THE INFLUENCE OF HIGH-PRESSURE CARBON DIOXIDE ON THE PHASE BEHAVIOR OF PDMS/PEMS BLENDS: AN EXPERIMENTAL AND THEORETICAL INVESTIGATION

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ABSTRACT

In this work the effect of high-pressure CO_2 on the miscibility of low-polydispersity poly(dimethylsiloxane)/poly(ethylmethylsiloxane) (PDMS/PEMS) blends in which $M_{w,PDMS}$ = 44.5 kg/mol and $M_{w,PEMS}$ = 14.6 kg/mol is investigated by complementary experimental and theoretical methods. Experimental measurements of phase equilibria in ternary PDMS/PEMS/ CO_2 systems are obtained as functions of blend composition and CO_2 pressure by high-pressure spectrophotometry. Results indicate that the cloud point of the blend (T_{cp}) increases with increasing CO_2 pressure. This observation reveals that CO_2 serves to reduce blend miscibility by translating the entire phase envelope of our PDMS/PEMS blend to higher temperatures, in marked contrast to previous studies of PDMS/PEMS blends subjected to hydrostatic pressure (which enhances blend miscibility by depressing T_{cp}).

We have modeled the phase behavior of these PDMS/PEMS/CO_2 systems using the SAFT equation of state, which is a molecular-based formalism that is designed to account for the effects of molecular association and chain flexibility, as well as repulsive and dispersion interactions. The SAFT parameters for PDMS are obtained from binary cloud curves previously reported in the literature for PDMS/CO_2 mixtures, whereas PEMS parameters are obtained from an extended group contribution approach established for PDMS systems. The ability of the model to predict the phase behavior of the ternary PDMS/PEMS/CO_2 system is corroborated by comparing theoretical predictions with the experimental data reported herein.

INTRODUCTION

Most commercially relevant polymer blends exhibit upper critical solution temperature (UCST) behavior in which increasing temperature (or decreasing hydrostatic pressure) promotes an increase in miscibility. Horiuchi et al. [1] have demonstrated that the PDMS/ PEMS system is partially miscible, with an experimentally accessible UCST that may (depending on the molecular weights of the constituent polymers) reside near ambient temperature. These characteristics, along with the ability to design the shape of the phase boundary and position of the UCST through judicious choice of polymer molecular weights, make this blend attractive for the present study. Moreover, this system is also interesting for another reason: due presumably to its negative excess volume change upon mixing [2], it becomes more miscible when exposed to an increase in hydrostatic pressure. This is contrary

to the conventional UCST behavior of most polymer pairs and provides us with an opportunity to explore the effect of high-pressure condensable gas on blend phase behavior.

In this work we seek to elucidate the response of the PDMS/PEMS blend to high-pressure CO_2, which has been shown [3] to significantly swell PDMS. Recent efforts have demonstrated that high-pressure CO_2 can enhance the miscibility [4] of blends exhibiting UCST behavior and reduce the miscibility of LCST blends [5]. For this study, we have selected model polymers with relatively low polydispersity indices (M_w/M_n) so that the effect of polydispersity on the phase diagram can be neglected.

I- EXPERIMENTAL SECTION

The PDMS (M_w = 44.5 kg/mol, M_w/M_n = 1.09) and PEMS (M_w = 14.6 kg/mol, M_w/M_n = 1.13) homopolymers were purchased from Polymer Source (Dorval, Quebec, Canada) and subjected individually to pretreatment in high-pressure CO_2 to remove any low-molecular-weight (CO_2-soluble) fraction. Cloud point temperatures for various PDMS/PEMS blend compositions were determined by cooling blends from the homogeneous state at constant CO_2 pressures and measuring the change in turbidity with a 632 nm laser source in conjunction with a photometric power meter. The cloud points reported herein corresponded to the temperature at the inflection point of the power (intensity) *versus* temperature curve. The detailed experimental procedure for this measurement is described elsewhere [6].

II- EXPERIMENTAL RESULTS

PDMS/PEMS Blends

As a baseline for comparison with prior studies [1, 2, 7-10] of PDMS/PEMS blends, we have measured the cloud curve of our blend in the absence of CO_2. Figure 1 shows T_{cp} as a function of blend composition (w_{PDMS}) for three series of PDMS/PEMS blends, with the closed circles representing the results of this study. The coexistence curve measured by Kuwahara et al. [7] (open squares) for a mixture of PDMS (M_w = 19.1 kg/mol, M_w/M_n = 1.03) and PEMS (M_w = 14.0 kg/mol, M_w/M_n =1.02) is included for comparison. The critical temperature extracted from their high-precision data is located at 30.662°C and 55.04 wt% PEMS. Beiner et al. [2] have previously reported the critical points of three different blends. Only one of these, blend "C" composed of PDMS (M_w = 10.7 kg/mol) and PEMS (M_w = 12.4 kg/mol) with polydispersities between 1.04 and 1.12, is shown (as an open triangle) in Figure 1. In this case, the critical temperature lies below -50°C at 50 wt% PEMS. Note that $M_{w,PEMS}$ is approximately the same for the three blends displayed in Figure 1, whereas $M_{w,PDMS}$ nearly doubles in each series. This figure illustrates the dramatic effect that $M_{w,PDMS}$ can have on the cloud point temperatures of relatively low-molecular-weight PDMS/PEMS blends.

PDMS/PEMS Blends in Presence of Supercritical CO_2

Pressure can serve to either compatibilize or demix polymer blends, depending on the specific characteristics of the constituent polymers and their mutual interaction. It has been shown that (hydrostatic) pressure enhances the miscibility of model PDMS/PEMS blends that exhibit UCST behavior. Beiner et al. [2] have suggested that this unusual behavior is caused by a negative excess volume change upon mixing when pressure-induced mixing becomes

significant ($\delta T_c/\delta P \sim$ -25 K/kbar). Our studies of this blend under reasonably high pressure include an additional complication, the presence of CO_2, which swells polysiloxanes.
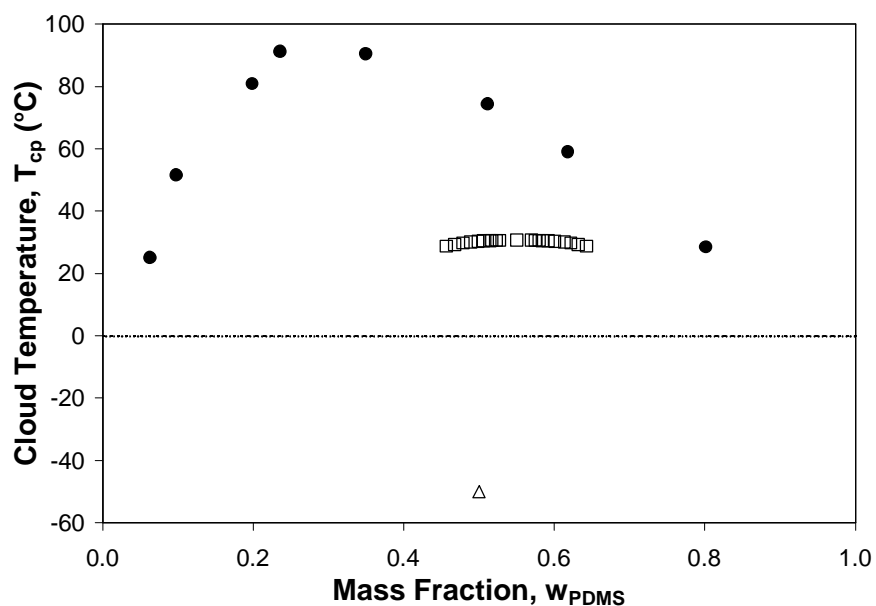

Figure 1. Cloud point temperatures of model PDMS/PEMS blends.

Figure 2 shows the experimental cloud point temperatures obtained in this study for the PDMS/PEMS blend as a function of PDMS mass fraction (solvent-free basis) and CO_2 pressure, as discerned by high-pressure spectrophotometry. At constant PDMS/PEMS mass fraction, an increase in CO_2 pressure increases the cloud temperature, thus reducing the miscibility of the UCST blend. It must be recognized, however, that an increase in CO_2 pressure implies an increase in the amount of CO_2 present in the system.
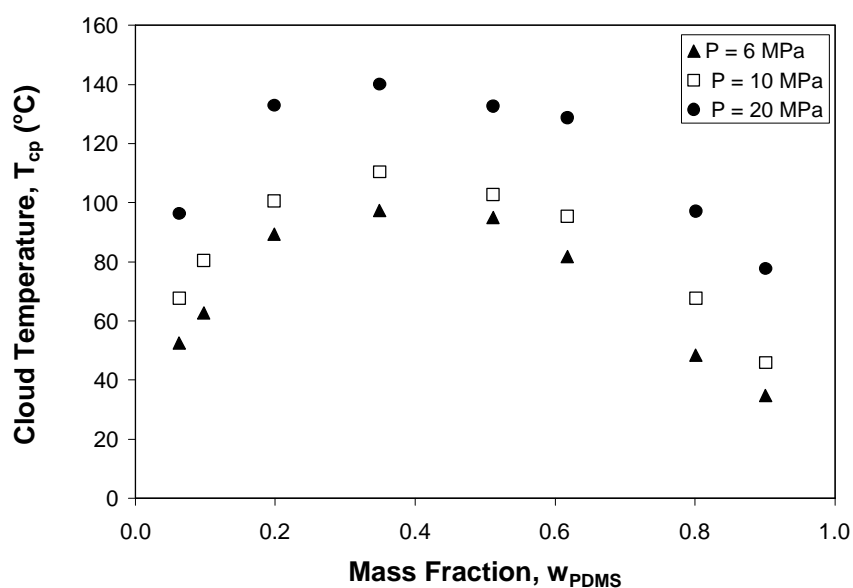

Figure 2. Cloud point temperatures of PDMS/PEMS blends as a function of blend composition (solvent-free) and CO_2 pressure.

III- MODELING

According to the SAFT equation of state [11], molecules are modeled as chains of covalently bonded spheres, and different molecules of homologous series (such as n-alkanes or polymers that only differ in molecular weight) are considered as chains of identical spheres. In this case the number of spheres in the chain is directly proportional to the molecular weight. Within the context of the SAFT framework, the residual Helmholtz energy, a^{res}, is of the form

$$a^{res} = a^{seg} + a^{chain} + a^{assoc} \qquad (1)$$

where a^{seg} reflects segment-segment interactions (interactions between repeat units in different molecules) usually modeled in terms of hard-sphere, LJ or square-well potentials; a^{chain} is the additional Helmholtz energy due to chain formation; and a^{assoc} is the contribution due to association between different molecules due, for example, to H-bonding. Therefore, in this work we set the parameters comprising a^{assoc} to zero. A detailed discussion of the mathematical form of the SAFT equation can be found elsewhere [12,13] and is not reproduced here.

Determination of Parameters

Since high-molecular-weight polymers do not possess a detectable vapor pressure and since they commonly undergo thermal degradation before exhibiting a critical point, equation-of-state parameters for polymers are generally determined from experimental pure-liquid molar volume data. Unfortunately, regression of polymer parameters from this procedure generally results in poor predictions of phase equilibrium afforded by the SAFT equation [14,15]. When parameters are determined from such restricted data, a variety of pure-component parameter sets fit the data. Recent efforts [16] have demonstrated that this shortcoming remains in newer versions of the SAFT equation of state (such as PC-SAFT).

An alternative approach to obtain polymer parameters is to regress a pure-component parameter for the polymer from binary phase equilibria data [14,15]. In this work, the SAFT parameters for PDMS are obtained from binary cloud curves reported elsewhere [17-19] for PDMS/CO_2 mixtures, and the relevant CO_2 parameters have been extracted from the literature [20]. Regrettably, data corresponding to PEMS/CO_2 phase equilibria are not presently available, in which case the PEMS parameters have been estimated from an extended group contribution approach proposed by Lora et al. [21] for acrylate polymers. Colina et al. [22] have recently used a similar pseudo-group approach to determine the parameters for poly(1,1,2,2-tetrahydroperfluorooctyl acrylate) (PTAN), estimating the contribution of the -CF_2- group, from high molecular weight poly(1,1-dihydroperfluorooctyl acrylate) (PFOA).

Lora et al. [21] argue that the number of segments (m) for a given acrylate polymer is determined by first calculating m for the base ester group. The m for a particular alkyl tail is calculated by summing the m values of the appropriate number of -CH_2- and -CH_3 groups. The values of m for -CH_3 and -CH_2- are obtained from regressions of alkane and alkene parameters. The value for the product of mv^{00}, where v^{00} represents the segment volume, for the base is determined from the same group contribution approach used to obtained m. Using

a similar approach for PEMS, we estimate the contributions of the –Si-O- group: $m_{SiO} = 5.742$ and $v^{00}_{SiO} = 15.597$ cm^3/mol.

Since the attractive energy of a segment (u^0/k) cannot be obtained by this method, we have elected to determine this energy parameter from one experimental cloud point. For PEMS, regression of u^0/k fitted to the 60°C data obtained in this work yields a value of 204 K, which compares well with that of PDMS (u^0/k = 200 K).

The binary interaction parameter k_{ij} is a fitted, binary mixture parameter that corrects the mean-field energy contribution to SAFT. This parameter is usually determined by fitting SAFT to experimental phase equilibrium data, and is expected to lie between ±0.10. From a careful analysis of binary and ternary blends of low-polydispersity blends, Horiuchi et al. [1] conclude that the PDMS/PEMS pair exhibits no evidence of specific interactions. On the basis of this finding, we have elected to set $k_{PDMS/PEMS}$ = 0 in this work. Moreover, we assume $k_{PEMS/CO2} = k_{PDMS/CO2}$ = 0.017, which is obtained from PDMS/CO$_2$ experimental data [17-19].

A comparison of predicted and experimental cloud point isobars for PDMS/PEMS blends in CO$_2$, with PDMS concentrations varying from 5 to 90 wt%, is provided in Figure 3. At any pressure, the homogeneous region lies above the cloud point temperature. The maximum temperature in the cloud curve is the UCST, where the compositions of the two coexisting phases become equal. We apply a freehand closure to our predicted curves in the immediate vicinity of the UCST. As this figure attests, the predictions from SAFT are in reasonably good quantitative agreement with the experimental data.
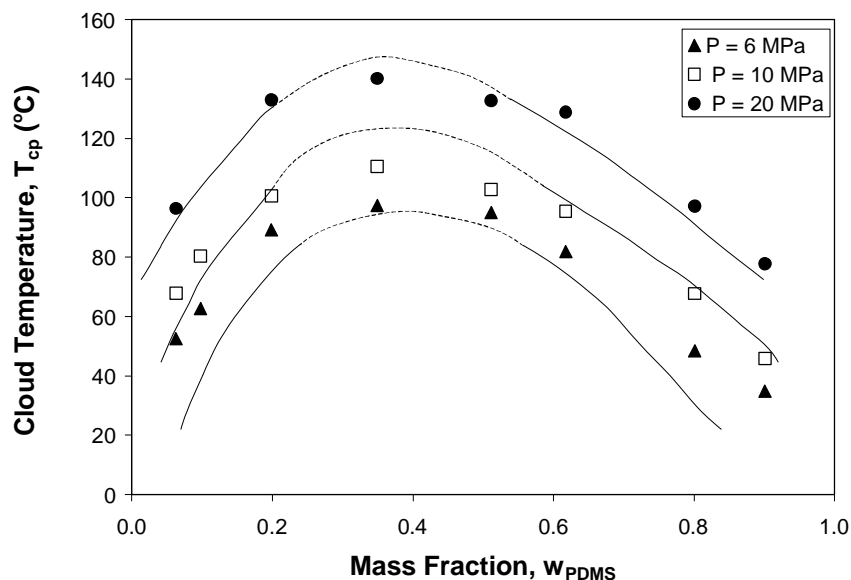

Figure 3. Cloud point temperatures of PDMS/PEMS blends in CO$_2$. Symbols denote experimental results; curves signify corresponding SAFT predictions.

CONCLUSIONS

We have measured cloud curves for the PDMS/PEMS/CO_2 system. Results indicate that the cloud point increases with increasing CO_2 pressure, which is contrary to the response of this blend to hydrostatic pressure. Predictions from the SAFT equation of state compare favorably with experimental results, confirming the versatility of this theoretical approach.

ACKNOWLEDGMENTS

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