ВИСОКОМОЛЕКУЛЯРНІ СПОЛУКИ ТА (НАНО)КОМПОЗИЦІЙНІ МАТЕРІАЛИ

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ТЕХНОЛОГІЧНІ ОСОБЛИВОСТІ ПЕРЕРОБКИ СУМІШЕЙ ПОЛІМЕРІВ НА ОСНОВІ НАДВИСОКОМОЛЕКУЛЯРНОГО ПОЛІЕТИЛЕНУ

Розроблено технологічну схему одержання полімерних сумішей на основі надвисокомолекулярного поліетилену. Доведено доцільність використання комбінованого способу змішуваня компонентів суміші. Визначено оптимальні умови змішування у шнековому пластикаторі литтєвої машини. Встановлено технологічні режими переробки композицій для промислових методів лиття під тиском та екструзії високов’язких (перехідних партій) композицій на основі надвисокомолекулярного поліетилену.

Ключові слова: технологічна схема, надвисокомолекулярний поліетилен, литтєва машина, шнековий пластикатор, лиття під тиском.

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TECHNOLOGICAL FEATURES OF POLYMER BLENDS PROCESSING BASED ON ULTRA-HIGH MOLECULAR WEIGHT POLYETHYLENE

The technological scheme of polymer blends obtaining which are based on of ultra-high molecular weight polyethylene has been developed. The advisability of using the combined method of components mixing of the blend has been proved. The optimum conditions of mixing in screw plasticizer of the injection molding machine are determined. The technological modes of compositions processing for the industrial methods of injection molding and extrusion of high-viscidity (transitional batches) compositions based on ultra-high molecular weight polyethylene are defined.

Key words: technological scheme, ultra-high molecular weight polyethylene, injection molding machine, screw plasticiser, injection molding.

Problem definition. A rather large group of industrial thermoplastics are polyolefins, that is the basis of many compositions [1]. The most widely used are the compositions based on polyethylene and polypropylene. Applying of polyethylene and its copolymers in compositions is caused by its rather valuable complex of properties such as: high impact strength, non-toxicity, resistance to aggressive environments, and the ability to hold properties in a wide range of compositions.

By the mixing in the melt of various polyolefins obtain the materials with the necessary specific properties that can not be obtained during the synthesis. Scientists know the compositions where the injection of ethylene and vinyl acetate copolymer in polyolefins can achieve improvement in impact strength with high processing ability [2, 3]. The improvement of strength is also achieved by the injection of thermoplastic blends, polyethylene-propylene rubbers, styrene-butadiene-styrenic blocks-copolymers into polyolefins [4].

Widespread blends are used with a small amount of low molecular weight polyethylene with a wide molecular weight division (MWD), added to linear low density polyethylene with small MWD, that improves its transparency and stability of the sleeve film at the blowing during extrusion, but worsens resistance to cracking in the direction of extrusion. Approximately the same properties are found in mixtures of low density polyethylene and polyethylene of high density, although the main advantage is the increase in tensile strength.

Due to the wide range of molecular masses, there is a conditional gradation of low pressure polyethylene (high density) according to their values. Following to the classification adopted, the low-pressure polyethylene is divided into pretended standard low pressure polyethylene with molecular weight from 30 thousand to 700 thousand and ultra-high molecular weight polyethylene (UHMWPE) of low pressure with a molecular weight of 1 million and more. UHMWPE has higher physical, mechanical and chemical properties, wear resistance, abrasion resistance, cracking and impact loads, frost resistance, low friction coefficient, and the ability to keep properties over a wide range of temperatures in comparison with standard grades of low density polyethylene (LDPE) [5**]**. On the other hand, during the melting UHMWPE passes over not into viscid state, which is typically for standard LDPE with M.W. 70000, but in highly elastic state, that means, melt has a high viscosity.

Analysis of recent experiments. UHMWPE processing is mainly carried out by hot pressing or sintering. Use of such methods as an extrusion or injection molding is difficult due to significant mechanical and thermal efforts. Extrusion and injection molding give the possibility of processing only for modified UHMWPE by polymer or non-polymer additives, namely, in the form of composites [6, 7].

One of the first additives for the UHMWPE modification were powdered sulfides of metals and graphites – solid lubricants. Mentioned additives led to the increase of the resistance of UHMWPE amortization to the steel level, reduced friction and improved processing conditions. Compositions containing UHMWPE, as well as polyolefins [8], were mainly filled during the polymerization, where kaolin (28–45 % by weight), Al (54 % by weight), $Al(OH)_3$ (51 % by weight) [9], $CaCO_3$ (0–50 % by weight) [10], bauxite (45 % by weight) were applied as fillers [11]. The adding of filler by such method increases the elastic modulus, improves mechanical properties.

Due to its unique properties, UHMWPE is applied to create a multilayer film with improved elastic modulus [8], shine and resistance to drops water, and due to its chemical resistance – in the production of microporous separators for accumulators [12].

The most well-known methods for composites processing based on UHMWPE include: sintering, hot pressing, plunger extrusion [5, 6]. The first two methods of composites processing are quite voluminous. Sintering is accompanied by a mechanical treatment of the product, and when hot pressing, the molding part of the mold should provide the shape of the product itself, with the method only obtaining monolithic products. Plunger extrusion requires the use of high mechanical and thermal loads, which can lead to mechanochemical destruction, in which the polymer flow in the extruders occurs in slip mode. As you can see, the use of the above-mentioned methods of composites processing is technologically unprofitable and limited.

Ultra-high molecular weight polyethylene can not claim the scope of the usage of polyethylene traditional grades, but its above-mentioned unique properties attract attention for the purpose of using it as a polymer matrix in composites [6] and make it a perspective material for the creation of composite materials of constructional purpose.

However, it should be noted that the processing of UHMWPE and its compositions, as you can see from the given data, is heavy. Therefore, it is quite reasonable to study the creation of technological compositions based on UHMWPE which would have high strength and stable properties of the appropriate polymer and, at the same time, would be able for processing by the traditional methods such as injection molding or extrusion.

The purpose of the work. To develop the technological scheme for the production of polymer blends based on ultra-high molecular weight polyethylene. Determine the optimum conditions for the technological mode of the compositions processing by the method of injection molding and extrusion.

Results and discussion. The most interesting from a technological and ecological point of view are studies aimed at creating of compositions based on transitional fractions of ultra-high molecular weight polyethylene, characterized by unregulated composition and properties.

As already mentioned [5], ultra-high molecular polyethylene is not suitable for processing by such industrial methods as an injection molding, even in extreme conditions close to destruction – T = 220 – 230 °C and P = 100 MPa. The processing of ultra-high molecular weight polyethylene due to the high viscosity and melt elasticity (MFI = 0,024 g / 10 min.) by injection molding is not possible even under the above-mentioned conditions, and therefore the attempt to process it by injection molding causes the obtaining underdone product formed only on 10 % (Fig. 1).

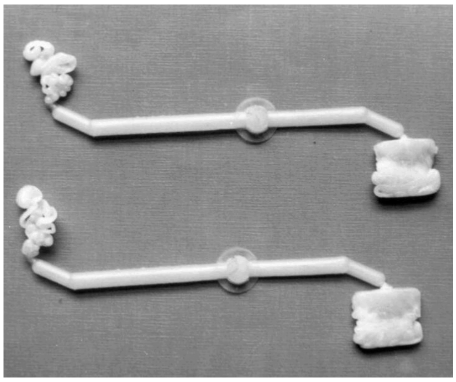

Fig. 1. Sample of the scapula form made of UHMWPE, obtained at T = 220 °C and P = 100 MPa

As we see, during processing by the injection molding of the original polymer, due to the high melt viscosity it is practically impossible to obtain a quality product.

The features of "transitional batches" are summarized in Table 1.

Table 1

Characteristics of "transitional batches"

№ of party	Density, g/10min	$MFI_{21,6}$ at 190°C	$MFI_{21,6}$ / $MFI_{5,0}$	Ash, %
1	0,948	12	20	0,07
2	0,950	15	90	0,05

The research of rheological properties [13] of blends based on UHMWPE, that is, waste production, created during the mode transition on the installation from one batch to the other (transitional batches) gives the grounds to affirm the possibility of their use for creating compositions of the developed contents.

Studies have proved [14] that the most suitable method for obtaining of homogeneous blend with good properties is the method of combined mixing – in the plunger cylinder, and then in a screw plasticizer. This method allows combine the final stage of mixing with the formation of the product by injection molding.

For the developed compositions based on UHMWPE the technological scheme of obtaining and processing has been offered in Fig. 2.

The powdered UHMWPE and polymer additives (PE, PP) from the hopper 1 through the dosing device enter the drum mixer 2 (volume – 3 liters), where at the room temperature there is a mechanical mixing of the components within 15–20 minutes. After that, the obtained mixture stays in a plunger injection cylinder of vertical type 3 at T = 190 °C for 15 minutes with the followed pushing of the melt through the nozzle d = 2,095±0,005 mm. The derived cold bars are ground with a rotary knife crusher 4. The granulated mixture goes into a mixer 5, where calcium carbonate and a stabilizer (surface modifier) are injected via the dosing device from bunkers 6. Previously the calcium carbonate is heated by a heater to 200 °C and is fed to the mixer 5, the process of "hot rubbing" of the material takes place. After that, the material with a tape dispenser 7 goes to the loading bunker 8 of the injection machines KuASY 260/100.

From the bunker 8 the blend captured by the screw of the casting machine and the plasticization of the mixture occurs, the temperature in the zones of the cylinder T_1 = 190 °C, T_2 = 210 °C, T_3 = 220 °C, the time of plastisation τ = 90s, the time of exposure under pressure t_{sp} = 5s, with the following injection the material in the form where the temperature of the form T_f = 50–70 °C, the cooling time τ_{ct} = 18 s, the velocity rotation of the screw is 100 rpm. After automatic removal of the product, the container 10, we check out a quality on the external features, if necessary, and machining the product manually. At the final stage it is necessary to carry out technical quality control of the product.

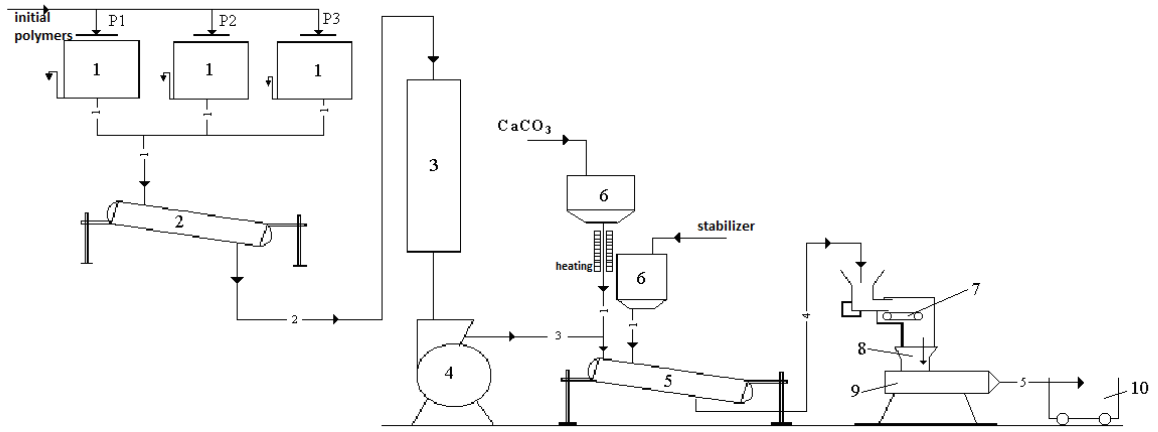

Fig. 2. The general technological scheme of obtaining and processing of composite based on ultra-high molecular weight polyethylene:

–1 – 1 – initial materials
–2 – 2 – mechanically obtained blend
–3 – 3 – crushed blend
–4 – 4 – filled polymer blend
–5 – 5 – final products

1 – bunkers for the initial materials;
2, 5 – mixers;
3 – plunger-injection cylinder of the vertical type;
4 – rotary knife crusher;

6 – auxiliary bunkers;
7 – tape dispenser;
8 – downloading bunker;
9 – injection molding machine;
10 – container for final products.

On the basis of the proposed technological scheme, a technological card of the injection molding process of the triple composition of UHMWPE/HDPE/PP = 19/76/5 % by weight was developed [14], Table 2.

The overall process includes the steps of: equipment preparation, the process of product formation, for instance, mechanical mixing of blend components, melting the mixture, grinding, filling of the composition, plastisation, injection, machining and technical control over the quality of the product. The typical technological process includes the stages of mixing and processing: general production time of the process, taking into account all operations, is 1620s = 27 min., including the time of the injection molding cycle is 120s = 2 min.

Table 2

Technological card of manufacture of products by injection molding

<table>
<tr><td>№</td><td>№ oper.</td><td colspan="2">Name of operation</td><td rowspan="2">Name of the equipment</td><td colspan="2" rowspan="2">Injection molding mashine</td><td colspan="2" rowspan="2">Kuasy 260/100</td><td colspan="3">Production method</td></tr>
<tr><td></td><td></td><td colspan="2">Injection molding</td><td colspan="3">Injection molding</td></tr>
<tr><td colspan="9">Materials</td><td colspan="3" rowspan="3"></td></tr>
<tr><td colspan="5">Name, brand</td><td>Color</td><td>Fluidity, g/10 min</td><td>Humidity, %</td><td>Shrinkage %</td></tr>
<tr><td colspan="5">Blends:
UHMWPE transitional batches ТУ-У 6-05743160.018-96
HDPE 21008 – 075 GOST 16337 – 77
PP 21060 ТУ 6-05-1105-73</td><td>
white
white
white</td><td>
< 0,1
6,4
12,52</td><td>
н
н
н</td><td>
2
2
1</td></tr>
<tr><td colspan="9">Injection form</td><td colspan="3">Armature</td></tr>
<tr><td>Type</td><td colspan="2">Code</td><td>Circle</td><td>Heating</td><td colspan="2">Cooling</td><td colspan="2">Name of the lubricant</td><td colspan="3"></td></tr>
<tr><td>fixed</td><td colspan="2">block 0611–4001</td><td>2</td><td>electro</td><td colspan="2">water</td><td colspan="2">silicone
ТУ 6-15-542-75</td><td>name</td><td>mark</td><td>numb er</td></tr>
<tr><td>Note</td><td colspan="11">Specify processing modes for each batch of material separately</td></tr>
</table>

№	Contents	Facilities and tools (code, name)	Injection molding				Temperature in zones of the cylinder, °C				Time t,s.
			temperature of the mztrix	pressure on manometer	endurance		I	II	III	nozzle	
					under pressure	at the cooling					
1	Lubrication of the molding form cavity (after every 15–20 melts)										
2	Enable heating machine and heated to a working condition	0–300 °C GOST 9736 – 80					190	210	220	220	1200
3	Close the barrier										1
4	Turn on the machine										1
5	Close the form										1
6	Loading the material										90
7	Injection the material into form		60				190	210	220	220	1
8	Staying under pressure	GOST 2405–80 MT–3; 0–160	60	100	0,1		190	210	220	220	5
9	Staying at the cooling					0,6					18
10	Shutting off the mold										1
11	Removing the barrier										1
12	Turn off the machine										1
13	Check the details on the quality of external appearances										80
14	Mechanical treatment of parts	hand tools for the treatment: pliers, knife									100
15	Technical control, quality control of the product (existence of imperfections, cracks, weights, detachments)	size, surface roughness									120

The introduction of polymer additives of different ratios allow improving manufacturability of UHMWPE transition fractions processing and obtain blends with sufficient physical – mechanical properties ($\sigma_{pl.}$ = 19–27 MPa, $\varepsilon_{t.}$ = 100–300 %) [14].

The development of a technological mode for the processing of injection molding of compositions based on ultra-high molecular weight polyethylene gave the possibilities to obtain blends with predicted working properties.**Conclusions.** A technological scheme and an operational map for the production of polymer blends based on ultra-high molecular weight polyethylene were developed. The expediency of usage the combined method of mixing the components of the mixture is proved. The optimum conditions of the mixing process in the screw plasticizer of the injection molding machine are determined: mixing time 1,5–2 min., temperature 200–220 °C at the screw velocity 50–120 rpm. The possibility of processing high-viscosity (transitional batches) of compositions based on ultra-high molecular weight polyethylene by industrial methods of the injection molding and extrusion was researched.

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