

8 Comparison of Theoretical Model with Experiments

8.1 Equipment

8.1.1 Photoresist Removal from Silicon Wafers

Polymer coating removal experiments were conducted on two different components: (1) silicon wafers (see Section 1.1), and (2) anodized aluminum photoconductor drums (see Section 1.2). All experiments were performed at the Supercritical Fluids Facility at the Los Alamos National Laboratory, utilizing two experimental setups. Experiments on the removal of photoresist from silicon wafers were carried out in a commercial 10 liter high-pressure vessel. This vessel is part of a computer controlled, closed-loop system, having real-time temperature and pressure control and a variable-speed internal impeller. The system operates in a dynamic mode with a flow rate of 2.7 liter/hr. Temperature control is maintained through a “process logic control” feedback loop with inputs from one thermocouple at the top of the pressure vessel and one thermocouple in the vessel bottom ($\pm 2^{\circ}\text{C}$). Equipment maximum temperature and pressure limitations are 90°C and 3000 psi, respectively. Figure 8-1(a) shows a view of the vessel, at the far right-hand side of the cabinets, along with the associated gas handling equipment and computers. Figure 8-1(b) is a view inside the vessel. An 8” silicon wafer can be seen mounted in the vessel, along with a high-pressure color CCD camera.



(a)



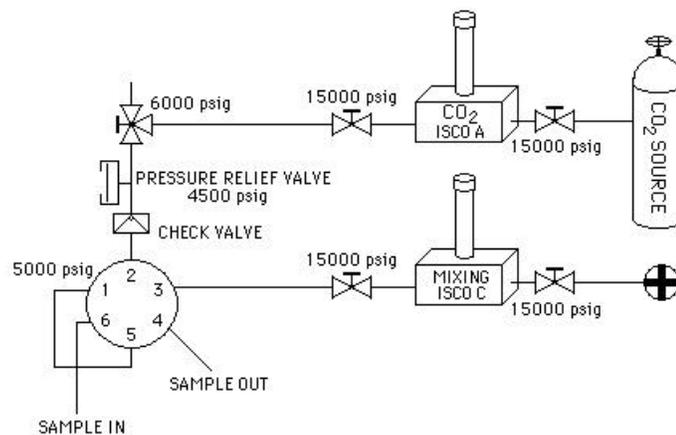
(b)

Figure 8-1. (a) View of the Los Alamos National Laboratory Supercritical Fluids Facility, showing the automated, 10-liter pressure system. (b) View inside the 10-liter high-pressure reaction vessel.

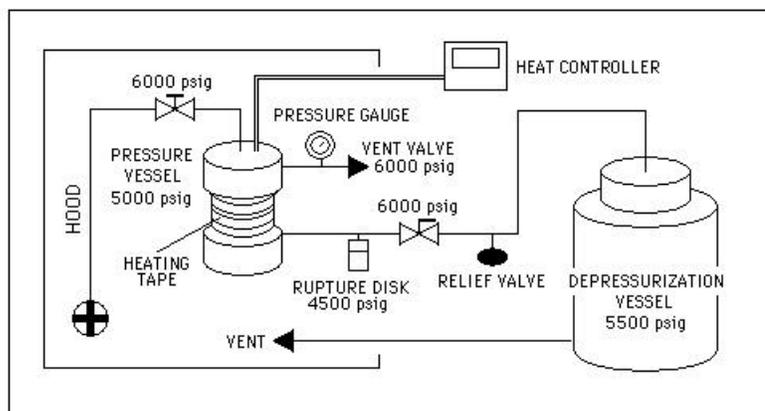
Experiments on many photoresist polymers have been conducted at the Supercritical Fluids Facility, using various combinations of T, P, and cosolvents. However, only the PMMA photoresist was sufficiently characterized in terms of composition to allow a comparison between experimental results and the predictions of the HSP model. The remaining photoresist polymers were either of unknown initial composition, or had been subjected to treatments such as ion implantation or plasma etching, again resulting in an unknown overall composition.

8.1.2 Polymer Removal from Photoconductor Drums

Experiments on the removal of polymer coatings from the aluminum photoconductor drums were conducted in a purpose-built, 105 ml bench-top high-pressure vessel. A schematic illustration of this equipment is shown in Figure 8-2(a) and (b).



(a)



(b)

Figure 8-2. Schematic illustration of the 105 ml bench top supercritical fluid system used for the photoconductor drum experiments. (a) CO₂ source, pumps, and cosolvent injection/mixing system. (b) High pressure cleaning vessel, temperature controls, and depressurization vessel.

Unlike the 10-liter vessel system, the bench top system was suitable only for static (non-continuous flow) experiments. However, the bench top system does allow for easy changing of cosolvents, minimum cosolvent usage (based on volume fraction), and rapid depressurization. The rate of depressurization was recognized to be an important variable early in the experimental testing. The swelling of a polymer with CO₂ results in a decrease in polymer/polymer molecular interactions, as described in Chapter 6, and a reduced polymer solubility parameter. Additional disruption of polymer/polymer

intramolecular interactions can also occur through specific interactions with the solubilized CO₂ and/or cosolvent. Upon depressurization, the solubilized CO₂, begins to expand as the vessel pressure decreases. This expansion of the gas, and the reduced hydrostatic pressure exerted on the polymer, often results in a temporarily-enhanced polymer swelling effect. Before the polymer/polymer interactions can be reestablished, stress cracks, bubbles or complete debonding of the polymer film can occur as the CO₂ rapidly desorbs. Rapid depressurization rates were not possible using the 10-liter vessel, although upgrades to the system are currently underway.

The pressure in the 105 ml vessel was controlled with two ISCO high-pressure syringe pumps, each with its own controller. The first pump, 'ISCO A' in Figure 8-2(a), pressurized and supplied pure CO₂ to pump 'ISCO C', which was used as a vessel for the mixing the CO₂ and cosolvent. Intermediate to pump 'ISCO C' is an injection valve, located to allow the CO₂ to deliver a measured amount of cosolvent to the mixing vessel and pump. The number of cosolvent injections was determined based on the desired overall mixture composition, with the injection loop supplying a maximum of 2.5 ml of cosolvent per injection. The cosolvent concentration typically varied from 2 to 3.8 vol.%. The volume of each syringe pump is 266 ml.

The vessel was heated to the desired processing temperature with an external heat tape. The vessel temperature was monitored with an external thermocouple, and adjusted to maintain the desired temperature during the experiment. Precise temperature control was not possible with this setup, but observed fluctuations were less than $\pm 7^{\circ}\text{C}$. Equipment maximum temperature and pressure limitations are 100°C and 3000 psi, respectively

8.2 Results

8.2.1 Photoresist Removal from Silicon Wafers

Silicon wafers, 3" in diameter, coated with approximately 12-14 μm of PMMA photoresist were supplied by Agilent Technologies. The resist was identified by Agilent as a positive acting photoresist (as described in Section 1.1), which had been baked at 160°C. Two removal experiments were conducted, with the treatment conditions shown in Table 8-1.

Table 8-1. Experimental conditions of the PMMA photoresist removal experiments.

Resist	T (°C)	P (psi)	cosolvent	vol.%	Time (min)
PMMA	50	3000	butylene carbonate	1.9	10
PMMA	60	3000	propylene carbonate	0.6	20

Butylene carbonate and propylene carbonate, Figures 8-3 and 8-4, are organic cyclic esters supplied by Hunstman Corporation. Both cosolvents contain carbonyl functional groups, which are expected to act as Lewis bases in CO_2 .

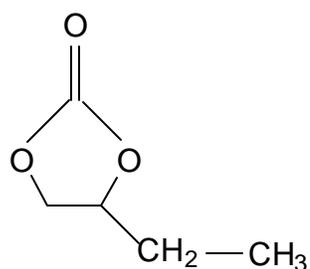


Figure 8-3. Butylene carbonate, HSP values⁵⁵⁰: $\mathbf{d}_l = 17.0 \text{ MPa}^{1/2}$, $\mathbf{d}_p = 6.1 \text{ MPa}^{1/2}$, and $\mathbf{d}_h = 9.8 \text{ MPa}^{1/2}$.

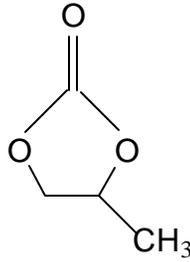


Figure 8-4. Propylene carbonate, HSP values⁵⁵¹: $d_t = 20.0 \text{ MPa}^{1/2}$, $d_p = 18.0 \text{ MPa}^{1/2}$, and $d_h = 4.1 \text{ MPa}^{1/2}$.

An as-received, photoresist-coated silicon wafer is shown in Figure 8-5(a), while Figure 8-5(b) shows a similar wafer after the successful removal of the polymer coating using CO₂/propylene carbonate at the conditions noted in Table 8-1.

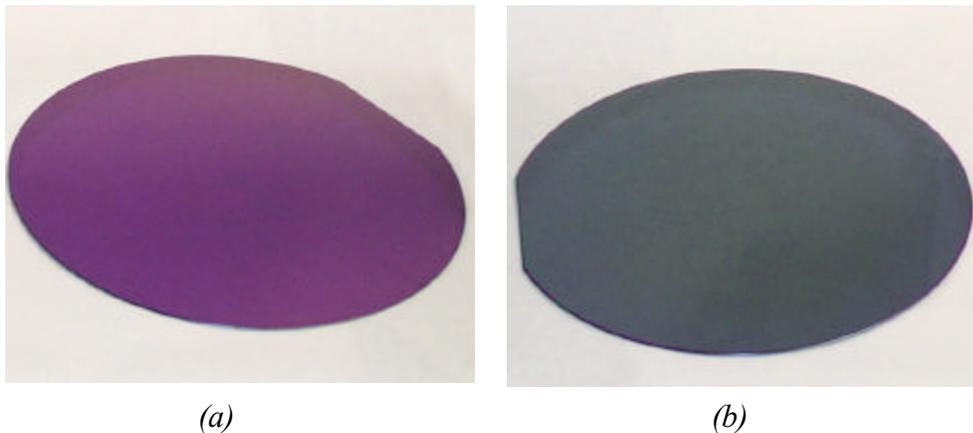


Figure 8-5. (a) Silicon wafer coated with PMMA photoresist, (b) Silicon wafer stripped of photoresist coating.

Figure 8-6 (a) and (b), shows higher magnification optical images of the edges of an untreated, Figure 1-6(a), and treated, Figure 1-6(b), silicon wafer. The left-hand image clearly shows the boundary of the polymer coating.

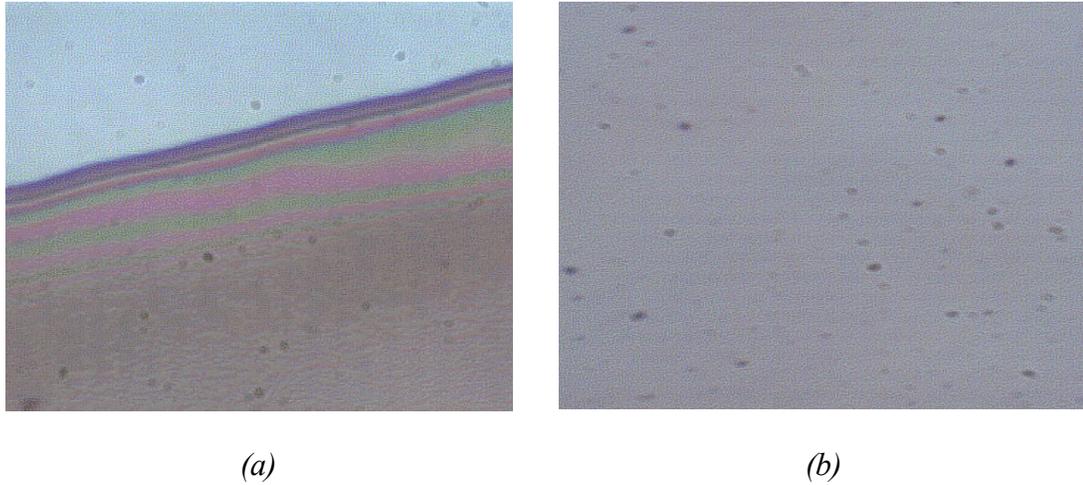


Figure 8-6. (a) As received silicon wafer coated with PMMA photoresist. (b) Silicon wafer stripped of photoresist coating after treatment with CO₂/propylene carbonate (0.6 % v/v) at T = 60°C and P = 3000 psi.

Table 8-2 gives the HSP values of the CO₂/cosolvent mixture, calculated using eqn. (6-22), as well as HSP values of the PMMA, and the value of *Ra*, calculated using eqn. (5-20) in Section 5.2.1. Recall that *Ra* is the distance (expressed as a radius) from the HSP value of PMMA at T and P, to the HSP value of the CO₂/cosolvent mixture at T and P. For clarity, eqn. (5-20) is given again as eqn. 8-1, with the calculation of *Ra* for the first treatment condition shown in Table 8-1.

$$\begin{aligned}
 (Ra)^2 &= 4(\delta_{d2} - \delta_{d1})^2 + (\delta_{p2} - \delta_{p1})^2 + (\delta_{h2} - \delta_{h1})^2 & (8-1) \\
 (Ra)^2 &= 4(10.7 - 10.3)^2 + (5.8 - 4.4)^2 + (4.0 - 4.8)^2 \\
 (Ra)^2 &= 3.24 \\
 Ra &= 1.8
 \end{aligned}$$

Table 8-2. HSP values of the solvent mixture and PMMA and *Ra* at the treatment conditions.

T (°C)	P (psi)	Solvent Mixture HSP's (MPa ^{1/2})			PMMA HSP's (MPa ^{1/2})			<i>Ra</i> (MPa ^{1/2})
		<i>d</i> ₁	<i>d</i> ₂	<i>d</i> _h	<i>d</i> ₁	<i>d</i> ₂	<i>d</i> _h	
50	3000	10.3	4.4	4.8	10.7	5.8	4.0	1.8
60	3000	9.3	4.3	4.5	11.2	5.9	4.0	4.3

For the two treatment conditions shown in Table 8-1, the PMMA is predicted to be significantly plasticized, with T_g estimated to be -125°C , using eqn. (6-12). In addition, the distance between the HSP values of the solvent mixture and of the PMMA, identified by Ra (see Table 8-2), is below the reported PMMA interaction radius of $8.6 \text{ MPa}^{1/2}$.⁵⁵² The PMMA interaction radius noted in the literature, $R_o^{liq} = 8.6 \text{ MPa}^{1/2}$, was determined on the basis of the dissolution behavior of PMMA in a range of liquid solvents. An interaction radius based on the swelling behavior of PMMA in a SCF is unknown. However, because of the enhanced diffusion of SCFs, an interaction radius larger than that noted for liquid solvents is anticipated. Therefore, the reported liquid interaction radius, R_o^{liq} , will be assumed to be a minimum radius for SCF's, R_o^{SCF} .

Because the T_g of PMMA is significantly depressed at both of the treatment conditions noted in Table 8-1, favorable swelling conditions exist (i.e. CO_2 sorption and polymer swelling increase with increasing pressure). In addition, for both treatment conditions the Ra value (see Table 8-2) is less than the R_o^{liq} value noted for dissolution of PMMA in liquid solvents. Therefore, based on the fact that $T_{\text{CO}_2} > T_g^{\text{CO}_2}$ and $Ra < R_o^{liq}$, the model framework predicts favorable conditions for the promotion of coating removal by polymer swelling for both of the experimental treatments in Table 8-1. These predictions are in agreement with the experimental results, where successful removal of the PMMA photoresist from the silicon wafers was achieved.

Figure 8-7 shows, in schematic form, the model predictions of the HSP values for PMMA and CO_2 /butylene carbonate mixture, and CO_2 /propylene carbonate mixture.

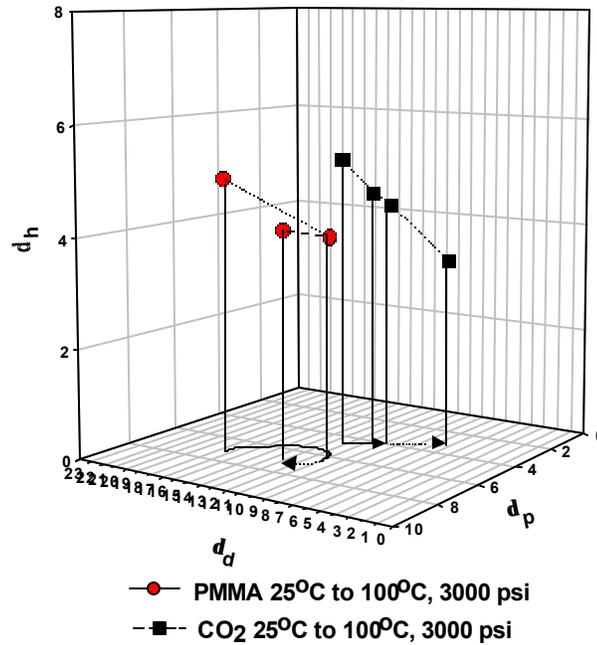


Figure 8-7. Predicted PMMA and CO₂ mixture HSP values as the temperature varies from 25 to 100°C and at 3000 psi.

From Figure 8-7, the HSP values of PMMA can be seen to approach those of the solvent as the temperature is increased, up to a temperature of approximately 70°C. Above 70°C, the PMMA HSP values begin to increase with increasing temperature. At the two treatment conditions of $T = 50^{\circ}\text{C}$ and 60°C and $P = 3000$ psi, the radius of interaction is minimized, i.e., $R_a < R_o^{liq} < R_o^{SCF}$, and the predicted conditions are optimal for experimental testing.

It should also be noted that the distance between the HSP values of pure CO₂ and of the PMMA, at the given experimental conditions, is $R_a = 1.9$ and $4.5 \text{ MPa}^{1/2}$, respectively. The estimated depression in T_g , and the match of HSP values, as quantified by R_a , indicates that pure CO₂ should also be a “good” solvent for PMMA.

8.2.2 Polymer Removal from Photoconductor Drums

Aluminum photoconductor drums were provided by Lexmark Corporation with three coating schemes, as seen in Figure 1-2; (1) PC only, (2) poly(vinyl butyral) only, and (3) poly(vinyl butyral) and PC,. The drums, originally 12 inches long, were cut into 1 inch lengths so that one of each of the three types of coated drums could be run simultaneously in the 105 ml pressure vessel. The vessel, with the drums placed inside, was heated to the desired processing temperature with an external heat tape. The vessel temperature was monitored with an external thermocouple, and adjusted to maintain the desired temperature during the experiment. This external thermocouple temperature was assumed to equal the drum temperature throughout the experiment. CO₂ or CO₂/cosolvent mixture was injected at the desired experimental pressure, but for all experiments the temperature of the solvent was initially equal to room temperature (approximately 25°C). At the end of each experiment the CO₂ or CO₂/cosolvent mixture temperature was assumed to equal the temperature noted by the external thermocouple.

All experiments using the bench top system were conducted for 20 minutes at static (non-flowing) conditions, followed by two pressure pulses; 3000 to approximately 1000 psi, or 1500 to 1000 psi; followed by a rapid depressurization to atmospheric pressure. The experimental conditions are given in Table 8-3. Also given in Table 8-3 are the HSP values for pure CO₂ or CO₂/cosolvent mixture (initial and final conditions), PC, and PVB at the experimental conditions. Unlike the wafer experiments discussed earlier, where the solvent and polymer temperatures are assumed to be equal throughout the experiment, the CO₂ and/or CO₂/cosolvent mixture temperature, and consequently the HSP values of the solvent, vary from values at room temperature (approximately

25°C) to the final experimental temperature (see Table 8-3). Therefore, there is an initial radius of interaction, Ra_i , and a final radius of interaction, Ra_f , reflecting the range of conditions between the solvent and polymer HSP's, where each Ra is the distance from the HSP's of the polymer at T and P to the HSP's of pure CO₂ or CO₂/cosolvent mixture at its initial and final T and P.

Presentations of the model results include plots of the HSP values of the solvent (pure CO₂ or CO₂/cosolvent mixture) at the initial and final experimental T and P, as well as the polymer HSP values at the experimental T and P. These HSP values, representing a point in three-dimensional solubility parameter space, can be represented in a two-dimensional diagram using fractional solubility parameters,

$$f_D = \frac{\delta_D}{\delta_D + \delta_P + \delta_H} \quad (8-2)$$

$$f_P = \frac{\delta_P}{\delta_D + \delta_P + \delta_H} \quad (8-3)$$

$$f_H = \frac{\delta_H}{\delta_D + \delta_P + \delta_H} \quad (8-4)$$

Plots of fractional solubility parameters, such as Figure 8-9, are known as a Teas plot.⁵⁵³ The fractional solubility parameters, as given in a Teas plot, along with the initial and final total solubility parameters, completely define the extent of HSP matching between the solvent and polymer as the solvent temperature varies from room temperature to the final experimental temperature. In terms of fractional parameters on the Teas plots, consideration must be given to the proximity of the points as well as the total solubility parameter value. As an aid in making this comparison, the initial and

final Ra values are given, as well as the R_o^{liq} for the polymer, which, again, is the radius of (dissolution) interaction of the respective polymer in liquid solvents. Optimum conditions are predicted for $T_{CO_2} > T_g^{CO_2}$ and $Ra < R_o^{SCF}$ (where R_o^{SCF} is assumed to be $> R_o^{liq}$). Photographs of the treated drums are also included for each experiment.

Table 8-3. Experiment conditions of temperature, pressure and cosolvent concentrations for the photoconductor drum experiments.

T (°C)	P (psi)	cosolvent	vol. %	Mix HSP (MPa ^{1/2}) (initial)			Mix HSP (MPa ^{1/2}) (final)			PC HSP (MPa ^{1/2}) Ra _i = initial radius Ra _f = initial radius					PVB HSP (MPa ^{1/2}) Ra _i = initial radius Ra _f = initial radius				
				d _i	d _f	d _h	d _i	d _f	d _h	d _i	d _f	d _h	Ra _i	Ra _f	d _i	d _f	d _h	Ra _i	Ra _f
45	1500	none		10.7	4.5	5.0	6.7	3.7	4.0	16	5.6	6.4	10.8	18.9	16.6	7.0	11.4	13.7	21.4
45	3000	none		12.2	4.7	5.3	10.6	4.5	4.8	16.3	5.7	6.8	8.4	11.6	16.7	7.0	11.5	11.2	14.1
75	1500	none		10.7	4.5	5.0	2.4	2.5	2.6	15.6	5.6	6.1	9.9	26.8	16.2	6.9	11.3	13.7	29.3
75	3000	none		12.2	4.7	5.3	7.8	3.9	4.1	16.0	5.6	6.7	7.8	16.7	16.3	6.9	11.4	11.2	18.7
100	1500	none		10.7	4.5	5.0	1.8	2.2	2.2	14.6	5.4	5.7	7.9	26.0	15.9	6.8	11.3	13.7	30.0
100	3000	none		12.2	4.7	5.3	5.7	3.5	3.5	15.2	5.5	6.6	6.2	19.4	16.0	6.9	11.3	11.2	22.3
75	3000	hexane	10.0	12.4	4.2	4.8	8.4	3.5	3.7	16.0	5.6	6.7	7.7	15.6	16.3	6.9	11.4	10.6	17.9
40	1500	ethanol	3.8	10.9	4.7	5.5	8.5	4.2	5.0	16.0	5.6	6.5	10.3	15.2	16.7	7.0	11.5	13.3	17.9
40	3000	ethanol	3.8	12.3	4.9	5.8	11.2	4.7	5.4	16.4	5.7	6.8	8.2	10.6	16.8	7.0	11.5	10.8	13.0
85	1500	ethanol	3.8	10.8	4.7	5.5	2.7	2.6	3.0	15.3	5.5	6.0	9.0	25.6	16.0	6.9	11.3	12.1	28.3
75	3000	ethanol	3.8	12.3	4.8	5.8	8.0	4.0	4.5	16.0	5.6	6.8	7.5	16.3	16.3	6.9	11.4	10.0	18.2
100	1500	ethanol	2.8	10.9	4.7	5.5	2.1	2.4	2.6	14.6	5.4	5.8	7.7	25.3	15.9	6.8	11.3	12.1	29.2
100	3000	ethanol	2.8	12.3	4.9	5.8	5.9	3.6	3.9	15.2	5.5	6.6	6.0	18.9	16.0	6.9	11.3	9.7	19.6
40	1500	acetone	3.8	10.9	4.7	5.1	8.5	4.2	4.5	16.0	5.6	6.5	10.4	15.3	16.7	7.0	11.5	13.5	18.1
40	3000	acetone	3.8	12.3	4.9	5.4	11.2	4.7	5.0	16.4	5.7	6.8	8.3	10.7	16.8	7.0	11.5	11.1	13.2
85	1500	acetone	3.8	10.9	4.7	5.1	8.0	4.1	4.2	15.3	5.5	6.0	9.1	25.7	16.0	6.9	11.3	12.3	28.5
75	3000	acetone	3.8	12.3	4.9	5.4	2.6	2.7	2.5	16.0	5.6	6.7	7.6	16.2	16.3	6.9	11.4	10.3	18.3
40	3000	cyclohexanone	1.5	12.3	4.7	5.3	11.1	4.5	4.9	16.4	5.7	6.8	8.4	10.8	16.8	7.0	11.5	11.2	13.4
65	1500	cyclohexanone	2.6	10.8	4.5	5.0	3.3	2.8	2.8	15.7	5.6	6.2	9.9	25.2	16.3	6.9	11.4	12.9	27.7.
65	3000	cyclohexanone	2.6	12.3	4.7	5.3	8.9	4.1	4.4	16.1	5.6	6.7	7.8	14.7	16.4	6.9	11.4	10.5	16.8
75	3000	cyclohexanone	2.6	12.3	4.7	5.3	8.5	4.1	4.2	16.0	5.6	6.7	7.5	15.2	16.3	6.9	11.4	10.3	17.4
100	1500	cyclohexanone	2.6	10.8	4.5	5.0	2.2	2.3	2.3	14.6	5.4	5.7	7.6	25.3	15.9	6.8	11.3	12.1	29.3
100	3000	cyclohexanone	2.6	12.3	4.7	5.3	4.5	5.9	3.6	15.2	5.5	6.6	6.0	18.8	16.0	6.9	11.3	9.8	21.8
40	3000	THF	3.0	12.3	4.7	5.4	11.2	4.5	5.0	16.4	5.7	6.8	8.3	10.7	16.8	7.0	11.5	11.1	13.2
75	1500	THF	2.8	10.8	4.5	5.1	3.0	2.6	2.8	15.6	5.6	6.1	9.6	25.7	16.2	6.9	11.4	12.7	28.2
100	1500	THF	2.0	10.8	4.5	5.1	2.1	2.3	2.3	14.6	5.4	5.7	7.7	25.5	15.9	6.8	11.3	12.2	29.5
100	3000	THF	2.0	12.3	4.7	5.4	5.9	3.5	3.6	15.2	5.5	6.6	6.1	19.0	16.0	6.9	11.3	9.8	21.9

Prior to discussing the results of the coatings removal experiments on the photoconductor drums a few comments regarding the poly(vinyl butyral) coating are necessary. While the surface of the silicon wafers were nearly atomically smooth, the surface of the photoconductor drums are anodized to provide a desired surface roughness and protective oxide coating. This surface roughness, combined with the thinness of the PVB coating ($\sim 1 \mu\text{m}$), produces a mechanical bond between the PVB and the drum surface, in addition to any chemical bond. The model framework developed here, however, does not account for substrate/polymer interactions nor mechanical bonding. The extreme thinness of the PVB coating results in a very limited ability of the PVB to swell, making this specific combination of substrate and polymer a particularly difficult application for the current model, which considers only intermolecular forces of attraction between the polymer and solvent). Visual results of the treatments on the PVB film are included in the following figures, however no direct comparisons with the HSP model are made.

Figure 8-8 shows examples of the three types of polymer-coated drums prior to treatment by supercritical fluid solvents.



Figure 8-8. Untreated aluminum photoconductor drums with polymer coatings; (left) $\sim 1 \mu\text{m}$ -thick poly(vinyl butyral) coating only, (center) $\sim 25 \mu\text{m}$ -thick polycarbonate coating only, (right) $\sim 25 \mu\text{m}$ -thick polycarbonate coating over $\sim 1 \mu\text{m}$ -thick poly(vinyl butyral) coating.

8.2.2.1 Pure CO₂

Photoconductor drums coated with PC only, PVB only, and PC/PVB were treated with pure CO₂ at T = 45°C, 75°C, and 100°C, and P = 1500 psi and 3000 psi. The resulting HSP values for CO₂ (initial and final) and PC at these conditions, are plotted in Figures 8-9, 8-11, and 8-13. Also indicated on these Teas plots is the initial Ra_i values and the final Ra_f values, where Ra is the distance from the HSP value of PC at T and P (open symbols), to the HSP values of CO₂ at its initial and final T and P (filled symbols), calculated using eqn. (5-20) in Section 5.2.1. The R_o^{liq} values indicated for PC⁵⁵⁴ represent the interaction radius for the polymer, based on its dissolution behavior in a range of liquid solvents. A corresponding interaction radius for PC in a SCF system is

not known, R_o^{SCF} , but its value is expected to be greater than, due to the increased diffusion capabilities of a SCF solvent versus a liquid solvent.

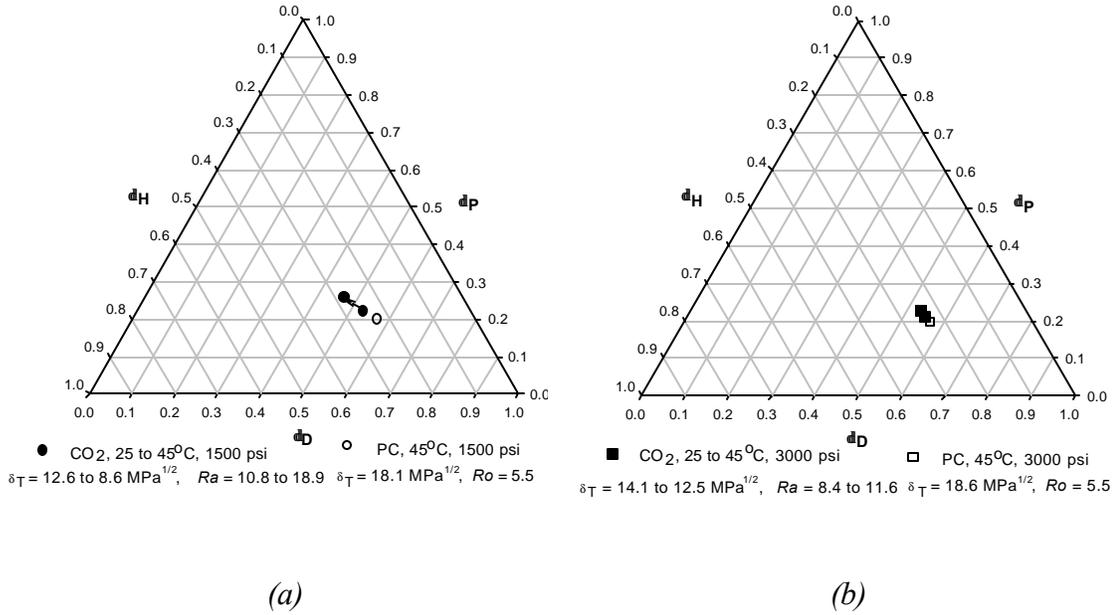


Figure 8-9. (a) HSP values of CO₂ and PC, at $T = 25$ to 45°C and $P = 1500$ psi. (b) HSP values of CO₂ and PC, at $T = 25$ to 45°C and $P = 3000$ psi.

Visual results of the pure CO₂ treatments, at the temperature and pressures indicated in Figure 8-9(a) and 8-9(b), are shown Figure 8-10(a) and 8-10(b).

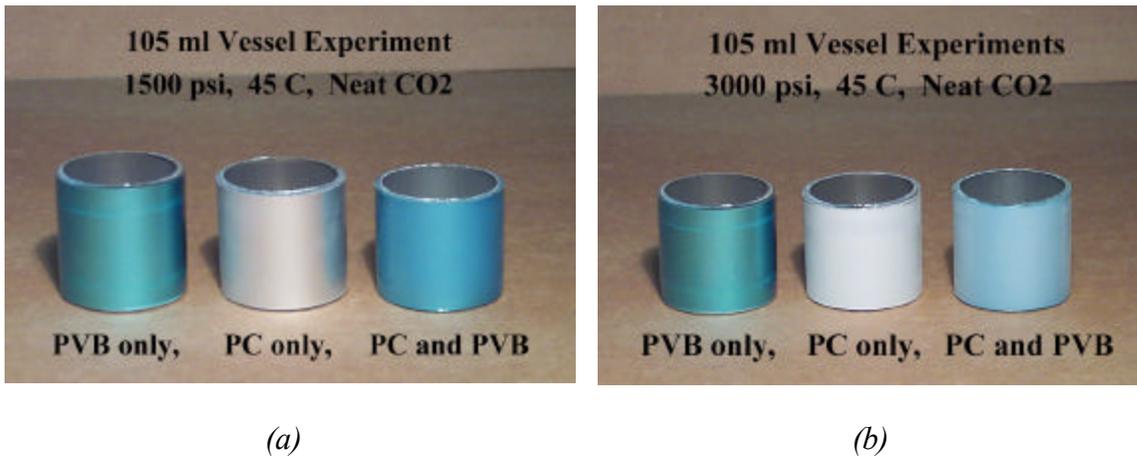
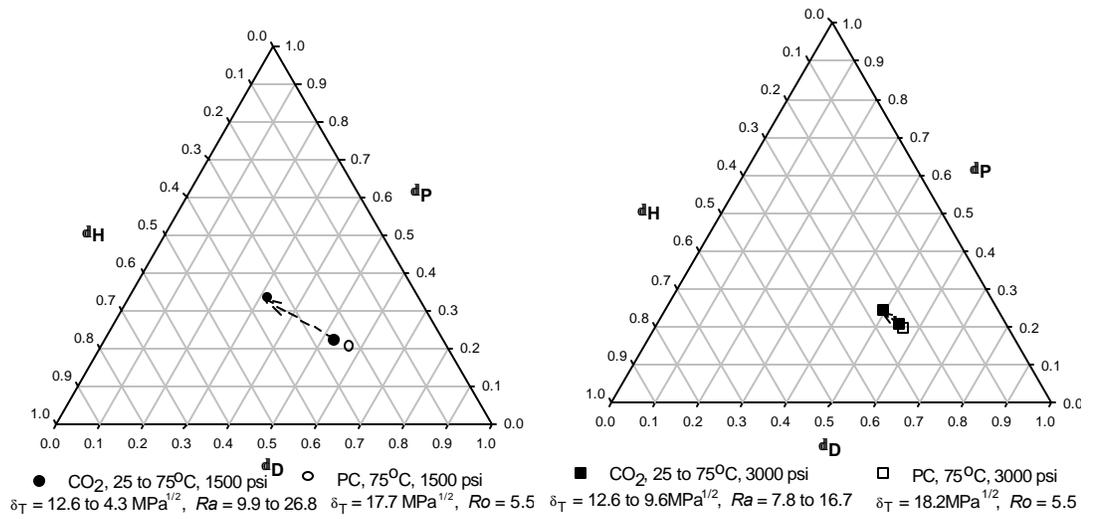


Figure 8-10. Appearance of polymer coated photoconductor drums treated with pure CO₂ at (a) $T = 25$ to 45°C , $P = 1500$ psi, (b) $T = 25$ to 45°C , $P = 3000$ psi.

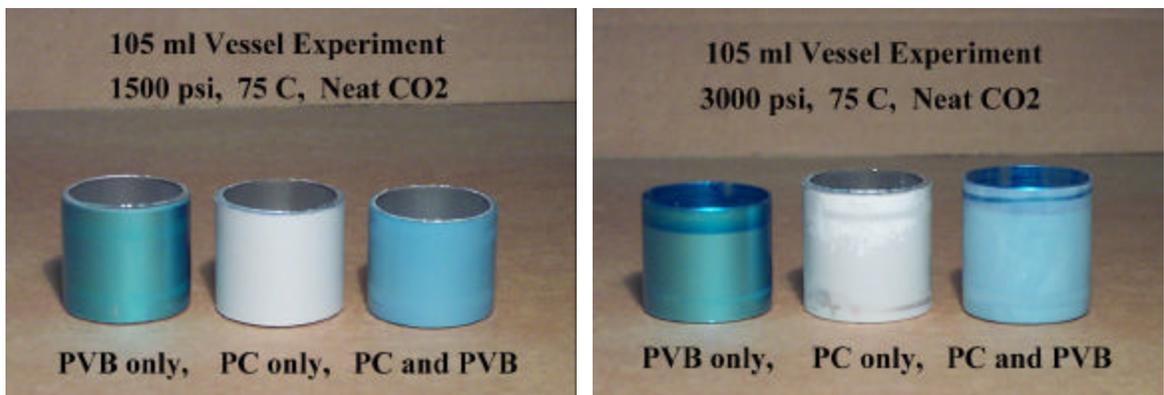


(a)

(b)

Figure 8-11. (a) HSP values of CO₂ and PC at $T = 25 \text{ to } 75^\circ\text{C}$ and $P = 1500 \text{ psi}$. (b) HSP values of CO₂ and PC at $T = 25 \text{ to } 75^\circ\text{C}$ and $P = 3000 \text{ psi}$.

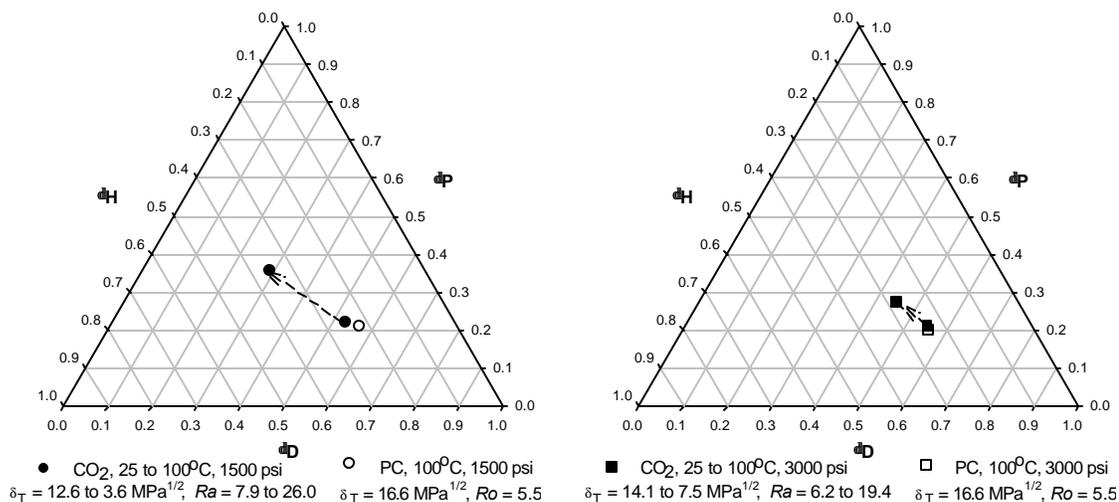
Visual results of the pure CO₂ treatment, at the temperature and pressures indicated in Figure 8-11(a) and 8-11(b), are shown Figure 8-12(a) and 8-12(b).



(a)

(b)

Figure 8-12. Appearance of polymer coated photoconductor drums treated with pure CO₂ at (a) $T = 25 \text{ to } 75^\circ\text{C}$ and $P = 1500 \text{ psi}$, (b) $T = 25 \text{ to } 75^\circ\text{C}$ and $P = 3000 \text{ psi}$.

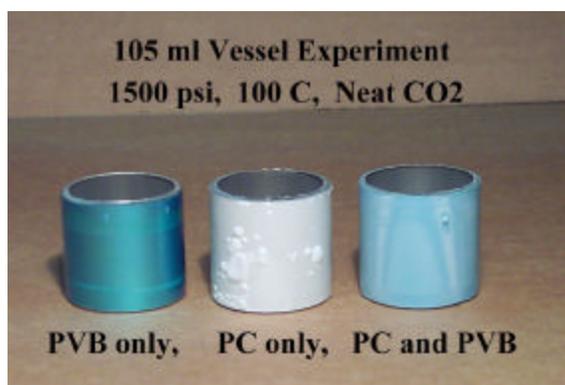


(a)

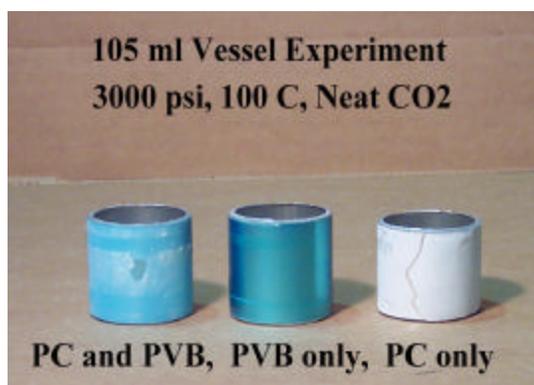
(b)

Figure 8-13. HSP values of CO₂ and PC at $T = 25$ to 100 °C and $P = 1500$ psi. (b) HSP values of CO₂ and PC at $T = 25$ to 100 °C and $P = 3000$ psi.

Visual results of the pure CO₂ treatment, at the temperature and pressures indicated in Figure 8-13(a) and 8-13(b), are given in Figure 8-14(a) and 8-14(b).



(a)



(b)

Figure 8-14. Appearance of polymer coated photoconductor drums treated with pure CO₂ at (a) $T = 25$ to 100 °C and $P = 1500$ psi. (b) $T = 25$ to 100 °C and $P = 3000$ psi.

8.2.2.1.1 Observations of Polymer Coating Removal Experiments using Pure CO₂

The results of the experiments described in Figures 8-10, 8-12, and 8-14 are ranked in Table 8-4, based on a visual assessment of the effect of the treatment on the PC coating. Since the ultimate objective of these experiments is the removal of the polymer coating through polymer swelling, a treatment is judged to have a favorable effect if the treatment results, in order of decreasing significance; complete coating removal (debonding), surface cracking, flaking, bubbling, or discoloration of the PC coating. The polymer glass transition temperature at the treatment conditions, T_g , is determined using eqn. (6-16). Column 4 in the table shows the difference between the treatment temperature, T_{CO_2} , and T_g of the polymer at the treatment temperature. In columns 5 and 6 give the initial and final Ra values, Ra_i and Ra_f , representing the distance (expressed as a radius) between the initial HSP values of CO₂, to the polycarbonate HSP values at $T = 25$ °C and P, Ra_i , and between the final HSP values of CO₂ to the polycarbonate HSP values, Ra_f , at T and P.

Table 8-4. Results of polymer removal experiments using pure CO₂.

T_{CO_2} (°C)	P_{CO_2} (psi)	Polymer T_g at (T_{CO_2} , P_{CO_2})	ΔT ($T_{CO_2} - T_g$)	Ra_i ($MPa^{1/2}$)	Ra_f ($MPa^{1/2}$)	R_o^{liq} ($MPa^{1/2}$)	Exp. result
100	3000	54.3	45.7	6.2	19.4	5.5	debonded
100	1500	85.6	14.4	7.9	26.0	5.5	bubbled
75	3000	88.0	-13.0	7.8	16.7	5.5	discolored
75	1500	103.0	-28.0	9.9	26.8	5.5	discolored
45	3000	88.0	-43.0	8.4	11.6	5.5	discolored
45	1500	103	-58.0	10.8	18.9	5.5	slight discoloring

Two important observations of the experimental summary presented in Table 8-4 are the increasingly favorable effects on the coating with increasing ΔT ($T_{CO_2} - T_g$) and the increasingly favorable effects on the coating as Ra_i decreases. As discussed in Chapter 6, absorption of CO_2 swells the polymer only when in the polymer is in its rubber state, i.e., $T_{CO_2} > T_g$. As $(T_{CO_2} - T_g)$ increases, it is expected that the amount of CO_2 absorption during swelling will increase, as would the amount of mechanical disruption of the polymer during depressurization. Also, as discussed earlier, experiments conducted in the bench top set-up did not include preheating of the solvent. Therefore the HSP values of the solvent vary from the initial values shown in Table 8-3 to the final values, also shown in Table 8-3. The exact path of these values is dependent on the heating rate of the solvent, which could not be measured in this work. However, the initial and final values are available, allowing the calculation of both an initial and final Ra value. From a review of Table 8-3, increasingly favorable effects are seen as the initial Ra_i values decrease and ΔT increases. These results are entirely consistent with model predictions, where favorable effects are predicted as the polymer is plastized and Ra (whether initial or final) approaches Ro .

On the basis of a polycarbonate interaction radius of $5.5 MPa^{1/2}$ (again, based on polycarbonate dissolution in organic liquid solvents) and $T = 45^\circ C$, the model predicts that a pressure of 9200 psi is required to achieve an Ra_f of $5.2 MPa^{1/2}$, a value intermediate between the HSP values of pure CO_2 and the HSP values of polycarbonate.

8.2.2.2 CO₂/Hexane

Hexane, Figure 8-15, is a nonpolar solvent, and is not expected to exhibit any specific Lewis acid/base interactions with CO₂, PC, or PVB. This compound is not identified as a (pure) solvent for either PC or PVB, which are both reported to be insoluble in aliphatic hydrocarbons.^{555,556}



Figure 8-15. Hexane, HSP values⁵⁵⁷ $\mathbf{d}_d = 14.9 \text{ MPa}^{1/2}$, $\mathbf{d}_p = 0.0 \text{ MPa}^{1/2}$, and $\mathbf{d}_h = 0.0 \text{ MPa}^{1/2}$.

The HSP values given in the caption of Figure 8-15 are ambient condition values and are taken from the literature. To adjust these parameters for temperature and pressure effects, we use the HSP equations derived in Section 5.3 and summarized in Table 5-8. These equations are given again as eqns. 8-5 to 8-11.

$$\mathbf{d}^2 = \left[\mathbf{d}_d + \left(\frac{\partial \mathbf{d}_d}{\partial T} \right)_P \Delta T + \left(\frac{\partial \mathbf{d}_d}{\partial P} \right)_T \Delta P \right]^2 + \left[\mathbf{d}_p + \left(\frac{\partial \mathbf{d}_p}{\partial T} \right)_P \Delta T + \left(\frac{\partial \mathbf{d}_p}{\partial P} \right)_T \Delta P \right]^2 + \left[\mathbf{d}_h + \left(\frac{\partial \mathbf{d}_h}{\partial T} \right)_P \Delta T + \left(\frac{\partial \mathbf{d}_h}{\partial P} \right)_T \Delta P \right]^2 \quad (8-5)$$

where

$$\left(\frac{\partial \mathbf{d}_d}{\partial T} \right)_P = -1.25 \mathbf{d}_d \mathbf{a}, \text{ and } \left(\frac{\partial \mathbf{d}_d}{\partial P} \right)_T = 1.25 \mathbf{d}_d \mathbf{b} \quad (8-6) \text{ and } (8-7)$$

$$\left(\frac{\partial \mathbf{d}_p}{\partial T} \right)_P = -\mathbf{d}_p \left(\frac{\mathbf{a}}{2} \right), \text{ and } \left(\frac{\partial \mathbf{d}_p}{\partial P} \right)_T = \mathbf{d}_p \left(\frac{\mathbf{b}}{2} \right) \quad (8-8) \text{ and } (8-9)$$

$$\left(\frac{\partial \mathbf{d}_h}{\partial T}\right)_P = -\mathbf{d}_h \left(1.32 \times 10^{-3} + \frac{\mathbf{a}}{2}\right), \text{ and } \left(\frac{\partial \mathbf{d}_h}{\partial P}\right)_T = \mathbf{d}_h \left(\frac{1.32 \times 10^{-3} \mathbf{b}}{\mathbf{a}} + \frac{\mathbf{b}}{2}\right) \quad (8-10) \text{ and } (8-11)$$

The data necessary for these adjustments are the thermal expansion coefficient, $\mathbf{a}(T)$, and isothermal compressibility, \mathbf{b} of the pure cosolvent compound. The thermal expansion coefficient is first used to adjust for temperature with eqn. (8-12),⁵⁵⁸

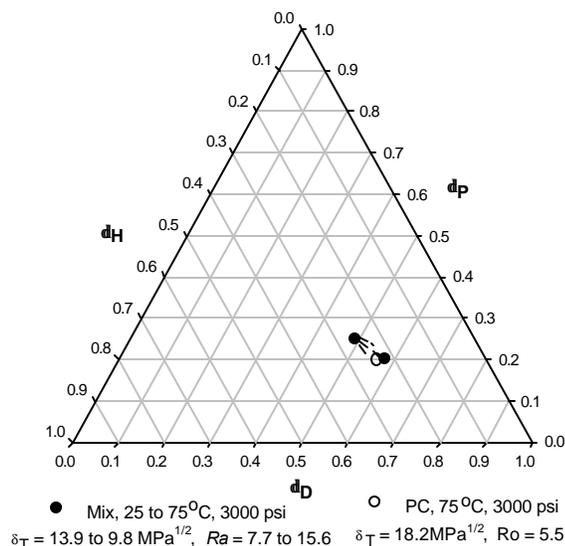
$$\alpha(T) = a \left(1 - \frac{T}{T_c}\right)^m \quad (8-12)$$

where $a = 0.000728$, $m = -0.7219$, and $T_c = 507.43 \text{ K}$.⁵⁵⁹ Next, the pressure adjustment is made using the compressibility. Isothermal compressibility values for all the cosolvent compounds have been made at high pressures,⁵⁶⁰ however, the variation of \mathbf{b} with temperature, in the pressure range of interest, is not known, and a constant value is assumed in each case. A compressibility value of $0.000117 \text{ (bar}^{-1}\text{)}$ ⁵⁶¹ was used for hexane. The adjusted HSP values for hexane are shown in Table 8-5.

Table 8-5. HSP values for hexane, adjusted for temperature and pressure.

T (K)	$\mathbf{a}(T) (K^{-1})$	$\mathbf{b}(\text{bar}^{-1})$	P (bar)	\mathbf{d}_h	\mathbf{d}_f	\mathbf{d}_h
298	0.001379	0.000117	1	14.9	0.0	0.0
348	0.001679	0.000117	200	13.8	0.0	0.0

An HSP value for the CO₂/hexane mixture is calculated using eqn. (6-22). The resulting HSP values for the CO₂/hexane mixture (initial and final), and for PC at T = 75°C and P = 3000 psi are plotted in Figures 8-16(a) and 8-16(b). Also indicated on the plots are the resulting Ra (initial and final) values, from eqn. (5-20), where Ra is the distance from the HSP value of PC at T and P (open symbols), to the initial and final HSP value of CO₂/hexane at T and P (filled symbols).



(a)

Figure 8-16. HSP values of CO₂/hexane and PC at $T = 25$ to 75°C and $P = 3000$ psi.

Visual results of the treatment using the CO₂/hexane mixture, at the temperature and pressure indicated in Figure 8-16, are given in Figure 8-17.

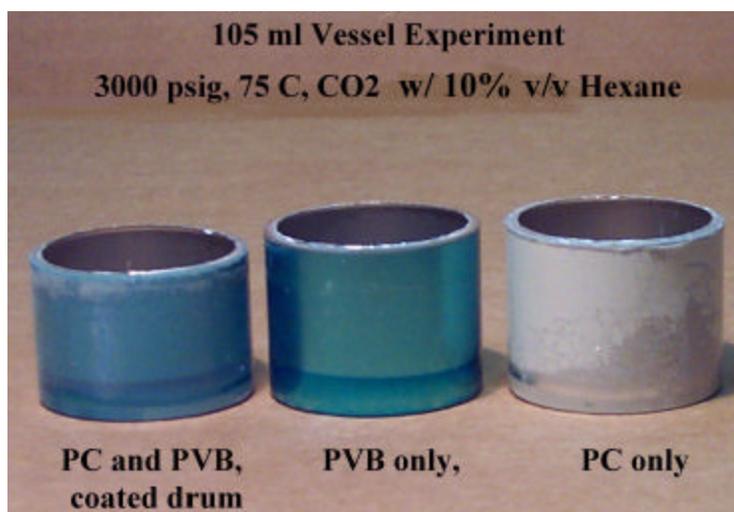


Figure 8-17. Appearance of polymer coated photoconductor drums treated with a CO₂/hexane mixture at $T = 25$ to 75°C and $P = 3000$ psi, hexane concentration = 10 vol.%.

8.2.2.2.1 Observations of Polymer Coating Removal Experiments using CO₂/Hexane Mixtures.

Only one treatment was conducted using a CO₂/hexane mixture, Table 8-6. The result of this treatment did not significantly differ from that using pure CO₂. This is an expected outcome, as no specific interactions between hexane and PC are anticipated. The only added benefit of hexane addition is a slight increase in the dispersion component of the mixture HSP's.

Table 8-6. Treatment conditions and results on polycarbonate coating using CO₂/hexane mixture.

T _{CO₂} (°C)	P _{CO₂} (psi)	Polymer T _g at (T _{CO₂} , P _{CO₂})	ΔT (T _{CO₂} - T _g)	R _{ai} (MPa ^{1/2})	R _{af} (MPa ^{1/2})	R _o ^{liq} (MPa ^{1/2})	Exp. result
75	3000	88.0	-13.0	7.7	15.6	5.5	discolored

8.2.2.3 CO₂/Ethanol

Ethanol, Figure 8-18, is a Lewis acid (see Table 6-1) and therefore specific interactions with Lewis bases are possible. PVB⁵⁶² is reported to have partial solubility in ethanol, and while not identified specifically, alcohols are reported to be nonsolvents for PC.⁵⁶³

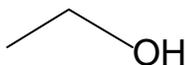


Figure 8-18. Ethanol, HSP's ⁵⁶⁴ $d_t = 15.8 \text{ MPa}^{1/2}$, $d_f = 8.8 \text{ MPa}^{1/2}$ and $d_h = 19.4 \text{ MPa}^{1/2}$.

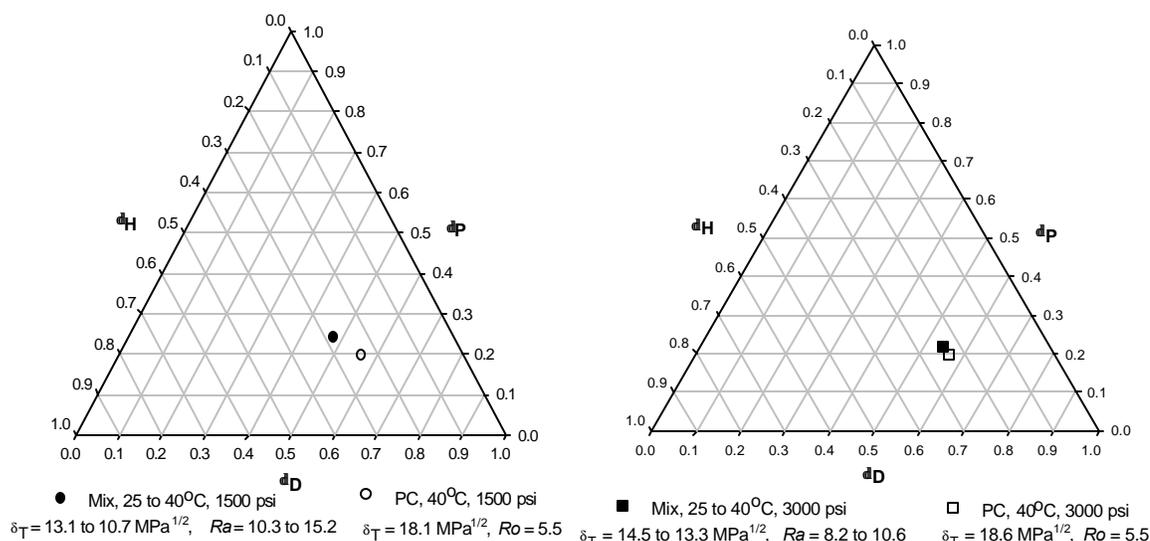
The thermal expansion coefficient, $\alpha(T)$, of ethanol is determined from eqn. (8-13) with $a = 0.000611$, $m = -0.7633$, and $T_c = 516.25 \text{ K}$ ⁵⁶⁵. The isothermal compressibility

value used for ethanol is $0.000063 \text{ (bar}^{-1}\text{)}$.⁵⁶⁶ Adjusted HSP values for ethanol are shown in Table 8-7.

Table 8-7. HSP values for ethanol adjusted for temperature and pressure.

$T \text{ (K)}$	$a(T) \text{ (K}^{-1}\text{)}$	$b \text{ (bar}^{-1}\text{)}$	$P \text{ (bar)}$	d_1	d_2	d_h
298	0.001178	0.000063	1	15.8	8.8	19.4
313	0.001244	0.000063	100	15.6	8.8	19.0
313	0.001244	0.000063	200	15.7	8.8	19.2
348	0.001437	0.000063	200	14.6	8.5	17.8
358	0.001506	0.000063	100	14.1	8.4	17.2
358	0.001506	0.000063	200	14.3	8.5	17.3
373	0.001625	0.000063	100	13.5	8.3	16.5
373	0.001625	0.000063	200	13.6	8.3	16.6

An HSP value for the CO₂/ethanol mixture is calculated using eqn. (6-22). The resulting HSP values for the CO₂/ethanol mixture (initial and final), and for PC at T = 40°C and P = 1500 psi and 3000 psi are plotted in Figures 8-19(a) and 8-19(b). Also indicated on the plots are the resulting Ra values, from eqn. (5-20), where Ra is the distance from the HSP value of PC at T and P (open symbols), to the initial and final HSP value of CO₂/ethanol at T and P (filled symbols).

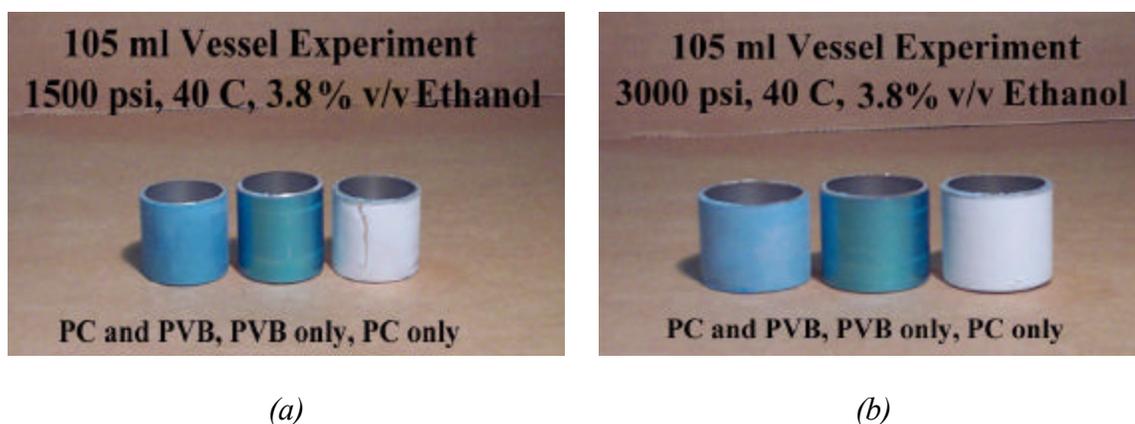


(a)

(b)

Figure 8-19. (a) HSP values of CO₂/ethanol and PC, at 25 to 40 °C and 1500 psi, (b) HSP values of CO₂/ethanol and PC, at 25 to 40 °C and 3000 psi.

Visual results of the treatment using the CO₂/ethanol mixture, at the temperature and pressures indicated in Figure 8-19(a) and 8-19(b), are given in Figure 8-20(a) and 8-20(b).



(a)

(b)

Figure 8-20. Appearance of polymer coated photoconductor drums treated with a CO₂/ethanol mixture at (a) $T = 25$ to $40 \text{ }^\circ\text{C}$, $P = 1500 \text{ psi}$, and ethanol concentration = 3.8 vol.%, (b) $T = 25$ to $40 \text{ }^\circ\text{C}$, $P = 3000 \text{ psi}$, and ethanol concentration = 3.8 vol.%.

The resulting HSP values for the CO₂/ethanol mixture (initial and final), and for PC at T = 85°C and P = 1500 psi; and at T = 75°C and P = 3000 psi are plotted in Figures 8-21(a) and 8-21(b). Also indicated on the plots are the resulting *Ra* values, from eqn. (5-20), where *Ra* is the distance from the PC HSP value at T and P (open symbols), to the initial and final HSP value of CO₂/ethanol at T and P (filled symbols).

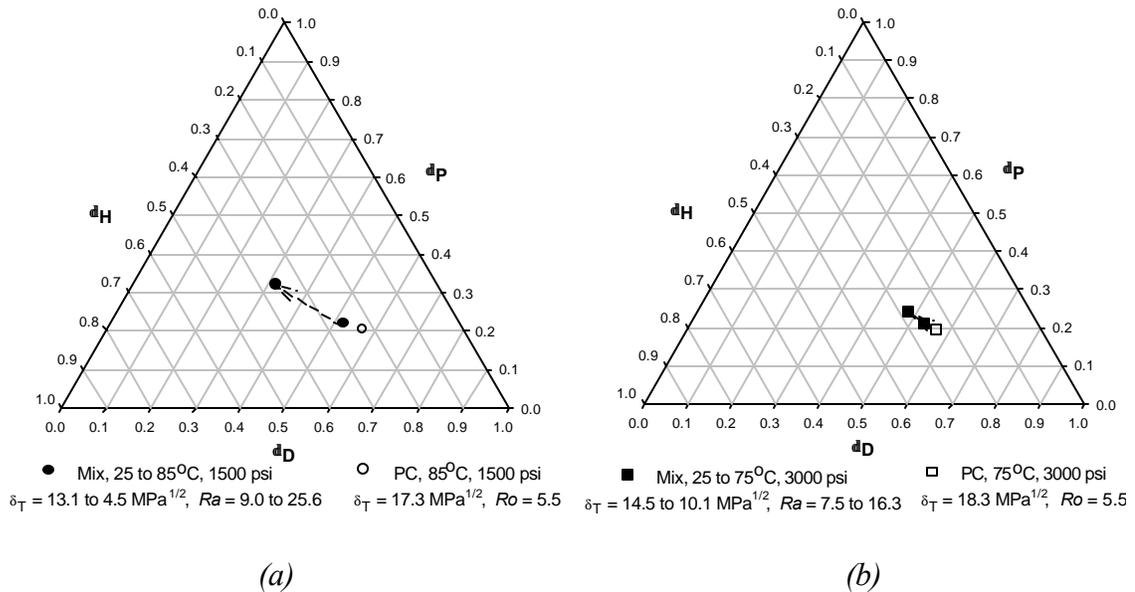
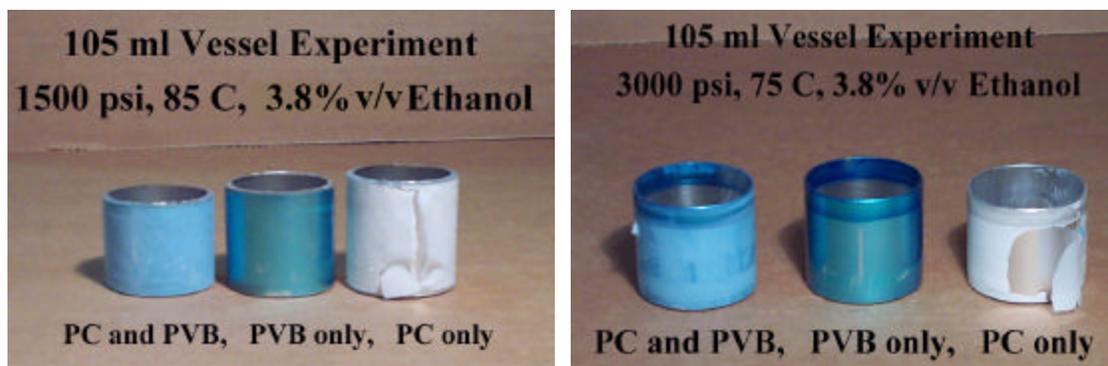


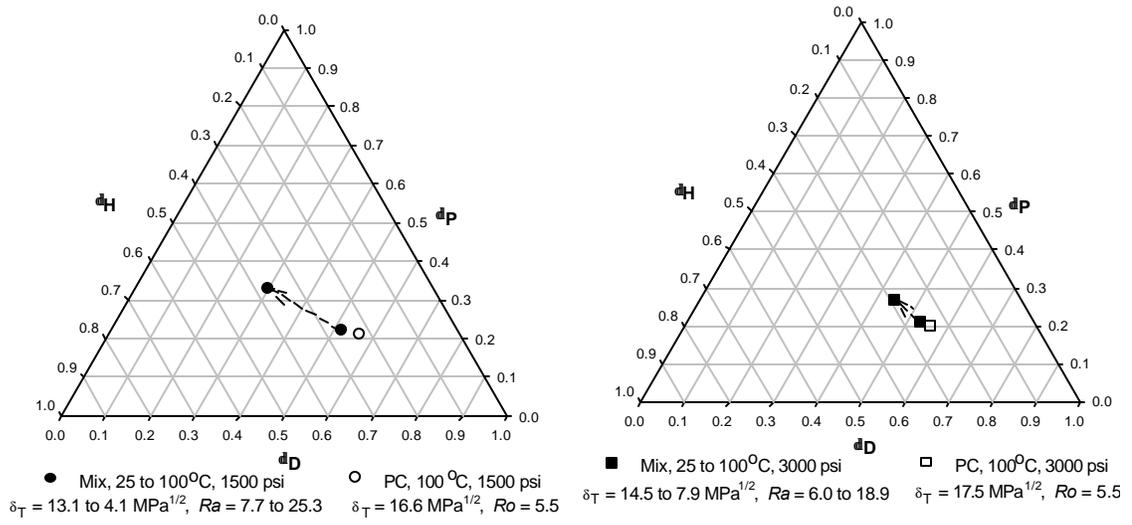
Figure 8-21. (a) HSP values of CO₂/ethanol and PC, at T = 25 °C to 85°C and P = 1500 psi. (b) HSP values of CO₂/ethanol and PC at T = 25°C to 75 °C and P = 3000 psi.

Visual results of the treatments using the CO₂/ethanol mixture, at the temperature and pressures indicated in Figure 8-21(a) and 8-21(b), are given in Figure 8-22(a), and 8-22(b).



(a) (b)
Figure 8-22. Appearance of polymer coated photoconductor drums treated with a CO_2 /ethanol mixture at (a) $T = 25$ to 85°C , $P = 1500$ psi, and ethanol concentration = 3.8 vol.%, (b) $T = 25$ to 75°C , $P = 3000$ psi, and ethanol concentration = 3.8 vol.%.

An HSP value for the CO_2 /ethanol mixture is calculated using eqn. (6-22). The resulting HSP values for the CO_2 /ethanol mixture (initial and final) and for PC at $T = 100^\circ\text{C}$ and $P = 1500$ psi and 3000 psi are plotted in Figures 8-23(a) and 8-23(b). Also indicated on the plots are the resulting Ra values, from eqn. (5-20), where Ra is the distance from the HSP value of PC at T and P (open symbols), to the initial and final HSP value of CO_2 /ethanol at T and P (filled symbols).

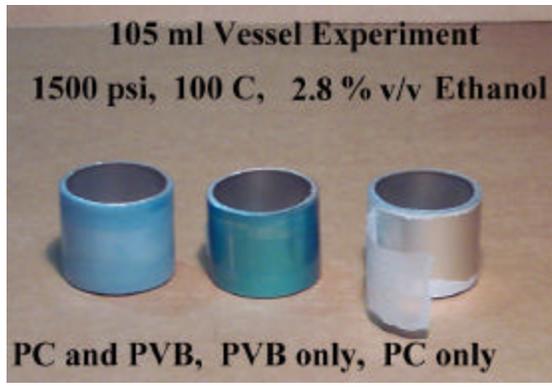


(a)

(b)

Figure 8-23. (a) HSP values of CO₂/ethanol and PC at T = 25 to 100°C and P = 1500 psi. (b) HSP values of CO₂/ethanol and PC at T = 25 to 100°C and P = 3000 psi.

Visual results of the treatments using the CO₂/ethanol mixture, at the temperature and pressures indicated in Figure 8-23(a) and 8-23(b), are given in Figure 8-24(a) and 8-24(b).



(a)



(b)

Figure 8-24. Appearance of polymer coated photoconductor drums treated with a CO₂/ethanol mixture at (a) T = 25 to 100°C, P = 1500 psi, and ethanol concentration = 2.8 vol.%, (b) T = 25 to 100°C, P = 3000 psi, and ethanol concentration = 2.8 vol.%.

8.2.2.3.1 Observations of Polymer Coating Removal Experiments using CO₂/Ethanol Mixtures

The results of the experiments described in Figures 8-20, 8-22, and 8-24, are ranked in Table 8-8 according a visual assessment of the effect on the PC coating, from most favorable to least favorable.

Table 8-8. Experimental results of polymer coating removal using CO₂/ethanol mixtures.

T _{CO₂} (°C)	P _{CO₂} (psi)	Polymer T _g at (T _{CO₂} , P _{CO₂})	ΔT (T _{CO₂} - T _g)	R _{a<i>i</i>} (MPa ^{1/2})	R _{a<i>f</i>} (MPa ^{1/2})	R _{o^{liq}} (MPa ^{1/2})	Exp. result
100	3000	54.3	45.7	6.0	18.9	5.5	debonded
100	1500	85.6	14.4	7.7	25.0	5.5	debonded
85	1500	91.1	-6.1	9.0	25.3	5.5	debonded
75	3000	88.0	-13.0	7.5	16.3	5.5	debonded
40	1500	88.0	-63.0	10.3	15.2	5.5	flaking
40	3000	103.0	-48.0	8.2	10.4	5.5	cracked

The results for the CO₂/ethanol mixtures are similar to those seen for the pure CO₂ experiments in that favorable effects become more pronounced as (T_{CO₂} - T_g) increases and the difference between R_a and R_{o^{liq}} is minimized. However, the addition of a cosolvent capable of Lewis acid/base interactions with the polymer, appears to significantly enhance the effects on the PC coating. Specifically, with the ethanol cosolvent, debonding of the PC coating occurred at all temperature and pressure conditions, except those at T= 40°C. This behavior suggests an increased sorption due to specific interactions between the cosolvent (ethanol) and PC that promote the removal at conditions of temperature and pressure not possible with pure CO₂.

Targeting this type of behavior is of significant importance to Industrial applications. Specifically, the ability to achieve a desired result, polymer coating removal, at lower pressures and temperatures directly results in lower capital equipment

costs (thinner pressure vessel wall thickness) and increased throughput (larger vessel size).

8.2.2.4 CO₂/Acetone

Acetone, Figure 8-25, is expected to act as a Lewis base in CO₂, and could participate in specific interactions with Lewis acids, such as PVB. However, acetone should not exhibit specific (favorable) interactions with PC, which should also act as a Lewis base. Pure acetone is reported to be a nonsolvent for both PC⁵⁶⁷ and PVB.⁵⁶⁸

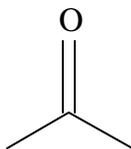


Figure 8-25. Acetone, HSP values⁵⁶⁹ $\mathbf{d}_t = 15.5 \text{ MPa}^{1/2}$, $\mathbf{d}_p = 10.4 \text{ MPa}^{1/2}$, and $\mathbf{d}_h = 7.0 \text{ MPa}^{1/2}$.

The thermal expansion coefficient for acetone, $\mathbf{a(T)}$, is determined using eqn. (8-13) with $a = 0.000798$, $m = -0.701$, and $T_c = 508.2 \text{ (K)}$ ⁵⁷⁰. The isothermal compressibility value used for acetone is $0.000061 \text{ (bar}^{-1}\text{)}$.⁵⁷¹ HSP values for acetone, adjusted for T and P effects, are shown in Table 8-9.

Table 8-9. HSP values for acetone adjusted for temperature and pressure.

$T \text{ (K)}$	$\mathbf{a(T)} \text{ (K}^{-1}\text{)}$	$\mathbf{b} \text{ (bar}^{-1}\text{)}$	$P \text{ (bar)}$	\mathbf{d}_t	\mathbf{d}_p	\mathbf{d}_h
298	0.001482	0.000061	1	15.5	10.4	7.0
313	0.001561	0.000061	100	15.2	10.3	6.8
313	0.001561	0.000061	200	15.3	10.3	6.9
348	0.001793	0.000061	200	14.0	10.0	6.3
358	0.001876	0.000061	100	13.4	9.9	6.1

An HSP value for the CO₂/acetone mixture is calculated using eqn. (6-22). The resulting HSP values for the CO₂/acetone mixture (initial and final) and for PC at T = 40°C and P = 1500 psi and P = 3000 psi are plotted in Figures 8-26(a) and 8-26(b). Also indicated on the plots are the resulting *Ra* values, from eqn. (5-20), where *Ra* is the distance from the HSP value of PC at T and P (open symbols), to the initial and final HSP value of CO₂/acetone at T and P (filled symbols).

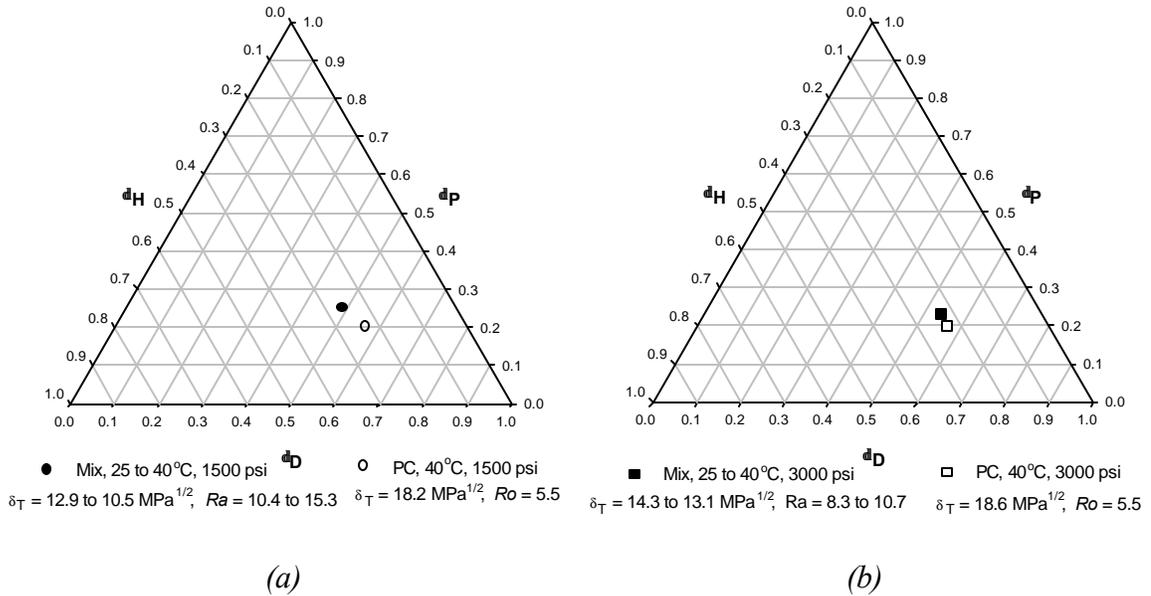


Figure 8-26. (a) HSP values of CO₂/acetone and PC at T = 25 to 40°C and P = 1500 psi. (b) HSP values of CO₂/acetone and PC at T = 25 to 40°C and P = 3000 psi.

Visual results of the CO₂/acetone treatment, at the temperature and pressures indicated in Figure 8-26(a) and 8-26(b), are given in Figure 8-27(a) and 8-27(b).

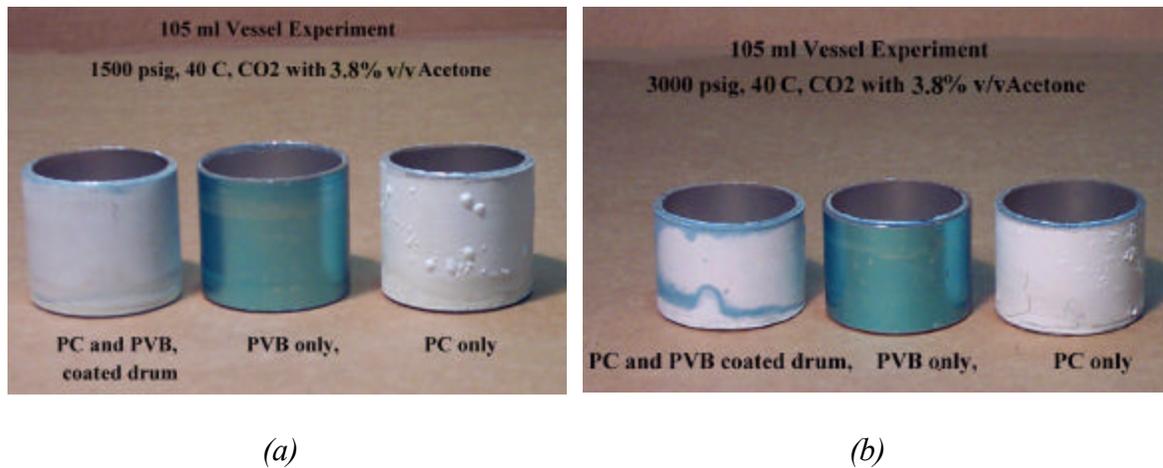
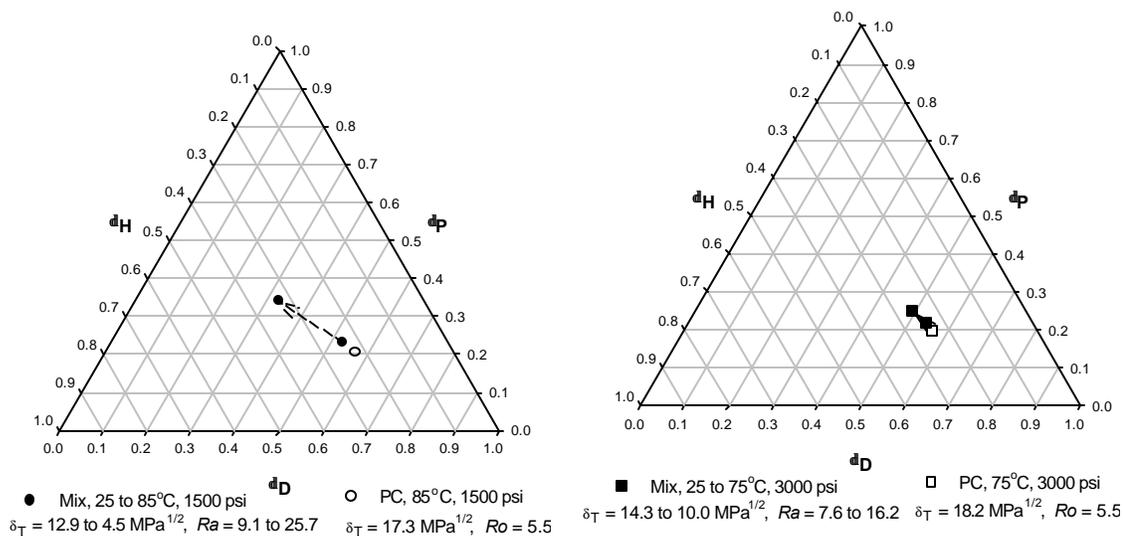


Figure 8-27. Appearance of polymer coated photoconductor drums treated with a CO₂/acetone mixture at (a) $T = 25$ to 40°C , $P = 1500$ psi, and acetone concentration = 3.8 vol.%, (b) $T = 25$ to 40°C , $P = 3000$ psi, and acetone concentration = 3.8 vol.%.

The resulting HSP values for the CO₂/acetone mixture (initial and final) and for PC at $T = 85^{\circ}\text{C}$ and $P = 1500$ psi; and $T = 75^{\circ}\text{C}$ and $P = 3000$ psi are plotted in Figures 8-28(a) and 8-28(b). Also indicated on the plots are the resulting Ra values, from eqn. (5-20), where Ra is the distance from the HSP value at T and P of PC (open symbols), to the initial and final HSP value of CO₂/acetone at T and P (filled symbols).

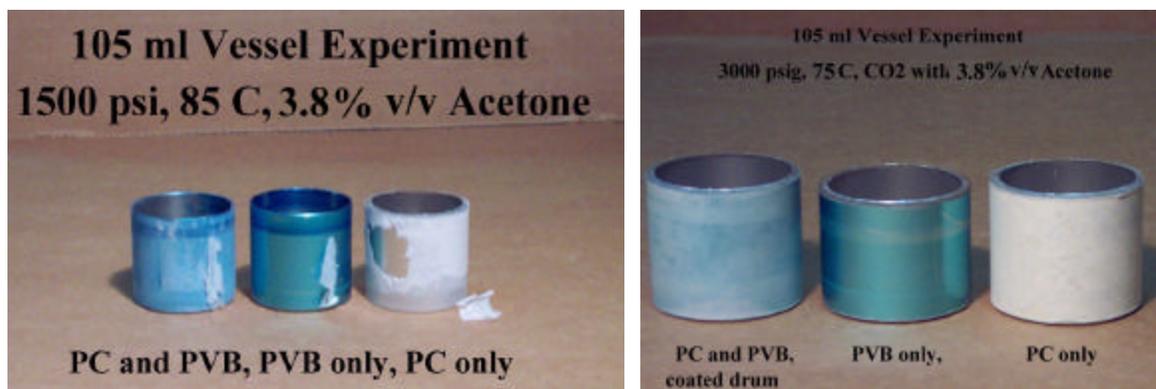


(a)

(b)

Figure 8-28. (a) HSP values of CO₂/acetone and PC at T = 25 to 85°C and P = 1500 psi, (b) HSP values of CO₂/acetone and PC at T = 25 to 75°C and P = 3000 psi.

Visual results of the treatments using the CO₂/acetone mixtures, at the temperature and pressures indicated in Figure 8-28(a) and 8-28(b), are given in Figure 8-29(a) and 8-29(b).



(a)

(b)

Figure 8-29. Appearance of polymer coated photoconductor drums treated with a CO₂/acetone mixture at (a) T = 25 to 85°C, P = 1500 psi, and acetone concentration = 3.8 vol.%, (b) T = 25 to 75°C, P = 3000 psi, and acetone concentration = 3.8 vol.%.

8.2.2.4.1 Observations of Polymer Coating Removal Experiments using a CO₂/Acetone Mixture

On the basis of visual observations, Table 8-10 gives a ranking of the results of the experiments using CO₂/acetone mixtures, according to most favorable to least favorable effect on the PC coating.

Table 8-10. Results on Polycarbonate coating to CO₂/acetone experiments.

T _{CO₂} (°C)	P _{CO₂} (psi)	Polymer T _g at (T _{CO₂} , P _{CO₂})	ΔT (T _{CO₂} - T _g)	R _{a_i} (MPa ^{1/2})	R _{a_f} (MPa ^{1/2})	R _{o^{liq}} (MPa ^{1/2})	Exp. result
85	1500	91.1	-6.1	9.1	25.7	5.5	flaking
40	3000	88.0	-48.0	8.3	10.7	5.5	cracked
40	1500	103.0	-63.0	10.4	15.3	5.5	bubbled
75	3000	88.0	-13.0	7.6	16.2	5.5	discolored

As with experiments discussed previously, the depression of the polymer T_g to below the treatment temperature, T_{CO₂}, leading to enhanced polymer sorption and swelling, promotes the most favorable results. However, unlike the CO₂/ethanol mixture, where the potential for specific cosolvent/polymer interactions exist, experimental results with the acetone (a Lewis base) cosolvent, at the same treatment temperature and pressure, produce far less favorable results.

8.2.2.5 CO₂/Cyclohexanone

Cyclohexanone, Figure 8-30, is expected to act as a Lewis base in CO₂, and could participate in specific interactions with Lewis acids, such as PVB. Pure cyclohexanone is reported to be a solvent for both PVB⁵⁷² and PC⁵⁷³.

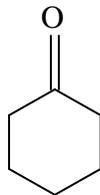


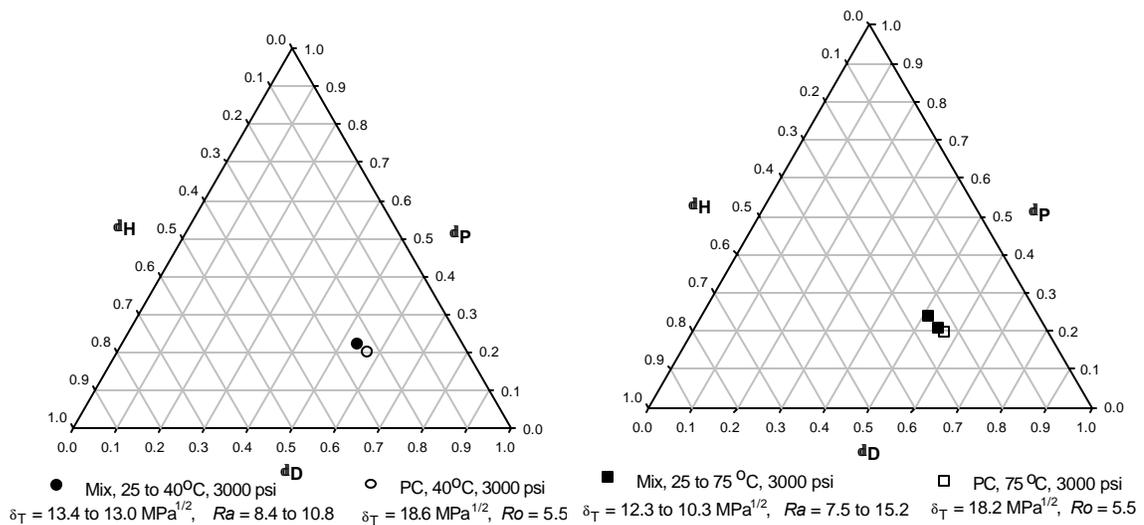
Figure 8-30. Cyclohexanone, HSP values⁵⁷⁴ : $\mathbf{d}_t = 17.8 \text{ MPa}^{1/2}$, $\mathbf{d}_p = 6.3 \text{ MPa}^{1/2}$, and $\mathbf{d}_h = 5.1 \text{ MPa}^{1/2}$.

Parameters used for determining the coefficient of thermal expansion of cyclohexanone are $a = 0.000563$, $m = -0.7283$, and $T_c = 629.15 \text{ K}$. The isothermal compressibility value used for cyclohexanone⁵⁷⁵ is $0.000066 \text{ (bar}^{-1}\text{)}$. Adjusted HSP values for cyclohexanone are shown in Table 8-11.

Table 8-11. HSP values for cyclohexanone adjusted for temperature and pressure.

$T \text{ (K)}$	$\mathbf{a}(T) \text{ (K}^{-1}\text{)}$	$\mathbf{b} \text{ (bar}^{-1}\text{)}$	$P \text{ (bar)}$	\mathbf{d}_t	\mathbf{d}_p	\mathbf{d}_h
298	0.000898	0.000066	1	17.8	6.3	5.1
313	0.000929	0.000066	200	17.8	6.3	5.1
328	0.000962	0.000066	200	17.5	6.3	5.0
338	0.000986	0.000066	100	17.1	6.2	4.8
338	0.000986	0.000066	200	17.2	6.2	4.9
343	0.000998	0.000066	100	17.0	6.2	4.7
348	0.001011	0.000066	200	17.0	6.2	4.8
363	0.001053	0.000066	100	16.4	6.1	4.6
373	0.001082	0.000066	100	16.1	6.1	4.5

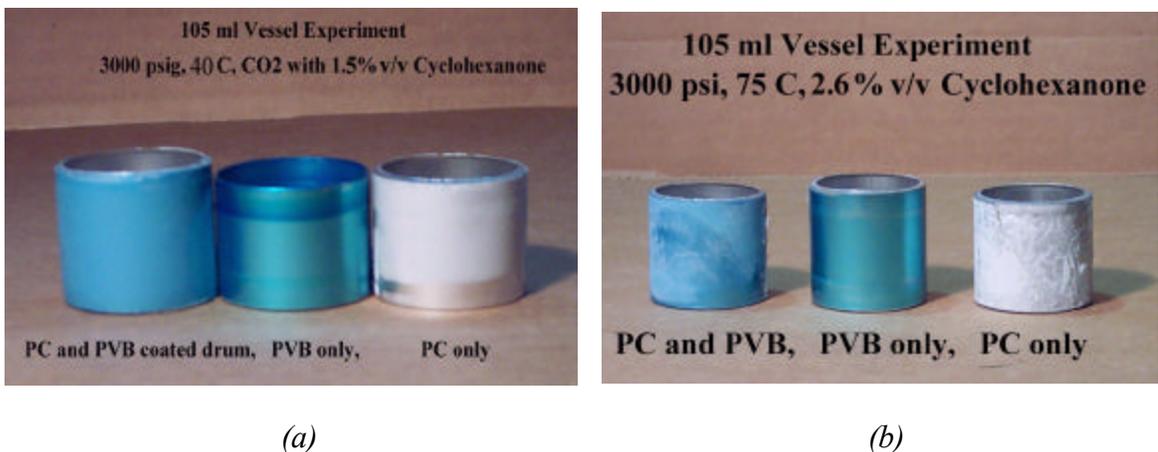
With the HSP values for both CO_2 and cosolvent adjusted for temperature and pressure, an HSP value for the CO_2 /cyclohexanone mixture is calculated using eqn. (6-22). The resulting HSP values for the CO_2 /cyclohexanone mixture (initial and final) and PC at $T = 40^\circ\text{C}$ and $P = 3000 \text{ psi}$; and $T = 75^\circ\text{C}$ and $P = 3000 \text{ psi}$ are plotted in Figures 8-31(a) and 8-31(b). Also indicated on the plots are the resulting Ra values, from eqn. (5-20), where Ra is the distance from the HSP value of PC or PVB at T and P (open symbols), to the initial and final HSP value of CO_2 /cyclohexanone at T and P (filled symbols).



(a) (b)

Figure 8-31. (a) HSP values of CO₂/cyclohexanone mixture and PC at T = 25 to 40°C and P = 3000 psi. (B) HSP values of CO₂/cyclohexanone mixture and PC at T = 25 to 40°C and P = 3000 psi.

Visual results of the CO₂/cyclohexanone treatments, at the temperature and pressures indicated in Figure 8-31(a) and 8-31(b), are given in Figure 8-32(a) and 8-32(b).



(a) (b)

Figure 8-32. Appearance of polymer coated photoconductor drums treated with a CO₂/cyclohexanone mixture at (a) T = 25 to 40°C, P = 3000 psi, and cyclohexanone concentration = 1.5 vol.%, (b) T = 25 to 75°C, P = 3000 psi, and cyclohexanone concentration = 2.6 vol.%.

The resulting HSP values for the CO₂/cyclohexanone mixture (initial and final) and for PC at T = 65°C and P = 1500 psi and P = 3000 psi are plotted in Figures 8-33(a) and 8-33(b). Also indicated on the plots are the resulting *Ra* values, from eqn. (5-20), where *Ra* is the distance from the HSP value of PC at T and P (open symbols), to the initial and final HSP value of CO₂/cyclohexanone at T and P (filled symbols).

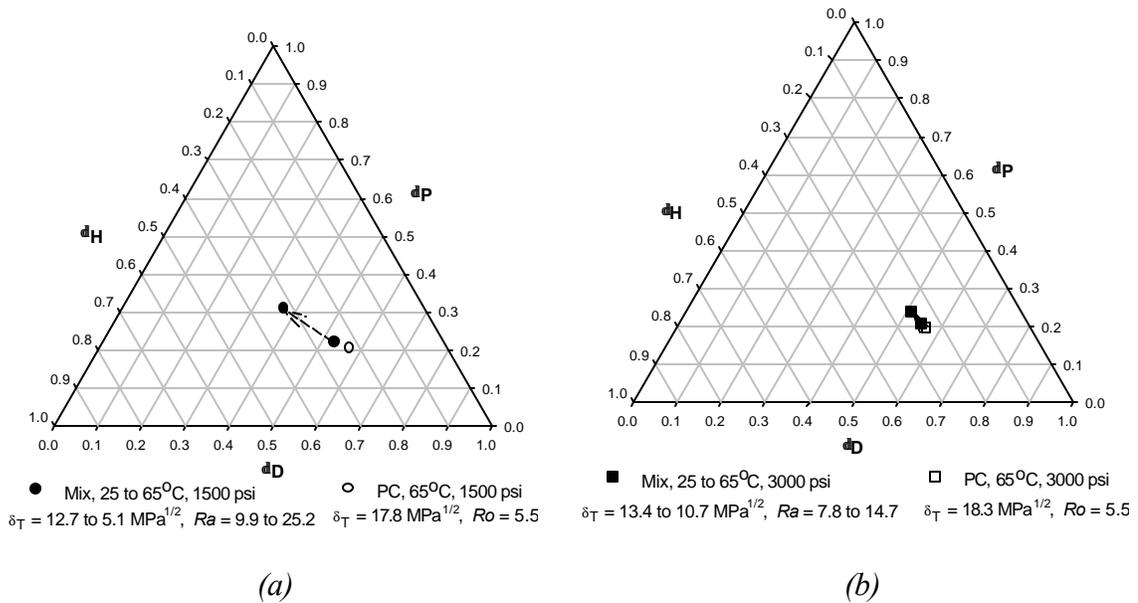


Figure 8-33. (a) HSP values of CO₂/cyclohexanone mixture and PC at T = 25 to 65°C and P = 1500 psi. (B) HSP values of CO₂/cyclohexanone mixture and PC at T = 25 to 65°C and P = 3000 psi.

Visual results of the CO₂/cyclohexanone treatments, at the temperature and pressures indicated in Figure 8-33(a) and 8-33(b), are given in Figure 8-34(a) and 8-34(b).

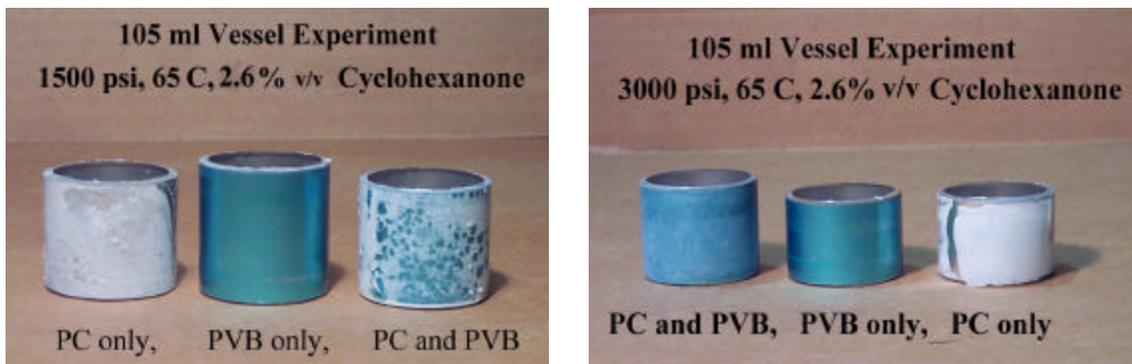


Figure 8-34. Results of CO₂/cyclohexanone treatment of polymer coated photoconductor drums. (a) $T = 25$ to 65 °C, $P = 1500$ psi, and cyclohexanone concentration = 2.6 vol.%. (b) $T = 25$ to 65 °C, $P = 3000$ psi, and cyclohexanone concentration = 2.6 vol.%.

The resulting HSP values for the CO₂/cyclohexanone mixture (initial and final) and for PC at $T = 100$ °C and $P = 1500$ psi and $P = 3000$ psi are plotted in Figures 8-35(a) and 8-35(b). Also indicated on the plots are the resulting R_a values, from eqn. (5-20), where R_a is the distance from the HSP value of PC at T and P (open symbols), to the initial and final HSP value of CO₂/cyclohexanone at T and P (filled symbols).

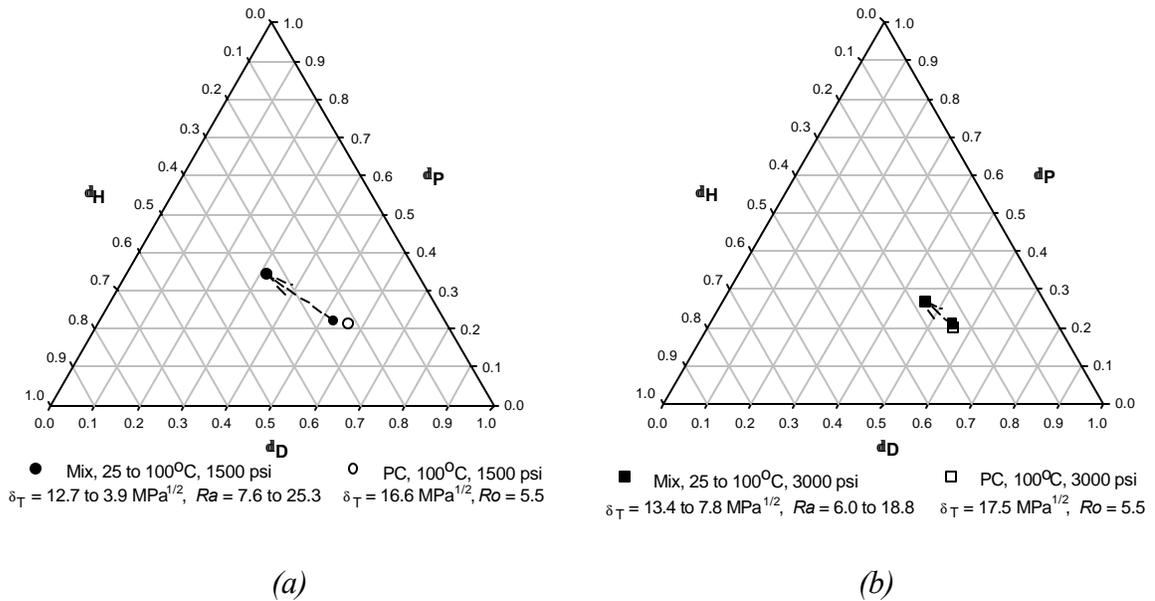


Figure 8-35. (a) HSP values of CO₂/cyclohexanone mixture and PC at T = 25 to 100°C and P = 1500 psi. (B) HSP values of CO₂/cyclohexanone mixture and PC at T = 25 to 100°C and P = 3000psi.

Visual results of the CO₂/cyclohexanone treatments, at the temperature and pressures indicated in Figure 8-35(a) and 8-35(b), are given in Figure 8-36(a) and 8-36(b).

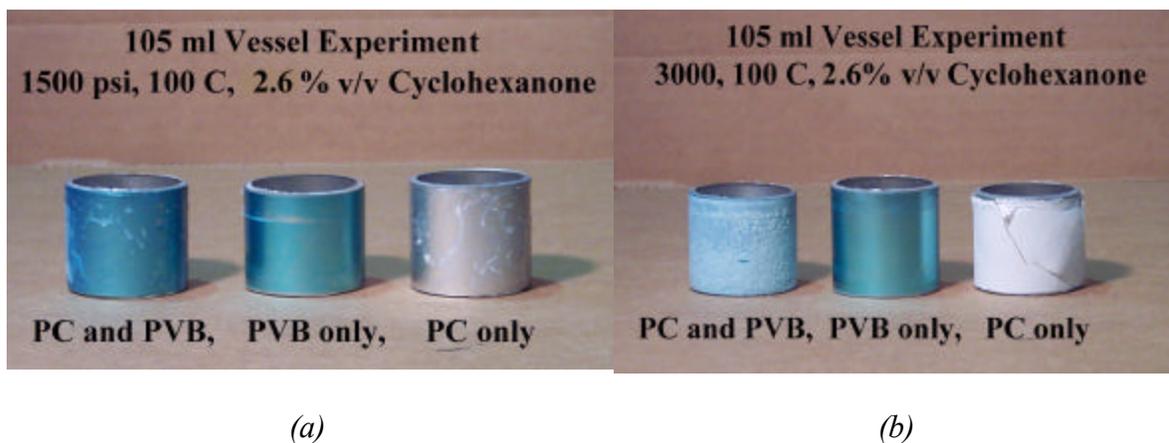


Figure 8-36. Results of CO₂/cyclohexanone treatment of polymer coated photoconductor drums. (a) T = 25 to 100°C, P = 1500 psi, and cyclohexanone concentration = 2.6 vol.%. (b) T = 25 to 100°C, P = 3000 psi, and cyclohexanone concentration = 2.6 vol.%.

8.2.2.5.1 Observations of Polymer Coating Removal Experiments using CO₂/Cyclohexanone Mixtures

On the basis of the visual observations, the results of the experiments shown in Figures 8-32, 8-34 and 8-36, are ranked in Table 8-12 according to most favorable to least favorable effects on the PC coating.

Table 8-12. Results on polycarbonate coating to CO₂/cyclohexanone experiments.

T _{CO₂} (°C)	P _{CO₂} (psi)	Polymer T _g at (T _{CO₂} , P _{CO₂})	ΔT (T _{CO₂} - T _g)	R _{a<i>i</i>} , (MPa ^{1/2})	R _{a<i>f</i>} , (MPa ^{1/2})	R _{o^{liq}} (MPa ^{1/2})	Exp. results
100	3000	54.3	45.7	6.0	18.9	5.5	debonded
65	3000	88.0	-23.0	7.8	14.7	5.5	debonded
75	3000	88.0	-13.0	7.5	15.2	5.5	flaking
100	1500	85.6	14.4	7.6	25.3	5.5	cracked
65	1500	103.0	-38.0	9.9	25.2	5.5	cracked
40	3000	88.0	-48.0	8.4	10.8	5.5	discolored

The results obtained with the CO₂/cyclohexanone mixtures follow a similar trend to those discussed previously for pure CO₂ and CO₂/ethanol, with a strong correlation between favorable effects on the polymer coating and ΔT = (T_{CO₂} - T_g). The result which contradicts this trend is the one conducted at T = 100°C and P = 1500 psi. Small surface cracks in the PC coating were evident, however, at the completion of this particular experiment the drum components were noted to have been in contact with liquid cyclohexanone. This was not a result noted with other experiments and solvent/cosolvent mixtures. The solubility of cyclohexanone in CO₂ was not evaluated at all experimental temperature and pressures, however, as a Lewis base with a carbonyl functional group, some level of solubility is expected. However, this solubility is reduced at higher temperatures and lower pressures, and the molecular weight of cyclohexanone

is larger than the other Lewis base cosolvents evaluated in this study, which is a rough indicator of lower solubility.

Also, unlike the CO₂/ethanol mixture, where the potential for specific cosolvent/polymer interactions exist, experimental results with the (Lewis base) cyclohexanone cosolvent, for a range of temperature and pressures, produce less favorable results.

8.2.2.6 CO₂/Tetrahydrofuran

Tetrahydrofuran (THF), Figure 8-37, is expected to act as a Lewis base in CO₂ and therefore specific interactions with Lewis acids, such as PVB, are possible. Pure, liquid THF is reported to be a solvent for both PVB⁵⁷⁶ and PC⁵⁷⁷.

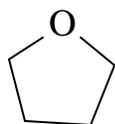


Figure 8-37. Tetrahydrofuran (THF), HSP values⁵⁷⁸ $d_t = 16.8 \text{ MPa}^{1/2}$, $d_p = 5.7 \text{ MPa}^{1/2}$, and $d_h = 8.0 \text{ MPa}^{1/2}$.

The HSP's given in the caption of Figure 8-37 are ambient condition values and are taken from the literature. These parameters are adjusted for temperature and pressure effects as described in Section 7.2.2. The thermal expansion coefficient, $\alpha(T)$, is determined from eqn. (8-13) with $a = 0.000685$, $m = -0.7088$, and $T_c = 540.15 \text{ K}$ ⁵⁷⁹. An isothermal compressibility value for THF could not be located, and the value for cyclohexanone was assumed, based on the similarity of their chemical structures. Adjusted HSP values for THF are given in Table 8-13.

Table 8-13. THF HSP values adjusted for temperature and pressure.

T (K)	$a(T)$ (K^{-1})	b (bar^{-1})	P (bar)	d_H	d_P	d_D
298	0.001209	0.000066	1	16.8	5.7	8.0
313	0.001265	0.000066	200	16.7	5.7	7.9
333	0.001351	0.000066	200	16.1	5.6	7.6
343	0.001399	0.000066	100	15.6	5.5	7.4
373	0.001572	0.000066	100	14.5	5.4	6.8
373	0.001572	0.000066	200	14.6	5.4	6.9

An HSP value for the CO₂/THF mixture is calculated using eqn. (6-22). The resulting HSP values for the CO₂/THF mixture (initial and final) and for PC at T= 75°C and P = 1500 psi; and T = 40°C and P = 3000 psi are plotted in Figures 8-38(a) and 8-38(b). Also indicated on the plots are the resulting Ra values, from eqn. (5-20), where Ra is the distance from the HSP value of PC at T and P (open symbols), to the initial and final HSP value of CO₂/THF at T and P (filled symbols).

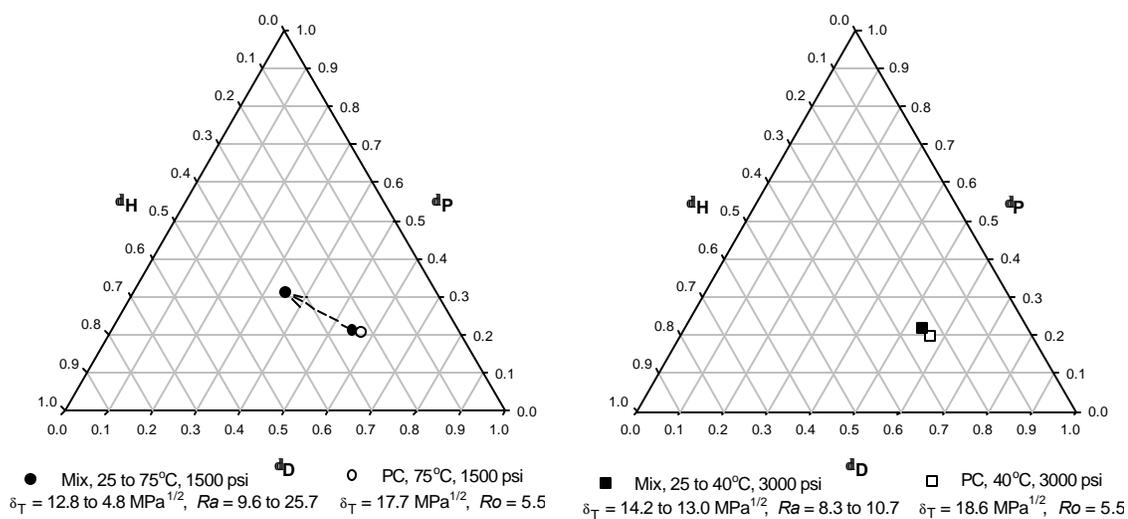


Figure 8-38. (a) HSP values of CO₂/THF and PC at T = 25 to 75°C and P = 1500 psi. (b) HSP values of CO₂/THF and PC at T = 25 to 40°C and P = 3000 psi.

Visual results of the CO₂/THF treatment, at the temperature and pressures indicated in Figure 8-38(a) and 8-38(b), are given in Figure 8-39(a) and 8-39(b).



(a)

(b)

Figure 8-39. Appearance of polymer coated photoconductor drums treated with a CO₂/THF mixture at (a) $T = 25$ to 75 °C, $P = 1500$ psi, and THF concentration = 2.8 vol.%, (b) $T = 25$ to 40 °C, $P = 3000$ psi, and THF concentration = 3.0 vol.%.

The resulting HSP values for the CO₂/THF mixture (initial and final) and for PC at $T = 100$ °C and $P = 1500$ psi and $P = 3000$ psi are plotted in Figures 8-40(a) and 8-40(b). Also indicated on the plots are the resulting R_a values, from eqn. (5-20), where R_a is the distance from the HSP value of PC at T and P (open symbols), to the initial and final HSP value of CO₂/THF at T and P (filled symbols).

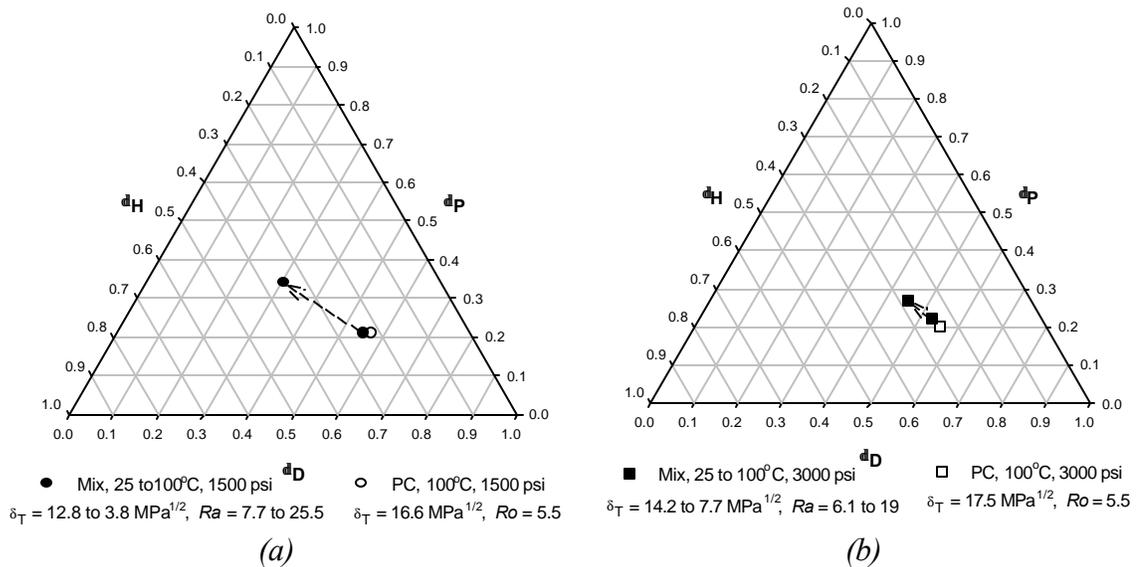
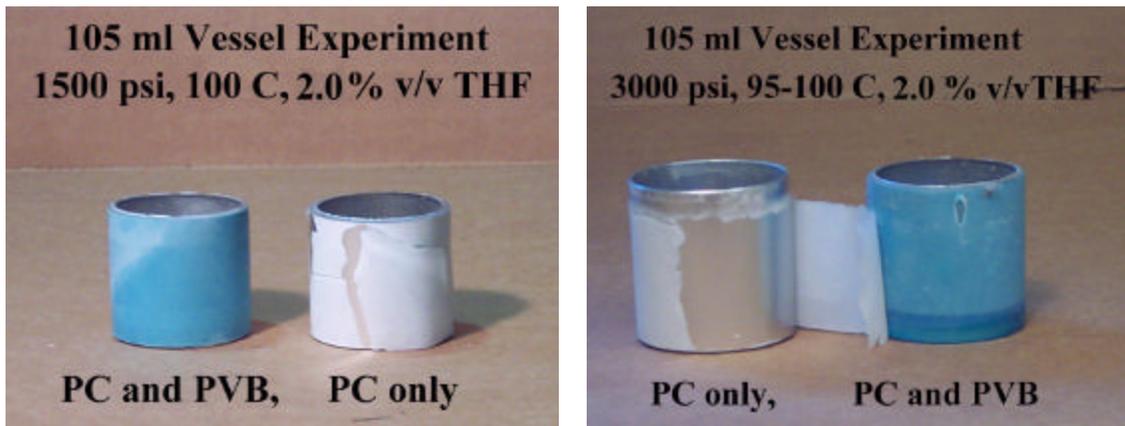


Figure 8-40. (a) HSP values of CO₂/THF and PC T = 25 to 100°C and P = 1500 psi
 (b) HSP values of CO₂/THF and PC T = 25 to 100°C and P = 3000 psi.

Visual results of the CO₂/THF treatments, at the temperature and pressures indicated in Figure 8-40(a) and 8-40(b), are given in Figure 8-41(a), and 8-41(b).



(a) (b)
Figure 8-41. Appearance of polymer coated photoconductor drums treated with a CO₂/THF mixture at (a) T = 25 to 100°C, P = 1500 psi, and THF concentration = 2.0 vol.%, (b) T = 25 to 100°C, P = 3000 psi, and THF concentration = 2.0 vol.%.

8.2.2.6.1 Observations of Polymer Coating Removal Experiments using CO₂/THF Mixtures

On the basis of the visual observations, the results of the experiments shown in Figures 8-39, and 8-41, are ranked in Table 8-14, according to most favorable to least favorable effects on the PC coating.

Table 8-14. Results of polymer removal experiments using CO₂/THF mixtures.

T _{CO₂} (°C)	P _{CO₂} (psi)	Polymer T _g at (T _{CO₂} , P _{CO₂})	ΔT (T _{CO₂} - T _g)	R _{a_i} (MPa ^{1/2})	R _{a_f} (MPa ^{1/2})	R _{o^{liq}} (MPa ^{1/2})	Exp. result
100	3000	54.3	45.7	6.1	19.0	5.5	debonded
100	1500	85.6	14.4	7.7	25.5	5.5	debonded
75	1500	103.0	-28.0	9.6	25.7	5.5	debonded
40	1500	88.0	-48.0	8.3	10.7	5.5	discolored

The results of the CO₂/THF mixtures are very similar to the results using the CO₂/cyclohexanone mixtures in that the effects on the PC correlate strongly with ΔT

8.2.2.7 Comparison of Polymer Coating Removal Experiments – Photoconductor Drums

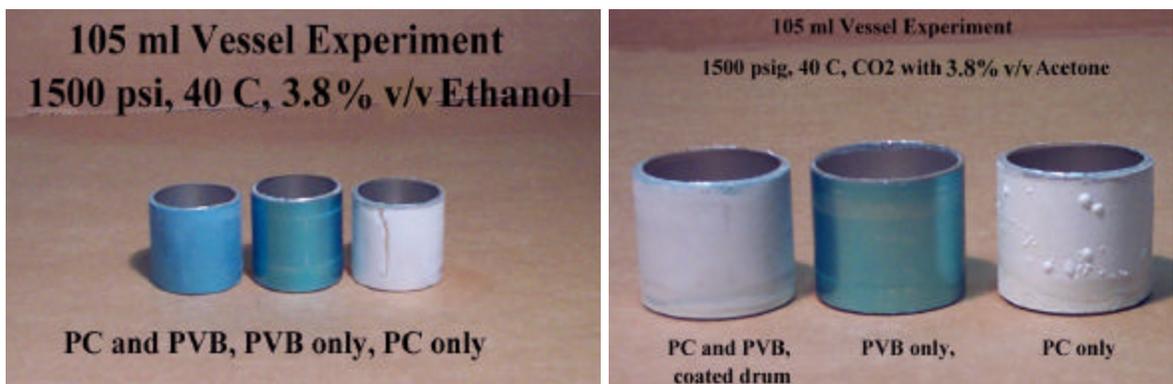
Table 8-15. Overall results on Polycarbonate coating removal experiments, ranked according to the effect on the PC coating.

Cosolvent	T _{CO₂} (°C)	P _{CO₂} (psi)	Polymer T _g at (T _{CO₂} , P _{CO₂})	ΔT (T _{CO₂} - T _g)	R _{a<i>i</i>} (MPa ^{1/2})	R _{a<i>f</i>} (MPa ^{1/2})	R _{o^{liq}} (MPa ^{1/2})	Exp. result
ethanol	100	3000	54.3	45.7	6.0	18.9	5.5	debonded
ethanol	100	1500	85.6	14.4	7.7	25.3	5.5	debonded
ethanol	85	1500	91.1	-6.1	9.0	25.3	5.5	debonded
ethanol	75	3000	88.0	-13.0	7.5	16.3	5.5	debonded
cyclohexanone	100	3000	54.3	45.7	6.0	18.9	5.5	debonded
THF	100	3000	54.3	45.7	6.1	19.0	5.5	debonded
THF	100	1500	85.6	14.4	7.7	25.5	5.5	debonded
CO ₂	100	3000	54.3	45.7	6.2	19.4	5.5	debonded
cyclohexanone	65	3000	88.0	-23.0	7.8	14.7	5.5	debonded
THF	75	1500	103.0	-28.0	9.6	25.7	5.5	debonded
cyclohexanone	75	3000	88.0	-13.0	7.5	15.2	5.5	flaking
ethanol	40	1500	103.0	-63.0	10.8	15.2	5.5	flaking
acetone	85	1500	91.1	-6.1	9.1	25.7	5.5	flaking
cyclohexanone	100	1500	85.6	14.4	7.6	25.3	5.5	cracked
ethanol	40	3000	88.0	-48.0	10.6	10.6	5.5	cracked
acetone	40	3000	88.0	-48.0	8.3	10.7	5.5	cracked
cyclohexanone	65	1500	103.0	-38.0	9.9	25.2	5.5	cracked
CO ₂	100	1500	85.6	14.4	7.9	26.0	5.5	bubbled

acetone	40	1500	103.0	-63.0	10.4	15.3	5.5	Bubbled
acetone	75	3000	88.0	-13.0	7.6	16.2	5.5	discolored
CO ₂	75	3000	88.0	-23.0	7.8	16.7	5.5	discolored
THF	40	3000	85.6	-48.0	8.3	10.7	5.5	discolored
CO ₂	45	3000	88.0	-43.0	8.4	11.6	5.5	discolored
cyclohexanone	40	3000	88.0	-48.0	8.4	10.8	5.5	discolored
CO ₂	75	1500	103.0	-28.0	9.9	26.8	5.5	discolored
hexane	75	3000	91.1	-16.1	7.7	15.6	5.5	discolored
CO ₂	45	1500	103.0	-58.0	10.8	18.9	5.5	discolored

Table 8-15 is a ranking of all of the photoconductor drum polymer coating removal experiments. The results, ranked according to the most desirable (top) to least desirable (bottom) effect on the PC coating, are based on visual observations. The ranking in Table 8-15 clearly indicate that, of the cosolvents examined, ethanol produces the best results for the PC coatings removal application. This supports the concept discussed in Section 3.4 where it was noted that specific interactions, such as Lewis acid/base interactions, generally have a greater influence than the combined van der Waals interactions. Direct comparisons of experimental results at the same temperature and pressure, using a Lewis acid or Lewis base cosolvent, are shown in Figures 8-42 and 8-43.

In Figure 8-42, a greater effect on the PC coating (partial debonding) is observed when a Lewis acid cosolvent is used versus the effect when a Lewis base is used (bubbling).

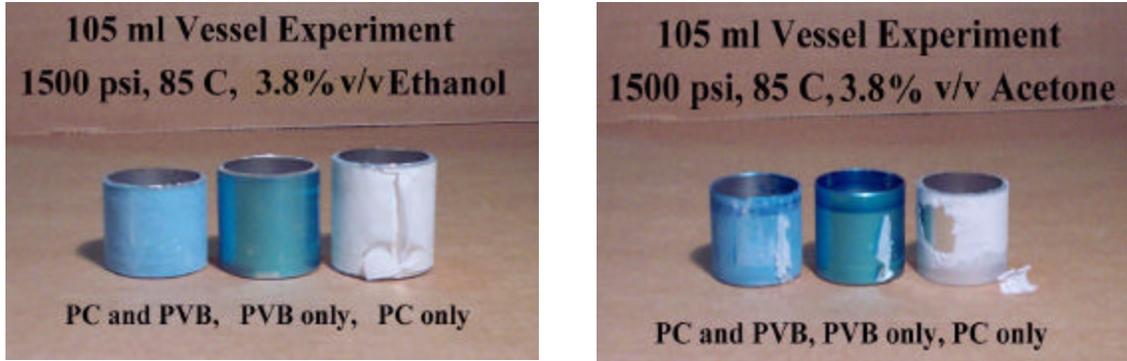


$$\begin{aligned} \Delta T &= T_{CO_2} - T_g^{CO_2} = -63^\circ C \\ Ra &= 11 \text{ to } 15.2 \text{ MPa}^{1/2} \\ &(a) \end{aligned}$$

$$\begin{aligned} \Delta T &= T_{CO_2} - T_g^{CO_2} = -63^\circ C \\ Ra &= 11 \text{ to } 15.2 \text{ MPa}^{1/2} \\ &(b) \end{aligned}$$

Figure 8-42. (a) Results of CO₂/Lewis acid treatment of polymer coated photoconductor drums, $T = 25$ to $40^\circ C$, $P = 1500$ psi, and ethanol concentration = 3.8 vol.%. (b) Results of CO₂/Lewis base treatment of polymer coated photoconductor drums, $T = 25$ to $40^\circ C$, $P = 1500$ psi, and acetone concentration = 3.8 vol.%.

In Figure 8-43, a similar comparison is made at a higher experimental temperature (85°C)



$$\begin{aligned}\Delta T &= T_{CO_2} - T_g^{CO_2} = -6^\circ C \\ Ra &= 9.5 \text{ to } 25.3 \text{ MPa}^{1/2} \\ &(a)\end{aligned}$$

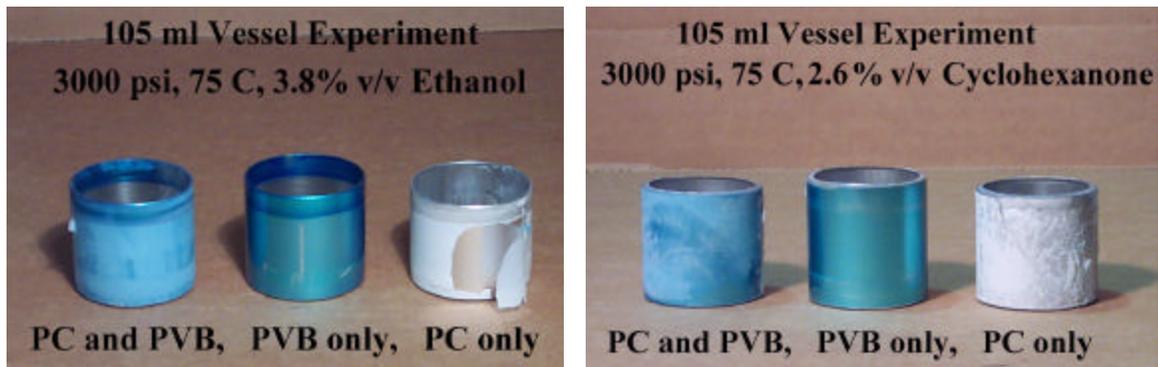
$$\begin{aligned}\Delta T &= T_{CO_2} - T_g^{CO_2} = -6^\circ C \\ Ra &= 9.5 \text{ to } 25.7 \text{ MPa}^{1/2} \\ &(b)\end{aligned}$$

Figure 8-43. (a) Results of CO₂/Lewis acid treatment of polymer coated photoconductor drums, $T = 25$ to $85^\circ C$, $P = 1500$ psi, and ethanol concentration = 3.8 vol.%. (b) Results of CO₂/Lewis base treatment of polymer coated photoconductor drums, $T = 25$ to $85^\circ C$, $P = 1500$ psi, and acetone concentration = 3.8 vol.%.

Again, the result with the Lewis acid cosolvent, debonding of the PC coating, is significantly better than the result observed with the Lewis base cosolvent, flaking of the PC coating. The initial and final Ra values, representing the distance (expressed as a radius) between the initial solvent mixture HSP values to the PC HSP value (Ra_i), and between the final mixture HSP values to the PC HSP value (Ra_f), at T and P , ranged from an initial value of 9.5 to a final value of approximately $25 \text{ MPa}^{1/2}$ versus values in Figure 8-42 of 11 to $15.2 \text{ MPa}^{1/2}$. An optimum radius of interaction, R_o^{SCF} , that can be used to design test conditions for the PC/SCF is unknown, although, as discussed earlier, it is expected to be greater than the optimum radius of interaction for the dissolution of PC in liquid solvents, $R_o^{liq} = 5.5$. Based on the results in Figure 8-42(a) and 8-43(a) an

optimum value of Ra for the CO_2 /ethanol/PC system appears to lie between 11 to $9.5 \text{ MPa}^{1/2}$.

Another set of comparisons, of experimental results at the same temperature and pressure, using a Lewis acid or Lewis base cosolvent that is a known solvent for the PC, are shown in Figures 8-44 and 8-45.



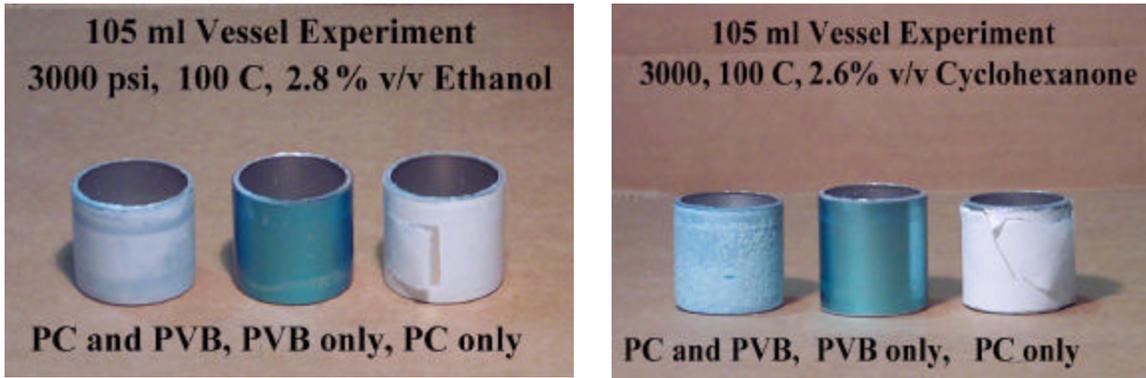
$$\begin{aligned}\Delta T &= T_{\text{CO}_2} - T_g^{\text{CO}_2} = -13^\circ \text{C} \\ Ra &= 7.5 \text{ to } 16.3 \\ (a)\end{aligned}$$

$$\begin{aligned}\Delta T &= T_{\text{CO}_2} - T_g^{\text{CO}_2} = -13^\circ \text{C} \\ Ra &= 7.5 \text{ to } 15.2 \\ (b)\end{aligned}$$

Figure 8-44. (a) Results of CO_2 /Lewis acid treatment of polymer coated photoconductor drums, $T = 25$ to 75°C , $P = 3000 \text{ psi}$, and ethanol concentration = 3.8 vol.%. (b) Results of CO_2 /Lewis base treatment of polymer coated photoconductor drums, $T = 25$ to 75°C , $P = 3000 \text{ psi}$, and cyclohexanone concentration = 2.6 vol.%.

As seen in the previous figure, the result with the Lewis acid cosolvent, debonding of the PC coating, is significantly better than the result observed with the Lewis base cosolvent, flaking of the PC coating. This also indicates a difference between supercritical and liquid solvent environments, as well as the change in the polymer behavior in the two environments. For although identifying typical liquid solvents that are noted to be good solvents for a particular polymer can still provide information in determining the HSP values of a polymer at atmospheric conditions, these same liquid solvents do not necessarily represent good cosolvent selections for the supercritical fluid

application discussed here. In Figure 8-45, a similar comparison is made at a higher temperature (100°C).



$$\Delta T = T_{CO_2} - T_g^{CO_2} = 46^\circ C$$

$$Ra = 6.2 \text{ to } 18.9$$

(a)

$$\Delta T = T_{CO_2} - T_g^{CO_2} = 46^\circ C$$

$$Ra = 6.2 \text{ to } 18.9$$

(b)

Figure 8-45. (a) Results of CO₂/Lewis acid treatment of polymer coated photoconductor drums, $T = 25$ to $100^\circ C$, $P = 3000$ psi, and ethanol concentration = 2.8 vol.%. (b) Results of CO₂/Lewis base treatment of polymer coated photoconductor drums, $T = 25$ to $100^\circ C$, $P = 3000$ psi, and cyclohexanone concentration = 2.6 vol.%.

As the temperature is increased from 75°C to 100°C, favorable effects on the PC coating are observed with either a Lewis acid or Lewis base cosolvent. At these conditions, the radius of interaction required for PC/SCF systems with Lewis base cosolvents also begins to emerge, and appears to be between 6.2 and 7.5 MPa^{1/2}, as determined from the comparison of Figure 8-44(b) and Figure 8-45(b).

In schematic form, the model predictions of HSP values for PC and CO₂ are plotted in Figure 8-46.

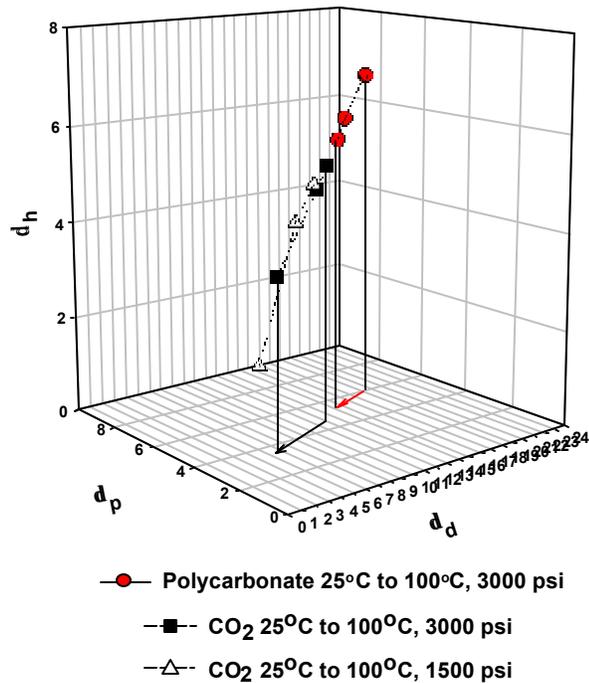


Figure 8-46. Predicted HSP values for PC and CO₂ as the temperature varies from $T = 25$ to 100°C at $P = 1500$ psi and 3000 psi.

From Figure 8-46 it can be seen that the HSP values of PC decrease with increasing temperature and pressure, and are nearest to the HSP values of CO₂ when the CO₂ and/or CO₂/cosolvent enters the pressure vessel at 25°C and 3000 psi. As the CO₂, and or CO₂/cosolvent temperature increases from these initial conditions, to the final vessel temperature, the solvent HSP values decrease, away from the PC values.

In addition to the proximity of the match in HSP's between the PC and solvent, plasitization of the polymer at the experimental temperature and pressure is a factor in predicting favorable results. From Table 8-4, and in the preceding images, it is observed that the greater the ΔT ($T_{\text{CO}_2} - T_g^{\text{CO}_2}$), in combination with a smaller Ra , the more favorable the effect on the PC coating. This emphasizes the importance of polymer

swelling, which can be significant when the polymer is in a rubber rather than glassy state. In addition, the relationship between Ra and ΔT should be appreciated. Whereby, the ability to swell the polymer, which occurs primarily above the polymer T_g , also affects the polymer HSP values in a manner that promotes a favorable interaction radius. This is readily seen in Figure 8-46 where the HSP values of PC, adjusted for temperature, pressure and swelling due to CO_2 absorption (ΔV^{CO_2}), approach those of CO_2 .

In terms of the model framework, complete characterization of the binary pairs (solvent/solvent, polymer/polymer, and solvent/polymer) in terms of HSP values allows for optimization of experimental conditions of temperature and pressure to ensure $Ra < R_o^{liq}$, or $Ra < R_o^{SCF}$ (if known), where $R_o^{liq} < R_o^{SCF}$. This situation, however, assumes experimental capabilities that are not limited by temperature or pressure. Where temperature or pressure limitations are encountered, the experimental results observed in this work indicate the enhanced favorable results are achievable by targeting specific interactions (Lewis acid/base) between a cosolvent and the polymer. This has direct effect not only on the design and construction on new equipment, but also allows facilities with existing equipment to operate supercritical fluid/polymer coating removal applications without new costly capital expenditures.

A direct effect of these interactions is the use of ethanol as a cosolvent in the PC/ CO_2 coatings removal application where removal of the PC coating was achieved in a Ra range of 9.5 to 11 $MPa^{1/2}$, versus a Ra range of 6.2 to 7.5 $MPa^{1/2}$ for the PC/ CO_2 /cyclohexanone system, and a value of less than 6.2 $MPa^{1/2}$ for pure CO_2 or 5.5 $MPa^{1/2}$ for a liquid solvent.