National Institute of Standards & Technology

Report of Investigation

Reference Material 8385

Ultra-High Molecular Weight Polyethylene Wear Particles

This Reference Material (RM) consists of five ampoules containing five distinct wear particle populations generated by rubbing gamma-irradiated, ultra-high molecular weight polyethylene (UHMWPE) pins against textured chromium-coated silicon surfaces with various sizes and shapes of micro-cutting edges. Controlled size and shape wear particles were generated by wear tests according to ASTM F-732 test method [1] in autoclaved distilled water. Three round particles with nominal diameters of 2 µm, 7 µm, and 12 µm and two elongated particles with nominal lengths of 9 µm and 18 µm and aspect ratios of 2 and 4, respectively, were produced. These narrowly distributed wear particles can be used for comparison purpose for retrieved particles analysis and for bioactivity testing. The particles are packed into 5 ml amber, flame-sealed vials.

Reference Values: A NIST Reference value is a non-certified value that is the best estimate of the true value; however, the value does not meet NIST criteria for certification and is provided with associated uncertainties that may reflect only measurement precision and may not include all sources of uncertainty [2]. The RM consists of five wear particle populations with distinct sizes and shapes. Three particle populations are round in shape and two particles are elongated in shape. Since the particles were generated by a wear process, precise control of size and shape was not feasible. Therefore, the particle size population is characterized by the median of the particle size distribution (i.e., the particle size at which half of the population is larger and half of the population is smaller). Since the particle size distribution is skewed by design, the median is a better indicator of the particle size. The references particle size population is given in Table 1.

The particles are contained in an amber vial, flame-sealed under Argon atmosphere. We certify that each ampoule contains at least a minimum number of 1×10^5 particles in distilled, autoclaved water containing HCl. The water is controlled at a pH of 3.7, which is the approximate isoelectric point of the particles in water.

Table 1. Reference Particle Size Populations

Particles	R1	R2	R3	E1	E2
Median Diameter (µm)	2.43 ± 0.13	6.62 ± 0.52	12.43 ± 1.40		
Median Major length (µm)				9.37 ± 0.36	18.28 ± 2.45
Median Aspect Ratio				1.89 ± 0.10	4.03 ± 0.39

Expiration of Reference Values: The certification of this RM is valid, within the measurement uncertainty specified, until **21 May 2012**, provided the RM is handled in accordance with instructions given in this certificate (see "Storage and Handling").

This RM was prepared by H.W. Fang, Y. Liang, and P.P. Kavuri (NIST Research Associates) in collaboration with S.M. Hsu of the NIST Ceramics Division. The reference value measurements were performed by Y. Liang.

Debra Kaiser, Chief
Ceramics Division

Gaithersburg, MD 20899
Certificate Issue Date: 05 October 2007

Robert L. Watters, Jr., Chief
Measurement Services Division

Statistical analysis was provided J. Lu and C.R. Hagwood of the NIST Statistical Engineering Division.

Support aspects involved with the certification and issuance of this RM were coordinated through the NIST Measurement Services Division.

Maintenance of RM Certification: NIST will monitor this RM over the period of its certification. If substantive changes occur that affect the reference values before the expiration of this report, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

Storage and Handling: These ampoules should be stored in a cool, dark place to avoid ultra-violet light exposure, which may cause oxidation of the polymer. The ampoule should be opened in a clean, preferably sterile environment and sterilized immediately, either by boiling water or immersed in a 50:50 alcohol to water solution before use.

PREPARATION AND ANALYSIS[1]

Material Acquisition and Preparation: The ultra high molecular weight polyethylene was from a reference material UHMWPE (GUR 415) obtained from The Hospital for Special Surgery (New York City, NY). This material is an industrial standard with well-defined material properties. Wear pins were machined from this stock and sent to Biomet Corporation (Warsaw, IN) for gamma irradiation prior to the wear process. The gamma irradiation was performed to simulate, as close as possible, how the hip replacement material is fabricated and sterilized as well as to induce a reasonable level of cross-linking similar to the current orthopedic joint replacement part materials.

Sterility: The particles are NOT certified to be sterile and the user is encouraged to sterilize the particles before use in bioactivity tests. However, every precaution has been taken to prevent extraneous particle contamination and each ampoule has been gamma irradiated at 28 kGy after bottling to minimize potential bio-contamination and to ensure stable shelf life.

CAUTION: Reference values are based on pre-irradiation data. The process of irradiation may slightly increase the particle size.

Packaging and Bottling: The particles were packed into 5-ml ampoules by using the ampouling machine (Cozzoli Machine Company) at NIST. Before packing, the particles were diluted in the purified water to a certain dilution rate. In order to pack the particles uniformly into the ampoules with the desired minimum particle number of 1.0×10^5 per ampoule, the crucial issue was that the particles must disperse in the solution uniformly before the packing. To solve this problem, the purified water, used as the packing solution, was adjusted via incorporation of HCl pH $\approx$ 3.7 (Zeta-potential measurement shows that the electric charging level of the generated particles tends to be zero as pH $\approx$ 3.7) and mechanical energy was introduced by using a stirring device. All the parts involved were cleaned with a 50:50 alcohol to water solution to provide a clean environment. The ampoules were flame-sealed immediately after bottling.

Generation of UHMWPE Particles: The wear particles were generated by rubbing gamma-irradiated UHMWPE pins against textured surfaces in distilled, filtered, and autoclaved water in several pin-on-disk reciprocating wear machines. The machines were cleaned with a 50:50 solution of alcohol to water and covered by cleaned plastic films during operation.

[1] Certain commercial equipment, instruments, or materials are identified in this report to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Five distinct sizes and shapes of wear particles were generated by using different surface textured patterns. Figure 1 shows the textured surfaces and typical particles are shown.

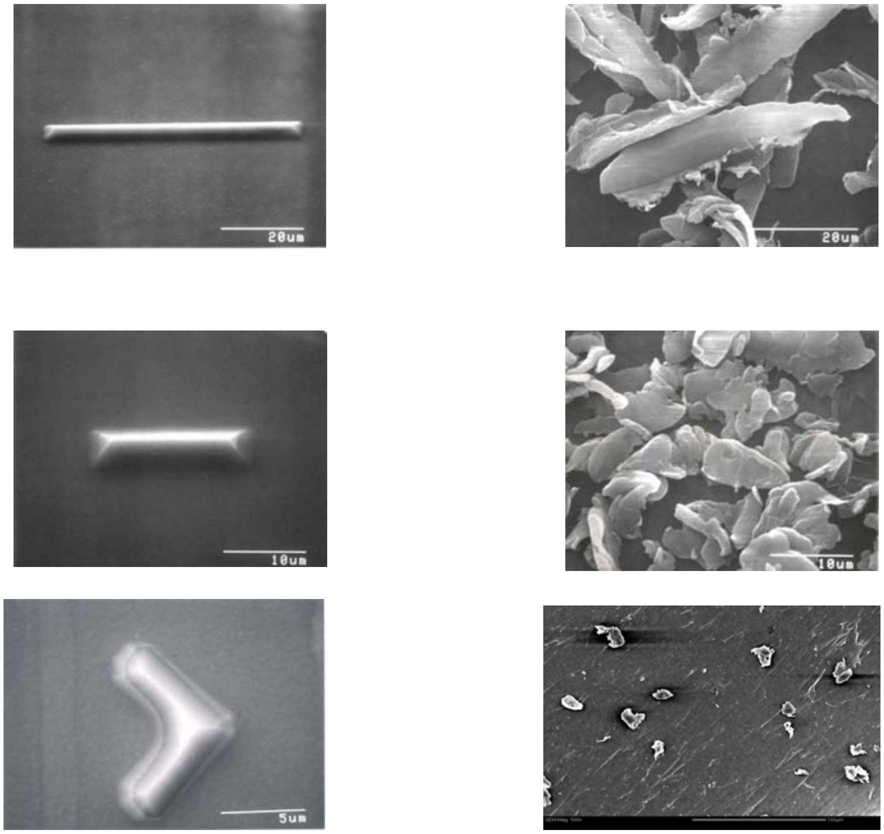

Figure 1. Surface textured patterns made on silicon surfaces using micro-lithography in order to generate a controlled size and shape of wear particles. A protective film of chromium oxide was deposited on the features for durability.

Three round particles with various diameters and two elongated particles with two different aspect ratios and lengths were generated.

Measurement of Particle Size and Shape: To characterize the size and shape of the generated particles, the packed particles were sampled and the particle size measured.

The Sampling Procedure: Ten random ampoules were taken from each particle batch and the contents were mixed with a surfactant (0.02 volume % surfactant) for dispersion control. The solution was ultrasonically mixed for 15 minutes to obtain a uniform dispersion. The contents were divided into four equal portions and each portion was filtered on a 0.1 µm Millipore filter. These filters were mounted on scanning electron microscope (SEM) stubs and gold-coated for SEM analysis.

Measurement of Particles: To measure the particle size, the filters were observed using a SEM. Seven areas on the filter were measured and the particles were measured by using particle analysis software (Scion Image, Scion Corporation; Frederick, MD). For round particles, the particle area (A) was measured and the equivalent diameter D calculated using

$$D = \sqrt{\frac{4A}{\pi}}\ .$$

For elongated particles, the major axis (L) and minor axis (W) were measured, and the aspect ratio

$$AR = \frac{L}{W}$$

and length (L) were determined. Shown below are the typical particle size distributions for round particles, R1-R3.

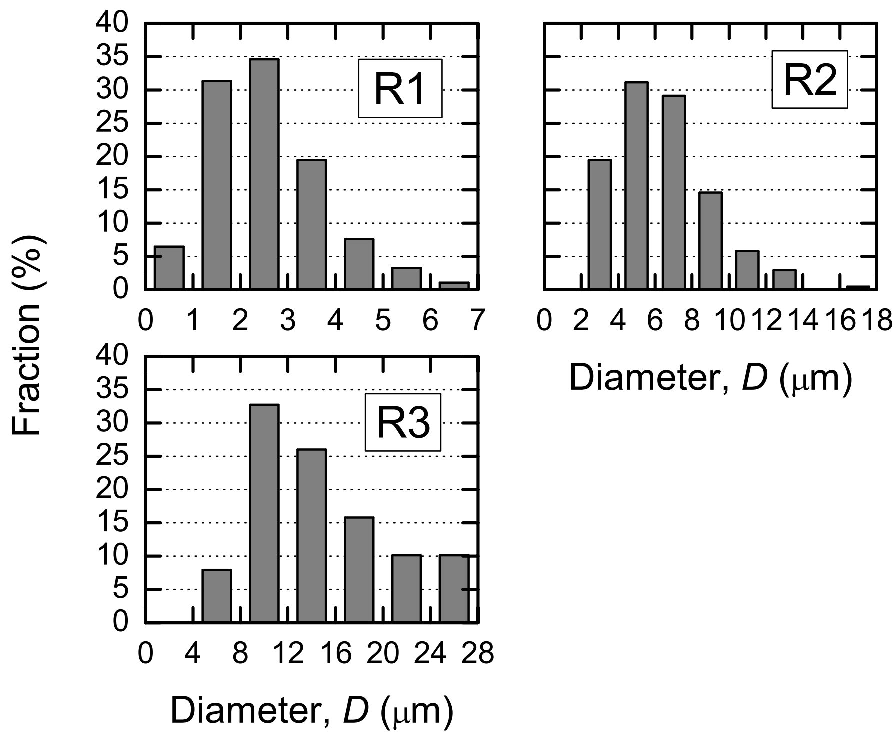

Figure 2. Typical distributions of round particles.

For elongated particles, distributions of the major length and aspect ratio for each population of particles are shown below (these distributions are typical distributions; variants are reflected by the reported statistics).

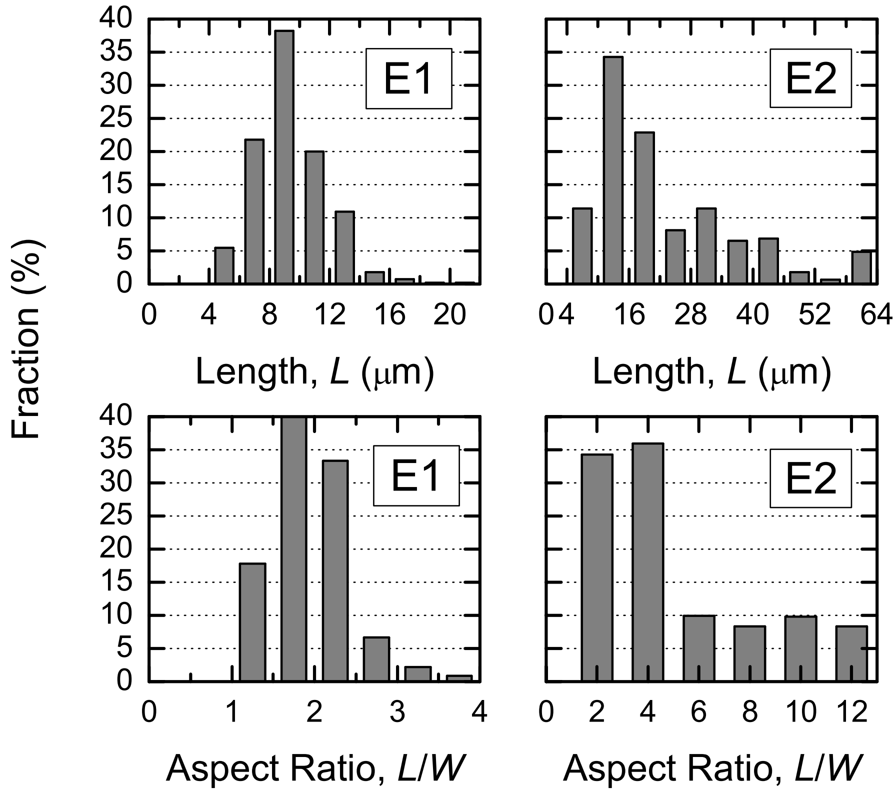

Figure 3. Particle size distributions for elongated particles and their aspect ratio distributions.

Statistical Analysis of Particle Size and Shape: The particle size data were analyzed by the Statistics Engineering Division at NIST. Since the particle size distribution is skewed and non-Gaussian, the sample median, defined as the particle size at which half of the population of particles is larger and half of the population is smaller, is chosen to certify the particle populations in this certification. The uncertainty for the sample median can be approximated by its asymptotic variance which is given by

$$\frac{1}{4 \times f^2(h)n},$$

where n is the sample size and f is the density function evaluated at median, h.

Inter-quartile range (IQR) was used to measure the spread of size distribution, which describes the distance between the 25 % quartile and 75 % quartile, and provides a measure of the breadth of the interval within which 50 % of the particles are contained.

Information Values: A NIST information value is considered to be a value that will be of interest and use to the RM user, but insufficient information is available to assess adequately the uncertainty associated with the value or only a limited number of analyses were performed. Information values pertaining to more detailed statistical analysis data are provided in Tables 2 and 3 for the round and elongated particles, respectively. The average median of the various ampoules from each particle is shown with the estimated standard error of the median. The standard uncertainty includes both the variation in individual sample medians (between-ampoule variation) and the uncertainty estimate based on bootstrap method (within-ampoule uncertainty); the expanded uncertainty interval (at 95 % level) for the median of an average ampoule may be interpreted as the predictive intervals for median for a typical ampoule in the population.

Table 2. Information Values for Diameter of the Packed Rounded UHMWPE Particles

Statistical Measurand	R1	R2	R3
Average Median for Particle Diameters (µm)	2.43	6.62	12.43
Standard Error of Median Estimate (MSE) (µm)	0.13	0.52	1.40
The Expanded Uncertainty Interval for Median (µm)	(2.17, 2.69)	(5.57, 7.66)	(9.63, 15.23)
The Average Interquartile Range (IQR) (µm)	1.45	3.74	7.80
Standard Error of Estimated IQR (µm)	0.23	0.55	1.60
The Expanded Uncertainty Interval for IQR (µm)	(0.99, 1.91)	(2.64, 4.84)	(4.0, 11.0)

Table 3. Information Values for Aspect Ratio and Length of the Packed Elongated UHMWPE Particles

Statistical Measurand	E1		E2	
	AR[(a)]	L[(b)] (µm)	AR[(a)]	L[(b)] (µm)
Average Median	1.89	9.37	4.03	18.28
Standard Error of Median Estimate (MSE)	0.10	0.36	0.39	2.45
The Expanded Uncertainty Interval for Median	(1.69, 2.09)	(8.65, 10.09)	(3.25, 4.81)	(13.38, 23.18)
The Average Interquartile Range (IQR)	0.57	2.65	3.47	15.77
Standard Error of Estimated IQR	0.10	0.73	0.76	4.10
The Expanded Uncertainty Interval for IQR	(0.37, 0.77)	(1.19, 4.11)	(1.95, 4.99)	(7.57, 23.97)

[(a)]AR – aspect ratio of the particles
[(b)]L – length of the particles

REFERENCES

[1] ASTM F723-00: Standard Test Method for Wear Testing of Polymeric Materials Used in Total Joint Protheses; Annu. Book ASTM., Vol. 13.01 (2007).

[2] ISO; *Guide to the Expression of Uncertainty in Measurement*; ISBN 92-67-10188-9, 1st ed., International Organization for Standardization: Geneva, Switzerland (1993); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297, U.S. Government Printing Office: Washington, DC (1994); available at http://physics.nist.gov/Pubs/.

Users of this RM should ensure that the Report in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.