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Ultra-high molecular weight polyethylene (UHMW-PE) and its application in microporous separators for lead/acid batteries

L.C. Wang [a,*], M.K. Harvey [a], J.C. Ng [b], U. Scheunemann [c]

[a] Ticona, 2525 South Shore Blvd., Suite 110, League City, TX 77573, USA
[b] Hoechst Singapore, 200 Cantonment Road, 16-02 South Point, Singapore, 0208, Singapore
[c] Ticona, Ruhrchemie Works, GUR R&D, D-46128 Oberhausen, Germany

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Abstract

The polyethylene (PE) used in separators for automotive lead/acid batteries is actually UHMW-PE (ultra high molecular weight polyethylene). Microporous PE separators were commercialized in the early 1970s. Since then, they have gained in popularity in the lead/acid battery industry, particularly in SLI (starting, lighting and ignition) automotive applications. This paper provides an introductory overview of the UHMW-PE polymer and its contributions to the PE battery separator manufacturing process, battery assembly and battery performance, in comparison with other conventional separators such as polyvinyl chloride (PVC) and glass fibre.

Keywords: Lead/acid battery; Polyethylene; Separator; Automotive batteries

1. Introduction

Ultra-high molecular weight polyethylene (UHMW-PE) was commercially introduced in the 1950s. Although it belongs to the polyethylene (PE) family, it offers superior performance to conventional PE types such as high density polyethylene (HDPE) and low density polyethylene (LDPE). UHMW-PE has an impact strength and an abrasion resistance superior to any other thermoplastic. The first commercial use of UHMW-PE in PE separators for lead/acid batteries was in the early 1970s. PE separators have contributed to improved battery specific energy and specific power, increased battery cycle life, and higher temperature operating capabilities. PE separators have gained in popularity and have replaced PVC, cellulose, glass fibre, and other conventional separators. Today, PE separators have captured almost 100% of the USA and more than 70% of the worldwide automotive markets [1]. Among the unique properties offered by PE separators are: excellent microporous structure for electrolyte flow with minimal lead particle deposits; excellent ductility, strength and toughness for envelopability and plate puncture resistance; excellent oxidation, chemical and thermal resistance to resist premature deterioration; good manufacturability with high production efficiency and low raw material cost to reduce overall manufacturing costs. Many of these characteristics are dependent on the type of polymer binder used in the ‘PE separator’. Today, the polymer of choice is UHMW-PE, which has more than 10 times the molecular weight of conventional HPDE.

2. What is UHMW-PE polymer?

Ultra high molecular weight polyethylene is a linear, low pressure, Ziegler-type catalyst, polyethylene resin. It is sold as a fine powder with a typical particle size of about 120–150 μm, either in natural form or containing a small amount of a processing additive. The resin is commercially available in grades with a molecular weight that ranges from 3×10^6 to 8×10^6 g mol^{-1}.

UHMW-PE has both the highest abrasion resistance and highest impact strength of any plastic. Figs. 1 and 2 show a comparison of its impact strength and abrasion resistance with other materials, respectively. In many applications, even steel is replaced by UHMW-PE if wear resistance is required. This resistance to abrasion is due to the long molecular chains of UHMW-PE and its semi-crystalline

* Corresponding author.

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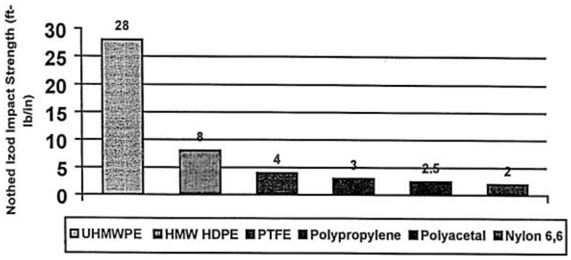

Fig. 1. Comparison of notched Izod impact resistance.

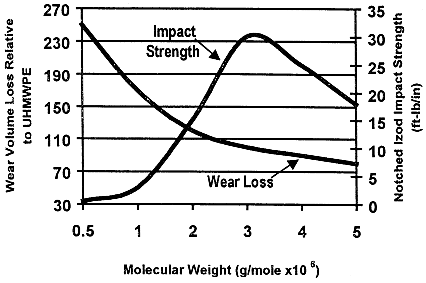

Fig. 3. Effect of molecular weight on impact strength and wear resistance.

structure. UHMW-PE not only has superior impact strength at ambient conditions, but also maintains its high impact resistance down to very low temperatures. As the molecular weight increases from 3×10^6 to 6×10^6, abrasion resistance improves significantly (by approximately 30%), whereas impact strength decreases slightly, as shown in Fig. 3.

The extremely high molecular weight of UHMW-PE makes it a unique material. Its special characteristics in moulded forms include:

–outstanding abrasion resistance
–highest impact resistance of any plastic
–low coefficient of friction
–non-stick, self-lubricating surface
–good chemical resistance
–negligible water absorption
–excellent properties at cryogenic conditions
–good stress cracking resistance
–good energy absorption and sound-damping.

The outstanding performance characteristics of UHMW-PE can be maintained from -269 to 90°C, and even higher for short periods of time. In addition, unlike lower molecular weight polyethylene, the melt flow viscosity of UHMW-PE is very high, such that it does not liquefy when heated above its crystalline melting point. This non-flow behaviour is due to the high degree of entanglement of the very long molecular chains. For the same reason, the thermal stability of UHMW-PE is superior to that of PE's of lower molecular weight. At low mechanical stress levels, the material can be employed at temperatures in the region 80 to 90°C without any substantial deformation taking place. Even at temperatures of

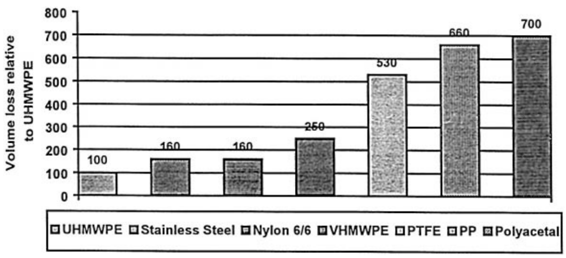

Fig. 2. Comparison of abrasion resistance.

~ 200°C, UHMW-PE shows fairly high dimensional stability because of its viscoelastic properties.

Like all polyethylenes, UHMW-PE has very good resistance to aggressive media (except for strong oxidizing acids). Aromatic, some aliphatic and halogenated hydrocarbons that would dissolve PEs of lower molecular weight cause only slight surface swelling at moderate temperatures with UHMW-PE.

3. UHMW-PE resin characterization

As mentioned above, the unique performance of UHMW-PE is determined by its molecular weight. The basic chemical unit of UHMW-PE is $–CH_2–$. Thus, a 4×10^6 molecular weight polymer contains approximately 285×10^3 carbon atoms in the polymer chain. The insolubility of UHMW-PE makes size exclusion chromatography (SEC) impractical. The molecular weight of UHMW-PE is usually determined by the measurement of the dilute solution viscosity (*alternately reduced solution viscosity RSV*), as detailed in ASTM D1601 and D4020. Extrapolating the RSV to infinite dilution leads to the intrinsic viscosity (IV). With these procedures, UHMW-PE is a polyethylene having values in the range of about 1600 to 2900 ml g^{-1}. The nominal molecular weight is approximated by means of the Mark–Houwink equation: $MW = 5.37 \times (IV)^{1.37}$, where IV represents the intrinsic viscosity [2].

A determination of what is termed elongational stress (*alternatively flow value / ZST*) (DIN 53493) provides an alternative means to characterize the resin with respect to its nominal molecular weight. The procedure is as follows: test pieces, each with a different weight attached, are suspended in a silicone bath heated to 150°C. Under the test loading, the specimens undergo tensile elongation. The length of time required for 600% elongation is recorded. From a logarithmic extrapolated plot, elongational stress is defined by the stress required for a 600% elongation in 10 min. Elongational stress values for different grades of UHMW-PE range between 0.1 and > 0.7 N mm^{-2}. The elongational stress of UHMW-PE can be statistically correlated to its intrinsic viscosity.

Other powder properties, such as bulk density, particle size and size distribution are frequently used to characterize the processibility of a rising for compression moulding, ram extrusion and PE separator extrusion. These properties can be accurately measured in accordance with ASTM and ISO standards. Due to the non-flow characteristic of UHMW-PE, the conventional thermoplastic processing methods, such as injection moulding and screw extrusion are impractical for this resin.

4. Major applications of UHMW-PE

UHMW-PE was developed initially for applications that demanded its superior abrasion resistance and impact strength. Because of its self-lubricating, non-stick, lightweight, and wear-resistant characteristics, it has been used for many years in both the bulk material handling (grain, cement, gravel, and aggregate) and the coal mining industries. Applications include liners for silos, hoppers, dump trucks, railcars and chutes; conveyor troughs and flights; wear strips; slide plates; and dry bearings and bushings.

At higher temperatures, aggressive hydrocarbons such as oil can form gels with UHMW-PE and act as a diluent rather than a solvent. Unlike UHMW-PE alone, the resulting gel can be extruded. Such technology was adapted for PE separator fabrication and fibre spinning. During the 1960s, the resin was first studied for use in lead/acid battery separators [3]. Today, PE (actually, UHMW-PE) separators offers excellent performance and manufacturing cost saving in the lead/acid battery industry, particularly in automotive applications. The so-called gel spun UHMW-PE fibre probably yields the highest specific tensile properties of any polymeric fibre. UHMW-PE fibre has its major applications in both the armour industry, such as bulletproof vests, and the non-armour industries, such as fishing lines and nets, safety gloves and nautical ropes.

5. UHMW-PE in separator application

More than 70% of the worldwide automotive markets use PE separators [1]. UHMW-PE, silica and oil are the primary components used to manufacture PE Separators. The major manufacturing process steps include compounding, calendering extrusion, oil extraction and solvent recovery, drying and winding. Prior to oil extraction, a typical PE separator formulation consists of 50–60% oil, 30–40% silica, and 10–20% UHMW-PE and some minor ingredients. PE separators have addressed the following needs of the automotive marketplace [4]:

(i) improved production efficiency with screw extrusion;
(ii) improved assembly efficiency and performance by automated enveloping;
(iii) excellent microporous structure;
(iv) excellent puncture resistance and mechanical properties;
(v) satisfactory chemical resistance and thermal stability.

The UHMW-PE provides the flow media and strong binder to process and hold the silica particles together in a strong and flexible matrix under the severe chemical, oxidative, and thermal conditions experienced in batteries.

6. Contribution of UHMW-PE to separator characteristics

6.1. Calendering extrusion significantly improves separator production efficiency

PE separators are processed by screw extrusion which, in comparison with the sintering process for PVC separators, significantly increases productivity and reduces process cost. The UHMW-PE creates a flow media for the silica. As the UHMW-PE comes into contact with oil in the extruder, under elevated temperatures and shear, it transforms into a viscous gelatinous (gel) state. This is not a chemical reaction process, but a mechanical transformation. The UHMW-PE/oil gel carries the silica particles and forms a continuous matrix. This gel has excellent strength and allows the matrix to be extruded and calendered into thin films. This allows for higher speed production of thinner backweb separators that is not possible with PVC, glass, or cellulosic separators. If a lower molecular weight polyethylene were used, it would generate a low viscosity matrix and greatly reduce the melt strength and processibility of the separator.

6.2. Automated separator enveloping notably increases battery assembly efficiency and battery life

The ductility of a separator is of crucial importance for enveloping separators. The microstructure of separators must be sufficiently flexible to permit enveloping without cracking. Since the silica structure is brittle, ductility of the separator is an inherent property of UHMW-PE. Typically, the tensile elongation of UHMW-PE at failure is over 350%. It also has the unique characteristic of maintaining its ductile properties well into cryogenic temperatures. The microstructure developed by UHMW-PE is thus sufficiently ductile to hold the fragile silica matrix together through high-speed enveloping equipment with no cracking at any normal operating temperature. Lower molecular weight polyethylene would not be able to provide this level of ductility at all operating temperatures.

Envelopability is one of the major reasons why PE separators have gained in popularity in recent years. Separator enveloping not only increases the assembly efficiency and quality, but also strongly reduces the potential for bottom and side shorts that are caused by dendrite growth or plate shedding, and hence, has improved battery service life.

6.3. Microporosity improves separator performance and life

The maximum, typical pore size of PE separators is less than 1 μm, compared with over 20 μm for PVC separators, over 30 μm for cellulose separators, and over 40 μm for glass–fibre separators [5]. The small pore size makes the PE separators much more resistant to small particles of lead depositing in the separator pores and causing short circuits. Separators with larger pore sizes are more susceptible to this phenomenon [6–8].

The silica is largely responsible for the microporosity. Separators made with UHMW-PE have a good total pore volume with pore sizes notably smaller than those of PVC, cellulose, and glass–fibre separators. The porosity of PE separators is created by the extraction of oil from the separator and silica's own porosity. The UHMW-PE forms a binder media for the silica particles by developing weblike structure to link the particles. This process is possible due to the high molecular weight characteristics of UHMW-PE and the development of the viscous UHMW-PE/oil gel. The gel smears over the silica particles in a weblike structure without flowing into the silica pores and clogging them. Once the calendered separator is extracted and cooled, the web structure hardens and links the silica particles while only minimally reducing the porosity of the silica particles. A lower molecular weight polyethylene would melt and create more of a continuous film that would cover the silica and block the pores.

6.4. Excellent puncture resistance safeguards the separator against premature failure

Puncture resistance is critical because any puncture of the separator offers a hole for lead particle deposition and, therefore, the possibility of premature battery failure. Studies [9,7,10] show that separators made with UHMW-PE have superior puncture resistance in comparison with PVC, cellulose, and glass fibre. Improving the puncture resistance is always one of the major focuses for manufacturers of PE separators.

Therefore, puncture resistance is a critical determinant of life. The separator structure must be sufficiently tough to resist plate puncture during enveloping and high vibration loads. The silica structure has little resistance to puncture. Most puncture-resistant characteristics are related to the UHMW-PE. Its properties of high flexibility, high tensile elongation and superior impact strength are well suited to fulfil these needs. Lower molecular weight PEs would not offer the same level of performance. The puncture resistance improves as the molecular weight of UHMW-PE increases [1].

6.5. Thermal stability and oxidation resistance ensures separator performance life

UHMW-PE has superior thermal stability and oxidation resistance compared with polyethylene of lower molecular weight. Due to its exceptionally high toughness, UHMW-PE can withstand significant mechanical stress without failure, even at cryogenic temperatures. Unlike lower molecular weight polyethylene, UHMW-PE by virtue of its viscoelastic properties also displays remarkably high dimensional stability even up to 200°C. Cycling test results [8] show that PE separators at 50°C, as required in DIN 43539E-1980, have the best thermal resistance and hence, the best cycle life compared with PVC and cellulose separators. Also, PVC separator, when exposed to high temperatures, can release chlorine gas that can have serious adverse effects on battery life [7].

Nevertheless, UHMW-PE will oxidize under battery conditions, although at a slow rate. As the polyethylene is attacked, the molecular chains are crosslinked or broken. This results in a slow degradation of some of the mechanical properties.

7. UHMW-PE separators

Today, major UHMW-PE suppliers to the battery industry include Ticona (a member of the Hoechst Group), Montell and DSM. Of the three, Ticona is by far the major world-wide supplier to the PE separator industry, offering UHMW-PE with molecular weights from 3 to 8 million g mol^{-1}. Ticona has two major production and technical service facilities, the Bayport Plant near Houston, TX, and the Ruhrchemie Plant in Oberhausen, Germany. Also, Ticona has a pilot plant located at the Ruhrchemie facility, and its research and development staff are located both at the Ruhrchemie facility and the Frankfurt research center.

Among the polyethylene family, only UHMW-PE is suitable for separator fabrication. Therefore, it would be more appropriate to call these separators 'UHMW-PE separators' rather than 'PE separators'.

References

[1] W. Bohnstedt, J. Power Sources 59 (1996) 45–50.
[2] H. Stein, Ultrahigh Molecular Weight Polyethylene (UHMW-PE), Engineered Materials Handbook, Vol. 2.
[3] D.W. Larsen, C.L. Kehr, US Patent 3,351,495, Nov. 7, 1967.
[4] L.C. Wang, The 12th Annual Battery Conference on Applications and Advances, January 1997, pp. 69–71.
[5] S.J. Strzempko, W.M. Choi, Battery separators—past, present and future, The Battery Man, March 1993, pp. 15–21.
[6] M.J. Weighall, J. Power Sources 53 (1995) 273–282.
[7] J.W. Reitz, Separator technology for lead/acid batteries, J. Power Sources 19 (1987) 181–188.
[8] W. Bohnstedt, A. Weiss, J. Power Sources 38 (1992) 103–110.
[9] P.J. McLaughlin, The strategy decision of leaf vs. envelope battery construction, 48th IBMA Convention, Oct. 1985.
[10] M.J. Weighall, Battery separators for the new millenium, 5th ELBC Convention, Sept/Oct. 1996.