



## Supercritical CO<sub>2</sub> sterilization of ultra-high molecular weight polyethylene

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### ABSTRACT

The aim of this study was to use a benign technique for the sterilization of ultra-high molecular weight polyethylene (UHMWPE), which is broadly used in artificial joints. The feasibility of using supercritical (SC) CO<sub>2</sub> modified with additives such as ethanol, water and hydrogen peroxide was assessed for the sterilization of UHMWPE. The operating conditions and the amount of modifiers were changed to achieve a complete inactivation of bacteria such as spores and fungi. Complete inactivation of all microorganisms including spores was achieved within 2 h at 37 °C and 170 bar CO<sub>2</sub>, when at least 25 μL hydrogen peroxide was mixed with equal volume of other modifiers. The physio-chemical properties of the polymer were tested for untreated, as well as treated samples. Mechanical strength and elongation of the polymer were measured using an Instron and the oxidation of the polymer was measured using FTIR. Both the physical and chemical properties of the polymer were unchanged after the SC CO<sub>2</sub> sterilization technique.

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### 1. Introduction

Every year, over 1.4 million implants made of ultra-high molecular weight polyethylene (UHMWPE) components are used in patients suffering from injury or disease making it the most widely accepted implant material [1]. In 2004, the US market for joint replacement implants was valued at over \$3.5 billion and this revenue is growing at 12% [2]. UHMWPE is a unique polymer with desirable physical and mechanical properties such as a high tensile and impact strength and resistance to corrosion and abrasion. Despite the success and worldwide acceptance of total joint arthroplasty and restorative procedures, wear and concomitant debris generation is still a major obstacle limiting the longevity of implanted UHMWPE components. Once significant wear has occurred, particulate wear debris can be released inside the joint capsule and this debris can activate macrophages. This often leads to inflammation of the surrounding tissues, and subsequently to necrosis and failure of artificial joints.

Some of the wear can be attributed to polymer weakening during the sterilization process. Commercial sterilization techniques for artificial joints are  $\gamma$ -irradiation, ethylene oxide gas, and gas plasma [3]. Sterilization of UHMWPE with  $\gamma$ -irradiation leads to the formation of polymer free radicals, which can then lead to oxidative polymer chain scission when the polymer is exposed to air [4].

This chain scission causes adverse effects on the elastic modulus, tensile strength, and shear strength of the polymer [5]. Sterilization using either ethylene oxide gas or gas plasma was adopted by the artificial joint industry because these techniques created no free radicals within the polymer [3]. Studies have shown that the chemical, physical, and mechanical properties of UHMWPE sterilized using ethylene oxide gas are nearly the same as the virgin polymer [6–9]. The largest downside to this type of sterilization is that ethylene oxide gas is highly toxic, flammable, carcinogenic [5], and its sterilization must conform to strict international and domestic standards. Gas plasma is the newest of the commercial sterilization techniques and it can be performed at temperatures below 50 °C [10]. Different molecules have been used for this type of sterilization, such as peracetic acid and hydrogen peroxide [3]. Some studies have shown that it does not adversely affect the chemical, physical, or mechanical properties of the UHMWPE [11–14]. However, gas plasma induces oxidation of the surface of the polymer [15], this could lead to long-term negative effects such as increased wear.

High pressure CO<sub>2</sub> has been used for the inactivation of bacteria and the sterilization of polymers [5,16]. Carbon dioxide is nontoxic, nonflammable, abundantly available, and inexpensive. Sterilization using CO<sub>2</sub> is potentially advantageous compared to ethylene oxide because it leaves no toxic residue, has no special requirements for handling, does not react with polymers (i.e., no chain scission will occur), and the process can be conducted at low temperatures due to its low critical temperature (31.1 °C) [16]. Supercritical CO<sub>2</sub> has gas-like transport properties and liquid-like densities, as well as low viscosity and zero surface tension [17]. All of these characteristics allow CO<sub>2</sub> to diffuse into bacteria and spores and biologically

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inactivate them. Zhang et al. [16] compiled an extensive review of the high pressure CO<sub>2</sub> sterilization studies. The overall mechanism for inactivation of bacteria is still not completely understood, but it is hypothesized that there are several different mechanisms that work synergistically. Carbon dioxide can diffuse through bacteria walls and extract vital contents, leaving the bacteria biologically inactive [18]. It also reacts with water in the bacteria to form carbonic acid, this lowers the pH and destabilizes the bacterial contents, such as enzymes [18]. Finally, the bacteria cell membrane can burst during either pressurization [19] or depressurization [20].

The primary objective of this study was to assess the feasibility of using SC CO<sub>2</sub> and low levels of chemical modifiers to minimize microbial contaminations, such as bacteria and fungus, on UHMWPE to levels accepted by FDA standards. The FDA requires a 6 log reduction of bacterial spores in order to approve a new sterilization technique [21]. The chemical modifiers (ethanol, H<sub>2</sub>O, H<sub>2</sub>O<sub>2</sub>) play an important role in the sterilization procedure. The volume of each modifier was varied in order to determine the conditions that required the least amount of modifiers and still resulted in a 6 log reduction.

It is critical to demonstrate that the SC CO<sub>2</sub> sterilization process had no significant impact on the physio-chemical properties such as mechanical strength and oxidation of the implants fabricated from UHMWPE. The tensile strength was used to assess the effect of CO<sub>2</sub> on the mechanical properties of UHMWPE. Any sterilization process may have a negative impact on the oxidation of UHMWPE. It has been found that  $\gamma$ -radiation increased the oxidation of UHMWPE, which resulted in deleterious changes to the physical, chemical, and mechanical behaviors of the polymer during its long-term shelf life [22]. The effect of CO<sub>2</sub>  $\pm$  modifiers on the oxidation of UHMWPE can be measured using FTIR. The goal of this study is to show proof of concept for a new, less destructive, more environmentally friendly sterilization technique for artificial joints, where improved longevity of the implanted joint can be realized.

## 2. Experimental

### 2.1. Materials

UHMWPE (GUR 1050) supplied by Ticona in Bayport, TX (average MW = 4–6 million). Carbon dioxide (food grade, 99.9%) was purchased from BOC. Ethanol (EtOH, 99.9%) and hydrogen peroxide (30% in water) were supplied by Ajax Fine Chemical Pty Ltd. Sabouraud-4% Dextrose Agar for microbiology (1.05438.0500) was supplied by Merck in Darmstadt, Germany. The buffered sodium chloride peptone solution (CM0982) and the Tryptone Soya Agar (CM0131) were supplied by Oxoid in Hampshire, England. A contaminant with a total microbial count of greater than  $5 \times 10^7$  bacteria/g and fungi was extracted from White American Ginseng (*Panax quinquefolius*) that was donated by The Simply Ginseng Company in Bungendore, Australia. *Bacillus Subtilis* spores were also in the contamination that was prepared from soybean product (natto). These sources of bacteria were used to generate diverse range of non-pathogenic gram positive, gram negative bacteria and fungi to minimize biohazard and safety concerns.

### 2.2. Preparation of agar plates

The plates for measuring the colony formation unit and detection of fungi were prepared as described previously [23]. Bacterial and fungus growth plates were created by mixing 40 g of Tryptone Soya Agar and 61 g of Sabouraud-4% Dextrose Agar with 1 L of distilled water, respectively. The solution was heated until transparent and then autoclaved for 15 min at 121 °C and 0.115 MPa, then it was poured into pre-sterilized Petri dishes, cooled to solidify under lam-

inar flow safety cabinet. The covered Petri dishes were then stored at 5 °C until use.

### 2.3. UHMWPE sample preparation

Polymer samples were compression molded from powdered UHMWPE. The powder was poured into a Teflon® film covered mold and heated to 200 °C before applying compressive force. A compression molder (Geo. E. & Son) was used to apply 4 MPa of pressure at 200 °C for 1.5 h to shape the powder into a solid sheet (4–5 mm thick). The sheet was cut into 9.5 mm  $\times$  63.5 mm rectangles to comply with ASTM D 638 type V tensile bars.

Polymer samples were cleaned with a solution of detergent and distilled water, disinfected with 70 wt% ethanol solution and placed under a sterile laminar flow cabinet (class 1) to dry. The disinfection procedure was validated prior to contaminating the samples. No bacterial colony formation units or fungi were detected on the disinfected samples. The samples were stored in a sterile container until intentional contamination.

Prior to conducting the sterilization by SC CO<sub>2</sub>, 0.5 mL of contaminated buffer solution was pipetted onto the surface of the UHMWPE samples (2 per experiment), the buffer solution was dried in a sterile laminar flow cabinet and the mass of contaminant was recorded.

### 2.4. Sterilization procedure

A schematic diagram of the high pressure apparatus used for the sterilization is shown in Fig. 1. The apparatus consists of a high pressure syringe pump (ISCO 500D), a controlled temperature water bath (Thermoline TSB1), and a high pressure vessel (volume 40 mL).

The high pressure vessel was disinfected prior to each run using 70 wt% ethanol. The disinfection procedure for the vessel was validated by conducting a blank run. After the disinfection of the vessel, two runs were performed using uncontaminated UHMWPE samples as controls. No microorganisms were detected on the samples after plating, corroborating that the vessel disinfection procedure was valid.

The contaminated samples and modifiers were added to the high pressure vessel under a sterile laminar flow cabinet, to avoid extraneous contamination. The modifiers were pipetted onto a sterilized Kimwipe® and it was placed at the bottom of the high pressure vessel. The polymer sample (2 per run) was then placed into the vessel; care was taken to avoid direct contact of the modifier with the contaminated sample. The vessel was placed in a constant temperature water bath and allowed to thermally equilibrate to a predetermined temperature. The system was slowly pressurized (5 bar/min) with CO<sub>2</sub> to a desired pressure, isolated from the pump for 2 h, and then it was depressurized (<5 min) to collect the samples for analysis. The operating conditions of using CO<sub>2</sub> at 37 °C and 170 bar for 2 h were adopted from previous study [23]. The amount of modifiers (i.e., ethanol, H<sub>2</sub>O and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)) was varied to achieve minimum 6 log reduction in total microbial count for the sterilization of UHMWPE.

### 2.5. Phase behavior of the CO<sub>2</sub> and modifiers

It is critical to investigate the phase behavior of CO<sub>2</sub> + EtOH + H<sub>2</sub>O + H<sub>2</sub>O<sub>2</sub> prior to sterilization to determine the conditions that the mixtures used theoretically maintained in one-phase region. To the best of our knowledge, no data is available in the literature for the above quaternary system, so we modeled the system as a pseudo ternary system by combining the mole fractions of H<sub>2</sub>O<sub>2</sub> and water and considered it as pure water. The phase equilibrium of the modifiers with CO<sub>2</sub> was estimated at

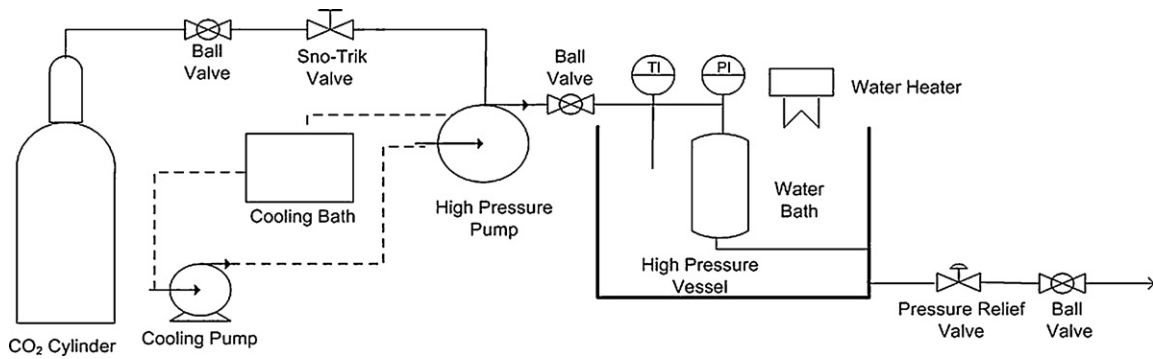


Fig. 1. Schematic diagram of supercritical fluid sterilization apparatus.

the operating condition used in this study using the data available in the literature for the  $\text{CO}_2 + \text{H}_2\text{O} + \text{EtOH}$  [24].

The results in Fig. 2 demonstrate that the ternary equilibrium data for  $40^\circ\text{C}$  and 142 bar,  $40^\circ\text{C}$  and 185 bar, and  $60^\circ\text{C}$  and 142 bar fall nearly on the same curve for this region of the phase diagram. The equilibrium curve is the phase boundary; data points left of the curve are in the two-phase region and data points right of the curve are in the one-phase region.

At each experimental condition, the volume of modifiers was used to determine their mole fraction in  $\text{CO}_2$  and assess the miscibility. The modified Benedict-Webb-Rubin equation of state was used to determine the density of  $\text{CO}_2$  at the experimental conditions. From this information and the volume of the high pressure vessel, the moles of  $\text{CO}_2$  in the system were determined. The moles of the modifiers were calculated from the volume of liquid and their respective density at ambient conditions, since the liquid was sealed in the high pressure vessel at ambient conditions and then heated and pressurized.

## 2.6. Detection of contamination

A standard method was used for viable bacteria counting and fungi determination in solid samples. The sample removed from the high pressure vessel and also the control sample (contaminated and non-sterilized), were placed in 10 mL of buffer solution individually, and shaken using vortex. Two serial 100-fold dilutions were

prepared for each sample by diluting 0.1 mL of suspended sample in 9.9 mL of autoclaved distilled water according to a standard serial dilution procedure. One mL of the diluted sample was then plated on Petri dishes containing Tryptone Soya Agar (for total aerobic microbial count) and Sabouraud Dextrose (for fungi detection). For each polymer sample at least three plates were prepared and then incubated at  $37^\circ\text{C}$  for 1–5 days. At the end of the incubation period, the colonies were counted. The active spores were counted after the plated Petri dishes were held at  $80^\circ\text{C}$  for at least 2 h, and then placed in an incubator at  $37^\circ\text{C}$  for 1–2 days.

Inactivation was expressed as  $\log N_0/N$ , where  $N_0$  is the number of microorganisms (CFU/gram) contained in the sample at the initial period (control sample), and  $N$  is the number of microorganisms counted after treatment at any time  $t$ . These values were normalized using Eq. (1) and the mass of the contamination. No fungal growth in any dilution corresponds to a log reduction of 6.

$$\frac{\text{CFU}}{\text{g}} = \frac{\text{number of bacterial colonies}}{\text{agar plating volume}} \times \frac{1}{\text{dilution factor}} \times \frac{\text{volume of contaminate}}{\text{mass of contaminate}} \quad (1)$$

where the dilution factor is  $5^E-2$ ,  $5^E-4$ , or  $5^E-6$ , agar plating volume is 1 mL, volume of contaminate is 0.5 mL and mass of contaminate is the measured mass of contaminate in gram.

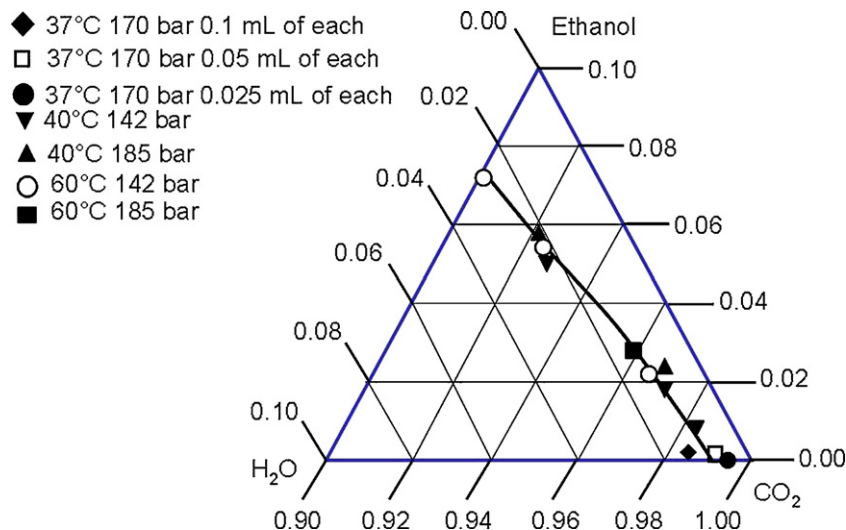


Fig. 2. Ternary phase diagram for  $\text{CO}_2 + \text{water} + \text{ethanol}$  adopted from Lim et al. [24] and experimental conditions used in this study.

**Table 1**  
Experimental conditions for sterilization.

Test #	Ethanol, $\mu\text{L}$ , (mol frac)	Water, $\mu\text{L}$ , (mol frac)	Hydrogen peroxide, $\mu\text{L}$ , (mol frac)	Bacterial log reduction	Fungal log reduction
1	0(0.0)	0(0.0)	0(0.0)	1.80	2
2	100 ( $2.3 \times 10^{-3}$ )	0(0.0)	0(0.0)	1.40	2
3	0(0.0)	100 ( $7.3 \times 10^{-3}$ )	0(0.0)	0.07	2
4	0(0.0)	0 ( $5.1 \times 10^{-3}$ ) <sup>a</sup>	100 ( $1.7 \times 10^{-3}$ )	6.00	6
5	0(0.0)	0 ( $2.6 \times 10^{-3}$ ) <sup>a</sup>	50 ( $8.3 \times 10^{-4}$ )	6.00	6
6	0(0.0)	0 ( $1.3 \times 10^{-3}$ ) <sup>a</sup>	25 ( $4.2 \times 10^{-4}$ )	2.20	2
7	25 ( $5.6 \times 10^{-4}$ )	0 ( $1.3 \times 10^{-3}$ ) <sup>a</sup>	25 ( $4.2 \times 10^{-4}$ )	6.00	6
8	0(0.0)	25 ( $3.1 \times 10^{-3}$ )	25 ( $4.2 \times 10^{-4}$ )	6.00	6
9	25 ( $5.6 \times 10^{-4}$ )	25 ( $3.1 \times 10^{-3}$ )	25 ( $4.2 \times 10^{-4}$ )	6.00	6
10	10 ( $2.3 \times 10^{-4}$ )	10 ( $1.2 \times 10^{-3}$ )	10 ( $1.7 \times 10^{-4}$ )	1.80	2
11	100 ( $2.2 \times 10^{-3}$ )	100 ( $7.2 \times 10^{-3}$ )	0(0.0)	2.20	2

<sup>a</sup> Mole fractions were calculated based on the amount of water presented in 30% (v/v)  $\text{H}_2\text{O}_2$  solution used in these experiments (the amount of  $\text{CO}_2$  was excluded in the calculation).

### 2.7. Mechanical strength testing

Tensile bars of UHMWPE were prepared according to ASTM D 638 type V bars. Tensile tests were performed using an Instron (4468) with a 10 kN load cell and cross-head speed of 100 mm/min. The maximum load and the elongation were normalized via dividing by the sample cross-sectional area. At least 12 untreated specimens and 29 treated samples with  $\text{CO}_2$  were tested for mechanical properties.

### 2.8. Fourier transform infrared spectroscopy (FTIR) analysis

Fourier transform infrared (FTIR) spectroscopy analysis (Varian 660-IR) was used to investigate the effect of  $\text{CO}_2 \pm$  modifiers on the oxidation of UHMWPE. The FTIR spectra for the untreated sample, treated sample by pure  $\text{CO}_2$ , and treated sample by  $\text{CO}_2 +$  modifiers were collected immediately after depressurization. The oxidation of UHMWPE can be determined based upon normalized measurements of the area under the carbonyl peak in the region of  $1650\text{--}1850\text{ cm}^{-1}$ . The oxidation index is obtained when the carbonyl peak area is normalized to the area under the peak at  $1370\text{ cm}^{-1}$ .

## 3. Results and discussion

The bacterial and fungal log reductions at every experimental condition are presented in Table 1. In systems that neat  $\text{CO}_2$  at  $37^\circ\text{C}$  and 170 bar was used, only 1.8 bacterial log reduction was achievable within 2 h sterilization. At these operating conditions, UHMWPE samples were not foamed by  $\text{CO}_2$ . The effect of addition of a modifier on the sterilization efficiency of  $\text{CO}_2$  in binary system of  $\text{CO}_2$ -modifier was determined; as shown in Table 1, the addition of 100  $\mu\text{L}$  ethanol or 100  $\mu\text{L}$  water as a single modifier (tests 2 and 3) had negligible effect on inactivation of bacteria. However, 6 log reduction was achievable in systems that 50  $\mu\text{L}$  hydrogen peroxide was used. At lower concentrations, such as 25  $\mu\text{L}$ , only 2.2 log reduction was achievable (test 6).

The synergistic effect of modifiers on the sterilization of UHMWPE was investigated. Complete inactivation was not achievable in the ternary systems that one phase  $\text{CO}_2 +$  ethanol +  $\text{H}_2\text{O}$  was used. However,  $\text{CO}_2 + 25\ \mu\text{L}\ \text{H}_2\text{O}_2 + 25\ \mu\text{L}\ \text{EtOH}$  or  $\text{H}_2\text{O}$  was efficient for complete inactivation (6 log reduction in tests 7 and 8).

A series of tests introduced the modifiers all in equal volumes to determine the minimum amount for complete sterilization. The results in Table 1 show that the minimum total amount of modifiers for complete sterilization was 75  $\mu\text{L}$  (test 9). Test 10 shows that at low volumes of each modifier (10  $\mu\text{L}$ ) only 1.8 log reduction was achievable. Utilization of water + ethanol had also negligible effect on the sterilization (test 11). At all conditions examined there were no obvious changes in the dimension of samples.

The operating conditions used in this study ( $37^\circ\text{C}$  and 170 bar) were similar to the data available from literature, thus, we assumed that the equilibrium curve for our system also lay on the same curve. The ternary phase diagram (Fig. 2) shows that a mixture of  $\text{CO}_2 + 100\ \mu\text{L}\ \text{water} + 100\ \mu\text{L}\ \text{EtOH} + 100\ \mu\text{L}\ \text{H}_2\text{O}_2$  was in the two-phase region, meaning that  $\text{CO}_2$  phase was saturated with these compounds. When 50  $\mu\text{L}$  of each of the three liquids was added to the system, the point lay slightly right of the equilibrium line, meaning that  $\text{CO}_2$  was nearly saturated at this condition. All other compositions tested were in the one-phase region of the ternary phase diagram.

Other researchers observed similar effects from adding modifiers; sterilization using SC  $\text{CO}_2$  was enhanced when a solvent such as water, ethanol, and hydrogen peroxide was added to the system [25,26,21]. It was found that a minimum amount of hydrogen peroxide was required for the complete sterilization using a SC  $\text{CO}_2$  process, however, addition of extra water to the system beyond saturation did not improve the sterilization efficiency [23]. In this study we also observed similar behavior; complete sterilization was achieved with a low mole fraction of  $\text{H}_2\text{O}_2$ . Zhang et al. also found that the log reduction was dramatically increased when they used  $\text{H}_2\text{O}_2$  instead of water or ethanol [21]. In other studies  $\text{H}_2\text{O}_2$  and SC  $\text{CO}_2$  were used effectively for sterilization [27–29].

### 3.1. Effect of $\text{CO}_2$ sterilization process on the physio-chemical properties of UHMWPE

The results of mechanical testing corroborated that modified  $\text{CO}_2$  used for complete sterilization of UHMWPE had negligible effect on the samples. The results in Table 2 demonstrate that the maximum load and elongation of processed samples were similar to the untreated ones. At each condition (maximum load)/(cross-sectional area) and (maximum elongation)/(cross-sectional area) were measured for at least six samples and the *t* test was conducted to compare untreated and treated samples; the *p* value of 0.84 and 0.92, respectively confirmed that there is no difference between these two groups of samples.

The FTIR spectra of the UHMWPE exposed to  $\text{CO}_2 \pm$  modifier at  $37^\circ\text{C}$  and 170 bar for 2 h were compared with untreated samples. The results in Fig. 3 demonstrate that the peak height of the carbonyl at  $1750\text{ cm}^{-1}$ , which corresponds to the degree of

**Table 2**  
Mechanical properties of treated and untreated UHMWPE samples.

	Elongation/area (mm/mm <sup>2</sup> )	Load/area (N/mm <sup>2</sup> )
Sterilized sample with modified $\text{CO}_2$	$4.47 \pm 1.1$	$35.1 \pm 4.8$
Untreated sample	$4.42 \pm 1.2$	$35.5 \pm 5.2$

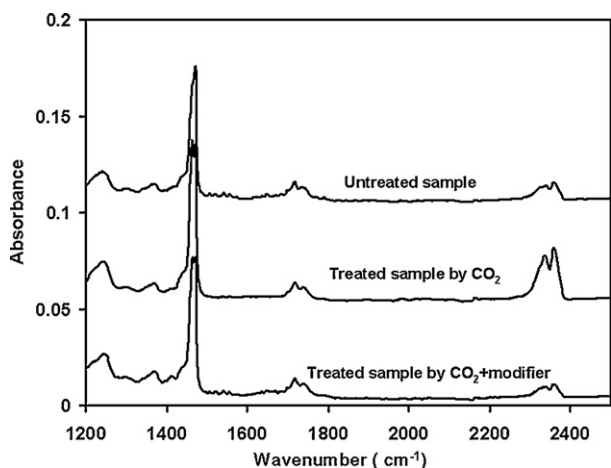


Fig. 3. FTIR spectrum of UHMWPE.

oxidation, did not increase after sterilization by  $\text{CO}_2 \pm$  modifier (25  $\mu\text{L}$  water + 25  $\mu\text{L}$  EtOH + 25  $\mu\text{L}$   $\text{H}_2\text{O}_2$ ), indicating that high pressure  $\text{CO}_2$  is a robust method for sterilization of UHMWPE without any effect on the chemical integrity of the material. This non-destructive SC  $\text{CO}_2$  sterilization technique can be an alternative to the commercial methods to sterilize UHMWPE; this will decrease the number of repeat joint replacement surgical operations because they will have a longer life-span.

#### 4. Conclusions

Complete sterilization, 6 log reduction, of bacteria (including spores) and fungi on ultra-high molecular weight polyethylene was accomplished by using  $\text{CO}_2$  (170 bar) with modifiers at 37 °C for 2 h. It was shown that of the modifiers, hydrogen peroxide had the greatest impact on log reduction, and that water had the least impact. Mechanical properties testing showed that this type of sterilization had no statistically significant negative effects on the tensile strength or elongation of the polymer. FTIR studies showed that the degree of oxidation did not increase due to the sterilization technique, even when hydrogen peroxide was present.

The three aims of this study have all been met: (1) A 6 log reduction was achieved, (2) mechanical properties of the polymer were unchanged after sterilization and (3) the surface of the polymer did not show signs of increased oxidation. This method of sterilization shows great promise to improve the longevity of human artificial joint implants, it is also safe to operate and environmentally friendly process due to the physical and chemical characteristics of SC  $\text{CO}_2$ . The supercritical fluid technology has been used in commercial scale for extraction, fractionation, cleaning and also for the sterilization of tissue allograft (e.g., Novasterilis). The outcome of this study can open an avenue to broaden the SC technology for the sterilization of implants fabricated from polymers in commercial scale.

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