Ultrahigh Molecular Weight Polyethylene as Used in Articular Prostheses (A Molecular Weight Distribution Study)

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Synopsis

Currently there is widespread use of ultrahigh molecular weight polyethylene (UHMWPE) acetabular components in total joint replacement prostheses. What has been most surprising about the wear of UHMWPE under such circumstances is the occurrence of brittle fracture. Such fracture had not been observed in the usual engineering tests done in the laboratory on UHMWPE. It was only when prostheses which had been removed from patients were examined or run in hip joint simulators with serum or synovial fluid as the lubricant, that brittle fracture was encountered. The problem of environment-enhanced brittle fracture in plastics dates back to 1946. Interestingly, the phenomenon was first described in polyethylene. The prime variables involved are polymer molecular weight, sensitizing environment, stress field, and temperature. Other things being equal, brittle behavior in polyethylene is extremely sensitive to the amount of low molecular weight polymer present. In the light of the foregoing we have studied the molecular weight distribution in six commercially available UHMWPE components. These were obtained from six different manufacturers. The specimens were characterized both on their bearing (wear) surfaces and in their interior bulk. The results obtained indicate that:

- 1. The UHMWPE components contain substantial amounts of low molecular weight polymer.
- 2. The UHMWPE components differ significantly in molecular weight distribution.
- 3. The UHMWPE components contain substantial amounts of crosslinked polymer.

Use of ultrahigh molecular weight polyethylene (UHMWPE) acetabular components in total hip joint replacement prostheses is estimated at about 40,000 such implantations this year in the United States.

What has been most surprising about the wear of high molecular weight polyethylene under such circumstances has been the occurrence of brittle fracture. This was first reported by Weightman et al. in 1973¹ and since confirmed by Walker.² The occurrence of brittle fracture had not been observed in the usual engineering tests done in the laboratory on ultrahigh molecular weight polyethylene.³⁻⁵ It was only when prostheses were examined which

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Sample	Low MW fraction, %	% Crosslinkeda	% Soluble	I.V. Soluble, dl/g	\overline{M}_w (soluble)
1	5-10	55	45	3.5	360,000
2	5-10	45	55	3.0	270,000
3	5-10	80	20	6.2	810,000
4	75	25	75	1.0	54,000
5	10	70	30	4.8	460,000
6	15	0	100	4.0	410,000
M _N	10	50	50	2.5	210,000
MO	5	40	60	7.0	1,000,000

TABLE I Molecular Weight Distribution Study (Surface)

^a Crosslinked and/or greater than 6×10^6 .

had been removed from patients or run in the hip joint simulators with serum or synovial fluid as the lubricant that brittle fracture was encountered.⁶

The concept of environment-enhanced stress reactivity in plastics dates back to 1946 as far as we know.⁷ Interestingly, the phenomenon was first described in polyethylene. The considerable research carried out in the ensuing decade^{8,9} led to the definition suggested by J. B. Howard¹⁰ in 1959:

"Environmental stress cracking is the failure in surface initiated brittle fracture of a polyethylene specimen or part under polyaxial stress in contact with a medium in the absence of which fracture does not occur under the same conditions of stress. Combinations of external and/or internal stress may be involved and the sensitizing medium may be gaseous, liquid, semisolid or solid."

The prime variables affecting this type failure were revealed to be polymer structure, sensitizing medium, stress field, and temperature. In particular polyethylenes with similar average molecular weights but different molecular weight distributions may have vastly different propensities for brittle fracture. Other things being equal, crack resistance in polyethylene is extremely sensitive to the amount of low molecular weight polymer present.

Sample	Low MW fraction, %	% Crosslinkeda	% Soluble	I.V. Soluble, dl/g	\overline{M}_{w} (soluble)
1	20	60	40	1.6	90,000
2	15	55	45	2.1	160,000
3	10	60	40	3.6	370,000
4	15	60	40	2.1	160,000
5	10	90	10	3.0	270,000
6	25	45	55	5.5	680,000
M _N	15	40	60	2.1	160,000
MO	10	50	50	6.5	900,000

TABLE II

^a Crosslinked and/or greater than 6×10^6 .

In light of the foregoing discussion, we have characterized a number of commercially available UHMWPE Mueller-type actabular components^{*} for molecular weight and molecular weight distribution. These were studied both on their bearing surface and in their interior bulk. The samples were cut from the prosthese with surgical scalpels. A new scalpel was used for each sample. The chips resulting from the hemispheral bearing surface were trapezoidal in shape varying in thickness from 1 to 3 mils. Forty to 50 such chips made up a sample. The chips from the interior were of same order thickness but perhaps more uniformly flat in cross section.

In the course of the investigation, it became apparent that the polymers were in part crosslinked either as a consequence of processing/fabrication and/or the irradiation-type sterilization they had undergone. The variables employed in the characterization were as follows:

A. Low molecular weight fraction, defined as that portion of the polymer which entered solution in normal xylene at 130°C and remained in solution after cooling to room temperature. The fraction so isolated was found to have an intrinsic viscosity of 0.34 dl/g in p-xylene at 105°C. This corresponds to an \tilde{M}_v of 9000.¹¹

B. Crosslinked fraction, defined as that portion of the polymer which was not soluble in decalin at 135°C. (Since we were able to dissolve polymers of a 6×10^6 molecular weight, strictly speaking, we are only sure that this fraction was either crosslinked or of molecular weight greater than 6×10^6 .)

C. I.V. Soluble, the intrinsic viscosity in decalin at 135° C of that polymer which dissolved under these conditions.

D. \bar{M}_w Weight-average molecular weight of the soluble fractions based on $[\eta]_{135^{\circ}C} = 6.77 \times 10^{-4} M_w^{0.67} dl/g^{.12}$

The results obtained are presented in Table I (surface) and Table II (interior). They indicate that the components tested have significant differences in molecular weight distribution and, perhaps more importantly, they can have substantial amounts of low molecular weight polymer.

Therefore, all the variables necessary for environment-enhanced brittle fracture appear to exist in the ultrahigh molecular weight polyethylene components. We assume that, since all UHMWPE acetabular components are fabricated in similar ways from similar materials, our findings would generally hold true for all polyethylene acetabular components. The sensitizing medium of polar nonsolvents serum or synovial fluid is always present under the conditions of implantations in the body. The stress field is clearly acting both from the very high impulsive loading cycle generated by walking and possibly by the internal stresses created by the fabrication of the component. The low molecular weight polyethylene fraction is in most components present in significant amounts in the bearing surface.

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References

- 1. B. Weightman, I. Paul, R. Rose, S. Simon, and E. Radin, J. Biomech., 6, 51 (1973).
- 2. B. L. Gold and P. S. Walker, Clin, Orthop., 100, 270 (1974).
- 3. H. C. Amstutz, J. Biomed. Mat. Res., 3, 547 (1968).
- 4. C. A. Homsey and J. W. King, J. Bone Joint Surg., 51A, 805 (1969).
- 5. J. O. Galante and W. Rostoker, Acta Orthop. Scand., Suppl. 145, (1973).
- 6. B. Weightman, I. Paul, R. Rose, S. Simon, and E. Radin, J. Biomech., 6, 299 (1973).
- 7. R. B. Richards, Trans. Faraday Soc., 42, 10 (1946).
- 8. Pinsky, J. Plast. Technol., 159 (April 1955).
- 9. P. Hittmair and R. Ullman, J. Appl. Polym. Sci., 6(19) 1 (1962).
- 10. J. B. Howard, S.P.E. J. 15, 397 (1959).
- 11. W. R. Krigbaum and Q. A. Trementozzi, J. Polym. Sci., 28, 295 (1958).
- 12. P. S. Francis, P. Cooke, and J. Elliot, J. Polym. Sci., 31, 453 (1958).

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