The plasticization of a polyurethane by carbon dioxide at high pneumatic stresses

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This paper describes a study of the interaction of high pressure subcritical and supercritical carbon dioxide with a polyurethane elastomer. A novel optical high pressure cell was employed to examine the gas–polymer interactions at a molecular level, using Fourier transform infra-red spectroscopy, at 42°C and at a range of ambient pressures. Infra-red spectroscopic measurements, at atmospheric pressure, of the effect of temperature on the same polymer and a measure of the effect of temperature on the modulus on the polymer, again at atmospheric pressure, are used to estimate the effect of the absorbed gas on the modulus of the polymer.

(Keywords: polyurethane, plasticization; modulus)

INTRODUCTION

The application of a high pressure gas environment to an organic polymer has two potential consequences. The gas molecules can be imbibed into the matrix, inducing swelling and plasticization as a result of an enhanced molecular mobility. Alternatively, the pneumatic stress may produce a compressive strain, with the converse effect on the molecular mobility. Both effects will compete with each other, as the ambient gas activity is proportional to the pneumatic pressure or fugacity. For the more condensable gases, like carbon dioxide, the plasticizing effect will dominate at low to medium pressures[1]. The relatively small gas molecules, when sufficiently absorbed in a polymer network, increase the mobility of the polymer chain segments, hence plasticizing the system. However, as the gas pressure reaches significant levels, the hydrostatic component of the pneumatic pressure tends to decrease the free volume, thus reducing segmental mobility. A consequence of plasticization is an increase in gas permeability: this phenomenon has been widely reported in the literature[2,3].

Plasticization and compression of a polymer may also result in a change in the mechanical behaviour of the polymer[4,5]. Many studies have been reported on the plasticization phenomena induced at ambient pressures by liquid solvents[6,7]. Similarly, there are many reported studies of the action of hydrostatic stresses on polymers[8,9]. There are, however, comparatively few reported studies on the influence of gaseous media on the mechanical properties of polymers. The work of Jones Parry[10] has reported changes to the shear modulus of polymers at nitrogen gas pressures up to 200 MPa. Such experiments are problematic for various reasons, and this paper examines a means of estimating mechanical properties indirectly.

This present paper reports data on one aspect of the interactions of carbon dioxide and a polyurethane elastomer, up to a pressure of around 16 MPa in a carbon dioxide environment at 42°C. Data are described for the effect of the gas on the molecular interactions of the polymer as measured by infra-red spectroscopy. The spectroscopic data are used to estimate the variation in the Young's modulus of the polymer with increasing gas pressure by the use of a fictive temperature argument which uses separate data on the temperature dependence of the polymer spectra and the mechanical properties at atmospheric pressure.

EXPERIMENTAL

Materials

The elastomeric material used in this study was a diphenylmethyl-4-4-diisocyanate (MDI) polyester-based polyurethane elastomer, with Shore A hardness 55 (Kemira Polymers, UK, Diprane 54 series). The carbon dioxide (CO_2) gas used was of 99.9% purity (BOC, UK).

High pressure equipment

The high pressure equipment consisted essentially of the gas feed (cylinder), an intermediate gas receiver, a reciprocating gas booster pump (Charles Madan, Altrincham) and a novel optical high pressure cell. A detailed description of the pumping system may be found elsewhere[11]. *Figure 1* shows the main design features of the high pressure cell. The cell was heated using a heating tape (RS Components) in conjunction with a temperature controller (British Electric Resistance Co.). The temperature of the vessel containing the prepared
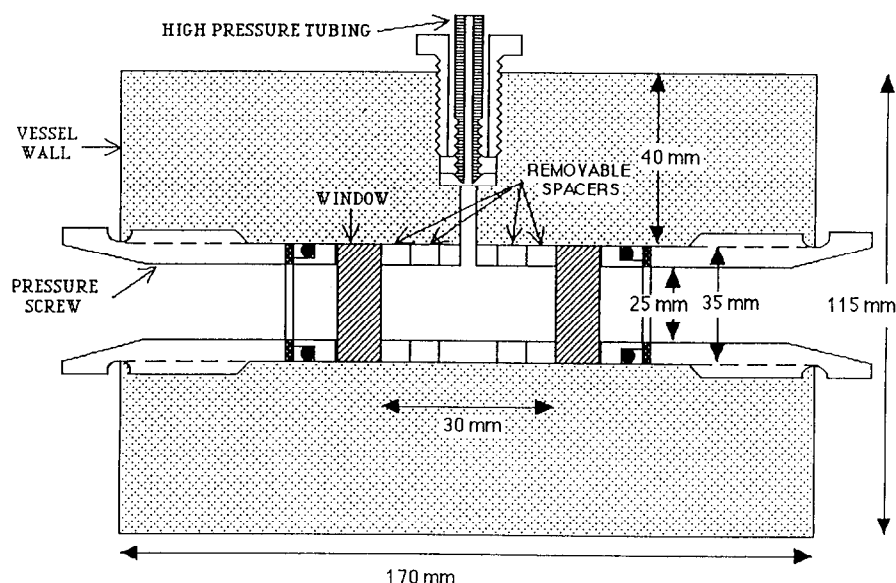
Figure 1 Main design features of the optical high pressure cell

specimens was maintained above the critical temperature of CO_2 (31°C) at 42°C.

Spectroscopic studies

The optical high pressure cell was fitted with zinc selenide windows (transmission range 0.58–21 μm; Harrick Scientific Corporation), 16 mm in thickness and 35 mm in diameter. The high pressure cell was linked to an infra-red spectrometer (Bomem Ramspec 152) via a transmitter/receiver fibre probe system (Graesby Specac Ltd) and microbeam interface (26400 Biomem Michelson 100). A 15 μm thick film of the polyurethane elastomer was placed in the cell cavity, and a spectrum recorded at ambient conditions. The carbon dioxide pressure was subsequently raised in steps of 2–3 MPa to a maximum of 16 MPa, with an infra-red spectrum of the gas–polymer system being recorded following each pressure increment. The gas–polymer system was allowed to equilibrate for 1 h at each pressure step before an infra-red spectrum was recorded. All spectra were obtained at a resolution of 4 cm^{-1} averaged over 1000 scans, using a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector.

The temperature dependence of the infra-red spectra of the polyurethane was recorded using a Linkham THMS 600 temperature cell attached to the spectrometer. The sample was scanned over the range 25–100°C in steps of 10°C. All spectra were recorded over 200 scans.

Dynamic mechanical thermal analysis

The modulus of the polyurethane sample was recorded as a function of temperature using a Polymer Laboratories MkII Dynamic Mechanical Thermal Analyser. The samples were tested in tensile mode over the temperature range 25–100°C, at a frequency of 5 Hz and a heating rate of 5°C min^{-1}.

RESULTS AND DISCUSSION

Polyurethane elastomers contain a high degree of polar entities, in particular the urethane functional groups and,

for the present polymer, ester functional groups. The interactions between these polar groups are of great importance in determining the properties of polyurethanes of all types. Hydrogen bond interactions are known to occur between the N–H and C=O of the urethane groups and between the N–H of the urethane and C=O of the polyester groups. Infra-red spectroscopy is particularly effective for characterizing hydrogen bonding groups[12], and in the infra-red study of the carbon dioxide–polyurethane system, the nature of the hydrogen bonding of the N–H group was seen to change as the ambient gas pressure was increased. This was reflected by the frequency shift of the infra-red absorption peak associated with the hydrogen bonded N–H group. *Figure 2* shows the hydrogen bonded N–H peak at atmospheric pressure and at 16 MPa, while *Figure 3* shows a plot of the frequency shift of the hydrogen bonded N–H peak as a function of carbon dioxide pressure. The effect of the high pressure gas is to gradually disrupt the hydrogen bonding in the polyurethane. At pressures above ~ 12 MPa, the shift of this absorption band is seen to attain a limiting value. The extent of gas absorbed and the corresponding dilation of this polymer have been reported elsewhere[13] and followed a similar trend. At pressures up to 12 MPa, the sorption and dilation increased rapidly as the gas pressure increased; however, at higher pressures, the rates of sorption and dilation were seen to decrease quite significantly. At lower pressures, the gas acts as a plasticizer for the polyurethane, causing significant swelling. At higher pressures, the hydrostatic component of the gas dominates, thus inhibiting further gas uptake.

The temperature-dependent spectra of the polymer, at atmospheric pressure, also revealed a gradual weakening of the hydrogen bonding with increasing temperature. *Figure 4* shows a plot of the frequency shift of the hydrogen bonded N–H peak as a function of temperature.

Figure 5 shows the modulus–temperature characteristic of the polyurethane elastomer, at atmospheric pressure. As can be seen, the modulus of the polyurethane decreases with increasing temperature. A
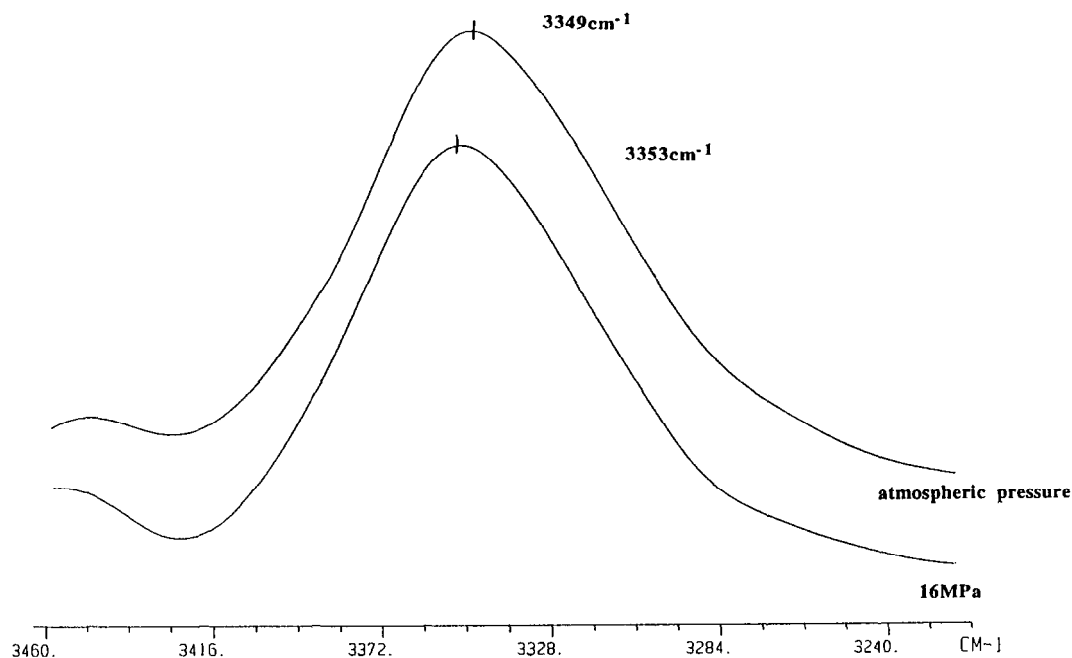
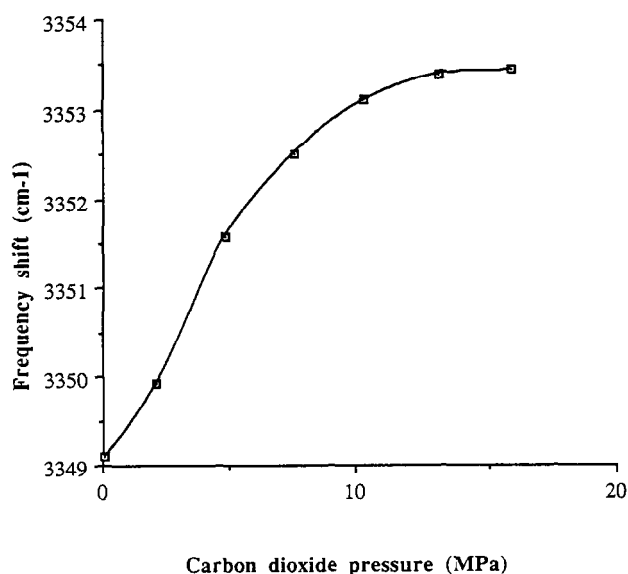**Figure 2** Hydrogen bonded N–H infra-red peak of the polyurethane at atmospheric pressure and 16 MPa

Figure 3 Frequency shift of the hydrogen bonded N–H peak as a function of carbon dioxide pressure
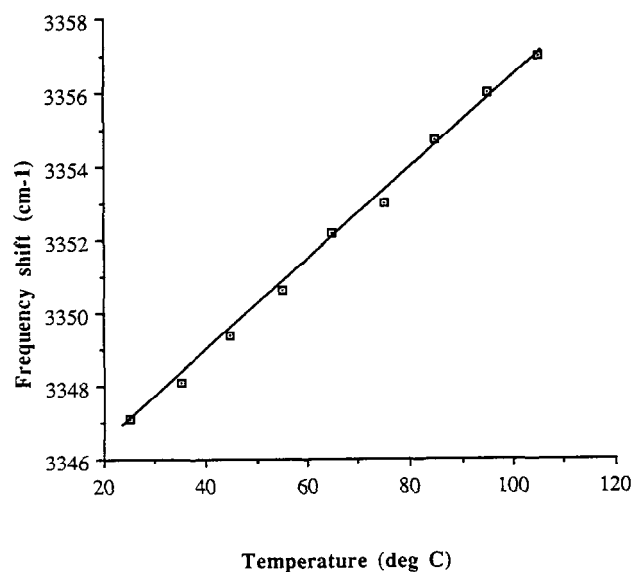

Figure 4 Frequency shift of the hydrogen bonded N–H peak as a function of temperature at atmospheric pressure

'fictive' temperature argument may be used to estimate the change in the modulus as a function of the gas pressure. By estimating the point at which the gas pressure produced an equivalent shift of the hydrogen bonded N–H peak in the temperature-dependent spectra (a 'fictive' temperature), the change in specimen modulus with an increase in gas pressure may be calculated, since the modulus–temperature characteristic of the poly-urethane is known. *Figure 6* shows the computed change in modulus as a function of gas pressure for the polyurethane elastomer. As can be seen, the modulus drops from 0.53 to 0.3 MPa over the range of pressure from atmospheric to 16 MPa, indicating that the high pressure gas plasticizes the polymer. A point worth noting is that the change in modulus attains a limiting

value at around 12 MPa, showing that the hydrostatic component of the gas is becoming the dominant process and retarding further gas sorption. For this system, the volumetric dilation and mass sorption also attain rather constant values at 12 MPa and beyond[13].

CONCLUSIONS

Infra-red spectroscopic measurements of the CO_2–polyurethane system indicated that the hydrogen bonding between the polymer chains was disrupted by the imbibed gas. This disruption attained a limiting point at around 12 MPa. The data were then used in conjunction with temperature-dependent spectral data and the modulus–temperature characteristic of the polymer, in
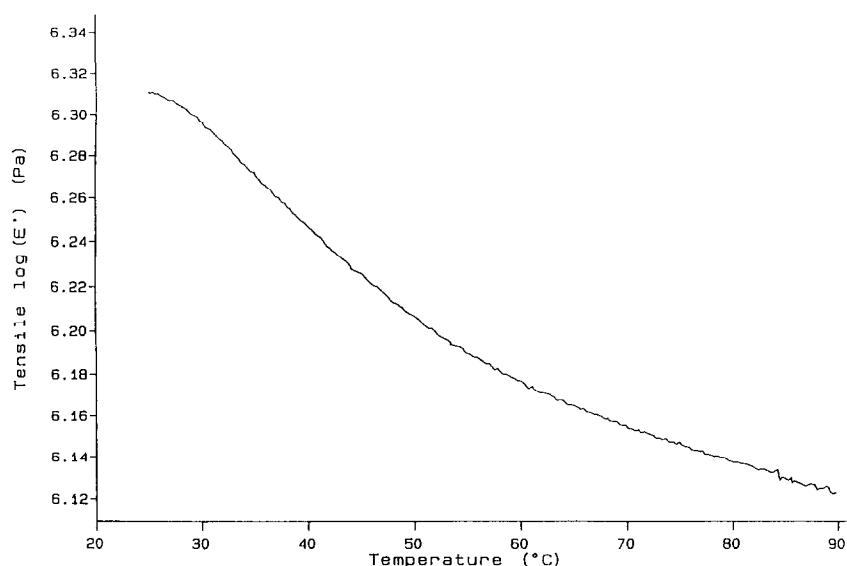
Figure 5 Modulus–temperature characteristic of the polyurethane elastomer at atmospheric pressure
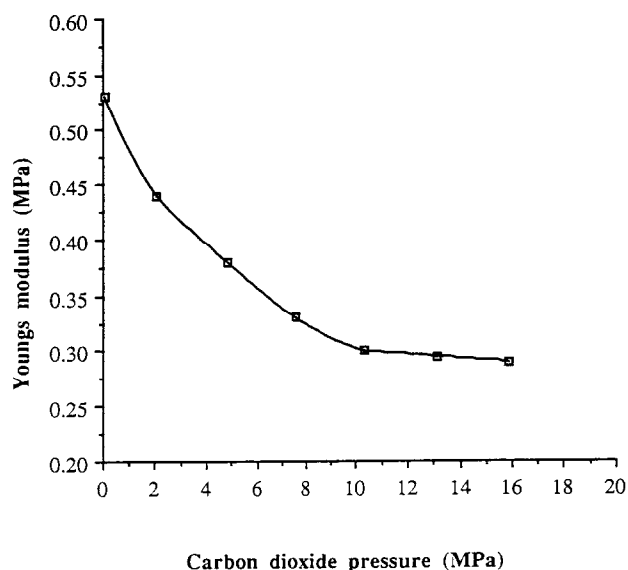

Carbon dioxide pressure (MPa)

Figure 6 Computed change in modulus as a function of gas pressure for the polyurethane elastomer

order to estimate the change in modulus of the polymer as a function of gas pressure. The predicted modulus of the polyurethane was seen to fall as the gas pressure was increased, indicating that the polyurethane was plasticized by the carbon dioxide. The plasticization effect became the less dominant process at pressures above 12 MPa. The procedure described provides a relatively convenient method for quantifying plasticization in polyurethane systems in the presence of high pneumatic stresses. Such data are valuable in predicting the consequences of gas-induced rupture during ambient gas decompression.

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