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Porous Shish-Kebab Structure Prepared from Oriented UHMWPE Films by Processing in Supercritical CO_2

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Abstract For the first time, a highly crystalline porous shish-kebab structure with a high degree of crystallinity was obtained by using a combination of two methods for the formation of porous polymeric materials. A treatment procedure using supercritical carbon dioxide ($scCO_2$) was carried out for oriented ultrahigh molecular weight polyethylene (UHMWPE) films, which provided special conditions for the crystallization of dissolved UHMWPE macromolecules on the surface of oriented UHMWPE crystals. The prepared porous materials were investigated by scanning electron microscopy (SEM) and differential scanning calorimetry (DSC). The particularity of the obtained porous shish-kebab is the absence of the amorphous phase between lamellar crystals (kebabs). The obtained pores had an oval shape, and they were oriented in the orientation direction of the UHMWPE macromolecules. The pore size ranged from 0.05 μm to 4 μm. Controlling the conditions for the crystallization of the UHMWPE macromolecules using supercritical CO_2 gives the possibility to control the size of both lamellar disks and pores formed.

Keywords UHMWPE; Supercritical CO_2; Porous shish-kebab structure

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INTRODUCTION

Porous polymeric materials based on polyolefins, such as polyethylene,[1–7] polypropylene,[8] polyamide,[9] polytetrafluoroethylene,[10] poly(vinylidene fluoride),[11] and poly(vinyl chloride),[12] are widely used in medical and industrial applications. Porous materials based on polyethylene are used as bone implants,[1,2] materials for cell culture cultivation,[3] heat insulating materials,[4] filters,[5] and separators in batteries.[6,7] Porous materials based on ultrahigh molecular weight polyethylene (UHMWPE) are not numerous though often have better mechanical properties, corrosion resistance and chemical resistance in comparison with traditional polymeric materials.[13–15] However, the preparation of porous materials based on UHMWPE has several limitations related to its high molecular weight and low melting index, which obstruct using the traditional methods of polymer foaming. In general, the formation of porous/cellular structures in UHMWPE is usually carried out by thermal sintering,[16,17] or by a hot pressing of a powdery UHMWPE mixture with water soluble salts followed by salt leaching.[18–20] However, these methods have some disadvantages, which deteriorate the properties of the prepared porous materials. For example, by the sintering method, the polymer macromolecules are poorly diffused between the sintered particles, which negatively affects the mechanical properties of the obtained bulk material, leading to obtaining a weak bonded porous structure. Moreover, using the salt introduction method, followed by a hot-pressing process, and then a salt leaching process, leads to a material with a high porosity, and the pore size in the prepared porous material will be dependent on the particle size of the introduced salt.

One such porous structure is a so-called "shish-kebab". This structure consists of a central fibrillar rod called a "shish" formed by crystals on extended chains and stacks of disc-shaped lamellae called "kebabs" crystallized on the surface of the fibrillar rod and stung perpendicular to it.[21–23] It is believed that the supramolecular shish-kebab structure predominates in highly oriented polymer fibers.[24,25] The central rod (shish) in the "shish-kebab" structure has a melting point that is 15–20 °C higher than the melting point of the lamellar structure of the kebab.[23] The lamellar folded crystals in the "shish-kebab" structure have two types: macro-kebab and micro-kebab. The micro-kebab is attached to the center fibrillar

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rod, whereas the macro-kebab is grown on the micro-kebab, and it is not connected to the central rod. Therefore, the macro-kebab can be removed from the center rod with a solvent or melted at heating, whereas micro-kebab is thermally more stable, and a strong solvent under special conditions is needed to dissolve it.[26]

Several studies described the appearance of a shish-kebab in extrusion-prepared UHMWPE membrane separators that have high mechanical and electrochemical properties, which makes them one of the best candidates for rechargeable batteries applications. Gao *et al*. prepared UHMWPE films by stretching at 120 °C in two perpendicular directions.[5] They obtained a uniformly distributed network of nanofibrillar structure with pores of an approximately 200 nm diameter. The authors reported that nanofibrils had a shish-kebab structure which consisted of extended shish crystal chains with a diameter of 6 nm and folded kebab chains with a diameter of 45 nm. He *et al*. prepared UHMWPE microporous membranes by using the extrusion of dilute UHMWPE/liquid paraffin oil solutions and a drawing process at 110 °C to stretch the film and to obtain the micro-porous UHMWPE.[27] The authors reported a uniform distribution of pore diameters and a good permeability at 30% UHMWPE concentration. Also, they reported a moderate porosity of the obtained structure (42%). In Li's work,[28] a porous membrane based on UHMWPE films was prepared by using a low-entanglement UHMWPE and biaxial stretching. The films with a thickness of 100 nm had a fibrillar structure and exhibited shish-kebab structure with a kebab diameter of 10 nm.

The formation of porous polymeric materials by using two preparation protocols together is considered an interesting direction.[29–31] In this work, oriented UHMWPE films were used as a material, which was treated by supercritical CO_2 to prepare a porous shish-kebab structure. The main aim of the proposed approach is providing special conditions for polymer crystallization under $scCO_2$ treatment. In the case of small pores, the capillary pressure can be very high, which leads to the destruction of the porous structure.[24] So, to avoid this effect, supercritical drying (SCD) is usually used.[30–35] This approach requires sequential washing of samples with a solvent and liquid carbon dioxide, which is then removed in a supercritical state at high pressure. This method makes it possible to produce materials with open porosity and uniform pore distribution.

We recently published the results of a treatment of a swollen UHMWPE in supercritical CO_2 leading to a formation of meso-(15–17 nm) and macropores (2–5 μm) in UHMWPE-based aerogels and aerogel-like materials with porosity up to 97%.[36,37] Such an approach (extraction of the solvent from meso- and macropores by $scCO_2$, which prevents pore collapse) provides a powerful tool for porous structure formation in UHMWPE. In our previous work,[36,37] we managed to prepare highly porous materials from a high-entanglement UHMWPE (GUR 4120). In the current work, we applied a $scCO_2$-based protocol to pre-oriented UHMWPE with the aim of developing a novel method of UHMWPE-based porous material preparation. As a result, a new method for the formation of a shish-kebab structure in UHMWPE treated by supercritical CO_2 is presented.

EXPERIMENTAL

UHMWPE (Kazanorgsynthesis Ltd., Russia) with an average molecular weight of 1×10^6 g/mol, an average particle size of 70 μm, and an intrinsic viscosity of 8.3 dL/g, was used to prepare the oriented films. Xylene was used for UHMWPE plasticizing with a concentration of UHMWPE in xylene of ~42 wt% (1 g of UHMWPE + 1.6 mL of xylene). Gel of UHMWPE in xylene was prepared by heating the UHMWPE/xylene mixture at 140±3 °C for 15 min. The ram extruder UE-MSL (Extrusion Machinery Sales Ltd.) was used for extrusion of UHMWPE/xylene films, and then the obtained films were dried at 50 °C for 48 h. The films were oriented at 110 °C to obtain a draw ratio of 10. The technique for obtaining UHMWPE films was described in detail earlier.[38,39]

Solvent Film Processing

The solvent film processing was carried out as seen in Fig. 1. A sample of the oriented UHMWPE film was placed in a glass flask; then an appropriate amount of the solvent (*o*-xylene) was added to reach a complete covering of a sample. After that, the sealed glass flask was heated up to 110 °C in a BINDER FD 53 laboratory oven with an accuracy of ±0.3 °C and kept at this

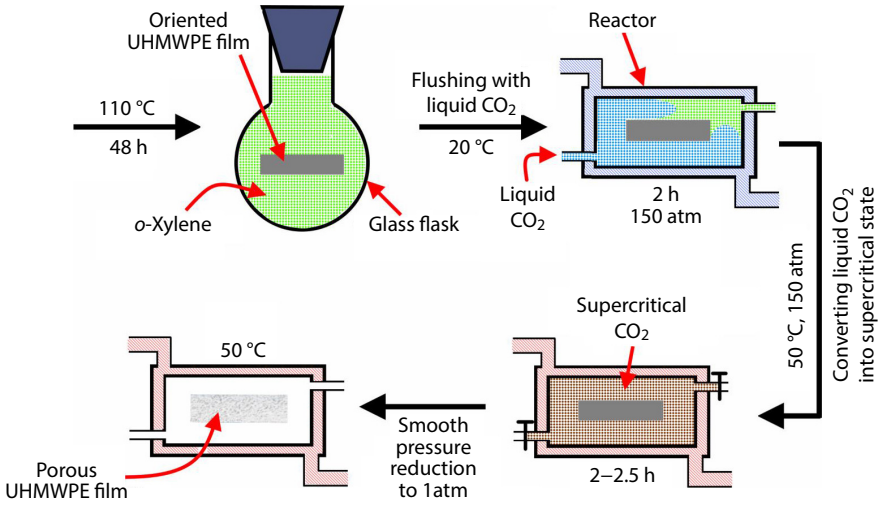

Fig. 1 Schematic diagram showing the process of porous material formation from oriented UHMWPE films under supercritical CO_2' conditions.

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temperature for 48 h. During this stage, *o*-xylene penetrated the amorphous phase and a partial melting of the UHMWPE crystalline phase occurred due to the swelling pressure of the solvent. After that, the sample was cooled to room temperature, placed into a high-pressure reactor, and flushed by liquid CO_2 for 2 h at a pressure of 150 atm to replace xylene by CO_2 in the UHMWPE pores completely. Then, the temperature in the reactor was raised to 50 °C and the sample was flushed by $scCO_2$ for 2–2.5 h. After that, the pressure was gradually reduced to atmospheric during 40–60 min, the rector was cooled, and the porous sample was taken out.

Characterization of Aerogels

Thermal analysis of samples was performed by using differential scanning calorimeter NETZSCH DSC 204 F1 in argon atmosphere according to ASTM D 3417–83. The measurements were performed under controlled heating and cooling regimes at a rate of 10 °C/min. The key parameters for DSC curves processing were T_m^{onset} (the onset of the melting peak), T_m (the melting temperature peak) and T_m^{end} (the end of the melting peak). The crystallinity was calculated as the ratio of the experimental sample melting enthalpy compared to the completely crystallized polyethylene melting enthalpy, which was set as 293 J/g.[40]

The microstructure of the samples was investigated using Vega3 Tescan scanning electron microscope (SEM). Two regions of samples were investigated by SEM: the external surface of porous UHMWPE film and the inside part of it. The inside part was reached by ripping the sample in the orientation direction of the films. The analysis of pores size distribution was performed using ImageJ software. The number of measured pores was at least 1000 per sample.

The specific surface area and a pore size distribution of the samples were measured by the low-temperature nitrogen adsorption method on a Nova 1200e analyzer (Quantachrome Instruments, USA), according to a BET equation. Prior to analysis, the samples were degassed at 50 °C in a vacuum for 17 h. The pore size distribution was calculated by a Barrett-Joyner Halenda model.

GPC investigation was carried out at 140 °C with 1,2,4-trichlorobenzene as solvent using Polymer Laboratories PL-GPC 220 chromatograph. The molecular weight was calculated by the standard procedure based on the universal calibration of polystyrene.[41]

RESULTS

Fig. 2 shows the SEM images of the external surface of the UHMWPE film after the treatment procedure by supercritical CO_2. As it can be seen in Fig. 2, the UHMWPE sample surface is porous. Pores have oval shape and their size ranges from 0.05 μm to 4 μm (Fig. 3a). The average pores size is 0.9 μm.

The full adsorption-desorption isotherm and pore size distribution is presented in Fig. 4. The specific surface area of the sample determined by a BET protocol S_{sp} was 50±5 m^2/g. All isotherms belong to type IV according to IUPAC classification

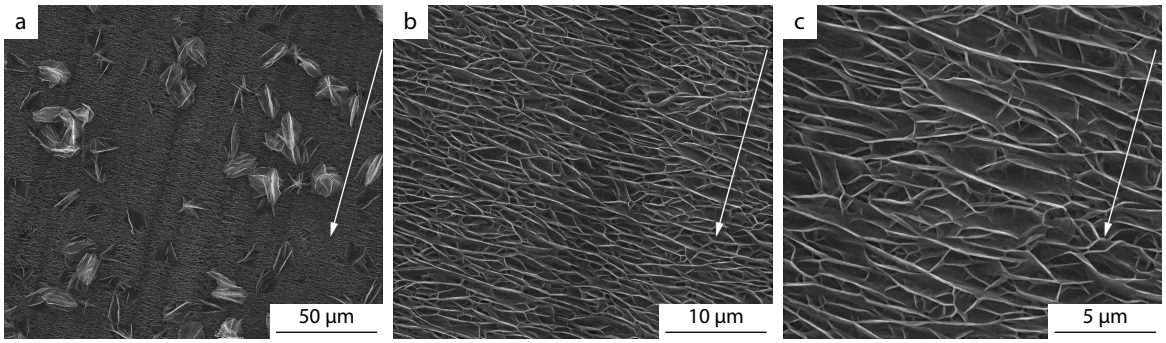

Fig. 2 SEM images of the external surface of porous UHMWPE film after cooling and crystallization in supercritical CO_2 at different magnifications. The arrows show the orientation direction of the film.

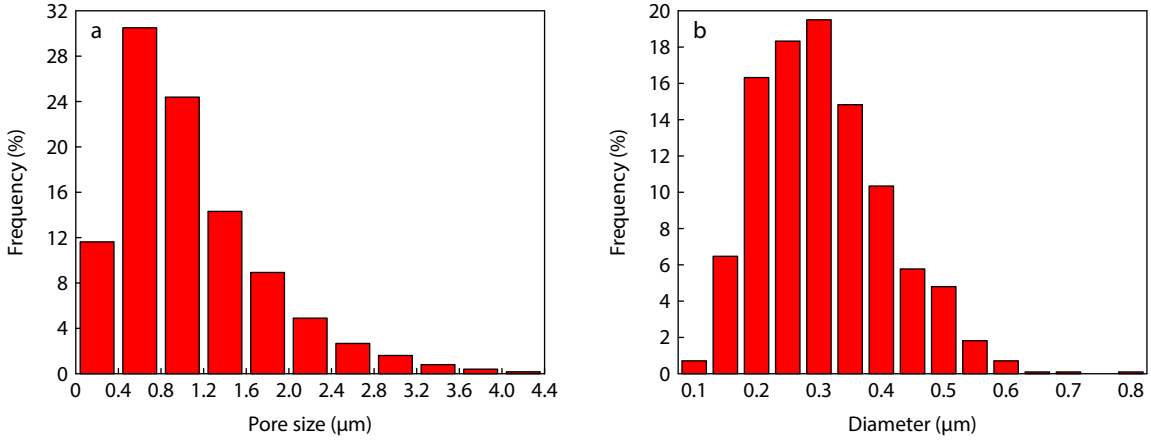

Fig. 3 (a) Pore size distributions of porous UHMWPE films and (b) "kebabs" diameter distribution in shish-kebab structure.

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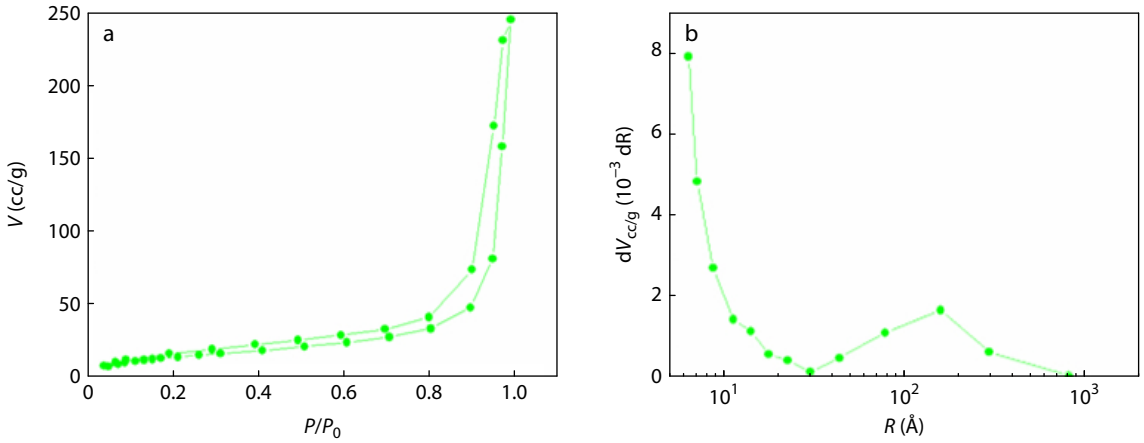

Fig. 4 Full adsorption-desorption isotherm (a) and pore size distribution (b) for a porous UHMWPE film.

and are characterized by a narrow hysteresis of type H1, typical for materials containing cylindrical mesopores. According to BJH analysis the mesopores radius varied in the range of 2–100 nm.

Fig. 5 presents the SEM image of the well-known shish-kebab structure for the internal part (inside) of the UHMWPE film. This structure consists of single extended-chains (a central fibrillar core), called "shish", which may consist of a single-crystal structure or even a single aligned chain; and an assembly of folded-chain lamellae, called "kebabs", which are oriented perpendicularly to the shish core.[21,22] The "kebabs" diameters distribution is shown in Fig. 3(b). The maximum diameter of "kebabs" reached 0.8 μm and the average size was ~0.3 μm. The particularity of obtained shish-kebab structure is the absence of the amorphous phase between the "kebabs" (lamellar crystals). Usually, the space between "kebabs" is filled with an amorphous phase, which requires additional sample processing to visualize the shish-kebab structure by SEM.[42,43] Undoubtedly, it is the presence of supercritical CO_2 which leads to unique conditions providing the practically complete crystallization of the UHMWPE macromolecules (formation of "kebabs") on extended UHMWPE chains (according to DSC data, the degree of crystallinity of the obtained UHMWPE film reaches 95%, see Table 1). This feature gives the possibility to obtain a textured porous structure due to the absence of the amorphous phase between "kebabs". Since the "kebabs" are aligned in one direction (orientation direction of the UHMWPE film), they form a textured porous structure.

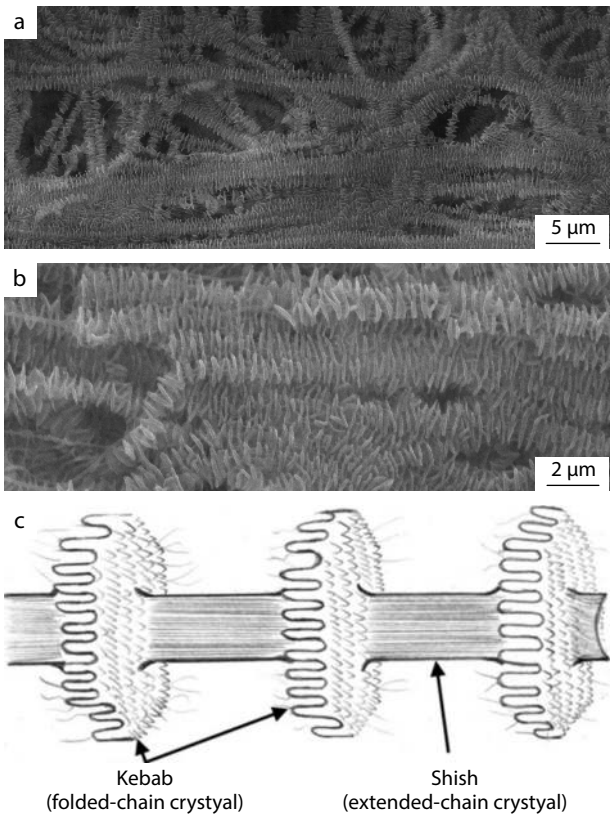

Fig. 5 (a, b) SEM images at different magnifications of shish-kebab structure inside the porous UHMWPE film. The surface was prepared by ripping the sample. (c) Schematic illustration of shish-kebab structure.

In order to elucidate the difference in the mat structure view between the external and internal regions of the prepared porous material (Figs. 2 and 5), the preparation conditions of the UHMWPE films and their processing with $scCO_2$ should be discussed. Using extrusion molding to prepare the polymer films, the high shear regions will be located near the xerogel walls, which means that the presence of the oriented macromolecules will be higher in the external regions in comparison with the internal regions of the xerogel.[44,45] In addition, after applying the orientation drawing for the polymer xerogels, the polymer macromolecules in the wall regions will have higher orientation degree in comparison with the ones that are in the internal regions, which in turn means that the crystallinity of the polymer in the wall regions will be higher. Moreover, the lamellae thickness of the UHMWPE macromolecules located on the wall regions will be smaller than the ones that are in the internal regions. In the swelling process of the oriented UHMWPE film in xylene, when the solvent penetrates the polymer amorphous phase, the swelling pressure on the folded-chain crystals that are located in the wall regions will be higher than the ones that are located in the internal regions of UHMWPE films, which in turn leads to the dissolu-

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Table 1 DSC data for the initial UHMWPE powder, initial oriented UHMWPE film and porous UHMWPE film.

Material	T_m^{onset} (°C)	T_m (°C)	T_m^{end} (°C)	Crystallinity (%)
Initial UHMWPE powder	118.2	128.3/141.0	144.5	78±2
Initial oriented UHMWPE film	124.6	132.0	136.2	63±3
Porous UHMWPE film	124.3	133.6/138.0	138.7	95±2

tion of more UHMWPE macromolecules located in the wall regions than the ones that are located in the internal regions. These differences in the dissolution condition and macromolecule orientation degree (lamellae thickness) between internal and external regions of the sample affect the crystallization process, which in turn leads to a difference in the size of the obtained kebab crystals. Figs. 2(a)–2(c) show the SEM images of the external surface of the porous UHMWPE film after the treatment with supercritical CO_2 picked from the top, bottom, and side places at the same magnification. As can be seen in Fig. 2(a), the mat structure of external regions of the prepared porous material is practically the same in all views, and it consists of central rod (shish) with folded UHMWPE crystals, which differ significantly from "kebabs" in the inner part of the material—inner "kebabs" are much smaller than external crystals (see Fig. 5). This fact confirms that the difference in dissolution and crystallization conditions between inner and outer layers of the UHMWPE film leads to a "shish-kebab" structure with distinct kebab discs in the inner region of the material.

Shish-kebab structure is considered a type of supramolecular structures for many oriented polymers including oriented UHMWPE films and fibers.[21,22,46] In the current work, the prepared oriented UHMWPE film has a fibrillar structure, which consists of chain-folded crystallites, extended-chain crystallites, and amorphous phase. Its crystallinity degree was 63%, whereas that of shish-kebab structure reached 95% (Table 1).

The melting temperature for polymers depends mainly on the crystalline phase size.[47] According to the Thomson-Gibbs equation,[47] small and defected crystallites have a lower melting temperature compared to larger size and non-defected crystallites. This explains the difference in the melting point values of the porous UHMWPE and its powders.

$$T_{rmm} = T_m^0\left(1 - \frac{2\sigma_e}{\Delta H}\cdot L\right) \quad (1)$$

where T_m^0 is the melting temperature of the lamellar crystallites of infinite size, σ_e is the surface energy, ΔH is the melting enthalpy, L is the lamellae crystallite thickness.

According to the DSC results, the initial UHMWPE powder has two distinct melting peaks at 128.3 and 141.0 °C (Fig. 6). In our opinion, two melting points are related to the presence of different size UHMWPE lamellae in the initial UHMWPE. The melting point of the oriented UHMWPE films was lower (~132 °C) due to the lamellae smaller size.[48] The porous UHMWPE melting point (133.6 °C) reveals some increase of lamellae size. Besides, a small melting peak at 138 °C appeared, which was related to the crystallites on extended chains (shish).[48]

The presence of the folded-chain crystals and bimodal distribution of molecular weight in the UHMWPE structure are the determining factors that explain the formation of the shish-kebab structure in porous UHMWPE film.[49–51] The

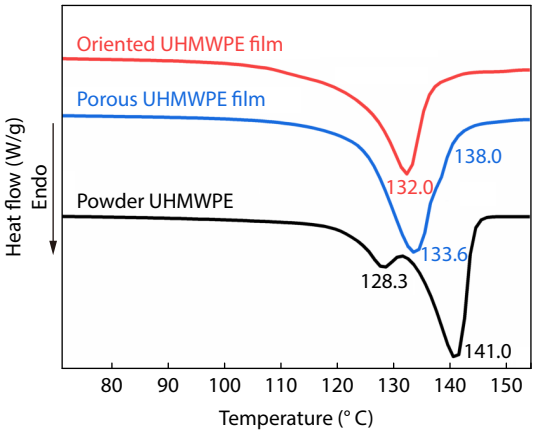

Fig. 6 DSC curves for the 1st heating for initial UHMWPE, UHMWPE film and porous UHMWPE film.

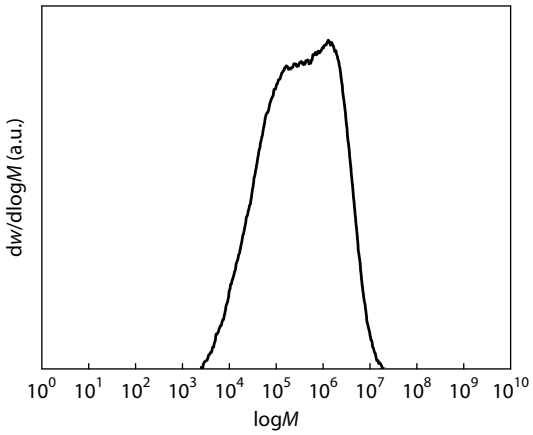

Fig. 7 GPC curve of the UHMWPE powder.

bimodal distribution of molecular weight of the UHMWPE powders is confirmed by GPC measurement. Fig. 7 and Table 2 show the GPC curve of the UHMWPE powder. As it can be seen, the M_w of the UHMWPE powder has a wide range. Polydispersity index (PDI) of the UHMWPE powder was 14.4 basing on GPC data.

In the swelling process of the oriented UHMWPE film in xylene, the solvent penetrates the polymer amorphous phase and dissolves the low molecular weight fraction. The solvent forms stresses on the folded-chain crystals (macro-kebabs) by the swelling pressure, which leads to a decrease in the melting temperature of the crystals. Under the influence of temperature and stress, some parts of the folded-chain crystals will transform into the amorphous phase. As a result, a system that consists of a dissolved amorphous phase, a crystalline phase in the form of extended-chain crystallites and micro-kebab will be formed (Fig. 8). Upon cooling, the crystalline phase acts as crystallization centers for the dissolved

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Table 2 Molecular weight characteristics of UHMWPE.

Material	M_n	M_w	M_z	M_z^{+1}	M_v	PDI
UHMWPE powder	77000	1112000	3990000	6800000	1024000	14.4

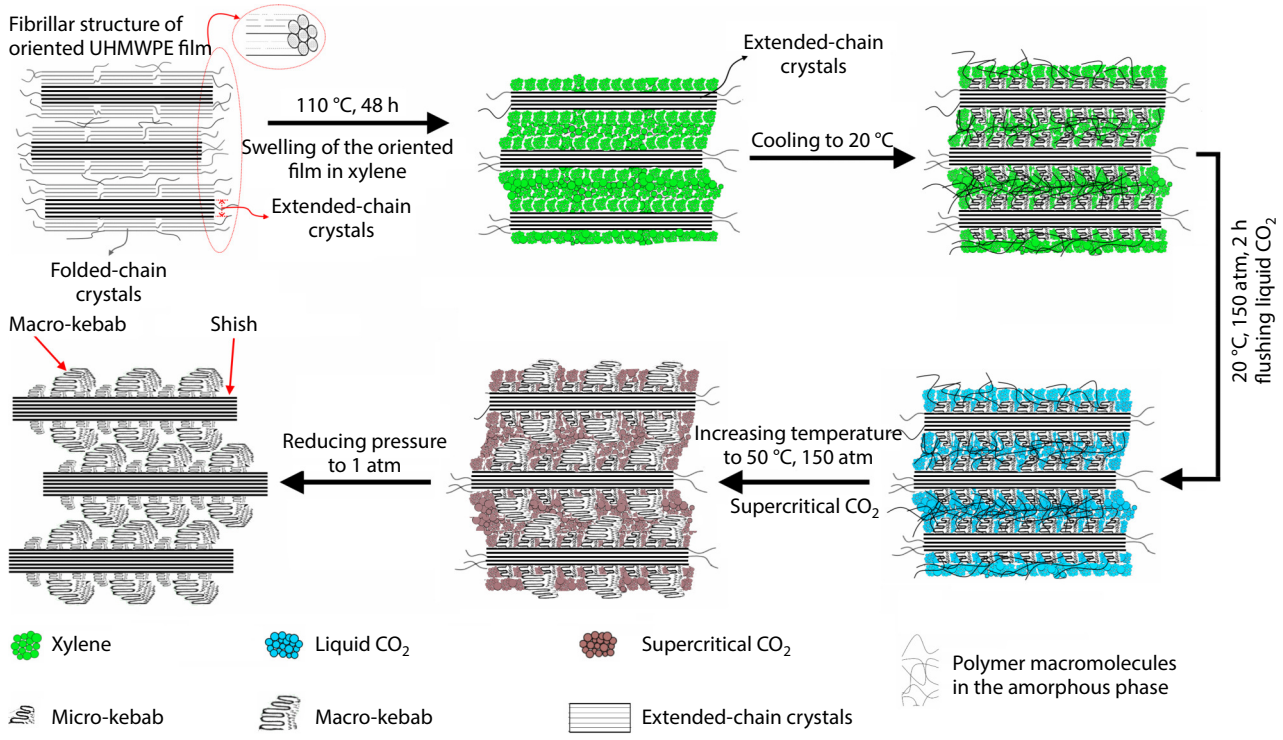

Fig. 8 Formation of porous UHMWPE shish-kebab structure during crystallization in supercritical CO_2.

macromolecules. The crystallization of the UHMWPE macromolecules in the presence of the solvent leads to the formation of new small lamellar crystals. At this stage, the crystallization of the dissolved macromolecules is limited due to the presence of the solvent in the inter-molecular space, which prevents the polymer macromolecules from approaching to the required critical distance but ensures crystal growth. After the replacement of xylene by liquid CO_2 and its transformation into a supercritical fluid state, unique crystallization conditions will be formed, in which macromolecules will practically completely crystallize in the form of a macro-kebab (Fig. 8).

Porous UHMWPE structures of this kind can be widely used as membranes.[27,28,52] Since separator is a permeable membrane located between the anode and cathode of the battery, the main function of the separator is to keep two electrodes apart to prevent electrical short circuits, as well as to allow the transport of ionic charge carriers, which are necessary to complete the circuit during the passage of current in an electrochemical cell.[53] In addition, the separator must have sufficient pore density to hold a liquid electrolyte that allows ions to move between the electrodes. So, the prepared porous UHMWPE material, which has a "shish-kebab structure" with the possibility to control the pore size, is considered the best option for membrane applications and separators.

CONCLUSIONS

Crystallization during SCD in supercritical CO_2 creates unique conditions, which allow UHMWPE macromolecules to crystallize completely into folded-chain crystals. According to DSC data, the degree of crystallinity of the obtained porous UHMWPE films reached 95%. Crystallization of UHMWPE macromolecules on the surface of extended-chain crystals in supercritical CO_2 formed the shish-kebab structure, which had oval-shaped pores and preferred orientation; pore size ranged from 0.05 μm to 4 μm under the presented experimental conditions.

For successful preparation of a shish-kebab structure, the initial oriented UHMWPE must contain more folded-chain crystals, which can be easier dissolved by a solvent than crystallites on extended chains that play a main role as nucleation centers for further crystallization of the dissolved macromolecules upon cooling and substitution of xylene by liquid and then supercritical CO_2.

Since the pores size in the obtained porous UHMWPE film obviously depends on the “kebabs” diameter, this can be used to prepare a porous structure with desired properties. By adjusting the conditions for obtaining such “shish-kebab” structure using the method of SCD in CO_2, it is possible to control the size of the formed lamellar disks, which in turn gives the possibility to change the size of the formed pores which can empower their use in practical applications. Such porous UHMWPE structures can be widely used as heat-insulating materials, filters, and separators in batteries.

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Conflict of Interests

The authors declare no interest conflict.

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