

INTERACTION OF CANDIDATE CLEANING SOLUTIONS FOR SENSITIVE EQUIPMENT DECONTAMINATION WITH POLYMERIC MATERIALS

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Chemical-polymer compatibility is an important criterion for the cleaning, decontamination, and extraction of hazardous chemicals from sensitive equipment (electronics, optics, and other advanced polymeric materials). Candidate cleaning fluids for sensitive equipment include fluorocarbons and supercritical fluids. The initial evaluation strategy involves the measurement of the sorption and desorption diffusion coefficients of the candidate cleaning fluid in a spectrum of polymer compositions. The objective was to characterize the complete desorption process by the continuous measurement of the entire diffusion process employing thermogravimetric instrumentation. These measurements and calculations provided an estimated 'time before reuse' after the cleaning process. The continuous measurement of desorption provided the high data density required to calculate a low concentration Fick's Law diffusion coefficient and equation for the extrapolations. The composition spectrum selected contains hydrogen bond donor, hydrogen bond acceptor, dipolar, and non-polar polymer structures; over 15 materials were studied.

INTRODUCTION

Chemical-material compatibility is a critical criterion in development of a decontamination system. The degradation of material properties and performance is especially important for sensitive equipment cleaning and decontamination. Sensitive equipment includes electronics, optics, and other high-value and unique equipment. The candidate cleaning fluids for sensitive equipment include supercritical carbon dioxide and fluorocarbons.

The overall material evaluation methodology for compatibility with decontaminants is under development (1-3). The selection of representative materials for compatibility testing is underway based on several parallel approaches. These include a top-down, material-to-material analysis that identifies surface materials in a spectrum of high-cost equipment; several material science based approaches were also applied to identify a spectrum of material physical states, molecular structures, and hydrogen bond and polarity classes (4).

The initial evaluation in any chemical-material evaluation test scheme usually involves measurement of sorption or solubility of the candidate cleaning fluid in a spectrum of relevant material compositions. The supercritical carbon dioxide processing conditions and material sorption experimentation is being reported separately. The experimentation reported herein concentrates on the desorption diffusion kinetic process for supercritical carbon dioxide from polymeric materials (5).

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The purpose is to characterize the complete desorption diffusion process by continuous measurement of the entire diffusion curve, with the exception of a few minute time increment at the start of the experiment and a few percent of the final weight-loss. The next purpose was to use the continuous desorption curve to provide an accurate extrapolation of the zero-time sorption value immediately after supercritical carbon dioxide decompression. This extrapolation from the high concentration region of the desorption curve allowed calculation of a corrected sorption value for each material that provided an accurate ranking of material solubility relative to the uncorrected values. The characterization of the plateau to equilibrium desorption allowed the measurement of extractables and, therefore, the correction of the sorption value for this fraction extracted. Another purpose of diffusion coefficient measurements was to provide an estimate of the time required for each material to completely desorb all of the carbon dioxide cleaning fluid and return the material to the original unplasticized condition. These measurements and calculations provide an estimated 'time before reuse' after the decontamination process. The continuous measurement of desorption provided the high data density required to calculate a low concentration Fick's Law diffusion coefficient and equation for the extrapolation to initial material sample weight before exposure. The experimental strategy includes mechanical, optical, thermal, and electrical property characterization to measure the influence of the sorbed decontaminant; in this initial screening stage, indentation hardness measurements of surface mechanical properties were completed.

EXPERIMENTATION

Extraction Instrumentation. The extraction instruments and cells employed to expose the materials to supercritical carbon dioxide have been documented (5). In general, the diffusion specimens were relatively small; therefore, the smaller cell sizes cited in the reference were employed.

Desorption Instrumentation. The thermogravimetric instruments employed to measure the continuous desorption of sorbed supercritical carbon dioxide were a TA Model TGA 2950 and Model TGA 951 (New Castle, DE 19720). The final values reported were all measured with a combination of the Model TGA 2950 and control software Version 8.10B (2.3A). Custom specimen holders were required for the unique research measurements and were constructed to clamp the ca. 1-cm diameter disk shaped specimens, while allowing free surface diffusion on all sides. The 0.62-0.64 mm diameter nichrome wire was formed to a shape that matched the TGA Model 2950 hang down wire hook, cleared the furnace sides, and avoided buoyancy fluctuations. The supercritical carbon dioxide and polymeric materials used have been documented (5).

PROCEDURES

Supercritical Exposure Procedures. The supercritical exposure procedures and conditions employed were based on conditions that were found to successfully remove contaminants from non-sorptive surfaces in previous exploratory experiments (B. MacIver, D. Sorrick; SBCCOM). The supercritical conditions are documented in Table 1. The first column in Table 1 lists the supercritical pressure, temperature, and exposure-time conditions. The second column documents the units. The remaining columns define codes that document the set of experimental conditions in the table. These codes are used in experimental data sheets and computer data file documentation. The difference in RT#1 and RT#2 is only the Sorption Weighing Time; this weighing time at 20 minutes allows a direct comparison with literature (last column) that reported the first weighing at 20 minutes. The extraction time refers to a static exposure without flow through the cell. The decompression time is a rapid but controlled pressure drop to ambient at an approximately linear rate. The "Sorption Weighing" time defines the time lag required to disassemble the cell and manipulate the material specimen to obtain the initial weight. Carbon dioxide desorption under ambient conditions occurred during this lag and can be corrected by an extrapolation back to the end of the decompression period.

TABLE 1. Comparison of Experimental Conditions for Super Critical Carbon Dioxide Sorption in Polymeric Materials: Measurement Conditions versus Similar Literature (6-8) Conditions

Experimental Conditions	Units	RT#1	RT#2	Literature C3
Pressure	Psig.	1399	1399	2000
Temperature	Degrees, C	50	50	40
Time: Static Extraction @ PT	Minutes	15	15	60
Time: Decompression	Minutes	1	1	60
Time: 1 st Sorption Weighing	Minutes	5	20	20

Kinetic Analysis Data Reduction Procedures. The basic data sets consisted of time, temperature, and weight measurements. These files were processed by various filtering techniques and data conversions to Fickian parameters. Interim results were processed with custom C++ code based on previous operational computational methods. A general description of the kinetic data analysis procedure has been provided (5). The final computations were performed using custom coded Excel functions.

RESULTS

Sorption Values Corrected for Fraction Extracted Employing Equilibrium Desorption Measurements. The sorption results in Table 2 are corrected for the fraction of mobile additives in the material that were extracted during the supercritical exposure. The value for the corrected sorption is followed by the uncorrected sorption value based on the fraction extracted. The relative error due to ignoring the extractables is calculated in the last column. Note that experimentation that ignores the extraction of the additives in the material causes considerable error that would change the relative ranking of materials for resistance to supercritical carbon dioxide sorption. The ‘Not Applicable’ entry refers to materials in which there was no measurable extraction. The methodology was capable of ranking the relative sorption levels for the spectrum of materials. The corrected sorption value was required to correctly rank the materials; the general trend in supercritical carbon dioxide was slightly influenced by fraction extracted, except for the combination of low sorption and high extractables. In these cases (for example, PEEK), the relative error was high but the ranking was only slightly in error.

Comparison of Sorption Values with Correction to Zero-time Mass Based on High Concentration Desorption Extrapolations. Most of the sorption values reported are based on an initial measurement that is often performed after considerable desorption has occurred. This measurement delay is due to the inherent lag between the end of the exposure or decompression time and the measurement time. Some modes of material damage may correlate with the maximum amount of decontaminant sorbed, therefore, accurate measurement of actual sorbed decontaminant is important. The reported measurements that ignore the desorption immediately after exposure give systematically low sorption values that underestimate the actual degree of interaction and solubility of fluids such as supercritical carbon dioxide in materials. In Table 3, the ‘zero-time corrected sorption’ values are calculated, followed by the error in ignoring the desorption immediately after the extractant exposure and decompression. Two delay periods are listed in the columns: the 7-12 minute delay inherent in the TGA experiment, reported herein, and the typical 20-minute measurement delay (U. Mass. Ref. 6-8). Large systematic relative errors of –15 to –86% were obtained by ignoring the extrapolation to zero-time. The methodology was capable of correcting for this measurement time lag after decompression and correctly ranking the materials. One can observe from the last two columns that there would be large ranking errors from not employing the methodology developed here.

TABLE 2. Supercritical Carbon Dioxide Sorption (%) into Polymeric Materials Based on Correction for Fraction Extracted: Conditions of 1400 psig and 50 degrees C after 15 minutes

No.	Polymer Codes	Sorption, Corrected, %	Sorption, Uncorrected, %	Extracted, %	Relative Error, %
1.	PDMS	0.44	0.44	-0.03	Not Applicable.
2.	PI	1.09	0.21	0.88	-80.7
3.	PEEK	1.49	1.20	0.28	-18.8
4.	PVC	1.65	1.65	-0.02	Not Applicable.
5.	PTFEP	2.39	2.24	0.15	-6.3
6.	PC	2.62	2.49	0.13	-5.0
7.	PBB	3.12	3.00	0.12	-3.8
8.	PEP	3.22	3.11	0.11	-3.4
9.	PPO	3.64	3.64	-0.24	Not Applicable.
10.	ABS	3.75	3.72	0.03	-0.8
11.	PIP	4.12	3.39	0.73	-17.7
12.	PSB	4.72	4.70	0.01	-0.2
13.	SMO	4.94	4.94	-0.20	Not Applicable.
14.	PMMA	6.24	6.24	-0.22	Not Applicable.
15.	PU	7.08	6.80	0.28	-4.0
16.	PSBR	7.32	6.58	0.74	-10.1
17.	PIB	7.88	7.88	-0.13	Not Applicable.

TABLE 3. Comparison of Sorption (%) Corrected for Extrapolation to Zero-time at the End of the Decompression Period Versus Uncorrected Sorption after 7-12 Minutes and 20 Minutes (6-8).

No.	Polymer Codes	Sorption, Zero-time Corrected	Sorption at 7-12 min, % (Relative Error, %)	Sorption at 20 min, % (Relative Error, %)
1.	PDMS	0.44	0.13 (-70.3)	0.06 (-86.8)
2.	PI	1.09	0.16 (-22.5)	0.04 (-80.0)
3.	PEEK	1.49	0.78 (-34.7)	0.60 (-50.3)
4.	PVC	1.65	1.37 (-17.2)	1.20 (-27.2)
5.	PTFEP	2.39	1.68 (-24.7)	1.31 (-41.3)
6.	PC	2.62	1.85 (-25.8)	1.48 (-40.5)
7.	PBB	3.12	1.41 (-52.8)	0.90 (-70.0)
8.	PEP	3.22	1.53 (-50.7)	0.93 (-70.0)
9.	PPO	3.64	2.57 (-29.5)	1.97 (-45.7)
10.	ABS	3.75	2.86 (-23.2)	2.37 (-36.3)
11.	PIP	4.12	1.08 (-68.2)	0.60 (-82.4)
12.	PSB	4.72	3.32 (-29.3)	2.76 (-41.4)
13.	SMO	4.94	3.92 (-20.8)	3.50 (-29.2)
14.	PMMA	6.24	5.26 (-15.7)	4.67 (-25.2)
15.	PU	7.08	5.07 (-25.5)	4.19 (-38.4)
16.	PSBR	7.32	3.67 (-44.3)	1.87 (-71.6)
17.	PIB	7.88	4.36 (-44.7)	2.72 (-65.5)

Time For Complete Desorption and Reuse of Sensitive Equipment After Exposure. The time required for complete desorption of all carbon dioxide from the material is important to establish the waiting time before equipment can be reused after decontamination and these values are provided in Table 4. The continuous measurement of desorption allowed the best possible estimate of the time to complete desorption since the high data densities provided robust extrapolations to the time required for the material specimen to regain its original weight. The approach to this final equilibrium can be extremely slow, however, and the continuous, high data densities combined with a Fick's Law diffusion coefficient allowed extrapolation to time axis zero-mass values. An example of a Fick's Law plot for Silicone Modified Organic (SMO) polymer is shown in the Figure. The mass has been normalized from 0 to 1 on the y-axis and the square root of time is employed on the x-axis. The Fick's Law equations for the linear portion of the initial and final desorption are shown adjacent to their respective section of the plot. The thinner line denotes the extrapolated section of the curve at both extremes of the plotted data. One can see the extrapolation to zero-time on the x-axis that defines the time-to-complete-desorption that can be used to specify the time-to-reuse for decontaminated items. The time for complete desorption is reported, followed by the Fickian diffusion equation and diffusion coefficient in the last two columns of Table 4. One can see that the methodology is capable of ranking the materials based on the time required to return to the unplasticized condition after super critical carbon dioxide exposure. For the materials studied, this period ranged from about 1 to 5 days.

TABLE 4. Time for the Complete Desorption of All Carbon Dioxide from Polymeric Materials Based on a Fick's Law Extrapolation of Low Concentration Desorption Diffusion.

No.	Polymer Codes	Time for Complete Desorption hrs (days)	Fickian Diffusion Equation: Relative Mass Fraction =	Diffusion Coefficient, cm-sq/second
1.	PEP	20.6 (0.9)	$0.038 - 1.38E-4 \text{ time}(1/2)$	$5.7250E-11$
2.	PU	20.7 (0.9)	$0.050 - 1.83E-4 \text{ time}(1/2)$	$7.5549E-11$
3.	PTFEP	22.4 (0.9)	$0.083 - 2.92E-4 \text{ time}(1/2)$	$1.5448E-10$
4.	PBB	23.5 (1.0)	$0.056 - 1.91E-4 \text{ time}(1/2)$	$7.9684E-11$
5.	PSB	24.2 (1.0)	$0.042 - 1.44E-4 \text{ time}(1/2)$	$1.4751E-10$
6.	PIP	24.4 (1.0)	$0.070 - 2.38E-4 \text{ time}(1/2)$	$1.2030E-10$
7.	SMO	30.3 (1.3)	$0.209 - 6.33E-4 \text{ time}(1/2)$	$2.8522E-09$
8.	PIB	31.5 (1.3)	$0.041 - 1.21E-4 \text{ time}(1/2)$	$3.0844E-11$
9.	PEEK	38.7 (1.6)	$0.163 - 4.38E-4 \text{ time}(1/2)$	$9.4139E-11$
10.	PSBR	40.5 (1.7)	$0.081 - 2.11E-4 \text{ time}(1/2)$	$9.3694E-11$
11.	ABS	42.8 (1.8)	$0.124 - 3.15E-4 \text{ time}(1/2)$	$4.8703E-10$
12.	PI	46.4 (1.9)	$0.363 - 8.88E-4 \text{ time}(1/2)$	$1.1647E-10$
13.	PC	57.9 (2.4)	$0.119 - 2.60E-4 \text{ time}(1/2)$	$1.1518E-10$
14.	PVC	60.0 (2.5)	$0.175 - 3.77E-4 \text{ time}(1/2)$	$3.2042E-10$
15.	PDMS	83.0 (3.5)	$0.110 - 2.02E-4 \text{ time}(1/2)$	$1.1404E-10$
16.	PPO	111.3 (4.6)	$0.124 - 1.96E-4 \text{ time}(1/2)$	$5.9724E-11$
17.	PMMA	130.1 (5.4)	$0.199 - 2.90E-4 \text{ time}(1/2)$	$1.6240E-10$

Indentation Hardness. Chemical exposure often influences the surface properties of materials that are critical to their performance. Indentation hardness is one of the most important of these surface properties and the values before versus after exposure were measured and are documented in Table 5. About a third of the materials exposed to supercritical carbon dioxide showed surface hardening of about 1 to 3 %.

Another one-third experienced surface softening of over ca 1%. Note that the measurement shows the relatively low level of surface change after the plasticizing supercritical fluid had completely desorbed. The methodology was capable of ranking the materials based on these longer term indentation effects.

TABLE 5. Indentation Hardness Changes to Polymeric Materials After Exposure to Supercritical Carbon Dioxide, Followed by Complete Desorption: Exposed to 1400 psig at 50 degrees C for 15 Minutes

No.	Polymer Codes	Scale	Initial	Final	Change, %
1.	PSB	Shore D	63.6	45.8	-28.0
2.	PVC	Shore D	73.4	71.5	-2.6
3.	PMMA	Shore D	82.0	81.0	-1.2
4.	PC	Shore D	76.9	76.1	-1.0
5.	PTFEP	Shore A	91.7	91.2	-0.5
6.	PI	Shore D	82.5	82.2	-0.4
7.	PU	Shore A	96.9	97.0	0.1
8.	PEP	Shore A	93.6	93.9	0.3
9.	PPO	Shore D	76.2	76.6	0.5
10.	SMO	Shore A	58.6	58.9	0.5
11.	PEEK	Shore D	76.4	77.0	0.8
12.	ABS	Shore D	72.6	73.4	1.1
13.	PSBR	Shore A	85.8	87.1	1.5
14.	PDMS	Shore A	63.9	64.9	1.6
15.	PIB	Shore A	66.2	67.7	2.3
16.	PIP	Shore A	66.9	68.7	2.7
17.	PBB	Shore A	65.9	67.8	2.9

CONCLUSIONS

A methodology was developed and applied for evaluation of desorption diffusion of decontamination extractants such as supercritical fluids and fluorocarbons. The instrumentation and methods were capable of ranking polymeric materials based on interaction with supercritical carbon dioxide for several types of measurements. These measurements included: sorption, corrected for fraction of polymer additives extracted; sorption, corrected for extrapolation to the end of decompression; time for complete desorption to the initial weight; low-concentration diffusion coefficient; and change in surface indentation hardness.

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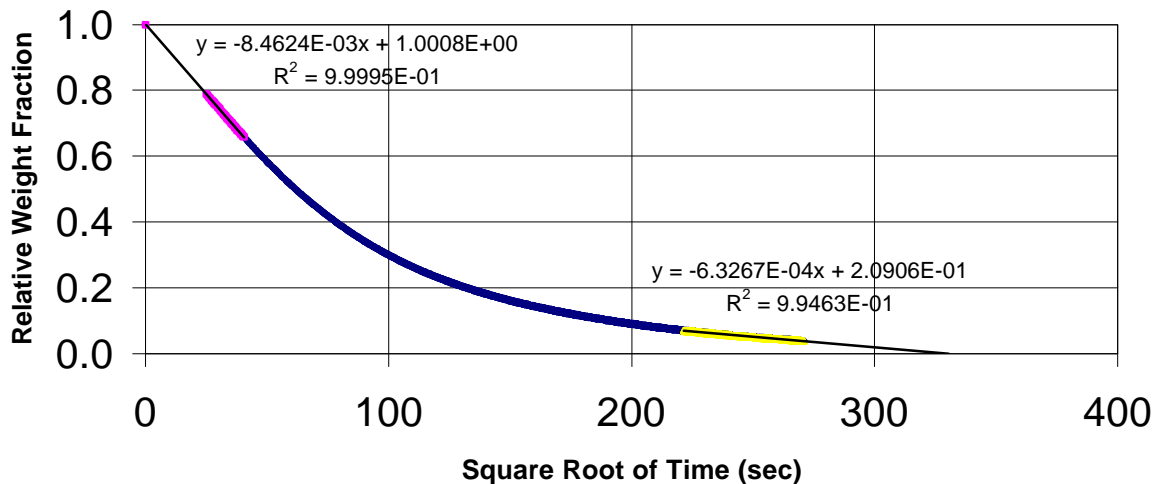


Figure. Desorption Plot for Determination of Low Concentration Diffusion Coefficient for a Fick's Law Calculation of Time-to-Complete-Desorption (Polymeric Material: SMO).