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Mechanical Measurement of the Plasticization of Polymers by High-Pressure Carbon Dioxide

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Abstract: A linear variable displacement transducer has been used to measure the central deflection of 2–3 mm thick polymer samples undergoing three-point bending while exposed to CO₂ at pressures of up to 120 bar. Significant reductions in the bending onset temperatures were observed on the application of CO₂ for polycarbonate, polystyrene, and poly(methyl methacrylate) of typically 20–40 K over the range of pressures applied. Initial onset temperatures correlated reasonably well with literature values for glass transition temperatures, but complete softening of the sample required further time for CO₂ to diffuse into the samples.

Keywords: Glass transition; LVDT; Softening; Supercritical; Thermoplastics

INTRODUCTION

The ability of CO₂ at high pressure to lower the glass transition temperature (T_g) of (i.e., plasticize) polymers is well documented and makes it ideal for extraction, impregnation, polymerization, foaming, and shape forming of polymers.^[1] The nontoxic nature of CO₂ also provides a strong impetus for its use.^[2] Therefore, there is a very real need to understand how CO₂ interacts with polymeric materials and how it might be used to modify process operations.

The sorption of CO₂ and subsequent plasticization effect on certain polymers has been investigated using a variety of methods such as

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differential scanning calorimetry (DSC) and gas sorption/gas permeation,^[1] FTIR,^[3] and NMR^[4]. Measurements of the softening temperature for the same polymer can differ between researchers, probably due to the different techniques and experimental procedures used. Typically, however, a 1 K reduction per bar of applied pressure is observed for polycarbonate (PC),^[5-7] poly(ethylene terephthalate) (PET),^[8] poly(vinylidene fluoride) (PVF),^[9] poly(vinyl chloride) (PVC),^[6] polystyrene (PS),^[6,10,11] and poly(methyl methacrylate) (PMMA).^[3,11-13]

Mechanical properties are, however, of prime importance when plasticization is used to aid extrusion or other shape-forming processes, and so a direct test would be of much benefit in such situations. Relatively few studies have directly examined the effect of CO₂ on the mechanical properties of polymers. These have included measurements of:

- The hardness of PMMA by an indentation test.^[14]
- The high-frequency elastic modulus of PS from its response to ultrasonic waves.^[15]
- The creep compliance of PS,^[15] PS and PMMA,^[11] and PMMA^[16] measured using either a linear variable displacement transducer (LVDT) or a sight gauge.
- The linear dilation of PVF, also measured by LVDT.^[9]
- The point where the central deflection of glycol-modified poly(ethylene terephthalate) (PETG) and PMMA exceeds a threshold value as indicated by a magnetic sensor.^[17]
- Dynamic mechanical analysis (DMTA) of samples after exposure to high-pressure CO₂ and quenching of the high-pressure cell in liquid nitrogen to trap the absorbed CO₂. The samples were analyzed outside the cell by DMTA as they slowly warmed.^[18]

However, few of the above studies exceeded 60 bar of CO₂ pressure. The experiments described here extend the three-point bending method of Yoon and Cha^[17] to continuously monitor the central deflection with time using a high-pressure cell equipped with an LVDT. Pressures of up to 120 bar were achieved, allowing CO₂ to be applied in the supercritical and liquid states.

EXPERIMENTAL SECTION

Materials

Three polymers were tested: PC (MW 29 400, T_g 151.8°C), PS (MW 184 000, T_g 102.6°C), and PMMA (syndiotactic, MW 179 000, T_g 110.8°C) (Polybron Ltd., Shepshed, UK). Molecular weights were determined by

the solution viscosity method, and T_g values by DSC (Q10, TA Instruments, New Castle, Del., USA). The polymers were supplied in sheets of different thicknesses: PC strips were 3 mm thick and PS and PMMA strips were 2 mm thick. The sheets were cut using a band saw into 8.0 cm \times 2.0 cm strips.

Experimental Method

Experiments were carried out in a cylindrical stainless steel high-pressure cell with dimensions 11.4 cm (high) \times 13.5 cm (diameter); see Figure 1. An LVDT (RS Components Ltd., UK) was suspended from the top of the cell to measure the central deflection of the polymer strips, which were placed horizontally at the base of the cell in a three-point bending configuration. The LVDT core (mass 2.2 g, with a flat tip of 2.4 mm diameter) was simply supported by the polymer. A platinum resistance thermometer (PRT) (Omega Engineering Ltd., UK) was located close to the sample to monitor its temperature. The cell was externally heated by a temperature-controlled oil bath. CO₂ was supplied from a cylinder via a high-pressure pump, with a back-pressure regulator used to control

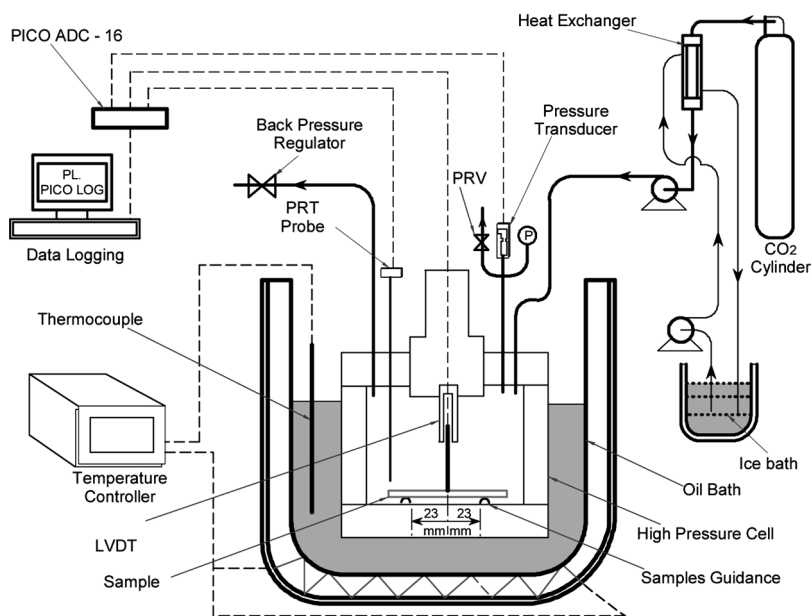


Figure 1. Experimental setup showing connections to the high-pressure cell.

the pressure in the cell. The cell pressure was measured using a PMP-1400 piezo transducer (Druck, UK). The voltage outputs from the LVDT, PRT probe, and pressure transducer were logged to a PC via a data acquisition card (Pico Technology Ltd., UK).

The experimental procedure was performed according to the following method:

1. The polymer strip was placed in the cell in contact with the LVDT, and the cell sealed and placed in the oil bath at ambient temperature.
2. CO₂ was introduced into the cell from a supply cylinder, using the pump where necessary. Pressures of 0, 20, 40, 54, 70, 85, 100, and 120 bar were employed in separate experiments.
3. The oil bath was then heated at a rate of 1°C/min, up to 160°C for PC and 140°C for PS and PMMA.
4. Heating was then stopped, the cell depressurized and cooled, and the sample extracted.
5. Softening points were extracted from the LVDT data using two alternative methods:
 - Method A: The softening value T_A was taken from the point where the increase in displacement first exceeded 0.01 mm over a 10 K temperature interval (lower temperature value quoted). This was chosen to provide a good initial indication of softening while filtering out noise in the data.
 - Method B: The softening temperature T_B was taken as the point where the deflection reached 0.5 mm from the initial value. This provides a marker where gross deformation of the sample can be considered to be occurring.

The same criteria for T_A and T_B were used regardless of the thickness of the strips, as the measurements are indicative only.

RESULTS AND DISCUSSION

Effect of CO₂ Pressure on Polymer Softening

The deflection versus temperature curves for all three polymers are presented in Figures 2 to 4. In all cases the deflection curve is initially relatively flat and then undergoes a dramatic increase as the temperature is raised over a 20 K interval. It can be safely assumed that this is due to softening occurring in the sample. The temperature of the increase varies with both the polymer and the pressure used. Increasing the pressure, in general, caused the curves to shift to lower temperatures, by typically

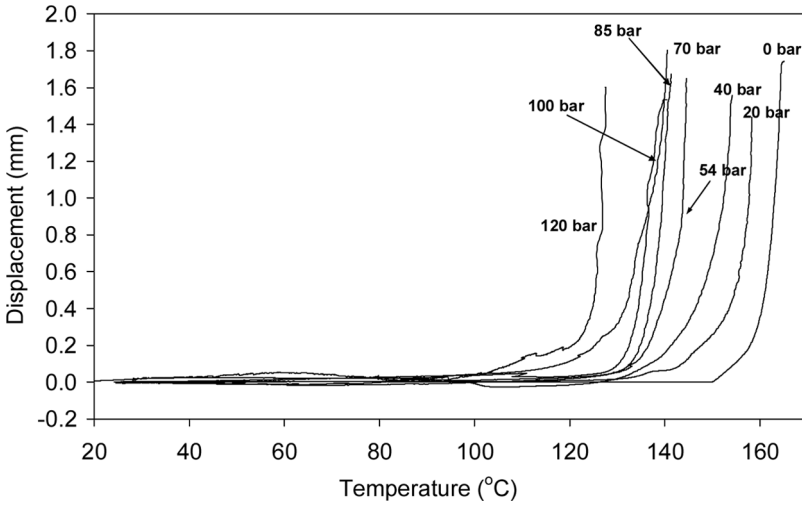


Figure 2. Central deflection vs. temperature of polycarbonate (PC) strips heated at 1°C/min in carbon dioxide at various pressures.

40 K (20 K for PMMA) over the full range of pressures. The variation is generally monotonic, although with some exceptions, which may be due to experimental error. PC showed the highest temperatures required to soften the sample (~120° to ~160°C), whereas lower temperatures were

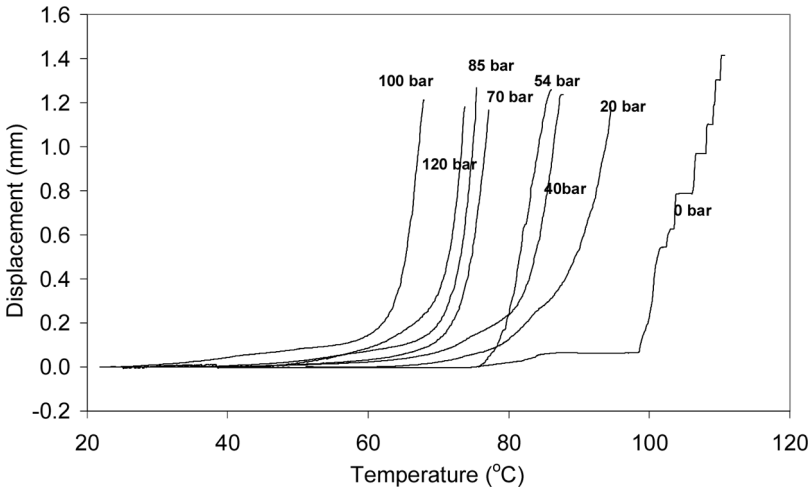


Figure 3. Central deflection vs. temperature of polystyrene (PS) strips heated at 1°C/min in carbon dioxide at various pressures.

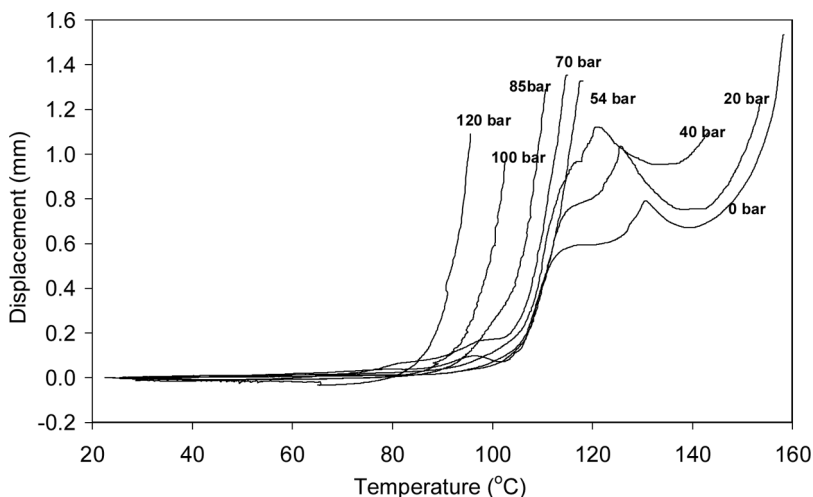


Figure 4. Central deflection vs. temperature of poly(methyl methacrylate) (PMMA) strips heated at $1^{\circ}\text{C}/\text{min}$ in carbon dioxide at various pressures.

sufficient for the other polymers ($\sim 60^{\circ}$ to $\sim 100^{\circ}\text{C}$ for PS; $\sim 80^{\circ}$ to $\sim 100^{\circ}\text{C}$ for PMMA).

It should also be remarked that the forms of the curves observed in Figures 2 to 4 also varied with pressure. At zero bar the deflection curves displayed a noticeable kink at the onset of softening. At intermediate pressures a more gradual onset of softening is observed. At high pressures (100 and 120 bar) a small but significant deflection is apparent even at low temperatures. It is well established that very high densities occur at ambient temperatures above the critical pressure of 70 bar, which may be enough to partially plasticize the sample at the beginning of the run. As the temperature is increased so-called retrograde vitrification may occur as the sample temporarily returns to the glassy state^[11,16] as the CO_2 phase expands.

Unusual behavior was observed for PMMA at low pressures (≤ 40 bar), as the increase of deflection with temperature was not monotonic. Although this was reproducible, the reason is unclear, but could be due to pre-stressing of the samples when they were originally formed.

Comparison of Glass Transition Temperatures with Literature Values

The extracted values of T_A and T_B are compared with literature values for PC^[5-7,13,19] in Figure 5, PS^[4,6,10,11,13,15,19,20] in Figure 6, and PMMA^[3,7,11-14,16,19] in Figure 7. The literature data range up to 60 bar

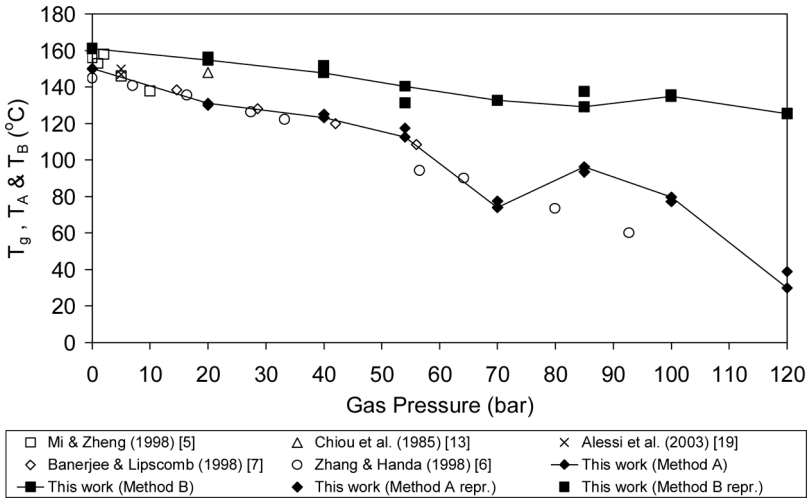


Figure 5. Softening temperature of PC vs. applied CO₂ pressure as measured by LVDT using methods A and B (with reproducibility checks), compared to glass transition temperatures reported in the literature for PC.

for PMMA and up to 90 bar for PC and PS. The data from different workers are generally consistent with one another, with a linear decrease of T_g below the normal (unplasticized) T_g with increasing pressure of

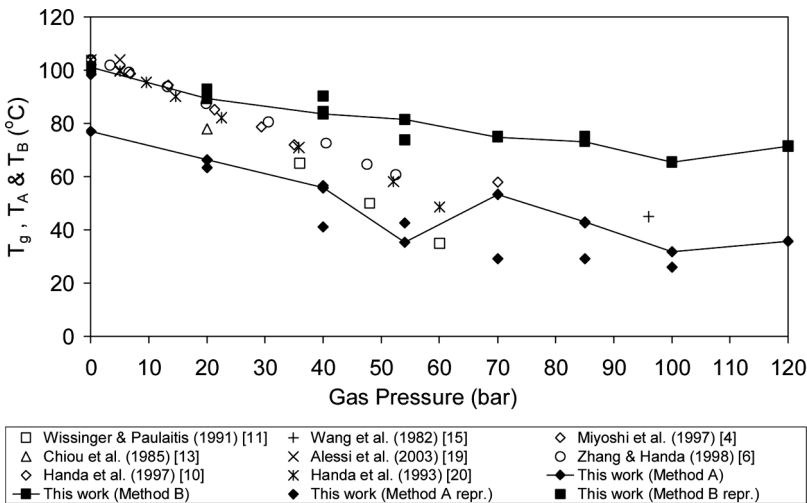


Figure 6. Softening temperature of PS vs. applied CO₂ pressure as measured by LVDT using methods A and B (with reproducibility checks), compared to glass transition temperatures reported in the literature for PS.

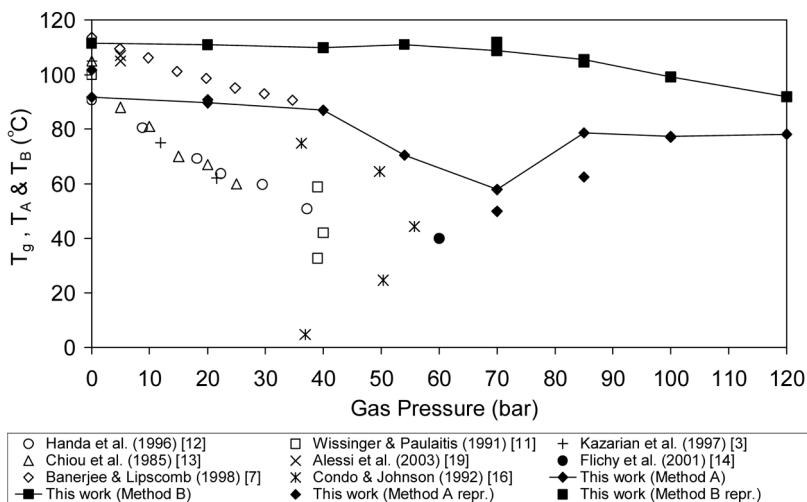


Figure 7. Softening temperature of PMMA vs. applied CO₂ pressure as measured by LVDT using methods A and B (with reproducibility checks), compared to glass transition temperatures reported in the literature for PMMA.

approximately 1 K/bar. Two exceptions are the data of Wissinger and Paulaitis^[11] and Condo and Johnston^[16] for PMMA. These both show a large departure from linearity at around 40–50 bar—evidence for retrograde vitrification, which appears to be a very strong effect for PMMA. There is also some variability in the PMMA data, possibly due to different molecular weights being used.

The T_A and T_B data extracted from Figures 2, 3, and 4 are joined by a line in Figures 5, 6, and 7, but also shown (as individual points) are the results of repeat experiments. The average discrepancy between repeat runs was 8.3 K for T_A and 2.3 K for T_B. The greater variability of T_A values reflects the more difficult problem of detecting an onset. It can be seen that T_A values for PC (Figure 5) lie reasonably close to the literature data for T_g and our own DSC measurement. The same is almost true for PS, with the only anomaly being at 0 bar (in air). However, inspection of the LVDT curve in Figure 3 shows a minor blip at around 80°C, which has led to this T_A value being used in Figure 6, whereas the more obvious increase of deflection at 98°C corresponds quite closely to the literature data and our DSC data for T_g. The T_A values for PMMA, however, lie well above the literature data with the exception of Banerjee and Lipscomb^[7] but are reasonably consistent with our DSC value.

The T_B values for all the samples, on the other hand, lie well above the literature values in all cases with a modest decrease of T_B with increasing pressure. Thus the degree of softening required for large

deformations is subject to a time lag. It is likely that this is caused by the time taken for CO₂ to diffuse into the center of the polymer strips to cause softening at the center of the sample. To test this hypothesis an order of magnitude estimate of the average diffusion coefficient (D) of the CO₂ in the polymer samples was performed.

Estimation of the Diffusivity of CO₂ in Polymer Strips

The standard solution for diffusion into both faces of a slab of thickness L (0 < x < L) is^[22]

$$\frac{c - c_e}{c_i - c_e} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{(2n + 1)} \sin\left(\frac{(2n + 1)\pi x}{L}\right) \cdot \exp\left(-\frac{(2n + 1)^2 \pi^2}{L^2} Dt\right) \quad (1)$$

where c is the concentration of CO₂ (at time t and distance x into the slab), and c_i and c_e are the initial and equilibrium concentrations respectively. Noting that c_i is zero, the centerline concentration, c_c, (at x = L/2) is thus:

$$\frac{c_c}{c_e} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{(2n + 1)} \cdot \exp\left(-\frac{(2n + 1)^2 \pi^2}{L^2} Dt\right) \quad (2)$$

Now the T_g is expressed as a linearly decreasing function of CO₂ concentration,^[11,16] i.e.:

$$T_g = T_{g0} - \beta c \quad (3)$$

The first (onset) softening point (T_A) is considered to correspond to softening of the surface regions where c = c_e. Therefore:

$$T_A = T_{g0} - \beta c_e \Rightarrow c_e = \frac{T_{g0} - T_A}{\beta} \quad (4)$$

We now hypothesize that the second softening point (T_B) occurs when the center of the sample has also reached the glass transition, that is:

$$T_B = T_{g0} - \beta c_c \Rightarrow c_c = \frac{T_{g0} - T_B}{\beta} \quad (5)$$

Substituting c_e and c_c from Equations (4) and (5) into Equation (2) yields:

$$\frac{c_c}{c_e} = \frac{T_{g0} - T_B}{T_{g0} - T_A} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{(2n + 1)} \cdot \exp\left(-\frac{(2n + 1)^2 \pi^2}{L^2} Dt\right) \quad (6)$$

Thus, an estimate of the diffusivity can be made by comparing the ratio of the decrease in the softening point by method B to that by method A.

Due to the large scatter of T_A values in our experiments we have opted to insert the following linearly decreasing functions of pressure to represent “ T_A ” values ($^{\circ}\text{C}$) in Equation (6). These are based on the literature values of T_g in Figures 5 to 6. For PMMA we chose to fit the data of Banerjee and Lipscomb^[7] as this better agrees with the DSC measurements at under nitrogen at 0 bar for our sample and also our T_A values.

$$\text{For PC : } T_A = 156 - 1.03 \times p \quad (7)$$

$$\text{For PS : } T_A = 104 - 1.15 \times p \quad (8)$$

$$\text{For PMMA : } T_A = 112.6 - 0.669 \times p \quad (9)$$

We have assumed that the time t corresponds to the time from when the polymer is initially exposed to the CO_2 to when the second softening occurs. The above analysis also assumes that D and c_e are constant. These are simplifying assumptions that will clearly affect accuracy, as both of these parameters vary with temperature, but they are reasonable for the order of magnitude calculations presented here.

Diffusivity evaluations were performed in MS Excel using the “Goal Seek” function to match the middle and right-hand terms of Equation (6) for each experimental data point by varying the diffusivity for each. Only the first three terms of the summation in Equation (6) were required to evaluate the function to the required accuracy. The average values and standard deviations for PC, PS, and PMMA were found to be $7.3 \pm 0.6 \times 10^{-11} \text{ m}^2\text{s}^{-1}$, $8.2 \pm 1.2 \times 10^{-11} \text{ m}^2\text{s}^{-1}$, and $2.7 \pm 1.0 \times 10^{-11} \text{ m}^2\text{s}^{-1}$ respectively. Thus, distinctly smaller values are found for PMMA.

Diffusion coefficients of CO_2 in polymers have been obtained from high-pressure sorption experiments by a number of workers.^[22–26] Published values are shown in Table I for each polymer for various combinations of temperature and pressure. The table shows that diffusivity varies considerably with both temperature and pressure, and as such the constant diffusivity model that we employed will lack accuracy. However, it is clear that the published diffusivities are of a similar order of magnitude to those extracted from our experimental data, and this confirms the lower diffusivity of CO_2 in PMMA than in PC and PS. This strongly suggests that the full softening of the samples is limited by diffusion of CO_2 into the sample.

This would also explain the difference between the very sharp onsets for the LVDT curves (Figures 2 to 4) at 0 bar (in air) compared to the smoother onsets at higher pressures. At 0 bar the softening is not diffusion limited as the CO_2 concentration gradient is low and little diffusion occurs, resulting in a sudden softening as the T_g is reached. However, at higher pressures the overall stiffness of the polymer strips is gradually reduced by the ingress of CO_2 plasticizing the sample to greater depths as time proceeds.

Table I. Published values of diffusion coefficients of CO₂ in PC, PS, and PMMA

| Polymer | Pressure (bar) | Temperature (°C) | D (10 ⁻¹¹ m ² s ⁻¹) | Ref. |
|---------|----------------|------------------|---|------|
| PC | 200 | 40 | 1.22 | 22 |
| | 200 | 50 | 1.68 | |
| | 200 | 60 | 3.36 | |
| PS | 24 | 100 | 8.1 | 23 |
| | 44 | 100 | 11.4 | |
| | 63 | 100 | 14.6 | |
| | 83 | 100 | 16.7 | |
| PS | Not specified | 25 | 3.0–4.0 | 24 |
| PS | 90 | 50 | 8.7 | 25 |
| | 90 | 65 | 15.7 | |
| | 125 | 50 | 12.7 | |
| | 125 | 65 | 29.8 | |
| PMMA | 105 | 40 | 10.4 | 26 |
| PMMA | 33 | 25 | 0.1 | 24 |
| | 65 | 25 | 1.0–2.5 | |

CONCLUSIONS

A high-pressure three-point bend testing cell has been successfully designed to measure mechanically the plasticization of PC, PS, and PMMA by CO₂ at pressures up to 120 bar. The technique was able to detect surface softening temperatures (subject to some error) that were similar to T_g values reported in the literature. Better data might be obtained by using a sharper probe tip rather than the flat end used in these experiments. It is also shown that full softening of the samples, accompanied by a large deformation of the strip, is limited by the diffusion of CO₂ into the sample. Some minor softening of the samples was observed at ambient temperatures at very high pressures (100 and 120 bar). This is in line with earlier literature findings^[1,16] that attribute the plasticization effect under these conditions to the high density of CO₂.

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