UDC 678.7

DOI: 10.15372/CSD20170612

Effect of Molecular Mass on Structure and Properties of Ultra-High Molecular Weight Polyethylene

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(Received August 25, 2017; revised October 1, 2017)

Abstract

The paper presents the results of a study into the effect of molecular mass on structure, properties, and behaviour of ultra-high molecular weight polyethylene under thermal action. Diversity in physical and thermal properties is due to the difference in the polymer structure, as demonstrated.

Keywords: ultra-high molecular weight polyethylene, UHMWPE, molecular mass, structure, properties, thermal behaviour

INTRODUCTION

Polyethylene is a large-tonnage polymer that finds use in various industries owing to low-toxicity, high chemical stability, relatively wide operating temperature range, and good processing properties that allow obtaining a broad assortment of various purpose products [1]. Low indicators of strength properties fall within to a significant disadvantage, which, on the one hand, leads to the generation of a large volume of wastes in the manufacture of products and, on the other hand, to rapid wear of products and transfer them into the category of waste.

One way to address the problem of increasing environmental friendliness of polyethylene is an increase in molecular mass (MM) of the polymer, which particularly leads to increasing strength characteristics [2, 3]. A polymer with MM up to 500 000 refers to so-called high molecular weight polyethylene and beginning with 500 000 amu, the material is classified already as ultra-high molecular weight polyethylene (UHMWPE). Ultra-high molecular weight and structure of this engineering thermoplast determines its high strength, hardness, a low coefficient of friction, lack of transition into the viscous flow state, *etc*. [2, 4–7]. This allows obtaining products not only with high exploitation qualities but also the high useful lifetime, which decreases the amount of the resulting waste from consumption of UHMWPE and makes this material more environmental compared to low, high, and medium density

polyethylenes.

On the other hand, a question arises concerning environmental friendliness of wastes of UHMWPE products, methods for their disposal, which of course requires the study of the chemical structure and polymer behaviour under thermal impact.

Due to lack of transition into the viscous flow state, processing of UHMWPE into products is carried out by a special cold pressing technique followed by thermal treatment. The market presence of UHMWPE with MM differed in several times and due to the insufficient information about properties of these materials, the study of structure and composition that determines technological parameters of processing and the properties of the resulting products is relevant.

The purpose of this work was the study of the effect of MM on structure, properties, and behaviour of UHMWPE under thermal impact.

OBJECTS AND METHODS OF RESEARCH

Ultra-high molecular weight polyethylenes with MM of 610 000 and 3 000 000 amu that are white powdery materials (Tomskneftekhim, OOO) were taken as objects of research.

The bulk density of polyethylene powders was determined according to GOST 11035.1–93 "Plastics. The determination of the apparent density of moulding material that can be poured from a special funnel"; the density according to GOST 15139–69 "Plastic. Methods for determining the density (mass density)"; the contents of moisture and volatile matter – by drying.

A microscopic study of the size and shape of particles, of the presence of voids in the samples was carried out using JEOL JSM-6390 LA scanning electron microscope with JED 2300 energy dispersive X-ray detector. Particle samples were deposited onto a bilateral carbon tape that was fixed on an aluminum sample stage. For contrast enhancement of surface images, samples were sputtered with gold. Micrographs of the surface of samples were obtained using secondary electron imaging (SEI) detector and reflected electron detector (RED) with the accelerating voltage of 5–30 kV in the JPEG format with resolutions of 1280×960 and 2560×1920 pixels.

Thermal analysis of UHMWPE samples was carried out in open platinum crucibles using STA-409 PG device. Sample mass is 2.2 mg. Heating was performed with a rate of 10 K/min in a flow of gas mixture of He (50mL/min)/O_2 (15 mL/min).

RESUTS AND DISCUSSION

Table 1 presents the results of the determination of technological parameters of UHMWPE. The findings demonstrate that the batches of UHMWPE under study are coarse powders, moreover, UHMWPE with MM of 610 000 amu contain fractions with average dispersibility (particle size from 10 to 40 μm). Volumetric characteristics of UHMWPE correspond to the values of similar parameters of HDPE (High-Density Polyethylene). The difference in the density of the batches under study is 3.5 %, moreover, a sample with a lower MM has a higher density.

A peculiarity of polymer materials is the ability to form supramolecular structures, the structure of which is driven by the chemical structure of macromolecules, their interaction among themselves, and also by processes occurring during obtaining polymer products, *i.e.* crystallization, orientation, *etc*.

Structure together with chemical structure and MM determine processing and operating characteristics of polymers and products obtained therefrom. Direct methods for studying polymers structure are electron and optical microscopy,

TABLE 1

Technological parameters of UHMWPE

MM of UHMWPE, amu	Particle size, μm	Bulk density, kg/m^3	Specific volume, m^3/kg	True density, kg/m^3
610 000	20–400	498±8	2.01	9598±21
3 000 000	40–600	472±2	2.12	9321±35

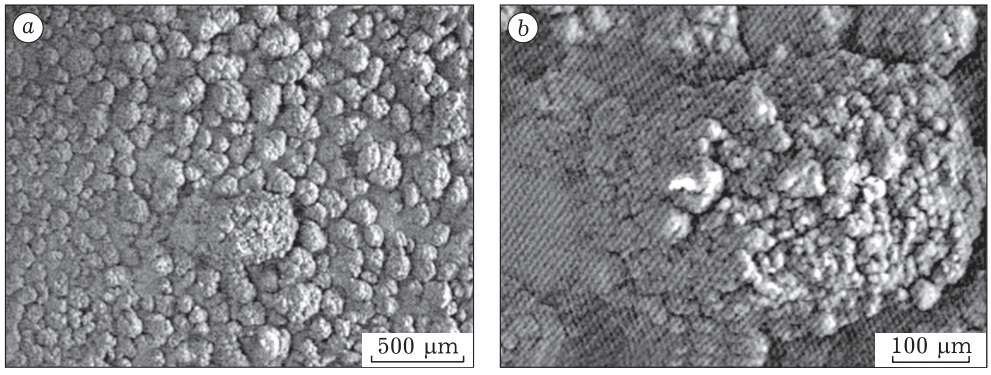

Fig. 1. Micrographs of species of UHMWPE with MM of 3 000 000 amu: *a* – general view; *b* – single particles with gold sputtering.

and electron, X-ray and light diffraction [3].

The present work studies UHMWPE structure using a scanning electron microscope. For UHMWPE with MM of 3 000 000 amu, there have been obtained micrographs: the general form of the polymer and a single species (Fig. 1), the surface of the species (Fig. 2, 3) with different magnifications. For UHMWPE with MM of 610 000 amu, there have been obtained micrographs: the general form of the polymer and the species that comprise it (Fig. 4), the polymer particle surface with different magnifications (Fig. 5).

The studied UHMWPE with different MM consist of round shaped particles united in agglomerates, as demonstrated by analysis of the images received. Particle size for UHMWPE with MM of 3 000 000 amu is found within 40–600 μm, for UHMWPE with MM of 610 000 amu – 20–400 μm (Fig. 1 and 4). The view of single particles (Fig. 2 and 5) points to the globular structure of the polymer.

Globules are ball-shaped species generated by twisted macromolecules (one or several). Globules consisting of macromolecular aggregates are generated resulting from joint twisting of several macromolecules or are comprised of single twisted macromolecules coupled to each other. Twisting of chain macromolecules to globules proceeds upon polymer synthesis in a medium where the resulting product is insoluble [3].

As demonstrated by surface analysis of UHMWPE globules (Fig. 3 and 5), there is a bond in the form of bridges between them, in other words, the species have a spatial structure, moreover, the presence of the spatial relationship is most pronounced for UHMWPE with MM of 610 000 amu.

Comparative analysis of the data showed that UHMWPE with MM of 3 000 000 amu has larger particles in which the globules are linked by chemical bonds to a greater extent than UHMWPE with MM of 610 000 amu.

Ultra-high molecular weight polyethylene refers to thermoplastic polymers, therefore, polymer melting is assumed during thermal impact, while the compound begins to

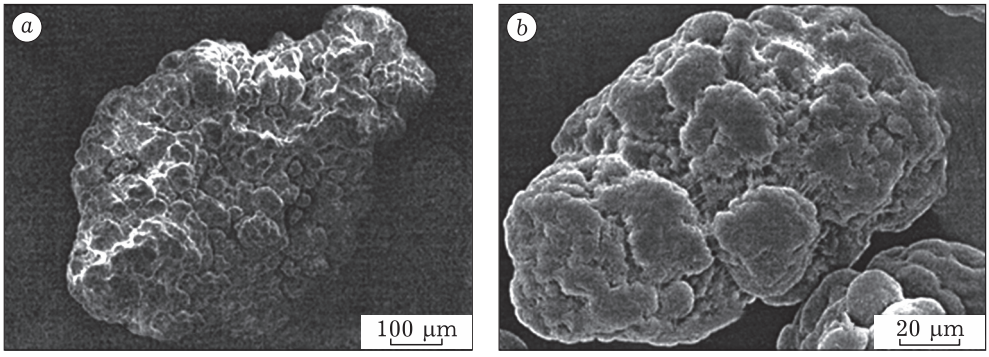

Fig. 2. Surface of species of UHMWPE with MM of 3 000 000 amu with gold sputtering at different magnifications: 130 (*a*) and 750 (*b*).

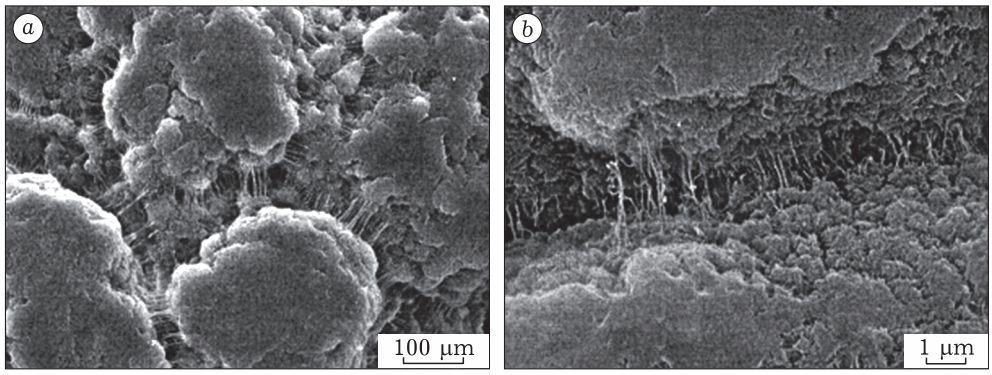

Fig. 3. Surface of species of UHMWPE with MM of 3 000 000 amu at different magnifications: 1500 (*a*) and 100 00 (*b*).

decompose, while destruction products are generated. Thermal oxidation proceeds in the studied case resulting in a decrease of polymer molecular mass.

A peculiarity of UHMWPE behaviour under thermal action is the fact that there is no melting of the polymer due to its high molecular mass and it does not pass to the viscous flow state. At the same time, a process similar to melting has been observed as an endothermal peak in the DSC curve. This quasi-melting process is associated with the restructuring of polymer structural elements, a transition from an ordered structure of supramolecular formations to an amorphous one.

Temperature range and heat effect of this transition increases with a rise in polymer molecular mass, as can be seen from the data of Fig. 6 and Table 2.

The molding process of products from the

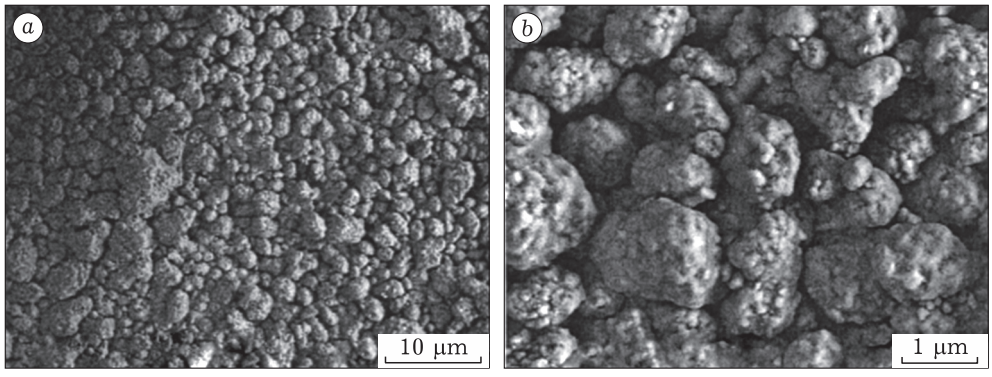

Fig. 4. Micrographs of species of UHMWPE with MM of 610 000 amu: *a* – general view; *b* – single particles.

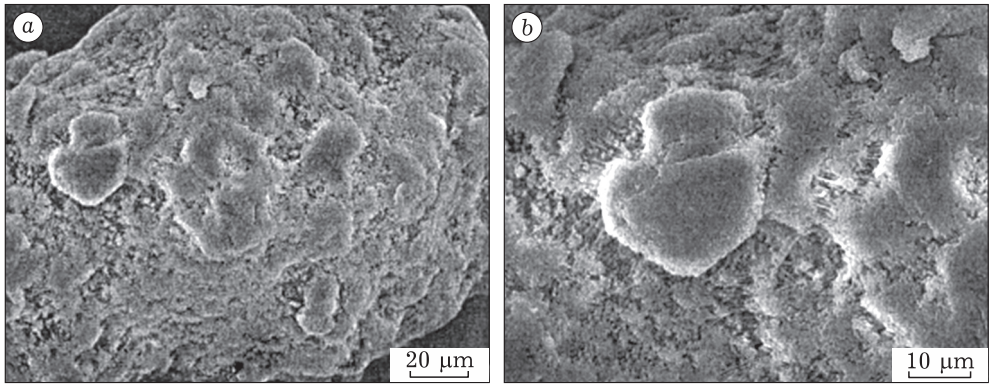

Fig. 5. Micrographs of the surface of single species of UHMWPE with MM of 610 000 amu at different magnifications: 750 (*a*) and 1500 (*b*).

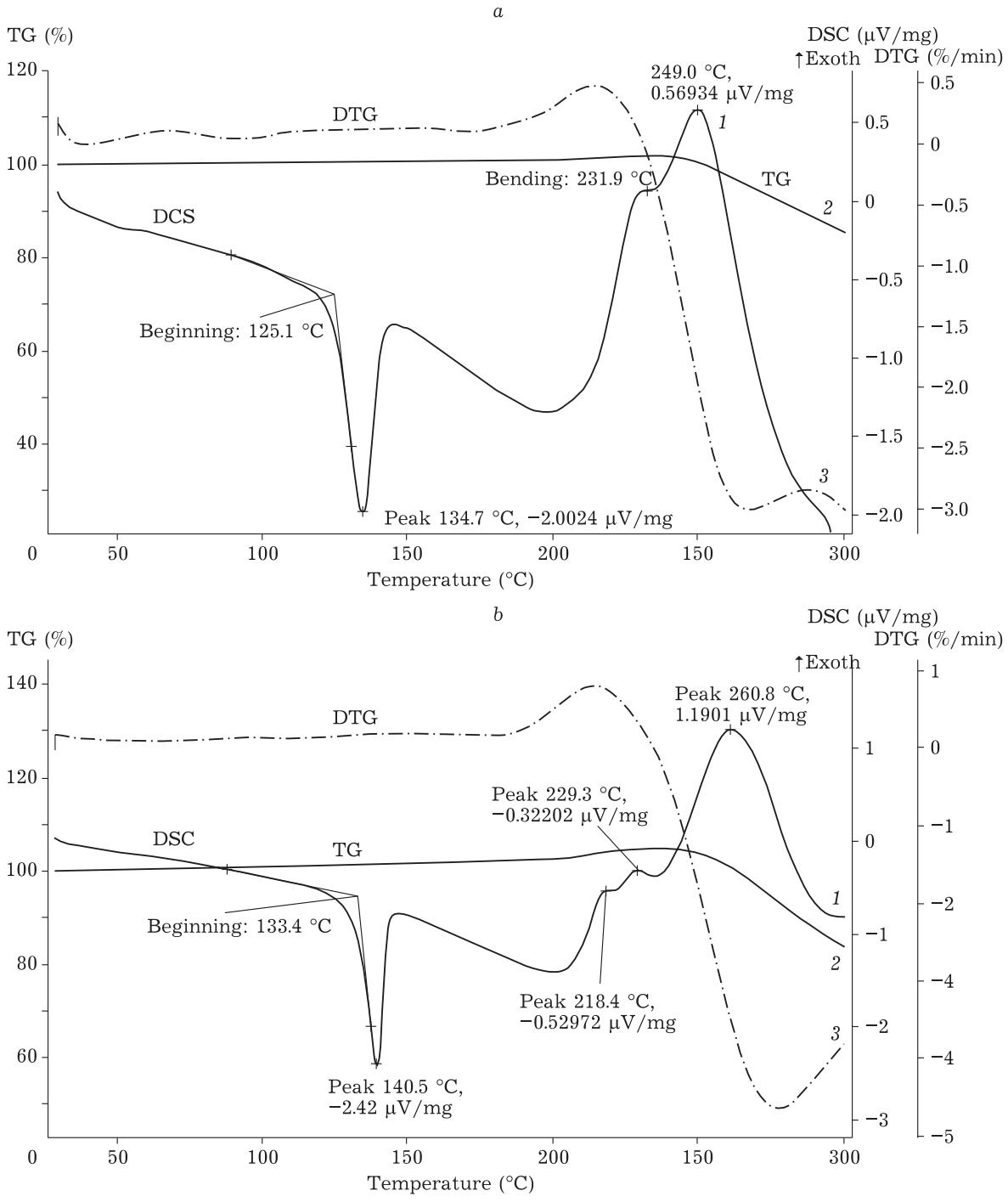

Fig. 6. Differential scanning calorimetry (DSC) of UHMWPE with MM of 610 000 (*a*) and 3 000 000 amu (*b*): DSC curve (*1*), TG curve (*2*), DTG curve (*3*).

considered batches of UHMWPE that provides for thermal treatment (sintering) should be carried out within certain temperature transitions. They are 125–145 °C and 133–150 °C for UHMWPE with MM of 610 000 and 3 000 000 amu, respectively. At a temperature above 215 °C, polymer oxidative destruction begins, as indicated by exothermal peaks in the DSC curve and by a decrease in sample mass due to the liberation of volatile products. Accordingly, the thermal treatment process of the studied UHMWPE grades should be carried out in different temperature ranges; processing of their mixture is probable only in the 133–145 °C

TABLE 2

Parameters for the process of quasi-melting of UHMWPE

MM of UHMWPE, amu	Process temperature range, °C		Melting heat, μV/mg
	Peak beginning	Peak maximum	
3 000 000	133.6	140.5	−2.42
610 000	125.2	134.7	−2.00

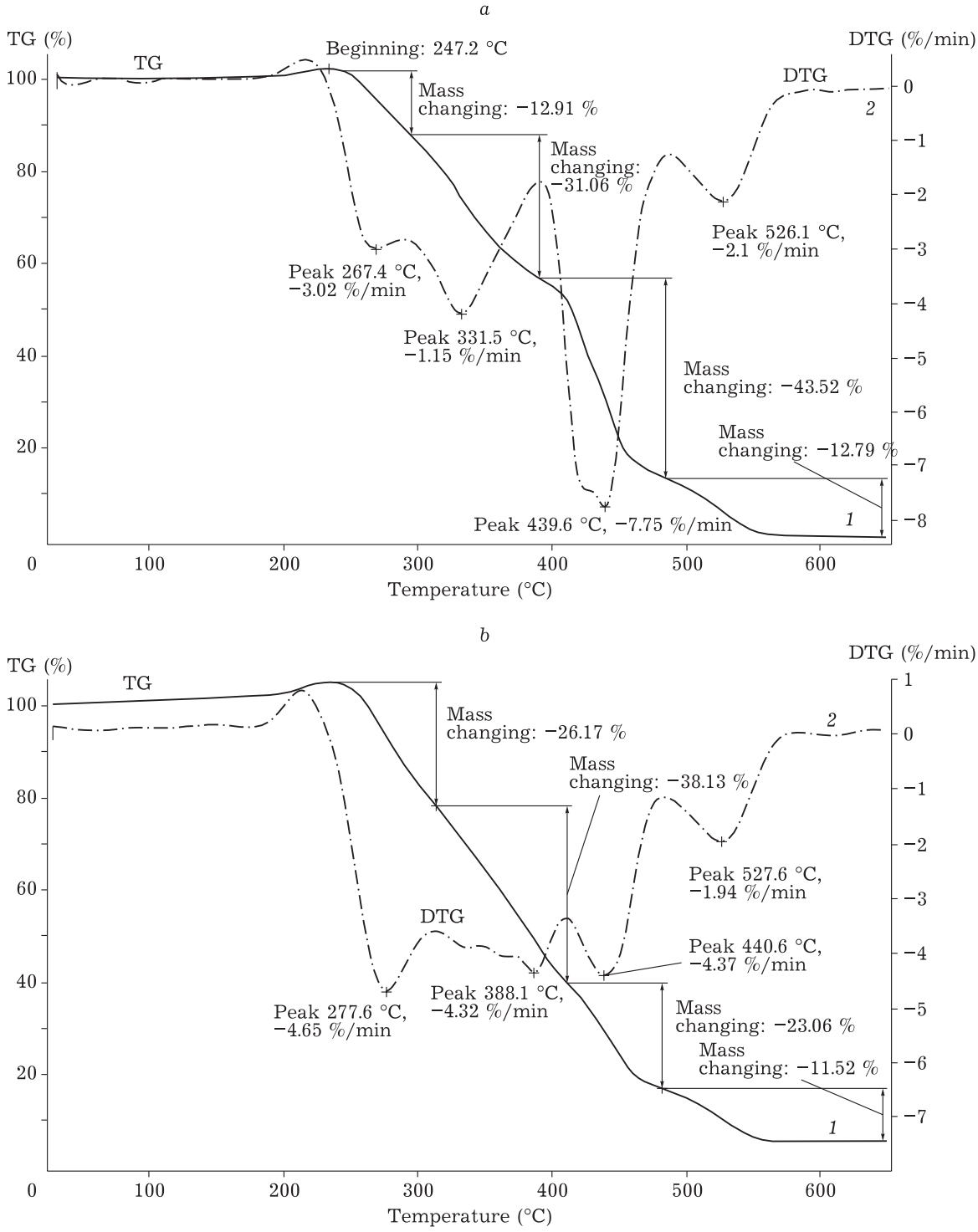

Fig. 7. . The thermogravimetric (TG) (*1*) and differential thermogravimetry (DTG) (*2*) curves of UHMWPE particles with MM of 610 000 (*a*) and 3 000 000 amu (*b*).

TABLE 3
Parameters for the process of UHMWPE destruction

Stage	MM of 610 000 amu		MM of 3 000 000 amu	
	Temperature range, °C	Mass loss, %	Temperature range, °C	Mass loss, %
1	249–290	13	260–314	26
2	290–390	31	314–413	38
3	390–484	43	413–483	23
4	484–600	12	484–600	12

range. At temperatures lower than 133 °C and above 145 °C, thermal treatment of blanks made of a mixture of UHMWPE grades would lead to the preparation of substandard products due to either incomplete pseudo-melting of a batch with MM of 3 000 000 amu or destruction of a batch with MM of 610 000 amu.

Oxidative destruction of batches of UHMWPE proceeds in 4 steps that are different in reaction rates, as demonstrated in curves (Fig. 7) and presented in Table 3. The total mass loss for both batches of UHMWPE is 100 %.

The differences of the destruction process between the studied batches lies in qualitative parameters of process stages. Ultra-high molecular weight polyethylene with MM of 610 000 amu begins to decompose at lower temperatures; the bulk of the polymer is degraded in 2 and 3 stages (mass loss in the 290–484 °Crange of 74 %); the fourth stage of the destruction process proceeds in the same temperature range (484–600 °C) for both batches with the same mass loss (12 %). For UHMWPE with a molecular mass of 3 000 000 amu, the bulk of the polymer decomposes at the first and second stages (mass loss in the 260–413 °C range of 64 %).

To assess processes proceeding during UHMWPE destruction, and also the toxicity of the resulting products, the additional research of the destruction process is assumed.

CONCLUSIONS

i) Ultra-high molecular weight polyethylene (UHMWPE) is particulates consisting of round shaped species with a diameter of 20–400 μm for a polymer with molecular mass of 610 000 amu and 40–600 μm for a polymer with molecular mass of 3 000 000 amu. The species have globular structure, characterized by interconnection of globules among themselves by bridges with different intensities, which causes the difference in processing and operational properties;

ii) The process of quasi-melting has different temperature limits for UHMWPE with different molecular mass and these differences in properties may be used to determine the temperature range of thermal treatment (sintering) of products.

iii) A thermal destruction process in the presence of oxygen also has different temperature limits for the studied batches of UHMWPE and is accompanied by the liberation of gaseous products. Thermal oxidative destruction of UHMWPE proceeds in four steps that differ in mass-loss rates and temperature limits. For UHMWPE with a molecular mass of 610 000 amu there is the main mass loss in the 290–484 °C range, with a molecular mass of 3 000 000 amu – in the 260–413 °C range.

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