Modelling the swelling of crosslinked elastomers by supercritical fluids

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(Received 12 November 1991; revised 15 February 1992; accepted 19 March 1992)

Despite the general knowledge that near-critical and supercritical CO_2 will swell elastomers extensively, there has been little work done to date on modelling the phenomenon. We have used the mean-field-lattice-gas model of Kleintjens *et al.* for the free energy of mixing with an additional elastic term due to Flory, in order to model the swelling of crosslinked silicones by supercritical CO_2. Whereas the model reproduces the pressure trends in both volume change and weight fraction fluid absorbed well for the poly(dimethylsiloxane)–CO_2 system, the absolute predictions of weight fraction CO_2 absorbed are too high in the vicinity of critical pressure.

(Keywords: modelling; swelling; elastomer; supercritical fluids)

INTRODUCTION

Supercritical fluids (SCFs), materials above their critical temperature (T_c), are of technological interest in that they exhibit properties intermediate to those of liquids and gases[1]. Specifically, the liquid-like density and gas-like viscosity of SCFs have generated interest in applications such as selective extraction and separation, where both good solubility and high rates of mass transfer of particular solutes are required. Further, because the density of a material near the critical temperature can be varied over a wide range, SCFs are, in effect, pressure-tunable solvents.

Previous work has demonstrated that supercritical CO_2 will swell polymers, the degree of swelling being a strong function of both pressure and the structure of the polymer[2–10]. Many elastomers, in particular, will absorb extremely large quantities of CO_2 at moderate pressures, an important point to consider when designing sealing systems for SCF apparatus[11].

Despite the general knowledge that near-critical and supercritical CO_2 will swell elastomers extensively, there has been little work to date on modelling the phenomenon. In a recent study[12], Shim and Johnston applied the Peng–Robinson equation of state to calculate the activity of CO_2 in the pure SCF phase, while the Flory–Huggins free energy expression was used to calculate the activity of CO_2 in the swollen polymer. Fleming and Koros[13] also examined the sorption of CO_2 by silicone rubber at pressures up to 60 atm†. Again the Flory–Huggins free energy expression was used to model the volume change on swelling. In each of these studies, the relationship between volume increase and weight fraction CO_2 absorbed was derived by assuming an average partial molar volume for CO_2, based on data from organic liquid mixtures. However, as shown by Briscoe and Zakaria[14], who measured both weight fraction CO_2 absorbed and volume change during swelling of poly(dimethylsiloxane) (PDMS), the partial molar volume of CO_2 can change significantly as pressure increases in the supercritical region.

The effect of changes in the volume, and consequently pressure on the free energy of polymer–gas mixtures, can be modelled using both cell-type equations of state[15] and lattice-gas free-energy expressions[16]. We have opted for the latter approach both because the lattice-gas method has been shown to model accurately the sorption of gases by polymers[17] and because an excess-free-energy model allows for easy incorporation of the elastic-free-energy contribution, a necessary part of modelling network behaviour. Kiszka *et al.*[18] employed the Sanchez–Lacombe equation of state to model Fleming and Koros's swelling data on the CO_2–silicone system. Their results demonstrate the power of lattice-type models in the description of gas–polymer phase behaviour. In this work, we will attempt to model the swelling of the CO_2–silicone mixture at pressures up to 300 atm. As shown by Briscoe, the partial molar volume of the absorbed carbon dioxide exhibits large changes in the pressure region 50–150 atm, providing a severe test for the model. We will also attempt to account for the contributions to the free energy owing to the presence of crosslinks in the system. In this paper we present a mean-field lattice-gas model which is based on the derivation of Kleintjens[19,20], yet is modified by the addition of an elastic term, thus allowing good descriptions of swelling of polymer networks by gases as a function of pressure and temperature. Further, the derivation allows generation of an equation of state for a rubbery network.

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†1 atmosphere ≈ 0.1 MPa

0032-3861/92/235032-08

THEORY

Mean-field lattice-gas model for networks

In the lattice-gas approach, which has been in use since the 1920s[21], a compound is represented as a mixture of molecular segments and vacancies, or holes. A pure component is therefore assumed to be a pseudo-binary mixture, and changes in volume with pressure or temperature are modelled by changes in the concentration of holes in the system. In the first approximation, the distribution of holes is assumed to be random, yet this is readily modified to include the effect of specific interactions[22,23] if desired.

The fundamentals of the mean-field lattice-gas (MFLG) model have been described previously[19,20], thus only a brief summary follows. The model assumes a compressible fluid to be a random mixture of segments and holes on a three-dimensional lattice. Further, the segments and holes are permitted to exhibit different contact surface areas (and thus, different effective coordination numbers) as first proposed by Staverman[24]. The lattice is therefore an abstract concept rather than a rigid construction. The internal energy of mixing of holes and segments is calculated using regular solution theory where surface fractions are used in place of the commonly applied volume fractions. The entropy of mixing is assumed to follow a Flory–Huggins–Staverman expression which has been modified by the addition of a term ($\phi_0\phi_1\alpha$), where α is a material parameter. For a pure component, the Helmholtz free energy of mixing is therefore derived as:

$$\frac{\Delta A_{\mathrm{MIX}}}{N_\phi RT} = \phi_0\, ln\, \phi_0 + \frac{\phi_1}{m_1}\, ln\, \phi_1 + \phi_0\phi_1\left[\alpha_1 + \frac{\beta_1(1-\gamma_1)}{(1-\gamma_1\phi_1)}\right] \tag{1}$$

where

$$\beta_1 = g_{10} + g_{11}/T \tag{2a}$$

$$\gamma_1 = 1 - \sigma_1/\sigma_0 \tag{2b}$$

$$N_\phi = n_0 + n_1 m_1 \tag{2c}$$

$$\phi_0 = n_0/N_\phi \tag{2d}$$

$$\phi_1 = n_1 m_1/N_\phi \tag{2e}$$

The quantities α_1, g_{10} and g_{11} are material parameters which include both entropic and energetic contributions to the free energy. For a crosslinked polymer structure of $n_1 m_1$ polymer segments, some are part of junction units and the others are part of the polymer chains between crosslinks. We define the segment fraction of the junctions as:

$$S_{\mathrm{j}} = \frac{n_{\mathrm{j}} m_{\mathrm{j}}}{n_{\mathrm{j}} m_{\mathrm{j}} + n_{\mathrm{m}} m_{\mathrm{m}}} = \frac{n_{\mathrm{j}} m_{\mathrm{j}}}{n_1 m_1} \tag{3}$$

For our purposes, we assume that the energetic characteristics of junctions and chain units are identical.

As shown originally by Flory[25], the free energy of a swollen polymer network can be modelled as the sum of a mixing contribution and an elastic term. We have used Flory's derivation[26] of the elastic-free-energy contribution which includes the effect of constraints on junction site movement, and which has been shown by Erman and Flory[27] to provide a good description of the swelling of polymer networks by liquids at atmospheric pressure. For isotropic three-dimensional swelling, this expression becomes:

$$\Delta A_{\mathrm{EL}} = \frac{1}{2}\xi RT(3\lambda^2 - 3) + \frac{3}{2}\mu RT[B + D - \ln(B+1) - \ln(D+1)] \tag{4}$$

where

$$B = \frac{\kappa^2(\lambda^2 - 1)}{(\lambda^2 + \kappa)^2} \tag{5a}$$

$$D = \frac{B\lambda^2}{\kappa} \tag{5b}$$

$$\lambda^3 = \frac{V}{V^0} \tag{5c}$$

$$\xi = \frac{\mu(F-2)}{2} \tag{5d}$$

In the context of the MFLG model, the volume of the system is given as:

$$V = N_\phi v_0 \tag{6}$$

where v_0, the volume/mole of lattice sites, is fixed at 25 cm^3 mol^{-1}. Previous work has shown that changing the value of v_0 does not significantly alter the quality of the pressure–volume–temperature (PVT) data fit, but merely adjusts the values of the material parameters[28]. Given equation (6) above, the ratio V/V^0 becomes:

$$\frac{V}{V^0} = \frac{N_\phi}{N_\phi^0} \tag{7}$$

Because our derivation allows holes (as well as solvent molecules) to act as a swelling agent for the polymer network, N_ϕ^0 in this case represents the volume of the system in the absence of free volume. Consequently:

$$\frac{N_\phi}{N_\phi^0} = \frac{n_0 + n_1 m_1}{n_1 m_1} = \frac{1}{\phi_1} \tag{8}$$

The parameter κ measures the effect of constraints on junction mobility during elastic deformation of the network. When $\kappa \to 0$, the junctions may pass through each other during network deformation (phantom limit); when $\kappa \to \infty$, the junctions are assumed to move proportionally to the macroscopic deformation (affine limit). Erman and Flory[27] define κ as:

$$\kappa = I\left(\frac{\langle r^2\rangle_0}{M}\right)^{3/2} \frac{M_{\mathrm{c}}^{3/2}\mu}{V^0} N_{\mathrm{A}} \tag{9}$$

The factor ($\langle r^2\rangle_0/M$) is a material constant for polymers. Initially, we assume that the crosslinking units are indistinguishable from the monomer units in both energetic characteristics and contact surface area. We then introduce a parameter Z, the ratio of crosslink units to monomer units, such that,

$$Z = \frac{n_{\mathrm{j}}}{\left(\dfrac{n_{\mathrm{m}} m_{\mathrm{m}}}{c_{\mathrm{m}} M_{\mathrm{m}}^0}\right)} \tag{10}$$

where $c_i = m_i/M_i$, and is a MFLG material constant for each material under consideration. Therefore, combining equation (10) with equation (3):

$$S_j = \frac{Zm_j}{Zm_j + c_m M_m^0} = \frac{Zc_j M_j^0}{Zc_j M_j^0 + cM_m^0} \tag{11}$$

and finally:

$$\mu = n_j = S_j\left(\frac{n_1 m_1}{c_j M_j^0}\right) \tag{12}$$

For the silicone network, if we further assume that the junctions and the chain units have identical segmental contact surface areas, and that the junction and chain units exhibit the same volume, then:

$$m_j M_j^0 = m_m M_m^0 = m_1 M_1^0 \tag{13}$$

Thus:

$$S_j = \frac{Z}{1+Z} \tag{14}$$

$$\mu = \frac{Z}{1+Z}\left(\frac{n_1 m_1}{c_1 M_1^0}\right) \tag{15}$$

Finally, the calculation of the molecular weight between crosslinks assumes a perfect network, i.e. no chain ends, or:

$$M_c = \left(\frac{2M_1^0}{ZF}\right) \tag{16}$$

And thus:

$$\kappa = \frac{1}{2}\left(\frac{\langle r^2\rangle_0}{M}\right)^{3/2}\left(\frac{2M_1^0}{ZF}\right)^{3/2}\left[\frac{Z/(1+Z)}{c_1 M_1^0 v_0}\right]N_A \tag{17}$$

Substituting these expressions into equation (4) provides the final form for the elastic contribution to the free energy. Following the usual procedure, we then differentiate the total free energy to find the equation of state:

$$\left(\frac{\partial \Delta A}{\partial V}\right)_{T,n_1} = -p \tag{18}$$

or

$$\left(\frac{\partial \Delta A}{\partial n_0}\right)_{T,n_1} = -pv_0 \tag{19}$$

which results in:

$$\begin{aligned}\frac{-pv_0}{RT} &= \ln\phi_0 + \phi_1\left(1 - \frac{1}{m_1}\right)\\ &\quad -\phi_0\phi_1\left[\alpha_1 + \frac{\beta_1(1-\gamma_1)}{Q^2}\right]\\ &\quad +\phi_1\left[\alpha_1 + \frac{\beta_1(1-\gamma_1)}{Q}\right]\\ &\quad +\xi\lambda^2 + \frac{3}{2}\mu\left(\frac{B'B}{1+B} + \frac{D'D}{1+D}\right)\end{aligned} \tag{20}$$

where

$$B' = \frac{2}{3}\lambda^2 B\left(\frac{1}{\lambda^2 - 1} - \frac{2}{\lambda^2 + \kappa}\right) \tag{21a}$$

$$D' = 1/\kappa(\lambda^2 B' + 2/3\lambda^2 B) \tag{21b}$$

MFLG model for mixtures of solvent and polymer network

An analogous procedure is used for the construction of the free-energy expression for a network/solvent mixture. The free energy of mixing becomes:

$$\begin{aligned}\frac{\Delta A_{\mathrm{MIX}}}{N_\phi RT} &= \phi_0\ln\phi_0 + \frac{\phi_1}{m_1}\ln\phi_1 + \frac{\phi_2}{m_2}\ln\phi_2\\ &\quad +\phi_0\phi_1\left[\alpha_1 + \frac{\beta_1(1-\gamma_1)}{Q}\right]\\ &\quad +\phi_0\phi_2\left[\alpha_2 + \frac{\beta_2(1-\gamma_2)}{Q}\right]\\ &\quad +\phi_1\phi_2\left[\alpha_M + \frac{\beta_M(1-\gamma_1)(1-\gamma_2)}{Q}\right]\end{aligned} \tag{22}$$

where

$$Q = 1 - \gamma_1\phi_1 - \gamma_2\phi_2 \tag{23a}$$

$$\beta_i = g_{i0} + g_{i1}/T \tag{23b}$$

and α_M, g_{m0} and g_{m1} account for interaction between solute and solvent due to mixing. Volume fractions are related to actual physical properties of the mixture via:

$$\phi_2 = \frac{c_2 w_2 v_0}{\bar{V}} \tag{24a}$$

$$\phi_1 = \frac{c_1 w_1 v_0}{\bar{V}} \tag{24b}$$

The general form of the elastic contribution to the free energy does not change, yet some modifications are required to model mixtures of network and solvent. First:

$$\frac{V}{V^0} = \frac{N_\phi}{N_\phi^0} = \frac{n_0 + n_1 m_1 + n_2 m_2}{n_0^0 + n_1 m_1} = \frac{\phi_1^0}{\phi_1} \tag{25}$$

where n_0^0 and ϕ_1^0 are the number of vacancies and the volume fraction of polymer segments in the unswollen network. Therefore:

$$\kappa = \frac{1}{2}\left(\frac{\langle r^2\rangle_0}{M}\right)^{3/2}\left(\frac{2M_1^0}{ZF}\right)^{3/2}\left(\frac{Z\phi_1^0}{c_1 M_1^0 v_0}\right)N_A \tag{26}$$

To model the swelling of a network by a fluid, we employ the equilibrium criteria:

$$\mu_0^{\mathrm{I}} = \mu_0^{\mathrm{II}} \tag{27a}$$

$$\mu_2^{\mathrm{I}} = \mu_2^{\mathrm{II}} \tag{27b}$$

where μ_0^i and μ_2^i are the chemical potentials of the holes and solvent segments in the swollen network and pure solvent phases (a perfect network is assumed, such that no polymer is in the solvent phase). Chemical potential is defined in the usual way:

$$\mu_i = \left(\frac{\partial \Delta A}{\partial n_i}\right)_{T,n_j} \tag{28}$$

The relevant expressions for the MFLG network model are shown in the Appendix.

Parameter fit

The determination of the model parameters was accomplished using a multivariate fitting program which finds the values of the parameters, ω_j, which are solutions to the minimization problem[29]:

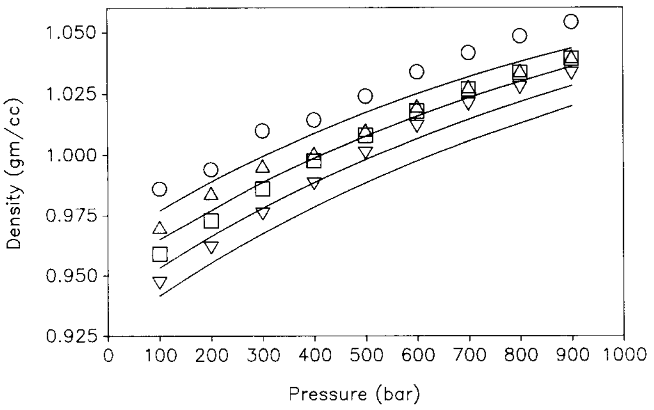

Figure 1 Experimental data[32] and model predictions of PVT behaviour of PDMS; ○, 25°C; △, 40°C; □, 55°C; ▽, 70°C. $\bar{M}_n = 594$, $\bar{M}_w = 665$

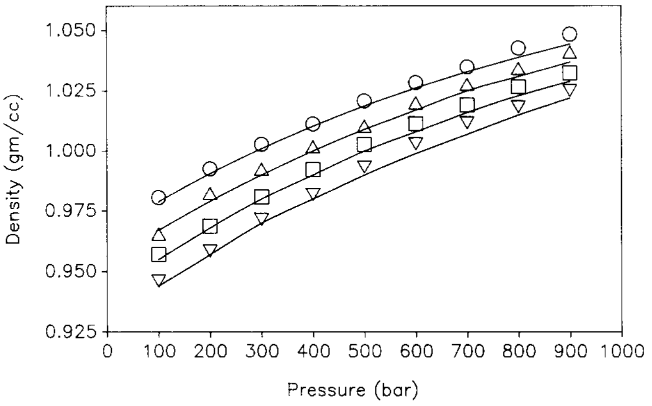

Figure 2 Experimental data[32] and model predictions of PVT behaviour of PDMS: ○, 25°C; △, 40°C; □, 55°C; ▽, 70°C. $\bar{M}_n = 958$, $\bar{M}_w = 1418$

Minimize

$$\sum_{i=1}^{n} (x_i - x_i^0)^{\mathrm{T}} \Omega^{-1} (x_i - x_i^0) \qquad (29)$$

subject to the constraints

$$f(x_i, \omega_j) = 0 \qquad (30)$$

where x_i are the calculated data points and x_i^0 are the true values. The constraints are the appropriate model equations in the implicit form as shown in equation (30). All variables are therefore assumed to have been measured with some error. The errors, or tolerances, from which Ω is calculated are assumed to be random in nature and are set using suggested values from literature. The errors can be assigned either absolute or relative (%) values. The best values for the parameters, therefore, are those that fit the surface represented by the constraints to the data x_i^0 such that the sum of the squares of the distance between x_i^0 and their projections onto the surface is minimal. The distances, $x_i - x_i^0$, are weighted by the corresponding tolerances. The problem is solved iteratively for the ω_j using a Gauss–Newton-type algorithm. The parameters are found as follows:

1. α, m, γ, g_{10} and g_{11} for CO_2 and poly(methyl methacrylate) are found by fitting the pure component data.
2. Swelling data for uncrosslinked polymer is fitted to find the mixing parameters g_{m0}, g_{m1} and α_m.
3. Swelling of crosslinked polymer is predicted based on the above.

RESULTS AND DISCUSSION

MFLG parameters for pure CO_2 have been derived previously[28]. Parameters for PDMS were found via fitting of literature PVT data[30–32] to the MFLG equation of state for uncrosslinked polymers ($\mu = \xi = 0$). Results are shown in *Figures 1–4*; parameters are given in *Table 1*. As can be seen, accuracy decreases as molecular weight decreases, probably due to the increasing effect of end groups on the free volume (ϕ_0) in the material. This deficiency could possibly be improved via conversion of the model to a group contribution basis[33], but we have employed the equations in their original form for simplicity. The average error in density for 164 data points is 0.2%, or approximately ±0.002 g cm^{-3}.

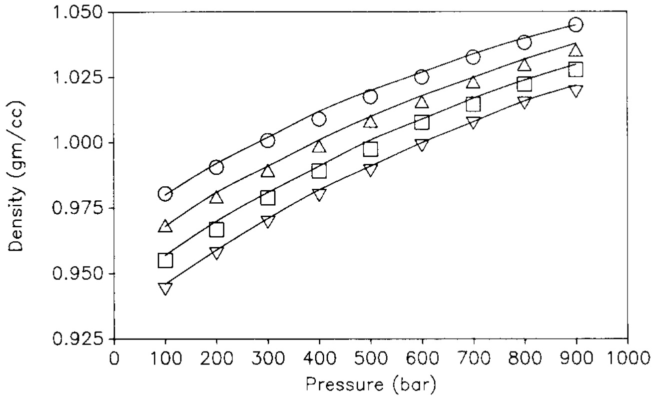

Figure 3 Experimental data[32] and model predictions of PVT behaviour of PDMS; ○, 25°C; △, 40°C; □, 55°C; ▽, 70°C. $\bar{M}_n = 1540$, $\bar{M}_w = 1879$

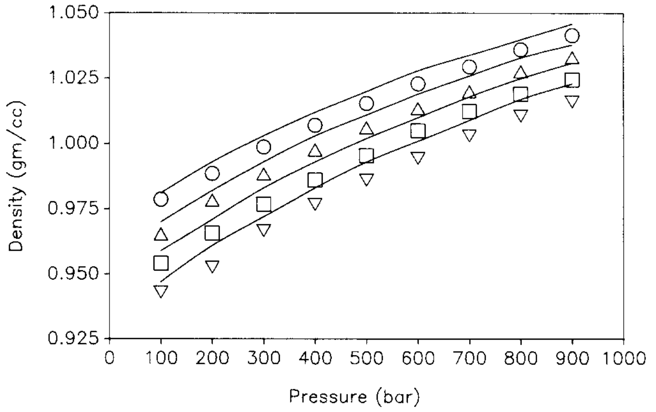

Figure 4 Experimental data[32] and model predictions of PVT behaviour of PDMS: ○, 25°C; △, 40°C; □, 55°C; ▽, 70°C. $\bar{M}_n = 6560$, $\bar{M}_w = 11\,218$

Table 1 MFLG parameters for CO_2 and PDMS

Parameter	CO_2	PDMS
m	1.31	2.70
α	0.91498	−2.5097
g_{10}	−1.1445	1.6038
g_{11}	519.82	606.89
γ	−1.2010	−0.90668

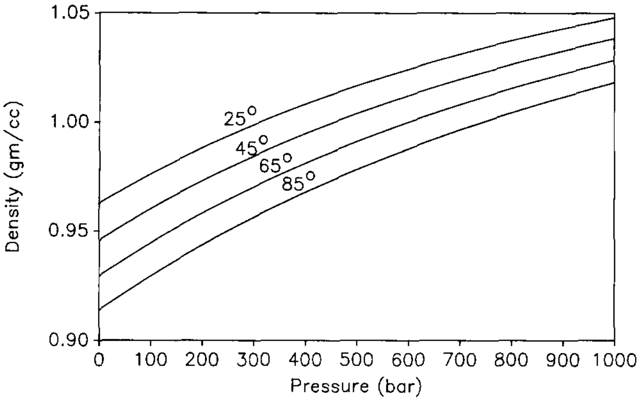

Figure 5 Predicted PVT behaviour of crosslinked PDMS ($Z = 0.0247$)

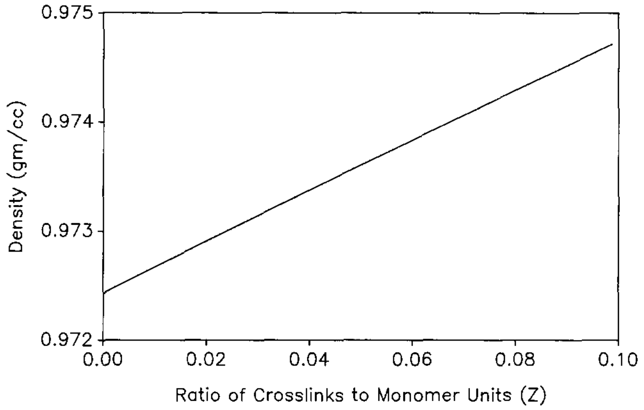

Figure 6 Predicted PVT behaviour of crosslinked PDMS at 45°C and 200 bar, assuming junction functionality of 3

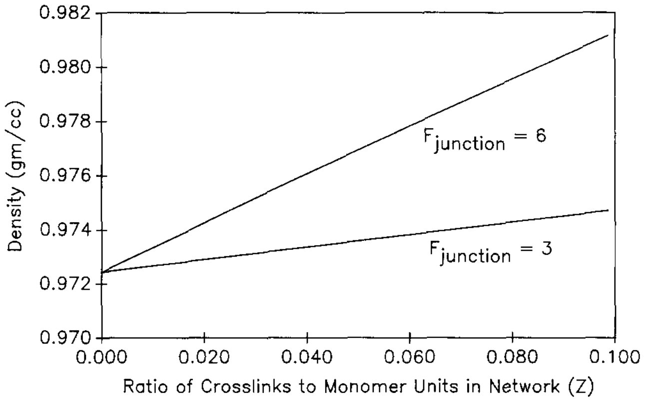

Figure 7 Predicted PVT behaviour of crosslinked PDMS at 45°C and 200 bar, at two junction functionalities

Using the parameters found above in conjunction with the equation of state (equation (19)), the density of a model network was calculated as a function of crosslink concentration, junction functionality, pressure and temperature. These results are shown in *Figures 5–7*. While PVT data for networks are not readily available, the predictions do show the expected trends, that density increases as crosslink density, junction functionality, or pressure increases.

Swelling of crosslinked PDMS by supercritical CO_2

The model equations for network swelling (equations (27a), (27b), (A1)–(A4)) were fit to data by Shim and Johnston[12], who measured volume change *versus* pressure for silicone rubber exposed to CO_2 at 35°C and 70°C, and by Briscoe and Zakaria[14], who measured both volume change and weight fraction CO_2 in silicone rubber *versus* pressure at 42°C. The values for Z used in the data fit were calculated using formulation information in refs 12 and 14. Binary mixture parameters for the PDMS–CO_2 system derived from the data fit are shown in *Table 2*.

Results, shown in *Figures 8–11*, demonstrate that the modified MFLG reproduces the volume change data (and thus the volume change on mixing) relatively well. The model reproduces the sigmoidal shape of the volume change *versus* pressure curves, but does not plateau to the extent that the data does. This may indicate that there are more 'effective junctions' than the number which we would calculate based on the chemical make-ups of the system, or that the junctions present exert a greater effect on swelling than that predicted by Flory's model. Chain entanglements would be one factor

Table 2 MFLG parameters for CO_2–PDMS mixture

Parameter	CO_2–PDMS
g_{m0}	2.5196
g_{m1}	320.03
α_m	−7.4521

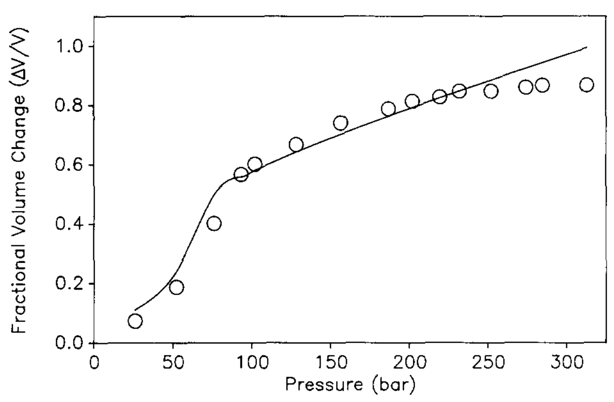

Figure 8 Experimental data[12] and model predictions of fractional volume change of PDMS due to swelling in CO_2 at 35°C as a function of gas pressure

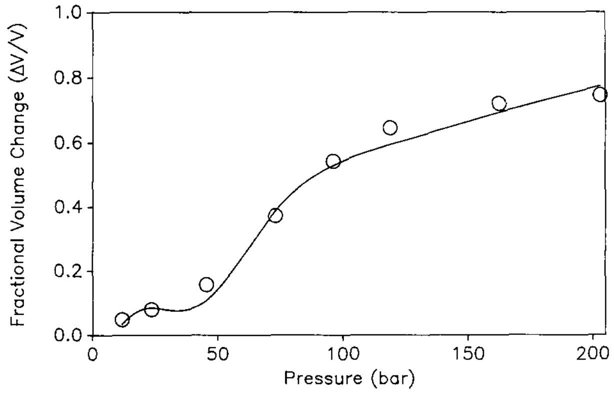

Figure 9 Experimental data[14] and model predictions of fractional volume change of PDMS due to swelling in CO_2 at 42°C as a function of gas pressure

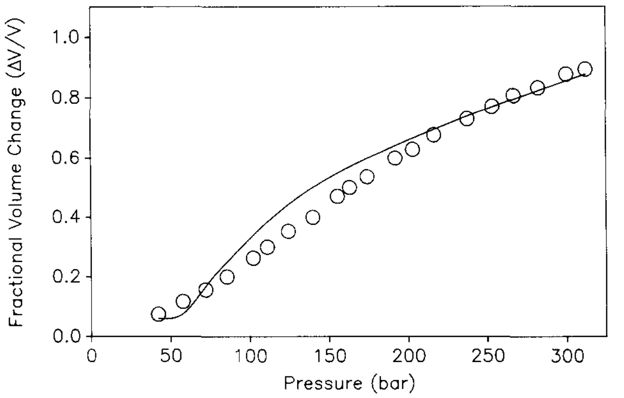

Figure 10 Experimental data[12] and model predictions of fractional volume change of PDMS due to swelling in CO_2 at 70°C as a function of pressure

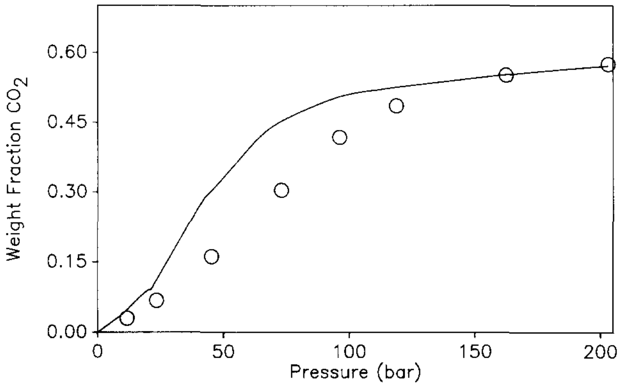

Figure 11 Experimental data[14] and model predictions of weight fraction CO_2 absorbed by PDMS as a function of pressure at 42°C

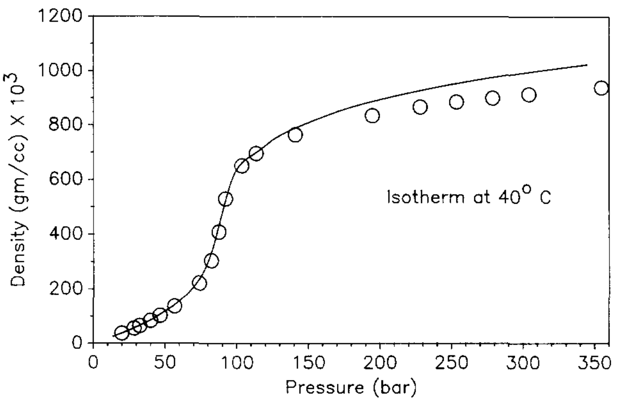

Figure 12 Experimental data[35,36] and model predictions of PVT behaviour of pure CO_2 at 40°C

which would increase the number of effective junctions in the system.

Although describing the sigmoidal shape of the weight fraction data, the model overpredicts the amount of CO_2 absorbed at moderate pressures. This is due partially to an overprediction of the density of pure CO_2 in this pressure regime (*Figure 12*) and also to incorrect predictions of the dependence of the partial molar volume of CO_2 on pressure.

The overestimation of weight fraction CO_2 absorbed by PDMS is also shown in predictions of CO_2 sorption *versus* pressure for uncrosslinked PDMS ($\mu = \xi = 0$) (*Figure 13*). These predictions, which make use of the mixture parameters calculated above, show the proper trends *versus* temperature but substantially overestimate the weight of CO_2 absorbed by the polymer.

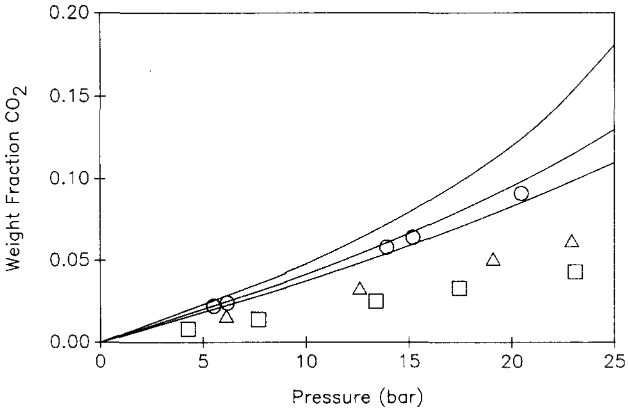

Figure 13 Experimental data[37] and model predictions of weight fraction CO_2 absorbed by uncrosslinked PDMS *versus* pressure: ○, 10°C; △, 35°C; □, 55°C

CONCLUSIONS

The mean-field lattice-gas model of Kleintjens *et al.* for the free energy of mixing has been modified by an elastic term due to Flory, in order to model the swelling of an elastomer by a supercritical fluid. In the absence of a diluent, the lattice vacancies, whose concentration determines overall system volume, are considered as swelling agents for the networks. This allows the derivation of an equation of state for a crosslinked elastomer. Predictions of volumetric behaviour for a crosslinked PDMS *versus* pressure, temperature, crosslink density and junction functionality show trends which are logical, although lack of PVT data for networks makes verification difficult.

The model represents the pressure trends in both volume change and weight fraction fluid absorbed well for the PDMS–CO_2 mixture. However, the absolute predictions of weight fraction CO_2 absorbed are far too high in the vicinity of the critical pressure (74 atm). A potential means by which to correct this deficiency has been suggested recently by Koningsveld[34]; given that the accessibility of a particular segment to contact by another will be dependent on the presence of neighbouring segments as well as on the freedom of motion of segments, it is not unreasonable to postulate that the contact surface area of a segment should be a function of the local free volume, as well as the presence of segments from other molecules. We are currently exploring this option for modifying the model.

In a forthcoming paper, we will show that predictions of the free volume in a PMMA network swollen by CO_2 conform well to trends measured using dielectric techniques.

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NOMENCLATURE

ΔA_{MIX}	Helmholtz free energy of mixing
ΔA_{EL}	Elastic free energy
c_i	MFLG material constant
F	Junction functionality
g_{ij}	MFLG material parameter
I	Universal constant ($\sim$0.5 for various polymers[27])
M	Molecular weight
M_c	Molecular weight between crosslinks
M_i^0	Molecular weight of a monomer unit
m_i	Segments per chain of species *i*
N_A	Avogadro's number
N_ϕ	Total number of sites
n_i	Number of (moles of) species *i*
P	Pressure
R	Gas constant
$\langle r^2 \rangle_0$	Unperturbed mean square end-to-end distance
S_j	Segment fraction of junction units
T	Temperature
V	Volume of swollen network
V^0	Volume of unswollen network
$\bar{V}$	Specific volume of swollen network (cm^3 g^{-1})
v_0	Volume/mole of lattice site
w_i	Weight fraction of component *i* in swollen network
Z	Ratio of junction units to monomer units
α_i	MFLG material parameter
κ	Parameter which accounts for constraints upon junction during network deformation
λ	Linear increase upon swelling
μ	Moles of junction units in network
μ_i	Chemical potential of species *i*
ξ	Network cycle rank
σ_i	Contact surface area of a segment of species *i*
ϕ_i	Volume fraction of species *i*
Ω	Error variance matrix

Subscripts

j	Junction
m	Monomer units
0	Hole
1	Component 1 molecules
2	Component 2 molecules

APPENDIX

The chemical potential, μ, for the holes and segments in the pure CO$_2$ phase is derived as:

$$\frac{\mu_0}{RT} = \ln \phi_0 + \phi_1\left(1 - \frac{1}{m_1}\right) - \phi_0\phi_1\left[\alpha_1 + \frac{\beta_1(1-\gamma_1)}{Q^2}\right] + \phi_1\left[\alpha_1 + \frac{\beta_1(1-\gamma_1)}{Q}\right] \qquad \text{(A1)}$$

$$\frac{\mu_1}{m_1 RT} = \left(\frac{1}{m_1} - 1\right) + \frac{1}{m_1}\ln \phi_1 + \phi_1\left(1 - \frac{1}{m_1}\right) - \phi_0\phi_1\left[\alpha_1 + \frac{\beta_1(1-\gamma_1)^2}{Q^2}\right] + \phi_0\left[\alpha_1 + \frac{\beta_1(1-\gamma_1)}{Q}\right] \qquad \text{(A2)}$$

where $Q = 1 - \gamma_1\phi_1$ and $\beta_1 = g_{10} + g_{11}/T$.

The chemical potential of holes and CO$_2$ segments in the swollen polymer phase is given by:

$$\frac{\mu_0}{RT} = \ln \phi_0 + \phi_1\left(1 - \frac{1}{m_1}\right) + \phi_2\left(1 - \frac{1}{m_2}\right) - \phi_0\phi_1\left[\alpha_1 + \frac{\beta_1(1-\gamma_1)}{Q^2}\right] + \phi_1\left[\alpha_1 + \frac{\beta_1(1-\gamma_1)}{Q}\right] - \phi_0\phi_2\left[\alpha_2 + \frac{\beta_2(1-\gamma_2)}{Q^2}\right] - \phi_1\phi_2\left[\alpha_{12} + \frac{\beta_{12}(1-\gamma_1)(1-\gamma_2)}{Q^2}\right]$$

$$+\phi_2\left[\alpha_2+\frac{\beta_2(1-\gamma_2)}{Q}\right]$$

$$+\xi\lambda^2+\frac{3}{2}\mu\left(\frac{B'B}{1+B}+\frac{D'D}{1+D}\right) \qquad \text{(A3)}$$

$$\frac{\mu_1}{m_1RT}=\left(\frac{1}{m_1}-1\right)+\frac{1}{m_1}\ln\phi_1+\phi_1\left(1-\frac{1}{m_1}\right)$$

$$+\phi_2\left(1-\frac{1}{m_2}\right)-\phi_0\phi_1\left(\alpha_1+\frac{\beta_1(1-\gamma_1)^2}{Q^2}\right)$$

$$+\phi_0\left(\alpha_1+\frac{\beta_1(1-\gamma_1)}{Q}\right)$$

$$-\phi_0\phi_2\left(\alpha_2+\frac{\beta_2(1-\gamma_1)(1-\gamma_2)}{Q^2}\right)$$

$$-\phi_1\phi_2\left(\alpha_{12}+\frac{\beta_{12}(1-\gamma_1)^2(1-\gamma_2)}{Q^2}\right)$$

$$+\phi_2\left(\alpha_{12}+\frac{\beta_{12}(1-\gamma_1)(1-\gamma_2)}{Q}\right)$$

$$+\xi\lambda^2+\frac{3}{2}\mu\left(\frac{B'B}{1+B}+\frac{D'D}{1+D}\right) \qquad \text{(A4)}$$

where $Q = 1 - \gamma_1\phi_1 - \gamma_2\phi_2$ and other symbols are as described in the Nomenclature.