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MATHEMATICAL MODELLING OF DISPERSED PHASE DROP DEFORMATION IN NANO-FILLED POLYNER MIXTURE MELTS

Purpose. *To study using mathematical modeling method of the influence of nano-additive on dispersed phase component drop deformation during polymer dispersion melt flow in the entry area of forming hole.*

Methods. *To study the process of drop deformation in a polymer dispersion the mathematical model developed on the standpoint of structural-continual approach was improved. The model takes into account the main provisions of classical fluid mechanics and changes in the structure of the dispersed phase during its flowing.*

Results. *It is shown that the modified mathematical model of deformation of the polymer dispersed phase drop adequately describes the process of structureformation during real nano-filled polymer compositions flowing. The values of polypropylene (PP) drops deformation, calculated using the model, correlate the experimental results: inter-phase tension reduce leads to drops in deformation increase and to the average diameter of PP microfibers reduction.*

Scientific novelty. *The mathematical model of deformation of dispersed phase polymer drop was improved in order to carry out for theoretical research of nano-filled polymer mixtures.*

The practical significance. *Using the developed mathematical model will accelerate researches and reduce material and energy costs of them.*

Keywords: mathematical model , nano-additives, dispersion, deformation.

Introduction. One promising way modification of polymers and their blends are creating nanocomposites, in which a set of desired properties is achieved through the optimal combination of components. The use of fillers of different sizes, shapes and chemical nature allows to improve mechanical properties of materials and provide them with new functional characteristics (incombustibility, bactericidal, conductivity, sorption capacity, etc.). Herewith essential is the ability of nanoparticles (NP) surface be getting wet by polymer and the nature and degree of interaction between the NP and macromolecules polymer on the interphase [1,2]. It is shown that the introduction of silica nanoparticles in a mixture melt of polypropylene / copoliamide (PP / SPA) allows to adjust the processes of structureformation of PP in the SPA matrix and thus improve the structure of the filter material (FM), obtained in processing of the said mixture. These filters combine high cleaning efficiency and productivity, and the presence of nanofiller in the FM structure provides them bactericidal properties[2]. To create new nanomaterials and regulation of their properties is necessary conducting basic research and the establishment of appropriate laws.

Problem. Polymers are generally thermodynamically incompatible with each other in the melt, but the section on individual phases prevents high viscosity of the components. Shear flow contributes to the formation of different types of structures by the component of dispersed phase: liquid cylinders (jets), layers, drops, etc To describe the rheological behavior of polymer

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dispersion melts are used the laws of classical mechanics, same as for modeling systems such as suspensions and emulsions [3]. At the same time a polymer mixture is a special class of colloidal dispersions of the "polymer in the polymer." An important difference is formation between the two its components interphase transition layer whose properties are very different from those of the characteristics of polymer melt in volume. In nano-filled polymer melts an interphase layer around the nanoparticles is formed as well at the interphase filler / polymer and its thickness ranges (0,0004 ÷ 0,16) mm [4]. Thus, depending on the degree of affinity between the polymer and additive nanoparticles can be localized in the bulk melt or at the interface and influence the magnitude of surface tension.

Purpose ─ studying by the mathematical modeling of the influence of nano-additives on deformation of dispersed phase component drop during polymer composition melt flow.

The main material. Study of flow patterns and structureformation in polymer dispersions subject of many articles and books. However, because of the complexity of such systems research experimental approaches outweigh theoretical. Today received a number of empirical regularities and mathematical models that describe with sufficient accuracy the behavior of such systems. In [5] from the standpoint of structural and continual approach developed a mathematical model that allows to determine the value of drop deformation depending on the volume concentration and the rheological properties of the components (viscosity of the dispersed phase and dispersion medium, their interrelation and flexibility). The advantage of this model is that it takes into account the main provisions of continuum mechanics (integrity protection, continuity of functions, describing its movement and state) and the particular structure of the dispersed phase. Form drops - is ellipsoid of revolution, which changes size during the interaction with its dispersion medium but retains volume. Deformation drops depending on the orientation in the flow accounted for using the tensor strain rate uniaxial tension. The model is a system of differential equations in dimensionless variables has the form:

$$
\begin{cases}
\dot{\varphi} = 0 \\
\dot{\theta} = -\dfrac{3}{4} u \lambda_3 \sin(2\theta) \\
\dfrac{\dot{q}}{q} = \dfrac{3}{2}\left(\lambda_1 + \dfrac{u}{2}(\lambda_2 r_0^2 q^{4/3} + \lambda_3)(2 - 3\sin^2\theta)\right)
\end{cases}
\tag{1}
$$

where: φ, θ - angles that define the orientation of the drop in the stream;

   u - the intensity of the current uniaxial stretching;

   q - the value of deformation (stretching dimensionless);

   $\lambda 1$, $\lambda 2$, $\lambda 3$ - values that take into account the rheological characteristics of the components.

In the above equation point means complete original in time.

It is known that solid fillers cause thickening thixotropic effect, which leads to an increase of viscosity of the polymer melt. In carrying out modifications of polymer mixture melts an additive is usually pre-injected into one component. In determining the value of drop deformation using model (1) the influence of nano-additive can be taken into account due to

changes in melt viscosity of the dispersed phase and dispersion medium, using Einstein's formula for dilute suspensions:

$$\eta_E = \eta_0 (1+2,5V) \qquad (2)$$

where: η0 - viscosity of the medium; V - volume concentration of suspended particles.

Experimental studies show that for compositions with a low content of nano-additive (0,05 ÷ 3,0) masses. %, the viscosity increases slightly within the error and it coincides with the effective viscosity (ηE) defined by the formula (2). Calculations made using the model showed that the concentration of nano-additive (0,05 ÷ 3,0) masses. % virtually no effect on the amount of strain drops of the dispersed phase. However, this is inconsistent with research on the impact of nanofillers on micro and macro-rheological processes in polymer mixture melt flowing. Thus, in [2] is shown that the introduction of (0,1 ÷ 3,0) masses. % silica in a mixture melt of polypropylene / co-poliamide improves fiberization PP in SPA matrix: an average microfibers diameter reduced and their uniformity of distribution by diameters increasing. The authors attribute this to the influence of nanoparticles on the interphase phenomena, namely with decreasing values of surface tension at the interphase.

From classic fundamental ratios that describe thermodynamic equilibrium in Low-molecular dispersion system it follows that the dispersion medium in a flow is acting on a drop dispersed phase therein with a force proportional to the gradient of shear velocity and medium viscosity and besides this is a function of the ratio of viscosities components. A drop of polymer dispersed phase reacts on deformation with force [6]:

$$T_\gamma = 2\gamma_{\alpha\beta} / r$$

where: γαβ - interphase tension; r - the radius of the drop.

At the same time, the ability to drop deformation is largely determined by its elasticity. In mathematical model (1) resistance of drop on its deformation is taken into account due to the value of the elastic modulus G, which is included into the relation to determine the rheological function λ1:

$$\lambda_1 = \frac{-2ab^2\beta_0'' G \dfrac{a}{a_0}(1-\dfrac{q}{q_0})}{\mu(2+3ab^2\beta_0''\dfrac{\eta}{\mu})}(1-M\Phi) \qquad (3)$$

where: a, b, a0, b0 - ellipsoid axis in deformed and undeformed state;

G, F - modulus of elasticity and volume concentration of the dispersed phase;

μ, η - viscosity of the dispersion medium and dispersed phase;

$$M = \frac{4}{ab^2(2+3ab^2\dfrac{\eta}{\mu}\beta_0'')} * \{ \frac{5}{6(\alpha_0+2\beta_0-2\beta_0'(a^2+b^2))} -$$

$$- \frac{100\beta_0' a^2(2\beta_0' a^2-\alpha_0-2\beta_0)}{(\alpha_0+2\beta_0)(\alpha_0+2\beta_0-2\beta_0'(a^2+b^2))} * [\frac{1}{24a\beta_0} - \frac{1}{2\beta_0'^2 a^2-(\alpha_0+2\beta_0)}] \}$$

The values of $\alpha_0, \beta_0, a_0', \beta_0', \alpha_o'', \beta_o''$ are obtained in [3].

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To assess the effect of the interfacial tension on the ability to deformation of the dispersed phase drops in the expression for the determination of rheological function λ1 were made changes based on the fact that G = Tγ. With the balance of the elastic power inside (G) and resistance (Tγ) equation to determine λ1 will look like:

$$\lambda_1 = \frac{-2ab^2\beta_0^{"} \dfrac{\gamma_{\alpha\beta}}{R_0} \dfrac{a}{a_0} q^{2/3}}{\mu(2 + 3ab^2\beta_0^{"} \dfrac{\eta}{\mu})}(1 - M\Phi) \qquad (4)$$

where: a_0 - ellipsoid axis, which volume is equivalent to the volume of sphere drop with radius r.

The system of differential equations (1) was solved numerically by the Runge-Kutta method using specially written program in Delphi environment with Object Pascal language. Modified model tested for adequacy, ie the ability to predict the results of research in some area with the required accuracy by comparing the amount of strain drops obtained when using it with experimental data. This was used in the investigation results of about 1.0. methyl silica % additive (MC) on the value of interfacial tension ($\gamma_{\alpha\beta}$) and average diameter jets (micro) mixtures PE / spa and polypropylene / polyvinyl alcohol (PE / PVA) of the 30.6 / 68.4 vol. % (Table).

Table

The dependence of the deformation of the dispersed phase drops on the value of interphase tension

Mixture	$\gamma_{\alpha\beta,}$ мН/м$^{-1}$	$\overline{d}$ мкм	q
PP / SPA	2,60	4,0	125
PP / SPA / MS	0,75	2,6	620
PP / PVA	0,73	3,5	273
PP / PVA / MS	0,47	1,7	531

The table shows that the values of interfacial tension obtained by using the theory of fracture liquid cylinder for nano-filled compositions are much lower compared to the initial mixture. This results in reduction of energy consumption in the formation of new surfaces dispersed phase, that promotes the dispersion and deformation of the droplets in the matrix polymer PP, PP microfiber average diameter lower than in the initial mixture of (1,5 ÷ 2,1) times. Improved model actually describes the process of deformation of a PP drop in matrix: γαβ reduction in nano-filled mixtures is accompanied by increasing values of deformation. The results produced by the model are in good agreement with the experimental data on the influence of nano-filler on processes of structure -formation. Introduction filler reduces the average diameter polypropylene microfibers by reducing the surface tension at the interface.

Conclusion. It is shown that the improvement of previously established mathematical model of deformation of drop dispersed phase polymer in a of polymer mixture melt flow in the entry area forming hole can expand its capabilities and to use it to predict droplets deformation of component dispersed phase in nano-filled mixtures. Found that the modified model includes the effect of Nano-additive on droplet deformation in the terms of interphase tension at the interphase of the components.

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МАТЕМАТИЧНЕ МОДЕЛЮВАННЯ ДЕФОРМУВАННЯ КРАПЛІ ДИСПЕРСНОЇ ФАЗИ В РОЗПЛАВАХ НАНОНАПОВНЕНИХ СУМІШЕЙ ПОЛІМЕРІВ

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Мета – дослідження методом математичного моделювання впливу нанодобавки на деформацію крапель компоненту дисперсної фази при течії розплаву полімерної дисперсії у вхідній зоні формуючого отвору.

Методика. Для вивчення процесу деформації краплі в полімерній дисперсії вдосконалено математичну модель, розроблену з позицій структурно-континуального підходу, яка враховує основні положення класичної механіки рідини та зміни структури дисперсної фази при течії.

Результати. Показано, що модифікована математична модель деформації краплі полімеру дисперсної фази адекватно описує процеси структуроутворення при течії реальних нанонаповнених полімерних композицій. Величини деформації краплі поліпропілену (ПП), розраховані за допомогою моделі, корелюють з експериментальними даними: зниження міжфазного натягу приводить до збільшення показників деформації краплі та до зменшення середнього діаметра ПП мікроволокон.

Наукова новизна. Вдосконалено математичну модель деформації краплі полімеру дисперсної фази для проведення теоретичних досліджень нанонаповнених сумішей полімерів.

Практична значимість. Використання розробленої математичної моделі дозволить прискорити дослідження та зменшити матеріальні і енергетичні затрати на їх проведення.

Ключові слова: *математична модель, нанодобавка, дисперсія, деформація*

МАТЕМАТИЧЕСКОЕ МОДЕЛИРОВАНИЕ ДЕФОРМАЦИИ КАПЛИ ДИСПЕРСНОЙ ФАЗЫ В РАСПЛАВАХ НАНОНАПОЛНЕННЫХ СМЕСЕЙ ПОЛИМЕРОВ

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Цель – исследование методом математического моделирования влияния нанодобавки на деформацию капель компонента дисперсной фазы при течении расплава полимерной дисперсии во входовой зоне формующего отверстия.

Методика. Для изучения процесса деформации капли в полимерной дисперсии усовершенствована математическая модель, разработанная с позиций структурно-континуального подхода, которая учитывает основные положения классической механики жидкости и изменение структуры дисперсной фазы при течении.

Результаты. Показано, что модифицированная математическая модель деформации каплі полимера дисперсной фазы адекватно описывает процессы структурообразования при течении реальных нанонаполненных полимерных композиций. Величины деформации каплі полипропилена (ПП), рассчитанные с помощью модели, кореллируют с экспериментальными данными: снижение межфазного натяжения приводит к увеличению величин деформации капли и к уменьшению среднего диаметра ПП микроволокон.

Научная новизна. Усовершенствована математическая модель деформации капли полимера дисперсной фазы для проведения теоретических исследований нанонаполненных смесей полимеров.

Практическая значимость. Использование разработанной математической модели позволит ускорить исследования и уменьшить материальные и энергетические затраты на их проведение.

Ключевые слова: *математическая модель, нанодобавка, дисперсия, деформація.*