

On Abrasive Wear of Polyethylene

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ABSTRACT: Despite widespread and growing use of polymers in applications where abrasion is present, ranging from gearboxes to prosthetic joints, abrasive wear of these materials is ill-understood. We present a study that for commercially relevant polyethylene (PE) points to the effective number of physical cross-links per macromolecular chain as the principal—remarkably simple—factor that dictates the intrinsic abrasive wear resistance. This new insight has permitted us, among other things, to identify a polyethylene of a hereto unknown matrix of desirable properties, i.e., ultra-wear-resistant and—unlike the commonly used ultrahigh molecular weight version (UHMW PE)—melt-processable, which should open a host of novel applications.

Introduction

Abrasive wear, which may occur and manifest itself in many different forms, is generally thought to be dependent on numerous factors that include the physicochemical nature of the various materials, surfaces and interfaces involved, such as roughness and polarity, and the presence or absence of lubricating agents or other foreign matter.¹ A particularly illustrative example where such complex conditions can be encountered are implanted artificial hip joints in which typically a steel or ceramic femoral ball, which is fixed onto a metal stem, moves against an UHMW PE acetabular cup in the presence of body fluids.^{2,3} The latter motion results in removal of small (often submicrometer) particles of the polymer material (an estimated 500000 particles per step²) and, ultimately, aseptic loosening and failure of the prosthesis and inflammatory periprosthetic bone loss. Besides various attempts to improve lubrication in such joints⁴ and modify the size of the debris to reduce inflammatory responses,⁵ numerous efforts have been directed toward the enhancement of the abrasive wear resistance of UHMW PE itself. These include cross-linking of the macromolecules by irradiation or with the aid of peroxides,^{6,7} sintering of the polymer at elevated pressures and temperatures (~ 1 kbar, 220 °C) via a transient hexagonal crystal phase,⁸ and adding high-performance aramide fibers.⁹

Unfortunately, a fundamental and predictive understanding of the origin of abrasive wear is still lacking, and UHMW PE continues to be the material of choice in applications where resistance to wear is demanded, despite its major drawbacks with respect to poor processability and associated unfavorable microstructure.

It is generally believed that the abrasive wear resistance of polymers correlates with the reciprocal product of their ultimate tensile stress and the elongation at break (Ratner–Lancaster correlation¹⁰), and increases with increasing molecular weight.^{11,12} In a brief study of branched polyethylenes, Khanin et al.¹¹ have argued that the number-average molecular weight, \bar{M}_n , is the relevant moment of the molecular weight distribution.

However, claims also have been made that weight-average molecular weight, \bar{M}_w , or the viscosity are the more critical correlating characteristics.^{13–15} In addition, some authors have suggested that abrasive wear is related to the degree of crystallinity of polymeric materials.¹²

In this work, we investigated abrasive wear of linear polyethylenes of an extraordinary broad range of molecular weights (spanning more than 3 orders of magnitude), different distributions (mono- and bimodal), and a variety of polydispersities (from nearly monodisperse to \bar{M}_w/\bar{M}_n values exceeding 80) in an attempt to re-examine the above suggested conflicting correlations and to elucidate the (macro)molecular origin of abrasive wear of this polymer.

Experimental Section

Materials. The various grades of linear polyethylenes employed in this study were obtained from DSM (Stamylan), Polyscience, U.S. National Institute of Standards and Technology (NIST), and Societe National Elf Aquitaine Production (SNEAP).

Blends of various polyethylene grades (all compositions in weight percentage) were prepared with a small-scale (sample volume 4 cm³) laboratory, recycling, co-rotating twin-screw extruder (MicroCompounder, DACA Instruments, Santa Barbara, CA), the temperature of which was kept at 180 °C. The material residence time was 10 min at 120 rpm, after which the product was discharged. Gel permeation chromatography (see below) showed that no shear degradation occurred during the preparation of these blends.

Methods. Unless indicated otherwise, values of \bar{M}_n and \bar{M}_w were either provided by suppliers or determined by high-temperature gel permeation chromatography (HT-GPC) carried out at Montell Polyolefins, Ferrara, Italy, with a Waters 150 °C ALC/GPC instrument with the following specifications: column type, TSK GMHXL-HT (13 pm); mobile phase flow rate, 0.5 mL min⁻¹; solvent and mobile phase antioxidant, 1,2,4-trichlorobenzene and 2,6-di-*tert*-butyl-*p*-cresol; detector, refractive index; column temperature, 135 °C. Standard polystyrene samples (Easy Cal Kit, Polymer Laboratories, U.K.) were used for calibration; the total elution duration was about 120 min.

Thermal analysis was conducted with a Netzsch differential scanning calorimeter (DSC, model 200), calibrated with indium. Samples of about 5 mg were heated at a rate of 10 °C/min under a nitrogen atmosphere. Crystallinities were calcu-

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lated from the enthalpies of fusion, which were determined from the endothermal peak of once molten (at 180 °C) and cooled (at 10 °C/min) material, adopting the value of 293 J/g for 100% crystalline PE.¹⁶

Samples for abrasive-wear tests were compression molded from the molten state at 180 °C in a Carver press (model M, 25T) for 10 min at 1 metric ton and 10 min at 10 ton and then cooled to room temperature during 4 min under 4 ton in a water-cooled Carver press. The test coupons typically were of a thickness of 0.3 mm and a diameter of 25 mm.

Abrasive wear measurements reported here were carried out using a custom-built device according to specifications and the method described by Hutchings et al.¹⁸ In this device, a hard sphere (1 in. tungsten carbide ball with a 400 nm surface roughness; Atlas Ball & Bearing Co. Ltd.) clamped between two coaxial driving shafts, rotated at a constant speed of 200 rpm. The sample was placed against the ball with a normal force of 0.25 N using a pivoted L-shaped arm, while an abrasive slurry (0.75 g of SiC (mean particle size of 4–5 μm) per cm³ of distilled water) was dripping onto the ball at a feed rate of 0.5 cm³/min. The sizes of the resulting abrasive wear craters were measured with an optical microscope (Leica, MS5 at 25×) and on occasion additionally by profilometry, which was carried out at the Eidgenössische Materialprüfungs- und Forschungsanstalt, Dübendorf, Switzerland, with a Profilometer Tencor P10. In all cases, spherical craters were observed (cf. Figure 1A). The corresponding wear volume V was calculated according to

$$V = \left(\frac{\pi d^4}{64R} \right) \quad (1)$$

where R is the ball radius and d is the surface chordal diameter of the crater.¹⁹ To correct the measured diameter of the wear craters (d'), which typically consist of a central spherical crater surrounded by a roughened or "scuffed" annular region, the following empirical rule (according to Trezona et al.²⁰) was applied:

$$d = \left(\frac{d' - 0.1407}{0.9358} \right) \quad \text{for } 0.5 \text{ mm} \leq d \leq 2.193 \text{ mm} \quad (2)$$

$$d = d' \quad \text{for } d > 2.193 \text{ mm}$$

For three-body abrasive wear of homogeneous materials, the wear volume is proportional to the product of the sliding distance S and the normal force N

$$V = \kappa S N \quad (3)$$

which defines the wear coefficient κ . In all tests the total amount of ball rotations was 9000, which corresponds to a sliding distance of 718 m. In a typical test, the crater diameter was measured every 3000 cycles to verify the applicability of eq 3 (cf. Figure 1C).

Results and Discussion

The molecular characteristics and degrees of crystallinities of the various linear polyethylenes used are collected in Table 1. Abrasive wear of melt-compression molded samples were analyzed by the microscale or ball-cratering test method after Hutchings et al.¹⁸ on all materials, and for samples of which sufficient quantities were available, also according to the well-known sand-water slurry test²¹ and pin-on-disk method.²² Gratifyingly, within experimental error, identical trends were observed in all tests, and, therefore, only the more complete set of wear coefficients, κ , obtained in the microscale abrasive-wear tests are listed in Table 1 (see Figure 1). Parts A–C of Figure 2 are plots of the values of κ vs, respectively, the number- and weight-average molecular weights (M_n and M_w) and the degree of crystallinity of the various polyethylene samples (no plot

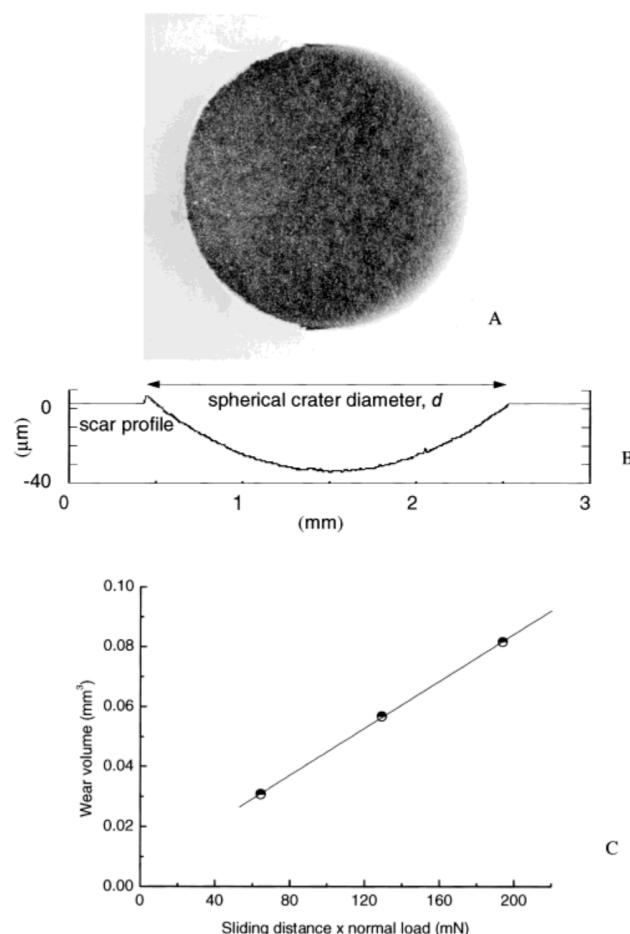


Figure 1. Typical results obtained with the microscale abrasive-wear test according to Hutchings et al.¹⁸ Optical micrograph, reflected light (A), and profilometer trace (B) of an abrasion scar after 9000 cycles and (C) plot of microscale abrasive-wear volume as a function of the product of sliding distance and normal load (held constant at 0.25 N), here shown for the polyethylene sample designated HD 8621 (●) (Table 1). The observed linear correlation between wear volume and sliding distance \times normal load is indicative of three-body wear.

is shown of κ vs the z -average molecular weight because of the notorious unreliability of the latter values in the high molecular weight regime and the meaningless correlation noted). As is evident from these data, neither the commonly used molecular weight averages, M_n and M_w , nor the crystallinities correlate in a satisfactory and predictive manner with the measured wear coefficients. This observation, in fact, is consistent with the conflicting results reported in the literature. Particularly illustrative for this lack of a direct correlation is the wear coefficient of the near-monodisperse sample with $M_n = 16$ kg/mol and $M_w = 17$ kg/mol (○). Figure 2A appears to indicate that this material has a substantially higher wear coefficient than polymers of similar M_n , while the data in Figure 2B, by contrast, suggest that this sample is more wear resistant (lower value of κ) than material of significantly higher M_w .

In other attempts to correlate macroscopic mechanical and rheological properties of polymers to (moments of) its molecular weight distribution, it has been recognized that (macro)molecules of a molecular weight below a critical value actually do not effectively contribute to the property of interest, but merely functions as diluent. Examples are the Bueche treatment of polymer rheol-

Table 1. Molecular Weights, Polydispersities, Crystallinities, $\phi\bar{M}_n^*$ (See Text), and Wear Coefficients of Different Polyethylenes

symbol ^a	sample ^b	\bar{M}_n (kg/mol)	\bar{M}_w (kg/mol)	\bar{M}_w/\bar{M}_n	crystallinity ^c (%)	ϕ ^d	$\phi\bar{M}_n^*$ (kg/mol)	wear coeff, ^e $10^4\kappa$ (mm ³ /mN)
●	PE 2000, Polyscience ^{f,g}	2	2	1.0	90.1	0	0.0	44.1
●	HD 8621, DSM	7	230	32.9	66.9	0.84	23.9	4.20
●	HD 7048, DSM	21	91	4.3	63.2	0.96	28.7	4.02
○	UH 210, DSM	285	2063	7.2	53.6	1	286.0	2.57
◆	50/50 PE 2000/HD 7048	4	47	12.8	78.8	0.48	14.3	7.44
■	40/60 PE 2000/HD 7048	4	56	12.7	73.8	0.57	17.2	6.68
◆	30/70 PE 2000/HD 7048	5	65	11.8	74.3	0.67	20.0	5.70
▲	20/80 PE 2000/HD 7048	7	73	10.1	72.6	0.77	22.9	5.46
▼	10/90 PE 2000/HD 7048	11	82	7.6	65.8	0.86	25.9	4.46
□	90/10 HD 8621/UH 210	8	414	50.0	66.6	0.86	27.2	3.90
▲	80/20 HD 8621/UH 210	9	522	58.0	65.6	0.87	31.4	3.72
▼	60/40 HD 8621/UH 210	12	978	81.5	61.8	0.89	37.7	3.31
□	90/10 HD 7048/UH 210	24	289	12.0	62.0	0.96	31.8	3.59
▲	80/20 HD 7048/UH 210	26	529	20.3	57.2	0.96	35.2	3.60
▼	60/40 HD 7048/UH 210	35	967	27.6	56.6	0.97	46.6	3.21
○	fraction, SNEAP ^{g,h}	16	17	1.1	71.2	1	16.1	6.41
□	PE 1484a, NIST ^{g,h}	102	120	1.2	60.9	1	102.2	2.80
◇	fraction, SNEAP ^{g,h}	267	329	1.2	49.7	1	267.4	2.57
△	fraction, SNEAP ^{g,h}	360	448	1.2	49.5	1	360.4	2.56
▽	fraction, SNEAP ^{g,h}	450	490	1.1	54.3	1	450.1	2.44

^a Corresponding to denotation in Figures 2 and 3. ^b Blends prepared according to procedure in the Experimental Section. ^c Crystallinity calculated from the enthalpy of fusion of once-molten polymer with 293 J/g for 100%-crystalline material.¹⁶ ^d Calculated according to eqs 4–6, using a value of 5000 g/mol for $(n + 1)M_c^0$. ^e Average value from three measurements. ^f Assumed to be monodisperse, molecular weight estimated from the peak melting temperature (125 °C) according to ref 17. ^g \bar{M}_n and \bar{M}_w according to supplier; except for PE 2000 (see ref 6). ^h $\phi\bar{M}_n^*$ calculated assuming a log-normal distribution.

ogy,²³ the gelation of gelatin,²⁴ the concept of the effective number of entanglements for craze fibril stability in deformation of glassy polymers,^{25,26} and the criterion of elastic percolation for semicrystalline polymers.²⁷ In all these approaches it is assumed and, in fact, asserted that macroscopic mechanical response, such as plastic flow of polymers, involves molecular “connectivity” throughout the material, which is provided by covalent chains which are engaged to each other through friction loci, such as entanglements and crystallites. In the case of polyethylene, both types of friction loci are operative and to some extent indistinguishable since they involve very similar distances. Macroscopic connection, or percolation, starts to develop when the polymer chains take part in at least two of such physical cross-links and, thus, need to be of an average length (or molecular weight) of about 3–5 (“ $n + l'$) times the separation between these loci^{25,26,27} which corresponds to a molar mass $(n + 1)M_c^0$. Here, M_c^0 is the molar mass between the loci, which is expected for polyethylene to be in the order of the entanglement molar mass M_e , ($M_e = 1250$ g/mol³⁰).

For a given continuous molecular weight distribution $w(M)$, the weight fraction w of chains that are large enough ($M > (n + 1)M_c^0$) to effectively participate in the polymer network, is given by

$$w = \int_{(n+1)M_c^0}^{\infty} w(M) dM \quad (4)$$

Assuming molecular weight independent density, this weight fraction “effective” polymer w equals the volume fraction “effective” polymer ϕ .

The chains, which are so small ($M < (n + 1)M_c^0$) that they do not effectively participate in the polymer network, will dilute this network according to:²⁹

$$M_c = \frac{M_c^0}{\phi} \quad (5)$$

where M_c is the value of M_c^0 corrected for the volume fraction “effective” polymer ϕ .

Finally, \bar{M}_n^* is the number-average molecular weight adjusted for the fraction “diluent”:²⁶

$$\bar{M}_n^* = \frac{\int_{(n+1)M_c^0}^{\infty} w(M) dM}{\int_{(n+1)M_c^0}^{\infty} \frac{w(M)}{M} dM} \quad (6)$$

We now propose that the limiting, or intrinsic wear resistance (that is of homogeneous, defect-free materials) is governed by the average number of effective physical cross-links per macromolecular chain, \bar{N}_c , which equals:

$$\bar{N}_c = \frac{\bar{M}_n^*}{M_c} \left[1 - \frac{n M_c}{\bar{M}_n^*} \right] = \frac{\phi \bar{M}_n^*}{M_c^0} \left[1 - \frac{n M_c^0}{\phi \bar{M}_n^*} \right] \sim \phi \bar{M}_n^* \quad (7)$$

Here, as before, the scalar, n , defines the strand length that is weak in the sense that strands of molar mass less than $(n + 1)M_c^0$ are easily pulled out through crystals or entanglement loci. From eq 7 above it is clear that, if the wear behavior indeed depends on the average number of physical cross-links per chain, the wear coefficient should correlate with $\phi \bar{M}_n^*$; and not simply with \bar{M}_n . A plot of the measured wear coefficients κ vs $\phi \bar{M}_n^*$ here with $(n + 1)M_c^0 = 5000$ g/mol is presented in Figure 3. In contrast to results in Figure 2A–C, now a simple, unique and predictive correlation is observed for materials covering the entire range of molecular weights and polydispersities, including the above-discussed polyethylene with $\bar{M}_n = 16$ kg/mol and $\bar{M}_w = 17$ kg/mol (○). Graphs of κ as a function of $\phi \bar{M}_n^*$ calculated with smaller or larger values of $(n + 1)M_c^0$ yielded similar correlations, but with a larger and, hence, undesirable spread.

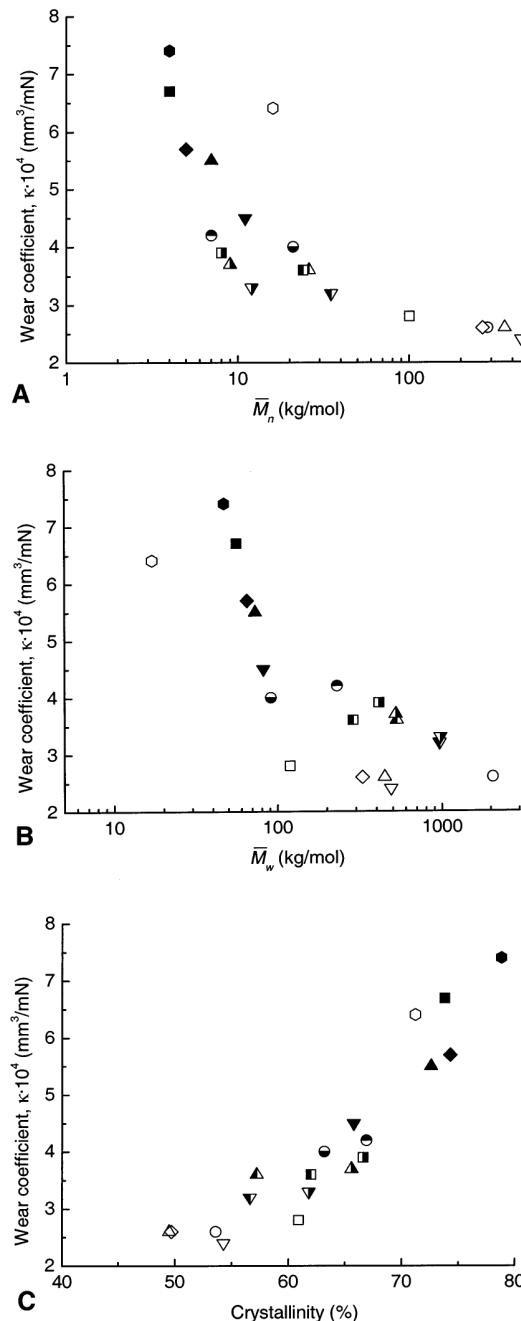


Figure 2. Abrasive-wear coefficient, κ (eq 3), vs (A) number-average molecular weight, \bar{M}_n , (B) weight-average molecular weight, \bar{M}_w , and (C) degree of crystallinity of the various linear polyethylenes (Table 1). Note that in this particular measurement a material with value of $\kappa = 0 \text{ mm}^3/\text{mN}$ represents a “wear-less” species. At the other end of the spectrum, the extremely poor wear-resistant PE wax (PE 2000) displayed a value of $\kappa = 44.1 \times 10^{-4} \text{ mm}^3/\text{mN}$ (not included in the graphs).

Instead of relating the wear coefficient to the average number of physical cross-links per chain, it is, of course, also possible to choose the fraction of noneffective cross-links per chain as controlling parameter. This fraction (the second term in between the brackets in eq 7) will be small for high molar mass polymers and approach unity for low molar mass polymers and is proportional to $1/\phi\bar{M}_n^*$. Interestingly, a plot of the reciprocal wear coefficient, $1/\kappa$ (a measure of the wear resistance),

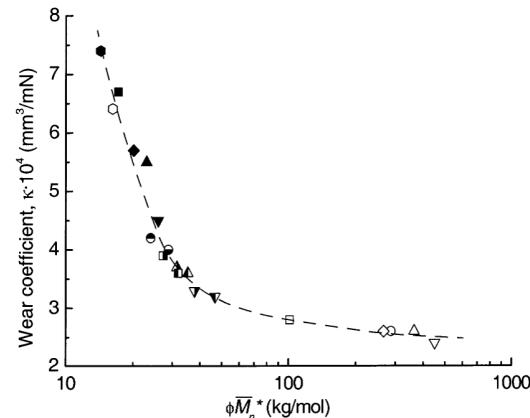


Figure 3. Graph of the abrasive-wear coefficient, κ , as a function of $\phi\bar{M}_n^*$ for $(n + 1)M_c^0 = 5000 \text{ g/mol}$ (see text) of the various polyethylene samples, revealing an unique correlation between those two quantities. The dashed line in this graph merely is a guide to the eye.

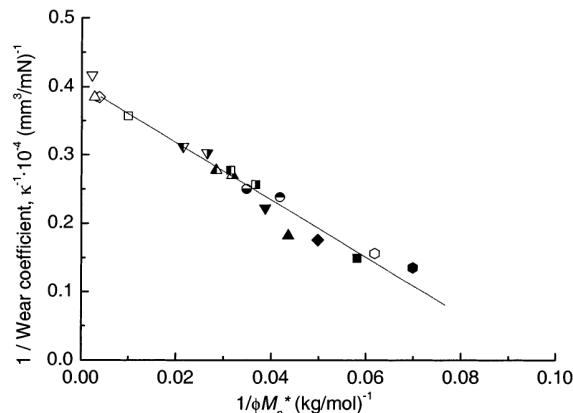


Figure 4. Graph of the reciprocal wear coefficient, $1/\kappa$, as a function of $1/\phi\bar{M}_n^*$ for $(n + 1)M_c^0 = 5000 \text{ g/mol}$ (see text) of the various polyethylene samples. The line is a least-squares fit of all data.

against $1/\phi\bar{M}_n^*$ yields to a good approximation a straight line (see Figure 4).

Of particular interest are the wear characteristics of polyethylenes of modest molecular weight and of low polydispersity (~ 1 ; cf. Table 1 and Figure 3). These grades exhibit a high value of $\phi\bar{M}_n^*$ and high abrasion resistance already at a relatively low weight-average molecular weight. Since it is \bar{M}_w that largely dictates the steady-state shear viscosity at a given shear rate, which is of paramount importance in polymer processing, the above observation opens the possibility of the creation of polyethylenes with a heretofore unknown, unique matrix of desirable characteristics: i.e., ultrahigh wear resistance and melt-processability. Inspection of the data in Table 1 reveals that, as a matter of fact, this extraordinary useful combination of properties indeed is found for the polyethylene grade with $\bar{M}_n = 450 \text{ kg/mol}$ and $\bar{M}_w = 490 \text{ kg/mol}$. Samples of this particular polymer were found to exhibit a wear coefficient of $2.44 \times 10^{-4} \text{ mm}^3/\text{mN}$, which actually is lower than that of the grade UH 210 with $\bar{M}_w = 2063 \text{ kg/mol}$. The latter material has a zero-shear viscosity of approximately $10^8 \text{ Pa}\cdot\text{s}$, which is prohibitively high for standard melt-processing techniques such as injection molding. Hence, polymers of such (ultra-)high molecular weights commonly are processed by compaction, sinter-

ing, and machining into final articles such as the aforementioned acetabular cups. This process not only is cumbersome and uneconomical, but also yields incompletely fused materials and products that comprise machining marks. In particular the incomplete fusion and therewith associated particulate nature of processed UHMW PE is highly undesirable, as previous studies indicate that the original polymer powder particles may constitute the debris that is removed during abrasion and ultimately responsible for phagocytic reactions.³¹ In sharp contrast, the polyethylene grade of $M_w = 490$ kg/mol, which has a zero-shear viscosity of about 1.6×10^7 Pa·s can be readily processed at modest shear rates from the melt, fuses completely and shows no memory of its original particle structure. It has not escaped the attention of the authors that polyethylenes produced with modern metallocene catalysts³² may yield polymers of relatively narrow molecular weight distributions ($\text{polydispersity} \approx 2$), and that the latter materials may be a particularly viable commercial alternative to the present near-monodisperse laboratory samples.

Conclusions

We have shown for the practically relevant system of polyethylene that a unique correlation exists between the polymer molecular weight distribution and the abrasive wear coefficient, which resides in the *effective* number of physical cross-links per macromolecule. From this it follows that the relevant measure of the molecular weight distribution is not just the number-average molecular weight \bar{M}_n , but $\phi\bar{M}_n^*$, which is the number-average molecular weight corrected for the fraction of chains which are not long enough to contribute to the connectivity in the material but merely act as a diluent, multiplied by the volume fraction “effective” polymer.

Since the rheological behavior of polymer melts is predominantly determined by the higher moments of the molecular weight distribution, the above implies that polymer grades of narrow molecular weight distributions constitute a more attractive compromise between resistance to abrasive wear, the property of interest here, and processability. Indeed, the low polydispersity polyethylene samples with molar masses in the range of 100–490 kg/mol, which are readily processable, had a similar or even superior resistance against abrasive wear compared to the intractable ultrahigh molecular weight polyethylene grade studied in this work.

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