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# All Polyethylene Compositions Based on Ultrahigh Molecular Weight Polyethylene Synthesized over Binary Catalyst including Zirconocenes of Various Designs

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**Abstract** Single-step ethylene polymerization over a binary catalyst, including zirconocene precatalysts of various designs, has been studied to obtain polymer compositions based on ultrahigh-molecular-weight polyethylene (UHMWPE) and low-molecular-weight HDPE (LMWPE) directly in synthesis. Zirconocenes *rac*-$(CH_3)_2SiInd_2ZrCl_2$ (**Zr-1**) and *rac*-$(C_6H_{10})CpIndZrCl_2$ (**Zr-2**) activated with methylaluminoxane (MAO) were used as the components of the binary catalyst. It has been shown that the use of **Zr-1**/MAO and **Zr-2**/MAO in ethylene polymerization at 30 °C leads to the production of UHMWPE with $M_w$=1000 kg·mol$^{-1}$ and LMWPE with $M_w$=18 kg·mol$^{-1}$, respectively. Reactor polymer compositions (RPC) with LMWPE fraction contents ranging from 9 wt% to 42 wt% were obtained when a molar fraction of **Zr-2** in the binary catalyst (**Zr-1**+ **Zr-2**)/MAO varied in the range from 0.3 to 0.85. A study of the molecular weight characteristics of RPC showed that it has a wide bimodal molecular weight distribution (MWD) and includes UHMWPE ($M_w$=1000 kg·mol$^{-1}$) and LMWPE ($M_w$=18 kg·mol$^{-1}$) fractions. The degree of crystallinity of the polymer products was determined using the DSC method. The tensile properties and melt indices of the materials were studied depending on the LMWPE fraction content in the polymer composition. UHMWPE/LMWPE compositions with high tensile properties and fluidity at a load of 5 kg were obtained.

**Keywords** Ultrahigh molecular weight polyethylene; Reactor polymer compositions; Polymerization; Organometallic catalysts; Tensile properties; Melt indexes

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## INTRODUCTION

The creation of bimodal polyolefin compositions provides great opportunities for the development of new types of materials with practically important properties.[1–4] Compositions based on high density polyethylene (HDPE) with extremely high molecular weights ($M_w \geq 10^6$ g/mol) are of particular interest. The performance properties, such as high mechanical strength, abrasion resistance, impact resistance, dielectric properties, high energy absorption, chemical inertia, solvent resistance, *etc.* offered by ultrahigh molecular weight polyethylene (UHMWPE) make it attractive for practical use.[1] UHMWPE applications range from joints for endoprosthetics in biomechanics[3,5] to more common industrial applications, such as gears, liners, bearings, seals, and protective equipment.[1,6,7] The requirements for products made of this material are increasing owing to the development of new technologies and expansion of UHMWPE applications. Therefore, it is important to improve the technological and operational properties of polyolefins. Most investigations on the modification of UHMWPE are aimed at improving the rheological properties by reducing the viscosity of the melt.[8,9] These include studies on the post-reaction mixing of UHMWPE with other high-flow polyolefins, such as HDPE and linear low-density polyethylene.[10–12]

HDPE-s with various molecular weights, including polyethylene waxes,[6,13] have also been applied to create such polymer-polymer compositions with a bimodal molecular weight distribution. The use of HDPE is reasonable because of the identical structures of the molecular chains of the linear polyethylenes.[6,14] The properties of HDPE (strength, plasticity, and rheological *etc.*) depend on the molecular weight of the polymer and meet the requirements of a wide range of applications.[1] Low-molecular-weight polyethylene waxes introduced into UHMWPE act as plasticizers; their presence leads to an improvement in the recyclability of the material without a significant loss of UHMWPE ten-

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sile properties.[13,15] Compositions of UHMWPE/HDPE obtained by the method of mechanical mixing of components in a melt have been widely studied.[16–18] However, it was noted that owing to the high viscosity of the melt, UHMWPE is present in the mechanical composition in the form of agglomerates located in polymer matrices with high melt indices.[12,19] This leads to a decrease in the impact and tensile properties of materials.[10–12,19]

The synthesis of UHMWPE compositions with polyolefins *in situ* (the "reactor" method) is an effective alternative to the post-reaction mixing of components. This method is based on the ability to control the properties of polymer products by selecting the catalysts, monomers, reactor types, and reaction conditions. "Reactor" methods include multi-step polymerization processes over organometallic catalysts using reactor cascades.[12,20–23] Single-step polymerization in the presence of two catalysts (binary catalysts) belonging to the same type or different types of catalytic systems is also an effective approach for producing reactor polymer compositions (RPC).[12] Each catalyst simultaneously produces separate polymer fractions, which are part of the RPC. The molecular weights and properties of the fractions were determined based on the catalytic properties of the binary system components. There are many studies in the literature on the possibility of controlling the molecular weight distribution (MWD) of reactor compositions obtained in one-step ethylene polymerization.[24–28] However, the number of publications concerning the physical and mechanical properties of such materials is limited.

Muelhaupt *et al*. developed graphene-supported dual- and multi-site catalysts for the production of RPC with bi- and trimodal MWD in the single-step ethylene polymerization.[29,30] The multisite systems included catalysts producing UHMWPE and HDPE with intermediate molar masses and PE waxes. RPC-s with increased melt indices relative to UHMWPE were synthesized. The presence of a fraction of low molecular weight PE wax made it possible to include up to 30 wt% UHMWPE and get RPC with a good mix of components. These materials can be processed using classical injection molding and have high mechanical properties.

Previously, we synthesized a series of reactor polymer compositions of UHMWPE and HDPE with a lower molecular weight relative to UHMWPE. Two-step sequential ethylene polymerization and one-step polymerization in the presence of a metallocene catalyst and a combination of metallocene and post-metallocene catalysts, respectively, have been used.[31,32] The RPC series significantly differed in the properties of low-molecular-weight HDPE (LMWPE) fractions modifying UHMWPE: molecular weight (160 and 48 kg·mol$^{-1}$), crystallinity (62% and 81%), which exceeded the crystallinity of unmodified UHMWPE (55%), tensile properties, and fluidity. The presence of 30 wt% of low molecular weight fractions (70% UHMWPE), a uniform distribution of fractions in the compositions ensured an increase in the fluidity of the material[33] while maintaining high mechanical properties.

An important task for creating compositions based on UHMWPE with improved technological and operational properties is to establish a balance between fluidity, mechanical properties, and the content of polyethylene fractions modifying UHMWPE. It was interesting to obtain and study compositions based on UHMWPE and LMWPE with a reduced molecular weight and higher fluidity relative to the low molecular weight fractions in UHMWPE/HDPE described in Refs. [31] and [32]. The compositions were synthesized by ethylene polymerization over a binary catalyst, including homogeneous metallocene precatalysts *rac*-$(CH_3)_2Si(Ind)_2ZrCl_2$ (**Zr-1**) and *rac*-$(C_6H_{10})CpIndZrCl_2$ (**Zr-2**), activated by methylaluminoxane (MAO). The molecular weight characteristics, crystallinity, and tensile and rheological properties of the material were studied depending on the percentage of LMWPE in RPC.

## EXPERIMENTAL

### Materials

The zirconocene compound *rac*-$(CH_3)_2Si(Ind)_2ZrCl_2$ (**Zr-1**), acquired from Aldrich, and *rac*-$(C_6H_{10})CpIndZrCl_2$ (**Zr-2**), synthesized according to a previously described method[34], were used as precatalysts. MAO as a 10 wt% solution in toluene with a density $\rho$=0.875 g·cm$^{-3}$ was applied as received from Aldrich. Toluene (spectroscopic grade, Aldrich) was held over molecular sieves (5 Å) and distilled in the presence of sodium wire in an argon atmosphere. Ethylene has a polymerization degree of purity.

### Ethylene Polymerization

Ethylene polymerization was carried out in a 0.4 L stainless reactor equipped with an electromagnetic stirrer and a thermostat jacket. The reactor was preliminarily evacuated at 70 °C and cooled to room temperature and supplied with 250 mL of toluene and 5 mL MAO solution, as well as calculated amounts of **Zr-1** and **Zr-2** components of the tandem catalyst. Both zirconocene compounds were individually fed in the form of complexes with MAO. Then, the reactor was heated to 30 °C and ethylene was supplied. The ethylene pressure was kept constant at 7 bar, the temperature at 30 °C, and the stirring speed was 1000 rpm. Typically, the molar ratio of Al/(**Zr-1**+**Zr-2**) was t2000 and the amount of precatalyst (**Zr-1**+**Zr-2**) was 6.5×10$^{-3}$ mmol. The polymerization time was 2 h. The mole fraction ($\alpha$) of **Zr-2** in (**Zr-1**+**Zr-2**) was varied from 0.3 to 0.85. A 5 wt% solution of HCl in ethanol was added to the reactor to stop the polymerization. The resulting polymer products were filtered off, washed with ethanol, and dried under vacuum at 60 °C.

The amount of RPC synthesized over (**Zr-1**+**Zr-2**)/MAO for 2 h ($Q_{HDPE}$, g) was calculated from the consumption of ethylene during the polymerization process. The percentage of LMWPE in the polymer composition ($\Delta_{HDPE}$, wt%) was calculated by the formulas:

$$Q_{\mathbf{Zr\text{-}2}/MAO} \times \alpha = Q_{\mathbf{Zr\text{-}2}} \quad (1)$$

$$Q_{\mathbf{Zr\text{-}2}} \times 100/Q_{HDPE} = \Delta_{HDPE} \quad (2)$$

where $Q_{\mathbf{Zr\text{-}2}/MAO}$ (g) is the amount of HDPE synthesized over the **Zr-2**/MAO catalyst during 2 h and $Q_{\mathbf{Zr\text{-}2}}$ (g) is the calculated amount of HDPE synthesized over (**Zr-1** + **Zr-2**)/MAO at the molar fraction of **Zr-2** equal to "$\alpha$" during 2 h.

The method of decomposing the MWD curves into two components, low molecular weight and high molecular weight, was also used to calculate the content of LMWPE in the compositions ($\Delta_{MWD}$).

### Characterization of Polymer Products

The molecular weight characteristics of the polymers were de-

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termined by gel permeation chromatography using a GPC Tosoh HLC-8321 GPC/HT (Japan) at temperature 160 °C, equipped with a column TSKgel GMHHR-H (20)HT2. 1,2,4-Trichlorobenzene (Thermo Scientific, 99% pure, India) was used as solvent. To stabilize and prevent the destruction and oxidation of polymers during the dissolution period, Irganox 1010 was added to the solvent as a stabilizer.[35] Sample preparation was performed at 160 °C for 3–5 h in accordance with the $M_w$. Samples concentration and flow rate were 1.0 mg·cm$^{-3}$ and 1.0 cm$^3$·min$^{-1}$ respectively. Molecular weight characteristics were calculated using a universal calibration curve with linear approximation obtained by PS standards with a narrow molecular weight distribution in the range of 2700 Da to 11.6×10$^6$ Da. The Mark-Houwink coefficients for PE in 1,2,4-trichlorobenzene were $K$=2.1×10$^{-4}$; $k$=0.73.[36]

The degree of crystallinity ($\chi$, %) of the polymers was determined using DSC. A Netzsch scanning calorimeter (Germany), model DSC-204 F1. Samples were heated to 160 °C at a heating rate of 10 °C·min$^{-1}$, cooled at a rate of 10 °C·min$^{-1}$ to room temperature, and heated to 160 °C at 10 °C·min$^{-1}$ rate to record melting endotherms. $\Delta H$=293 J/g was considered as the heat of fusion of an ideal PE crystal to calculate $\chi$.[37]

Tensile properties were determined in accordance with ISO 527-2:2012 using universal testing machine (Instron 3365) at 21 °C in the mode of uniaxial stretching (equivalent length 50 mm) at a rate of sample deformation of 50 mm·min$^{-1}$. The tensile modulus values of the samples were determined at a sample deformation of 1 mm·min$^{-1}$. Dumbbell samples were cut from plates with a thickness of 1 mm. The plates were prepared by the method of hot pressing at 190 °C and pressure of 10 MPa. All reported mechanical parameters were based on the average values of a minimum of five samples. Statistical processing of the data for each parameter was performed in accordance with ISO 2602:1980.

The sample melting indexes were measured on an IIRT-5 instrument at 190 °C and loads of 2.16, 5, 10 and 21.6 kg (ISO 1133-1).

## RESULTS AND DISCUSSION

The selection of binary catalyst components for the synthesis of polymer compositions in single-step ethylene polymerization is difficult. The organometallic precatalysts included in this catalytic system must ensure the formation of RPC fractions with desired properties under the same process conditions (nature of the co-catalyst, temperature, ethylene concentration, polymerization time, *etc.*). According to the results we received earlier, ethylene polymerization over the zirconocene catalyst *rac*-$(CH_3)_2SiInd_2ZrCl_2$/MAO (**Zr-1**/MAO) (Fig. 1) at 30 °C leads to the production of UHMWPE with $M_w$=1000 kg·mol$^{-1}$.[31,38] The choice of *rac*-$(C_6H_{10})CpIndZrCl_2$ (**Zr-2**) (Fig. 2) as a component of the binary system responsible for the formation of the low-molecular-weight fraction was based on the data presented in a review.[39] The authors noted that, in many cases, low molecular weight polyethylene was obtained using zirconocene complexes with bulky bridges. The polymerization of ethylene over such catalysts is characterized by rapid chain transfer reactions.

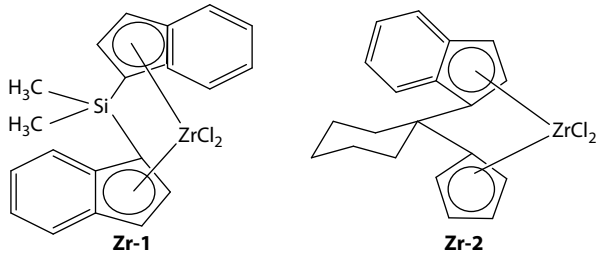


**Fig. 1** Structural formulas of: *rac*-$(CH_3)_2SiInd_2ZrCl_2$ (**Zr-1**) and *rac*-$(C_6H_{10})CpIndZrCl_2$ (**Zr-2**).

Preliminarily, single-site catalysts **Zr-1**/MAO and **Zr-2**/MAO were tested in ethylene polymerization under the same conditions (30 °C, Al/(**Zr-1**+**Zr-2**)=2000, ethylene pressure 7 bar, 2 h) to determine the activity of each catalyst and the properties of polymer products (molecular weight characteristics, crystallinity, tensile properties, melt indexes) as analogs of the RPC factions. The activity of **Zr-1**/MAO was about three times higher than that of the **Zr-2**/MAO catalyst. The values of their activities calculated on the basis of ethylene consumption after 2 h of polymerization were 320 and 94 kgPE·(mmolZr·bar)$^{-1}$ and the yields of PE were 2150 and 660 kgPE·(mmolZr)$^{-1}$, respectively (Table 1). Ethylene polymerization over **Zr-1**/MAO gave UHMWPE with $M_w$=1000 kg·mol$^{-1}$ and narrow MWD=3.0 (Table 1). The **Zr-2**/MAO catalyst produced LMWPE with $M_w$ = 18 kg·mol$^{-1}$ and MWD=13 (Table 1, Fig. 2). However, there are two narrow peaks in the MWD curve: a strong peak in the low molecular weight region and a very weak peak in the high molecular weight region. According to calculations based on the decomposition of the MWD curve into components of a low molecular weight and high molecu-

**Table 1** Ethylene polymerization over **Zr-1**/MAO, **Zr-2**/MAO catalysts and binary (**Zr-1**+**Zr-2**)/MAO system at different mole fraction of **Zr-2** in (**Zr-1**+**Zr-2**).

| Run | $\alpha$ [a] | $A$ [b], kgPE (mmolZr·bar)$^{-1}$ | $Q$ [c], kgPE (mmolZr)$^{-1}$ | $Q_{HDPE}$ [d] (g) | $\Delta_{HDPE}$ [e] (wt%) | $\Delta_{MWD}$ [f] (wt%) | $M_w$ (kg/mol) | MWD |
|---|---|---|---|---|---|---|---|---|
| 1 | 0 | 310 | 2150 | 14 | 0 | n.d. | 1000 | 3.2 |
| 2 | 1 | 94 | 660 | 4.1 | 100 | n.d. | 18 | 13 |
| 3 | 0.3 | 298 | 2080 | 13.6 | 9.0 | n.d. | 915 | 3.2 |
| 4 | 0.4 | 270 | 1890 | 12.3 | 13 | 15 | 730 | 4.0 |
| 5 | 0.5 | 260 | 1820 | 11.9 | 17.5 | 20 | 670 | 6.0 |
| 6 | 0.6 | 210 | 1470 | 9.6 | 27 | 26 | 470 | 10.7 |
| 7 | 0.85 | 180 | 1260 | 8.3 | 42 | 45 | 440 | 16.5 |

[a] $\alpha$ is the mole fraction of **Zr-2** in (**Zr-1**+**Zr-2**); [b] $A$ is activity of catalysts calculated by the consumption of ethylene in 2 h; [c] $Q$ is the yield of RPC in 2 h; [d] $Q_{HDPE}$ is the amount of HDPE synthesized during 2 h; [e] $\Delta_{HDPE}$ is the percentage of LMWPE in the RPC calculated using the bimodality criterion; [f] $\Delta_{MWD}$ is the percentage of LMWPE fraction in the RPC calculated by the method of MWD curve decomposition.

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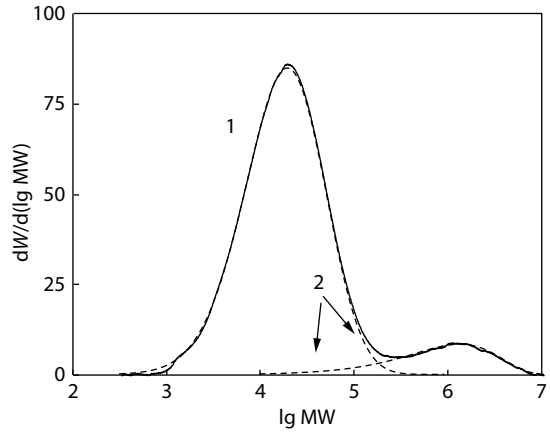


**Fig. 2** MWD curve of pure LMWPE (1) and the curves obtained by decomposing the MWD curve 1 into components of a low molecular weight and high molecular weight fractions (2).

lar weight polymer, the contribution of the second peak is < 7 wt% of the total product.

Table 1 shows the data on the polymerization of ethylene over the binary catalyst (**Zr-1**+**Zr-2**)/MAO, which includes various mole fractions of less active **Zr-2**. An increase in α from 0.3% to 0.85% led to a decrease in catalyst activity, polymer yield, and an increase in the percentage of LMWPE in the RPC from 9 wt% to 42 wt%. The $\Delta_{HDPE}$ values were calculated using the bimodality criterion proposed by Soares and D'agnillo.[26, 27] According to this criterion, the proportion of each polymer fraction depended on the activity and mole fraction of the corresponding zirconocene compound in the binary catalyst. This criterion has been widely used in studies on the synthesis of RPC in the presence of binary catalysts, including homogeneous single-site catalysts[40,41] and catalysts of different natures.[24]

As shown in Table 1, the addition of 9 wt% of LMWPE has practically no effect on the width of material MWD. There are weak shoulders in the low molecular weight region on the MWD curves of compositions with 13 wt% and 17.5 wt% of modifying fraction (Figs. 3 and 4, curves 1). The MWD of these materials were 4.0 and 6.0. The compositions including 27 wt% and 42 wt% of LMWPE have a wide bimodal MWD of 10.7 and 16.5, with peaks in the high molecular and low molecular regions (Fig. 5, curves 3 and 4). Their positions coincided with the peak positions on the curves of pure UHMWPE and LMWPE (Fig. 5, curves 1 and 2), respectively. The coincidence of the peak locations in the high molecular weight part of the MWD curves of RPC with 13 wt% and 17.5 wt% of LMWPE with the peak on the MWD curve of pure UHMWPE (Figs. 3, 4 and 5 (curve 1) respectively). This indicates the formation of the UHMWPE fraction with $M$ =1000 kg·mol$^{-1}$ and the LMWPE fraction with $M_w$=18 kg·mol$^{-1}$ during the single-step ethylene polymerization over the studied binary catalyst at different mole fractions of **Zr-2**.

The MWD curve decomposition method was used to calculate the content of the LMWPE fraction in RPC ($\Delta_{MWD}$). Decomposition of the MWD curves for UHMWPE/LMWPE containing 13 wt% and 17.5 wt% of the modifying fraction is shown in Fig. 3 and Fig. 4, respectively, for an example. These results were close to the values calculated using the bimodality criterion (Table 1). It can be assumed that there is no interaction between components **Zr-1** and **Zr-2** in the binary catalyst.

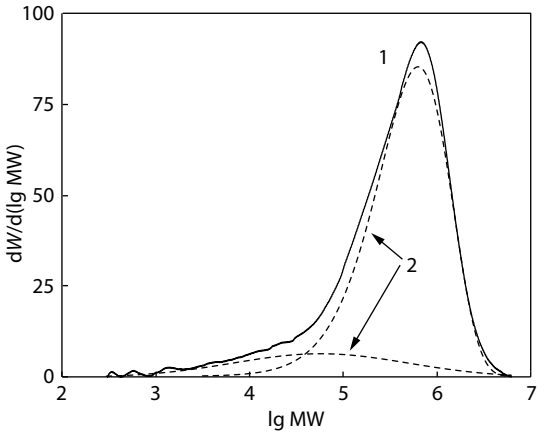


**Fig. 3** MWD curve of UHMWPE/LMWPE compositions containing 13 wt% of LMWPE. 1: MWD curve, 2: curves obtained by decomposing the MWD curve into components of a low molecular weight and high molecular weight fractions.

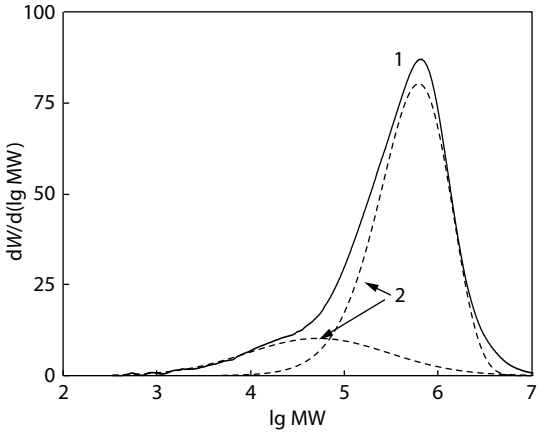


**Fig. 4** MWD curve of UHMWPE/LMWPE composition containing 17.5 wt% of LMWPE. 1: MWD curve, 2: curves obtained by decomposing the MWD curve into components of a low molecular weight and high molecular weight fractions.

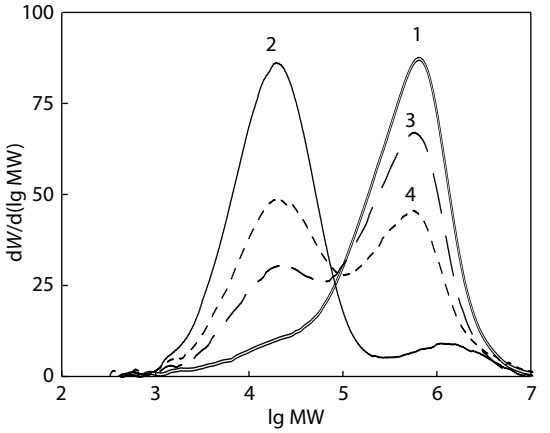


**Fig. 5** MWD curves of pure UHMWPE, LMWPE and compositions UHMWPE/LMWPE with different LMWPE contents. 1: 0 wt% (UHMWPE), 2: 100 wt% (LMWPE), 3: 27 wt%, 4: 42 wt%.

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The properties of the polymer fractions formed simultaneously during ethylene polymerization were determined by the catalytic properties of **Zr-1**/MAO and **Zr-2**/MAO.

Figs. 6 and 7 show the stress-strain curves of pure UHMWPE, LMWPE, and UHMWPE/LMWPE compositions with different contents of low molecular weight fraction and the initial sections of these curves, respectively. A significant difference was observed between the tensile properties of the pure UHMWPE and LMWPE. There is a peak with a maximum corresponding to the yield strength ($\sigma_y$), followed by pronounced deformation hardening of the sample on the stress-strain curve of unmodified UHMWPE (Fig. 6, curve 1). Pure LMWPE, unlike UHMWPE, collapsed at a very low strain of 2.3% (Fig. 7, curve 2, Table 2).

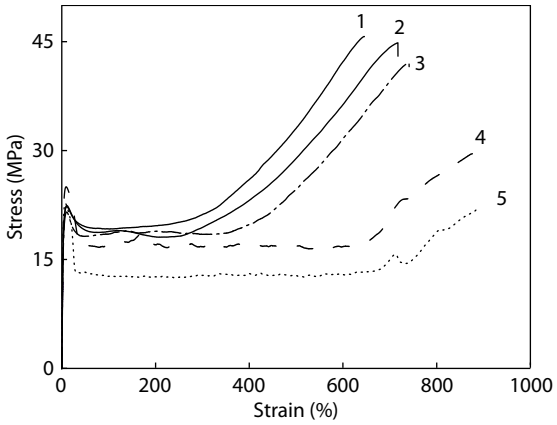


**Fig. 6** Stress–strain curves of pure UHMWPE and UHMWPE/LMWPE with different LMWPE contents. 1: 0 wt% (UHMWPE), 2: 9 wt%, 3: 17.5 wt%, 4: 27 wt%, 5: 42 wt%.

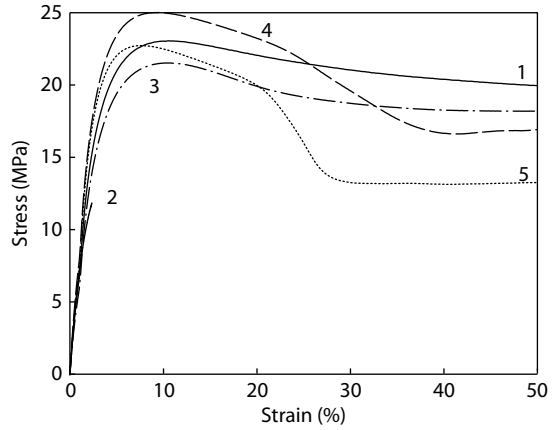


**Fig. 7** The initial sections of the stress–strain curves of pure UHMWPE, LMWPE and UHMWPE/LMWPE with different LMWPE contents. 1: 0 wt% (UHMWPE), 2: 100 wt%, 3: 17.5 wt%, 4: 27 wt%, 5: 42 wt%.

The curve for UHMWPE/LMWPE with 9 wt% of LMWPE (Fig. 6, curve 2) practically coincides with this one for unmodified UHMWPE. The composition containing 17.5 wt% of LMWPE shows the peak corresponding to $\sigma_y$, elongation under tension with the formation of a stable neck and intensive hardening in the zone of large deformations. The curves of the RPC with 27 wt% and 42 wt% of LMWPE are typical for HDPE (Fig. 6, curves 4, 5).

The introduction of LMWPE with a crystallinity ($\chi$) of 54% into UHMWPE with a crystallinity of 55% had practically no effect on the degree of crystallinity of RPC. This characteristic varied within a narrow range from 51% to 57% (Table 2). The increase in the proportion of the low molecular weight fraction from 9 wt% to 42 wt% does not affect the values of the material $\sigma_y$ (Fig. 7, Table 2). This result is consistent with the literature data. A linear increase in the yield strength of HDPE with increasing degree of crystallinity was reported in.[42] It is also known about the relationship between $\chi$ and the modulus of elasticity ($E$) of mechanical blends UHMWPE/HDPE.[10,19,43] Unmodified UHMWPE and LMWPE are characterized by close and relatively low $E$ values of 850±12 and 950±30 MPa, respectively. An increase in the proportion of the LMWPE from 9 wt% to 42 wt% is accompanied by the very slight increase in the $E$ value of the compositions from 810±20 MPa to 980±40 MPa (Table 2).

The unmodified UHMWPE was characterized by a high tensile strength ($\sigma_b$) of 46±1 MPa (Table 2). The high-strength properties of this polyolefin are due to the peculiarities of its structure and the massive entanglement of passage chains in the amorphous phase. This has an important effect on the resistance of a material to high deformation.[1,16,44] The elongation at break ($\varepsilon_b$) of UHMWPE is small compared to that of HDPE with high and medium molecular weights and equal to (650±20)%. Pure LMWPE with $M_w$=18 kg·mol$^{-1}$ breaks down brittle with $\varepsilon_b$= (2.3±0.8)% and has a low tensile strength ($\sigma_b$=12±2 MPa). Despite the large differences in the strength properties of UHMWPE and LMWPE, the introduction of less than 20 wt% of the low molecular weight fraction has very weakly effect on the value of material $\sigma_b$. These characteristics varied in the range of 46±1 MPa to 42±2 MPa. A further increase in the proportion of modifying fraction from 27 wt% to 42 wt% leads to a decrease of $\sigma_b$ to 32±2 MPa and to 23±1 MPa respectively. The presence of the LMWPE fraction improved the plastic properties of the UHMWPE compositions.

**Table 2** Crystallinity and tensile properties of UHMWPE, LMWPE and UHMWPE/LMWPE with different content of low molecular weight fraction.

| Run | $\Delta_{HDPE}$ [a] (wt%) | $\chi$ [b] (%) | $\sigma_y$ (MPa) | $\varepsilon_y$ (%) | $\sigma_b$ (MPa) | $\varepsilon_b$ (%) | $E$ (MPa) |
|---|---|---|---|---|---|---|---|
| 1 | 0 | 55 | 22±0.1 | 11±0.2 | 46±1 | 650±20 | 850±10 |
| 2 | 100 | 54 | – | – | 12±2 | 2.3±0.8 | 950±30 |
| 3 | 9 | 51 | 22±0.1 | 11±0.2 | 45±1 | 710±20 | 810±20 |
| 4 | 13 | 55 | 24±0.2 | 10±0.2 | 44±1 | 745±20 | 800±20 |
| 5 | 17.5 | 57 | 22±0.1 | 10±0.1 | 42±2 | 740±40 | 920±10 |
| 6 | 27 | 57 | 24±0.4 | 9±0.1 | 32±2 | 870±50 | 980±30 |
| 7 | 42 | 56 | 23±0.2 | 8±0.1 | 23±1 | 920±50 | 980±40 |

[a] $\Delta_{HDPE}$ is the percentage of LMWPE in the RPC calculated using the bimodality criterion; [b] $\chi$ is the crystallinity determined by the DSC method.

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The $\varepsilon_b$ values varied from (650±20)% for the pure UHMWPE to (920±50)% for the RPC containing 42 wt% of the modifying fraction.

Table 3 shows the data obtained in the study of the melt indices (MI) of RPC-s, which are an important technological characteristic of polyolefins, demonstrating their ability to process. It can be seen that the fluidity of the composition melts increases depending on the content of the low molecular weight fraction with high MI (30 g·(10min)$^{-1}$ at 190 °C and load 2.16 kg). Unmodified UHMWPE and RPC with 9 wt% of LMWPE do not flow at the load of 21.6 kg. Introduction of 13 wt% of LMWPE leads to the appearance of very weak fluidity of the material melt at the maximum load of 21.6 kg. A further increase in the low molecular weight fraction content was accompanied by an increase in MI-s. The composition including 17.5 wt% shows the ability to flow at the load of 10 kg. The presence of the 27 wt% and 42 wt% of LMWPE ensures the flowability of the material at the load of 5 kg with MI-s, respectively, equal to 0.07 and 0.09 g·(10min)$^{-1}$. In addition, these RPC flows at a load of 2.16 kg with MI-s of 0.02 g·(10min)$^{-1}$.

**Table 3** Melt indexes of UHMWPE, LMWPE and compositions UHMWPE/LMWPE.

| Run | $\Delta_{HDPE}$ (wt%) | MI, g·(10min)$^{-1}$ at 190 °C and load (kg) | | | |
|---|---|---|---|---|---|
| | | 21.6 | 10 | 5 | 2.16 |
| 1 | 0 | 0 | 0 | 0 | 0 |
| 2 | 100 | – | – | – | 30 |
| 3 | 9 | 0 | 0 | 0 | 0 |
| 4 | 13 | 0,03 | 0 | 0 | 0 |
| 5 | 17.5 | 0.17 | 0.03 | 0 | 0 |
| 6 | 27 | 2.65 | 0.31 | 0.07 | 0.02 |
| 7 | 42 | 2.54 | 0.37 | 0.09 | 0.02 |

## CONCLUSIONS

The study showed that single-step ethylene polymerization over a binary zirconocene catalyst, including *rac*-$(CH_3)_2SiInd_2ZrCl_2$ and *rac*-$(C_6H_{10})CpIndZrCl_2$ activated by MAO, is an effective method for the synthesis of UHMWPE compositions with controlled content and properties of the modifying polyethylene fraction. The obtained polymer products are characterized by a wide MWD and bimodal reactor polymer compositions based on UHMWPE with $M_w$=1000 kg·mol$^{-1}$ and LMWPE with $M_w$=18 kg·mol$^{-1}$.

It was found that the introduction of LMWPE fractions with a low content of crystalline phase into low-crystalline UHMWPE had a weak effect on both the crystallinity of RPC and its behavior in the region of small deformations, yield strength, and modulus of elasticity. This corresponds to the literature data on the effect of the crystallinity of polyolefins and their compositions on the specified characteristics of the materials.

The presence of the UHMWPE fraction in compositions with linear LMWPE, which breaks down brittleness, provides a transition to viscous deformation of the material. RPC-s containing up to about 20 wt% LMWPE have a high strength close to the value of the ultimate tensile strength of UHMWPE. The plastic properties increased with the enrichment of compositions with LMWPE and exceeded the properties of UHMWPE. A comparison of the data on the deformation and strength characteristics of the RPC and their melt indexes shows that for the studied reactor polymer compositions, a balance between their mechanical characteristics and rheological properties can be achieved by introducing 20 wt%–30 wt% of the low molecular weight fraction into UHMWPE.

## Conflict of Interests

The authors declare no interest conflict.

## Data Availability Statement

The data that support the findings of this study are available on request from the corresponding authors upon reasonable request.

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