UDC 620.186.12
DOI https://doi.org/10.32782/2663-5941/2024.1.2/18

Melnyk L.I.
National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute"

Cherniak L.P.
National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute"

Yevpak V.V.
National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute"

COMPOSITES BASED ON FLY ASH WITH DIFFERENT POLYMER MATRIXES

Burshtyn TPP generates electricity through coal combustion, which produces significant volumes of ash, which are accumulated and amount to approximately 40 million tonnes. One of the promising areas of utilisation of this ash is its use in the production of polymer composite materials (PCM). The key aspect in this process is the choice of a polymer binder as a matrix, which determines the main characteristics of PCMs, such as strength, stiffness, thermal and chemical resistance, etc.

The combination of fly ash and a polymer matrix results in a material with improved mechanical and thermal properties compared to traditional materials. The ash component provides heat resistance to the composite, while the polymer matrix adds flexibility and durability.

The use of traditional plastics in the creation of composites leads to an increase in the energy intensity of PCM production due to the significant consumption of thermal energy to convert the polymer into a melt to optimise the mixing process. Therefore, we propose to use a polymer matrix in the form of aqueous polymer dispersions in the development of composite materials. This simplifies and reduces the cost of production of polymer composite materials.

A technology for the production of polymeric composite materials (PCM) is proposed, which includes several stages: mechanical activation of the filler and polymer matrix, forming of blanks and their drying, heat treatment of blanks with subsequent cold pressing.

The process of forming the composite structure and the peculiarities of interaction in the ash-polymer matrix system were studied. The influence of different types of polymer binder on the formation of the porous structure and physical and mechanical characteristics of composites at high filler concentration was evaluated. The possibility of adjusting the properties of composites in a wide range was demonstrated: water absorption from 4.2% to 10.9%, open porosity from 6.03% to 18.40%, Young's modulus from 1.6 MPa to 60.6 MPa.

Key words: c*omposite, filler, fly ash, latex, composition, structure, physical and mechanical properties.*

Introduction. Polymeric composite materials (PCMs) are a unique class of composites that consist of a polymer matrix and fillers. These materials acquire a set of properties by combining the advantages of both the matrix and the filler. They are widely used in various industries such as aerospace, mechanical engineering, construction, electronics, sports goods and others.

The choice of starting materials for the production of composites for various purposes is the subject of many studies [1–2]. In particular, an important aspect of consideration is the possibility of using secondary products and waste from various industries as fillers [3–4].

Among the large amount of waste from the thermal power industry, a special place is occupied by ash and fly ash [5].

Coal combustion at thermal power plants in Ukraine produces 7–9 million tonnes of ash and slag annually (50 to 200 grams of ash per 1 kWh of electricity produced) [6], including about 40 million tonnes of ash accumulated at Burshtynska TPP [7].

A promising area of utilisation of TPP fly ash is its use for the manufacture of polymer composite materials. In this case, the choice of a polymeric binder as a matrix is of great importance, as it plays a key role in determining the properties of PCM and determines such characteristics as strength, stiffness, resistance to temperature, chemical resistance, etc.

Fly ash and polymer matrix composites have attracted considerable attention due to their unique properties [8–10]. The combination of ash and polymer matrix results in a material that has improved mechanical and thermal properties compared to traditional materials. The fly ash component provides the composite with inherent heat resistance, while the polymer matrix provides flexibility and durability.

There are studies [11] on the creation of a composite using up to 40 wt.% of fly ash and household waste PVC as a matrix. It is indicated that the mechanism of surface phenomena at the interface in the fly ash – PVC system is adhesion. Similar results were obtained when creating a composite with up to 40 wt.% fly ash when using LDPE as a matrix [12].

However, the use of polymeric binders in the form of plastic masses (PM) in these works increases the energy intensity of the manufactured composites, since a significant amount of thermal energy is consumed to convert the PM into a melt.

In this regard, studies on the creation of composites using polymeric binders in the form of aqueous dispersions, which simplify and reduce the cost of manufacturing PCM, are of particular interest [13]. In this direction, the present work was carried out, the purpose of which was to identify the features of the structure and properties of polymeric composites based on fly ash during the differentiation of polymeric binders.

Objects and methods of research. A set of physicochemical methods for analysing and testing properties was used in the study.

The mineralogical composition of ash microspheres and the quantitative ratio between phases were determined by X-ray structural analysis using a DRON-3M diffractometer (CuKα radiation, voltage 40 kV, current 20 mA, speed 2 degrees/min). The surface of the samples was examined using an optical microscope with an H5D digital camera. IR spectra in the range of 4000-400 cm-1 were recorded on a Specord IR-75 spectrophotometer (manufactured by Carl Zeis, Germany).

The parameters of the porous structure were determined on evacuated samples by the low-temperature N_2 adsorption-desorption method (T=-196°C) (Quantachrome NOVA-2200e Surface Area and Pore Size Analyzer, USA). The results were processed using the ASiQwin™ V 3.0 software. The specific surface area (S_{BET} , m^2 /g) was measured by multipoint BET method (Brunauer-Emmett-Teller) [14]. The total pore volume (V_P , cm^3 /g) was calculated using the maximum adsorbed volume of nitrogen at a relative pressure P/P $_0$ of 0.99. The volume of micropores (V_μ , cm^3 /g) was determined by the t-plot method, and their percentage was calculated using the following formula:

$$V\mu , \% = (V\mu /V\sum)*100\% \qquad (1)$$

The mechanical properties of ’deformation-loading’ diagrams under uniaxial compression were studied at room temperature using an automated arrangement consisting of IMAIII-20-78, analog-digital converter (ADC), personal computer (PC), and connecting cables. The measurements were performed in a vacuum of 10–5 Torr [15].

The technology of manufacturing a composite based on the polymer-filler water dispersion system consisted of the following operations:

– mechanical activation of the filler and polymer matrix in a ball mill (20 minutes);

– forming of blanks (by mould volume) and their maturation (48 hours at room temperature);

– heat treatment of the workpieces (gradual increase in temperature and holding for 1 hour at 80°C);

– cold pressing of cylindrical samples with a diameter of 10 mm. The object of study was composite materials based on water polymer dispersion – filler systems. The fly ash from Burshtynska TPP (Ash) (Ukraine) was chosen as a filler.

Aqueous dispersions of Latex 2012 copolymer and Policril 590 polymer were used as a matrix for the composite (Table 1).

Table 1

Characteristics of binders

Features.	Indicators.	
	Latex 2012	Policril 590
Chemical composition	Styrene-butadiene	Acrylic
Styrene content, %.	30	-
Physical condition	White aqueous dispersion	White aqueous dispersion
Dry matter content, %.	51,0	53,5–55,0
Particle size, nm	140	200
Viscosity, MPa-s	200	<1000
pH	5,5	5,5–7,5
Temperature (MTU), °C	< 5	0

According to the chemical composition (Table 2), the ash is acidic and is characterised by a quantitative ratio of SiO oxides :$_2$ Al O_{23} = 2.6, and a content of alkaline earth and alkaline oxides of 22.2 %.

Table 2

Chemical composition of raw materials

Sample of fly ash	Oxide content, wt.%.								
	SiO2	Al O23	Fe O23	TiO2	CaO	MgO	SO3	K O2	n.p.
Burshtynskaska	46,12	18,00	22,17	1,78	4,03	1,46	0,21	2,10	1,49

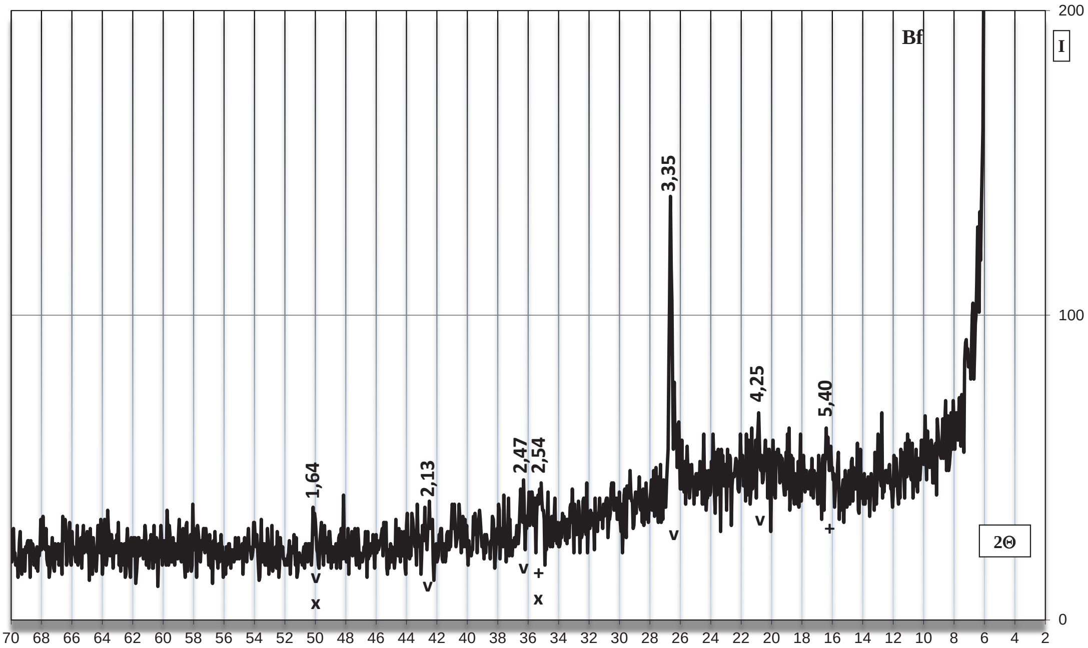


Fig. 1. Diffractogram of fly ash from Burshtynska TPP: v-quartz, +-mullite, x-haematite

Table 3

Characteristics of the pore structure of composite materials of the waterdispersion – ash system

Dispersion mark	Ash concentration, C, wt. %	Indicators			
		Water absorption after 24 h, %	Open porosity, %	Total porosity, %	Averagedensity, g/cm^3
Policril 590	65	4,2	6,03	18,04	1,44
	75	4,6	7,07	21,19	1,54
	85	7,8	12,50	21,74	1,56
	90	10,3	16,23	22,06	1,57
Latex 2012	65	7,2	9,17	13,74	1,28
	75	7,3	11,61	17,17	1,52
	85	8,5	12,90	18,21	1,59
	90	10,9	18,40	22,62	1,68

The analysis of the mineralogical composition of the studied ash showed that the sample of fly ash from Burshtynska TPP is characterised by the presence of glassy phase and crystalline phases of quartz, hematite, and mullite (Fig. 1).

Experimental part. The studied compositions provided for a high concentration of fly ash as a filler from 65 to 90 wt. % (Table 3).

It has been established that the obtained compositions differ in the characteristics of the pore structure, evaluated by physical and mechanical parameters, with obvious differences related to the type of polymeric binder used.

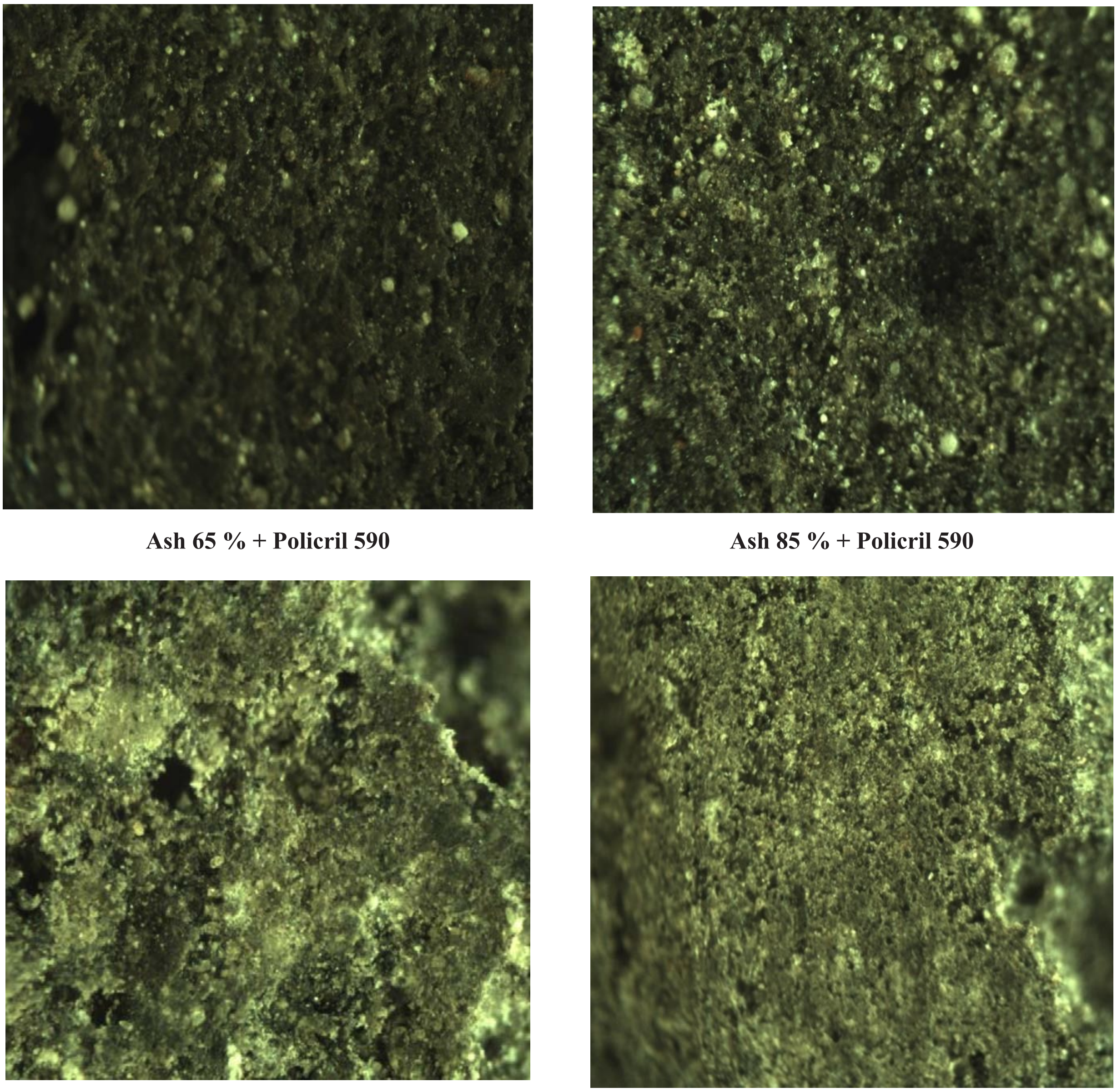
Thus, the indicators of water absorption and open porosity reach a minimum at an ash concentration of 65 wt. %, but differ quantitatively depending on the type of polymer binder. These indicators for the system with Latex 2012 are 7.2 % and 9.17 %, respectively, and for the system with Policril 590, 4.2 % and 6.03 %, respectively.

In the same range of changes in filler concentrations C = 65–90 wt. % when using Latex 2012 in comparison with Policril 590, the total porosity values are 13.74–22.62 % vs. 18.04–22.06 %.

The results of optical microscopy were a clear confirmation of these features of the pore structure of composites based on the studied systems (Fig. 2).

An important stage of the work was the analysis of the energy state of the surface of the filler particles as a factor in the degree of interaction with different types of polymer binder.

When studying the structure of composites according to the modified de Boer classification, the nitrogen sorption isotherms (Fig. 3) on the materials under study belong to type II (b) isotherms [16].



Ash 65 % + Policril 590 | Ash 85 % + Policril 590

Ash 65 % + Latex 2012 | Ash 85 % + Latex 2012

Fig. 2. Optical analysis of the pore structure of composites

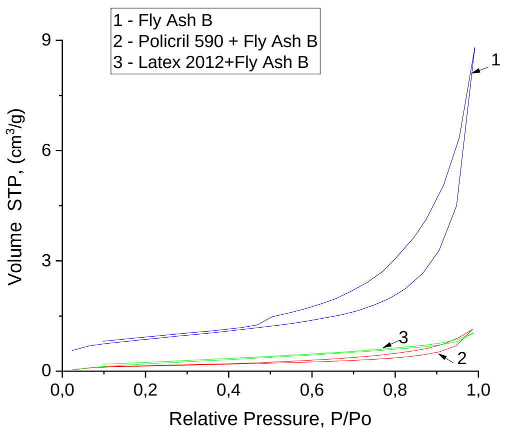


Fig. 3. Adsorption-desorption isotherms of N2 of 1 – Fly Ash B, 2 – Policril 590 + Fly Ash B, 3 – Latex 2012+Fly Ash B

The narrow hysteresis loop on the isotherms is caused by capillary condensation in the ash structural elements. In addition, the narrow hysteresis indicates the presence of micropores. The calculated parameters of the porous structure of the samples are given in Table 4.

Thus, the particles of the filler – fly ash with a developed surface intensively interact with the matrix – Policril 590. This is confirmed by a 5-fold decrease in the specific surface area of the particles of the composition of ash + Policril 590 compared to the original ash.

When using the copolymer Latex 2012, the specific surface area of the composite particles decreased by 1.2 times.

The results of infrared spectroscopy correlate with the above data. When analysing the interaction

Table 4

Characteristics of the porous structure

Samples	BET specific surface, m/g^2	Total porevolume at P/P_0 =up to 1, cm /g^3	Micropore volume see/g^3	Average pore size,nm
Ash	3,10	13,6*10^{-3}	1,56*10^{-4}	8,79
Ash + Policril 590	0,80	1,76*10^{-3}	4,52*10^{-4}	4,39
Ash + Latex 2012	2,64	1,61*10^{-3}	3,54*10^{-4}	1,21

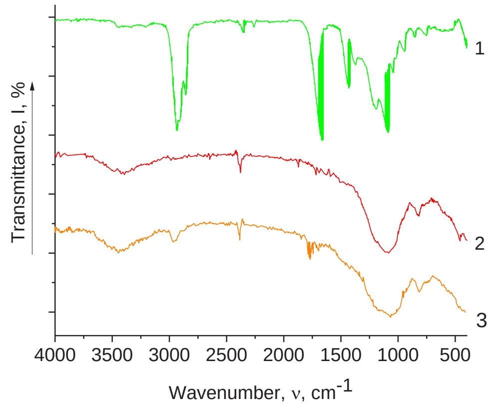


Fig. 4. a. Infrared spectroscopyof samples: 1 – Policril 590, 2 – Ash, 3 – Ash + Policril 590

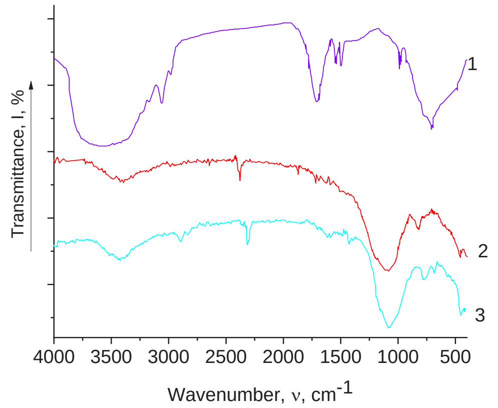


Fig. 4. b. Infrared spectroscopyof the samples: 1 – Latex 2012, 2 – Ash; 3 – Ash + Latex 2012

between the filler and the binder (Fig. 4. a, curve 1), it was found that the acrylic dispersion of Policril 590 has an absorption band at 1670 cm^{-1} , which corresponds to the monomeric links of acrylate [17]. This band is the result of asymmetric and symmetric valence vibrations of C=O in the carboxyl group. The absorption band at 1435 cm^{-1} reflects the vibrational vibration of the C=C bond, and the bands at 1100 cm^{-1} indicate the presence of the CH bond [18].

In the Policril 590-Ash system (Fig. 4. a, curve 3), changes in the curve are observed, indicating the interaction between the components. The formation of a small absorption band at 2250 cm^{-1} , corresponding to the C=C bond, and at 1720 cm^{-1} , characteristic of the C=O bond of the polymer, in addition to their slight displacement, indicates the interaction of the Policril 590-Ash system.

Regarding the IR spectrum of the styrene-butadiene dispersion Latex 2012 (Fig. 4. b, curve 1), the saturation band at 2980 cm^{-1} corresponds to the CH bond in the aromatic ring, and the saturation band at 1525 cm^{-1} indicates the presence of the ring itself. The absorption bands at 2852 cm^{-1} and 1500 cm^{-1} indicate the presence of the CH_2 group and the styrene double bond [19].

For the composite material based on the Latex 2012-Ash system (Fig. 4. b, curve 3), a decrease in the intensity of the peak at 2980 cm^{-1} with its shift to 2910 cm^{-1} and the disappearance of the peak at 1720 cm^{-1} was detected. These changes indicate an intermolecular interaction between the styrene-butadiene dispersion and the ash from Burshtynska TPP.

The revealed structural features of the studied composites result in significant changes in their mechanical properties. Thus, in particular, when determining the Young's modulus associated with the elasticity characteristics of the material (Fig. 5), a significant effect of the polymer matrix on the properties of PCM can be observed.

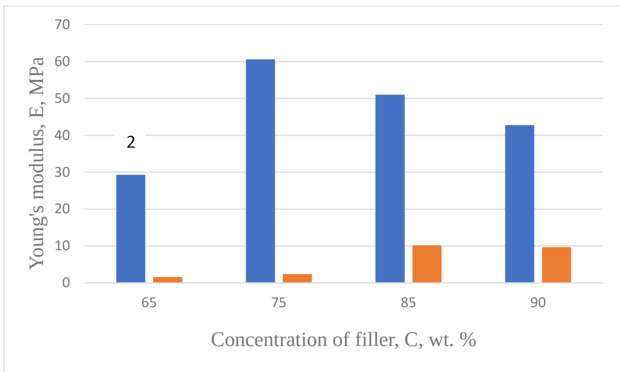


Fig. 5. Dependence of Young's Modulus on ash concentration for the systems: Ash + Policril 590 (1), Ash + Latex 2012 (2)

As can be seen, PCMs based on styrene-butadiene aqueous dispersion are characterised by significantly higher strength values. Their Young's modulus ranges from 29.3–60.6 MPa compared to 1.6–10.2 MPa for acrylic dispersion.

The analysis of the obtained characteristics of the mechanical properties of the experimental composites determines their possible scope of practical use.

Conclusions:

1. The use of thermal power waste as a filler is a promising area for expanding the raw material base for the production of polymer composites.

2. In the development of new composites with a high content of fly ash from thermal power plants, it is important to take into account the peculiarities of their composition and the energy state of the surface as a factor of interaction with different types of polymer matrix.

3. The test results indicate the possibility of adjusting the properties of polymer composites by varying the types and concentration of the polymer matrix. It is noted that the range of changes in property indicators includes: water absorption from 4.2 % to 10.9 %, open porosity 6.03–18.40 %, Young's modulus from 1.6 MPa to 60.6 MPa.

Bibliography:

1. Landel R.F., Nielsen L.E. Mechanical properties of polymers and composites. In CRC Press eBooks, 1993. 580 p. https://doi.org/10.1201/b16929.

2. Melnyk L.I., Chernyak L.P., Sviderskyy V.A., Belousov O.Yu., Nehreyko A.V. Structure and properties of polymer composite based on natural zeolite. *French-ukrainian journal of chemistry*, 2020. № 8. P. 12–18. https://doi.org/10.17721/fujcV8I1P12-18.

3. Haluschak M.O., Ralchenko V.G., Tkachuk A.I., Freik D.M. Methods of Measuring the Thermal Conductivity of Bulk Solids and Thin Films (Review). *Physics and Chemistry of Solid State,* 2013. Vol. 14. №. 2 P. 317–344.

4. Demchenko V., Simyachko O., Svidersky V. Research of mineralogical composition, structure and properties of the surface of Ukrainian ash microspheres. *Technology Audit and Production Reserves*. 2017. Vol. 6. № 1(38). P. 28–34. https://doi.org/10.15587/2312-8372.2017.118958.

5. Кашковський В.І., Євдокименко В.О., Каменських Д.С., Ткаченко Т.В., Вахрін В.В. Зольні та золошлакові відходи як багатофункціональна сировина. *Наука та інновації.* 2017. № 13(4). С. 54–63. https://doi.org/10.15407/scin13.03.054.

6. Дворкін Л. Й. Ефективні зольні цементи, бетони та розчини: монографія. Рівне: НУВГП, 2022. 419 с.

7. Перков Е., Перкова Т. Утилізація золи-виносу Придніпровської ТЕС. *Mining of Mineral Deposits,* 2017. № 11(1). С. 106-112. https://doi.org/10.15407/mining11.01.106.

8. Hadbaatar A., Mashkin N.A., Stenina N.G. Study of Ash-Slag Wastes of Electric Power Plants of Mongolia Applied to their Utilization in Road Construction. *Procedia Engineering,* 2016. Vol. 150. P. 1558–1562. https://doi.org/10.1016/j.proeng.2016.07.111.

9. Яцишин А.В., Матвєєва І.В., Ковач В.О., Артемчук В.О, Каменева І.П. Особливості впливу золовідвалів підприємств теплоенергетики на навколишнє середовище. *Проблеми надзвичайних ситуацій,* 2018. № 2 (28). С. 57-68. https://doi.org/10.5281/zenodo.2594489.

10. Mironyuk I.F., Tatarchuk T.R., Vasylyeva H.V., Yaremiy I.P., Mykytyn I.M. Morphology, Phase Composition and Radiological Properties of Fly Ash Obtained from the Burshtyn Thermal Power Plant. *Physics and chemistry of solid state,* 2019. V. 19, № 2. P. 171–178.

11. Костюкова Є., Барахтенко В.В. Суміші полімерних відходів і летючої золи для виробництва штучної деревини. *Всесвітня екологічна конференція з пластмас.* Орландо, Флорида, США, 2010. С. 74–82.

12. Мельниченко М. А., Єршова О. В., Чупрова Л. В. Вплив складу наповнювача на властивості полімерних композиційних матеріалів. *Молодий вчений*. 2015. № 96(16). С. 199–202.

13. Водно-дисперсійна теплоізоляційна композиція: пат. 122837 України: МПК C09D4/02, C09D5/00, C09D 5/02. № 201902367; заявл. 11.03.2019; опубл. 06.01.21, Бюл. № 1. 3 с.

14. Brunauer S, Emmett P.H., Teller E. Adsorption of gases in multimolecular layers. *Journal of the American chemical society*, 1938. № 60(2). P. 309-19. https://doi.org/10.1021/ja01269a023.

15. Vovchenko L.L., Matzui L.Y., Zhuravkov A.V., Samchuk A.P. Electrical resistivity of compacted TEG and TEG-Fe under compression. *Journal of Physics and Chemistry of Solids*, 2006. № 67(5-6). P. 1168–1172. https://doi.org/10.1016/j.jpcs.2006.01.042.

16. Kuila U., Prasad M. Specific surface area and poresize distribution in clays and shales. *Geophysical Prospecting,* 2013. Vol. 61, № 2, 341–362. https://doi.org/10.1111/1365-2478.12028.

17. Fischer E., Cuccato D., Storti G., Morbidelli M. Effect of the charge interactions on the composition behavior of acrylamide/acrylic acid copolymerization in aqueous medium. *European Polymer Journal*, 2018. Vol. 98. P. 302-312, https://doi.org/10.1016/j.eurpolymj.2017.11.022.

18. Crompton TR. Practical Polymer Analysis. New York: Springer. 1993. 822 p. https://doi.org/10.1007/978-1-4615-2874-6

19. Guo T., Song J., Jin Y., Sun Z., Li L. Thermally stable and green cellulose-based composites reinforced by styrene-co-acrylate latex for lithium-ion battery separators. *Carbohydrate Polymers*, 2019. Vol. 206, P. 801–810. https://doi.org/10.1016/j.carbpol.2018.11.025

Мельник Л.І., Черняк Л.П., Євпак В.В. КОМПОЗИТИ НА ОСНОВІ ЗОЛИ ВИНОСУ З РІЗНОВИДАМИ ПОЛІМЕРНОЇ МАТРИЦІ

Під час виробництва електроенергії на Бурштинській ТЕС, в результаті спалювання вугілля, утворюються значні обсяги золи, що накопичуються та становлять приблизно 40 мільйонів тон. Одним з перспективних напрямків утилізації цієї золи є її використання у виробництві полімерних композиційних матеріалів (ПКМ). Ключовим аспектом у цьому процесі є вибір полімерного зв'язуючого як матриці, що визначає основні характеристики ПКМ, такі як міцність, жорсткість, термічна та хімічна стійкість та інші.

Поєднання золи та полімерної матриці призводить до створення матеріалу, що відрізняється покращеними механічними та термічними характеристиками порівняно з традиційними матеріалами. Зольний компонент забезпечує термостійкість композиту, в той час як полімерна матриця додає гнучкість і довговічність.

Використання традиційних пластичних мас при створенні композитів призводить до збільшення енергоємності виробництва ПКМ через значне споживання теплової енергії для переведення полімеру в розплав для оптимізації процесу змішування. Тому нами запропоновано використовувати полімерну матрицю у вигляді водних дисперсій полімерів при розробці композиційних матеріалів. Це спрощує та здешевлює технологію виробництва полімерних композиційних матеріалів.

Запропоновано технологію виробництва полімерних композиційних матеріалів (ПКМ), що включає кілька етапів: механоактивацію наповнювача та полімерної матриці, формування заготовок та їх висушування, термообробку заготовок з наступним холодним пресуванням.

Вивчено процес формування структури композиту та особливості взаємодії в системі зола-полімерна матриця. Проведено оцінку впливу різних типів полімерного зв'язуючого на формування пористої структури та фізико-механічних характеристик композитів при високій концентрації наповнювача. Демонстровано можливість регулювання властивостей композитів в широкому діапазоні: водопоглинання від 4,2% до 10,9%, відкрита пористість від 6,03% до 18,40%, модуль Юнга від 1,6 МПа до 60,6 МПа.

Ключові слова: *композит, наповнювач, зола виносу, латекс, склад, структура, фізико-механічні властивості.*