Modeling of the process of mechano activation of filler particles in polymer composites

Umida Ziyamukhamedova[1,2*], *Hatice* Evlen[1,2], *Jasurbek* Nafasov[1], *Zilola* Jalolova[3], and *Elbek* Turgunaliyev[1,3], and *Erkin* Rakhmatov[4]

[1]Tashkent State Transport University, Tashkent, Uzbekistan
[2]Karabuk University, Turkey
[3]Andijan machine building institute, Andijan, Uzbekistan
[4]University of Economics and Education, Uzbekistan

Abstract. The article presents the results of the study of the filler particles activation mechanism in the production of composite polymeric materials modified by mechanical activation. The studies were conducted in simulated conditions of motion of filler particles taking into account the trajectory of motion during milling in progressive-rotational activation units using analytical expression of velocity distribution of each filler particle in the composite material.

1 Introduction

Materials with improved mechanical and technological properties, both solid metal materials [1-3] and plastic ones based on various polymers [4-6] and elastomers [7-9], used in mechanical engineering cover more and more applications in practice in production conditions. The development of materials science, especially related to composite materials in many cases is based on the methods and conditions of their production, where one of the most common and effective is mechanical and mechanochemical activation of the components [10, 11]. Mechanochemistry is a science that develops on the edge of chemistry and mechanics: it is also closely related to other fields of science and technology, physics, especially solid-state physics, biophysics, physical chemistry, polymer technology, chemistry and technology of inorganic substances, biochemistry, molecular biology, and bionics [10]. Mechanochemistry, by selecting and processing certain facts and regularities taken from all these fields of science, in turn puts forward its own regularities and conclusions that contribute to the development and enrichment of the originating sciences. In the most general definition, mechanochemistry can be called a science that studies the mutual transformations of mechanical and chemical energy occurring in bodies. But the creation of a single, comprehensive representation that comprehensively reflects all aspects of the mechanochemical process must be based on knowledge of the complex structure of the object under study, which is determined by the number of levels of supramolecular organization. The mechanochemical phenomenon includes two main components: mechanochemical, which determines the transformation of mechanical energy into

*Corresponding author: z.umida1973@yandex.ru

chemical energy, and chemo mechanical, which represents the release of mechanical energy, due to the course of chemical reactions [10]. From the above review, it follows that mechanical activation is one of the main indicators of the effectiveness of the activation process itself, so it is important to study the mechanism of the processes, depending on the activity of the particles of the components involved in this process.

In practice, various varieties of installations providing fast and fine grinding of the processed materials are widely used in production conditions [10]. Most often vibromills of different types and designs are used, which differ mainly by technological and design features. In accordance with technological features, they are subdivided according to the type of grinding (dry grinding or wet) and the nature of work (batch or continuous). Structural features include the type of exciter (eccentric or unbalanced), the shape of the mill body (cylindrical, rectangular), the type of its support, etc.

A wide choice of mechanical activation units gives an opportunity to choose equipment for modification of composite materials of various purposes, but in our opinion more profound theoretical research of the process is required in order to increase the capabilities of this modification method. In this connection an interest arose to study the mechanism of particle motion during mechanical activation and its influence on the process itself.

2 Objects and methods of research

At reception of a composite material, structural appointment the basic purpose of filling is reception of the strengthened polymeric composite material, i.e. a material with the improved complex of physical and mechanical properties. It is achieved both by introduction of fibrous reinforcing fillers and fine-dispersed fillers.

Dispersed fillers used to impart special wear properties to the material include minerals, carbon black, graphite, metal powders, etc. Another group of disperse fillers, which are increasingly being used nowadays, are modified materials in the form of disperse particles. Their chemical composition, which can be both simple elementary (AB) and multicomponent ($A_nB_mX_p$, $A_m(B_nX_c)_{m-x}(D_iG_f)_{m-y}$) of complex structure with many strong primary and weak secondary, such as hydrogen and Van Derwalas, plays important role in choosing fillers. It should be noted that the above-mentioned set of compositions can mainly fit minerals, which contain metal oxides and their complex structure associated multicomponent. One of the representatives of minerals of complex structure with a multi-component composition is kaolin, in addition, its production marks produced by enrichment (AKF-78, 80, AKS-30, AKT-10), which was used in our studies in obtaining composite polymeric materials.

Both thermoplastics and reactoplastic polymers can be used as binders. But in the process of reinforcement of any composite polymers with filling there is a change of physical and mechanical properties mechat their limits in relation to amount and correlation of heterogeneous components, which is the reason of considering the necessity of their plasticization with organic and inorganic components in particular ecological and accessible ones.

The world petrochemical industry is one of the largest industries [12-15], which produces olefin products, where as in any production enterprise annually generates more than 109 thousand tons of waste products - pyrolysis condensate, which we used as a carbon-containing plasticizer.

To study the process of mechanical activation under laboratory conditions, the installation “Rocker mill” was developed (Figure 1).

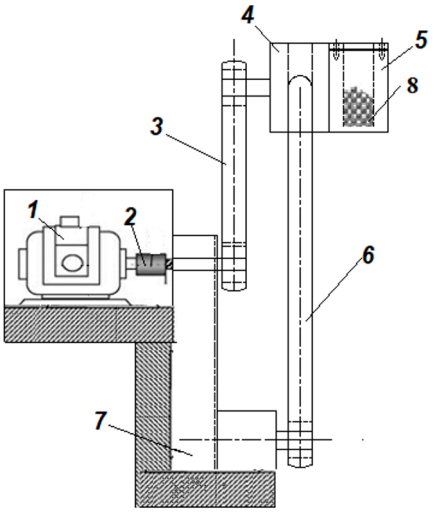

Fig. 1. Schematic of a rocker mill: 1 - electric motor; 2 - connection sleeve; 3 - crank; 4 - stone; 5 - beaker; 6 - rocker; 7 - mill body; 8 - grinding bodies.

The principle of operation of the unit is as follows: the rotation of the crank causes the vibrations of the beater, and the beater in turn provides torsional and onset motion of the stone, where the mill body, loaded with grinding bodies and grinded material, is attached. The frequency of rotation of the shaft is from 1000 to 3000 rpm, the amplitude of vibration of the mill body is 600 mm.

The grinding bodies, receiving frequent impulses from the walls of the mill shell, make complex movements. They bounce, collide and slide on the walls of the mill shell. As a result of friction against the walls of the mill, they begin to rotate. The particles of the ground material are subject to impact, compression and shearing forces of variable magnitude. The impact impulse of a single grinding body in a rocker-type mill is relatively large compared with the impact impulse in a rotating ball mill.

3 Results and their discussion

To study the motion of composite polymeric materials, particles of kaolin filler with pyrolysis containing carbon and residual paraffins in an oscillatory-rotational unit occurs along a truncated cone trajectory. Each filler particle participates in structural changes between solid dispersed and liquid polymer components. The filler particles in the process of mechanocativation are activated by the volume of the particles depending on the abrasion trajectory depending on the direction of movement depending on the trajectory of the equipment container where the activation process takes place.

In this regard, we set the task of modeling the dynamics of particle motion in the process of mechanoactivation of heterocomposite materials. In the section of truncated cone type, taking into account that the approximation of an arbitrary point of the truncated cone is equal (Figure 2):

$$z = (r - r_0)tg\theta \qquad (1)$$

But as we know from figure 1, the height of the truncated cone also has an expression of the following form:

$$H = (r_1 - r_0)tg\theta \qquad (2)$$

where, $r_0 \le r \le 1$. From where we obtain the coordinate for the driving filler particles in hetero-composites:

$$z = \frac{r - r_0}{r_1 - r_0} H \qquad (3)$$

As is known from analytical geometry, the cross-sectional area of a truncated cone S, S_0, S^* is defined by the equations:

$$S_0 = \pi r_0^2 ; S_1 = \pi r_1^2 \text{ and } S^* = \pi r^{*2} \qquad (4)$$

Then the second flow rate of milling particles of heterocomposites in the beaker is determined by the equations:

$$Q_1 = S_1 V_1 = \pi r_1^2 H \qquad (5)$$

$$Q_0 = S_0 V_0 \qquad (6)$$

and

$$Q^* = S^* V^* \qquad (7)$$

If there is no inflow of particle mass of components from outside, the second flow rate through the cross section will be constant [16] i.e. (1):

$$Q = SV = const \qquad (8)$$

In the rotational motion of the center of the section, there is a compression of the flow, there is a change in density - the particles of the components of mechanoactivation.

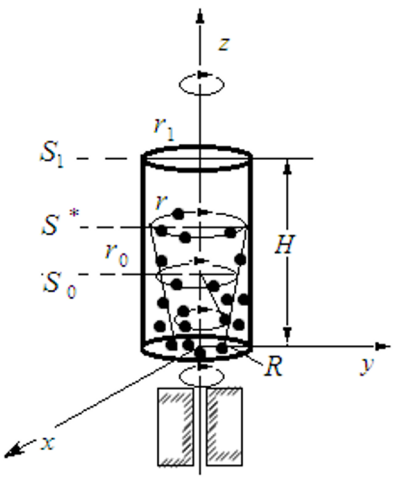

Fig. 2. Scheme of motion of filler particles of composite materials in the oscillatory-rotational machine of mechanical activation

But from the mass conservation condition of the particle flux [17] we have:

$$\rho Q = \rho VS = const \tag{9}$$

where ρ -is the density of the particle at each arbitrary point of the inner part of the beaker area of the mechanically activated unit.

From the condition of non-breakable flow of filler particles of the components in obtaining wear-resistant hetero-composites of the assumed continuous area we get the equality:

$$d(\rho VS) = 0 \tag{10}$$

or in differential form:

$$\frac{dp}{\rho} + \frac{dS}{S} + \frac{dV}{V} = 0 \tag{11}$$

where p - is the pressure on the particles during the rotational motion of the beaker, and is defined by the following formula:

$$p = p_0 \left(\frac{\rho}{\rho_0} \right)^n \tag{12}$$

p_0 and ρ_0 — pressure and density of the particle of wear-resistant hetero-composites , in the position of equilibrium; n - polytropy index;

In a polytropic process, the flow of a filler particle of composite materials is modeled as an ideal medium. Then, in the absence of vortexing, we obtain expressions for pressure, density and temperature from the Bernoulli integral as

$$p = p_0 \left(1 - \tau_0 \frac{V^2}{V_1^2} \right)^{\beta+1} \tag{13}$$

$$\rho = \rho_0 \left(1 - \tau_0 \frac{V^2}{V_1^2} \right)^{\beta} \tag{14}$$

and

$$T = T_0 \left(1 - \tau_0 \frac{V^2}{V_1^2} \right)^{\beta} \tag{15}$$

where

$$\beta = \frac{1}{n-1} \tag{16}$$

$$\tau_0 = \frac{V_1^2}{V_{\max}^2} \tag{17}$$

$$\tau_0 = \frac{V_1^2}{a^2}\frac{n-1}{n+1} \tag{18}$$

$V_{\max}$- maximum flow velocity of inseparably bonded particles of hetero-composites.

From equality (5) for the change inside the activator beaker of particle flux density of composite polymeric materials we have:

$$\rho_1 = \rho_0\left(1-\tau_0\frac{V_0^2}{V_1^2}\right)^{\beta} = \rho_0\left(1-\tau_0\right)^{\beta} \tag{19}$$

The pattern of relative changes in the density of hetero-composite materials particles in a rotating beaker follows from the following:

$$\frac{\rho}{\rho_1} = \left(\frac{1-\tau_0\frac{V_0^2}{V_1^2}}{1-\tau_0}\right). \tag{20}$$

From equality (4) we find $\frac{\rho}{\rho_1} = \frac{SV}{S_1V_1}$ and given the last equations we get:

$$\frac{SV}{S_1V_1} = \frac{\left(1-\tau_0\frac{V_0^2}{V_1^2}\right)^{\beta}}{\left(1-\tau_0\right)^{\beta}}. \tag{21}$$

Given the smallness of $\left(\tau_0\frac{V^2}{V_1^2} << 1\right)$ the friction of the particles of the components of composite materials, the last equality can be written in the form:

$$\frac{V}{V_1}\frac{S}{S_1} = \frac{1-\tau_0\beta\frac{V^2}{V_1^2}}{1-\tau\beta}. \tag{22}$$

Then we obtain a quadratic equation for the particle velocity distribution of hetero-composites. As a ratio of particle velocity:

$$\frac{V^2}{V_1^2}\tau_0\beta + \frac{r^2}{r_1^2}\frac{V}{V_1} - 1 = 0 \tag{23}$$

From there we get the expression for the flow velocity distribution of wear-resistant hetero-composites:

$$V = V_1\left(\sqrt{\left(\frac{r}{r_1}\right)^2 + 4\tau_0\beta} - \frac{r^2}{r_1^2}\right)\frac{1}{2\tau_0\beta} \qquad (25)$$

or

$$V = V_1\frac{2}{\frac{r^2}{r_1^2} + \sqrt{4\tau_0\beta + \frac{r^4}{r_1^4}}} \qquad (26)$$

Knowing the incompressibility of the particle flow of the activated filler when using the process of mechanical activation in obtaining composite materials with improved physical and mechanical properties, we can write that the tangential stress of the particle flow $\tau_0 << 1$ and the velocity distribution we get:

$$V = V_1\frac{r_1^2}{r^2} \qquad (27)$$

Thus, the distribution of the velocity of filler particles during mechanical activation to obtain composite materials in the progressively rotating motion of the installation at each point of the medium, provided that there is no gravity is obtained:

$$V = V_1\frac{\hat{r}_1^2}{r_0^2 + (\hat{r}_1 - \hat{r}_0)z}. \qquad (28)$$

As we mentioned above, one of the most common methods of modification is the mechanochemical method, which is increasingly used in studies of interstructural phenomena at the phase boundary [10, 17-20]. In order to study the effect of mechanoactivation as one of the methods of physical modification of mineral filler, we conducted structural studies of AKT-10 filler together with soot-containing waste after mechanoactivation.

When the filler is mechanochemically treated at four different values of the rotation frequency of the vibro-planetary mechanism electrode, n_1=750 rev/min, n_2=1000 rev/min, n_3=1500 rev/min, n_4=3000 rev/min, different rotation frequencies values, we can see the graph of the dependence of the tensile strength on the time of mechanoactivation from Figure 3.

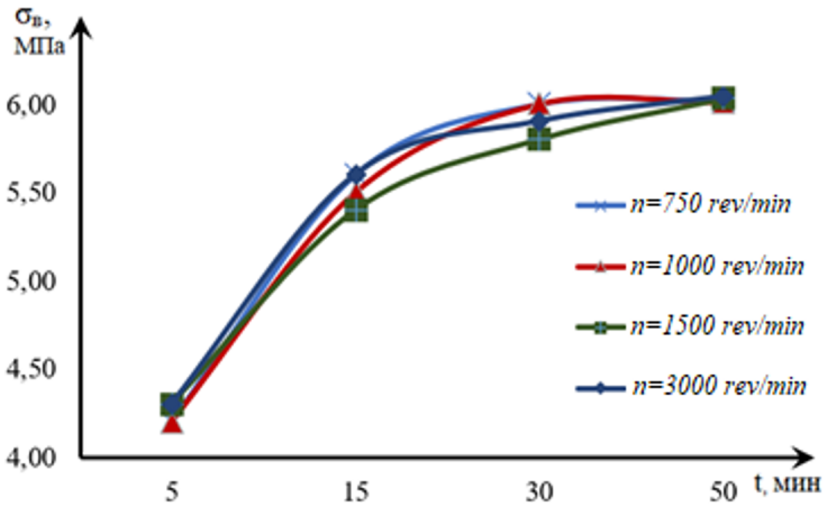

Fig. 3. Graph of dependence of extensor stiffness on mechanoactivation time at different values of rotation frequency

As can be seen from the graph, the optimum value of the mechanochemical processing time of dispersed mineral materials, which are included as fillers in polymer composite materials, is 30-35 minutes. For more than this time, the effect of mechanochemically treated materials on the mechanical properties of the obtained polymer composite material has not changed significantly. When the number of rotations of the mechanoactivator electrode reaches 1000 times per minute, the degree of dispersion of processed fillers has a certain value. We can see that the degree of dispersion of the processed material remains almost unchanged at further values of the rotation frequency (Figure 4).

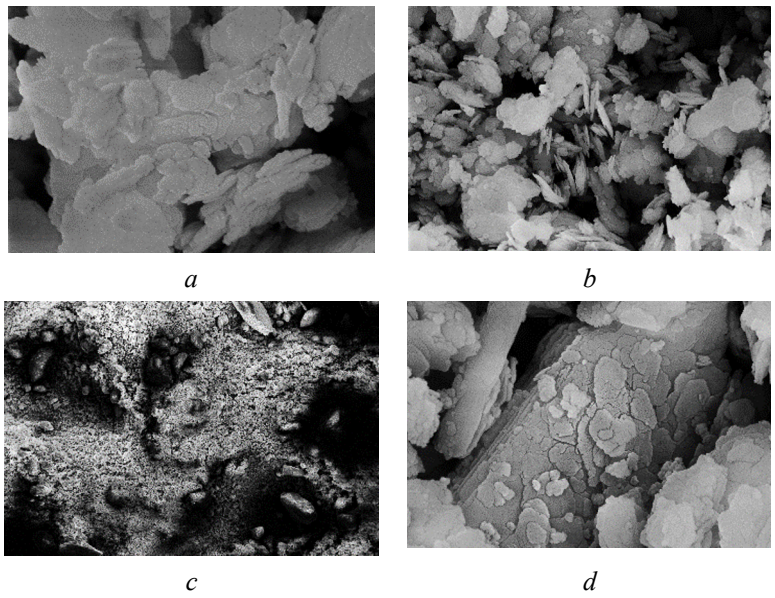

Fig. 4. Gemini 500 (FE-SEM) Scanning Electron Microscope Analysis of Mechanically Activated Fillers at Different Times, ×30.00 K
a) t_1= 5 min; b) t_2= 15 min; c) t_3= 30 min; d) t_4= 50 min

Microscopic analysis shows that the materials used as fillers form active surfaces during mechanochemical processing in grinders when certain values of time are reached. If the processing process is continued, the increase in the density of the processed filler particles due to the joining and formation of agglomerates leads to a decrease in the interstructural connection of the fillers with the polymer (Figure 4-d).

4 Conclusions

Analyses made by formula (28) show that the particle velocity distribution of hetero-composites of the inclined wall of the truncated cone inside the beaker decreases, depending on the angle of inclination.

Progressive - rotational motion of each particle of hetero-composite materials moves with a variable radius, under the action of gravity and the intensity of the flow.

The optimal duration of time for mechanochemical processing in vibro-planetary mechanisms for materials that are planned to be included as fillers in polymer composite materials is 30-35 minutes. Since during this time the dispersed fillers have enough charge to form interstructural bonds, increasing the duration of time can be considered uneconomical.

In the process of mechanical activation of fillers, increasing the frequency of rotations of the electric motor shaft from 1000 revolutions per minute does not significantly affect the tensile strength of the obtained material.

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