A Szilikátipari Tudományos Egyesület lapja

építőanyag

Journal of Silicate Based and Composite Materials

A TARTALOMBÓL:

- Critical state desiccation induced shrinkage of biomass treated compacted soil as pavement foundation
- Rheology and strength of concrete made with recycled concrete aggregates as replacement of natural aggregates
- The role of explosive ordnance decontamination in the field of building trade
- Electrochemical characterization of polymeric sensor of poly-acrylonitrile self-modified with carbon nanotubes (CNT)
- Potentials of calcined clay as a pozzolan
- Thermal and mechanical properties of fabricated plaster of Paris filled with groundnut seed coat and waste newspaper materials for structural application

2020/2

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Critical state desiccation induced shrinkage of biomass treated compacted soil as pavement foundation

Biomasszával kezelt tömörített járda alap talajának kritikus állapotbeli kiszáradás okozta zsugorodása

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Abstract

Volumetric shrinkage critical state induced by desiccation of compacted earth treated and improved with Rice Husk Ash (RHA) and utilized as pavement foundation has been investigated in the laboratory. The critical state study was important to determine at what level of earth improvement with the biomass material can be considered safe in terms of shrinkage behavior of treated soft soil utilized in pavement construction. Rice Husk (RH) is an agricultural waste discharged during rice production and is disposed on landfills. It causes land pollution in places like Abakaliki and Ebonyi State, Nigeria as whole where rice farming is the predominant occupation. Ground and soil improvement with the use of rice husk ash has contributed in the management of solid waste in the developing countries where rice production is a common occupation with its attendant solid waste generation. However, the use of biomass-based binders like RHA has reduced the rate at which oxides of carbon are released into the atmosphere, which contribute to greenhouse emission effects. This exercise is an environmentally conscious procedure that keeps the environment safe from the hazards of carbon and its oxides. the preliminary investigation on the test soil showed that it is classified as an A-7-6 soil group according to AASHTO classification. The index properties showed that the soil was highly plastic with high clay content. The RHA was utilized at the rate of 2%, 4%, 6%, 8% and 10% by weight of treated solid to improve the soil volumetric shrinkage induced desiccation at molding moisture conditions of 2% dry, 0%, 2% wet, and 4% wet of optimum moisture. This was necessary to establish the behavior of hydraulically bound foundation materials subjected to dry and wet conditions during the rise and fall of water tables. Results of the laboratory investigation have shown that at 2% dry of optimum moisture, the volumetric shrinkage (VS) behavior performed best and reduced below the critical line of 4% at 8% by weight addition of RHA and maintained that consistent reduction at 10% addition of RHA. Generally, the critical point was achieved at 8% by weight addition of RHA at all the molding moisture conditions. This is an indication that at molding moisture conditions between -2% to 4%, 8% by weight addition of the admixture, RHA can be utilized as an environmentally conscious construction material to improve the VS of soils for use as hydraulically bound materials in pavement foundation construction.

Keywords: critical state, volumetric shrinkage, desiccation, biomass pavement foundation, treated compacted earth, lignocellulosic material
Kulcsszavak: kritikus állapot, térfogati zsugorodás, kiszáradás, biomassza járda alap, kezelt tömörített föld, lignocelluláris anyag

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1. Introduction

Solid waste handling and management around the world and especially in the third world countries have contributed to the alarming amounts of carbon oxides emission and on the threat of global warming. On the other hand, Laterite has served as foundation material for pavement ever since road existed, the need to analyze this material and subsequently improve on the quality of roads has been a serious issue to highway Engineers. One critical concern in the use of laterite is the swell – shrink property of the lateritic material. Expansive soils (lateritic soils with high plasticity index above 17) are prone to large volume changes that are directly proportional to moisture exposure. Therefore, the low bearing strength and compressibility behavior as a result of constant exposure to moisture under hydraulically bound conditions causes severe damage and deterioration to subgrade. Due to the rise and fall of the water table which is triggered by rainfall percolation and subsequent capillary action or suction, the compacted sub-grade layer is constantly subjected to swelling and shrinkage cycle [1-4]. The road embankment is regularly under hydraulically bound condition, and the compacted earth serves as hydraulic barrier in waste containment facilities [5] and also as subgrade/embankment layer of the road. Swelling and shrinkage properties of laterite have contributed immensely to road failures, and therefore measures to ameliorate these would be of great importance to the Engineer.

The swelling and shrinkage properties of soil are not excluded in stabilized soil but can be minimized, this is due to the physical and chemical properties of soil, swelling occurs during water absorption and shrinks when water dries up. Generally, swelling and shrinking are major factors which affect the development of fissures in lateritic soil [6]. These fissures separate the soil surface and gradually close down into the deeper soil and in turn give rise to different problems of stability. Clayey soil is observed to give different characteristics in wet and dry conditions, it possess desirable sorption characteristics when wet and crack with dust emitted when dry [7]. These cracks break down continuity of soil mass, thereby reducing its strength and soil stability is affected. It grants surface water easy infiltration into the soil. When laterite is soaked with infiltrated water, it collapses and loose strength. Structures built on a soil with stability problem such as this, especially pavements, will in turn collapse with the soil. To a large extent, fissures are closely related with the swell - shrink characters.

Modification and stabilization are two basic soil improvement technique [8], these enhance the mechanical behavior to suit construction requirements. Additives such as cement, lime, fly ash and bituminous materials have been used in common practice to improve the strength and other characteristics of laterite [9]. This has kept the cost of roads construction increasingly high due to increasing cost of the stabilizing agents. Thus, the use of agro-industrial wastes (such as rice husk ash) will lead to a considerably reduced cost of construction, minimize environmental hazards and enhance economical value chain of the farmers [10].

Rice husk ash has been validated through several researches as an effective partial replacement for stabilizing agents such as cement, lime etc. Globally, it is estimated that an average of about 160 million tons of rice husk ash are produced annually [10]. The addition of RHA reduces the plasticity and increase volume stability as well as the strength of the soil [11]. Combined application of RHA and lime can modify the expansive soil by reducing the swelling index and improve its strength and bearing capacity. In the above background analysis, it can be observed that relatively new and sustainable approach, which are environmentally conscious soil improvement has emerged. It is also important to note at this stage that for materials to be considered to be utilized in geotechnical engineering works, a maximum requirement of 4% for the volumetric shrinkage strain is recommended [12].

This paper seeks to study the effect on critical state desiccation of rice husk ash treated soil compacted earth when used as pavement foundation.

2. Materials and methods

2.1 Materials

Soil: The soil utilized in the laboratory experimentation was obtained by disturbed sampling method at depths of 1 to 3 meters from a borrow site located in Amaoba, Ikwuano Local Government Area, Abia State, Nigeria. The map location of the soil sample source is presented in *Fig. 1*.

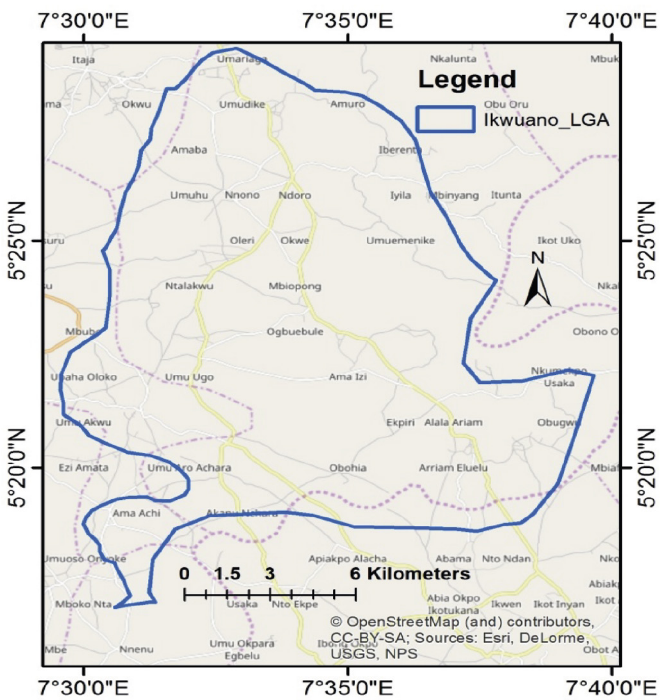

Fig. 1 Test soil sample location map
1. ábra Vizsgált talajminták földrajzi elhelyezkedése

Rice Husk Ash: Rice Husk (RH) is an agricultural solid waste belonging to the lignocellulosic biomass discharged from the harvesting and milling of rice. It is normally disposed on landfills and this practice constitute pollution of the environment. The RH used in this laboratory exercise was collected from Rice Mills in Abakaliki, Ebonyi State, Nigeria where rice farming and production is prevalent and common. Conversely, Rice Husk Ash (RHA) is derived from the direct combustion of the above lignocellulosic biomass released from rice production.

2.2 Methods

Rice Husk Combustion:

Rice Husk (RH) is a biofuel that combusts releasing high amount carbon and its oxides. The method of combustion employed here is the controlled incineration method developed by K. C. Onyelowe *et al.* [13] known as the Solid Waste Incineration NaOH Oxides of Carbon Entrapment Model. In this method, the oxides of carbon released are entrapped in a reaction jar containing 40 v/v NaOH solution, which has very strong affinity with oxides of carbon. At the end of the process, ash is derived and soda ash, baking soda and hydrogen gas are released through the outlet as presented in the waste valorization and gas sequestration cycle (see *Fig. 2*).

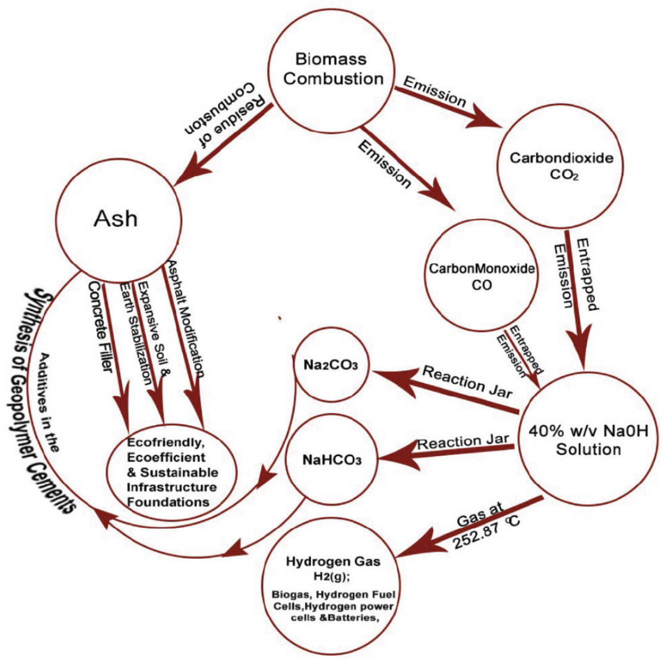

Fig. 2 Biomass valorization, carbon sequestration and hydrogen gas separation and capture cycle
2. ábra Biomassza hasznosítás, szén megkötés, hidrogén gáz elválasztás és megkötés körforgása

Preparation of Specimens: 2000 g of crushed open-air dried soil sample passing through sieve number 4; aperture of 4.76 mm was secured and readied for the experimentation. The specimens were prepared by deep and thorough blending and mixing at molding moisture contents of 2% dry, 0%, 2% wet and 4% wet of optimum moisture content, of the soil and varying percentages of the RHA in proportions of 2%, 4%, 6%, 8% and 10% by weight of treated solid. The standard proctor mold was used in this exercise to compact the specimen in accordance with appropriate standards.

Index Properties: Moisture content of the natural soil, specific gravity, and gradation characteristics were determined in accordance with experimental protocols presented in British Standard International [14].

Atterberg Limits: The consistency limits; liquid limit, plastic limit and plasticity index values were determined for the both the natural and treated soils in accordance with British Standard International [14; 15]. It was observed that the liquid limits decreased from 54% for the natural soil to 31% at the RHA treatment of 8% and increased to 36% at the RHA treatment of 10%. The plastic limit showed similar behavior and decreased from 26% for the natural soil to 17% at 8% treatment with RHA and increased again to 10% treatment of RHA. Generally, the plasticity index consequently showed the same trend and reduced to medium plastic condition of 14% at 8% treatment with RHA from a highly plastic condition of 28% for the natural soil.

Compaction Properties: The treated specimens were compacted using the standard proctor mold in accordance with British Standard International requirements presented in BS 1377 [14] and BS 1924 [15] to determine the maximum dry density (MDD) and the optimum moisture content (OMC).

Volumetric Shrinkage: In an effort to determine the volumetric shrinkage (%) of the specimens, the compacted materials were extruded from the standard proctor compaction mold and air dried for 12 days under temperature conditions of 24±2°C and measurements of diameters and heights were taken every other three (3) with the aid of a Vernier caliper of 0.01 mm precision. The changes in dimensions of the specimens with drying days were observed and recorded.

3. Discussion of results

3.1 Index and preliminary properties of the natural and treated soil

Table 1 represents the index and preliminary properties of the test soil. From *Table 1* the following can be observed and deduced;

Soil Classification using AASHTO System: AASHTO soil classification system classified soils in accordance with their performance as subgrade. To classify the soil, laboratory tests including sieve analysis, hydrometer analysis, and Atterberg limits are used to determine the group of the soil. In the AASHTO system [16], the soil is classified into seven major groups: A-1 through A-7 and the soil under investigation is classified as A-7-6 as more than 35% of the sample passed through sieve no 200, i.e., 38%, and its liquid and plastic limits are 54% and 26%, which exceeds 41% and 11% respectively, being the minimum requirements for liquid and plastic limits of soils in this category. However, soils in this category are generally rated for subgrade use as fair to poor.

Unified Soil Classification System: On the basis of the Unified Soil Classification System (USCS), soil with > 50 % of sample mass retained on the 0.074 mm sieve is term coarse-grained and if > 50 % of the coarse fraction is retained on 4.76 mm sieve, the soil is classified as gravel but if ≥ 50 % of the coarse fraction passes 4.76 mm sieve, such soil is sandy soil. Also the gravelly of sandy soil is classified further as well graded gravel/sand (GW or SW) or poorly graded gravel/sand (GP or SP) if percentage of the soil fines is < 5 %, but if the percentage of the soil fines is > 12 %, the soil plasticity index is plotted against its liquid limit and the soil is classified as gravel/sandy clayey (GC or SC) or gravel/sandy silty soil (GM or SM) depending on its position on the chart. On the other hand, if ≥ 50 % of the sample mass passes the 0.074 mm sieve, the soil is classified as fine-grained soil. The plasticity index of the soil fine-grained is then plotted against its liquid limit on plasticity chart to further distinguish the soil as silt or clay of low, medium, or high plasticity. Based on the Unified Soil Classification System (USCS) results shown in *Table 1*, the soil is poorly graded (GP) and is a clayey soil of high plasticity (CH). However, it was observed that addition of RHA at 4%, 6%, 8% and 10% improved the soil to clayey soil of medium plasticity (CL).

Sieve Analysis: The grain size analysis test results for the soil sample were summarized in *Table 1*. The values which were obtained from the gradation tests were analyzed with respect to the effect of pre-treatment and soil variations along lateral and depth wise. According to British Standard [14] the %passing the 0.075mm BS sieve should be < 35% for subgrade. From the sieve analysis result carried out, 38% of the particles passed through the 0.075mm sieve. Hence the soil is not suitable for use as pavement subgrade.

Soil Consistency Index: Soil consistency index examined was Atterberg limit and widely used to differentiate soil types and states. The liquid limit, w_L and plastic limit, w_p, plasticity index I_p, and linear shrinkage of the soil were determined in order to examine the influence of RHA contents used in its treatment. In *Table 1* above, the results of Atterberg limits were represented, and it was clearly indicated that the values of the liquid limit w_L (54%) and plastic limit (26%) w_p decreased with increasing proportion of RHA, from 54% to 48% and 26% to 23% at 2%, 48% to 42% and 23% to 20% at 4%, 42% to 36% and 20% to 19% at 6% and from 36% to 31% and 19% to 17% at 8% for liquid limit and plastic limit respectively. An increase was also observed in the values of liquid and plastic limits at 10% addition of RHA, from 31% to 36% and 17% to 20% respectively. According to BS 1377 [14], subgrade/fill material should have liquid limit ≤50% and plasticity index ≤30% while for sub-base, liquid limit should be ≤ 30% and plasticity index ≤ 12%. However, it can be observed that this soil is unsuitable for use as a pavement subgrade in its original state, but stabilizing same using RHA reduced the liquid limit and plasticity index, making it very suitable for use as pavement subgrade.

Specific Gravity: Specific gravity of the soil samples under investigation was determined using AASHTO T22 03, T85-91 procedures [17]. The specific gravity of the soil sample from the result above gave 2.05 and it is perfect for identifying poorly graded soils. It was also observed that addition of RHA at 2%, 4%, 6% and 8% increased the specific gravity of the soil sample to 2.08, 2.25, 2.42 and 2.70 respectively. At 10% addition of RHA, a decrease in specific gravity of the soil from 2.70 to 2.50 was observed. This however shows that RHA is a very good stabilizer for poorly graded soils.

MDD (mg/m³) and OMC (%): Compaction Test was carried out and tabulated to determine the compaction properties i.e., Maximum Dry Density and Optimum Moisture Content of the studied soil. The compaction result shows that the maximum dry density (MDD) of the sample has a value of 1.85mg/m³ and optimum moisture content (OMC) of 12%. The range of values that may be anticipated when using the standard proctor test methods are: for clay, maximum dry density (MDD) may fall before 1.44 mg/m³ and 1.685 mg/m³ and optimum moisture content (OMC) may fall between 20-30%, for silty-clay MDD is usually between 1.6 mg/m³ and 1.845 mg/m³ and OMC ranged between 15-25% and for sandy clay, MDD usually ranged between 1.76 mg/m³ and 2.165 mg/m³ and OMC between 8 and 15%. Thus, looking at the results of the soil samples, it is observed that the sample is sandy-clay. The low values of the dry density indicate that the natural deposits are loose and accounts for the high void ratio. However, the addition of RHA increased the value of the MDD, while decreasing the value of the OMC respectively from 1.85 mg/m³ and 12% to 2.00 mg/m³ and 11% at 2%, 2.30 mg/m³ and 9% at 4%, 2.70 mg/m³ and 8% at 6% and 2.85 mg/m³ and 8% at 8%. A decrease in value of MDD and increase in OMC was also observed at 10% addition of RHA 2.85 mg/m³ and 8% to 2.75 mg/m³ and 10% respectively. These substantial improvements recorded on the addition of RHA are due to the high binding strength and the aluminosilicate composition of the additive (see *Table 2*)

pH Value: Soil pH is a measure of the acidity or alkalinity of the water held in its pores. The pH scale goes from 0 to 14, with 7 representing neutral. From pH 7 to 0 the soil is increasingly acidic, while from 7 to 14 it is increasingly alkaline. *Table 1* shows that the soil has a pH value of 7.2 and the addition of RHA at higher proportions further increases the soil's alkalinity.

Property	0%	2%	4%	6%	8%	10%
Natural Moisture Content, %	14	-	-	-	-	-
Liquid Limit, %	54	48	42	36	31	36
Plastic Limit, %	26	23	20	19	17	20
Plasticity Index, %	28	25	22	17	14	16
Linear Shrinkage, %	8	6.5	5.5	5.2	4.5	3.2
Percentage Passing BS sieve No. 200 (0.075mm)	38	41	43	47	51	55
AASHTO Classification	A-7-6	-	-	-	-	-
USCS Classification	GP, CH	GP, CH	GP, CL	GP, CL	GP, CL	GP, CL
Specific Gravity	2.05	2.08	2.25	2.42	2.70	2.50
Maximum Dry Density, g/cm³	1.85	2.00	2.30	2.70	2.85	2.75
Optimum Moisture Content, %	12	11	9	8	8	10
pH Value	7.2	7.4	7.6	7.8	8.1	8.3
Color	Red	Reddish brown	Reddish brown	Reddish brown	Reddish ash	Reddish ash
Dominant Clay Mineral	Illite	-	-	-	-	-

Table 1 Physical properties of the untreated and RHA treated soils
1. táblázat Kezeletlen és RHA kezelt talajok fizikai jellemzői

Materials	Oxides composition (content wt %)												
	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	K_2O	Na_2O	TiO_2	LOI	P_2O_5	SO_3	IR	Free CaO
study soil	35	12.09	7.36	8.66	5.90	12.0	13.4	-	-	5.5	-	-	-
RHA	86.0	3.3	3.6	3.2	0.45	-	-	-	3.45	-	-	-	-

*IR is Insoluble Residue, LOI is Loss on Ignition, RHA: rice husk ash.

Table 2 Oxides composition of the materials used in this paper
2. táblázat A cikben használt anyagok oxidos összetétele

3.2 Effect of Rice Husk Ash (RHA), Drying Time (DT) and Molding Moisture (MM) on the Volumetric Shrinkage of Treated Soil

Up to 10% by weight of RHA was utilized in the treatment of soft soil and the volumetric shrinkage (VS) behavior as a result of this treatment procedure was observed. These blending and mixing were achieved with four various molding moisture conditions of -2%, 0%, 2% and 4% of optimum moisture and subjected to different drying periods to a maximum of 12 days and measurements were recorded on 0, 3, 6, 9 and 12 days. *Figs. 3, 4, 5* and 6 and *Tables* 3, 4, 5 and 6 present the graphical behavior of VS against percentage RHA treatment and tabulated behavior of the soil treated with RHA, molded under different moisture conditions and dried at different days. It can be observed that the VS reduced consistently with increased RHA where the soil was treated under 2% dry of optimum moisture in *Fig. 3*. Throughout the curing period, the VS also reduced considerably and all fell below VS of 4%, which according to standard requirements is the critical point above which a material cannot be considered good for use as a subgrade foundation under hydraulic bound conditions. This shows that RHA can be used to treat soft soils of similar properties under 2% dry of optimum molding conditions beyond 8% by weight. This behavior is attributed to the highly pozzolanic properties of RHA, which acted as an environmental conscious binder improving hydration reaction, cementation, calcination, and flocculation and reduced consistently the tendency for the treated material to be affected by shrinkage [18; 19]. Another reason for this behavior was because of the cation exchange that took place at the interface between soil polarized ions and those of the admixture within the diffused layer. Thirdly the fineness of the ash material contributed to filling process within the voids, which improved the space-mass index of the treated material. In *Fig. 4*, the treatment process was achieved under optimum moisture molding conditions i.e. 0% of optimum moisture. This condition is hardly experienced in the field where foundations are subjected to rise and fall of water table like the pavement foundation. This is due to the fact that water table rises when it rains and drops during dry seasons. In Nigeria for example, during spring and fall in many parts of the country, there always rain and this brings about the rise in water table while during winter, the water table falls considerably. So, pavement foundations, which are hydraulically bound structures suffer as a result. It can be observed that at 8% by weight addition of RHA, the VS fell below the critical point (4%), which is safe for treated soil materials to be utilized as subgrade foundation materials. In *Fig. 5*, wetting moisture condition of molding started where the treated material was molded with 2% wet of optimum moisture. This happens when the water table rises and expose foundation materials to moisture ingress or migration through the poorly compacted or cracked layers. It can also be observed that at 8% by weight addition of RHA, the VS dropped to below 4% point safe for materials to be used but beyond that to 10% addition, the VS abruptly increased again beyond the critical line. This shows that, at the molding moisture condition of 2% wet of optimum, the RHA cannot be utilized beyond 8% again (see *Table 3*). This behavior was due to the added moisture which restarted the hydration reaction and created space for volume changes thereby increasing the shrinkage properties again in a renewed cycle. In *Fig. 6*, the molding moisture was increased and the condition wasn't encouraging as the behavior of the VS resided above the critical line except also at 8% by weight addition of RHA and at 12 days drying time. This is due to excessive molding moisture within the clayey mass of treated soil, which increase swelling properties and VS properties. On the hand, *Figs. 7, 8, 9* and *10* show the response of VS with respect to the various drying periods in days. It can be observed that the VS reduced with increased exposure to drying conditions corresponding also to increased addition of RHA. The best result was obtained at 2% dry of optimum molding moisture condition and at the RHA treatment rate of 8% by weight. This shows that the longer the foundation materials treated with RHA stay through the drying period, the better and more reliable the strength development and a corresponding improvement in the volumetric shrinkage (VS) [20]. It is also important to remark that the VS obtained at the optimum moisture condition is reliable but beyond that line, on the molding moisture side, the treated material start to suffer the effect of moisture exposure. It is obvious that at molding moisture of 4% wet of optimum, the treated soil fails to meet the VS requirements.

Volumetric Properties	Air Drying Period (Days)	RHA treated soil compacted at 2% dry (-2%) of optimum (%)					
		0	2	4	6	8	10
Volumetric Shrinkage Strain (%)	0	10	9	7.5	5.5	4	3.5
	3	9.5	8	7	5.2	3.8	3.2
	6	8.5	7.5	6.5	5	3.5	3
	9	7.8	7.2	6	4.8	3.3	2.8
	12	7.5	7	5.5	4.5	3.1	2.5

Table 3 Desiccation of RHA treated soil compacted at 2% dry (-2%) of optimum
3. táblázat RHA-val kezelt talaj száradása az optimálisnál 2%-kal szárazabban tömörítve

Volumetric Properties	Air Drying Period (Days)	RHA treated soil compacted at 0% of optimum (%)					
		0	2	4	6	8	10
Volumetric Shrinkage Strain (%)	0	12	10	7.5	5.5	4	5.2
	3	11	8.5	6.5	5	3.8	4.8
	6	9	7.5	6	4.5	3.5	4.5
	9	7	6.8	5.5	4.2	3.2	4.3
	12	6	5.5	5	4.1	3	4.2

Table 4 Desiccation of RHA treated soil compacted at 0% of optimum
4. táblázat RHA-val kezelt talaj száradása az optimálisan tömörítve

Volumetric Properties	Air Drying Period (Days)	RHA treated soil compacted at 2% wet (+2%) of optimum (%)					
		0	2	4	6	8	10
Volumetric Shrinkage Strain (%)	0	15	12	8	6.5	4.1	5.5
	3	11	9	7.5	5.8	4	5.2
	6	8	7.5	6	5.2	3.8	4.8
	9	6	5.5	5	4.5	3.5	4.5
	12	6	5	4.5	4.3	3.5	4.3

Table 5 Desiccation of RHA treated soil compacted at 2% wet (+2%) of optimum
5. táblázat RHA-val kezelt talaj száradása az optimálisnál 2%-kal nedvesebben tömörítve

Volumetric Properties	Air Drying Period (Days)	RHA treated soil compacted at 4% wet of optimum (%)					
		0	2	4	6	8	10
Volumetric Shrinkage Strain (%)	0	18	14	12	9	7	5.5
	3	17	13	10	7.5	6.5	4.5
	6	15	12	9.5	6.8	5.5	4.2
	9	11	8.5	7.5	5.5	4	4
	12	8	7.5	5.8	4.5	4	4.2

Table 6 Desiccation of RHA treated soil compacted at 4% wet (+4%) of optimum
6. táblázat RHA-val kezelt talaj száradása az optimálisnál 4%-kal nedvesebben tömörítve

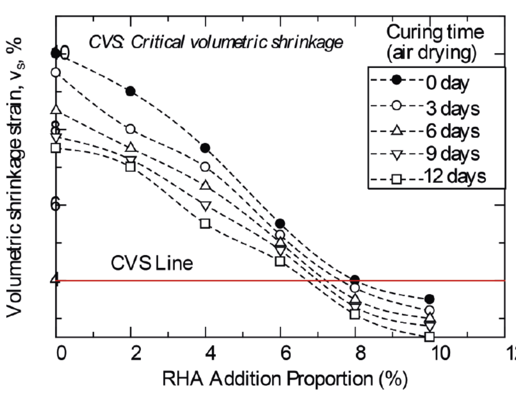

Fig. 3 Volumetric shrinkage of RHA treated soil compacted at 2% dry (-2%) of optimum moisture
3. ábra Optimális víztartalomnál 2%-kal szárazabban tömörített RHA kezelt talaj térfogati zsugorodása

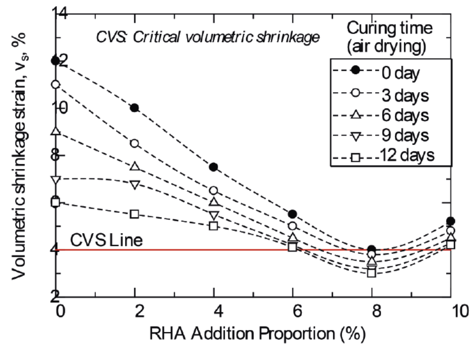

Fig. 4 Volumetric shrinkage of RHA treated soil compacted at optimum moisture
4. ábra Optimális víztartalom mellett tömörített RHA kezelt talaj térfogati zsugorodása

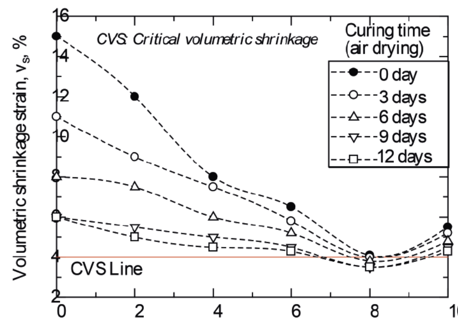

Fig. 5 Volumetric shrinkage of RHA treated soil compacted at 2% wet (2%) of optimum moisture
5. ábra Optimális víztartalomnál 2%-kal nedvesebben tömörített RHA kezelt talaj térfogati zsugorodása

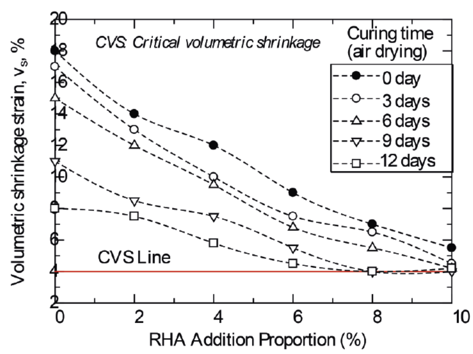

Fig. 6 Volumetric shrinkage of RHA treated soil compacted at 4% wet (+4%) of optimum moisture
5. ábra Optimális víztartalomnál 4%-kal nedvesebben tömörített RHA kezelt talaj térfogati zsugorodása

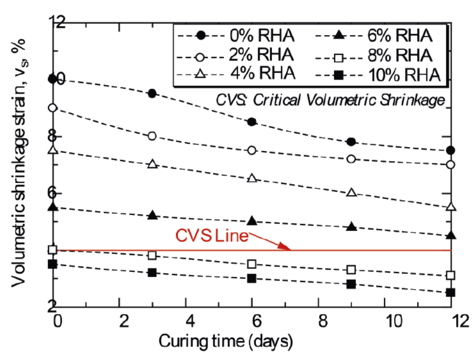

Fig. 7 Volumetric shrinkage against curing time of soil treated with RHA at 2% dry of optimum moisture molding condition
7. ábra RHA kezelt talaj térfogati zsugorodása az utókezelési idő függvényében optimális nedvességtartalomnál 2%-kal szárazabban készítve

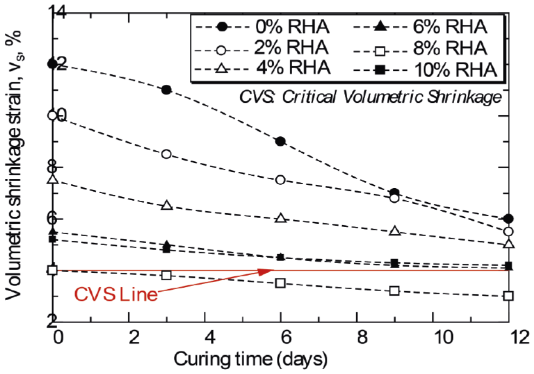

Fig. 8 Volumetric shrinkage against curing time of soil treated with RHA at optimum moisture molding condition
8. ábra RHA kezelt talaj térfogati zsugorodása az utókezelési idő függvényében optimális nedvességtartalom mellett készítve

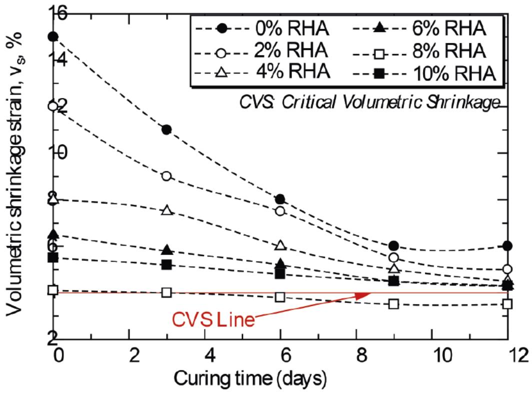

Fig. 9 Volumetric shrinkage against curing time of soil treated with RHA at 2% wet of optimum moisture molding condition
9. ábra RHA kezelt talaj térfogati zsugorodása az utókezelési idő függvényében optimális nedvességtartalomnál 2%-kal szárazabban készítve

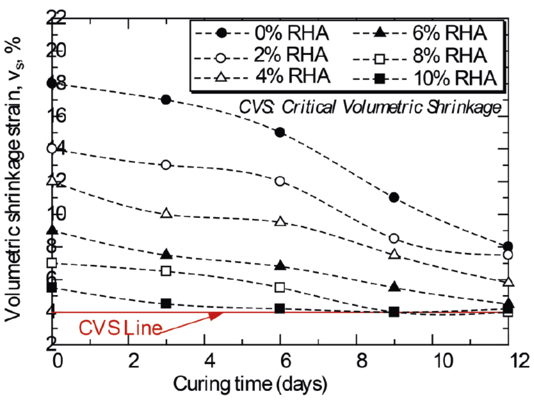

Fig. 10 Volumetric shrinkage against curing time of soil treated with RHA at 4% wet of optimum moisture molding condition
10. ábra RHA kezelt talaj térfogati zsugorodása az utókezelési idő függvényében optimális nedvességtartalomnál 4%-kal szárazabban készítve

4. Conclusion

The following remarks can be made from the laboratory investigation of the critical state volumetric shrinkage of compacted earth treated and improved with rice husk ash;

a. The index properties of the test soil showed that it is an A-7-6 soil group according to AASHTO method, it is highly plastic with the I_p above 17%, it is poorly graded and expansive with high shrinkage properties, which made it undesirable to be used as a pavement foundation soil subjected to hydraulically bound conditions.

b. The RHA as a lignocellulosic and amorphous material has high pozzolanic reaction on the treated soil thereby improving the shrinkage properties under different molding moisture conditions.

c. The VS of the treated soil reduced consistently with the addition of RHA and with the days of exposure (drying) and important to note is that the VS reduced below the critical line 4% at 8% by weight addition of RHA and was established as the proportion that met the condition for the soil material improvement under varying molding moisture conditions between -2% and 4%. Meanwhile, the drying period proved that the longer the days within the drying conditions, the better the VS. it shows that water migration and ingress during rise in water table for hydraulically bound structures like the pavement foundation causes the VS to increase above the critical level thereby causing failures of the pavement facilities.

d. Finally, and once again, Rice Husk Ash (RHA) has proven to serve as an environmentally conscious construction material with the potentials to improve soils and the ground for use as foundation materials. With the above results, it can comfortably replace the conventional cement and completely rid our planet with the sources of greenhouse emission for a healthier world of construction activities.

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Rheology and strength of concrete made with recycled concrete aggregates as replacement of natural aggregates

Újrahasznosított beton adalékanyag hatása a beton szilárdságára és reológiai tulajdonságaira

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Abstract

This paper presents the results of an experimental study carried out to evaluate the influence of the nature and the content of the recycled fine and coarse aggregates from concrete construction and demolition wastes on the rheological and strength properties of concrete. For this purpose, concretes mixtures were made with different percentages (15, 30, 50, 70 and 100%) of recycled sand and recycled gravel. Three different cement / admixture ratios were used. At fresh state, tests applied include slump, yield stress, plastic viscosity, air content and fresh density. Moreover, in order to follow the evolution of these properties over time, the tests were carried out at different times: directly after mixing, 30 minutes, 60 minutes and 90 minutes after completion of the mixing). At hardened state, compressive strength was determined at age of 7 and 28 days. The results show that, the properties of the concretes made with recycled aggregates depend up on the cement / admixture ratio and the substitution level of recycled aggregates. This means that there is indeed an influence of the recycled aggregates on the compatibility (physicochemical equilibrium) of the cement / admixture ratio. This influence is more noticeable on the sand than on the gravel. The results also show that, increasing the percentage of substitution of recycled aggregates in concrete mixture increases the yield stress and the plastic viscosity of fresh concrete. However, a decrease in the compressive strength was found with increasing the content of recycled aggregate.
Keywords: concrete, admixture, recycled aggregates, yield stress, rheology, mechanical strength
Kulcsszavak: beton, adalékszer, újrahasznosított adalékanyag, folyáshatár, reológia, szilárdság

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1. Introduction

Given the strong demand and supply for material resources and the need to preserve the environment in a sustainable development vision, it has become essential to investigate all possibilities for the reuse and recycling of wastes and industrial by-products in the field of civil engineering [1,2]. Indeed, concrete is the most widely used construction material in the field of civil engineering, despite its high environmental impact. The cement is made from limestone and requires a very high-temperature heating of 1450°C, engendering high CO_2 emissions. So, about 8% of the worldwide emissions are stemming from the manufacturing of cement. As an example, the production of a ton of Portland cement generates 930 kg of CO_2. The manufacturing of the cement establishes then an important source of greenhouse gas. The extraction of aggregates participates in the high carbon assessment of the concrete as well.

Every year, 3 billion tons of waste are produced in Europe, among which approximately 900 million by the construction industry, is more than 25% of all produced waste [3]. Indeed, the demolition of damaged or obsolete structures generate a huge quantity of concrete waste which creates serious ecological and environmental problems [4]. One way to minimize this impact is the use of recycled concrete aggregates [5–11]. Actually, the incorporation of recycled aggregates from construction waste or demolition significantly improves the ecological footprint of concrete. The concrete mixtures have rheological properties that are characterized by the parameters of Bingham material model (the yield stress and the plastic viscosity). The constituents' properties and mixtures composition affect commonly these parameters [12–15].

Slump is the most practical and widely accepted measure of the rheological behavior of concrete. Slump is not only an index of flow behavior, which includes the workability and implementation of fresh concrete, but is also used to quantify the consistency of mixtures. Variations of slump in concrete may be caused by factors related to concrete mix-design, particularly the quantity of water, as well as aggregate properties such as granular distribution, shape, and water absorption. In the field of construction, with the development of new concretes and new installation techniques such as pumping and projection, the control of the rheological behavior of fresh concrete becomes principal factor to facilitate its implementation [16]. It is also necessary to define the basic parameters that are used in the rheological behavior of a material as well as the most common behavioral models. Several rheological behaviors which are divided into two major families: Newtonian fluids and non-Newtonian fluids [8,17]. In the case of fresh concrete, workability is studied. The first, consistency, is an index of the mobility (ability to flow) of fresh concrete. The second is an indication of stability (ability to prevent segregation). For only a few decades, more characterizations that are precise have appeared to determine quantities related to the Bingham parameters.

The rheological test is essential for the execution of a construction project. During the mix-design of concrete in the laboratory to the test, the workability of concrete can be predicted on site. At the time of the construction of the structure, it is used for quality control, thus making it possible to take the necessary precautions before placing the concrete in case of an accident that can occur during manufacturing. The test therefore, avoids or minimizes economic loss. Many tests essentially empirical have been developed to evaluate the workability of concrete [18]. However, the complexity of the concrete mixture makes it difficult to study the rheology of this material. Some authors, then, propose a simplification that considers the fresh concrete as a two-phase material (cement paste and aggregates). Nevertheless, the interaction between these two phases does not consist in a simple lubrication between paste and aggregates, but in a complicated combination of the viscous effect of the paste and the mass of the aggregates. Therefore, it is useful to understand the rheology of cement paste, which has much in common with that of concrete. Some factors influencing the rheology of fresh concrete are related to the nature of the materials and water absorption capacity, which is higher for recycled aggregates than natural aggregates [1,19]. Other factors are related to the composition of the concrete itself. These factors are determining its rheology then concern the formulation of the concretes (water / cement (W/C), gravel / sand (G/S), paste volume, additions). The time factor is an important in the evaluation of the rheology of concrete, since it is not intrinsically part of the composition of the concrete. The duration of the period during which the fresh concrete remains sufficiently workable is limited due to the hydration process. When this limit is exceeded, the concrete loses its workability and its rheological behavior is changed.

In this context, the main objective of this research is to study the effect of recycled aggregate concrete (RAC) with different substitution percentages of 15, 30, 50, 70, and 100% of coarse and/or fine natural aggregate (NA) by recycled aggregate (RA), and the cement / admixture combination on the rheological behavior of concretes. Three different times T0, T30 and T90 were considered corresponding to 0 min, 30 min and 90 min after completion of mixing.

2. Materials

2.1 Cement

Three types of cement, CEM I 52.5R CE CP2 (C1), CEM I 52.5R CE (C2) and CEM I 52.5N CE CP2 ES (C3) from LAFARGE in France were used. The chemical and physical properties of these cements are summarized in *Table 1*. From *Table 1*, cement C1 has a higher C_3A and a lower C_3S than those of cement C2 and C3.

Cement	C1	C2	C3
Nomination	CEM I 52.5R CE CP2	CEM I 52.5R CE	CEM I 52.5N CE CP2 ES
Blaine Fineness (cm²/g)	4520	3250	4110
Median diameter (µm)	9.7	16.5	12.3
Water demand (%)	27.2	26.0	26.5
Initial setting time (min)	120	165	140
Hydration heat at 41h (j/g)	328	300	320
S_iO_2	19.54	20.19	20.1
Al_2O_3	5.70	3.81	5.5
Fe_2O_3	3.06	2.99	4.8
CaO	60.10	61.50	59.70
SO_3	3.71	3.31	2.31
MgO	1.85	1.96	3.26
K_2O	0.86	0.81	1.81
Na_2O	0.19	0.17	0.22
Cl^-	0.07	0.02	0.06
Loss on ignition	0.33	0.68	0.78
Clinker (%)	99	98	99
Alite (C_3S) (%)	53.4	67.0	46.4
Belite (C_2S) (%)	15.8	7.4	22.7
Aluminate (C_3A) (%)	9.9	5.0	6.5
Ferrite (C_4AF) (%)	9.2	9.1	14.6

Table 1 Chemical analysis and physical properties of cements used
1. táblázat Az alkalmazott cementek kémiai összetétele és fizikai tulajdonságai

2.2 Fine aggregates

Natural sand (NS) (0/4 mm) from limestone quarries and recycled concrete sand (RS) from concrete construction and demolition wastes (0/4 mm) from a recycling plant were used. Steps used to prepare recycled aggregates (RA) are detailed in [1]. The grain size distribution and morphological appearance of recycled and natural aggregates are presented in [1]. Water absorption and density are given in *Table 2*. The fineness modulus of RS (3.27) is significantly higher than that of NS (2.25).

Type of aggregate	Water absorption (%)	Density (%)
NS (0/4 mm)	0.9	2.59
RS (0/4 mm)	10.0	2.71
NG (4/10 mm)	0.5	2.71
RG (4/10 mm)	5.1	2.17
NG (10/20 mm)	0.4	2.31
RG (10/20 mm)	5.7	2.29

Table 2 Water absorption and density of aggregates used
2. táblázat Az alkalmazott adalékanyagok vízfelvétele és sűrűsége

2.3 Coarse aggregates

Two natural limestone gravels (NG) of fractions (4/10 mm and 10/20 mm), and two recycled gravels (RG) of fractions (4/10 mm and 10/20 mm) concrete construction and demolition wastes are used in this study. The grain size distribution of recycled and natural aggregates is presented in [1]. Density and water absorption are given in *Table 2*. Recycled aggregate (RA) shows relatively higher water absorption compared to NA.

2.4 Admixtures

Three admixtures (A1, A2 and A3) are used. Their physical properties and chemical analysis are summarized in *Table 3*.

Admixtures	A1	A2	A3
Chemical Type	Polycarboxylate	Ether polycarboxylique	Polycarboxylate
Type	High water reducing	Water reducing	Water reducing
Solids content	22.5%	22.5%	20%
Shape	liquid	liquid	liquid
Colour	light yellow	light brown	light yellow
pH	4 up to 6	6 up to 8	4.5 ± 1.0
Recommended Dosage	0.1% up to 3.0%	0.2% up to 1.9%	0.1% up to 3.0%
Content Na_2O Eq.	≤ 1%	≤ 1%	≤ 0.5%
Content ions Cl^-	≤ 0.1%	≤ 0.1%	≤ 0.1%

Table 3 Chemical analysis and physical properties of used admixtures
3. táblázat Az alkalmazott adalékszerek kémiai összetétele és fizikai tulajdonságai

3. Experimental program

3.1 Mixture proportioning

Three concretes (with cement C1, Cement C2 and Cement C3) and 36 different concrete mix proportions have been used, keeping the same quantity of cement and the same granular selection. Either coarse aggregates or natural sand were partially replaced by RA with percentages of replacement of 15, 30, 50, 70 and 100% respectively to the amount of aggregate. All the mixtures proportions of concretes are summarized in *Table 4*.

3.2 Casting and testing

The recycled aggregates were used in a saturated state, and steps used to prepare recycled aggregates are detailed in [1]. The rheological behavior of concretes made with recycled sand is studied using a concrete rheometer developed by Soualhi et al [21]. The principle consists in rotating a blade in a cylindrical sample of fresh concrete at different speed stages. The torques applied to rotate the blade at different speed levels are measured. The rheological parameters (the yield stress and the plastic viscosity) are then calculated.

The compressive strength was measured at the ages of 7 and 28 days according to NF P 18-455 [20].

4. Results and discussion

4.1 Workability

In all concrete mixes, constant slump of 200 +/- 20 mm is used, in order to limit the number of mixes. Slump results of concrete mixes with recycled sand is shown in *Fig. 1*. It is evident that slump is almost constant for mixes with 30% of RS, but beyond this percentage, the slump is reduced with 55% to 65% when RS content increases. This is due to the particle packing and surface roughness of the particles of RS. these results are similar to those reported by [21,22]. On the other hand, regardless of the cement / admixture ratio, low rheology is with 100% recycled sand. This is due to particle packing of recycled sand and surface roughness. It is observed that, irrespective of RS used, concrete made with cement C2 prove higher slump than that with cement C3 and C1. This can be explained by the lower amount of C_3A in cement C2. So, the degree of hydration of the cement is delayed and the workability of the mixture is increased [23]fillers and superplasticisers are typically added to the binder system. It is clear that cement, filler and admixture interact, and influence concrete properties. By means of an experimental programme on concrete with different types of Portland cement, with and without partial cement replacement by silica fume, and considering a naphthalene sulphonate superplasticiser, the interaction between C3A, silica fume and naphthalene sulphonate superplasticiser has been investigated. A higher C3A content of the Portland cement leads to a higher required dosage of superplasticiser. Partial cement replacement by silica fume leads to an acceleration of the second hydration peak (hydration of C3S.

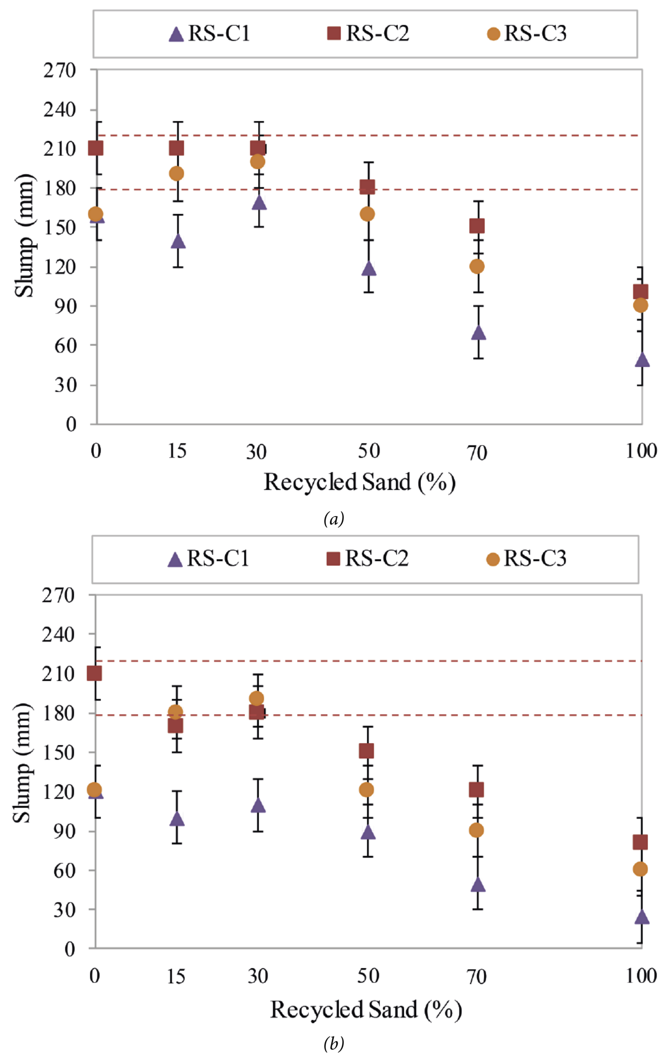


Fig. 1 Variation of slump with percentage of substitution in RS: (a) T30; (b) T90
1. ábra A roskadás változékonysága az újrahasznosított homok (RS) mennyiségének függvényeként: (a) T30; (b) T90

Cement (C)	Mixture	C	NS	RS	NG (4/10)	NG (10/20)	RG (4/10)	RG (10/20)	SP (%)	Water (kg/m³)	w/c
				(kg/m³)							
C1	0RS0RG	320	852	0	325	696	0	0	0.40	188	0.59
	15RS0RG		724	105					0.40	196	0.61
	30RS0RG		596	211					0.40	206	0.64
	50RS0RG		426	350					0.40	218	0.68
	70RS0RG		256	492					0.40	231	0.72
	100RS0RG		0	702					0.30	250	0.78
	0RS0RG		852	0	325	696	0	0	0.40	188	0.59
	0RS15RG				276	592	42	87	0.40	193	0.60
	0RS30RG				228	487	84	173	0.58	200	0.63
	0RS50RG				163	348	140	288	0.65	205	0.64
	0RS70RG				98	209	195	404	0.78	217	0.68
	0RS100RG				0	0	279	578	0.78	200	0.63
C2	0RS0RG	320	852	0	325	696	0	0	0.20	176	0.55
	15RS0RG		724	105					0.40	185	0.58
	30RS0RG		596	211					0.40	195	0.61
	50RS0RG		426	350					0.40	205	0.64
	70RS0RG		256	492					0.40	220	0.69
	100RS0RG		0	702					0.40	238	0.74
	0RS0RG		852	0	325	696	0	0	0.20	176	0.55
	0RS15RG				276	592	42	87	0.67	182	0.57
	0RS30RG				228	487	84	173	0.51	189	0.59
	0RS50RG				163	348	140	288	0.50	200	0.63
	0RS70RG				98	209	195	404	0.48	206	0.64
	0RS100RG				0	0	279	578	0.42	218	0.68
C3	0RS0RG	320	852	0	325	696	0	0	0.30	180	0.56
	15RS0RG		724	105					0.40	195	0.61
	30RS0RG		596	211					0.40	203	0.63
	50RS0RG		426	350					0.40	215	0.67
	70RS0RG		256	492					0.40	230	0.72
	100RS0RG		0	702					0.40	245	0.77
	0RS0RG		852	0	325	696	0	0	0.30	180	0.56
	0RS15RG				276	592	42	87	0.50	188	0.59
	0RS30RG				228	487	84	173	0.50	190	0.59
	0RS50RG				163	348	140	288	0.45	200	0.63
	0RS70RG				98	209	195	404	0.45	220	0.69
	0RS100RG				0	0	279	578	0.42	228	0.71

Table 4 Mixtures proportions of concrete
4. táblázat Beton keverékek összetétele

Fig. 2 shows slump of concrete mixes with RG. It can be seen that regardless of cement / admixture ratio, slump decreases slightly with increasing of the percentage of RG. The slump of concrete with cement C2 is higher than that of concrete with cement C3 and C1. It can be seen also that (i) workability of RAC with cement C2 is better; (ii) workability reduces with higher percentage of recycled aggregates. Up to 30% recycled sand, slump values are similar. However, beyond 30% recycled sand, reduction was significant; 80% for 100% of recycled sand, (iii) reduction in workability of RAC with RS is higher than with RG, and this is due to the interaction between C_3A and superplasticizer [23,24]fillers and superplasticisers are typically added to the binder system. It is clear that cement, filler and admixture interact, and influence concrete properties. By means of an experimental programme on concrete with different types of Portland cement, with and without partial cement replacement by silica fume, and considering a naphthalene sulphonate superplasticiser, the interaction between C3A, silica fume and naphthalene sulphonate superplasticiser has been investigated. A higher C3A content of the Portland cement leads to a higher required dosage of superplasticiser. Partial cement replacement by silica fume leads to an acceleration of the second hydration peak (hydration of C3S.

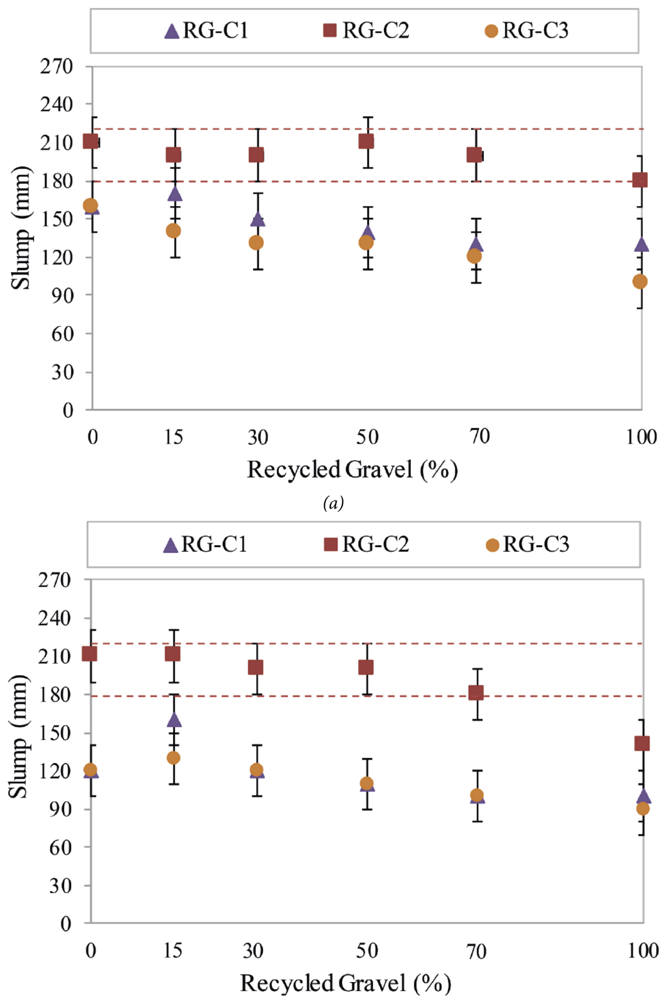


Fig. 2 Variation of slump with percentage of substitution in RG: (a) T30; (b) T90
2. ábra A roskadás változékonysága az újrahasznosított durva adalékanyag (RG) mennyiségének függvényeként: (a) T30; (b) T90

4.2 Air content and density

Air content and density results of concrete are shown in *Fig. 3* and *4*. It can be seen that beyond 30% of RS, and whatever the type of cement used in mixtures, the air content is higher than mixture with 0% of RS. Effectively, because of the roughness and shape of the recycled sand and the formation and immobility of air bubbles during vibration of concrete, since the recycled sand has a higher porosity than natural sand [25]. The results also show that the air content of RAC are affected by cement / admixture ratio. Concretes with the cement C3 and C2 have lower air content than those made with cement C1. Similarly, the figures indicate that with an increase in recycled gravels, the air content increases. However, this increase is slightly less than that the one observed with RS. This result indicates that the fine portion of RA influences negatively the behavior of RAC.

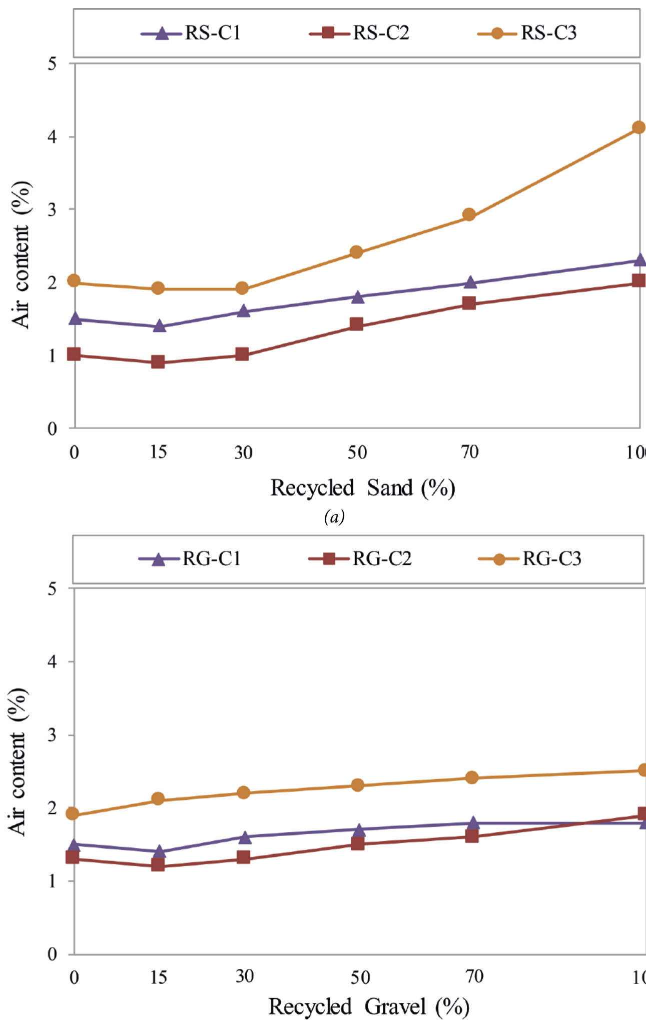


Fig. 3 Variation of air content with percentage of substitution of RA: (a) RS; (b) RG
3. ábra A levegőtartalom változása az újrahasznosított adalékanyag (RA) mennyiségének függvényeként: (a) RS; (b) RG

Fig. 4 indicates that densities of NAC (reference concrete) are higher than those of RAC. Up of 30% of substitution, the density of RAC with RS decreases and then remains constant. This is because of adhered old mortar included in RA surrounding the NA. The figures also indicate that with RG content, density decreases slightly. This is due to the more porous nature and lightweight of adhered old cement mortar to the RA. The density of sand aggregate reduction is within 6% and 4% of the gravel aggregate. This means that where lightweight concrete is needed, the RA can be used. Therefore, for using the RA of low density and with adequate strength, 30% RS can be used in concrete mixtures.

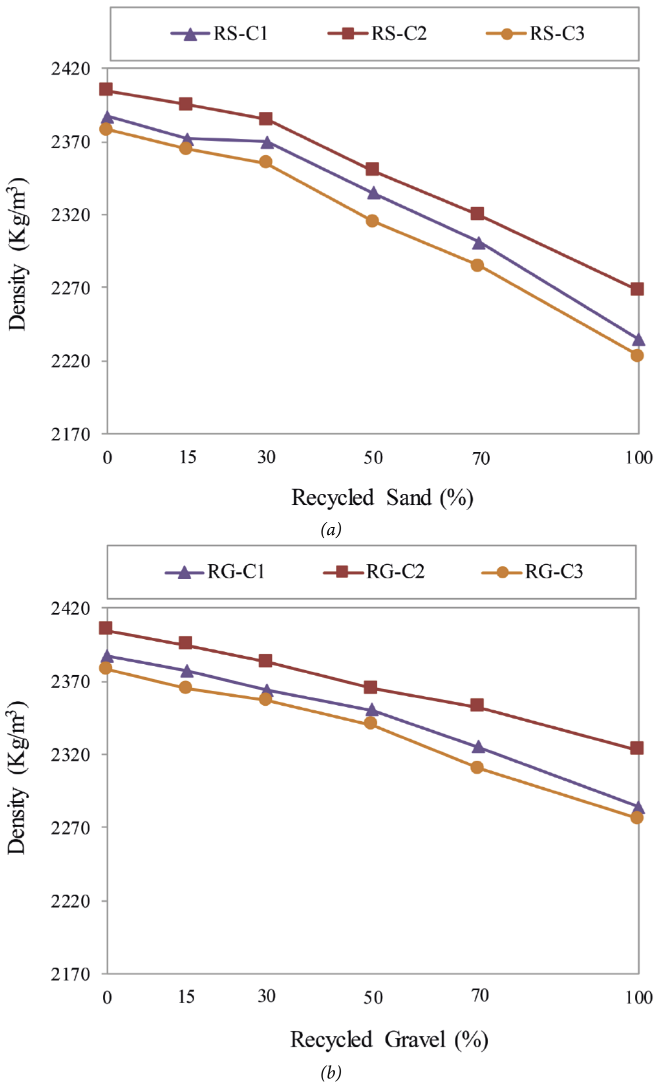


Fig. 4 Variation of density with percentage of substitution of RA: (a) RS; (b) RG
4. ábra A sűrűség változása az újrahasznosított adalékanyag (RA) mennyiségének függvényeként: (a) RS; (b) RG

4.3 Rheology

4.3.1 Effect of recycled fine aggregate

Fig. 5 show the evolution of torque as a function of the rotational speed at T0 for the several of cement / admixture ratios for concrete with recycled fine aggregates. The results show, firstly, that torques are increasing linearly with speed. On the other hand, these results show a distinction between different cement / admixture ratio. It can be said that, the rheological behavior of recycled sand concrete exhibits a Bingham fluid. Indeed, the graphs are linear and do not pass through the origin. These results are explained by the low amount of C_3A in the cements C2 of the RS-C2 couple, thus delaying the setting of concrete, and then conferring good fluidity at the fresh state. A high percentage of C_3A for cements C1 of the RS-C1 couple accelerates the setting of the concrete and reduces its fluidity. The cements C3 of the RS-C3 couple present an average quantity of C_3A.

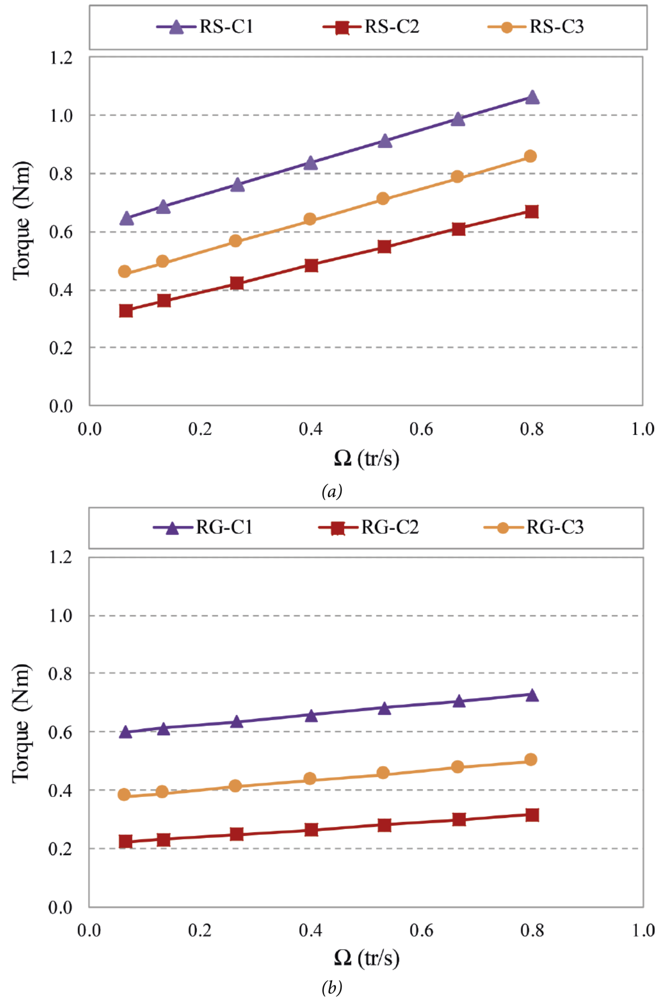
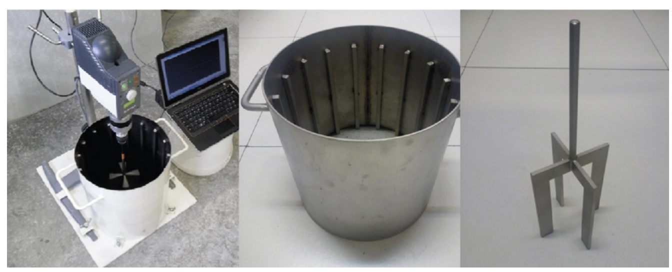


Fig. 5 Variation of torques with speed of RA: (a) RS; (b) RG
5. ábra A forgatónyomaték változása az újrahasznosított adalékanyag (RA) mennyiségének függvényeként: (a) RS; (b) RG

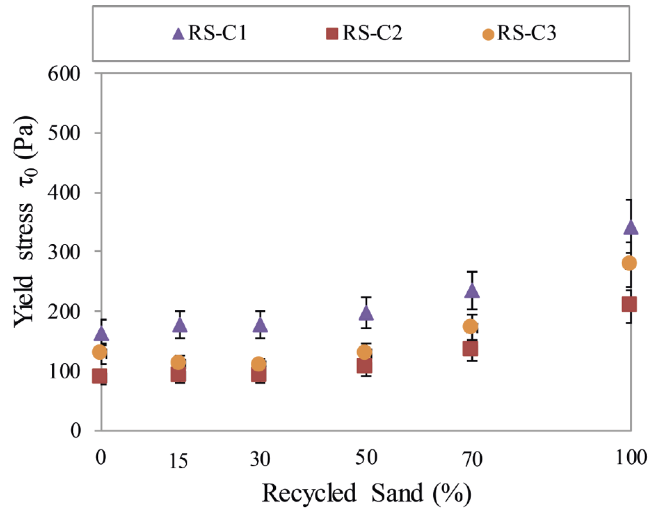


(a) Rheometer (b) Cylindrical sample (c) Blade

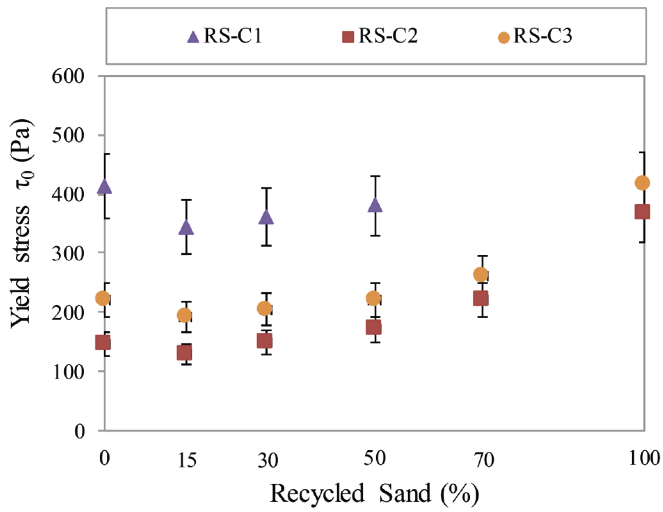
Fig. 6 The configuration of the rheometer used and its constituents [21]
6. ábra Az alkalmazott reométer mérési összeállítása és alkotóelemei [21]

a. Development of the yield stress τ_0

This part of the study is devoted to the analysis of the evolution of the yield stress at T0 (just after completion of the mixing) and at T90 (after 90 minutes), as a function of the percentage of substitution for the three cement / admixture ratio. *Fig. 7* shows the evolution of the yield stress as a function of the percentage of recycled sand for the three cement / admixture ratio. According to *Fig. 7*, it should be noted that:



(a)



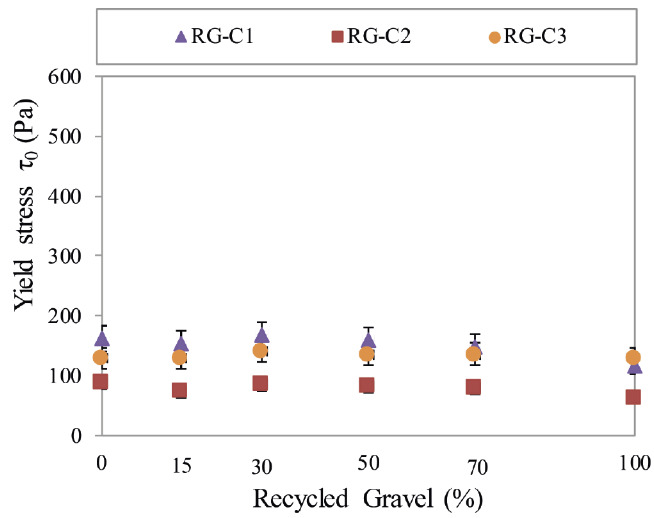
(b)

Fig. 7 Variation of yield stress with percentage of substitution in RS: (a) T0; (b) T90
7. ábra A folyási feszültség változása az újrahasznosított homok (RS) mennyiségének függvényeként: (a) T0; (b) T90

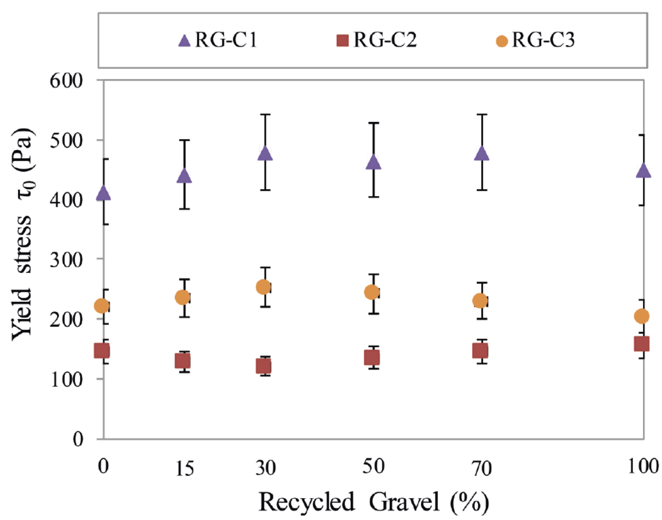
At a percentage less than 30% of substitution, the yield stress is nearly constant at T0 and at T90. Beyond this, the yield stress increases quasi-linearly, whatever the cement / admixture couple at T0 and T90. The "yield stress-substitution percentage" graphs present clearly the three torques versus time (T0, T90). The first torque has low yield stress (RS-C2 concretes). The second one has higher yield stress (RS-C1 concretes) and the third one has average yield stress (RS-C3 concretes). Finally, whatever the torque and the percentage of substitution, the yield stress at T90 is always higher than that at T0. These differences in results between torques of different mixes can be explained by the fact that the yield stress varies significantly according to slump [26–30]. RS-C2, concretes have higher slump than RS-C1 and RS-C3 concretes, regardless of the substitution percentage.

b. Development of the plastic viscosity μ

The purpose of this section is to study the evolution of the plastic viscosity at the outlet of the mixer and after 90 minutes according to the percentage of substitution of natural sand by recycled sand for three ratios of cement / admixture. *Fig. 9* shows the evolution of the plastic viscosity as a function of the percentage of recycled sand for the three cement / admixture ratio. *Fig. 9* shows an increase in the plastic viscosity with increasing of the percentage of substitution of recycled sand. This increase in the plastic viscosity can be explained by the increase in the ratio (∅ / ∅ ^ *) of concrete when adding recycled sand due to the action of two mechanisms. On the one hand, increase in the volume concentration of sand (natural sand + recycled sand) (∅), and on the other hand, the reduction in the compactness of the granular mixture (natural sand + recycled sand + natural gravel) (∅ *) when the substitution content of natural sand by recycled sand in the concrete increases. The plastic viscosity of concrete is proportional to this ratio (∅ / ∅ ^ *) according to the literature [15,31,32]. The increase in the ratio (∅ / ∅ ^ *) therefore leads to an increase in the plastic viscosity of the concretes. In addition, the same type of rheometer should be used to measure, and then compare the rheological parameters of the concretes (yield stress and plastic viscosity). Indeed, each type of rheometer gives results that differ significantly according to its configuration.

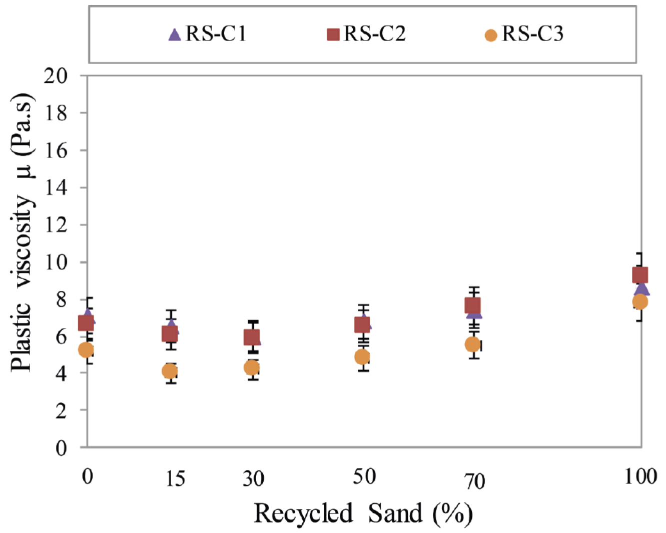


(a)

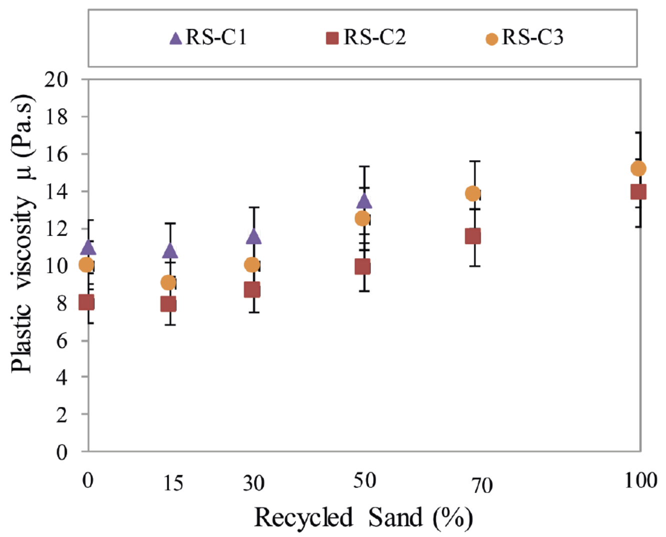


(b)

Fig. 8 Variation of yield stress with percentage of substitution in RG: (a) T0; (b) T90
8. ábra A folyási feszültség változása az újrahasznosított durva adalékanyag (RG) mennyiségének függvényeként: (a) T0; (b) T90



(a)



(b)

Fig. 9 Variation of plastic viscosity with percentage of substitution in RS: (a) T0; (b) T90

9. ábra A plasztikus viszkozitás változása az újrahasznosított homok (RS) mennyiségének függvényeként: (a) T0; (b) T90

c. Discussion

The following conclusions can be drawn from the assessment of the rheological parameters of concrete made from recycled sand:

- For substitution content less than or equal to 30%: Recycled sand has little influence on the amount of admixture to be introduced into the concrete mixtures (for a slump of 200 ± 20 mm). The slump is maintained constant at T30 and T90 for the different ratio, except for RS-C1. Regardless of the cement / admixture couple, the slump decreases slightly as a function of time compared to the reference concrete. The air content and densities of concrete mixtures are almost constant. The yield stress is practically constant at T0 and T90.
- For substitute content more than 30%: The demand for admixture increases to reach the desired workability. Regardless of the time and the cement / admixture couple, the slump decreases. The slump loss for RS-C1 mixtures with 100% recycled sand is up to 70% compared to natural concrete. Regardless of the cement / admixture couple, air content increases and densities decrease.
- Regardless of the cement / admixture couple at T0 and T90, the yield stress increases linearly.
- Independently of the substitution percentage, the slump decreases with time for each cement / admixture couple. Concretes made with low C_3A cements have a higher reduction and better maintenance of slump as a function of time compared to those made with higher C_3A cements. Therefore, the yield stress of concretes made with C_3A of RS-C3 cements is lower.
- Regardless of the cement / admixture couple, the yield stress at T90 is always higher than at T0. Whatever the time (T0 or T90), the plastic viscosity increases steadily and the total replacement of the natural sand by the recycled sand increases double the value of the plastic viscosity. The cement / admixture couple influences the yield stress and the viscosity of the concrete with recycled sand.

4.3.2 Effect of recycled coarse aggregate

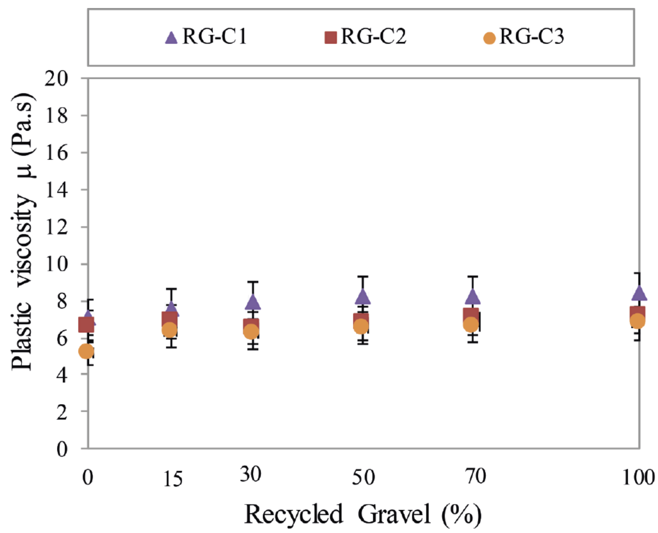
Fig. 5b shows the torque evolution at different rotational speed at T0 for concretes made with recycled gravel and natural sand. The results show that the torques increase slightly in a linear way as a function of speed. Moreover, the torque-speed curves are distinguished from the cement / admixture ratio.

a. *Development of the yield stress τ_0*

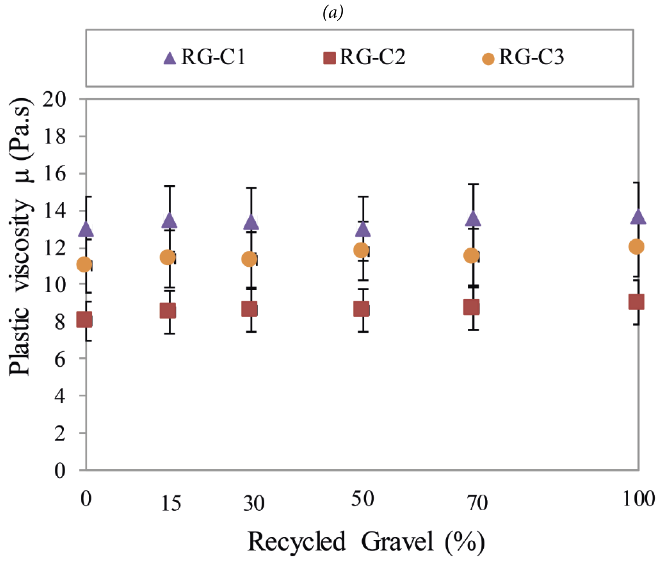
The yield stress of concrete made with recycled gravels is measured by a Couette rheometer (*Fig. 6a*). The measurement of this parameter was performed on the three cement / admixture ratio at times T0 and T90. *Fig. 8* shows the development of the yield stress as a function of the percentage of recycled gravels in concrete mixtures. As seen from *Fig. 8*, whatever the percentage of substitution at T0 and T90, the yield stress increases slightly as compared to concrete made with natural gravel. Three ratio of concrete are used in this test. The first one has a low yield stress (RG-C2 concretes), up to 60 Pa at T0 and 100 Pa at T90. The second one has a higher yield stress (RG-C1 concretes), up to 210 Pa at T0 and 500 Pa at T90 for 100% recycled gravels. The third one has an average yield stress (RG-C3 concretes). The difference in results between these three ratios can be explained by same logic as those invoked for concretes made with recycled sand, specifically that the yield stress is a function of the slump. Indeed, it has been found that the RG-C2 ratio has a good hold with respect to the other ratio (RG-C3 and RG-C1). The evolution of the yield stress for each substitution percentage is due to its significant variation as a function of slump [26–30].

b. Development of the plastic viscosity μ

This part presents the evolution of the plastic viscosity (μ) of the concretes manufactured with recycled gravels as a percentage of substitution, for various cement / admixture ratio at T0 and T90. *Fig. 10* shows the obtained graphs. According to the results, the plastic viscosity of the concretes based on recycled aggregates increases slightly in comparison with concretes manufactured with natural aggregates, regardless of the percentage of substitution. In addition, the concrete mixture C1 has the highest plastic viscosity and it reaches a value of 14 Pa.s at T0 and 19 Pa.s at T90. This is due to a significant amount of C_3A in this cement, which accelerates the setting and thus makes the concrete more viscous and less workable. On the other hand, the pair of concrete C2 that has a small amount of C_3A is characterized by lower plastic viscosity (5 Pa.s at T0 and 3 Pa.s at T90). The cements C3 of the RS-C3 couple present a medium quantity of C_3A.



(a)



(b)

Fig. 10 Variation of plastic viscosity with percentage of substitution in RG: (a) T0; (b) T90

10. ábra A plasztikus viszkozitás változása az újrahasznosított durva adalékanyag (RG) mennyiségének függvényeként: (a) T0; (b) T90

c. Discussion

Following the assessment of the rheological properties of concretes made with recycled gravel, the following conclusions can be made:

- To maintain a slump of 200 ± 20 mm, the amount of admixture increases gradually in the concrete when the percentage of substitution of the recycled gravel increases.
- At T30 the slump is maintained for the different torques except for the RG-C1 concretes. In addition, 100% maintenance loss of concrete made with recycled gravels (up to 55% for RG-C1 concretes) should be noted.
- A gradual decline in subsidence for the three ratio was noted up to T90.
- Between the measurement at the mixer outlet (T0), and the measurement after 90 minutes (T90), for reference concrete (0% substitution), a loss of workability of up to 25% is recorded. For concretes with 100% recycled gravels, a loss of workability of 40% is retained, except for RG-C1 concrete, which has a loss of workability of 70%.
- Whatever the cement / admixture couple, the slump of the concretes decreases slightly as a function of time. This decrease is less remarkable in the case of concretes made from recycled sand.
- The time-dependence of the concretes based on recycled gravel depends on the cement / admixture ratio.
- The air content increases slightly as the percentage of recycled gravels increases. This increase follows a lower slope than concretes made with recycled sand concretes, regardless of the cement / admixture couple.
- The air content measured at T90 increases more pronouncedly as a function of the percentage of recycled gravels than that measured at T0.
- The cement / admixture couple influences the yield stress and the plastic viscosity, whatever the measurement time (T0 or T90) and the percentage of substitution.
- Whatever the percentage of substitution and whatever the measurement time (at T0 and T90), the yield stress increases slightly compared to that of the concrete made with natural gravel.

4.4 Compressive strength

Fig. 11 and *12* present the results of the compressive strength for concrete mixes with cement C1, C2 and C3. It can be seen that compressive strength of RAC decreases with the increase in RA content. Two reasons are possible for this state: the first one is that the strength loss due to the recycled sand adhered paste contains un-hydrated cement [5]; and the second one is the increasing porosity is due to the increased paste of the RS. On the other hand, when the RG percentage increases, compressive strength of RAC decreases slightly because air content and density of concrete have a slight variation when the content of RG increases. Further, the small amount of the old cement stuck in the RG weakened the structure of concrete with RS [33]. It should be noted that, the type of cement affects compressive strength [34,35]. Thus, the combinations C1 and C3, in which the C_3S dosage is lower than of C2, presents weak early strength, however, concrete with 100% recycled sand exhibits a reduction in compressive strength of 45%. This is because of concrete with RS, which has a low air content and density. Further, the structure of the mixture is weakened by cement mortar content in RS. From *Fig. 11*, it is evident that the combination cement / admixture at 7 days regardless of the percentage of RA affects the compressive strength. The RAC with cement C2 achieved higher compressive strength at 7 days than that with cement C3 and C1. However, from *Fig. 12*, 28 days compressive strength is not significantly affected by the cement / admixture ratio.

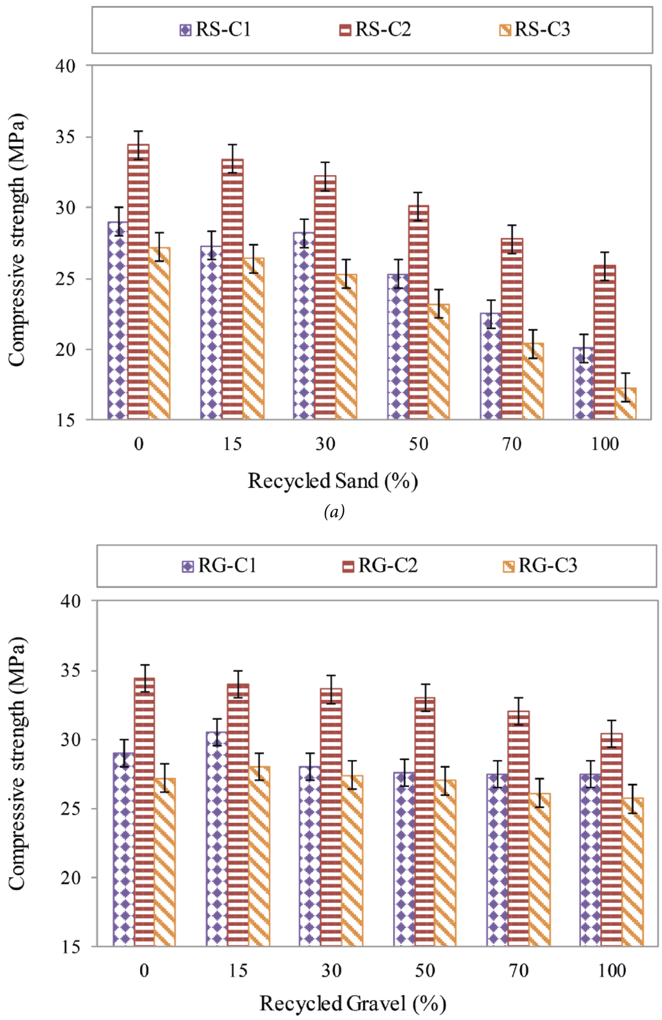


Fig. 11 Compressive strength evolution of RAC with three cement / admixture and with RA substitution rate at 7 days: (a) RS; (b) RG

11. ábra Újrahasznosított adalékanyag tartalmú beton nyomószilárdsága (3 különböző cement/adalékszer típus esetén) az adalékanyag helyettesítési mennyiségének függvényében 7 napos korban: (a) RS; (b) RG

5. Conclusions

The aim of this paper is the comparison of the fresh behavior of concrete made from recycled sand and recycled gravel. The results lead to the following conclusions:

- Slump of the concretes produced with recycled gravels decreases slightly as a function of time, regardless of the cement / admixture couple tested. This decrease is less pronounced in the case of recycled sand concretes. Recycled gravels therefore affect less than recycled sand on maintaining the workability of concrete.
- The air content increases slightly as the percentage of recycled gravels increases. The slope that represents this increase is less than that of concretes made with recycled sand. This observation is evident whatever the cement / admixture pair used.
- For both types of aggregate substitution, whatever the dosages, the cement / admixture ratios at T0 and T90 influence the yield stress and the plastic viscosity. These parameters increase in both substitution cases but more significantly for recycled sand (this increase is slight in the case of substitution by recycled gravel).
- Recycled gravel concretes have workability, air content and density that develop slightly as a function of the percentage of substitution. Concretes based on recycled sand exhibit the same behavior when the substitution percentage is less than or equal to 30%. Beyond this dosage, the behavior is not well determined.

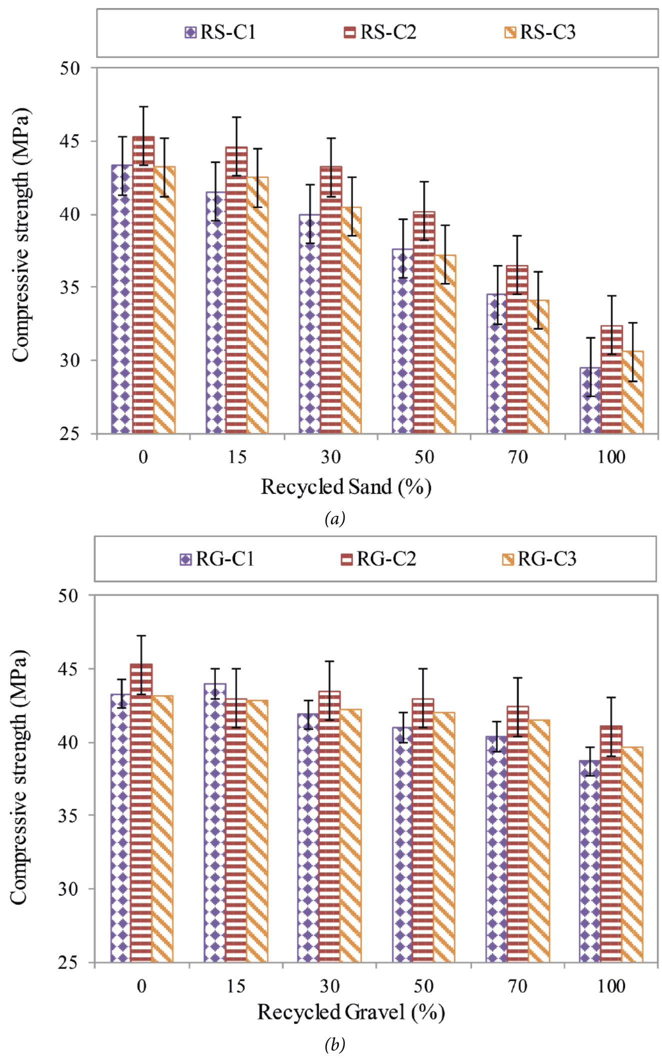


Fig. 12 Compressive strength evolution of RAC with three cement / admixture and with RA substitution rate at 28 days: (a) RS; (b) RG

12. ábra Újrahasznosított adalékanyag tartalmú beton nyomószilárdsága (3 különböző cement/adalékszer típus esetén) az adalékanyag helyettesítési mennyiségének függvényében 28 napos korban: (a) RS; (b) RG

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A lőszermentesítés szerepe az építőiparban

The role of explosive ordnance decontamination in the field of building trade

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Kivonat
A katonai eredetű fel nem robbant robbanótestekhez kapcsolódó riasztások Magyarország teljes területéről érkeznek a tűzszerészekhez. Minden földmunka során, minden építési területen számításba kell venni a veszélyes eszközök okozta nehézségeket. Ezek a gránátok és bombák napjainkban is képesek felrobbanni, veszélyességük miatt pedig speciális módszereket és eszközöket kell alkalmazni a felkutatásukhoz és hatástalanításukhoz. A lőszermentesítés jelentősen csökkentheti egy-egy építkezés szervezési feladatait, költségeit, ezért érdemes alaposabban megvizsgálni a lehetőségeket.

Abstract
The explosive ordnance disposal unit receives alerts to military origin unexploded ordnances from the whole region of Hungary. Difficulties make by these dangerous devices has to be considered during every earthwork or construction works. These projectiles and bombs are able to blow up and their localization and deactivation requires special methods and equipment. The explosive ordnance decontamination may significantly reduce the organizational process and the costs of construction works therefor it is worthy to make a thorough examination of the possibilities.

Kulcsszavak: lőszermentesítés, tűzszerészet, építési terület, gránát, bomba
Keywords: explosive ordnance decontamination, explosive ordnance disposal work, construction site, grenade, bomb

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1. Bevezetés

Magyarország méretét tekintve nem volt a II. világháború legnagyobb résztvevői közé sorolható, azonban a földrajzi elhelyezkedése következtében mégis komoly szerepe volt az európai hadszíntéren. A hazánk területén folytatott háborús cselekmények során jelentős számban alkalmaztak különböző robbanótesteket.

A II. világháború azonban több mint hét évtizede befejeződött és ez felveti a kérdést, hogy mekkora veszélyt jelentenek a napjainkban előkerülő katonai eredetű robbanótestek. Szükséges-e erőforrásokat áldozni a felkutatásukra? Képesek-e halát és anyagi károkat okozni?

A fenti kérdések megválaszolására egy kifejezetten határozott igen a válaszom, és a kutatásommal megpróbálom alátámasztani ezt a hipotézist, annak érdekében, hogy a jövőben folyó építőipari beruházások, talajmegmunkálások előtt ne legyen kérdéses a tűzszerészeti mentesítés végrehajtása.

2. Mi rejtőzik a földben?

Először is meg kell határozni, hogy milyen robbanótestek lapulnak a talajban. A köznyelv nagyon egyszerűen bombaként azonosít mindent, hiszen ez a szó hordozza a figyelemfelkeltéshez szükséges hátteret, de valójában csak a levegőből „ejtett" robbanótesteket hívhatjuk szakmai értelemben bombának. A robbanótesteket az alábbi felosztás szerint tagolhatjuk: gyalogsági lőszerek, kézigránátok, puskagránátok, aknák, kézi páncélelhárító eszközök és komplexumok, aknagránátok, tüzérségi gránátok és lőszerek, legvégül pedig a légibombák.

A fenti típusok mindegyike előkerült már hazánkban és az *1. táblázat* jól szemlélteti, hogy 2019-ben a teljes spektrumot hatástalanították a tűzszerész katonák. A legnagyobb számban gyalogsági lőszerek kerültek elő, majdnem 28000 darab, azonban szakmai szempontból nem ez a legmeghatározóbb típus. A közel 2500 darab tüzérségi gránát és a közel 750 db aknagránát jelentős mennyiségnek számít, még akkor is, ha jelentős szórásról beszélhetünk méretük vonatkozásában egy-egy típuson belül is. Ebben az értelmezésben tüzérségi gránátnak számít egy 20-30 mm átmérőjű, 100-200 g tömegű és egy 203 mm átmérőjű, 100 kg-nál nehezebb robbanótest is. Ami viszont a közhiedelemmel ellentétben jól kiolvasható, hogy aknák elenyésző számban kerülnek elő, köszönhetően a II. világháború után folytatott igen eredményes aknamentesítő tevékenységnek.

Fsz.	Típus	Mennyiség [db]	Összesen [db]
1.	Aknagránát	747	34768
2.	Tüzérségi	2486	
3.	Kézigránát	364	
4.	Bomba	386	
5.	Akna	16	
7.	Gyalogsági lőszer	27931	
8.	Egyéb	~2838	
9.	Nem robbanótest	3476	3476

1. táblázat A 2019-ben előtalált robbanótestek
Table 1 Unexploded ordnances founded in 2019 [8]

Az is fontos tisztázni, hogyan kerültek a talajba a robbanótestek, hiszen ez nagyban hatással lesz a kezelésük, hatástalanításuk módjára, ami jelentősen befolyásolja a feladat időszükségletét.

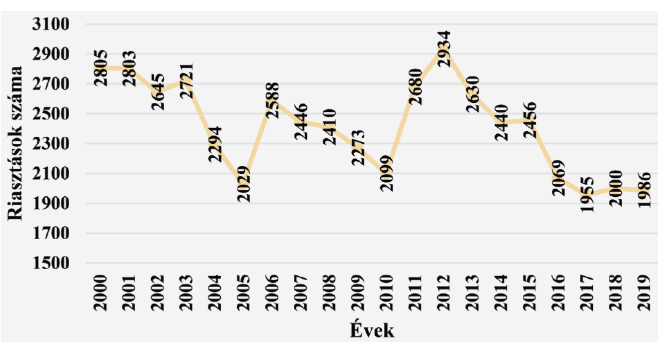
Ebben a vonatkozásban megkülönböztethetünk alkalmazás előtti (tárolási helyzetben van, alkalmazásra előkészített helyzetben van stb.) és alkalmazott (vetett, kilőtt, kidobott stb.) állapotot. Az első esetben kissé könnyebb helyzetben lesznek a tűzszerész szakemberek, hiszen az eszközök gyakorlatilag tárolási helyzetben vannak, bár nem éppen raktározási körülmények között. Ilyenkor is számolni kell nehézségekkel, hiszen a környezet hatásai ilyen esetben is képesek olyan fizikai és kémiai változásokat okozni, melyek megnehezítik a hatástalanítást, másrészt egyes típusok esetében irreleváns az állapota, mert minden állapotában jelentős veszélyt hordoz. Az alkalmazott eszközök esetében számolni kell azzal, hogy a működtető szerkezetben vagy gyújtószerkezetben az élesítés lezajlott és mechanikai hatásra a gyújtás megtörténhet, az eszköz felrobbanhat. Ezek alapján kijelenthető, hogy mindkét típus esetében fennállhat a fokozott veszély, melyet kizárólag a hatástalanításra felkészített és felhatalmazott tűzszerész szakember kezelhet.

Ezek a világháborús robbanótestek tapasztalataim szerint leggyakrabban alkalmazott formában kerülnek elő. Nem ritka azonban az olyan „lerakat", ahol egy egykori tüzelőállás deponált harcanyagkészletét egyszerűen csak betemették, vagy az utánpótlás szállítás során döntötték a robbanótestekből álló készlet hátrahagyása mellett.

Fontos megemlítenem, hogy léteznek terror jellegű robbanótestek, pokolgépek, melyeket a szaknyelvben improvizált robbanótestnek nevezünk. *„Az improvizált robbanóeszközök előállításához használhatnak katonai vagy polgári célból gyártott robbanóanyagokat, esetenként házilag elkészített robbanóanyagot, elegyet."* [1]. Ezek az eszközök nem képezik dolgozatom tárgyát, azok megjelenése nem a jelenleg vizsgált körülmények között várható.

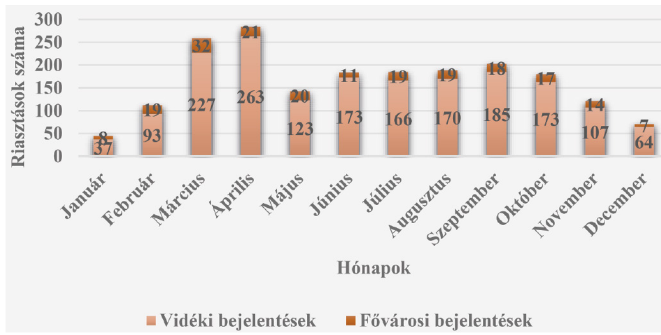
3. A robbanótestek előfordulása

Mivel Magyarország teljes egészében műveleti terület volt a II. világháború alatt, ezért kijelenthető, hogy az egész ország területe szennyezett lehet robbanótestekkel. Nyilván az egykori harcok intenzitása nem volt egyforma az ország minden pontján, ezért regionálisan jelentős különbségek lehetnek. Ettől függetlenül azonban nem lehet kijelenteni egy országrészről sem, hogy teljesen robbanótest-mentes. *„Kiemelten szennyezett területek a Balaton északi és déli oldala, Székesfehérvár és környéke, a Margit-vonal menti települések és haszonterületek, a Főváros és környéke, Győr, Nagybajom térsége, és a Duna"* [2].



1. ábra Feltételezett robbanótest bejelentések száma 2000-től
Fig. 1 Number of alerts of supposed unexploded ordnances since 2000 [8]

Az elmúlt több mint 70 év során folyamatosan dolgoztak a szakemberek az ország területének biztonságosabbá tételén. Minden évben több ezer helyszínről érkezik bejelentés, hogy feltételezett robbanótestek kerültek elő. Az elmúlt 20 év során átlagosan több mint 2400 esethez kellett a tűzszerészeknek vonulni. Ez a szám is jól mutatja, hogy olyan tevékenység ez, mely az ország mindennapjainak szerves része (naponta átlagosan 6-7 bejelentés) annak ellenére, hogy nem minden eset kerül a médiaérdeklődés középpontjába.



2. ábra A 2019-es év bejelentéseinek megoszlása
Fig. 2 Target-diagram of alerts in 2019 [9]

A Magyar Honvédség 1. Honvéd Tűzszerész és Hadihajós Ezred (rövidítve: MH 1. HTHE) tűzszerészei 2019-ben is kiemelkedő munkát végeztek. 1986 db bejelentés érkezett a Tűzszerész Ügyeletre, ami korántsem elenyésző, tekintve, hogy Magyarország legtávolabbi részein is el kell végezni hatástalanítási feladatokat. Ez a szám 205 db budapesti és 1781 db vidéki bejelentést tartalmaz. Jól látszik tehát, hogy a bejelentések több mint 10% a fővárosból érkezett, de az alábbi táblázat megmutatja, hogy minden megye érintett. Békésmegye nevéhez híven a legkevesebb feltételezett robbanótest bejelentést produkálta, de a lista végén van Nógrád, Zala és Tolna is. A legtöbb veszélyes feladatot Fejér-megye adta 355 db bejelentéssel, ami az éves szám közel 18%-a. Veszprém, Pest, Budapest, Komárom-Esztergom, Baranya, Győr-Moson-Sopron a 100 feletti bejelentési számmal pedig a lista előkelő helyén szerepel.

A Budapesten bejelentett feltételezett robbanótestek a XII. és XIV. kerületekben kerültek elő kimagasló esetszámban, míg a VIII. kerületből gyakorlatilag egyetlen egy ilyen esetet láthatunk.

4. A rozsdásodó halál

Sokszor felmerül a kérdés a laikus emberekben, hogy szükséges-e egyáltalán ezeket a robbanótesteket ilyen érzékenységgel kezelni. Megmaradt-e a robbanásképességük? A válasz egyértelmű, de nem csak kizárólag a triviális értelmezésében.

A robbanótestek nem várt felrobbanása alapvetően valamilyen mechanikai behatáshoz köthető. Ezt nagyban befolyásolja, hogy a gyújtószerkezetben lezajlott változások (pl.: korrózió) milyen eredményt hordoznak. Előfordulhat, hogy sokkal kisebb energiaközlésre elműködik a szerkezet, mert a belső gátló, vagy biztosító szerkezeti egységek már nem tudják ellátni feladataikat, de ennek az ellenkezője is előfordulhat. Meg kell említeni a kémiai átalakulásokat is, melyek jelentősen képesek

Megye / hónap	Jan	Feb	Már	Ápr	Máj	Jún	Júl	Aug	Sze	Okt	Nov	Dec	Össz.
Budapest	8	19	32	21	20	11	19	19	18	17	14	7	205
Bács-Kiskun	3	3	3	6	2	7	2	1	1	3	2	1	34
Baranya	3	4	8	11	6	14	14	12	18	12	12	9	123
Békés	1	0	1	2	2	0	1	1	0	1	2	1	12
Borsod-Abaúj-Zemplén	1	5	12	18	4	4	12	7	15	11	3	3	95
Csongrád	1	1	6	8	5	10	4	7	4	5	5	1	57
Fejér	2	21	60	73	16	30	23	34	35	31	20	10	355
Győr-Moson-Sopron	2	6	18	8	11	5	10	8	15	14	5	0	102
Hajdú-Bihar	1	5	8	8	7	7	10	7	6	7	6	8	80
Heves	1	4	11	13	7	5	5	4	10	12	3	1	76
Jász-Nagykun-Szolnok	2	1	8	7	3	2	1	11	5	4	4	0	48
Komárom-Esztergom	5	6	18	14	6	9	15	13	12	9	5	9	121
Nógrád	1	2	1	4	2	0	2	5	1	1	1	1	21
Pest	7	17	41	45	25	32	28	27	27	35	21	9	314
Somogy	1	2	5	10	7	10	8	8	5	2	3	4	65
Szabolcs-Szatmár-Bereg	1	4	4	8	5	3	3	5	4	4	2	1	44
Tolna	0	1	7	5	3	3	2	2	1	3	1	0	28
Vas	3	1	4	6	2	6	2	7	4	3	3	0	41
Veszprém	1	7	10	13	8	24	22	10	19	13	8	5	140
Zala	1	3	2	4	2	2	2	1	3	3	1	1	25
Összesen	45	112	259	284	143	184	185	189	203	190	121	71	**1986**

2. táblázat Feltételezett robbanótest bejelentések országosan 2019-ben
Table 2 Alerts of supposed unexploded ordnances in Hungary in 2019 [9]

Kerület / hónap	Jan	Feb	Már	Ápr	Máj	Jún	Júl	Aug	Sze	Okt	Nov	Dec	Össz
I.	1	1	0	1	0	1	0	0	0	0	0	1	5
II.	1	3	3	3	1	0	1	1	2	1	0	0	16
III.	1	0	2	0	2	1	2	1	1	0	1	1	12
IV.	1	0	0	1	0	0	0	0	1	1	0	0	4
V.	0	0	1	0	0	0	1	0	0	0	0	0	2
VI.	0	0	1	0	0	0	1	0	0	1	1	0	4
VII.	0	0	0	0	0	0	1	0	0	2	0	0	3
VIII.	0	0	0	0	1	0	0	0	0	0	0	0	1
IX.	0	0	0	1	0	0	2	0	0	2	0	2	7
X.	0	2	3	1	1	0	2	2	0	0	0	0	11
XI.	2	0	2	0	1	1	0	3	3	1	4	0	17
XII.	1	5	9	3	1	3	1	4	1	3	0	0	31
XIII.	0	1	1	1	1	0	0	1	0	0	1	1	7
XIV.	0	1	3	3	0	2	2	3	2	4	1	0	21
XV.	0	1	1	1	0	1	2	0	2	0	1	0	9
XVI.	0	0	1	1	2	0	0	1	1	0	2	0	8
XVII.	1	0	0	5	0	2	1	0	0	1	1	0	11
XVIII.	0	1	0	0	4	0	0	1	2	0	1	0	9
XIX.	0	2	1	0	0	0	0	0	0	0	0	0	3
XX.	0	0	1	0	3	0	0	0	1	0	0	0	5
XXI.	0	1	1	0	2	0	0	1	1	0	0	1	7
XXII.	0	0	1	0	1	0	1	0	0	1	0	0	4
XXIII.	0	1	1	0	0	0	2	1	1	0	1	1	8
Összesen	8	19	32	21	20	11	19	19	18	17	14	7	205

3. táblázat Feltételezett robbanótest bejelentések Budapesten 2019-ben
Table 3 Alerts of supposed unexploded ordnances in Budapest in 2019 [9]

a veszélyességi fok növelésére. A különböző robbanóanyagok sok esetben olyan vegyületeket képezhetnek a fémekkel, melyek az adott robbanóanyagra jellemző érzékenységet sokszorosára növelik. Példaként a Trinitro-toluolt szeretném felhozni. Ennek a széles körben ismert és használt robbanóanyagnak a *„fémvegyületei olyan robbanóanyagok, amelyeknek lényegesen alacsonyabb a gyulladáspontjuk, és nagyobb az ütésérzékenységük”* [3].

Az energiaközlés egy másik lehetséges módja, mely vétlen elműködtetéshez vezet: a tűz. *„A primer robbanóanyagokat nem tekintve a feketelőpor az egyedüli olyan robbanóanyag, mely valóban láng hatására közvetlenül felrobbantható”* [4]. Éppen ezért érdemes elkerülni, hogy ezek a robbanótestek extrém hőnek, lángoknak legyenek kitéve (pl.: erdőtűz során), vagy számolni kell felrobbanásukkal.

Mindezeken túl a robbanóanyagok mérgező tulajdonságait is ismernie kell annak, aki a kezébe vesz egy veszélyes eszközt. Ez alapvetően kevéssé jelentős probléma, mivel ezek a robbanótestek jól zártak, sok esetben hermetikusak az eltelt idő ellenére. Azonban az esetek jelentős számában törötten vagy sérülten kerülnek elő. Ez egyrészt növeli a kémiai átalakulás kockázatát, másrészt a robbanóanyag töltet fizikailag hozzáférhetővé válik. Ilyen tipikusnak számító eszköz a szovjet 82 mm-es repesz aknagránát, melynek tetrilből készült detonátora van. Ez a brizáns robbanóanyag erősen toxikus [3], és sok esetben ez valódi veszélyt is hordoz, mert az aknagránát bakelit gyújtószerkezete könnyen letörhetett a becsapódás erejétől.

Ezekből a tényekből egyenesen fakad, hogy ezeket az eszközöket megérinteni kizárólag tűzszerész szakembereknek szabad, akik sok éven keresztül tanulják kezelésük mesterfogásait. A tűzszerész szakma olyan ismerethalmazon alapul, melyet laikusként, önjelölt szakértőként megszerezni nem lehet, ezért el kell kerülni a felesleges kockázatokat és minden egyes esetben értesíteni kell a hatóságokat, ha feltételezzük, hogy az előkerült fémtárgy egy robbanótest.

Mindenkinek kötelező bejelenteni a rendőrhatóságnak, esetleg a település jegyzőjének, ha robbanótestnek tűnő tárgyat talál, vagy annak hollétéről tudomást szerez. Itt fontos megjegyezni, hogy a Magyar Honvédség Tűzszerész Ügyelete nem fogad közvetlenül bejelentést az állampolgároktól, mert a vonatkozó jogszabály alapján a Rendőrség feladata a helyszínen meggyőződni a bejelentés részleteiről. A rendőrök a helyszín és az eszköz szemrevételezése után elhelyezik a robbanásveszélyre figyelmeztető jelzést, megjelölik a helyszínt és bejelentést tesznek, majd szükség szerint követik a Tűzszerész Ügyeletes útmutatását. Ezt követően a Rendőrség bejelentését az MH 1. HTHE rendszerében kategóriába sorolják, mely szerint lehetséges soron kívül intézkedni tűzszerész alegység kirendelésére, vagy normál esetben 30 napon belül elvégezni a feladatokat. A meghatározott kategóriáról a bejelentő tájékoztatást kap, mivel a folyamat csak néhány percet vesz igénybe. [5]

A jogszabály 3.§ (3) bekezdése szerint a soron kívüli kirendelés akkor szükséges és lehetséges, ha az alábbi helyszínek valamelyikén került elő feltételezett robbanótest:

„a) lakóépületben,
b) oktatási, nevelési, szociális, egészségügyi vagy más közintézmény területén,
c) vízi vagy szárazföldi útvonalon, közforgalmú repülőtéren,
d) közterületen,
e) vízi létesítmény belső védőterületén lelték fel és a vízszolgáltatást akadályozza; illetve
f) az egyéb helyen talált robbanótest sürgős tűzszerész mentesítése alapos okból indokolt”. [5]

Minden egyéb esetben pedig a 30 napos határidő érvényes, az MH 1. HTHE közszolgálati leterheltségének függvényében. A példa kedvéért ilyen lehet egy családi ház hátsó kertje, ahol rendezett kerítés van és egyéb körülmény nem befolyásolja a kategorizálást, de egy külterületei szántóföld, vagy erdő szintén ebbe a kategóriába esik. Szeretném megjegyezni, hogy a gyakorlati tapasztalat alapján a második kategóriában sem kell 30 napot várni a robbanótestek hatástalanítására, mert a szakemberek ennél jóval korábban megérkeznek.

5. A tűzszerész területmentesítés

Mindezek alapján ahhoz már kétség sem férhet, hogy országunk bármelyik pontján jelentős eséllyel fogunk robbanótestre bukkanni egy komolyabb földmunka során, mely szinte minden építőipari beruházás kezdő mozzanata. Sokan úgy gondolhatják, hogy ez a veszély nem áll fenn, ha például egy régi épület elbontása után kezdenek az építkezésbe. Ezt megcáfolandó, személyes esetet szeretnék ismertetni, mely során egy Budapesten elbontott épület törmelékét egy főváros közeli telephelyen aprították, zúzták kívánatos méretűre további felhasználás céljából. A törmeléket tehát a rombolás után deponálták, felrakodták, elszállították, a telephelyen lerakodták, majd ismét deponálták és betöltötték a gépbe. Szerencsére idejében fedezték fel a zúzógépbe került szovjet FAB-100 típusú romboló légibombát, melynek tömege 100 kg. A hihetetlen szerencsés munkafolyamatban hét olyan alkalom volt, ahol a robbanótest elműködhetett volna. Miközben a kollégáimmal hatástalanítottuk, kiderült, hogy az APUV típusú gyújtószerkezete éles állapotban volt, ezért a mielőbbi megsemmisítés mellett döntöttem. Ezek alapján a különböző foghíj telkek beépítése során, különösen ahol a II. világháborút megelőző az utcakép [6], is felmerülhet a lőszermentesítés kérdése.

A fenti eset jól rámutat, hogy az építőipari munkálatok során még a viszonylag nagyméretű robbanótestek sem keltenek feltűnést, ezért érdemes még a munkagépek megérkezése előtt eltávolítani a veszélyes eszközöket. A terület lőszermentesítésére több megoldás kínálkozik. A piaci szereplők között több vállalkozás is képes felderíteni a talajban lévő robbanótesteket. A MH 1. HTHE szintén végez ilyen jellegű tevékenységet, azonban ezeket a feladatokat térítés ellenében, non profit szervezetként hajtja végre [5].

Ezt a tevékenységet nagyban meghatározza és behatárolja az adott vállalkozás technikai felszereltsége, mert a fémtárgyak detektálására különböző elveken és teljesítményen üzemelő eszközök alkalmazhatók [7]. Fontos megemlítenem, hogy sok esetben az átvizsgálási mélység, a talaj típusa, fémszennyezettsége olyan kombinációban áll össze, hogy nem lehetséges kizárólag műszeres átvizsgálásra alapozni. Ilyen esetben az előzetes műszeres felderítést folyamatos helyszíni biztosítással kell kombinálni a földmunkák alatt, mert csak a szakemberek állandó vizuális felderítésével garantálható a biztonság.

Mindkét választásnak van előnye és hátránya egyaránt, melyet a beruházónak, megrendelőnek érdemes és kell is mérlegelnie. A Magyar Honvédség bevonása a projektbe teljeskörű megoldást tesz lehetővé a felkutatástól, a robbanótest hatástalanításáig vagy elszállításáig, de az árképzés a végrehajtás teljes önköltségét (haszontermelés nem lehetséges) felöleli, mely nem igazodik a piaci versenyhez, és természetesen nem alkuképes. A civil szektor vállalkozásai azonban versenyhelyzetben vannak, ami hatással van az árképzésre, de lehetőségeik kizárólag a robbanótestek felkutatásáig terjednek. Megérinteni és elmozdítani nekik is szigorúan tilos a feltételezett robbanótesteket, bejelentési kötelezettség terheli őket a bemutatott módon, melynek végén a MH 1. HTHE tűzszerészei a jogszabályban rögzített határidőkkel hatástalanítják az eszközöket. Ebben az esetben a hatástalanítás és elszállítás közszolgálati feladat keretében történik, melynek nincs további költségvonzata.

Az elvégzett területmentesítés vagy lőszermentesítés sok kellemetlenségtől kímélheti meg a beruházót, és a projekt költségeiből normál esetben viszonylag kis részt szükséges erre fordítani. Az építkezés menetében egy-egy előkerült robbanótest rengeteg kárt képes okozni, nem is beszélve a szervezési káoszról, amit a kiürítések, állampolgári korlátozások okoznak. Ezeknek jelentős pénzügyi teher lehet a vonzata, míg a mentesítés – jól ütemezve – lehetővé teheti, hogy az építési munkák ebből a szempontból zökkenőmentesen haladjanak.

Érdemes tehát az életveszélyes eszközök felkutatására erőforrást áldozni, de nélkülözhetetlen, hogy ezt jól időzítve, a partnercéget jól megválasztva (nem kizárólag az ár számít, mert a technikai felszereltség, tapasztalat kincset érhet) és körültekintő szervezéssel tegyük meg. Érdemes fontolóra venni hatástanulmány készítését szakértő bevonásával, melynek eredménye megmutatja a mentesítés vélhető szükségességét. A leendő partnerünk kiválasztására és a szakmai munkájának ellenőrzésére szintén jól képzett szakember megbízásával garantálja az elvárt célt. Amennyiben a robbanótest szennyezettség miatt indokolt a munkaterületen dolgozók számára – a biztonság növelése érdekében – előzetes robbanótest felismerő felkészítést is rendelhetünk.

6. Megállapítások

A dolgozat összegzéseként kijelenthető, hogy Magyarország területének szinte minden részén előkerülhetnek II. világháborús robbanótestek, melyek képesek az emberi élet kioltására. A pusztító képességükre az elmúlt évtizedek környezeti eseményei, valamint a lehetséges kémiai folyamatok jelentős hatással lehettek, és ez tovább fokozhatja veszélyességüket. Ez a veszély és képesség mindazon túl, hogy életeket tud elvenni, komoly károkat is okozhat egy baleset során.

A talajból előkerülő robbanásra képes katonai eredetű eszközök bejelentését nem lehet félvállról venni, az mindenkire nézve kötelező érvényű, és kizárólag a tűzszerész szakemberek számára lehetséges a robbanótestek megérintése és elmozdítása.

Érdemes átgondolni a projektek megkezdése előtt a lőszermentesítés végrehajtását, hiszen a folyamatban lévő beruházásokra jelentős negatív hatással van egy-egy előkerült robbanótest. Biztonsági és anyagi értelemben véve is fontos mérlegelni az adott terület mentesítését, mert mindkét vonatkozásban előnyös lehet. Szakértő bevonásával magasabb szintre emelhető a végrehajtás minősége, optimalizálhatók a költségek a várható eredmények tükrében.

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Electrochemical characterization of polymeric sensor of poly-acrylonitrile self-modified with carbon nanotubes (CNT)

Szén nanocsövekkel (CNT) módosított poliakrilnitril elektrokémiai jellemzése

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Abstract

A new conductive material was fabricated from polymer (poly-acrylonitrile) modified with carbon nanotubes. The polymeric material was used to produce of self – modified electrode in cyclic voltammetry. It is well known that when using solid electrodes in electrochemistry, especially in cyclic voltammetry, the electrode works independently in electrolytic conductivity. Therefore, we modify the electrode using carbon nanotubes or other nanomaterials to increase electrical conductivity and obtain high oxidation – reduction current peaks with clear chemical reaction comparing with the electrode in its natural state, (such as glass electrode, platinum electrode, gold electrode and other commercial electrodes). The modification of commercial electrode with carbon nanotubes was acted either mechanical method (manually) by modifying the working electrode with multi attachment of the electrode surface with carbon nanotube (about 30 times). The fabrication electrode is characterized by its special properties, as it is inert, with high potential area, excellent reliability, high hardness, resist to high temperature, water and organic solvents, its low cost (relative to the commercial electrode), non-toxicity, high stability and high accuracy in the analysis of oxidation-reduction process. And has high sensitivity to the chemicals, pollutants and has excellent selectivity.
Keywords: cyclic voltammetry, poly-acrylonitrile, CNT, polymer self-modified with CNT
Kulcsszavak: ciklikus voltammetria, poliakrilnitril, szén nanocsövek (CNT), CNT-vel módosított polimer

1. Introduction

Some advanced techniques in conductive polymers were presented using nanoparticles within to produce different applications in the electrochemical field [1-5], such as working electrode of cyclic voltammetry with high electro-conductivity [6].

It was observed that in mixed nanomaterials, high damping can be achieved by using friction between the nanotubes and the polymeric material. The aim of this research is to study the damping properties in the structures of the mixed material supported by nanotubes of various rubber ratios. The damping properties of samples for pipe ratios between 0-0.6% were studied and tested in practice. By comparing the raw material of the base and the base with the additive, it was observed that the damping was improved by adding nanotubes to the mixture. Practical results showed that the maximum damping ratio (damping factor) was 0.4% of carbon nanotubes [7].

The effect of carbon nanotubes on the electrical properties of polyvinyl chloride has been studied. Examples of polyvinyl chloride composites and carbon nanotubes prepared using thermal pressing technology. Weight ratios of carbon nanotubes are (0, 5, 10 and 20) wt.%. The results show that continuous electrical conductivity increases with increasing weight ratios of carbon nanotubes. Continuous electrical conductivity also changes with increasing temperature for different concentrations of carbon nanotubes. The activation power of the continuous electrical conductivity decreases with increasing the concentration of carbon nanotubes [8].

Carbon nanotubes were used to strengthen the epoxy mixture with polysulfide and assessed the tensile and wear characteristics. In order to achieve a better evaluation of properties, several ratios of nanomaterials were used and mixed with epoxy resin. Poly sulfide was then added to the mixture. Nanocarbon coefficient has increased from 245-273 MPa and the tensile strength of 30.5-38.9 MPa and fracture stress from 12.4% to 14.2%. Electronic elements [9].

Carbon nanotubes were employed using covalent recruitment and in two phases. The employed carbon nanotubes were coated with copper metal using (Electroless coating process). Three groups of superposed copper nanoparticles were prepared using powder technology with different weight ratios of carbon nanotubes. The first group contained carbon nanotubes as they were, the second group contained the employed carbon nanotubes, while the third group contained coated carbon nanotubes. The comparison of these samples showed that the coating process significantly improved the hardness and wear resistance of the superposed nanomaterial. The improvement in properties can be attributed to increased adhesion to the ground and dispersion of carbon nanotubes. SEM, XRD, and FTIR were used to characterize the coating process as well as to characterize metal-based nanomaterials [10].

2. Experimental

2.1 Apparatus

Cyclic voltammetry (CV) was performed with an EZstat apparatus (NuVant Systems, USA) consisting of an electrochemical cell connected to a computer [11]. Reference silver chloride electrodes were placed in 3mol potassium chloride. A 1mm platinum wire used as counter control electrodes [12]. A glassy carbon electrode (GCE) was polished with alumina solution and ultrasonic waterpath 10 min to maintain performance and remove impurities [13-15].

2.2 Materials

Poly-acrylonitrile was received from SCRC, (China), carbon nanotubes (purity 99%) were supplied by Fluka company (Germany), Potassium ferrous cyanide $K_4Fe(CN)_6$ (Merck Sante SAS, Germany), KCl, $KClO_4$, K_2SO_4, K_2HPO_4, and KNO_3 (Technicon chemicals, Tournai, Belgique). deionized water and added 0.1 mM of $K_4Fe(CN)_6$ solution in a cyclic voltammetric cell with the GCE, reference and counter electrodes immersed in the fluid as shown in *Fig. 1*.

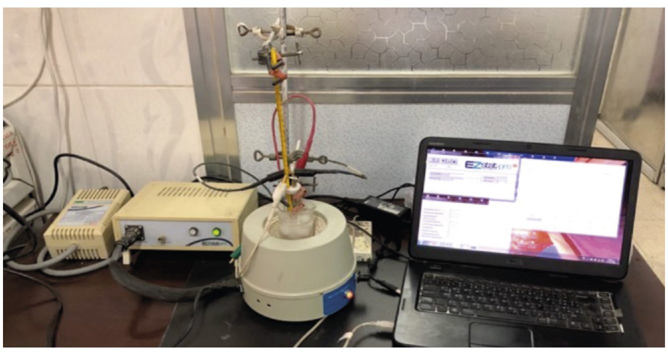

Fig. 1 *Cyclic voltammetry experimental setup*
1. ábra *Ciklikus voltammetria kísérleti összeállítása*

2.2.1 Manufacture of poly-acrylonitrile modified with carbon nanotubes (CNT)

Poly-acrylonitrile was modified with carbon nanotubes were manufactured using the thermal method [16].

2 g of poly-acrylonitrile was mixed with 1 mg of carbon nanotubes using 50 mL of chloroform as a solvent and heated at 50 °C with continuous mixing using a magnetic bar (magnetic bar) for 72 hours for use in diagnostic analyzes and electrode fabrication.

2.2.2 Fabrication of self-modified polymer with carbon nanotubes

The working electrode is made of self-modified polymer with carbon nanotubes by taking a piece of it in a circular diameter of 5 mm and a thickness of 2 mm. The other is connected with a copper wire and all the parts are covered with a glass tube and fixed with epoxy adhesive as shown in *Fig. 2*.

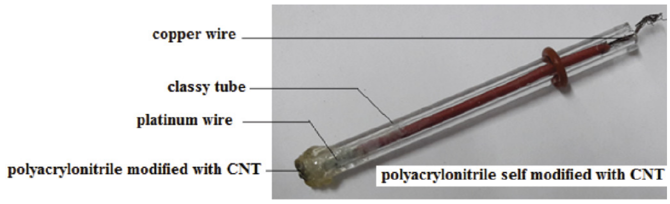

Fig. 2 *Poly-acrylonitrile self-modified with CNT as working electrode*
2. ábra *CNT-vel módosított poliakrilnitril munkaelektróda*

2.3 Characterization studies of the new modified polymer

2.3.1 FTIR infrared spectra

The infrared spectra of the poly-acrylonitrile alone is shown in *Fig. 3* and its comparision with the polymer modified carbon nanotubes in *Fig. 4*.

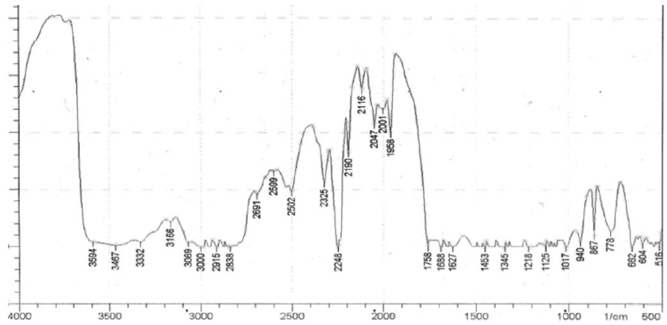

Fig. 3 *Infrared spectrum of poly-acrylonitrile*
3. ábra *A poliakrilnitril infravörös spektrum elemzésének eredménye*

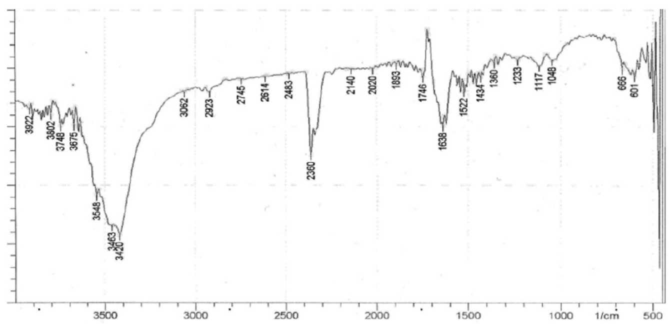

Fig. 4 *Infrared spectrum of polyacrylonitrile after modification with carbon nanotubes rile*
4. ábra *A CNT-vel módosított poliakrilnitril infravörös spektrum elemzésének eredménye*

3.2.2 X-ray study of the new modified polymer

The study of X-ray spectra of the polymer material (poly-acrylonitrile) emergenced of two peaks as shown in *Fig. 5* comparing with the modified polymer material with carbon nanotubes which showed the emergence of a new third summit in the polymer composition of the nanomaterial as shown in *Fig. 6*.

3.2.3 Study of polymer modification with nanomaterials

One of the three methods indicated by Manas, 2006 and Zinco, 2010 was used to modify the polymers either by the free radicals of the gamma rays, the ionic method or the thermal method. The thermal method was adopted in the preparation of the modified polymeric material with nanomaterials. The composition of the nanomaterial entry through the poly-acrylonitrile was proposed as per the scheme proposed in *Fig. 7* [17].

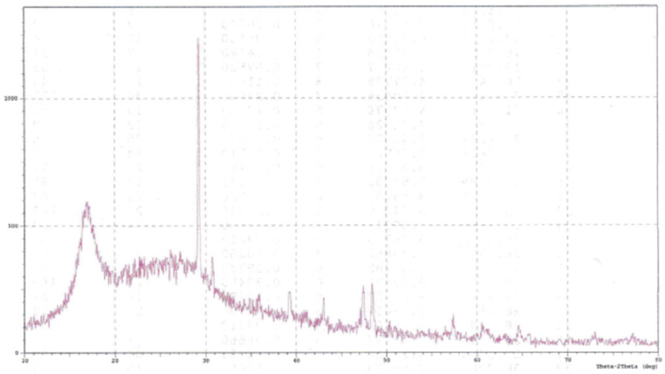

Fig. 5 X-ray spectrum of poly-acrylonitrile
5. ábra A poliakrilnitril röntgenspektruma

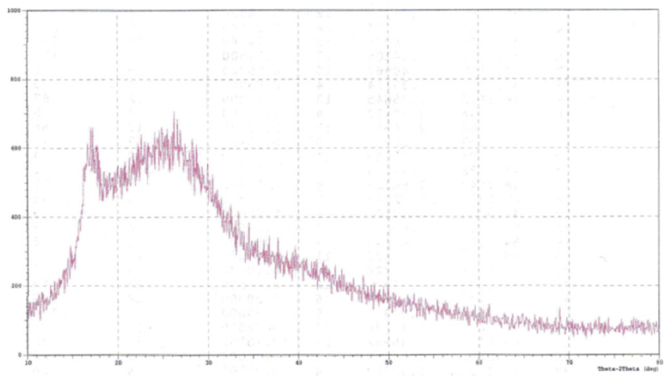

Fig. 6 X-ray spectrum of poly-acrylonitrile after modification with carbon nanotubes
6. ábra A CNT-vel módosított poliakrilnitril röntgenspektruma

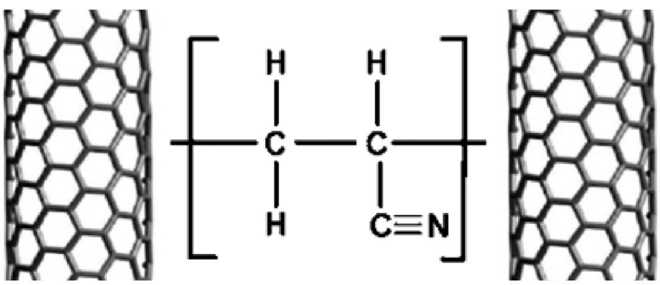

Fig. 7 Proposed formula for carbon nanotube-modified poly-acrylonitrile
7. ábra A CNT-vel módosított poliakrilnitril javasolt formulája

3. Results and discussion

3.1 Effect of potential area

The potential area of the polymeric electrode (polymer modified with carbon nanoparticle) was compared with commercial working electrode such as glassy carbon electrode (GCE) in KCl 1 molar solution. It was noted that the area of potential of the polymer electrode is greater than the potential area of the glassy carbon electrode. The polymer electrode covers an area of -1.8 to + 2.0 volts, while the commercial electrode (GCE) covers an area of less than -1.5 to +1.8 volts.

3.2 Effect of different electrodes

The standard 0.1 molar compound of $K_4[Fe(CN)_6]$ was used to calibrate the cyclic voltammeter in aqueous solutions. Oxidation - reduction peaks of the iron were observed in Fe (III) / Fe (II) as shown in *Fig. 8* of the both working electrodes, modified polymer electrode and glassy carbon electrode (GCE). It was observed that the potential difference between the oxidation and reduction peaks is E_{pc-a} ≈100 mV and the ratio of the current value of the cathode-to-anode peaks (I_{pc} / I_{pa}) is equal to 1, which represents the standard value of the reversible electrodes.

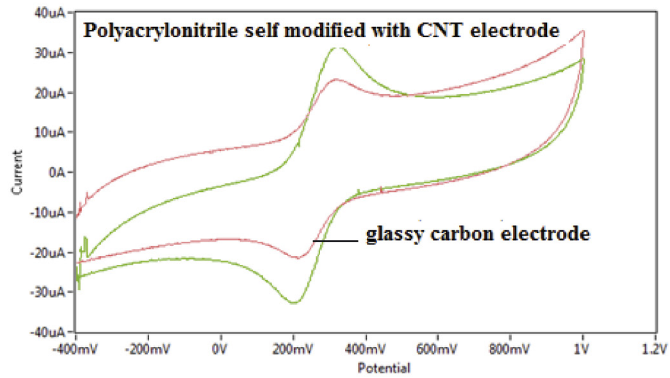

Fig. 8 Cyclic voltammogram of 0.1M Fe ions in 0.1M KCl using (green line) polymer electrode modified with CNT and (red line) glassy carbon electrode
8. ábra 0.1M KCl-ben lévő 0.1M Fe ion ciklikus voltammogramja CNT-vel módosított polimer elektródát használva (zöld) valamint karbon elektródát használva (piros)

3.3 Effect of scan rates on self - modified polymer electrode

At the different scan rates (0.01 - 0.1 Vs-1) of 0.1 mM $K_4[Fe(CN)_6]$ in 0.1 M KCl solution the CV were studied using polymer electrode modified with CNT manufactured in the laboratory. It has been observed that the electric current of the oxidation and reduction peaks of Fe(III)/Fe(II) increases with increasing scanning rate, which indicated that the phenomenon of heterogeneous kinetics is shown in *Fig. 9*. When plotting oxidation and reduction (Ipa and Ipc) versus scan rate, a straight line was shown as in *Fig. 9* and *10* respectively, and the sensitivity values were high because the graphical line matched the device results [18].

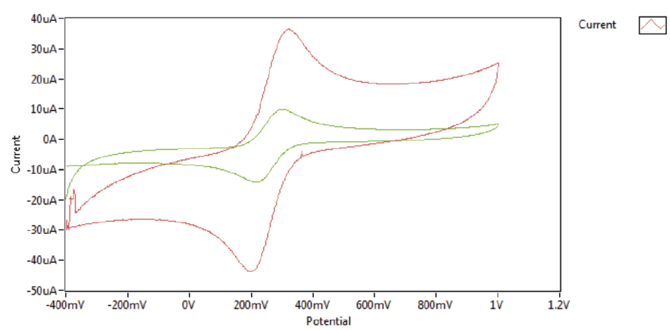

Fig. 9 Cyclic voltammogram of 0.1M $K_4[Fe(CN)_6]$ in 0.1M KCl at different scan rates (red line) SR=0.1 mV/sec (green line) SR==0.01 mV/sec using polymer electrode modified with CNT.
9. ábra 0.1M KCl-ben lévő 0.1M $K_4[Fe(CN)_6]$ ciklikus voltammogramja CNT-vel módosított polimer elektródát használva különböző mintavételi sebességeken (Zöld: SR=0.1 mV/sec; Piros: SR=0.01 mV/sec)

3.4 Measurement of Fe(II)/Fe(III) in different concentration

The new electrode is a highly sensitive electrode in detecting low concentrations of aqueous solutions and, as evidenced by the use of the standard solution $K_4[Fe(CN)_6]$ in a 0.1M KCl solution.

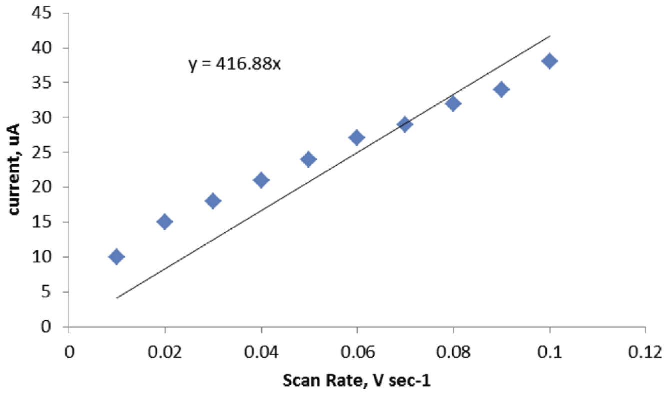

Fig. 10 Plot the oxidation current peak of $K_4[Fe(CN)_6]$ at different scan rates on working electrode of polyacrylonitrile self-modified with CNT

10. ábra $K_4[Fe(CN)_6]$ oxidációs áramcsúcsa különböző mintavételi sebesség mellett CNT-vel módosított polimer elektródát használva

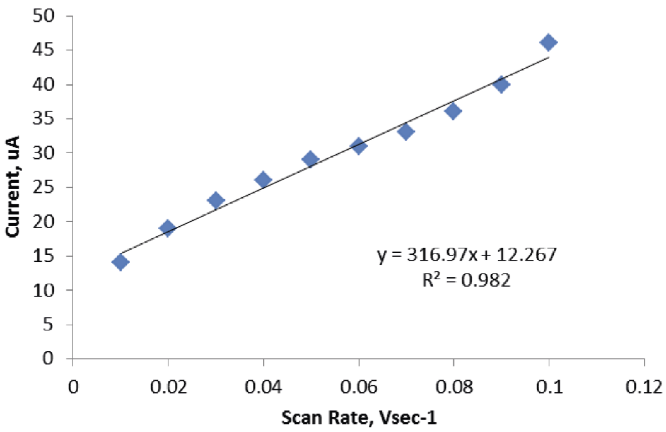

Fig. 11 Plot the reduction current peak of $K_4[Fe(CN)_6]$ at different scan rates on working electrode of polyacrylonitrile self-modified with CNT

11. ábra $K_4[Fe(CN)_6]$ redukciós áramcsúcsa különböző mintavételi sebesség mellett CNT-vel módosított polimer elektródát használva

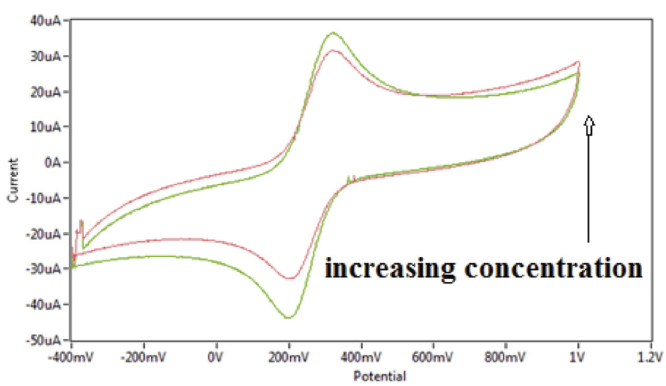

Fig. 12 Cyclic voltammogram of 0.1M $K_4[Fe(CN)_6]$ at different concentrations in 0.1M KCl using polymer electrode self-modified with CNT at SR=0.1 mV/sec versus Ag/AgCl

12. ábra 0.1M $K_4[Fe(CN)_6]$ ciklikus voltammogramja CNT-vel módosított polimer elektródát használva különböző koncentrációk mellett (SR=0.1 mV/sec; vs. Ag/AgCl)

3.5 Study the polymer self-modified with CNT in different pH

The CV technique demonstrated the high sensitivity of the synthesized electrode in different pH levels (for both acidic and alkaline medium) on the oxidation and reduction peaks of 1 mM $K_4[Fe(CN)_6]$ in 0.1 M KCl as an electrolytic solution on the self-modified polymer with carbon nanotubes where shows in *Fig. 13*, a significant sensitivity in various acidic and basic solutions. *Fig. 14* shows the relationship between the pH medium against to oxidation current peak of the iron ions.

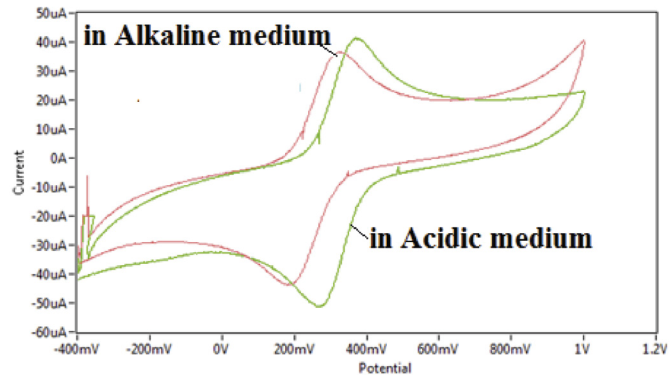

Fig. 13 Cyclic voltammogram of 0.1M $K_4[Fe(CN)_6]$ in 0.1M KCl using polymer electrode modified with CNT in alkaline pH and acidic medium at SR=0.1 mV/sec versus Ag/AgCl

13. ábra 0.1M KCl-ben lévő 0.1M $K_4[Fe(CN)_6]$ ciklikus voltammogramja CNT-vel módosított polimer elektródát használva savas és lúgos közegben (SR=0.1 mV/sec; vs. Ag/AgCl)

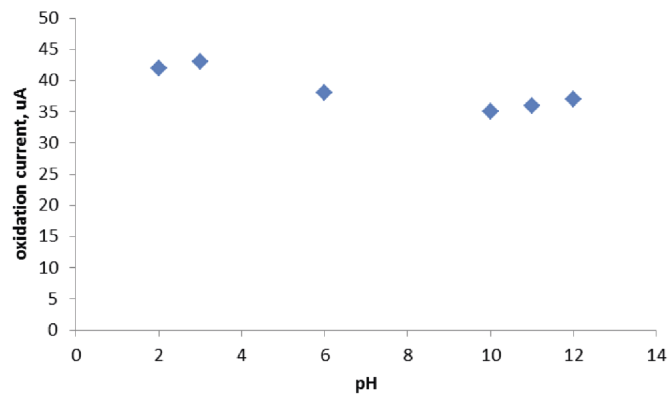

Fig. 14 Plot of oxidation current peak of $K_4[Fe_3(CN)_6]$ at different pH (acidic and alkaline) using polymer electrode self-modified with CNT against to Ag/AgCl as reference electrode and scan rate at 0.1Vsec^{-1}

14. ábra $K_4[Fe(CN)_6]$ oxidációs áramcsúcsa különböző pH (savas és lúgos) mellett CNT-vel módosított polimer elektródát használva vs. Ag/AgCl mint referencia elektróda (SR = 0.1Vsec^{-1})

3.6 Effect of different electrolytes

The different electrolytic solutions have a clear effect on the oxidation and reduction peaks of 1 mM $K_4[Fe(CN)_6]$ in terms of the current as well as voltage when using the polymer electrode. It was found that the highest degrees of the electric current was increaseed the oxidation and reduction peaks according to the following sequence:

Anodic current: KCl> $KClO_4$> K_2SO_4> K_2HPO_4> KNO_3

Cathodic current: KCl> $KClO_4$> KNO_3> K_2SO_4> K_2HPO_4

On this basis, the best electrolyte solution supported in the study of the modified polymer with carbon nanotubes is KCl.

3.7 Scanning Electron Microscopy (SEM) for polymer modified with CNT

The scanning electron microscopy of the polymer modified with carbon nanotubes have been studied as shown in *Fig. 15*.

It was noted that the figure shows the surface of the electrode was overlapped, impermeable, compact and punctuated by strings represented by carbon nanotubes.

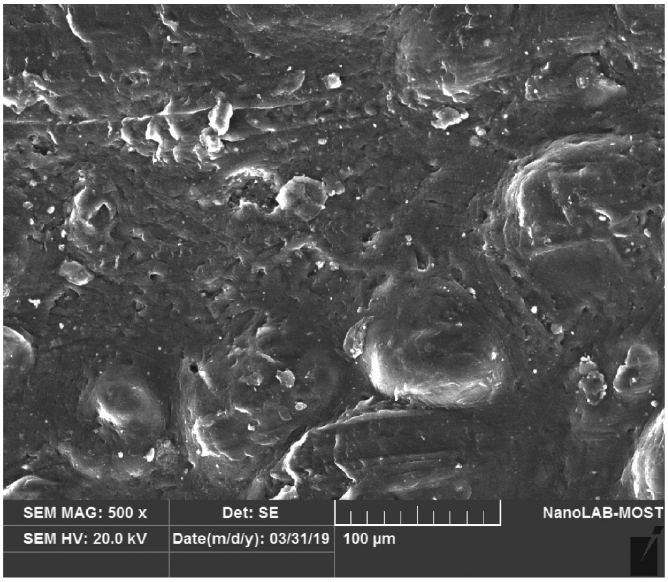

Fig. 15 SEM of polymer modified with CNT
15. ábra A CNT-vel módosított polimer pásztázó elektronmikroszkóp alatt

3.8 Study Atomic Force Microscopy (AFM) of polymer modified with CNT

Fig. 16 shows the atomic force microscopy of the surface of the synthetic electrode in the regular image of the polymer, which overlaps with carbon nanotubes and highly homogeneity and regulation was the high proportion of the measurement of carbon nanotubes of 20-100 nanometers as shown in *Fig. 17*.

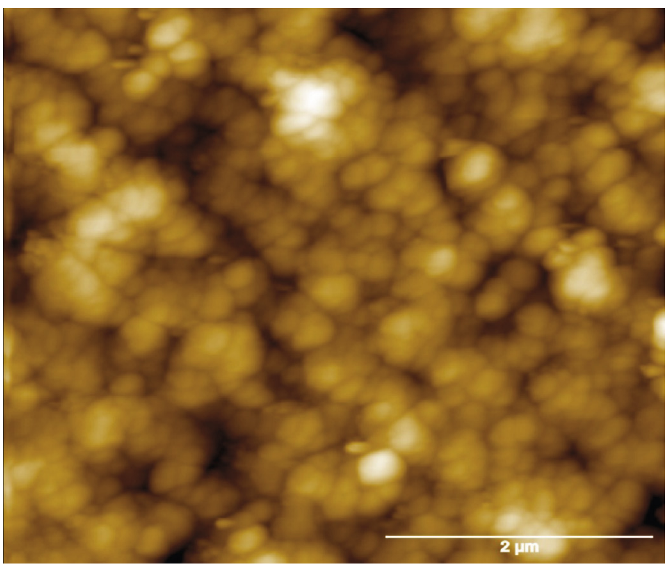

Fig. 16 AFM of the polymer modified with CNT
16. ábra A CNT-vel módosított polimer atomerő-mikroszkóp alatt

3.9 Study of reproducibility and stability of self-modified polymer with carbon nanotubes

The potential and current stability of the new electrode was studied by the standard solution of $K_4[Fe(CN)_6]$ in KCl solution. The CV is obtained by proving the redox peaks in the relation between current and voltage. *Fig. 19* shows the overlapping of cyclic voltammogram of ten times of redox peaks of Fe(II)/Fe(III), which indicated the stability of the new fabricated electrode.

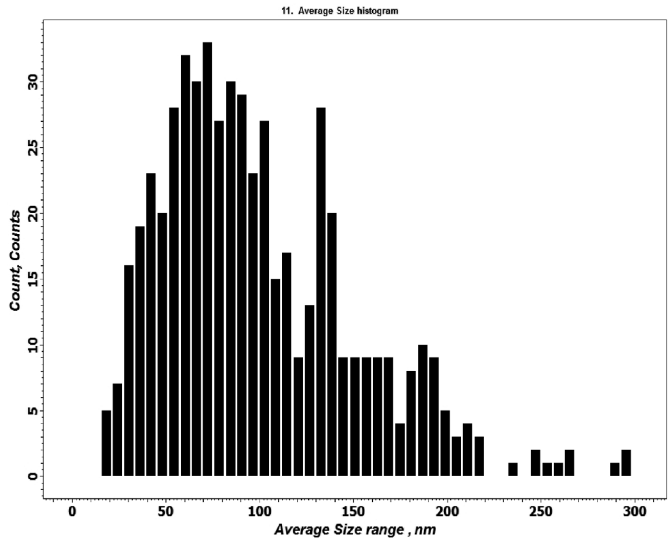

Fig. 17 The diagram of the percentage average dimension of nanoparticles in the polymer modified with CNT from AFM analysis
17. ábra A CNT-vel módosított polimer nanorészecskék méretének százalékos eloszlása az AFM elemzés alapján

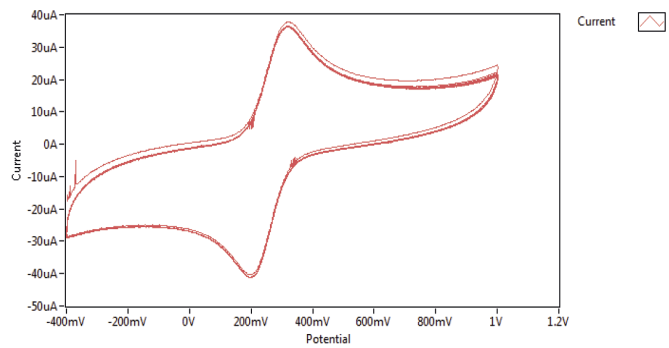

Fig. 18 Cyclic voltammogram of 0.1M $K_4[Fe(CN)_6]$ in 0.1M KCl at ten times using polymer working electrode modified with CNT
18. ábra 0.1M KCl-ben lévő 0.1M $K_4[Fe(CN)_6]$ ciklikus voltammogramja 10-szer ismételve CNT-vel módosított polimer elektródát használva

4. Conclusions

The new polymeric working electrode was manufactured because of its importance in the analysis of electrochemistry, especially in the cyclic voltmeter can be used in several aspects:

1. Used as an alternative to commercial solid electrodes used in the cyclic voltmeter because it is better than electrochemical analysis (in terms of electrical conductivity).
2. It can be used as an alternative to electrodes used in acidity measurement (pH meter).
3. The electrode can be used as a self-modified carbon nanotube in the rotary electrode technique which can be used with high efficiency by electrolysis since the oxidation and reduction current at high value.

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Potentials of calcined clay as a pozzolan

Kalcinált agyag puccolános anyagként való használatának lehetőségei

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Abstract

Calcined clay (CC) is a promising pozzolan recently attracting research attention globally. Various investigations have shown the desirable attributes of the material as a Supplementary Cementitious Material (SCM) in cement concrete systems. This paper captures the compressive strengths impact of calcined clay-Portland cement (CC-PC) as binders in both concrete and soil systems. Grade 20 concrete cubes were prepared and tested; adopting five CC-PC binder blends obtained by replacing PC with CC at 0(control), 5, 10, 15, and 20%; designated as PC100, PC95, PC90, PC85, and PC80, respectively. Similarly, four CC-PC binder blends PC100(control), PC75, PC50, and PC25 were adopted to stabilise samples of A-2-6 lateritic soils at increasing content of 0, 2.5, 5, 7.5, 10% of the soil's weight. Results show that compressive strengths of the concrete samples increase with cement replacement. PC80 impacts the highest strengths with 7, 28 and 56-day strength activity indices (SAIs) of 174.7, 126.0 and 144.9%, respectively. In soil stabilisation, unconfined compressive strength (UCS) of the soil was found to increase with binder contents (2.5% to 10%) for the four binder designations. Compared to control (PC100), the PC75, and PC50 binders were better stabilisers with 7 and 28-day SAIs ranging between 105 and 275%, respectively. From the results, for applications across concrete and soil stabilisation works, CC has been shown to be a potential supplementary material for mitigating carbon emission without compromising on strength enhancement.

Keywords: calcined clay, compressive strength, binder blends, cement concrete, soil stabilisation
Kulcsszavak: nyomószilárdság, kötőanyag keverékek, beton, talaj stabilizálás

1. Introduction

The need for reduction in carbon footprints has continued to be a front-burning discussion in environmental sustainability. In response to this, research efforts have been geared towards finding eco-friendly, cost-effective alternatives to Portland cement, which contributes about 10% of carbon emission globally [1-2]. Moreover, considering the likelihood of increased cement demands (especially in developing countries), possible supplements should have an appreciable level of commercial availability to meet up with these demands.

Calcined kaolin clay (calcined clay, CC) has been reported as a promising supplementary binder in civil engineering works. It has been regarded as reactive and its production eco-friendlier than cement's [1-4]. This paper documents the comparative performances of CC in cement concrete and soil stabilization works. The idea is to project the broader view of the applicability of this pozzolan across different civil engineering uses.

2. Materials and methods

Raw kaolinite clay was obtained from a deposit reported to have abundance of the material with the kaolinite mineral content being as high as 95% [5]. Chemical properties are also typical of kaolin clay [6]. The clay was milled and calcined 700°C for 1 hour based on the previous findings of the authors [6]. The calcined samples sieved using 90μm sieve to have samples whose fineness compares closely with cement.

The work was executed in two stages. The first was to use calcined clay (CC) in cement concrete. CC-PC concrete cubes of grade 20 were prepared with ordinary Portland cement (PC) grade 32.5, CC and aggregates (fine and coarse aggregates in line with standard [7]). Five sets of 150mm concrete cubes were produced and designated as PC100, PC95, PC90, PC85, and PC80; corresponding to replacement of Portland cement (PC) with CC at five levels of 0%, 5%, 10%, 15% and 20% respectively. The samples were tested for their compressive strengths at increasing curing ages. The sprinkler curing method was applied to simulate a typical curing technique at construction sites. The concrete cubes were uniformly sprayed twice daily (sunrise and by sunset) with water to obtain thin films of water round them.

The second stage was to stabilise samples of fine-grained (A-2-6) lateritic soils using four CC-PC blends designated as PC100, PC75, PC50 and PC25; corresponding to PC replacement levels of 0%, 25%, 50% and 75% respectively. Each blend was applied at 0%, 2.5%, 5%, 7.5% and 10% of the soil's weight, respectively; the 10% limit considered as adequate in line with [8]. The soil-stabiliser mixes were compacted, cured and tested for the unconfined compression strength (UCS).

3. Results and discussion

Table 1 presents the compressive strengths of the CC-PC concretes. Generally, the strengths of the PC95, PC90, PC85, PC80 specimens were comparable to control's (PC100). These were typical of grade 20 concretes. The PC80 samples produced the highest 28-day and 56-day strengths of 24.36 N/mm² and 28.00 N/mm², respectively. The corresponding strength activity indices (SAIs) were 126% and 144.9%; indicating that the strengths were enhanced with the adoption of CC as cement supplement up to the 20% level. Thus, apart from the potential of reducing dependence on cement and mitigating the associated carbon emissions, strength enhancements are achievable with CC-PC blends.

Binder Designation	7-day strength	28-day strength	56-day strength
PC100	9.06 (100.0%)	19.33 (100.0%)	21.15 (100.0%)
PC95	8.41 (92.8%)	19.29 (99.8%)	22.64 (117.1%)
PC90	9.11 (100.6%)	17.60 (91.1%)	20.00 (103.5%)
PC85	16.00 (176.6%)	20.74 (107.3%)	23.82 (123.2%)
PC80	15.83 (174.7%)	24.36 (126.0%)	28.00 (144.9%)

Note: Strength Activity Indices are presented as a % of PC100

Table 1 Compressive strengths (N/mm²) of the CC-PC concretes
1. táblázat CC-PC betonok nyomószilárdsága (N/mm²)

The results of the UCS are also presented in *Table 2a* and *2b*.At 0% stabiliser content, the 7-day strength (0.8 N/mm²) did not vary significantly from the 28-day strength (0.9N/mm²) since there were no binders whose impact can improve the soil strength. These UCS values are lower than the minimum of 1.8 N/mm² recommended for base course materials for flexible road pavement [9-11]; indicating a weak soil which requires stabilisation. The results show that the binders PC100 (control), PC75 and PC50 successfully improved the strength of the soil above the required threshold.

Binder Designation	Total binder %				
	0%	2.5%	5%	7.5%	10%
PC25	0.80	0.40 (48.8%)	0.55 (45.8%)	0.70 (42.4%)	1.20 (40.8%)
PC50	0.80	2.24 (273.2%)	2.34 (195.0%)	2.59 (157.0%)	3.11 (105.8%)
PC75	0.80	1.50 (182.9%)	3.04 (253.3%)	3.74 (226.7%)	4.64 (157.8%)
PC100	0.80	0.82 (100.0%)	1.20 (100%)	1.65 (100.0%)	2.94 (100.0%)

Note: Strength Activity Indices are presented as a % of PC100; for each binder content

Table 2a 7-day unconfined compressive strength of stabilised soil (N/mm²)
2a táblázat Stabilizált talaj 7 napos nyomoszilárdsága (N/mm²)

Binder Designation	Total binder %				
	0%	2.5%	5%	7.5%	10%
PC25	0.90	0.97 (87.4%)	1.76 (88.9%)	2.13 (83.2%)	3.36 (91.1%)
PC50	0.90	2.97 (267.6%)	3.19 (161.1%)	3.58 (139.8%)	4.47 (121.1%)
PC75	0.90	2.31 (208.1%)	4.63 (233.8%)	4.98 (194.5%)	5.80 (157.2%)
PC100	0.90	1.11 (100.0%)	1.98 (100.0%)	2.56 (100.0%)	3.69 (100.0%)

Note: Strength Activity Indices are presented as a % of PC100; for each binder content

Table 2b 28-day unconfined compressive strength of stabilised soil (N/mm²)
2b táblázat Stabilizált talaj 28 napos nyomoszilárdsága (N/mm²)

The SAIs indicate that PC75 and PC50 can comparatively replace the control (PC100) with satisfactory performances. PC50 presented comparably higher strength while optimum strengths were obtained with PC75. Thus, for soil stabilisation, potential savings of up to 50% in PC usage (by extension, 50% reduction in accruable carbon emission) can be achieved with CC-PC blends, as indicated in the result. The PC25 did also improve strength but at a later curing age.

4. Conclusions

The optimal strengths achieved in adopting CC in concrete and soil stabilisation works indicates possible benefits accruable from adopting this pozzolan in civil engineering works. The material has shown the potential of mitigating carbon emission by replacing cement by as much as 20 to 50%, respectively, depending on the required engineering use and without compromise on strengths.

The details of the mechanism of reaction of this pozzolan, especially in soil-binder systems remain to be fully investigated. This will help capture the reactive phases with the CC based systems. With this, the protocol for the application of CC as binder can be established for stakeholders. Research progress on the durability of the CC-based systems needs be properly documented, as well, in details.

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Thermal and mechanical properties of fabricated plaster of Paris filled with groundnut seed coat and waste newspaper materials for structural application

Földimogyoró héjjal és hulladék papírral készült szerkezeti felhasználású alabástromgipsz hőtani és mechanikai tulajdonságai

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Abstract

This work sought to assess the suitability of using boards produced with plaster of Paris (P.O.P) and various weight proportions of groundnut seed coat (GSC) as well as P.O.P and similar proportions of waste newspaper paste (WNP) as ceiling in building design. The results obtained from the investigation of thermal and mechanical properties of the fabricated boards revealed that with the use of GSC as filler, the samples were of higher mean values of specific heat capacity, thermal conductivity, thermal absorptivity, but lower mean values of bulk density, thermal diffusivity, percentage water absorption, flaking concentration and flexural strength when compared to the samples with similar proportions of WNP as filler content. Also, the sample with 13.8% content of GSC and the one containing 22.5% of WNP were found to exhibit an impressive performance. Generally, it was observed that the samples filled with either GSC or WNP were lighter than pure P.O.P samples and the recorded values for all the measured properties favoured them for use as ceiling material in buildings. It is noteworthy that the proportion of the filler can be adjusted for optimum performance of such environmentally-friendly and cost-effective ceilings. Utilizing groundnut seed coat and waste newspapers as filler materials in fabrication of P.O.P ceiling can help to reduce environment pollution level, ensure better thermal insulation of buildings and solve the lingering problem of high cost of using P.O.P or other conventional materials as ceiling in buildings by the end-users.

Keywords: ceiling, flaking concentration, flexural strength, recycling, specific heat capacity, thermal conductivity, waste materials

Kulcsszavak: födém, hajlító szilárdság, újrahasznosítás, fajlagos hőkapacitás, hővezető képesség, hulladék anyagok

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1. Introduction

In any building design, ceiling is one of the most important structural elements that require consideration with priority. Energy consumption increases as demand in thermal comfort of building raise [1]. Ceiling plays a vital role in shielding the occupant from direct heat absorbed from an external environment by the building roof. Stating in another way, ceiling is a finished surface that conceals the underside of a building roof to impart aesthetic appeal and also prevent thermal influx to the room, thereby promoting comfort as well as safety of individuals. Based on the used materials, various types of false ceiling include asbestos ceiling, gypsum ceiling, polyvinylchloride (PVC) ceiling, Plaster of Paris (P.O.P) ceiling, among others.

It has been reported that even at low concentration, asbestos has a significant health risk [2]. The findings made by [3, 4] also supported such report. Therefore, when considering the fact that gypsum ceiling can be easily damaged by water from a leaked roof and PVC ceiling is not heat-resistant, P.O.P ceiling becomes preferable among them. Usually, P.O.P is manufactured as a dry powder and when it is mixed with water, it is possible to produce paste which in turn is used for ceiling. The mixing process generates heat through crystallization and the hydrated P.O.P then hardens in mold after few minutes.

Apart from its attractive nature, P.O.P ceiling almost requires no maintenance and has a long-life-span. Such tendencies make it a suitable material for sustainability in real estate industry.

But sustainable building materials have to be cheap [5] in order to make housing affordable, accessible, easy to own and maintain [6, 7]. In that case, there is no doubt that the high cost of P.O.P experienced for years now has contributed immensely to the bane of development of housing in particular and construction sub-sector at large. Also, it is obvious that one way of solving the evolving problem due to high rise in the cost price of building materials is the production of new engineering materials that are cheap but can perform optimally when used for structural applications.

This research work, therefore, seeks to develop a new kind of composite material using P.O.P with groundnut seed coat (also known as testa) and waste newspaper (un-useful and discarded newsprint materials). The choice of groundnut seed coat and waste newspaper is primarily due to their cheap availability in addition to high volume generation as municipal solid wastes [8, 9] without safe disposal techniques. Kaz et al [10] opined that if this situation persists, the current annual production of about 2.01 billion metric tons of such solid wastes will increase by 70% with the possibility of their overall generation increasing to 3.40 billion metric tons by 2050 as estimated by world bank. Due to the global problems associated with solid waste management [11], it has been observed in recent times that the waste materials in question are usually disposed of by burning in an open air. This practice has the potential of bringing about serious environmental issues that can substantially affect human health and climate. Specifically, this work is aimed at using recycling method to prevent the accumulation of the said waste materials in our environment. The thermal and mechanical properties of the developed composite boards will be investigated in order to ascertain their suitability to be used as a ceiling in building design. Among other advantages, it is hoped that this work will provide useful information to engineers, builders, researchers and so on.

2. Experimental perspective

2.1 Materials

The following major materials were used in this research work; water, groundnut seed coat (collected from groundnut sellers as waste product of blanching process), waste newspapers (obtained from newspaper vendors) and P.O.P (ABS 3Se bought from building materials store). These materials were sourced within Uyo metropolis, Akwa Ibom State, Nigeria.

2.2 Method

2.2.1 Processing of the groundnut seed coat and waste newspapers

A large quantity of the as-received groundnut seed coat was soaked in cold water in a plastic bucket at 30°C. This process helped to remove any dirt and unwanted materials from it. After 10 hours, it was removed and sun-dried completely before being blended by means of an electric blender. Also, the waste newspaper was shredded into tiny pieces with the aid of an electrical paper shredder (Rexel V125). Warm water was put into another plastic bucket and the paper pieces produced were soaked in it for 24 hours. This was necessary in order to make the paper smooth, soft and unable to affect the amount of water needed for plaster reaction. On removing them from the water, they were lightly squeezed with hand (to remove some water absorbed) and then pounded by means of mortar and pestle to form paste. The paste was subjected to continuous sun-drying and weighing until its weight remained constant. *Fig. 1* shows the dry forms of the blended groundnut seed coast (GSC) and waste newspaper paste (WNP).

Fig. 1 Dry forms of (a) blended GSC and (b) WNP
1. ábra (a) GSC és (b) WNP szárított formában

2.2.2 Fabrication of test samples

Using hand lay-up technique, samples containing the P.O.P and various weight proportions of the blended groundnut seed coat were prepared. Then after, other samples of similar proportions but with the dry waste newspaper paste as content were formed. The weight ratio of water to the sample composition was 1:2 throughout the preparation process. While the prepared samples for thermal conductivity test were cast in a 240mm x 240mm x 18mm mold, those for other tests were poured into a mold of dimensions 210mm x 120mm x 10mm. For each composition, five representative samples were developed per proportion, precured for 40 minutes at room temperature and then sun-dried until there was no reduction in the weight of each of them before they were used for tests in this work.

2.3 Tests implementation

2.3.1 Bulk density

This property expresses the degree of compactness of matter in a given material considered. In this work, the sample was cut into a reasonable size and its mass was determined by weighing using analytical balance (METTLER TOLEDO, PL 203). Then after, the bulk volume of the sample was determined by modified water displacement method [12]. In this case, white candle wax discarded as waste was melted and used in surface-coating the sample. The thickness of the glass cylindrical tube was measured with digital micrometer screw gauge and the external diameter of the tube was measured using digital vernier calipers. Complete immersion of the coated sample was ensured after which the height through which water was displaced in the tube was measured with metre rule. The bulk density of the sample (uncoated) was computed using the relation

$$\rho = \frac{M}{V_m - V_s} \qquad (1)$$

where ρ = bulk density of the sample, M = mass of the sample, V_s = volume of the candle wax coating on the sample, V_m = volume of the coated sample and (V_m – V_s) = bulk volume of the sample.

2.3.2 Specific heat capacity

Determination of this property was done by using mixture method of calorimetry, employing temperature-cooling correction [13, 14]. However, instead of using boiling water to heat the sample under investigation, a modified procedure was applied in this work. The mass of an empty copper calorimeter with its stirrer and that of the sample were measured. After filling the calorimeter with a reasonable amount of cold water, the mass of the water alone was determined. Then after, the system was well lagged and its initial temperature was measured by means of a copper-constantan thermocouple. Also, a stainless-steel container was filled to about 18mm of its depth with dry sharp river sand (free from impurities) screened with mesh No. 10 of US sieve. The sample was embedded in the sand in such a way that it did not make any direct contact with the container. While heating the container, when the temperature of its content remained unchanged for some seconds, the sample was quickly transferred by tongs into the water contained in the calorimeter. In order to determine the actual final steady temperature of the gently stirred mixture, the temperature-cooling correction value was added to the observed steady temperature value. Also, for any component of the system, the quantity of heat lost or gained in the process, as the case may be, was calculated as the product of its mass, specific heat capacity and change in temperature (in relation to the actual final temperature of the mixture). By assuming that there were no heat losses to the surroundings, the specific heat capacity, c of the sample was calculated using the formula

$$c = \frac{Q_c + Q_w}{M\Delta T} \qquad (2)$$

where Q_c = quantity of heat gained by the calorimeter and its stirrer, Q_m = quantity of heat gained by water in the calorimeter, M = mass of the sample used and $\Delta\Theta$ = change in temperature of the sample on cooling.

2.3.3 Thermal conductivity and thermal diffusivity

Measurement of data for determination of thermal conductivity of each sample in this work were carried out in accordance with ASTM C518 procedure [15]. The data were obtained using Heat Flow Meter (HFM 100 series) as described elsewhere [16]. This meter is equipped with Peltier heating / cooling plates for rapid temperature control. Its two flux sensors are for accurate monitoring of heat flux generated as a result of difference in temperature between the top and bottom plates at regular intervals. Based on Fourier's law, when the steady-state heat flux was observed, the data obtained were applied to calculate the sample's thermal conductivity value according to the relation

$$k = \frac{xQ}{A\Delta\theta} \qquad (3)$$

where k = thermal conductivity of the sample, x = thickness of the sample, Q = amount of heat flowing through the sample, and $\Delta\Theta$ = temperature difference between the top and bottom plates.

For each of the samples, the values of thermal conductivity, bulk density and specific heat capacity got were used to compute its thermal diffusivity, λ as [17]

$$\lambda = \frac{k}{\rho c} \qquad (4)$$

2.3.4 Water absorption

Porous ceiling materials are known to have the tendency to absorb and retain water if it gets in contact with them. Since, as ceiling materials, the samples are likely to come in contact with water if there is leakage in the building roof, this test was performed to assess the extent to which the samples in this work can behave in such situation, Each dry sample was weighed before all of them were immersed immediately in water at 32°C. After 24 hours, they were removed from the water and allowed to surface-dry before each of them was reweighed. The data obtained were used to determine the percentage water absorption based on the equation [16]

$$W.A = \left(\frac{M_w - M_d}{M_d}\right) 100\% \qquad (5)$$

2.3.5 Flaking concentration and flexural strength

The durability of materials that can undergo tear and wear when they are worked on can be predicted from the degree of their abrasion resistance. Such prediction is possible with a known value of a material's flaking concentration. In this work, a Taber Linear Abraser (Model 5750) was used for the test. The machine has a mechanical arm to which a free-floating test system is attached. Both sides of the sample were cleaned using a lint free cloth after which the mass of the sample was measured. The sample was then placed on the table and secured with sample holder in such a way that the area to be tested lined up with the abradant. Also, the abradant was refaced with a bristled brush pad before the commencement of the test. For each of the test samples, a test speed of 70 strokes per minute was used with 50 cycles of back-and forth movement of the arm. At the end of each test, both sides of the sample (flaked) were cleaned and the sample was weighed. The data obtained were utilized in the calculation of flaking concentration using the formula

$$F_c = \frac{m_f}{m_o} \qquad (6)$$

where F_c = flaking concentration of the sample, m_f = difference in the mass of the sample after the abrasion test, m_o = mass of the sample before being subjected the abrasion test.

The flexural strength was tested for each of the samples using a three-point bending method as stated in [18]. A test speed of 50.0mm.min^{-1} was maintained for each test schedule until fracture occurred [16]. Then the value of maximum load, L applied at that instant, length of the support span, d as well as the width, b and thickness, x of the sample were applied in the computation of flexural strength, σ as

$$\sigma = \frac{3Ld}{2bx^2} \qquad (7)$$

All the tests in this work were carried out at room temperature with ± 2°C variations. For each test, the five representative samples developed were made use of and also, the results obtained were tabulated and analysed.

3. Results and discussion

The experimental data got from the analysis involving samples with groundnut seed coat (GSC) and those associated with samples containing waste newspaper paste (WNP) are recorded in *Table 1* and *Table 2* respectively. For 0.0% content of either GSC or WNP, the data are meant for pure plaster of Paris (P.O.P) samples. The mean values of the data are presented, with their uncertainty, as the experimental results in *Table 3*.

It can be seen from *Table 3* that the addition of either GSC or WNP to the P.O.P decreases the mean values of bulk density and thermal conductivity. Samples containing the GSC are observed to have lower values of mean bulk density and higher values of mean thermal conductivity than their counterparts containing the WNP. In the case of bulk density, this shows that the densest material among the three is P.O.P followed by WNP. Also, in the case of thermal conductivity, it is due to the capability of the WNP to create more pores within the samples and that consequently gives rise to existence of more enclosed dead air space (void) after the fabrication process. Thus, since air is a poor conductor of heat, the samples with WNP content then become more thermally insulating than those containing GSC of similar proportion. As can be deduced from *Table 3*, the mean thermal resistivity (reciprocal of mean thermal conductivity) value of the P.O.P is (3.829 ± 0.059) $W^{-1}mK$ while the highest mean value for the samples with GSC content and the highest mean value for the samples containing WNP are (6.557 ± 0.013) $W^{-1}mK$ and (8.097 ± 0.118) $W^{-1}mK$ respectively. These mean thermal resistivity values portray improvement in thermal insulation ability at 31.3% by (41.62 ± 0.92) % for GSC content and (52.72 ± 1.80) % for using WNP as a component of the samples. The implication of this observation is that although the developed samples with GSC are lighter than those with WNP content of similar proportion, they are not as effective as the later in terms of ability to restrict heat transmission across their thickness.

From *Fig. 2*, it is obvious that the mean values of both bulk density and thermal conductivity decrease with the proportion of either GSC or WNP added to the P.O.P. This finding is fully supported by the report of Faiza et al [19]. The possibility of this phenomenal trend is based on the fact that since the size of the fabricated samples is fixed in this work, increasing the GSC or WNP content leads to decrease in the proportion of the P.O.P which eventually results to decrease in bulk density of the sample because of increase in its number of interstices through which air may pass easily.

Weight fraction of GSC	Sample Code	Bulk Density, ρ (kgm^{-3})	Specific Heat Capacity, c ($Jkg^{-1}K^{-1}$)	Thermal Conductivity, k ($Wm^{-1}K^{-1}$)	Thermal Diffusivity, λ ($10^{-7}m^2s^{-1}$)	Water Absorption, W.A (%)	Flaking Concentration, F_c (10^{-3})	Flexural Strength, σ (N/mm^2)
0.0%	S1	1360.89	1586.34	0.2637	1.221	13.28	0.038	5.230
	S2	1353.29	1622.85	0.2528	1.151	14.24	0.041	5.210
	S3	1363.83	1577.34	0.2730	1.269	12.92	0.037	5.236
	S4	1356.62	1596.66	0.2539	1.172	14.08	0.040	5.211
	S5	1360.49	1610.69	0.2625	1.198	13.68	0.038	5.217
7.5%	G1	1175.00	1757.81	0.2347	1.136	15.87	0.778	1.343
	G2	1162.00	1775.95	0.2267	1.099	15.99	0.779	1.342
	G3	1152.66	1820.70	0.2182	1.040	16.02	0.919	1.330
	G4	1154.46	1817.58	0.2257	1.076	16.00	0.848	1.333
	G5	1150.21	1831.46	0.2173	1.032	16.04	0.991	1.322
13.8%	G6	1011.79	2000.80	0.1800	0.889	20.45	1.277	0.525
	G7	1020.91	1953.55	0.1808	0.907	20.23	1.226	0.526
	G8	1030.14	1952.00	0.1934	0.962	19.52	1.097	0.543
	G9	1027.48	1948.98	0.1873	0.935	19.73	1.157	0.540
	G10	1025.73	1949.28	0.1865	0.933	19.95	1.212	0.528
22.5%	G11	898.99	2207.74	0.1680	0.847	22.54	1.533	0.460
	G12	924.07	2177.33	0.1744	0.867	22.47	1.524	0.501
	G13	899.77	2200.96	0.1688	0.852	22.53	1.530	0.477
	G14	927.64	2170.69	0.1796	0.892	22.45	1.473	0.503
	G15	922.89	2186.34	0.1736	0.860	22.49	1.529	0.480
31.3%	G16	843.89	2460.21	0.1524	0.734	29.15	2.192	0.165
	G17	856.69	2409.97	0.1533	0.743	29.12	2.188	0.169
	G18	842.32	2466.89	0.1521	0.732	29.21	2.274	0.162
	G19	851.66	2438.81	0.1527	0.735	29.13	2.191	0.167
	G20	839.83	2484.61	0.1518	0.727	29.26	2.281	0.160

Table 1 Experimental data from the analysis involving the samples with GSC
1. táblázat A GSC-vel készült mintákon végzett vizsgálatok mérési eredményei

Weight fraction of WNP	Sample Code	Bulk Density, ρ (kgm^{-3})	Specific Heat Capacity, c ($Jkg^{-1}K^{-1}$)	Thermal Conductivity, k ($Wm^{-1}K^{-1}$)	Thermal Diffusivity, λ ($10^{-7}m^2s^{-1}$)	Water Absorption, W.A (%)	Flaking Concentration, F_c (10^{-3})	Flexural Strength, σ (N/mm^2)
0.0%	S1	1360.89	1586.34	0.2637	1.221	13.28	0.038	5.230
	S2	1353.29	1622.85	0.2528	1.151	14.24	0.041	5.210
	S3	1363.83	1577.34	0.2730	1.269	12.92	0.037	5.236
	S4	1356.62	1596.66	0.2539	1.172	14.08	0.040	5.211
	S5	1360.49	1610.69	0.2625	1.198	13.68	0.038	5.217
7.5%	W1	1217.41	1566.20	0.2106	1.105	20.99	1.433	3.058
	W2	1222.95	1561.85	0.2116	1.108	20.82	1.544	3.068
	W3	1209.95	1567.98	0.2074	1.093	21.08	1.374	3.052
	W4	1189.99	1597.57	0.2063	1.085	21.16	1.491	3.049
	W5	1189.87	1604.56	0.2053	1.075	21.34	1.436	3.040
13.8%	W6	1088.63	1553.25	0.1783	1.054	27.08	2.081	2.397
	W7	1090.14	1545.17	0.1792	1.064	26.98	2.043	2.403
	W8	1081.17	1558.23	0.1767	1.049	27.19	2.082	2.386
	W9	1116.09	1534.21	0.1829	1.068	26.69	1.985	2.424
	W10	1098.66	1543.49	0.1804	1.064	26.88	1.986	2.418
22.5%	W11	1049.54	1531.35	0.1457	0.907	33.79	4.279	1.258
	W12	1028.34	1549.92	0.1378	0.865	33.77	4.331	1.251
	W13	1036.59	1535.01	0.1381	0.868	33.77	4.332	1.279
	W14	1051.55	1529.49	0.1463	0.910	33.88	4.279	1.279
	W15	1055.59	1520.73	0.1484	0.924	34.14	4.199	1.283
31.3%	W16	936.15	1505.64	0.1274	0.904	41.87	7.713	0.858
	W17	913.78	1521.79	0.1183	0.851	43.00	7.891	0.845
	W18	922.01	1514.25	0.1253	0.897	42.54	7.790	0.850
	W19	919.54	1521.36	0.1198	0.856	42.78	7.878	0.848
	W20	927.19	1512.15	0.1269	0.905	41.96	7.721	0.852

Table 2 Experimental data from the analysis involving the samples with WNP
2. táblázat A WNP-vel készült mintákon végzett vizsgálatok mérési eredményei

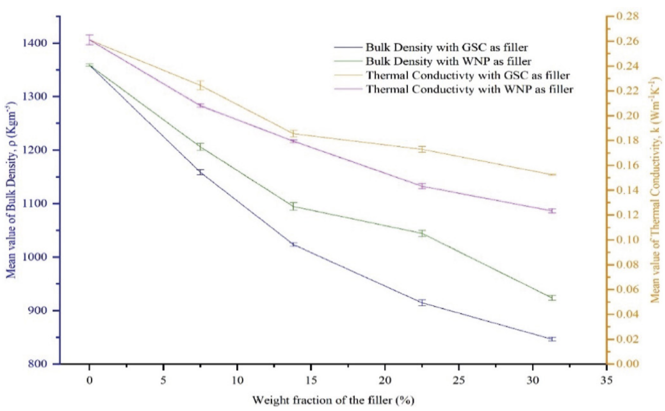

Fig. 2 Mean values of bulk density and thermal conductivity with filler proportion added to P.O.P.
2. ábra Testsűrűség valamint hővezető képesség az alabástromgipszhez adagolt kitöltőanyag mennyiség függvényében

The results registered in *Table 3* also reveal that, while increase in the proportion of GSC causes increase in the mean specific heat capacity values of the samples, the reverse is shown when the content of WNP increases. This portrays the fact that the specific heat capacity value of the P.O.P is less than that of GSC but greater than that of the WNP. It means that more heat will be required by samples containing GSC than those fabricated with WNP content in order to effect a change in the temperature of their unit mass.

In the case of thermal diffusivity, the mean values for samples containing GSC are slightly lower than those recorded for the samples with WNP content. This may be attributed to the GSC having a higher value of specific heat capacity than that of WNP. Despite the opposite trend observed in terms of the mean specific heat capacity values, a direct relationship exists between the mean values of thermal diffusivity and thermal conductivity with respect to the variations in the contents for both cases of GSC and WNP in the prepared samples. The fact portrayed by such link involving thermal conductivity and thermal diffusivity is that as the ability of the samples to allow heat pass across their thickness decreases, the speed at which such heat diffuses through them decreases as well. This is certainly in agreement with their mathematical relationship adopted (for use) and expressed as equation 4 in this work. By considering the reported thermal diffusivity value of 1.8 – 2.0 × $10^{-7}m^2s^{-1}$ for dry wood panel products [20], there is no doubt that although the spread of heat will be slower within samples with GSC component than in their counterparts containing WNP, the samples (used in this work) have lower rates of distribution of thermal disturbance than dry wood panel products.

Moreover, samples developed with the WNP as filler have higher values of mean water absorption than those containing the GSC. This may be due to the impermeable tendency of GSC and hydrophilic nature of WNP. In other words, the WNP has

Waste Content	Weight Fraction n	Mean values of the test properties						
		Bulk Density, ρ (kgm^{-3})	Specific Heat Capacity, c ($Jkg^{-1}K^{-1}$)	Thermal Conductivity, k ($Wm^{-1}K^{-1}$)	Thermal Diffusivity, λ ($10^{-7}m^2s^{-1}$)	Water Absorption,W.A (%)	Flaking Concentration, F_c (10^{-3})	Flexural Strength, σ (N/mm^2)
GSC	0.0%	1359.02 ± 2.11	1598.78 ± 9.10	0.2612 ± 0.0040	1.202 ± 0.024	13.64 ± 0.26	0.039 ± 0.001	5.221 ± 0.005
	7.5%	1158.87 ± 4.96	1800.70 ± 14.73	0.2245 ± 0.0035	1.077 ± 0.021	15.98 ± 0.03	0.863 ± 0.043	1.334 ± 0.004
	13.8%	1023.21 ± 3.67	1960.92 ± 10.36	0.1856 ± 0.0027	0.925 ± 0.015	19.98 ± 0.19	1.194 ± 0.036	0.532 ± 0.004
	22.5%	914.67 ± 5.73	2188.61 ± 7.41	0.1729 ± 0.0023	0.864 ± 0.009	22.50 ± 0.02	1.518 ± 0.011	0.484 ± 0.009
	31.3%	846.88 ± 3.37	2452.10 ± 14.93	0.1525 ± 0.0003	0.734 ± 0.003	29.17 ± 0.03	2.225 ± 0.019	0.165 ± 0.002
WNP	0.0%	1359.02 ± 2.11	1598.78 ± 9.10	0.2612 ± 0.0040	1.202 ± 0.024	13.64 ± 0.26	0.039 ± 0.001	5.221 ± 0.005
	7.5%	1206.03 ± 6.62	1579.63 ± 8.54	0.2082 ± 0.0013	1.093 ± 0.007	21.08 ± 0.10	1.456 ± 0.034	3.053 ± 0.006
	13.8%	1094.94 ± 6.98	1546.87 ± 4.81	0.1795 ± 0.0012	1.060 ± 0.004	26.96 ± 0.10	2.035 ± 0.019	2.406 ± 0.008
	22.5%	1044.32 ± 5.45	1533.30 ± 5.84	0.1433 ± 0.0021	0.895 ± 0.012	33.87 ± 0.07	4.284 ± 0.027	1.265 ± 0.006
	31.3%	923.73 ± 4.47	1515.04 ± 3.23	0.1235 ± 0.0018	0.883 ± 0.011	42.43 ± 0.23	7.799 ± 0.036	0.851 ± 0.003

Table 3 Statistics of the measured properties of the samples
3. táblázat A vizsgált tulajdonságok mérési eredményeinek statisztikai elemzése

a stronger affinity for water compared to the GSC. The nature of both GSC and WNP also plays a critical role in the abrasion resistance of the prepared samples. As can be seen from the results presented in *Table 3*, the flaking concentration increases with the filler content and results in the highest recorded mean value at 31.3% content of the GSC or WNP. Based on the value of 2.0×10^{-2} reported by Berge [20] to be the flaky concentration of asbestos, it can be rightly remarked that the samples developed in this work are less flaking than asbestos by at least (88.87 ± 0.09) % with GSC content and (61.00 ± 0.18) % with WNP as component. This simply means that the said samples are better than asbestos in maintaining their original structure and appearance by resisting mechanical wear. Although the abrasion resistance is higher in the case of using GSC than that of WNP as fillers, the samples with WNP content exhibit better flexural strength than those formed with similar proportion of GSC.

Fig. 3 clearly depicts how the mean percentage values of water absorption as well as mean flexural strength values vary with the proportion of the filler used. For instance, it can be deciphered that as the mean percentage values of water absorption increase with the added proportion of the GSC or WNP, a slight stability tends to occur between 13.8% and 22.5% of the filler content in the case of samples containing GSC. On the contrary, the mean values of flexural strength decrease with increase in the filler proportion and this observation resonates with the research findings reported by Al-Shabander [21].

In general, the results obtained in this work reveal that the mean thermal conductivity values of the samples fall within the range (0.023 – 2.900) $Wm^{-1}K^{-1}$ recommended by [22], for good heat-insulating and construction materials. Also, all the materials fabricated with either the GSC or WNP content are lighter than the pure P.O.P sample and this is an enviable characteristic of the new engineering material sought for. Again, at 0.05 level of significance, Chi-square test of the recorded results reveals that there is a significant effect of varying the proportion of the fillers on the samples' mean values of the properties investigated. Though the mechanical performance reduces as the thermal properties of the samples improve, it is likely that the sample with 13.8% of GSC content and the one containing 22.5% of WNP can exhibit an impressive performance when used in buildings as ceiling.

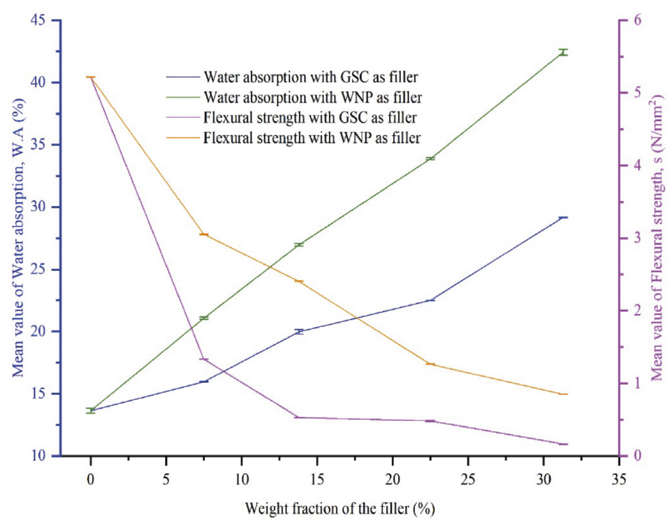

Fig. 3 Mean values of percentage of water absorption and flexural strength with filler proportion
3. ábra Vízfelvétel valamint hajlító szilárdság a kitöltőanyag mennyiség függvényében

4. Conclusions

Based on the experimental results obtained in this work, it was found that mixing P.O.P with either GSC or WNP resulted in new engineering materials with improved thermal properties. Also, it was observed that whether GSC or WNP is chosen for use as filler, its weight proportion can be adjusted to obtain a new material with P.O.P which can then be used as ceiling that is capable of exhibiting desirable physical, thermal and mechanical properties. Again, the new materials formed are cost-effective and environmentally-friendly. Therefore, since groundnut seed coat and waste newspapers are readily available as waste materials, using them as fillers in making P.O.P ceiling will enhance their utilization instead of allowing them to accumulate in the environment, help to reduce the cost of using P.O.P as ceiling in buildings and ensure better thermal insulation of buildings, and so on, thereby meeting the needs of end-users.

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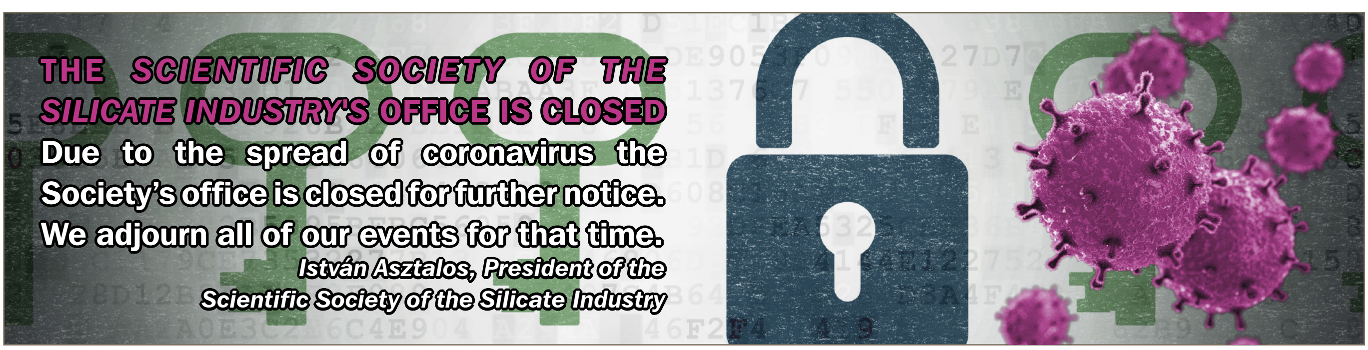

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