Ultrahigh molecular weight polyethylene: the new reality of the Russian polyolefin industry

E. A. Maier, V. K. Dudchenko, A. N. Poddubnyak, and O. L. Arkatov
Tomsk Petrochemical Works Open Joint Stock Company

The specific, and often unique, properties of ultrahigh molecular weight polyethylene (UHMWPE) have been described in detail in the literature, as have their widest areas of application: engineering, the chemical industry, electrical engineering, medicine, and so on. In the more than forty year history of the industrial production of UHMWPE, leaders of the world market such as Hoechst, DSM, and Ticona have increased the volumes of UHMWPE production to tens of thousands of tons per year; a range of grades has been developed with the optimum properties for different processing technologies and end uses; improved production equipment has been created, for example, for injection moulding, which has made it possible most productively to process the polymer which does not pass into the viscous flow state after melting and can be produced in a technologically ineffective powder form [2].

Likewise, in the 1970s and 1980s, research and pilot-plant work was carried out in the Soviet Union on the production of UHMWPE, showing the inaccuracy of the conclusion by Andreeva et al. [1] concerning the possibility of producing high-quality polymers on any production lines for the synthesis of high-density polyethylene (HDPE).

In view of the urgency of the task of developing Russian technology for UHMWPE synthesis, and taking into account the available scientific and technical potential, with the guidance of the Tomsk Petrochemical Integrated Works, in the middle of the 1990s the decision was made to create a pilot unit for the suspension polymerisation of ethylene. Specialists of the Board for Scientific and Technical Development and the planning and design department of the enterprise developed the initial data, technological layout, and design of the unit. In the development work, use was made of titanium–magnesium catalysts of the Institute of Catalysis of the Siberian Section of the Russian Academy of Sciences, and the given partnership continued both at the stage of investment in the project and in experimental optimisation of the technology.

With a constant shortage of recycling facilities, crises in the Russian economy, and an even more complicated position at the enterprise, construction and assembly and start-up and adjustment work on the unit was carried out by chief specialists without involving specialised enterprises, which slowed down somewhat the delivery of the unit for complex testing.

In 2000, the unit for UHMWPE synthesis was put into service using the two-reactor layout shown in Figure 1.

The synthesis process consists of the following technological operations.

A solution of organoaluminium cocatalyst (AlEt₃, Al(i-Bu)₃) in heptane is transferred from container V-12 into measuring tank V-1, and a suspension of titanium–magnesium catalyst (TMC) in heptane is transferred from container V-15 into measuring tank V-2. The polymerisation of ethylene is carried out in two parallel operating reactors R-1 and R-2 at a temperature of 45–80°C and a pressure of 2–4 kgf/cm² with the continuous feeding of components of the catalytic system from measuring tanks, ethylene through valves HSA-2 and HSA-3, and heptane from collection tank V-5 for dilution of the suspension. Typical polymerisation conditions in the reactors are as follows: bath modulus of the order of 130–170 g/l, concentration of organoaluminium matter 0.5–1.0 g/l, and average residence time 3–5 h. The TMC concentration is set according to laboratory tests of activity and the problem
being addressed. When the reactors are 80% filled with suspension, the suspension is partially discharged through spherical control valves into degasser V-3, where, by throttling, precipitation of dissolved ethylene from suspension occurs, and, by feeding heptane, dilution of the suspension is carried out. The suspension prepared in this way is fed to centrifuges C-1 and C-2, where it is separated into centrifugate (heptane, organoaluminium matter, impurities of dustlike polyethylene, and low molecular weight polymer) and solid phase. The degree of forcing out of solid phase in the centrifuge is controlled by the concentration of suspension fed, by the rotational speed of the rotor, and by the degree of opening of the centrifugate discharge windows. The powder is discharged continuously into bins B-1 and B-2, and the centrifugate into vessel V-6.

The polymer is dried in a periodic regime in a rotary vacuum dryer DR-1. The dryer is evenly heated, with simultaneous feeding of steam into the jacket of the housing and hot water into the rotor, powder is charged from bin B-1 (B-2), the housing is sealed, and the dryer is evacuated by the vacuum system to a residual pressure of 0.013 MPa. The drying operation ends at a residual content of volatiles in the powder of no more than 0.25%, and the dry polymer is discharged into one of the bins B-3 or B-4, where it is stored beneath a nitrogen blanket. The polymer from the bins is analysed, rated, and packaged in fabric polypropylene bags with a polyethylene liner.

Analysis of the product obtained is carried out according to the following principal and optional indices: the density of UHMWPE according to GOST 1539, the bulk weight according to GOST 11035.1, the mass fraction of the volatiles according to GOST 26359, the mass fraction of ash according to GOST 15973, the physicomехanical properties of pressed specimens according to GOST 11262, the intrinsic viscosity of the solutions in decalin according to ISO 1628-3, the particle size distribution by sieve analysis according to ASTM D1921, and the calorimetric characteristics by differential scanning calorimetry (DSC) according to ASTM D3418 D3417.

The group of certified catalysts (TMCs) and the permissible variations in operational regimes on the synthesis unit showed the possibility of producing a wide grade range of UHMWPE in terms of the particle size distribution of the powder, the achieved values of the molecular weight (up to 5 million nominal units), and the purity of the polymer (according to the residual content of ash and volatiles). Table 1 gives comparative analyses of UHMWPE specimens from the pilot unit and commercial grades of similar designation of the leading producer companies, from which it can be seen that the polymer, in its properties, occupies an intermediate position between the best commercial grades on the market and fully meets the requirements for material for the production of accumulator strip (analyses were carried out by a foreign expert).
The annual calculated productivity for operation on one reactor, according to the results of a 2 week trial run, was of the order of 300 t (prolonged tests using the two-reactor scheme are not carried out for economic reasons).

Furthermore, the unit makes it possible to carry out the synthesis of UHMWPE in a periodic regime when the user needs a minimum amount of polymer with prescribed properties, or when it is necessary to test a new type of catalyst. For the latter case, at present the unit is equipped with a hydrogen feed line, which will also make it possible to test catalysts for the synthesis of HDPE that have been developed by Russian scientists.

As practice with operation of the unit has shown, there is practically no Russian market for UHMWPE consumption – roughly 20 companies engaged in specialist use of the polymer and having production equipment for its processing are consuming something of the order of 30–40 t/year. The largest-capacity markets in theory, such as engineering, the chemical industry, and electrical engineering, are continuing to use materials that have similar properties (fluoroplastics, polyamides) but are more expensive, as they do not have specific equipment for the processing of UHMWPE, and other markets, such as medicine, traditionally work with imported endoprostheses. And all this against a background of new ways of specialist use of UHMWPE that are constantly being proposed by scientists [3–5].

We offer our services to the Kazan’orgsintez Open Joint Stock Company, the leader of the Russian polyethylene market, which is involved in drawing up investment policy, in setting up a pilot-plant unit for ultrahigh molecular weight polyethylene [6]. The Tomsk Petrochemical Works is ready to supply the needs of the enterprise for UHMWPE and to take part in the development of the production layout using experience gained.

We invite all enterprises engaged in (or planning) the processing or application of ultrahigh molecular weight polyethylene to collaborate with us for the more successful and effective advancement of the material on today’s technology market.

REFERENCES


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