Interaction of Supercritical Carbon Dioxide with Polymers. II. Amorphous Polymers

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SYNOPSIS

In continuation of our goal to implement supercritical fluid (SCF) technology for various applications such as precision cleaning, foaming, and impregnation of materials, a systematic study has been performed involving amorphous polymers. Eleven different polymers of amorphous nature have been subjected to supercritical carbon dioxide (SC CO_2) treatment under a wide pressure and temperature range (1000–3000 psi and 25–70°C, respectively). The influence and impact of such treatment on the appearance, weight change, and thermal and mechanical properties were followed systematically. In addition, the effect of treatment conditions and dimension of the samples on weight changes were also monitored. It has been found that amorphous polymers can absorb carbon dioxide to a greater extent than crystalline polymers and, in turn, the phenomenon of plasticization was also very high. In addition to morphology, the polarity of the polymer is also crucial in determining the solubility in carbon dioxide. Comparison was also made with the behavior of crystalline polymers. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Supercritical fluid (SCF) technology has recently begun to be studied as a substitute for chlorofluorocarbons [CFCs, ozone-depleting substances that are used as cleaning agents in many industrial processes], because they are being phased out of production and use.[1] With an aim to realize applications involving polymeric materials, one can expect that polymers will show greater variety of response with supercritical (dense gas) fluid such as carbon dioxide (SC CO_2) than would other materials such as metals and ceramics. SCFs are materials above their critical temperature and pressure conditions, and exhibit interesting behavior by combining the properties of conventional liquids and gases.[2] Although the gas like low viscosities lead to higher rates of flow and diffusion, their liquidlike densities permit higher solvent power.

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, $T_c = 31°C$ and $P_c = 1070$ psi, the solubility of CO_2 in many polymers is as high as that of typical organic liquid swelling agents, ranging from around 10 to more than 30% by weight.[3] In addition, carbon dioxide also has a strong plasticizing effect; for example, concentrations of 8–10 wt % can depress the glass transition temperature of common glassy polymers from 80–100°C to below room temperature. It has been demonstrated that SC CO_2 acts as a very good plasticizer for poly(methyl methacrylate) (PMMA), resulting in a retrograde vitrification of polymer.[4] Although these attributes of CO_2/ polymer systems are typical of organic liquid/polymer systems, CO_2 has the high diffusivity in polymers that is characteristic of gases of similar molecular sizes. This phenomenon allows the impregnation and reimpregnation of polymers and copolymers of polystyrene and PMMA[5] with

the impregnation and reimpregnation of polymers and copolymers of polystyrene and PMMA[5] with CO_2. Further, CO_2 also acts as a pressure-transmitting medium as well as a diluent, whose interaction with materials varies significantly, depending on the treatment and decompression pressures and temperature. Our recent report[6] has addressed the interaction of supercritical carbon dioxide (SC CO_2) with nine different crystalline polymers. The present article shows that the acceleration of absorption and plasticizing effect are much more pronounced in amorphous polymers than in the crystalline polymers and extends the understanding reached through the earlier investigation.

EXPERIMENTAL

Materials

Eleven different polymers of amorphous nature (listed in Table I) have been employed to investigate the interaction of SC CO_2 and evaluate the impact on different parameters. All of them are from commercially available sources in sheets of varying thicknesses ranging from 0.80–6.63 mm (Table I). The carbon dioxide gas used in all experiments is pure grade (Grade 2.8, Bone dry) from US Airgas, Inc. Polymer samples of 1 × 4 cm sizes were cut out using a guide mold to have uniform surface.

Methods

The supercritical carbon dioxide treatment was performed in a similar experimental setup as discussed earlier.[6] Each experiment has been performed with five identical samples treated under similar conditions, so each reported data is an average of five values, with a standard deviation of < 2%. The gravimetric procedure used here involves treatment of supercritical CO_2 with polymer film or sheet samples in a simple pressure vessel, followed by venting and transfer of the samples to a balance for recording weight changes (up to ten thousandths of a gram) at seven different time intervals. The samples were stored in dust-free polyethylene bags before and after SC CO_2 treatment. Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) evaluations were performed using a Perkin–Elmer DSC-2C. Experiments were run at various pressures and temperatures, sorption times, and sample thicknesses for each polymer studied.

RESULTS AND DISCUSSION

The systematic supercritical carbon dioxide treatment involving a wide pressure range of 1000–3000 psi and temperature from 25 to 70°C with 11 different commercially available polymers has been performed. The changes in physical, thermal, and

Table I   Employed Polymers

Polymer ID	Polymer	Commercial Name	Thickness of Employed Polymers (mm)
ABS	Acrylonitrile butadiene styrene	Royalite	1.60
			2.40
CAB	Cellulose acetate butyrate	Uvex	1.50
			2.40
HIPS	High-impact Polystyrene		1.00
			1.50
PC	Poly(carbonate)	Lexan	3.00
PEI	Poly(etherimide)	Ultem	1.74
PETG	Poly(ethylene terephthalate) glycol modified	Vivak	1.00
			2.40
PMMA	Poly(methyl methacrylate)	Plexiglas	1.50
			3.00
PPO	Poly(2,6-dimethyl phenylene oxide)	Noryl	6.63
PSF	Poly(sulfone)	Thermalux	1.46
PU	Poly(urethane)		3.05
PVC	Poly(vinyl chloride)		2.24

mechanical properties due to the treatment have been monitored.

Changes in Appearance

Severe distortion and/or foam formation was visually apparent for the amorphous polymers PMMA, PETG, CAB, ABS, and HIPS as a result of SC CO_2 treatment at pressures higher than 2000 psi. This distortion and/or foam formation is readily apparent upon visual examination. Photographs of the various test specimens of PMMA and PETG (Figs. 1 and 2, respectively) clearly demonstrate the observed changes. Of the investigated 11 materials, PMMA was the most vulnerable one to distortive effects caused by treatment with carbon dioxide. Other materials showed little or no gross deformation. For example, PC and PVC were found to have slight dissolution on their edges after treatment at 3000 psi and 70°C. Although PP turned to a light yellow from its initial white color under the treat-

ment condition C6 (marked in Table II), LDPE and Teflon were observed to have bubbles. The presence of such defects as pronounced bubble formation or changes in color may be obvious upon inspection of the samples or may require more careful inspection of the samples to note the presence of voids or defects in the polymer contiguity caused by such bubbles. For example, presence of color in the polypropylene samples suggests the formation of scattering domains (bubbles) leading to Rayleigh/Mie (particle)-type scattering, which imparts the yellow color to the samples (bubble dimensions that may roughly be on the order of the wavelength of visible light or smaller).[7]

Weight Changes of Polymers

The polymers were treated under conditions noted in Table II, and changes in the weight of polymers were monitored gravimetrically. We have observed significant changes in the investigated amorphous
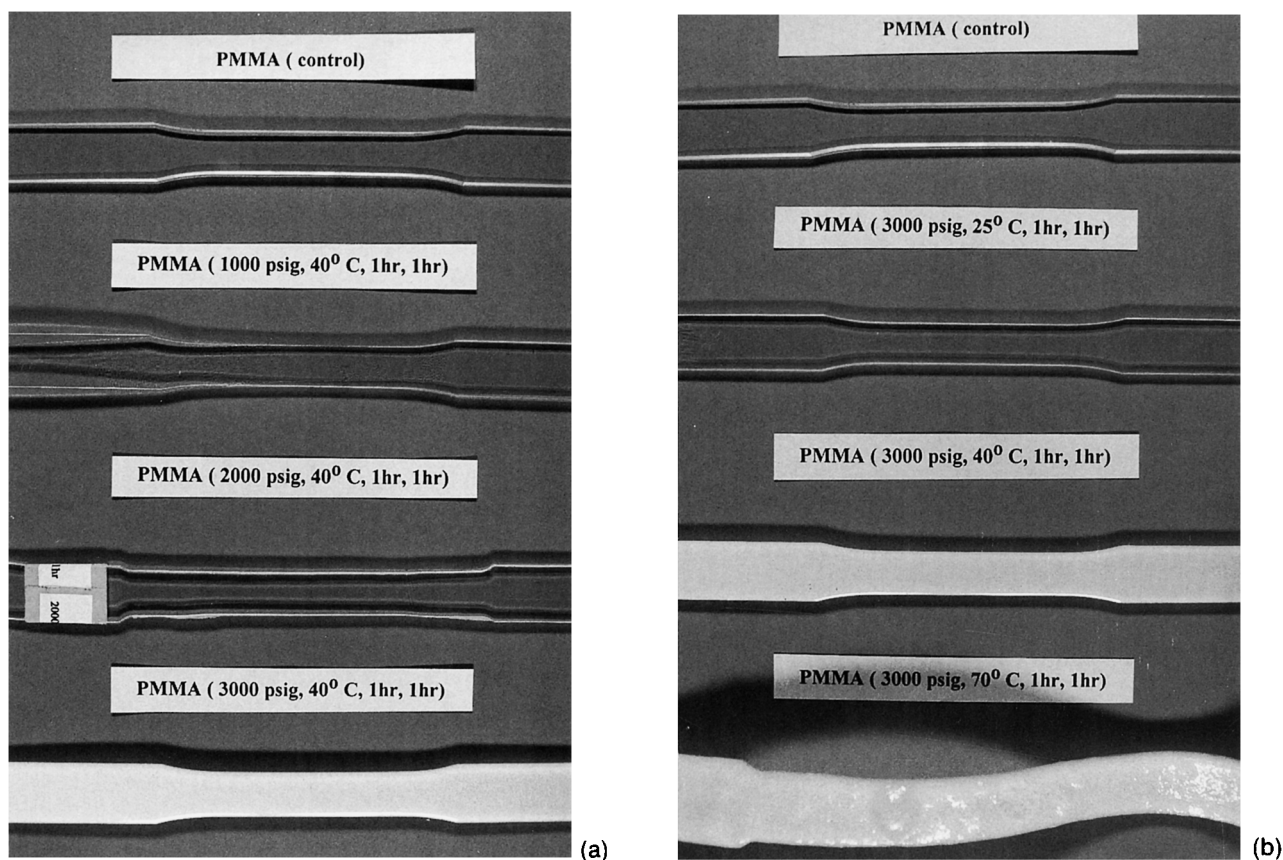

Figure 1 (a) Photographs of the untreated and treated PMMA samples, showing the effect of treatment pressure under constant treatment temperature and time. (b) Photographs of the untreated and treated PMMA samples, showing the effect of treatment temperature under constant treatment pressure and time.
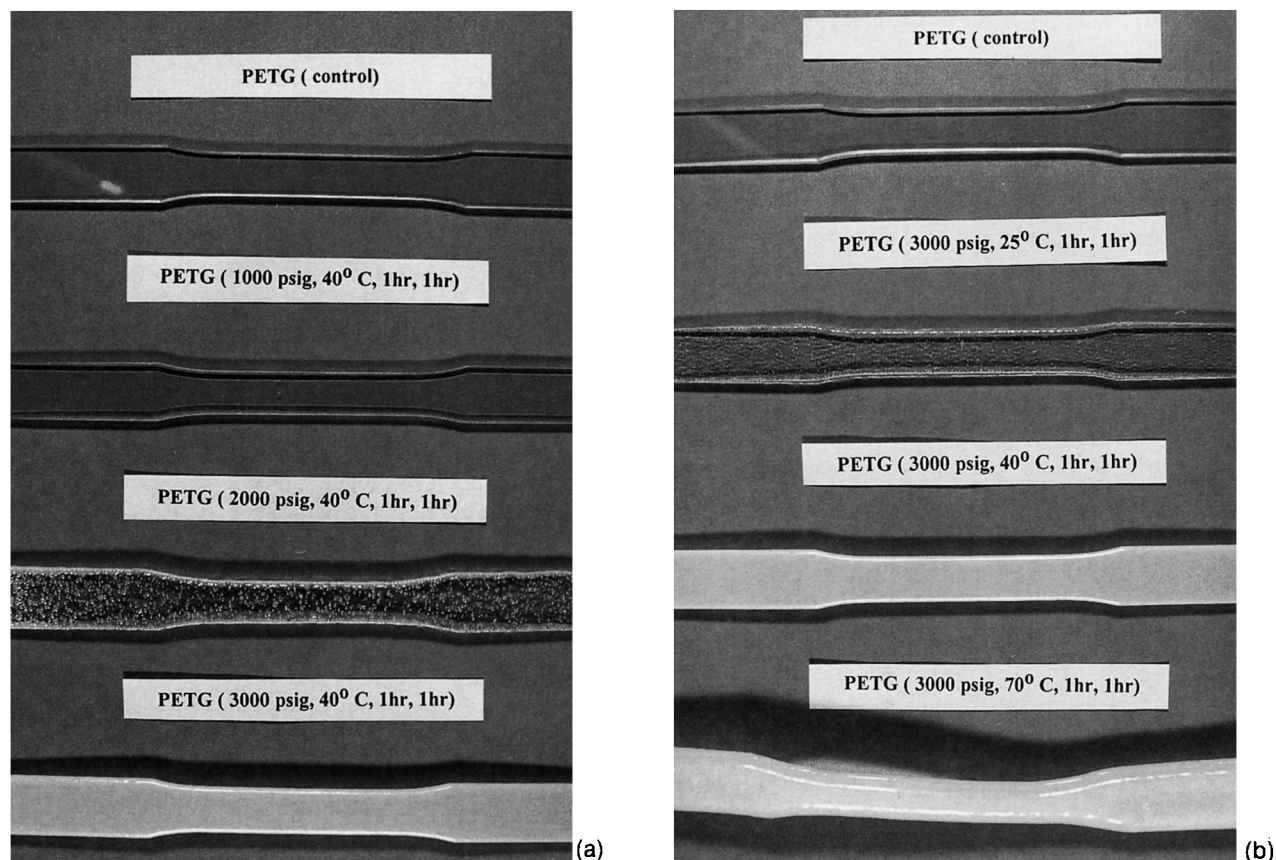
Figure 2 (a) Photographs of the untreated and treated PETG samples, showing the effect of treatment pressure under constant treatment temperature and time. (b) Photographs of the untreated and treated PETG samples, showing the effect of treatment temperature under constant treatment pressure and time.

polymers compared to the crystalline polymers, as investigated earlier.[6] Table III presents the observed weight changes for polymers of different thicknesses at three different pressures, namely, 1000, 2000, and 3000 psi at 40°C. The weight changes for amorphous materials, such as PMMA, PETG, ABS, CAB, HIPS, PU, and PSF, were found

to be more significant (up to 16%) than those for crystalline materials such as Teflon, LDPE, etc., where a maximum weight change (%) of 3.0% was observed for Polyvinylidine fluoride (PVDF) at 3000 psi and 40°C among them.[6] The absorption/dissolution of CO_2 into a material is readily noted either (a) by observing a large positive change in

Table II Carbon Dioxide Conditions Employed in Polymer Treatments

Condition	Pressure (psi)	Temperature (°C)	Exposure Time (h)	Decompression Time (h)	CO_2 Phase
C (Control)	14.7	25	—	—	—
C1	1000	25	1	1	Liquid
C2	1000	40	1	1	Gas
C3	2000	40	1	1	SCF
C4	3000	25	1	1	Liquid
C5	3000	40	1	1	SCF
C6	3000	70	1	1	SCF
C7	3000	70	1	5	SCF

Table III   Observed Weight Changes for Polymers Treated with Carbon Dioxide at Different Temperatures and Pressures

| Polymer | Thickness (mm) | Weight Change (%) | | | | |
| | | 1000 psi 40°C | 2000 psi 40°C | 3000 psi | | |
				25°C	40°C	70°C
ABS	1.60	4.32	4.87	6.49	7.35	0.08
	2.40	3.16	4.14	4.57	7.24	
CAB	1.50	1.90	−2.10	−4.40	−1.03	−5.16
	2.40	6.61	0.19	15.29	7.92	
HIPS	1.00	1.83	1.09	1.92	2.17	0.08
	1.50	1.99	2.04	3.51	4.48	
PC	3.00	0.87	0.93	1.16	1.88	—
PEI	1.74	0.56	0.88	0.52	1.04	2.06
PETG	1.00	2.99	5.22	5.36	5.14	0.28
	2.40	1.47	2.35	2.52	4.18	
PMMA	1.50	5.85	8.45	11.30	12.96	7.70
	3.00	4.10	7.86	9.51	11.27	
PPO	6.63	0.72	1.33	0.63	1.32	3.43
PSF	1.46	1.25	2.27	1.25	2.23	4.09
PU	3.05	2.25	4.39	2.48	3.54	2.78
PVC	2.24	0.52	0.83	0.84	1.55	—

Treatment time and decompression time were fixed as 1 h each. Weight changes (wt %) were measured the same day as the treatments.

the weight of the sample and/or (b) by the presence of extensive foam or bubble formation in the sample. These effects indicate that the treated polymer is significantly plasticized by the carbon dioxide as observed earlier.[3]

Further, note that ABS, HIPS, PETG, PMMA, and PU absorbed less CO_2 at 3000 psi and 70°C than at 40°C under same pressure. In general, the extensive foam formation leads to more open structure of the polymer and, in turn, increased surface area that further leads to rapid loss of carbon dioxide. At lower treatment temperatures and pressures polymers do not get as much or any foaming and, therefore, CO_2 loss is strictly due to the diffusional phenomena and not from the mechanical foaming of polymers.

The mechanisms that can contribute to the observed changes are: (a) the carbon dioxide is absorbed by or dissolved in the polymers, which leads to an increase in the weight of the samples; and (b) either the polymers or some agents, such as monomers, oligomers, additives, or plasticizers in the polymers, are dissolved or extracted from the polymer material, which leads to a decrease in the weight of the samples.[6] The second mechanism can be obviously evidenced by a decrease in weight in

the case of CAB after treatment at 2000 psi. Other obvious changes such as the loss of precise or well-defined edges may also contribute to the decrease in weight.

Effect of the Treatment Conditions on the Weight Changes of Polymers

The effect of treatment pressures and temperatures on the observed weight changes of polymeric materials can be ascertained from the data in Table III. Contrary to the crystalline polymers' interaction with supercritical carbon dioxide, amorphous materials such as PMMA and ABS had large weight changes under all experimental conditions, and the weight changes appear to be directly proportional to the treatment pressure and temperature. Further, the effect of temperature was also monitored by carrying out experiments from 25 to 70°C at a constant pressure of 3000 psi also [Figs. 1(b) and 2(b)]. The temperature of treatment leads to more deformation in the samples at a constant treatment pressure and time. Although the two mechanisms described in the previous section contribute to the weight changes, there are other additional factors, such as structures, morphologies, values of T_g and T_m of materials, and
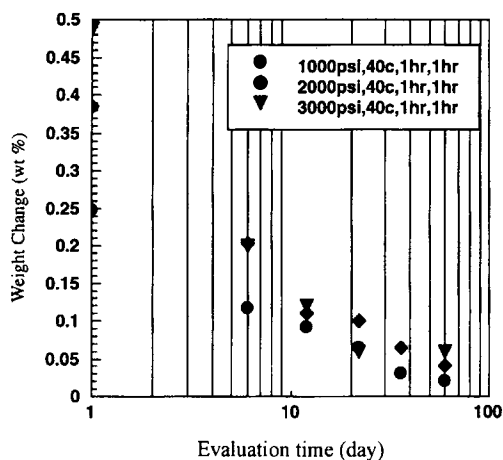
Figure 3   Weight changes for poly(2,6-dimethyl phenylene oxide) as a function of evaluation time.

dimensions of samples, that may affect variations in the data.

Effect of the Dimensions of Samples on the Weight Changes of Polymers

Polymer samples with two different thicknesses were treated with SC CO_2 to ascertain the effect of dimensions on the weight changes under similar treatment conditions, as shown in Table III. However, no general relationship could be derived between the dimensions of samples and weight change data, because samples with a wide range of varying thicknesses were not subjected to treatment. Considering the example of thin and thick samples of CAB, thin samples were found to lose the weight, contrary to thick ones. The different cooling and annealing processes of polymer manufacturing may play a role in polymer morphology and, in turn, the morphology of thick and thin polymer sheets may be different. Subjecting polymer sheets made of similar processing techniques to a systematic supercritical fluid treatment will give more information on this specific aspect.

Desorption of Carbon Dioxide

As discussed earlier, the increase in weight of the polymers after SC CO_2 treatment attributes to the absorption/dissolution of CO_2 in polymers. The loss of CO_2 from polymers was determined by the change in mass of polymers with the logarithm of time, and generally showed a linear dependence. A typical example of weight changes observed for poly(2,6-dimethyl phenylene oxide) as a function of evaluation time is shown in Figure 3. It also indicates that the

trend of desorption from the different treated pressures is: 3000 > 2000 > 1000. In contrast, plots of the weight change as a function of the square root of time ($t^{1/2}$) consistent with a purely diffusive effect showed highly nonlinear behavior. Amorphous polymers also showed similar non-Fickian behavior, as was observed with the crystalline materials.[6]

Solubility of Polymers in Carbon Dioxide

The solubility of polymers in carbon dioxide was evaluated by gravimetry at two different time periods: (1) on the same day, and (2) 8 months after treatment, as explained earlier. The measurement after 8 months allowed a maximum desorption of dissolved carbon dioxide.

Weight loss for some polymers is evident even under the most mild conditions explored (for example, C1), as shown in Table II. Dissolution under these conditions was found to be significant for PMMA, CAB, ABS, PETG, PSF, and PU polymers. The changes in the weights of polymer specimens may be caused by dissolution/extraction of either monomers, oligomers, polymer, additives, stabilizers, processing aids, plasticizers, etc. The data in Table IV clearly shows that the solubility in carbon dioxide was more significant than that observed in the case of crystalline materials.[6] For example, a maximum of 1.8 and 1.3 wt % of solubility was observed for Nylon 66 at similar treatment conditions of C1 and C3, respectively.

ABS had an unexpectedly low uptake of carbon dioxide under condition C6 and showed extensive

Table IV   Total Solubility of Carbon Dioxide in Polymers

Polymer	Solubility Parameter	Solubility of CO_2 (wt %)			
		C1	C3	C6	C7
ABS	9.8	2.5	5.0	0.2	5.9
CAB	12.0	1.9	1.8	5.3	—
HIPS	8.8	0.8	1.1	0	0.5
PC	10.0	—	—	—	—
PEI				1.5*	
PETG	10.6	2.1	—	—	0.8
PMMA	9.3	6.3	9.3	—	10.5
PPO	8.9	—	—	3.4*	—
PSF	10.5			3.6*	—
PU	10.0	—	—	2.2*	
PVC	9.5	—	0.1	—	—

Determined gravimetrically 8 months after treatment for all the polymers except *, for which the evaluation time was 5 months.

foam formation, which led to nearly complete desorption of carbon dioxide during decompression. Thus, it is believed that much of the absorbed carbon dioxide, consistent with the weight changes seen for the other conditions tested, was lost in foaming the polymer. As a general trend, it has been found that these materials have polar groups such as COOR, CN, S$=$O, and Ph$-$O. Thus, in addition to the morphology factor, polarity of the polymer is also crucial in determining the solubility in carbon dioxide.

Influence on the Thermal Properties

Plasticization is an important phenomenon in polymer processing. By treating the polymers with CO_2, they get plasticized and showed a marked reduction in the glass transition temperature. On the other hand, the effect of plasticization may induce or increase crystallization or microcellular structure.[8] The time for treatment and decompression was also set for 1 h each, and the treated samples were subjected to DSC and TGA evaluations at four different time intervals: (a) same day, (b) 1 day, (c) seventh day, and d) sixteenth day.

Coupon-shaped samples of 1 × 4 cm were made from poly(methyl methacrylate) (PMMA) and poly(ethylene terephthalate) glycol modified (PETG) sheets of thickness 3.0 and 1.0 mm, respectively, and subjected to carbon dioxide treatment at 3000 psi and 25°C, and the treatment was held for 1 h and then the high pressure chamber was decompressed to atmospheric pressure for an additional hour. The SC CO_2-treated samples were immediately subjected to differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) evaluations. The TGA traces for SC CO_2-treated PMMA samples are presented in Figure 4. The TGA profile for treated polymer sample measured immediately shows a big difference than the control samples, due to supercritical fluid treatment. Returning to the control state after 16 days indicates that the effect of SC CO_2 diminishes with time. Both PMMA and PETG showed significant swelling as well as extensive bubble/foam formation in the bulk of the material, in contrast to our earlier observation with crystalline polymers,[6] in which significant changes were not observed under identical conditions.

The weight loss in the range of about 120–150°C has been assigned to the outgas of carbon dioxide from the polymers, while weight losses occurring in the range of 290–400°C are due to the decomposition of polymers. The outgas temperature of PMMA was
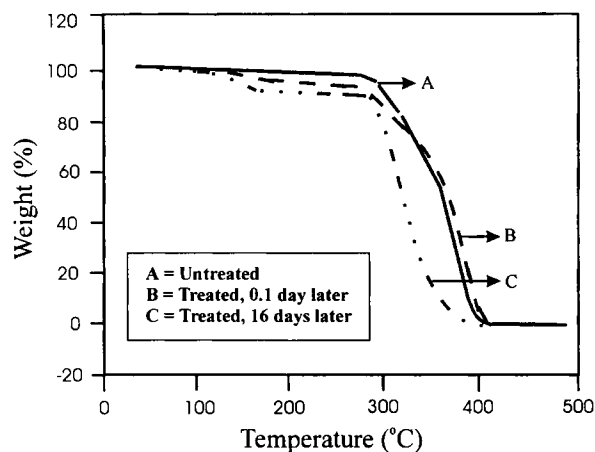

Figure 4   TGA traces for SC CO_2-treated PMMA samples as a function of evaluation time. The treatment condition was CO_2 at 3000 psi and 25°C. Treatment and decompression time = 1 h each.

higher than that of PETG because the glass transition temperature of PMMA is higher than that of PETG. The amount of CO_2 uptake in polymers has been obtained as a function of evaluation conditions employed. Thermogravimetric data showing the amount of carbon dioxide uptake and glass transition temperature for PMMA and PETG are shown in Table 5.

Figure 5 gives the observed glass transition temperature of PMMA and PETG (from DSC measurements) samples treated in CO_2 at 3000 psi and 25°C for 1 h, as a function of carbon dioxide content (evaluated from the TGA data). As expected, the glass transition temperature of both the polymers decreases as carbon dioxide contents in the polymers increase. This evidence clearly suggests that plasticization by carbon dioxide occurs in the investigated polymers. The most dramatic change in T_g was noted immediately after treatment of the polymer samples and was, surprisingly, 22 and 42°C for PMMA and PETG, respectively.

Of the samples investigated, PMMA showed the greatest uptake of carbon dioxide while PETG showed progressively lesser amounts when evaluated approximately 2 h after the treatment, inspite of a higher T_g for PMMA. Because both the materials are amorphous in nature, it can be hypothesized that the presence of a side-chain ester functionality, as compared with the main-chain ester functionality of PETG, allows for the greater dissolution of carbon dioxide in PMMA. Hence, the side-chain ester functionality appears to interact more strongly with CO_2 than one in the main chain. Similarly, Table VI presents the effect of different treatment con-

ditions (varying pressure and temperature) on the glass transition temperature for six different polymers. In general, increase in treatment pressure and temperature was found to increase the dissolution of CO_2 and, as a consequence, T_g was found to decrease.

It is also interesting to note that the T_g values are lower for PC, PMMA, and PETG (Table VI) at 3000 psi, 70°C, 1 h, 5 h, compared to those at similar treatment pressure, temperature, and time, but a shorter decompression time of 1 h (3000 psi, 70°C, 1 h, 1 h), indicating the less loss of CO_2. In fact, when samples are treated with longer decompression period, the CO_2 absorption in the polymer increases due to the pressure gradient change. It can also be explained as follows. When the samples are treated with a desired pressure and decompressed over two different periods of 5 h and 1 h, the samples are in contact with the supercritical fluid at the desired pressure for a longer period of time in the former case than the later. Although it can be assumed that the longer decompression period facilitates the removal of more volatiles from the samples and, in consequence, T_g would increase, in reality both treatment process and removal of volatiles occur simultaneously, leading to the observed results. Amorphous materials showed significantly more uptake of carbon dioxide than the crystalline materials and showed property changes that resulted from the absorption of carbon dioxide.

Influence on the Mechanical Properties

Three different tensile properties, namely, (a) yield strength (tensile strength at yield), (b) ultimate elongation (elongation at break), and (c) modulus of elasticity of amorphous polymers, have been tested to indicate the implications of supercritical
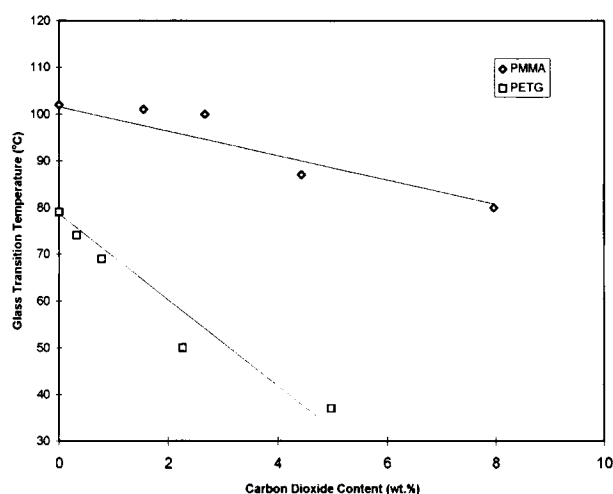

Figure 5 The glass transition temperature of amorphous polymers as a function of carbon dioxide content. The treatment condition was CO_2 at 3000 psi and 25°C for 1 h.

carbon dioxide treatment. The stress–strain measurements and the experimental procedure are essentially the same as detailed earlier.[6] Samples treated with SC CO_2 were evaluated 30 days after treatment, to allow for the significant loss of dissolved CO_2. The yield strength, ultimate elongation, and modulus of elasticity were obtained from the stress–strain curves employing the standard procedures (Table VII). Detailed remarks were also made for the observed visual changes in polymers after different treatments.

Samples were subjected to CO_2 treatment at three subcritical and four supercritical conditions in order to evaluate the effect of these treatments on the mechanical properties of the polymers. For illustration purposes, the treatments at two extreme conditions can be compared: (a) a pressure of 3000 psi at 70°C

Table V   Thermogravimetric Data for PMMA and PETG Showing the Amount of Carbon Dioxide Uptake and Glass Transition Temperature

Evaluation Time (Days)	PMMA			PETG		
	Weight Loss at 200°C (%)	CO_2 Uptake (%)	T_g (°C)	Weight Loss at 170°C (%)	CO_2 Uptake (%)	T_g (°C)
Untreated	−1.03	0	113	−0.45	0	79
0.1	−8.99	7.96	80	−5.43	4.98	37
1.0	−5.46	4.43	87	−2.71	2.26	50
7.0	−3.69	2.66	100	−1.23	0.78	69
16.0	−2.57	1.54	101	−0.77	0.32	74

Treated in carbon dioxide at 3,000 psi and 25°C for 1 h.

Table VI   Glass Transition Temperature (in °C) of Various Polymers as a Function of Treatment Conditions

Polymer	Control	Treatment Conditions				
		1000 psi, 25°C, 1 h, 1 h	2000 psi, 40°C, 1 h, 1 h	2300 psi, 70°C, 15 min, 5 m	3000 psi, 70°C, 1 h, 1 h	3000 psi, 70°C, 1 h, 5 h
PC	153.2	154.4	152.9	151.7	154.1	153.0
PMMA	113.4	112.9	116.3	111.8	117.4	115.2
PETG	79.2	77.1	76.5	77.9	75.8	75.0
CAB	106.7	114.0	122.2	112.4	127.1	123.3
HIPS	104.4	—	105.9	104.1	104.1	106.2
ABS	106.6	—	—	110.8	—	109.3

with a treatment time of 1 h and a decompression (pressure-release) time of 1 h (which is summarized as 3000 psi, 70°C, 1 h, 1 h); and (b) keeping all the other conditions constant except the decompression time as 5 h (which is summarized as 3000 psi, 70°C, 1 h, 5 h).

PMMA and PVC showed high values in yield strength and modulus and a low value in elongation. Interestingly, the bulky and polar side group —COOCH₃ and high dipole C—Cl bond somewhat simulate the effects of crystallinity to restrict disentanglement or slippage among polymer chains

Table VII   Yield Strength, Ultimate Elongation, and Modulus of Elasticity for Various Polymers before and after Treatment with Supercritical Carbon Dioxide

Polymer	Thickness (mm)	SCF Treatment Condition	Yield Strength (MPa)	Ultimate Elongation (%)	Modulus of Elasticity (MPa)	Remarks
ABS	2.40	Control	41.9	8	1920.7	Black in color.
		C1	41.1	4	1677.2	Light dissolution on edges.
		C3	43.2	6	1837.2	Bent.
		C6	—	—	—	Extensive foam formation.
		C7	—	—	—	Extensive foam formation.
CAB	2.40	Control	38.2	59	1442.7	Transparent.
		C1	41.1	44	1505.5	Light dissolution on surface.
		C3	—	—	—	Foam formation.
		C6	—	—	—	Extensive foam formation.
		C7	—	—	—	Extensive foam formation.
PC	3.00	Control	67.8	69	1943.4	Transparent.
		C1	66.7	57	1942.1	Transparent.
		C3	64.9	09	2153.8	Transparent.
		C6	63.9	08	2057.2	Light dissolution on surface.
		C7	63.6	35	1983.4	Light dissolution on surface.
PMMA	3.00	Control	63.9	3	2648.9	Transparent.
		C1	55.2	3	2426.2	Light dissolution on surface.
		C3	67.2	5	2168.9	Dissolution and bubbles were seen.
		C6	—	—	—	Extensive foam formation.
		C7	—	—	—	Extensive foam formation.
PVC	2.24	Control	61.0	9	3006.2	Dark gray in color.
		C1	60.8	12	2811.0	Dark gray in color.
		C3	59.3	10	2793.1	Light dissolution on edges.
		C6	49.6	12	2211.0	Bent.
		C7	49.2	13	2531.7	Bent.

C: Control; C1: 1000 psi, 25°C, 1 h, 1 h; C3: 2000 psi, 40°C, 1 h, 1 h; C6: 3000 psi, 70°C, 1 h, 1 h; and C7: 3000 psi, 70°C, 1 h, 5 h.

during stress–strain measurements. In brief, crystallinity, chain flexibility, bulkiness of side group/ main chain, and polarity (including dipole forces and hydrogen bonding) determine the mechanical property values and can be used to explain how the specific values can be compared for the investigated amorphous materials (Table I).

In samples of PC, light dissolution was seen after SC CO_2 treatment at both conditions. On increasing the temperature and pressure from 25–70°C and 1000–3000 psi, respectively, the material shows a slight reduction in the yield strength and modulus of elasticity, and a significant change in ultimate elongation. These data suggest that the PC has become plasticized by the treatment with SC CO_2 and also likely to be crazed. The material became brittle with a concurrent decrease in ultimate elongation. From the experiments carried out by Beckman and Porter[9] on bisphenol A polycarbonate, it has been found out that crystallization begins with 1 h of exposure to CO_2. Percentage crystallinities of over 20%, comparable to that achieved using acetone or other organic liquids, have been obtained after 2 h of exposure to SC CO_2. Here, caution should be made before concluding that only crystallization plays a role, because a study of Lexan®,[10] polycarbonate immersed and subjected to loading in several liquids such as alcohols, hydrocarbons, and esters, showed that those liquids with solubility parameters slightly higher or lower than that of polycarbonate caused crazing and those with solubility parameters approximately equal to polycarbonate caused cracking and fracture.

On the other hand, the decrease in the yield strength resulted from the plasticization caused by the absorption of carbon dioxide in the amorphous regions after treatment.[11,12] Longer decompression times appear to favor increased plasticization of the material. CAB, which is completely amorphous, showed extensive foam formation after treatment at both conditions like PMMA. This suggested the occurrence of high diffusivity, which led to high uptake of carbon dioxide in the material. Apparently, both the $COOCH_3$ and $COO(CH_2)_2CH_3$ groups led to increase in CO_2 absorption. The dimensions of the foam resulting from 1-h decompression were larger than those resulting from 5-h decompression.

Like CAB, PMMA, which is an amorphous material with a side-chain ester group, had extensive foam formation after treatments at both conditions. The dimensions of the foam resulting from 1-h decompression were larger than those resulting from 5-h decompression. Weight change data for PMMA (Table III) indicated a tremendous amount of CO_2

uptake, which led to extensive foam formation during decompression. The large decrease in T_g (see Tables V and VI) also suggested the occurrence of a large amount of CO_2 uptake. The $COOCH_3$ group must have played a special role in the high amount of carbon dioxide uptake. Like CAB and PMMA, ABS also showed extensive foam formation after treatments at both conditions, which is exacerbated by the rubbery nature of the material due to the butadiene moieties. Similarly, PVC samples also showed a significant decrease in yield strength and modulus after treatment at both conditions, which indicated the occurrence of a high extent of plasticization.

CONCLUSIONS

Through the systematic study involving 11 different amorphous polymers treated with supercritical carbon dioxide under a wide pressure and temperature range, it has been demonstrated that the amorphous materials showed a greater amount of carbon dioxide absorption and, in turn, a significant amount of plasticization of the materials was found to occur. Although the increase in treatment temperature and pressure increase the dissolution of CO_2, polarity of the polymers also plays a crucial role in determining the solubility of CO_2 into them. These results indicate that SC CO_2 treatment will generally be more suitable for crystalline materials than amorphous materials in realizing applications such as precision cleaning under extreme conditions. On the other hand, amorphous materials will be ideal candidates for applications such as foaming of the polymer, impregnating and reimpregnating selective additives into them, surface modification, and to induce crystallization or microcellular structures.

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