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Basalt-Polyester Hybrid Composite Materials for Demanding Wear Applications

Faisal AbuSahmin¹, Ahmed Algellai², Nataša Tomić³, Marija M. Vuksanović^{4*}, Jelena Majstorović¹, Tatjana Volkov Husović², Vladimir Simić¹, Radmila Jančić Heinemann², Marinko Toljić¹, Jovan Kovačević⁵

¹The University of Belgrade, Faculty of Mining and Geology, Djusina 7, 11070 Belgrade, Serbia

²The University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4. 11070 Belgrade, Serbia

³Innovation Centre of Faculty of Technology and Metallurgy, Karnegijeva 4. 11070 Belgrade, Serbia

⁴The University of Belgrade, Vinča Institute of Nuclear Science, P.O. Box 522, 11001 Belgrade, Serbia

⁵Geological Survey of Serbia, Rovinjska 12, 11000 Belgrade, Serbia

Abstract:

Basalt as a filler in a polymer-based composite material fulfils the demand of being natural, environment-friendly material for the production of various composite materials. The material could be used as protective layer and the abrasion should be tested in order to evaluate the properties of the material. The cavitation test enables the evaluation of the possible service in conditions that simulate the extensive erosion. The presence of basalt in the matrix improves the resistance to cavitation. The possibility to further improve the material could be obtained using the reinforcement of the matrix itself by incorporation of submicron ceramic particles into the composite. The obtained hybrid composite material with the addition of reinforcement in the matrix further improves the cavitation resistance.

Keywords: Basalt; Composite materials; Cavitation erosion; Alumina particles.

1. Introduction

Composite materials reached a new era in the 20th century with the use of polymer matrix and the properties of the material became tuneable in terms that by a selection of components the properties could be adjusted. The micro-composite materials where the reinforcing phase has grains of micrometer size the rule of mixing rule applies and the general properties such as density, thermal conduction can be calculated from the component properties. There are also models to predict the modulus and strength of those materials. On the other hand, when nanoparticles are added to a composition, a small addition, such as 1 wt.% reinforcement greatly increases mechanical properties that can be increased by over 30 % [1, 2].

The growing demands for composite materials are often supplied using environmentally unfriendly materials. The demand for inventing the materials using natural sources is growing. The mineral rocks such as basalt are well known for their good mechanical and chemical resistance [3]. Among the oldest applications of basalt rocks was in

*) **Corresponding author:** mdimitrijevic@tmf.bg.ac.rs

Roman time in the production of roads and marks for the roads. Basalt is an abundant mineral, having good mechanical properties and aesthetical appearance and is used as structural parts of buildings [4]. Most of the studies of the use of basalt-based material in the building construction industry are based on the use of basalt fibres [5] but the number of studies that consider basalt powder as filler is much smaller.

In Libya, the basalt rocks are present in several locations and some of them were only recently studied and the use of some minerals is envisaged. The use of large parts of the rock is possible in the aggregate industry as they are mechanically. During the production, some waste creates dust, which provides a good mineral source for several applications. The authors here want to propose the use of this waste mineral in composite materials as filler [6]. Resistance to erosion could be evaluated through the exposition of the material to a cavitation fluid jet [7]. In the present research, authors approached those conditions by exposing the composite to cavitation. In order to provide better cavitation resistance, the material was improved by the addition of alumina particles that enable obtaining better mechanical properties when added to the polymer [8]. The proposed material can be treated as a hybrid one [9, 10] as the added particles are of submicron dimensions and enable obtaining better matrix material that is surrounding the basalt particles [11-13]. As the matrix material, a commercial polyester resin was used.

2. Materials and Experimental Procedures

2.1 Materials

The polymer matrix used for composite preparation was C-RESIN AC200TP kindly supplied by Sinteza Smola Ltd Belgrade, Serbia. Aluminium hydroxide chloride (Locron L; $\text{Al}_2(\text{OH})_5\text{Cl}\cdot 2,5\text{H}_2\text{O}$, Clariant company) was used for the preparation of alumina-based particles. Iron chloride ($\text{FeCl}_3\cdot 6\text{H}_2\text{O}$) was purchased from Sigma-Aldrich (Germany). Methyl ethyl ketone peroxide (MEKP) was obtained from Sigma-Aldrich (Germany). Basalt originated from the Tibesti volcanic province, the Jabal Eghei area [17, 18]. In total 17 basalt samples were studied using optical petrography. Finally, a selected sample of basalt from the third volcanic phase was used for testing.

The ferrous oxide doped alumina particles were synthesized via the sol-gel technique with the addition of 1.5 wt.% $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ to $\text{Al}_2(\text{OH})_5\text{Cl}\cdot 2,5\text{H}_2\text{O}$ as described in the previously published study [1]. The particles were calcinated at 900 °C. The particle size was determined by the laser particle size analyzer (PSA) Mastersizer 2000 (Malvern Instruments Ltd., UK) and the values obtained are: $d(0.1) = 0.412 \mu\text{m}$, $d(0.5) = 0.608 \mu\text{m}$, $d(0.9) = 1.208 \mu\text{m}$ [14, 15].

2.2. Preparation of composite

Alumina based particles doped iron oxide was prepared with a sol-gel technique starting from aluminium chloride hydroxide. The preparation of particles is described in our previous paper [1].

The composites made of pure resin were prepared in order to compare the properties of the matrix to the properties of obtained composites. Two types of composites were prepared: the composites reinforced with 40 wt.% basalt and composites reinforced with basalt (40 wt.% in relation to the resin) and with 1, 3 and 5 wt.% alumina particles doped with ferrous oxide (in relation to the resin). A two-component system is used to prepare the samples: resin and 1.5 wt.% of MEKP in relation to the resin. The samples were polymerized at room conditions during 24 h and then heat-treated at 60 °C for 4 hours in order to complete the process. Samples were cylinders having 25.0 mm diameter and 4.0 mm height.

2.3. Characterization methods

The hybrid composite material consisted of a basalt powder added to a matrix that was itself composed of polyester resin and alumina particles. Basalt rocks were tested using the dynamic modulus measurements, the material was then grinded and the obtained material was observed under the optical microscope to get information about the forms of the material. Diameter distribution of the grinded basalt powder was measured. Dynamic modulus of the prepared composites was measured using the same testing procedure. The hardness of the composite was measured using the Shore manual tester.

Morphology and shape of the basalt particles were observed using an optical microscopy Carl Zeiss – Jena, NU2. A.A morphological analysis of the composite cross-section was performed using field emission scanning electron microscopy (FE-SEM), TESCAN MIRA3 XMU, operated at 20 kV. Image-Pro Plus 4.0 software package tools (Media Cybernetics, Rockville, MD) was used for image data processing and quantification of the damage characteristics. Ultrasonic method (measuring velocity of ultrasonic waves) is performed by using equipment OYO model 5210 by standard testing procedure (ICS 81,080 SRPS D. B8. 121).

Cavitation resistance was tested using ASTM G32-92 Standard (the stationary specimen method) [16]. The device consisted of a 360 W high-frequency generator, electrostrictive transducer, transformer for mechanical vibrations and water bath containing the test specimen. Cavitation testing was accomplished using the recommended standard values:

- frequency of vibration: 20 ± 0.5 kHz
- the amplitude of vibrations at the top of the transformer: 50 μm
- the gap between the test specimen and the transformer: 0.5 mm
- the temperature of water in the bath: 25 ± 1 °C
- ordinary water flow: from 5 to 10 ml/s

3. Results and Discussion

3.1. Mineralogy and petrography of studied basalts

General mineralogy of studied basaltic rock samples is very similar, as it consists of olivine, clinopyroxene, and plagioclase as essential minerals, and accessory spinel group mineral \pm volcanic glass residuum. The main difference between different basalt samples is the relative abundance of those minerals and occasional absence of pyroxene and/or plagioclase in phenocryst phases. Considering fabric variety there are much more differences such as massive to vesicular/amygdaloidal structure, or/and texture features (ophitic, porphyritic, intersertal, intergranular) with holocrystalline to hypo crystalline groundmass. Texture features range from picritic-like (hypocrystalline porphyritic) to doleritic-like (ophitic).

The completely tested basalt belongs to the third volcanic phase, dark grey to black, with porphyritic to intersertal texture and vesicular structure with vesicles >2 mm in diameter. Thin section of the sample revealed it is composed of olivine micro phenocrysts, and hypocrystalline groundmass made of predominant pyroxene, rare plagioclase laths, opaque (metallic) mineral – magnetite/ilmenite and glass residuum. Olivine phenocrysts (5 % vol.) are hypidiomorphic to idiomorphic (up to 0.5 mm large), mostly fresh, with some fissures. Groundmass is finer-grained, made of clinopyroxene (elongated hypidiomorphic forms, up to 0.3 mm), rare plagioclase laths (subhedral, elongated forms, up to 0.2 mm long), a bit of volcanic glass residuum, and opaque (metallic) minerals \pm leucoxene, spread all over the

groundmass, like fine dusty aggregates – magnetite \pm ilmenite (2 vol.%). Vesicles are locally filled with secondary calcite (Figure 1).



Fig. 1. Bulk specimen of basalt rock.

Tab. I The corresponding measured dynamic modulus of elasticity of the rock used in composite preparation.

Sample	γ , (kN/m ³)	Direction of measurements	E_{dyn} , (GN/m ²)	μ_{dyn}
1337	20.55	1-1'	25.39	0,35
		2-2'	20.06	0.36
		3-3'	21.60	0.36

3.2. Mechanical properties testing

The mineral samples were tested using the ultrasound dynamic modulus technique. Table I presents the results of the homogeneity and mechanical properties of the rock. The modulus was measured in three directions in order to evaluate the rock homogeneity. The results indicate that the rock is rather homogenous and has the dynamic modulus of elasticity of between 20 and 25 GPa depending on the direction. Those materials are considered as a promising source for further use as filler.

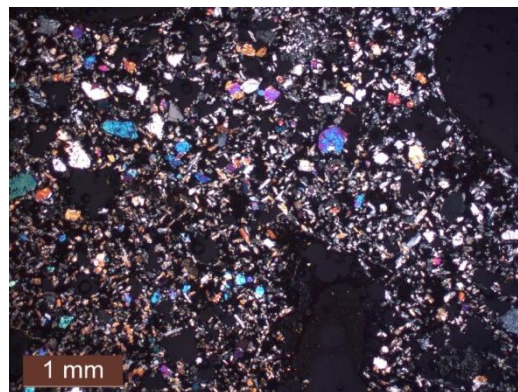


Fig. 2. Microphotograph of the thin section of the basalt used for technological tests observed under polarized light.

The basalt was grinded and milled in order to be used in the preparation of the composite. The obtained particles were classified and the finest obtained fraction having diameter under 46 μm was used for the composite preparation (Figure 2). The optical micrograph of the obtained basalt powder is given in Figure 3.

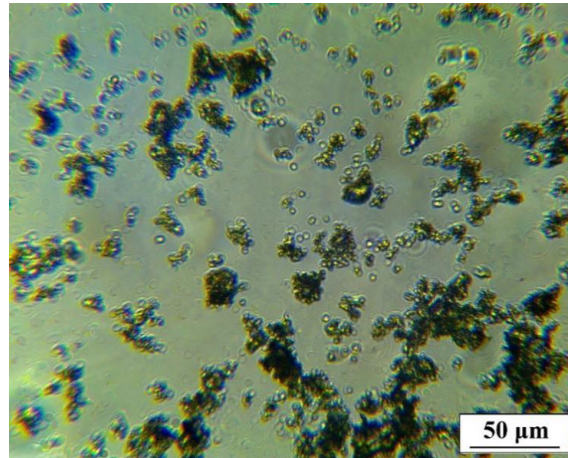


Fig. 3. Optical micrograph of basalt powder used in composite preparation.

Figure 4 shows the micrograph of the cross-section of the composite having 40 wt.% of basalt and 5 wt.% of alumina particles doped with iron (III) oxide.

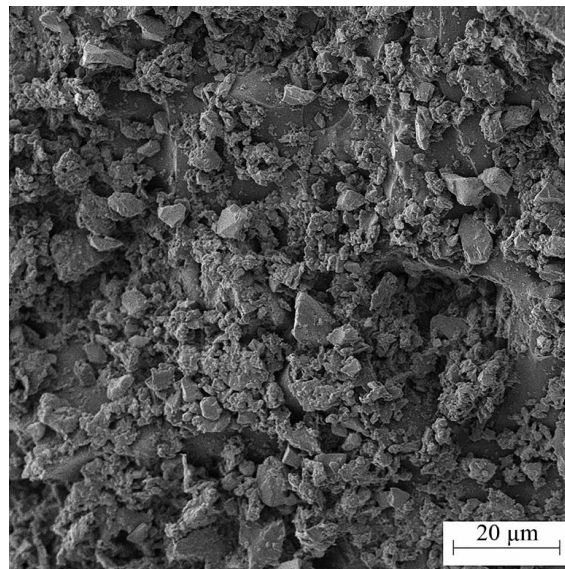


Fig. 4. FESEM micrograph of the fracture surface of composite with 40 wt.% of basalt and alumina particles doped iron (III) oxide.

Obtained composites were tested using the ultrasound tester, the same used to measure the dynamic modulus of elasticity of the rock, the dynamic elastic modulus of the obtained composite. The results indicate that there is a slight improvement of the elastic modulus when the alumina particles are added into the composite matrix giving the material having better mechanical properties. The obtained mechanical properties are given in Table II. Modulus was measured as dynamical modulus of elasticity; the hardness was measured using the Shor DS, hardness method that is suitable for this sort of materials.

Tab. II Mechanical properties of composite materials.

Amount of basalt, %	Amount of particles, %	γ , kN/m ³	Vp, m/s	Vs, m/s	Edyn GN/m ²	HS	μ_{dyn}
0	0	12.50	1270	630	1.156	84	0.33
40	0	18.30	1030	480	1.337	88	0.36
40	1	18.40	1180	550	1.183	87	0.36
40	3	18.73	1030	480	1.528	90	0.36
40	5	19.02	1080	510	1,322	85	0.36

As it could be concluded from Table II, the addition of alumina particles does not improve the mechanical properties. The mechanical properties remain stable and do not differ in a sensible way. The addition of alumina particles does not improve the mechanical properties of more than 8 %.

3.3. Cavitation resistance measurements

The cavitation resistance was observed in regular time intervals and the specimens were measured with the precision of 0.01 μg . The mass loss of composite materials is shown in Figure 5. This corresponds to the standard method of cavitation testing.

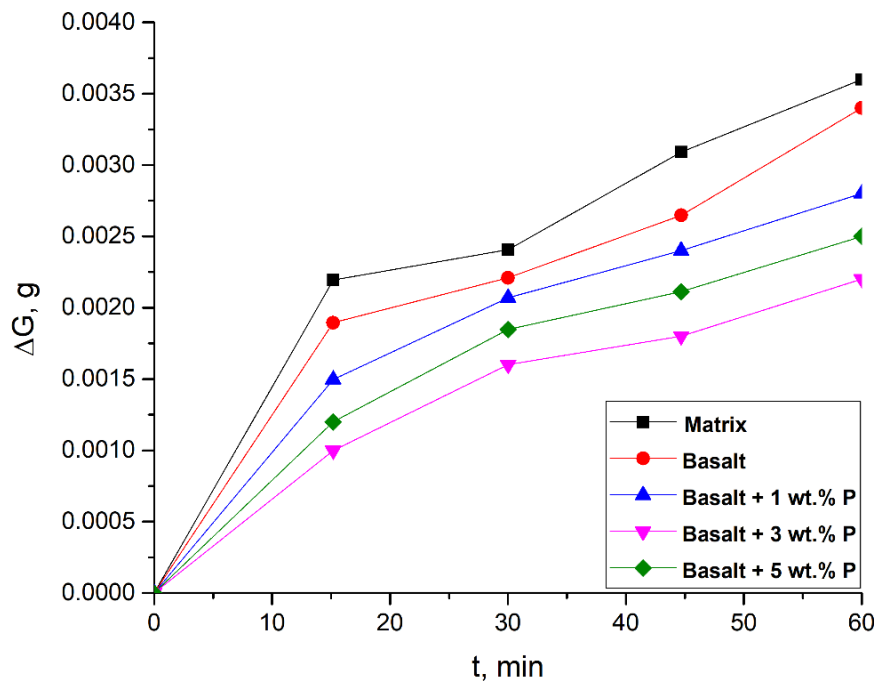


Fig. 5. The mass loss of the specimens containing 40 wt.% of basalt and 1 wt.%, 3 wt.% and 5 wt.% of alumina particles added to improve the overall properties of the composite compared to the pure matrix specimen.

The image analysis program was used for the determination of the surface deterioration level. The imaging technique required to observe the destruction of the surface was high-resolution imaging in the form of high-resolution scanning. Those images give the resolution of 600 dpi which enables the visualization of the 2,54 cm/600 size defects which were considered to be enough for the study. The results are given in Figure 6. The image analysis program was applied for surface analysis during testing.

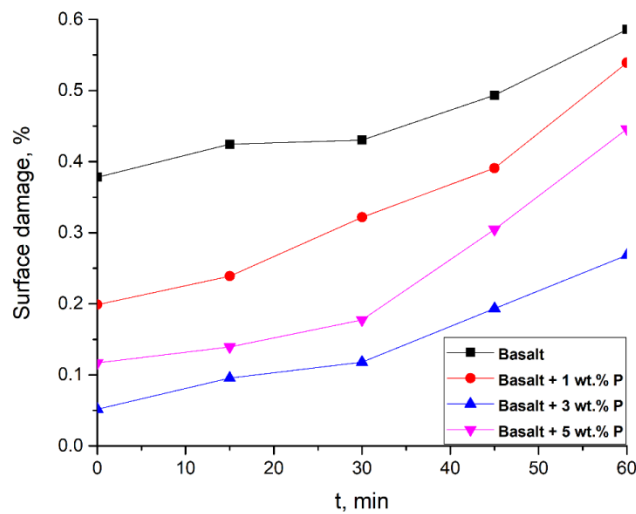


Fig. 6. Surface erosion results during cavitation determined using an image analysis technique.

The surface damage was concentrated and the flows observed on the surface corresponded to those of metal specimen having isolated defects that were rather small (Figure 7). The defects were separated and did not represent a large amount of the surface. This is different compared to less hard polymers such as PMMA [19]. The addition of alumina particles, however, improved the resistance measured by the mass loss and measured by surface destruction, Table III. The amount of surface destruction is up to 5 times lower compared to that of a polymer alone. Basalt is hard filler improves cavitation resistance but adding alumina particles to the matrix, as reinforcement, improves the matrix properties and the composite improves overall cavitation resistance measured as mass loss and surface destruction level.

From the measured data, it can be concluded that the addition of fillers improves cavitation resistance. Improvement of matrix properties improves the overall properties of the composite as well as the hardness of the obtained material.

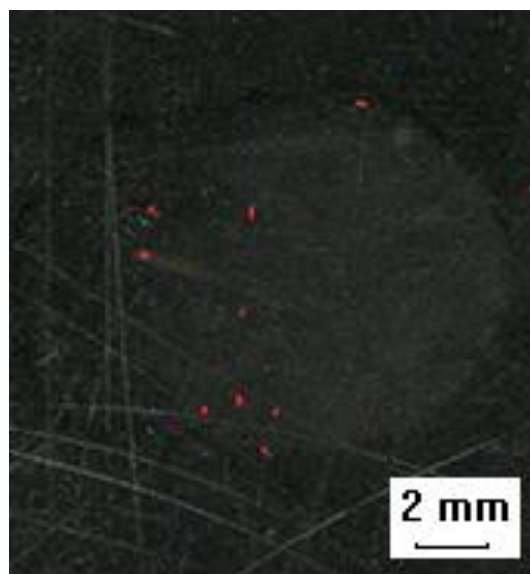


Fig. 7. Observed pits for sample after 1 h of testing.

Tab. III Pits characterization for samples during testing.

	t, min	d_{av}, mm	P_{av}, mm²	N
without particles	15	0.0321	0.0008	26
	30	0.0379	0.0011	13
	45	0.0538	0.0023	8
	60	0.3858	0.1168	11
1% of particles	15	0.0204	0.0003	2
	30	0.0799	0.0051	2
	45	0.0571	0.0026	4
	60	0.4769	0.1786	12
3% of particles	15	0	0	0
	30	0.0415	0.0014	3
	45	0.0388	0.0012	6
	60	0.0330	0.0008	8
5% of particles	15	0.0233	0.0004	
	30	0.2763	0.0599	3
	45	0.0214	0.0004	6
	60	0.0530	0.0022	5

From Figure 7, it could be observed for pure sample growth and merging of the formed pit is the dominant mechanism, and after 45 minutes, new pits are forming simultaneously with merging and growth. The addition of alumina particles changes the mechanism, in a way that for all samples, the formation of new pits was observed for all samples during the time (Figure 8).

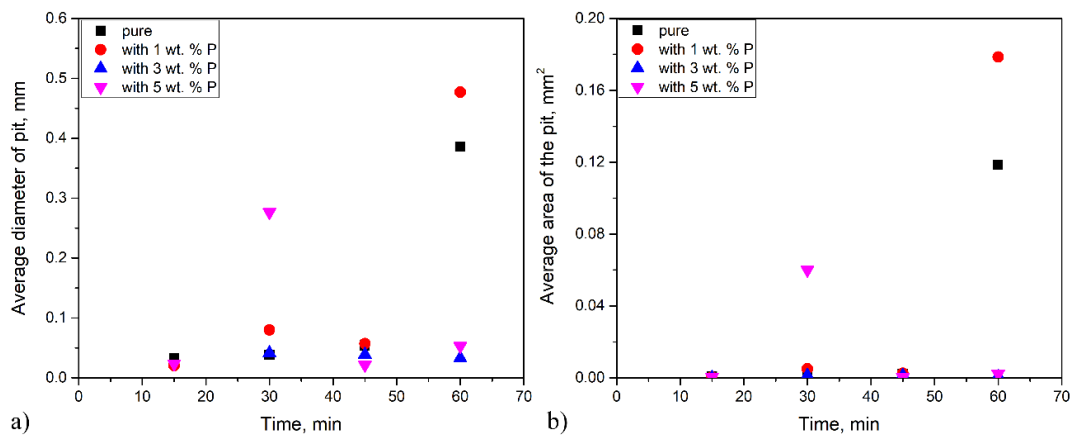


Fig. 8. a) The average diameter of the pit for samples during testing and b) The average area of the formed pit for samples during testing.

4. Conclusion

The basalt powder as a filler was tested to determine the possibility of preparing a composite material suitable to be exposed to cavitation. Cavitation is a method used to evaluate the abrasion resistance of a material, and the results show that a hybrid composite material consisting of basalt powder and alumina particles has improved cavitation resistance with respect to a pure matrix and a micro composite consisting of basalt powders and matrix materials. The improvement is sensible and could be considered as a promising material. This

material, in addition, has very good aesthetic properties and has the properties of hard abrasion-resistant material.

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Сажетак: Базалт, као пунилац у полимерном композитном материјалу на бази полимера представља природан, еколошки материјал за производњу различитих композитних материјала. Материјал се може користити као заштитни слој, а абразија се треба испитати да би се проценила својства материјала. Тест кавитације омогућава процену могуће услуге у условима који симулирају велику ерозију. Присуство базалта у матрици побољшава отпорност на кавитацију. Могућност даљег побољшања материјала може се добити употребом ојачања саме матрице убацивањем субмикронских керамичких честица у композитни материјал. Добијени хибридни композитни материјал, са додатком ојачања у матрици, додатно побољшава отпор композита на кавитацију.

Кључне речи: Базалт, композитни материјали, отпорност на кавитацију, алуминијум оксидне честице.

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