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НИЗКОТЕМПЕРАТУРНАЯ ТЕХНОЛОГИЯ СИНТЕЗА ПОЛИАМИДА-6 И ЕГО СВОЙСТВА

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Для получения полимерных композиционных материалов в первую очередь необходимо ориентироваться на физико-химические свойства полимеров, которые являются основой для их производства. Одним из востребованных полимеров для производства изделий промышленного и бытового применения в России и в мире является полиамид-6. Разрабатывается и совершенствуется технология получения данного полимера методом низкотемпературной гидролитической полимеризации капролактама. На первой стадии - двухступенчатого синтеза капролактама при использовании воды в качестве катализатора при последовательном понижении температуры - получен форполимер полиамида-6. Для получения продукта с низкой вязкостью полученный форполимер с целью снижения содержания исходного мономера подготавливается к переработке с помощью процесса совмещенной демономеризации и сушки. Для получения продукта с высокими показателями вязкости и молекулярной массы последовательно проводили процессы твердофазного дополиамидирования и совмещенной демономеризации и сушки. Подобраны оптимальные технологические параметры для проведения каждой стадии процесса. Установлены основные физико-химические показатели полученного продукта: содержание капролактама и низкомолекулярных соединений, относительная вязкость, молекулярная масса. Показано влияние технологических особенностей разрабатываемой технологии на свойства конечного продукта. Разработанные технологические параметры позволяют за счет встраивания мономера и его олигомеров в макромолекулу полимера повысить выход целевого продукта, а также соответствующие характеристики гранулята. Доказано, что конечный продукт отвечает требованиям к полиамиду-6, готовому к переработке в полимерные композиционные материалы. Низковязкий полиамид-6 используется для получения нитей и волокон, а высоковязкий – для получения конструкционных изделий и пластических масс.

Ключевые слова: полиамид-6, капролактам, дополиамидирование, совмещенная сушка-демономеризация

LOW TEMPERATURE TECHNOLOGY FOR SYNTHESIS OF POLYAMIDE-6 AND ITS PROPERTIES

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To obtain polymer composite materials, it is first necessary to focus on the physical and chemical properties of polymers, which are the basis for their production. One of the popular polymers for the production of products for industrial and everyday use in Russia and in the world is polyamide-6. The technology for producing this polymer by low-temperature hydrolytic polymerization of caprolactam is being developed and improved. Polyamide-6 prepolymer was obtained used a two-stage synthesis of caprolactam using water as a catalyst with a sequential decrease in temperature. To obtain a product with low viscosity, the resulting prepolymer is prepared for processing

using a combined demonomerization and drying process in order to reduce the content of the monomer. To obtain a product with high viscosity and molecular weight, the processes of solid-phase polyamidation and combined demonomerization and drying were carried out sequentially. Optimal technological parameters were selected for each stage of the process. The main physicochemical parameters of the resulting product have been established: the content of caprolactam and low-molecular compounds, relative viscosity, molecular weight. The influence of the technological features of the developed technology on the final product properties is shown. The developed technological parameters make it possible, by incorporating the monomer and its oligomers into the polymer macromolecule, to increase the yield of the product, as well as the corresponding characteristics of the granulate. The final product has been proven to meet the requirements for polyamide-6, ready for processing into polymer composite materials. Low-viscosity polyamide-6 is used to produce threads and fibers, and high-viscosity polyamide is used to produce structural products and plastics.

Keywords: polyamide-6, caprolactam, polyamidation, combined drying-demonomerization

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INTRODUCTION

Composite materials obtained by processing polymers are subject to very serious requirements for their more durable and efficient operation [1-2]. Physical-chemical and physical-mechanical properties of materials significantly influence the processes of destruction when using the products [3-4]. As a result of chemical transformations during the aging process of polymers, processes of oxidation and destruction or cross-linking occur, leading to a deterioration in their consumer properties [5-6]. The strength and elasticity of the material decreases, staining occurs, and processability deteriorates when polymers are recycled [7-8].

On the one hand, this pattern can be influenced using various filler additives [9-10]. On the other hand, the characteristics of polymer composite materials directly depend on the properties of the primary polymers, which are the basis for their production [11].

Polyamide-6 (PA-6), due to its valuable set of consumer properties such as strength, elasticity, abrasion resistance, is widely used in the light, food, textile industries, construction, mechanical engineering, and medicine. The main part of polyamide-6 produced industrially is used in the production of polyamide threads, fibers and composite materials, which are increasingly used in technology and everyday life [12-14]. Polyamide threads are widely used for the production of hosiery and knitwear, ropes, fishing nets, cord, and technical fabrics. Also, recently the use of polyamide-6 has significantly expanded for the manufacture of machine parts and structural elements of aircraft and ground equipment: propellers, bearings, gears, bushings, etc. [15-17]. Membranes and food films based on polyamide-6 have also become widespread [18-19].

In this regard, there is a need to increase the production volume of polyamide-6 and improve its quality [20]. To solve these problems, a process for producing this polymer by low-temperature hydrolytic polymerization of caprolactam is being developed. The technological features of this process make it possible to increase productivity and reduce production costs of the final product – polyamide-6 granulate.

EXPERIMENTAL METHODS

To obtain various composite materials based on polyamide-6, described above, low-viscosity and high-viscosity polymer granules are used. To obtain a low-viscosity granulate, two-stage hydrolytic polymerization of caprolactam was carried out sequentially in the presence of an initiator – water, followed by the production of polyamide-6 granulate from a prepolymer melt and continuous combined drying-demonomerization in the solid phase of the resulting equilibrium polyamide-6 granulate in a flow of inert gas – nitrogen. To obtain a high-viscosity granulate, the processes of two-stage hydrolytic polymerization of caprolactam in the presence of an initiator – water were carried out, followed by the production of polyamide-6 granulate from a prepolymer melt, solid-phase polyamidation of polyamide-6 granulate in a flow of inert gas – nitrogen and continuous combined drying-demonomerization in the solid phase of the resulting equilibrium polyamide-6 granulate in a flow of inert gas – nitrogen.

It was previously shown that the properties of the final product - polyamide-6 granulate – are greatly influenced by the technological features of the process of obtaining a prepolymer. In the course of this work, the prepolymer was obtained according to the optimal technological parameters of this process, developed previously and described in [21].

The feasibility and necessity of carrying out the processes of solid-phase polyamidation and combined drying-demonomerization in order to obtain a high-quality product – polyamide-6 granulate – has been proven and shown in works [22-23].

To obtain the finished product, the process of two-stage hydrolytic polymerization of caprolactam was carried out sequentially under the following parameters: the first stage: temperature – 250 °C, time – 10 h, the second stage: temperature – 210 °C, time – 10 h. The solid-phase polyamidation process was carried out at a temperature of 175-180 °C, the process time was 28 h, the combined drying-demonomerization process was carried out at a temperature of 150-160 °C, the process time was 28 h.

ANALYSIS METHODS

In the process of obtaining prototypes of low-viscosity and high-viscosity polyamide-6 granulates with the above-described technological parameters of the process of low-temperature hydrolytic polymerization in the melt and solid phase, the properties of the granulate were constantly studied using standard methods:

- determination of the content of low molecular weight compounds ([LMC], %) was carried out in accordance with GOST 17824-2005 (gravimetric);

- determination of caprolactam content ([CL], %) was carried out in accordance with GOST 30351-2001 (gas-liquid chromatography method);

- relative viscosity (η_{rel}) of polyamide solutions was measured in accordance with GOST 11034-2018.

RESULTS AND DISCUSSION

The low-viscosity polyamide-6 granulate obtained during experimental work has the following properties: η_{rel} = 2.37 ± 0.03, [CL] = 0.46 ± 0.01%, [LMC] = 1.48 ± 0,02%, molecular weight – 17000-20000.

The high-viscosity polyamide-6 granulate obtained during experimental work has the following properties: η_{rel} = 3.50 ± 0.03, [CL] = 0.42 ± 0.01%, [LMS] = 1.45 ± 0,02%, molecular weight – 29000-32000.

Thus, it has been experimentally proven that lowering the temperature of the polyamide-6 synthesis process at the stage of solid-phase polyamidation promotes the further conversion of caprolactam into polyamide macromolecule chains, which leads to an increase in the molecular weight and viscosity of the finished product. And in the process of combined drying-demonomerization the polyamidation process of caprolactam oligomers occur, leading to an increase in the yield of the product and an increase in the molecular weight of the polymer.

The technological features of the developed technology make it possible to obtain a finished product - polyamide-6 granulate with a given set of physical and chemical parameters, which fully meets modern requirements for granulate processed into composite polymer materials.

The author declares the absence a conflict of interest warranting disclosure in this article.

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