

Phase Behavior of Semicrystalline Polyester Resin in Supercritical Fluid Solvents and Solvent Mixtures: Implications for Supercritical Fluid Processing

S. E. CONWAY,¹ J. S. LIM,² M. A. McHUGH,³ J. D. WANG,⁴ F. S. MANDEL⁴

¹ Department of Chemical Engineering, Johns Hopkins University, Baltimore, Maryland 21218

² Korean Institute of Science and Technology, Cheongryang, Seoul 130-650, Korea

³ Department of Chemical Engineering, Virginia Commonwealth University, Richmond, Virginia 23284

⁴ Ferro Corporation Technical Center, Independence, Ohio

Received 10 June 2000; accepted 15 November 2000

ABSTRACT: Cloud-point data between 40 and 240°C and pressures to 2750 bar are presented for a low molecular weight, semicrystalline polyester resin of 53.4 mol % adipic acid and 46.6 mol % 1,4-cyclohexanedimethanol in supercritical CO₂, dimethyl ether (DME), and chlorodifluoromethane (CDFM), and in mixtures of CO₂ with DME, CDFM, methanol, ethanol, butanol, octanol, hexafluoroisopropanol, acetone, and cyclohexane. Carbon dioxide, by itself, is an extremely weak supercritical fluid (SCF) solvent because this polyester only dissolves at pressures in excess of 2000 bar and at temperatures over 180°C. However, DME and CDFM are excellent solvents for this polyester, which dissolves at 16 bar and 40°C in CDFM and at 167 bar and 55°C in DME. The melting point of this polyester is reduced from 105 to 40°C in CDFM and to 55°C in DME, which makes the polyester amenable to high intensity mixing for the efficient dispersion of inorganics or crosslinking agents and other hard to deposit materials. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2642–2648, 2001

Key words: phase behavior; semicrystalline polyester resin; supercritical fluid; solvents

INTRODUCTION

Classical techniques used to process crystalline resins rely on elevated temperatures so that the resin is above its melt point. However, these materials are difficult to process with melt-mixing techniques because of the thinning of the resin

that occurs upon melting at high temperatures. Additionally, the application of these resins in heat-sensitive environments is precluded with conventional processing because of the elevated processing temperatures needed to intimately mix the resin with reactive additives. An alternative processing protocol for crystalline resins was recently described that makes use of the interesting properties of supercritical fluid (SCF) solvents or solvent mixtures. Although it can take significant pressures to dissolve a polymer in a low molecular weight SCF solvent,¹ it does not take much pressure to dissolve an SCF solvent into a

Correspondence to: M. McHugh (mmchugh@saturn.vcu.edu).

Contract grant sponsor: National Science Foundation; contract grant numbers: CTS-99729720; GER-9454136.

Journal of Applied Polymer Science, Vol. 81, 2642–2648 (2001)
© 2001 John Wiley & Sons, Inc.

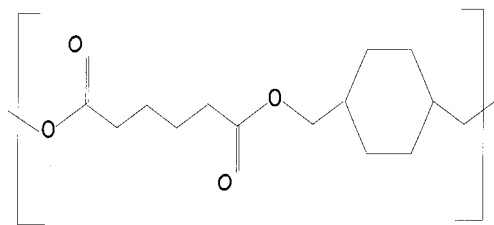


Figure 1 The repeat unit of poly(adipic acid-co-cyclohexanedimethanol).

molten polymer. Significant polymer plasticization occurs as the polymer absorbs the SCF solvent, which lowers the viscosity, depresses the glass-transition temperature (T_g), reduces surface tension, and modifies the ultimate pore structure.²⁻⁶ The SCF processing of crystalline resins capitalizes on the decreased resin viscosity at temperatures well below the melt point, which means that high intensity mixing can be used to efficiently disperse materials such as inorganic or crosslinking agents into the polymer matrix. When the pressure is let down, the SCF solvent is vented from the polymer, allowing it to rapidly crystallize and encapsulate guest materials. Mandel and coworkers describe an array of innovative products using supercritical CO_2 as a processing aid for mixing and polymerizing refractory materials with thermally labile additives to produce crystalline materials for high performance market applications.⁷⁻⁹ For many market applications SCF CO_2 is the solvent of choice because it is readily available, inexpensive, and environmentally benign. This article investigates the phase behavior of a low molecular weight, semicrystalline polyester resin comprising 53.4 mol % adipic acid and 46.6 mol % 1,4-cyclohexanedimethanol (AA-CHDM, weight-average molecular weight 5960, number-average molecular weight 2060, T_{melt} 105°C, see Fig. 1) in a variety of SCF solvents with and without cosolvents. This polyester is used as a coatings resin in the powder coatings industries.

Table I lists the physical properties of the SCFs and the liquid cosolvents used in this study.^{10,11} Carbon dioxide was the primary SCF solvent investigated here because of its potential industrial relevance. It exhibits specific intermolecular interactions with electron-donating functional groups, such as carbonyl groups.¹² Even though these interactions favor polymer dissolution in CO_2 , high pressures and temperatures are required to solubilize main chain polyesters in

CO_2 .¹³ Supercritical dimethyl ether (DME) and chlorodifluoromethane (CDFM) were also investigated because literature data suggested these are good solvents for ester-containing polymers.¹⁴⁻²¹ DME has a large polarizability and a significant dipole moment that makes it a stronger solvent than CO_2 . CDFM also has a larger polarizability than CO_2 and a large dipole moment. In addition, CDFM is a proton donor and DME is a proton acceptor that, in both cases, provides enhanced solvent power relative to CO_2 , which is a weak electron acceptor.

Liquid cosolvents expand the region of miscibility by increasing the solvent density and by introducing or augmenting polar interactions and hydrogen bonding. DME and CDFM are also used as cosolvents with CO_2 . Another cosolvent of choice is acetone because of its high polarizability (8.88 Å³) and its large dipole moment (2.9 debye). Relative to acetone, ethanol has a smaller polarizability (5.11 Å³) and a weaker dipole moment (1.7 debye), but the hydroxyl group can hydrogen bond with the carboxylic acid in the backbone of the polyester considered in this study. Methanol, butanol, and octanol were examined as cosolvents so the polarizability was systematically varied while maintaining a relatively constant dipole moment and maintaining specific interactions associated with the hydroxyl group. Because 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) is widely used as a conventional solvent for polyesters, including nylon 66,^{22,23} poly(ethylene terephthalate),^{24,25} and polycaprolactone,²⁶ it was also investigated here as a viable cosolvent for AA-CHDM. Nonpolar cyclohexane was used as a cosolvent to elucidate the impact of increased solvent density as opposed to solvent energetics.

Table I Physical Properties of Solvents and Cosolvents Used in Study^{10,32}

Solvent	T_c (°C)	P_c (bar)	α (Å ³)	μ (debye)
CO_2	31.0	73.8	2.65	0.0
DME	126.9	52.4	5.29	1.3
Acetone	234.9	47.0	6.39	2.9
Ethanol	240.8	61.4	5.11	1.7
Methanol	239.5	80.9	3.32	1.7
Butanol	289.9	44.2	8.88	1.8
Octanol	379.4	28.6	16.2	2.0
Hexafluoroisopropanol	195.3	34.2	7.11	—
Chlorodifluoromethane	96.2	49.7	4.44	1.4
Cyclohexane	280.4	40.7	11.0	0.3

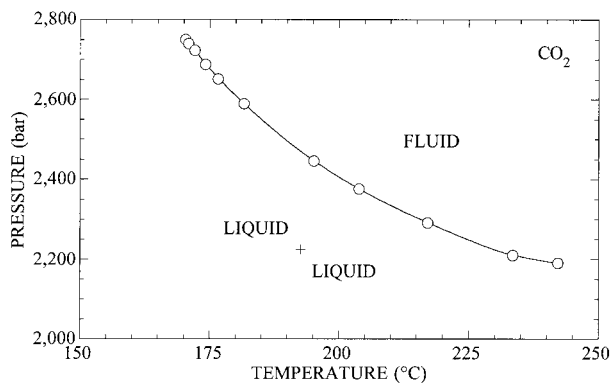


Figure 2 The phase behavior of ~5 wt % poly(adipic acid-co-cyclohexanedimethanol) in CO₂.

EXPERIMENTAL

Cloud-point data were obtained using a high-pressure, view cell apparatus described in detail elsewhere.^{17,27} The AA-CHDM cloud points were obtained at a fixed polymer composition of ~5 wt %, the expected maximum in the pressure–composition isotherms.^{20,28,29} The cloud points were reproduced several times to within ± 5.0 bar. The pressure was measured with a digital pressure transducer (0–3450 bar, accurate to within ± 3.5 bar, model 245, Viatran Corp.) or a Heise Gage (0–3450 bar, accurate to within ± 3.5 bar, Heise model CM-108952 or CM-105952, Dresser Industries). The temperature was measured and maintained to within $\pm 0.5^\circ\text{C}$. The solution in the cell was mixed with a magnetic stir bar driven by a rotating external magnet.

RESULTS

Figure 2 shows cloud-point data for AA-CHDM in pure CO₂ at temperatures higher than 170°C and pressures in excess of 2200 bar. The cloud-point pressure increased as the temperature decreased as a consequence of the weak quadrupolar character of CO₂, which was unable to overcome the energetics associated with AA-CHDM self-interactions. Although AA-CHDM has a normal melting point (T_m) of approximately 105°C, a polymer-rich fluid phase was observed with CO₂ at temperatures as low as 75°C. The SCF solvent depressed the resin T_m , so that low temperature processing could be performed while still obtaining favorable wetting characteristics for coating powders or inert particles. However, to reduce the

operating temperature below 75°C, other SCF solvents or liquid cosolvents must be used.

Figure 3 compares AA-CHDM-CO₂ cloud points to those in DME and in a mixture of CO₂ with 13.7 wt % DME (on a polymer-free basis). It was obvious that DME was a much better solvent for AA-CHDM than CO₂. The AA-CHDM-DME curve had a positive slope and it was only at ~500 bar at 180°C whereas the AA-CHDM-CO₂ curve was at 2700 bar at this temperature. The AA-CHDM-DME cloud-point pressures decreased as the temperature was decreased, which implied that the temperature-dependent interactions between DME and the ester group in the resin were stronger than DME–DME or resin–resin self-interactions. When 13.7 wt % DME was added to the CO₂, the cloud-point pressures decreased significantly, but they were still much higher than those observed with pure DME. The AA-CHDM-CO₂-13.7 wt % DME curve exhibited a negative slope at pressures in excess of 1700 bar as the temperature decreased from 180 to 80°C. The addition of DME as a cosolvent reduced the pressure required to attain a single phase by as much as 1000 bar, and it also extended the one-phase region by nearly 90°C at high pressures. The advantage of DME was that the melting point of AA-CHDM was depressed to 55°C at only 200 bar and a single phase could be obtained at low pressures whereas two phases were observed with CO₂ at temperatures below 180°C and pressures below 2700 bar.

Figure 4 shows the cloud-point data for AA-CHDM in CO₂ with 5.3, 31.0, 50.6, and 100 wt % CDFM as a cosolvent. These data reaffirmed the observation that CDFM was an excellent solvent

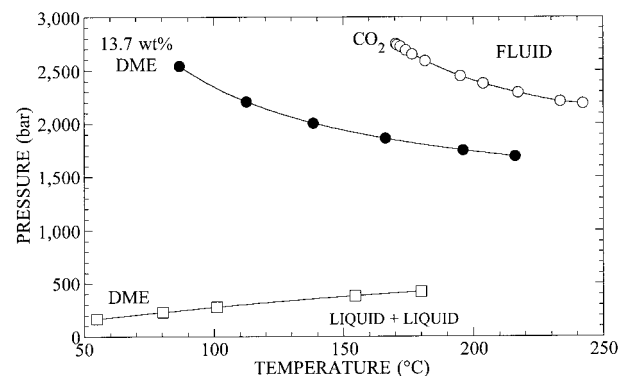


Figure 3 A comparison of the phase behavior of ~5 wt % poly(adipic acid-co-cyclohexanedimethanol) in CO₂, dimethyl ether (DME), and a solvent mixture of 13.7 wt % DME plus CO₂.

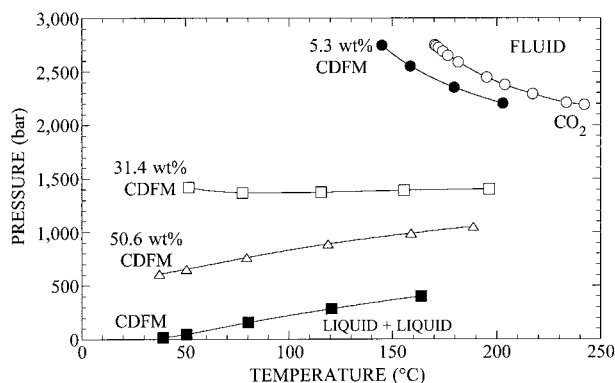


Figure 4 The effect of chlorodifluoromethane (CDFM) cosolvent concentration on the phase behavior of ~ 5 wt % poly(adipic acid-*co*-cyclohexanedimethanol) in CO_2 .

for polyesters, which was more than likely due to the strong, temperature-dependent specific interactions between the hydrogen in CDFM and the ester group in AA-CHDM. The addition of 5.3 wt % CDFM lowered the cloud-point pressures by approximately 200–325 bar, although the shape of the curve closely resembled that observed with pure CO_2 . By increasing the CDFM concentration to 31.4 wt %, the shape and location of the cloud-point curve were drastically altered. Not only did the pressures drop by more than 1300 bar, but also the slope of the curve was close to zero so that the cloud-point pressures remained virtually constant until the crystallization boundary was reached near 50°C . The cloud-point pressures were further lowered when 50.6 wt % CDFM was added to the solution, and then the curve exhibited a positive slope. Pure CDFM was an excellent solvent because the cloud points were only 350 bar at 170°C and 50 bar at 50°C . At temperatures below 50°C the cloud-point curve intersected the AA-CHDM bubble-point curve that was expected to superpose onto the pure CDFM vapor pressure curve.¹ It is interesting to note that the resin rapidly dissolved into CDFM at room temperature, even though the pressure was only 10 bar. Therefore, it would be necessary to heat the solution to temperatures in excess of 50°C to force the resin to precipitate at the end of a process. It may not be economically feasible to recover the resin with a small change in the system pressure because a very small second phase was formed that was essentially pure CDFM. This led to the dilemma that CDFM, by itself, was too strong of a solvent for AA-CHDM. However, the cosolvent data shown in Figure 4 suggested that it was

feasible to separate an AA-CHDM-CDFM solution by adding modest amounts of CO_2 to the mixture, which induced the formation of a concentrated polymer-rich phase.³⁰

Figure 5 compares the effect of 13.7 wt % DME; 11.6 wt % acetone; and 6.7, 12.0, and 26.9 wt % ethanol on the cloud-point behavior of the AA-CHDM- CO_2 system. DME at 13.7 wt %, acetone at 11.6 wt %, and ethanol at 12.0 wt % were at approximately the same molar loading because all three molecular weights were very close to one another. Acetone was a better cosolvent than DME because the acetone cloud-point curve is at lower pressures and temperatures for the same concentration of cosolvent. Acetone was likely to be denser than DME because the critical temperature of acetone is more than 100°C higher than that of DME. In addition, acetone has a much larger dipole moment than DME. Although both of these physical properties made acetone a better cosolvent than DME, the shift in the cloud-point curve was still quite modest. In contrast, the shift in the cloud-point curve with only 6.7 wt % ethanol was equal to that observed with 11.6 wt % acetone added to the solution. The location of the AA-CHDM- CO_2 -6.7 wt % ethanol cloud-point curve was a result of hydrogen bonding between the hydroxyl group on the ethanol and ester groups in the polymer because the dipole moment of ethanol is lower than that of acetone and both cosolvents should have similar densities. The cloud-point curve shifted to even lower temperatures and pressures when 12.0 and 26.9 wt % ethanol were added to the solution. The extent of hydrogen bonding increased with decreasing temperature, which was the reason the cloud-point

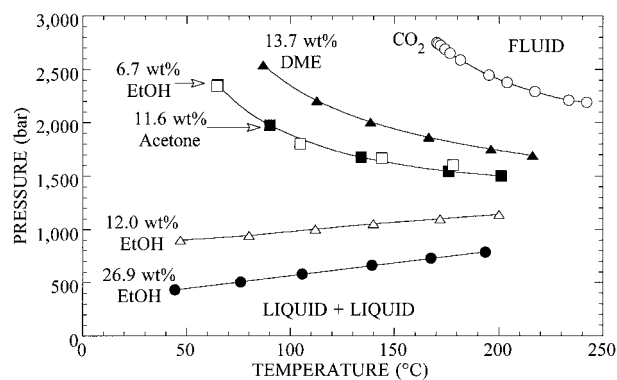


Figure 5 A comparison of the phase behavior of ~ 5 wt % poly(adipic acid-*co*-cyclohexanedimethanol) in CO_2 with 13.7 wt % dimethyl ether (DME), 12.0 wt % ethanol (EtOH), and 11.6 wt % acetone.

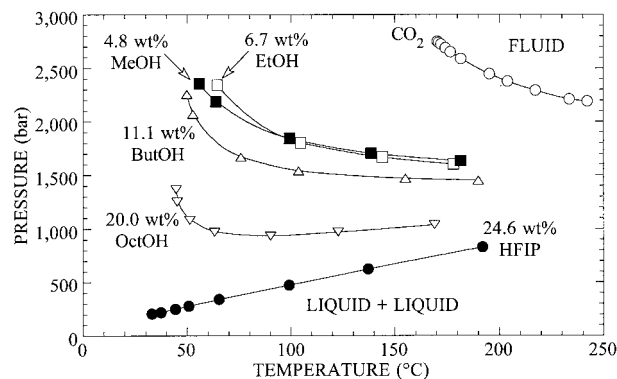


Figure 6 A comparison of the phase behavior of ~5 wt % poly(adipic acid-co-cyclohexanedimethanol) in CO₂ with methanol (MeOH), ethanol (EtOH), butanol (ButOH), octanol (OctOH), and hexafluoroisopropanol (HFIP).

curve exhibited a positive slope for the solutions with large amounts of ethanol.

It was apparent that increasing the cosolvent concentration of ethanol had a large impact on the location of the cloud-point curve. However, it remained a challenge to determine whether the decrease in cloud-point pressures was directly related to an increase in ethanol-ester hydrogen bonding or to an increase in solvent density, which decreased the free volume difference between the solvent mixture and the resin. Figure 6 shows the cloud-point behavior for AA-CHDM in CO₂ with 4.8 wt % methanol, 11.1 wt % butanol, 6.7 wt % ethanol, 20.0 wt % octanol, and 24.6 wt % HFIP. The mass loading of the alcohol was chosen to maintain a fixed ratio of the number of alcohol hydroxyl groups to the number of resin acid groups. The cloud-point curve for the CO₂ and 4.8 wt % methanol system virtually superposed onto the curve for the CO₂ and 6.7 wt % ethanol system, which showed that methanol was a more effective cosolvent than ethanol. The shape of the cloud-point curve for the butanol system was very similar to that of the ethanol and methanol systems. Butanol appeared to be a better cosolvent than methanol or ethanol because the cloud-point pressures were reduced by 200–300 bar. The cloud-point curve for the octanol system exhibited a slightly positive slope until the temperature dropped to about 80°C, where the pressures again rapidly increased with decreasing temperature. Because the magnitude of the dipole moments of methanol, ethanol, butanol, and octanol are very similar, it was probably the polarizability-driven nonpolar dispersion interac-

tions between octanol and AA-CHDM that caused the cloud-point curve to be so much lower than those of the other alcohols. The CO₂ and HFIP system exhibited a positive slope, a marked pressure reduction, and no sharp pressure increase upon a decrease in temperature. At approximately 190°C the cloud-point pressure was 800 bar, and as the temperature decreased the pressure consistently decreased to 200 bar at 25°C.

Experiments were performed with nonpolar cyclohexane as a cosolvent so that the density of the solution could be increased without introducing any strong intermolecular interactions associated with hydrogen bonding or polar moments. Cyclohexane at ambient conditions has a density within 1.5% of that of ethanol.¹⁰ Figure 7 compares the cloud-point curves for AA-CHDM in CO₂ with cyclohexane to those with ethanol. The cloud-point pressures decreased as the concentration of cyclohexane increased from 0.0 to 28.2 wt %. However, the addition of smaller amounts of ethanol definitely had a stronger effect on the location of the phase boundary. With 10.2 wt % of cyclohexane the cloud-point pressures were still 100–600 bar higher than those obtained with 6.7 wt % ethanol. The cloud-point curve for the AA-CHDM-CO₂-28.2 wt % cyclohexane was nearly identical to the curve for the 12.0 wt % ethanol system. The effect of nonpolar cyclohexane showed that increasing solution density decreased the cloud-point pressures, but at a lower rate compared to the addition of a polar cosolvent.

A key question when working with cosolvents is whether the effect of the cosolvent concentration can be predicted or at least correlated to some physical properties of the system. The prediction

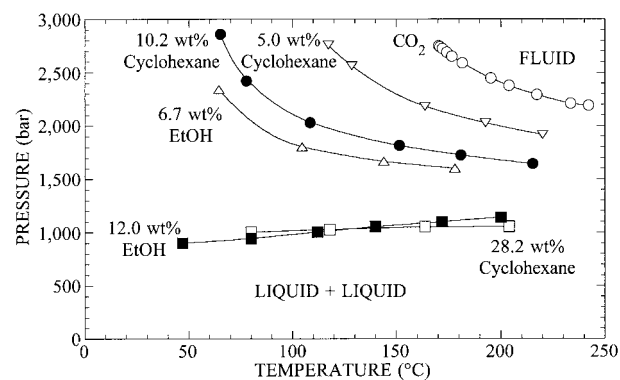


Figure 7 A comparison of the phase behavior of ~5 wt % poly(adipic acid-co-cyclohexanedimethanol) in CO₂ with ethanol (EtOH) and cyclohexane as cosolvents.

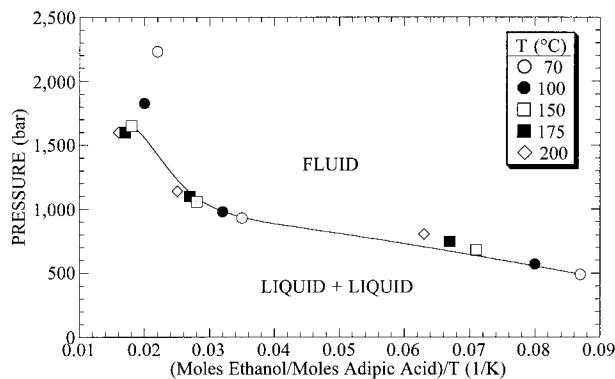


Figure 8 The impact of ethanol on the cloud-point pressure of ~5 wt % poly(adipic acid-co-cyclohexanedimethanol) in CO_2 .

of the cosolvent effect is less than quantitative in most cases when an equation of state for polymer-solvent-supercritical solvent mixtures are used.¹ The cloud-point data for the ethanol and CDFM cosolvent systems were correlated to the ratio of moles of cosolvent relative to moles of ester groups in the resin divided by the system temperature because increased thermal energy effectively reduces the strength of configuration-specific interactions as noted by Prausnitz and coworkers³¹ (Fig. 8). All of the ethanol cloud-point data in Figure 5 collapses to a single curve in Figure 8. If this curve is indeed universal, it would only be necessary to measure a single cloud-point curve at a fixed ethanol concentration because all other concentrations fell on the same curve.

Figure 9 shows the cloud-point pressure as a function of the molar ratio of CDFM to ester groups in the resin divided by the absolute system temperature. The curve for the CDFM system showed the same trends found with the ethanol cosolvent system. At the lowest cosolvent concentration the data had a larger spread and the curve did not fit well at these conditions. At the higher CDFM concentrations the data exhibited less scatter from the master curve. For the ethanol and CDFM systems the hydrogen bonding between the cosolvent and the polymer was the driving force of the phase behavior. The molar ratio analysis provided an excellent qualitative fit to the cloud-point data for both of these systems. Therefore, we surmised that the same analysis would provide a similar fit to other systems that have hydrogen bonding cosolvents. A single experiment at a moderate cosolvent concentration could then be used to create a plot similar to

Figures 8 and 9. The resulting curve could be extrapolated to provide reasonable estimates of the cloud-point pressures at other cosolvent concentrations. This type of analysis failed with the cyclohexane cosolvent system, probably because of the type of interactions present with these mixtures. Dispersion and dipolar interactions are physical not chemical interactions, which means that they do not become saturated, or, stated in another way, the strength of the interaction does not scale with the moles of each of the components in solution.³¹ In addition, the strength of chemical interactions is much greater than physical interactions; therefore, the chemical interactions can dominate the solution behavior. Therefore, the method of how to scale nonspecific mean-field and polar interactions with the moles of each component in solution is not apparent.

CONCLUSIONS

Although CO_2 requires elevated pressures and temperatures to completely solubilize AA-CHDM, at low pressures it plasticizes this resin and thus lowers the resin melting point by $\sim 30^\circ\text{C}$. Polar SCF solvents, such as DME and CDFM, can be used to obtain a single phase at much more moderate conditions, because the magnitude of the intermolecular interactions is greater between these polar solvents and AA-CHDM than between CO_2 and AA-CHDM. Both of these polar solvents can be used as a cosolvent with CO_2 to considerably expand the region of miscibility.

Liquid cosolvents enhance the solubility of AA-CHDM in CO_2 by increasing the solvent density and by introducing more favorable intermolecular

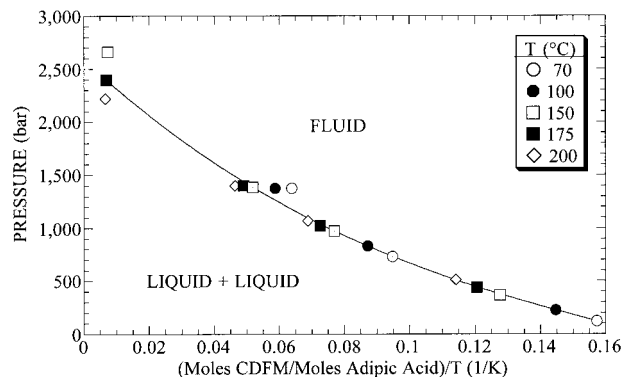


Figure 9 The impact of chlorodifluoromethane (CDFM) on the cloud-point pressure of ~5 wt % poly(adipic acid-co-cyclohexanedimethanol) in CO_2 .

interactions between the mixed solvent and the polyester. Cyclohexane, a dense liquid cosolvent with a large polarizability, does not provide any specific interactions with the ester groups, but it is still able to significantly reduce the cloud-point pressures, as well as extend the one-phase region to lower temperatures. The single-phase region increases significantly if the liquid cosolvent forms hydrogen bonds or other specific interactions with the resin repeat units. The cloud-point curves obtained with the hydrogen bonding cosolvents can be correlated with a single empirical curve that relates cloud-point pressure to the ratio of moles of cosolvent to moles of resin ester units divided by the absolute temperature. This curve can then be used to anticipate the phase behavior for other cosolvent concentrations.

The first (S.E.C.) and third (M.A.M.) authors acknowledge the National Science Foundation for partial support of this project.

REFERENCES

- Kirby, C. F.; McHugh, M. A. *Chem Rev* 1999, 99, 565.
- Smith, P. B.; Moll, D. J. *Macromolecules* 1990, 23, 3250.
- Wissinger, R. G.; Paulaitis, M. E. *Ind Eng Chem Res* 1990, 30, 842.
- Kalospiros, N. K.; Paulaitis, M. E. *Chem Eng Sci* 1994, 49, 659.
- Wen, W.-Y. *Chem Soc Rev* 1993, 117.
- Wissinger, R. G.; Paulaitis, M. E. *J Polym Sci Polym Phys Ed* 1987, 25, 2497.
- Mandel, F. S.; Green, C. D.; Scheibelhoffer, A. S. U.S. Pat. 5,399,597, 1995.
- Mandel, F. S.; Green, C. D.; Scheibelhoffer, A. S. U.S. Pat. 5,548,004, 1996.
- Mandel, F. S. U.S. Pat. 5,698,516, 1997.
- Reid, R. C.; Prausnitz, J. M.; Polling, B. E. *The Properties of Gases and Liquids*, 4 ed.; McGraw-Hill: New York, 1987.
- Lide, D. R., Ed. *Physical Constants of Organic Compounds*, CRC Handbook of Chemistry and Physics; Chemical Rubber Company: Boca Raton, FL, 1992.
- Kazarian, S. G.; Vincent, M. F.; Bright, F. V.; Litta, C. L.; Eckert, C. A. *J Am Chem Soc* 1996, 118, 1729.
- Lele, A. K.; Shine, A. D. *Polym Prepr* 1990, 31, 677.
- Haschets, C. W.; Shine, A. D. *Macromolecules* 1993, 26, 5052.
- Haschets, C. W.; Blackwood, T. A.; Shine, A. D. *Polym Prepr* 1993, 34, 602.
- Lele, A. K.; Shine, A. D. *AIChE J* 1992, 38, 742.
- Meilchen, M. A.; Hasch, B. M.; McHugh, M. A. *Macromolecules* 1991, 24, 4878.
- Hasch, B. M.; Meilchen, M. A.; Lee, S.-H.; McHugh, M. A. *J Polym Sci Polym Phys Ed* 1992, 30, 1365.
- Meilchen, M. A.; Hasch, B. M.; Lee, S.-H.; McHugh, M. A. *Polymer* 1992, 33, 1922.
- Lee, S.-H.; Lostracco, M. A.; Hasch, B. M.; McHugh, M. A. *J Phys Chem* 1994, 98, 4055.
- Lee, S.-H.; McHugh, M. A. *Polymer* 1997, 38, 1317.
- Jackson, C.; Barth, H. G.; Han M. C. *Polym Mater Sci Eng* 1993, 69, 270.
- Samanta, S. R. *J Appl Polym Sci* 1992, 45, 1635.
- Chalykh, A. Y.; Surovtsova, O. B.; Busygin, V. B.; Zanehin, V. D.; Ronzhin, N. K.; Gerasimov, V. I. *Vysokomol Soed* 1992, 34, 92.
- Sonnenschein, M. F.; Roland, C. M. *J Polym Sci Polym Phys Ed* 1991, 29, 431.
- DeKesel, C.; Lefevre, C.; Nagy, J. B.; David, C. *Polymer* 1999, 40, 1969.
- Mertdogan, C. A.; Byun, H.-S.; McHugh, M. A.; Tuminello, W. H. *Macromolecules* 1996, 29, 6548.
- Allen, B.; Baker, C. H. *Polymer* 1965, 6, 181.
- Irani, C. A.; Cozewith, C. *J Appl Polym Sci* 1986, 31, 1879.
- Guckes, T. L.; McHugh, M. A.; Cozewith, C.; Hazelton, R. L. U.S. Pat. 4,946,940, 1990.
- Prausnitz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1986.
- Miller, K. J.; Savchik, J. A. *J Am Chem Soc* 1979, 101, 7206.