The study of fly ash filler behaviour in the polymer matrix of polyethyleneterephthalate

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The purpose of the investigation was to study the behavior of mechanically activated fly ash filler containing carbon in a polymer matrix of polyethylene terephthalate (PET). By means of the methods of optical and electron microscopy the change of physical and chemical properties of fly ash after intensive grinding in planetary mills of centrifugal type was considered. The research showed that mechanically activated filler, in contrast to its non-activated analog, structures the polymer matrix and provides improving the characteristics of the composite material.

Keywords: fly ash; mechanical activation; filler; a polymer composition.

Механикалық белсендірілген ұшпа күлді полиэтилентерефталат полимерлі матрицасында толтырғыш ретінде қолдануды зерттеу

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Зерттеу мақсаты – полиэтилентерефталатты полимерлі матрицасында көміртегі бар, механикалық белсендірілген ұшпа күл толтырғышының қасиетін зерттеу. Оптикалық және электронды микроскопия әдістері көмегімен центрден тепкіш күш типтес планетарлы диірмендерде қарқынды ұсақтаудан кейінгі ұшпа күлдің физика-химиялық қасиеттері зерттелінді. Сонымен қатар, ұшқыш күлдің осындай механикалық өңдеуден кейін полиэтилентерефталатты полимерлі маптериалдарға толтырғыш ретінде қолданылу мүмкіндігі қарастырылды. Механикалық өңделген және өңделмеген күлді толтырғыштары бар полимерлі материалдардың механикалық беріктігі, суды сіңіру қабілеті және қышқылға төзімділігі зерттелініп, салыстырмалы талдау жасалынды. Зерттеулер нәтижесінде механикалық белсендірілген толтырғыш белсендірілмеген аналогымен салыстырғанда полимерлі матрицаның құрылымын түзіп, композиционды материалдың сипаттамаларын жақсартқанын көрсетті.

Түйін сөздер: ұшпа күл; механикалық белсендіру; толтырғыш; полимерлі материалдар.

Исследование применения механически активированной золы уноса в качестве наполнителя в полимерной матрице полиэтилентерефталата

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Целью исследования было изучение поведения механически активированного наполнителя золы-уноса, содержащего углерод, в полимерной матрице из полиэтилентерефталата (ПЭТФ). С помощью методов оптической и электронной микроскопии рассматривалось изменение физико-химических свойств золы-уноса после интенсивного измельчения на планетарных мельницах центробежного типа, а также возможность использования летучей золы после такой механической обработки в качестве наполнителя для полимерного материала, представленного полиэтилентерефталатом. Были изучены и сопоставлены механическая прочность, водопоглощение и кислотостойкость полимерных материалов, наполненных механически обработанным и необработанным зольными наполнителями. Исследования показали, что механически активированный наполнитель, в отличие от его неактивированного аналога, структурирует полимерную матрицу и обеспечивает улучшение характеристик композиционного материала.

Ключевые слова: зола уноса; механическая активация; наполнитель; полимерные материалы.

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1. Introduction

In recent years, polymer-based compositions have found wide application in various branches of industrial and civil construction; it makes high demands on both the performance characteristics and the decorative properties of the polymer material. Generally, the properties of polymers depend not only on the properties of the polymer matrix but also on the properties of the filler. Nowadays, there are lots of fillers that provide the required properties of the composite. In addition to well-known various minerals such as gypsum, talc and carbonates [1, 2] for a long time the household waste, such as eggshells [3-6], rice husks [7], coconut husks [8]) and as well the industrial wastes, ash and slag of energy enterprises [9-13], sawdust and wastes from pulp mills [14, 15, 16], etc. are used as fillers. In this case application of fly ash as filler is beneficial not only from the economic site but also from the environmental perspective due to the reduction of the man-caused environmental load [17].

However, the amount of the utilized ash is much less than the number of its producers, which is associated with high content of harmful compounds including unburned carbon in fly ash composition. This fact limits the applications of fly ash in a high-capacity production of building materials, including cement, concrete, bricks, etc. Due to this reason there is a necessity to develop alternative research technologies where can fly ash will be also used. The purpose of this work is studying the applicability of ash and slag wastes of Kazakhstan thermal power plants as filler for polymer matrix based on polyethylene terephthalate (PET).

2. Experiment

Coal energy is predominating in the Republic of Kazakhstan with the share of about 70% in the general energy balance of the country [18]. Power plants in Kazakhstan work with the coals of different deposits but one of the most common is the coal from the Ekibastuz deposit [18]. It was noted that the technological scheme of coal combustion at thermal power plants in Kazakhstan is based on the traditional scheme of joint slag removal when combustion products, ash and slag, discharged by water through common channels and stored in one slag dump.

The description of fly ash from Ekibastuz coals are given in monographs [19, 20] but the absence of references to later literature sources was served as the basis for further carrying out chemical and grain size analysis of the ash composition. The results of the analysis are presented in Table 1 [21].

The fly ash (up to 95%) consists of oxides of silicon, aluminum, and iron (Table 1) represented by quartz, mullite, and hematite. The content of oxides of alkali and alkaline earth metals in total is 2,3%, and the amount of carbon is more than 3%. In accordance with the standard [22], the ash material with low carbon content (less than 1%) is classified in class F and

Table 1 – Data of the phase composition of fly ash from Ekibastuz deposit coal

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	K_2O	Na_2O	P_2O_5	MnO_2	SO_3	LOI
61,5	27,4	5,65	1,17	0,49	1,49	0,42	0,32	0,52	0,17	0,57	5,1

recommended as filler for concretes which are resistant to the impact of sulfate solutions and groundwater [23]. From the results of the grain sizes' analysis of the initial material, it follows that the largest number of particles (more than 60%) belongs to the class 0.25-0.1 mm. The total amount of other particle sizes is about 40% or about 10% of each class (Figure 1), which indicates the possibility of direct ash processing in the mills-activators without the stage of preliminary crushing.

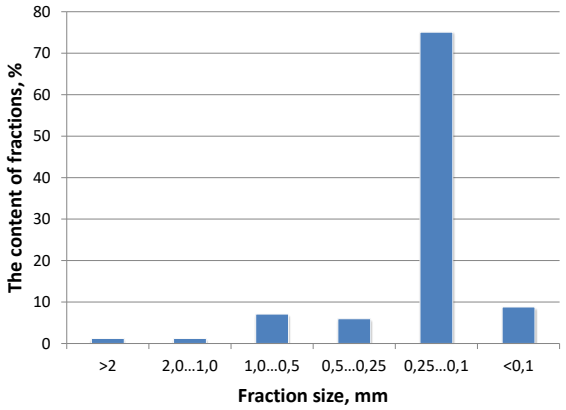

Figure 1 – The diagram of granulometric composition of ash from Ekibastuz deposit coal

Mechanical treatment of ash was carried out in centrifugal mill "Activator 2SL" (Russia) with the closest modes of obtaining the fillers at industrial conditions (in contrast to [24]): the activation time were 5, 10 and 15 min; the ratio of the material mass to the grinding bodies mass was 1:2 and 1:4; rotated speed of the drums mill was 400 rpm. Measurement of the specific surface area before and after mechanical activation was performed by BET method at the analyzer Sorbtometr-M (Russia). The scanning electron microscopy (SEM) was carried out in order to investigate the morphology of the samples surface before and after mechanical treatment using the scanning electron microscope Quanta 3D 200i Dual system, FEI.

Determination of carbon in fly ash material was carried out by means of Raman spectroscopy using Solver Spectrum device with 473 nm wavelength. Differential thermal analysis of samples was carried out in order to study the phase transformations using analyzer NEITZSCH STA 449 F3Jupiter, in the temperature intervals up 20 to 1000°C, with a heating rate of 20°C per a min. Polarizing microscopy was carried out in order to study the behavior of fly ash filler in the polymer matrix using the microscope Axio VERT1 with optical magnification x100 and x200. In addition, a series of tests for obtaining the composite material of the following composition were conducted: PET, hardener (Butanox) and fly ash filler. The mass ratio of mixture M (PET): M (fly ash) was 1:1. The polymer material was poured into special forms of 2×2×2 cm size, with subsequent vibratory compaction of the mixture. The drying process of the samples was implemented at room temperature for 10-12 h.

3. Results and Discussion

Nowadays, targeted improvement of the tribological properties of polymers that combine excellent mechanical and chemical resistant properties remains a major problem. Effective management of these properties is achieved by introducing into a polymer matrix of micro- and nanometer sized fillers. However, expensive methods of synthesis of nano-disperse-sized fillers require a search of alternative technological solutions. The most acceptable from a technical and economic point of view is the technology of mechanical activation. Therefore, for averaging of particle size and increasing their reaction activity, mechanical treatment of the fly-ash in a ball mill of planetary type was conducted, which allows providing uniform distribution of filler particles in the volume of the binding agent.

After mechanical fly ash processing a large part of the studied samples had the particle size of 5-15 microns. Larger particles have almost never occurred. The decrease in particle size accompanied by an increase in the specific surface area from 1.3 m^2/g to 3.6 m^2/g.

The sizes of particles first influence the bulk density of fly ash, and, therefore, the bulk density of mixture which contains the ash. After mechanical treatment with different mass ratios of the milled materials to the grinding bodies, the dispersity of the particles increases and bulk density decreases for 15%. The values of the bulk density of the fly-ash before and after mechanical activation are shown in Table 2.

Table 2 – Specific bulk density of fly ash

Fly ash	Bulk density g/cm^3
Activated (1:2, 5 min)	0.593
Activated (1:2, 10 min)	0.581
Activated (1:2, 15 min)	0.573
Activated (1:4, 5 min)	0.568
Activated (1:4, 10 min)	0.561
Activated (1:4, 15 min)	0.557
Non-activated	0.657

It was found that the best characteristics were demonstrated by the samples of polymers with filler obtained at the 15-minute mode of mechanical treatment when the mass ratio of ash to the mass of balls was equal to 1:4. We used this activation mode in our subsequent experiments.

The studied fly ash contained a large number of the microspheres' inclusions (Figure 2). However, after grinding the

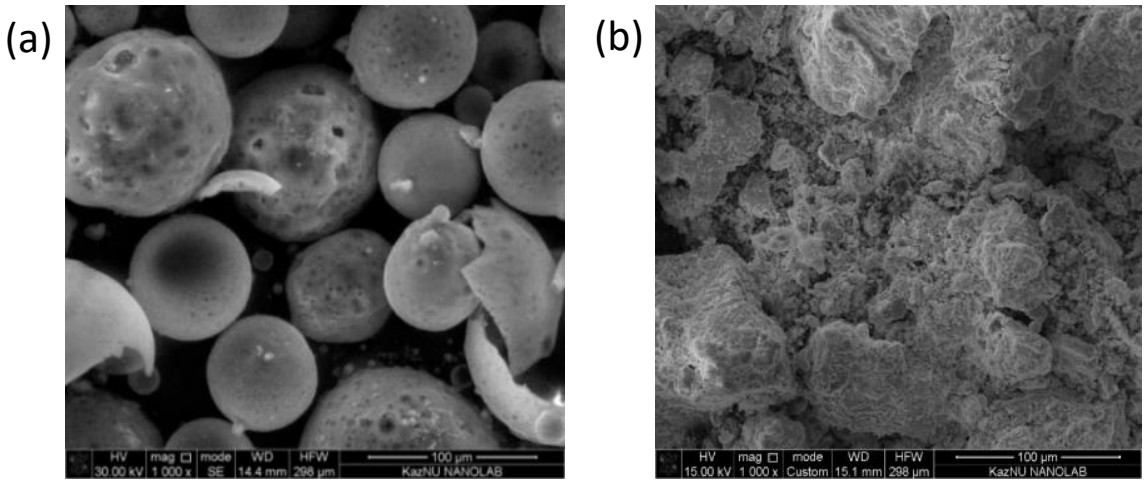

Figure 2 – SEM-analysis of fly ash: a) before mechanical activation; b) after mechanical activation

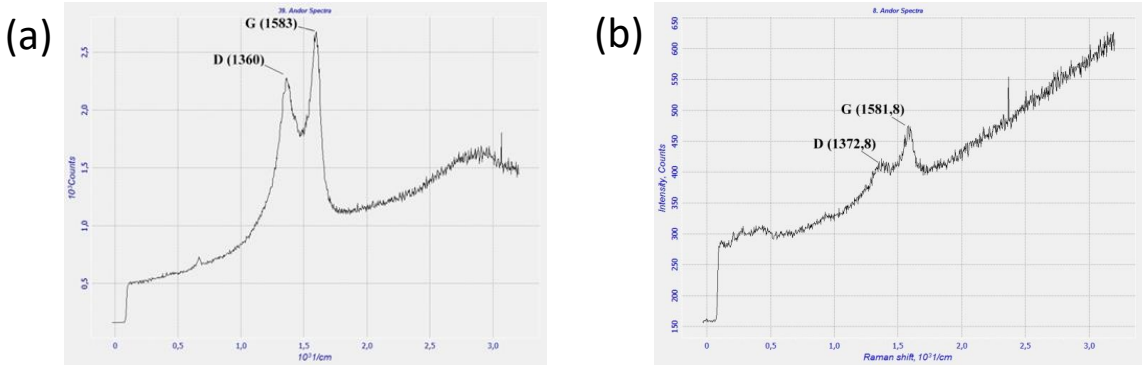

Figure 3 – Raman spectroscopy of fly ash before (a) and after mechanical activation (b)

particles of microspheres got a fragmentary rough particle form with a loose structure of surface due to covering the surface with carbon in the mechanical activation process.

The structure of pointed duplet peaks of the Raman spectra is shown at Figure 3 (a, b). It demonstrates the characteristic peaks of crystalline carbon at D 1360 cm^{-1} and G 1583 cm^{-1} wavelengths that correspond to graphite. However, in a greater degree the peak at 1360 cm^{-1} can be associated with a defect of the carbon structure resulting from temperature drop during ash cooling. The results of Raman spectroscopy of crushed filler demonstrated the shift of peaks G and D carbon in the low-frequency area with broadening the peaks indicating uniform distribution of carbon. Sloping peaks D 1372.8 cm^{-1} and for G 1581.8 cm^{-1} (Figure 3 b) indicate the distribution of carbon across the surface of the sample.

The carbon presence on the sample surfaces after mechanical treatment was proved by the change of the contact angle of wetting in aqueous solutions; the definition of which was carried out by the method described in [24]. It is seen from the results of measurements that before mechanical activation the contact angle was Θ=41°, and after mechanical treatment it became Θ=29°. The change in contact angle downward indicates increase in hydrophilicity of the powder material, which can be explained only by the presence of carbon on the surface of the particles.

The view of curves of differential thermal analysis for non-activated and activated samples (Figure 4 a, and b) has a complex form characterized by the occurrence of parallel processes. In the low-temperature area up to 200°C competing reactions are taking place: the losses of adsorbed water from the ash particles, and the start of carbon oxidation. For non-activated fly ash sample, the mass loss was about 2.2%. At the same time for the samples subjected to mechanical impact mass loss in this temperature interval was negligible. It was due to the fact that the process of mechanical reduction of particle size was accompanied by increase of temperature of particles over than 100°C that led to the loss of adsorbed water.

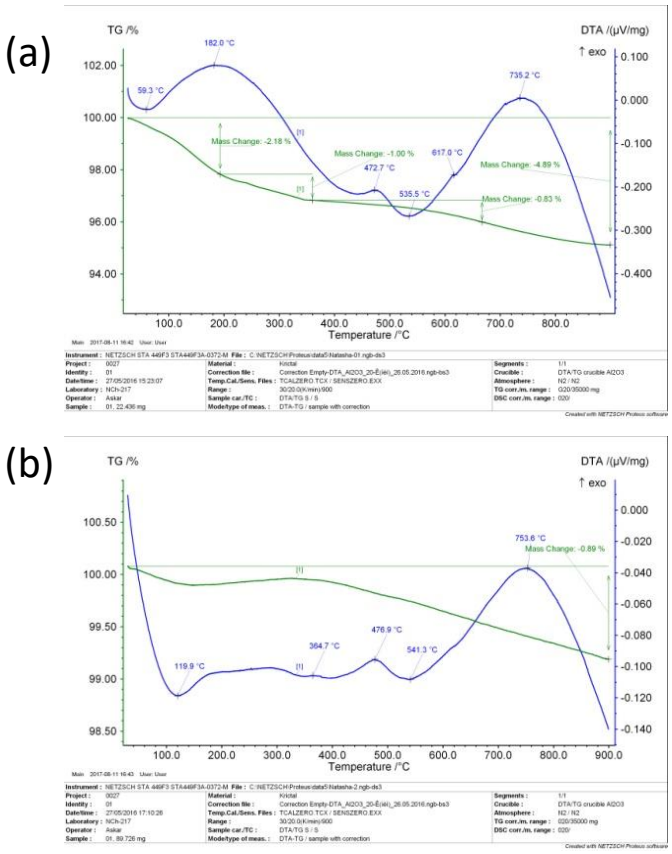

Figure 4 – DTA analysis of fly-ash: a) before mechanical activation; b) after mechanical activation

On the DTA curve of the mechanically activated samples Figure 4 b is noted intensive process of oxidation of the coal part of fly ash from 400°C, while for non-activated sample the peak was shifted to 430°C with the end of the process of oxidation for both simples at temperatures above 500°C. Exothermic effects in the temperature interval 735-750°C can be associated with the transformation of quartzite into tridymite and the inevitable changes that occur in the glass phase of the ash under the heat. In addition, the sintering process can result to additional broadening the lines of the curve of differential thermal analysis.

Generally, the use of fly ash as filler for composite materials based on cement is limited by the presence of unburned carbon in the composition of the fly ash. However, for polymer compositions carbon presence is not a critical feature. It is known that under mechanical mixing the polymer with the filler (carbon black) polymer radicals interact with the active sites of the filler particles forming the chemical bond 'polymer-filler'. When elastomers are mixed with carbon black there is formed a gel-like structure where the elastomer is chemically associated with the filler [25-29]. The phenomena of hardening the elastomers by carbon black were discovered as far back as 1912 and are actively explored to this day. In general, the mechanism of the phenomenon of strengthening the polymer durability is determined by a set of geometrical, physical and chemical properties of carbon [27, 28]. In fact, it occurs as a result of ordering the macromolecules that related to each other.

Therefore, with the aim of establishing the interaction between the fly ash filler and binding agent polarizing microscopy at optical magnification ×100 and ×200 was carried out. As it is seen from Figure 5 (a and b), the sample from the non-activated material presents a heterogeneous system of solid and liquid phases with an accurately defined interface. The samples filled with a mechanical activated fly ash material (Figure 5 c, d) with carbon on its surface represents a homogeneous system, indicating the interaction between the polymer matrix and carbon.

Measurement of properties of the polymer composition was carried out in accordance with the standards [30-33] and the results are presented in Table 3.

According to the obtained data (Table 3) it was found that the strength of polymer compositions was collected within 14 days and then remained almost unchanged. For samples with mechanically activated filler the maximum value of the strength in compression was 1.1 MPa; for non-activated ash powders the strength value was 0.4 MPa.

Thus, polymer materials based on mechanically activated fillers demonstrated better strength values that can be

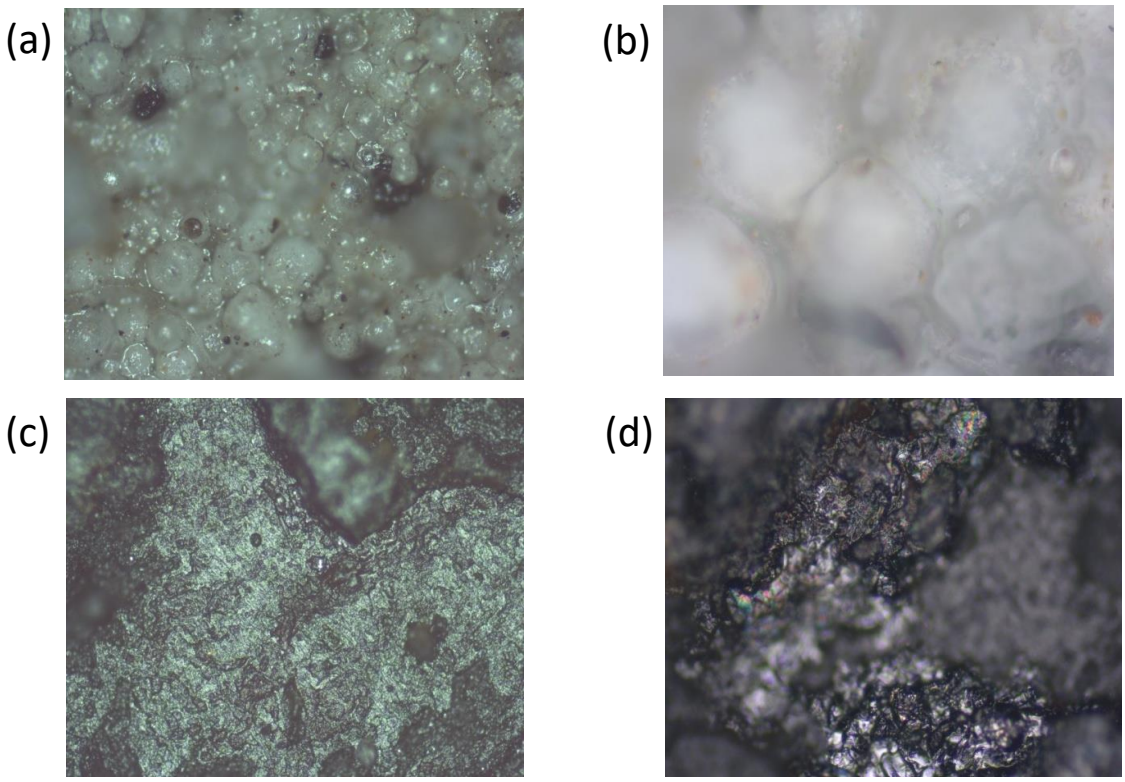

Figure 5 – Polarizing microscopy of polymer composite material filled with ash material: a) non-activated (×100); b) non-activated (×200); c) activated (×100); d) activated (×200)

Table 3 – Measured properties of the polymer composition

Strength characteristics	Non-activated filler	Mechanical activated filler
Strength in compression at 14th day, MPa*	0.4	1.1
Water absorption, %**	0.5	0.1
Acid resistance, %***	96	97

*The strength in compression of the samples was determined on a hydraulic press Cyber-Plus Evolution Mod YIMC109NC.

**When determining the water absorption of the samples, the exposition time was conventionally equal to 24 h.

*** When determining the acid resistance of the samples, the exposition time was conventionally equal to 24 h. Two acids were used: sulfuric and nitric acid, with concentration of 34%.

associated not only with the better distribution of the filler in the polymer matrix but with the additional interaction of the components of the composite mixture.

Water absorption of all samples regardless of the type of filler was almost always equal to zero. The reason was because most polyesters are resistant to water.

Acid resistance of all samples was 96-97%, which corresponds to the established norms of standards.

Conclusions

During this research the effect of preliminary mechanical activation on fly ash properties of Almaty Thermal power plant-2, as well as the possibility of its use as fillers for polymers, was studied.

The role of carbon in the formation of the ordered structure of a polymer composite material was shown, and it resulted to the greater mechanical strength of samples with mechanically activated fly ash filler.

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