Absorption of Low Molecular Weight Solutes into Polyurethane in Supercritical Carbon Dioxide

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ABSTRACT: Absorption of a series of low molecular weight solutes into polyurethane was investigated in supercritical carbon dioxide with different conditions. The effect on the amount of solutes absorbed in polyurethane due to these factors such as pressure, temperature, absorption time, decompression time, the character of solutes, and the amount of cosolvent was examined by a gravimetric method. The absorption mechanism was discussed. The desorption of solutes in polyurethane showed a dependence on the logarithm of time. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 3162–3168, 2000

Key words: supercritical carbon dioxide, polyurethane, absorption

INTRODUCTION

Applications of supercritical fluids, particularly supercritical carbon dioxide (SC-CO_2), have received considerable attention during the past 20 years, not only because of the inherent potential of supercritical fluids themselves, but also of an environmentally benign alternative to organic solvents.[1,2] SC-CO_2 has a critical temperature of 31.06°C and a critical pressure of 7.38 MPa. It offers many advantages including low human toxicity, natural occurrence, low cost, and ready availability. Therefore, SC-CO_2 has been widely used in extraction, purification, chromatography, and reaction processes.[3,4]

It has been found that CO_2 accelerates the absorption of many low molecular weight solutes into a number of polymers. This effect is partly due to the high diffusivity, low surface tension, and plasticizing action of compressed CO_2 in poly-

mers. Upon release of the pressure, absorbed CO_2 rapidly diffuses out from the polymer while other compounds desorb more slowly.[5] The earlier reports show that many substances such as fragrances, pest-control agents, pharmaceutical drugs,[6–8] organometallic compounds,[9,10] inorganic additives,[11–13] and monomers,[14] can be absorbed in a polymers by exposing the polymer to SC-CO_2. The absorption of low molecular weight solutes into polymer offers considerable possibilities for modification of specific polymer properties and preparation of materials. Though there are so many reports about absorption of solutes into polymers, the amount of solutes absorbed in polymer with these factors such as the temperature, pressure, absorption time, decompression time, the character of solutes, and the amount of cosolvent, has not been completely addressed. However, it is important to understand the effects on absorption due to these factors for it will favor enhancement and control the amount of solute absorbed in polymer. Polyurethane, as an amorphous polymer, has good response to SC-CO_2. So it can be used as absorbent to absorb solutes. Moreover, much of the recent research has found that cosolvents usually produce much larger solubility of solutes in SC-CO_2. The cosolvent has
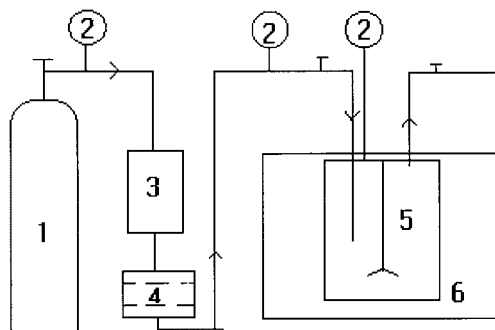
Figure 1 Experimental system. (1) High pressure steel cylinder, (2) manometer, (3) condenser, (4) high pressure pump, (5) autoclave, and (6) heating furnace.

been used in the supercritical fluid extraction process to enhance the solubility of solute,[15] but it is seldom used in supercritical absorption process, it may be expected to show a special effect on absorption.

EXPERIMENTAL

Materials

Polyurethane (PU, Bagflex 50T) is the product of Bayer Chemical Corp. of German. The carbon dioxide gas (99.9% purity) used in all experiments was purified by molecular sieve. The solutes include thymol (C.P.), benzyl carbinol (BC, C.P.), benzoic acid (BA, C.P.), ethyl alcohol (ethanol, A.R.), 2-propanol (A.R.), butanol (A.R.), amyl alcohol (C.P.), hexanol (C.P.), octanol (C.P.), acetone (C.P.), ethyl acetate (C.P.), and anisole (C.P.).

Preparation of Polyurethane Samples

Polyurethane was prepared into sheets by compression molding with a planet vulcanizing machine at 170°C. The sheets were cut out into the size of 1×4 cm to have uniform surface area for all the samples.

Absorbing Experiments

The surface of PU sheets was cleaned with ethyl alcohol before absorption. The absorption was performed in a system comprised of a 0.1 L, high-pressure equipment described in the chart (Fig. 1). PU and solute were placed into the autoclave and a glass net was used to prevent solutes coming directly into contact with PU. The average weight of PU used to absorb thymol was 0.505 g and the average weight of other PU is 0.495 g. After absorption, the weight of PU was monitored gravimetrically (by taking the weights up to 0.1 mg) at once, and then did it again at different time intervals. The amount of solutes absorbed in PU was decided when the weight loss of PU became much slower or virtually stops. The experiments were repeated twice at the same condition, and the reported data was an average of two values, with a standard deviation of 2%. The PU after absorption were stored in cleaned, dust-free room at temperature (23~26°C), relative humidity (65°70%).

RESULTS AND DISCUSSION

A systematic study to evaluate the effect on the amount of solutes absorbed in PU due to these factors such as pressure, temperature, absorption time, decompression time, the character of solutes, and the amount of cosolvent had been undertaken by a simple gravimetric method.

The Effect of Absorption Condition

Under CO_2 pressure, the polymer absorbs solutes and its weight will be changed. The contribution

Table I   The Amount of Solute (%) Absorbed in PU with Temperature and Pressure[a]

			Amount of Solute (%) Absorbed in PU					
			40°C			60°C		
Solute	Mass (g)	Thickness of PU (mm)	8.0 MPa	10.0 MPa	12.0 MPa	8.0 MPa	10.0 MPa	12.0 MPa
CO_2	—	1.0	3.7	6.8	5.0	2.0	—	—
Thymol	0.4	1.1	48.4	32.4	20.7	48.6	51.7	42.2
BC	0.51	1.0	19.9	41.1	24.4	41.2	53.6	59.3
BA	0.50	1.0	5.6	16.9	14.2	13.6	26.1	34.3

[a] Absorption time = 4 h; decompression time = 1 h. Mass is the amount of solute placed in the autoclave at the beginning of experiment.

Table II   The Amount of Solute (%) Absorbed in PU with Temperature and Absorption Time[a]

Solute	Mass (g)	Thickness of PU (mm)	Amount of Solute (%) Absorbed in PU					
			40°C			60°C		
			1 h	2 h	4 h	1 h	2 h	4 h
CO_2	—	1.0	3.9	3.6	3.7	1.8	1.3	2.0
Thymol	0.40	1.1	28.3	35.0	48.4	28.0	37.6	48.6
BC	0.51	1.0	13.1	19.4	19.9	17.5	25.2	41.2

[a] Pressure of SC—CO_2 = 8.0 MPa. Decompression time = 1 h.

to the weight changes is as follows: (a) the carbon dioxide and solutes are absorbed by the polymers, which leads to an increase in the weight of the samples; and (b) either the polymers or some agents, such as remains of monomers, oligomers, additive, or placticizers in the polymers are dissolved or extracted from polymer, which leads to a decrease in the weight of the samples.[16] However, when the pressure is released, CO_2 is rapidly desorbed and the weight loss of PU becomes much slower or virtually stops after the CO_2 has largely escaped. A series of alcohol are absorbed into PU to examined the contribution of second case and the results show that second case contributes to the weight changes less than 1.6%. So the remaining weight gain of PU above its initial weight is a close approximation of the amount of solutes present in PU at the end of the absorption.

The effect of absorption conditions on the amount of solutes absorbed in PU can be ascertained from the data noted in Tables I–IV. The results indicate that the change of the amount of solutes absorbed in PU has a similar trend for all the different solutes. The data of Table I is the effect of pressure and temperature. The result

show that the amount of solutes absorbed in PU increases with temperature at a constant pressure while it initially increases with pressure and beyond a certain pressure of SC-CO_2 starts to decrease at a constant temperature. The data of Table II and Table III is the effect of absorption time. The amount increases with absorption time at low pressure (8.0 MPa) for the rate of swelling of PU is slow at low pressure, but has slight change at high pressure (12.0 MPa).The data of Table IV is the effect of decompression time. The decompression time has insignificant effects on the weight changes of PU after absorbing those solutes with a large specific evaporation velocity.

The Effect of the Character of Solutes

The weight change of PU after absorption depend on the character of solutes, which is shown in Table V–VII. One character of the solute is the solubility parameter δ, which is defined by the square of the cohesive energy density. Generally, the solubility parameter of solute is closer to that of the polymer—the interaction force between them is stronger, which benefits the absorption of

Table III   The Amount of Solute (%) Absorbed in PU with Pressure and Absorption Time[a]

Solute	Mass (g)	Thickness of PU (mm)	Amount of Solute (%) Absorbed in PU					
			8.0 MPa			12.0 MPa		
			1 h	2 h	4 h	1 h	2 h	4 h
CO_2	—	1.0	3.9	3.6	3.7	4.2	4.8	5.0
Thymol	0.4	1.1	28.3	35.0	48.4	20.2	22.4	20.7
BC	0.51	1.0	13.1	19.4	19.9	25.8	23.3	24.4
BA	0.50	1.0	6.3	6.3	5.6	14.9	14.1	14.2

[a] Temperature of SC—CO_2 = 40°C. Decompression time = 1 h.

Table IV   Weight Changes of PU After Absorbing Solute with Decompression Time[a]

Solute	Mass (g)	SEV[b]	0.2 h	0.5 h	1 h
			Weight Change (%) of PU		
Ethanol	0.79	203	21.3	20.6	19.1
Ethyl acetate	0.90	525	14.5	15.0	15.4
Acetone	0.79	720	11.1	11.4	10.9

[a] Pressure = 8.0 MPa; temperature = 40°C; absorption time = 2 h; thickness of PU = 1.0 mm.
[b] SEV: specific evaporation velocity; SEV of butyl acetate = 100.

solute into polymer.[7,17] However, the principle is not consistent with our results (Table V), for example, the δ values of hexanol and acetone are more close to the one of PU [δ = 20.4 $(J/cm^3)^{1/2}$] than that of butyl alcohol, but the butyl alcohol shows greater absorption amount. In addition, hexanol and acetone have the same δ value, but hexanol is absorbed more than acetone, which indicates that the amount of solute absorbed in polymer also depends on its structural character. Furthermore, the aromatic compounds have a higher degree of absorption in PU than the aliphatic compounds (Table VI). Table VII showed that the solubility of solutes in SC-CO_2 also effected the absorption because the weight changes of PU did not increase with the amount of solute placed in the autoclave at the beginning of experiment.

The Effect of Cosolvent

Much of the recent research has been shown that cosolvents usually produce much larger solubility

of solutes in SC-CO_2 and it has been used in supercritical fluid extraction process to enhance the solubility of solute.[15] However, the cosolvent used in supercritical absorption process has seldom been addressed. The cosolvent usually can not only enhance the solubility of solutes in SC-CO_2, but also may be expected to play two roles: (1) the cosolvent in polymer will increase the amount of solutes absorbed in polymers for cosolvent has an interaction with solutes; (2) the pure cosolvent or the one in SC-CO_2 will decrease the absorption amount.

Ethyl alcohol was used in the experiment as the cosolvent to evaluate the effect of cosolvent on the amount of solutes absorbed in PU. Experiment indicates that ethyl alcohol has largely escaped after 48 h, so when the pressure is released, CO_2 and ethyl alcohol are rapidly desorbed, and the weight loss of PU becomes much slower or virtually stops after 48 h. The remaining weight gain of PU above its initial weight is a close approximation of the amount of solutes present in the sample at the end of the absorption. The results of the effect of cosolvent are shown in Table VIII. With the exception of absorption of thymol, the amount of solute absorbed in PU initially increases with the amount of ethyl alcohol at the same absorption conditions and beyond a certain amount of ethyl alcohol starts to decrease. The result indicates that ethyl alcohol can enhance or control the absorption amount of some solutes absorbed in polymer with relatively moderate temperature and pressure of SC-CO_2.

Desorption of CO_2 and Solutes

The absorption/dissolution of CO_2 and solutes in polymers is indirectly indicated by the weight

Table V   Weight Change for 1.0 mm Thick PU After Absorbing Aliphatic Compounds with Pressure[a]

Solute	Mass (g)	δ $[(Jcm^{-3})^{1/2}]$	8.0 MPa	9.0 MPa	10.0 MPa	12.0 MPa
			Weight Change (%) of PU			
CO_2	—	12.3	3.4	—	7.6	4.4
Ethanol	0.79	26	19.1	17.5	13.0	10.2
2-propanol	0.78	23.4	19.4	15.0	12.0	10.1
n-Butanol	0.81	23.3	22.8	18.2	13.2	10.1
n-Amyl alcohol	0.81	21.7	20.6	19.9	15.1	11.9
n-Hexanol	0.82	20.5	17.7	19.3	12.0	10.2
n-Octanol	0.82	19.8	14.1	16.7	14.1	9.4
Acetone	0.79	20.5	10.9	7.0	5.5	—
Ethyl acetate	0.90	18.4	15.4	10.8	9.5	6.2

[a] δ: Solubility parameter; temperature = 40°C; absorption time = 2 h; decompression time = 1 h.

Table VI Weight Change for PU After Absorbing Aromatic Compounds with Pressure[a]

| Solute	Mass (g)	Thickness of PU (mm)	Weight Change (%) of PU		
			8.0 MPa	10.0 MPa	12.0 MPa
Thymol	0.4	1.1	52.8	37.9	23.8
Benzyl carbinol	0.51	1.0	25.2	47.6	27.1
Benzoic acid	0.50	1.0	9.9	22.7	19.6
Anisole	0.50	1.0	43.4	15.0	13.8

[a] Temperature = 40°C; absorption time = 4 h; decompression time = 1 h.

change of polymers after absorption. In accordance with Fickian diffusion kinetics, this changes vs the square root of desorption time ($t^{1/2}$) is initially linear.[7,18] But in our experiments, this change in mass with time shows a dependence on the logarithm of time (see Figs. 2 and 3), which is consistent with the result of Yeong-Tarng Shieh.[19]

Mechanism of Absorption

Two possible mechanisms by which CO_2 promotes polymers absorbing solutes were introduced in other works. One is that the solute dissolves in the CO_2, then the polymer is swollen by the CO_2 solution of the solute.[20] However, CO_2-miscible butanol and octane are not absorbed by CO_2-swollen PVC, while the slightly CO_2-soluble naphthalene is highly absorbed,[7] so the mechanism is not completely reasonable. Another[7] is the CO_2-assisted impregnation process, which involves the approach toward an equilibrium distribution of three components (polymer, solute, and CO_2). The absorption process can be considered as the partitioning of the solute between these phases (CO_2-swollen polymer phase and pure CO_2 phase). The amount of solute absorbed by the polymer will depend on the relative interaction of the solute with the polymer and CO_2 phase. In this light, the amount of solute absorbed by the polymer will

decrease if the pressure of SC-CO_2 is increased or there is the existence of new phase such as ethyl alcohol. However, the second mechanism does not seem consistent with this case that solute and polymer is not in contact directly or the amount of solute placed in the autoclave at the beginning of experiment is much higher than its solubility limit. Taking into account our results, the following absorption process is presented:

$$\text{Solute (A)} \xrightarrow{K_D} \text{SC-CO}_2\text{(A)} \underset{}{\overset{K_P}{\rightleftharpoons}} \text{Polymer(A)}$$
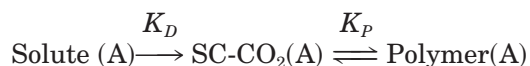
In accordance with the absorption process, the amount of solute absorbed in polymer will depend on the dissolution constant (K_D) and the partition coefficient (K_P) of solute between these phases (CO_2-swollen polymer phase and pure CO_2 phase). If solute is favored to dissolve into SC-CO_2, that is, K_D is very large, or if K_P is very small, the absorption process will change into mechanism two. It is why CO_2-miscible butanol and octane are not absorbed by CO_2-swollen PVC. However, if K_P is very large, even if the solute is slightly soluble in SC-CO_2, it will be highly absorbed, for example, naphthalene is highly absorbed in CO_2-swollen PVC. In addition, when the amount of solute placed in the autoclave at the

Table VII Weight Change for 1.0 mm Thick PU with the Amount of Solute[a]

Amount of Solute (mL)	Weight Change (%)					
	Ethanol	2-Propanol	*n*-Butanol	*n*-Amyl Alcohol	*n*-Hexanol	*n*-Octanol
1.0	19.1	19.4	22.8	20.6	17.7	14.1
2.0	17.8	18.7	19.5	19.1	16.9	15.5

[a] Pressure = 8.0 MPa; temperature = 40°C; absorption time = 2 h; decompression time = 1 h.

Table VIII   The Amount of Solute Absorbed in PU with the Amount of Ethyl Alcohol[a]

Solute	Mass (g)	Thickness of PU (mm)	Amount of Solute (%) Absorbed in PU with the Amount of Ethyl Alcohol (g)				
			0	0.08	0.16	0.24	0.40
Thymol	0.40	1.1	48.4	37.8	21.4	25.9	27.3
BC	0.51	1.0	19.9	27.2	28.8	29.4	26.7
BA	0.50	1.0	5.6	10.1	14.1	21.1	18.3

[a] Pressure = 8.0 MPa; temperature = 40°C; absorption time = 4 h; decompression time = 1 h.

beginning of experiment is much higher than its solubility limit in SC-CO_2, its amount absorbed in polymer will depend on these constants (K_D and K_P). The constant K_D increases with pressure, but the constant K_P decreases with pressure, so the amount of solute absorbed in polymer initially increases with pressure and beyond a certain pressure starts to decrease. K_D and KP both increase with temperature, so the amount of solute absorbed in polymer increases with temperature. At constant pressure and temperature, K_D and K_P are constant, so the amount of solute absorbed in PU does not increase with the amount of solute placed in the autoclave at the beginning of experiment (Table VII).

The cosolvent may be expected to have three effects on the absorption. First, it can enhance the solubility of solutes in SC-CO_2, that is, enhance KD. Second, cosolvent can be absorbed into polymer, and the one absorbed in polymer will show an interaction with solutes and increase the partitioning of solutes in polymers, that is, it can increase K_P. Third, the pure cosolvent or the one in SC-CO_2 will decrease K_P. Due to these three effects, the amount of benzyl carbinol and benzoic

acid absorbed in PU initially increases with the amount of cosolvent at the same absorption conditions and beyond a certain amount of cosolvent starts to decrease.

CONCLUSIONS

1. The amount of solutes absorbed in PU increases with temperature at a constant pressure while it initially increases and beyond a certain pressure of SC-CO_2 starts to decrease with pressure at a constant temperature.
2. The higher pressure, the shorter the absorption time to equilibrium state.
3. The decompression time has insignificant effects on the weight changes of polyurethane.
4. PU is more favored to absorb aromatic compounds than aliphatic compounds.
5. Solubility of solutes in SC-CO_2 is also an important factor that effected the absorption.
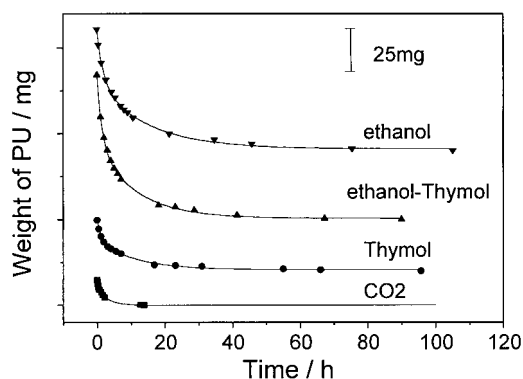6. The amount of benzyl carbinol and benzoic

Figure 2   Weight change of PU after absorbing thymol, alcohol, and CO_2 for 2 h in 40°C, 8.0 MPa SC-CO_2.
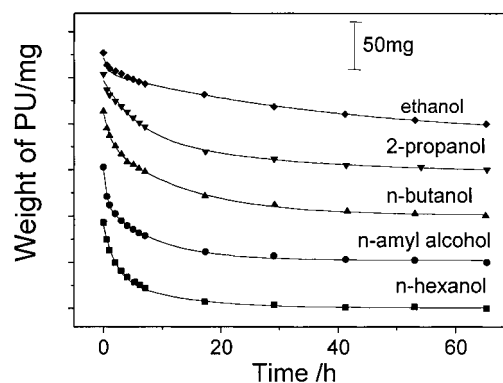

Figure 3   Weight change of PU after absorbing a series of alcohol for 2 h in 40°C, 8.0 MPa SC-CO_2.

acid absorbed in polyurethane initially increases with the amount of cosolvent(ethyl alcohol) at the same absorption conditions and beyond a certain amount of cosolvent-(ethyl alcohol) starts to decrease.

7. The weight changes of polyurethane after absorption in mass with time show a dependence on the logarithm of time.

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