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Compatibility of Medical-Grade Polymers with Dense CO₂

A Jiménez,

Department of Chemical Engineering, University of South Carolina, Columbia SC 29208 USA

G L Thompson,

Department of Chemical Engineering, University of South Carolina, Columbia SC 29208 USA

M A Matthews*,

Department of Chemical Engineering, University of South Carolina, Columbia SC 29208 USA

T A Davis,

Department of Chemical Engineering, University of South Carolina, Columbia SC 29208 USA

K Crocker,

Department of Mechanical Engineering, University of South Carolina, Columbia SC 29208 USA

J S Lyons, and

Department of Mechanical Engineering, University of South Carolina, Columbia SC 29208 USA

A Trapotsis

Consolidated Stills and Sterilizers, Boston MA 02134 USA

Abstract

This study reports the effect of exposure to liquid carbon dioxide on the mechanical properties of selected medical polymers. The tensile strengths and moduli of fourteen polymers are reported. Materials were exposed to liquid CO₂, or CO₂ + trace amounts of aqueous H₂O₂, at 6.5 MPa and ambient temperature. Carbon dioxide uptake, swelling, and distortion were observed for the more amorphous polymers while polymers with higher crystallinity showed little effect from CO₂ exposure. Changes in tensile strength were not statistically significant for most plastics, and most indicated good tolerance to liquid CO₂. These results are relevant to evaluating the potential of liquid CO₂-based sterilization technology.

Keywords

supercritical fluids; carbon dioxide; mechanical test; polymethylmethacrylate; polyvinylchloride; polyethylene

1 INTRODUCTION

Synthetic polymers are important in many biomedical applications, such as artificial joints and vascular implants. Medical devices used in invasive procedures must be cleaned and sterilized prior to use. Sterilization is the destruction of living organisms, and must be done without damaging the material surface and without compromising the bulk material strength or

*Corresponding author. Tel. 803-777-0556., Fax: 803-777-8265, matthews@enr.sc.edu.

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biocompatibility of implantable devices. It is well known that established sterilization processes may have adverse effects on certain biomaterials, including metals and polymers [1]. Common sterilization processes include steam autoclaving, gamma irradiation, and chemical treatments with ethylene oxide or hydrogen peroxide plasma [1–3]. Parameters such as temperature, pressure, energy intensity, sterilant concentration, and cycle time vary, [4] and the process chemistry and conditions determine the applicability of each process for a given material or device. New sterilization processes continue to be investigated, with emphases on reducing the process temperature and minimizing contamination. A novel approach to sterilization is based on carbon dioxide (CO₂) technology; reviews and patents have recently appeared [2,3,5–8]. The deactivation of vegetative bacteria using liquid CO₂ in a single step has been demonstrated many times and a comprehensive review has been prepared by Zhang *et al.* 2006 [8]. Because of its potential for cleaning, disinfecting, or sterilizing at mild temperatures (typically between ambient and 79°C), and because of the cost advantages of liquid CO₂ over supercritical, this study focuses on the bulk mechanical properties of selected polymeric biomaterials before and after exposure to liquid CO₂.

CO₂ technology is attractive in part because CO₂ is non-flammable, non-toxic, physiologically safe, chemically inert and readily available [5,9–11]. When heated and compressed above its critical point (7.38 MPa and 304.2K) CO₂ exhibits a liquid-like density ($0.6\text{--}1.0\times 10^{-3}\text{kg.m}^{-3}$) [12] but gas-like diffusivity ($10^{-7}\text{--}10^{-8}\text{m}^2\text{s}^{-1}$) and viscosity ($3\text{--}7\times 10^{-5}\text{N.s.m}^{-2}$), and zero surface tension [11]. These properties allow CO₂ to penetrate porous structures easily. Typical process temperatures are on the order of 0 to 40°C, so there is the potential for developing a low-temperature sterilization technology. Research has shown that compressed CO₂ kills many clinically relevant gram positive (*Listeria monocytogenes*, *Staphylococcus aureus*, and *Enterococcus faecalis*) [13,14] and gram negative (*Salmonella typhimurium*, *E. coli*, and *Pseudomonas aeruginosa*) vegetative bacteria [2,15]. Bacterial spores can also be sterilized with CO₂-based processes [2,7,16–18]. A 6-log reduction of *B. pumilus*, *B. atrophaeus*, and *G. stearothermophilus* spores was achieved at relatively low temperatures and treatment time (40°C, 27.58 MPa for 4 hours) [19]. Several groups are now actively working on development of CO₂ technology for biomaterial sterilization [7].

The objective of this work is to evaluate the tensile strength of several polymers before and after exposure to liquid CO₂, or to liquid CO₂ plus aqueous H₂O₂. The polymers under investigation are used in manufacturing flexible surgical and diagnostic instruments, such as endoscopes. Loss of tensile strength will lead to degradation of the mechanical performance. The focus of the present study is on whether the materials will be tolerant to temperatures and elevated pressures (typically higher than 5.0 MPa) typical of liquid CO₂ processing. Many polymers absorb significant amounts of gases and vapors when exposed at high pressures [11]. In particular, CO₂ absorption can induce plasticization, swelling, and a decrease in the glass transition temperature [21]. Several reports examine the effect of high pressure CO₂ on certain specific polymers, including silicone rubber [20–23], cellulose acetate [24], poly(vinylidene fluoride) [20], poly(vinyl chloride) [20], poly(methyl methacrylate) [20,25], polystyrene [20,26], poly(vinyl benzoate) [27], low density polyethylene [28,29] and polysulfone [29,30]. The solubility of CO₂ in polymers [24,29] and the resultant swelling and absorption behavior [23–25,29–32] have been recently investigated.

2 MATERIALS AND METHODS

Materials

A total of eighteen different commercial polymers were initially selected for study because of their relevance to the manufacture of flexible medical instruments. Four polymers were obtained from Laird Plastics (ultra high molecular weight polyethylene (UHMWPE), polystyrene (PS), low density polyethylene (LDPE), and high density polyethylene (HDPE)).

The rest were obtained from Laboratory Devices Company (natural rubber latex (NRL), ethylene propylene diene monomer (EPDM) elastomer, poly (methyl methacrylate) (PMMA), silicone rubber (SI), polyurethane (PUR), acrylonitrile-butadiene-styrene (ABS) rubber, polycarbonate (PC), poly (ethylene terephthalate) (PET), poly(phenylene oxide) (PPO), poly (vinylidene fluoride) (PVDF), Teflon[®], polyvinylchloride (PVC), Nylon (PA), and acetal). Liquid CO₂ from Holox (Coleman Grade, 99.99%) was used, and in some experiments aqueous hydrogen peroxide (H₂O₂, 30%) from Fisher Scientific was added.

ASTM D638 tensile testing

ASTM Procedure D638 was used to evaluate tensile properties of polymers before and after exposure to liquid CO₂. Thickness was measured with a caliper (Central Tools, Incorporated) and mass was determined both before and after treatment with a Mettler AE 240 balance. Polymers were obtained in sheet form, from which the standard tensile “dogbone” specimens were prepared as specified by the ASTM D638 (Figure 1). A high pressure water jet was used to cut specimens; the use of the water jet allowed precision cutting at ambient temperature (i.e. without the friction heating from a conventional blade) and minimized the introduction of residual stresses in the samples. The specimens were washed in cool water to remove residue, dried, and weighed. The length, width (specimen maximum and minimum for dogbones) and thickness of the specimens were measured prior to CO₂ processing. Also, specimens were weighed before treatment, immediately after treatment, and after degassing for 24 hours post-treatment. Specimen thickness varied from 0.16 cm for UHMWPE to 0.688 cm for PET. Qualitative observations of color, unique markings and flexibility were also recorded.

2.3 Processing with CO₂

All specimens were exposed to liquid CO₂ in a 1L high pressure vessel from Pressure Products Industries, Inc, schematically represented in Figure 2. The vessel is capable of operating in a range of 0°C to 60°C (32°F to 140°F) and up to 44.5 MPa (445 bar). Up to six specimens were mounted in the vessel for simultaneous exposure to the CO₂ environment. Liquid CO₂ from the CO₂ supply was drawn through a 0.2 cm porous steel filter to a liquid CO₂ pump (Thar Designs, P-200). The CO₂ was preheated in 10 feet of coiled tubing to the desired temperature; a circulating bath (Fisher Scientific, Isotemp 1013S) provided temperature control. The pre-heated CO₂ was filtered a second time with a 0.025 cm filter at the vessel inlet. Vessel temperature was maintained with an internal coil of tubing connected to the circulating bath. A thermocouple (Fluke 54) mounted in the built-in thermowell was used to monitor the internal temperature. An outlet at the top of the vessel was used to purge air before pressurization, and the drain valve at the bottom was used for depressurization. The temperature of the fluid exiting the drain valve was monitored by a thermocouple (Fluke 54) fastened into a high-pressure tee fitting. The vessel outlets and vessel bypass line were joined to allow flow through either a manual valve or a pressure regulator (Tescom, 26-1724-24-154) before venting to the atmosphere.

The vessel was flushed with gaseous CO₂ for about 10 s before pressurizing. The process temperature was ambient, typically between 17°C and 24°C. To ensure that CO₂ remained liquid, the pressure was set to 6.5 MPa. For experiments that required H₂O₂, approximately 200 µL of aqueous H₂O₂ (about 0.07 M) were injected at approximately 6 min. into the pressurization step. To ensure uniform mixing of H₂O₂ and CO₂, the internal six-blade impeller was rotated at about 525 rpm during treatments. The density and viscosity of CO₂ at ambient temperature and 6.5 MPa are 0.797 g/mL and 1.5*10⁻⁵ kg/m*s respectively. Specimens were maintained at the prescribed conditions for one hour after the pressure stabilized at 6.5 MPa, then the regulator-bypass valve was opened slowly to depressurize the vessel. The time required to depressurize the vessel (15 to 20 min) was recorded. The specimens were visually inspected immediately after opening the pressure vessel. Specimen weight and dimensions were recorded

along with the time required for depressurization and removal from the vessel. Mechanical tests were initiated after a 24-hour holding time to ensure that CO₂ had desorbed. Any further changes in the specimen after 24 hours were noted.

Miscibility of aqueous H₂O₂ and CO₂ at these conditions was confirmed in separate experiments by direct observation in a Thar variable volume, stirred view cell shown in Figure 3. CO₂ was fed into the variable volume view cell with a magnetic mixer using an ISCO 500HP syringe pump controlled by an ISCO series D controller. 10 µL of 30% H₂O₂ were carried quantitatively into the CO₂ pressurized chamber through the use of a Valco Instruments (Houston, TX) six-port liquid injection valve. H₂O₂ droplets observed at the beginning of the process disappeared once the process pressure was reached.

2.4 Mechanical Testing

Mechanical testing was performed on treated and control specimens. ASTM D638 tensile strength tests were performed with a 311 N-capacity Tinius Olsen universal testing machine, with a loading rate set at 0.005 m/min. Labtech NotebookTM was used for data acquisition. At least four replicate specimens were used for the untreated controls and for each CO₂-treated material. An extensometer with a 10% strain range was used to record the strain during the initial elastic response of each specimen. This strain and force data were used to calculate the modulus of elasticity. The extensometer was removed prior to sample yielding (i.e., at approximately 9% strain) and each specimen was further loaded until failure. The peak force was recorded and used to calculate the ultimate tensile strength. The cross-sectional dimensions at the point of rupture were measured to determine the percent-reduction in area after fracture. As will be described below, four of the polymers proved incompatible with CO₂ processing and therefore were not subjected to a full range of mechanical testing.

2.5 Data Analysis

Quantitative data presented in this work are the results of at least four replicate tests. As indicated for the specific results shown in the figures, certain means of different treatments were compared using a two-sided Student's t-test with a confidence level $\alpha = 0.01$. All the results are presented as mean $\pm$ standard deviation.

3 RESULTS AND DISCUSSION

The results of all tests are summarized in the form of bar graphs in Figures 4 and 6–8. All bars represent the average property of at least four replicate tests, and in many cases if sufficient material was available, five or six specimens were tested. The error bars shown represent one standard deviation.

Figure 4 shows the weight change after treatment with CO₂ or CO₂/H₂O₂ followed by degassing for 24 hours. The “X” in Figure 4 designates a statistically significant difference between treatments (CO₂, CO₂ + H₂O₂), as determined by a two-sided Student's t-test with a confidence level $\alpha = 0.01$. The more amorphous polymers (Latex rubber, PMMA, ABS, PUR, EPDM, PS, PC, LDPE, PPO, PTFE and PVC) are on the left, and the more crystalline polymers (UHMWPE, HDPE, POM, PVDF, PET, PA, SI) are to the right in Figure 4. Amorphous polymers have little molecular orientation and large free volume, thus CO₂ penetrates even if no specific intermolecular interactions are present. Crystalline polymers, in contrast, have highly ordered molecular arrangement and relatively less free volume, so CO₂ will not absorb as readily [33]. Figure 4 reflects these generalizations.

Latex rubber gained more mass than any other polymer, about 7% under pure CO₂ and about 5.5% under CO₂/H₂O₂. The behavior of PMMA was comparable to that for latex rubber;

PMMA showed a mass uptake of over 6% when exposed to either CO₂ or to CO₂ plus H₂O₂. PMMA was slightly distorted and softened, and specimens were deformed at areas of contact with the reactor. ABS, polyurethane and EPDM also gained significant mass, on the order of 5%. EPDM deformed during treatment, but polyurethane and ABS did not deform. Of the amorphous polymers, latex rubber specimens were most swollen and distorted. After two days, the specimens returned to their original sizes and shapes. Because of excessive swelling, latex rubber was not subjected to tensile tests. With crystalline polymers, the weight uptake was small and there were no observable changes in the materials after CO₂ or CO₂ plus H₂O₂ treatment.

The ability of a polymer to solubilize CO₂ depends on both chemical interactions and the degree of crystallinity. Polymers possessing electron donating or Lewis base functional groups, for example, exhibit specific attractive interactions with CO₂ [34]. The weight gain in latex rubber, PMMA and EPDM can be interpreted in terms of intermolecular forces. Latex rubber and EPDM are non-polar polymers and do not exhibit any specific intermolecular interaction with CO₂. The weight increase after exposure of CO₂ is attributed primarily to the amorphous structure. The degree of cross-linking and effects of chain branching also increase the free volume. PMMA contains a carbonyl functional group in the backbone chain, which is an electron-donor or Lewis base. The presence of this carbonyl group enhances the solubility of CO₂ and induces a change in weight after treatment. Compared to crystalline polymers, amorphous polymers show more weight gain and swelling due to CO₂ absorption.

The more crystalline polymers, nylon and PET, showed the least weight change. Polar amide groups in the backbone chain of nylon form strong hydrogen bonds that promote crystallinity. In PET, crystallinity is induced by the polar ester groups as well as the orderly arrangement of aromatic rings. Highly crystalline lattices inhibit penetration and adsorption of CO₂.

A practical sterilization process should be accomplished in as short a time as possible; significant CO₂ uptake and degassing times are detrimental. However, previous work on sterilization processes [8,35] and mechanisms [19] indicate that processing times on the order of 0 seconds to 4 hours may be necessary to achieve complete sterilization. It is therefore of interest to estimate the relative degree of CO₂ absorption under the experimental conditions used in this work. In a simple model, the specimens are treated as flat planes, and Fickian diffusion is assumed. The Fickian sorption and desorption of fluids into or out of a flat polymeric membrane can be modeled according to Crank and Park [36] by equation (1):

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{e^{-D((\frac{2n+1}{2})\frac{\pi}{L})^2 t}}{(2n+1)^2} \quad (1)$$

In this equation M_t is the total amount of diffusing fluid that has entered the polymeric membrane at time t , M_∞ represents the saturation amount of CO₂ that can be absorbed, L the sample thickness and D the diffusion coefficient. In this dimensionless model, M_t/M_∞ describes the extent of CO₂ adsorption at a time t relative to the maximum equilibrium absorption at $t = \infty$. The important parameter in this model is D . The diffusion coefficient of SC CO₂ has been measured in a variety of polymers, including PVC with a diffusion coefficient of 0.24×10^{-11} m²/s [37]. As a sensitivity check, equation (1) is also solved using $D = 0.24 \times 10^{-9}$ m²/s; this higher diffusion coefficient is representative of CO₂ diffusing in an amorphous polymer. Figure 5 shows calculations of M_t/M_∞ over time for PVC for $L = 0.0016$ m, i.e., the thinnest specimen tested. As observed from this figure, after 1 hour the amount of CO₂ adsorbed is approximately 10% of the equilibrium amount. Since PVC is crystalline, CO₂ will not easily penetrate. As observed in Figure 5, the treatment time required for the CO₂ to completely penetrate the crystalline matrix is about a month. In contrast, CO₂ uptake is comparatively rapid in the case

of $D=0.24 \times 10^{-9} \text{ m}^2/\text{s}$. For amorphous polymers, the amount of CO_2 adsorbed is about 70% of the equilibrium amount after 1 hour and the treatment time necessary for the CO_2 to completely penetrate the matrix is about a day. This behavior is consistent with the swelling of polymers shown in Figure 4. It is emphasized that this is a simple model for order of magnitude calculations.

Figure 6 shows the ASTM D638 tensile strength of fourteen plastics (latex, PUR, and SI are not reported because they were too elastic, while EPDM was too brittle). Figure 6 shows data for CO_2 - and CO_2 plus H_2O_2 -treated specimens, respectively. An “X” above a bar indicates a statistically significant difference from the untreated control group, as determined by a two-sided Student’s t-test with a confidence level (α) of 0.01. Each bar represents the average of 4 to 6 replicate specimens.

The tensile strength of PMMA decreased about 19% after exposure to CO_2 , while for ABS it decreased about 10%. The tensile strength of PC shows a statistically significant decrease of about 6% after exposure to either treatment. PVC shows a statistically significant decrease, similar to PC. PET shows a very slight decrease in tensile strength when treated with CO_2 plus H_2O_2 . Other plastics did not show statistically significant changes in tensile strength.

Figure 7 shows the area reduction of the specimens after treatment. This is the decrease in the cross-sectional area of the neck of the dogbone (Figure 1) after failure. Rigid polymers like PMMA and PS showed only slight area reduction before failure. The area reduction increases with the pliability of the material, and so the strain before failure will likewise increase. Note that PMMA and PS, for example, show very little area reduction. CO_2 plus H_2O_2 treatment increased the area reduction in PC and HDPE. ABS and HDPE, after treatment with pure CO_2 , show a statistically significant (though small numerically) increase in the area reduction. The area reduction for the remaining polymers was not affected by CO_2 processing.

Figure 8 shows Young’s modulus (modulus of elasticity) calculated from the stress/strain curve. The modulus is strongly correlated with variations in the polymer structure, the molecular weight and the density among specimens of the same material [38]. PMMA showed a statistically significant decrease in the modulus after exposure to CO_2 , suggesting CO_2 plasticization [30]. PS demonstrated a statistically significant increase in the modulus when treated with CO_2 plus H_2O_2 . PVC also showed a statistically significant increase in modulus after exposure to pure CO_2 .

4 CONCLUSIONS

The mechanical properties of several medically-relevant polymers have been evaluated before and after exposure to liquid CO_2 at ambient temperature and 6.5 MPa. There was appreciable CO_2 uptake even after 24 hours of degassing for some of the amorphous polymers (latex rubber, ABS, PMMA, polyurethane, and EPDM). Crystalline polymers showed little weight change. A statistically significant decrease in the tensile strength was observed for PMMA (CO_2), ABS ($\text{CO}_2/\text{H}_2\text{O}_2$), PC ($\text{CO}_2/\text{H}_2\text{O}_2$), PVC ($\text{CO}_2/\text{H}_2\text{O}_2$), and this may be clinically significant also. PET ($\text{CO}_2/\text{H}_2\text{O}_2$) showed a slight decrease in tensile strength. PMMA showed a statistically significant decrease in Young’s modulus after exposure to CO_2 , probably because of induced plasticization, whereas PS ($\text{CO}_2/\text{H}_2\text{O}_2$) and PVC (CO_2) demonstrated a statistically significant increase in modulus when treated with CO_2 plus H_2O_2 that could be due to an increase in the degree of crystallinity.

Liquid CO_2 , proposed for cleaning and sterilizing medical devices, may be used at realistic processing conditions with certain polymeric biomaterials. However, one must take into account the interactions between CO_2 and the materials of interest. Crystalline polymers show little if any uptake, swelling and distortion, and devices made from these materials would likely

be compatible with a CO₂-based process. In contrast, some amorphous polymers showed more pronounced effects with CO₂ that could compromise bulk material strength, and a CO₂ sterilization process might not be feasible for medical devices containing those polymers. It should be emphasized that all these data are for a single cycle of exposure to liquid CO₂. For development of a process to sterilize reusable instruments, it remains to be demonstrated that a material or instrument could withstand multiple cycles. Finally, it should be noted that liquid CO₂ may extract low molecular weight oligomers, plasticizers, or other components blended with commercial polymers. There is evidence that extraction occurred with certain systems as indicated by the weight changes shown in Figure 4, namely polystyrene, polyurethane, acrylic, silicone, latex, LDPE, HDPE, PET, PPO, acetal, PVDF, and EPDM.

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Figure 1.
Dimensions of specimens used for ASTM D638 tests

Figure 2.
Schematic representation of the one-liter high pressure reactor

Figure 3.
Thar Technologies Inc. variable volume view cell

Figure 4.

Weight change due to uptake of CO₂ in the specimens. The “X” designates a statistically significant difference between treatments.

Figure 5. CO_2 uptake in a planar polymer as predicted by the Crank and Park [36] model. The diffusion coefficient of SC CO_2 in PVC is $0.24 \times 10^{-11} \text{ m}^2/\text{s}$; $D = 0.24 \times 10^{-9} \text{ m}^2/\text{s}$ is representative of CO_2 diffusing in an amorphous polymer.

Figure 6. Tensile strength of plastic specimens, as measured by ASTM D638. The “X” designates a statistically significant change compared to the control.

Figure 7. Area reduction in plastic specimens. The “X” designates a statistically significant change compared to the control.

Figure 8.

Modulus of elasticity of plastic specimens. The “X” designates a statistically significant change compared to the control.