

Application of Compressed Carbon Dioxide in the Incorporation of Additives into Polymers

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SYNOPSIS

It has been found that carbon dioxide remarkably accelerates the absorption of many low molecular weight additives into a number of glassy polymers. This effect is due to the high diffusivity, solubility, and plasticizing action of compressed CO₂ in polymers. The transport of CO₂ and the effects of CO₂ pressure on the transport of other low molecular weight compounds in polymers have been studied by a simple gravimetric method: Polymer film samples were contacted in a pressure vessel with compressed CO₂, or with CO₂ plus various organic liquids or solids, and the sample weight was followed with a fast-response electronic balance during subsequent desorption at atmospheric pressure. Upon release of the pressure, absorbed CO₂ rapidly diffuses from the polymer, while the other compounds desorb much more slowly. The amount of additive absorbed can be determined from the plateau weight of the sample after most of the CO₂ has escaped. Extensive kinetic and equilibrium data are reported for the model system poly(vinyl chloride)/dimethyl phthalate/CO₂, and a number of other examples of CO₂-assisted additive absorption are given. This "infusion" process, in effect, amounts to the partitioning of the additive between the CO₂- and polymer-rich phases; consequently, the relative solubility of the additive in CO₂ and in the polymer is a major factor governing the amount of additive absorbed. Data reported here illustrate the generality and potentially broad applicability of CO₂-assisted polymer impregnation.

INTRODUCTION

Recent studies in this laboratory¹ and elsewhere²⁻⁸ have demonstrated that carbon dioxide under high pressure shows an unusual combination of effects in its interactions with high polymers: At temperatures and pressures approaching its critical conditions, $T_c = 31^\circ\text{C}$ and $P_c = 73$ atm, the solubility of CO₂ in many polymers is as high as that of typical organic liquid swelling agents, ranging from around 10 to more than 30% by weight. Carbon dioxide also has a strong plasticizing effect; concentrations of 8–10 wt % depress the glass transition temperature of

common glassy polymers from the 80–100°C range to below room temperature. Although these attributes of CO₂/polymer systems are typical of organic liquid/polymer systems, CO₂ has the high diffusivity in polymers that is characteristic of gases of similar molecular size.

Other recent works^{9,10} have reviewed the effects of the molecular size of the diffusing species and the state of the polymer on the kinetics of transport of small molecules in polymers. To illustrate the major trends, diffusivities, D , of a number of gases, vapors, and liquids in both glassy (unplasticized) and rubbery (plasticized) poly(vinyl chloride) are plotted vs. molecular diameter in Figure 1.¹⁰ In the glassy state, D is an extremely strong function of the molecular size of the penetrant, decreasing by roughly 10 orders of magnitude from the small fixed gases, He and H₂, to solvent molecules such as *n*-C₆H₁₄ and CCl₄. In the rubbery state, the dependence of D on molecular size is more moderate. Consequently, the difference in D between the glassy and rubbery states increases sharply with increasing size of the

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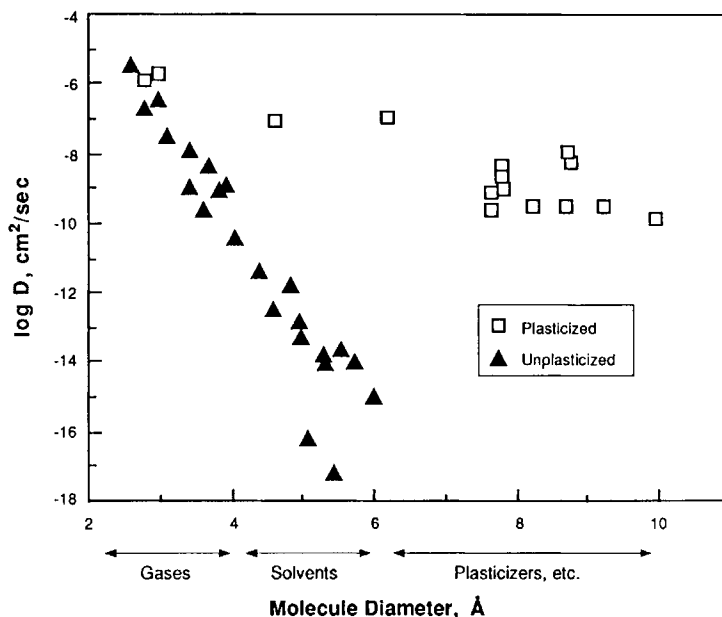


Figure 1 Diffusivities of penetrants in rigid and plasticized PVC vs. molecular diameter.

diffusing species. Thus, for the small gases, D may increase by about one order of magnitude upon plasticization, whereas for common solvents, the increase may be by a factor of 10^6 or 10^8 , and for plasticizers and other polymer additives, it may be still greater.

Consideration of the trends illustrated in Figure 1, in combination with the high solubility, diffusivity, and plasticizing action of CO_2 , led us to suggest that compressed CO_2 could be useful as a temporary plasticizer to facilitate the absorption of additives into glassy polymers.¹¹ The concept was to expose a polymer sample simultaneously to an additive substance and to CO_2 under high pressure; the CO_2 would rapidly diffuse into the polymer, plasticizing it and accelerating the absorption of the additive. When the CO_2 pressure was released, the gas would rapidly diffuse out of the polymer, deplasticizing it and sharply reducing the additive diffusivity; the additive would then be left in the polymer to desorb at the slow rate governed by its diffusivity in the CO_2 -free polymer. We have applied the terms "CO₂-assisted impregnation" or simply "infusion" for brevity in referring to this process.

In this paper, we describe a simple gravimetric procedure that provides transport kinetics and solubility equilibrium data for both polymer/ CO_2 binary systems and polymer/ CO_2 /additive ternary systems, and we present results demonstrating the efficacy and scope of the CO_2 -assisted impregnation process. Some of the complexities and limitations

of the process are also illustrated and explanations are suggested.

In the course of this work, a patent on a very similar impregnation process was published.¹² The present paper shows that the acceleration of absorption is much more pronounced in glassy polymers than in the rubbery and semicrystalline polyolefins and olefin copolymers cited in this patent's examples.

EXPERIMENTAL

The gravimetric procedure used here involves sorption of CO_2 , or CO_2 plus an additive, into polymer film or sheet samples in a simple pressure vessel, followed by rapid venting and transfer of the samples to a balance for recording weight changes during desorption at atmospheric pressure. All experiments were carried out at 25°C , and pressures ranged up to the saturated vapor pressure of CO_2 : 6.53 MPa (950 psia). Samples included a wide range of polymer types, which were compression-molded to thicknesses from 0.1 to 1 mm.

Polymer/ CO_2 Binary Systems

The procedure for CO_2 sorption experiments is illustrated schematically in Figure 2. A preweighed polymer sample (20–200 mg) was placed in a 100 mL pressure vessel fitted with a pressure gauge,

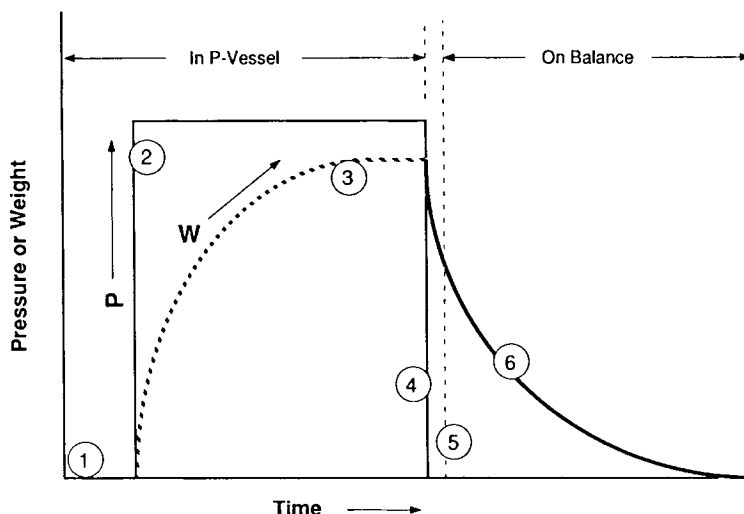


Figure 2 Schematic curves for pressure and sample weight vs. time during sorption/desorption experiments on polymer/CO₂ binary systems: ① load film sample and evacuate; ② apply CO₂ pressure; ③ polymer absorbs CO₂; ④ rapidly release pressure; ⑤ transfer sample to balance; ⑥ record weight during desorption.

valve, and a screw closure that could be opened quickly. The vessel was evacuated, then filled to the desired sorption pressure from a cylinder of liquid CO₂ and left at this pressure for an appropriate sorption period. Experiments were run at various pressures, sorption times, and sample thicknesses for each polymer studied. At the end of the sorption period, the CO₂ pressure was rapidly vented to atmospheric, the vessel opened, and the sample quickly placed on the pan of a fast-response electronic digital balance readable to 0.00001 g (Mettler AE163). Using a computerized data acquisition system, sample weights during desorption were recorded at intervals as short as 5 s beginning within 10–20 s after venting the vessel.

Plots of sample weight vs. the square root of desorption time were initially linear, in accord with Fickian diffusion kinetics. The diffusivity of CO₂ was readily estimated from the slope of these plots and the initial sample thickness. Linear extrapolation to zero desorption time gave the weight of CO₂ in the sample at the end of the sorption period. Repeated experiments at a series of sorption times then defined the absorption kinetics, and the attainment of sorption equilibrium was evidenced by reaching a constant level of CO₂ uptake. Experiments at varied pressures provided the sorption isotherms, i.e., the equilibrium solubility of CO₂ in the polymer as a function of CO₂ pressure. Thus, a complete description of both the transport kinetics and the equilibrium solubility of high-pressure CO₂ in a polymer could be developed from gravimetric data

obtained only during the desorption process at atmospheric pressure.

Polymer/CO₂/Additive Ternary Systems

Experiments on ternary systems closely paralleled those on the binaries with only these changes in procedure: The liquid or solid additive was charged to the pressure vessel, along with the polymer sample, before closing, evacuating, and pressurizing with CO₂, and the polymer and additive were in direct contact to minimize any mass-transfer barrier. The amount of the additive, in most cases, was in excess of its expected uptake by the polymer. When the vessel was opened, after the period of absorption under CO₂ pressure, the unabsorbed excess additive was wiped or blotted from the surface of the polymer sample. This step added only a few seconds to the time between opening the vessel and placing the sample on the balance to record weight during desorption.

The sorption/desorption sequence for the ternary systems is shown schematically in Figure 3. While under CO₂ pressure, the sample absorbs both CO₂ and, presumably, some of the additive, at an undetermined rate. When the pressure is released, CO₂ is rapidly desorbed, as in the binary case. But now, extrapolation of the initially linear weight vs. $t^{1/2}$ plot for desorption gives the sample weight gain due to sorption of both components. Because of the much higher diffusivity and volatility of CO₂ compared to

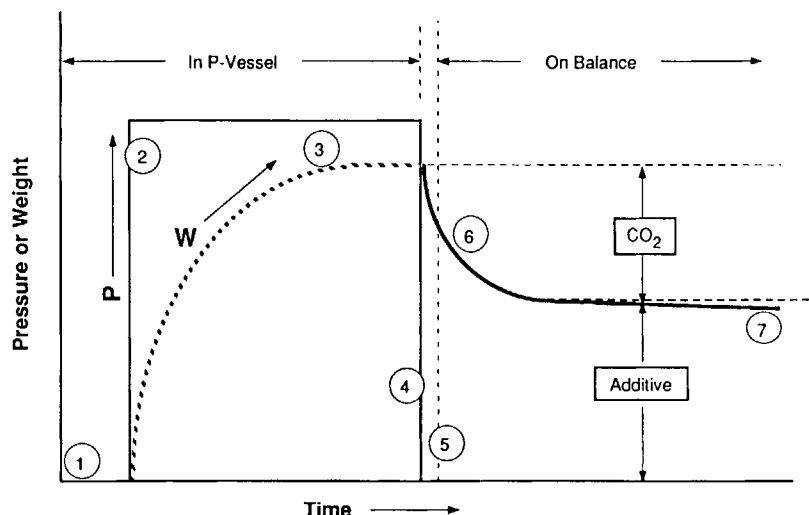


Figure 3 Schematic curves for pressure and sample weight vs. time during sorption/desorption experiments on polymer/ CO_2 /additive ternary systems: ① load polymer film sample and additive and evacuate; ② apply CO_2 pressure; ③ polymer absorbs CO_2 and additive; ④ rapidly release pressure; ⑤ transfer sample to balance to record weight; ⑥ CO_2 is rapidly desorbed; ⑦ additive desorbs very slowly.

the typical additives, the desorption of CO_2 is much faster than that of the additive; the time scale for CO_2 desorption can be estimated from binary experiments on samples of the same polymer at similar thickness. When the CO_2 has largely escaped, the weight loss becomes much slower or virtually stops; the remaining weight gain of the polymer, above its initial weight, is then a close approximation of the amount of additive present in the sample at the end of the absorption period. Just as in the CO_2 /polymer binary systems, the absorption kinetics and equilibria of the additive in the CO_2 -swollen polymer at various CO_2 pressures can be defined by a series of experiments using varied absorption times.

RESULTS AND DISCUSSION

Polymer/ CO_2 Systems

Results of our gravimetric desorption experiments on the interactions of compressed CO_2 with a number of polymers have been reported elsewhere.¹ Both equilibrium solubility and kinetic data provide evidence of the plasticization of most glassy polymers by CO_2 ; illustrative data are repeated here for ready reference.

Figure 4 shows the 25°C sorption isotherms, at pressures up to 6.53 MPa (950 psia, liquid CO_2), for

four common glassy polymers: poly(vinyl chloride) (PVC), polycarbonate (PC), poly(methyl methacrylate) (PMMA), and poly(vinyl acetate) (PVA). The solubility of CO_2 in all these polymers is substantial, though it varies markedly with the polymer structure. The downward curvature of the PVC and PC isotherms illustrates the "dual-mode" form typical for gases absorbed in glassy polymers. The reverse curvature for PMMA and PVA is characteristic for swelling agents in rubbery polymers and suggests that these two polymers are plasticized into the rubbery state by CO_2 at sufficiently high pressure, i.e., their glass transition temperature is depressed below 25°C by the absorbed CO_2 .

In Figure 5, D_d (mean diffusivities for desorption over the concentration interval of the experiment) of CO_2 in PVC, PMMA, cellulose acetate (CA), and polystyrene (PS) at 25°C are plotted vs. the initial CO_2 concentration. At low concentrations, there are substantial differences in CO_2 diffusivity between these polymers; the order of D_d , $\text{PS} \gg \text{PVC} > \text{PMMA}$, is the same as previously found for organic vapors in these glassy polymers⁹ and presumably reflects differences in packing or stiffness of the polymer chains. The diffusivity of CO_2 increases with concentration in all four polymers, approaching a range of 10^{-6} to 10^{-7} cm^2/s , typical for CO_2 in rubbery polymers.¹³ The transport kinetics thus provide further evidence of the plasticizing action of CO_2 in glassy polymers.

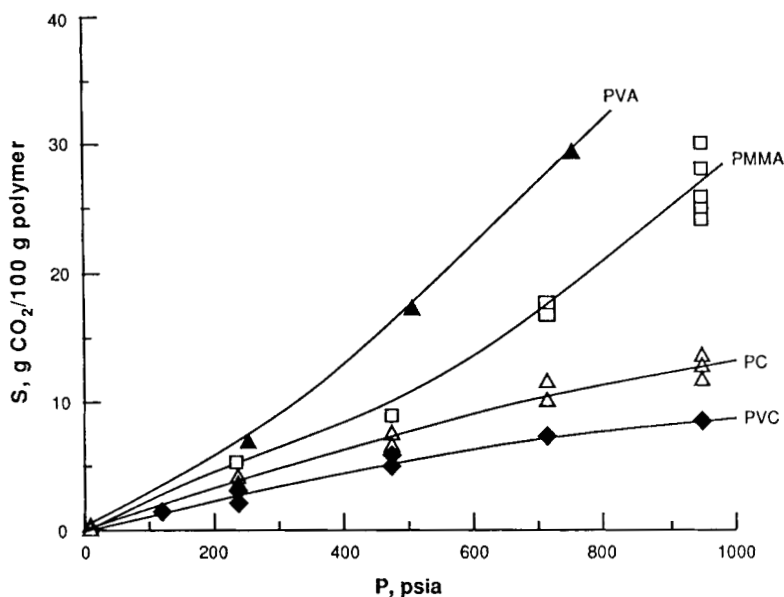


Figure 4 Sorption isotherms for CO₂ in four glassy polymers at 25°C.

The System PVC/CO₂/Dimethyl Phthalate

We have used the combination of PVC with dimethyl phthalate (DMP) as a model polymer/additive system for exploring the effects of CO₂ on the transport kinetics and equilibria of an additive in a

glassy polymer. DMP is well known to be a plasticizer for PVC, i.e., it has a substantial solubility in the polymer. From published values of the polymer/solvent interaction parameter for this pair,¹⁴ it is estimated that PVC in equilibrium with pure liquid DMP would be swollen at least 300%. The rate of

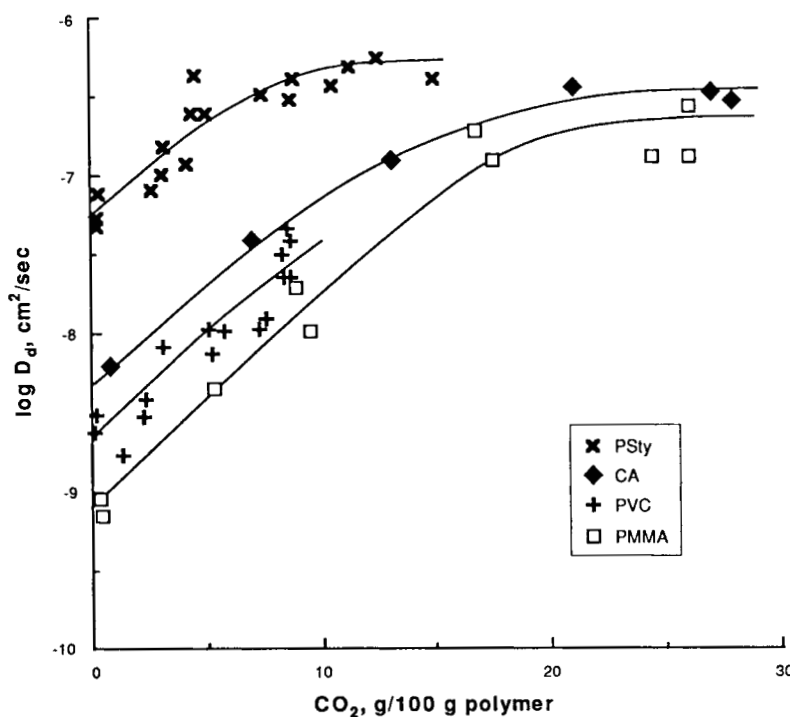


Figure 5 Diffusivity of CO₂ vs. concentration in four glassy polymers.

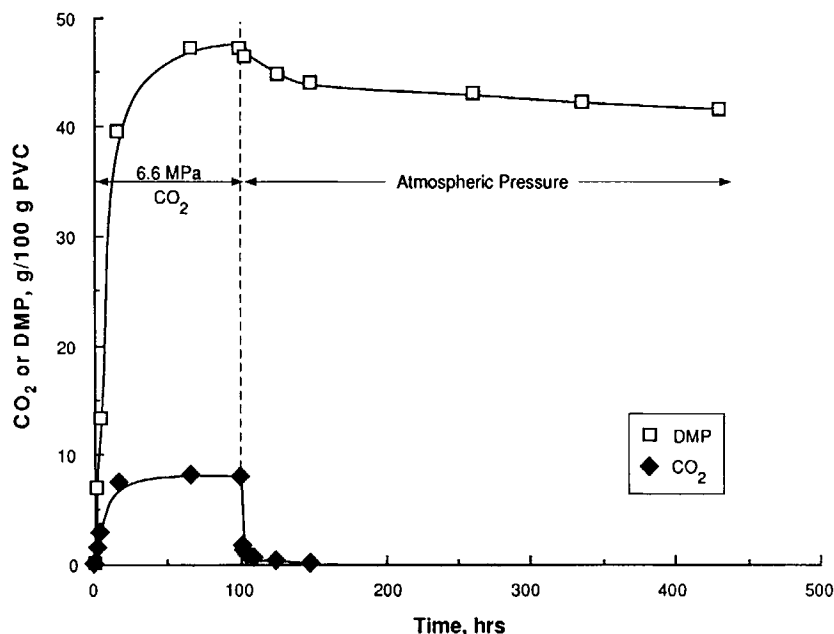


Figure 6 Sorption/desorption in CO₂/DMP/PVC system, 0.6 mm film.

absorption of DMP by PVC at room temperature, however, is extremely slow: Immersion of PVC film samples in excess DMP for times up to 64 h resulted in absorption of no more than 1 wt % of DMP. Thus, the absorption of DMP by PVC is thermodynamically favored, but kinetically limited at room temperature. DMP has limited miscibility with liquid CO₂; Francis¹⁵ reports the compositions of the two phases of the CO₂/DMP system at equilibrium at 25°C to be 94/6 and 43/57 wt % CO₂/DMP, respectively.

Results of a typical series of sorption/desorption experiments on the ternary PVC/DMP/CO₂ system are presented in Figure 6. Here, samples of 0.6 mm PVC film were exposed to an excess of DMP under 6.53 MPa (950 psia) CO₂ pressure (liquid CO₂) for times up to 64 h. Amounts of CO₂ plus DMP absorbed were determined from the sample weights at zero desorption time (extrapolated). The amount of DMP absorbed was estimated from the weight after 24 h desorption, the time for about 95% CO₂ desorption in comparable binary runs. The sorption of DMP appeared to reach an equilibrium level near 45% of the PVC weight by 64 h. After the rapid desorption of the CO₂, the data show a continued very slow weight loss attributable to desorption and evaporation of the slightly volatile DMP. Even after more than 1000 h, however, more than 80% of the absorbed DMP remained within the PVC. Clearly, the absorption of DMP was strongly accelerated by the presence of CO₂, while its slow desorption is

the normal behavior for a simple PVC/plasticizer system.

The effects of PVC film thickness and CO₂ pressure on the absorption of DMP are illustrated in Figure 7. Amounts of DMP absorbed by PVC of four different thicknesses, in the presence of CO₂ at 6.53 MPa (950 psia), are plotted vs. the square root of sorption time in Figure 7(A); the equilibrium uptake is about 45 wt % for all the films, but the time required to approach sorption equilibrium increases with film thickness. Figure 7(B) shows results of similar experiments under 3.78 MPa (550 psia) CO₂ pressure; here the approach to equilibrium is much slower, but the equilibrium uptake is substantially higher, compared to results at the higher CO₂ pressure. The shifts in sorption kinetics from apparent Fickian to non-Fickian swelling observed with changes in CO₂ activity and with changing film thickness are reminiscent of similar behaviors observed for organic solvent/PVC systems described and discussed in detail in a recent publication from our laboratory.¹⁶ Such behaviors seem typical of glassy polymer/penetrant systems when large variations in penetrant activities and sample thickness are studied.

The effect of CO₂ pressure on the kinetics of DMP absorption into PVC is further illustrated in Figure 8, where M_t/M_∞ , the fraction of equilibrium sorption, is plotted vs. $t^{1/2}/l$, with l the film thickness. Such plots are initially linear for sorption following Fickian diffusion kinetics, with slopes proportional

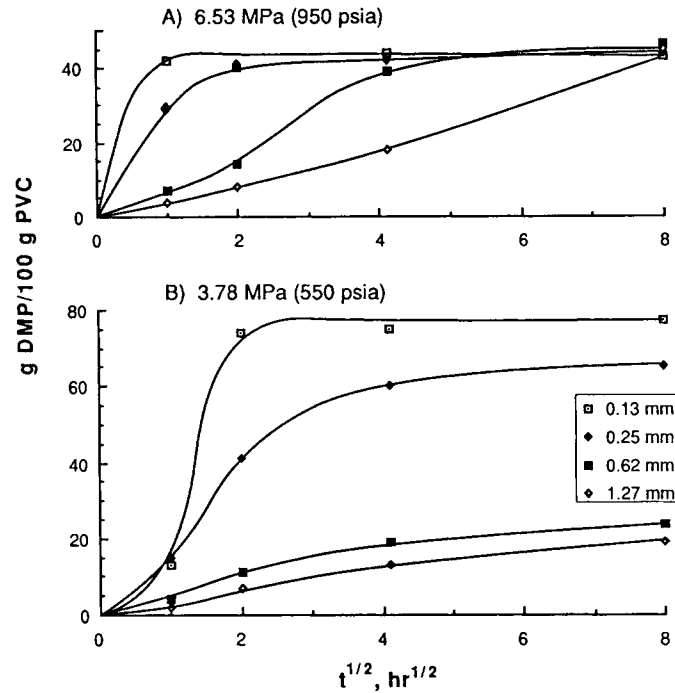


Figure 7 DMP sorption by PVC under CO₂ pressure: weight absorbed vs. $\sqrt{\text{time}}$, varied film thickness.

to $D^{1/2}$. The initial uptake data are sufficiently linear to allow estimation of apparent Fickian diffusivities for DMP in PVC at varied CO₂ pressures, with the results shown in Table I. D for DMP alone

in PVC has not been measured, but the correlation with molecular size (Fig. 1) indicates that D for DMP in unplasticized PVC would be $\leq 10^{-15}$ cm²/s. It therefore appears that the diffusivity of DMP

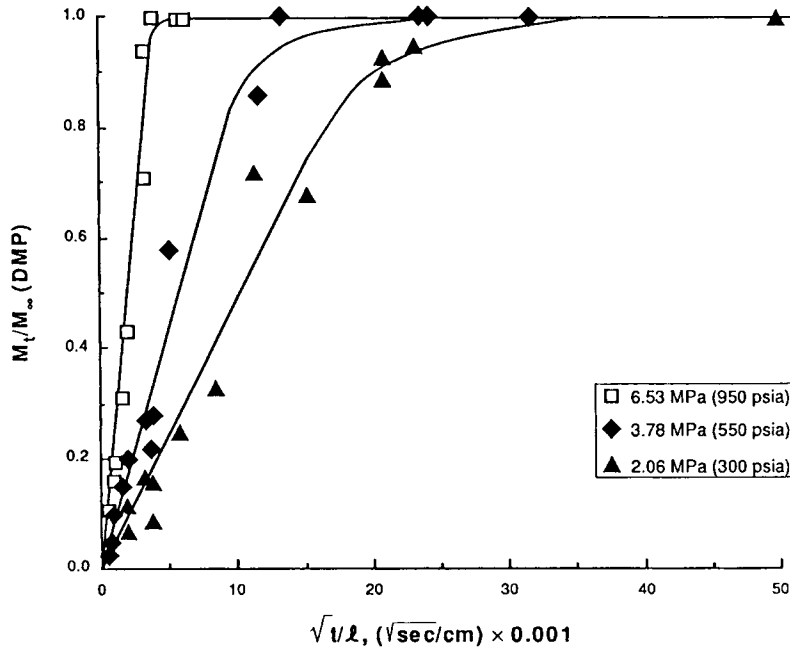


Figure 8 DMP sorption by PVC: fractional uptake, M_t/M_∞ vs. \sqrt{t}/l , at varied CO₂ pressure.

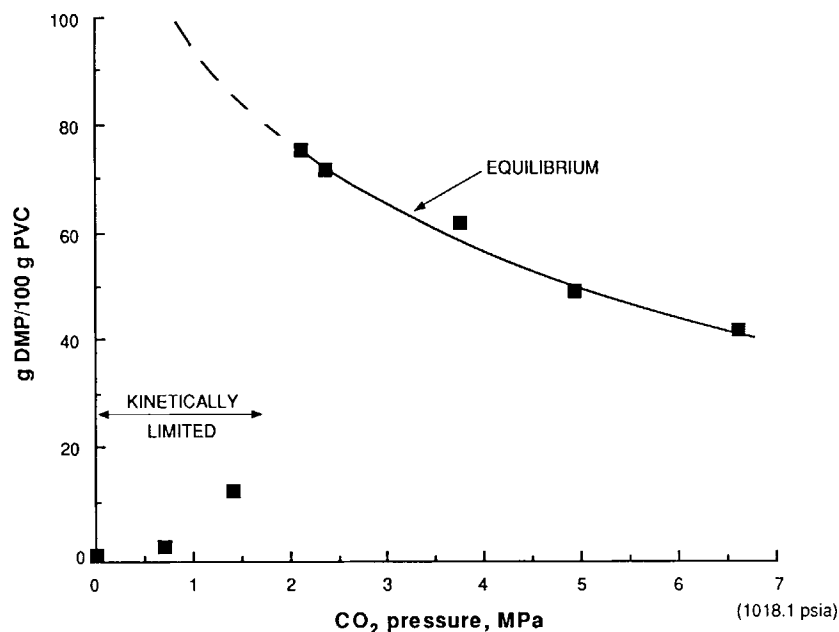


Figure 9 DMP uptake by PVC vs. CO₂ pressure; 0.1 mm film, 17 h exposure.

in CO₂-swollen PVC may be larger than that in pure PVC by a factor of at least 10⁶.

Figure 9 shows the effect of CO₂ pressure on the amount of DMP absorbed by 0.13 mm PVC films in 17 h at 25°C. The uptakes as functions of sorption time showed that equilibrium was reached in 17 h at pressures of 2.06 MPa (300 psia) and higher. At lower CO₂ pressure, however, the DMP sorption had not approached equilibrium in 17 h; hence, the observed uptake was kinetically limited. The clear trend of the equilibrium data is a decrease in the amount of DMP absorbed with increasing CO₂ pressure. The probable explanation of this effect is that increasing CO₂ pressure increases the concentration of CO₂ dissolved in the DMP, thus reducing the thermodynamic activity of the DMP in the DMP/CO₂ phase. The decrease of equilibrium concentration of DMP in PVC with increasing CO₂ pressure is thus the normal effect of decreasing DMP activity.

Table I Apparent Diffusivity of DMP in PVC at Varied Pressures of CO₂

CO ₂ Pressure (MPa)	Apparent D (cm ² /s)
0	($\ll 10^{-15}$)
1.4	1.0×10^{-11}
2.3	4.0×10^{-10}
3.8	1.3×10^{-9}
6.5	8.0×10^{-9}

A reinforcing factor may be the increasing concentration of CO₂ in the PVC; given the low solubility of DMP in CO₂, it is reasonable to expect increased CO₂ in the polymer to reduce the solubility of DMP in that phase.

Other PVC/CO₂/Additive Systems

In an effort to define, at least qualitatively, the scope, limitations, and governing parameters of the CO₂-assisted polymer impregnation process, exploratory experiments have been carried out with a variety of compounds as "additives." These have included other plasticizers, model compounds of varied chemical type, bioactive compounds for potential slow-release applications, and others. With most of the candidate additives, experiments were less extensive and systematic than with DMP, as the objective was mainly to learn what types of compounds could be infused into PVC with the help of compressed CO₂.

In one series of experiments, PVC samples from 0.1 to 1.2 mm thick were exposed for 71 h, in the presence of liquid CO₂, to each of the "additives" DMP, naphthalene, *n*-butanol, and octane. The amounts of each additive absorbed, determined from the sample weights after most of the CO₂ had desorbed, are listed in Table II as percent of the PVC sample weight. Octane and butanol are miscible with liquid CO₂,¹⁷ but are nonsolvents for PVC; the absorption of these compounds was negligible.

Naphthalene and DMP, on the other hand, have limited solubility in liquid CO₂,¹⁵ but are quite soluble in PVC. The results of these experiments, and analogous results with other additive compounds, seem to show a direct correlation between additive solubility in the PVC and amounts infused into the polymer; infusion levels do not directly correlate with the solubility of the additive in CO₂.

Other Polymer/Additive/CO₂ Systems

A number of polymers other than PVC have also been used in exploratory CO₂-assisted impregnation trials. The variables of sorption time, CO₂ pressure, etc., were not explored in sufficient detail to define the kinetics or equilibrium solubilities for each system, but it was established that the presence of CO₂ at high pressure could greatly accelerate the absorption of additives in many different polymers. A few examples are cited here to illustrate the scope and limitations of the infusion process.

One type of experiment compared the absorption of a particular additive in several different polymers under similar conditions. For example, 0.1 mm films of PVC, PS, PMMA, and PC were contacted with an excess of 1-hexanol and CO₂ at 6.53 MPa (950 psia) pressure for 1 h at room temperature. The amounts of hexanol absorbed, as a percent of the sample weight, were determined from the sample weight after essentially all the CO₂ had desorbed. For comparison, similar films were exposed to hexanol for 1 h with no CO₂ present. Table III gives the results. A substantial amount of infusion occurred only in PMMA, the one polymer in the group in which hexanol is appreciably soluble. It is presumably the very low diffusivity of hexanol in PMMA that accounts for its low uptake in the absence of CO₂. This experiment again shows a direct correlation between the solubility of the additive in the polymer and the concentration resulting from the infusion process.

The following examples illustrate the infusion of pharmaceutical compounds into glassy polymers:

Table II Additive Infusion into PVC (0.1–1 mm Films, 71 H in Liquid CO₂)

Additive	Wt % Infused
Octane	< 2
<i>n</i> -Butanol	< 1
DMP	8–37
Naphthalene	13–15

Table III Absorption of 1-Hexanol by Four Polymers (0.1 mm Films, 1 H Exposure)

Polymer	Wt % Hexanol Absorbed	
	At 6.53 MPa CO ₂	Without CO ₂
PVC	0.5	~ 0
PS	1.2	< 1
PMMA	24	< 1
PC	0.9	~ 0

Films of poly(caprolactone) (PCL), ethyl cellulose (EC), and cellulose acetate (CA), 0.25 mm thick, were contacted with their own weight of either indomethacin or aspirin in the presence of liquid CO₂ for 64 h at room temperature. The amounts of additives infused, as percent of the polymer weight, are listed in Table IV. As in the previous examples, the amounts infused vary with both the additive and the polymer, again indicating the importance of specific additive/polymer solubility.

Nearly 100 polymer/additive combinations, involving about 20 different polymers and over 40 additives, have now been tested in this study of CO₂-assisted impregnation. Rather than cite further specific examples here, we may simply say that most cases seem to follow the general, qualitative rule that CO₂ will markedly accelerate the absorption of additives that are soluble in the particular polymer used. Additives incompatible with the polymer generally are not absorbed to a significant extent even in the presence of high-pressure CO₂.

Desorption of Additives

After impregnation, the rapid desorption and consequent deswelling of the polymer matrix generally results in deplasticization of the polymer before significant loss of the additive can occur. From their molecular size, typical additives would be expected to have extremely low diffusivities in glassy polymers

Table IV Absorption of Pharmaceuticals by Glassy Polymers (0.25 mm Films, 64 H Exposure in Liquid CO₂)

Polymer	Wt % Indomethacin	Wt % Aspirin
PCL	< 1	8
EC	4	12
CA	2.4	3

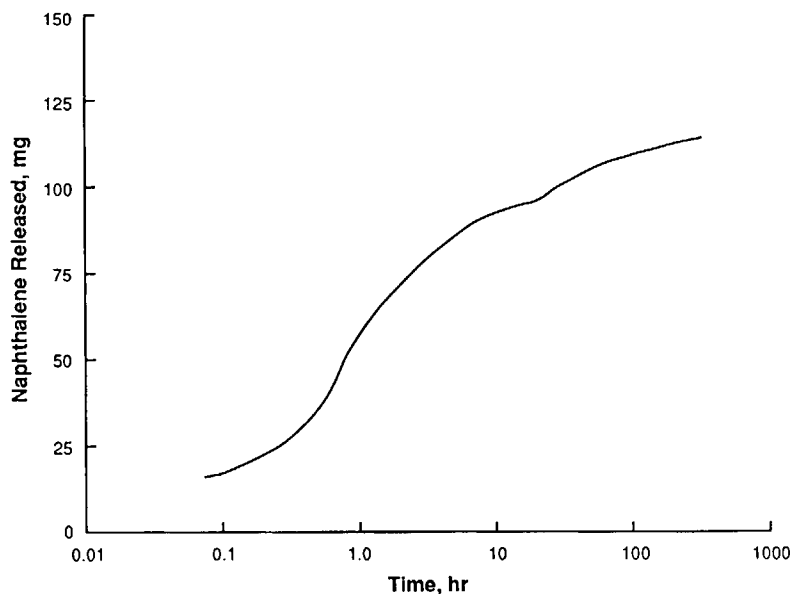


Figure 10 Release of infused naphthalene from a PVC suspension resin (Geon 103EP) into 50/50 v/v ethanol/water at room temperature.

(cf. Fig. 1) and, consequently, very long desorption times. Indeed, the release rates are sufficiently slow that such systems have potential for controlled-release materials and devices.

To illustrate, Figure 10 shows the release of naphthalene (still a useful insect repellent) from 1 g of a typical PVC suspension resin powder (Geon 103EP, BFGoodrich Co.) into 100 mL of a 50/50 v/v mixture of ethanol and water. The wash mixture was changed periodically to minimize the buildup of the external naphthalene concentration. The naphthalene concentrations in the wash solutions were determined using a calibrated UV spectrophotometer. Although the liquid CO₂-assisted infusion of naphthalene into the resin was accomplished in only 1 h at 25°C, the release of the additive from the resin continued after more than 300 h.

Progesterone was infused into a 0.014 cm (5.5 mil) film of polycarbonate (M39F, Mobay Chemical Co.) to a level of 0.5 wt % after exposure of the film to the additive in the presence of CO₂ at 5.95 MPa (~865 psia) for 66 h at 25°C. After CO₂ desorption, a 1 g sample of the infused film was washed with 100 mL of a 75/25 v/v mixture of ethanol and water with periodic solution changes and measurements as above. The release of progesterone from the film is graphed in Figure 11 and shows nearly linear release of the additive over a period approaching 400 h. In both the naphthalene and progesterone experiments, a rapid initial release of the additive was observed and is believed due to a small quantity of

additive left adhered to the surface of the polymer after infusion.

Mechanism

There seem to be two possible interpretations of the mechanism by which CO₂ promotes the impregnation of polymers with additives: One is that the additive dissolves in the CO₂ and the polymer is then swollen by the CO₂ solution of the additive.⁸ If this were the case, one would expect that any additive soluble in CO₂ would be infused into any polymer that CO₂ will swell, and the concentration of the additive in the CO₂ would be the major factor affecting the amount of additive impregnated into the polymer. This concept does not seem consistent with our results; however, for example, CO₂-miscible butanol and octane are not absorbed by CO₂-swollen PVC, while the slightly CO₂-soluble naphthalene is highly absorbed.

An alternative interpretation considers that the CO₂-assisted impregnation process actually involves the approach toward an equilibrium distribution of three components (polymer, additive, and CO₂) among the phases present. The phase relations in three-component systems involving CO₂ are highly varied and complex,¹⁵ but a somewhat simplified view seems appropriate for the systems and conditions considered here. The polymers we have used have negligible solubility in CO₂ and are swollen only to the extent of 30% or less by CO₂, and the volume

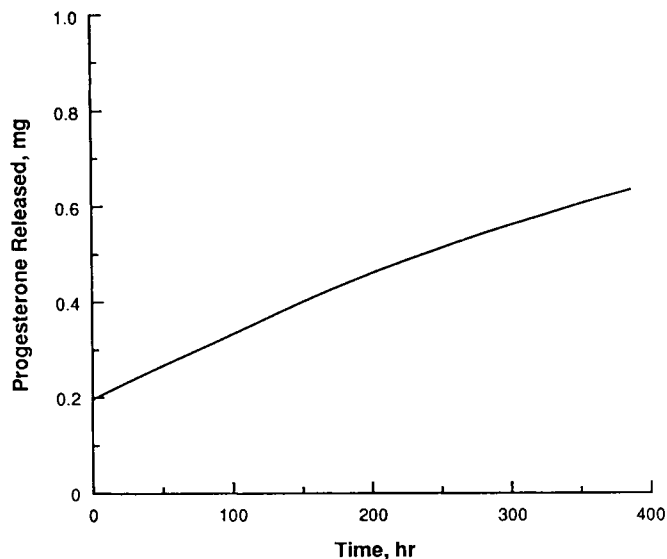


Figure 11 Release of infused progesterone from 0.014 cm-thick polycarbonate film into 75/25 v/v ethanol/water solution at room temperature.

of our pressure vessel is large compared to the volume of swollen polymer. Thus, in the absence of additive, our systems consist of a CO₂-swollen polymer-rich phase and essentially pure CO₂, present as vapor only, or vapor and liquid, depending on the pressure and temperature. It then seems to be a useful and valid approximation to consider the impregnation process as the partitioning of the additive between these phases, followed by rapid removal of the CO₂. In this light, the concentration of additive absorbed by the polymer will depend upon the relative solubility of the additive in the polymer-rich and CO₂ phases. Preferential partitioning of the additive toward the polymer phase, i.e., a high degree of impregnation, will be favored if the additive is relatively more soluble in the polymer than in CO₂. This seems to be the case, for example, in the PVC/DMP/CO₂ system. The partitioning concept, indeed, does seem qualitatively consistent with most of our results. The major effect of the CO₂, then, is to accelerate the kinetics of additive absorption when this is thermodynamically favored by the polymer/additive interaction. In principle, then, it should be possible to predict infusion results from knowledge of the relative solubilities of additive compounds in CO₂ and in polymers. Unfortunately, such solubility data are not plentiful.

In the absence of data allowing quantitative prediction of infusion results, the use of solubility parameters seems to be of some value in estimating the suitability of untested polymer/additive combinations for CO₂-assisted infusion. For all of the

polymers tested, additives that exhibit good infusionability generally have solubility parameters, δ , fairly close to the reported δ values of the polymers.¹⁸ An example of this correlation is shown in Figure 12, where additive uptakes in liquid-CO₂-assisted infusion into PVC are plotted against the solubility parameter of the additive. Although the data show considerable scatter, it appears that the probability of good infusionability is greatest for additives whose δ values lie in a band from about 2 MPa^{1/2} below to 5 MPa^{1/2} above that of PVC. The asymmetry of the correlation seems reasonable, since δ values farther below that of the polymer would suggest greater solubility in liquid CO₂ ($\delta \approx 12.3$ MPa^{1/2})¹⁹ and consequent partitioning of the additive toward the CO₂ rather than the polymer phase during the infusion process.

CONCLUSIONS

- Useful equilibrium solubility and transport kinetic data on both CO₂/polymer binary and CO₂/polymer/additive ternary systems are readily obtained through a simple gravimetric procedure involving rapid periodic weighing of samples during desorption after exposure to high-pressure CO₂.
- Carbon dioxide under high pressure is rapidly absorbed by many glassy polymers, plasticizing them into the rubbery state at room temperature; upon the release of pressure, CO₂ is rapidly desorbed and the plasticizing effect is reversed.

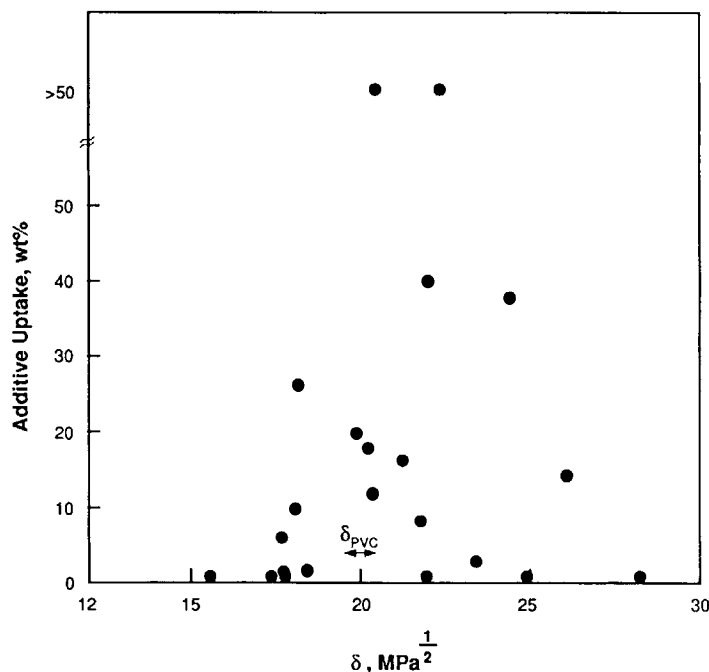


Figure 12 Additive absorption in liquid- CO_2 -assisted infusion in PVC vs. additive solubility parameter.

- The impregnation of glassy polymers with many additive compounds is dramatically accelerated by the presence of CO_2 at sufficiently high pressure.
- The CO_2 -assisted impregnation process amounts, in effect, to the partitioning of the additive between the CO_2 and polymer phases; therefore, the major factor in producing a substantial concentration of absorbed additive is solubility of the additive in the polymer.
- Upon the release of pressure on a CO_2 /polymer/additive system, CO_2 is rapidly desorbed and the degree of plasticization is sharply reduced, leaving the absorbed additive trapped in the polymer to diffuse at the normal rate for the polymer/additive binary composition.

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