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DEVELOPMENT OF MULTIFUNCTIONAL POLYMER COMPOSITES WITH HIGH RED MUD CONTENT

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Red mud (RM) is one of the large-scale by-products of alumina production, posing significant environmental challenges due to its high alkalinity, toxicity, and substantial accumulation volumes. The object of this study is polymer composite based on styrene-butadiene aqueous dispersion with RM and chamotte (Pa2) as fillers at high concentrations (up to 90 wt. %). The primary problem addressed in this research is finding effective ways to utilize RM as secondary raw material to enhance its recycling efficiency and create multifunctional materials with adjustable properties.

The study established that RM has an irregular plate-like structure with a high active surface area, which facilitates the formation of an open porous composite structure, while Pa2 forms a dense matrix due to its aluminosilicate content. Infrared spectral analysis confirmed the presence of functional groups (OH, Si–O, Al–O) that ensure the interaction of fillers with the polymer matrix. Thermogravimetric analysis demonstrated that RM and Pa2 exhibit similar behavior under heating. Mechanical tests revealed that RM-based composites exhibit high plasticity and energy absorption capacity, whereas Pa2-based composites are characterized by greater stiffness and strength (elastic modulus up to 129.8 MPa).

The results indicate that the choice of filler type and concentration effectively regulates composite properties. The proposed approach enables the recycling of industrial waste and the development of multifunctional materials suitable for use in construction, protective coatings, and the production of structural elements capable of withstanding significant loads

Keywords: red mud, polymer composite, technogenic fillers, industrial waste, specific surface area

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1. Introduction

In the modern era of technology and materials science, much attention is paid to the creation of environmentally friendly, functional and economically beneficial materials that can meet the needs of various industries. Among such materials, polymer composites occupy a leading place due to their unique properties, they are characterized by low density, high mechanical strength, chemical resistance and adjustable thermal insulation properties. Due to these characteristics, PCM are widely used in various industries: from construction and transport to energy and household products.

Scientific research in the field of polymer composites is extremely important, as they contribute to solving such global problems as reducing the use of natural resources, minimizing waste and creating materials with specified properties. One of the key aspects in the development of composites is the selection and modification of fillers that determine the structure, physical and mechanical properties and areas of use.

Among the promising areas is the use of industrial waste as fillers for polymer composites. This allows solving two important problems at the same time: reducing waste accumulation and creating accessible materials with improved characteristics. In particular, red mud (RM), a by-product of alumina production using the Bayer process, is a valuable resource due to its chemical composition, which includes oxides of iron, aluminum, silicon and other components that give it unique physicochemical properties.

The practical value of research on the use of red mud is due to its high potential as a filler for polymer composites. Its use allows to reduce the cost of final materials, improve their mechanical strength, thermal stability and environmental characteristics. RM modification, for example in the form of chamotte (Pa2), expands the range of its applications, ensuring the creation of multifunctional materials for the construction, transport and other industries.

Research on this topic is needed in practice, since optimization of the composition of composites using RM and chamotte can contribute to the creation of materials with specified characteristics for specific operating conditions. For example, such materials can provide high thermal insulation at the same time low density or withstand high mechanical loads at elevated temperatures.

Therefore, the relevance of research in this area is determined by the need to create innovative materials using industrial waste that meet modern requirements for economy, functionality and environmental sustainability. Studying the influence of concentration, particle size and chemical properties of RM and chamotte on the characteristics of composites is an important scientific task, the results of which can significantly contribute to the development of materials science and industry.

2. Literature review and problem statement

Red mud (RM), the main by-product of the Bayer process for alumina production from bauxite, presents both significant challenges and opportunities in materials science. For every ton of aluminum produced, about 4 tons of RM are generated [1], resulting in an annual global production of 70–120 million tons with total reserves of over 2.7 billion tons worldwide [2]. The chemical composition of RM varies significantly depending on the origin of the bauxite and the alumina production technology, typically including the oxides SiO_2, Al_2O_3, Fe_2O_3 and CaO [3]. The high alkalinity of RM (pH 10.3–12.3) is due to the use of sodium hydroxide during production [1], as well as the presence of toxic metals such as lead, nickel and zinc [4].

Traditional disposal methods, such as landfilling and sea dumping, pose serious environmental risks, including groundwater contamination due to leaching of toxic metals and alkaline suspensions, and air pollution due to RM dust inhalation [2, 5]. Catastrophic incidents such as the Aica accident (Hungary, 2010) highlight the urgent need to develop sustainable solutions [6].

Attempts to reuse RM include its application in wastewater treatment [1, 7], toxic metal removal [1], and valuable metal recovery [8]. However, despite the progress made, only a small fraction of RM is effectively utilized, with recovery rates of only 4 % in countries such as China [9, 10]. The main challenges in the RM use have been identified as the complexity of the pre-treatment of the material, including alkalinity neutralization and removal of toxic components. The lack of availability of technologies reduces the scale of RM utilization even in countries with large industrial resources.

In the construction industry, RM is used to create materials such as glass ceramics, ceramic pigments, refractories, geopolymers and cement [11, 12]. The paper [13] considered the possibilities of using RM for the manufacture of ceramic products. It was shown that RM can replace up to 30 % of natural raw materials, while maintaining the mechanical strength and thermal stability of ceramics. However, the issues of controlling the uniformity of the porosity of the material remain unresolved, as they require improving the methods of forming the structure of products.

Geopolymers integrate RM as a replacement for Portland cement, which allows reducing CO_2 emissions and improving the properties of materials [14]. However, issues related to optimizing the formulation to consistently obtain the required mechanical characteristics remain unresolved. The reason for this is the variable chemical composition of RM, which depends on the origin of the raw materials and the conditions of the technological process. To overcome these difficulties, it is proposed to use additives that compensate for chemical fluctuations, but their effect on long-term strength requires further research.

In [15], a study of the utilization of red mud in the production of cements and other hydraulic materials was conducted. The authors indicate that the inclusion of red mud allows to improve the thermophysical properties and reduce the cost of materials. However, the issue of high alkalinity of red mud remains unresolved, since it complicates the hydration processes of cements and requires special measures for neutralization. This is explained by the high content of Na_2O, which is difficult to remove without a significant increase in costs.

Modern studies confirm the effectiveness of using red mud as a filler in polymer composites, which can significantly improve their functional properties [16].

In [17], the use of red mud in the creation of polymer composites is considered. It is proven that red mud as a filler can increase the heat resistance and reduce the density of materials. However, it was noted that a high content of red mud in the composition reduces the adhesion between the polymer matrix and the filler, which negatively affects the mechanical properties. This is due to the high hydrophilicity of red mud, which limits its compatibility with hydrophobic polymer matrices. Surface modification of red mud is a possible solution, but requires additional costs and research. Despite the significant potential of red mud (RM) in construction materials, its application remains insufficiently effective due to its variable chemical composition, high alkalinity and insufficient mechanical characteristics. Further research is needed to address these problems, particularly in the field of polymer composites, where the RM properties can be optimized to create multifunctional materials. The integration of additional fillers, such as chamotte Pa2, as well as the improvement of processing technologies open up new opportunities to overcome existing limitations. This study aims to develop and optimize composite materials containing RM and chamotte, with a focus on achieving high mechanical, thermal and environmental characteristics.

3. The aim and objectives of the study

The aim of the study is to develop multifunctional polymer composites based on red mud and chamotte Pa2 as fillers with their high content (65–90 wt. %). This will make it possible to optimize the properties of materials to ensure their high mechanical, thermal and environmental characteristics, which will contribute to the expansion of the areas of their practical use in the construction, heat-insulating and environmental industries.

To achieve the aim, the following objectives were set:

– to analyze the physicochemical properties of red mud and chamotte (Pa2);

– to investigate the processes of interaction between the components of the experimental systems based on styrene-butadiene aqueous dispersion as a matrix and RM and chamotte as fillers;

– to investigate the influence of the concentration and granulometric composition of fillers on the structural, mechanical and thermal properties of composites.

4. Materials and methods

4. 1. Object and hypothesis of the study

The object of the study is a composite material based on the “copolymer-filler” system.

The use of red mud and chamotte as fillers for polymer composites with a high concentration (up to 90 wt. %) will allow creating materials with adjustable mechanical, thermal and environmental properties. This can be achieved due to the specific structural features and chemical composition of the fillers, which contribute to optimal interaction with the polymer matrix.

The hypothesis is based on the assumption that:

– red mud with an irregular lamellar structure will contribute to the formation of open porous structures, increasing plasticity and energy absorption capacity;

– chamotte, due to its stable aluminosilicate structure, will form a dense matrix, which will ensure high stiffness and strength of the composites;

– the choice of filler concentration and their granulometric composition will allow optimizing the properties of composites for various applications, including construction, thermal insulation and structural elements.

4. 2. Materials

Red mud obtained from PrJSC "Zaporizhzhia Aluminum Combine" (Ukraine) was used as a filler. Chamotte (Pa2) was produced by mixing red mud with 20 wt. % clay with subsequent joint firing at a maximum temperature of 900 °C.

According to the chemical composition (Table 1), red mud and chamotte are characterized by a high content of Fe_2O_3 and TiO_2, as well as a total concentration of alkaline earth and alkali metal oxides ($RO+R_2O$), which is 8.62 wt. % for red mud and 8.08 wt. % for red mud.

Table 1

Chemical composition

Material	Oxide content, wt. %								
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	SO_3	K_2O	LOI
RM	7.10	16.60	50.00	5.28	6.34	0.18	0.11	2.10 (Na_2O)	11.7
Pa2	21.98	19.23	44.96	4.82	5.76	0.30	0.13	2.02	0.80

Mineralogical analysis of the studied materials revealed that the RM samples [18] and chamotte (Fig. 1) contain goethite ($Fe_2O_3{\cdot}H_2O$), hematite (Fe_2O_3), gibbsite ($Al_2O_3{\cdot}3H_2O$), rutile (TiO_2) and ilmenite ($FeTiO_3$) [19], and the technological process of sample preparation is described in [20].

In the mineralogical composition of the studied materials, including RM and chamotte (Fig. 1), as already noted, the presence of goethite ($Fe_2O_3{\cdot}H_2O$), hematite (Fe_2O_3), gibbsite ($Al_2O_3{\cdot}3H_2O$), rutile (TiO_2) and ilmenite ($FeTiO_3$) was detected. The phase distribution and quantitative composition of the fillers were determined by X-ray structural analysis (XRA) on a DRON-3M diffractometer (Cu Kα 1–2 radiation, voltage 40 kV, current 20 mA, scanning speed 2°/min).

4. 3. Methods

The morphology of the sample surface was studied using a JSM scanning electron microscope. Infrared (IR) spectra were recorded in the range of 4000–400 cm^{-1} using a Specord IR-75 spectrophotometer (Carl Zeiss, Germany).

The specific surface area of the powders was measured using the BET method, which involves the adsorption of nitrogen vapor at –195 °C to calculate the surface area of the monolayer [21]. The particle size distribution was estimated using sieve analysis, while the contact angle was calculated using the Washburn equation [22], and the porosity was determined according to the standards set forth in DSTU B V.2.7-170:2008.

The mechanical properties were evaluated using load-unload diagrams recorded at room temperature using an automated testing system consisting of a JMAIII-20-78 unit, an analog-to-digital converter (ADC), and a personal computer. All measurements were performed in a vacuum environment of 10^{-5} Torr [23].

5. Results of the study of the use of red mud and its modification as fillers for polymer composite materials

5. 1. Analysis of the physicochemical properties of red mud and chamotte Pa2

Based on literature data [24], the mineral composition of red mud (RM) varies significantly depending on the size of its granulometric fractions. The 100–250 µm fraction consists mainly of quartz, hematite and calcite. The 50–100 µm fraction is dominated by hematite and aluminum goethite, 5–8 % Fe is replaced by Al. The 10–50 µm fraction contains hematite, aluminum goethite and aluminum goethite with partial substitution of Fe by Al within 7–12 %. In addition, this fraction demonstrates an increased concentration of hydrogarnets. The smallest fraction, less than 10 microns, includes hydrous aluminosilicates (e.g., cancrinite), hydrogarnets, secondary carbonates, aluminum goethite with approximately 25 % Fe replaced by Al, as well as dispersed hematite and rutile.

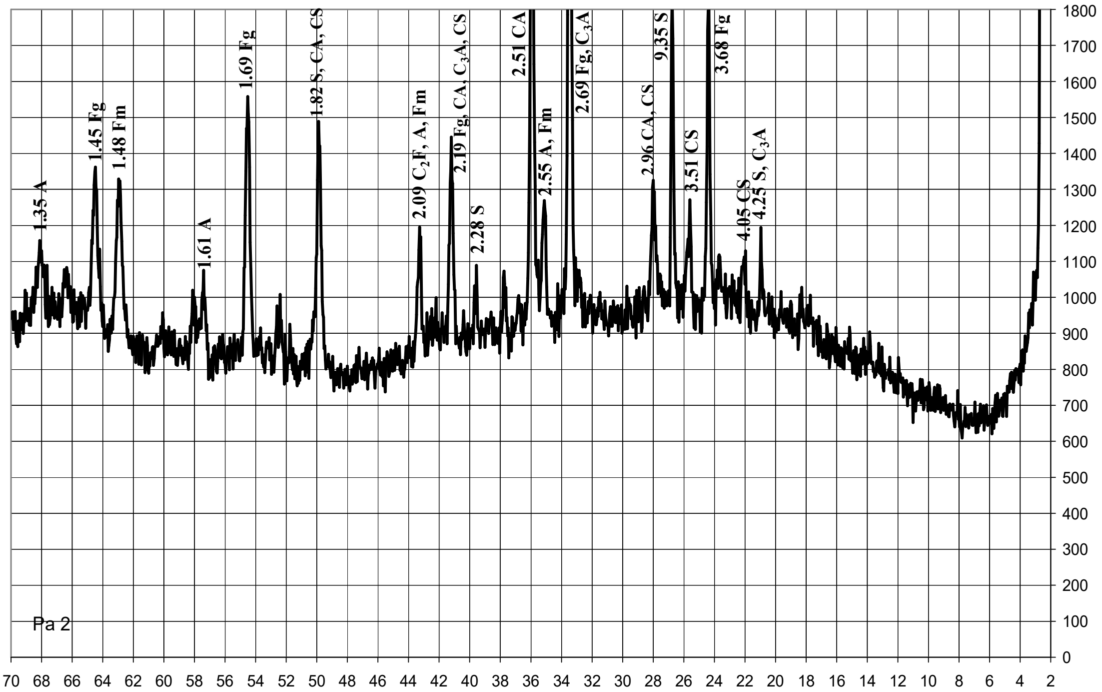


Fig. 1. X-ray diffraction of sample Pa2: x — goethite; + — hematite; T — rutile; o — hydrargilite

During storage, RM undergoes chemical transformations under the influence of alkaline process water (pH=11–13), carbon dioxide from the air, and oxygen. These transformations are enhanced by elevated temperatures, which can reach 50 °C in summer. The main active phases of red mud include calcium hydrosilicates, which decompose into calcium bicarbonates and amorphous silica within 1–3 years under the influence of carbon dioxide. The rate of this transformation is affected by the silica content in the hydrosilicates, which slows down the process, as well as the presence of isomorphic impurities of iron and titanium. At higher temperatures, calcium bicarbonates decompose into calcium carbonate and gibbsite. Meanwhile, aluminum goethite and hematite in long-term stored red mud remain largely unchanged.

Sodium hydroaluminosilicates in sludge storage conditions undergo low-temperature causticization due to CaO dissolved in the process water. This process involves the ion exchange of Na for Ca and is assumed to lead to the formation of calcium hydrosilicates such as hydrogarnets, although this has not yet been confirmed experimentally. Over time, the chemical composition of red mud changes towards a decrease in alkalinity and an increase in SiO_2 content.

Given these observations, it became necessary to determine the particle size distribution of the test samples (Fig. 2) and to conduct their IR spectroscopic analysis.

Granulometric analysis (Fig. 2) shows that for red mud the fraction in the range of 63–160 µm prevails, which is 48.6 wt. %. This fraction mainly consists of quartz, hematite, calcite and aluminum goethite. For chamotte (Pa2), the largest share falls on the fraction of 200–315 µm, which is 37.3 wt. %. Such a particle distribution can significantly affect the interaction of fillers with the polymer matrix in composites.

The morphological features of red mud and chamotte Pa2 particles were analyzed using electron microscopy (Fig. 3, 4).

Both materials have an irregular, lamellar structure, which increases their active surface area. Some particles are nanosized, which can improve adhesion to the polymer matrix and affect their distribution in the composite.

According to infrared spectroscopy data (Fig. 5), the main minerals found in the red mud are sodium hydroaluminosilicates and kaolinite. A broad absorption band in the range of 3632–3457 cm^{-1} indicates the presence of hydroxyl groups. The presence of aluminum in the form of hydroxide, partly in the composition of gibbsite ($Al(OH)_3$), is confirmed by the absorption band at 537 cm^{-1}. In addition, the presence of kaolinite ($Al_2Si_2O_5(OH)_4$) is confirmed by the band at 1068 cm^{-1}.

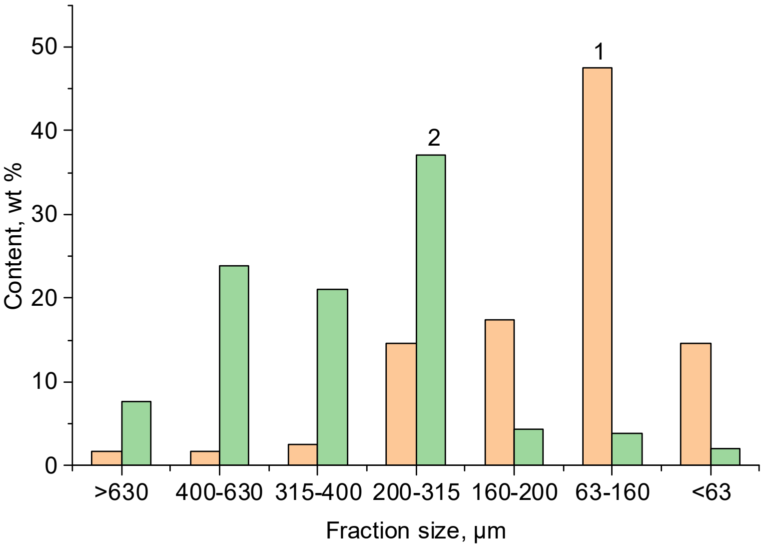
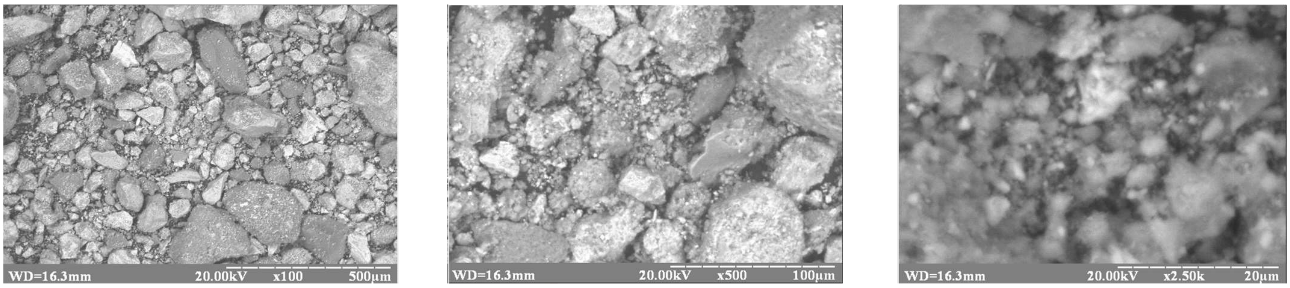
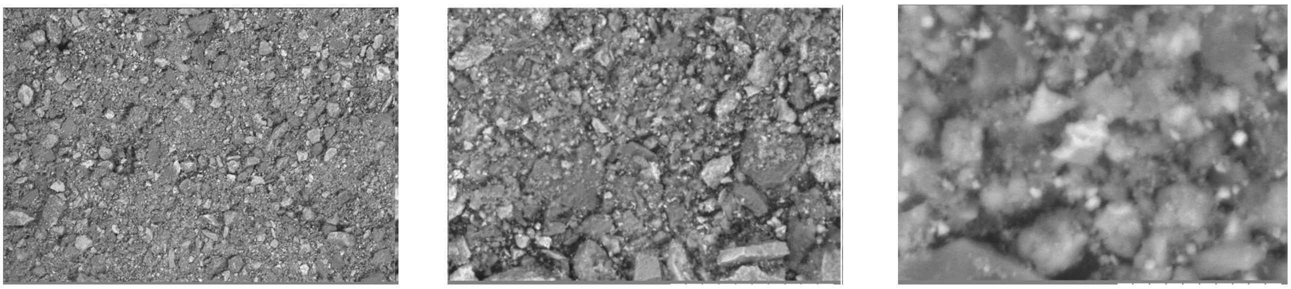


Fig. 2. Particle distribution by fractions for samples: 1 — RM; 2 — Pa2



a *b* *c*

Fig. 3. Electron microscopy of samples of chamotte Pa2 at magnification: *a* — 100 times; *b* — 500 times; *c* — 2500 times



a *b* *c*

Fig. 4. Electron microscopy of red mud samples at magnification of: *a* — 100 times; *b* — 500 times; *c* — 2500 times

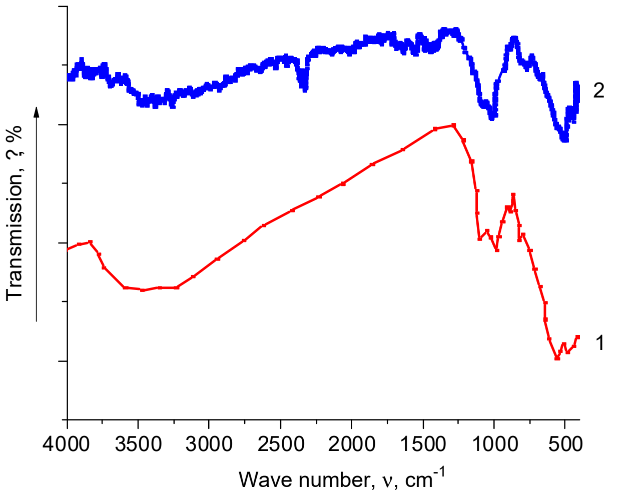


Fig. 5. IR spectrum of particles of the experimental fillers: 1 – red mud, 2 – Pa2

The band with a peak at 810 cm^{-1} corresponds to the Fe–O vibrations characteristic of hematite (Fe_2O_3). The Si–O vibrations observed in the range of 1100–1200 cm^{-1} indicate the presence of silicates or aluminosilicates. These spectral features emphasize the complex mineral composition of red mud [25].

Comparison of the IR spectra of pure red mud and chamotte (Pa2) shows that both samples exhibit broad peaks in the range of 3200–3600 cm^{-1}, which correspond to OH groups. The peaks at 1100 cm^{-1} and 537 cm^{-1}, which correspond to Si-O and Al-O vibrations, respectively.

The appearance of a peak in the range of 1600–1650 cm^{-1} indicates the presence of OH groups from adsorbed moisture, which is held in the layered structure of clay minerals.

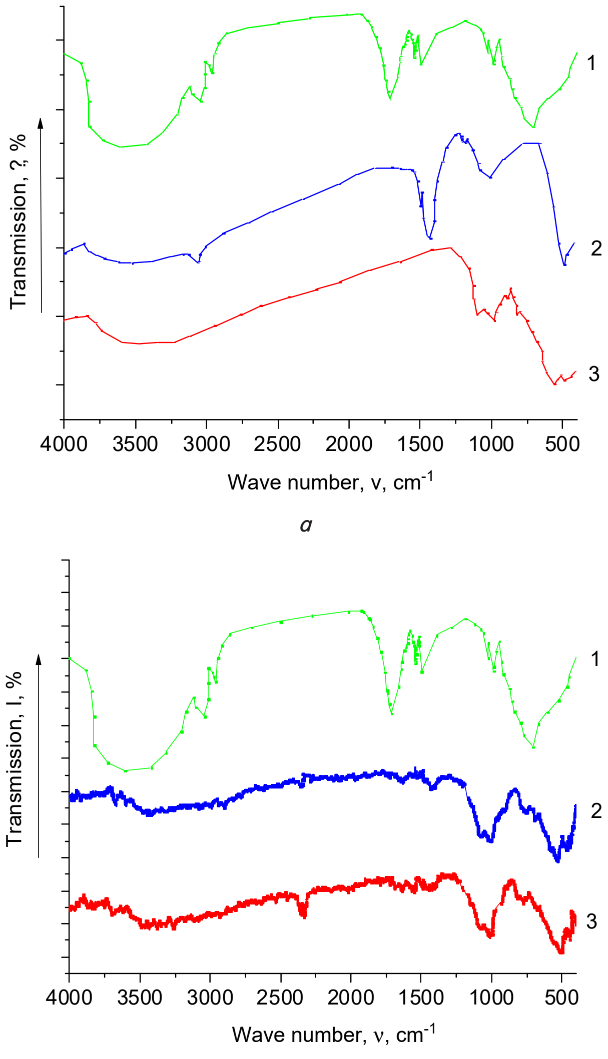
Thermal analysis (DTA-TG) of red mud and chamotte Pa2 showed similar weight losses: 10.8 % and 10.2 %, respectively, with the most significant weight loss in the temperature range of 200–650 °C (Fig. 6). Detailed analysis indicates that the gradual decrease in weight with increasing temperature may be due to the evaporation of physically bound water, dehydration of hydroxyl groups, or decomposition of organic and carbonate impurities.

The DTA curve exhibits both endothermic and exothermic peaks. Endothermic peaks are likely due to loss of adsorbed water or dehydration of hydroxyl groups, characteristic of aluminosilicates, which are the main components of red mud. On the other hand, exothermic peaks may indicate crystallization or phase transitions, such as the transformation of Fe_2O_3 (hematite) or other oxide phases upon heating.

In chamotte Pa2 (Fig. 6, *b*) similar thermal processes are observed as in red mud. In general, the results of DTA-TG analysis show that both red mud and chamotte Pa2 undergo significant mass losses due to the removal of water (physically and chemically bound in the form of hydroxyl groups) and the decomposition of certain components. Endothermic and exothermic peaks indicate the presence of phase transitions characteristic of minerals based on aluminum and iron.

To assess the possibility of using these materials as fillers in polymer composites, the surface energy state and specific surface area were determined. The results of these studies are given in Table 2.

The wetting angle at the interface of the 3 phases was determined using the standard method [26]. For red mud it was 74°, and for chamotte Pa2 it was 77°, which indicates the poor wettability of these materials.



a

b

Fig. 6. DTA-TG analysis: *a* – red mud; *b* – chamotte Pa2

Table 2

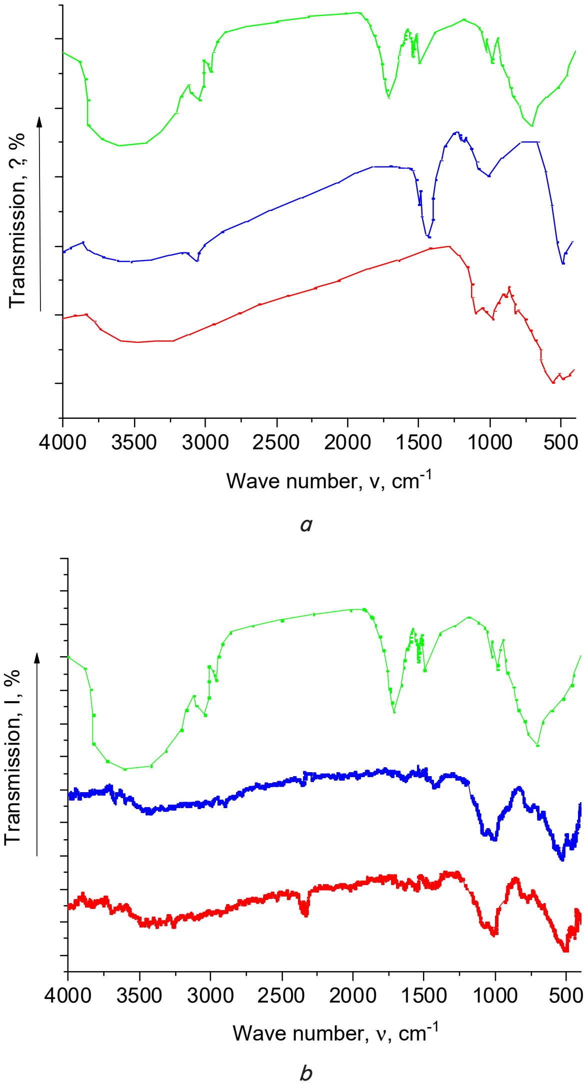
Effective specific surface area and surface energy state of RM and Pa2 samples

Material	BET specific surface area BET, m^2/g	Total pore volume, cm^3/g	Average pore diameter, nm	Wetting angle, deg	Surface energy, mJ/m^2
RM	19.63	0.010	2.29	74	45.02
Pa2	17.69	0.010	2.29	77	42.49

Another important characteristic of powder materials is their specific surface area (Table 2), which plays a key role in determining the interaction between the filler and the matrix. According to BET measurements, red mud has a larger specific surface area (19.63 m^2/g) compared to chamotte Pa2 (17.69 m^2/g), despite similar total pore volumes and average pore diameters. This difference is directly related to their granulometric and mineral-phase composition.

5. 2. Study of interaction processes in the Latex 2012-filler system

The analysis of the IR spectrum of the Latex 2012 butadiene-styrene dispersion (Fig. 7, *a*, *b*, curve 1) revealed characteristic absorption bands. The band at 2980 cm^{-1} corresponds to the stretching vibrations of the –CH– groups, while the bands at 3020 cm^{-1} and 1525 cm^{-1} are related to vibrations of the benzene ring. The absorption at 2852 cm^{-1} indicates the presence of CH_2 groups, and the band at 1500 cm^{-1} corresponds to the double bond in styrene. In addition, the band at 700 cm^{-1} is attributed to the deformation vibrations of the aromatic ring. The absorption band with a peak at 960 cm^{-1} corresponds to the stretching vibrations of the =C–H bonds in the butadiene moiety. This detailed spectral analysis provides insight into the structural features of the dispersion, which is important for understanding its interactions with the filler.



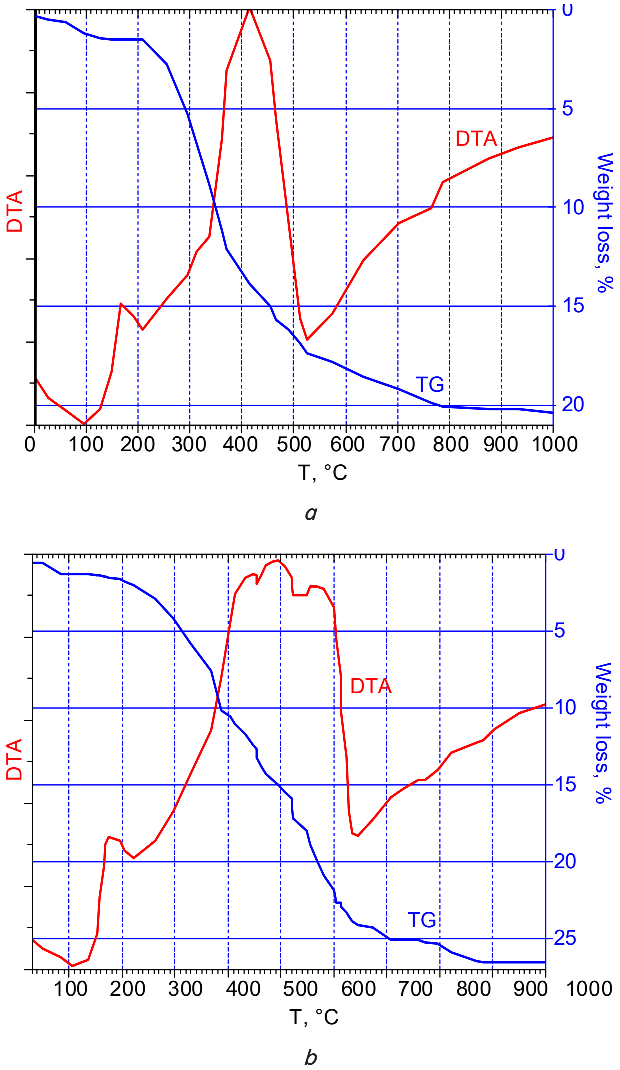
a

b

Fig. 7. IR spectroscopy of samples for the systems: *a* – Latex 2012 + RM; *b* – Latex 2012+Pa2; 1 – Latex 2012, 2 – PCM, 3 – filler

For the composite material (Fig. 7, *a*, curve 2), noticeable changes in the peaks associated with stretching vibrations of the benzene ring are observed. In particular, the intensity of the peak at 3020 cm^{-1} decreases and shifts to 2910 cm^{-1}, and the peak at 1525 cm^{-1} shifts to lower frequencies. These shifts confirm that the introduction of red mud as a filler into the Latex 2012 copolymer is accompanied by intermolecular interactions.

For systems using chamotte Pa2, the IR spectra are shown in Fig. 7, *b*. Based on the IR spectrum of the Latex 2012+Pa2 system (Fig. 7, *b*, curve 2), it can be stated that the presence of inorganic oxides in Pa2 does not significantly change the main characteristics of the polymer matrix, and the interaction with the binder is confirmed by a shift to lower frequencies and a decrease in the intensity of the peak at 1600 cm^{-1} associated with vibrations of the aromatic ring. To assess the thermal stability and determine the operating temperature ranges of the developed composites, thermogravimetric (TG) and differential thermal analysis (DTA) were performed for the Latex 2012+RM and Latex 2012+Pa2 systems (Fig. 8). The results obtained allow to compare the thermal behavior of composites based on Latex 2012 with the addition of RM and Pa2 as inorganic fillers, as well as to identify potential interactions between components in the studied systems.



a

b

Fig. 8. DTA-TG analysis of systems: *a* – Latex 2012+RM; *b* – Latex 2012+Pa2

The total mass loss for the Latex 2012+Pa2 system is 26.8 wt. %, while for the Latex 2012+RM system – 20.2 wt. %.

5. 3. Study of the influence of the concentration and type of fillers on the structural and mechanical properties of composites

The samples of composite materials were prepared on the basis of binary systems. The concentration of the filler, with a particle size ≤1 mm, varied from 65 to 90 wt. %. The composition and properties of the composites are given in Table 3.

Table 3

Composite composition and properties

PCM composition	Filler concentration, C, wt. %	Water absorption in 24 hours, %	Open porosity, %	Total porosity, %	Average density, g/cm^3
Latex 2012+RM	65	5.96	9.07	10.46	1.52
	75	8.64	15.23	29.17	1.76
	85	9.40	18.38	40.84	1.95
	90	10.05	21.37	47.56	2.13
Latex 2012+Pa2	65	13.69	19.49	22.74	1.42
	75	14.04	23.08	28.19	1.54
	85	20.27	31.25	35.78	1.64
	90	26.38	35.26	40.23	1.68

The results of the studies show that the characteristics of the pore structure of the composites significantly depend on the filler concentration. For both fillers, a linear dependence of water absorption and density on concentration is observed. With an increase in the filler concentration from 65 to 90 wt. %, water absorption increases from 5.96 % to 10.05 % for RM and from 13.69 % to 26.38 % for Pa2. At the same time, the density increases from 1.52 to 2.13 g/cm^3 for RM and from 1.42 to 1.68 g/cm^3 for Pa2.

It is noted that the change in the average density in the studied range of filler concentrations is insignificant. Thus, for RM it increases by 1.4 times, and for Pa2 by 1.2 times, while water absorption increases by 1.7 times for both systems. These differences indicate variations in the pore structure of the studied composites.

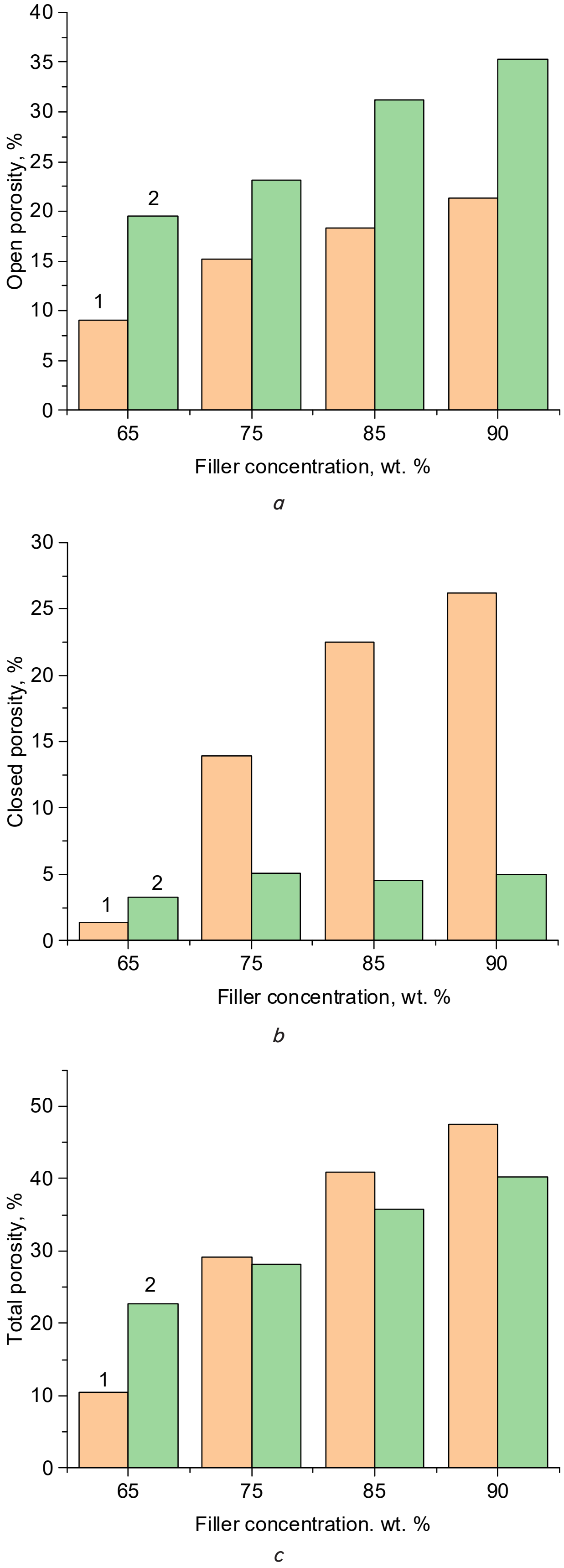
Structural differences of composite samples are mainly determined by the formation of open pores (Fig. 9). With an increase in the filler concentration from 65 to 95 wt. %, the number of open pores increases by 2.4 times for RM and by 1.8 times for Pa2. This confirms the dependence of the porous structure of the composite on the type and concentration of the filler used.

Analysis of open porosity (Fig. 9, *a*) shows a significant increase in this parameter with an increase in the filler concentration from 65 to 90 wt. % for both systems. However, the Latex 2012+RM system demonstrates a more dramatic increase, and the open porosity values for RM exceed the similar indicators for Latex 2012+Pa2 at the highest filler concentration. This indicates that RM contributes to the formation of a more interconnected pore structure.

Closed porosity (Fig. 9, *b*) also increases with an increase in the filler concentration in the Latex 2012+RM system, which reflects a large number of isolated pores in the composite. In contrast, in the Latex 2012+Pa2 system, the growth of closed porosity occurs more slowly, indicating that the addition of chamotte contributes to the creation of a composite structure with a smaller number of isolated pores.

The total porosity (Fig. 9, *c*) confirms these trends. The Latex 2012+RM system has a higher total porosity at all filler concentrations, especially at 90 wt. %, compared to the Latex 2012+Pa2 system. This emphasizes the influence of RM on the formation of a more porous composite structure, while Pa2 provides a denser matrix with lower total porosity.

The results of the study of elastic and strength characteristics are obtained from the "load-unload" diagrams (Fig. 10), they provide data on elastic and plastic deformations, as well as the effective elasticity modulus (Table 4).

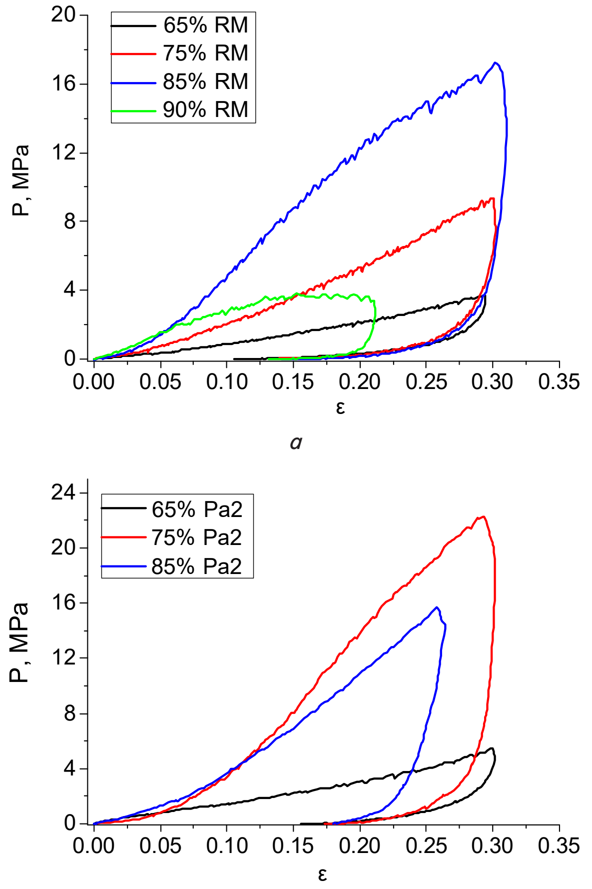


a

b

c

Fig. 9. Porosity of composites depending on the filler concentration for the systems: 1 – Latex 2012+RM, 2 – Latex 2012+Pa2; *a* – open; *b* – closed; *c* – total



a

b

Fig. 10. Dependence of deformation on load for systems: *a* — Latex 2012+RM; *b* — Latex 2012+Pa2

For the Latex 2012+RM system, the load-strain curves indicate a noticeable increase in the bearing capacity with increasing filler concentration. At 65 wt. % RM, the composite demonstrates a lower peak load of approximately 8 MPa and fails at a strain of about 0.25. With an increase in the RM concentration to 90 wt. %, the composite reaches a maximum load of 20 MPa and demonstrates a larger strain at failure (~0.35), which indicates increased plasticity. The area bounded by the hysteresis loop on the load-unload curves increases with increasing filler content, which indicates better energy dissipation through plastic deformation. Residual (plastic) deformation is observed for all samples, but no clear correlation with filler concentration is found.

For the Latex 2012+Pa2 system, the curves show higher load-carrying capacity compared to the RM-based composites. At 85 wt. % Pa2, the composite withstands a maximum load of 24 MPa, failing at a strain of around 0.3. Compared to the RM-based composites, the Pa2 composites have a lower strain at peak load, indicating a stiffer and less ductile structure. As in the RM-based system, the residual strain is significant for all filler concentrations, and the area of the hysteresis loop increases with increasing filler content, reflecting better energy absorption.

The Pa2-based composites exhibit higher mechanical strength and stiffness, while the RM-based composites exhibit greater ductility and higher strain at failure.

It is evident that all samples exhibit significant residual strain (ε_{pl}), which is not initiated at the threshold load but occurs at arbitrary values. In addition, no clear relationship between plastic deformation and filler content was found (Table 4).

Table 4

Strength and elasticity characteristics of the test specimens

Filler concentration. wt. %.	Maximum load, *P*, MPa	ε_{total}	ε_{pl}	ε_{el}	Elasticity modulus, *E*, MPa
PCM of the Latex 2012+RM system					
65	3.7	0.29	0.08	0.21	17.6
75	9.4	0.30	0.10	0.20	46.8
85	17.2	0.30	0.116	0.184	93.5
90	3.8	0.21	0.103	0.107	34.6
PCM of the Latex 2012+Pa2 system					
65	5.52	0.30	0.123	0.177	31.2
75	22.2	0.30	0.093	0.207	75.5
85	15.7	0.26	0.140	0.12	129.8

Analysis of the strength and elasticity characteristics of the composite material systems Latex 2012+RM and Latex 2012+Pa2 (Table 4) revealed significant differences in their behavior under load depending on the type and concentration of the filler. In the Latex 2012+RM system, increasing the filler content from 65 wt. % to 85 wt. % causes a significant increase in the maximum load from 3.7 MPa to 17.2 MPa, which indicates an improvement in strength. However, at a filler concentration of 90 wt. %, the maximum load decreases sharply to 3.8 MPa, which indicates structural weaknesses at very high filler concentrations. The residual plastic strain (ε_{pl}) increases with increasing filler concentration, reaching a maximum of 0.116 at 85 wt. %, but decreases slightly at 90 wt. %. The elastic strain (ε_{el}) decreases with increasing filler concentration: from 0.21 at 65 wt. % to 0.184 at 85 wt. %. The elastic modulus increases significantly with increasing filler content, reaching a peak of 93.5 MPa at 85 wt. %, but decreases to 34.6 MPa at 90 wt. %, indicating a decrease in stiffness at excessive filler concentrations. Mechanical tests have shown that the composites with Pa2 exhibit higher strength and stiffness. The maximum load for the Latex 2012+Pa2 system is 22.2 MPa at 75 wt. % filler, and the elastic modulus reaches 129.8 MPa at 85 wt. %. In contrast, the composites with RM have higher ductility and greater deformation at failure. The maximum load for Latex 2012+RM is 17.2 MPa at 85 wt. %, and the elasticity modulus is 93.5 MPa.

6. Discussion of the results of the study of the influence of the concentration and type of fillers on the structural and mechanical properties of composites

The results of the study showed that the structural and mechanical properties of polymer composites significantly depend on the type and concentration of fillers. This can be explained by the peculiarities of the morphology, chemical composition and thermal behavior of the fillers. Morphological analysis (Fig. 3, 4) showed that red mud (RM) has a lamellar structure with a high specific surface area (19.63 m^2/g; Table 2), which contributes to the formation of an open porous structure of the composite. At the same time, chamotte Pa2, due to the content of aluminosilicates, forms a dense matrix with reduced porosity.

IR spectroscopy (Fig. 5) confirmed the presence of functional groups (OH, Si–O, Al–O) in the fillers, which ensure effective interaction with the polymer matrix. In particular, a broad peak in the range of 3200–3600 cm^{-1}, which is characteristic of hydroxyl groups, explains the high level of adhesion with the polymer matrix.

DTA-TG analysis of fillers (Fig. 6) showed similar thermal behavior of RM and Pa2, with the main mass losses of 10.8 % and 10.2 %, respectively, in the range of 200–650 °C, caused by dehydration of hydroxyl groups and decomposition of carbonates. As for composites based on them (Fig. 8), the situation is somewhat different. The total mass loss for the Latex 2012+Pa2 system is 6.6 wt. % higher than for the Latex 2012+RM system. This can probably be explained by the fact that Pa2, due to its higher chemical activity compared to RM, can react with the components of the polymer matrix. These reactions form unstable intermediates that decompose at temperatures up to 650 °C, contributing to greater mass loss.

Mechanical tests (Table 4) revealed that composites with RM have high ductility and energy absorption capacity, making them suitable for applications with dynamic loads. In contrast, composites with Pa2 demonstrate greater stiffness and strength, with an elastic modulus of up to 129.8 MPa at a filler concentration of 85 wt. %. At a concentration of 90 wt. %, a decrease in strength is observed for both systems, which is explained by the formation of an excessively porous structure and a decrease in adhesion between the filler particles and the polymer matrix.

Comparing the results with the literature data obtained by other authors [16], it can be noted that RM provides unique mechanical and thermal insulation properties due to increased porosity, while Pa2 allows for composites with high structural strength. At the same time, the results confirm that the particle size distribution of fillers plays an important role in regulating these properties [24].

However, the study has certain limitations. First, the results obtained are relevant for a polymer matrix based on styrene-butadiene dispersion; other types of polymers may show different behavior during interaction with fillers. Second, the studies were conducted in laboratory conditions, which does not fully reflect the long-term operation of materials in real conditions. Among the shortcomings of the work, it should be noted the insufficient number of experiments devoted to the influence of aggressive environments on the properties of composites. This issue will be addressed in future studies.

Further development of the study may include chemical modification of the surface of RM and Pa2 to improve their compatibility with various polymer matrices. One of the challenges will be to ensure the stability of the properties of composites in a wide concentration range when using different matrices. In addition, an interesting prospect is the study of the influence of nanoimpurities to create materials with new functional properties.

Thus, the results confirm that the proposed approach allows for the effective use of RM and Pa2 to create multifunctional composites with tunable properties suitable for a wide range of industrial and construction applications.

7. Conclusions

1. The analysis of the physicochemical properties of red mud and chamotte Pa2 was carried out, which showed that red mud has an irregular lamellar structure and a high active surface, which contributes to the formation of a porous structure of the composite. In contrast, chamotte is characterized by a stable aluminosilicate structure, which provides high density and thermal stability. These properties are explained by the difference in the mineralogical composition of the fillers.

2. The study of the interaction between the components of the composites revealed that RM and chamotte interact differently with a polymer matrix based on butadiene-styrene aqueous dispersion. For the RM, an increase in intermolecular interactions is characteristic, which is manifested by a shift of peaks in the IR spectra, while chamotte demonstrates higher chemical inertness. These differences are due to the different surface chemistry of the fillers.

3. The study of the influence of the concentration and granulometric composition of fillers on the properties of composites showed that systems with RM provide high plasticity and an open porous structure (with an increase in the RM content from 65 to 90 wt. %, the open porosity increases by 2.4 times), which contributes to energy dissipation. In contrast, systems with chamotte are characterized by greater stiffness, a higher elasticity modulus (129.8 MPa at a concentration of 85 wt. %) and lower total porosity (40.2 % versus 47.6 % for HS at the maximum filler concentration), which makes them suitable for use in conditions of high mechanical loads.

Conflict of interest

The authors declare that they have no conflict of interest regarding this study, including financial, personal, authorship or other, which could affect the study and its results presented in this article.

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Data availability

Data will be provided upon reasonable request.

Use of artificial intelligence

The authors used artificial intelligence technologies within the permissible framework to provide their own verified data, which is described in the research methodology section.

References

1. Ahmed, S., Meng, T., Taha, M. (2020). Utilization of red mud for producing a high strength binder by composition optimization and nano strengthening. Nanotechnology Reviews, 9 (1), 396–409. https://doi.org/10.1515/ntrev-2020-0029

2. Power, G., Gräfe, M., Klauber, C. (2011). Bauxite residue issues: I. Current management, disposal and storage practices. Hydrometallurgy, 108 (1-2), 33–45. https://doi.org/10.1016/j.hydromet.2011.02.006
3. Liu, S., Guan, X., Zhang, S., Dou, Z., Feng, C., Zhang, H., Luo, S. (2017). Sintered bayer red mud based ceramic bricks: Microstructure evolution and alkalis immobilization mechanism. Ceramics International, 43 (15), 13004–13008. https://doi.org/10.1016/j.ceramint.2017.07.036
4. Zhang, M., Zhao, M., Zhang, G., Mann, D., Lumsden, K., Tao, M. (2016). Durability of red mud-fly ash based geopolymer and leaching behavior of heavy metals in sulfuric acid solutions and deionized water. Construction and Building Materials, 124, 373–382. https://doi.org/10.1016/j.conbuildmat.2016.07.108
5. Liu, R.-X., Poon, C.-S. (2016). Utilization of red mud derived from bauxite in self-compacting concrete. Journal of Cleaner Production, 112, 384–391. https://doi.org/10.1016/j.jclepro.2015.09.049
6. Mišík, M., Burke, I. T., Reismüller, M., Pichler, C., Rainer, B., Mišíková, K. et al. (2014). Red mud a byproduct of aluminum production contains soluble vanadium that causes genotoxic and cytotoxic effects in higher plants. Science of The Total Environment, 493, 883–890. https://doi.org/10.1016/j.scitotenv.2014.06.052
7. Mesgari Abbasi, S., Rashidi, A., Ghorbani, A., Khalaj, G. (2016). Synthesis, processing, characterization, and applications of red mud/carbon nanotube composites. Ceramics International, 42 (15), 16738–16743. https://doi.org/10.1016/j.ceramint.2016.07.146
8. Liu, Y., Naidu, R. (2014). Hidden values in bauxite residue (red mud): Recovery of metals. Waste Management, 34 (12), 2662–2673. https://doi.org/10.1016/j.wasman.2014.09.003
9. Liu, W., Yang, J., Xiao, B. (2009). Review on treatment and utilization of bauxite residues in China. International Journal of Mineral Processing, 93 (3-4), 220–231. https://doi.org/10.1016/j.minpro.2009.08.005
10. Mukiza, E., Zhang, L., Liu, X., Zhang, N. (2019). Utilization of red mud in road base and subgrade materials: A review. Resources, Conservation and Recycling, 141, 187–199. https://doi.org/10.1016/j.resconrec.2018.10.031
11. Abdel-Raheem, M., Santana, L. M. G., Cordava, M. A. P., Martínez, B. O. (2017). Uses of Red Mud as a Construction Material. AEI 2017, 388–399. https://doi.org/10.1061/9780784480502.032
12. Carneiro, J., Tobaldi, D. M., Capela, M. N., Novais, R. M., Seabra, M. P., Labrincha, J. A. (2018). Synthesis of ceramic pigments from industrial wastes: Red mud and electroplating sludge. Waste Management, 80, 371–378. https://doi.org/10.1016/j.wasman.2018.09.032
13. Mi, H., Yi, L., Wu, Q., Xia, J., Zhang, B. (2021). Preparation of high-strength ceramsite from red mud, fly ash, and bentonite. Ceramics International, 47 (13), 18218–18229. https://doi.org/10.1016/j.ceramint.2021.03.141
14. Chen, Y., Li, A., Jiang, S. (2024). Wettability and Mechanical Properties of Red Mud–Al2O3 Composites. Materials, 17 (5), 1095. https://doi.org/10.3390/ma17051095
15. Melnyk, L., Svidersky, V., Chernyak, L., Dorogan, N. (2018). Aspects of making of a composite material when using red mud. Eastern-European Journal of Enterprise Technologies, 2 (6 (92)), 23–28. https://doi.org/10.15587/1729-4061.2018.125702
16. Hendricks, H. L., Buchanan, V. E. (2020). Effect of material parameters on the mechanical properties of chemically treated red mud HDPE composites. Polymers and Polymer Composites, 29 (8), 1126–1134. https://doi.org/10.1177/0967391120954064
17. Bhat, A. H., Abdul, H. P. S., K., A. (2011). Thermoplastic Polymer based Modified Red Mud Composites Materials. Advances in Composite Materials - Ecodesign and Analysis. https://doi.org/10.5772/14377
18. Melnyk, L. I. (2023). Kompozyt na osnovi system sopolimer – chervonyi shlam. Modern science: challenges of today. Bratislava, 6–38. Available at: https://ela.kpi.ua/handle/123456789/67229
19. Melnyk, L. I., Cherniak, L. P., Yevpak, V. V. (2024). Composites based on fly ash with different polymer matrixes. Scientific Notes of Taurida National V.I. Vernadsky University. Series: Technical Sciences, 2 (1), 106–112. https://doi.org/10.32782/2663-5941/2024.1.2/18
20. Melnyk, L. (2024). Formation of composite with variation of dispersity of filler and type of binder. Technical Sciences and Technologies, 1 (35), 198–203. https://doi.org/10.25140/2411-5363-2024-1(35)-198-203
21. Brunauer, S., Emmett, P. H., Teller, E. (1938). Adsorption of Gases in Multimolecular Layers. Journal of the American Chemical Society, 60 (2), 309–319. https://doi.org/10.1021/ja01269a023
22. Bodnar, R. T. (2016). Ekspres-metod vyznachennia kraiovoho kuta zmochuvannia porystykh til. Metody ta prylady kontroliu yakosti, 1 (36), 30–38.
23. Vovchenko, L., Matzui, L., Zhuravkov, A., Samchuk, A. (2006). Electrical resistivity of compacted TEG and TEG-Fe under compression. Journal of Physics and Chemistry of Solids, 67 (5-6), 1168–1172. https://doi.org/10.1016/j.jpcs.2006.01.042
24. Hubina, V. H., Kadoshnikov, V. M. (2005). Red mud from the Mykolaiv Alumina Plant – A valuable technogenic raw material. Geological and Mineralogical Bulletin, 2, 122–126.
25. Palmer, S. J., Reddy, B. J., Frost, R. L. (2009). Characterisation of red mud by UV–vis–NIR spectroscopy. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 71 (5), 1814–1818. https://doi.org/10.1016/j.saa.2008.06.038
26. Wang, Q., Wang, D., Chen, H. (2017). The role of fly ash microsphere in the microstructure and macroscopic properties of high-strength concrete. Cement and Concrete Composites, 83, 125–137. https://doi.org/10.1016/j.cemconcomp.2017.07.021