

Thermo-Mechanical Approach to Evaluate Softening Behavior of Polystyrene: Validation and Modeling

Salah Al-Enezi, Rashed Al-Zufairi, Naseer Ahmad

Abstract—A Thermo-mechanical technique was developed to determine softening point temperature/glass transition temperature (T_g) of polystyrene exposed to high pressures. The design utilizes the ability of carbon dioxide to lower the glass transition temperature of polymers and acts as plasticizer. In this apparatus, the sorption of carbon dioxide to induce softening of polymers as a function of temperature/pressure is performed and the extent of softening is measured in three-point-flexural-bending mode. The polymer strip was placed in the cell in contact with the linear variable differential transformer (LVDT). CO_2 was pumped into the cell from a supply cylinder to reach high pressure. The results clearly showed that full softening point of the samples, accompanied by a large deformation on the polymer strip. The deflection curves are initially relatively flat and then undergo a dramatic increase as the temperature is elevated. It was found that increasing the pressure of CO_2 causes the temperature curves to shift from higher to lower by increment of about 45 K, over the pressure range of 0-120 bars. The obtained experimental T_g values were validated with the values reported in the literature. Finally, it is concluded that the deflection model fits consistently to the generated experimental results, which attempts to describe in more detail how the central deflection of a thin polymer strip affected by the CO_2 diffusions in the polymeric samples.

Keywords—Softening, high-pressure, polystyrene, CO_2 diffusions.

I. INTRODUCTION

GLASS transition is considered as a characteristic nature of amorphous polymeric materials, and naturally affects the processability and final application. Glass transition happens between the highly elastic and glassy states of the material. Considering the chemical structure, the glass transition temperature T_g reflects the relaxation of the amorphous phases of the polymer from the super cooled frozen state to the soften state [1], [2]. Under the T_g , the polymer is in a glassy state, in which the molecular chain movement is forbidden. However, the segmental mobility starts when the temperature increases, establishing high elastic properties. When the temperature is elevated consecutively, the entire molecular chain exhibits a viscous property. Glass transition is often caused by variations in pressure, temperature, and other thermodynamic parameters [3]. Analytical and experimental studies of glass transition are important due to widespread applications of glass in everyday life. The assessment of T_g at high pressure assumes prime importance when plasticization is used to aid processing. Moreover, in such cases, a better correlation study with any deterioration in its mechanical

properties would be possible based on the real-time T_g values. The scope of this technique is to measure T_g of polymeric materials as a function of pressure in a gaseous environment. The sorption of fluids, including gases in the supercritical state, would induce significant plasticization, which would result in a substantial decrease of the glass-transition temperature [4]-[7]. With the wide use of supercritical carbon dioxide to swell and plasticize polymers in various processes, it would be appropriate to simulate the intended end-use environment of high pressure and measure in-situ the T_g . Thus, the depression in glass transition behavior of polymers must be studied when the material is in direct contact with the gas, rather than measuring the polymer in isolation. This would equip researchers to predict the glass transition behavior of polymers which may be subjected to contact with gases. T_g is primarily determined using the following techniques: Differential Scanning Calorimetry (DSC), Thermo-Mechanical Analysis (TMA), Dynamic Mechanical Analysis (DMA). DSC defines the glass transition as a change in the heat capacity as the polymer matrix goes from the glass state to the rubber state. For TMA, a change in volume or a change in the coefficient of thermal expansion represents the glass transition. In DMA, a decrease in storage modulus signifies the onset of the glass transition or the peak of the $\tan \delta$ is often used to characterize the glass transition temperature, even though the glass transition happens over a range of temperatures. In this work, a patented apparatus used to determine the glass transition temperature (T_g) of polymeric materials exposed to a gaseous environment at ambient and high temperatures over a broad range of temperatures. This article describes the glass transition temperature, transformation range, new method of detecting glass transition, determination of glass temperature and thermodynamic relations at the glass transition. The recent developments in the modeling of glass transition are also presented.

II. EXPERIMENTAL

A. Materials and Methods

Polystyrene (PS) sheets (Mw 184 000, T_g 102.6 °C) obtained locally and used as received.

Experiments were carried out in a cylindrical stainless steel high-pressure cell with dimensions 11.4 cm (high) 13.5 cm (diameter); see Fig. 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

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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. CO₂ was supplied from a cylinder via a high-pressure pump, with a back-pressure regulator used to control 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).



Fig. 1 Experimental set-up [8]

Deflection Model

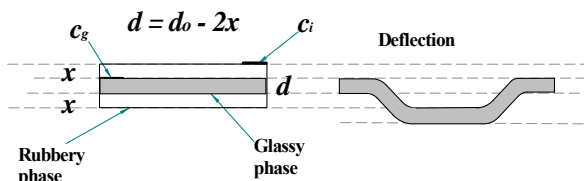


Fig. 2 Generalized deflection diagram

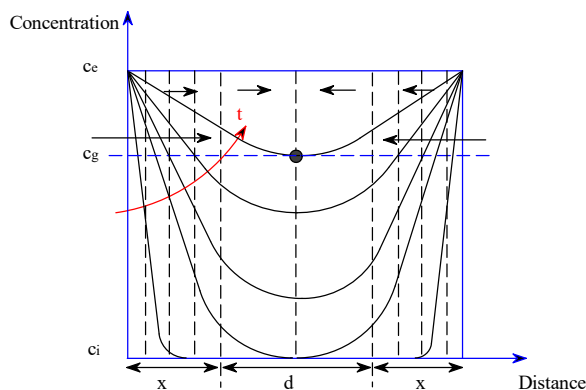


Fig. 3 General diffusion description

This model attempts to describe in more detail how the central deflection of a thin polymer strip supported at its ends varies with time as CO₂ diffuses in and the polymer softens [9]. If one postulates that only the glassy regions provide any significant mechanical strength then one can use the position of the front (which can itself be modelled as a function of time) to estimate the bending of the polymer. This model will be used to generate an equation for central deflection versus time which can be fitted to the experimental data (Isothermal experiments of PS/CO₂) gained. Figs. 2 and 3 express this

estimation:

$$\frac{c_g - c_i}{c_e - c_i} = 1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) = 1 - \operatorname{erf}(z) \quad (1)$$

For values of $z < 0.7$ the following approximation can be made

$$\begin{aligned} \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right) &\approx \frac{x}{2\sqrt{Dt}} \\ \Rightarrow \frac{x}{2\sqrt{Dt}} &= 1 - \frac{c_g - c_i}{c_e - c_i} = \frac{c_e - c_i - (c_g - c_i)}{c_e - c_i} \\ \Rightarrow \frac{x}{2\sqrt{Dt}} &= \frac{c_e - c_g}{c_e - c_i} \end{aligned}$$

Noting that c_i is zero, therefore:

$$\frac{c_g - c_e}{-c_e} = \frac{x}{2\sqrt{Dt}} \quad (2)$$

$$x = 2\sqrt{Dt} \left(\frac{c_g - c_e}{-c_e} \right) \quad (3)$$

The deflection of a slab of effective thickness d is:

$$\text{Deflection} = \frac{5WL^3}{384EI}, \left(\frac{Nm^3}{(N/m^2)m^4} \rightarrow m \right) \quad (4)$$

where:

$$\text{Moment of inertia, } I = \frac{bd^3}{12}, (m^4) \quad (5)$$

and, L : overall length (m), W : point load (N), I : moment of inertia (m^4), E : modulus of elasticity (N/m^2), b : width of the sample strips (m), d : thickness of the strip (m).

Substituting I from above equation is:

$$\text{Deflection} = \frac{5WL^3}{384E} \frac{12}{bd^3} \quad (6)$$

If the effective thickness d is given by:

$$d = d_0 - 2x \quad (7)$$

where d_0 is the thickness of the strip and x is the depth of the front then:

$$\text{Deflection} = \frac{5WL^3}{384E} \frac{12}{b(d_0 - 2x)^3} \quad (8)$$

Substituting x from (3) into (8):

$$\text{Deflection} = \frac{5WL^3}{384Eb} \frac{12}{(d_0 - 4\sqrt{Dt} \cdot (\frac{c_g - c_e}{-c_e}))^3}$$

$$\text{Deflection} = \frac{5}{32} \frac{WL^3}{Eb} \frac{12}{(d_0 - 4\sqrt{Dt} \cdot (\frac{c_g - c_e}{-c_e}))^3} \quad (9)$$

III. RESULTS AND DISCUSSION

The displacement versus temperature results for polystyrene (PS) at different pressures are shown in Fig. 4.

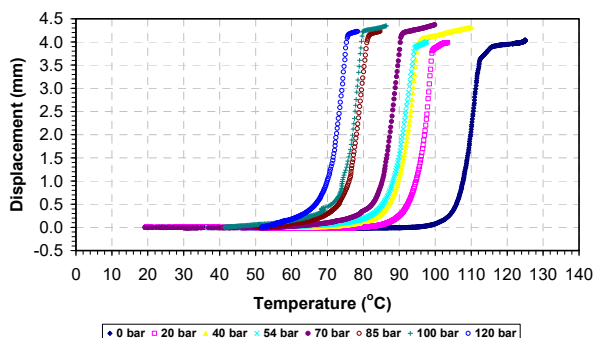


Fig. 4 Central deflection versus temperature of polystyrene (PS) strips heated at 1 °C/minute in carbon dioxide at various pressures

The deflection curves are initially relatively flat and then undergo a dramatic increase as the temperature is raised over 5 – 10 K interval, due to softening occurring in the sample. Increasing the pressure, in general, caused the curves to shift to lower temperatures, by about 45 K, over the pressure range of 0 – 120 bar. Appearance of samples after depressurization was shown in Fig. 5.

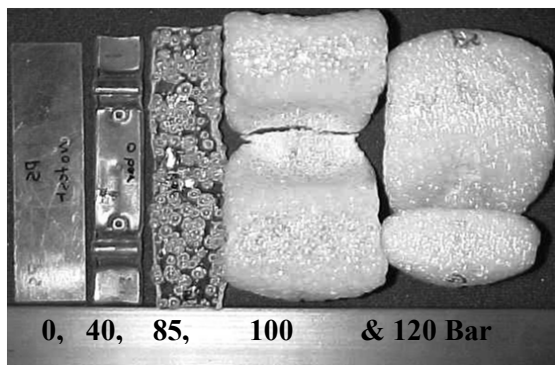


Fig. 5 Photographs of PS strips after depressurization from various pressures after passed through the softening point

As shown on Fig. 6, the softening points extracted from our LVDT data lie reasonably close to the literature data [10]-[15] for T_g, with the only 5 – 10 °C higher around 70 bar and above. This is because this technique measures the softening temperature of the interior polymer specimen, which suggests that at high pressure the degree of softening required for large

deformations is subject to a time lag.

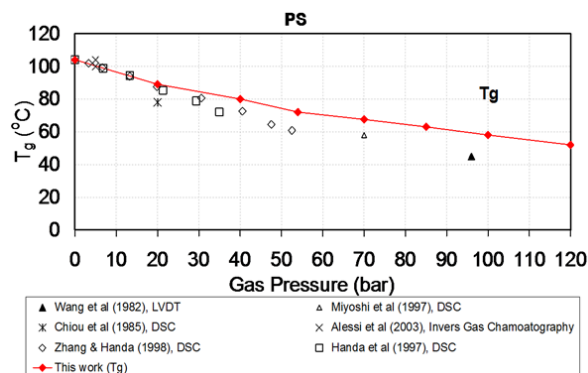


Fig. 6 Softening temperature of PS versus applied CO₂ pressure as measured by LVDT compared to T_g reported in the literature for PS

Deflection Model of Polystyrene/CO₂

In this section the experimental isothermal deflection data are fitted to the deflection model outlined in previous section. The fit equation is:

$$\text{Deflection} = \frac{5}{32} \frac{WL^3}{Eb} \frac{12}{(d_0 - 4\sqrt{Dt} \cdot (\frac{c_g - c_e}{-c_e}))^3}$$

$$\text{Or Deflection} = A \left(\frac{1}{d_0 - B\sqrt{t}} \right)^3 \quad (10)$$

$$\text{where, } A = \frac{5}{32} \frac{WL^3}{Eb}$$

$$B = 4\sqrt{D} \left(\frac{c_g - c_e}{-c_e} \right) \quad (11)$$

The above equation predicts an initial deflection of $\frac{A}{0.002^3}$

As experimental deflection values are quoted relative to the initial deflection, the model equation requires an adjustment so that it also represents the change in deflection relative to $t = 0$. Therefore, the modified equation used to fit the experimental data is:

$$\text{Deflection} = A * \left(\frac{1}{(0.002 - B\sqrt{t})^3} - \frac{1}{(0.002)^3} \right) \quad (12)$$

A least squares fit is applied to the data to extract the fit constant A and B. From the first constant (A), we can calculate the Young's modulus (E), but for the second constant (B) we need to estimate the concentration ratio $(\frac{c_g - c_e}{-c_e})$, before estimating the diffusivity (D). It is recalled from the previous section that the assumption $z \approx \text{erf}(z)$ was made where

$z = \frac{x}{2\sqrt{Dt}}$. This requires values of z of less than 0.7 [16].

This was tested by noting that z can be evaluated from concentration data.

$$z = -\left(\frac{c_g - c_e}{c_e}\right) \quad (13)$$

Values of z are plotted in Fig. 7. It can be seen that the high the assumption is valid, with the exception of the high pressure at 90 °C. However, this is only a small transgression.

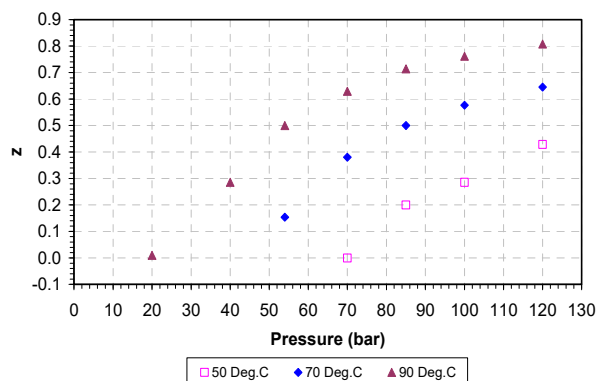


Fig. 7 z values

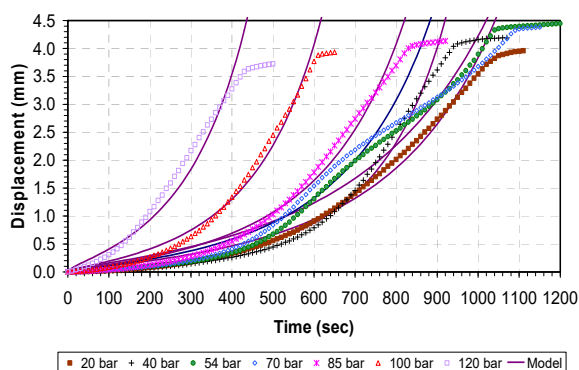


Fig. 8 Experimental versus Deflection Model at 90 °C

As shown in Fig. 8, the deflection model provides good fits to the experimental data. However, with some exceptions; this model can work very well with longer time, but with shorter time the model has small intervals, this probably because of the viscosity flow, which with long times the viscosity is insignificant but with shorter time the viscosity is holding the deflection rate. In all cases, the model provided good fits with experimental data until 1 mm and it far away from the starting softening point (T_g), which still can express the deflection rates. In general, this basic model is good and can express our experimental data.

IV. CONCLUSION

Three-point bend testing of polymer strips under carbon dioxide at various pressures has successfully been used to

mechanically demonstrate the plasticisation of polystyrene, by carbon dioxide at high pressures. The technique was able to detect surface softening temperatures (subject to some error) which were similar to glass transition temperatures reported in the literature. It is also shown that full softening of the samples, accompanied by a large deformation of the strip is limited by the diffusion of carbon dioxide into the sample. Some minor softening of the samples was observed at ambient temperatures at very high pressures. The plasticization effect of gases in the supercritical state can be better controlled based on the T_g values of the polymer/gas phase system, measured using this apparatus. The pressure dependence of the glass transition temperature, T_g , which is one of the key issues regarding the validity of existing free volume theories, can be studied easily and accurately with this equipment.

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