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Analysis of the effect of pressure on compression moulding of UHMWPE

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Ultra-high molecular weight polyethylene (UHMWPE) powder is effectively processed by compression moulding due to its very high melt viscosity. Compression moulding involves application of temperature and pressure as a function of time. The pressure applied during processing has a significant influence on the part properties. The effect of pressure applied during compression moulding was studied by moulding parts at different pressures. Increase in the applied pressure causes increase in the melting and recrystallization temperatures. An increase in the pressure applied at the melt temperature (~140 °C) from 7.8 MPa to 15.6 MPa caused the crystallinity to increase from 54% to 61%, the stiffness of the moulded part to increase from 257 MPa to 435 MPa and oxidative index to increase from 0.055 to 0.059. Further increase in the pressure applied at the melt to 23 MPa caused the crystallinity to fall to 49%, the modulus to reduce significantly to 302 MPa and the oxidative index to change to 0.063. Increase in the pressure applied at the recrystallization temperature (~91 °C) from 38 MPa to 78 MPa increased the crystallinity from 54% to 65%, increased the modulus from 257 MPa to 279 MPa and increased the oxidative index from 0.055 to 0.065. Further increase in the applied pressure to 97 MPa, caused the crystallinity to drop slightly to 61% the modulus to reduce to 269 MPa, and the oxidative index to reduce to 0.057. The experiments showed that for obtaining maximum crystallinity and stiffness, the applied pressure should be within a narrow range. The highest recrystallization pressure (97 MPa) indicated the formation of extended-chain crystals in addition to the chain-folded crystals. The change in pressure applied at the melt temperature had a significantly greater effect on Young's modulus, as compared to change in pressure applied at the recrystallization temperature. Fourier transform–infrared spectroscopy analysis of the samples moulded at different pressures revealed that the increase in crystallinity and stiffness was accompanied by increase in oxidation within the part. By filling the die in a nitrogen atmosphere instead of air, the oxidation level in the moulded parts was reduced by almost 60%, without adversely affecting the crystallinity and the modulus. © *1998 Chapman & Hall*

1. Introduction

UHMWPE is a material of choice for tribological applications including orthopaedic implants due to its excellent wear-resistant properties and high toughness. The cyclic contact stresses at the articulating surface can cause pitting and delamination, leading to the formation of wear debris. The wear debris can lead to osteolysis and bone resorption which can cause further degradation of the joint [1–4]. Unfused powder particles within the implant degrade the properties, and increase wear within the implant [5]. Wang *et al.* [6] studied wear within acetabular cups and developed a model for predicting wear within the cups. The model related the wear rate to the rate of cyclic inelastic wear accumulation within the UHMWPE under contact that was subjected to repeated microscopic asperity passes. Many researchers [7–9] have recently focused on the wear and degradation due to sterilization-induced oxidation of UHMWPE implants. Wear and oxidative degradation are interrelated and are the major factors in reducing the life of implants.

Tanner *et al.* [10] showed that wear within orthopaedic implants depended on starting raw materials and processing methods used for manufacturing. Zachariades *et al.* [11] showed that physical and mechanical properties of extrudates were dependent on the initial morphology of the polymer. There are currently two different manufacturing processes widely used for producing orthopaedic implants. One of them is compression moulding and the other is ram extrusion followed by machining. The quality of compression-moulded parts is better compared to parts that are ram extruded. Bankston *et al.* [12] showed that compression-moulded parts show much lower wear rates as compared to parts machined from extruded bar stock.

Compression moulding is emerging as the preferred processing route for orthopaedic implants, because it offers good process and morphological control.

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Compression moulding involves application of pressure and temperature in a proper sequence to produce parts of highest quality. The pressure applied at melt reduces the voids, removes the entrapped air and reduces the porosity. The pressure applied at recrystallization increases the crystallinity. Although the effect of pressure on the crystallization of polyethylene under the experimental setup has been studied [13–15], the effect of the change in applied pressure during processing, on the properties of the moulded parts, has not been thoroughly studied. Hence, a quantitative study of the effect of pressure applied at melt and at recrystallization is necessary. In this study, the compression-moulding pressure is applied as three step functions, an initial high compaction pressure ($\sim$38 MPa), followed by a low pressure ($\sim$7–23 MPa) at melt and a final high pressure ($\sim$38–97 MPa) during recrystallization.

The chemical and morphological changes occurring during compression moulding were investigated using a differential scanning calorimeter (DSC). An increase in pressure applied at melt was found to increase the polymer crystallinity and consolidation until a certain critical pressure was reached. Any increase in pressure beyond the critical pressure led to a decrease in polymer crystallinity and poor consolidation. An increase in pressure applied at the recrystallization temperature caused a steady increase in the crystallinity and stiffness. The effect of pressure on oxidation was studied using Fourier transform–infrared spectroscopy (FT–IR). This study showed that the oxidative index increased until a certain pressure was reached and then reduced. The maximum crystallinity, modulus and oxidation occurred at the same pressure levels. An additional step involving filling of the die in a nitrogen atmosphere was observed to significantly reduce the oxidation in the moulded components without affecting crystallinity and modulus.

2. Materials and Methods

2.1. Material systems

The UHMWPE powder used for the study was Hostalen GUR 4150 provided by Hoecsht Celanese. The bulk density of the powder was 400 kg m^{-3}, and the average molecular weight was 7.3 × 10^6. The laser diffraction technique was used to obtain particle-size distribution of UHMWPE powder particles (Fig. 1). The number average powder particle size was 200.2 μm.

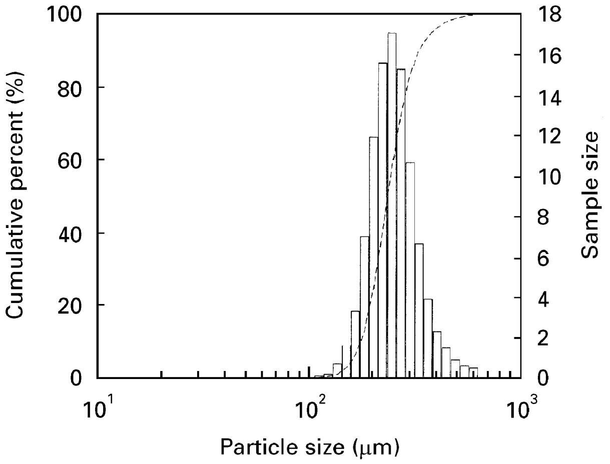

Figure 1 Particle size distribution for UHMWPE powder. (– – –) Cumulative per cent, (—) sample size.

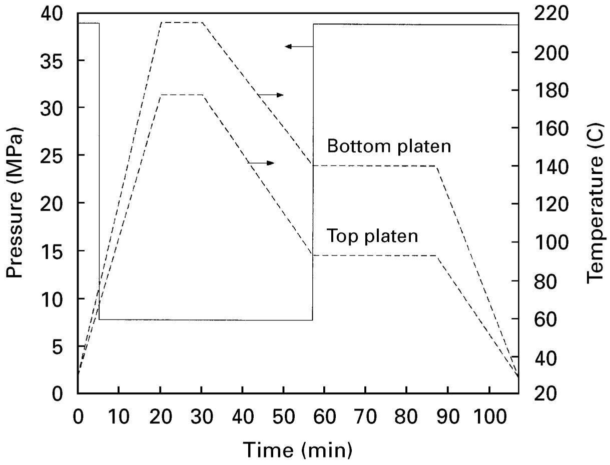

Figure 2 A typical processing cycle used during experiments. (—) Pressure, (– – – –) temperature.

TABLE I A typical processing cycle

Step number	Time (min)	Terminology for applied pressure	Pressure (MPa)	Temperature (°C)	
				Top	Bottom
1	0	Compaction	38.9	29	29
2	5	Melt	7.8		
3	20	Melt	7.8	177	215
4	30	Melt	7.8	177	215
5	57	Recrystallization	38.9	93	140
6	87	Recrystallization	38.9	93	140
7	107	–	0.0	29	29

2.2. Experiments

Samples were compression moulded by using 12 g UHMWPE powder. A typical processing cycle is shown in Fig. 2. Table I lists the temperatures and pressures used during a typical compression-moulding cycle. During the initial 5 min period of the heating cycle, a high pressure of 38 MPa was applied. The high initial pressure helped in compacting the powder and in removal of the voids. After 5 min, the pressure was reduced to 7.8 MPa. Thus, near the polymer melt temperature ($\sim$140 °C) the pressure applied was low enough to avoid squeeze flow. The polymer was then soaked at the melt temperature for 10 min. After, the soak the polymer was cooled to its recrystallization temperature ($\sim$93 °C) using air cooling. At the recrystallization temperature, the pressure was increased to 38 MPa, and the polymer was soaked for 30 min. After the soak at recrystallization, the polymer was cooled to room temperature and then the pressure was released.

Five different values of melt pressures and four different values of recrystallization pressures were

TABLE II Different pressures used during the experiments

	Melt pressure (MPa)	Recrystallization pressure (MPa)
1	7.79	38.93
2	11.68	58.40
3	15.57	77.87
4	19.47	97.33
5	23.36	–

selected (Table II) for this study. The recrystallization pressure used for the samples moulded at different melt pressures was 38 MPa, and the melt pressure value used for samples moulded at different recrystallization pressures was 7.8 MPa.

The maximum value of melt pressure was selected such that any further increase in pressure would cause squeeze flow, and the minimum value was the lowest pressure that ensured positive contact between the ram and the polymer powder. The maximum value of recrystallization pressure was governed by the machine capacity, and the minimum value was just greater than the maximum melt pressure. Three parts were moulded for each test case to ensure repeatability.

2.2.1. Differential scanning calorimetry

Compression-moulded samples were cut and tested with a Perkin–Elmer DSC2C differential scanning calorimeter. A section through the centre was used for taking three specimens from each moulded sample for the DSC. The specimens were around 2 mm × 2 mm cross-sections, with their mass ranging from 3.5–8.0 mg. The DSC scans were conducted by heating the samples from 300–550 K at a rate of 20 K min^{-1}, followed by a soak at 550 K for 5 min and a final cool down to 300 K at a cooling rate of 20 K min^{-1}.

The heat of crystallization was obtained as the area under the melt peak of the DSC scan. A sigmoidal curve was used as the baseline. The crystallinity was calculated using the ratio of the heat of fusion of the sample to the heat of fusion of a 100% crystalline sample (288 J g^{-1} [16]).

2.2.2. Tensile testing

Subtle differences in consolidation of the part can be revealed using a film tensile testing of thin films microtomed from the samples. Tensile tests on films taken from the compression-moulded samples were conducted using an Instron tensile testing machine. Five films from each moulded sample were microtomed and tested. The results from the tensile tests were used to calculate the Young's modulus using the slope of the stress–stain curve and the energy absorbed before failure (toughness) using the area under the stress–strain curve.

The thickness of the microtomed films was measured at three different sections of each film using dead weight calipers and was observed to be consistent. The average thickness of the microtomed films ranged from 120–190 μm. The sample width was 13.2 mm and the specific gauge length used was 12.7 mm. The samples were mounted using friction grips between the crosshead. The crosshead speed used was 0.42 mm s^{-1} (1.0 in. min^{-1}). Five films were tested from each sample and the strength and modulus of these films were obtained.

2.2.3. Fourier transform–infrared spectroscopy

FT–IR experiments were conducted on the microtomed films with a Nicolet magna series 550 spectrometer in transmission mode using a resolution of 4 cm^{-1}. Each microtomed film was scanned at two different places and the readings averaged. Oxidation within the part was characterized through the ketone (1712 cm^{-1}) and carbonyl ester peaks (1740 cm^{-1}). The oxidative index was obtained by normalizing the area under the curve between 1660 and 1800 cm^{-1} with area under the curve for methylene scissoring vibration from 1400–1500 cm^{-1}.

3. Results

The results from DSC scans (Fig.3), tensile tests and FT–IR scans for parts moulded at different melt pressures are listed in Table III. The crystallinity of the sample increased from 54% to 61% as the melt pressure was increased from 7.8 MPa to 15.6 MPa (Fig. 4). The increase in applied pressure caused an increase in

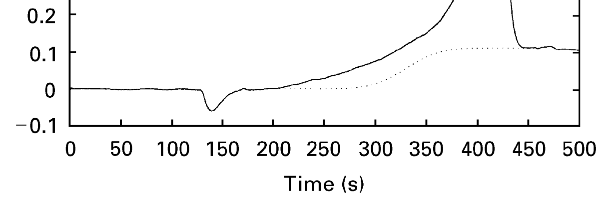

Figure 3 Typical DSC scans showing effect of melt pressure on crystallinity. (—) DSC scan, (– – –) baseline.

TABLE III Effect of melt pressure on tensile characteristics of patella button

Melt pressure (MPa)	Crystallinity (%)	Young's modulus (MPa)	Energy absorbed (J)	Oxidative index
7.79	54.44	257.15	1.35	0.0555
11.68	59.74	282.02	1.25	0.0630
15.57	60.94	435.51	0.63	0.0590
19.47	51.93	430.29	0.57	0.0655
23.36	48.58	302.95	1.07	0.0630

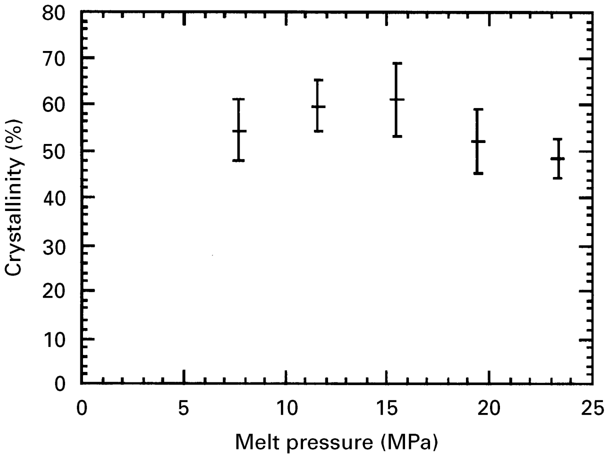

Figure 4 Effect of melt pressure on crystallinity (recrystallization pressure = 38 MPa).

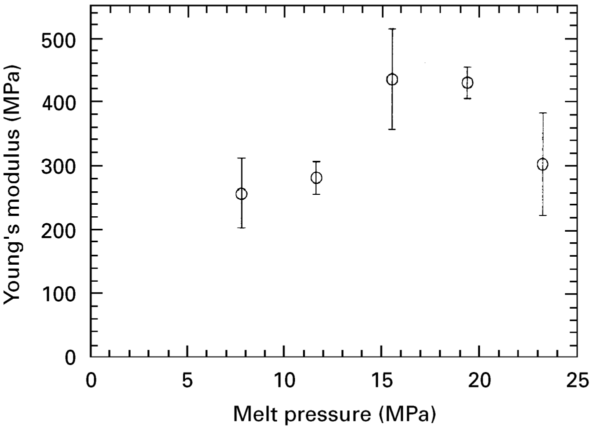

Figure 5 Effect of melt pressure on Young's modulus (recrystallization pressure = 38 MPa).

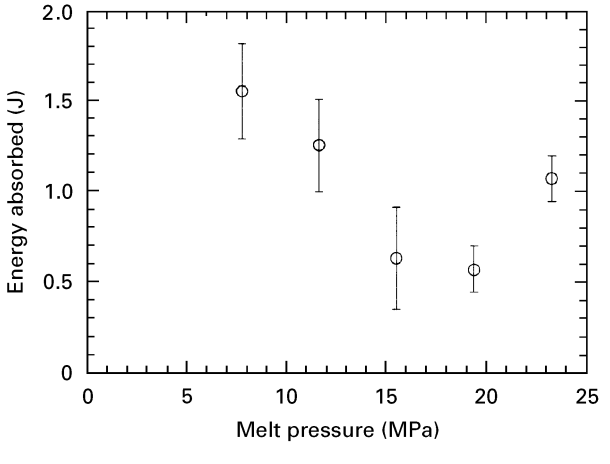

Figure 6 Effect of melt pressure on tensile toughness (recrystallization pressure = 38 MPa).

the Young's modulus of the moulded parts increased by almost 70% from 257 MPa to 436 MPa (Fig. 5) and a decrease in tensile toughness of the specimen from 1.35 J to 0.63 J (Fig. 6). FT–IR results showed that the oxidative index varied from 0.055–0.065 (Fig. 7). Further increase in the melt pressure to 23 MPa led to a fractional decrease in the crystallinity to 49%, the Young's modulus dropped to 303 MPa and the energy absorbed during the tensile testing increased to 1.07 J. The oxidative index also reduced to 0.063. An increase in pressure caused an initial increase in the modulus and decrease in the strength followed by a decrease in the strength and an increase in the modulus. The oxidative index also increased, until a certain pressure (~15 MPa) was reached; beyond that value, the oxidative index reduced.

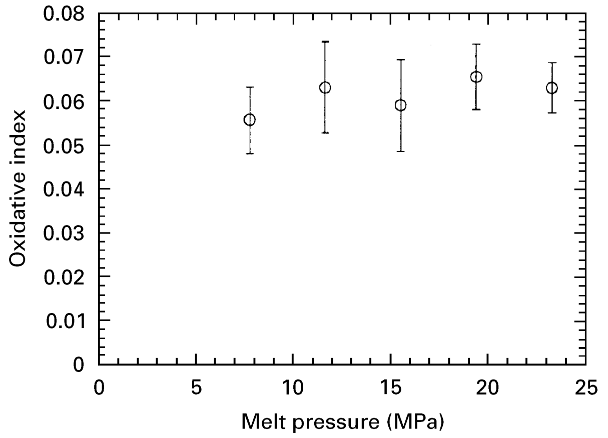

Figure 7 Effect of melt pressure on oxidation (recrystallization pressure = 38 MPa).

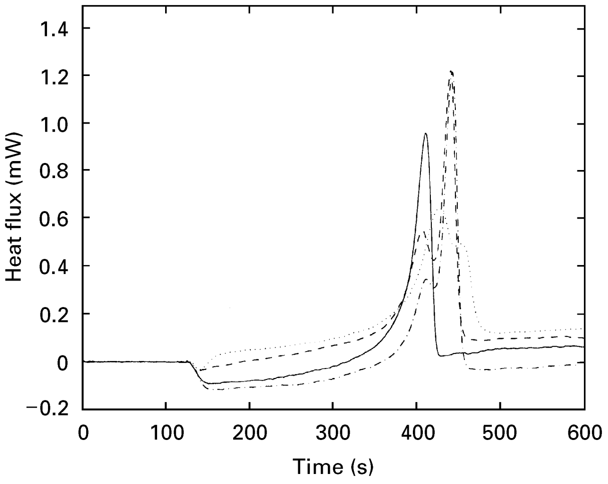

Figure 8 Change in DSC scans due to change in recrystallization pressure: (—) 38 MPa, (– – –) 58 MPa, (– –) 78 MPa, (– · –) 97 MPa (melt pressure = 7.8 MPa)

TABLE IV Effect of recrystallization pressure on tensile characteristics of patella button.

Recrystallization pressure (MPa)	Crystallinity (%)	Young's modulus (MPa)	Energy absorbed (J)	Oxidative index
38.93	54.44	257.15	1.55	0.0555
58.04	59.49	273.52	1.38	0.0645
77.87	64.67	279.40	1.18	0.0610
97.33	61.21	269.35	1.28	0.0570

Fig. 1 shows variation in the heat flow curves for samples moulded at different recrystallization pressures. Some of the curves clearly show two melting peaks. Table I has the tabulated results for crystallinity, young's modulus, energy absorbed and oxidative index measured for parts moulded at different recrystallization pressures.

As the recrystallization pressure was increased from 38 MPa to 78 MPa the crystallinity increased from

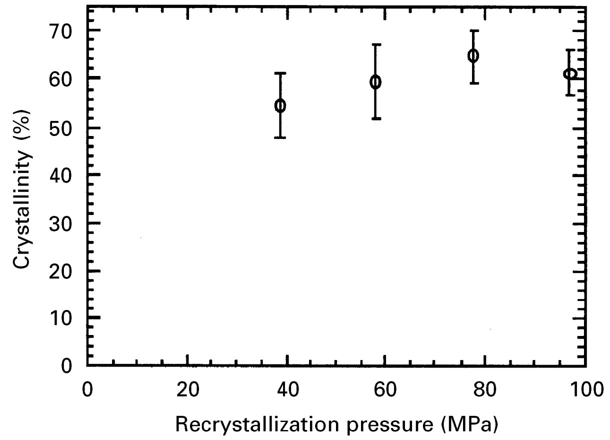

Figure 9 Effect of recrystallization pressure on crystallinity (melt pressure = 7.8 MPa).

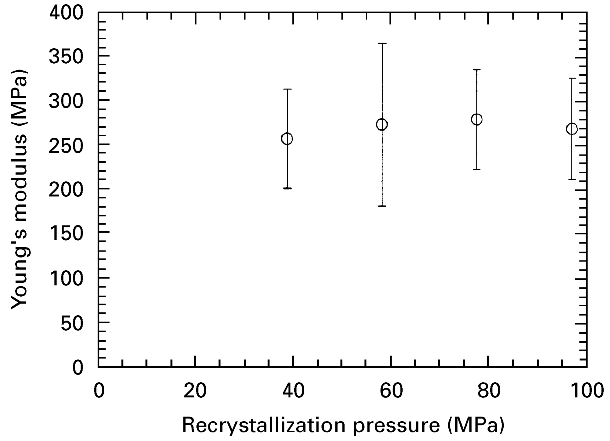

Figure 10 Effect of recrystallization pressure on Young's modulus (melt pressure = 7.8 MPa).

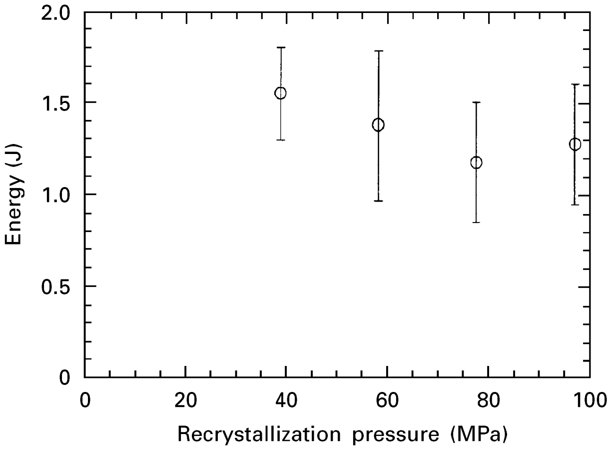

Figure 11 Effect of recrystallization pressure on tensile toughness (melt pressure = 7.8 MPa).

54% to 65% (Fig. 9). The Young's modulus increased slightly from 257 MPa to 279 MPa (Fig. 10). The tensile toughness reduced from 1.55 to 1.18 J due to an increase in the recrystallization pressure from 38 MPa to 78 MPa. Further increase in the recrystallization pressure to 97 MPa led to an increase in the tensile toughness to 1.28 J (Fig. 11). The oxidative index increased from 0.055 to 0.065 (Fig. 12). Further increase in the recrystallization pressure to 97 MPa caused a slight reduction in crystallinity to 61%, the Young's modulus dropped slightly to 269 MPa, the tensile toughness increased to 1.28 J and the oxidative index reduced to 0.057. The DSC scans revealed two melting peaks for some of the samples tested. There was no statistical correlation between the second melt peak and the applied recrystallization pressure, except for a pressure of 97 MPa. Seven out of the nine samples, moulded at a recrystallization pressure of 97 MPa, tested with the DSC showed two melt peaks. The first melt peak for all the samples was within 129–132 °C, and the second ;melt peak was within 137–142 °C.

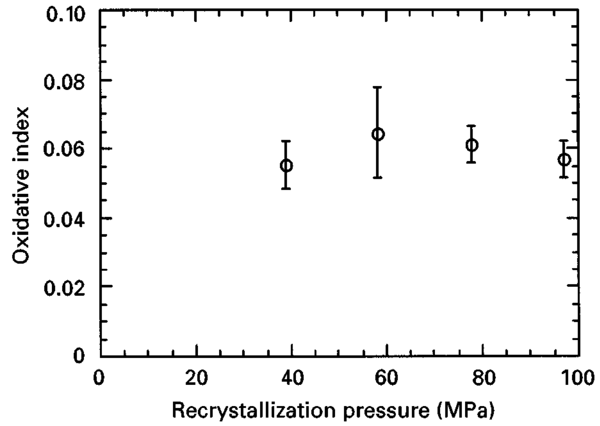

Figure 12 Effect of recrystallization pressure on oxidation (melt pressure = 7.8 MPa).

4. Discussion

The pressure applied during the melting of the polymer increases the melting point of the polymer. As the melting point is increased, a greater portion of the initial crystallinity is retained in the polymer, hindering growth of newer crystals. Although the equilibrium melting point of UHMWPE is 130 °C, Zachariades and Kanamoto [17] showed that complete fusion of crystalline phase occurs only at elevated temperatures when sufficient disentanglement and chain transition occurs. Gao and Mackley [18] have demonstrated the memory effect in UHMWPE while explaining the structure within molten UHMWPE. Crystallinity, modulus and oxidation increase with applied pressure, attain a maximum value and then reduce. The changes in crystallinity are of the order of ~10%–20%, whereas the modulus changes by ~100%. The change in modulus can be explained by studying the sintering behaviour of the polymer powder. The increased pressure improves the consolidation of the polymer powder up to the compressive strength of the polymer powder (~17 MPa), beyond which any increase in pressure does not have a significant effect on the sintering. However, there is a significant increase in the melting point at pressures of 25 MPa which hinders flow and consolidation of the polymer powder. The consolidation of the moulded part has a direct effect on the tensile properties. Well-consolidated parts have a higher modulus compared to poorly consolidated parts. The micrograph of a polymer film taken from a sample moulded at 15.6 MPa melt pressure shows no unconsolidated flakes or fusion defects. The micrograph of a sample from a part moulded at 23 MPa shows significant unfused flakes. The effect of change in applied pressure is much more significant on the Young's modulus and on the energy absorbed than on crystallinity. The Young's modulus is the highest around 15 MPa pressure (at melt) and drops off for any value either higher or lower. The initial increase in pressure helps in consolidation and fusion of flakes (Fig. 13). The energy absorbed is minimum at 15 MPa pressure and is higher for any other pressure. At very high melt pressures, the increase in melting point is significant, leaving a greater number of unfused flakes within the moulded part (Fig. 14). There is a slight improvement in crystallinity, which is accompanied by increased oxidation levels. A closer look at the oxidation leading to the formation of carboxyl groups shows a steady increase in the carboxyl group formation. Iring and Tudos [19] have shown that oxidation within polyethylene due to carboxyl group formation causes chain scission.

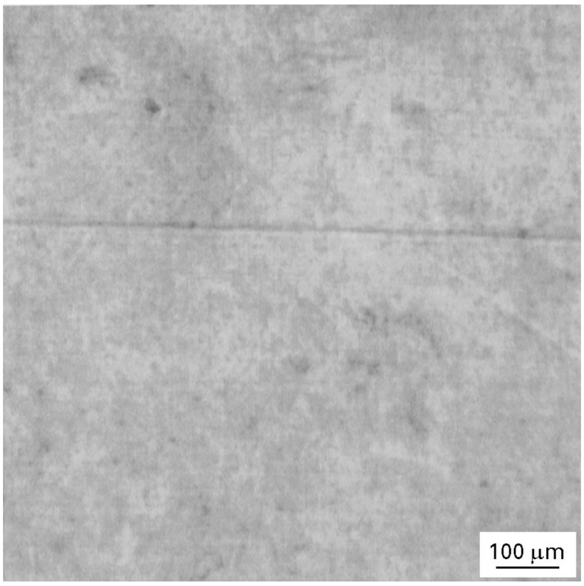

Figure 13 Parts moulded at medium melt pressure show good consolidation (recrystallization pressure = 38 MPa).

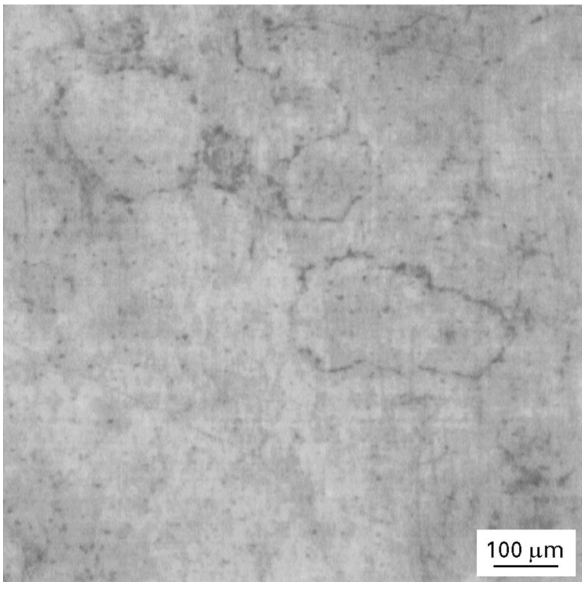

Figure 14 Parts moulded at high melt pressure show unfused flakes and poor consolidation (recrystallization pressure = 38 MPa).

Pressure applied during recrystallization of the polymer increased the recrystallization temperature. Simultaneously, the high pressure causes high stresses within the part and destroys the unstable smaller crystals, helping in melting. The increased pressure leads to increased crystal thickness as the crystallites get packed together. The DSC scans showed that the second phase in the melting scan increased with increasing recrystallization pressure. The results can be intepreted in terms of chain-folded and chain-extended crystal lamellae [13, 14]. At pressures lower than 90 MPa, chain-folded crystals appear. Above the recrystallization pressure of 90 MPa, chain-extended crystals appear. The melting point values obtained in the experiments compare favourably with those obtained by other researchers [13, 14]. The increased crystallinity causes an improvement in the tensile modulus of the part, and a simultaneous reduction in the energy absorbed during failure, as the brittleness within the part increases. Stresses within the part, increase due to the high applied pressure, leading to chain scission. Chain scissions provide additional sites for oxidation, leading to an increase in the oxidative index. The FT–IR results show that an increase in crystallinity and modulus are accompanied by an increase in oxidation, and a decrease in crystallinity and modulus are accompanied by a decrease in oxidation. The increase in crystallinity and modulus are beneficial effects. Oxidation brings about an increase in crystallinity, decrease in tensile strength and reduction in ultimate elongation [20]. The chain scission is indicated by an increase in the number of carboxyl groups formed (Figs. 15 and 16). The reduced molecular weight causes a reduction in the melting point of the moulded samples as indicated by the DSC results. Recrystallization of broken tie chains occurs immediately following chain scission in amorphous regions.

Single-factor ANOVA analysis of the effect of melt pressure and of the effect of recrystallization pressure on crystallinity was conducted. The analysis showed that melt pressure had a statistically significant effect

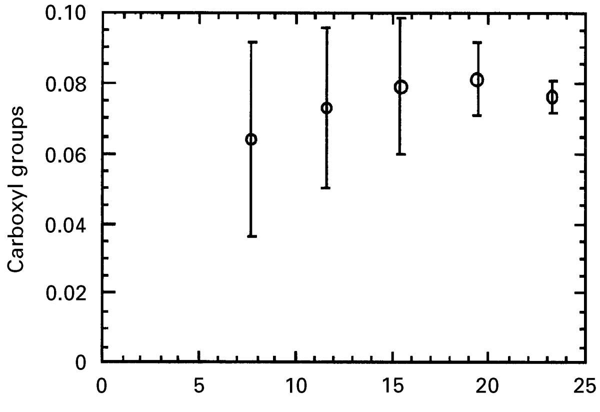

Figure 15 Effect of melt pressure on carbonyl group formation (recrystallization pressure = 38 MPa).

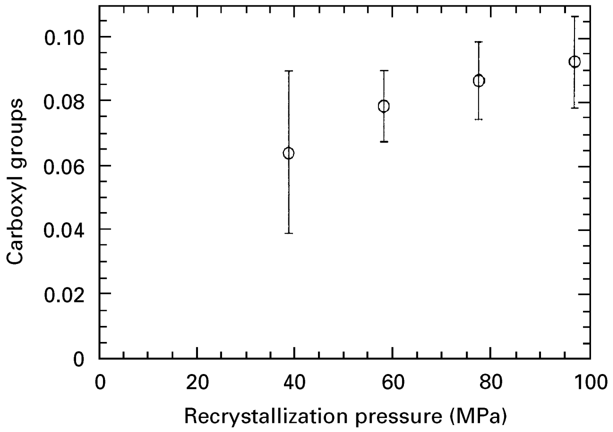

Figure 16 Effect of recrystallization pressure on carbonyl group formation (melt pressure = 7.8 MPa).

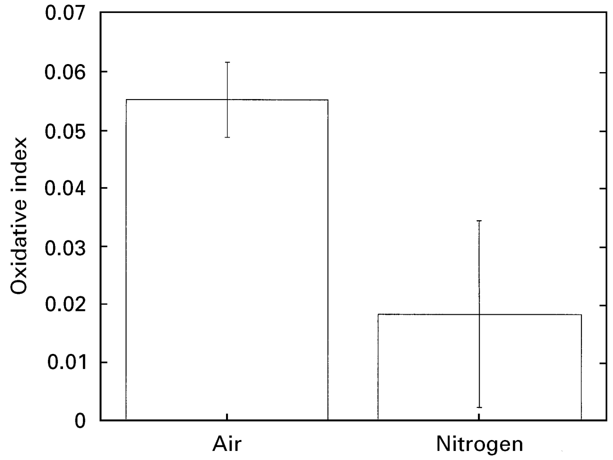

Figure 17 Effect of die-filling atmosphere on oxidation.

on crystallinity, whereas recrystallization pressure had a statistically insignificant effect on crystallinity of the moulded part. Pressure applied at melt has significantly greater effect on the tensile properties of the moulded part than the pressure applied at recrystallization. The greater effect on the tensile properties can be traced to the unfused flakes and incomplete consolidation. Significant portions of the mechanical strength and stiffness are developed during consolidation and sintering. Increase in crystallinity does increase the stiffness and strength, but not to a second order.

Particulate debris is a major factor in reducing the life of orthopaedic implants. Among the major factors affecting wear is oxidation. To avoid the increased oxidation accompanying the high crystallinity and modulus, an additional processing step was used. The die filled with the polymer was placed in an evacuated chamber. A vacuum of 91.18 kPa (27 in. Hg) was applied for 1 min, followed by filling the chamber with nitrogen under 34.5 kPa (5 p.s.i.) pressure for 1 min. This cycle was repeated three times before compression moulding. The FT–IR analysis of these specimens revealed that the oxidation level decreased from 0.055 to 0.018 (Fig. 17). The crystallinity and strength of the parts were, however, comparable to the parts with normal die filling (Table V). The possible reason for this could be that most of the oxidation is occurring at elevated temperatures and pressures inside the mould and is caused by oxygen in the entrapped air. The die filling in an evacuated chamber removes most of the traces of air/oxygen inside the die. Although air is free to flow into the die during moulding, it does not replace the entrapped inert gas, nitrogen.

TABLE V Effect of die filling atmosphere on quality of the moulded part

Die filling atmosphere	Crystallinity (%)	Young's modulus (MPa)	Energy absorbed (J)	Oxidative index
Air	62.04	435.51	0.63	0.0555
Nitrogen	61.17	405.21	0.79	0.0180

5. Conclusion

Increase in the pressure applied at melt improved the sintering and consolidation polymer powder. However, the increased pressure also increased the melting point of the polymer. Hence, the pressure applied at melt increased the crystallinity and modulus, until a certain pressure was reached, beyond which the crystallinity and modulus reduced. The quality of consolidation of the moulded part had a significant effect on the modulus of the part. An increase in the pressure applied at recrystallization helps in increasing the crystallinity of the part. Very high recrystallization pressure leads to the formation of chain-extended crystals. High crystallinity and modulus were accompanied by a low strength and high oxidation levels. For obtaining the highest crystallinity and modulus, the processing should be carried out within a small window of applied pressures. If the applied pressures are significantly higher or lower than this window, parts of low crystallinity and modulus are produced, often accompanied by incomplete consolidation.

High oxidation levels accompanying the high crystallinity and stiffness were avoided by a simple initial step of filling the die in a nitrogen atmosphere. The nitrogen filling does not affect the crystallinity and modulus of the part.

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