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**STUDIES ON
STRUCTURE AND MECHANICAL PROPERTIES OF
SLIGHTLY CROSS-LINKED UHMWPE CRYSTALLIZED
UNDER UNIAXIAL COMPRESSION
FOR
ARTIFICIAL JOINTS**

MAKOTO OHTA

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GENERAL INTRODUCTION

Replacement joints and orthopaedic implants have had a great impact on orthopaedic surgery since the 1960's¹⁾. Typically, metal or ceramic bearing surfaces articulate with a counterface of ultra high molecular weight polyethylene (UHMWPE). For total hip joints, the metal or ceramic ball articulates in a relatively conformable fashion with a hemispherical UHMWPE cup²⁾.

Although total joint replacements have been highly successful for many years, both wear and the accumulation of wear debris (primarily UHMWPE) cause adverse cellular responses, leading to inflammation, release of damaging enzymes and even bone cell lysis (death), and eventual loosening and revision of the implant³⁻¹⁶⁾. Wear mechanisms revealed¹⁷⁻²⁷⁾ that minimizing the production rate of debris may be essential to avoid the above cellular responses and potential revision of the implant, because small amounts of UHMWPE debris released at slow rates can be well tolerated.

To improve wear properties, a number of different material combinations of the bearing surfaces in total artificial joints have been studied over the last three decades. Pairs of highly polished cobalt chromium alloy surfaces have been used in limited numbers in hip prostheses. Although due to the high hard materials tend to propagate stress, there is concern about the high level of friction, which might affect the loosening processes²⁸⁾. In addition, sophisticated manufacturing processes are required to achieve the high quality surface finish and the three dimensional tolerances required in this type of bearing.

Many kinds of different types of polymers sliding on smooth metal surfaces have

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been examined as the bearing surfaces. Polytetrafluoroethylene (PTFE) was first used by Charnly³⁰⁾ due to its low frictional resistance of sliding on metal. It soon became evident that the wear of this polymer was unacceptably high and the volume of wear debris produced could not be tolerated by the body.

To improve the wear factor of UHMWPE, several attempts were performed. For example, Hylamer (manufactured by DePuy-Dupont) had a very high level of crystallinity (about 70%), the wear factor was very high and the attempt failed³¹⁻³⁴⁾. It was conformed that increasing crystallinity and modulus markedly depressed the impact relaxation due to decreasing the proportion of amorphous phase.

The use of γ -ray irradiation for sterilization of UHMWPE implants can change the mechanical properties and wear resistance³⁵⁻⁴¹⁾. These findings suggested that γ -ray irradiation reduces their abrasion resistance of cyclic loading and, subsequently, may contribute to the associated fatigue-related failures.

The molecular orientation of UHMWPE has been investigated in its material properties since the 1960's to enhance wear resistance⁴²⁻⁵²⁾. Macroscopic anisotropy caused by the orientation of long-chain molecules in the structure, should be well controlled for the purpose of usage. The macroscopic deformation of UHMWPE, either in the molten or the solid state, orientated molecular chains parallel to the deformed direction. However, since the molecular orientation cannot be simply and directly related to the macroscopic deformation, it is quite difficult to critically control the molecular orientation.

Deformation of molecular chains of slightly cross-linked UHMWPE has rubbery elasticity in the molten state and the deformation of molecular chains in the structure may be described by the macroscopic deformation. Hence, when the UHMWPE is cooled to room temperature, while maintaining the deformation, the crystallization

can be performed under controlled molecular orientation.

Suong-Hyu Hyon *et al.* reported the structure and properties of a slightly cross-linked UHMWPE prepared under uniaxial stretching. They elucidated the mechanism of crystallization under molecular orientation by stretching the polymers to various extents in the molten state. When a cross-linked UHMWPE film was stretched during the molten state and cooled, a super structure with a very unique phase structure was produced, in which highly oriented crystallites coexisted with unorientated and relaxed amorphous molecular chains. If cross-linked polyethylene molecules with adequate cross-link density are uniaxially compressed in the molten state, a very unique orientation of the crystal planes appears. The (200) planar orientation appears at a relatively low degree of compression and the (110) planar orientation follows at high degrees of compression. It is suggested that this unique orientation of the crystal planes was caused by the crystallographic structure intrinsic in this polymer. Such planar orientation of this polyethylene is suggested to be closely related to the mechanism of the crystallization regardless of the presence of the cross-linked units.

It has been difficult to make clear the wear behavior of materials, because the wear properties depend on an extremely large number of factors. However, the material properties affect strongly on its wear behavior. Therefore, the present study mainly focuses on the relationship between material properties and their wear behaviors to obtain deeper insights about wear resistance of UHMWPE used in artificial joints.

In Chapter 1, the relationship between orientation and the anisotropic material properties was clarified. The structure and dynamic mechanical properties of the compressed sample were studied using wide angle X-ray diffraction and viscoelastic

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rheometer. It was found that the (200) crystalline plane of the compressed sample was orientated parallel to the compressed surface.

The conduction velocity of ultrasonic waves on the compressed surface was faster than the others, also the surface was hardened about 10% compared with the non-compressed surface. The storage modulus of the compressed sample was also higher than that of the non-compressed sample at room temperature, and the intensity of the γ -relaxation in the loss modulus with the compressed sample was lower than that of the non-compressed one.

However, the peak of the α_c loss modulus of the compressed sample shifted to the higher temperature side when increasing the compression ratio. The reciprocating wear test results revealed that the wear resistance of the compressed UHMWPE was higher than that of the non-compressed one. Wear particle sizes of the non-compressed materials were greater than 1 μm , while those of the compressed were several hundreds micrometer. The transference volume from the non-compressed specimen to the counterface was larger than that from the compressed, which were consistent with the findings of weight loss.

In Chapter 2, friction and wear tests were carried out using a six-station reciprocating pin-on-flat apparatus. It was revealed that the wear factor of the compressed sample was 1/3-fold lower than that of the non-compressed sample. The weight loss was observed from about 30,000 m sliding distance and the loss was linearly increased with the increasing sliding distance. In addition, the compressed surface appeared harder than the uncompressed samples in Vickers hardness measurements. The hardness increased with the increasing compression ratio. These findings from Vickers hardness, wear test, and AFM observations provided clear experimental evidence for the improved wear resistance properties

of the compressed UHMWPE.

Chapter 3 shows wear volume with several wear tests. To confirm the results of the wear test in Chapter 2, it is necessary to perform wear tests with other machines, for example the pin-on-disc tester. The findings of the wear tests with pin-on-disc suggested that the wear factor of the compressed UHMWPE was enhanced and also the findings from Chapter 2, that the wear factor depended on the compression ratio, was confirmed. The findings of pin-on-flat wear test in NRIM ((National Research Institute of Metals) showed that the wear factor of the compressed UHMWPE was 1/35 -fold higher than that of the non-compressed sample. The orientation of the NRIM specimen was revealed from the findings of WAXD, where the pattern showed six distinct maxima points for the (110)-diffraction observed. These points would be caused by the relatively rather perfect orientation of both the (200) and (110) crystal planes. An additional pin-on-flat reciprocating wear test was carried out using specimens that were cut from different directions. The one specimen base was cut from the X-Y plane and the other was cut from the X-Z plane. The wear factor of the X-Y plane was lower than that of the X-Z plane.

In Chapter 4, measurements of residual stresses were performed with ultra-high molecular weight polyethylene (UHMWPE) for an artificial joint in order to investigate the effect of compression. When a crystalline piece of sample is elastically deformed in such a manner that the strain is uniformly applied over relatively large distances, the lattice plane spacing in the crystal form change from their stress-free value to some new value corresponding to the magnitude of the applied stress. The uniform macrostrain causes a shift in the diffraction lines to new 2θ positions. From this degree of shift, the strain may be calculated and, knowing the strain, the applied stress can be determined. In general, the effect of residual stresses

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is the same as the effect of stress with a mechanical load, therefore, a compressed residual stress causes increasing fatigue, while a tensile one causes decreasing fatigue. However, when both residual stresses are released by wear, the shape may be markedly deformed, which would lead the accuracy of artificial joints to deteriorate. The $\sin^2\psi$ method with the X-ray diffraction technique was carried out and 135° of 2θ was used for measurements. The stress constant of samples was based on the results of the dynamic modulus. Three samples were prepared. One was a compression of a slightly cross-linked UHMWPE during molten state (Sample A), and the other (Sample B: compressed at 120°C , Sample B': compressed at 80°C) was a compression of non-irradiated UHMWPE under melting point. The residual stresses of Sample A and an original UHMWPE were not observed, while tensile stresses were observed in Sample B and Sample B'. Measurements of shrinkage, as a function of temperature, indicated the existence of residual stresses in the amorphous phase of Sample B and Sample B'. When the temperature of all samples was increased from 0°C to 130°C at $2^\circ\text{C} / \text{min}$, Sample B was shrunk at 80°C and, moreover, Sample B' was shrunk at less than 60°C , while Sample C and Sample A was not shrunk over 130°C . These findings show that all these orientated samples including Sample A showed a property of shrinkage as a function of temperature, because of the existence of orientation in the crystalline phase. It was confirmed that the differences of shrinkage between Sample B and Sample A depended on the of states in amorphous phase. The amorphous phases in Sample B and B' were strained, while the phase in Sample A was relaxed.

In Chapter 5, two kinds of molding methods were investigated to compare with wear properties for an artificial joint bearing material. One was a compression of a slightly cross-linked UHMWPE during the molten state (Sample A), and the other

(Sample B) was a compression of an original UHMWPE below the melting point. The intensity distributions of the (200) crystalline planes of Samples A and B were similar judging from the measurement of each half-width. The heat of fusion and the density of Sample A were higher than those of Sample B. The storage modulus of Sample A was always higher than the original untreated UHMWPE (Sample C), while the storage modulus of Sample B was decreased suddenly with increasing temperature based on the measurements of dynamic moduli as a function of temperature. The α_c -peak of Sample A was shifted about 5°C higher, however, Sample B was shifted to a lower temperature and the β -peak disappeared. The wear factor of sample A was the lowest among the samples, while the wear factor of Sample B' was the highest. It was confirmed that the wear factor of UHMWPE depended on the mobility of the molecular chain.

In the last Chapter 6, a slight cross-linked UHMWPE was crystallized under 3-D compression during the molten state and the crystal planer orientation of the sample was studied using a wide angle X-ray diffraction technique. The sample surface was compressed with a brass ball to dent it along the ball and was compressed to a hollow, like an artificial acetabular cup. When X-ray beams were irradiated perpendicular to the surface of the cupped sample, it was observed that the crystal planes (110) and (200) were orientated parallel to the cupped surface. The direction from the bottom of the cup to the vertical direction was named the bottom direction, and the line crossing at the center of the cup to the bottom direction with an angle of 30° was defined as the 30-degree direction. The degree of orientation in the 30-degree direction was gradually lower at deeper positions from the surface, while the orientation in the bottom direction was maintained up to 4 mm depth. The melting point and the density near the cupped surface were relatively high compared

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with the bottom part. The knee mold sample had also orientation similar to the cup sample. This newly molded method suggested the fabrication possibility of manufacturing the artificial acetabular cup with excellent wear properties. The wear tests were performed using hip and knee simulators, and these findings suggested that the wear resistant properties of the orientated samples increased compared with the conventional cut sample.

In summary, the crystalline phase of slight cross-linked ultra-high molecular polyethylene, crystallized under uniaxial compression, was orientated parallel to the compressed surface. The mechanical properties were enhanced and it also was confirmed that the structure and the material properties were consistent with the wear properties.

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Chapter 1

Dynamic Mechanical Properties of Slightly Cross-linked Ultra-High Molecular Weight Polyethylene Crystallized under Uniaxial Compression

INTRODUCTION

Ultra high molecular weight polyethylene (UHMWPE) has been utilized well as a bearing material of acetabular prosthesis components in total joint replacement for more than thirty years. Although it has been used widely, friction between bearing surfaces of both acetabular and femoral components leads to generation of wear debris in a contact parts of joint cavities. It is found that the dislocation and the failure in total hip and knee arthroplasty are closely associated with osteolysis problems and caused by the UHMWPE wear debris¹⁻⁸⁾.

The purpose of the present chapter was to represent that the improvement of the wear resistance is discussed from the view point of reology. It was clarified that the anisotropic modulus in each surface was given by compression. And also it was discussed that the relationship between wear properties and the motion of the molecular chain.

EXPERIMENTAL

Preparation of Samples

The starting material for this work was a commercial UHMWPE from Mitsui Chemical Co. Japan, with a viscosity average molecular weight of 5.5×10^6 .

Figure 1 shows the method of the compression. At first, blocks of UHMWPE were irradiated using ^{60}Co γ -rays under reduced pressure at room temperature and the irradiation dose was 0.5 Mrad.

The irradiated UHMWPE was compressed at 200°C, which was higher than the melting point (about 140°C). The compressed speed was about 10 mm/min, and the total compression weight was about 42000 N.

The samples were cooled to room temperature over a period of 2 hours while maintaining of the deformation. The cooling speed from 140°C to 80°C demanded by the Japanese Industrial Standard (JIS), was about 1 hour. In this procedure, the sample thickness was reduced in accordance with increase in the compression. The compression ratio (CR) was defined by the ratio of the final thickness to the original thickness of the sample.

Wide Angle X-ray Diffraction

The crystalline orientation was studied by wide angle X-ray diffraction technique. The radiograph was taken by a Ru-3H, Rigaku Co., Japan, with a flat camera and with Cu-K_α radiation monochromatized with a graphite monochromator generated at 40 kV and 60 mA. The compressed sample was cut a cube to about 1mm^3 at room temperature. Then, the X-ray beam was introduced into the three directions. The non-compressed sample was only introduced into one direction.

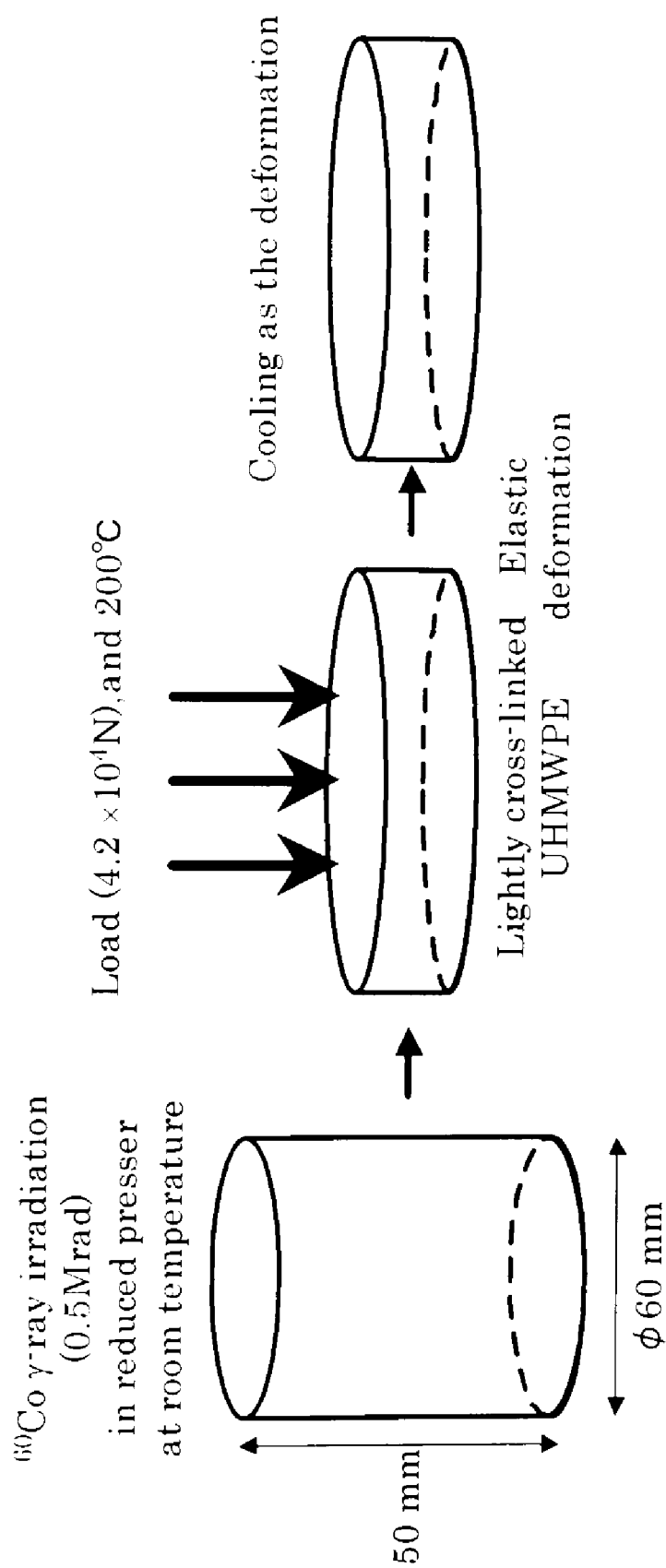


Figure 1: Scheme for preparation of specimens

Optical Microscope

The samples surfaces were observed by using an optical microscope. Both the non-compressed and the compressed samples were sliced to thin films at room temperature, especially the surface parallel to the compressed axis was observed.

Conduction Velocity of Ultrasonic Waves

Figure 2 shows a diagram of the apparatus for measurements of conduction velocity of ultrasonic. The probes for radiator and for receiver were made of PZT (lead zirconate titanate) and P(VDF-co-TrFE), respectively. The photo in Fig. 2 is the receiver probe of which diameter is about 2.6mm. The frequency of 6MHz was irradiated to sample in water bath at 25°C and measured the conduction time. The measured direction and cut sample is shown in Fig. 3. The compressed sample (CR = 4) was cut to 9 rectangular parallelepipeds of which shapes were about $4 \times 10 \times 8 \text{ mm}^3$. The velocities of Samples 1, 2, 3, and 4 were taken averages of 1 and 1', 2 and 2', 3 and 3', and 4 and 4', respectively.

Vickers hardness

The micro-hardness measurements were carried out at a room temperature by HMV-2000 (Shimadzu Scientific Instruments, Inc). The Hardness Apparatus has a Vickers square pyramidal diamond¹⁶⁻¹⁸⁾. The micro-hardness value was calculated by following formula:-

$$MH = 2 \sin 68^\circ \frac{P}{d^2} (MPa) \dots\dots (1)$$

Where P and d are the load in grams and the diagonal length of the indented surface (μm), respectively. The weighed load and the loading cycle time were 10 g

and 20 s/cycle through all measurement, respectively. The names of the measured surfaces were defined in Fig. 3.

Dynamic Mechanical Measurements

The dynamic tensile measurements were carried on viscoelastic analyzer (Rheogel-E4000, UBM Co. Ltd). The storage modulus (E') and the loss modulus (E'') were measured as a function of temperature from -150°C to 150°C at $2^{\circ}\text{C}/\text{min}$. The continuous sine wave was performed at the frequency of 10 Hz. The surface perpendicular to the compressed axis was cut to a rectangular parallelepiped. Complex moduli and $\tan \delta$ values determined are related thus:

$$E = E' + iE''$$
$$\tan \delta = \frac{E''}{E'} \dots \dots (2)$$

E : complex modulus, i : imaginary number

Reciprocating Pin-on-flat Wear Test

Wear tests were performed using a reciprocating pin-on-flat wear test device. The schematic representation⁵⁾ of the wear test machine has been reported in a previous publication. The machine has 6 arms thus 6 samples can be tested at the same time. Wear tests were performed at a frequency of 1.2 Hz for a minimum of 1.4 million cycles in saline. The unidirectional sliding distance of the motion was 14 mm. Thus the average of sliding speed was 33 mm/s, and the top speed was 52 mm/s as shown in Fig. 4 of diagram of wear test.

Samples were cut into flat-ended vertical cylinder 10 mm long, 6.0 mm in diameter.

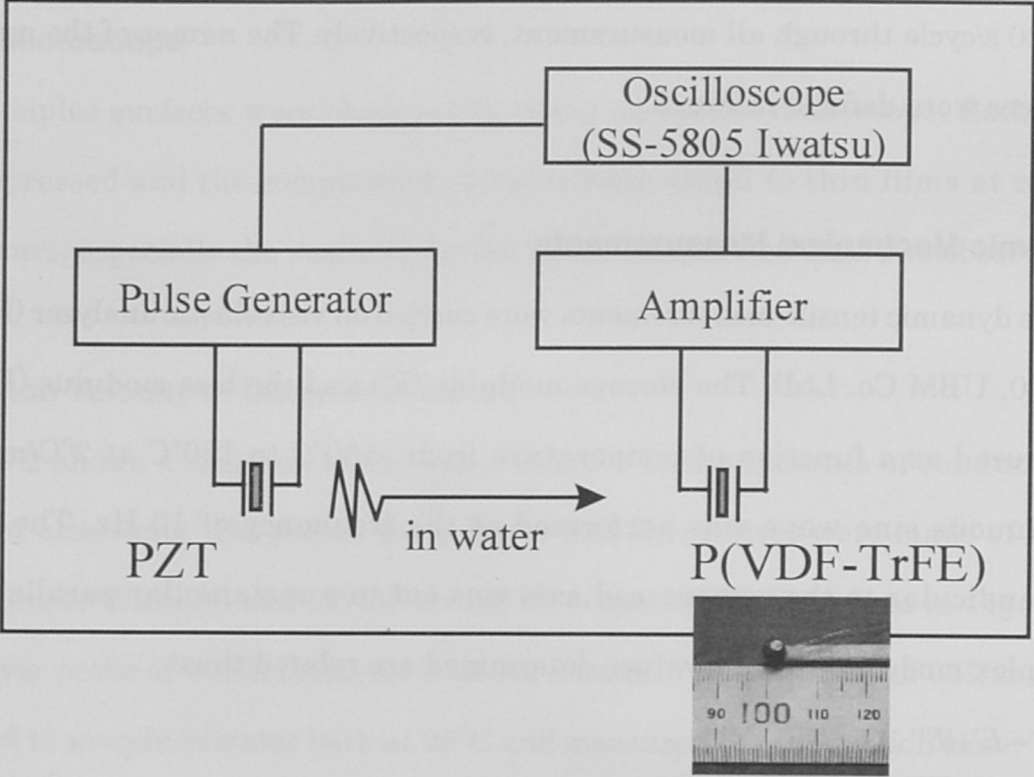


Figure 2: Scheme of measurements of conduction velocity of ultrasonic waves

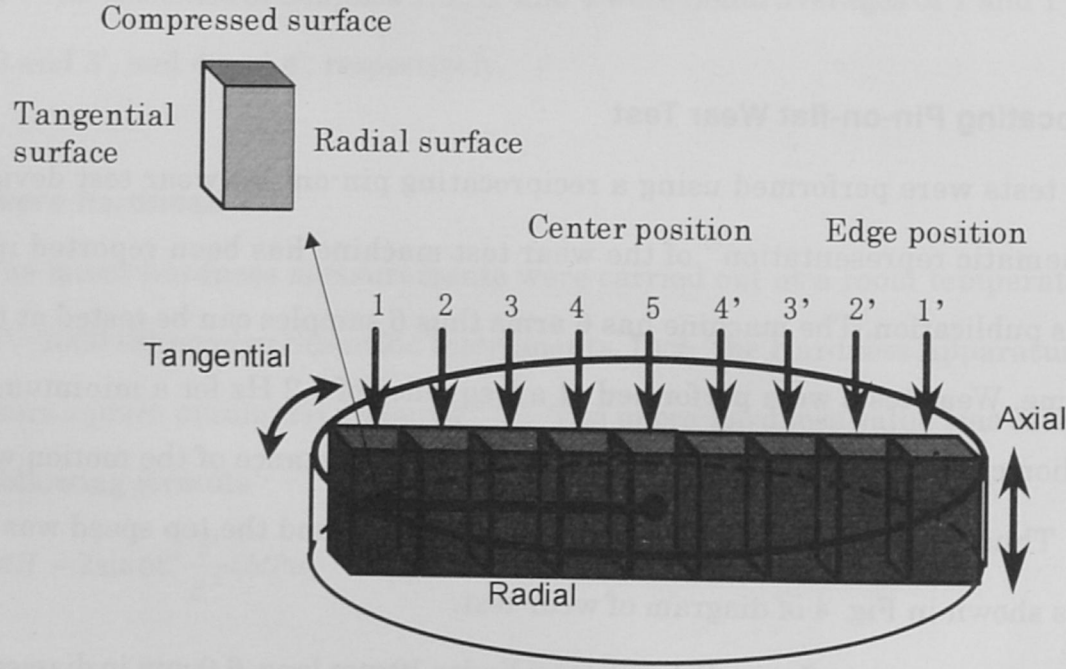


Figure 3: Sample's defined name

providing a cross-sectional area of 28 mm^2 . The sample surface was polished at the mean roughness (R_a) of $0.1 \text{ }\mu\text{m}$. The test load of 3.47 MPa was applied along the longitudinal axis of the samples. Co - Cr - Mo alloy plates were used for the counter face, of which the mean roughness was $0.01 \text{ }\mu\text{m}$. The chemical composition of the alloy was Co (63.72 wt%), Cr (28.06 wt%), Mo (6.20 wt%), Si (0.80 wt%), Fe (0.45 wt%), Mn (0.31 wt%), C (0.26 wt%), and Ni (0.2 wt%). The Rockwell C hardness was $28 \sim 30$.

After the samples were cleaned ultrasonically in research grade acetone and the reduced pressure desiccated, the weight losses of the samples were measured. The weights of the samples were recorded immediately after the desiccation.

RESULTS

Observation of Particles with Optical Microscope

The surfaces in each sample were observed by optical microscope. Figures 5 and Figure 6 shows the micrograph of the particles structures on the radial surface as defined in Fig. 3. The non-compressed particles got out of shape. The size of the particles was about $100 \text{ }\mu\text{m}$. These particles are thought as the original powders of UHMWPE. However, the compressed particles were keeping their shape and were very smaller (about $20 \text{ }\mu\text{m}$) than those of the non-compressed.

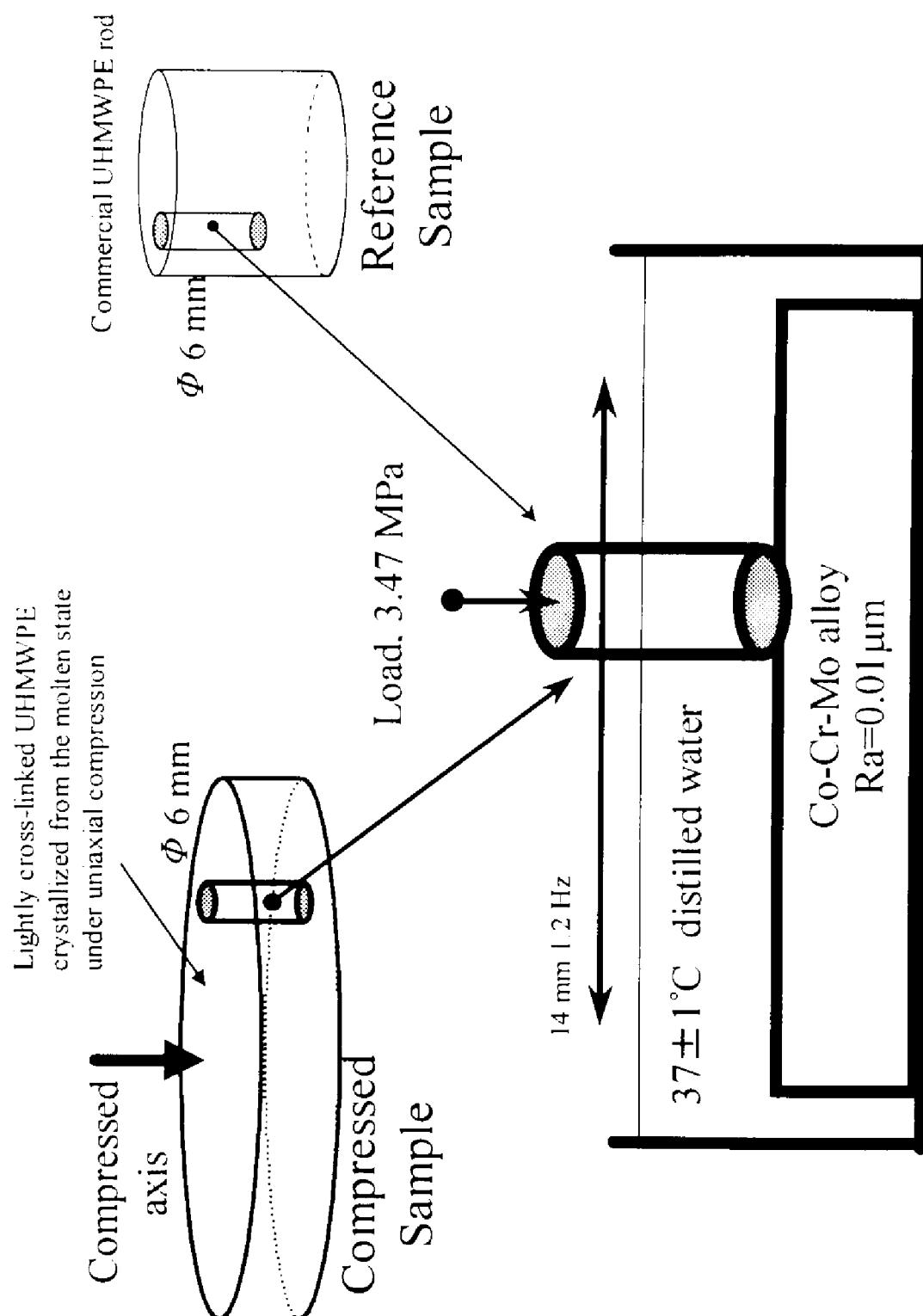


Figure 4: Diagram of reciprocating pin-on-flat wear machine

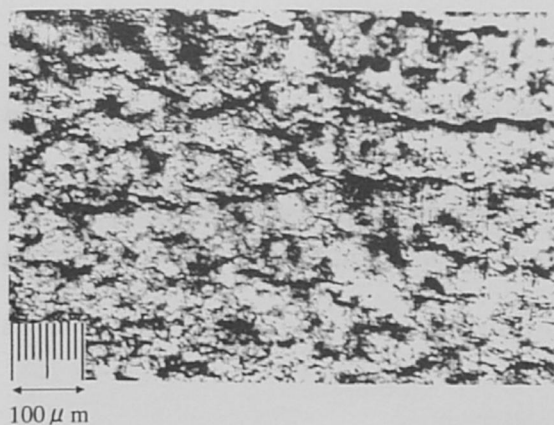


Figure 5: Optical microscope microgram of the non-compressed sample

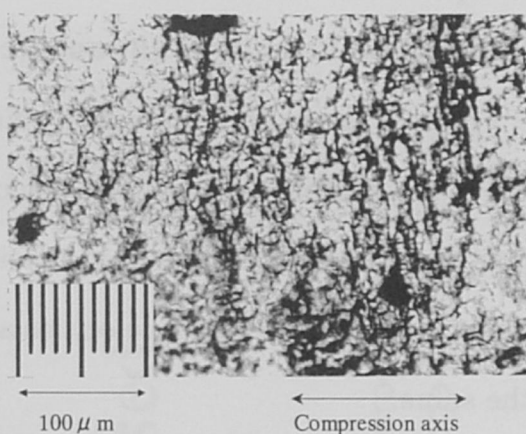


Figure 6: Optical microscope microgram of the compressed sample in the radial surface

Wide Angle X-ray Diffraction Technique

Figure 7 shows X-ray diffraction patterns from the compressed surface. The left photo is the pattern from the center position of the compressed surface and the right is from the edge of the compressed one. The pattern of the center was similar to that of the edge. The (020) crystalline plane was slightly orientated in the edge position, and the other crystalline planes are almost rings without orientation.

However, Fig. 8 shows patterns photos from the radial surface. The left one is of the non-compressed sample, the middle and the right are the center and the edge positions in the radial surface of the compressed sample, respectively. The (200) crystalline plane was orientated parallel to the compressed surface. These results show that the crystalline plane of the compressed sample was orientated.

Conduction Velocity of Ultrasonic Waves

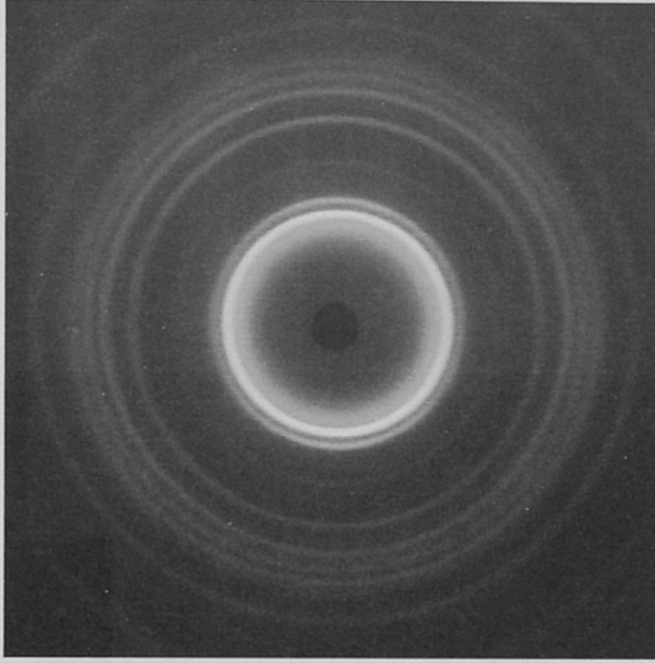
Figure 9 shows the conduction velocity of ultrasonic waves in each direction. The CR of the sample was 4.0. The velocity in the axial direction was the lowest. This means that the modulus of elasticity is higher in the tangential and the radial direction. The conduction velocities are similar among of the sample 1 · 5 are almost the same.

Vickers Hardness

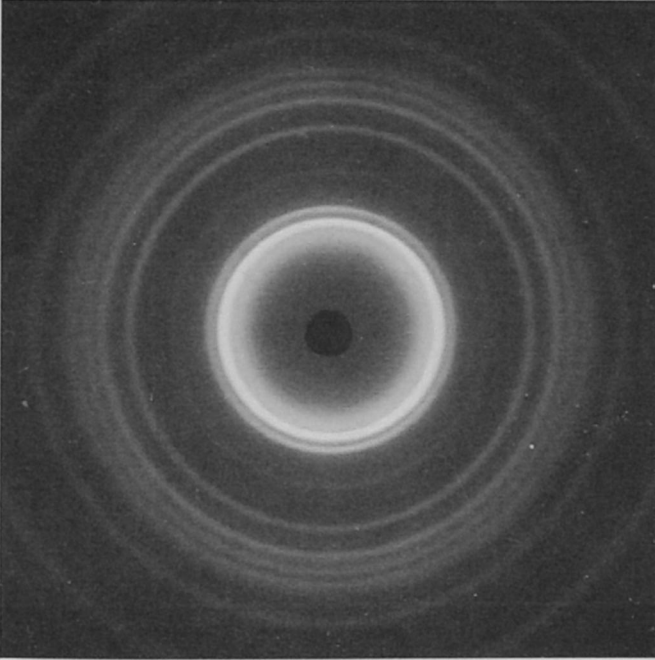
Vickers hardness on the each surface is shown in Fig. 10. The compressed sample (CR = 2.3) was used for measurement. The result indicated that the compressed surface was the hardest among 3 surfaces. It was no difference between the center and the edge position. It is confirmed that there is a relationship between the direction of conduction velocity of ultrasonic waves and the hardness on the surface.

Dynamic Modulus

Figures 11 and Figure 12 shows the storage modulus E' , and the loss modulus E'' of the non-compressed and the compressed samples respectively, as a function of temperature. Figure 13 shows $\tan \delta$ defined by the formula (2). It can be seen that both E' decrease moderately with temperature increase, and E'' has three apparent dispersion peaks at 70°C, -10°C, and -115°C. They are assigned as α_c , β , γ -relaxation respectively. The β peaks of both samples are at the same temperature (-10°C), and the γ peaks were also the same temperature (-115°C). On the other hand, the α_c peak of the compressed sample was shifted to 5°C higher temperature. The γ -relaxation is generally known as the molecular relaxation phenomena such as the chain ends or the dislocation of such defects in the crystalline part. The β -relaxation



Compressed
(Center)



Compressed
(Edge)

Figure 7: Wide angle X-ray photographs (left: X-ray beam was incident perpendicular to the compressed sample surface at the center position, right: at the edge position)

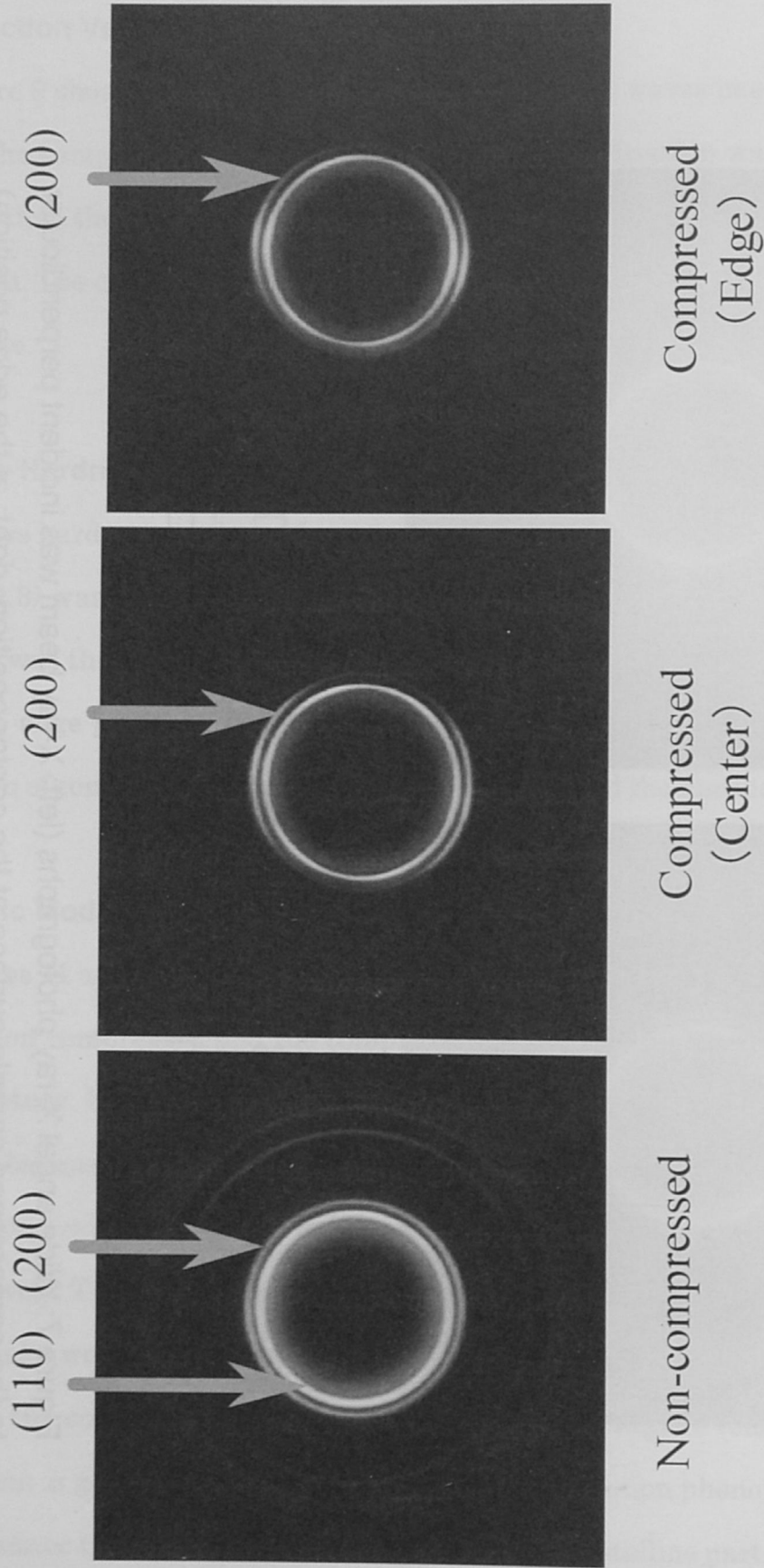


Figure 8: Wide angle X-ray photographs (left: the non-compressed sample, middle: X-ray beam was incident parallel to the compressed sample surface at the center position, right: at the edge position)

is explained as the micro-Brownian motion in the amorphous part. The α_c -relaxation is observed for the relaxation phenomena of the molecule in the crystalline part. In the α -relaxation, the thermo-vibration of the molecular chain in the crystal phase was occurred actively and the anharmonic oscillators of the intermolecular potential were increased. Then the crystalline phase became visco-elastic. The increases of the α -relaxation intensity and the peak shift to a higher temperature mean that the increases of the thickness of single crystal.

Wear Test

Weight losses of the compressed and the non-compressed specimens are shown in table 1. Figure 14 shows the graph of the mean weight loss of each kind. The mean of the weight loss of the non-compressed sample was 3.7×10^{-4} g. In contrast, that of the compressed sample was 2.7×10^{-5} g. There was a significant difference in the mean of the weight loss between the compressed sample and the non-compressed sample.

The distribution of samples on the counterface was also different. The optical micrograph of the each counterface was shown in Fig. 15 and Fig. 16. It was found that the counterface had many adhered samples like islands. Also the volume of the transferred sample of the non-compressed samples was more than that of the compressed. Moreover, the islands of the non-compressed were larger in size than that of the compressed sample. It is thought that there is an intimate relationship between the difference on the micrograph and the amount of weight loss.

Figure 17 shows the wear particles from the non-compressed. The size of particle was about over 1 mm, and several cracks that crossed to the traces on the wear particle were observed. While Fig. 18 shows the wear particles from the compressed,

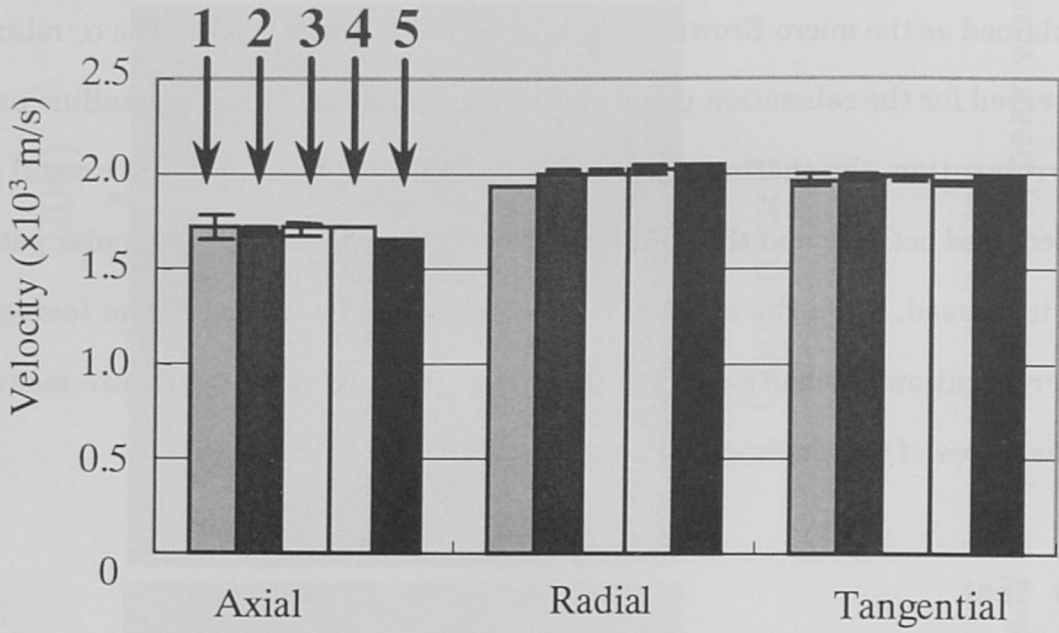


Figure 9: Conduction velocity of ultrasonic waves in each direction

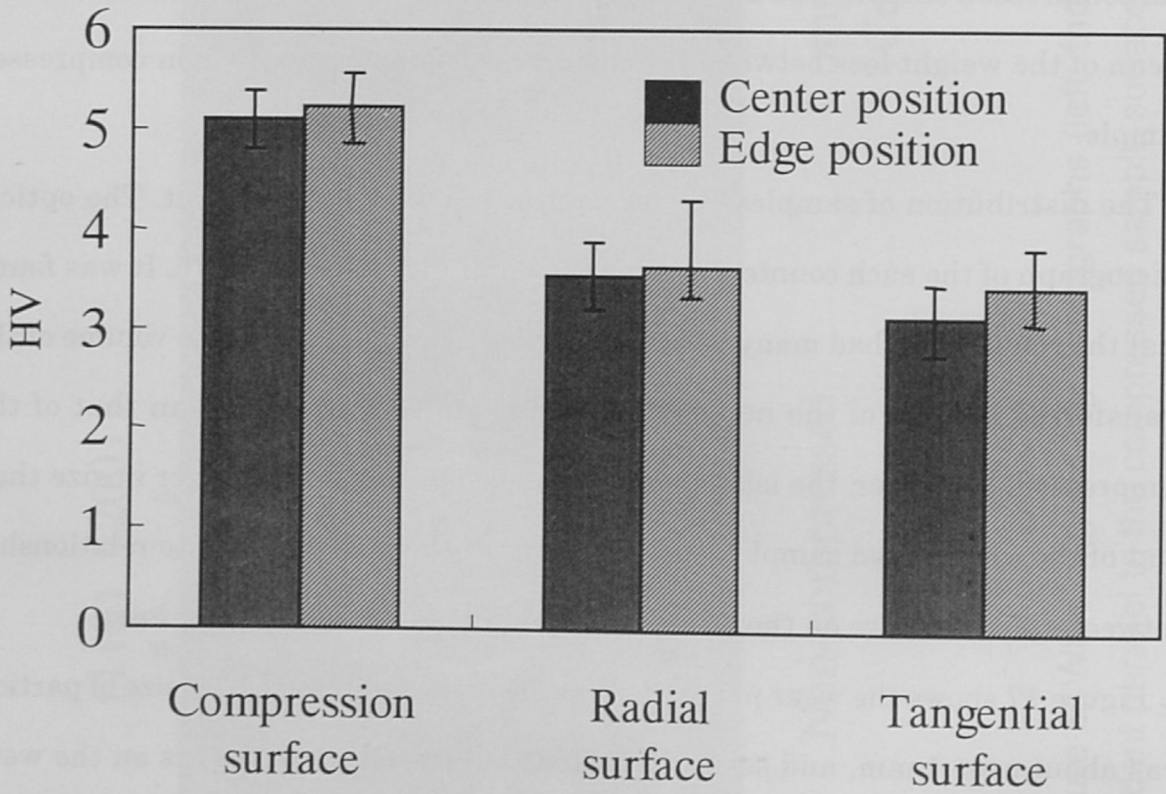


Figure 10: Vickers hardness on each surface

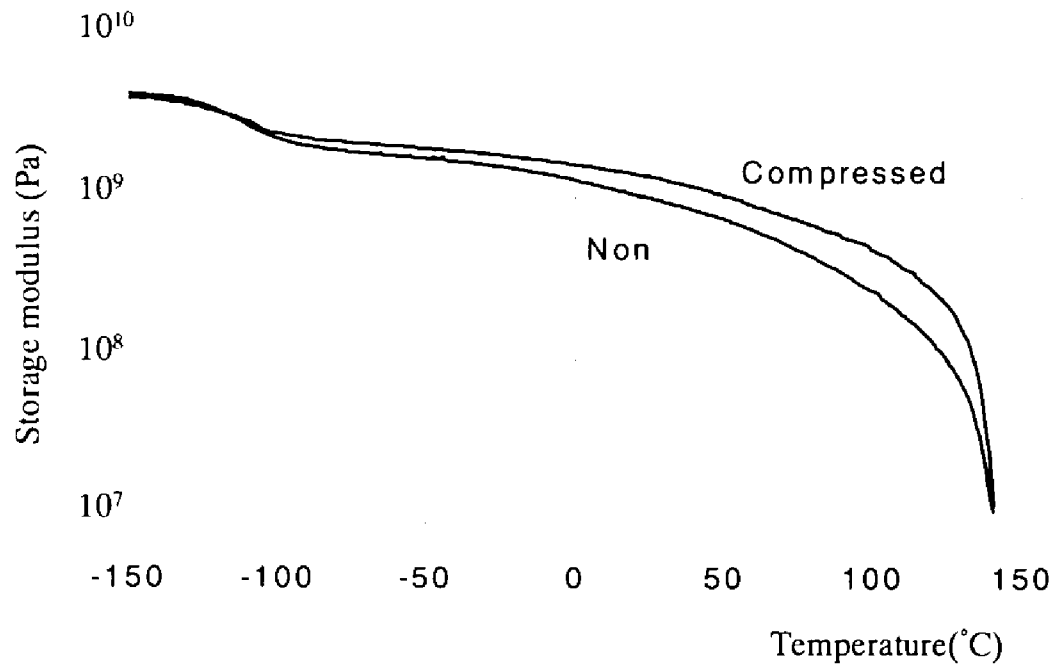


Figure 11: Storage modulus as a function of temperature (from -150 $^{\circ}\text{C}$ to 150 $^{\circ}\text{C}$)

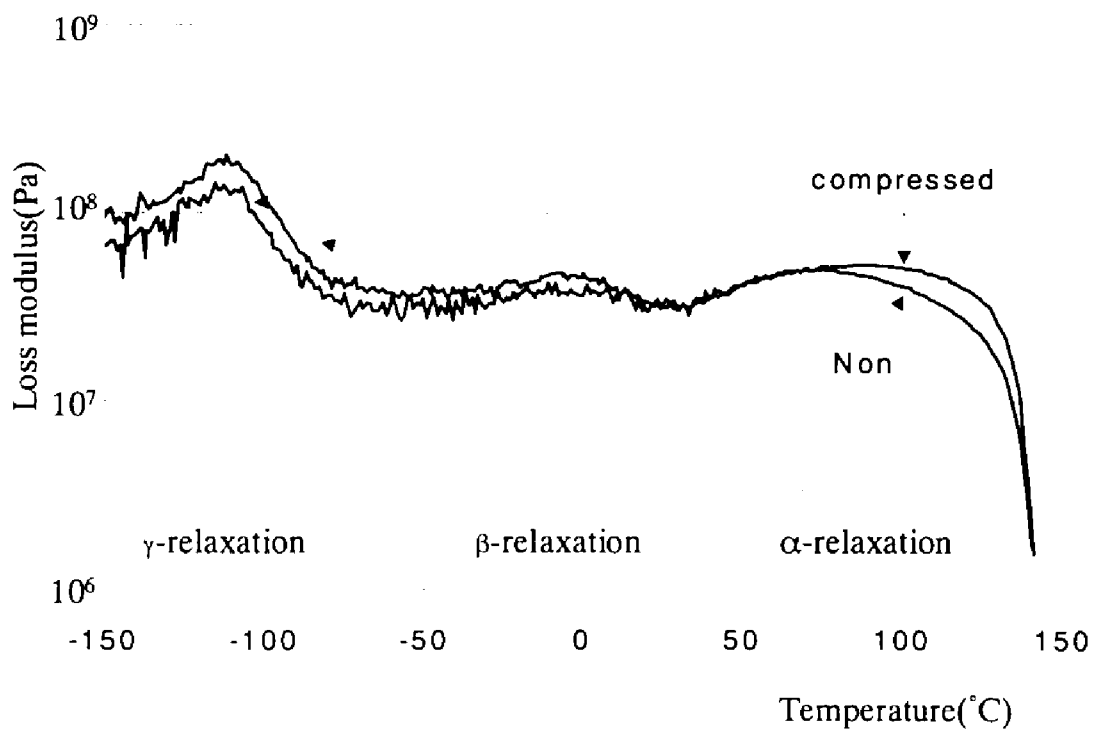


Figure 12: Loss modulus as a function of temperature (from -150 $^{\circ}\text{C}$ to 150 $^{\circ}\text{C}$)

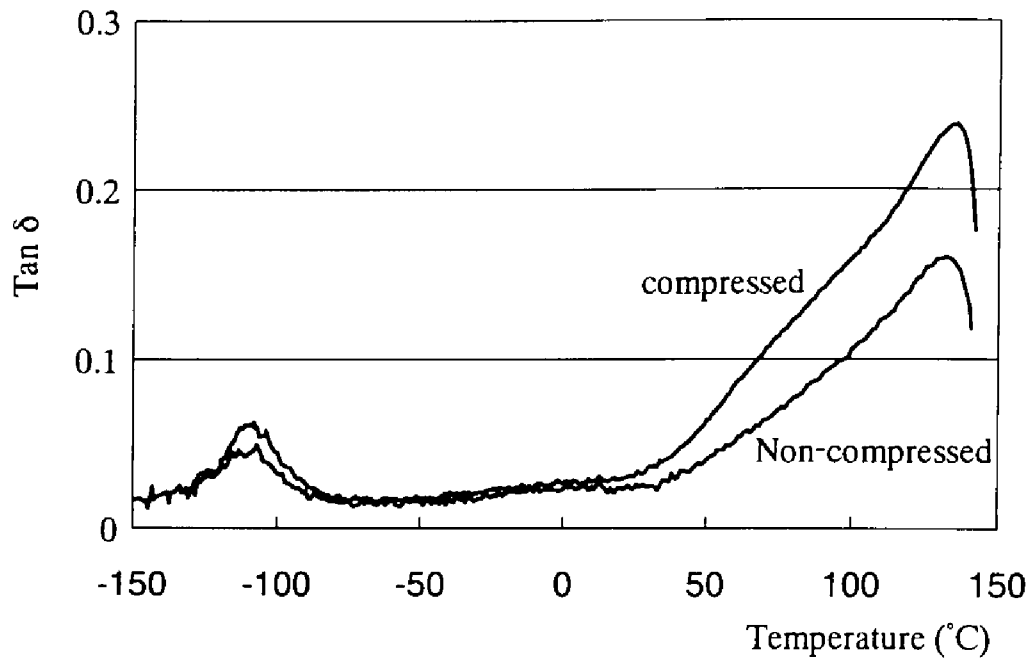


Figure 13: $\tan \delta$ as a function of temperature (from -150°C to 150°C)

which were about several hundreds micrometer. The surface on the counterface of the compressed was shown in Fig. 19. The black islands like were considered to be wear debris transported from the UHMWPE specimen. Figure 20 shows the counterface surface of the non-compressed, and it was found that both patterns were random. Therefore, it was confirmed that the differences of the wear factor was based on the difference of the UHMWPE sample, not on the differences of the counter face surface.

DISCUSSION

The most important point of this study was that the relationship of the weight loss of the wear test and the dynamic modulus from the rheological analysis point

view was clarified. In the experimental procedure, the slightly cross-linked UHMWPE was compressed uniaxially in molten state and crystallized maintaining the deformation. It was found that the crystal planes (110) and (200) of the compressed sample were orientated parallel to the compressed surface from the findings of the X-ray diffraction technique. And, it was appeared that the orientation increased the Young's modulus on the compressed surface from the findings of the conductive velocity of ultrasonic waves. It is also confirmed that Young's modulus of the compressed was higher than that of the non-compressed indicated by the results of the measurements of dynamic modulus as a function of temperature. It was showed that these findings lead to the relationships with the hardness of the compressed surface.

In spite of the having higher Young's modulus, the amorphous phase is indicated

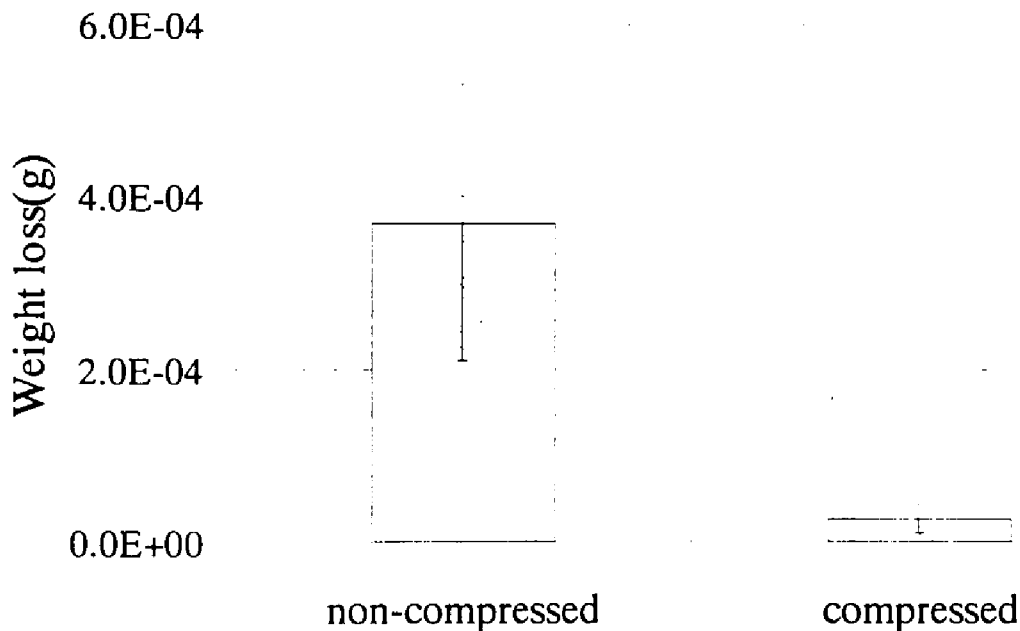


Figure 14: Weight loss with reciprocating wear test



Figure 15: Optical micrograph of the counterface surface after wear test against the non-compressed sample

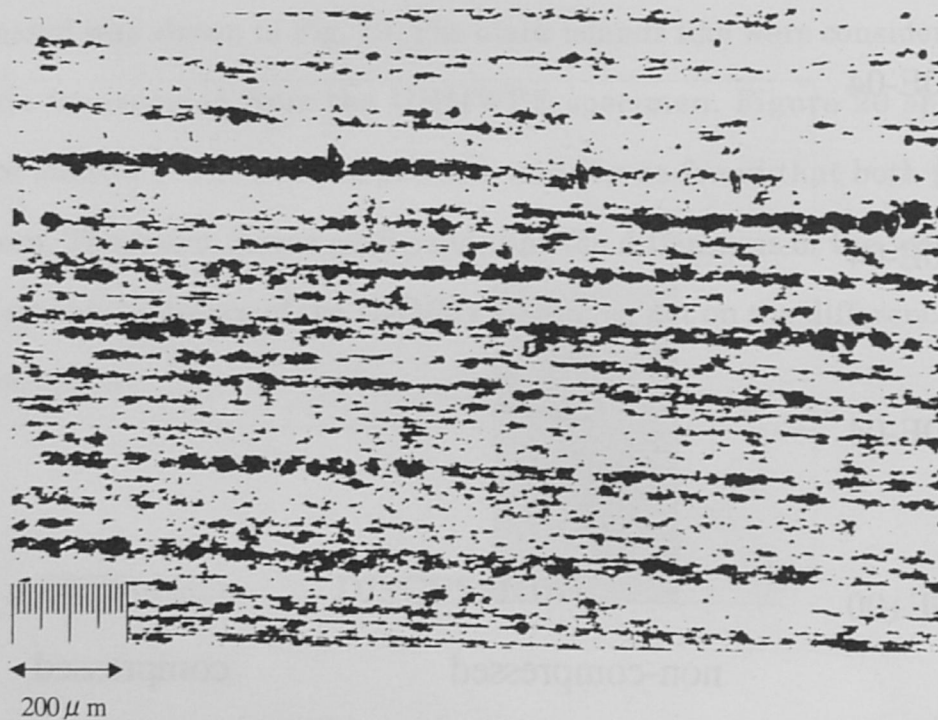


Figure 16: Optical micrograph of the counterface surface after wear test against the compressed sample

Table 1: Weight loss of each sample by reciprocating wear test

Sample	Weight(before test)(g)	Weight(after test)(g)	Weight loss(g)
1	0.27118	0.27117	0.00001
2	0.26706	0.26685	0.00021
3	0.27098	0.27096	0.00002
4	0.26940	0.26887	0.00053
5	0.27064	0.27059	0.00005

1,3,5: Compressed sample, 2,4: Non-compressed sample

to be relaxed like an original UHMWPE, based on the findings of both the β and the γ -relaxation peaks were not shifted and not decreased. Moreover, the lower dispersion of γ -relaxation means that the disordering in the amorphous phase was decreased. Meanwhile, the crystalline phase has a perfect crystal structure. It was clear that these phenomena are caused by the preparation process of the sample. The slightly cross-linked UHMWPE was heated and compressed at the molten state, which means that the sample was compressed without the crystal phase. The compression caused the cross-linked molecular chain to be orientated. After the procedure, the orientated molecular chain was crystallized. Consequently, the molecular chain in the amorphous phase was relaxed through the crystallization, therefore, the β and the γ -relaxation peaks were not changed.

When the compression was performed below the melting point, the following process produced the orientation. First, the molecular chain in the amorphous phase was orientated, and then the crystals are deformed. Therefore, both the phases were orientated and both the chains would be tensile state. The thermo-stability of the sample was lower than that of the compressed sample, moreover, the orientation

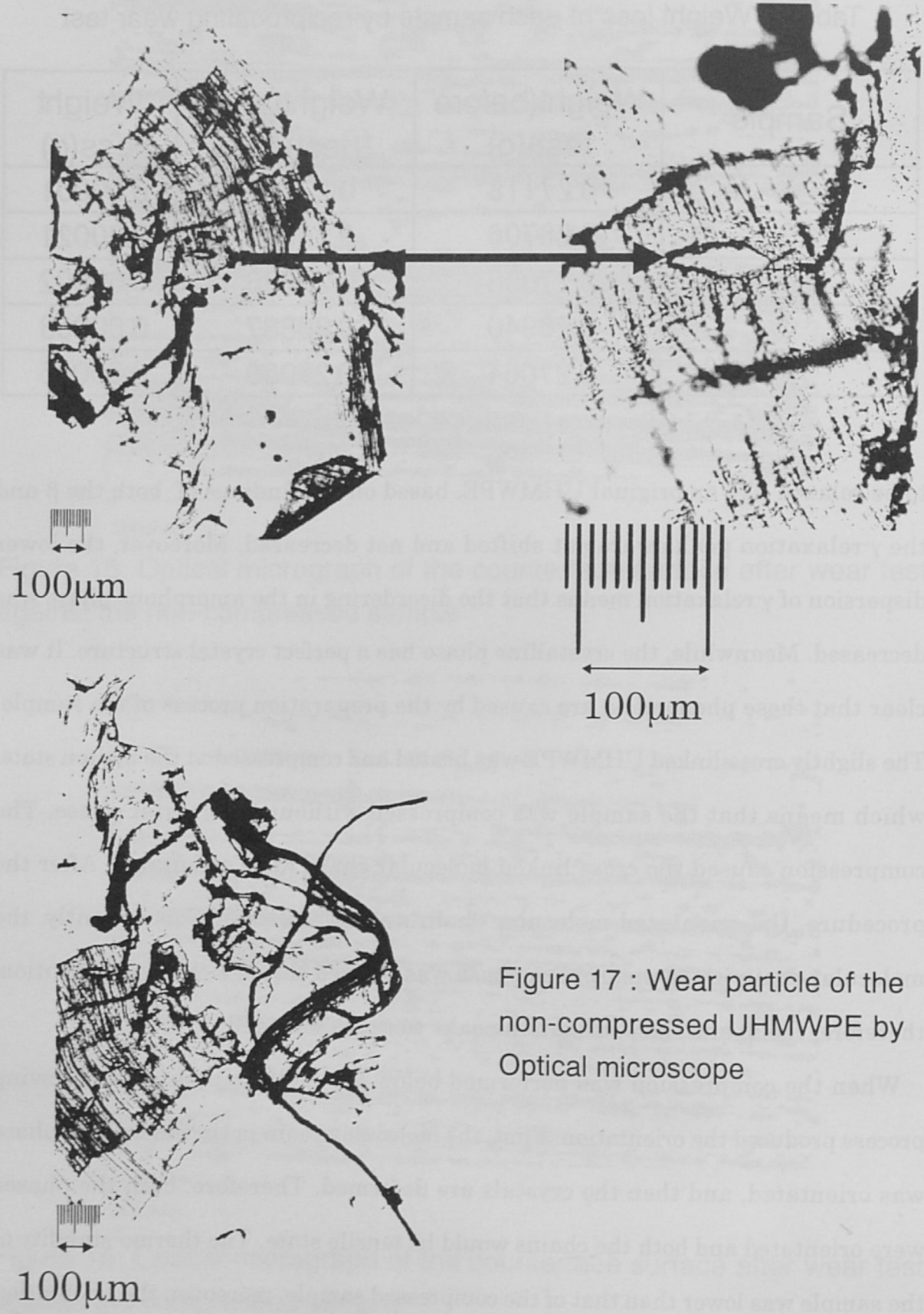


Figure 17 : Wear particle of the non-compressed UHMWPE by Optical microscope

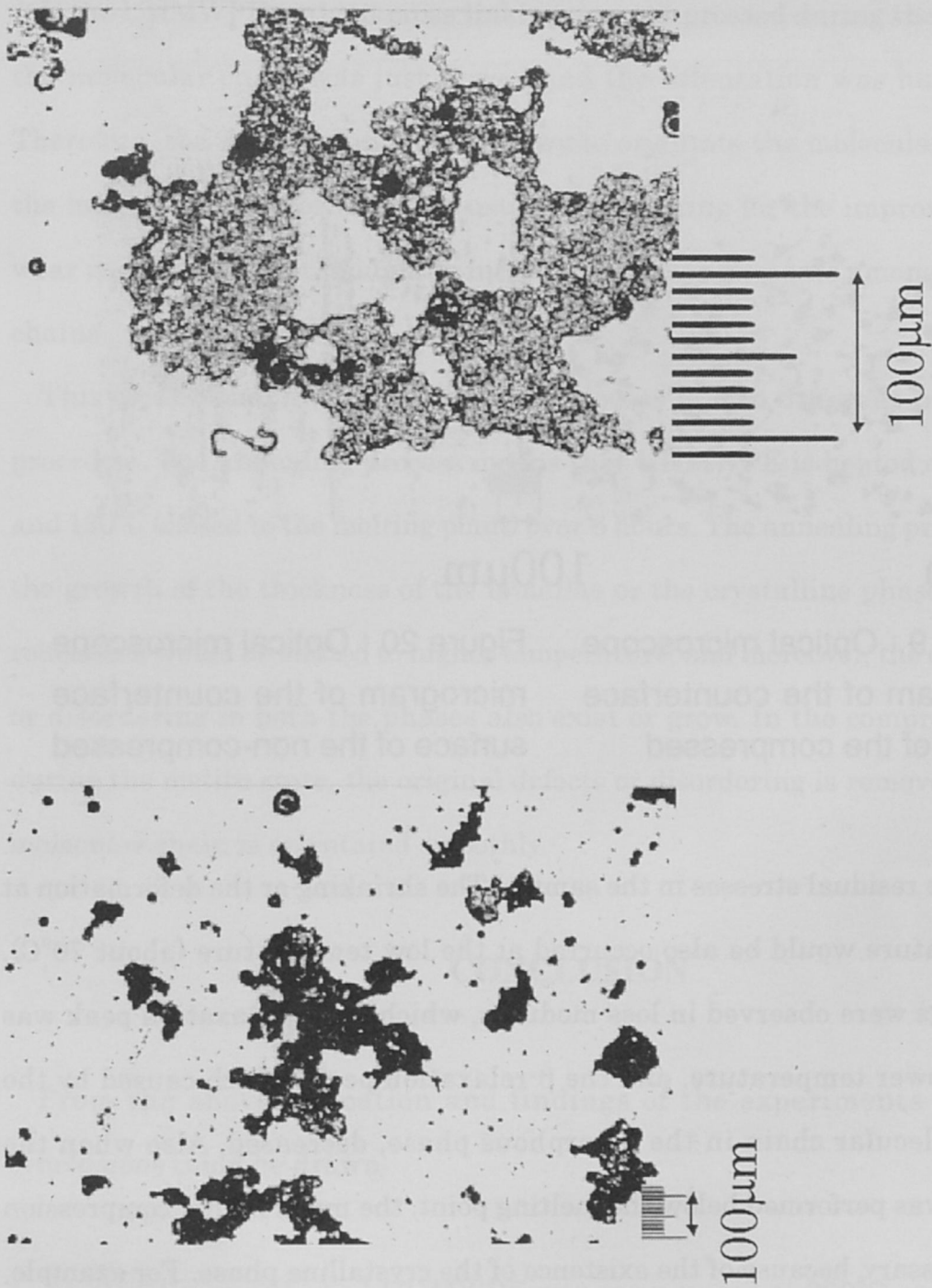


Figure 18 : Optical microscope micrograph of wear particles from the compressed sample



100 μ m

Figure 19 : Optical microscope microgram of the counterface surface of the compressed



100 μ m

Figure 20 : Optical microscope microgram of the counterface surface of the non-compressed

would produce residual stresses in the sample. The shrinking or the deformation at room temperature would be also occurred at the low temperature (about 70°C). These findings were observed in loss modulus, which the α -relaxation peak was shifted to a lower temperature, and the β -relaxation peak, which caused by the motion of molecular chain in the amorphous phase, decreased. Also when the compression was performed below the melting point, the much higher compression load was necessary, because of the existence of the crystalline phase. For example, in Fig. 11, the Young's modulus of the non-compressed sample at 100°C was about 300 MPa, while, at over the melting point, the modulus was only about 24 MPa.

Therefore, it is found that the compression process below the melting point is very different and difficult from the compression process during the melting state.

If the UHMWPE without cross-linking was compressed during the melting state, the molecular chain was just flowed and the orientation was hardly occurred. Therefore, the cross-linking is necessary to orientate the molecular chain during the melting point. However, the usual cross-linking for the improvements of the wear resistance is just thought to increase the entanglements among the molecular chains.

This orientation and crystallization process is also different from annealing processes. The annealing process means that UHMWPE is heated at between 110 and 130°C (closed to the melting point) over 6 hours. The annealing process promotes the growth of the thickness of the lamellae or the crystalline phase. Therefore α -relaxation would be shifted to higher temperature, and moreover, the original defects or disordering in both the phases also exist or grow. In the compression process during the melting state, the original defects or disordering is removed because the molecular chain is orientated smoothly.

CONCLUSION

From the above indication and findings of the experiments the following conclusions could be drawn:

1. A slightly cross-linked UHMWPE was compressed at 200°C and cooled while maintaining the deformation.

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2. The (200) crystalline plane of the compressed sample was orientated parallel to the compressed surface.
3. The conduction velocity of ultrasonic waves along the compressed surface became higher.
4. The compressed surface was the hardest among the surfaces.
5. The dynamic mechanical experiments appeared the properties of the molecular chain.
6. The molecular chain in the amorphous phase was relaxed and only the crystalline phase was orientated perfectly.
7. The compressed surface had excellent wear resistance properties.

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Chapter 2

Wear Resistance of Slightly Cross-linked UHMWPE Crystallized from the Melt under Uniaxial Compression

INTRODUCTION

Ultra high molecular weight polyethylene (UHMWPE) has been used as a bearing material of an acetabular prosthesis component in hip and knee total joint replacement for more than thirty years. However, friction between bearing surfaces of both acetabular and femoral components leads to generation of wear debris in a contact part of joint cavities. It was found that dislocation and failure in total hip and knee arthroplasty are closely associated with osteolysis problems and caused by produced UHMWPE wear debris¹⁻³⁾.

Many improvements have been reported concerning the raw material and the component designs, composed of hard material including acetabular liner prosthesis without cementing. Oka et al.⁴⁾ reported a relationship between the kind of interface material and the volume of wear debris produced by the friction. Wear mechanism about UHMWPE was presumed in other reports⁵⁻⁸⁾. There were many reports in past concerning a relationship in which an abrasion volume is reduced with an increase in the molecular weight of UHMWPE⁹⁾. Although the weight-average molecular weight of the UHMWPE at present has been increased to approximately six million, it is difficult to make a UHMWPE having a far ultra high molecular

Chapter 2

weight. Further, considerable improvement in dynamic mechanical properties can scarcely be expected even if UHMWPE having a weight-average molecular weight of ten million could be synthesized. Thus, it is regarded that any improvement in dynamic mechanical properties of the UHMWPE by chemical modification has reached its limit. Also, though the γ -ray irradiation of UHMWPE was reported to reduce wear in other studies¹⁰⁻¹²⁾, but the reported results show an increase in both the coefficient and abrasion volume.

The author reported in the previous chapter that UHMWPE was slightly cross-linked, deformed compressively in the molten state, and oriented in molecular level to improve wear resistance¹³⁻¹⁵⁾.

The present chapter was carried out to eliminate the wear resistance by the compression ratio and provide experimental verification data by employing a reciprocal pin-on-flat wear test machine.

EXPERIMENTAL

Sample Preparation

A raw material for this study is an UHMWPE of GUR4150HP sold in the market by Hoechst.

Figure 1 shows a flow chart of sample preparation. At first UHMWPE blocks are irradiated by ^{60}Co γ -ray under reduced pressure at room temperature.

As the next step, the slightly cross-linked UHMWPE is compressed at 200°C which is higher than melting temperature (140 °C). The compressed speed and pressure are 1cm/min and 20 MPa, respectively. And then, the samples are cooled

until a room temperature for more than 3 hours. While the cooling speed of 140 to 80°C shown in the Japanese Industrial Standard (JIS) is about 1 hour. In this procedure, the sample thicknesses are reduced in accordance with a compression increase. The compressed ratio (CR) is defined as a ratio of the final to the original thickness of the sample, namely, the ratio of the sample thickness before and after compression.

The annealing method is that non-irradiation samples are left at 120°C under reduced pressure for 6 hours and then cooled down to room temperature.

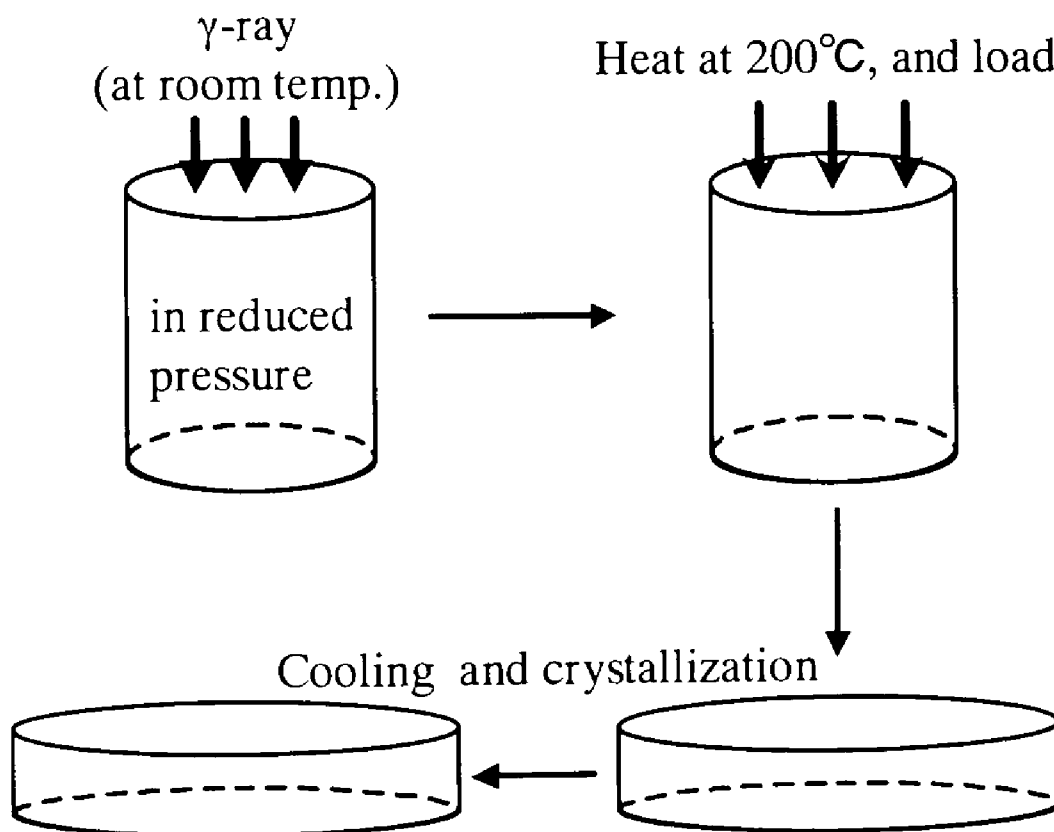


Figure 1: Scheme for preparation

Chapter 2

Wide Angle X-ray Diffraction

The crystalline structure analysis of the samples was studied by wide angle X-ray diffraction techniques. The diffraction photographs were taken by a flat camera of Rigaku Ru-3H which is equipped Ni-filtered Cu-K_α radiation at 40 kV × 60 mA. The compressed samples were cut to a cubic shape of about 1 mm at a room temperature. Then, the X-ray beam was introduced to the samples from three directions in the case of compressed samples and from only one direction in the case of uncompressed samples.

Thermal Properties

The heat fusion of the uncompressed and the compressed samples were measured by a differential scanning calorimetry (DSC, fabricated by Seiko Instruments Inc. DSC-6200). The heating rate was 10°C/min and alumina was employed as a reference.

Hardness Test

The micro-hardness measurements were carried out at a room temperature by Shimadzu Scientific Instruments, Inc. Hardness Apparatus with a Vickers square pyramidal diamond¹⁶⁻¹⁸⁾. The micro-hardness value was calculated by following equation.

$$MH = 2 \sin 68^\circ \frac{P}{d^2} (MPa) \dots\dots (1)$$

Where P and d are a load in gram and the diagonal length of an indented surface (μm) and the weighed load and the loading cycle time were 10 g and 20 s/cycle through all measurement, respectively.

Reciprocating Pin-on-flat Wear Test

Wear test was performed using a reciprocating pin-on-flat wear tester. Figure 2 shows the schematic representation of the wear tester. The tester is comprised of 6 arms so that 6 samples can be tested at the same time and condition. The wear test was tried in saline at 1.2Hz frequency for 2 million cycles at least. As unidirectional sliding distance at 14mm at one motion, the average and the maximum sliding speed are 33 and 52 mm/s, respectively.

Samples were cut to a flat-ended vertical cylinder shape of 10 mm in a length, 6.0mm in a diameter, and thus 28 mm² in a cross-sectional area. The sample surface was polished until 0.1µm roughness. The 3.47 MPa test load was applied along the longitudinal axis of the samples, while Co-Cr-Mo alloy plates were employed as the counter face of 0.01µm roughness. The chemical composition of the alloy was Co(63.72wt%), Cr(28.06wt%), Mo(6.20wt%), Si(0.80wt%), Fe(0.45wt%) , Mn(0.31wt%), C(0.26wt%), and Ni(0.2wt%) respectively. And the Rockwell C hardness was 28 - 30.

After the samples were ultrasonically cleaned in a desiccated vessel filled with a research grade acetone, reduced pressure, and then the weight loss of the samples were measured. The sample weights were immediately recorded after removing from the above vessel. Wear factor is defined as following equation.

$$\text{Wear Factor} = \frac{\text{Wear volume(g)}}{\text{Load(MPa)} \times \text{Sliding distance(m)}} \dots\dots (2)$$

AFM observation

Surface morphology of UHMWPE is observed at an aired room by atomic force microscope (AFM, OLYMPUS OPTICAL CO., LTD., NF-2000) of scanning 256 lines

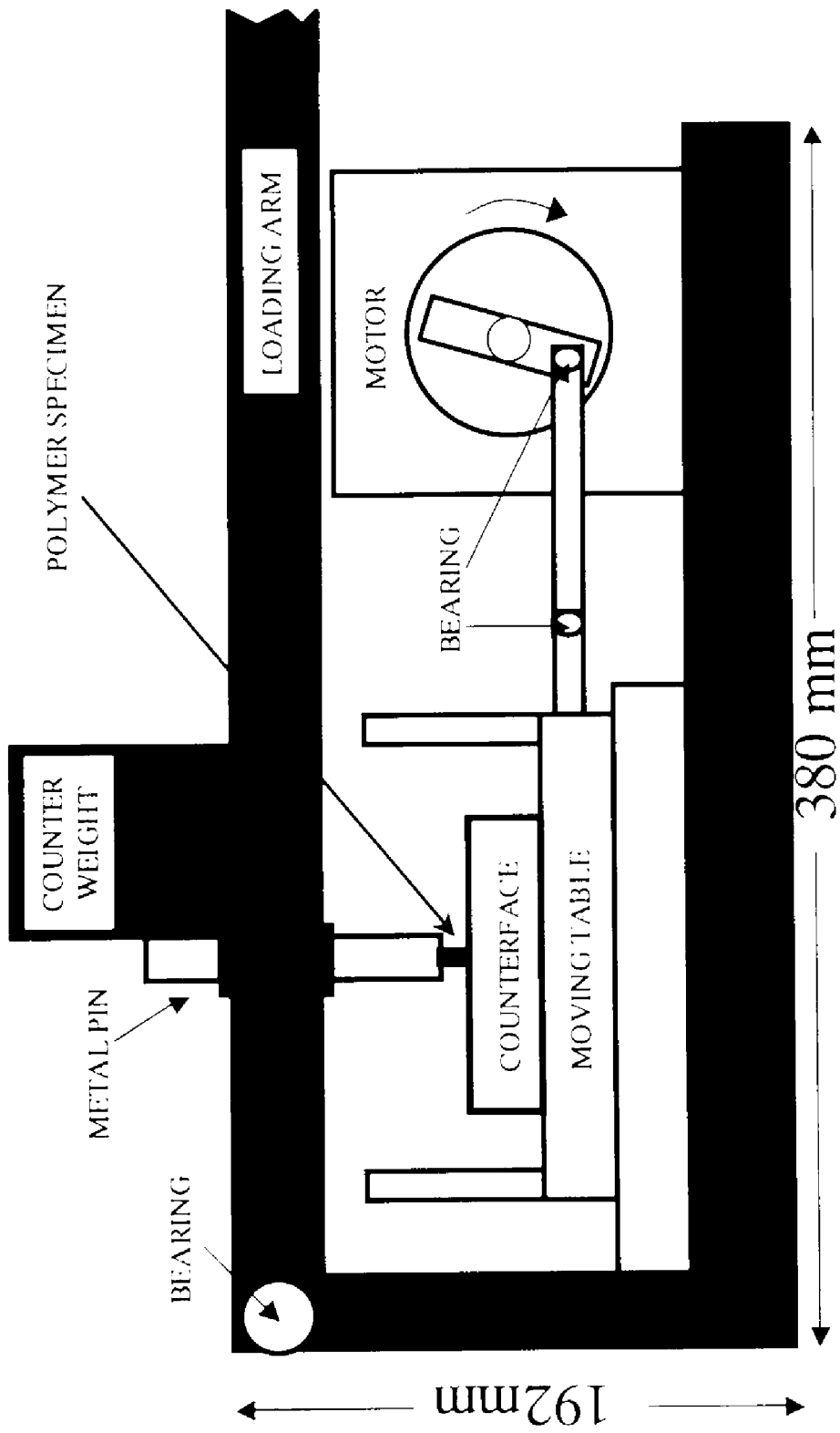


Figure 2: Diagram of reciprocating pin-on-flat wear machine

in every $30\ \mu\text{m}^2$ square area of a sample surface. The spring constant of the cantilever is measured about 0.09 N/m when 10 nN load is applied on the sample.

RESULTS

The effect of γ -ray irradiation of polyethylene was primarily to introduce cross-links, while accompanied by random scission of polyethylene chains to a minor extent. Because of the extremely high molecular weight of the molecules in specimens, a small amount of cross-linking was expected to be sufficient to cause to formation of network structure. Figure 3 shows the undissolved gel fraction determined for

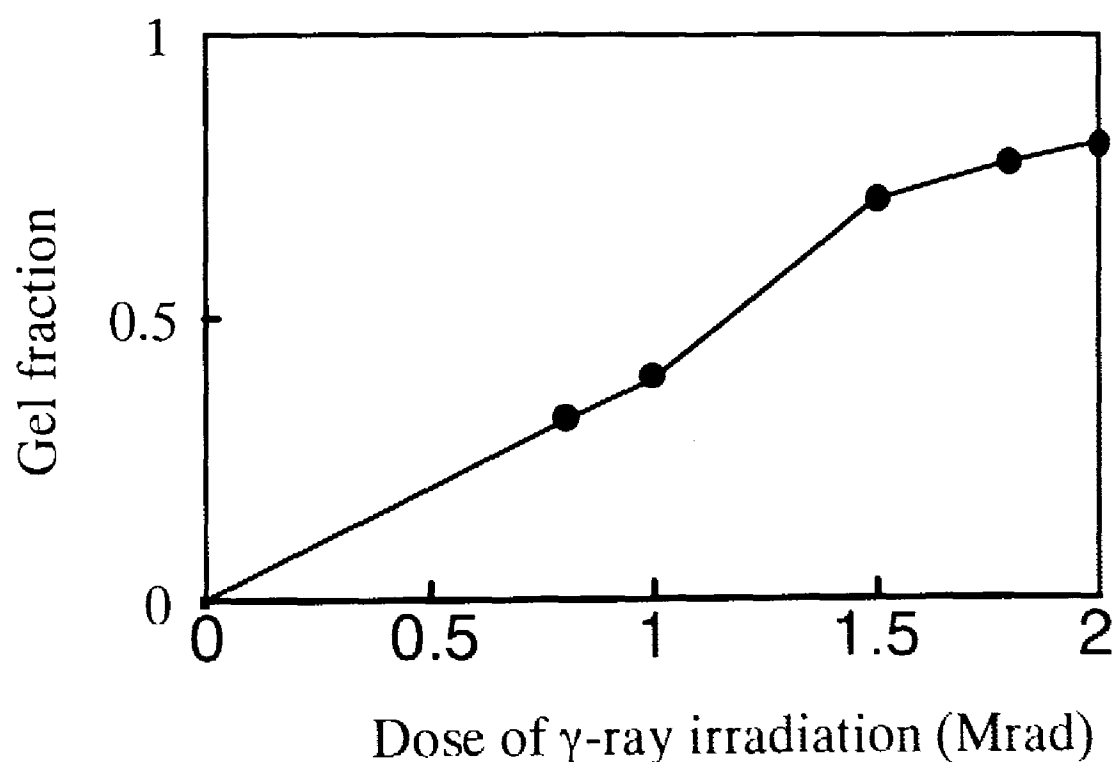


Figure 3: Relation between gel fraction and dose of γ -ray irradiation

specimens irradiated to various doses, as determined under the condition of 24 hr dissolution time.

This plot indicates that when irradiation dose is too high, the density of the intermolecular cross-links becomes so high that the cross-linked UHMWPE is difficult to be oriented. Therefore, the irradiation dose is preferable to be less than 1.8 Mrad. Then, the UHMWPE is slightly cross-linked and its gel fraction ratio is about 0.85, as a result.

The both uncompressed and compressed samples were observed by using a wide angle X-ray diffraction photograph technique taken by an equipped flat camera. Figure 4(a) shows the taken pattern of the uncompressed samples, and uniform circular rings indicate a random distribution of crystalline phase or crystal planes. Furthermore, Fig. 4(b) shows the pattern of the compressed samples taken by the method that X-ray beam was parallel incident to the compressed surface. And Fig. 4(c) shows the pattern taken by the method that the beam was perpendicular incident of the compressed surface. The both patterns mean that the crystalline planes, especially (200) plane, are parallel orientated along the compressed surface.

Figure 5 shows the relationship between the heat of fusion measured by DSC and the compression ratio; the heat of fusion increases in accordance with the compression ratio. The heat of fusion for the compressed samples (the compressed ratio CR is 4.02) was 6.9% higher than the uncompressed samples while the annealed sample was about 5.1% higher. This means that the crystallinity of the compressed and the annealed samples are higher than that of the uncompressed samples, and that the compression ratio increases in accordance with a hardness increase on the sample surface.

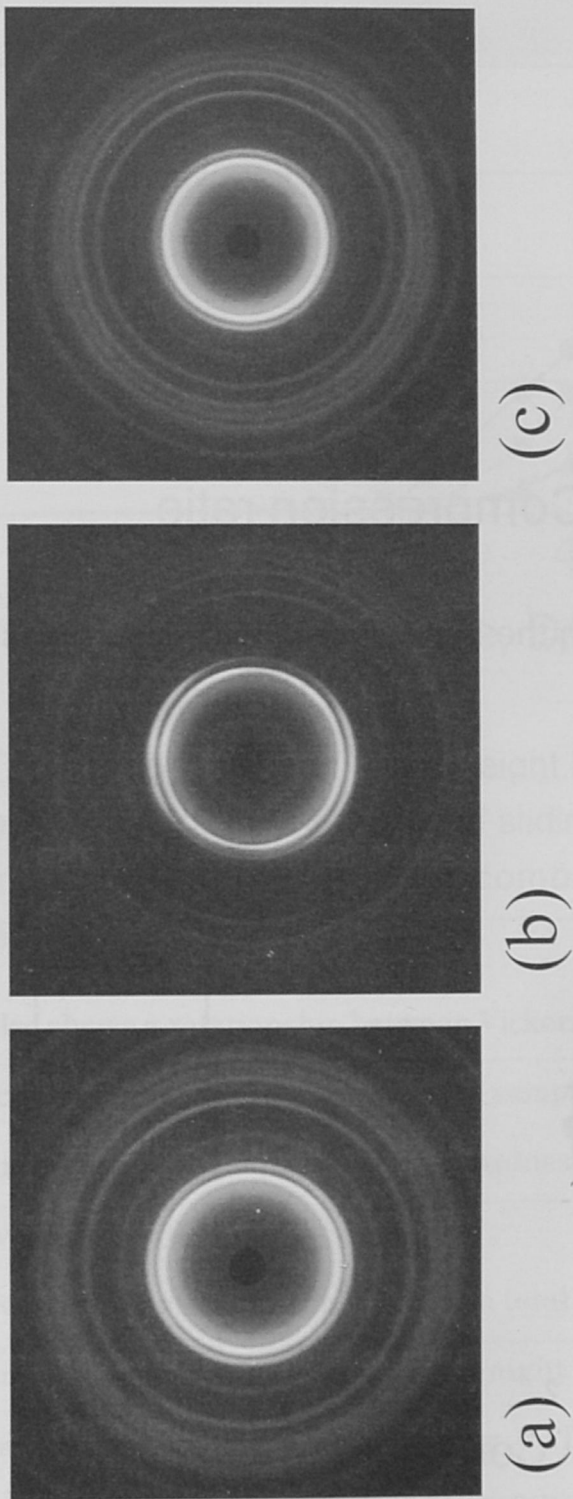


Figure 4: Wide angle X-ray photographs for uncompressed and compressed UHMWPE. (a): uncompressed (b): compressed (CR = 2.7), (c): X-ray beam was incident perpendicular to the compressed sample surface

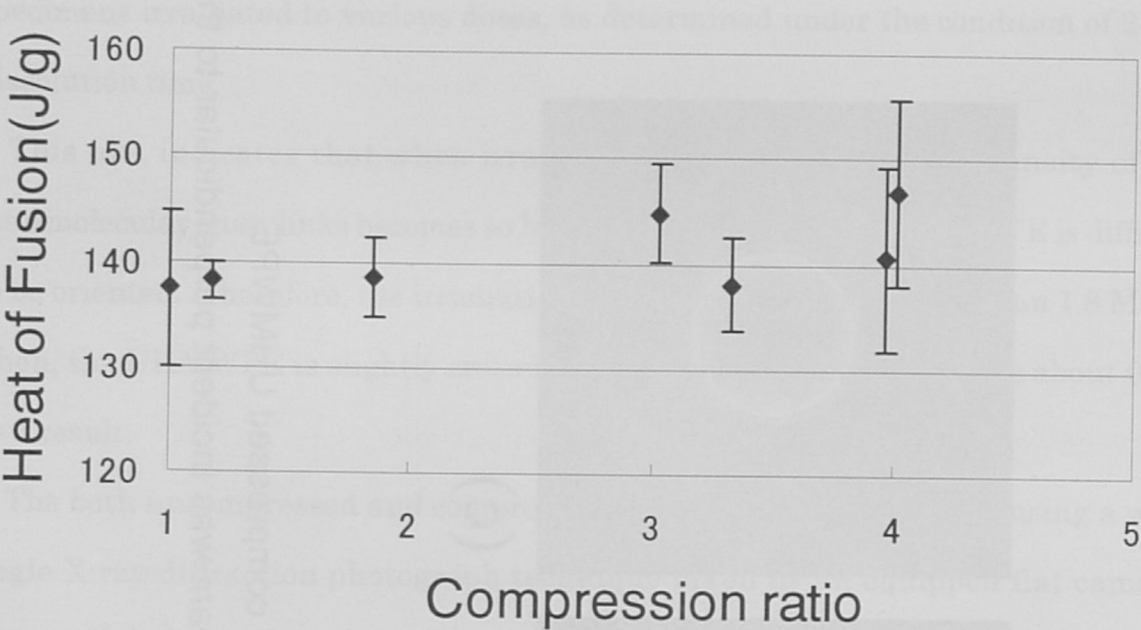


Figure 5: Relation between the heat of fusion and compression ratio

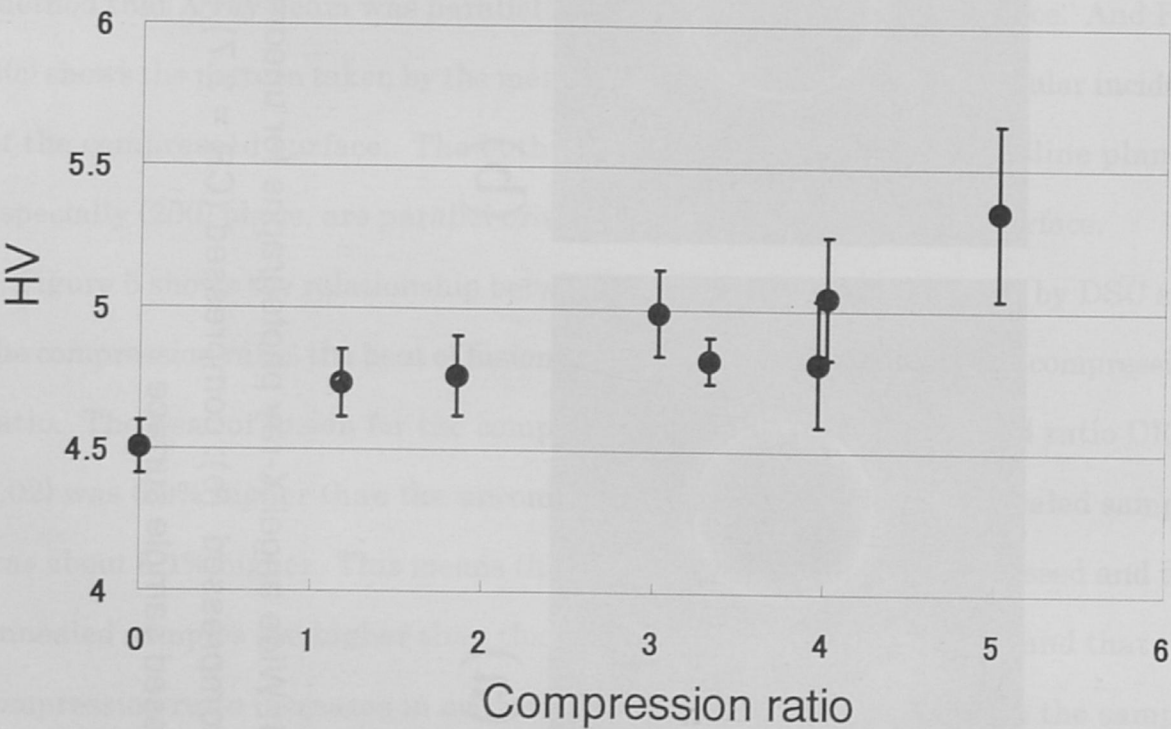


Figure 6: Relation between the hardness of sample surface and compression ratio

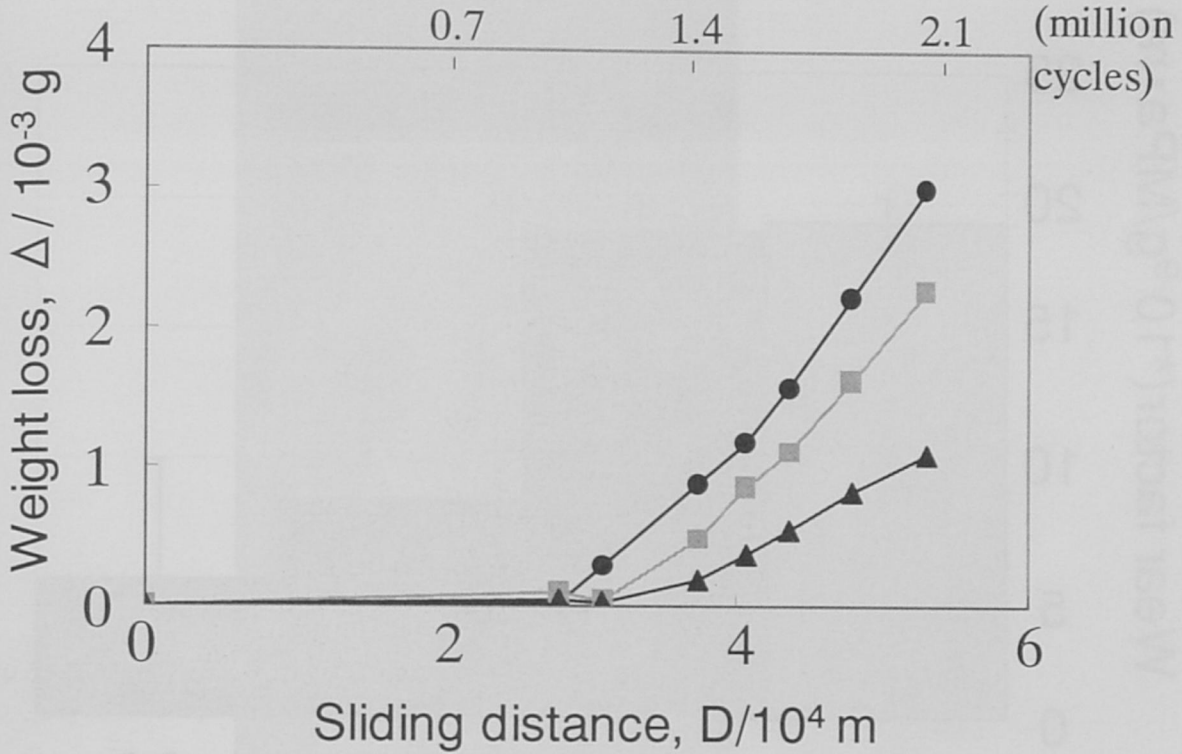


Figure 7: The changes in cumulative weight loss for uncompressed and compressed UHMWPE as a function of sliding distance

● : uncompressed (CR = 1), ■ : compressed (CR = 2.1), ▲ : compressed (CR = 2.7)

Figure 6 also shows a relationship between Vickers hardness and the compression ratio, in which the hardness of the compressed sample (CR is 5) was 10% higher than that of the uncompressed sample while the hardness of the annealed sample was in a range between 4.32 ± 0.13 .

Wear test was tried by sliding about 60,000m total distance, equivalent to 2 million cycles. From the wear test, the average weight loss of the UHMWPE sample compressed and uncompressed, is shown in Fig. 7. The weight loss of the UHMWPE was lower than that of the uncompressed UHMWPE and was also dependent on the compression ratio. No significant difference of weight loss between the both samples

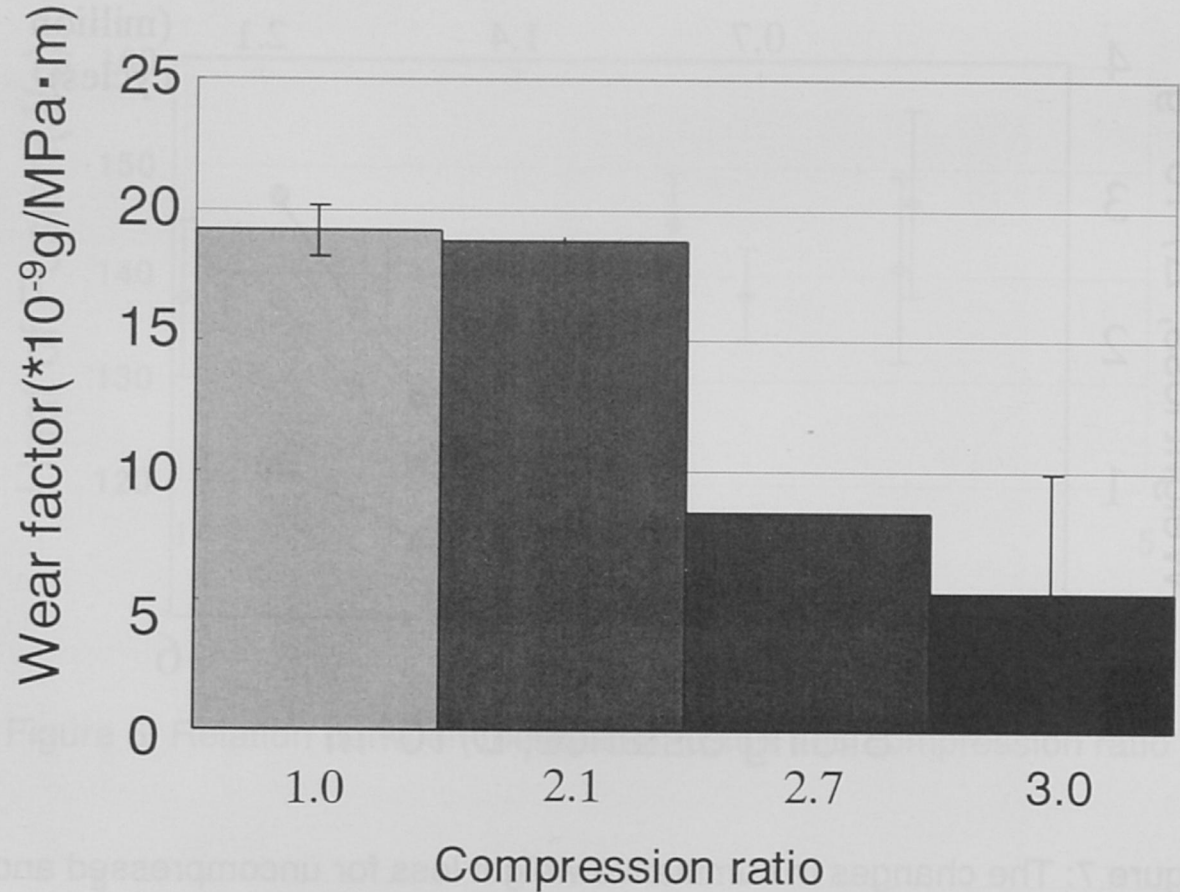
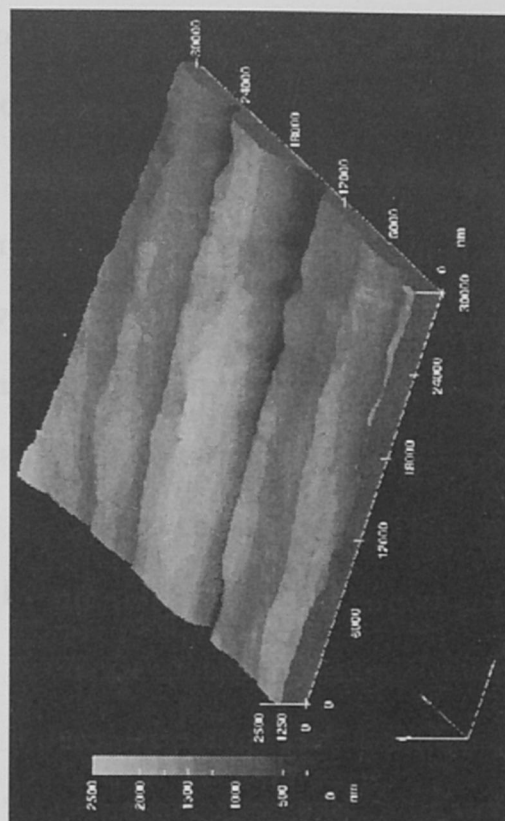


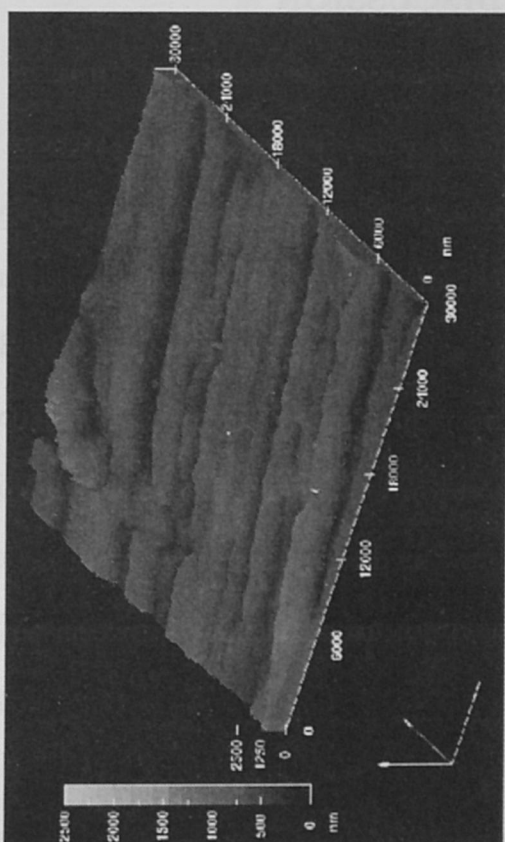
Figure 8: The changes of wear factor as a function of compression ratio

was observed until 20,000m sliding. However, the weight loss volumes of the uncompressed samples are higher than that of the compressed samples in the range of sliding distance more than 20,000m, in which the weight loss (shown in sample of CR 2.1) decreases in accordance with an increase of the compression ratio (shown as compression of CR 2.7).

The wear factor was calculated according to the above data and equation (1), in which the sliding distance and the employed load were about 60,000m and 3.47 MPa, respectively. Figure 8 shows the wear factors of each samples, in which the wear factors are gradually decreased in accordance with the increase of



(a)



(b)

Figure 9: AFM images of worn UHMWPE sample surfaces after 2×10^6 cycles
(a): uncompressed (b): compressed

compression ratio, especially the wear factor of the compression ratio 3.0 is reduced to one-third of the uncompressed samples. While the wear factor of the annealed sample was higher than the uncompressed sample.

Figures 9(a) and (b) show images of the uncompressed and the compressed samples, and the worn pin surface after slide test taken by AFM, respectively. Abrasion patterns of the uncompressed samples, shown in the images, were composed of various kinds of wide, deep, narrow and shallow ridges, while abrasion patterns of the compressed samples are only composed of wide and deep ridges. Table 1 shows the ridge depths of the worn sample surfaces in the compressed and uncompressed samples.

DISCUSSION

The above experimental results show the relationship between the crystalline structures of UHMWPE and their wear resistances. In the experimental procedure, the slightly cross-linked UHMWPE samples are compressively deformed in molten state, cooled while maintaining the deformation and then oriented parallel along the compression plane. The author point out that there are many advantages in the above procedure, including easy to orient the crystal plane so that the dose of γ -ray irradiation is possibly a little as a result, because of deforming compressively in the molten state.

The above test data of the wear resistance suggests that the compressed sample is a superior acetabular prosthesis component to the uncompressed sample, as the wear factor of the compressed samples is lower than the uncompressed samples.

Table 1: Roughness of worn surface

	$P_a(*10^2)$	$P_{max}(*10^3)$	$R_z(*10^2)$	$P_p(*10^2)$	$P_v(*10^2)$
uncompressed	1.35	1.00	6.06	3.00	7.04
compressed	2.50	1.56	7.08	6.98	8.65

P_a : Average of profile roughness
 P_{max} : Maximum value of profile
 R_z : Ten points average of profile roughness
 P_p : Maximum value of average line
 P_v : Maximum depth value of average line

Chapter2

The above wear resistance tests were performed in a similar condition to that of ASTM except for lubricant saline in the present study.

A crystal structure is one of very important factors for the wear resistance, because the main molecular chains are slightly oriented along the radial direction judging from WAXD photographs. We have already reported that a crystalline planar orientation increases in accordance with an increase of the compression ratio, and therefore, there is a certain relationship between the compression ratio and the wear resistance. When the slightly cross-linked UHMWPE samples are compressively deformed against a metal ball shape, it can be predicted that the (200) crystal plane is possibly oriented along a sphere surface of the ball.

It is found that as the wear factor of the oriented UHMWPE makes unimproved in spite of crystallinity increase, an increase of crystallinity as a whole is not a main factor for improving the wear resistance or the wear factor. In a conclusion, the main factor for improving the wear factor seems to be not the crystallinity degree as a whole but a crystal structure on the sample surface.

As compared the worn surfaces of the compressed with the uncompressed samples by AFM images, there are observed a lot of narrow and shallow ridges in the uncompressed sample photographs as mentioned above. This means that the samples are rapidly worn out in the case of soft samples, and the order of the softness agrees with that of Vickers hardness. On the contrary as shown in upper left of Fig. 9, none of the narrow and shallow ridges were observed in the compressed sample surface, because the compressed sample surfaces are composed of uni-axially crystalline structures.

CONCLUSION

1. When UHMWPE, which was cross-linked slightly by γ -rays (less than 1.8Mrad), are compressively deformed in molten state and cooled while maintaining the deformation, the (200) crystal plane becomes oriented along compression plane; this crystalline planar orientation is confirmed by WAXD observation.
2. According to the reciprocating pin-on-flat wear test data, the wear factor of the compressed samples is improved.
3. The high compression ratio reduces the wear factor, as compared to that of the uncompressed sample.
4. The compressed samples appear harder than the both of annealed and uncompressed samples in Vickers hardness measurements. The hardness increases with an increase in the compression ratio increase.
5. The results of Vickers hardness, wear test, and AFM observations provided clear experimental evidences for the improved wear resistance properties of the compressed UHMWPE.
6. Lightly cross-linked UHMWPE crystallized from the melt under uni-axial compression is expected to be useful for artificial joint applications.

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Chapter 3

Comparison of Wear Properties with Several Wear Machines

INTRODUCTION

The superior wear, fatigue, and fracture properties of ultrahigh molecular weight polyethylene (UHMWPE) in its pristine form have made it the material choice for the last 30 years in the replacement of damaged or diseased articulating cartilage for total joint replacement surgery¹⁻¹⁴⁾.

In previous chapters¹⁵⁻¹⁹⁾, we reported on the wear resistance when compressing slightly cross-linked UHMWPE uni-axially during the molten state with subsequent cooling. It is found that the wear resistance of the compressed sample was enhanced based on the findings of a reciprocating wear test. The (200) and the (110) crystal planes of the compressed sample were orientated preferentially parallel to the compressed surface as shown by X-ray diffraction. It was confirmed that the compressed sample had a high level of crystallinity and an extremely high melting point based on the measurements of the density and enthalpy fusion.

Although it is found that the compressed UHMWPE was enhanced, it is necessary to perform wear tests with the other machines, because the principal of the wear mechanism was difficult to understand perfectly with one machine. Therefore the purpose of in the present chapter is that the comparison of wear tests with several wear machines. And the effects of the compression ratio on wear properties are also reported.

EXPERIMENTAL

Preparation of Samples

The starting material for this work was a commercial UHMWPE from Mitsui Chemical Co. Japan with a viscosity average molecular weight of 5.5×10^6 . Figure 1 shows the schematic diagram and photo of the procedure.

At first, blocks of UHMWPE were irradiated by ^{60}Co γ -rays under vacuum at room temperature and the irradiation dose was 0.5 Mrad.

The irradiated UHMWPE was compressed at 200°C , which was higher than the melting point (about 140°C in original UHMWPE). The compression speed was about 1 cm/min, and the total compression weight was about 4200 kgf.

The samples were cooled to room temperature over a period of 2 hours while maintaining of the deformation. The cooling speed from 140°C to 80°C demanded by the Japanese Industrial Standard (JIS), was about 1hour. In this procedure, the sample thickness was reduced in accordance with increases in the compression.

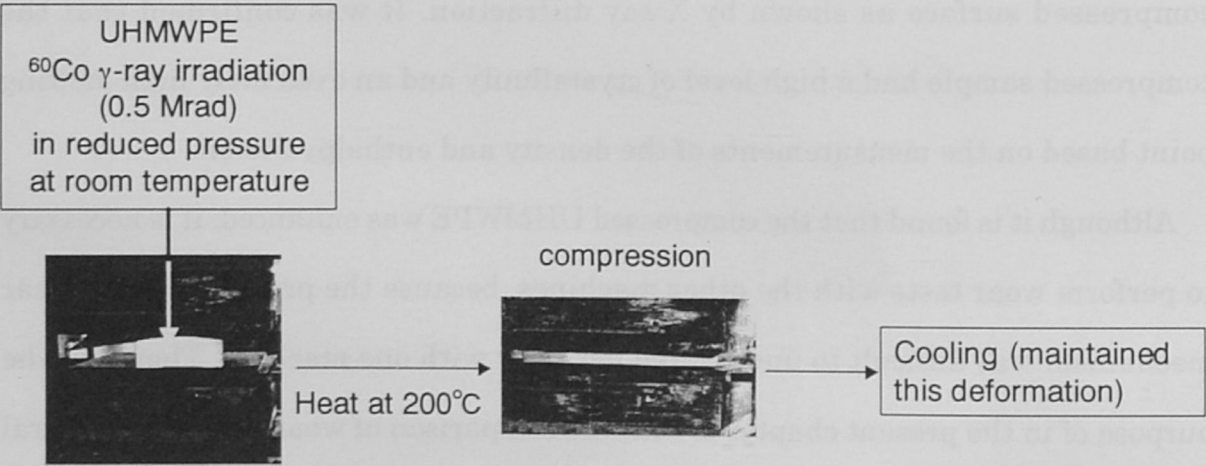


Figure 1: Schematic diagram for preparation of samples

The compression ratio (CR) was defined by the ratio of the final thickness to the original thickness of the sample.

Wide Angle X-ray Diffraction Technique

The crystalline structure analysis of the samples was studied by wide angle X-ray diffraction techniques. Imaging plates (MAC-Science Type DIP220) with an IP film were able to record two-dimensional patterns by shifting the drum along its axle. The rotating anode X-ray generator Cu-K α was monochromatized by a Rigaku type RU-200 and radiated at 40 kV and 100 mA. The X-ray beams were introduced to all samples parallel to the compressed surface.

Thermal Properties

Enthalpy changes in fusion and melting points were measured using a differential scanning calorimeter (DSC, Seiko Instruments Inc. DSC-6200). The heating rate was 10°C/min from room temperature to 200°C with alumina used as a reference. Each sample, weighting approximately 10 mg, was placed in a closed (but not airtight) aluminum pan. The degree of crystallinity was measured by DSC and calculated from the following formula using 288.9 J/g as the enthalpy for fusion in a perfect crystalline phase.

$$\text{The degree of crystallity} = \frac{\text{measured enthalpy of fusion}}{288.9} \dots\dots(1)$$

Density Measurements

Densities of samples were measured in a density gradient column at 30°C. Toluene was gradually added to carbon tetrachloride to make the gradient solution. The density range of the gradient solution was between 0.910 g/cm³ and 0.950 g/cm³. The degree of crystallinity calculated by the following formula using 1.00 g/cm³ as the density of the perfect crystalline phase and 0.85 g/cm³ as the density of the perfect amorphous phase.

$$\frac{1}{\rho} = \frac{x}{\rho_c} + \frac{1-x}{\rho_a} \dots\dots\dots (2)$$

where ρ is the measured density, ρ_c is the perfect crystalline density, and ρ_a is the perfect amorphous density.

Measurement of Extension

The extension was carried out by increasing temperature from -150°C to 140°C at 2°C/min in order to investigate the existence of residual stresses in amorphous phase. The surface perpendicular to the compressed axis was cut to a rectangular parallelepiped and measured the length. Extension was calculated using the following formula:-

$$\text{extension} = \frac{\text{length} - \text{original length}}{\text{original length}} \dots\dots\dots (3)$$

Where original length was defined as the length at 0°C.

Measurements of Dynamic Mechanical Properties

The principle of dynamic mechanical analysis was based on the following: Dynamic mechanical properties of a material are obtained, when a specimen is subjected to a periodic stress. The deformation lags behind this stress by an angle δ , because the material is viscoelastic. It is conventional to separate the viscoelastic properties into 'in-phase' and 'out-phase' components; the former comes from the elastic (completely recoverable) stored energy while the latter shows the dissipation of energy when the specimen is deformed. Therefore, the modulus of elasticity, E (Young's modulus), is given by:-

$$E = E' + jE'' \dots \dots (4)$$

Reciprocating Pin-on-flat Wear Test in NRIM

The reciprocating pin-on-flat wear test was performed at National Research Institute for Metals (NRIM). The test was followed with ASTM standard, the load was 3.54 MPa, the reciprocation was carried out up to 2×10^6 times with 25 mm stroke at 1 Hz. The lubricate was HBSS of pH 7.4 at 37°C. The number of specimen was 3, respectively, and the counterface was alumina plate. Figure 3 shows a shape of the specimen and introduced directions with X-ray in order to observe crystalline phase.

Wear Test of Uniaxial Direction Pin-on-disc

Using a pin-on-disc unidirectional wear device, wear tests were performed in saline for 48 hours. An unsterilized UHMWPE cylinder, 4 mm diameter, with a contact surface area of 12.56 mm^2 was pressed endwise under a constant axial stress of 3 MPa against the flat surface of the counterface disc. The wear chamber

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was driven in a clockwise direction by a variable speed electric motor at a constant speed of 60 mm/s. The wear rate was evaluated by the decrease in the UHMWPE pin length, and the frictional force was determined by the deformation of the leaf spring. Zirconia ceramics were used as a counterface material. The surface roughness, Ra, of the ceramic was polished to approximately 0.2 mm intentionally for the purpose of the decreasing the wear test time. The decrease of the UHMWPE pin length was measured by the laser displacement meter. Wear factor was calculated as follows:-

$$\text{Wear Factor} = \frac{\text{Wear volume}(g)}{\text{Load}(N) \times \text{Sliding distance}(m)} \dots\dots(5)$$

Reciprocating Pin-on-flat Wear Test

To investigate the relationship between the wear factor and the surface of the compressed UHMWPE, wear tests were performed using a reciprocating pin-on-flat wear test device. The schematic representation of the wear test machine has been reported previously. The machine has 6 arms, so 6 samples can be tested simultanelusly. Wear tests were performed at a frequency of 1.2 Hz for a minimum of 1.4 million cycles in distilled water. The unidirectional sliding distance of the motion was 14 mm. Thus, the average sliding speed was 33 mm/s, and the top speed was 52 mm/s.

Samples were cut into a flat-ended vertical cylinder and the base surface was polished at a mean roughness (Ra) of 0.1 μm . Two directions specimens were prepared, which one sample had the base of the X-Y plane, the other had the base of the X-Z plane shown in Figure 3. The test load of 98.11 N was applied to the samples along the longitudinal axis. Co - Cr - Mo alloy plates were used for the counter face,

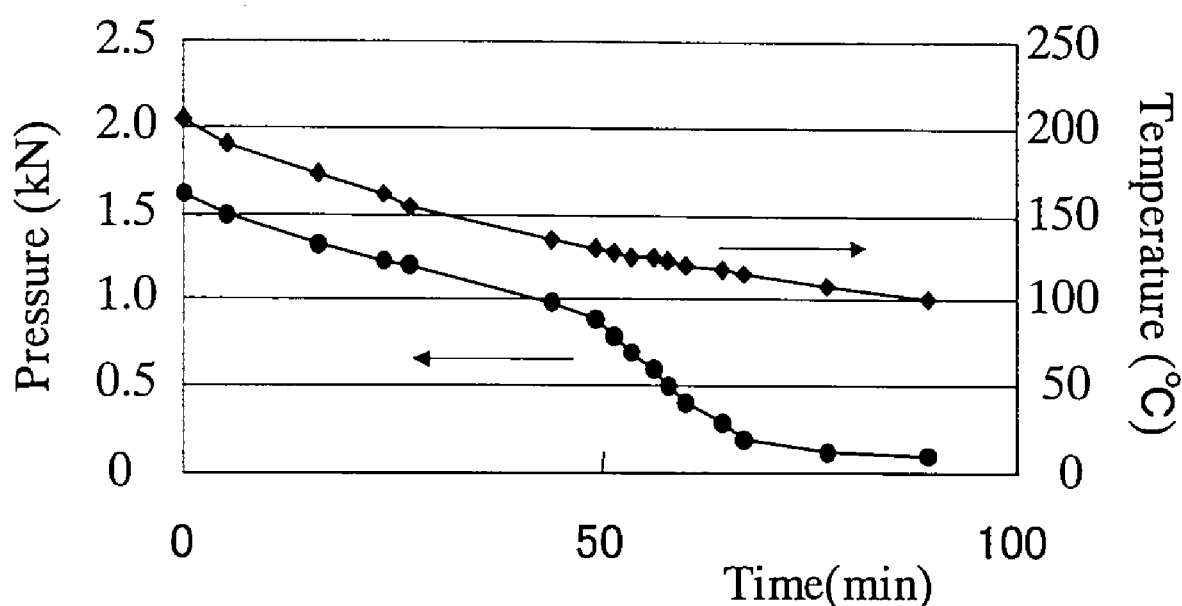


Figure 2: Pressure and temperature variations with time

of which the Ra was 0.01 μm . The chemical composition of the alloy was Co (63.72 wt%), Cr (28.06 wt%), Mo (6.20 wt%), Si (0.80 wt%), Fe (0.45 wt%), Mn (0.31 wt%), C (0.26 wt%), and Ni (0.2 wt%). The Rockwell C hardness was 28 - 30.

After the wear test, the samples were cleaned ultrasonically in research grade acetone and vacuum desiccated, the weight losses of the samples were measured. The weight was recorded immediately after the reduced pressure desiccation.

RESULTS

Figure 2 shows the variations in temperature and pressure with time when the cross-linked sample was cooled from the melting state with maintaining the compression. The temperature was gradually decreased with time, while the pressure

was quickly decreased between 50 and 70 minutes. The rapid decrease in pressure can be attributed to shrinkage and exothermic transition for crystallization.

Wide Angle X-ray Diffraction

Figure 4 shows that the X-ray diffraction patterns at the three directions shown in Figure 3. The left image in Figure 4 was taken a picture when X-ray was introduced to the compressed direction, and also the middle and the right photos were taken perpendicular to the compressed direction, respectively. In the right photos, there are white spots, which come from mica diffraction, because the small cubic sample was put between the mica when the photo was taken. The (200) and the (110) crystalline planes were orientated parallel to the compressed surface. Suong-Hyu Hyon *et al.* reported that the six distinct maxima points for the (110)-diffraction observed at the compression ratios larger than the CR=6. These points would be caused by rather perfect orientations of both crystal planes, the (200) and (110), shown in Figure 5 and Figure 6. The two maxima points on the meridian would be originated by an imperfect (110)-orientation, and the four maxima points would be composed of superposed maxima by the (200) and (110) orientation, respectively.

Figure 7 shows the change in WAXD imaging. Figures 7a, 7b, and 7c show diffraction patterns of compression ratios 1, 2, and 5, respectively. Slight orientation was observed at a wider angle in the CR=1 sample. It was suggested that the non-compressed sample was pre-orientated, because the conventional UHMWPE was a ram extruded sample and shear flow occurred in the extrusion. The direction of compression is shown in Figure 7. It was found that the (200) crystal plane of the CR=2 sample was orientated perpendicular to the compressed direction (i.e. parallel

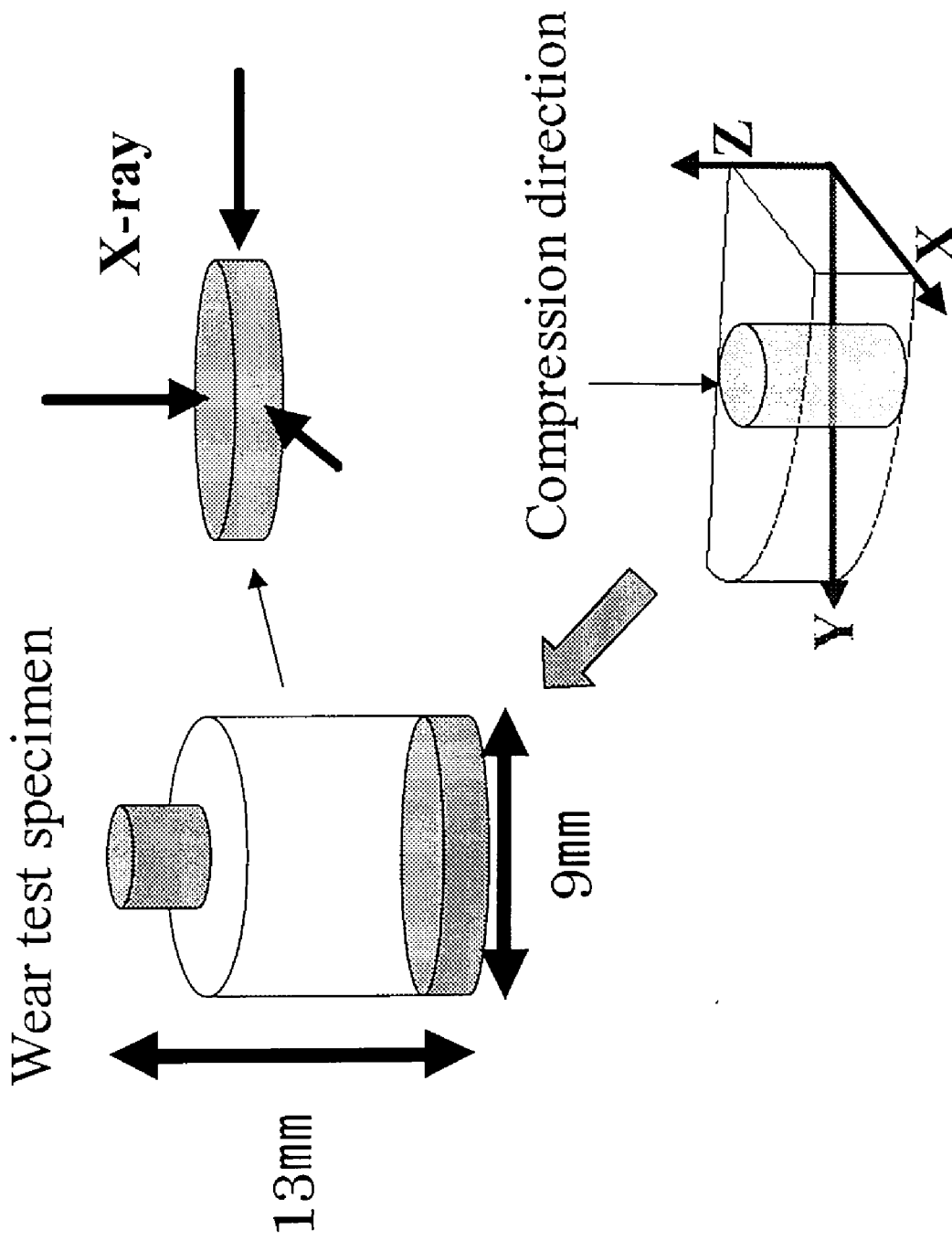


Figure 3: Schematic diagram of specimen for wide angle X-ray diffraction and wear test

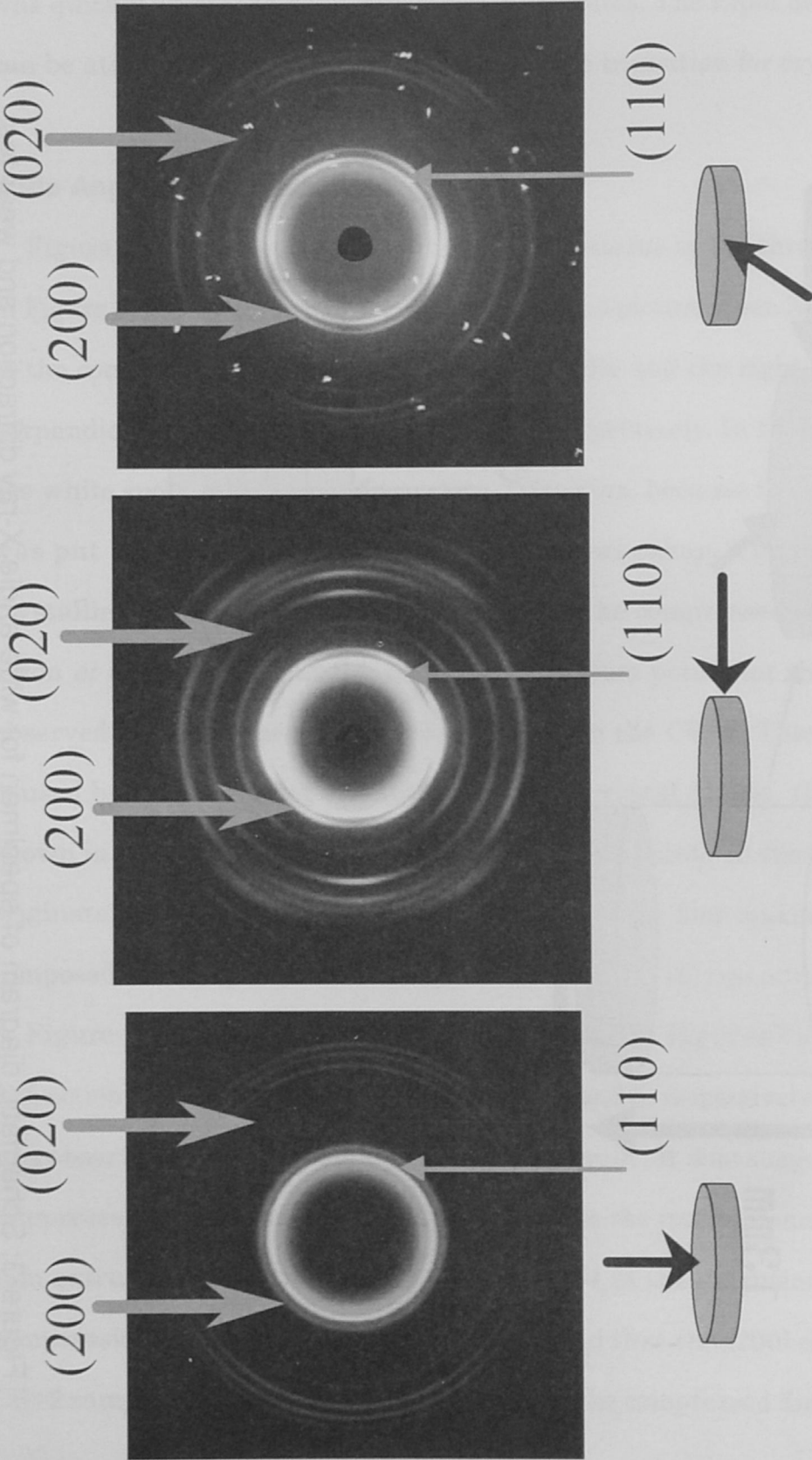


Figure 4: Wide angle X-ray diffraction patterns from three direction of the compressed UHMWPE

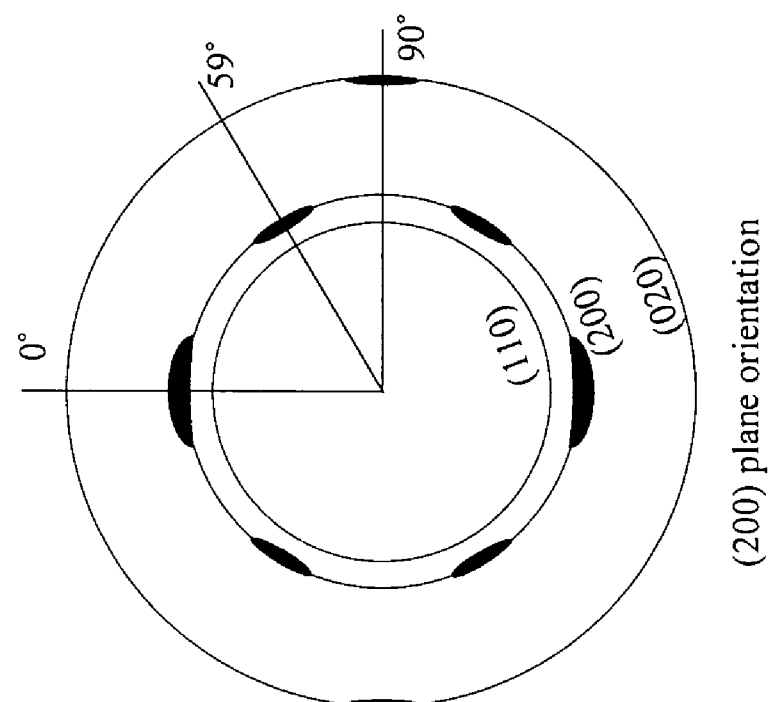


Figure 6: Schematic diagram of (200) crystalline plane orientation

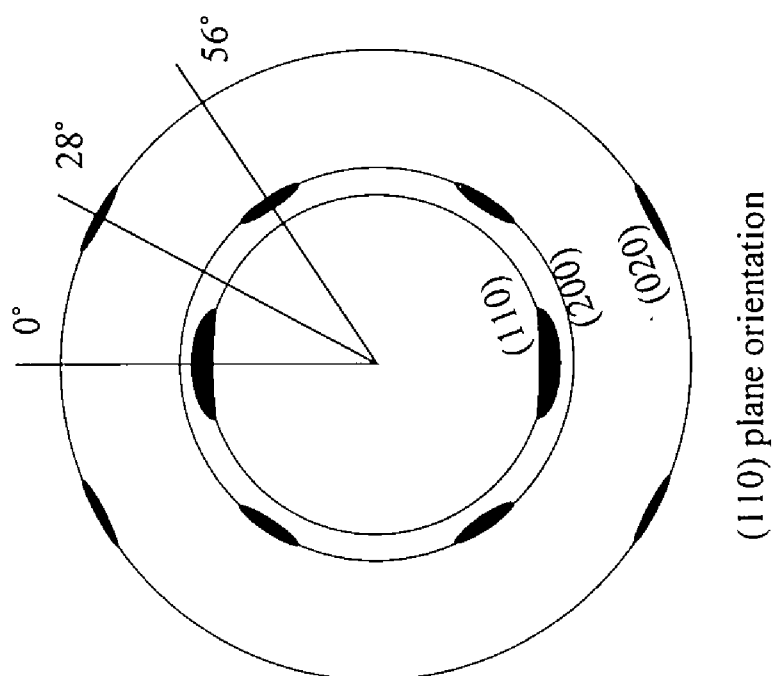


Figure 5: Schematic diagram of (110) crystalline plane orientation

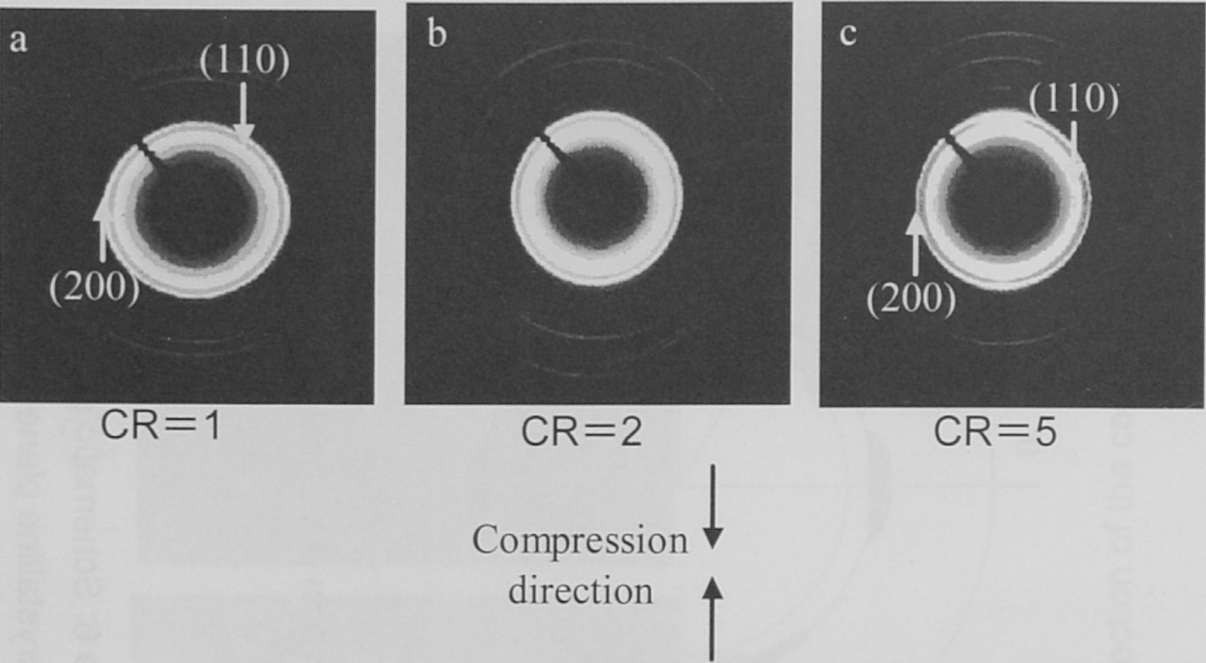


Figure 7: Wide angle X-ray diffraction images (a:CR=1, b:CR=2, c:CR=5)

Table 1: Density variations with different compression ratios

CR	1	2	3	4
Density(g/cm ³)	0.9283±0.0012	0.9257±0.0017	0.9267±0.0003	0.9302±0.0002

to the compressed surface), which means that the molecular chain was orientated parallel to the compressed surface. The (200) and also (110) crystal plane was orientated perpendicular to the compressed direction in the CR=5 sample, and furthermore the degree of orientation was higher than that of the CR=2 sample.

Density Measurement

Table 1 shows the relationship between the compression ratio and density. These findings show that the density increased with the increase in the compression ratio. The degree of crystallinity was calculated from Eq. (2), hence, the CR=2 sample was 49.3%, and the CR=4 sample was 53.5%.

DSC Measurement

The thermodynamic properties were measured using DSC and Figure 8 shows the endotherm curves. The peak at around 140°C of each sample indicates the melting point. The main feature of these findings was the increase in melting point with the increase in compression ratio (Table 2). The shift in the melting point to a higher temperature was related to the presence of the thick lamellae. Moreover, it was observed that the peak of the CR=2 was broader than CR=1 and CR=3.

Dynamic Mechanical Properties

Figure 9, Figure 10, and Figure 11 show storage modulus (E'), loss modulus (E''), and $\tan \delta$, respectively. In all samples, the E' value gradually decreases as the temperature rises. The CR=2 sample showed an elastic modulus which was equal to sample CR=1 at room temperature, and there was minimal lowering of the elastic modulus at approximately 50°C. The elastic modulus of the CR=5 sample was high

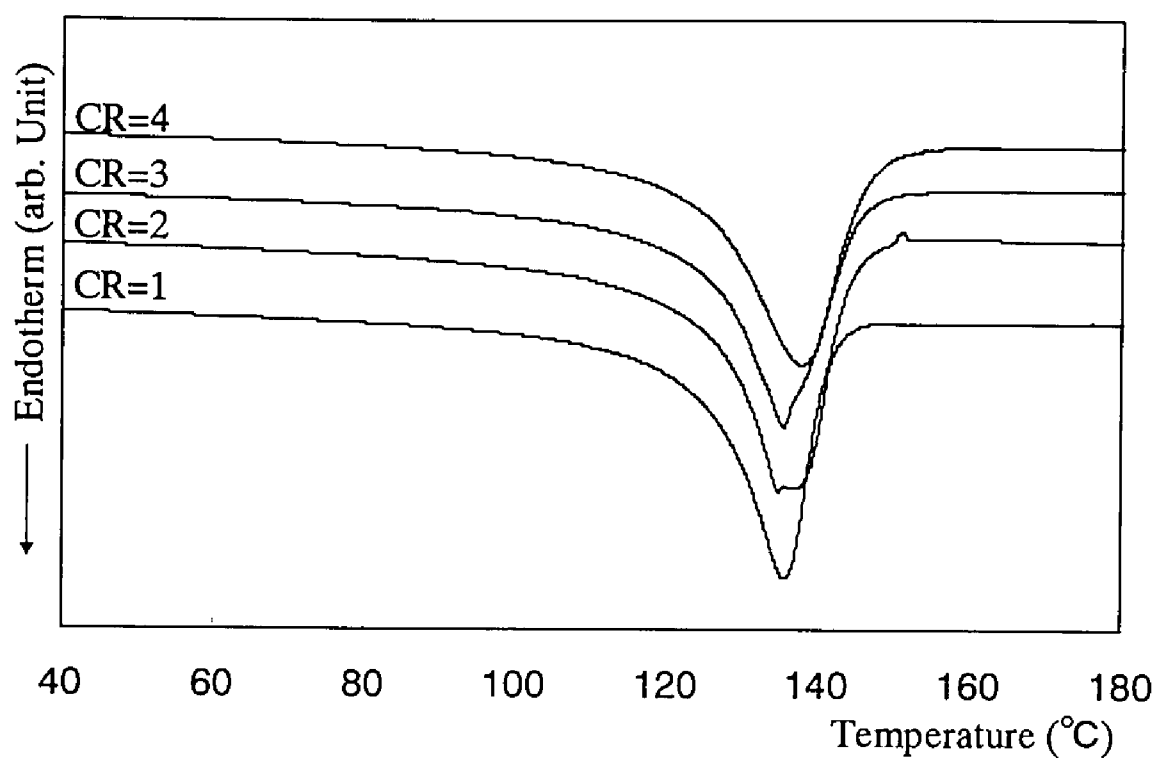


Figure 8: DSC fusion scans for several compression ratios

Table 2: Thermodynamic properties

CR	1	2	3	4
T_m (°C)	135.3	137.2	137.1	138.0
ΔH (J/g)	157.4	156.4	160.5	172.7

throughout the total temperature range. The loss modulus (E'') had three apparent dispersion peaks at 70°C, -10°C, and -115°C that were designated as α_c , β , γ -relaxation, respectively. The α -relaxation was observed for the relaxation phenomena of the molecules in the crystalline part. In the α_c -relaxation, the thermo-vibration of the molecular chain in the crystal phase actively occurred and the inharmonic oscillators of the intermolecular potential were increased. Then the crystalline phase became viscoelastic. It was observed that the α_c peaks of CR=2 and CR=5 shift to a higher temperature and increased in intensity.

The β -relaxation is explained as the micro-Brownian of the main chain motion in the amorphous part. No β peaks are were moved, although the intensity of the CR=2 sample decreased slightly.

The γ peak temperatures of all samples were also similar (at about -115°C). The γ -relaxation is generally known as the molecular relaxation phenomena such as the chain ends or the dislocation of such defects in the crystalline part. The broadening of the γ -relaxation of the CR=2 sample indicated an increase in the variety and amount of the crystalline disorder.

Measurement of Extension

Variations in extension for the CR=1, 2 and 5 samples are plotted as a function of temperature in Figure 12. Although all samples showed expansion of 4 - 6% at approximately 100°C, this was the thermal expansion. They also had an inflection point at around -110°C, which was related to γ -relaxation. The CR=1 sample shrunk rapidly at 135°C, while there was extension of other compressed samples without observing this shrinkage phenomenon. Moreover, the extension ratio of CR=5 was higher than that of the CR=2 sample.

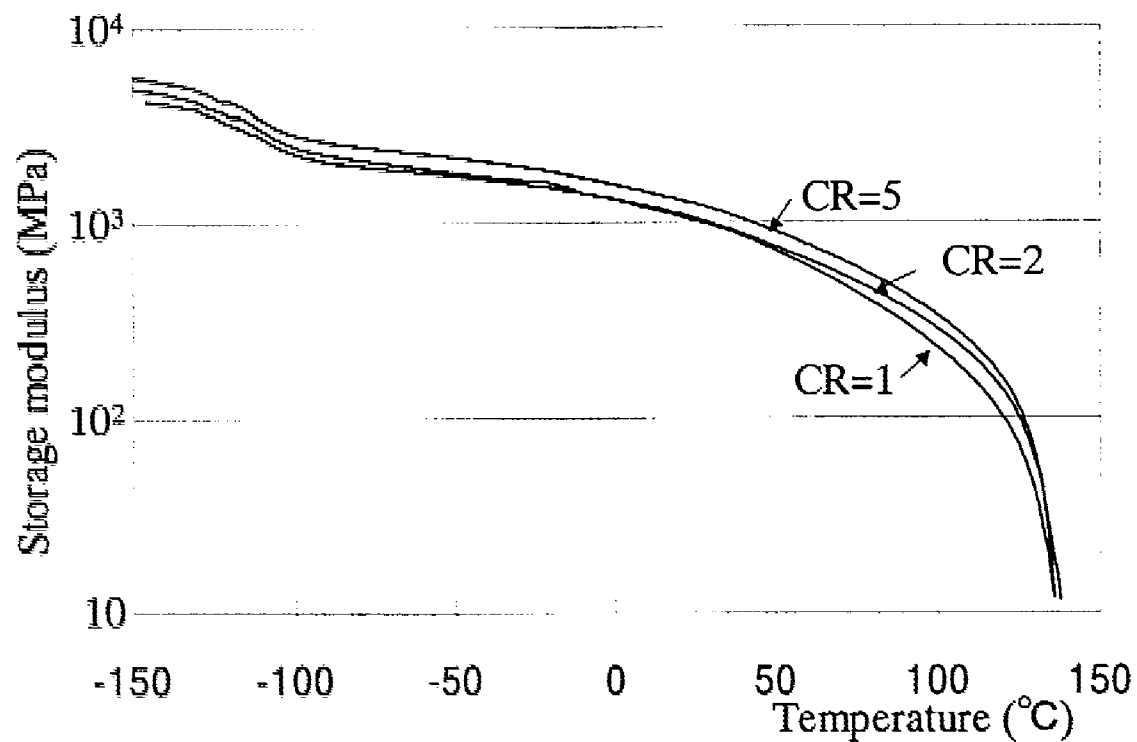


Figure 9: Storage modulus as a function of temperature

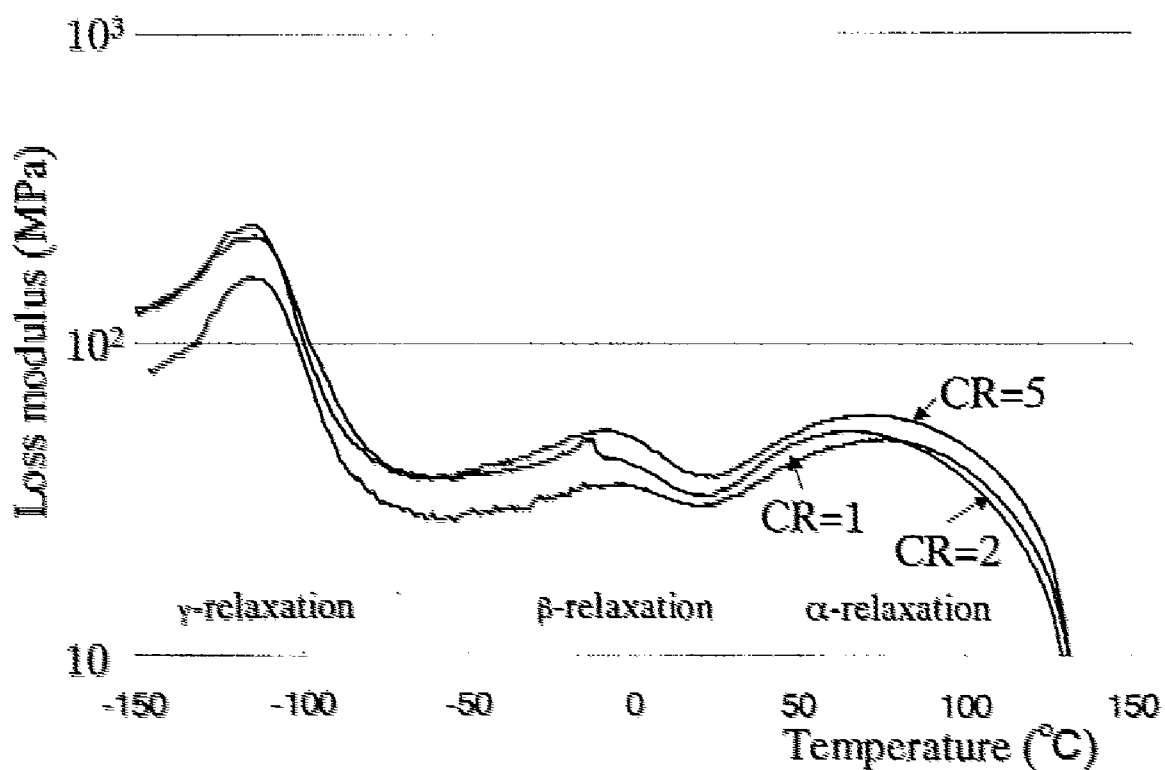


Figure 10: Loss modulus as a function of temperature

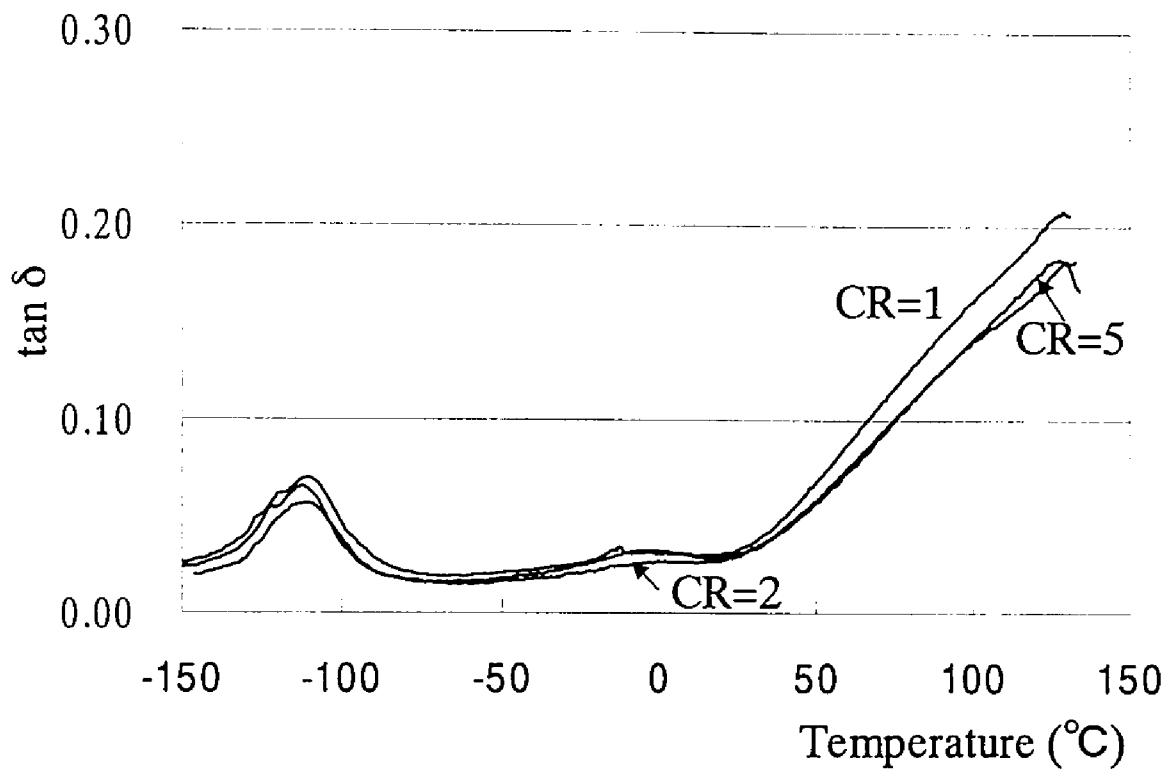
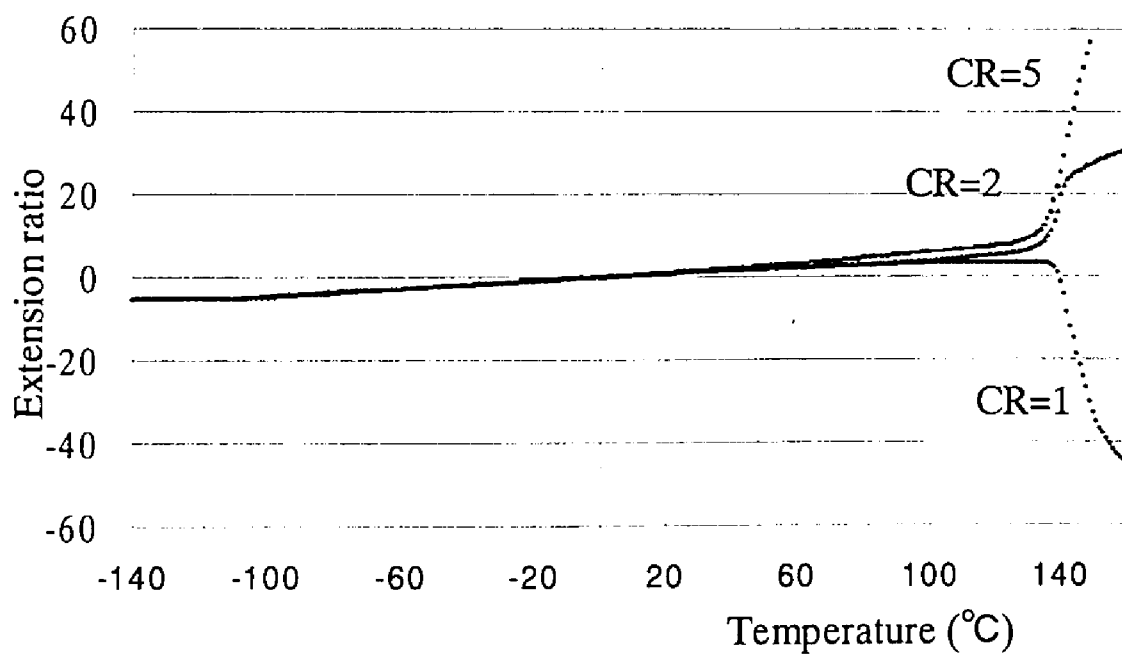
Figure 11: $\tan \delta$ as a function of temperature

Figure 12: Extension ratio as a function of temperature

Table 3: Comparison of wear factors and the compression ratios using the pin-on-disc and pin-on-flat wear test

	1	2	3	5
Pin-on-disc (g/N·m)	$(3.9 \pm 1.6) \times 10^{-10}$	$(5.2 \pm 0.93) \times 10^{-10}$	—	$(0.0 \pm 0.0) \times 10^{-12}$
Pin-on-flat (g/N·m)	$(2.8 \pm 2.1) \times 10^{-10}$	$(3.5 \pm 0.94) \times 10^{-10}$	$(1.8 \pm 1.6) \times 10^{-10}$	$(5.5 \pm 3.6) \times 10^{-12}$

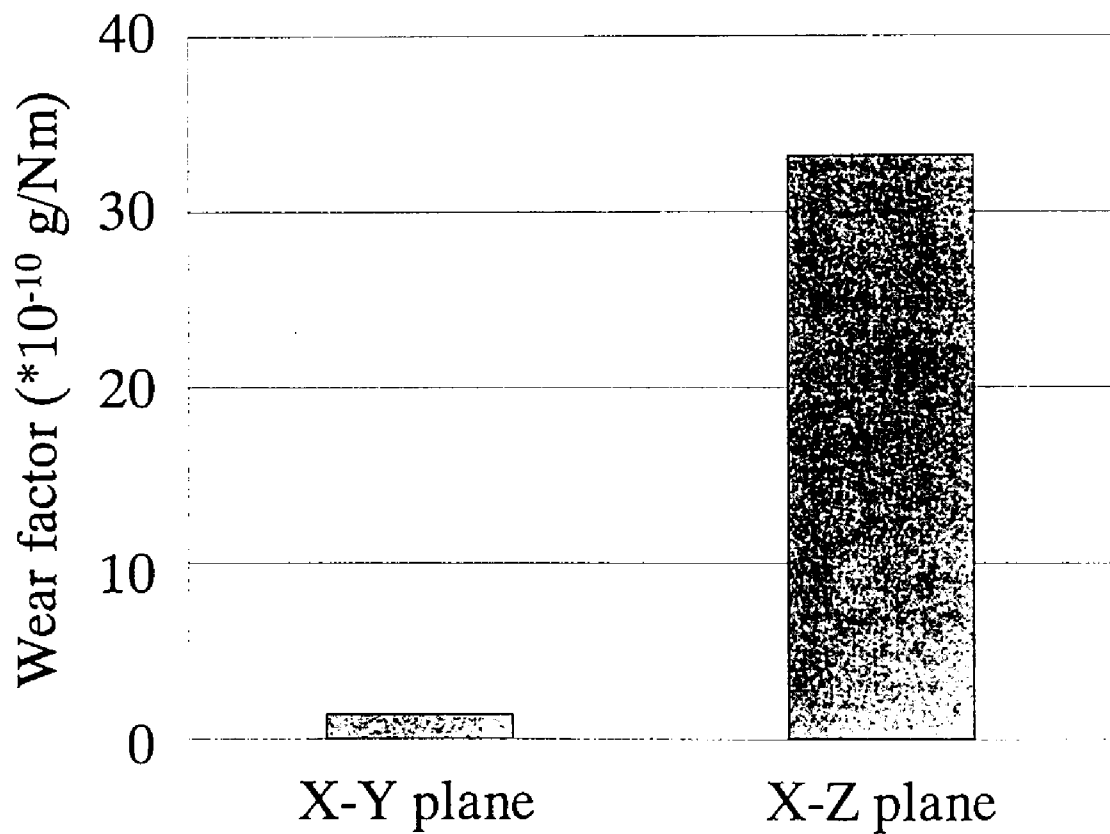


Figure 13: The relationship between the wear factor and the surface of the compressed UHMWPE

Wear Test

The results of the pin-on-disc and the pin-on-flat wear tests are shown in Table 3. For the pin-on-disc wear test, the wear factor of CR=1 was slightly lower than that of CR=2. However, the weight loss of the CR=5 sample was less than 0.1 mg, therefore, the wear factor was nearly 0.0. This suggested that the wear factor decreased with increasing compression ratio.

For the pin-on-flat wear test, the wear factor of the CR=5 sample decreased significantly compared with those of CR=1 and 2. The wear factor of CR=2 was slightly higher than that of CR=1, which were similar to findings the pin-on-disc test. Figure 14 shows the surface image of the counter face of CR=5 during the pin-on-flat test. The image was taken from the edge of the reciprocated position. It can be observed from the image at the upper part that there are many solidifications on the counter face, which was made of chromium. The UHMWPE debris remained on these solidifications. The counter face image of CR=1 is shown in Figure 15. It was confirmed that the distribution and the structure of solidification was similar to the counter face in CR=5. The wear debris image of CR=1 on the counter face was a glue-like material, while that of CR=5 was similar to powder.

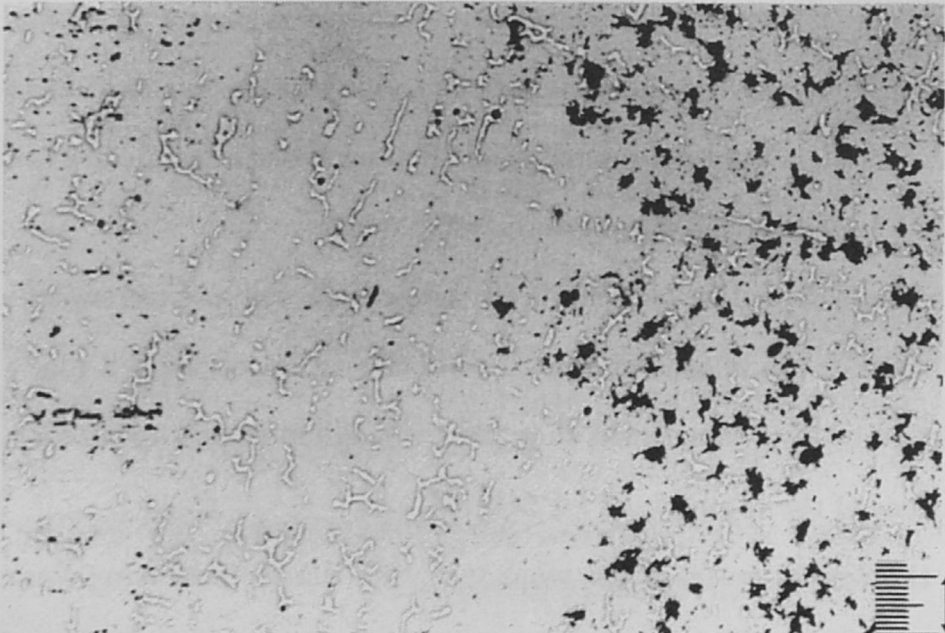
Figure 16 shows wear factors of two directions specimen of the compressed sample. The wear factor of the X-Y plane specimen was lower than that of the X-Z plane specimen. It was confirmed from this results that there was the relationship between wear factor and surface of the compressed UHMWPE.

Figure 17 shows the weight losses of the wear test with the reciprocating wear machine. The weight loss of the non-compressed sample was 0.1291 g while that of the compressed sample is 0.0037 g, which means that the wear factor of the non-



100 μm

Figure 15: Counterface surface of CR=1 by optical microscope



100 μm

Figure 14: Counter face surface of CR=5 by optical microscopy

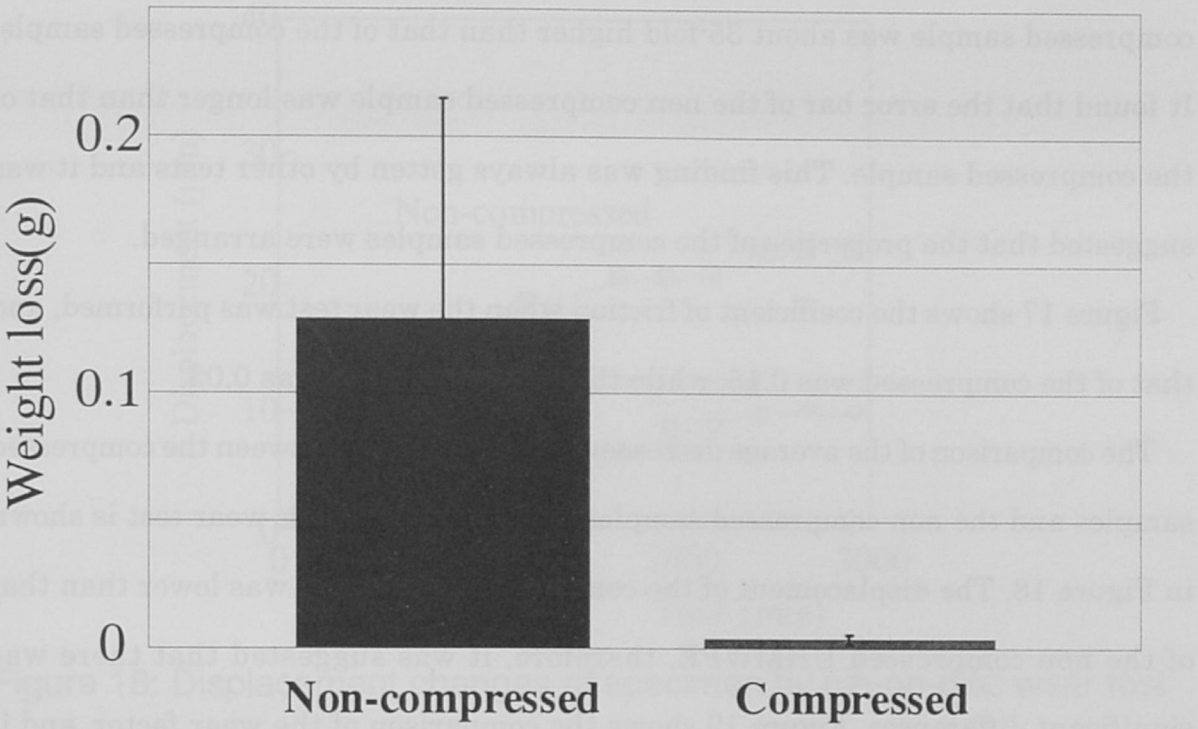


Figure 16: Weight loss of specimen by the reciprocating wear test

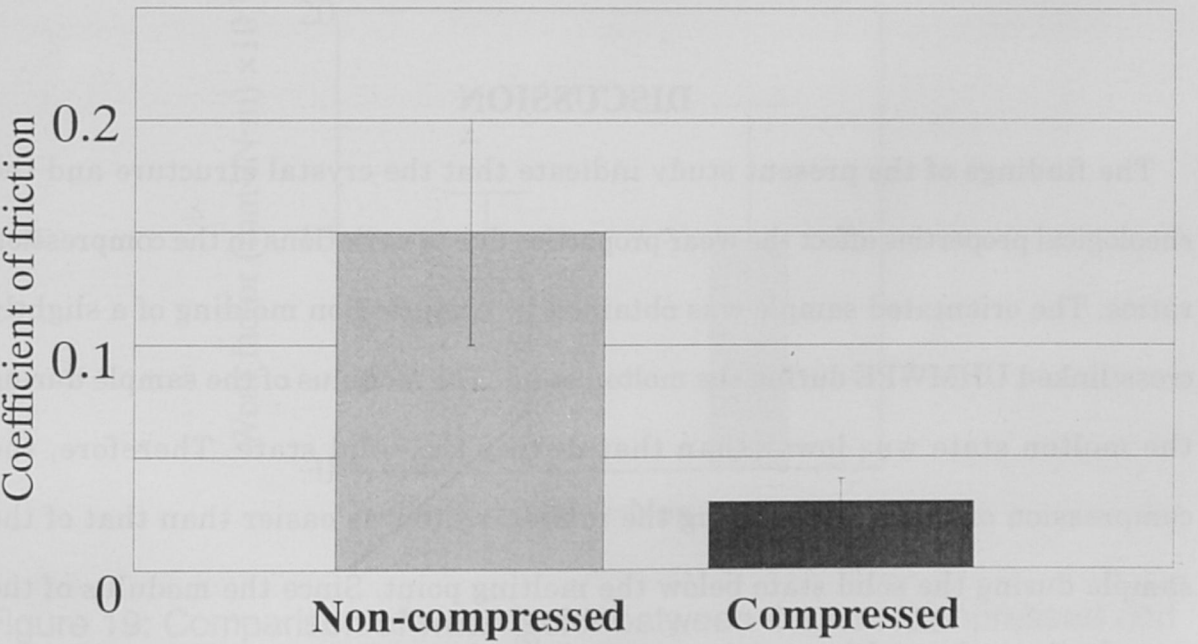


Figure 17: Coefficient of friction between the UHMWPE and the counterface by the reciprocating wear test

compressed sample was about 35-fold higher than that of the compressed sample. It found that the error bar of the non-compressed sample was longer than that of the compressed sample. This finding was always gotten by other tests and it was suggested that the properties of the compressed samples were arranged.

Figure 17 shows the coefficient of friction when the wear test was performed, and that of the compressed was 0.15, while the non-compressed was 0.03.

The comparison of the average decreased of the pin length between the compressed samples and the non-compressed samples with the pin-on-disc wear test is shown in Figure 18. The displacement of the compressed UHMWPE was lower than that of the non-compressed UHMWPE, therefore, it was suggested that there was significant differences. Figure 19 shows the comparison of the wear factor, and it was revealed that that of the compressed UHMWPE was statistically lower than the non-compressed UHMWPE.

DISCUSSION

The findings of the present study indicate that the crystal structure and the rheological properties affect the wear properties due to variations in the compression ratios. The orientated sample was obtained by compression molding of a slightly cross-linked UHMWPE during the molten state. The modulus of the sample during the molten state was lower than that during the solid state. Therefore, the compression of the sample during the molten state was easier than that of the sample during the solid state below the melting point. Since the modulus of the sample above the melting point was steady¹⁶⁾, the temperature effect on flowing molecular chains is minimal.

The X-ray diffraction image showed that the (200) crystalline plane was orientated

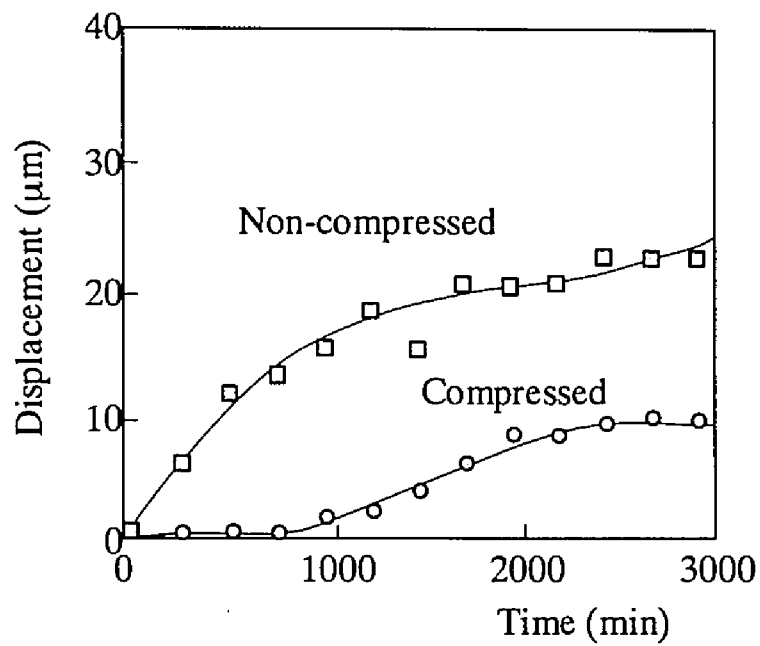


Figure 18: Displacement changes of specimen by pin-on-disc wear test

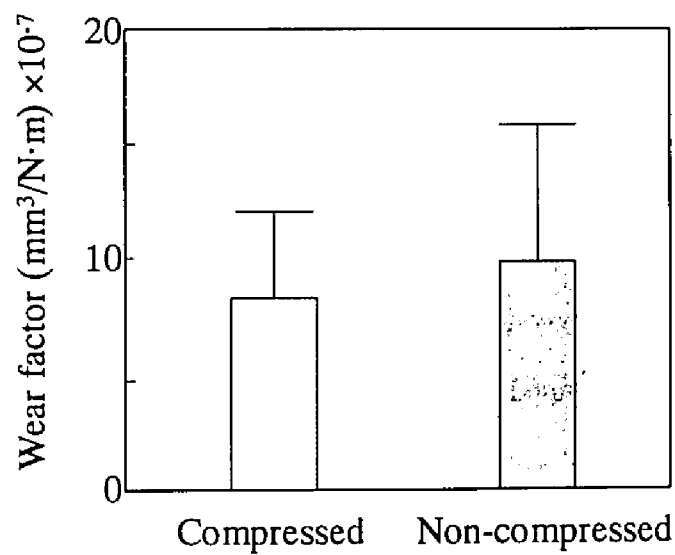


Figure 19: Comparison of wear factor between the non-compressed and the compressed UHMWPE

Chapter 3

parallel to the compression surface. This indicated that the *c*-axis of the orthorhombic crystal was orientated parallel to the deformed direction. In addition, it was revealed that the degree of the crystal planar orientation increased with increasing compression ratio. The (200) crystalline plane was only orientated parallel to the compression plane in the CR=2, however, in the case of the CR=5 sample, both the (200) and the (110) crystalline planes were orientated parallel to the compressed surface.

The thermodynamic properties and the density also increased. It was confirmed from these findings that the compression molecular chains to flow and the cooling caused crystallization. However, in the case of the CR=2 sample, the DSC, density, and dynamic mechanical measurements showed that an imperfect crystal form was generated. The broadening of the thermogram of the CR=2 peak indicated the variety of lamellae thickness or reorientation of the crystal phase. The experimental findings of the loss modulus measurements support these interpretations. The intensity of the α_c -peak of the CR=2 sample was lower, than that of CR=1, although the peak position was at a higher temperature. However, the intensity of the α_c -peak of CR=5 was higher, and the position was also at a higher temperature. It appears likely that the present findings correlate with those of DSC.

The extension with increased in temperature rapidly changed at approximately 130°C in all samples. If the compressed deformation of a sample was below the melting point and the sample was correctly orientated, the extension of the sample occurred at about 80°C²¹⁾. This suggested that the amorphous phase in the sample had tensile residual stresses. However, the amorphous phases in the CR=2 and CR=5 samples were relaxed like the original UHMWPE (CR=1), based on the findings of the extension measurements.

E' of CR=1 was similar to that of CR=2 at about room temperature, based on the findings of the storage modulus as a mechanical property.

Wear factors of CR=1 and CR=2 were not significantly different, while those of CR=3 and CR=5 were reduced. It was confirmed that wear factors depended on the compression ratio, and the present findings appeared to show that wear factor decreased in accordance with increases on the degree of orientation.

It was found that the findings from the pin-on-disc experiment were similar to these from the pin-on-flat wear test. These findings showed that there was the correlation between the wear tests.

CONCLUSION

1. Slightly cross-linked UHMWPE was compressed during the molten state and crystallized while maintaining the deformation.
2. Two different pin-on-flat uni-axial wear tests were performed. And it was revealed that the wear factor of the compressed sample was enhanced.
3. The pin-on-flat reciprocating wear test was also carried out up to 50 km of the sliding distance. The findings were that the weight loss of the compressed sample was 35-fold lower than that of the non-compressed. And the coefficient of friction with the compressed sample was also lower than that of the non-compressed.
4. The (200) and (110) crystalline plane of the compressed sample were orientated parallel to the compressed surface.
5. The wear factor depended on the surface of the compressed UHMWPE.

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Chapter 4

Residual Stress Measurements of Slightly Cross-linked UHMWPE Crystallized under Uniaxial Compression for Artificial Joints

INTRODUCTION

Wear particles generated during functioning of joint replacements have been associate with metallosis, osteolysis and prosthetic loosening, the factors which often necessitate revision surgery¹⁻⁸⁾. Many attempts to improve the wear performance have been reported concerning the raw material and the component designs⁹⁻¹⁶⁾.

The previous chapters¹⁷⁻²¹⁾ reported that the wear resistance of a slightly cross-linked ultra-high molecular weight polyethylene (UHMWPE) was compressed uniaxially during the molten state and then crystallization. It was found that the wear resistance of the compressed sample was enhanced from the results of reciprocating wear tests. Wide angle X-ray studies revealed that the compressed samples had a very special spatial orientation in the crystalline phase. The crystalline plane (200) was preferentially orientated parallel to the compressed surface, which means that the c-axis of the orthorhombic crystal form was located almost perfectly parallel to that surface.

When a crystalline piece of sample is deformed elastically in such a manner that the strain is uniform over relatively large distances, the lattice plane spacing in the

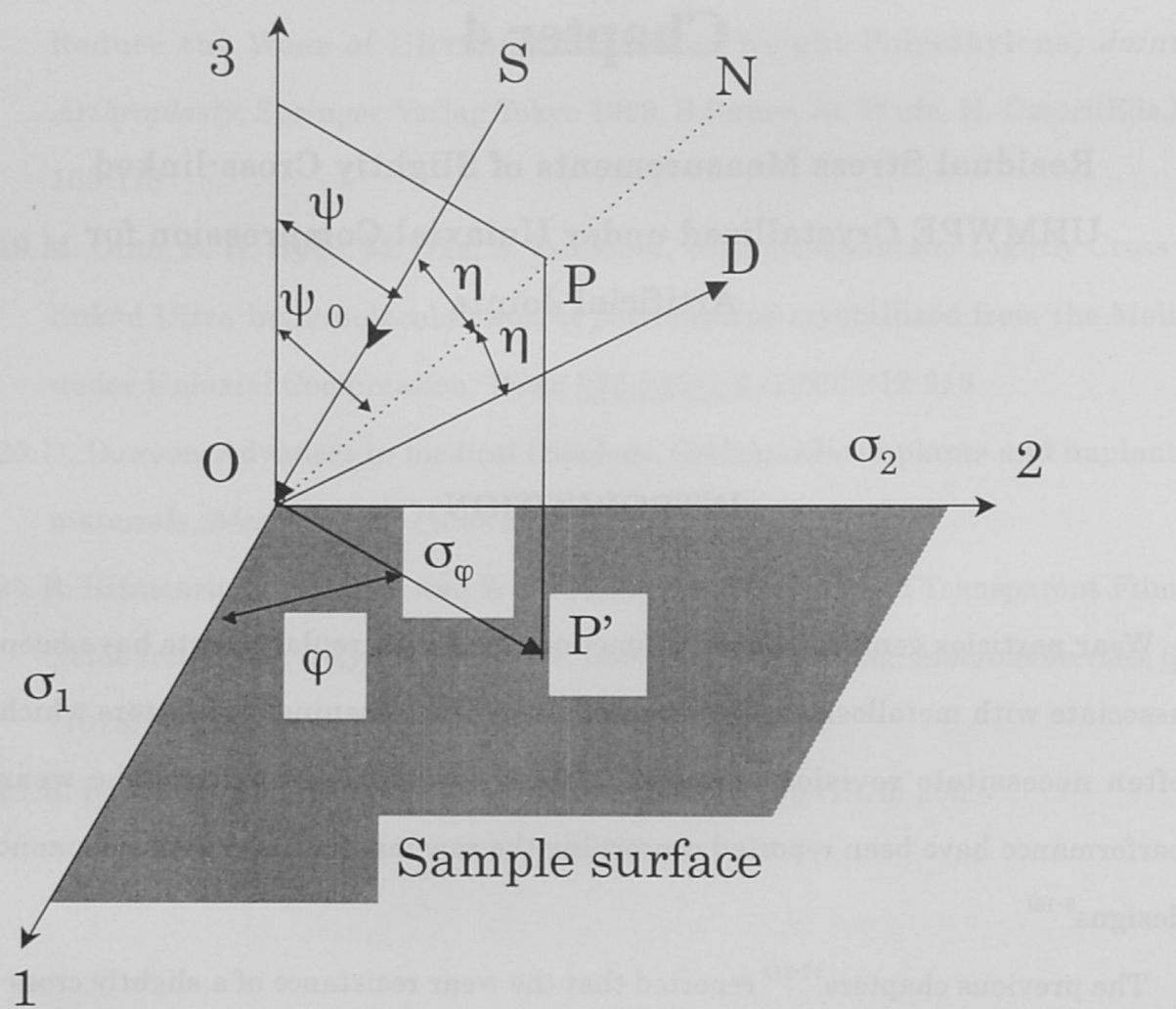


Figure 1 : Stresses at the surface of a stressed body.

crystal form change from their stress-free value to some new value corresponding to the magnitude of the applied stress²²⁾. The uniform macrostrain causes a shift of the diffraction lines to new 2θ positions. From this shift the strain may be calculated and, knowing the strain, the stress present can be determined. Generally speaking, the effect of residual stresses is the same as the effect of stress with a mechanical load, therefore a compressed residual stress causes increasing fatigue, while a tensile one causes decreasing fatigue.

The purpose of this chapter is measurements of residual stress with UHMWPE.

EXPERIMENTAL

Preparation of Samples

Two different molding methods were prepared. The starting materials for these methods were a commercial UHMWPE (Sample C) from Mitsui Chemical Co. Japan, with a viscosity average molecular weight of 5.5×10^6 .

First, the compression method of a slightly cross-linked UHMWPE during the molten state was performed. Blocks of original UHMWPE were irradiated by ^{60}Co γ -rays under reduced pressure at room temperature. Sample C_0.8 means the sample, which was irradiated dose of Sample C was 0.8 Mrad and this sample was prepared that compressed sample without γ -rays irradiation at 200°C, to investigate the affect of γ -rays (named as Sample D). The block was a column that was 80 mm in diameter and 70 mm in length. Sample C_0.5 was compressed at 200°C, which was higher than the melting point (about 140°C). The compression speed was about 1cm/min, and the total compression load was about 4200 kgf. Then, the samples were cooled to room temperature over a period of 2 hours. The cooling speed from 140°C to 80°C demanded by the Japanese Industrial Standard (JIS), was about 1 hour. In this procedure, the sample thickness was reduced in accordance with increases in the compression. The compression ratio (CR) was defined by the ratio of the final thickness to the original thickness of the sample.

The following process relates to Sample B. Blocks of original UHMWPE were heated at 120°C, which was below the melting point, for more than 3 hours. After the heating, the UHMWPE was compressed at the same speed as Sample A. The load was more than 10000 kgf.

To make clear the affect of annealing on Sample C was put at 110°C for 22 hours

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and the sample was named as Sample_Ca.

Principles of $\sin^2\psi$ Method

Figure 1 shows the schematic diagram of $\sin^2\psi$ method. When X-rays are introduced along SO line at an angle of ψ_0 to the sample surface, the diffraction is occurred at the lattice plane that is perpendicular NO line. SO line crosses NO line at an angle of η and X-ray was reflected along to OD line. The strain, $\varepsilon_{\varphi\psi}$, perpendicular to the lattice plane is expressed the following formula using principal stresses σ_1 and σ_2 that are parallel to the surface:-

$$\varepsilon_{\varphi\psi} = (1+\nu) \times \frac{(\sigma_1 \cos^2 \varphi + \sigma_2 \sin^2 \varphi)}{E} \times \sin^2 \psi - \nu \times \frac{(\sigma_1 + \sigma_2)}{E} \dots\dots(1)$$

Where $\varphi = \varphi_0 + \eta$ and ν is Poisson's ratio of the sample. σ_φ is defined as the stress located on OP' line and has a relationship to :-

$$\sigma_\varphi = \sigma_1 \cos^2 \varphi + \sigma_2 \sin^2 \varphi$$

Therefore, the equation (1) is rewritten the following equation:-

$$\varepsilon_{\varphi\psi} = (1+\nu) \times \frac{\sigma_\varphi}{E} \times \sin^2 \psi - \nu \times \frac{(\sigma_1 + \sigma_2)}{E}$$

When the distance of the lattice plane is defined as δ_0 , stresses leave the space to $\Delta\delta$, and using diffraction angle, θ ,:-

$$\varepsilon_{\varphi\psi} = \frac{\Delta\delta}{\delta_0} = -\frac{\Delta\theta}{\tan \theta}$$

$$\sigma_\varphi = -\left\{ \frac{E}{2(1+\nu) \times \tan \theta} \right\} \times \left\{ \frac{\partial 2\theta}{\partial \sin^2 \psi} \right\}$$

Put

Table 1: Stress constant of various samples

Sample	Stress constant(MPa)
Sample A	-3.02
Sample B	-2.87
Sample B'	-2.14
Sample C	-2.47
Sample Ca	-2.64
Sample C_0.8	-2.47

$$K = -\left\{ \frac{E}{2(1+\nu) \times \tan \theta} \right\}$$

$$M = \left\{ \frac{\partial 2\theta}{\partial \sin^2 \psi} \right\}$$

Then

$$\sigma_{\varphi} = K \times M \dots\dots(2)$$

Where K is called as stress constant. If a 2θ and $\sin^2\psi$ line is fallen, the σ_{φ} has a positive value and there is compressed stress in the sample. However, when the line is increased, the σ_{φ} has a negative value and the sample has tensile stress.

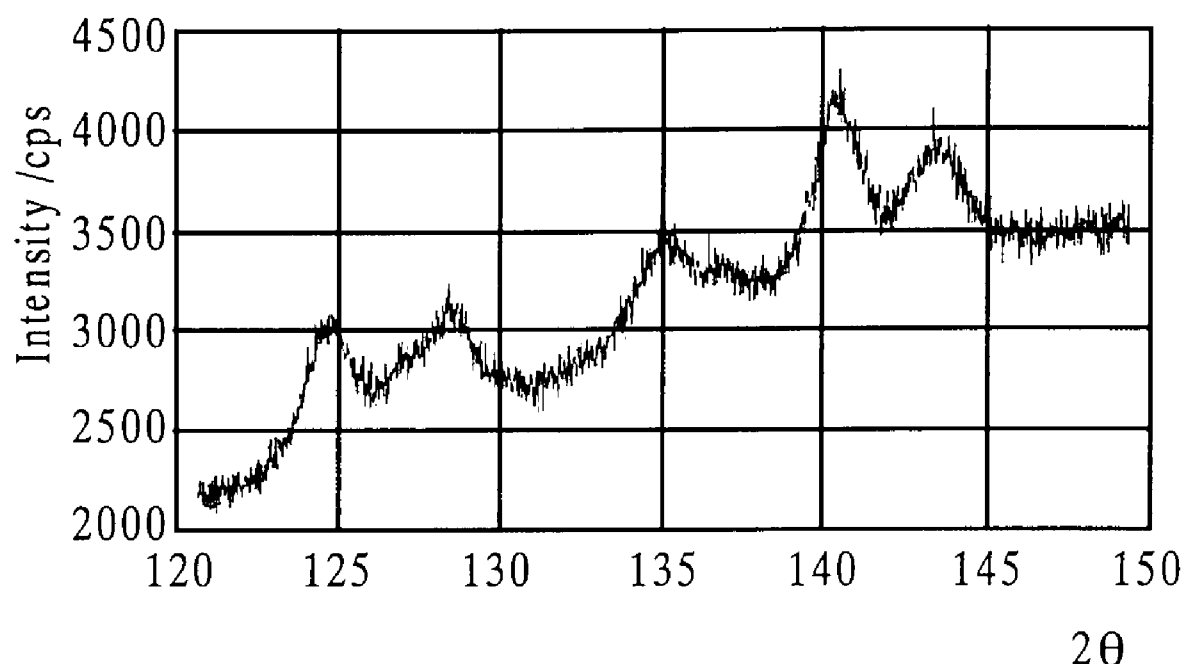


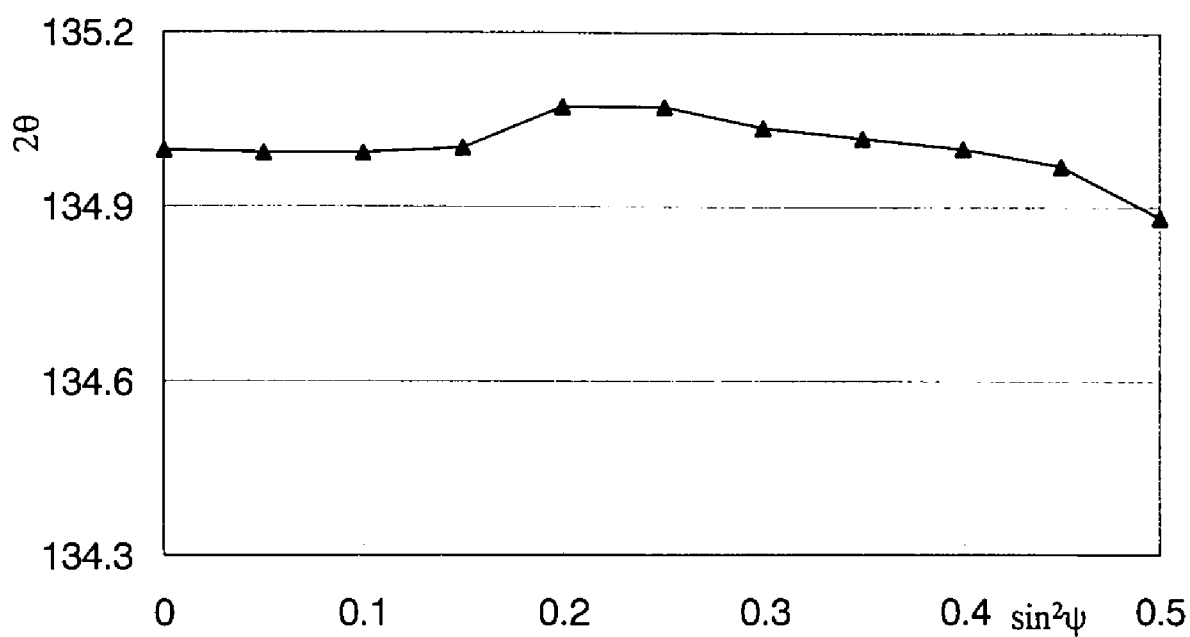
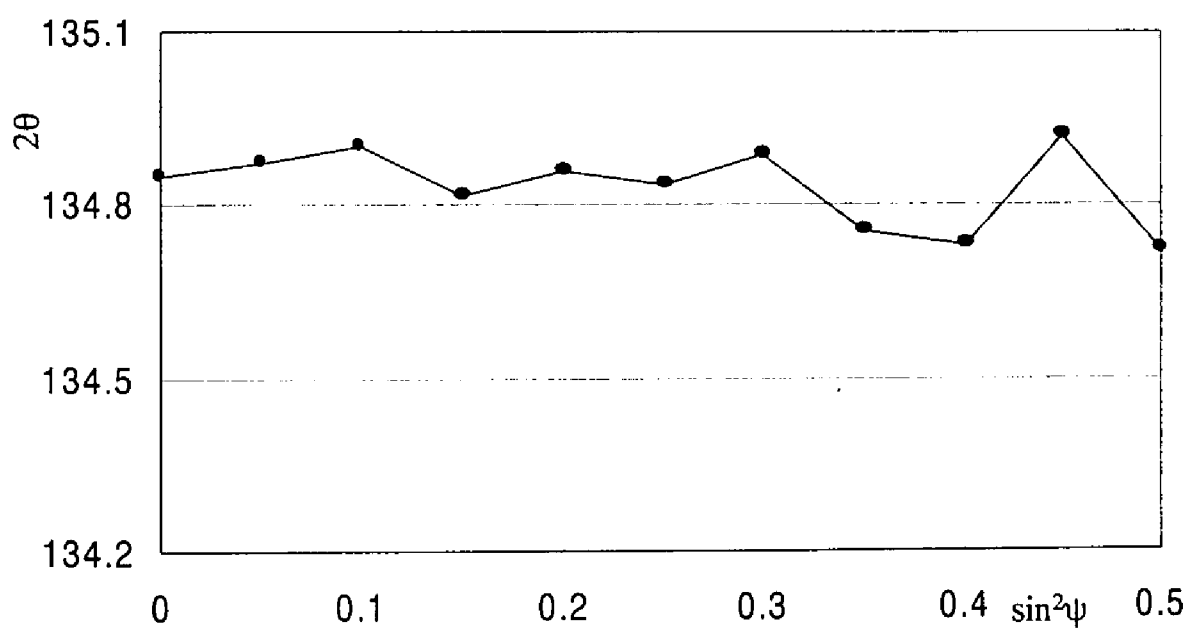
Figure 2: Intensity of X-ray diffraction as a function of 2θ from 120° to 150°

Measurement of X-ray Diffraction

The measurements of residual stresses in the crystalline phase were performed by a Residual Stress Analysis (V1.1.5, Rigaku Co., Japan) with Cr-K_α radiation (2.28970 angstrom) generated at 40 kV and 40 mA. The scan step was 0.1000 degree and the step time was 1.00 second. 10 points from 0.00 to 0.50 every 0.05 was selected as values of $\sin^2\psi$.

Measurement of Shrinkage

The shrinkage was carried out with increasing temperature from -150°C to 130°C at $2^\circ\text{C}/\text{min}$ to investigate the existence of residual stresses in the amorphous phase.

Figure 3: 2θ and $\sin^2\psi$ line of Sample CFigure 4: 2θ and $\sin^2\psi$ line of Sample A

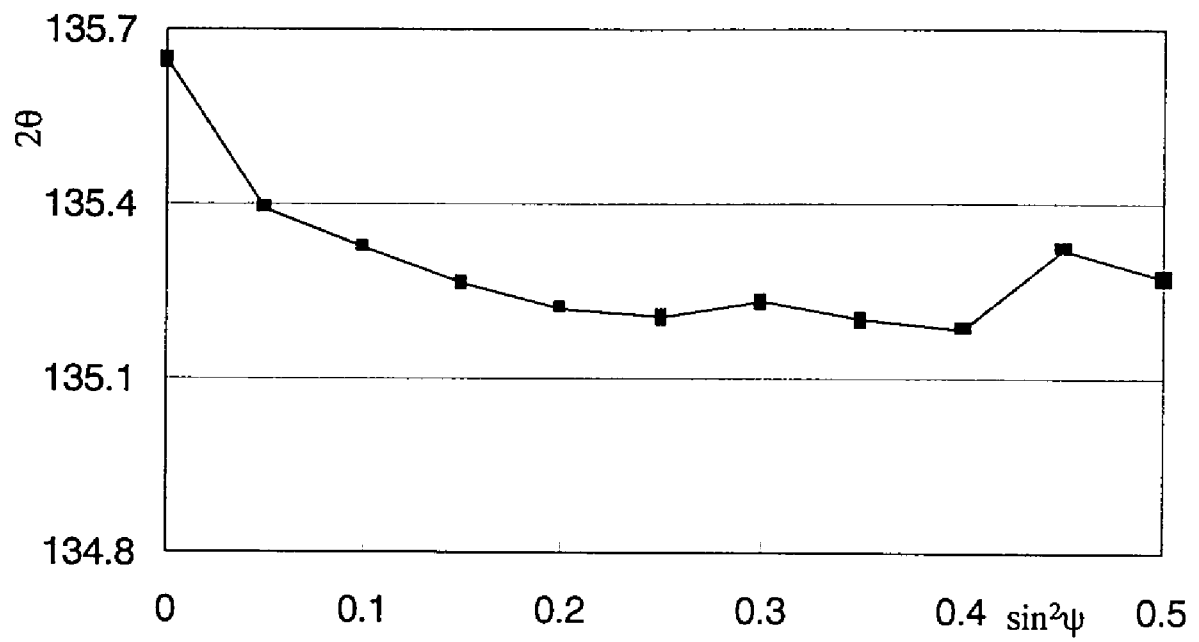


Figure 5: 2θ and $\sin^2\psi$ line of Sample B

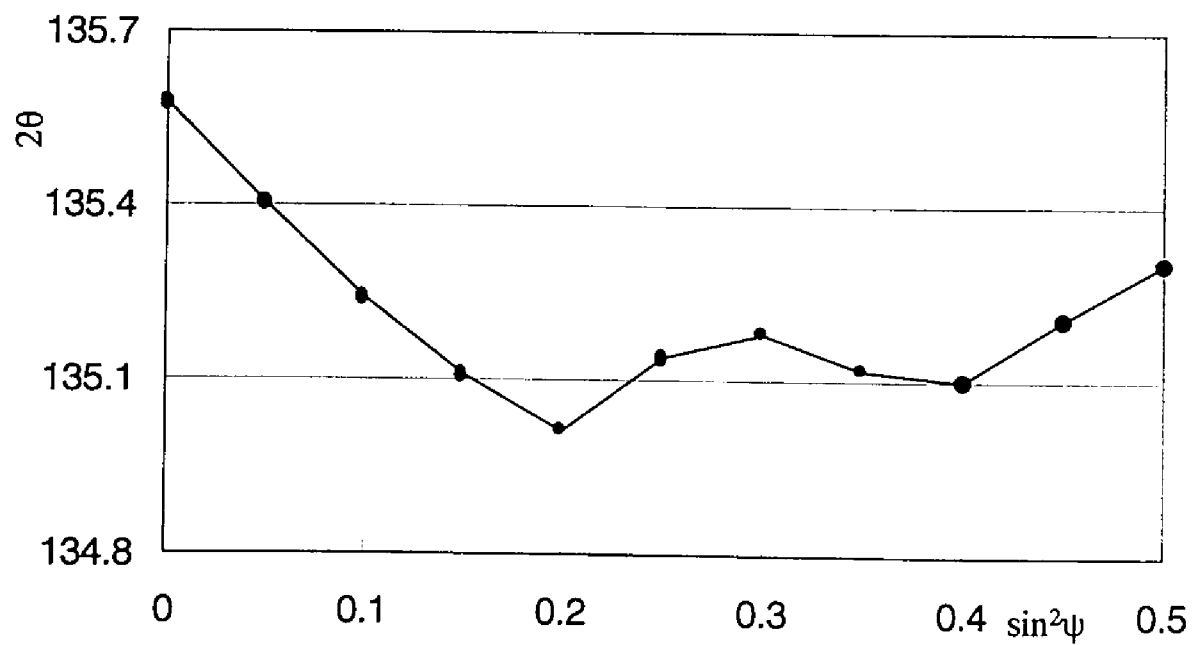


Figure 6: 2θ and $\sin^2\psi$ line of Sample B'

The surface perpendicular to the compressed axis was cut to a rectangular parallelepiped and measured the length. Shrinkage was calculated using the following formula:-

$$\text{Shrinkage} = \frac{\text{Sample length} - \text{The original length}}{\text{The original length}} \dots\dots (3)$$

Where the original length was defined as the length at 0°C.

Decision of Stress Constant

The stress constant of each sample was decided using the findings of dynamic modulus²²⁾. The storage moduli of Sample A, B, B', C, Ca, and C_0.8 at room temperature 27°C were 1.21 GPa, 1.15 GPa, 0.86 GPa, 0.99 GPa, 1.06 GPa, 0.99 GPa, respectively. The Poisson's ratio of 0.45 was applied to all samples. From these decisions, stress constants of various samples were calculated, shown in table 1.

RESULTS AND DISCUSSION

Figure 2 shows that the intensity of X-ray diffraction as a function of 2θ . It was observed that there were several peaks from 120° to 150° and the 135° peak and the 140° peak were selected as a single measurable peak, respectively.

Figure 3 shows 2θ and $\sin^2\psi$ line of Sample C. The inclination of the line was -0.118 ± 0.103 and also the stress was 0.291 ± 0.254 MPa, where the confidence limit 68.3% was used as the error.

The inclination of the line of Sample A was -0.195 ± 0.129 calculated by Figure 4. The stress was 0.588 ± 0.389 .

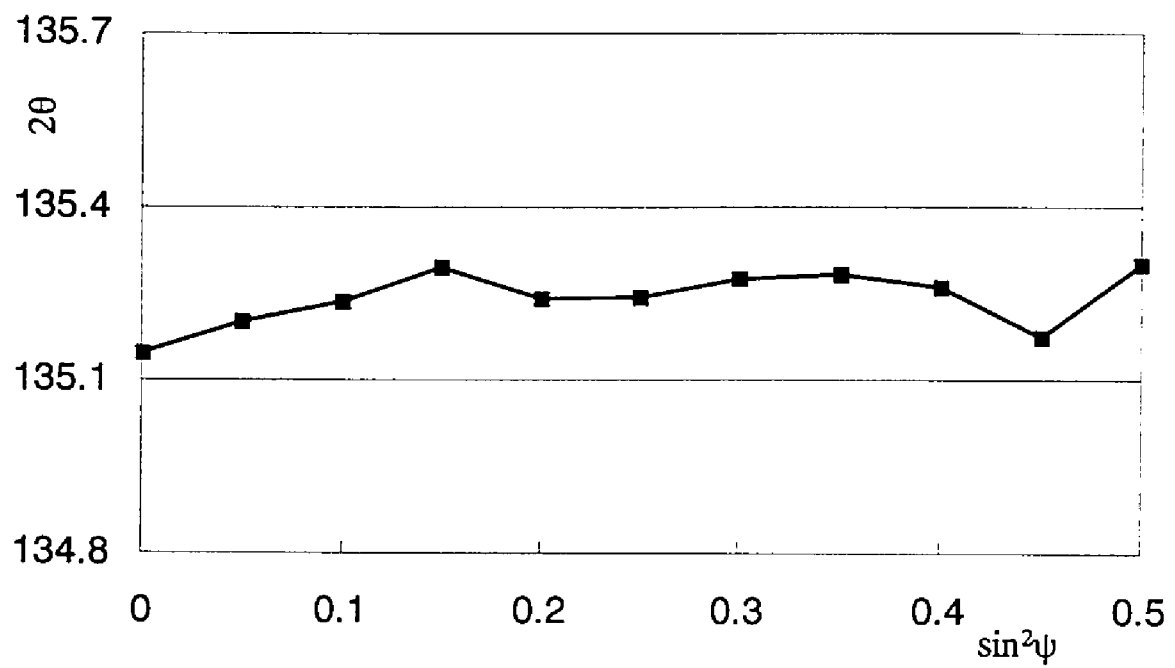


Figure 7: 2θ and $\sin^2\psi$ line of Sample_0.8

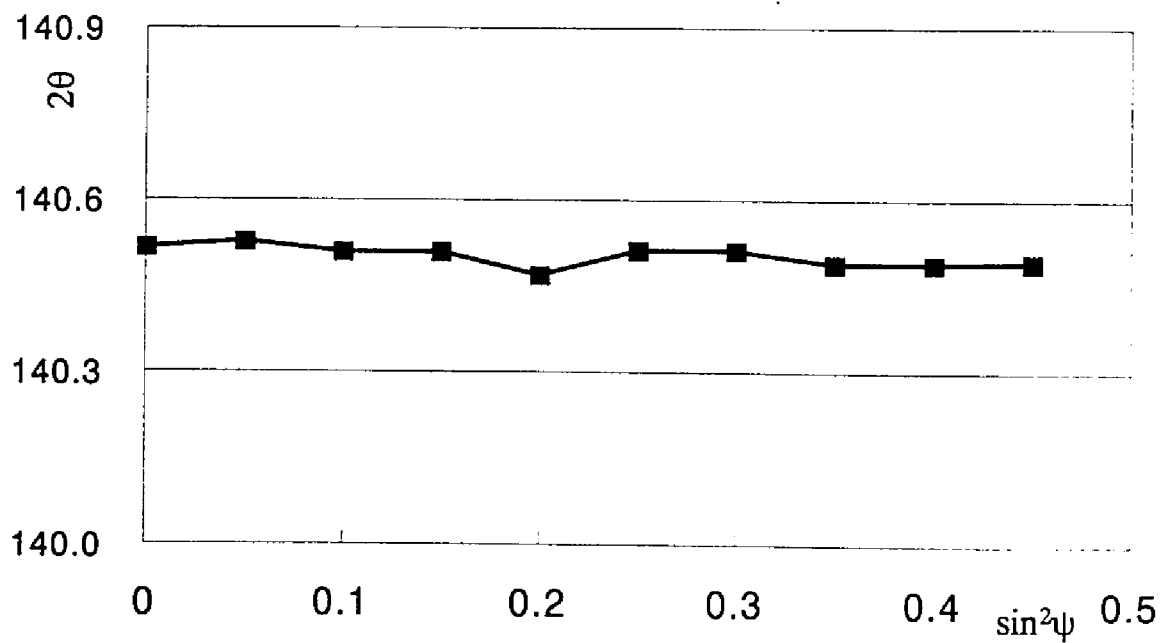


Figure 8: 2θ and $\sin^2\psi$ line of Sample D

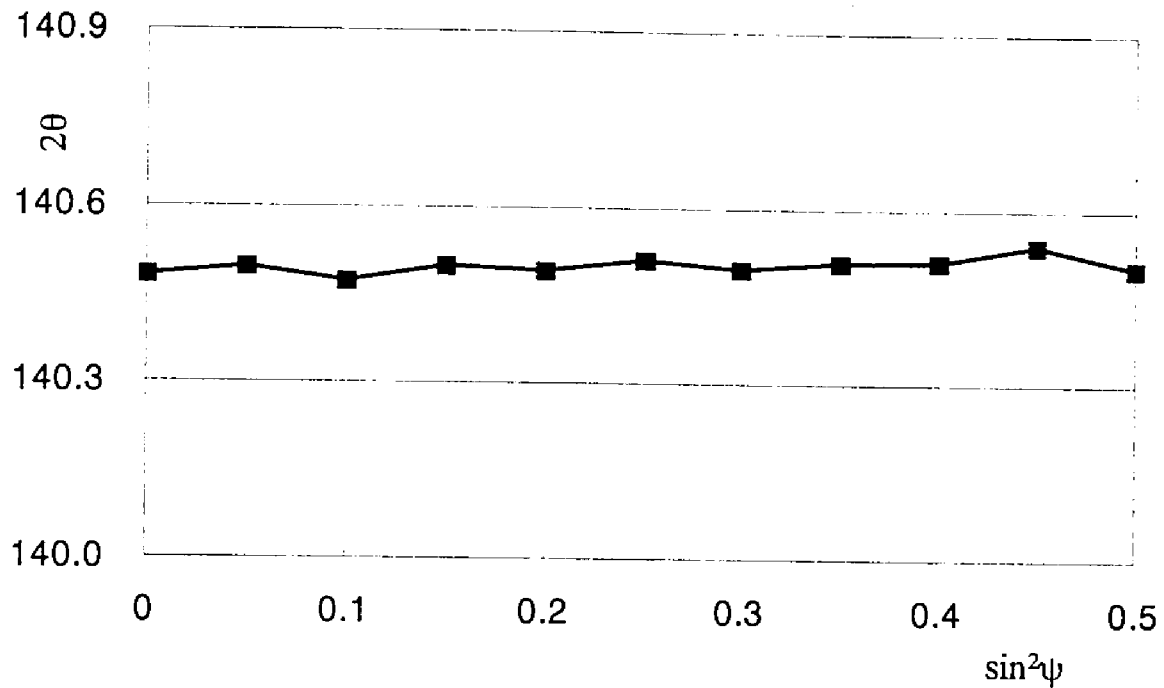
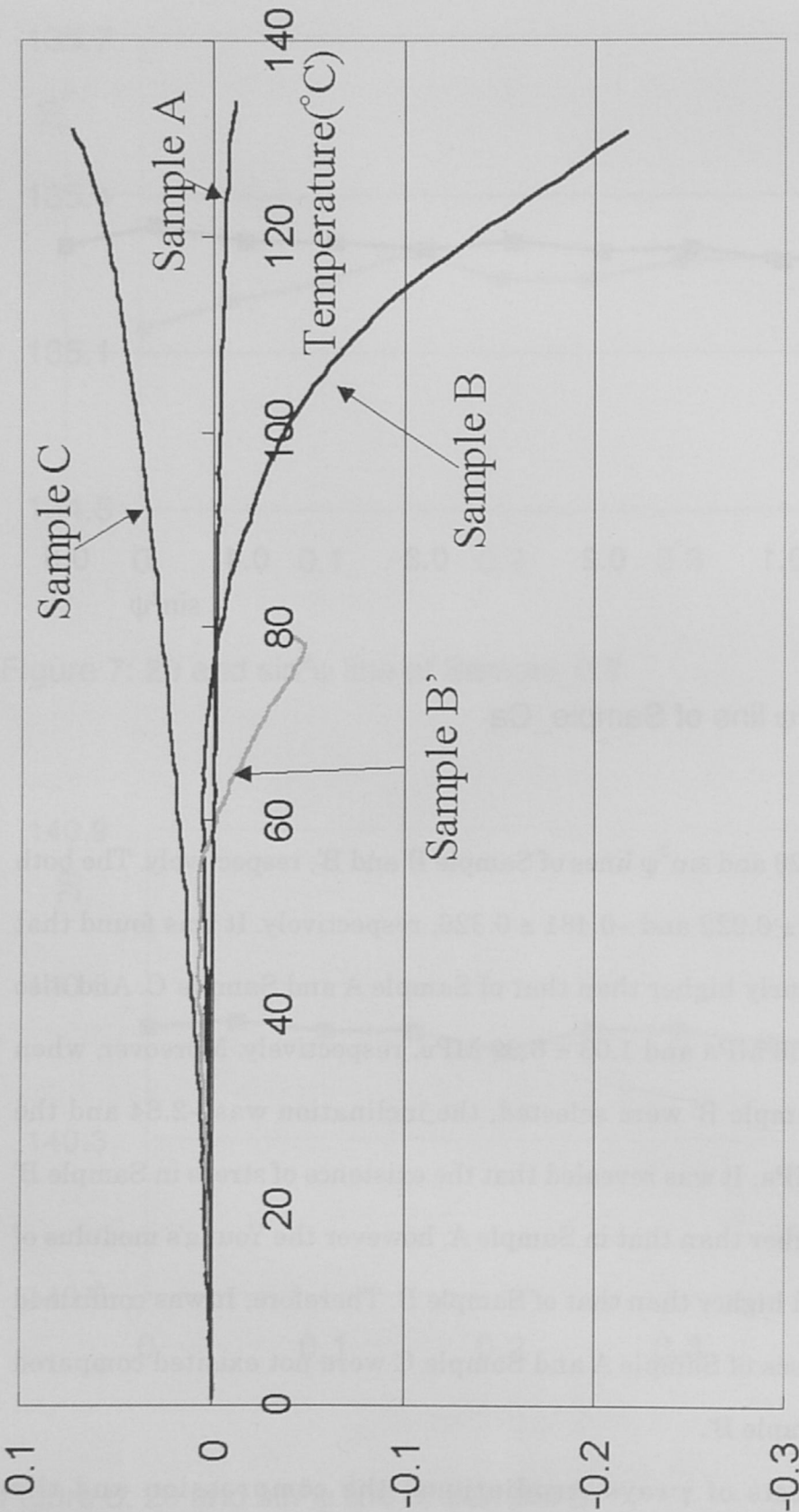


Figure 9: 2θ and $\sin^2\psi$ line of Sample_Ca

Figure 5 and 6 show 2θ and $\sin^2\psi$ lines of Sample B and B', respectively. The both inclination was -0.485 ± 0.222 and -0.481 ± 0.326 , respectively. It was found that these volumes were clearly higher than that of Sample A and Sample C. And also stresses were 1.39 ± 6.36 MPa and 1.03 ± 6.99 MPa, respectively. Moreover, when the first 5 points of Sample B' were selected, the inclination was -2.84 and the stress value was 6.08 MPa. It was revealed that the existence of stress in Sample B' was about 10.3-fold higher than that in Sample A, however the Young's modulus of Sample A was 1.40-fold higher than that of Sample B. Therefore, It was confirmed that the residual stresses of Sample A and Sample C were not existed compared with Sample B and Sample B'.

To investigate affects of γ -rays irradiations, the compression and the



The length at 0°C was defined as the original length.
Shrinkage = (length – original length) / original length

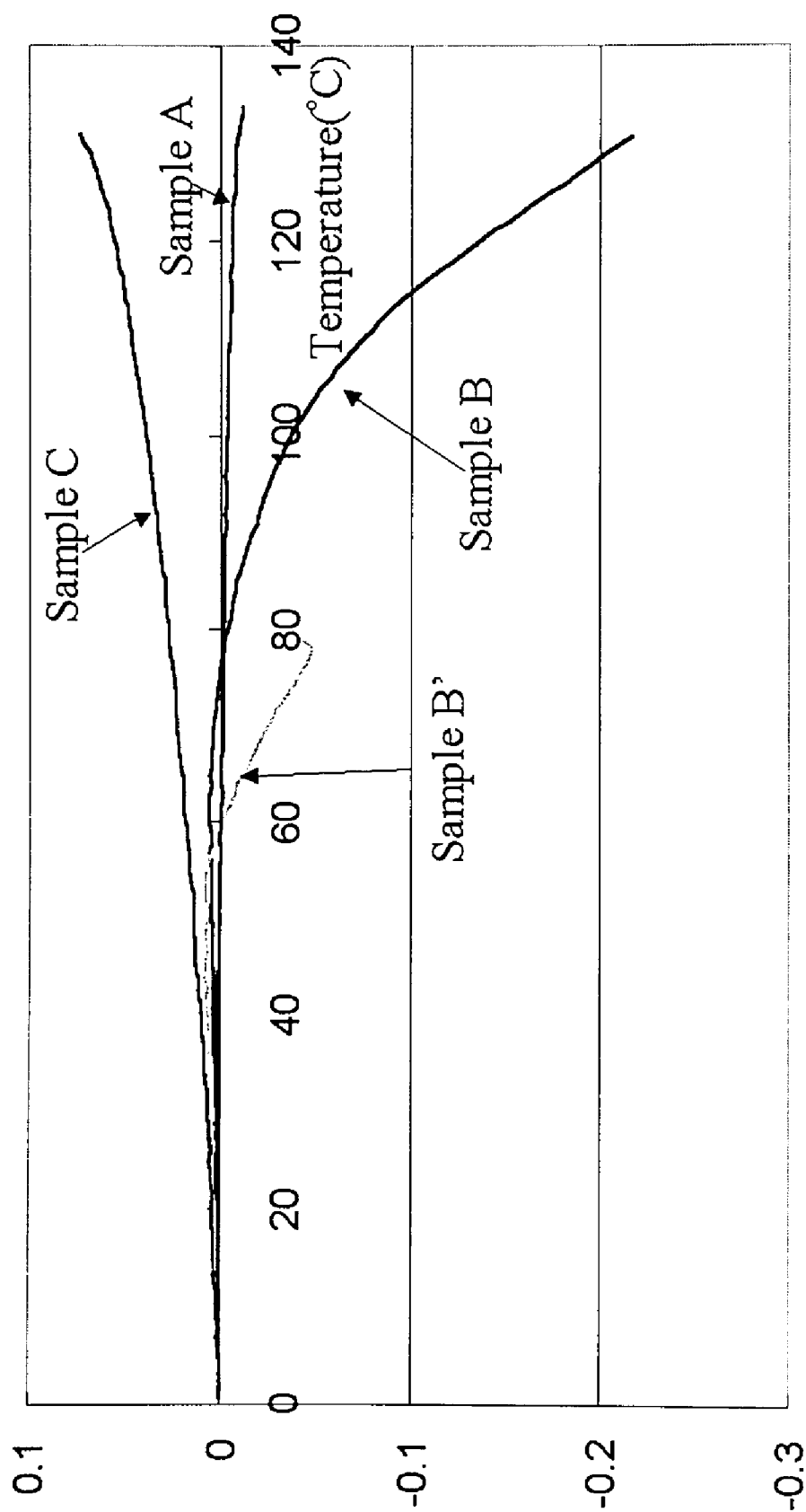
Figure 10: Shrinkage as a function of temperature

crystallization, the residual stresses of Sample C_0.8, Sample D, and Sample Ca. Figure 7 shows 2θ and $\sin^2\psi$ lines of Sample_0.8 and the inclination was 0.135 ± 0.094 . The stress value was -0.76 ± 0.0627 MPa. Figure 8 shows that of Sample D, and Figure 9 shows that of Sample Ca. The inclinations were -0.061 ± 0.035 and 0.076 ± 0.027 , respectively. It was found that the residual stresses of these samples were similar and nearly zero, which means that the both methods of the γ -rays irradiations and the compression without γ -rays irradiations had not influence to residual stresses. And also the crystallization had not affects. Needless to say, the more detail investigation may lead to the affects, but it was thought that the stress was too low to lead the affects of macroscopic material properties.

Figure 10 shows measurements of shrinkage as a function of temperature. Sample B was shrunk at 80°C and moreover, Sample B' was shrunk below 60°C , while Sample C and Sample A was not shrunk over 130°C . These findings show that all these orientated samples including Sample A have a property of shrinkage with a function of temperature, because of the existence of the orientation in the crystalline phase. It was confirmed that the differences of shrinkage between Sample B and Sample A depended on the differences of circumstance in the amorphous phase. The amorphous phases in Sample B and Sample B' were strained, while the phase in Sample A was relaxed.

CONCLUSION

From the above indication and findings of the experiments, the following conclusions could be drawn:



The length at 0°C was defined as the original length.
 $\text{Shrinkage} = (\text{length} - \text{original length}) / \text{original length}$

Figure 10: Shrinkage as a function of temperature

crystallization, the residual stresses of Sample C_0.8, Sample D, and Sample Ca. Figure 7 shows 2θ and $\sin^2\psi$ lines of Sample_0.8 and the inclination was 0.135 ± 0.094 . The stress value was -0.76 ± 0.0627 MPa. Figure 8 shows that of Sample D, and Figure 9 shows that of Sample Ca. The inclinations were -0.061 ± 0.035 and 0.076 ± 0.027 , respectively. It was found that the residual stresses of these samples were similar and nearly zero, which means that the both methods of the γ -rays irradiations and the compression without γ -rays irradiations had not influence to residual stresses. And also the crystallization had not affects. Needless to say, the more detail investigation may lead to the affects, but it was thoght that the stress was too low to lead the affects of macroscopic material properties.

Figure 10 shows measurements of shrinkage as a function of temperature. Sample B was shrunk at 80°C and moreover, Sample B' was shrunk below 60°C , while Sample C and Sample A was not shrunk over 130°C . These findings show that all these orientated samples including Sample A have a property of shrinkage with a function of temperature, because of the existence of the orientation in the crystalline phase. It was confirmed that the differences of shrinkage between Sample B and Sample A depended on the differences of circumstance in the amorphous phase. The amorphous phases in Sample B and Sample B' were strained, while the phase in Sample A was relaxed.

CONCLUSION

From the above indication and findings of the experiments, the following conclusions could be drawn:

Chapter 4

1. Residual stresses were measured by shrinkage and $\sin^2\psi$ methods. The $\sin^2\psi$ method was performed at 2θ of 135° .
2. Several samples were prepared. The one was a compression of a slightly cross-linked UHMWPE at the molten state (Sample A), and the others (Sample B, Sample B') were a compression of an original UHMWPE (Sample C) below the melting point.
3. The residual stresses of Sample A and Sample C were not observed.
4. There were residual stresses in Sample B and Sample B' that were tensile state.
5. The shrinkages of Sample B and B' were started at 80°C and 60°C , respectively, while Sample A was not shrunk over 130°C . Therefore, the amorphous phases in Sample B and B' had tensile residual stresses.
6. It was confirmed that the differences of residual stresses depended on their temperatures when the samples were compressed.

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Chapter 5

Comparison of Wear Properties of UHMWPE Orientated under Uniaxial Compression during the Melted State and at Lower Temperatures than the Melting Point

INTRODUCTION

Wear and generation of wear particles has been recognized as one of the major reasons for long term failure in total joint replacements¹⁻⁶⁾. Many attempts to improve the wear performance have been reported concerning the raw material and the component designs⁷⁻¹⁴⁾.

There are several methods of orientation, including the present method and the compression below the melting point. It is important to clarify the relationship between the orientation method and wear resistance.

The purpose of the present chapter was to compare the wear properties, mechanical properties and orientation using two methods of orientation. One sample (Sample A) was a slightly cross-linked UHMWPE orientated under compression during the molten state, and the other (Sample B) was UHMWPE orientated under compression at a lower temperature than the melting point.

EXPERIMENTAL

Preparation of Samples

Two different molding methods were prepared. The starting materials of both methods were a commercial UHMWPE (Sample C) from Mitsui Chemical Co. Japan, with a viscosity average molecular weight of 5.5×10^6 . Figure 1 shows the schemes of the compressions.

First, the compression method of a slightly cross-linked UHMWPE during the molten state was performed. Blocks of original UHMWPE a column of 60 mm diameter and 50 mm length were irradiated by ^{60}Co γ -rays under reduced pressure at room temperature. The irradiated UHMWPE was compressed at 200°C, which was higher than the melting point (about 140°C). The compression speed was about 1 cm/min, and the total compression load was about 4200 kgf. Then, the samples were gradually cooled to room temperature (not quenching) over a period of 2 hours while maintaining the deformation. The cooling speed from 140°C to 80°C demanded by the Japanese Industrial Standard (JIS), was about 1 hour. In this procedure, the sample thickness was reduced in accordance with the increase in the degree of compression. The compression ratio (CR) was defined by the ratio of the final thickness to the original thickness of the sample.

The following process relates to Sample B. The original UHMWPE blocks of which diameter was 30 mm and 30 mm long were heated to a temperature 120°C lower than the melting point for more than 3 hours. After heating, the UHMWPE was compressed at a speed of the same as sample A under a load greater than 10000 kgf.

As the fourth sample, an original UHMWPE was compressed at 80°C, which was named as Sample B'. The CR of Sample B and B' were 2.5 and 4, respectively.

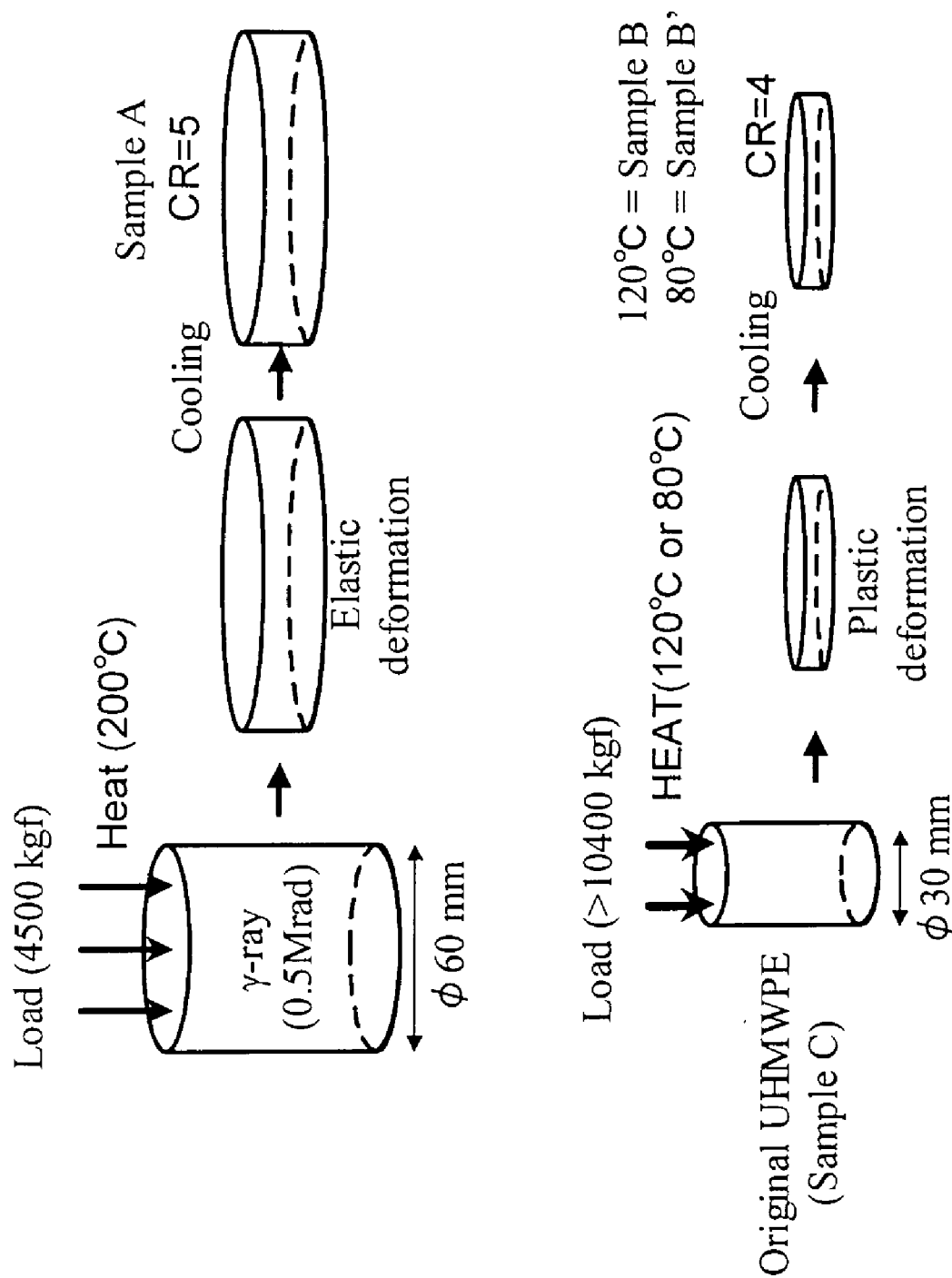


Figure 1: Scheme for preparation (Upper: slightly cross-linked UHMWPE crystallized from the melt under uniaxial compression, Lower: UHMWPE compressed below melting point)

Wide Angle X-ray Diffraction Analysis with Imaging Plate (IP) System

Imaging plates (MAC-Science Type DIP220)²⁰⁻²²⁾ had an IP film that was able to record two-dimensional patterns by shifting the drum along its axle. The rotating anode X-ray generator Cu-K α that was monochromatized by a Rigaku type RU-200 was radiated at 40 kV and 100 mA.

Thermal Properties

Enthalpy changes in the fusion and melting points of the non-compressed sample and the compressed ones were measured using a differential scanning calorimeter (DSC, Seiko Instruments Inc. DSC-6200). The rate of heating was 10°C/min and alumina was used as the reference. The degree of crystallinity calculated from DSC is the following expression using 288.9 J/g as the heat for fusion in a perfect crystalline phase.

$$\text{The degree of crystallinity} = \frac{\text{Measured enthalpy of fusion}}{288.9} \dots\dots(1)$$

Density Measurements

The densities of samples were measured in a density gradient column at 30°C. Toluene was added to gradually to carbon tetrachloride to make the gradient solution. The density range of the gradient solution was between 0.910 g/cm³ and 0.950 g/cm³. The degree of crystallinity was calculated using the following formula with 1.00 g/cm³ used as the density of the perfect crystalline phase and 0.85 g/cm³ as the density of the perfect amorphous phase.

$$\text{The degree of crystallinity} = \frac{\text{Measured density} - 0.85}{1 - 0.85} \dots\dots(2)$$

Dynamic Mechanical Measurements

The following is a principle of dynamic mechanical analysis. The dynamic mechanical properties of a material are obtained, when a specimen of the material is subjected to a periodic stress^{23,26}. The deformation (and hence strain) lags behind this stress by an angle δ , because the material is viscoelastic. It is conventional to separate the viscoelastic response into 'in-phase' and 'out-phase' components; the former comes from the elastic (completely recoverable) stored energy while the latter shows the in dissipation of energy as the specimen is deformed. Therefore, the modulus of elasticity, E (Young's modulus), is given by:-

$$E = E' + jE'' \dots \dots (3)$$

where E' is the in-phase (storage) modulus, E'' is the out of phase (loss) modulus, and $j = (-1)^{1/2}$. These parameters, together with $\tan\delta (= E'' / E')$, are the most fundamental dynamic mechanical properties of dynamic viscoelasticity. The dynamic tensile measurements of these samples were carried out by a viscoelastic analyzer (Rheogel-E4000, UBM Co. Ltd). E' and E'' were measured as a function of temperature between -150°C and 150°C at $2^\circ\text{C}/\text{min}$. The surface perpendicular to the compressed axis was cut to a rectangular parallelepiped. The continuous sine wave was subjected to the sample at the frequency of 10 Hz.

Reciprocating Pin-on-flat Wear Test

Wear tests were performed using a reciprocating pin-on-flat wear test device. The schematic representation of the wear test machine was described by the previous chapter. The machine had 6 arms, and thus, 6 samples were tested simultaneously. Wear tests were performed at a frequency of 1.2Hz for a minimum of 1.4 million

cycles in distilled water. The unidirectional sliding distance of the motion was 14 mm. Thus, the average sliding speed was 33 mm/s, and the top speed was 52 mm/s.

Samples were cut into a flat-ended vertical cylinder and the surface was polished to a mean roughness (Ra) of 0.1 µm. The test load of 98.11 N was applied along the longitudinal axis of the samples. Co - Cr - Mo alloy plates were used for the counter face, of which the Ra was 0.01 µm. The chemical composition of the alloy was Co (63.72 wt%), Cr (28.06 wt%), Mo (6.20 wt%), Si (0.80 wt%), Fe (0.45 wt%), Mn (0.31 wt%), C (0.26 wt%), and Ni (0.2 wt%). The Rockwell C hardness was 28 - 30.

After samples were cleaned ultrasonically in research grade acetone and reduced pressure desiccated, the weight losses of the samples were measured. The weights of the samples were recorded immediately after vacuum desiccation. The wear factor was defined as following equation:-

$$\text{Wear Factor} = \frac{\text{Wear volume(g)}}{\text{Load (N)} \times \text{Sliding distance(m)}} \dots\dots (4)$$

RESULTS

Wide Angle X-ray Diffraction with Imaging System

Figure 2(a) shows diffraction patterns when the X-ray was introduced to the surface perpendicular to the compressed axis. From the left images in figure, the diffraction pattern were from Sample A, from Sample B, from Sample B' and the last right is from Sample C, respectively. In Samples A, B and B', it was found that the (200) crystalline plane was orientated parallel to the compressed surface. The (200) crystalline plane of Sample C was also orientated slightly off parallel. Figure

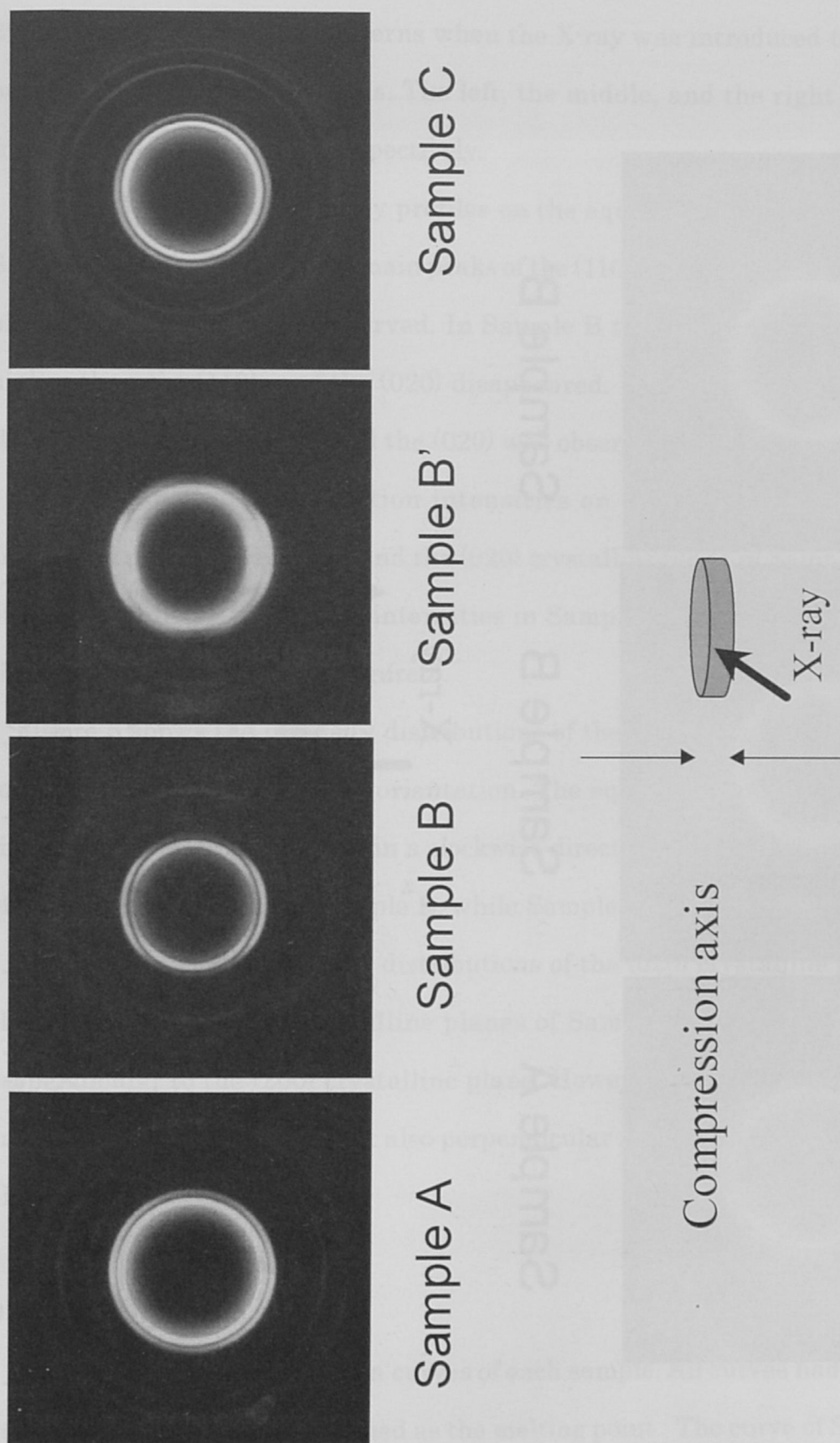


Figure 2(a): Wide angle X-ray photographs for each sample. X-rays were introduced perpendicular to the compressed axis (From left, Sample A, Sample B, Sample B' and Sample C)

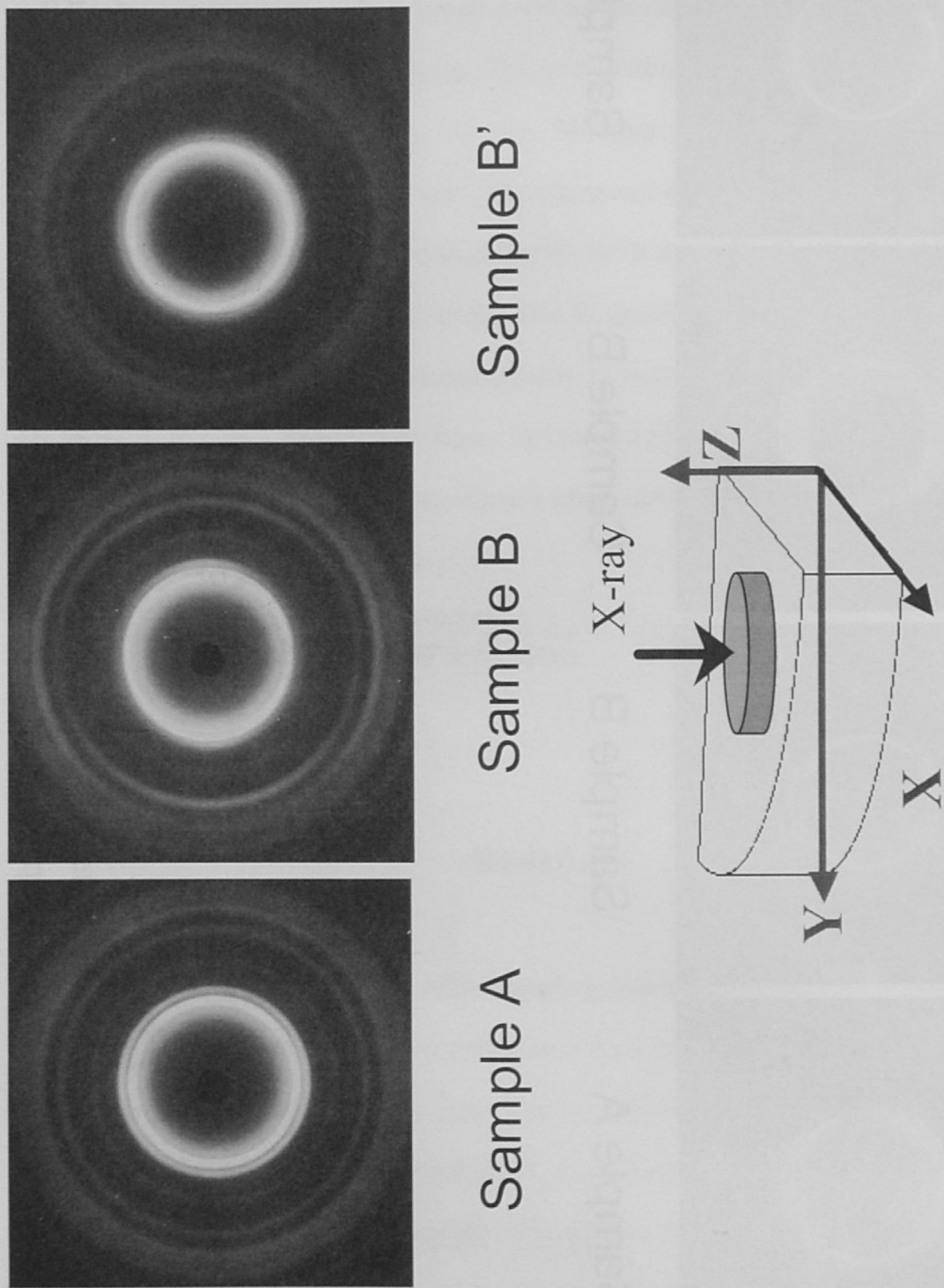


Figure 2(b): Wide angle X-ray photographs for each sample. X-rays were introduced parallel to the compressed axis (From left, Sample A, Sample B, Sample B')

2(b) shows the diffraction patterns when the X-ray was introduced to the surface parallel to the compressed axis. The left, the middle, and the right patterns are from Samples A, B, and B', respectively.

Figure 3 shows the intensity profiles on the equator of the WAXD patterns of Samples A, B and C. The three main peaks of the (110), the (200), the (020) crystalline planes, respectively were observed. In Sample B the (200) crystalline plane was higher than the (110), and the (020) disappeared. However, the (110) was higher than the (200) in Sample A and the (020) was observed.

Figure 4 shows the diffraction intensities on the meridian axis. The (200) crystalline plane in Sample B and the (020) crystalline plane in Sample C were not observed, while all diffraction intensities in Sample A were lower compared with those of Sample A shown in Figure 3.

Figure 5 shows the intensity distributions of the (200) crystalline plane, which indicates means the degree of orientation. The equatorial line in the diffraction ring was started from 0 degree in a clockwise direction. There were are peaks at 0° and 180° in Sample A and Sample B, while Sample C had a peak at 90°.

Figure 6 shows the intensity distributions of the (020) crystalline plane. It was observed that the (020) crystalline planes of Samples B and C were orientated perpendicular to the (200) crystalline plane. However, the (020) of Sample A was orientated not only parallel but also perpendicular slightly to the (200) crystalline plane.

DSC Measurements

Figure 7 shows the endotherm curves of each sample. All curves had a large peak at about 140°C, which was defined as the melting point. The curve of Sample A fell

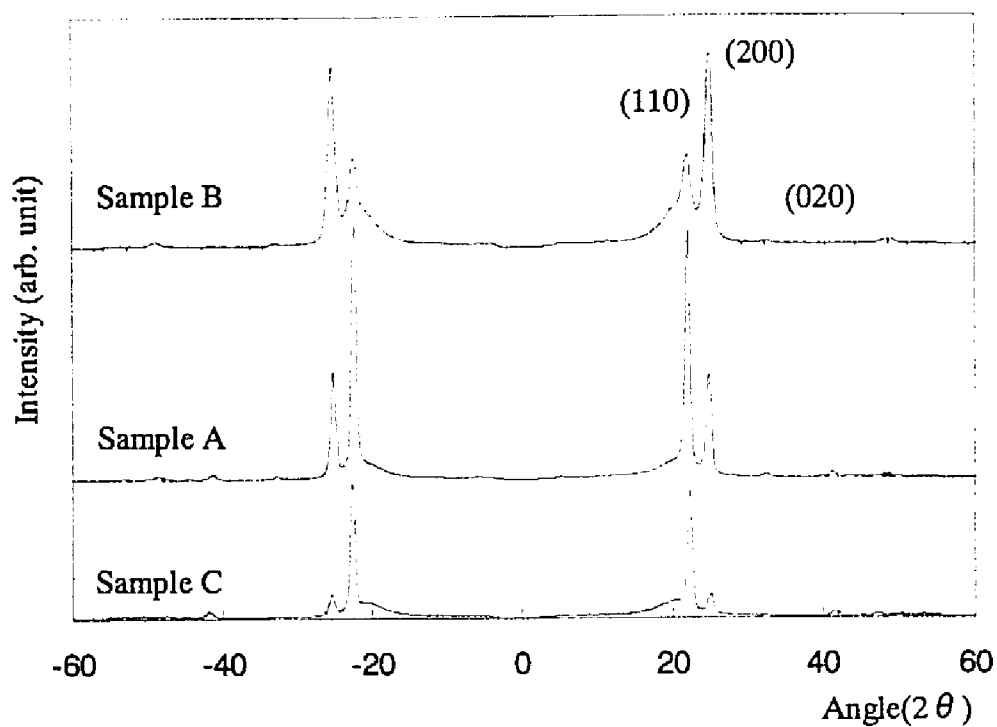


Figure 3: Intensity profiles on the equator line of the WAXD patterns

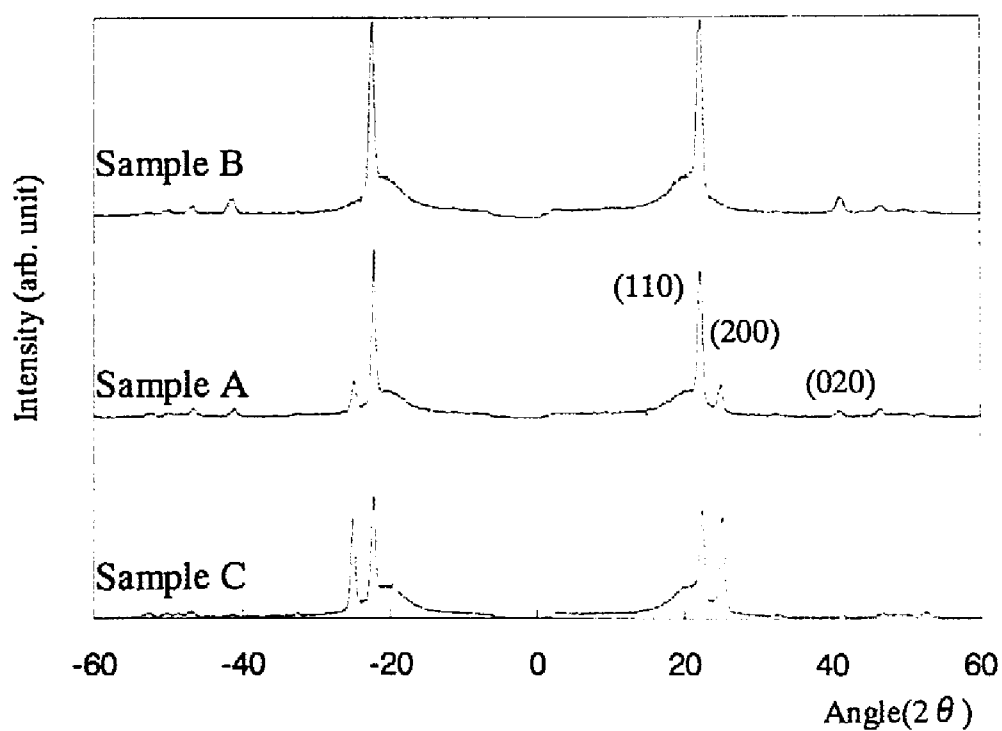


Figure 4: Intensity profiles on the meridian line of the WAXD patterns

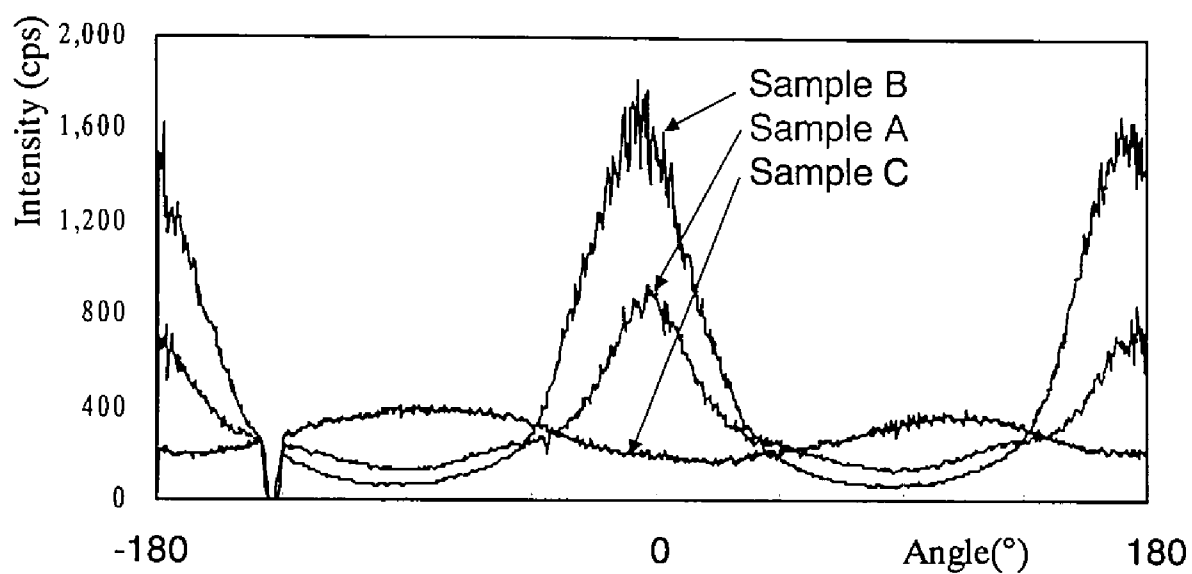


Figure 5: Intensity distributions of the (200) crystalline plane

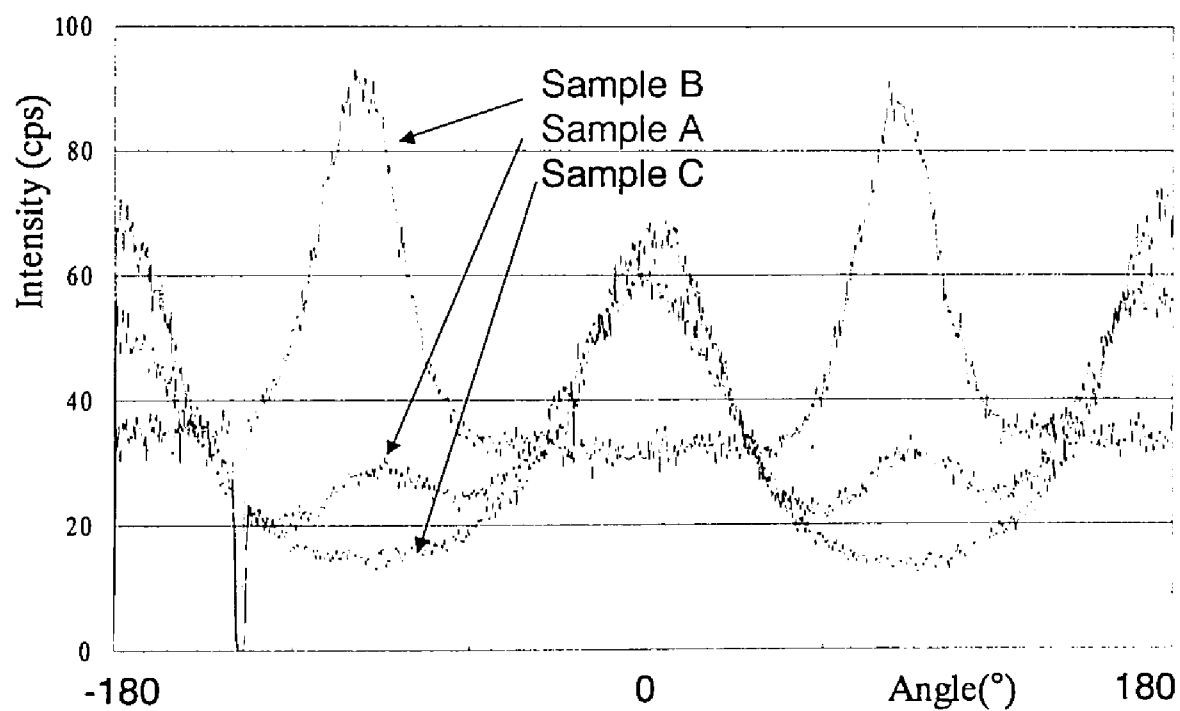


Figure 6: Intensity distributions of the (020) crystalline plane

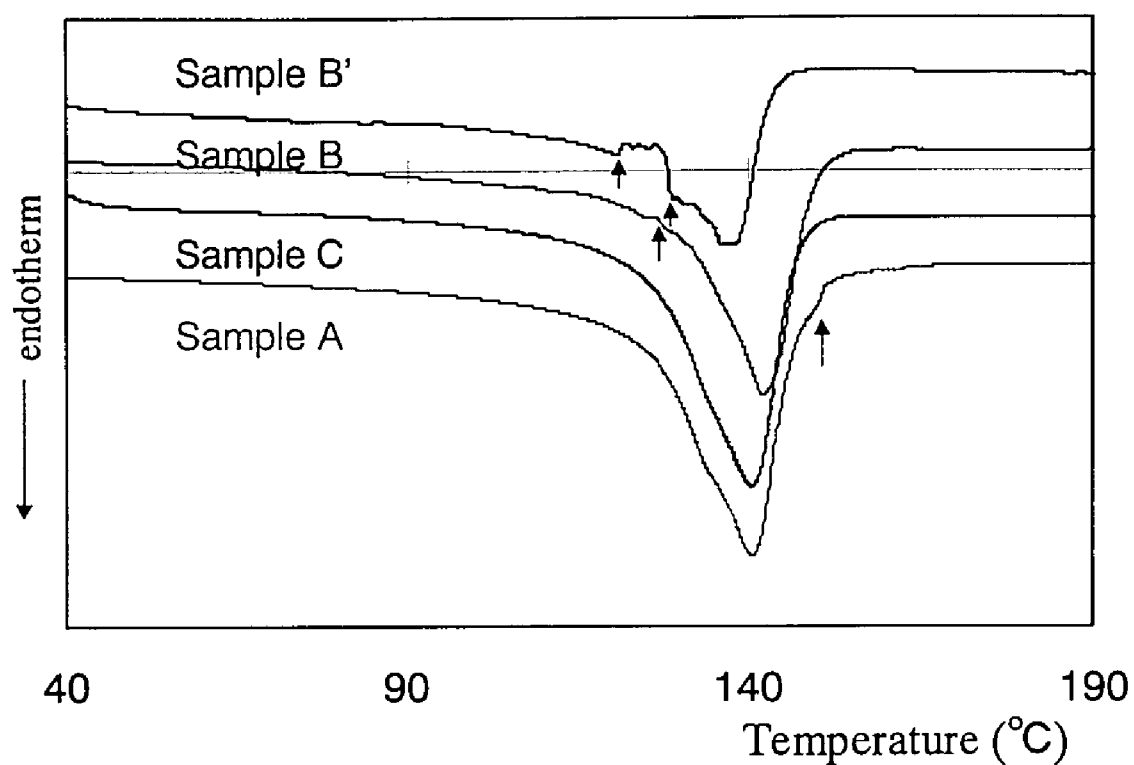


Figure 7: Endotherm curves as a function of temperature

Table 1: Thermodynamic properties

Sample Name	$T_1(^{\circ}\text{C})$	$T_2(^{\circ}\text{C})$	$T_m(^{\circ}\text{C})$	$T_h(^{\circ}\text{C})$	$\Delta H \text{ (J/g)}$
Sample C	-	-	140.6	-	174
Sample B'	120.8	128.8	137.9	-	153.6
Sample B	114	126	142.3	-	157.6
Sample A	-	-	140.8	155.6	209.8

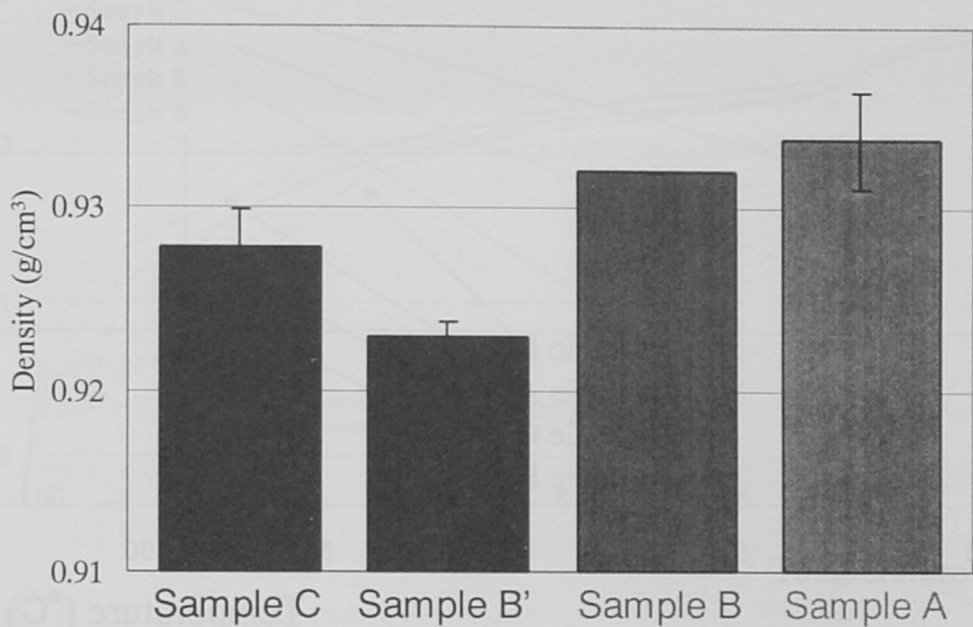


Figure 8: Comparison of densities

suddenly at about 120°C and the peak was formed at about 140.8°C, however, the curve of Sample B decreased gradually and then peaked at 142.3°C. Moreover, there were two small peaks below the melting point in Samples B and B', and there was one small peak at the higher temperature (at 155.6°C) in Sample A.

Table 1 shows temperatures of the peaks and heat of fusion. The heat of fusion of Sample A was the highest in all samples, which means that Sample A was 1.3-fold higher than that of Sample B. The degree of crystallinity, calculated using formula (1) was that Sample C was 60.2%, Sample B was 54.6%, and Sample A was 72.6%. It was found that Sample A was 1.2-fold higher than that of Sample A. Sample B' was 53.2% of the lowest among all samples.

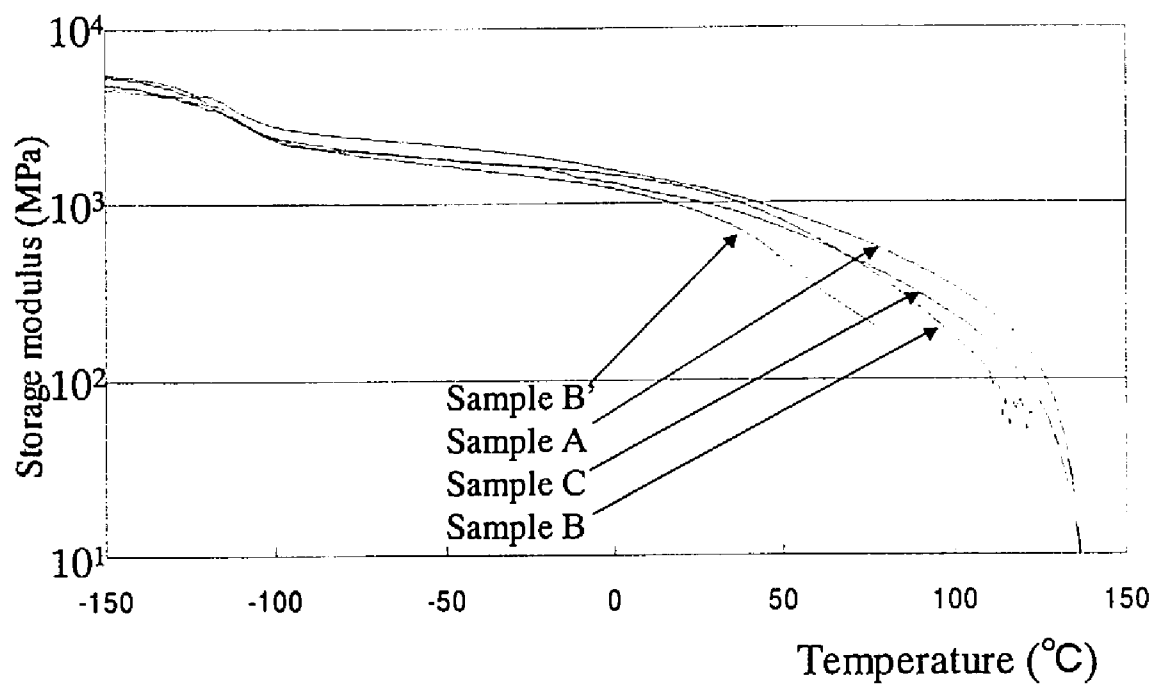


Figure 9: Storage modulus as a function of temperature

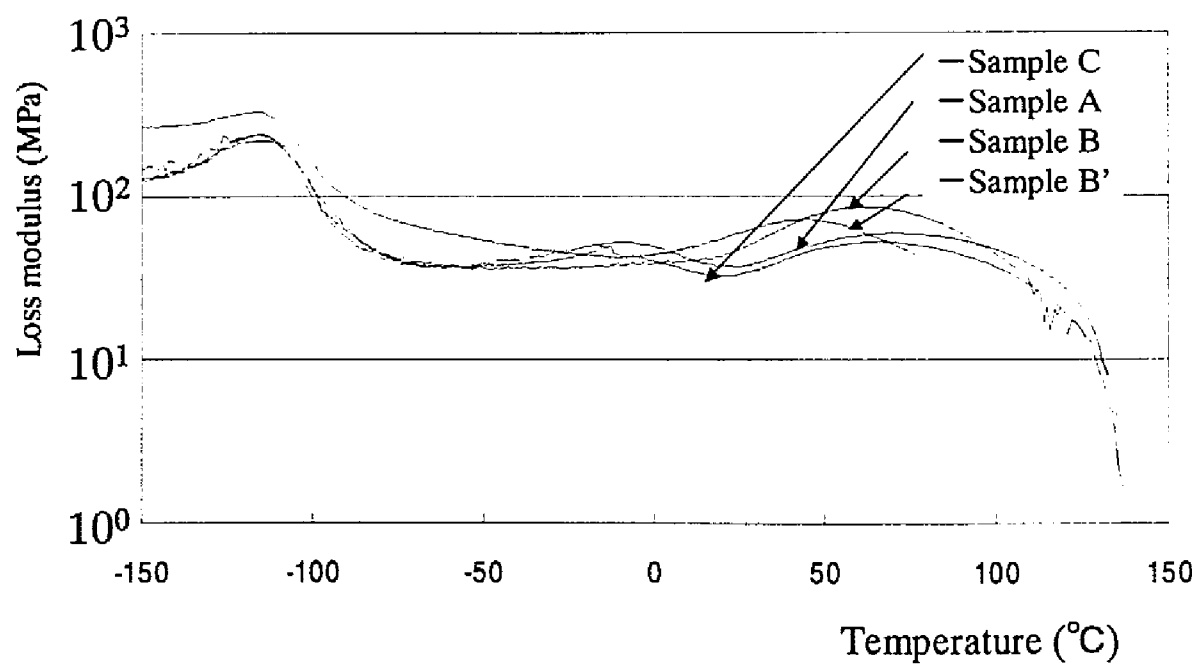


Figure10: Loss modulus as a function of temperature

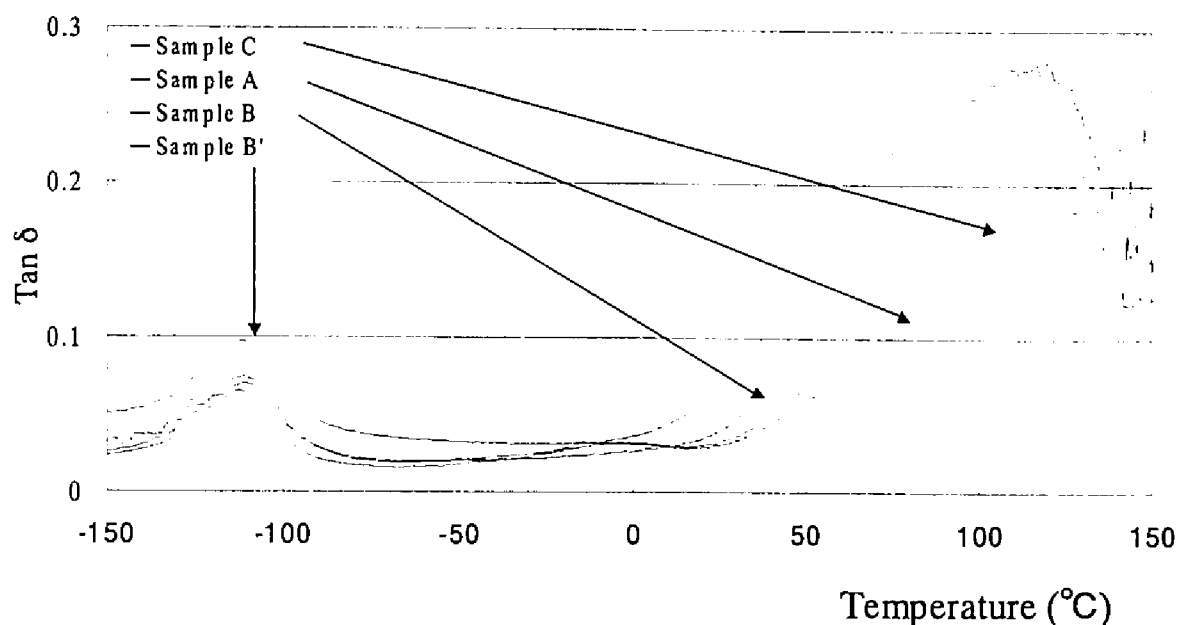


Figure 11: Tan δ as a function of temperature

Measurement of Density

The density was drawn depending on the various samples were shown in figure 6. The density of Sample A was 0.934 g/cm^3 , which was the highest of all samples. Sample B was 0.932 g/cm^3 , the second highest, because the density of Sample C was 0.928 g/cm^3 , it was revealed that the densities Sample A and B were both increased. The degree of crystallinity calculated using (2) was that Samples A, B, C were 56.0%, 54.7%, and 52.0%, respectively. The density and crystallinity of Sample B' were 0.923 g/cm^3 , 48.7%, respectively, and were also the lowest.

Dynamic Mechanical Measurements

Figures 9, 10, and 11 show the storage modulus E' , and the loss modulus E'' and the tan δ as a function of temperature of various samples. All E' values were moderately decreased with increasing temperature, and the E' of Sample A was

always higher than that of Sample C. Although the E' of Sample B was also higher than that of Sample C around room temperature, it rapidly decreased with increasing temperature.

E'' had three apparent dispersion peaks at 70°C, -10°C, and -115°C that are designated as α_c , β , γ -relaxation, respectively. The γ peaks of all samples were similar temperatures (at about -115°C). The γ -relaxation is typically due to molecular relaxation phenomena such as the chain ends or the dislocation of such defects in the crystalline part. The β peaks of Samples A and C were at similar temperatures (at about -10°C), while Sample B showed no peak at approximately -10°C. The β -relaxation suggested to derive from the micro-Brownian motion in the amorphous part. The α_c peak of Sample A was shifted to 9°C higher compared with the Sample C peak (at about 64°C), however, the α_c peak of Sample B was shifted to 62°C. The α_c -relaxation was observed for the relaxation phenomena of the molecular in the crystalline part. The α_c -relaxation is explained as the actively occurring thermo-vibration of the molecular chain in the crystal phase, as the anharmonic oscillators of the intermolecular potential are increased. Then the crystalline phase became viscoelastic. The increase of α_c -relaxation intensity and peak shifting to higher temperatures are related to increases in the crystalline thickness. As Sample B' was significantly shrunk, the viscoelastic properties could be measured in a range between -150°C and 76°C. E' of Sample B' rapidly dropped to be lowest among the samples. The α_c peak of Sample B' was at 44°C, suggests that the peak was shifted to 20°C lower than Sample C.

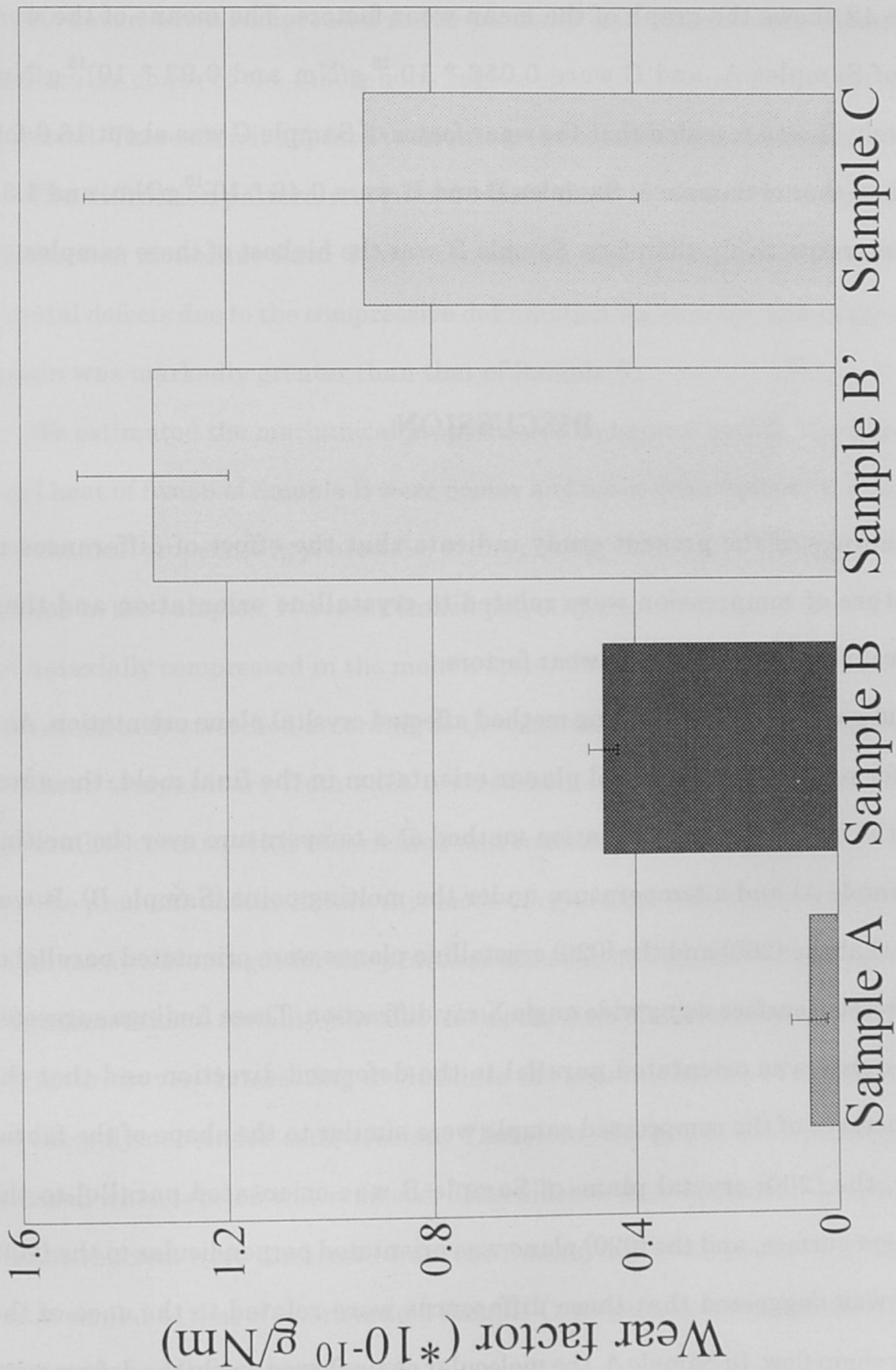


Figure 12: Comparison of wear factors

Reciprocating Wear Test

Figure 12 shows the graph of the mean wear factors. The means of the wear factors of Samples A, and C were 0.056×10^{-10} g/Nm and 0.93×10^{-10} g/Nm, respectively. It was revealed that the wear factor of Sample C was about 16.6-fold higher than that of Sample A. Samples B and B' were 0.46×10^{-10} g/Nm, and 1.3×10^{-10} g/Nm, respectively, therefore, Sample B' was the highest of these samples.

DISCUSSION

The findings of the present study indicate that the effect of differences in temperature of compression were related to crystalline orientation and their mechanical properties including wear factors.

First, it was shown that molding method affected crystal plane orientation. As a method for producing the crystal planar orientation in the final mold, the author adopted the compressive deformation method at a temperature over the melting point (Sample A) and a temperature under the melting point (Sample B). It was observed that the (200) and the (020) crystalline planes were orientated parallel to the compression surface using wide angle X-ray diffraction. These findings suggested that the c-axis was orientated parallel to the deformed direction and that the superstructures of the compressed sample were similar to the shape of the fabric. However, the (200) crystal plane of Sample B was orientated parallel to the compression surface, and the (020) plane was orientated perpendicular to the (200) plane. It was suggested that these differences were related to the ease of the molecular chain flow. In Sample A, the molecular chain flowed easily the deformation

direction, although a cross-link point existed in the structure.

However, when compressed in the partially crystallized state (Sample B), the molecular chain of the amorphous region showed deformation when stress was received. Thereafter, it appeared to orientate the crystals in the deformation direction.

The diffraction pattern recognized inside the (110) plane in Sample B' was the diffraction monocline form. It was considered that the monoclinic was created by crystal defects due to the compressive deformation because the flow of the molecular chain was markedly greater than that of Sample B.

We estimated the mechanical properties of Samples A and B. The heat stability and heat of fusion of Sample B were poorer and lower than Sample A. Differences in mechanical properties appeared due to morphology differences during the amorphous phase in the samples. If a cross-linked polyethylene of adequate cross-link density is uniaxially compressed in the molten state, the molecular chains in the structure are elastically stretched according to the macroscopic deformation. Upon cooling to a lower temperature from such a stretched state, in which highly orientated crystallites coexist with unioriented and relaxed amorphous molecular chains.

The products obtained from this mode of crystallization were not only associated with many advantages for the practical use such as high melting temperature and high dimensional stability, but also the mechanism of the formation of such a unique structure is very interesting to elucidate the general feature of the crystallization of the polymer under compression. Therefore, the amorphous phase was easily relaxed when tension was removed. The evidence that amorphous phase of Sample A was relaxed, were confirmed from the finding that the β peaks of E'' in Sample A were similar to that of unorientated Sample C, which was different from the findings of the disappearance on β peak in Sample B.

In contrast, in compression in the partially crystallized state, the amorphous phase, which had a lower modulus, was at first stretched and then orientated. After that, orientation of the crystalline phase occurred, so both these phases were orientated in the deformed direction and tensile state. Therefore, the stability of the sample was decreased. The large deformation of Sample B' produced crystalline disordering, monoclines and decreased heat stability in the crystalline phase.

The wear resistance of Sample A was markedly improved in comparison with original starting articles (Sample C), but opposite that of Sample B', which was significantly lowered. It was confirmed that heat stability of crystals and their mechanical properties in the molded article were highly related to the wear properties.

CONCLUSION

From the present experimental findings, the following conclusions could be drawn:-

1. Two different molding method were used to orientate the molecular chains. One was a compression of a slightly cross-linked UHMWPE during the molten state (Sample A), and the other (Sample B and Sample B') were compressed original UHMWPE at temperatures lower than melting point.
2. The degrees of orientation and the (200) crystalline plane of both samples were similar orientated parallel to the compression surface.
3. The heat of fusion and the density of Sample A were larger than those of Sample B.
4. The α_c -peak was shifted about 5°C higher, however, Sample B was shifted to

lower temperature and the β -peak disappeared. It was confirmed that the stability of heat of Sample B was poorer than that of Sample A and the amorphous phase of Sample B was a restricted state.

5. The wear factors of Sample A were the lowest and those of Sample B' the highest among the samples examined.

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Chapter 6

Slightly Cross-linked UHMWPE Crystallized and 3-D orientated under the Compression for Artificial Joints

INTRODUCTION

Ultra high molecular weight polyethylene (UHMWPE) has been used for a major bearing surface of total hip joint replacements for the past thirty years. The success of UHMWPE as a bearing surface is attributed to its excellent wear and abrasion resistance. However, friction between bearing surfaces of both acetabular and femoral components leads to generation of wear debris in a contact part of joint cavities. It was found that dislocation and failure in total hip and knee arthroplasty are closely associated with osteolysis reason and caused by produced UHMWPE wear debris¹⁻¹⁰⁾.

In previous chapters¹¹⁻¹⁵⁾, the method of a slightly cross-linked UHMWPE, crystallized under the uniaxial compression to improve of wear resistance was proposed. It was found that the (200) and the (110) crystalline plane were orientated parallel to the compressed surface. The density and the enthalpy change of fusion were increased in accordance with the compression ratio increase. Moreover, the wear factors of the compressed samples were showed decrease by reciprocating pin-on-flat wear tests. Regarding these findings, the slightly cross-linked UHMWPE crystallized from the melt under the uni-axial compression is expected to be useful for artificial joint applications.

However, it was not clear in the case that the sample could be molded to cup shape, as the above findings were gotten from compressions with two flat plates. It was also not appeared that the orientations of the crystalline plane in molded cup were similar to the results of the plane compression.

The present chapter is reported the study of orientation and material properties when the slightly cross-linked UHMWPE samples were compressed by using a ball mold and a knee mold. The orientation was confirmed by X-ray diffraction techniques and the quantity of the orientation was determined by imaging plate. The material properties were studied by density and DSC. In addition, to estimate wear properties, hip and knee simulators were performed.

EXPERIMENTAL

Preparation Samples

The raw material for this study is UHMWPE of GUR4150HP sold in the market by Hoechst. The detail explanation about crystallization under uni-axial compression is described in previous chpters¹¹⁻¹⁵⁾.

At first, 20mm-thick block of UHMWPE was irradiated by ^{60}Co γ -rays of 1.11 - 1.12 Mrad under reduced pressure at room temperature. The molecular chains were slightly cross-linked by the irradiation and the block sample became gel form. The slightly cross-linked UHMWPE was compressed at 200°C by pushing a brass ball with 22 mm diameter of a typical artificial hip joint. The temperature (200°C) means to be sufficiently higher than the melting point of UHMWPE (about 140°C).

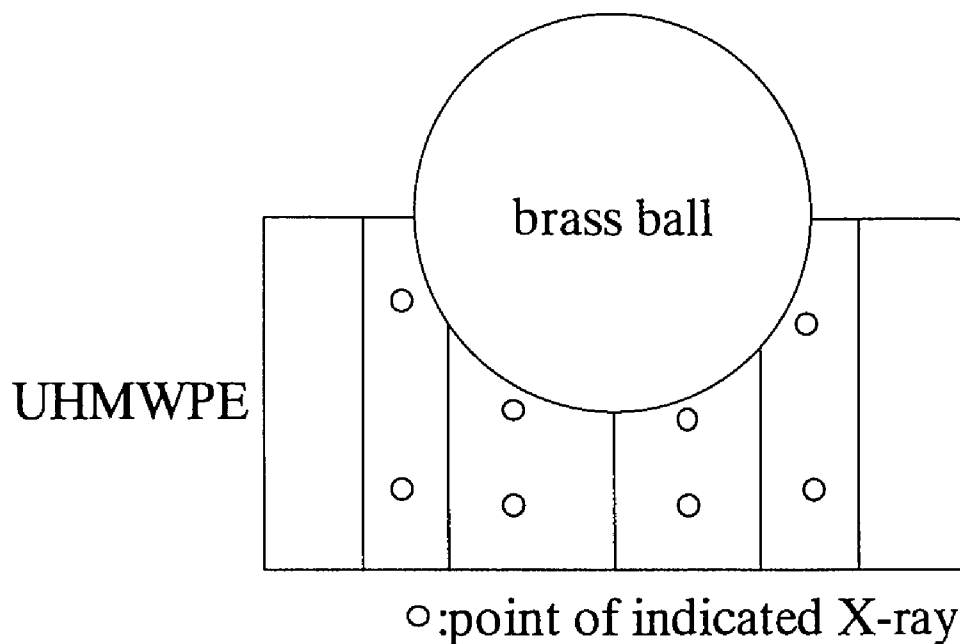


Figure 1: Positions for X-ray indication

Therefore, the crystalline phase in the sample was completely melted and compressed, and in consequence, the molecular chain was orientated. The ball was buried into 11 mm depth at the compression speed of 10 mm/min. Furthermore, the melted and compressed sample was cooled until room temperature for more than 3 hours, while maintaining of the ball buried. The hollow sample was defined as the cupped sample in this study.

The knee form was molded by knee mold, which was similar to the method of the hip mold.

Wide Angle X-ray Diffraction

The orientation analysis of the crystalline phase in the cup and the knee samples were studied by wide angle X-ray diffraction techniques. Figure 1 shows the positions of photographs of the sample. At first, the cupped samples were sliced as the thickness

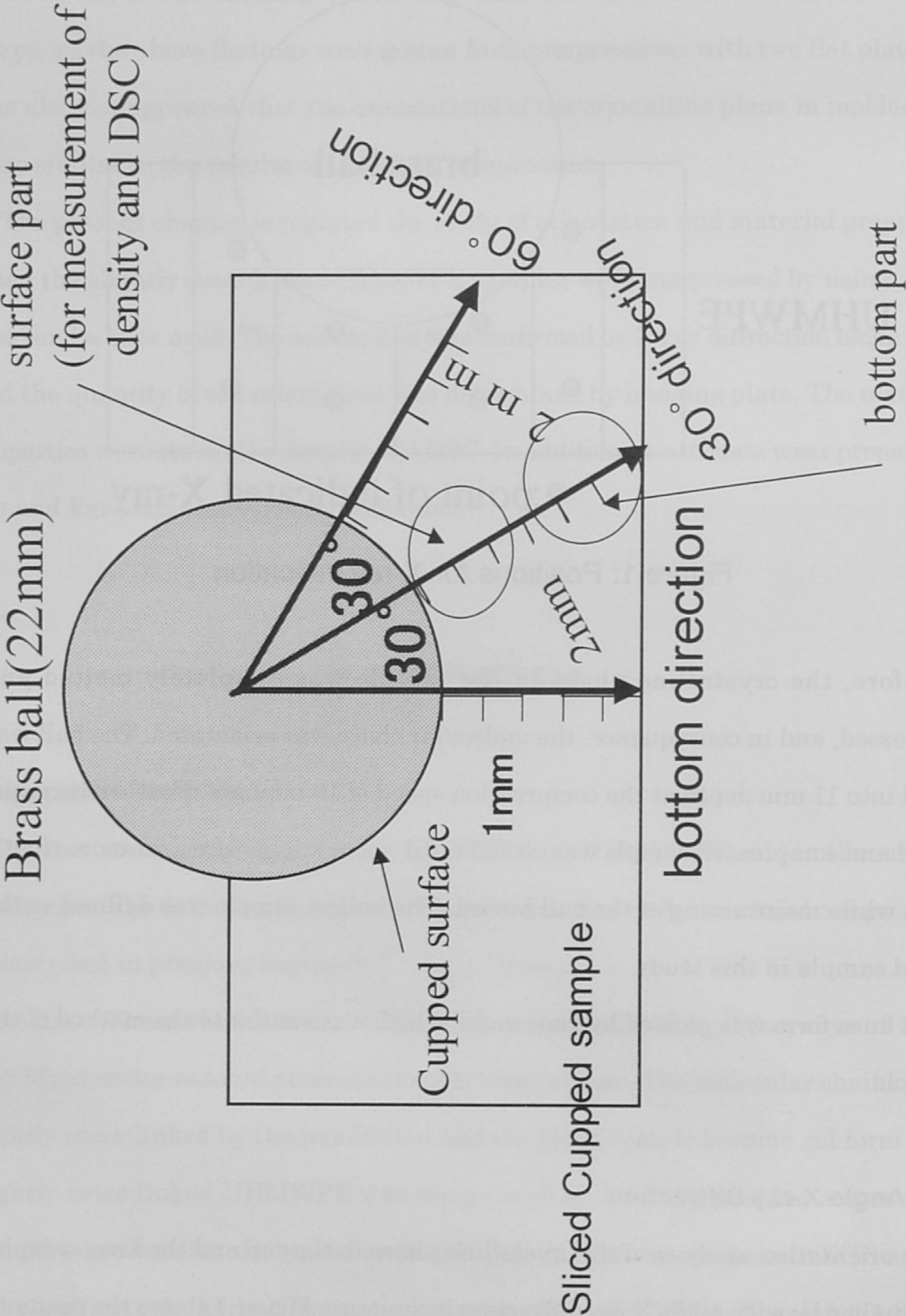


Figure 2: Positions named on sliced cupped sample

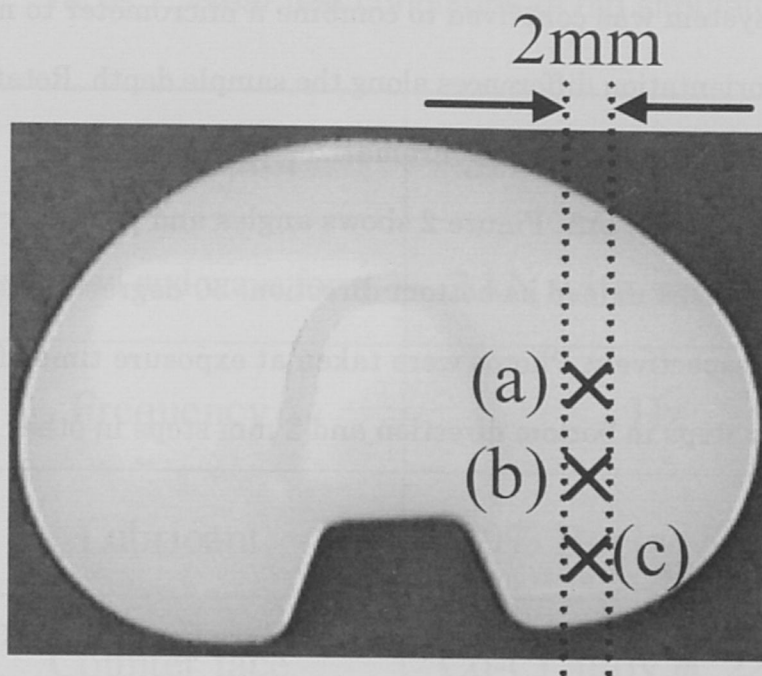


Figure 3: Positions on the knee surface for X-ray irradiation.

of 1 mm from the cupped surface to the bottom. Radiographs were taken with a flat camera that radiations were generated at 40 kV and 60 mA. The camera was made by a Rigaku Ru-3H, that has Cu- K_{α} X-ray beams monochromatized with a graphite monochromator.

The crystalline phase was measured by applying imaging plate to quantitatively investigate the detailed orientation.

The orientation of the knee sample was studied by X-ray diffraction similar to the cup sample. Figure 3 shows positions on the knee sample for X-ray irradiation. The X-ray beam was introduced parallel to the knee surface on the three positions.

Wide Angle X-ray with Imaging Plate (IP) System

Imaging plates (MAC-Science Type DIP220)¹⁶⁻¹⁸⁾ is equipped with an IP film that is able to record two-dimensional patterns by shifting the drum along its axle. In

addition, the IP system was contrived to combine a micrometer to move sample, and measure the orientation differences along the sample depth. Rotating anode X-ray generator Cu-K α that was monochromatized by a Rigaku type RU-200 was radiated at 40 kV and 100 mA. Figure 2 shows angles and positions taken on the sample. Each angle was named as bottom-direction, 30-degree direction, and 60-degree direction respectively. Photos were taken at exposure time of 900 seconds per photo by 1mm steps in bottom direction and 2 mm steps in other directions.

Density Measurements

Densities of samples were measured in a density gradient tube at 30°C. Toluene was gradually added to carbon tetrachloride to make the gradient solution. The density range of the gradient solution was between 0.910 g/cm³ and 0.950 g/cm³. The sample parts were cut from the cupped sample at 30-degree direction and divided into two parts of the surface and the bottom as shown in Figure 2.

The following formula concerns the crystallinity degree of the experimental samples while densities of the perfect crystalline and the amorphous are 1.00g/cm³ and 0.85g/cm³, respectively.

$$\text{The degree of crystallinity} = \frac{\text{Measured density} - 0.85}{1 - 0.85} \dots\dots (1)$$

Thermal Properties

Enthalpy changes of fusion and melting points of the non-compressed and the cupped samples were measured using a differential scanning calorimeter (DSC, Seiko Instruments Inc. DSC-6200) at the heating rate of 10°C / min with alumina

Table 1: Wear test conditions of hip simulator

Hip simulator	Shore Western Inc.
Peak load and wave form	2 kN with sine wave
Frequency	1 Hz
Lubricant	30% Bovine Serum
Counter face	Co-Cr alloy, ϕ 22mm

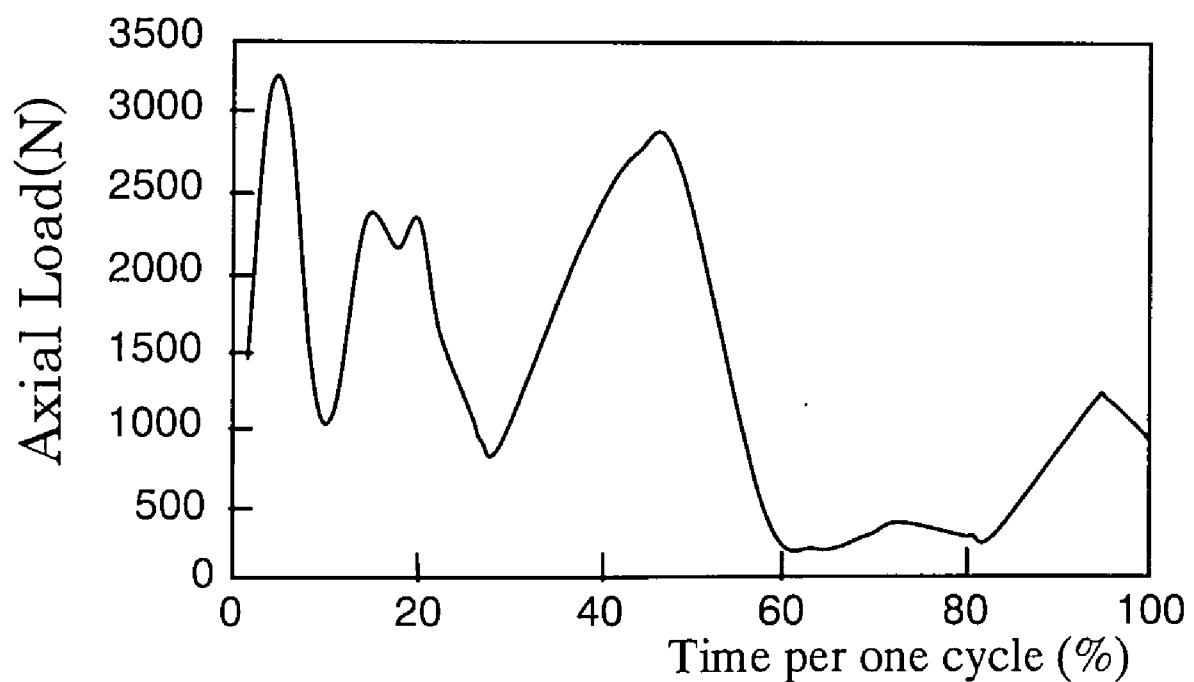


Figure 4: Wear test condition of knee simulator (Variation of axial force with cycle time)

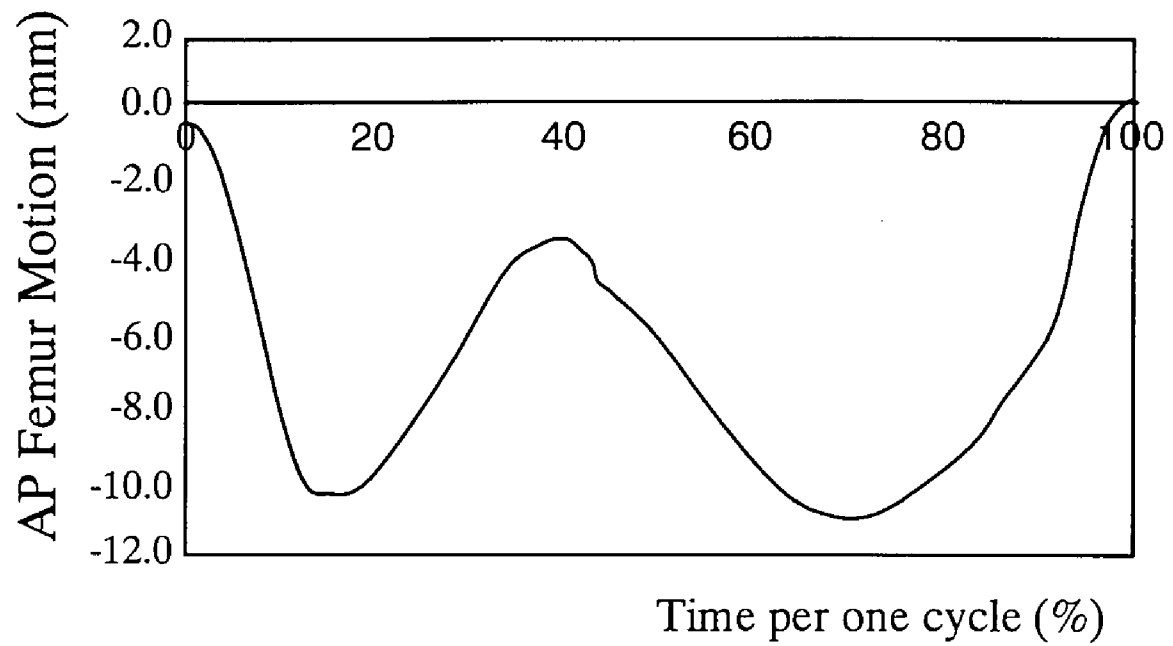


Figure 5: Wear test condition of knee simulator (Variation of AP motion with cycle time)

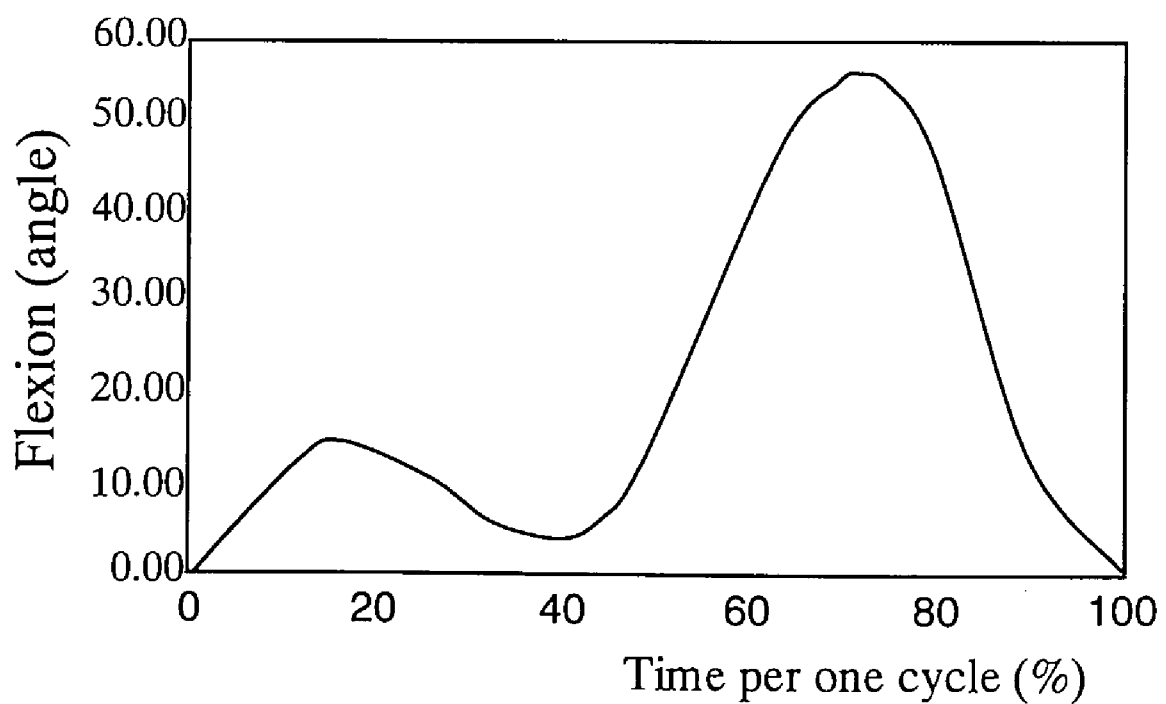


Figure 6: Wear test condition of knee simulator (Variation of flexion angle with cycle time)

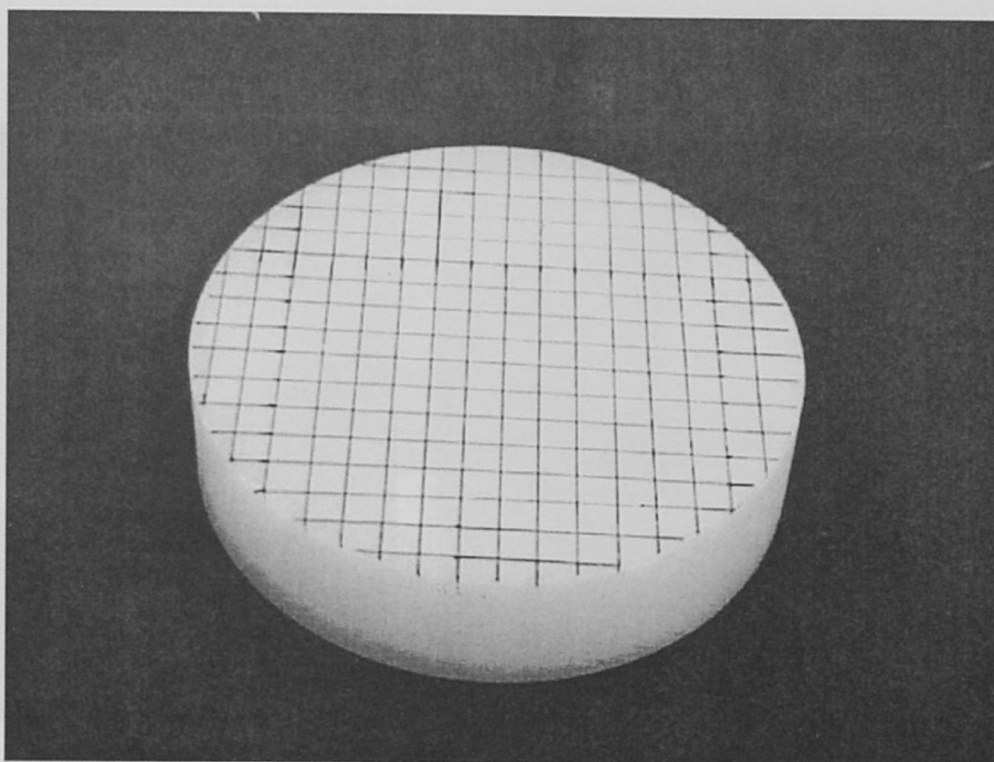


Figure 7: Before the compression of slightly cross-linked UHMWPE. The intervals of the grid line on the compressed surface are 5 mm

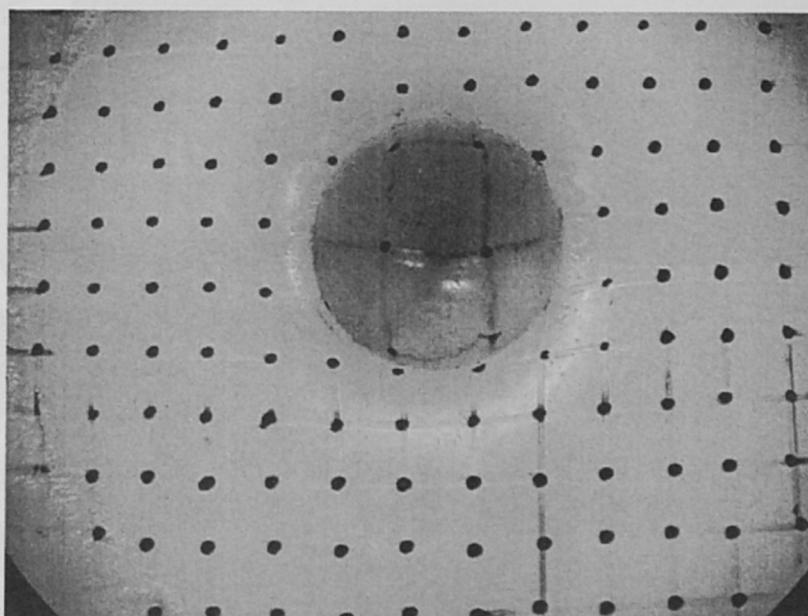


Figure 8: After the compression with brass ball. This sample was named as cupped sample

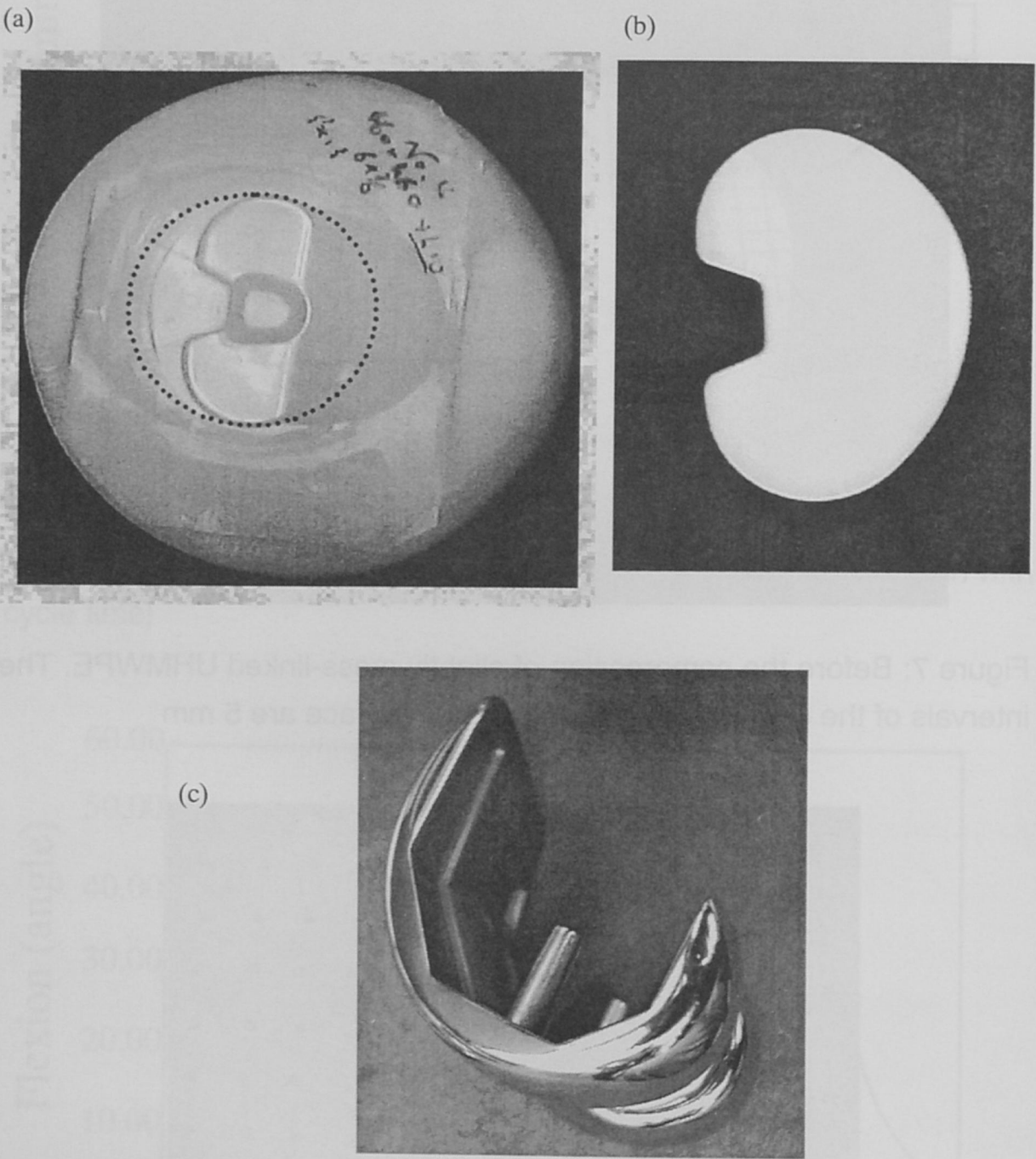


Figure 9: a: After the compression by knee mold.
b: After cut from the above compression.
c: Counter face of artificial knee joint

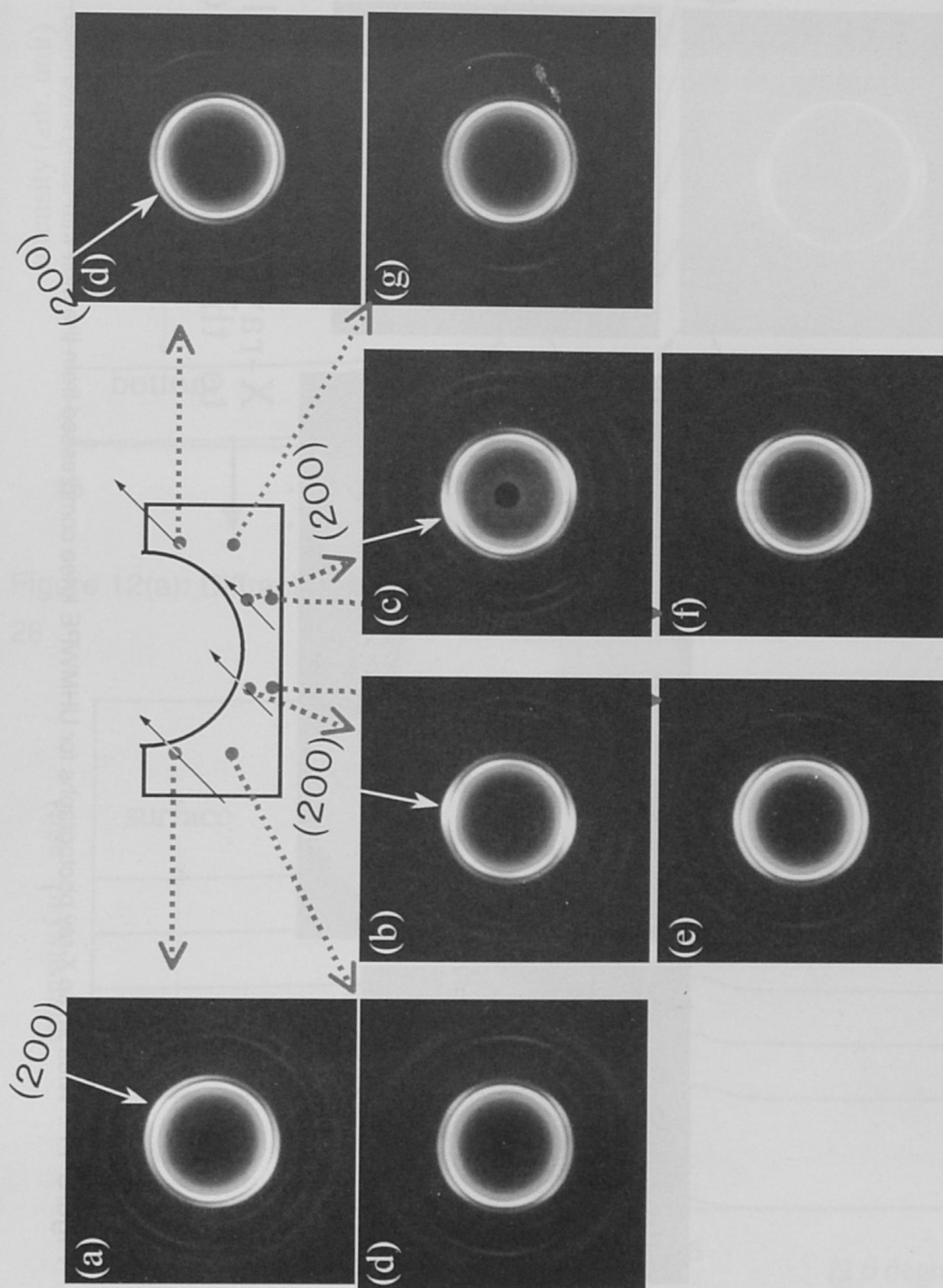


Figure 10 : Wide angle X-ray photographs for UHMWPE cup compressed from the melt with brass ball

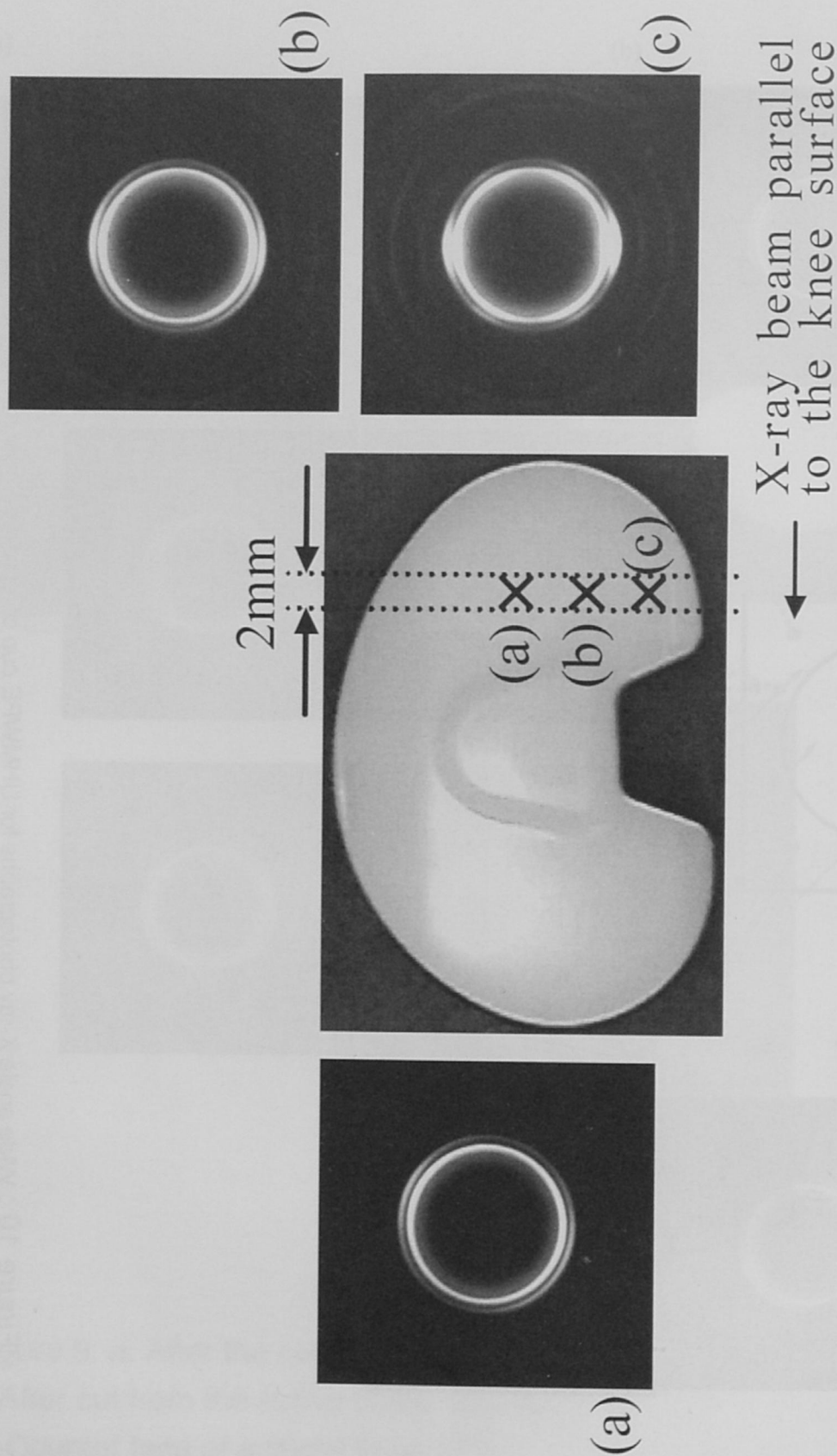


Figure 11 : Wide angle X-ray photographs for UHMWPE knee compressed from the melt with using knee mold

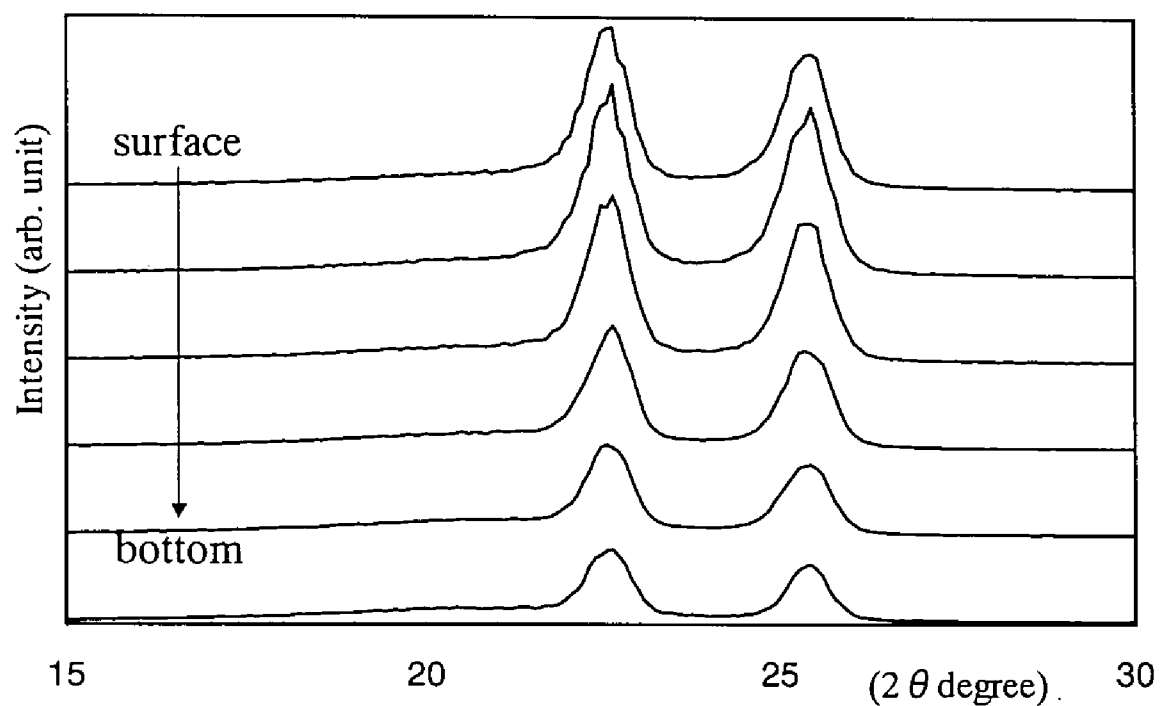


Figure 12(a): Diffraction intensities in the bottom-direction as a function of 2θ

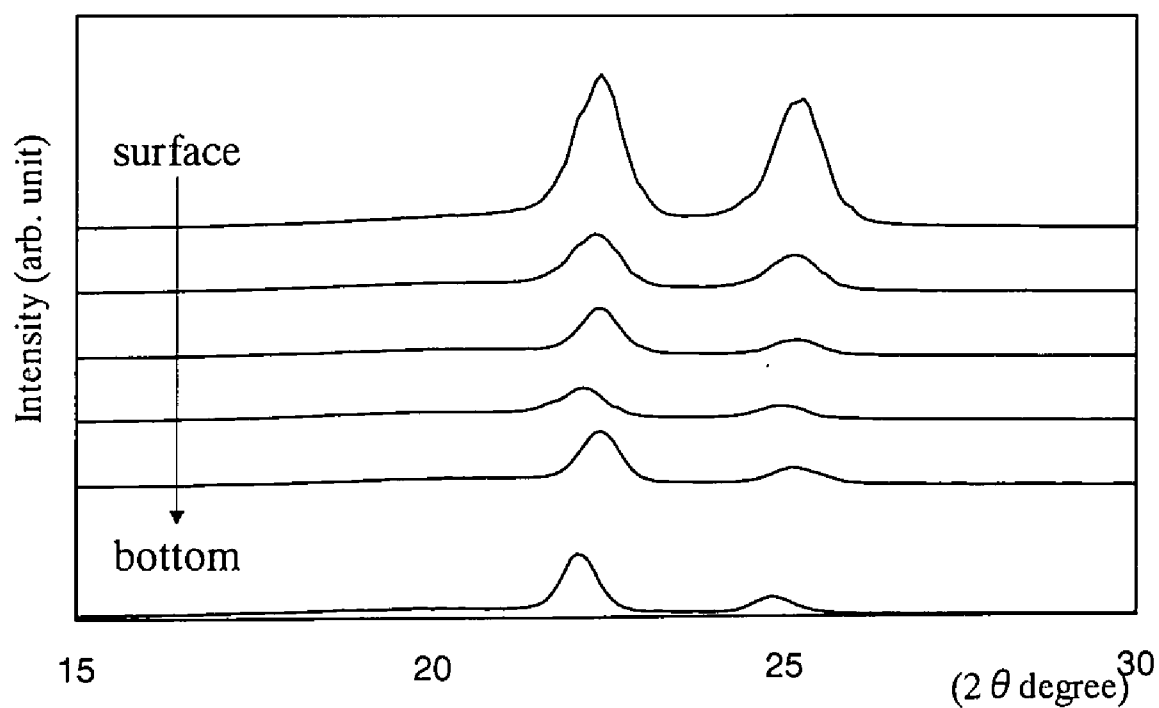


Figure 12(b): Diffraction intensities in the 30° -direction as a function of 2θ

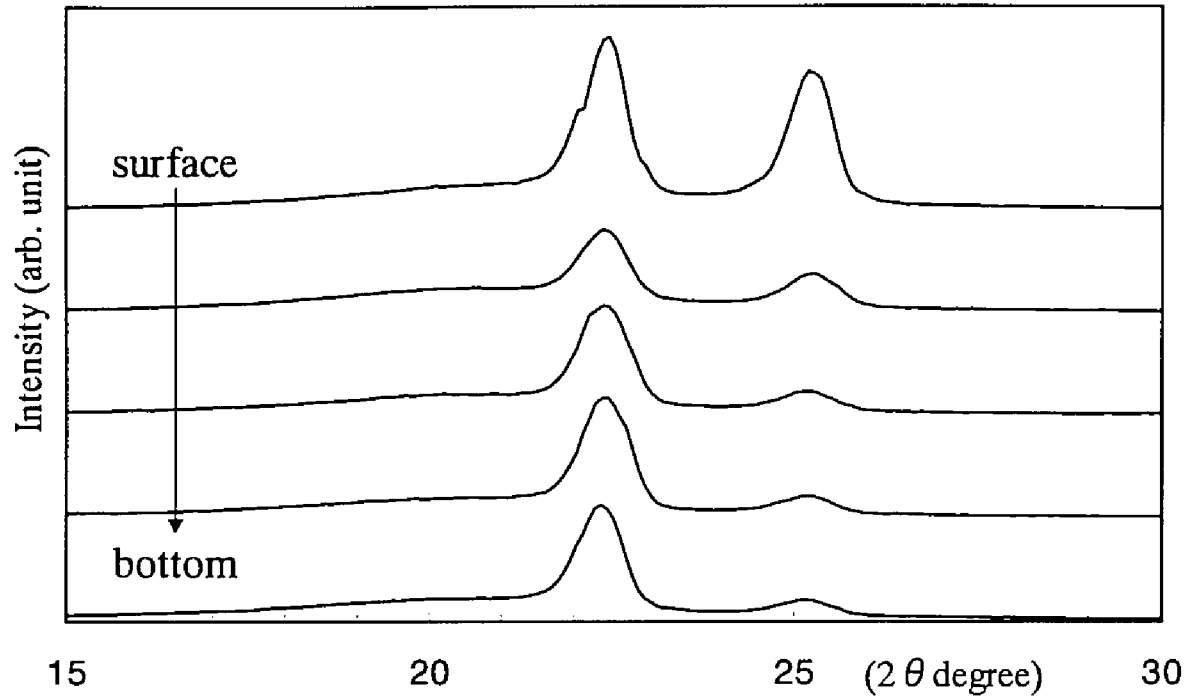


Figure 12(c): Diffraction intensities in the 60°-direction as a function of 2θ

used as a reference. The cupped samples were employed for both thermal properties and densities. The degree of crystallinity calculated from the following formula using 288.9 J/g as the enthalpy of fusion in a perfect crystalline phase.

$$\text{The degree of crystallinity} = \frac{\text{Measured enthalpy of fusion}}{288.9} \dots\dots (2)$$

Wear Tests by Hip and Knee Simulators

Hip wear test of the hip sample were performed by hip simulator. The compression ratio of the hip sample was CR=3. The test condition was shown in Table 1. The weight loss were measured and were compared with that of the conventional cut sample. The numbers of the two kinds were three, respectively. The test was carried

out up to 1.25 million.

Knee wear test of the knee sample were performed by knee simulator. The compression ratio of the hip sample was $CR=5$. The test condition was set by ISO-14243-3 and the loads is shown in Figure 4, 5, and 6, respectively. The weight loss were measured and were compared with that of the conventional cut sample. The numbers of the two kinds were one, respectively. The test was carried out up to 1 million.

RESULTS

Figure 7 and Figure 8 show the slightly cross-linked UHMWPE before and after the compression using the brass ball, respectively. The sample surface was deformed by the contacting and buried the brass ball.

The Grid lines were drawn on the sample surface at intervals of 5 mm shown in Figure 7. After the compression, the intervals of the grid line were enlarged to about 10 mm, which meant that the sample surface was deformed to about 2×2 times. Also the amount of the deformation in the bottom part was the larger than that in the other surface of the cup sample.

Figure 9 shows the slightly cross-linked UHMWPE after the compression using knee mold. The knee formed was translated to the compressed surface.

Wide Angle X-ray Diffraction

The cupped sample was sliced to 1 mm thick, to observe the orientation of the crystalline phase by wide angle X-ray diffraction photograph technique. Figure 10 (a) - (g) shows respective diffraction patterns taken at corresponding points in Fig.

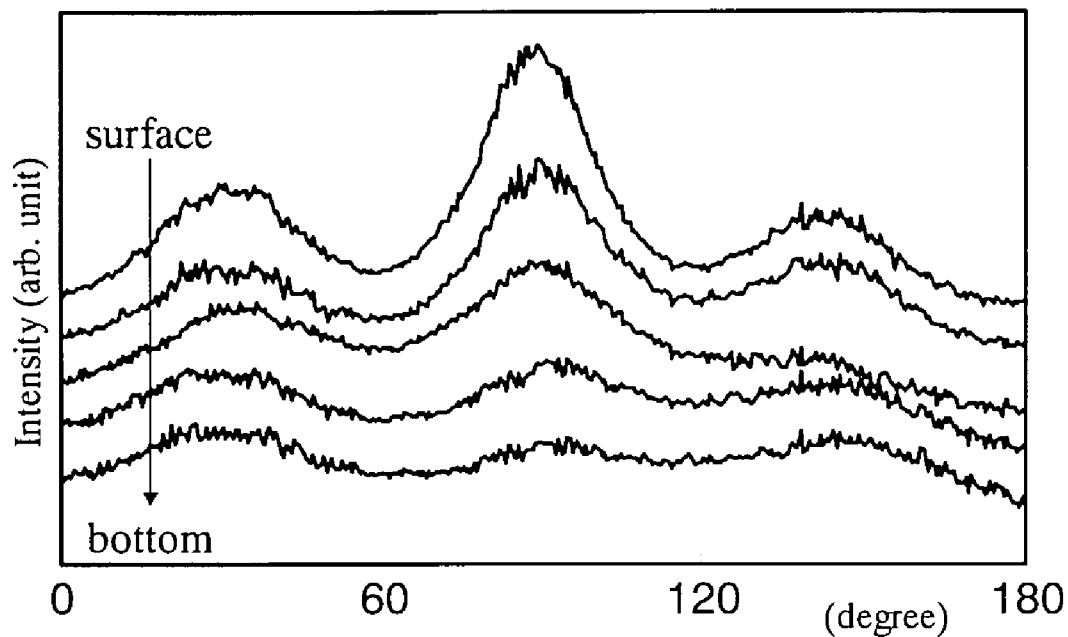


Figure 13(a): Intensity distributions of the circular ring of the (110) crystalline plane (in the bottom-direction)

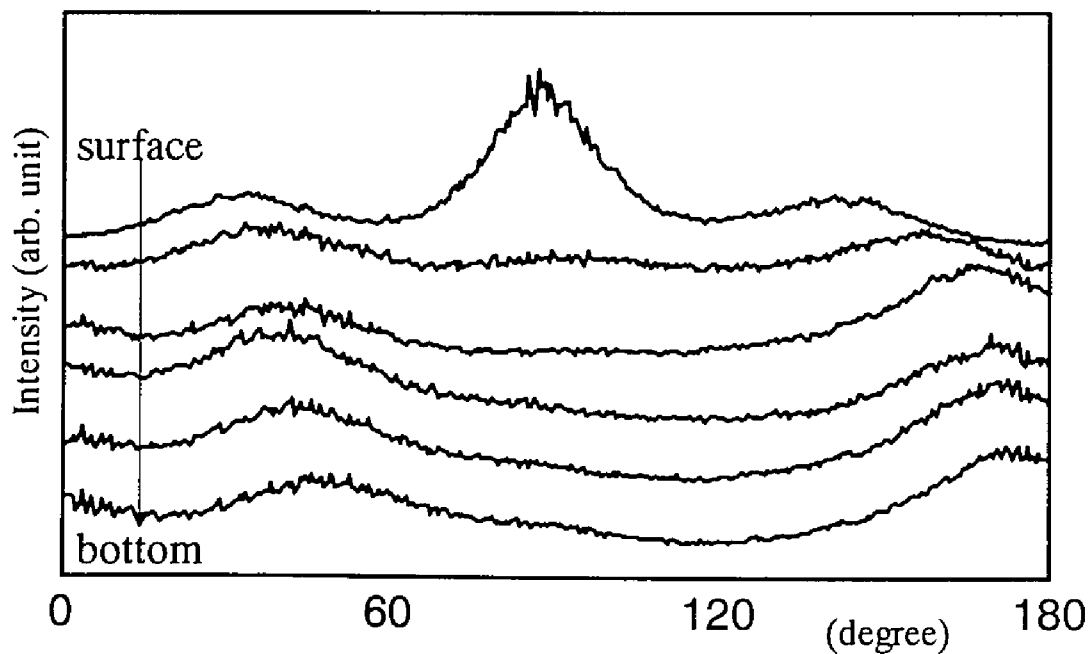


Figure 13(b): Intensity distributions of the circular ring of the (110) crystalline plane (in the 30° direction)

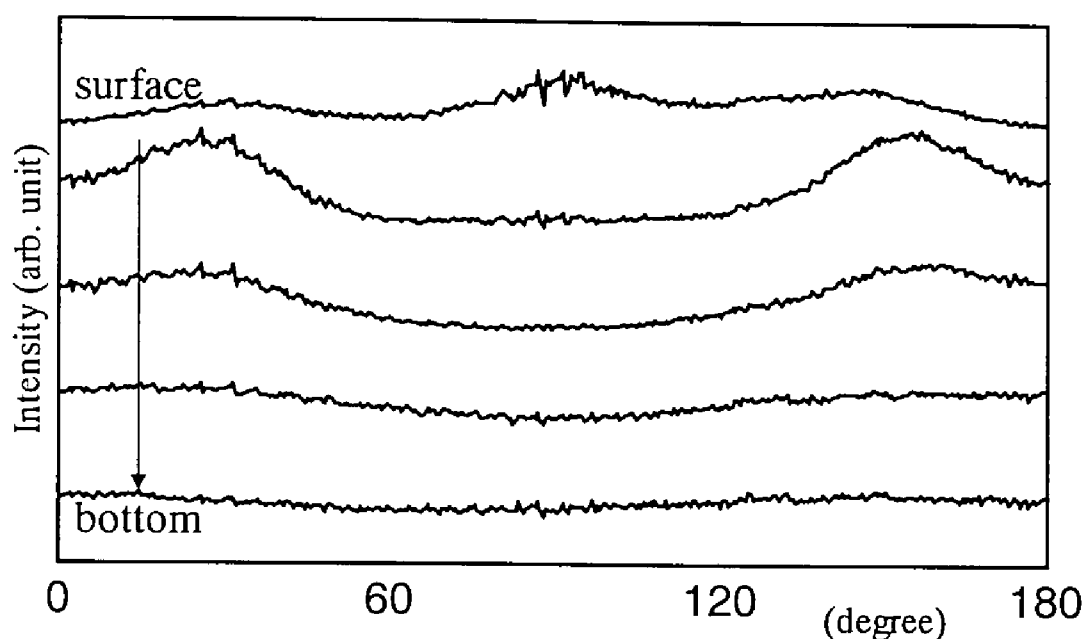


Figure 13(c): Intensity distributions of the circular ring of the (110) crystalline plane (in the 60° direction)

1. It was revealed that all photo patterns were orientated, especially patterns of (b) and (c) were strong orientation. The orthorhombic (110) and (200) reflections of all photos were orientated parallel to the cupped surface, also the (020) crystalline planes of all photos were orientated to perpendicular to the orientation of the (200) crystalline plane. Moreover the (020) in Figure 10 (b) and (c) were not only perpendicular to the (200), but also orientated parallel to the (200), that were orientated parallel to the cupped surface.

The diffraction patterns from the hip sample are shown in Figure 11. The (200) crystalline plane in each photo was orientated parallel to the compressed surface. The (200) crystalline plane in the (c) position may be located off the parallel to the horizontal axis, because the compressed surface drew curve slightly.

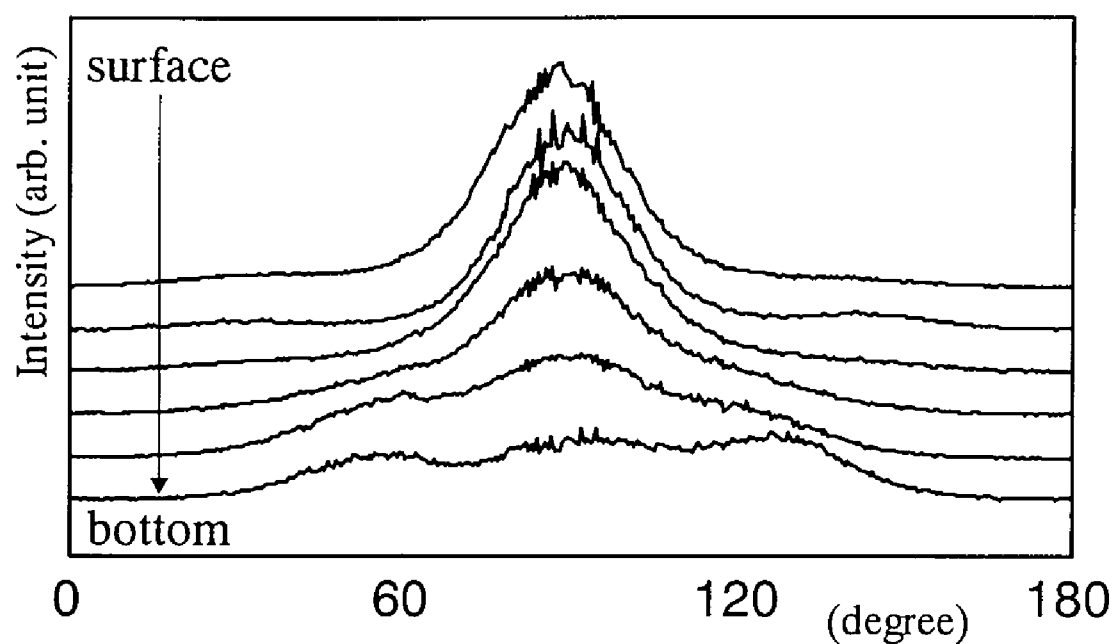


Figure 14(a): Intensity distributions of the circular ring of the (200) crystalline plane (in the bottom-direction)

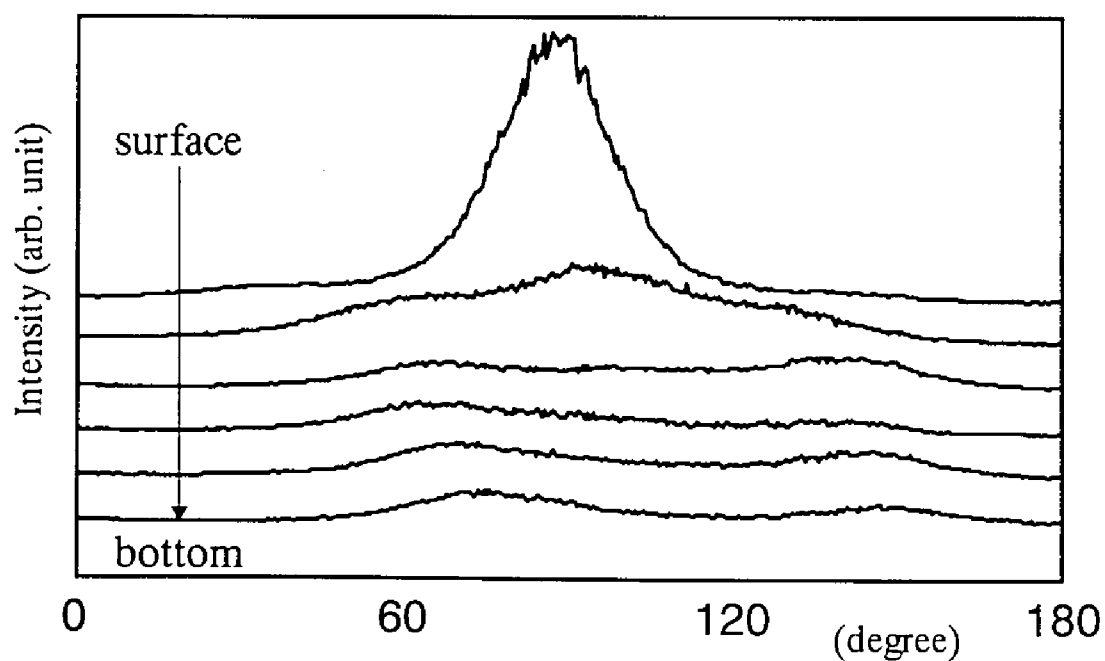


Figure 14(b): Intensity distributions of the circular ring of the (200) crystalline plane (in the 30° direction)

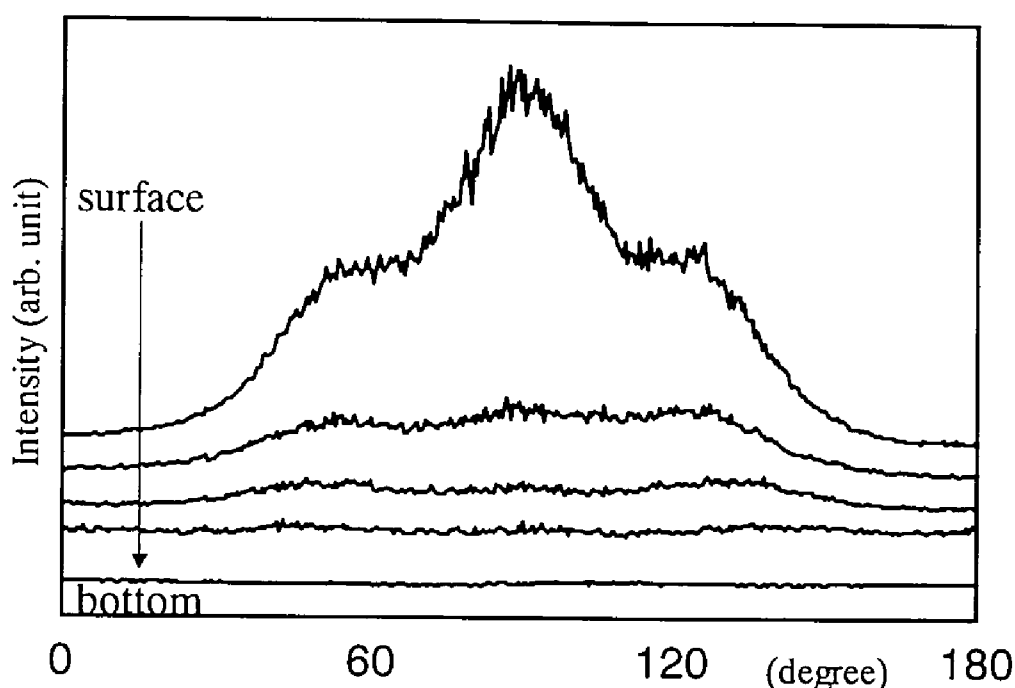


Figure 14(c): Intensity distributions of the circular ring of the (200) crystalline plane (in the 60° direction)

Wide Angle X-ray Diffraction with Imaging Plate

Figure 12 shows curves of X-ray diffractions graph of which the horizontal axis are 2θ at a range between 15° and 30° . There were two peaks in all curves, caused by the diffractions of the (110) and the (200) crystalline planes, respectively. Figure 12(a), 12(b) and 12(c) show curves of diffractions from the bottom direction, the 30° direction, and the 60° direction corresponding to Fig. 2. In the graph of 12(a), six curves show diffraction patterns by every 1 mm steps from the cupped surface to the bottom (referred to Fig. 2). The two peaks near the cupped surface were the highest and the sharpest, also the intensities were gradually decreased in accordance with the depth from the surface. Meanwhile, the peak ratio between the (200) and

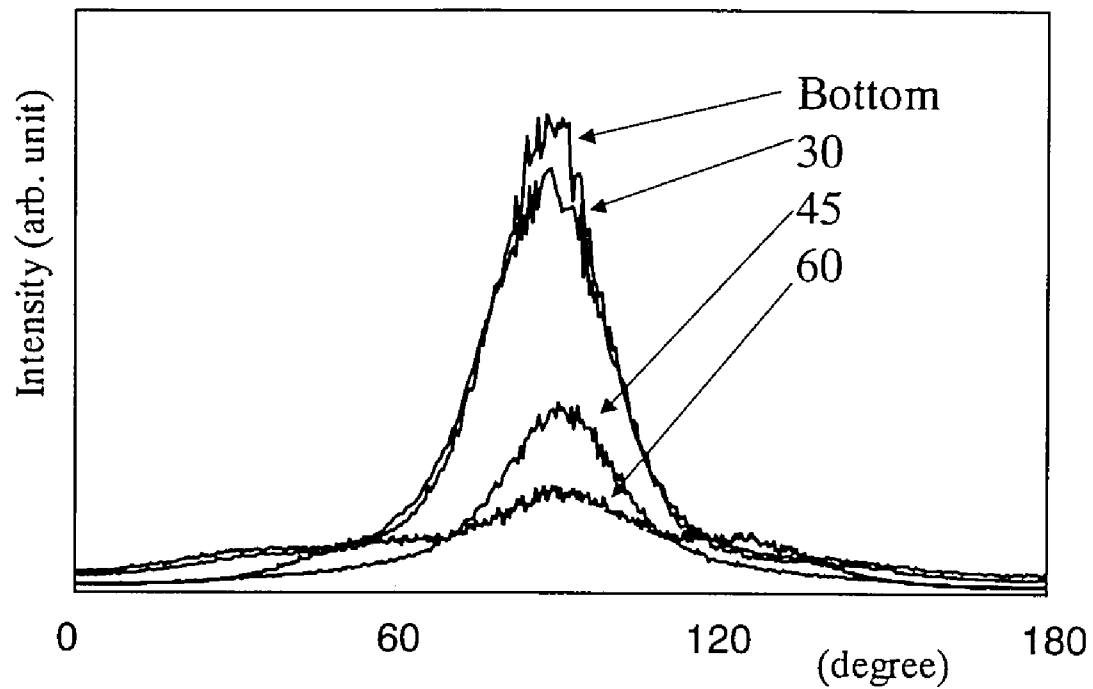


Figure 15: Comparison of the diffraction intensity of (200) crystalline plane from various directions in the 1 mm depth from the cupped surface

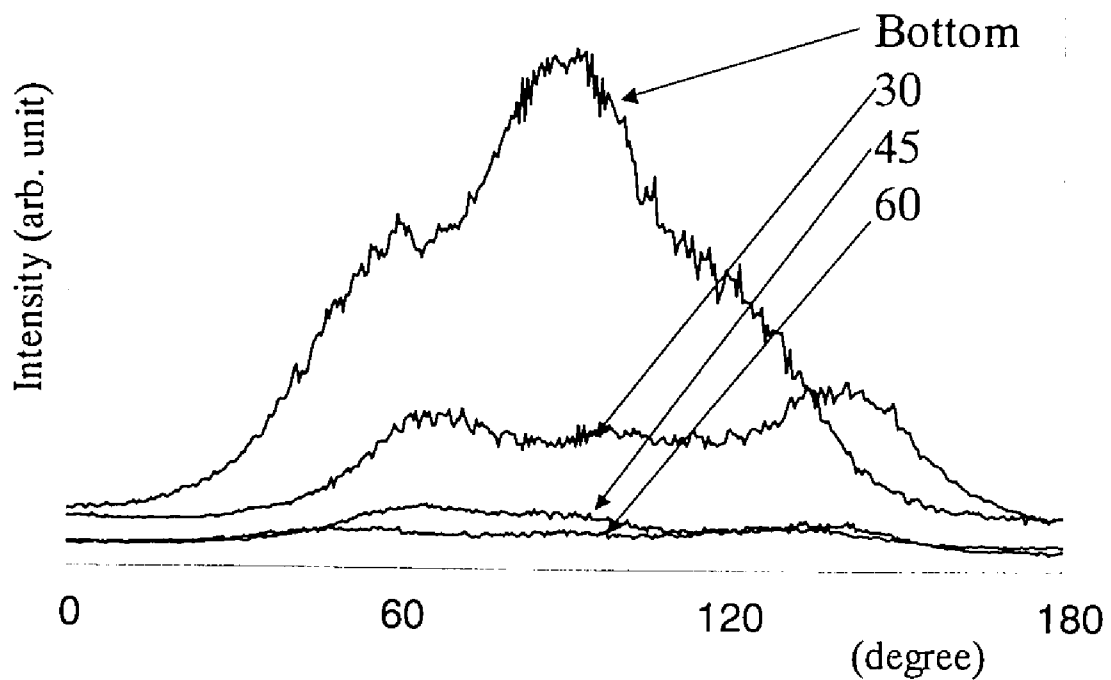


Figure 16: Comparison of the diffraction intensity of (200) crystalline plane from various directions in the 4 mm depth from the cupped surface

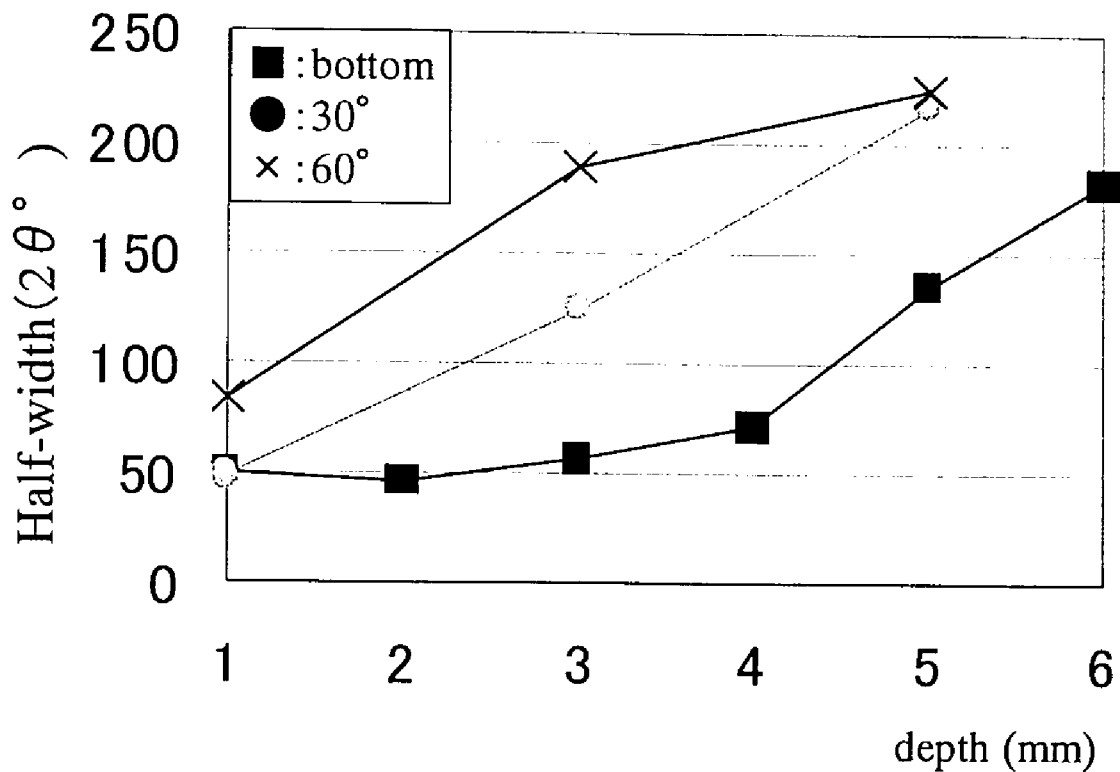


Figure 17: Relationship between the depth and half-width of the (200) crystalline plane

the (110) was high at the deep position, while lower near the cupped surface.

Figure 13 shows intensity distributions of the circular rings from the (110) crystalline plane to investigate the degree of the orientation. Figure 13(a), 13(b) and 13(c) indicate intensities from the bottom-direction, the 30-direction, and the 60-direction, where curves are, similar to Fig. 12, arranged orderly from the cupped surface to the bottom. The equatorial line in the diffraction ring is started from 0 degree a clockwise direction.

There were 3 peaks of the (110) crystalline in all figures, where the peak at 90 degree suggested an orientation parallel to the cup surface. Although there were 3 peaks near the cup surface in Figure 13(b) and 13(c), no peak of 90 degree was

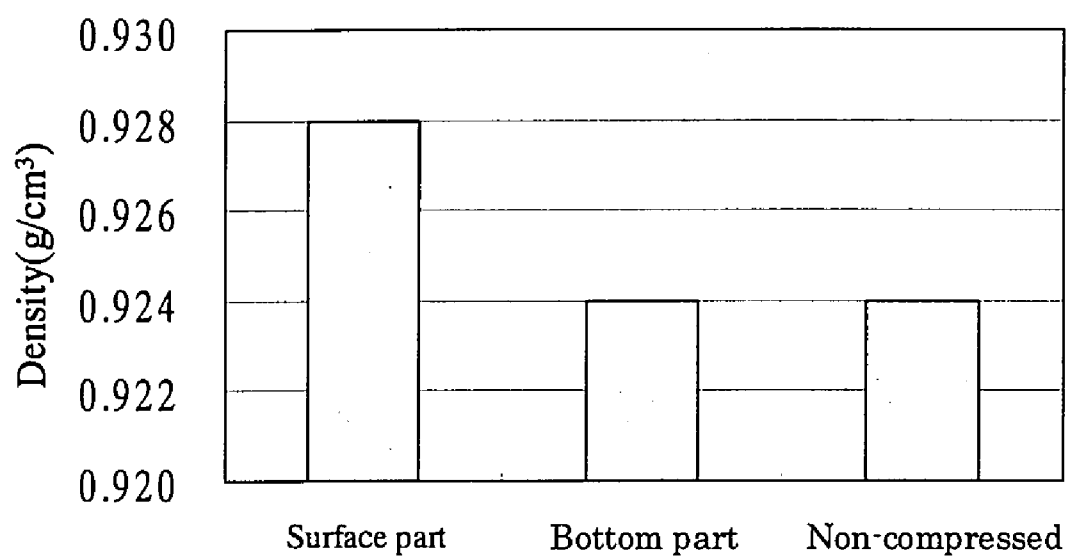


Figure 18: Densities of various parts

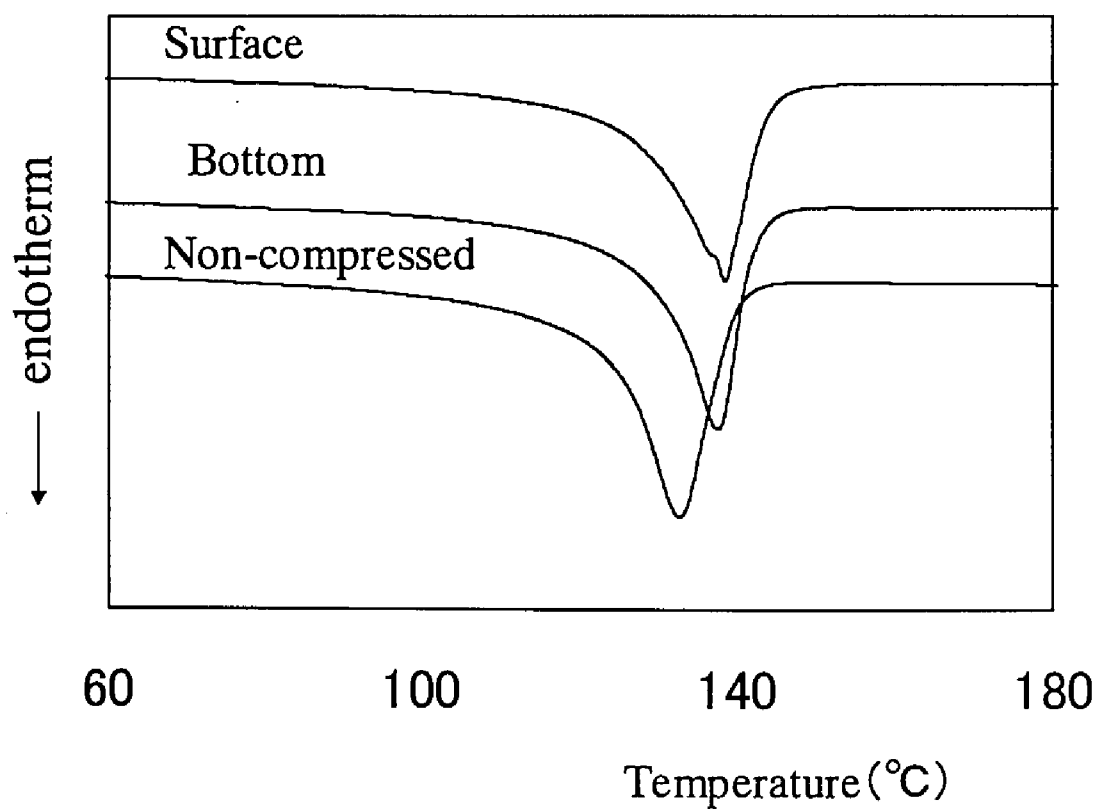


Figure 19: DSC curves of various parts

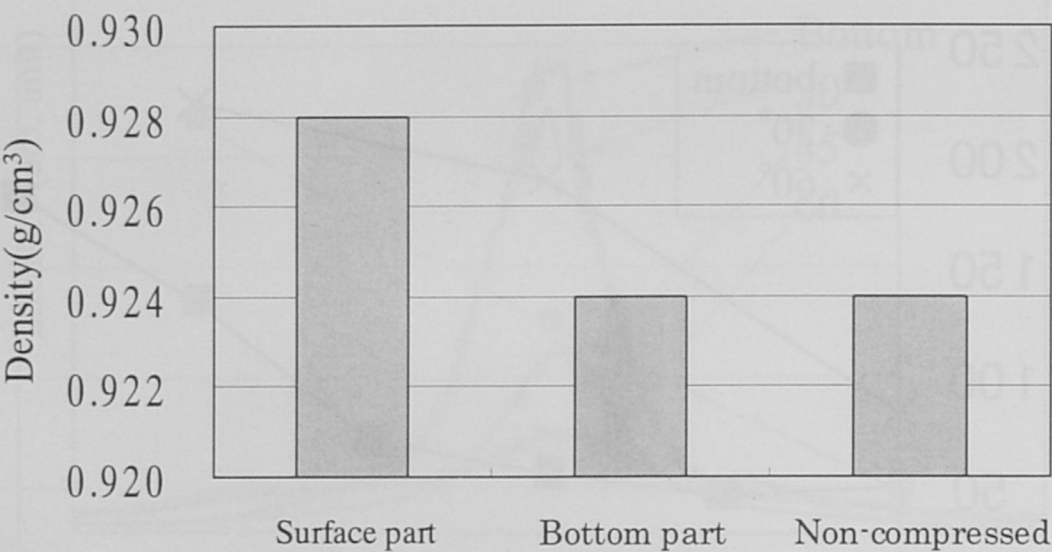


Figure 18: Densities of various parts

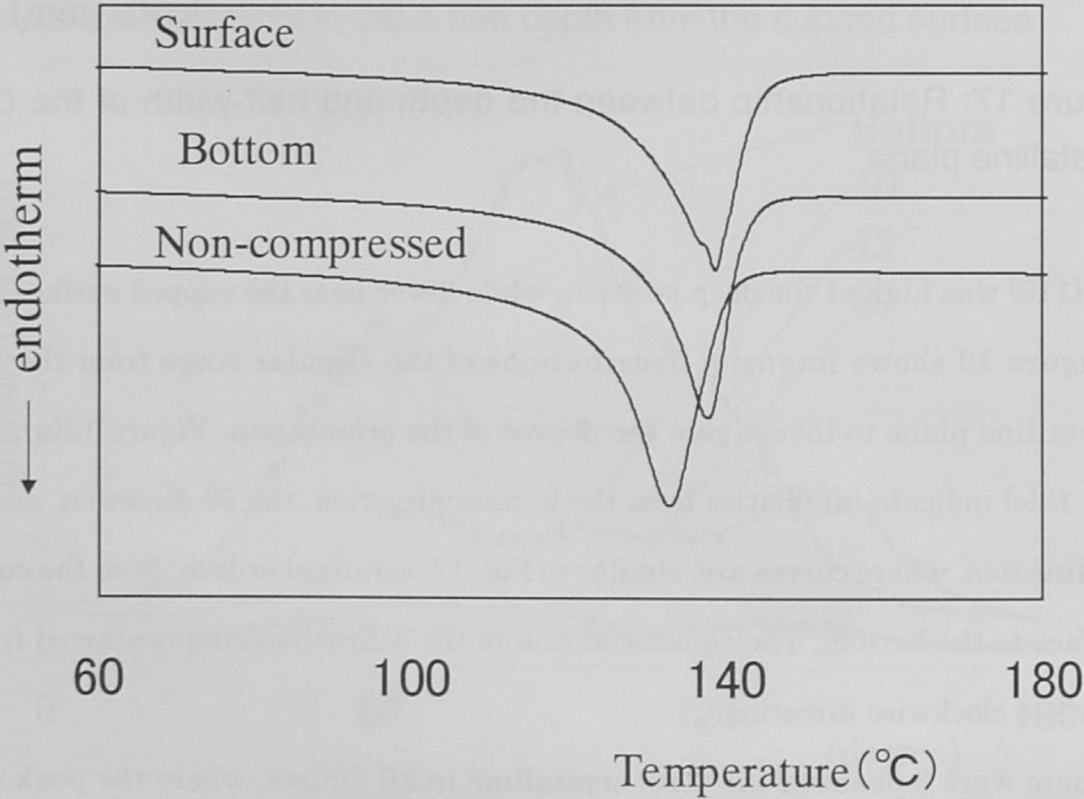


Figure 19: DSC curves of various parts

shown at the deeper depth than 2 mm.

Figure 14(a) shows that the intensity distribution of the (200) crystalline plane in the bottom-direction, also Fig. 14(b) is from the 30°-direction and Fig. 14(c) is the 60°-direction. The diffraction curves formed a peak at about 90-degree in the bottom-direction graph, which meant that the (200) crystalline plane was orientated parallel to the cupped surface. However the peaks at about 90° were also observed in Figure 14(b) and 14(c), the peaks intensities were weakened in accordance with the further deep in the surface, which indicated that the orientation intensities of both Figure 14(b) and 14(c) were weakened fast compared with Figure 14(a). The peak intensity at 1mm depth was about 2.2 times as high as that of 4 mm depth in Figure 14(a), on the other hand, was about 8.5 times high in a case of Figure 14(b).

Figure 15 shows diffraction intensities of the (200) crystalline plane in 1 mm depth from the cupped surface from various directions. The diffraction intensity of the bottom-direction was the highest among all other directions, which means that the degree of orientation of the bottom-direction was the highest in any other directions. The diffraction peak and the degree of orientation were decreased in accordance with the direction angle increase although it was no intensity difference between the bottom and the 30° direction. Figure 16 shows diffraction intensities in 4 mm depth from the surface, and it was revealed that all peaks were broadened, moreover the intensity of 30° direction was observed low compared with the bottom.

Figure 17 shows half-widths of various directions as a function of depth. It was observed that the half-width intensity of the bottom direction was kept up to 4 mm depth and was straightly increased after the 4 mm depth, which was different from the other directions in which half-widths were increased straightly from the surface.

Density measurements

Figure 18 shows densities of various samples, and the upper part of the cupped was the highest among three samples. The degree of crystallinity was calculated from the formula (1) and the upper part was 52.1%, and that of the bottom part was 49.6%. However, that of the non-compression part was 49.3%, therefore it was found that the degree of crystallinity of the upper part was the highest among these samples. It is revealed from these results that there is the difference of 1.1-fold between the degree of crystallinity of the upper part and that of the bottom part, also the degree of crystallinity of the upper part was about 5.6% higher than that of the non-compressed.

Thermal properties

The graph of endotherm curves against temperature measured by DSC was shown in Figure 19. The enthalpy of fusion of the upper part was 166.5 J/g, and that of the bottom part was 160.4 J/g, then it was appeared that the enthalpy of fusion of the upper part was 3.8 % higher than that of the bottom one. The degrees of crystallinity of the upper and the bottom samples were calculated as 57.6% and 55.5%, respectively by using expression 2. However, the enthalpy of fusion of the non-compressed sample was 146.4 J/g, and the degree of crystallinity was calculated as 50.7%, therefore it was revealed that the degree of crystallinity of the upper part was about 13.7% increased compared with that of the non-compressed one. In addition, the melting point of the upper part was 138.7°C, and that of the non-compressed was 132.8°C.

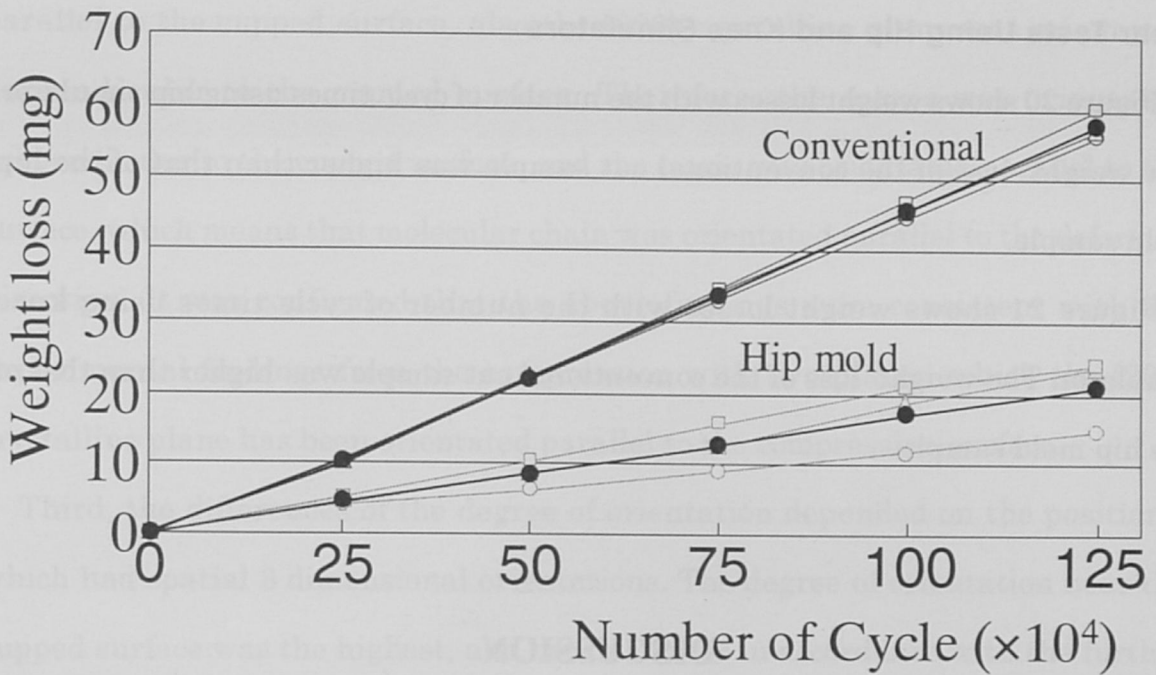


Figure 20: Weight losses of conventional cut sample and hip molded using hip simulator

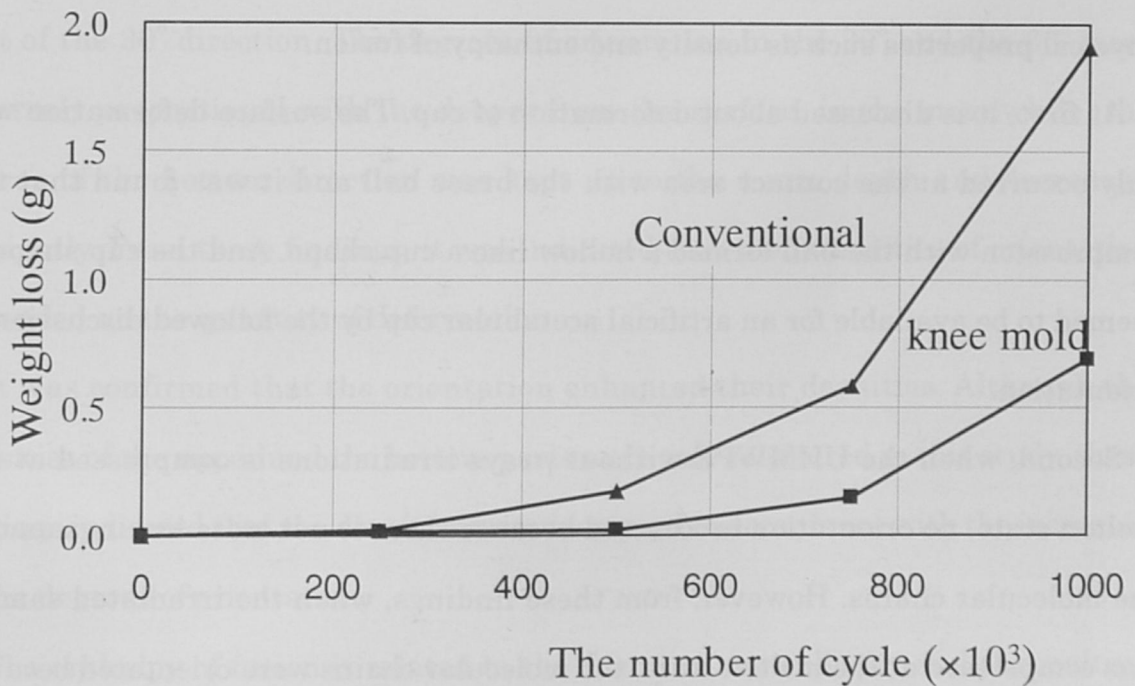


Figure 21: Weight losses of conventional cut sample and hip molded using knee simulator

Wear Tests Using Hip and Knee Simulators

Figure 20 shows weight losses with the number of cycle times using hip simulator. The weight loss of the conventional cut sample was higher than that of the hip mold sample.

Figure 21 shows weight losses with the number of cycle times using knee simulator. The weight loss of the conventional cut sample was higher than that of the hip mold sample.

DISCUSSION

The results of this study clearly indicate that the relationship between the 3-dimensional orientation of the crystalline plane by a ball compression and their physical properties such as density and enthalpy of fusion.

At first, it is discussed about deformation of cup. The surface deformation was only occurred at the contact area with the brass ball and it was found that the compression with the ball formed a hollow like a cup shape. And the cup shape is seemed to be available for an artificial acetabular cup by the followed discussion of orientation.

Second, when the UHMWPE without γ -rays irradiations is compressed at the molten state, no orientation is occurred because there is not cross-linkings among the molecular chains. However, from these findings, when the irradiated sample was compressed at the molten state, the molecular chains were orientated because of cross-linking. It was observed that the (200) crystalline plane was orientated

parallel to the cupped surface, also the (020) crystalline plane was orientated perpendicular to the cupped surface. Therefore, the a-axis was orientated perpendicular to the cupped surface, and the c-axis was orientated parallel to the surface, which means that molecular chain was orientated parallel to the deformed direction. It was confirmed that the above findings were consistent with the experimental findings from the compression with two plates, which the (200) crystalline plane has been orientated parallel to the compression surface.

Third, the differences of the degree of orientation depended on the positions, which had spatial 3 dimensional orientations. The degree of orientation near the cupped surface was the highest, and became lower in accordance with the further the surface. In addition, the orientation also depended on the directions. There were differences of the decline rates of orientation among directions, and it was shown that the decline rate of orientation of the bottom direction was lower than that of the 30° direction. The degrees of orientation in the 30° and the 60° were inversely proportional with the deeper from the surface, in the meanwhile, the degree of the bottom direction was kept up to the 4 mm depth and decreased straightly. From these findings, it was indicated that the intensities of orientation depended on the quantity of deformation.

It was confirmed that the orientation enhanced their densities. Although the densities of the upper and the bottom parts were only measured in this study, these findings indicated that the densities were increased in accordance with the increases of the degrees of orientation.

The enthalpy of fusion is related to the degree of crystallinity and the melting point is connected with the thickness of lamella. The enthalpy of fusion and the melting point of the upper sample were enhanced compared with the non-compressed,

also it was appeared that the findings of the density were consistent with the DSC findings.

From these discussions, it was suggested that the 3-D orientation had the gradient orientation that combined raw and new material properties. Therefore it was indicated that the new UHMWPE was maintained a raw property such as an impact resistant properties.

The wear test findings suggested that the compressed sample decreased the wear resistant properties of artificial hip and knee joints. From the previous chapter, the wear tests were only performed using pin-on-disc and pin-on-flat. The findings in this chapter was based on the simulators. Thus, these wear conditions were similar to the joints. Moreover, the findings suggested that the orientated crystallization increased their wear resistant properties and the orientation method can develop the artificial joints with excellent wear resistance.

CONCLUSION

These experiment results revealed these following characteristics.

1. A slightly cross-linked UHMWPE was compressed with a brass ball, and a hollow was formed along the ball on the surface, which the hollow surface was available to an acetabular cup surface.
2. When the X-ray was irradiated perpendicular to the cupped surface in order to study orientation, it was observed that the crystal plane (110) and (200) were orientated parallel to the cupped surface.
3. There were differences of the degree of orientation in various positions, and the

difference depended on the depth. The degree of orientation of upper sample was higher than that of the bottom.

4. The degree of orientation also depended on direction to the cupped surface. The degree of orientation at the bottom direction was the highest among other directions.
5. The density, the enthalpy of fusion, and the melting point of the upper part was higher than those of the bottom part. And it was confirmed that there were relationship between the orientation and those material properties.
6. The wear resistances of the compressed sample were higher than those of the non-compressed sample based on hip and knee simulators.
7. Slightly cross-linked UHMWPE, which was crystallized from the melt under uni-axial compression with 3-D orientation, was useful for artificial joint cup.

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SUMMARY

Chapter 1. Ultra high molecular weight polyethylene (UHMWPE) has been performed well as a bearing material of acetabular prosthesis components in total joint replacement for more than thirty years. Although it has been used widely, friction between bearing surfaces between acetabular and femoral components leads to generation of wear debris in a contact parts of joint cavities. In this chapter, the relationship between orientation and the anisotropic material properties was clarified. The structure and the dynamic mechanical properties of the compressed sample were studied by wide angle X-ray diffraction and viscoelastic rheometer. It was found that the (200) crystalline plane of the compressed sample was orientated parallel to the compressed surface.

The conduction velocity of ultrasonic waves on the compressed surface was faster than the other surfaces, also the compressed surface was about 10% hardened. The storage modulus of the compressed sample was also higher than that of the non-compressed sample at room temperature and the intensity of the γ -relaxation of the compressed sample was lower than that of the non-compressed one. However, the peak of the α_c loss modulus of the compressed sample shifted to higher temperature according to the compression.

Chapter 2. In this chapter, friction and wear tests were carried out using six-station reciprocating pin-on-flat apparatus. It was revealed that the wear factor of the compressed sample was lower than that of the non-compressed sample. The high compression ratio decreased the wear factor, as compared to that of the uncompressed

Summary

sample. And also, the compressed samples appeared harder than the both of annealed and uncompressed samples in Vickers hardness measurements. The hardness increased with the increase in the compression ratio increase. The findings of Vickers hardness, wear test, and AFM observations provided clear experimental evidence for the improved wear resistance properties of the compressed UHMWPE.

Chapter 3. The purpose of in this chapter is that the comparison of wear test with a compressed UHMWPE and an original one using several wear machines. The findings of the wear tests with pin-on-disc suggested that the wear factor of the compressed UHMWPE was enhanced and also the findings from chapter 2 that the wear factor depended on the compression ratio was confirmed. The findings of pin-on-flat wear test in NRIM showed that the wear factor of the compressed UHMWPE was 1/35 -fold as high as that of the non-compressed one. The orientation of the NRIM specimen was revealed from the results of WAXD that the pattern had distinct six points maxima for the (110)-diffraction observed. These points would be caused by rather perfect orientation of both crystal planes, (200) and (110). The pin-on-flat reciprocating wear test was carried out using specimens that were cut from different directions. The one specimen base was from the X-Y plane and the other was from the X-Z plane. The wear factor of the X-Y plane was lower than that of the X-Z plane.

Chapter 4. When a crystalline piece of sample is deformed elastically in such a manner that the strain is uniform over relatively large distances, the lattice plane spacing in the crystal form change from their stress-free value to some new value corresponding to the magnitude of the applied stress. The uniform macrostrain

causes a shift of the diffraction lines to new 2θ positions. From this degree of shift the strain may be calculated and, knowing the strain, the stress present can be determined. In general, the effect of residual stresses is the same as the effect of stress with a mechanical load, therefore a compressed residual stress causes strength of fatigue to increase, while a tensile one causes fatigue to decrease. In this chapter, measurements of residual stresses were performed with UHMWPE for an artificial joint to investigate affect of compression. If compressed residual stresses are existed in a sample, the fatigue of the sample can be enhanced. However, when residual stresses are released by wear, the shape may be deformed markedly. The $\sin^2\psi$ method with the X-ray diffraction technique was carried out and 135° of 2θ was used for measurements. The stress constant of samples was based on the findings of the dynamic modulus. Two different samples were prepared. The one is a compression of a slightly cross-linked UHMWPE at molten state (Sample A), and the other one (Sample B: compressed at 120°C , Sample B': compressed at 80°C) is a compression of an original UHMWPE below the melting point. The residual stresses of Sample A and the original UHMWPE were not observed, while there were tensile stresses in Sample B. Measurements of shrinkage as a function of temperature, were indicated the existence of residual stresses in the amorphous phase of Sample B and Sample B'. When the temperature of all samples was increased from 0°C to 130°C at $2^\circ\text{C} / \text{min}$, Sample B was shrunk at 80°C and, moreover, Sample B' was shrunk under 60°C , while Sample C and Sample A were not shrunk over 130°C . These findings show that all these orientated samples including Sample A have a property in shrinkage with a function of temperature, because of the existence of orientation in the crystalline phase. It was confirmed that the differences of shrinkage between Sample B and Sample A depended on the differences of state in

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the amorphous phase. The amorphous phases in Sample B and Sample B' were strained, while the phase in Sample A was relaxed.

Chapter 5. Two kinds of molding method were investigated, to compare with wear properties for an artificial joint bearing material. One was a compression of a slightly cross-linked UHMWPE at the molten state (Sample A), and the other (Sample B) was a compression of an original UHMWPE below the melting point. Half-widths of both samples with the (200) crystalline plane were the almost same. The heat of fusion and the density of Sample A were higher than those of Sample B. The storage modulus of Sample A was always higher than the original untreated UHMWPE (Sample C), while Sample B was decreased suddenly with increasing temperature. The α_c -peak was sifted to about 5°C higher temperature, however, Sample B was shifted to lower a temperature and the β -peak disappeared. The wear factor of sample A was extremely lower than that of Sample B which was the same as Sample C.

Chapter 6. A slight cross-linked UHMWPE was crystallized from the molten state under 3-D compression and the orientation of the sample was studied by using a wide angle X-ray diffraction. The sample surface was compressed by pushing a brass ball to dent it along the ball and was compressed to a hollow. The hollow was like an artificial hip cup. When X-ray beams were irradiated perpendicular to the surface of the cupped sample, it was observed that the crystal planes (110) and (200) were orientated parallel to the cupped surface. The degree of orientation in 30-degree direction was gradually lower at deeper positions from the surface, while the orientation in the bottom direction was maintained up to 4 mm depth. The

melting point and the density near the cupped surface were relatively high compared with the bottom part. This newly molded method suggested the fabrication possibility of manufacturing the artificial acetabular cup with excellent wear properties. The wear tests were performed using hip and knee simulators, and these findings suggested that the wear resistant properties of the orientated samples increased compared with the conventional cut sample. In summary, the crystalline phase of slight cross-linked ultra-high molecular polyethylene, crystallized under uniaxial compression, was orientated parallel to the compressed surface. The mechanical properties were enhanced and it also was confirmed that the structure and the material properties were consistent with the wear properties.

Summary

LIST OF PUBLICATIONS

Chapter 1.

- (1) Makoto Ohta, Suong-Hyu Hyon, Yu-Bong Kang, Sadami Tsutsumi, Masanori Oka, Syozo Murakami, Shinzo Kohjiya, Dynamic Modulus Measurements of a Slightly Cross-linked Ultra-high Molecular Weight Polyethylene Crystallized under Uniaxial Compression, *Russian J. Biomech*, vol. 3(4) (1999) pp.34-48

Chapter 2.

- (2) Makoto Ohta, Suong-Hyu Hyon, Masanori Oka, Sadami Tsutsumi, Wear Resistance of Lightly Cross-linked Ultra-high-molecular-weight polyethylene crystallized from the Melt under Uniaxial Compression, *Wear*, vol. 225-227/1-2 (1999) pp.312-318

Chapter 3.

- (3) Makoto Ohta, Suong-Hyu Hyon, Yu-Bong Kang, Masanori Oka, Sadami Tsutsumi, Syozo Murakami, Shinzo Kyohjiya, Wear Properties and Mechanical Properties of Slightly Cross-linked Ultra-high Molecular Weight Polyethylene Crystallized under Uniaxial Compression, *Zairyo*, vol. 49(12) (2000), in press

Chapter 4.

- (4) Makoto Ohta, Suong-Hyu Hyon, Yu-Bong Kang, Masanori Oka, Sadami Tsutsumi, Effect of Compression Ratio on Wear Properties of Slightly Cross-linked Ultra-high Molecular Weight Polyethylene Crystallized under Uniaxial Compression, *Wear* (2000), to be submitted

Chapter 5.

- (5) Makoto Ohta, Suong-Hyu Hyon, Yu-Bong Kang, Masanori Oka, Sadami Tsutsumi,

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Syozo Murakami, Shinzo Kohjiya, Comparison of Wear Properties of Orientated UHMWPE under Uniaxial Compression at Melted State and at Under Melting Point, J. Biome. Mater. Res. (2000) to be submitted

Chapter 6.

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- (11) Suong-Hyu Hyon, Makoto Ohta, Yu-Bong Kang, Sadami Tsutsumi, Masanori Oka, New molding method of UHMWPE cup for artificial hip joint, Japanese Society of reconstructive arthroplasty, vol.29 (1999) pp.271-272
- (12) Makoto Ohta, Suong-Hyu Hyon, Yu-Bong Kang, Sadami Tsutsumi, Hiroataka Tanabe, Yoshio Miyoshi Residual stress measurements of lightly cross-linked UHMWPE crystallized under uniaxial compression for artificial joints, Journal of Japanese Society for Clinical Biomechanics and Related Research, vol.21 (2000) pp.319-322

List of Publications

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