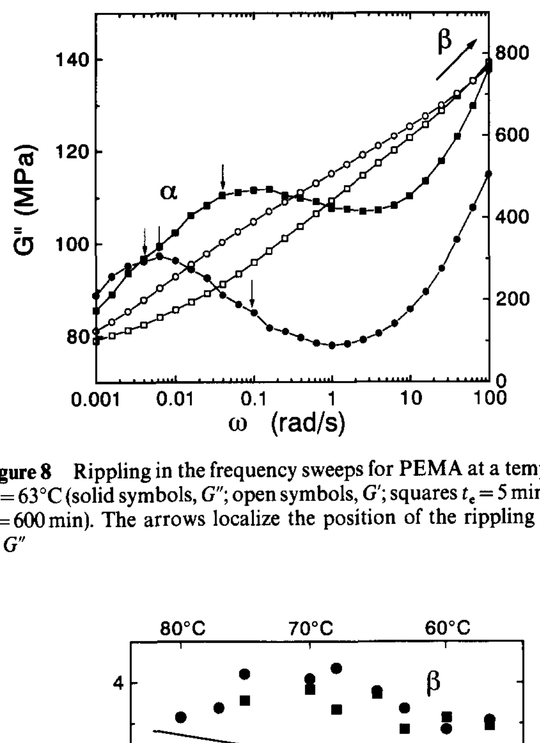

Figure 8 Rippling in the frequency sweeps for PEMA at a temperature $T_e = 63°C$ (solid symbols, G''; open symbols, G'; squares $t_e = 5$ min; circles, $t_e = 600$ min). The arrows localize the position of the rippling maxima in G''

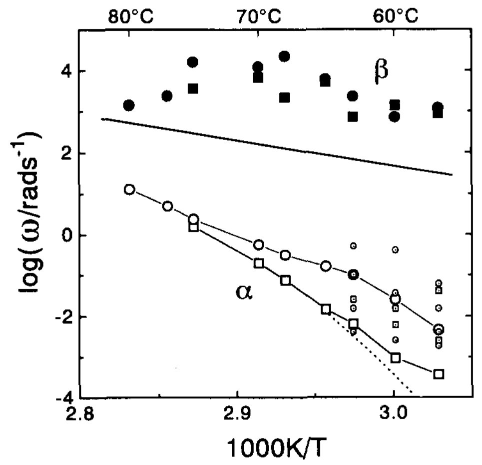

Figure 9 Arrhenius diagram for the G'' maxima of PEMA. The large symbols are the values taken from a fit of the experimental data by a superposition of two logarithmic Gauss functions (●, β ($t_e = 5$ min); ■, β ($t_e = 600$ min); all the β maxima are extrapolated; ○, α ($t_e = 5$ min); □, α ($t_e = 600$ min); (——) β fit from dielectric measurements over a wide frequency–temperature range; (····) interpolated equilibrium curve for the α relaxation. Small symbols represent the rippling maxima for different ageing times (⊙, $t_e = 5$ min; ⊡, $t_e = 600$ min). No rippling was detected above $T_e = 70°C$

DISCUSSION

Two problems complicate the evaluation of equilibrium moduli in the splitting region of the two poly(alkyl methacrylate)s: the large time-dependent non-equilibrium effects and the fine structure in the frequency sweeps. Both render it more difficult to determine a single α relaxation maximum in the usual manner.

Ageing process

Below T_g, an increase of the mean α relaxation time up to two decades and a per cent range increase of the shear modulus G' around the α maximum were observed during physical ageing (*Figures 6* and *8*). These tendencies are also known from measurements in other polymers[25,26] below the T_g. As concluded from the frequency–temperature shift, equilibrium dynamic shear measurements for $\omega > 0.1\,\mathrm{rad\,s^{-1}}$ can be made above $T_g - 10\,\mathrm{K}$. In this temperature region the time to reach practical equilibrium, $t_e(T_e)$, is manageable and is usually $< 10\,\mathrm{h}$.

In the splitting region the frequency–temperature equivalence is, of course, invalid because the two relaxation processes (α and β) are overlapping and diverging at lower temperatures. It is necessary to go well below T_g ($T_e < T_g - 10\,\mathrm{K}$) in the two poly(alkyl methacrylate)s to gather information about the developing α relaxation (*Figure 1*). At such temperatures the equilibrating time rapidly increases. In both investigated systems (PnBMA and PEMA), at temperatures $T_e = T_g - 20\,\mathrm{K}$, i.e. 20 K below the d.s.c. T_g, the equilibrium was not reached in practicable times ($t_e = 1200\,\mathrm{min}$). The ageing effect is logarithmic in time: $T_g - T_e$ is roughly proportional to the logarithm of the time necessary to reach practical equilibrium, $\log[t_{eq}(T_e)]$ or, in other words, the logarithm of all equilibrating times, $\log[t_{eq}(T_e)]$, is in good agreement with the beginning of the deviation from the equilibrium frequency trace of the α relaxation at the corresponding temperature T_e (*Figure 4*). Therefore, it is nearly impossible to realize equilibrium measurements below the temperature $T_e = T_g - 20\,\mathrm{K}$ in our samples.

Thus, ageing restricts the low frequency region around the onset of the α transition that can be investigated in equilibrium in our experiments. Other methods to extrapolate the non-equilibrium measurements at lower temperatures to equilibrium would be very helpful. In the splitting region of our methacrylates, this seems to be possible only by means of a complex analysis including a numerical multiparameter fitting procedure. The following things should be kept in mind:

1. The relatively narrow frequency window of the mechanical measurements, although nearly five decades, does not allow the simultaneous determination of both outer wings for the α and β processes.
2. It is an open question as to whether the usual formulae for the shape of α and β relaxation are applicable in the splitting region and whether the change in shape during ageing can be modelled by a simultaneous change in several parameters.
3. There are a lot of uncertainties in the understanding of the physical ageing process in the splitting region. We found indications of a superposition of shift and sharpening of the α relaxation during the ageing process, probably accompanied by an intensity change of (or exchange between) α and β relaxation (the α intensity increases while the β intensity decreases).

The different properties are related (e.g. the intensity, shape and position of α and β relaxation) especially with respect to the intensity changes. In future we intend to make a systematic comparison in a series of different poly(alkyl methacrylate)s, in the hope of fixing some of the free parameters in this multiparameter fitting problem. Our main aim will be to confirm the separate α onset well below (about one or two decades) the β relaxation.

Rippling

The rippling structure appears in the frequency sweeps at lower temperatures ($T_e \lessapprox$ about $T_g - 10\,\mathrm{K}$) around the maximum of the α relaxation and between α and β (*Figures 4* and *9*). We see two possibilities for an explanation. Rippling could be: (1) a property of the developing α relaxation in equilibrium; or (2) the result of non-equilibrium processes.

With regards to the first possibility, there are concepts assuming that the α process is co-operative with a characteristic length ξ_a of the order of a few nanometres[5,10]. According to this, it could be understood that, on going from β to α, the rippling is due to the successive incorporation of more and more 'co-ordination shells' into the co-operative movement. Consequently, fine structure is especially pronounced near the α onset where the co-operative motions are assumed to start.

There are some arguments against the equilibrium hypothesis. The temperature region mentioned above is related to the T_g. Furthermore, the rippling structure is partially smoothed by ageing. This could mean that rippling is due to, or at least amplified by, non-equilibrium.

During the dynamic measurements time flows so that the frequency dependence of G'' is superposed by a time dependence from ageing effects. The measured modulus values become a function of frequency and time. The frequency sweeps at lower temperatures are inevitably modified by physical ageing.

During a continuous ageing process without simultaneous changes of shape, intensity and position of the α relaxation we would see no reason for multiple maxima in a frequency sweep. However, the situation is much more complex because there are simultaneous changes in intensity, shape and position of the relaxations due to physical ageing.

The concept of sequential ageing in time[27], extended later to length[28], tries to describe the ageing by means of a structural relaxation including successively longer time and length scales. This concept assumes a continuous spectrum of modes between α and β relaxation, similar to that in equilibrium between α and β. The slower part of these modes freezes-in during the cooling from the melt to the glassy state at T_g, e.g. with a finite cooling rate $\dot{T}$. The frozen modes and length ranges (coupled by a general scaling assumption[7]) relax afterwards step by step during the isothermal ageing process at T_e (sequential structural relaxation). This leads to time-dependent rearrangements of the relaxation spectrum and could be, in combination with the time–frequency program of our linear measurements, a reason for the rippling structure (or its amplification) in the isothermal frequency sweeps. This effect could be especially pronounced near the onset of the α relaxation, because here the underlying motions have only a small co-operativity and will be especially affected by the discreteness of the molecular elements involved.

In addition to the 'first-order effect' of non-equilibrium just described, we also expect a second-order ageing effect during a single point measurement. In particular, at very low frequencies (a single point measurement at 0.001 rad s^{-1} requires ≈ 300 min) a systematic modification of the measured values by ageing also seems to be possible.

The rippling in poly(alkyl methacrylate)s and possible explanations of this phenomenon will be the subjects of further investigations. Experiments of the time dependence at different fixed temperatures and frequencies are planned. Such measurements guarantee the best stability of the measuring devices.

CONCLUSIONS

The temperature region around the onset of the dynamic shear relaxation in PnBMA and PEMA was found to be sensitive to freezing-in processes. This was expected because the α onset frequencies are low, i.e. in the hertz (PnBMA) and kilohertz (PEMA) regions. Isothermal ageing in both samples leads to a shift of the α relaxation towards equilibrium which means longer relaxation times with increasing ageing time t_e. This shift is accompanied by an intensity increase of the α relaxation and an intensity decrease of the local β mode. At temperatures T_e below $T_g - 20$ K equilibrium cannot be reached in practicable equilibrating times ($t_e < 1200$ min).

The rippling observed seems to be an inherent part of the α onset. Two possible explanations for this phenomenon are discussed: (1) the fine structure is a manifestation of an equilibrium dispersion near the onset of the α relaxation; or (2) rippling is due to a superposition of the four different time-scales during the dynamic measurements (internal relaxation spectrum for α and β, probing time and ageing time). We assume that rippling is connected with the discreteness of particle arrangements (e.g. co-ordination shells) in the range of small cooperativity.

ACKNOWLEDGEMENTS

The authors are grateful for financial support from the Deutsche Forschungsgemeinschaft (DFG). Rheometrics Europe is acknowledged for allowing some dynamic mechanical measurements to be performed in their laboratories in Frankfurt (Main). Thanks are due to Dr S. Höring and Professor K. Schlothauer for characterization of the polymers.

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