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Synthesis of a composite material based on coal mining waste using wave chemistry methods

Studies for developing composite materials based on coal waste in combination with coal and polymer raw materials under the influence of ultrasound have been carried out within the framework of creating effective and environmentally friendly technologies for the deep processing of coal waste and the production of new valuable import-substituting chemical products for various purposes. Burned rocks (BR) are used as a filler in the composite material that is a product of oxidative self-firing of waste rock extracted along with coal to the surface. Sodium humate (HNa) obtained by alkaline extraction from oxidized coals from the Shubarkol deposit was used as a modifier. A polymer was introduced into the matrix to increase the chemical resistance and increase the life cycle of the composite material. Polystyrene was used as a polymer in the matrix of the composite material. The choice of polystyrene is due to its widespread application in construction, medicine, and food industry as well as its ease of processing. It is distinguished by high rigidity, hardness and excellent transparency values. Composite material was obtained by the traditional method of impregnation using ultrasonic exposure. By varying the composition of the matrix and the filler, a composite material was obtained properties of which were quantitatively and qualitatively different from the properties of each of its components. The X-ray phase composition of new composite materials was studied on a DRON-2.0 diffractometer using Co(Kα) radiation. Microscopic analysis was performed using a scanning electron microscope to study the surface morphology of the synthesized composite. The resulting composite can be used as a building material.

Keywords: burnt rock, sodium humate, ultrasound, polymerization, reaction initiator, styrene, polystyrene, composite material.

Introduction

Questions on the creation of efficient and environmentally friendly technologies for the deep processing of coal waste and the production of new, valuable import-substituting multi-purpose chemical products that are globally competitive are promising and relevant. Burnt rocks that are products of oxidative self-firing of waste rock extracted along with coal to the surface should be considered as an important object of study. Every year in Kazakhstan, about 40 million cubic meters of burnt rock are produced with the underground mining of coal deposits, which are stored in dumps of various shapes and sizes, occupying a large area of land, polluting the air basin and adversely affecting the environment.

Burned rock of coal deposits, resulting from natural self-firing, should be attributed to promising minerals that can be used as raw materials for processing into various products. The disposal of such wastes and the development of methods for obtaining industrially important products on their basis are of current importance for the Republic of Kazakhstan.

The scope and properties of burned rocks are determined by the conditions of formation, namely the composition of the mineral part and the firing temperature. The importance of burnt rocks as a raw material for processing into various products of construction and filtration purposes is confirmed by significant foreign experience [1–5]. Burnt rocks can be used in the production of binding materials in addition to the construction industry [6, 7]. High adsorption activity and adhesion with organic binders allow their use in asphalt and polymer compositions. Burned rock has a ceramic nature and can also be used in the production of heat-resistant concretes and porous aggregates. Some burnt rocks have a lower average density, which allows their use as aggregates for light mortars and concretes [8, 9].

Currently, there is a considerable interest in research related to the development of new methods for producing composite materials based on coal mining waste and polymer raw materials using ultrasonic exposure and the study of their properties.

The combination of coal waste with polymers leads to the creation of new composite materials those properties are quantitatively and qualitatively different from the properties of each of its components. By varying the composition of the matrix and filler, one can get a wide range of materials with the desired set of properties. Therefore, many composite materials are superior to traditional materials in their mechanical properties. It should be noted that very little attention has been paid to the development of composite materials based on burnt rocks with synthetic polymers. One of the most important problems arising from the creation of such composites is associated with the need for a uniform distribution of the polymer matrix. Improvement of the technology of synthesis of composite materials allows the use of ultrasound (US).

The method for producing new multi-purpose composite materials based on coal mining waste and polymer raw materials using ultrasonic activation has been developed in order to improve chemical resistance, reduce porosity, increase density, water resistance, as well as to improve the strength and deformative indicators. In this regard, it is advisable to develop composite materials based on burnt rocks in combination with coal and polymer raw materials under the influence of ultrasound. Such work with such objects has not been described yet in the literature.

Experimental

Polystyrene (PS) was used as a polymer to create a composite material. Pure styrene $C_6H_5CH{=}CH_2$ was used to obtain polystyrene, which is a colorless transparent liquid, with boiling point 145.2 ºC and refractive index n^{20}_4=1.5468. The polymerization of styrene was carried out by a block method in the absence of a solvent, where only monomer and initiator were present in the reaction medium. The initiator used was benzoyl peroxide, the content of which ranged from 0.1 % by weight of styrene. The polymerization process was carried out at a temperature of 80 ºC for 1 hour. There was formed yellowish mass, soluble in benzene, insoluble in water and ethanol. The polymer yield was 48.02 %.

Burned rocks (BR) were used as filler in composite materials that is a product of oxidative self-firing of waste rocks extracted along with coal to the surface modified by the modifier.

Sodium humate obtained by the method of alkaline extraction from oxidized coal from the Shubarkol deposit was used as a modifier. Characteristics of HNa are as follows: ∑COOH + OH — 4.5 mEq/g, ∑COOH — 3.0–3.5 mEq/g, A — 13–15 %, W^a — 10–12 %, nitrogen content — less than 1 % [10].

The ultrasound unit IL-100-6/2 with a maximum power of 1200 W and a cylindrical waveguide was used as an ultrasound source. The device was equipped with an ultrasonic IL-10 generator with a magnetostrictive transducer with an operating frequency of 22 kHz.

Composite material composition polystyrene-burnt rock-sodium humate (PS+BR+HNa, 2:1:1) was synthesized as follows. The objects of study were obtained by the traditional method of impregnation of filler (burnt rock) with a modifier solution (sodium humate) of a given concentration under the influence of ultrasonic treatment for 10 minutes (ultrasound frequency 22 kHz). Next, the mixture was left for impregnation for 24 hours. The composite was dried in a stream of air at 80 ºC for 4 hours after impregnation. The resulting composite material composition (BR+HNa, 1: 1) was further impregnated with hot styrene at a ratio: polystyrene – burnt rock – sodium humate (PS+BR+HNa) that was equal to 2:1:1.

The surface modification of the burned rock was carried out by the methods of impregnation with modifier water solutions at a ratio of BR+HNa (Solid:Liquid = 2:1, 1:1 and 1:2) at 25 ºC, holding suspensions for 1 day, and also under ultrasound conditions radiation, ultrasonic processing time was 0–15 minutes. The control of reactions of modification of the burning rock was carried out by the methods of IR-spectroscopy.

X-ray phase analysis was used to identify mineralogical composition of burnt rock. Phase composition of composites was studied using diffractometer DRON-2.0 with Co(Kα)-radiation λ = 1,7902 Å in interval 10º–90º (2θ), velocity of counter rotation was 2 grad/min, I = 10 mA, U = 30 kV.

Scanning electron microscope MIRA-3 by TESCAN was used for microscopic analysis to study morphology of the composite synthesized.

Results and Discussion

Burnt rocks from the dumps of the mine named after Gorbachev, Karaganda region were used in the work. The burned rocks extracted from the mine's waste heaps are a brick-red fissured, comminuted stones, and washed away with plenty of water to eliminate carbonaceous and other inorganic impurities. The physicochemical characteristics of the burnt rock are presented in Table 1.

Table 1

Burned rock parameters

Sample	Density, kg/m^3	Bulk specific weight, kg/m^3	Porosity, %	Water absorption, %	Mechanical strength, %	
					Grindability	Abrasion
Burnt rocks	2.66	1000	15	5.2	3.7	0.4

Burnt rock used has the following chemical composition, namely silicon (59 %), aluminum (25 %), iron (4–5 %), potassium, calcium, magnesium up to 2 %, sodium, titanium, and phosphorus up to 1 %. The composition of burned rocks includes valuable natural cement that is the result of burning of limestone and clay in the process of burning coal.

Modification was carried out using sodium humate based on oxidized coals from the Shubarkol deposit in order to improve the technical parameters and reduce the porosity of the burned rock. The effectiveness of sodium humate as chemical and structural modifiers for the filler is due to the peculiarities of its molecular structure, polyfunctionality, the ability to various chemical reactions, as well as donor-acceptor and hydrophobic interactions. The method is based on the immobilization of humate in the porous structure of the burnt rock using ultrasonic dispersion.

The optimal ratio of the initial components is the 1:1 ratio and the optimal ultrasound treatment time is 10 minutes. Ultrasonic processing allows achieving a uniform distribution of sodium humate over the entire volume of the rock. The results of silicate analysis of the impregnation of the burnt rock with sodium humate solution of a given concentration under the influence of ultrasonic treatment for 10 minutes showed that ultrasound promoted the change in the content of silicon and aluminum oxides in composites. Thus, under the influence of US in composites, the content of silicon oxides was significantly reduced (58 %) and the content of aluminum oxides (28 %) increased, which significantly reduced the silicate module in comparison with the module of the initial burnt rock. Upon obtaining the composite BR+HNa removal of oxides of iron, titanium, phosphorus and calcium in the filtrate was observed. The content of exchangeable sodium increased significantly. At the same time, the composites were enriched with calcium and magnesium ions, iron and potassium ions went to the filtrate.

The main disadvantage of composite material (BR+HNa) is its poor chemical resistance when operating in real conditions, when the material is influenced by many factors, namely temperature, aggressive environment, mechanical loads, etc. One way to increase the life cycle of composites is to impregnate the surface of a material with polymers and epoxy resins.

We used polystyrene as a polymer in the composite material. The choice of polystyrene is due to its widespread use in construction, medicine, food industry, electrical engineering as well as its ease of processing. Being a rather fragile material, it is distinguished by high rigidity, hardness and excellent transparency values. The main features of polystyrene include lightness, good mechanical properties and low cost compared with other polymers. Polystyrene is relatively low heat resistant, but very water resistant and frost resistant and has exceptional electrical insulating properties. It has the greatest application in the electrical industry. Recently its use has been expanding for the manufacture of building products and materials, in particular in the manufacture of concrete products with improved quality indicators, the so-called polymer concrete.

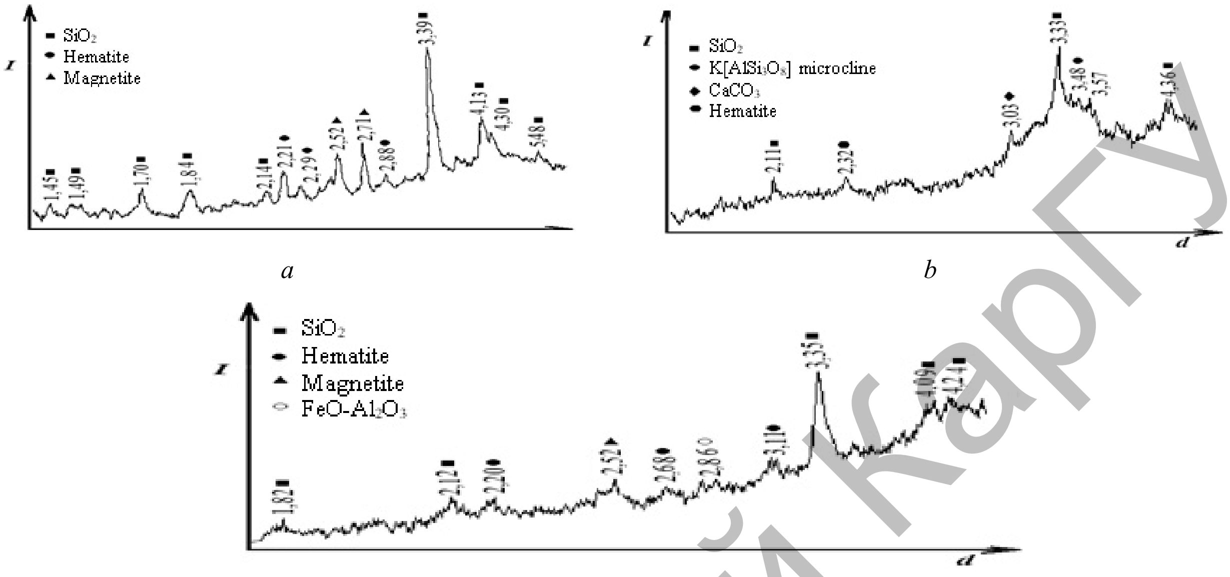
Composite material of polystyrene-burnt sodium-humate rock was obtained by the traditional impregnation method of a modified modifier (sodium humate) of a given concentration under the influence of ultrasound of the filler (burnt rock) with a hot polystyrene solution at a ratio: polystyrene-burnt sodium-humate rock (PS+BR+HNa) that was equal to 2:1:1 and 3:2:1. When cooled, the composite mass hardens. The results of the study are shown in Table 2.

Table 2

Effect of various factors on the yields of composites (PS+BR+HNa)

Composite	Ratio (L:S:S)	US, min	Yield, %
PS+BR+HNa	2:1:1	0	87.40
		10	80.48
	3:2:1	0	79.58
		10	72.20

Among composites PS+BR+HNa = 2:1:1 and PS+BR+HNa = 3:2:1 the composition of PS+BR+HNa = = 2:1:1 (US) is the most promising. Ultrasonic pre-treatment of burnt rock with sodium humate provides a tighter binding between the components. The low content of sodium humate (1/4 of the mass in comparison with the composition of PS+BR+HNa = 3:2:1, where the content of sodium humate is 1/6 of the mass) reduces the chemical resistance of the composite.

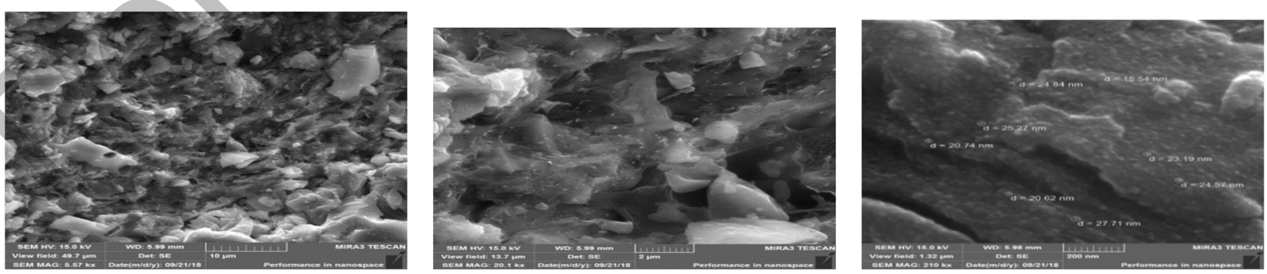


a — the original burning rock; *b* — the composite BR+HNa=1:1 (US=10 min);
c — the composite PS+BR+HNa=2:1:1 (US=10 min)

Figure 1. Radiograph

The inorganic part of burned rocks was represented by feldspar minerals, quartz magnetite and hematite according to X-ray phase analysis (XRA). The main component is α-SiO_2 quartz. The heights are indexed in the interplanar spacing for composite PS+HNa (US), namely d = 2.11 Å, d = 2.32 Å (hematite), d = 3.03 Å (calcite), d = 3.33 Å, d = 3.48 Å (microcline), d = 3.57 Å, d = 4.36 Å. The main component is α-quartz SiO_2 with d = 2.11 Å, d = 3.33 Å, d = 4.36 Å. The heights are indexed in the interplanar spacing for composite PS+BR+HNa (US), namely d = 1.82 Å, d = 2.12 Å, d = 2.20 Å, d = 2.52 Å, d = 2.86 Å, d = 3.11 Å, d = 3.35 Å, d = 4.09 Å, d = 4.24 Å. The main component is α-quartz SiO_2 with d = 1.82 Å, d = 2.12 Å, d = 3.35 Å, d = 4.09 Å, d = 4.24 Å. α-Fe_3O_4 is converted into γ-Fe_2O_3 in the range of 2.52 Å, γ-Fe_2O_3 — d = 2.20 Å, d = 2.68 Å, d = 3.11 Å and $FeO \cdot Al_2O_3$ (microcline) with d = 2.86 Å.

The results of the study of the synthesized composite (PS+BR+HNa=2:1:1) surface morphology are shown in Figure 2.



a — ×5,570 *b* — ×20,100 *c* — ×210,000

Figure 2. Microphotographs of composite PS+BR+HNa = 2:1:1 (US = 10 min)

Pictures of the PS+BR+HNa composite produced by US (Fig. 2) show a rough surface, which consists of two distinct structures, namely darker substrates and lighter inhomogeneous grains that are 10–11 microns in size. Lighter grains rise and have an irregular structure. Troughs and elevations are distinguishable in both structures. An increase of 24,200 times (Fig. 2*b*) shows a part of a dark substrate, which looks like consisting of smoother and more uniform growths with rounded edges, and grainy-like rounded protrusions that are 1–2 μm in size are also distinguishable on them. A further increase (Fig. 2*c*) gives a flat and homogeneous, although not devoid of roughness, surface. The grain is almost completely absent; there are extremely small protrusions, the dimensions of which are much less than a micron, which testifies to the positive influence of the US on the distribution in the composite of components.

Conclusions

Thus, a new composite material was developed using the methods of ultrasonic exposure. By varying the composition of the matrix and filler, the mechanical strength of the composite has been increased. Microscopic analysis was performed using a scanning electron microscope MIRA-3 to study the surface morphology of the composite synthesized. The results of the mapping of the elemental composition of the obtained composites fully confirm their composition. The phase composition of new composite materials was studied on a DRON-2.0 diffractometer using Co(Kα) radiation. The resulting composite can be used as a building material.

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Толқынды химия әдістерін пайдалану арқылы көмір өндіру қалдықтарының негізінде композициялық материалды синтездеу

Көмір өндіру қалдықтарын терең өңдеу және көп мақсатта қолдануға арналған жаңа құнды импорталмастыратын химиялық өнімдерді өндіру бойынша тиімді және экологиялық қауіпсіз технологияларды құру аясында ультрадыбыстың әсерімен көмір және полимер шикізатымен бірге тіркестікте көмір өндіру қалдықтары негізінде композиттік материалдарды әзірлеу бойынша зерттеулер жүргізілді. Композиттік материал құрамында толтырғыш ретінде модификатормен модификацияланған, көмірмен бірге жер бетіне шығарылатын, бос жыныстарды тотықтырғыш өздігінен күйдіру өнімі — жанғыш жыныс қолданылған. Модификатор ретінде Шұбаркөл кен орнының тотыққан көмірінен сілтілі экстракция әдісімен бөлінген натрий гуматы қолданылды. Химиялық төзімділікті жоғарылату және композиттік материалдың өмірлік циклін арттыру үшін матрица құрамына полимер енгізілген. Полимер ретінде композиттік материал матрицасында полистирол қолданылды. Полистиролды таңдау оны өңдеу қарапайымдылығының арқасында құрылыста, медицинада, тамақ өнеркәсібінде кеңінен қолдануға негізделген. Ол жоғары қаттылығы, беріктігі және мөлдірліктің тамаша көрсеткіштерімен ерекшеленді. Композитті материал ультрадыбыстық әсерді пайдалана отырып, дәстүрлі сіңдіру әдісімен алынған. Матрица мен толтырғыштың құрамын түрлендіре отырып, қасиеттері оның әрбір құрамдас қасиеттерінен сандық және сапалық жағынан ерекшеленетін композитті материал алынды. Жаңа композиттік материалдардың рентгенофаздық құрамы ДРОН-2,0 дифрактометрінде Co(Kα)-сәулеленуді пайдалана отырып, зерттелді. Синтезделген композит бетінің морфологиясын зерттеу үшін растрлық электрондық микроскопты қолдану арқылы микроскопиялық талдау жүргізілді. Алынған композитті құрылыс материалы ретінде пайдалануға болады.

Кілт сөздер: жанғыш жыныс, натрий гуматы, ультрадыбыс, полимеризациялау, реакция инициаторы, стирол, полистирол, композитті материал.

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Синтез композиционного материала на основе отходов угледобычи с использованием методов волновой химии

В рамках создания эффективных и экологически безопасных технологий по глубокой переработке отходов угледобычи и производству новой ценной импортозамещающей химической продукции многоцелевого назначения проведены исследования по разработке композитных материалов на основе отходов угледобычи, в сочетании с угольным и полимерным сырьем под воздействием ультразвука. В качестве наполнителя в составе композитного материала использована горелая порода — продукт окислительного самообжига пустых пород, извлекаемых вместе с углем на поверхность, модифицированная модификатором. В качестве модификатора использован гумат натрия, выделенный методом щелочной экстракции из окисленных углей Шубаркольского месторождения. Для повышения химической стойкости и увеличения жизненного цикла композитного материала в состав матрицы введен полимер. В качестве полимера в матрице композитного материала использован полистирол. Выбор полистирола обусловлен его широким применением в строительстве, медицине, пищевой промышленности благодаря простоте переработки. Его отличают высокая жесткость, твердость и отличные показатели прозрачности. Композитный материал получен традиционным методом пропитки с использованием ультразвукового воздействия. Варьируя состав матрицы и наполнителя, получен композитный материал, свойства которого количественно и качественно отличаются от свойств каждого из его составляющих. Рентгенофазовый состав новых композитных материалов изучен на дифрактометре ДРОН-2,0 с использованием Co(Kα)-излучения. Для изучения морфологии поверхности синтезированного композита проведен микроскопический анализ с использованием растрового электронного микроскопа. Полученный композит может быть использован в качестве строительного материала.

Ключевые слова: горелая порода, гумат натрия, ультразвук, полимеризация, инициатор реакции, стирол, полистирол, композитный материал.

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