

Ultra High Molecular Weight Polyethylene (UHMWPE)

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Reprinted from
ENGINEERED MATERIALS HANDBOOK™
Volume 2: Engineering Plastics



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SAN:204-7586

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Ultra High Molecular Weight Polyethylene (UHMWPE)

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ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE (UHMWPE) is a linear, low-pressure, Ziegler-type catalyst, polyethylene resin. Its weight-average molecular weight of 4×10^6 is approximately ten times that of high molecular weight high-density polyethylene (HMW-HDPE) resins. The extremely high molecular weight of this resin, which is commercially available in grades ranging in molecular weight from 3.5×10^6 to 6×10^6 g/mol (ASTM calculation), yields several unique properties.

UHMWPE has both the highest sliding abrasion resistance and highest notched impact strength of any commercial plastic. Figures 1 and 2 show a comparison of abrasion and impact strengths with those of other materials.

Combined with abrasion resistance and toughness, the low coefficient of friction of UHMWPE yields a self-lubricating, nonstick surface. Static and dynamic coefficients of friction are significantly lower than steel and most plastic materials (Table 1).

The basic chemical unit of UHMWPE is $-CH_2-$. Thus, a 4×10^6 molecular weight resin contains approximately 285×10^3 carbon atoms or units in the polymer chain. The insolubility of UHMWPE makes gel permeation chromatography (GPC) impractical. Molecular weight is therefore determined by the measurement of dilute-solution viscosity, as detailed in ASTM D 1601 and D 4020 (Ref 1, 2). With these procedures, UHMWPE is defined as a substantially linear polyethylene (PE) having a relative viscosity of 1.4 or greater at a concentration of 0.02% at 135 °C

(275 °F) in decahydronaphthalene. The nominal molecular weight (ASTM calculation) is approximated using the Mark-Houwink equation $M = 5.37 \times 10^4 (IV)^{1.37}$, where IV represents intrinsic viscosity. This method is not valid on thermally converted UHMWPE materials because of inadequate solubility and possible cross-linking. However, a relative indication of molecular weight can be determined by density, sand slurry abrasion and notched impact tests of molded or extruded specimens.

As molecular weight increases from 3×10^6 to 6×10^6 , abrasion resistance improves significantly (by approximately 30%), whereas impact strength decreases from 140 to 80 kJ/m² (67 to 38 ft · lbf/in²). By comparison, most HDPE grades range from 13 to 40 kJ/m² (6 to 19 ft · lbf/in²). A special test specimen had to be devised to determine the toughness of UHMWPE because no break occurs with conventional test methods. The ASTM D 256 (Ref 3) Izod impact test specimen was modified with two opposing 15° notches rather than the standard 45° notch. Double-notched Izod values typically exceed 1.6 kJ/m (30 ft · lbf/in) notch for UHMWPE. Figures 3 and 4 show the relationship between notched impact strength and temperature. Most other mechanical, thermal, and physical properties remain essentially constant throughout the molecular weight range of UHMWPE.

Because of the relatively low density of 0.93 g/cm³, the price per cubic inch of standard grade virgin resins is currently lower than for any other engineering resin. UHMW-PE is supplied as a free-flowing, near-white powder. Available packaging includes bags (25 kg, or 55 lb), containers or bulk packs (545

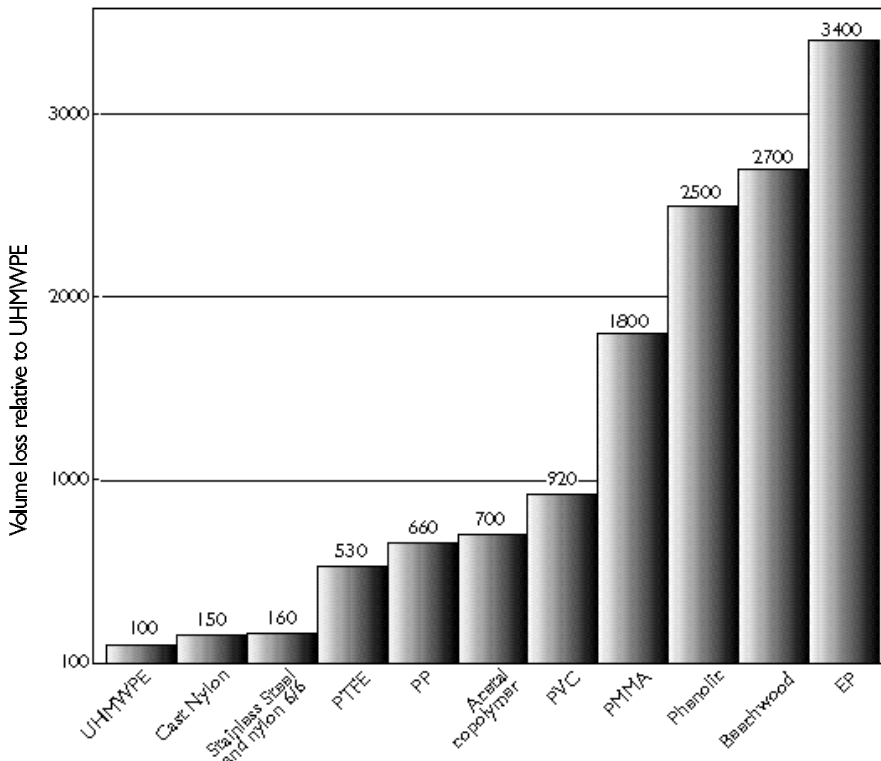


Fig. 1 Comparative abrasion resistance of different engineering resins. PTFE, polytetrafluoroethylene; PVC, polyvinyl chloride; PMMA, polymethyl methacrylate; EP, epoxy

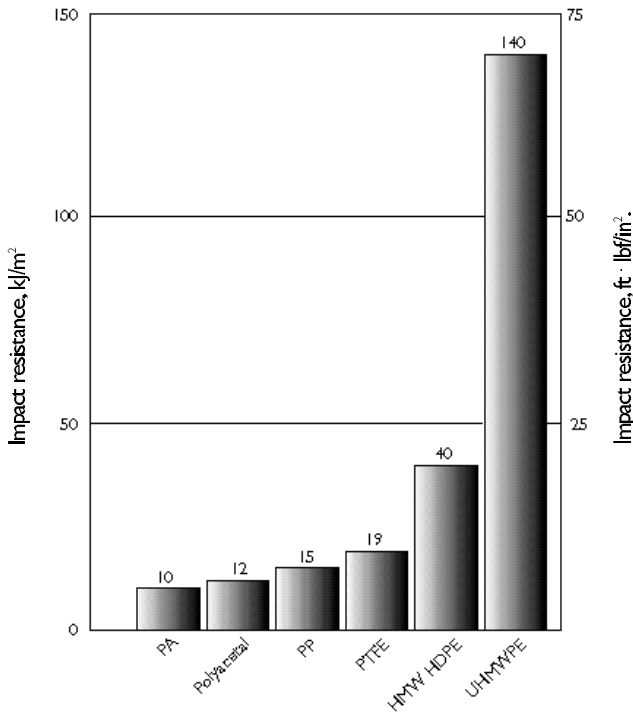


Fig. 2 Comparative impact resistance of different engineering resins

Table 1 Comparison of dynamic coefficient of friction on polished steel.

| Resin | Dry | Water | Oil |
|-------------------------|-----------|-----------|-----------|
| UHMWPE | 0.10-0.22 | 0.05-0.10 | 0.05-0.08 |
| Nylon 6/6 | 0.15-0.40 | 0.14-0.19 | 0.02-0.11 |
| PA/molybdenum disulfide | 0.12-0.20 | 0.10-0.12 | 0.08-0.10 |
| Polytetrafluoroethylene | 0.04-0.25 | 0.04-0.08 | 0.04-0.05 |
| Acetal copolymer | 0.15-0.35 | 0.10-0.20 | 0.05-0.10 |

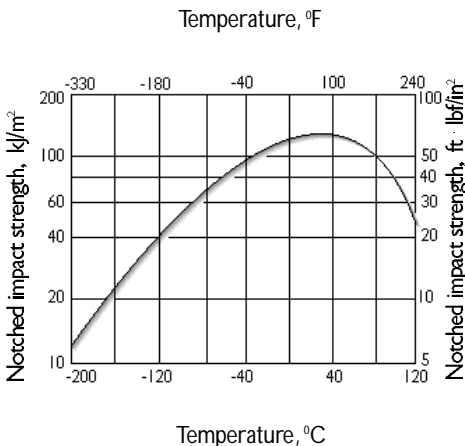


Fig. 3 Notched impact strength of UHMWPE as a function of temperature, using sharp V-notched test bar with double 15° V-notch

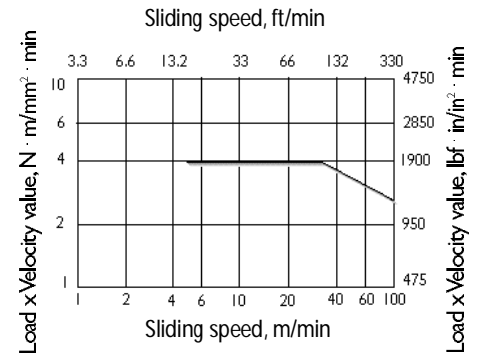


Fig. 5 Load limits for unlubricated bearings made from UHMWPE

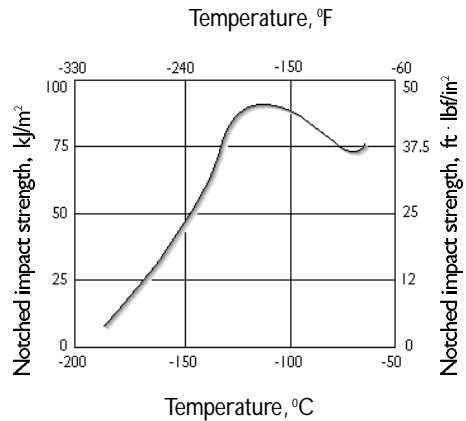


Fig. 4 Notched impact strength of UHMWPE as a function of temperature, based on a single 45° V-notch

kg, or 1200 lb), and railcars (63.5 X 10³ kg, or 140 X 10³ lb).

Typical Applications

Because of its self-lubricating, nonstick, lightweight, and wear-resistant characteristics, UHMWPE has been used for many years in the bulk material handling (grain, cement, gravel, and aggregate) and ore/coal mining industries. Typical applications include liners for silos, hoppers, dump trucks, railcars, and chutes; conveyor troughs and flights; wear strips; slide plates; and unlubricated bearings and bushings. Additional benefits of UHMWPE include increased product flow, reduction or elimination of caking (particularly in wet or icy conditions), noise abatement, and reduced energy consumption during use.

The absorption capacity for shock stress is extraordinary, even at temperatures approaching absolute zero. Thus, cryogenic and cold-weather applications are ideal for UHMWPE, whereas lower molecular weight HDPE resins could fail. Seals, pistons, and pumps have performed satisfactorily in liq-

uid hydrogen pumps at -253 °C (-423 °F).

The textile industry uses UHMWPE because of its excellent impact resistance and sound-dampening characteristics. It is used in highly stressed parts, including loom pickers, shuttles, sticks, straps, caps, buffers, gears, pinions, and small rollers.

Prime virgin UHMWPE grades are in compliance with U.S. Food and Drug Administration regulations and have received U.S. Department of Agriculture approval. Certain grades have been tested and comply with 3A requirements or have been listed at NSF.

The food, beverage, and pharmaceutical industries extensively use UHMWPE because oil and grease can be eliminated from most bearing applications. Furthermore, the growth of fungus and bacteria is discouraged because the material is nonporous. Common applications include bottling plant star wheels and guard rails.

Examples of other applications include pump impellers, pump housings, valve seats and valve gaskets for the chemical process industry; doctor blades, suction box covers,

and chain conveyor wear plates for the pulp and paper industry; and ski and snowboard bottom surfaces, snowmobile drive sprockets, golf ball cores, truck bed linings and maritime industry dock fenders. The special sintering processes can produce porous parts, including marking pen nibs, and filters for potable water, as well as industrial aeration and filtration uses. Nautical rope and personnel protection items are produced from UHMWPE fibers. UHMWPE is also an important component of lead-acid battery separators that isolate the electrode plates from one another.

Metal shafts can rotate freely in UHMWPE bushings despite misalignment or the presence of sand, dust, or dirt particles. In the design of bushings and bearings, dry PV (pressure times velocity) values should be limited to $4 \text{ N} \cdot \text{m}/\text{mm}^2 \cdot \text{min}$ ($1900 \text{ ft} \cdot \text{lb}/\text{in}^2 \cdot \text{min}$), whereas lubricated applications range from 6 to $7 \text{ N} \cdot \text{m}/\text{mm}^2 \cdot \text{min}$ ($2850 \text{ to } 3330 \text{ ft} \cdot \text{lb}/\text{in}^2 \cdot \text{min}$) (Fig. 5). Load and speed limits are 10 MPa (1.5 ksi) and 120 m/min (400 ft/min), respectively. Bearing temperatures below $40 \text{ }^\circ\text{C}$ ($104 \text{ }^\circ\text{F}$) should be maintained.

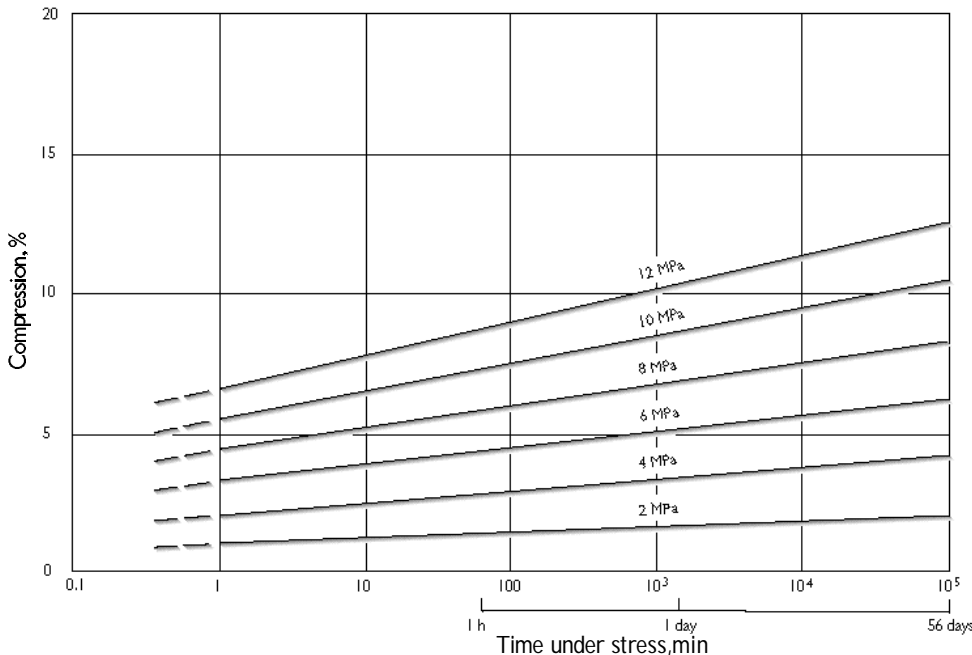


Fig. 6 Creep properties of UHMWPE under varying compressive stress rates, measured at $20 \text{ }^\circ\text{C}$ ($68 \text{ }^\circ\text{F}$)

Family Characteristics

The extremely high molecular weight of UHMWPE makes it a unique material. Its special characteristics, some of which have already been described, include:

- Outstanding sliding abrasion resistance
- Highest notched impact resistance of any plastic material
- Low coefficient of friction
- Nonstick, self-lubricating surface
- Good chemical resistance
- Negligible water absorption
- Excellent properties at cryogenic conditions
- Stress-cracking resistance exceeding 3000 h in surfactants
- Energy absorption and sound-dampening properties
- Excellent dielectric and insulating properties

The outstanding characteristics of this material can be maintained from $-269 \text{ }^\circ\text{C}$ ($-452 \text{ }^\circ\text{F}$) to $90 \text{ }^\circ\text{C}$ ($194 \text{ }^\circ\text{F}$) and even higher for short periods of time. Because the resin does not melt-flow or liquefy at its 138 to $142 \text{ }^\circ\text{C}$ ($280 \text{ to } 289 \text{ }^\circ\text{F}$) melting point, the resin retains excellent dimensional stability at temperatures up to $200 \text{ }^\circ\text{C}$ ($392 \text{ }^\circ\text{F}$). In a special application described in Ref 4, UHMWPE was used at temperatures up to $450 \text{ }^\circ\text{C}$ ($840 \text{ }^\circ\text{F}$) for sulfuric acid spray nozzles, because rapid carbonization of the surface occurred, forming a protective skin.

Table 2 UHMWPE properties

| Property | Typical Values | ASTM test method |
|--|-------------------|-----------------------|
| Mechanical | | |
| Density, g/cm^3 | 0.926-0.934 | D 792 |
| Tensile strength at yield, MPa (ksi) | 21 (3.1) | D 638 |
| Tensile strength at break, MPa (ksi) | 48 (7.0) | D 638 |
| Elongation at break, % | 350 | D 638 |
| Young's modulus, GPa (10^9 psi) | | |
| At $23 \text{ }^\circ\text{C}$ ($73 \text{ }^\circ\text{F}$) | 0.69 (0.10) | D 638 |
| At $-269 \text{ }^\circ\text{C}$ ($-450 \text{ }^\circ\text{F}$) | 2.97 (0.43) | D 638 |
| Izod impact strength, kJ/m ($\text{ft} \cdot \text{lb}/\text{in}$) notch | | |
| At $23 \text{ }^\circ\text{C}$ ($73 \text{ }^\circ\text{F}$) | 1.6 (30) | D 256(a) |
| At $-40 \text{ }^\circ\text{C}$ ($-40 \text{ }^\circ\text{F}$) | 1.1 (21) | D 256(a) |
| Hardness, Shore D | 62-66 | D 2240 |
| Abrasion resistance | 100 | ... |
| Water absorption, % | Nil | D 570 |
| Thermal | | |
| Crystalline melting range, powder, $^\circ\text{C}$ ($^\circ\text{F}$) | 138-142 (280-289) | Polarizing microscope |
| Coefficient of linear expansion, $10^{-4}/^\circ\text{K}$ | | |
| At 20 to $100 \text{ }^\circ\text{C}$ ($68 \text{ to } 212 \text{ }^\circ\text{F}$) | 2 | D 696 |
| At $-200 \text{ to } -100 \text{ }^\circ\text{C}$ ($-330 \text{ to } -150 \text{ }^\circ\text{F}$) | 0.5 | D 696 |
| Electrical | | |
| Volume resistivity, $\Omega \cdot \text{m}$ | $>5 \times 10^4$ | D 257 |
| Dielectric strength, kV/cm (V/mil) | 900 (2300) | D 149 |
| Dielectric constant | 2.30 | D 150 |
| Dissipation factor, $\times 10^{-4}$ | | |
| At 50 Hz | 1.9 | D 150 |
| At 1 kHz | 0.5 | |
| At 0.1 MHz | 2.5 | |
| Surface resistivity, wt% carbon black, | | |
| 0.2% for color | $>10^{14}$ | D 257 |
| 2.5% for UV protection | 10^{13} | D 257 |
| 6.5% for antistatic applications | 10^5 | D 257 |
| 16.7% for conductive applications | 10^3 | D 257 |

(a) Samples had two notches ($15^\circ \pm 1/2^\circ$) on opposite sides to a depth of 5 mm (0.20 in.).

Table 3 UHMWPE chemical resistance of dumbbell-type test specimens after 30 days

+, resistant (mechanical properties not appreciably affected); —, not resistant (decrease in yield stress and ultimate tensile strength greater than 20%); X, limited resistance decrease in yield stress and ultimate tensile strength less than 20%

| Reagent | Temperature | | | Reagent | Temperature | | |
|---|------------------|-------------------|-------------------|--|------------------|-------------------|-------------------|
| | 20 °C (68 °F) | 50 °C (120 °F) | 80 °C (175 °F) | | 20 °C (68 °F) | 50 °C (120 °F) | 80 °C (175 °F) |
| Inorganic acids | | | | Hydrocarbons and halogenated hydrocarbons | | | |
| Chromic acid (80%) | + | + | X | Benzene | X | X | |
| Hydrochloric acid (concentrated) | + | + | + | Carbon tetrachloride | X | | |
| Hydrocyanic acid | + | + | | Cyclohexane | + | + | |
| Hydrofluoric acid | + | + | | Dichloroethylene | — | — | |
| Nitric acid (concentrated) | — | — | — | Diesel oil | + | + | X |
| Nitric acid (50%) | X | — | — | n-heptane | + | + | |
| Nitric acid (20%) | + | + | X | Petroleum ether | + | | |
| Phosphoric acid (85%) | + | + | + | Trichloroethylene | X | — | |
| Sulfuric acid (concentrated) | + | — | — | Toluene | X | — | |
| Sulfuric acid (75%) | + | X | X | White spirit | + | X | |
| Sulfuric acid (50%) | + | + | + | Xylene | X | X | — |
| Alkalies | | | | Alcohols, ketones, ester and amines | | | |
| Aqueous ammonia | + | + | | Acetone | + | + | |
| Potassium hydroxide solution | + | + | + | Aniline | + | + | X |
| Sodium hydroxide solution | + | + | + | Benzyl alcohol | + | + | + |
| Aqueous solutions of inorganic salts | | | | Butyl alcohol | + | + | + |
| Aluminum chloride | + | + | + | Cyclohexanol | + | + | + |
| Ammonium nitrate | + | + | + | Ethanol | + | + | |
| Bleaching powder | + | + | + | Ethyl acetate | + | + | |
| Calcium chloride | + | + | + | Ethylene glycol | + | + | + |
| Sodium carbonate | + | + | + | Glycerine | + | + | + |
| Sodium chloride | + | + | + | Lauryl alcohol | + | + | + |
| Sodium hypochlorite | + | + | + | Propyl alcohol | + | + | + |
| Zinc chloride | + | + | + | Miscellaneous | | | |
| Organic acids | | | | Beer/Wine | + | + | + |
| Acetic acid (99%) | + | + | X | Detergents in aqueous solution | + | + | + |
| Acetic acid (10%) | + | + | + | Distilled water | + | + | + |
| Butyric acid | + | + | + | Hydrogen peroxide 30% (perhydrol) | + | + | |
| Citric acid | + | + | + | Linseed oil/olive oil | + | + | + |
| Formic acid | + | + | | Milk | + | + | + |
| Oleic acid | + | + | X | Seawater | + | + | + |

Outdoor ultraviolet (UV) light can degrade this material, as well as other olefinic materials, leading to cracking within a 1 year period, unless UV stabilizers are added during processing. An allowance for creep, or cold flow (such as 2% at 2 MPa at 20 °C, or 0.290 ksi at 68 °F), should be made. Creep properties under compressive stress are shown in Fig. 6. Other properties of the processed resin are listed in Tables 2 and 3.

Chemical resistance to aggressive media, including most strong oxidizing agents, is excellent. Exposure to aromatic and halogenated hydrocarbons results in only slight surface swelling if moderate temperature levels are maintained.

Processing Parameters. The extremely high processing viscosities require special processing procedures because the resin does not exhibit a measurable melt index and is more like an amorphous solid. The most common methods for fabrication of UHMWPE are ram extrusion and compression molding. In both cases, the individual UHMWPE particles are fused into an appar-

discrete particles, although there is a level of segmented diffusion between particles. Ram extrusion is accomplished by continuously feeding resin through a hopper into the extruder throat and then packing the material in frequent intervals with a reciprocating plunger, thus expelling the air phase. The compressed powder then moves through heated zones, where it is fused. The cross section of the barrel or die corresponds to the profile of the product. The hydraulic system, heater capacity, the die length, and the strength of the construction material influence production rates. Typical extrusion rates are 10 to 20 kg/h (22 to 44 lb/h). Controller set-point temperatures are 160 to 230 °C (320 to 446 °F).

Compression molding of sheets ranging from 1.2 X 2.4 m (4 X 8 ft) to 1.5 X 3.7m (5 X 12 ft) and larger is performed by homogeneous filling of the mold to 2.2 to 2.5 times the desired sheet thickness and then carefully leveling the powder with a straight edge. The powder is then cold compressed for 5 to 10 min at 7 to 10 MPa (1 to 1.5 ksi) to expel air and compact the material. At a minimum of

cycle is begun and continues until the entire charge is fused. Pressure is then increased to 10 MPa (1.5 ksi) during cool-down to prevent voids inside the block and sink marks on the surface. Sheets can be subsequently sliced (skived) if preheated to 140 to 150 °C (285 to 300 °F) before slicing. After being sliced, sheets are placed between thin aluminum steel plates, reheated to 150 °C (300 °F) and slowly cooled to room temperature to remove processing stresses.

Porous parts are produced by the compaction and sintering method, possibly including vibratory compaction. A cavity is filled with resin and vibrated to ensure uniform packing. The volume is then enclosed and heated to 175 to 205 °C (350 to 400 °F) without pressure, and then cooled. Predictable porosities are attained by careful selection of particle size distribution and bulk density. Resins with extremely low bulk densities (200 to 250 g/L, as opposed to a normal 350 to 500 g/L) are particularly suitable for these applications.

Other fabrication techniques include direct compression molding of parts, hot stamping, forging, and hot plate or spin welding.

Semi-finished parts can be easily sawed, turned, planed, milled, drilled, or punched with standard wood or metal fabricating machines. Sharp tools with wide-tooth spacing are necessary for adequate chip clearance and heat removal.

Adhesion of UHMWPE to substrates is poor, even with surface roughening and heat treatment. The difference between the coefficient of thermal expansion of UHMWPE and those of metals makes mechanical methods of fastening preferable. These include weld washers, stud welds, rivets, and flat-head elevator bolts. The fastener head is normally countersunk below the surface and then capped with a UHMWPE plug to provide a smooth surface.

Resin Compound Types and Properties.

This resin is sold as a fine powder, either in natural form or containing a small amount of metallic stearate, which acts as a corrosion inhibitor. Fabricators typically process UHMWPE into rods, tubes, boards, or profiles by ram extrusion and into billets and sheets by compression molding. Pigmentation, UV light stabilization, antistatic, cross-linking and thermal/electrical-conductivity formulations, as well as reinforcements can easily be added to the virgin resin during processing.

Although numerous modifications to

UHMWPE can be made with additives and fillers, it is difficult to improve its two outstanding properties, abrasion resistance and impact strength, because no chemical bonding occurs between the resin and the additive. In fact, one must consider the amount of decrease of either property that can be tolerated. Normally, any modification made to satisfy the application requirements compromises properties. Because the resin is viscoelastic, any additive must be homogeneously mixed prior to processing. Furthermore, the particle size distribution of the modifier should be comparable to or smaller than that of the UHMWPE particles.

Reinforcement. Hardness, creep resistance, dimensional stability, and coefficient of thermal expansion, which is normally 1.5 to $2.0 \times 10^{-4}/^{\circ}\text{K}$, can be improved with the proper selection of reinforcing filler. Wood flour, glass spheres, glass fibers, graphite, aluminum powder, talc, chalk, silicates, and carbonates have been used in concentrations of 5 to 30%. The addition of 5% micro-glass spheres increases wear resistance and is commonly used for suction box covers in the pulp and paper industry (Ref 5).

Cross-Linking and Antioxidants. Chemical cross-linking with 0.3 to 0.5% (active ingredient) organic peroxides has been found to improve wear resistance by as much as 30% over nonmodified resins, while reducing deformation under load. Thin-film transparency improves, and density is lowered because of a reduction in crystallinity. Cross-linking can also be accomplished by beta or gamma radiation although polymer chain scission leading to degradation can occur, particularly when radiation occurs in

the presence of oxygen. For continued exposure to high temperatures (80°C , or 175°F), it is desirable to add 0.1 to 0.2% antioxidant to minimize degradation.

Metal Powder Additives. The heat conductivity of UHMWPE components can be improved by adding metal powders such as copper, aluminum, and bronze. A 400% increase in conductivity (1.65 versus $0.4 \text{ W/m} \cdot ^{\circ}\text{K}$, or 11.4 versus $2.8 \text{ Btu} \cdot \text{in/h} \cdot \text{ft}^2 \cdot ^{\circ}\text{F}$) occurs with the addition of 50 wt% (28.5 vol%) aluminum powder. Graphite improves thermal conductivity even more efficiently. In both cases, however, toughness and strength are significantly reduced. A mixture of 30 wt% aluminum powder and 10 wt% graphite results in a thermal conductivity of $2.5 \text{ W/m} \cdot ^{\circ}\text{K}$ ($17 \text{ Btu} \cdot \text{in/h} \cdot \text{ft}^2 \cdot ^{\circ}\text{F}$) and is used for pile driver pads (Ref 5).

UHMWPE is an effective electrical insulator with a dielectric constant of 2.3 at 2 MHz. The surface resistivity of the natural resin is greater than 10^{13} . It can be reduced to the antistatic region (10^9 to 10^6), a level required for many mining applications, by the addition of 5 to 6.5 wt% conductive carbon black. Concentrations of 15 to 20 wt% carbon black provide resistivities in the conductive range of less than 10^3 .

UV Resistance. The addition of light-absorbing substances provides UV light resistance, with 2.5% carbon black being the most commonly used additive. When the finished product cannot be black, satisfactory UV resistance, which is a minimum of 5 years, can be obtained by 0.5 wt.% UV stabilizer.

Pigments and Lubricants. UHMWPE is typically sold in its natural color, which is

opaque white. However, it can be produced in any color with the proper selection of organic or inorganic pigments. Normally, 0.1 to 0.3 wt% is sufficient to obtain good color. Silicone oil, waxes, greases, and molybdenum disulfide (normally, 2 to 5 wt%) can be added to UHMWPE to reduce by a slight amount the already low coefficient of friction properties.

Flammability. The flammability of UHMWPE is similar to that of PE. It ignites readily when in contact with flame and continues to burn when the source of ignition is removed.

Resin Suppliers. Domestic resin producers of UHMWPE are Ticona LLC, Summit, NJ and Montell, Inc., Wilmington, DE.

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See example below for rate information:

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