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Use of Rubber Waste in the Ceramic

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Investigation of ceramic products is presented in the article. It shown that the rubber waste may be used in production of ceramic. The work contains description of rubber characteristics and also presents physical mechanical properties (dry and burning contraction, density, compressive strength, water absorption) and structural parameters (total open porosity, reserve of pore volume) of samples from fusible hydro clays, sand, crushed bricks and foaming mass that 5 % and 10 % of rubber waste. The influence of rubber additive on the mentioned properties of ceramic samples has been determined.

Keywords: ceramics, waste, rubber tyre, utilization of waste.

INTRODUCTION

Solving the waste utilization problems the main three ways of waste handling can be selected: waste reuse, burning of waste or storage in the specially equipped dumps [1].

It has been determined that burning 1 ton of rubber waste (used tyres, conveyor belts, rubber hoses) emits to an ambient air: CO – 0.1 t.; NO_x – 0.007 t.; SO_2 – 0.14 t.; hard particles – 0.1 t (burning down the waste the hard particles are assigned to the II group of pollution) [2].

In recent years various articles on use and utilization problems of rubber waste are presented periodically in the scientific literature.

Rubber waste is a valuable raw material. Modifying various building materials by rubber waste changes their properties.

It has been determined [3] that part of usual sand may be replaced by shredded rubber waste in the production of concrete items. Such additive decreases the elasticity modulus of concrete and improves structural (porosity) parameters.

The authors [4 – 8] state that the rigidity and elasticity of the portlandcement modified by rubber waste is always bigger compared to the ordinary concrete, while the elasticity modulus is lower. Moreover the frost resistance is larger.

In the last years the rubber waste is more rapidly applied in pavement of roads and as an additive of asphalt blacktop [9 – 12]. Investigations show that modifying the road asphalt concrete mixes by rubber waste the fraction of tyres' rubber should be very fine, all additives of steel and other polymeric materials should be removed.

The shredded rubber waste may be applied in the production of bitumen mastics [13, 14]. Applying bitumen-rubber mastics for roof covers the rubber filler improves deformation properties of mastic, however their disadvantage – low flame up temperature and intensive vaporization of solvent. But these disadvantages are insignificant applying such mastics to hydroisolation of foundations, priming of alloyed roof cover bedding.

However mostly the rubber waste of reprocessed auto tyres are used as a fuel in cement industry, furnaces of clinker manufacture [15, 16]. The turning furnace of clinker production has very high temperatures, under which all elements of tyres burn out; the cord melts replacing the usual additive in clinker – iron. Also the heat emitted during the burning of rubber waste is used effectively.

In the paper the results of experiments are presented. The goal of the experiments was to apply the waste of auto tyres in construction ceramics. The physical-mechanical properties and some structural parameters of these samples have been determined.

INVESTIGATION METHODOLOGY, RAW MATERIALS

Chemical compositions of the main raw material were determined by the classical methods of chemical analysis for silicate material [17].

Density of burned ceramic samples was determined according to LST 1272-92 "Ceramics bricks. Specifications". Compressive strength was determined according to LST EN 772 – 1:2003.

Water absorption of samples after 72 hours, total open porosity and reserve of pore volume were determined according to the methodology [18].

Water absorption after 72 hours (%) is determined as:

$$W = \frac{m_1 - m_0}{m_0} \cdot 100\ \% , \qquad (1)$$

where m_0 is the mass of sample dried up to the constant weight (g), m_1 is the mass of sample saturated with water (g).

Parameter of total open porosity characterizes total open porosity space of ceramic sample in the aspect of macrostructure and microstructure. Total open porosity from the water absorption in the vacuum process (%) is:

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$$W_R = \frac{m_2 - m_0}{V} \cdot 100\,\%, \qquad (2)$$

where m_0 is the mass of sample dried up to the constant weight (g), m_2 is the mass of samples saturated by the vacuum process in air (g), V is the volume of samples with open pores (cm^3).

Reserve of pore volume (3) characterises the amount of reserve pores and capillaries, where water hardly penetrates. The larger the reserve of pore volume, the bigger usually is the frost resistance of ceramic body.

$$R = \left(1 - \frac{W_e}{W_p}\right) \cdot 100\ \%, \qquad (3)$$

where W_e is the effective porosity according to the water absorption after 72 h (%), W_p is the total open porosity according to the water absorption in the vacuum process (%).

Phase analysis of burned samples was carried out by X-ray diffraction. The diffraction meter DRON-2 (Russia) with Cu anti-cathode and Ni filter / Fe anti-cathode and Mn filter was used when $U = 30$ kV, $Ia = 8$ mA and rotation speed of the sample was 1°min^{-1}. X-ray diffraction patterns were registered on paper and decoded comparing with the data of PDC catalogues [19].

The fusible hydro-micous clay was selected for investigation (Clay A). Granulometric composition of this clay was in following: amount of sand particles > 0.05 mm is from 0.09 % to 0.77 % amount of dust particles (0.05 – 0.005) mm is from 9.26 % to 21.39 %, and amount of clay particles < 0.005 mm fluctuates from 72.11 % to 96.04 %.

And the fusible devonian clay – B (Lithuania) was selected for the research (Clay B). According to the chemical composition the clay B is semiacid, because the quantity of Al_2O_3 in the heated clay is 15.8 %, the clay belongs to the group with a big amount of colorific oxides as 6.42 % Fe_2O_3, has low dispersion, is impure of coarse carbonaceous inserts ≥3 %, has lot of sand fraction, the amount of free quartz ranges (30 – 60) %. Chemical compositions of the clays are presented in the Table 1.

Table 1. Chemical compositions of the clay

Chemical composition, %	Raw material	
	Clay A	Clay B
SiO_2	47.60	66.33
Al_2O_3+TiO_2	17.79	15.80
Fe_2O_3	7.66	6.42
CaO	6.27	1.80
MgO	3.59	2.72
MnO	0.09	–
K_2O	4.49	1.63
Na_2O	0.55	–
L.o.l.	11.55	5.30

Non-plastic materials used in the work are: crushed bricks, sand. Crushed bricks of encaustic samples were passed through 2.5 mm sieve. Granularity modulus of sand 0.9, amount of dust and clay particles 0.6 %, they grading of the sand present in the Table 2.

Table 2. Grading of the sand

Fraction	Grading [mass, %]	
	Part	Full
2.5	0.02	0.02
1.25	0.044	0.064
0.63	1.89	1.954
0.315	21.13	23.08
0.14	41.76	64.84
< 0.14	35.16	100

The rubber powder with diameter from 0.1 to 1 mm was used in the work. Enlarging the rubber powder (Fig. 1) we can see that there is a cord polymeric splint among them, however there is still no method in the world for separating completely the cord from the rubber during utilization.

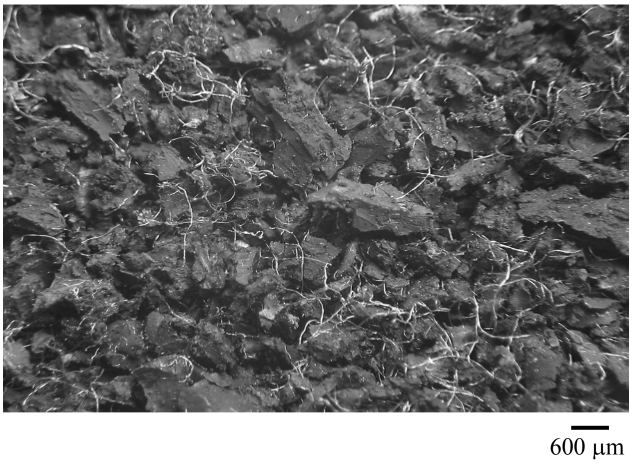

Fig. 1. Picture of the tyre rubber waste (×12 times)

It is difficult to determine the exact chemical composition of tyres' rubber as the tyres of different producers were shredded. As known, composition of tyres may differ widely. Auto tyres may be modified by additives of quartz, variety of silica and alike. We think that after shredding and mixing, the composition of different tyres' rubber equalizes.

The X-ray analysis of the rubber waste burned at 1000 °C temperature has shown (Fig. 2) that there are identified: Zn_2SiO_4 (0.404; 0.348; 0.282; 0.63; 0.232; 0.201; 0.193; 0.186; 0.163; 0.160; 0.155; 0.152; 0.142 nm) and ZnO (0.282; 0.260; 0.247; 0.191; 0.163; 0.148; 0.141; 0.138; 0.136 nm). However the identification of ZnO peaks is quite problematic, because ZnO, $ZnAlO_3(ZnO)_{15}$ or Zr_3O peaks overlap.

In order to determine the physical-mechanical properties, total open porosity, reserve of pore volume, samples

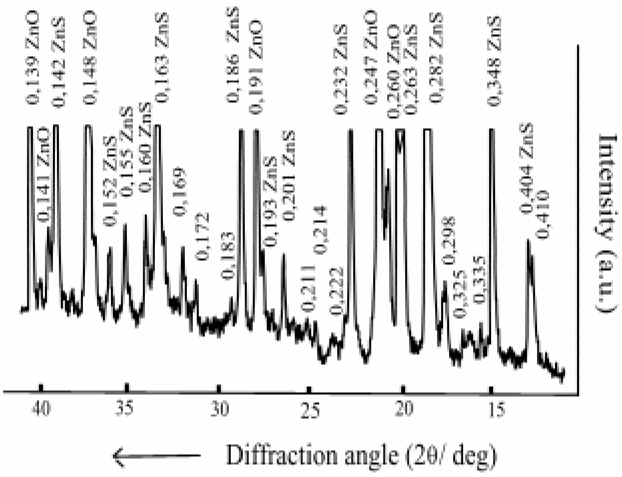

Fig. 2. X-ray diffraction pattern of the rubber waste at burning temperature 1000 °C (notation of index as in the text)

were made by a plastic formation way from the formation mixes presented in Table 4.

The laboratory samples were shaped into the dimensions (70×70×70) mm. At first the prepared samples were dried in a laboratory under natural conditions, later they were left to dry for three days in the electric furnace under temperature from 100 °C to 110 °C.

Table 4. Composition of forming mixtures

No.	Composition, %				
	Clay A	Clay B	Sand	Crushed bricks	Rubber waste
1	17	56	15	5	5
2	15	65	5	5	10
3	20	60	15	5	–

Dried samples were burned in the electric furnace with automatic regulator SNOL-30/1300 (Lithuania) with accuracy of ±1 °C. The sample burning temperature was 950 °C (T1), 1000 °C (T2). The burning time was 40 h, and exposure to the highest burning temperature was 1 h.

The process of burning was programmed in the way the velocity of increasing the samples with or without rubber additive to the temperature 420 °C would reach only (30 – 40) °C per hour. Such low velocity was selected in order the rubber additive would burn out and the cracks worsening properties of ceramic samples would not appear. Subsequent increase of temperature of all formation mixtures under investigation to the highest burning temperature was performed by the speed of (80 – 90) °C per hour.

The dangerous cooling of samples when transformations of quartz phases proceed [20] approximately to the temperature 500 °C was performed slowly – (50 – 70) °C per hour, in order the additional stresses would not occur and the samples would not crack. The very thin, sometimes even invisible cracks would not appear. The cooling in the secure interval was performed faster, at the speed about (100 – 120) °C per hour.

EXPERIMENTAL RESULTS AND DISCUSSION

The contraction of formed mixtures during drying and burning is presented in Fig. 3. One can notice that the contraction of formation mixes during drying is similar, while the contraction during burning is very diverse. The contraction of samples with the rubber additive during burning is ≈7 bigger than the ones without rubber additive. Increasing the burning temperature the contraction during burning changes only slightly.

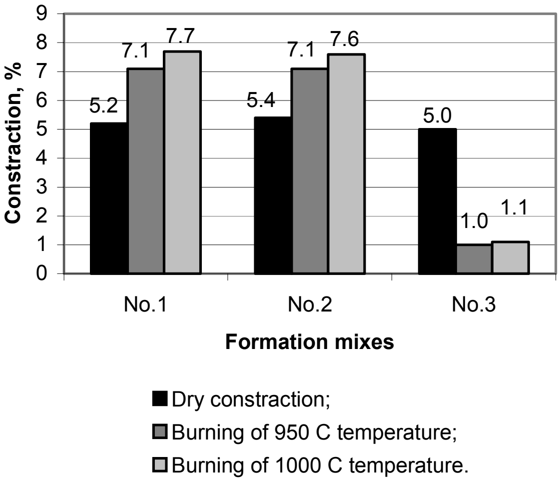

Fig. 3. The contraction of formation mixes during drying and burning

Dependence of density, compressive strength, water absorption after 72 hours and total open porosity on the burning temperature presented in Fig. 4 – 7 (T1 – burning at 950°C temperature, T2 – burning at 1000 °C temperature).

Applying rubber waste in the formation of mixtures, the density and compressive strength decrease, while water saturation increases.

Applying 5 % of rubber additive to the formation of mixture and burning the samples at the temperature 950 °C the density of these samples is 1720 kg/m^3, compressive strength only 6.5 MPa, and water saturation 13.9 %. Increasing the quantity of rubber additive in the formation mixture to 10 %, and burning the samples at the temperature 950 °C their density is smaller – 1575 kg/m^3, compressive strength – 10.2 MPa and water saturation – 15.8 %. Increasing the burning temperature to 1000 °C the values of the mentioned properties change only slightly.

Average compressive strength of the 2nd formation mixture is bigger than the one for the 1st formation mixture. According to our opinion, this is influenced by the amount of non-plastic materials in a formation mixture. The quantity of non-plastic materials in the 1st formation mixture is 20 %. Namely such a big mixture of sand and crushed bricks decreases the compressive strength of samples.

Certainly, the changes of the before-mentioned properties are also influenced by the rubber additive. Rubber powder is assigned to the burning-out additives. During the burning they form various pores and capillaries in a sample due to which the changes in properties occur. This is proved by the obtained total open porosity (Fig. 7).

Total open porosity of a formation mixtures without rubber additive ranges (25 – 27) % depend on the highest burning temperature. Total open porosity of the first formation mixture burned under different temperatures is approximately 33 %. Total open porosity of the formation mixture with 10 % of rubber additive is the biggest, depending on the burning temperature changes from 35 % to 37 %.

Parameter of porous volume reserve is an important feature having large influence on frost resistance of the ceramic samples, because it determines the part of ceramic body porous space that is initially unfilled with water, but fills up gradually under cyclic freezing of sample.

The biggest values of porous volume reserve are determined for the samples of the 1st formation mixture burned under different burning temperatures (Fig. 7). Burning this formation mixture at the temperature 950 °C the parameter *R* (reserve of pore volume) is 37.7 %, burning at the temperature 1000°C – 35.3 %. The values of porous volume reserve of the 2nd formation mixture with 10 % of rubber additive and of the 3rd formation mixture without rubber additive are smaller.

Burning the samples with rubber additive it has been noticed that after burning the core of black colour is formed inside the sample (Fig. 8). During the burning CO, H_2, other gas and water vapour emit and block the way oxygen can enter the sample, i.e. the internal burning of sample proceeds in a reduction medium.

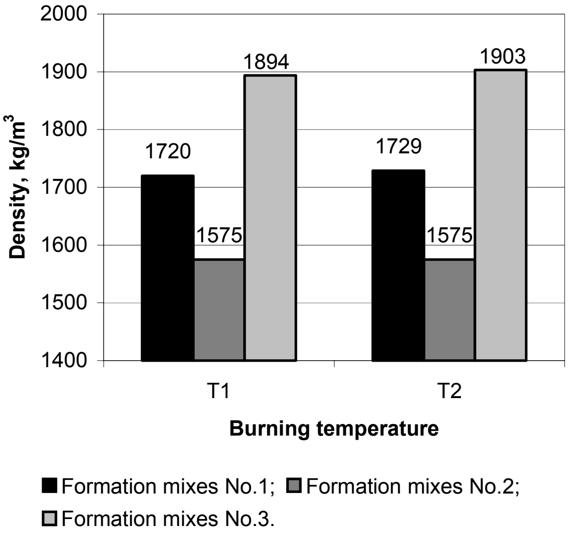

Fig. 4. Dependence of density on the burning temperature

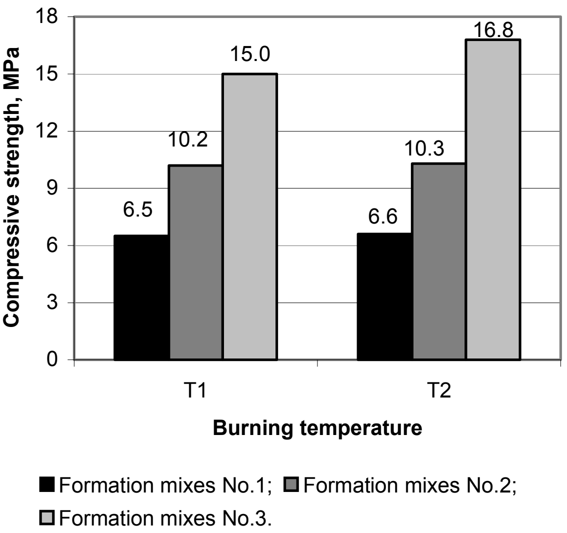

Fig. 5. Dependence of compressive strength on the burning temperature

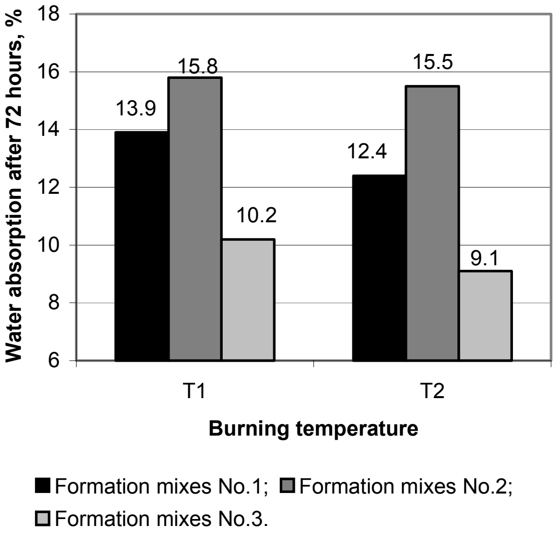

Fig. 6. Dependence of water absorption after 72 hours on the burning temperature

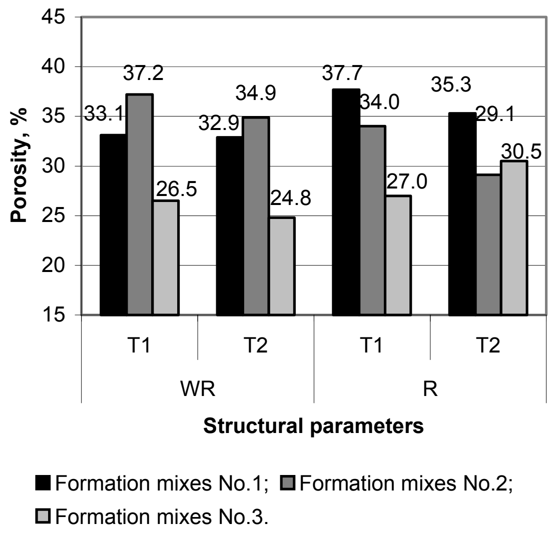

Fig. 7. Dependence of total open porosity (WR) and reserve of pore volume (R) on the burning temperature

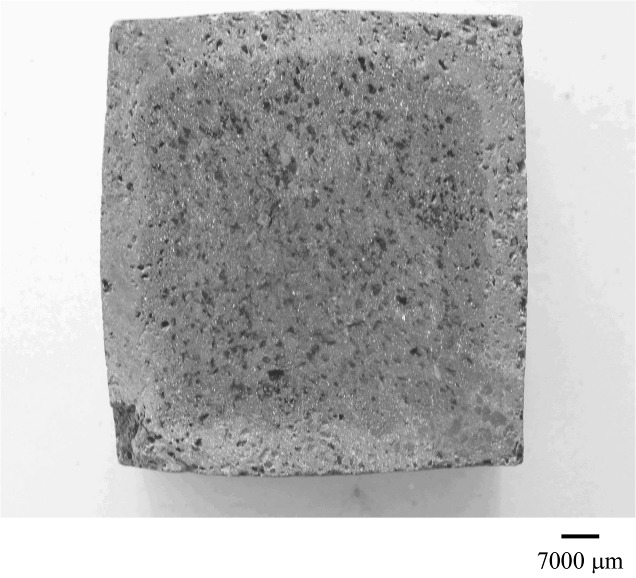

Fig. 8. Picture of the sample with 5 % rubber waste after burning at the highest 950 °C temperature (×1 times)

The author [20] states that in this way the inhomogeneous structure of pores-capillaries in samples is created, internally the structure is coarser, on the surface – finer. Such inhomogeneous structure of pores-capillaries may decrease the exploitation frost resistance.

In the literature [21], it is indicated that the black core may increase or decrease the compressive strength of samples, it depends on the mineralogical composition of a sample.

The X-ray diffraction patterns of sample of the ceramics body without of 10 % rubber waste additive are presented in Fig. 9.

The identified mineral are: quartz – Q (0.425, 0.335, 0.246, 0.227, 0.224, 0.213, 0.198, 0.182, 0.167, 0.154 nm), anortite – A (0.404, 0.370, 0.346, 0.320, 0.253 nm), hematite – He (0.269, 0.253, 0.221, 0.185, 0.169 nm), spinel – Sp (0.246, 0.202, 0.157 nm), dioxide – D (0.299, 0.294, 0.289, 0.173 nm).

CONCLUSIONS

The rubber waste of shredded auto tyres as an additive applied in ceramic products influences physical and mechanical properties of samples – contraction during burning, density, compressive strength and water saturation, also the investigated structural parameters – total open porosity and reserve of porous volume. During burning the rubber powder forms various pores and capillaries, due to which the changes of the mentioned properties take place.

Applying 5 % of rubber additive to a formation mixture, the density of samples is approximately 1725 kg/m^3, compressive strength – 6.5 MPa, water saturation – 13 %. Total open porosity of such ceramic body is 33 %, and the value of porous volume reserve is the biggest – 36 %. Therefore it could be expected that the frost resistance of this formation mix would be the biggest.

Light ceramic samples are obtained applying 10 % of rubber additive to a formation mixture; density of these samples is 1575 kg/m^3. Compressive strength of this ceramic body is 10 MPa, water saturation – 15 %.

It has been determined that the gas comprising during burning of formation mixes with rubber additive colours a ceramic body black, i. e. the internal burning of a sample proceeds in a reduction medium and during cooling the surface oxidizes. The burning out additive affects the parameters of burning process therefore additional investigations should be carried out further on.

The X-ray analysis has shown that application of rubber additive to a formation mixture does not change the mineralogical composition of the samples.

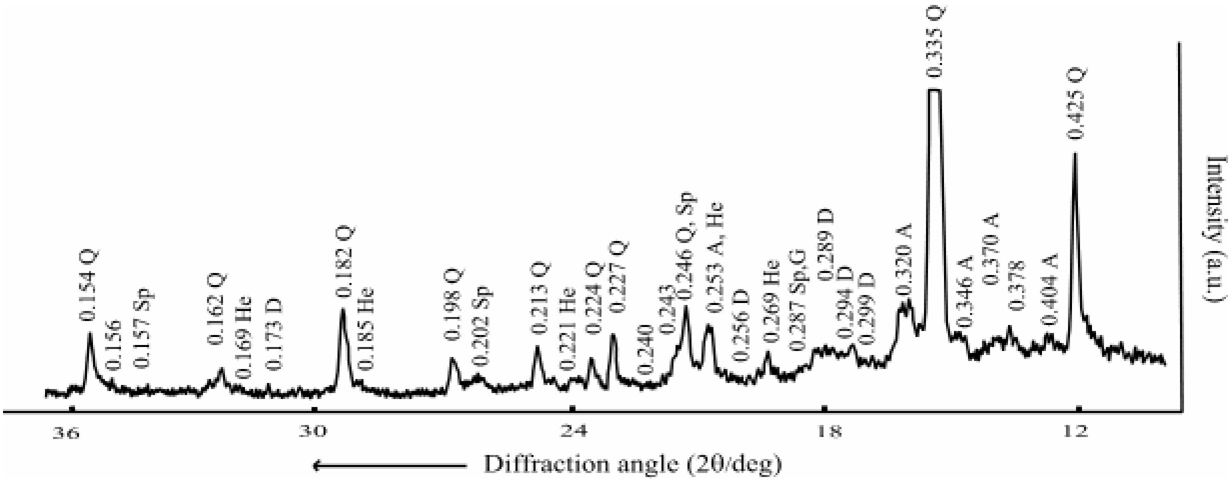

Fig. 9. X-ray diffraction pattern of examples of the ceramics body with 10 % of rubber waste additives at burning temperature 1000 °C (notation index as in the text)

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