JOURNAL OF MATERIALS SCIENCE **37** (2002) 4273–4277

FTIR investigation of structural modifications during low-temperature ageing of polycarbonate

N. HEYMANS*, S. VAN ROSSUM‡
Physique des Matériaux de Synthèse 259, Université Libre de Bruxelles, B-1050 Belgium
E-mail: nheymans@ulb.ac.be
E-mail: vanrossum.s@pg.com

Conformational changes are sought during low-temperature ageing of solution-cast films of BPA-polycarbonate, by observing the conformationally sensitive IR aromatic breathing band at 1600 cm^{-1}. Preliminary results using the carbonyl band at 1775 cm^{-1} had shown some indication of ageing-induced changes in the distribution of conformations. The present results obtained on the 1600 cm^{-1} band show no indication whatever of conformational rearrangements. This result, at variance with observations of conformational rearrangements accompanying sub-T_g annealing, lends support to the concept that sub-T_g annealing and low temperature ageing are two distinct processes.

1. Introduction

This work is part of an ongoing program of investigations aiming towards an improved understanding of physical modifications occurring during thermomechanical treatments of solid polymers. It has been known for some time that the effects of heat treatments on mechanical behaviour of solid polymers depend on the temperature range. Treatments just below the glass transition are accompanied by volume contraction and enthalpic relaxation, and lead to an increase in the yield stress of the polymer. Treatments well below the glass transition do not give rise to any measurable enthalpic relaxation, are accompanied by very little volume contraction, do not give rise to any change in yield or post-yield behaviour, but reduce the polymer's capacity for low-stress anelastic deformation. As a result these treatments affect the dynamic modulus and loss tangent in the linear range of viscoelasticity, and also affect low-stress creep behaviour. Although the term "physical ageing" is applied loosely in the literature to either treatment, in this paper and related work we apply the term "ageing" to the lower temperature process, and "annealing" to the higher temperature process. The annealing range depends to some extent on the time scale of observations and on prior thermomechanical treatment; as a rule of thumb this range extends from T_g to $T_g - 50$ K. The ageing range extends from below the annealing range down to the first secondary transition (β transition). The two ranges are well separated in BPA-polycarbonate, which has a T_g of approximately 145°C and T_β of approximately -100°C.

Although the effects of thermomechanical treatments on mechanical behaviour are well known, this is not true of the molecular mechanisms involved. In a preliminary investigation by FTIR of conformational changes occurring in BPA-polycarbonate during thermomechanical treatments, the conformationally sensitive C=O absorption band at 1775 cm^{-1} was observed [1]. These observations suggested that during room-temperature ageing, a narrowing of distributions of carbonate conformations about locally stable *trans-cis (t-c)* and *trans-trans (t-t)* conformations occurs. These conformations are defined on Fig. 1. No shift from *t-c* to *t-t* conformations was observed; such shifts are however observed during sub-T_g annealing [1, 2]. The 1775 cm^{-1} band is sensitive to Fermi resonance, which might either obscure or enhance small modifications such as those which are expected to occur during physical ageing or annealing. In a previous paper, conformational changes during annealing were investigated more thoroughly, using the potentially cleaner band at 1600 cm^{-1}. In this paper, room-temperature ageing is investigated using the same band.

2. Experimental

2.1. Thin film preparation

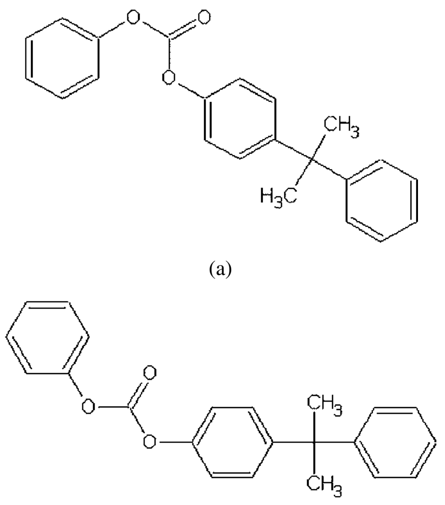
The material used was commercially available Makrolon® (Bayer) in a 2 mm thick sheet. This sheet was used because it was the same material as had been used previously in investigations of thermomechanical effects in this laboratory [1–6]. Thin films were prepared by solution-casting from a 6% solution of PC cuttings in 1,2-dichloroethane onto glass slides, and annealed at 165°C for 1 h to eliminate residual solvent and reduce internal stresses, as described previously [2].

---

[*] Author to whom all correspondence should be addressed.

[‡] *Present address:* Procter and Gamble Eurocor, Temselaan 100, B-1853 Strombeek-Bever.

0022–2461 © *2002 Kluwer Academic Publishers*



(a)

(b)

Figure 1 Conformations of BPA-PC, defined as *trans* (a) or *cis* (b) with respect to the carbonate group. (Schematic; the aromatic groups are not coplanar).

2.2. Ageing treatments

After the preliminary heat treatment at 165°C, the samples were transferred to a specially designed environmental chamber fitted in the sample compartment of a Perkin–Elmer 1725X FTIR spectrometer. During the heat treatment and transfer, samples were placed in a sample holder having high thermal inertia designed to avoid indirect quenching effects. Such effects are liable to lead to considerable data scatter. Special care was taken to leave the film stress-free. Ageing was carried out at temperatures ranging from 25°C to 60°C. This range was selected because it is well below the annealing range, which extends from T_g (approximately 145°C) to approximately $T_g - 50$ K, and also well above the β transition temperature (approximately -100°C), which is the lower limit for ageing.

2.3. Infrared measurements

In previous work, conformational changes were monitored using the conformationally sensitive C=O stretching absorption at 1775 cm^{-1}. This band is, however, complicated by Fermi resonance [7], and five components appear on deconvolution, casting doubt on reliability of quantitative or even semiquantitative estimates of conformational changes using this band. In the present work, the conformationally sensitive in-plane aromatic group stretching vibration at 1600 cm^{-1} is investigated; this band contains clearly identifiable contributions from *t-t* and *t-c* conformers at approximately 1594 cm^{-1} and 1604 cm^{-1} respectively. An optimal trade-off between low absorbances in the linear range of Beer's law, and high absorbances required for adequate sensitivity to small modifications, is obtained for a film thickness of approximately 80 μm; for various reasons detailed in [2], two films approximately 40 μm thick were superposed.

Spectra were obtained at 4 cm^{-1} resolution. An initial spectrum was taken immediately after transferring the sample to the environmental chamber after the heat treatment; the corresponding time was taken as the start of ageing. The following spectrum was taken 10 minutes later, following which spectra were taken at time intervals on a logarithmic scale of ratio 2. At each temperature ageing was allowed to proceed for approximately 10 days. A fresh sample was used for each ageing temperature. Details of the experimental procedure are given in [2].

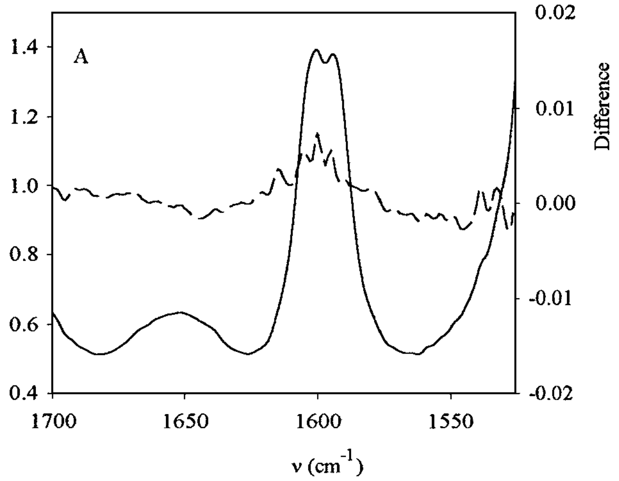


Figure 2 Full line: aromatic breathing band of polycarbonate after 13 days ageing at 60°C; dashed line: difference on subtraction of 20 min spectrum. Note different scales.

2.4. Data analysis

Spectra were analysed in the range 1525–1700 cm^{-1}, following various procedures. An initial analysis was performed by subtracting the reference spectrum from the current spectrum, following the procedure given in detail in [2]. This method is extremely sensitive to small modifications in the spectra. However, as discussed below, no modifications were observed after initial rapid changes attributed to thermal equilibration of the sample. A typical example is given in Fig. 2; the difference between the spectra obtained after 13 days and 20 minutes at 60°C contains no recognisable features whatever.

The spectra were then analysed individually using a commercially available curve fitting program specially adapted to spectroscopy (PeakFit®). However, this package was found unsatisfactory, mainly because it automatically assumes identical widths for all peaks; also, the investigated region of the spectrum contains contributions from neighbouring bands, which are difficult to take into account using the baseline shapes provided in the package. Furthermore, the package claims uncertainties in fitted parameters of order of 1%, which is considerably larger than any modifications expected during ageing. (Modifications obtained during sub-T_g annealing did not exceed 0.5% [2]).

Because of these limitations, the spectra were finally analysed by assuming a Lorentzian:

$$A(\nu) = \frac{h}{1 + ((\nu - \nu_m)/w)^2} \tag{1}$$

for each band influencing the investigated region (i.e., the two components of the 1600 cm^{-1} band, the neighbouring 1505 cm^{-1} band which saturates for films of this thickness, the carbonyl band centered at 1775 cm^{-1}, and a low, broad absorption at 1650 cm^{-1}),

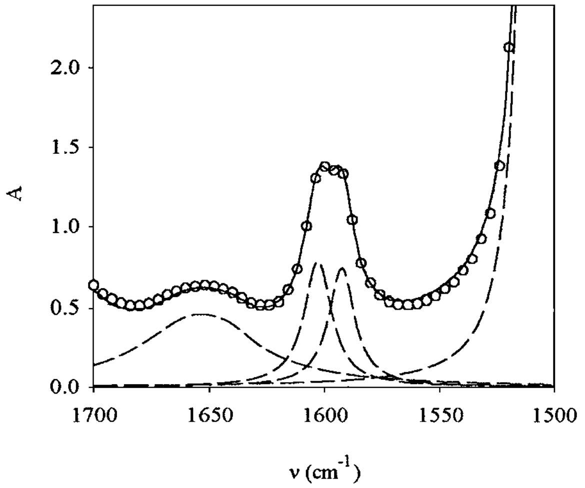


Figure 3 Contributions of 1600 cm^{-1} components and neighbouring bands to absorbance in 1700–1530 cm^{-1} range. Sample freshly quenched to 60°C. Circles: experimental data; dashed lines: calculated components; full line: adjusted spectrum.

also adding a linear baseline. In Equation 1, A is absorbance at wavenumber v, v_M is wavenumber at maximum, h is maximum amplitude and w is half width at half height. Curve fitting was carried out using the non linear regression capabilities of SigmaPlot®. This procedure allows the height, half width and wavenumber of each component to be adjusted independently.

Because of the large number of parameters, an iterative procedure was used to obtain them. Initially, reasonable starting values were assigned to the parameters describing the 1505, 1650 and 1775 cm^{-1} absorptions, and the remaining parameters, i.e., those of the two contributions to the 1600 cm^{-1} absorption, were fitted using the data between 1625 and 1575 cm^{-1}. Next the parameters of the 1505 cm^{-1} peak were adjusted using the data between 1625 and 1530 cm^{-1}. Then the parameters of the broad absorption at 1650 cm^{-1} were adjusted using the data between 1700 and 1625 cm^{-1}. Finally, the parameters of the 1600 cm^{-1} contributions were adjusted again as in the first step, but accounting for the newly obtained values for the other contributions. If necessary the whole process was repeated until convergence. An example of the resulting decomposition and a comparison between the data and the fitted absorbance is given on Fig. 3.

3. Results

None of the procedures described above was successful in showing up any conformational changes whatever in the course of low-temperature ageing. A typical example showing peak half widths, and the ratio S_{1603}/S_{1593} of peak areas ($S = \pi h w$) is given on Fig. 4. The present data show, however, as found by Dybal *et al.* [8] and by Tekely and Turska [9] that conformational rearrangements do indeed occur even well below T_g; the peak area ratio, and peak half widths and wavenumbers are all temperature dependent. This is demonstrated on Fig. 5, where each data point represents the time average of the appropriate quantity for a different sample. Two samples were slightly hazy, probably indicating some degree of crystallinity. Data from these samples are represented by cross-haired symbols on Fig. 5. It is interesting to note that the only quantity that appears to be affected by crystallinity is the wavenumber of the 1603 cm^{-1} peak, which is slightly lower for the partially crystalline samples. For all other parameters, data for the partially crystalline samples falls within scatter. The general trends observed are a decrease in S_{1603}/S_{1593}, a decrease in peak wavenumbers, a decrease of the half width of the 1603 cm^{-1} component and an increase

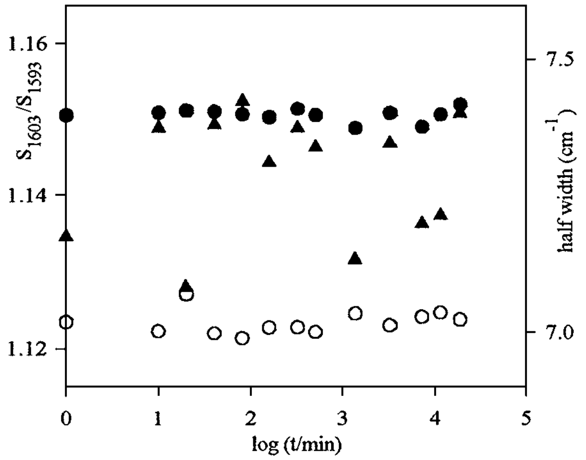


Figure 4 Peak half widths w_i and ratio S_{1603}/S_{1593} of peak areas during ageing of polycarbonate at 60°C. Circles: half widths, filled: 1603 cm^{-1}, open: 1593 cm^{-1}. Triangles: S_{1603}/S_{1593}.

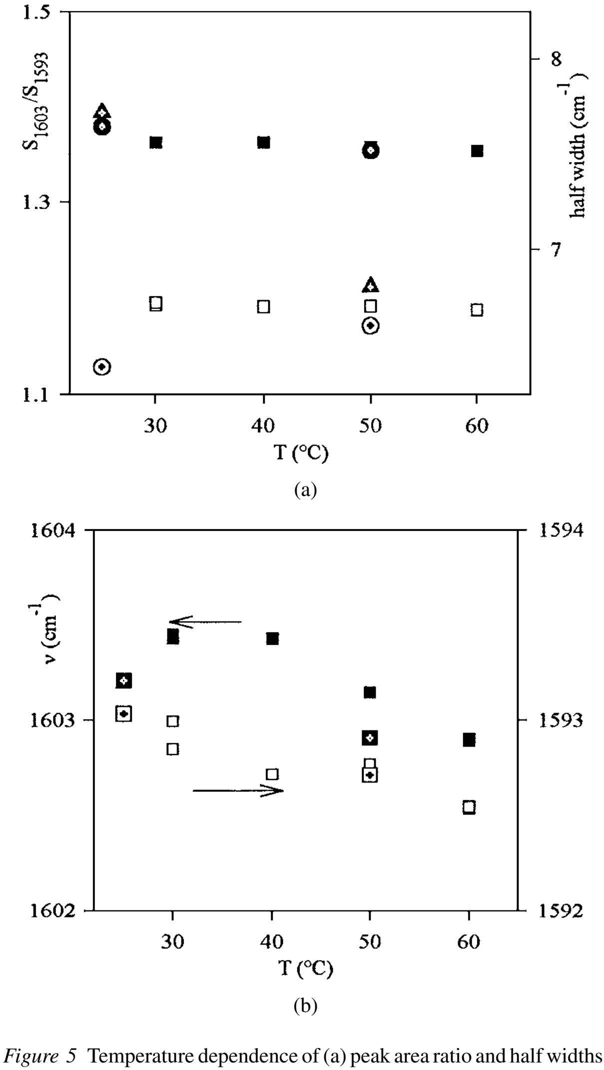


Figure 5 Temperature dependence of (a) peak area ratio and half widths, and (b) wavenumbers (1600 cm^{-1} band, polycarbonate). Symbols as Fig. 4, and squares: wavenumbers.

of the half width of the 1593 cm^{-1} component with increasing temperature.

4. Discussion

The present results obtained using the 1600 cm^{-1} band do not confirm preliminary observations [1] which indicated a change in width of conformer populations with ageing. However, the preliminary result was obtained by taking a spectrum on a well-aged sample, treating the sample at 160°C for 1 h, and then taking a spectrum on the unaged sample after cooling it to room temperature. In the light of more recent work, it is not at all unlikely that this procedure altered the reference state of the sample. At the time, it was also not realised how sensitive the peak half widths were to small temperature fluctuations. Thus, the previous result was probably an artefact.

It might be argued that the ageing times used in this work were insufficient, and that there might be a long induction time before the start of ageing. However, observations of the α' loss peak by Othmezouri–Decerf [10] indicate that ageing in PC starts after at most a few hours at room temperature, and also that the activation energy for ageing is approximately 213 kJ/mol. This means that 10 days at 60°C is equivalent to approximately 300 years at room temperature, so if no modifications of conformationally sensitive bands show up during ageing for 10 days at 60°C, it can safely be concluded that ageing is not accompanied by changes in conformer population distributions.

This behaviour is different from that observed previously [2] during sub-T_g annealing, where a distinct shift from the 1591 cm^{-1} to the 1601 cm^{-1} component occurred. This brings fresh support to the concept that sub-T_g annealing and low temperature ageing are two distinct processes: for instance, the former is linked with enthalpy and volume relaxation and produces an increase in the yield stress of amorphous materials, whereas the latter does not affect the yield stress and does not produce any visible modification of DSC scans, but leads to a decrease of the low stress anelastic component of deformation and of the loss tangent [11].

Thus the present results appear at first sight to lend support to the conclusions reached by Bauwens–Crowet [6] and Othmezouri–Decerf [10], namely that annealing and ageing are two distinct processes. They found it possible to describe the α' shoulder in aged samples of polycarbonate that had been previously quenched, cold rolled or anelastically deformed by taking two processes into account: ageing which is mainly active at temperatures far beneath the glass transition, and annealing which is active at temperatures closer to the glass transition, in particular during the temperature sweep itself. Although both processes are thermomechanically activated, their time dependencies are dissimilar. In particular, the activation energies found for the two processes are quite different. The activation energy for annealing is 267 kJ/mol, whereas it is only 213 kJ/mol for ageing after quenching or low strain deformation [10] and 125 kJ/mol for ageing after plastic deformation [6].

The molecular mechanism of low temperature ageing remains unelucidated. Some degree of molecular mobility is required for physical ageing, which does not occur below the β transition. Results obtained from a combination of DMS, DSC and NMR measurements are consistent with a picture involving small regions of chain alignment, or "bundles," defined by the volume within which cooperative motion occurs during phenyl ring π-flips [12]. Motion within such a bundle does not require any change in conformer distribution, but can lead to closer packing and hence to a loss of mobility. Ageing at room temperature is indeed accompanied by a very small amount of volume contraction after a quench [13], but contraction is imperceptible after slow cooling [14], hence volume contraction does not at first sight appear to be essential for ageing to occur. This interpretation may be misleading, however. A recent model developed by Drozdov [15] explains physical ageing in terms of the concept of traps, using extreme value statistics. In this model, physical ageing is connected with the time dependence of the energy landscape, leading to slowing down of molecular rearrangements as these lead to an increase of the depth of potential wells (or traps). This model affords insight into some aspects of physical ageing, in particular the fact that changes in packing density that are barely perceptible when averaged can induce measurable changes in mobility. Drozdov's model must in the present state be taken as purely phenomenological, since it contains a number of ad hoc assumptions. This model, however, allows an alternative interpretation of the present and previous results, namely that plastic deformation, ageing and annealing may be several aspects of a single process. This point of view is compatible with a comparison of the activation energies obtained under various conditions: the highest activation energy is obtained for plastic deformation (316 kJ/mol), followed respectively by annealing, ageing after quenching and lastly ageing after plastic deformation. The fact that the kinetics of ageing depend on the pretreatment suggests that a single process is active, governed by a distribution of activation energies. The pretreatment or the temperature range where the thermal treatment is carried out then acts as a thermomechanical window investigating a particular range of activation energies. Annealing can then be thought of as a high-temperature aspect governed by average value statistics, whereas ageing would be a low-temperature aspect governed by extreme value statistics. If this interpretation is correct, it is unlikely that experimental methods which are sensitive to average values of properties will be able to yield information on processes active during ageing.

5. Conclusions

The present work shows that there is no indication of any conformational changes during physical ageing in polycarbonate far below the glass transition. This result is compatible with observations by Lani Lee *et al.* [12] showing that low-temperature mobility does not require conformational rearrangements, and also seems to lend support to the concept that annealing close to T_g and low-temperature ageing are two distinct processes.

However, the possibility that ageing and annealing are governed by a single process cannot be ruled out.

Further work, particularly in the intermediate temperature range where both processes may be expected to interact, is required to investigate this possibility.

References

1. N. HEYMANS, *Polymer* **38** (1997) 3435.
2. N. HEYMANS and B. DEQUENNE, *ibid.* **42** (2001) 5337.
3. C. BAUWENS-CROWET and J.-C. BAUWENS, *ibid.* **27** (1986) 709.
4. *Idem.*, *ibid.* **31** (1990) 248.
5. *Idem.*, *ibid.* **31** (1990) 646.
6. C. BAUWENS-CROWET, *J. Mater. Sci.* **34** (1999) 1701.
7. P. SCHMIDT, J. DYBAL, E. TURSKA and A. KULCZYCKI, *Polymer* **32** (1991) 1862.
8. J. DYBAL, P. SCHMIDT, J. BALDRIAN and J. KRATOCHVÍL, *Macromolecules* **31** (1998) 6611.
9. P. TEKELY and E. TURSKA, *Polymer* **24** (1983) 667.
10. J. OTHMEZOURI-DECERF, *J. Mater. Sci.* **34** (1999) 2351.
11. J.-C. BAUWENS, *Plastics and Rubber Processing and Applications* **7** (1987) 143.
12. P. LANI LEE, T. KOWALEWSKI, M. D. POLIKS and J. SCHAEFER, *Macromolecules* **28** (1995) 2476.
13. R. PIXA, B. GRISONI, T. GAY and D. FROELICH, *Polymer Bulletin* **16** (1986) 381.
14. R. WIMBERGER-FRIEDL and J. G. dE BRUIN, *Macromolecules* **29** (1996) 4992.
15. A. D. DROZDOV, *Computational Materials Science* **15** (1999) 422.

Received 8 May
and accepted 8 July 2002