PREPARAÇÃO DE COMPOSIÇÕES DE MISTURAS BASEADAS EM POLIPROPILENO SECUNDÁRIO COM PROPRIEDADES FÍSICO-MECÂNICAS CONTROLADAS

PREPARATION OF BLENDING COMPOSITIONS BASED ON SECONDARY POLYPROPYLENE WITH CONTROLLED PHYSICO-MECHANICAL PROPERTIES

ПОЛУЧЕНИЕ СМЕСЕВЫХ КОМПОЗИЦИЙ НА ОСНОВЕ ВТОРИЧНОГО ПОЛИПРОПИЛЕНА С РЕГУЛИРУЕМЫМИ ФИЗИКО-МЕХАНИЧЕСКИМИ СВОЙСТВАМИ

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RESUMO

Foi investigado o efeito do método de obtenção de compósitos poliméricos com base na mistura de polímeros sobre uma ampla gama de suas proporções nas propriedades reológicas e físico-mecânicas. Os compósitos foram preparados (utilizando prensagem ou fundição sob pressão) com base em polipropileno secundário (PP) e os seguintes polímeros: 1) polietileno de ultra alto peso molecular (UHMPE); 2) monômero de etileno-propileno-dieno (EPDM); 3) polietileno secundário de baixa pressão (LPPE). A prensagem foi realizada em uma prensa hidráulica automática "AutoMH-NE" (Carver, EUA) a 210 °C e resistência sob pressão de 7000 kgfs em 3 min. A moldagem por injeção foi realizada utilizando uma máquina de moldagem automática Babyplast do tipo horizontal com um volume de injeção de até 15 cm³. Em ambos os casos, as composições também passaram por um estágio de mistura preliminar na estação de laboratório (plastograf) de "PlastographEC" (Brabender, Alemanha) em 15 min a uma carga de 200 N. A estimativa das propriedades reológicas das fusões da composição do polímero foi realizada usando um reômetro Haake Mars III. As propriedades de resistência à deformação foram estudadas de acordo com a norma estadual GOST 11262-80 com uma máquina de ensaio de tração "Shimadzu AGS-X". Utilizando os dados de reometria relativa, foi determinado para todos os sistemas estudados (misturas PP com UHMPE, EPDM e LPPE) que a variação do torque máximo com a composição composta é não-aditiva. Isto parece ser devido à reversão de fase ocorrente. O presente fato encontra seu suporte ao realizar investigações reológicas utilizando a reometria absoluta. Foi demonstrado que variações na estrutura de fase dos compósitos ocorrendo na área de reversão de fase levam às mudanças correspondentes nas propriedades de resistência à deformação dos compósitos.

Palavras-chave: polietileno secundário de baixa pressão, polietileno de peso molecular ultra alto, composições poliméricas, mistura de polímeros, investigações reológicas

ABSTRACT

It was investigated the effect of the method of obtaining polymer composites based on the blend of polymers over a wide range of their ratios on the rheological and physical-mechanical properties. The composites were prepared (using pressing or pressure die casting) on the basis of secondary polypropylene (PP) and the following polymers: 1) ultra high molecular polyethylene (UHMPE); 2) ethylene propylene diene monomer (EPDM); 3) secondary low pressure polyethylene (LPPE). Pressing was carried out on an automatic hydraulic press "AutoMH-NE" (Carver, the USA) at 210 °C and endurance under pressure of 7000 kgfs within 3 min. Injection molding was performed using a Babyplast automatic molding machine of the horizontal type with an injection volume of up to 15 cm³. In both cases, the compositions also went through a stage of the preliminary mixture at the laboratory station (plastograf) of "PlastographEC" (Brabender, Germany) within 15 min at a load of 200 N. Estimation of rheological properties of the polymer composition melts was performed using a Haake Mars III rheometer. The deformation-strength properties were studied according to the State

Standard GOST 11262-80 with a tensile testing machine "Shimadzu AGS-X". Using the data of relative rheometry, it is determined for all the systems studied (blends PP with UHMPE, EPDM, and LPPE) that variation of the maximum torque with composite composition is non-additive. This seems to be due to the occurring phase reversal. The present fact finds its support when performing rheological investigations using absolute rheometry. It is shown that variations in the phase structure of composites occurring in the phase reversal area lead to the corresponding changes in the deformation-strength properties of composites.

Keywords: *secondary low pressure polyethylene, ultra high molecular polyethylene, polymer compositions, polymer blend, rheological investigations.*

АННОТАЦИЯ

В работе исследовано влияние метода получения полимерных композиций на основе смеси полимеров в широком диапазоне их соотношений на реологические и физико-механические свойства. Композиции были изготовлены на основе вторичного полипропилена (ПП) и следующих полимеров: 1) сверх высокомолекулярного полиэтилена (СВМПЭ), 2) синтетического каучука этилен-пропиленового (СКЭПТ), 3) вторичного полиэтилена низкого давления ПНД методами прессования и литья под давлением. Прессование осуществляли на автоматическом гидравлическом прессе «AutoMH-NE» (Carver, США) при 210 °С и выдержке под давлением 7000 кгс в течение 3 мин. Литье под давлением осуществлялось на термопластавтомате Babyplast горизонтального типа с объемом впрыска до 15 см³. В обоих случаях композиции также прошли стадию предварительного смешения на лабораторной станции (пластограф) «Пластограф ЭК» (Брабендер, Германия) в течение 15 мин при нагрузке 200 Н. Оценка реологических свойств расплавов полимерных композиций была произведена с помощью реометра Haake Mars III. Деформационно-прочностные свойства изучали согласно ГОСТ 11262-80 на разрывной машине "Shimadzu AGS-X". Установлено, что для всех изученных систем (смесей ПП с СВМПЭ, СКЭПТ и ПНД) изменение максимального крутящего момента по данным относительной реометрии с изменением состава композиции происходит не аддитивно, что, очевидно, обусловлено имеющим место обращением фаз. Данный факт находит свое подтверждение и при проведении реологических исследований методом абсолютной реометрии. Показано, что изменения в фазовой структуре композиций, имеющие место в области обращения фаз, приводят к соответствующим изменениям в деформационно-прочностных свойствах композитов.

Ключевые слова: *вторичный полиэтилен низкого давления, сверх высокомолекулярный полиэтилен, полимерные композиции, смесь полимеров, реологические исследования.*

1. INTRODUCTION

The polyolefines – polypropylene (PP) and polyethylene (PE) – occupy the leading place among the industrially produced large tonnage polymers (Bazunova *et al.*, 2018; Belokurova and Ageeva, 2011; Cobkallo, 2006; Guseva, 2009; Sadritdinov *et al.*, 2018; Salikhov *et al.*, 2018). This is caused by the complex of their useful properties and, of course, low cost (Makio and Fujita, 2012). The modification of polyolefines by physical blending with other polymers seems to be the simplest and low cost way to make new materials (Blom *et al.*, 1998; Doroudaini *et al.*, 1996; Jose *et al.*, 2004; Karian, 2003). For example, on the one hand, the homopolymers (HP) are characterized by sufficiently high rigidity, but also have low impact strength. On the other hand, the block copolymers have better impact resistance than HP, but demonstrate a low modulus of elasticity, which considerably limits their applications. An addition of small quantities

of PE or EPDM to PP is capable of increasing impact strength and cold resistance of PP, as well as its oxidation resistance (Shibryaeva *et al.*, 2006; Tai *et al.*, 2000; Utracki, 1998). In its turn, the addition of PP to PE makes it possible to increase mechanical strength and composite rigidity as well as high temperature strength. An important practical aspect of studying the composition and structure of PE/PP blends is that they represent one of the raw materials for recycling (Radusch and Ding, 1998; Hechavarria *et al.*, 2018). As is known, at present separation of PP and PE in hard domestic wastes is an enormous difficulty because their densities are similar (Utracki, 2002; Savinykh and Lang, 2018). So recycling of polyolefines wastes by their conversion into blends known as "polymer mix" or "light fraction" is actively developing now. The laboratory research of PP/PE blending compositions will expand the utilization of the products of their recycling which also determines the significance of such research from the

viewpoint of ecology.

The properties of polymer composites based on polymer blends primarily depend on the compatibility of polymers and phase structure of the composite material. Single-phase blends are solid solutions of mutually soluble polymers having a good thermodynamic affinity to each other (Tugov and Kostyrykina, 1989). However, most polymers are soluble in one another at the rate of less than 1%, and their critical mixing temperature is very high. Nevertheless, in certain conditions (say, when blending polymers are in melt in an extruder or in roll mills), one can obtain formally homogeneous systems of two polymers. Despite the fact that such a system is nonequilibrium and should divide into two macroscopic phases, this does not occur owing to the ability of polymers to mutual segmental solubility and enormous relaxation time. Thereby, there is a possibility to purposefully regulate the structure of polymer blend (by varying the composition content or the method of its obtaining), i.e., the complex of its properties.

The objective of this work is obtaining of blending compositions based on the secondary PP over a wide range of polymer ratios and analysis of their rheological and physical-mechanical properties.

2. MATERIALS AND METHODS

As a polymer base to prepare polymer compositions, we used blends based on the most common large tonnage polyolefine – the secondary PP, corresponding to the primary PP brand FF/3350, and the following polymers: 1) UHMPE; 2) EPDM, 3) a test sample of secondary LPPE corresponding to the primary PE brand LPPE 273-83.

The composites were obtained in two ways:

1) pressing at an automatic hydraulic press "AutoMH-NE" (Carver, USA) at 210 °C and keeping under pressure of 7000 kgs for 3 min (is denoted in the text of the article as pressing). The composition was previously blended at the laboratory station (plastograph) "PlastographEC" (Brabender, Germany) for 15 min at a load of 200 N;

2) pressure die casting using of a thermoplast automat Babyplast of horizontal type with an injection volume of up to 15 cm³ (is denoted in the text of the article as pressure die casting). Similarly to the pressing method, the compositions were previously blended at the laboratory station (plastograph) "PlastographEC"

(Brabender, Germany) for 15 min at a load of 200 N.

The rheological measurements of melt composition based on a blend of polymers were performed at a modular dynamic HaakeMars III rheometer at 220 °C; the oscillation frequencies varied from 0.01 to 100 Hz. The physical-mechanical properties of polymer composites were determined according to the State Standard GOST 11262-80 at a tensile-testing machine "ShimadzuAGS-X" (Shimadzu, Japan).

3. RESULTS AND DISCUSSION:

A blend of two polymers is a colloidal system in which (at specified ratios between components) one polymer is a dispersed phase while another is a dispersive medium. As the component ratios change, a phase reversal occurs, i.e., a polymer may transform from a dispersed phase into a dispersive medium, and vice versa. A phase reversal in polymer blends may occur at changing not only the components ratio but also the blending conditions. This may result in variation of a complex of the physical-mechanical (deformation strengthening) properties of the composite, since the properties of any heterogeneous system are determined to the greatest extent by the properties of the dispersion medium.

Recycling of secondary polymer material or composites based on it begins practically from the estimation of processability whose criterion is manufacturability. The term "manufacturability" means a complex of rheological characteristics, because there is no single universal indicator whose value could enable one to judge of the technological properties of a polymer material (Ivanovskii *et al.*, 2014; Mantia, 2002). In this case, the primary estimation of the recycled secondary polymer has to begin from determining the limits of the fluid zone with subsequent determination of the rheological characteristics within that state (Eliasov *et al.*, 2001). When preparing polymer compositions, simulation of real process conditions (that take place during polymer recycling and formation of compositions on their basis) can be achieved using relative rheometry (torque rheometers or Brabender plastographs) (Schram, 2000; Baek *et al.*, 2001). They are designed so as to produce the maximum possible turbulent flow, high level of shear stress and optimal blending of all the heterogeneous components under the conditions when nonlinear viscoelasticity of materials appears. Thereby, the Brabender plastograph makes it possible to estimate the polymer

systems under the conditions coincident with the practical conditions of rolling and calendaring, as well as partially extrusion. In this connection, the relative rheometry (along with the absolute one) can contain important information about materials capacity for processing. In other words, if the absolute rheometry can deal with objects in the area of laminar flow and linear viscoelasticity, then in the torque rheometers the samples can be considered at processing in the nonviscous flow mode.

The performed investigations showed that, when preparing a composition with pressing at the preliminary blending of components in the chamber of Brabender plastograph, the torque varies regularly when the components are blended (Figure 1). In this case, as the chamber is being filled with material, the torque is increasing and peaks at the end of loading. In what follows, the torque decreases and in 3-5 min achieves its minimum value. The maximum torque value is a function of composition content. The obtained data are presented as a diagram in Figure 2. One can state that the maximum torque variation with composition content is not additive for all the examined systems (PP and UHMPE blends, EPDM and LPPE blends). One can see that with UHMPE content in the blend of about 40-50 mass%, EPDM content of 80 mass% or LPPE of about 60-70 mass%, the character of the maximum torque variation changes. This seems to be because of the phase reversal.

The data of absolute rheometry also indicate the phase reversal occurring at the variation of the composition content. It is clear that some composition contents have viscosity above the additive values, while others have it below the additive values; this is definitely related to the phase reversal. In this case, the dependence of the phase reversal area on the composition preparation method is clearly observed for the PP-UHMPE composition. For example, in the case of composition obtained by pressing, the phase reversal area corresponds to 40 mass% UHMPE in the blend, while for compositions prepared by pressure die casting, the phase reversal area is strongly shifted towards higher UHMPE content in composition and corresponds to ≈ 80 mass% UHMPE (Figure 3).

For the PP-EPDM composition, the phase reversal area corresponds to the EPDM content of about 80 mass% in the compositions obtained by pressing and 60 mass% to those prepared by pressure die casting (Figure 4). In the case of the PP-LPPE composition, the phase reversal area

occurs at about 60-70 mass% content of the second polymer in the compositions prepared by both methods.

It is important that the variations in the phase structure of compositions occurring in the phase reversal area lead to the corresponding changes in the deformation-strength properties of composites. Shown in Figure 3 and Figure 4 are presented variations occurring at a break in the values of the modulus of elasticity and strength for the compositions based on the secondary PP and UHMPE obtained by pressing and pressure die casting.

An analysis of the dependences presented in Figure 5 and Figure 6 makes it possible to state that the regularities in a variation of the deformation-strength properties correlate with the changes in viscosity (and the maximum torque) occurring at the phase reversal. One can see from the presented data that variations of the modulus of elasticity with changing the composition content become much as variations of viscosity. Until the PP matrix served as a continuous phase (dispersion phase), the values of the modulus of elasticity and breaking stress were over the additive values. And only after the phase reversal when the second polymer became the continuous phase, the values of the modulus of elasticity and breaking stress became below the additive values. One should stress that there is a distinction of the samples prepared using the different methods also in the case of deformation-strength characteristics of the composites.

It should be noted that for composites based on PP with EPDM and LPPE they were similar. In such cases, the variations of the modulus of elasticity and breaking stress also correlated with the phase reversal area, and their values were higher than the additive ones where the PP matrix is the continuous phase.

Thereby, a possibility appears to vary also the physical-mechanical (deformation-strength) properties of the obtained composites by varying their composition and the method of its preparation.

4. CONCLUSIONS:

In the course of the investigation, the phase reversal areas were determined for the composites based on the secondary PP with UHMPE, EPDM, and LPPE. For the composites based on PP with UHMPE and EPDM, the influence of the way for obtaining composite on

the composition was revealed at which the phase reversal occurs.

The result of changing the phase structure of the samples (as indicated by the phase reversal) is a regular variation of the deformation-strength properties of composites. In all cases studied, the variations of modulus of elasticity and breaking stress correlate with the phase reversal area and are over the additive ones in the region where the PP matrix is the continuous phase, and are below the additive ones if the second polymer is the continuous phase.

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Figure 1. Dependence of torque of composition on the basis of secondary software (90% PP) and SVMPE (10% UHMPE) from time of mixture of composition in the camera of a plastograf Brabender

Figure 2. Dependence of the maximum torque in the blending chamber of plastograph on the composition for the PP blends with UHMPE (1), EPDM (2) and LPP (3)

Figure 3. Dependence of the complex viscosity on composition of the secondary PP-UHMPE obtained using pressing (1) and pressure die casting (2) determined at 0.01 Hz from the volume fraction of the dispersed phase of the second polymer

Figure 4. Dependence of the complex viscosity on composition of the secondary PP-EPDM obtained using pressing (1) and pressure die casting (2) determined at 0.01 Hz from the volume fraction of the dispersed phase of the second polymer

Figure 5. Dependence of the modulus of elasticity on composition based on the secondary PP-UHMPE obtained using pressing (1) and pressure die casting (2)

Figure 6. Dependence of breaking stress on composition based on the secondary PP-UHMPE obtained using pressing (1) and pressure die casting (2).