

THERMODYNAMIC MODELING OF CO₂ – POLYSTYRENE/POLY (METHYLMETHACRILATE) AND POLYSTYRENE/ POLY (VINYL PYRIDINE) BLOCK COPOLYMERS

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A thermodynamic model which couples the lattice fluid theory and the Gibbs-Di Marzio criterion, which states the entropy of the system zero at the glass transition temperature, is applied to describe the sorption in presence of carbon dioxide (CO₂) of polystyrene (PS), poly (methyl methacrilate) (PMMA), poly (vinyl pyridine) (PVD) and of styrene-methyl methacrilate and styrene-vinyl pyridine block copolymers. The model requires only one binary interaction parameter that successively is used to predict qualitatively the glass transition temperature (T_g) behavior as a function of the CO₂ pressure. For the block copolymers, both for sorption and T_g behavior, the model evidences a continuous transition from one homopolymer to the other.

INTRODUCTION

Supercritical fluids (SCF) can interact not only with polymers at temperatures higher than softening temperature but also with polymers in the glassy state. Three concomitant effects must be considered: the ability of SCFs to dissolve in a considerable extent into amorphous glassy polymers (polymer sorption); the swelling of the polymer matrix; the plasticization of the polymer [1].

The so called plasticization effect, i.e. the depression of the glass transition temperature (T_g), is an important feature: the sorbed gas acts as a kind of “lubricant”, making it easier for chain molecules to slip over one another, and thus causing polymer softening. This effect induced by CO₂ has an impact on many polymer-processing operations and the evaluation of the T_g depression of the polymer [2-5] plays an important role in the definition of operating conditions.

For all these processes involving a polymer and a supercritical fluid is very important to know how the pressure of the diluent solved into the macromolecule affects the T_g of the polymer.

The thermodynamic model adopted in this study, proposed by Condo et al. [6], combines the lattice fluid theory and the Gibbs-Di Marzio criterion asserting that the entropy of the system is zero at the glass transition. The model requires only one interaction parameter. In this work the parameter is calculated from the fitting of the experimental sorption data taken from literature and it is used to predict the glass transition depression [7].

I - THERMODYNAMIC MODEL

The model, described in details in references [3] and [7], is essentially based on the use of a well known lattice fluid equation of state coupled with the Gibbs Di Marzio assumption which asserts that the entropy of the system is zero at the glass transition.

In the case of the pure polymer this criterion allows the determination of the so-called flexibility parameter. In the case of binary mixtures diluent-polymer the Gibbs-Di Marzio equation is used for the determination of the binary interaction parameter starting from experimental data of T_g depression; the sorption of the fluid can be consequently predicted. On the contrary from sorption data the T_g depression can be evaluated.

II - SORPTION MODELING

The characteristic parameters of lattice fluid equation of state for CO_2 and the investigated polymers are reported in table 1.

Substance	T^* (K)	P^* (bar)	r^* (Kg/m^3)
CO_2	309	57.4	1505
PMMA	696	50.3	1269
PS	735	35.7	1105
PVD	755	40.1	1121
80PS 20PMMA	727	38.6	1138
50PS 50PMMA	716	43.0	1187
40PS 60PMMA	712	44.4	1203
50PS 50PVD	745	37.9	1113
25PS 75PVD	750	39.0	1117

Table 1: Parameters of the lattice fluid equation for CO_2 and polymers.

The modeling of CO_2 sorption isotherms, based on the experimental work of Zhang *et al.* [5], is presented in figures 1 and 2 for PS/PMMA and PS/PVD copolymers. The determined ζ_{12} values are reported in table 2.

As reported in figure 1, there is a continuous transition from the PS behavior to the one of PMMA. This is confirmed by the binary interaction parameter variations: ζ_{12} is equal to 1.11 for pure PS while it reaches the value of 1.12 for pure PMMA. The fittings of the experimental data for the three copolymers give the following results: 1.115, 1.116 and 1.118 for the copolymer with 20%, 50% and 60% of PMMA.

In the case of pure PMMA and for the copolymer with 40% of PS the model is in agreement with experimental data till 80 bar while for the other copolymers and for pure PS the correlations are satisfactory for pressures below 60 bar.

Polymer	T_g (K)	z_{12}
PMMA	378	1.12
PS	373	1.11
PVD	410	1.13
80PS 20PMMA	374	1.115
50PS 50PMMA	375	1.116
40PS 60PMMA	376	1.118
50PS 50PVD	391	1.1198
25PS 75PVD	400	1.125

Table 2: T_g values of the polymer investigated

Similar consideration can be made for the PS/PVD copolymers as reported in figure 2 which shows a continuous transition from pure PS to pure PVD behavior: the binary interaction parameters achieved from the fittings of CO_2 in pure PS and pure PVD are 1.11 and 1.13, respectively. Intermediate values are obtained for the two copolymers: 1.1198 and 1.125 for 50% and 75% in PVD. Once more the model is in agreement with the experimental CO_2 sorption isotherm for pure PVD and the two copolymers for pressures till 70 bar.

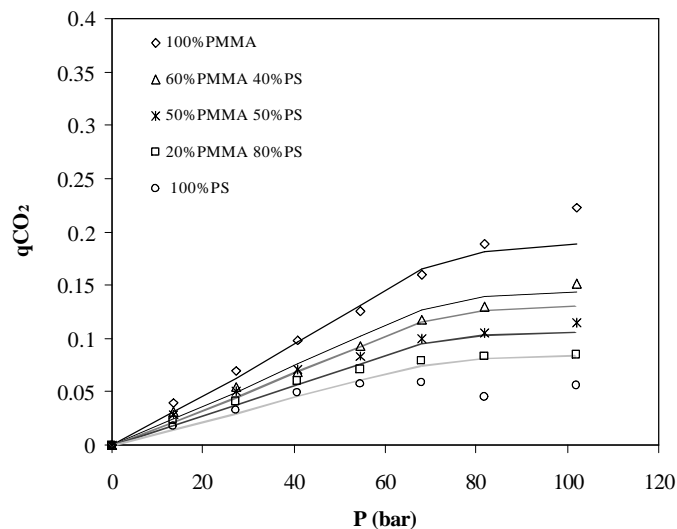


Figure 1: Modeling of CO_2 sorption data at 308 K with the lattice fluid equation of state for the copolymers PS/PMMA and for the two homopolymers ($q_{\text{CO}_2} = \text{g CO}_2/\text{g Polymer}$).

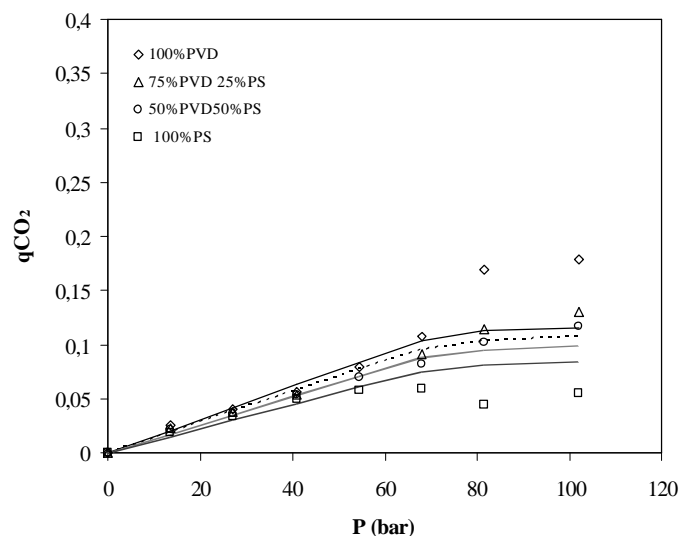


Figure 2: Modeling of CO₂ sorption data at 308 K with the lattice fluid equation of state for the copolymers PS/PVD and for the two homopolymers (q_{CO_2} =g CO₂/g Polymer).

III – GLASS TRANSITION TEMPERATURE PREDICTION

The binary interaction parameters obtained from the fitting of sorption data were successively adopted for the T_g behavior predictions. These investigations were not compared with experimental data because, in the work of Zhang *et al.*, the CO₂ plasticization effects were not reported.

The T_g behavior predictions for pure PS and PMMA and PS/PMMA copolymers are illustrated in figure 3. The polymers present a type IV behavior with the unusual phenomenon of the retrograde vitrification, which justify the presence of two T_g values at a fixed pressure.

All the curves pass through a cross point at about 363 K and 20 bar: above this pressure for a fixed T_g value the pressure increases as the PMMA percentage decreases, evidencing the dependence of the T_g behavior from the copolymer composition. Below the cross point the difference between the curves is not so evident because the atmospheric T_g values of pure PS and PMMA are closed one to the other.

Confirming the sorption data modeling, the T_g behavior shows a continuous transition from pure PS to pure PMMA.

The T_g behavior predictions for pure PS and PVD, and PS/PVD copolymers in CO₂ are presented in figure 4. For these systems the thermodynamic model evidences a type II behavior for the copolymer with 25% of PS and a type III for the one with 50% of PS while for pure PS and PVD the model predicts a type IV behavior. At a fixed T_g each curve increases with the PVD percentage, showing also for these polymers a continuous transition from the behavior of one homopolymer to the other. Finally at low temperatures (less than 253 K) the curves became close one to the other, showing a T_g behavior independent from the composition of the copolymers.

Differing from the PS/PMMA systems, there is a big discrepancy between the T_g values of the homopolymers at atmospheric pressure, as shown in figure 4.

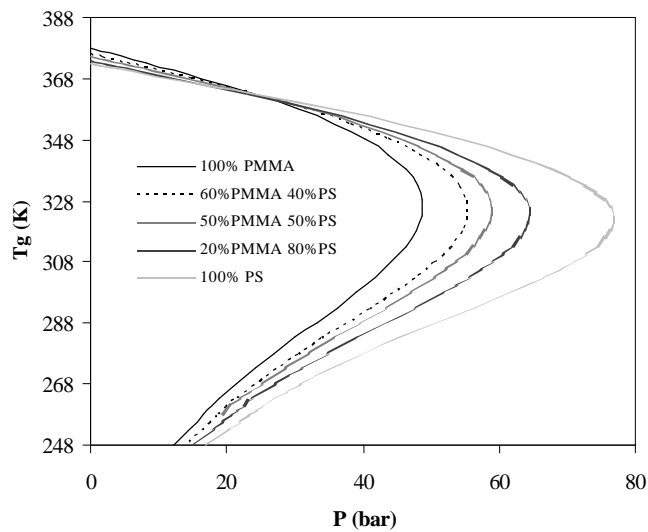


Figure 3: T_g versus P behavior for PS, PMMA and PS/PMMA copolymers.

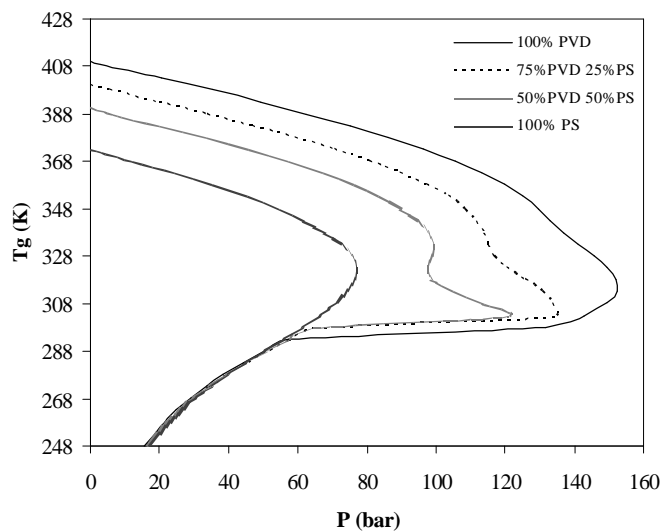


Figure 4: T_g versus P behavior for PS, PVD and PS/PVD copolymers.

CONCLUSIONS

A study on the behavior of two systems (PS/PMMA and PS/PVD block copolymers) in the presence of supercritical CO_2 is carried out by means of a thermodynamic model based on the lattice fluid theory and the Gibbs-Di Marzio criterion.

The analysis begins with the fitting of the CO_2 sorption isotherms at 308 K to find the value of the binary interaction parameter for each system. These parameters are then used to perform a qualitative prediction of T_g depressions as a function of the pressure of the CO_2 solved into the polymer.

A continuous transition between the behavior of one homopolymer and the other is confirmed both from the modeling of the CO₂ sorption isotherms and the T_g predictions showing for the latter a different behavior of the two systems examined.

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