Compaction of reactor powders of ultrahigh molecular weight polyethylene

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In previous publications (refs. 1 and 2) an examination was made of features of the processing of ultrahigh molecular weight polyethylene (UHMW PE) by die stamping and the properties of the articles produced.

Setting up of the cost-effective production of articles from UHMW PE by the given method is being held back by the need for preliminary production of semiproducts exposed to strain. Owing to features of the given material, its processing by high-performance methods is difficult and the production of semiproducts requires the creation of special technology. The advantages of forming methods in the solid state are largely lost in this case. In view of this, the present work is devoted to the development of a process for the production of compacted semiproducts.

The semiproduct for subsequent die stamping should have a shape similar to the configuration of the article and have an identical mass if the process is to be waste free. An analysis of published data showed the possibility of producing such semiproducts from UHMW PE by sintering, which is used to produce articles from difficult-to-process materials (refs. 3 and 4). Sintering is the process of the transition during heating of powder compacted to different degrees into a solid or porous substance.

The process of producing articles from polymers by sintering includes the following stages:

- compaction of polymer powder at room temperature into a semiproduct of the required shape;
- sintering of the formed semiproduct in the free state at a temperature exceeding the melting point of the polymer, and in vacuum to prevent degradation processes;
- preliminary experimental investigations and published data showed that the main parameters of this process are: the compaction pressure \( P_c \), the sintering temperature \( T_s \), and the sintering time \( \tau_s \).

A study was made of the influence of the parameters of the sintering process and the initial characteristics of the reactor powders on the quality (solidity) of the semiproducts produced. The selected criterion for quality evaluation was the density \( \rho \), as a quantity sensitive to the presence of porosity in the semiproduct obtained. In this case, ‘solid semiproduct’ means a polymeric substance formed as a result of temperature and force action that ensures breakdown of the initial structure and shape of the powder or granulated polymer and the formation from it of a single mass. Control specimens produced by hot compression were assumed to correspond to the definition ‘solid’.

In view of the fact that different producers use different catalytic systems and mechanisation of the production process, the initial properties of powders differ considerably. For the investigation, four grades of UHMW PE were selected: home-produced UHMW PE-1 and UHMW PE-2, Bulen 2 (Bulgaria), and Hostalen GUR-412 (Germany). Table 1 presents values of the densities and data obtained by differential scanning calorimetry (DSC), characterising the thermodynamic properties of the reactor powders and of compacted semiproducts obtained from them.

It can be seen that the initial reactor powders have higher values of the temperature of the start of melting \( T_{s,m} \), the temperature of the peak of melting \( T_p \), and the degree of crystallinity \( \alpha \), and a narrower interval of melting (\( \Delta T = T_p - T_{s,m} \)).
This is due to the fact that the supermolecular structure of the nascent (the structure formed during polymerisation) powder is largely ideal. According to data given in ref. 5, it is characterised by a small number of entanglements in the amorphous regions, and by fairly ideal crystallites of uniform size, which are formed by macromolecules in straightened conformations. The supermolecular structure of UHMWPE crystallised from the melt differs considerably from the structure of the nascent powder. The degree of crystallinity and the size of the crystallites are considerably smaller, a wider size distribution of the crystallites is characteristic, and the crystallites are formed by macromolecules in folded conformations (refs. 6 and 7). The density of the polymer forming the particles of nascent powder is also considerably higher than the density of UHMWPE crystallised from the melt. For example, for Hostalen Gur-412, these values are respectively 956 and 935 kg/m³ (ref. 9).

With increase in $P_c$, the density increases and, on achievement of $P_c > 100$ MPa, hardly changes.

Semiproducts compacted from UHMWPE powders with a lower bulk density have better strength characteristics (the compression strength is 16.8 MPa for UHMWPE-1, and 0.4 MPa for GUR-412).

An analysis of data on the change in density of specimens after sintering as a function of sintering temperature and compaction pressure indicates the following. For all UHMWPE specimens, with increase in the sintering temperature, the density of the semiproducts initially increases, and then the density values either change little or decrease. The decrease in density is probably due to the development of degradation of the polymer under the prolonged action of high temperatures. For UHMWPE-1 and Bulen B₂ powders, the optimum parameters are $T_s = 438$ K, $P_c = 130$ MPa, and $\tau_s = 7$ min/mm, with which a density is achieved that is similar to the density of specimens produced by compression. For UHMWPE-2 and GUR-412, it was not possible to achieve density values obtained by compression at any sintering temperatures. The semiproducts had a porous structure that could be discerned visually. Here it was noted that, in the case of sintering, the density decreases with increasing compaction pressure, the height of the semiproduct increases, and its diameter decreases.

The differences observed in the compactability and compressibility of UHMWPE powders are probably due to differences in their particle size distribution and in the particle shape.

The particle size distribution of the powders was studied by sedimentation analysis, which was based on the differences in mass between the particles. Figure 1 presents differential curves of powder particle size distribution.
It can be seen that specimens of UHMWPE powders possessing better compactability and sinterability have a lower most probable particle radius and a greater proportion of particles of small size (<50 \( \mu m \)). However, on the whole, the nature of the dependences is fairly similar and makes it impossible to judge the reasons for differences in compactability and sinterability of the powders investigated.

In view of this, investigations were carried out using a Fritsch laser diffraction microanalyser, the principle of action of which is based on a direct evaluation of the geometric dimensions of particles from an analysis of the diffraction pattern. From the data presented in Fig. 2 in the form of differential curves of the particle size distribution it can be seen that powders that are more poorly compacted and sintered have a narrower particle size distribution, a greater average particle size, and contain practically no <40 \( \mu m \) fractions. Data of diffraction analysis are in good agreement with results obtained by the sedimentation method for all specimens of UHMWPE powders, with the exception of Bulen B\(_2\). According to data of the sedimentation method, Bulen B\(_2\) particles have the smallest (~45 \( \mu m \)) average diameter of the specimens investigated, but according to results of diffraction analysis they have the greatest average diameter (~250 \( \mu m \)). This contradiction is probably due to the structure of the Bulen B\(_2\) particles. They have a low mass and considerable size, which indicates a developed specific surface.

An analysis of micrographs of specimens of UHMW PE powders confirms data of laser diffraction analysis. The smallest size is possessed by particles of UHMW PE-1 powder, and the greatest size by Bulen B\(_2\). Specimens of UHMW PE-2 and GUR-412 powders occupy an intermediate position.

UHMW PE specimens with poor compactability and sinterability have particles with a near-spherical shape. Specimens with good compactability and sinterability consist of particles of irregular shape and a fibrous structure with a developed specific surface.

Thus, specimens of UHMWPE powders possessing good compactability and sinterability have a combination of the following characteristics: low bulk density, wide particle size distribution, the presence of a sufficient number of fractions of particles of small size, and an irregular particle shape.

Such characteristics are more typical of specimens of Bulen B\(_2\) and UHMW PE-1.

It is not possible to produce a semiproduct by sintering in the free state from grades GUR-412 and UHMW PE-2, which have a near-spherical particle shape, owing to breakdown of the formed packing of the powder particles at elevated temperatures on account of partial reversibility of the strains arising during compaction. In view of this, it is of interest to develop a process for the production of semiproducts for subsequent die stamping that makes it possible to process UHMW PE powders with the morphology indicated above. For subsequent investigations, the grade GUR-412 was selected, ensuring the production of articles possessing high service characteristics.

The investigations carried out showed that an effective method for producing semiproducts is compaction by sintering at low pressure. By experimental means it was established that it is sufficient to provide a pressure of ~0.8–1.0 M Pa. In contrast to the method of sintering in the free state, the semiproduct compacted at room temperature is placed in a thin-walled (thickness 1.5–2.0 mm) metal mould, in which, through an elastic element, a certain pressure is created. The metal mould increases the heat feed rate to the polymeric material, which increases the compaction rate by comparison with sintering in the free state. The presence of pressure in the system prevents breakdown of the powder structure produced by compaction and pore formation. Furthermore, the dimensions of the semiproduct are unchanged after sintering.

The optimum parameters for the production of semiproducts by sintering in a metal mould are \( T_s = 468 K \) and \( \tau_s = 4 \text{ min/mm} \). The characteristics of the semiproduct produced with the above values of the sintering parameters are presented in Table 2.

| Table 2 Properties of semiproducts of GUR-412 produced by different methods |
|---------------------------------|-----|------|--------|
| Production method | \( \rho_s \), kg/m\(^3\) | \( V_1^* \), m/s | Micro-hardness, MPa |
| 1. Compression | 935 | 2210 | 52.0 |
| 2. Sintering | 936 | 2230 | 54.0 |
As can be seen from the data presented in Table 2, a semiproduct produced by the given method has properties similar to the control (compressed) specimen. Thus, the method of sintering at low pressure can be recommended for the production of semiproducts of UHMW PE powders with a near-spherical particle shape.

REFERENCES

3. I.N. Andreeva et al., Ultrahigh molecular weight high-density polyethylene, Khimiya, Leningrad, 1982, p. 80

(No date given)