Effects of Calcium Stearate Addition of Ultrahigh Molecular Weight Polyethylene in Direct Compression Molding

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ABSTRACT: The effects of calcium stearate addition in molding of ultrahigh molecular weight polyethylene (UHMWPE) were investigated by tensile testing, scanning electron microscope (SEM), Fourier transform infrared (FT-IR) spectroscopy, and elemental analysis. Four types of UHMWPE specimens with varying contents of calcium stearate (<5, 50, 100, and 1000 ppm) were used in this study. SEM observation revealed that calcium stearate added specimens have smoother and more homogeneous microstructures. After accelerated aging, subsurface oxidative degeneration was observed in all specimens; however, calcium stearate added specimens had less oxidative degeneration in comparison with specimens without additives. Specimens showed better mechanical properties with increasing content of calcium stearate. Though all specimens aggravated their mechanical properties due to oxidation after accelerated aging, the specimens of 100 ppm of calcium stearate showed better properties at 3.7 MPa larger yield strength and four times larger value of elongation at fracture than the specimens without additives. These results indicate that calcium stearate addition produces dense packing of UHMWPE particles, which brings about stronger fusion among the particles and fewer structural defects, and results in better mechanical properties and better resistance to oxidative degeneration. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 87: 1602–1609, 2003

Key words: calcium stearate; molding; ultrahigh molecular weight polyethylene; tensile testing; scanning electron microscopy; Fourier transform infrared; elemental analysis

INTRODUCTION

Through the years, although use of higher molecular weight powder has seen improvement in ultrahigh molecular weight polyethylene (UHMWPE) products, decrease of moldability of UHMWPE particles due to lower lubrication among the particles has resulted. The content of calcium stearate is not more than 50 ppm for medical use. This content was determined by the minimum amount owing to neutralization of the catalyst. Calcium stearate at the content of 100 ppm or above has been used as an additive in the molding of UHMWPE, enables denser packing of UHMWPE particles, and raises melting fluidity of the UHMWPE for industrial uses.

In the past decade, quite a large number of severe degeneration and wear cases of UHMWPE artificial joint implants, the probable cause being oxidative degeneration, have been reported. Many studies revealed that oxidative degeneration of particle boundaries develop into severe subsurface oxidative degeneration of UHMWPE implants, which is a major cause of UHMWPE delamination wear.[1,2] Various research-

ers have produced different reasons for the cause of oxidative degeneration. However, one clear and certain cause of severe oxidative degeneration is γ-irradiation in air for sterilization.[3,4] γ-Irradiation in air doubtlessly aggravates UHMWPE properties and accelerates oxidative degeneration spreading along the particle boundary area. Thus, currently, all medical manufacturers have terminated sterilization of UHMWPE implants with γ-irradiation in air. Oxidative degeneration occurs where oxygen exists and spread along residual oxygen; therefore, even without γ-irradiation, weakness of particle fusion and structural defects cause severe oxidative degeneration.[2] Consequently, low manufacturing pressure, which brings about insufficient fusion among the particles and structural defects, allows the existence of residual oxygen inside products and aggravates resistance against oxidative degeneration.[5] To tighten fusion and decrease structural defects, some manufacturers choose compression mold manufacturing for higher and more constant manufacturing pressure in spite of high costs.[1,6] Medical grade UHMWPE powder has seen an increase in its molecular weight of up to six million from three million in order to improve properties. Additives, capable of improving moldability, have not been preferred over the lower moldability higher molecular weight UHMWPE in order to avoid foreign substances in medical products. Addition of
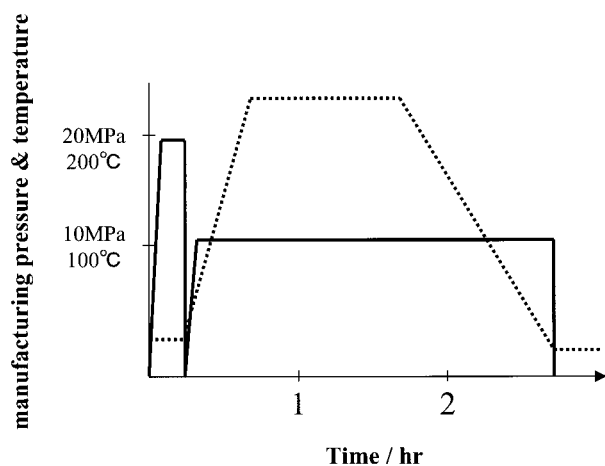
Figure 1 Molding procedure showing by manufacturing pressure (—) and temperature (----) plotted against time.

calcium stearate is effective for processing of UHMWPE in compression molding, but medical manufacturers for UHMWPE implants have choosing been additive-free UHMWPE powder recently. The use of calcium stearate is on the breach of disappearance in the manufacture of UHMWPE medical implants without detailed studies about the pros and cons of calcium stearate addition.

In this study, we examined effects of calcium stearate addition on the internal microstructure of UHMWPE and mechanical properties. We also analyzed the surface of mold metals to evaluate the effects of calcium stearate on neutralizing chlorine, a catalytic residual.

MATERIALS AND METHODS

Specimen preparation

Four sample groups of dumbbell-shaped test specimens [Japanese Industrial Standard (JIS) K7113-2 type, thickness = 1.2–3.0 mm] with molecular weights in the same range but with varying contents of calcium stearate were prepared for this study. All specimens were directly compression molded at 10 MPa, 220°C (Fig. 1). PE-0 specimens were medical commercial grade UHMWPE (GUR1050, Ticona, USA), not containing calcium stearate (<5 ppm). PE-50 specimens were medical commercial grade UHMWPE (GUR1150, Ticona, USA), containing 50 ppm of calcium stearate. PE-100 and PE-1000 specimens were prepared by mixing medical grade UHMWPE (GUR1050, Ticona, USA) with 100 and 1000 ppm of reagent grade calcium stearate in 2000 mL mechanical blender at 8500 rpm for 10 min intermittently (PE-100: 100 ppm, PE-1000: 1000 ppm). To simulate degradation of UHMWPE over many years, an accelerated aging technique was employed.[7,8] γ-Ray irradiation (a dose of 2.5 Mrad) was performed on half of the specimens from each group at room temperature in air. Next, irradiated specimens

were placed in an oven at constant temperature of 80°C for 23 days.

Scanning electron microscopic (SEM) observation

According to the specimen preparation method of Watanabe et al. virgin specimens and accelerated aged specimens were fractured in liquid nitrogen at extremely high strain rates to avoid stresses on fractured surface.[9] Observations of these freeze-fractured surfaces were performed in order to evaluate internal microstructure by a scanning electron microscope (S-4500, Hitachi).

### Fourier transform infrared (FTIR) spectroscopy

Using a Poly Cuts Microtome (Reichert-Jung), specimens were sliced at approximately 40-μm thickness rectangular to the compressed surface. The extent of oxidation in each UHMWPE specimens was determined by a Fourier transform infrared spectroscopy (model 2000 FT-IR, Perkin Elmer) from surface to surface. The oxidation index was defined as the ratio of the carbonyl peak area (1660 ~ 1800 cm^{-1}) to the methyl peak area (1400 ~ 1560 cm^{-1}), followed by former studies.[6,7]

Tensile testing

Tensile testing was carried out with crosshead speed of 1000 mm/min (corresponding strain rates: 0.4) and gauge length of 25 mm at 37°C by using a tensile tester (model 4502, Instron). Young's modulus, yield strength, and elongation at fracture of virgin and aged specimens were measured.

Elemental analysis of mold surface

In order to evaluate the damage of mold surfaces caused by chlorine, a catalytic residual in direct compression molding, the mold surfaces were analyzed after several moldings. Distributions of chemical elements on each mold surface after molding UHMWPE powder of PE-0 and PE-50 were analyzed by an optical microscope and an Electron Probe Micro Analyzer (JEOL JXA-8900R, EPMA). Virgin prehardened steel plates with polished surface exactly the same as mold surfaces were mounted on top of the mold. These molds were molded with each type of UHMWPE powder four times. Polishing surface procedures before molding and molding procedure were exactly same as manufacturing UHMWPE implants. After the fourth molding, these metal plates were removed from the molds, stored in air at room temperature with approximately 45% humidity for 48 h, and then analyzed. Three polished prehardened steel plates stored with test specimens were used as controls.
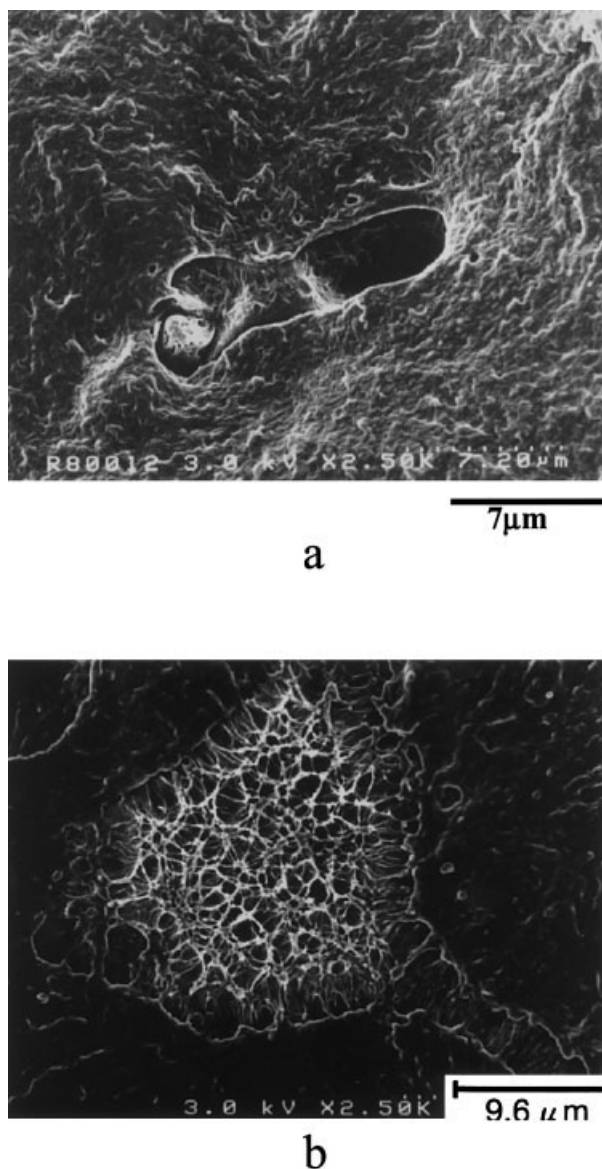
Figure 2 SEM micrographs of a void (a) and a fusion defect (b).

RESULTS

Scanning electron microscopy

To evaluate internal microstructure, we counted the number of structural defects such as voids and fusion defects larger than 5 μm in diameter in each observation area of 200 × 240 μm (Fig. 2).

Significant differences were evident between PE-0 and other specimens. In virgin specimens, an average of 3 structural defects per unit area of 72,000 μm^2 were found in PE-0, and an average of 0.8 structural defects per site were found in PE-50, PE-100, and PE-1000 (Fig. 3). Virgin PE-0, PE-50, PE-100, and PE-1000 showed smooth and homogeneous microstructure. No obvious differences between the specimen types were evident besides structural defects.

After the aging process, microstructure degeneration was observed in all specimens, making structural defects uncountable. It was undoubtedly evident that PE-50, PE-100, and PE-1000 were degenerated less than PE-0. PE-0 showed multifocal subsurface-degenerated areas, consisting of extremely rough structure. These degenerative changes resemble subsurface oxidative degeneration of retrieved UHMWPE implants[1,4] [Fig. 3(c)]. Although similar degenerative changes were evident in PE-50, PE-100, and PE-1000, the number and size of degenerative areas suggest calcium stearate added specimens had less degenerative changes than PE-0 [Fig. 3(d)]. Differences between PE-50, PE-100, and PE-1000 were relatively small compared to the differences between PE-0 and others. These degenerations occurred approximately 50–700 μm in depth from the surface of specimens in all specimens, which coincides with former reports of severe wear and delamination.[2,3]

Fourier transform infrared spectroscopy

Figure 4 shows the oxidation index according to depth from the surface. The oxidation index determined by IR spectroscopy for all virgin specimens was undetectable. After aging, the oxidation pattern of all specimens showed symmetrical peak with respect to the center of specimens. In all groups, two oxidation peaks existed at almost equivalent distances from both surfaces and almost no oxidation was detected in the center of the specimens. The area of oxidation ranged from 100 to 1000 μm depth under the surface, and almost no oxidation was detected deeper than 1000 μm from the surfaces. The oxidation pattern coincided with SEM observations, the oxidized area determined by FTIR matched with severely degenerated areas such as honeycomb structure, and no oxidation area matched with smooth and homogenous structure. The oxidation peak of PE-50, PE-100, and PE-1000 was respectively 0.07 at 350 μm in depth, 0.08 at 200 μm in depth, and 0.05 at 300 μm in depth. There was no remarkable difference in content of calcium stearate. PE-0 showed similar oxidation index values at 200–400 μm from the surface (0.08 at 300 μm in depth), but PE-0 had a higher peak of 0.12 at 550 μm in depth. Without contents of calcium stearate, oxidation index tended to show higher peaks at deeper areas.

Tensile testing

It is easier to recognize differences of Young's modulus between all groups by investigating stress vs strain curves (Fig. 5). All aged specimens significantly increased Young's modules. The aging process following γ-ray irradiation increased the modulus of PE-0 up to 145%. The modulus of PE-50, PE-100, and PE-1000 were also increased up to 140% after accelerated aging. No differences in modulus of virgin specimens between each group were observed; however, after
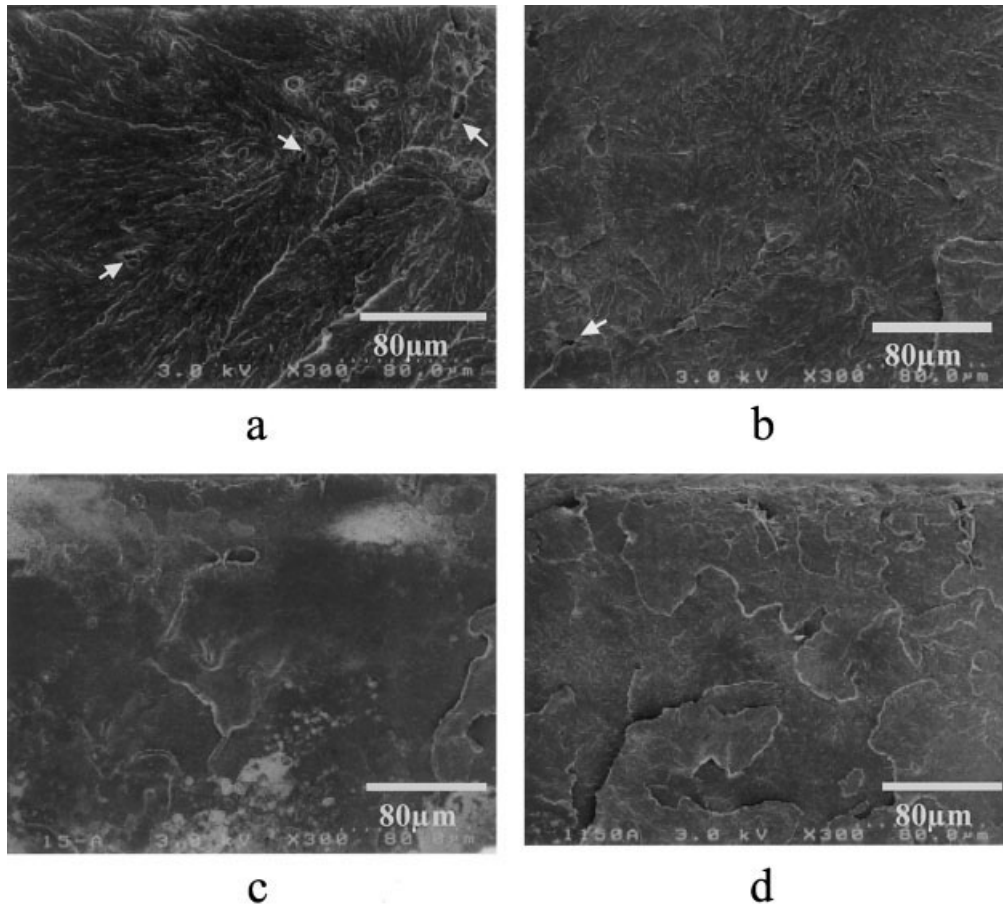
Figure 3 SEM micrographs of freeze-fractured surfaces of UHMWPE specimens: (a) virgin PE-0; (b) virgin PE-50; (c) accelerated aged PE-0; (d) accelerated aged PE-50. The molded surfaces of specimens are upper end of figures. The arrows in (a) and (b) indicate structural defects larger than 5 μm in diameter.

aging, the modulus tended to show lower values according to calcium stearate content.

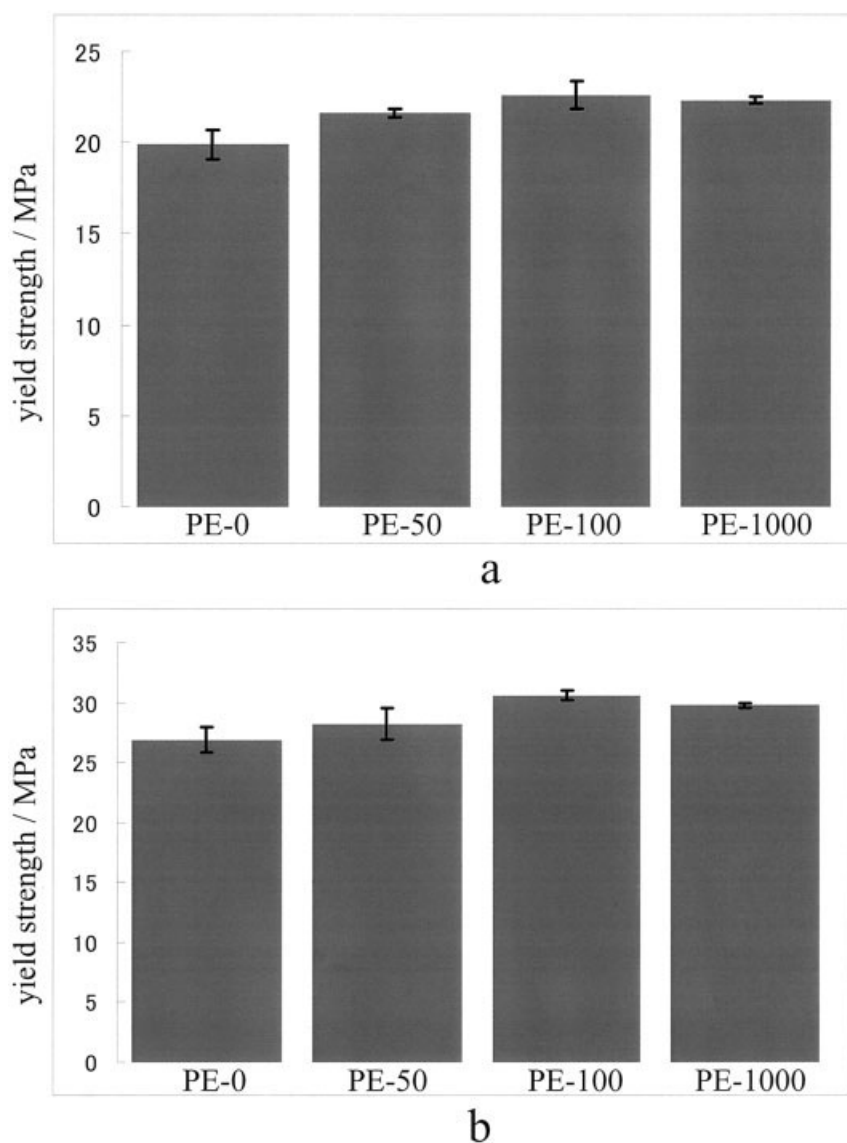Figure 6(a) shows yield strength of virgin specimens. Yield strength of PE-0 was 19.9 MPa. With increased contents of calcium stearate, yield strength increased up to a certain content level of calcium stearate. Yield strength of PE-50 was 21.5 MPa, and yield strength increased up to 22.6 MPa in PE-100. PE-1000 showed 22.3 MPa of yield strength, which was almost same as PE-100. Figure 6(b) shows yield
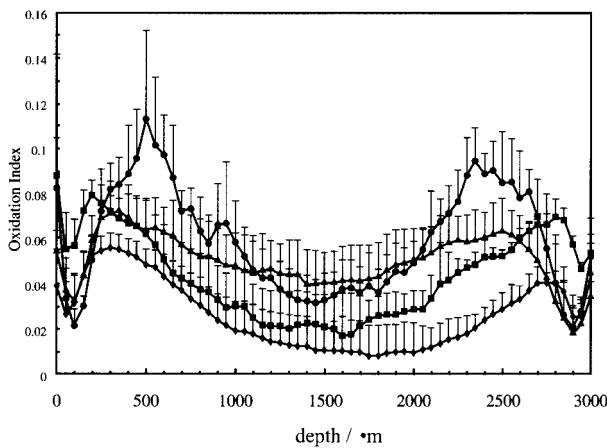
Figure 4 Oxidation index vs. depth curves obtained by FTIR: (—●—) PE-0; (—▲—) PE-50; (—■—) PE-100; (—◆—) PE-1000. The oxidation index was measured from the surface (0 μm in depth) to the other surface (3000 μm in depth).
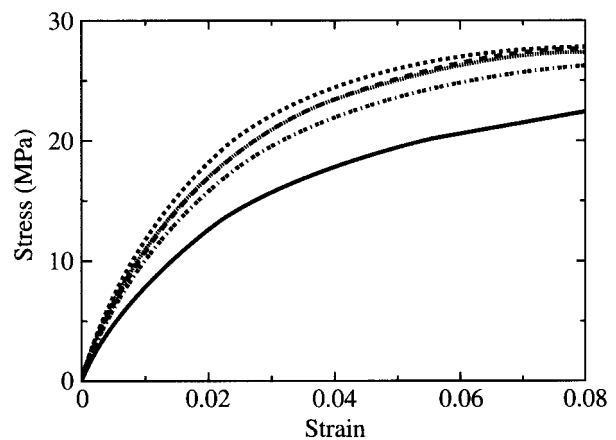
Figure 5 Stress vs strain curves of specimens up to the strain of 0.08. Curves of all virgin specimens fall on the same curve (—): (· · ·) accelerated aged PE-0; (- - -) accelerated aged PE-50; (▥) accelerated aged PE-100; (- - · - -) accelerated aged PE-1000.

Figure 6 Yield strength of specimens with different content of calcium stearate: (a) yield strength of virgin specimens; (b) yield strength of accelerated aged specimens.

strength of aged specimens. After an accelerated aging process, yield strength increased and the tendency for content-dependent increase until a certain content of calcium stearate in yield strength remained even after aging. Yield strengths of PE-0, PE-50, PE-100, and PE-1000 were respectively 26.9, 28.2, 30.6, and 29.8 MPa.
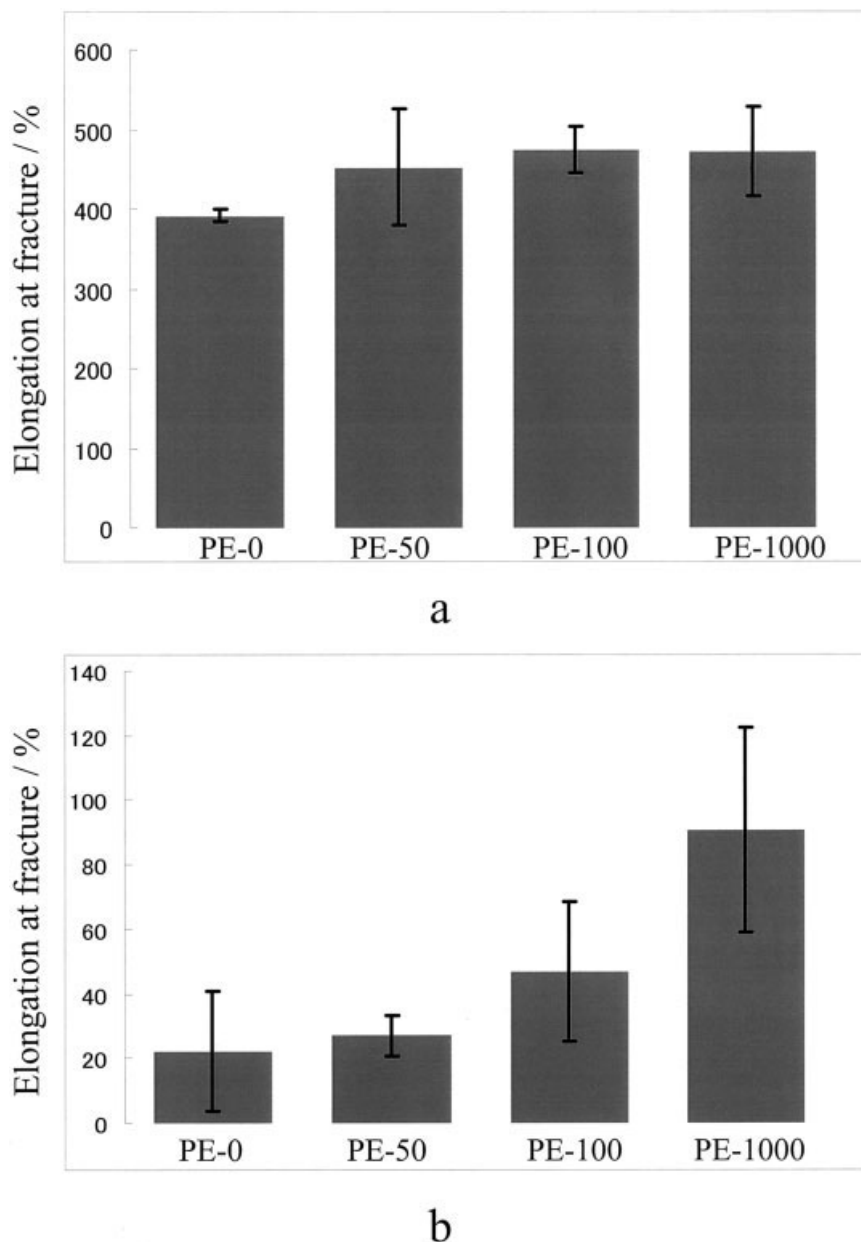
Figure 7 shows elongation at fracture of all specimens. Virgin specimens of PE-0 fractured at 390% of elongation on average; however, all calcium stearate added specimens, PE-50, PE-100 and PE-1000, withstood 450% of elongation, demonstrating a significant difference between PE-0 and other specimens. After the aging process, all specimens demonstrated striking decrease values in elongation at fracture. Elongation at fracture of PE-0, PE-50, PE-100, and PE-1000 was respectively 22, 27, 47, and 91%. Higher content of calcium stearate showed larger value of elongation at

fracture, and PE-1000 showed four times larger than the value of PE-0.

Elemental analysis of mold surface

All metal plates used for molding of PE-0 and PE-50 revealed relatively lusterless appearance after four moldings. After 48 h storage, the metal plates of PE-0 were totally rusted compared to a relatively lustered surface of PE-50. It was difficult to observe significant differences between PE-50 and control at microscopic observation (Fig. 8).

Elemental analysis of mold surface revealed existence of oxygen on all plates except the control, which indicates that molding surfaces have been oxidized by molding UHMWPE powder. PE-0 showed a remarkably larger ratio of oxygen existence than PE-50. The existence of 0.38 atom % of chlorine was detected only

Figure 7 Elongation at fracture of specimens with different content of calcium stearate: (a) elongation at fracture of virgin specimens; (b) elongation at fracture of accelerated aged specimens.
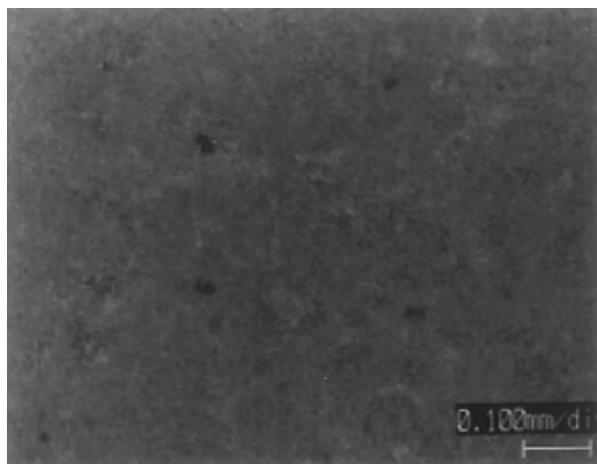
in PE-0 (Table I). This suggests that unneutralized chlorine—namely, a catalytic residual—corrodes molding surfaces, and is preventable by using small amount of calcium stearate as an additive.
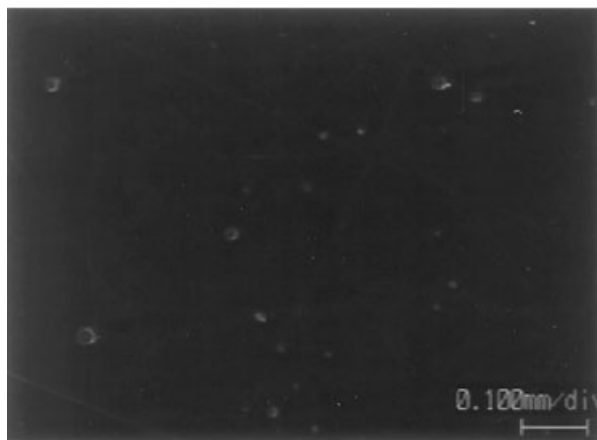
DISCUSSION

SEM observation of virgin specimens revealed smooth and homogeneous structure with only a few structural defects. Furthermore, calcium stearate addition revealed decrease of structural defects. After accelerated aging, SEM observation of all specimens demonstrated rough structure around 50–700 μm in depth from the surface. These rough structures resemble the honeycomb structure, which was reported as subsur-

face oxidative degeneration.[8] The peaks of oxidation index at 100–1000 μm under the surfaces measured by FTIR corroborate with findings that these rough structures were caused by oxidative degeneration. It is interesting that all specimens showed subsurface oxidation patterns, which has been reported to be caused by the spread of oxygen along particle boundaries.[2–4] With increasing content of calcium stearate, the size and extent of oxidative degeneration decreases on the SEM observation. Using Watanabe's oxidation grading for SEM observation, PE-0 was categorized in grade 3, while PE-50, PE-100, and PE-1000 were categorized in grade 2 after accelerated aging.[9] This suggests that even calcium stearate remains inside the UHMWPE product; PE-50, PE-100, and PE-1000 have
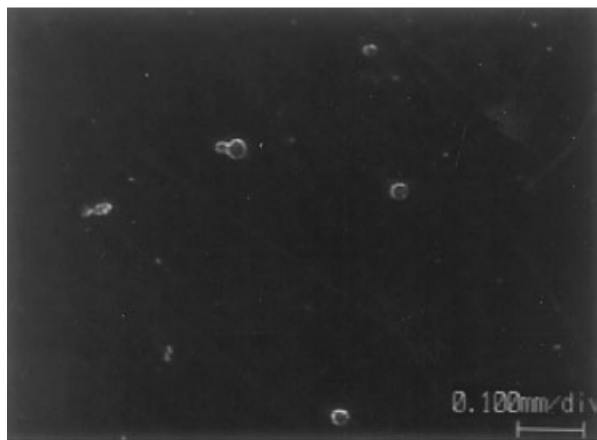
been demonstrated to have larger bonding strength of particle boundaries than PE-0. Calcium stearate is used generally as lubricant and slip agent in the molding processing of plastics and rubbers. The calcium

TABLE I
Distributions of Chemical Elements on Mold Surface Obtained by Electron Probe Microanalyzer (Atom %)

Element	PE-0	PE-50	Control
C	28.34	28.64	26.00
O	**26.86**	**6.64**	**ND**
Al	2.28	3.02	4.16
Si	1.09	0.70	0.94
Cl	**0.38**	**ND**	**ND**
Mn	0.87	1.14	1.43
Fe	37.96	56.06	63.02
Cu	0.85	1.43	1.45
Ni	1.37	2.36	3.00

a

b

c

Figure 8 The appearances of the mold surfaces obtained by optical microscope: (a) used for molding PE-0; (b) used for molding PE-50; (c) control.

stearate lowers the interaction between UHMWPE particles as its lubricant function. The pacing density of UHMWPE is improved by the prevention of aggregation of UHMWPE particles owing to the presence of calcium stearate on the surfaces of the particles. The fusion among adjacent UHMWPE particles was improved, because the addition of calcium stearate facilitates the melt flow UHMWPE in compression molding processing. Therefore, the calcium stearate addition has positive effects for preventing oxidative degeneration. Decrease of structural defects in virgin specimens suggests that calcium stearate addition raises fluidity of particles and concurrently produces dense packing of UHMWPE particles, which results in dense packing of particles and prevents diffusion of oxygen.

Fracture of UHMWPE in tensile testing occurs by the following mechanism: the deformation generates voids inside the structure. As strain increases, voids develop in number and size until fracture occurs. Innate structural defects cause concentration of stress and lead to the development of voids under strain force. Therefore, if UHMWPE has a large number of structural defects such as fusion defects and honeycomb structure, it could be broken at a lower strain than smooth and homogeneous UHMWPE.

Yield strength of PE-0 showed a lower value than PE-100 in virgin and aged specimens. Compound polymer, which contains micron glass beads inside, decreases its yield strength in comparison with unadulterated polymer. These micron glass beads can be regarded as voids, and increasing the number of these voids decreases yield strength of the polymer.[10,11] This suggests that PE-0 had larger number of voids within the structure than PE-100, and this coincides with the finding that PE-0 showed the largest number of voids in virgin specimens and the severest degeneration in aged specimens. Accelerated aging increased Young's modulus and made stress vs strain curves 40–45% steeper in all specimens. Yield strength was also increased nearly 40% in all specimens after aging. These changes due to accelerated aging can be explained by oxidation of UHMWPE, which causes an increase of crystallinity, which results in higher modulus and

yield strength. Many researchers have reported that the increase of the modulus of the samples after aging is owing to the increase of their crystallinity from differential scanning calorimetry measurement.[12–15]

According to the fracture mechanism of UHMWPE, elongation at fracture can be improved by decreasing structural defects. The elongation at fracture of virgin PE-50, PE-100, and PE-1000 showed 61–83% larger strain than PE-0. Moreover, PE-100 and PE-1000 showed two to four times larger values of elongation at fracture in comparison with PE-0 after accelerated aging, which brings about a striking decrease of elongation at fracture due to oxidative degeneration. Calcium stearate does not have the protective function for the oxidation of UHMWPE. The mechanical properties of UHMWPE compounded calcium stearate are not improved by the chemical reaction of calcium stearate. Therefore, these great differences of elongation at fracture among the specimens indicate that calcium stearate addition brings about stronger fusion among the UHMWPE particles for improvement of pacing density of the particles and melting flow of UHMWPE.

When UHMWPE is melted, UHMWPE does not flow easily like low molecular weight polyethylene such as LDPE and HDPE, owing to its high molecular weight and excessive entanglement. When UHMWPE is heated above its crystalline melting temperature (125–135°C), the resin become rubbery but does not flow. The method of fabricated forms for commonly used thermoplastics cannot be applied to process UHMWPE due to this extremely high melt viscosity. The processing of UHMWPE requires a proper combination of temperature, high pressure, and time to achieve complete plastification. It is necessary for processing of the UHMWPE plate to apply enough temperature and pressure to the UHMW-PE powder in order to ensure that the particles are fully sintered. These results suggest that calcium stearate addition brings about higher moldability and raises fluidity, concurrently producing dense packing of UHMWPE particles. These effects result in fewer structural defects and greater bonding strength among the particles, producing better mechanical properties and resistance to oxidative degeneration. Moreover, it also prevents corrosion of molding surfaces by neutralizing chlorine, a catalytic residual.

CONCLUSION

This study evaluated effects of calcium stearate addition in direct compression molding. Calcium stearate addition brings about dense and solid structure with fewer structural defects. Accordingly, this additive would be an asset in the molding of UHMWPE implants through compression molding on grounds of the following results.

1. SEM observation revealed that calcium stearate addition decreased structural defects and prevented extent of subsurface oxidative degeneration such as honeycomb structure.
2. FTIR spectroscopy revealed subsurface oxidation 100–1000 μm from the surface after aging. Calcium stearate addition brought about remarkable suppression of oxidation, and FTIR revealed lower oxidation peak in calcium stearate added specimens at a shallower depth from the surface in comparison with additive-free specimens. PE-100 showed an oxidation index value of 0.08 at 200 μm in depth from the surface while PE-0 showed 0.12 at 550 μm in depth.
3. At tensile testing, mechanical properties improve with an increase of content of calcium stearate. The yield strength of PE-100 was 22.6 MPa while PE-0 showed 19.9 MPa. After accelerated aging, PE-100 showed 30.6 MPa of yield strength, which was 3.7 MPa larger than PE-0. And calcium stearate added specimens (PE-50, PE-100, and PE-1000) withstood a 61–83% larger strain than PE-0 in tensile testing of elongation at fracture.

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