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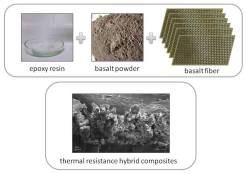

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Hybrid effects of basalt fibers and basalt powder on thermomechanical properties of epoxy composites

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Abstract:

The influence of basalt powder addition on thermomechanical properties of basalt fiber reinforced epoxy composites was investigated in this study. The dynamic mechanical thermal analysis was carried out in a torsion mode. The mechanical properties were evaluated by means of static tensile test and Charpy impact strength method. The thermal stability was investigated by thermogravimetric analyses in inert and oxidizing atmospheres. Results showed that combining basalt fibers with basalt powder improves stiffness and thermal resistance of the epoxy composites. The new hybrid composites are more resistant to temperature changes than the reference sample as proven by dynamic mechanical thermal analysis.

Key words: basalt fiber, epoxy composites, basalt powder, thermomechanical properties

Introduction

Investigations and design of new materials with specific properties are necessary to facilitate the manufacturing process of high quality products for different industry applications. Therefore, fiber reinforced composites are still the subject of many scientific publications and projects in the field of construction, automotive and marine industry. Epoxy matrix connected with rigid fiber allows to obtain construction materials with high stiffness and strength [1-3]. In order to limit negative impact of polymer materials on the environment, natural fibers are more and more often added in production of polymer-based composites. Jute, flax, hemp and mineral fibers prevail in use with polymer matrices [4,5]. Basalt fiber (BF) is obtained in an energy-saving process involving melting volcanic rock without additives [6,7]. Moreover, the advantages of basalt fiber compared to glass fiber are: better mechanical strength, thermal stability and chemical resistance [7-9]. Its large size allows for its safe application when shredded, without any risk of penetration of the body via inhalation. Introducing BF into polymer matrix improves its Young's modulus, impact resistance and bending and compression strength in comparison with the epoxy-glass composites [9-12]. It is worth noticing that in order to improve strength and roughness of basalt fibers, they can be modified with organic/inorganic hybrid coating technology [12,13]. Kuzmin et al described modification of basalt fiber surface by nano-SiO_2 and showed that nano-hybrid coating proved to be the most effective way to enhance interface between epoxy matrix and basalt fiber [14]. The introduction of both fibrous and mineral fillers into polymer matrix can improve mechanical and thermal properties of the composite [15,16]. Hybrid composites are manufactured from two or more components, for example fibers and powders, and their specific properties cannot be obtained with only one type of reinforcement [17]. Basalt fiber in combination with glass, flax, hemp and jute fibers has been recently applied in the hybrid composites [18-23], even if, to the best of the authors' knowledge, very limited works focus

on the using of basalt powder as a modifier of the polymer composites [24-27]. Many studies aimed to improve properties of composite materials by incorporating different micro or nanoparticles in combination with various forms of basalt fibers. However, the novelty in this paper, in comparison to the state-of-the art, is a simultaneous use of basalt materials in a form of powder and fibers in epoxy laminates [28-32].

Basalt powder has a fine grain structure and includes very hard phases like diopside and augite, as a result basalt base materials present superior abrasion, wear and chemical resistance. It should be underlined that basalt rocks are located in Poland and in many regions of Europe therefore, finding its new applications is highly desirable. The basalt powder can be applied as a cost effective filler for epoxy composites in comparison to synthetic materials like alumina, silica, graphene [33-34].

Therefore, the aim of this study was to verify the influence of basalt powder addition on thermomechanical properties of basalt fiber reinforced epoxy composites. Effect of interactions between the fillers was assessed in a context of changes in structure and properties of the composite material. Mechanical and thermomechanical properties were determined by means of static tensile test, Charpy impact strength method, dynamic mechanical thermal analysis and thermogravimetric analysis. Moreover, the structure of composites was characterized by Scanning Electron Microscopy.

Experimental

Materials

The following components were used in this investigation: epoxy resin Epidian 6 (EP6) based on bisphenol A (BPA) (viscosity at 25°C; 10000 - 15000 mPas), curing agent - triethylenetetramine (Z1), both produced by CIECH Sarzyna S.A., Poland. Epoxy resin was

mixed with Z1 at ratio 13 parts Z1 per 100 parts EP6 by weight, (composition pot life at 20°C; 33 min, properties after curing: tensile strength 50 MPa, flexural strength 120 MPa). Basalt fiber woven fabric (BF), type BAS 220.1270.P with weight of 210g/m^2 and plain weave type (BASALTEX), and basalt powder (Mine PGP BAZALT, Wilkowo, Złotoryia, Poland) were used as reinforcement. Natural basalt powder with lowered amount of heavy metals and ph=7.6 during preliminary investigations was characterized by means of scanning electron microscopy (SEM) (Fig. 1). Particle size distribution was also evaluated using laser particle sizer Fritsch ANALYSETTE 22 apparatus operated in a range of 0.08 – 2000 µm. In Figure 2 particle size distribution function (*Q3(x)*) and its derivative (*dQ3(x)*) as a function of particle size (*x*) were presented. According to data delivered by the producer, BP consists of: 49.5 SiO_2, 15% Al_2O_3, 9.6% CaO, 8.7% FeO, 6.8% MgO, 3.7% Fe_2O_3, 2.9% Na_2O, 1.2% K_2O, 0.4%P_2O_5, 0.2% MnO, 0.15% Mn, 0.0105% Zn, 0.0087% Cu, 0.0048% Co, 0.005% B, 0.00015% Mo.

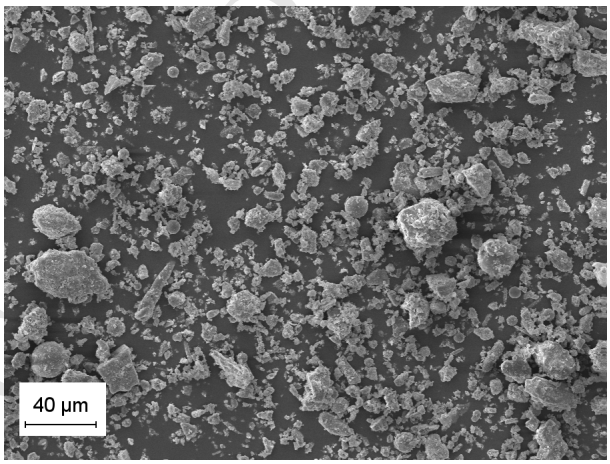

Fig. 1. Basalt powder SEM image (magnification 1000x)

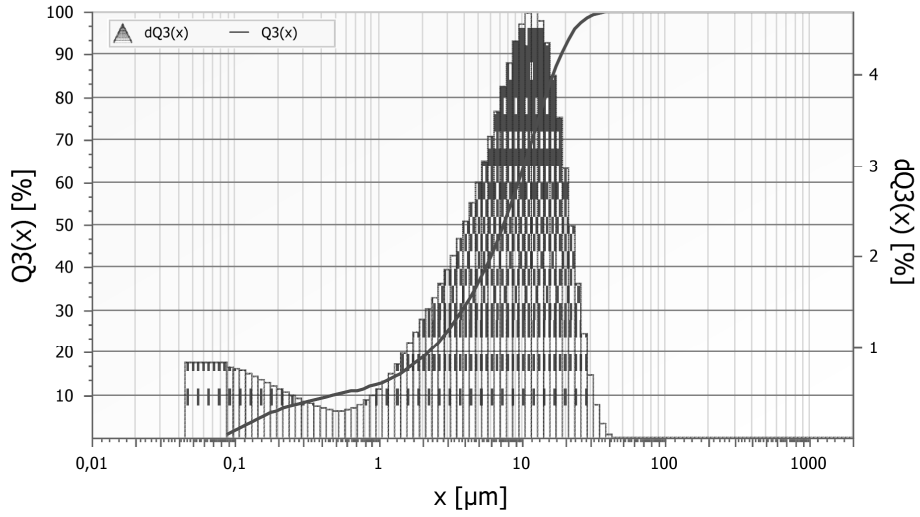

Fig. 2. Particle size distribution of basalt powder

Sample preparation

Epoxy matrix was mixed with a mechanical stirrer with 2.5, 5, 10 wt% of basalt powder respectively to the total weight. Next, the compositions were mixed with curing agent Z1. The epoxy composites were fabricated in a mold using hand lay-up, cured at ambient temperature (20°C) for 24h and post-cured at 80°C for 3 h. The composites contained 6 layers of basalt fibers. The samples were described as BF; 2.5BF; 5BF; 10BF adequately to the incorporated amount of basalt powder.

Methods

Determination of weight percentage of basalt in the composites

The basalt fiber content in the samples was determined by resin burn-off. A weighed amount of composite sample was taken and heated at 800°C to constant weight. The wt% basalt (x) was calculated according to the formula (1):

$$x = w_2/w_1 \cdot 100 \quad (1)$$

where: w_1 - the weight before heating and w_2- the weight after heating

Scanning Electron Microscopy (SEM)

The structure of composites was evaluated by Scanning Electron Microscopy (SEM). The fracture surfaces of the samples were investigated with magnifications of 1000x, 5000x and digitally captured using a scanning electron microscope Zeiss Evo 40. The electron accelerating voltage of 12 kV was applied. Fracture surfaces of the composites were obtained from the impact strength specimens. Prior to the tests, all the specimens were sputtered with a layer of gold.

Dynamic mechanical thermal analysis (DMTA)

The dynamic-mechanical properties of the composites, with 10x2,5x50 mm dimensions, were measured using DMTA methods (Anton Paar MCR 301, Austria) in a torsion mode, operating at frequency f = 1 Hz in the temperature range between 25°C and 200°C, and at the heating rate 2°C min. The position of tan δ at its maximum was taken as the glass transition temperature (Tg).

Thermogravimetry (TGA)

The thermal stability of composites was analyzed by thermogravimetric method (TGA) with temperatures ranging from 30 to 900°C at the heating rate of 10°C/min under nitrogen and air atmospheres using a TG 209 F1 Netzsch apparatus. Approximately 10 mg samples were placed in ceramic pans. The initial decomposition temperature T_i was determined as a 5%. weight loss temperature. The residual mass (ΔW%) was defined at about 900°C.

Tensile mechanical properties

Tensile mechanical properties were measured with INSTRON 4481 universal testing, machine in accordance with ISO 527-4. All tests were performed at ambient temperature (23°C) with testing speed 5 mm/min, with a load cell of 50kN.

Charpy impact strength

The impact strength of the unnotched samples with 10x4x80 mm dimension was measured using the Charpy method (ISO 179) at room temperature. The INSTRON Woolpert PW9 impact tester with 25 J hammer was used.

Results and discussion

Basalt weight content

Content of basalt fibers and powder in the composites is collected in Table 1. Percentage weight of basalt fibers in the composites was constant and equal to 40 wt%. Applied amounts of basalt powder, referred to total weight of epoxy matrix, were 2.5, 5, 10 wt%, respectively. In addition, the total basalt powder contents, referred to composite total weight, were calculated.

Table 1. Percentage weight of basalt fibers and powder in the composites

Name	wt% basalt fiber	wt% basalt powder
BF	40	0
2.5BF	40	1.5
5BF	40	3
10BF	40	6

Scanning Electron Microscopy (SEM)

Interfacial enhancement between reinforcement and the polymer matrix is necessary for effective stress transfer from matrix to fiber whereby, maximum utilization of the fiber strength in the composites is achieved [35]. In Figure 3, the SEM micrographs of the composites with different amounts of basalt filler are presented. The well dispersed basalt powder for the sample 2.5BF was visible in Figure 3b. Moreover, fiber pull-out effect was not observed for all composites as characteristic hollows in epoxy matrix were not observed. This may confirm good connection between the fibers and epoxy matrix [36]. The brittle-type fracture for all tested samples was noticed, what confirms the fact that the fibers on the fractured surfaces were clean [37]. Furthermore, in all cases a ridge in the epoxy matrix upon cracks was visible. As evidenced in Fig. 3 a-d, matrix contour occurred very close to fiber surface. This proves a sufficient interfacial adhesion between basalt fiber and epoxy resin [35]. Differences in SEM images between reference sample and composites were observed. In case of composites, fragments of basalt powder particles were distributed on the fiber surface. Good saturation of the inorganic fibrous filler may be denoted in SEM image with a magnification of 5000x presented in Figure 4a. Changes in composites' morphology with increasing content of basalt powder are presented in Fig. 4-b and 4-c. In Fig. 4-b, presenting the 2.5BF sample, basalt powder particle deeply immersed in the matrix was visible. Fig. 4-c presents the structure of 10BF sample where the basalt powder particle place in epoxy matrix and at the same time outside them were noticeable.

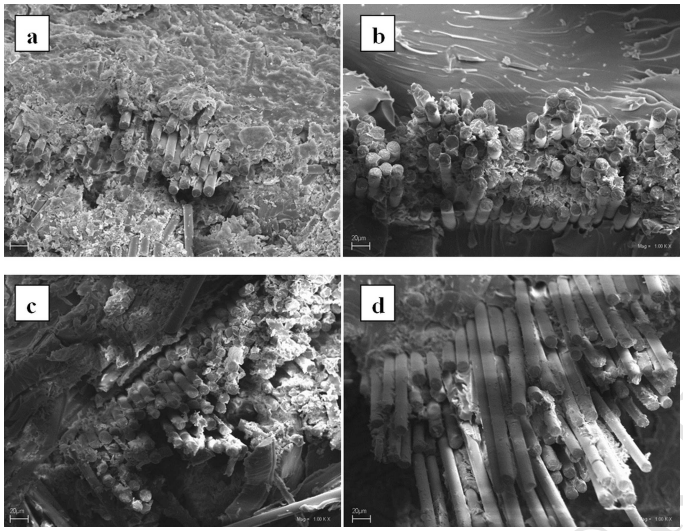

Fig. 3. SEM microphotographs of composites a) BF b) 2.5BF c) 5BF d) 10BF magnification 1000x

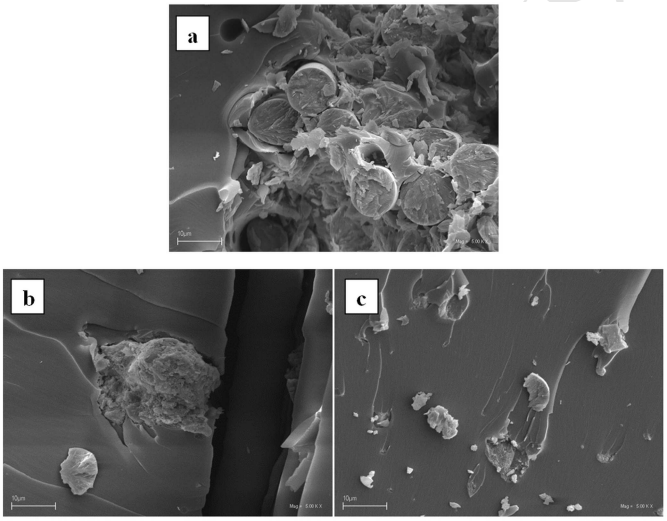

Fig.4. SEM microphotographs of composites structure a) 2.5BF and surface b) 2.5BF; c) 10BF, magnification 5000x

Dynamic mechanical thermal properties

Plots of the storage modulus G' and mechanical loss factor (tan δ) versus temperature T for the composites are shown in Figure 5. The values of the composite storage modulus G' at various temperatures, as well as glass transitions are listed in Table 2. The highest values of G'(3.4 GPa) and Tg (122°C) were recorded for the sample containing 2.5 wt% basalt powder.

These results are reflected by the reduced tan delta values [38]. The properties of the filled polymers are affected both by variations in the molecular mobility of the polymer matrix induced by interaction at the polymer interfaces, and coupling effects between phases [38]. The presence of the inorganic rigid basalt particles can restrict the motion of polymer chains [24]. On the other hand, a higher amount of this mineral filler does not improve viscoelastic properties of composites which may be due to their poor bonding strength. The main relaxation peak shown in Fig. 5 is related to the glass transition value and decreases together with the increase of basalt powder content. It is worth noticing that above glass transition temperature i.e. at 125°C, 2.5BF sample indicated higher G' value than the reference sample. This proves that the new hybrid composites will be more resistant to temperature changes above glass transition temperature.

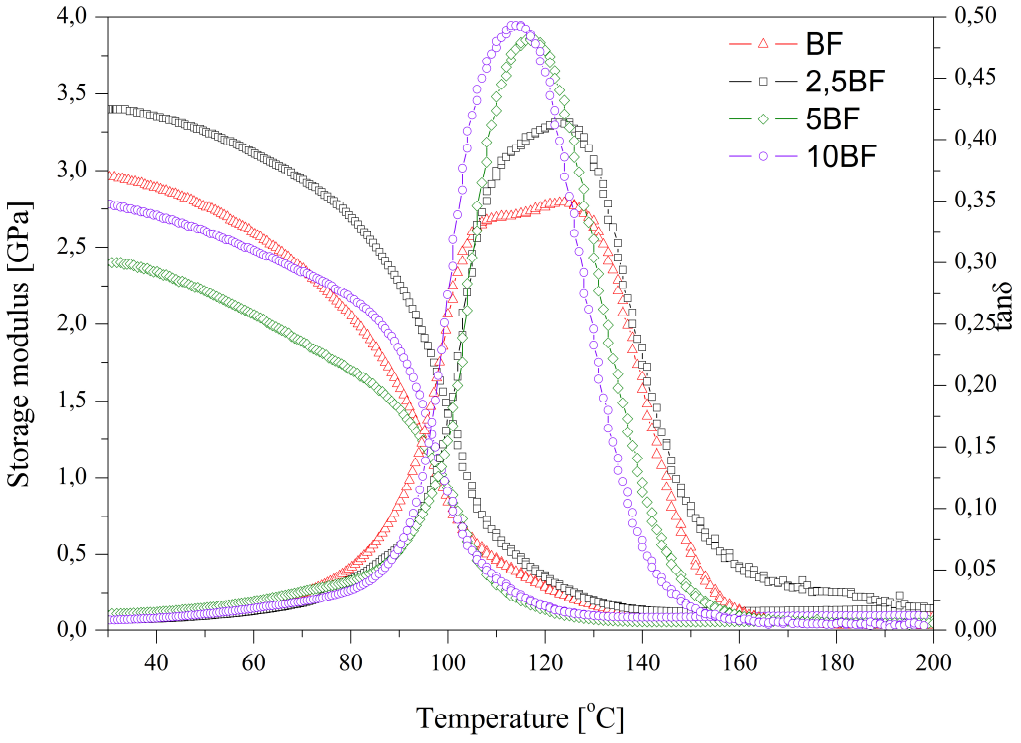

Fig. 5. The DMTA curves of the composites

Table 2. The values of composite storage modulus and glass transitions

Name	G'[GPa] at 30°C	G'[GPa] at 125°C	Tg [°C]	Tan δ peak
BF	2.96	0.29	114	0.35
2.5BF	3.40	0.36	122	0.41
5BF	2.39	0.12	114	0.48
10BF	2.90	0.19	116	0.49

Mechanical properties

The mechanical properties were determined and the comparison of the values of tensile strength, elasticity modulus, elongation at break and impact strength is presented in Figure 6. The value of tensile strength of the reference sample was approx. 210 MPa, while for the modified samples it reached 214 MPa, 154 MPa, 195 MPa, correspondingly to 2.5BF; 5BF; 10BF. The value of tensile strength for 2.5BF sample is comparable to the one for the reference sample. Therefore, it can be stated that this amount of filler supplements hybrid materials with valuable properties. In all cases basalt filler introduction led to an increase of the elasticity modulus of the composites and a reduction of their elongation at break. The highest elasticity modulus value was recorded for the sample with 2.5 wt.% of basalt powder. The elongation at break values for all modified samples were comparable. These results are in good agreement with the DMTA analysis. The most advantageous mechanical and thermomechanical properties were obtained for the sample containing 2.5 wt% of basalt powder, thanks to sufficient dispersion of basalt powder particles in epoxy matrix as proven in SEM photographs (Fig.4b).

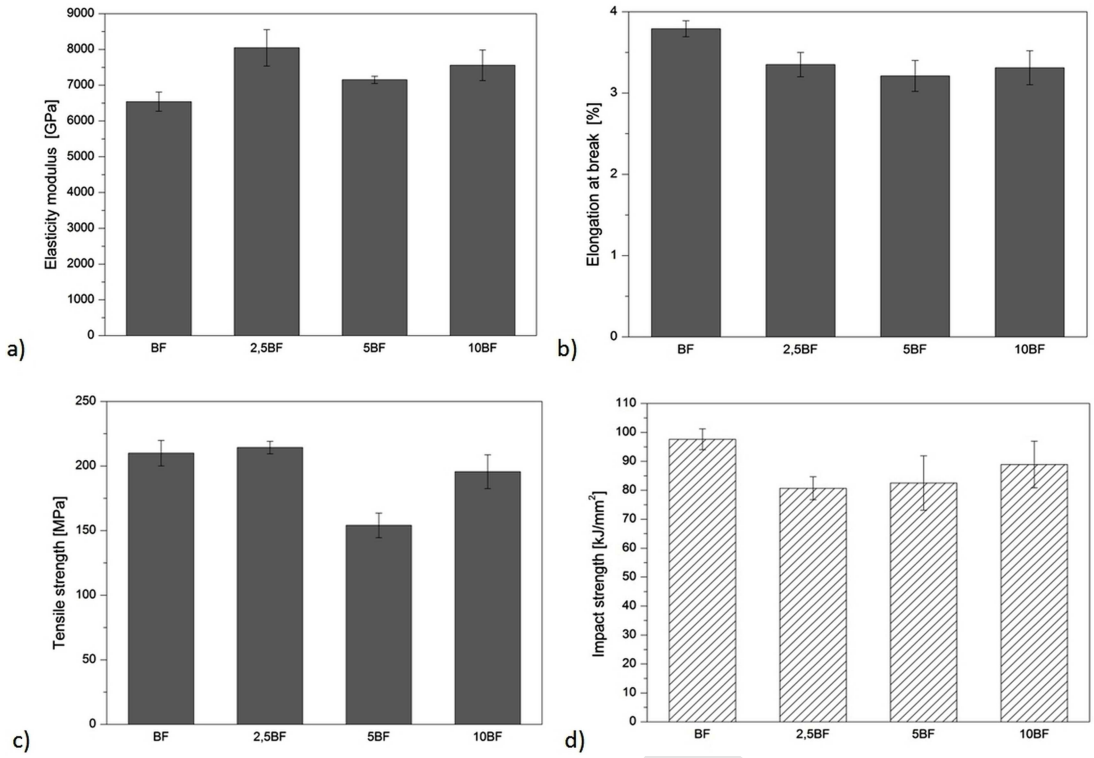

Fig 6. Mechanical properties of composites

The introduction of inorganic filler may increase the stiffness of the composite and consequently its ductile properties may deteriorate [39]. The impact strength of the composites decreased as a result of a higher filler powder amount. This is due to the filler particles being more rigid than epoxy resin, as well as pour resin–reinforcement interface between high amount of powder and epoxy matrix [40].

Brittleness evaluation

Composite materials modified with inorganic particle-shaped and fibrous fillers usually reveal an increased elasticity modulus and reduced elongation at break and impact resistance values in comparison with unmodified polymeric matrix. Changes in mechanical properties caused by simultaneous modification of epoxy resin with long basalt fibers and

basalt powder are complemented with evaluation of Brittleness *B*. Brittleness was calculated from the formulation (2) as described by Brostow et al. [41]:

$$B = 1/(\varepsilon_B \cdot E') \quad (2)$$

where: ε_B is elongation at break determined in tensile test measurements and E' is the storage modulus determined by dynamic mechanical thermal analysis (DMTA) at a defined temperature and 1.0 Hz frequency. It should be underlined that brittleness is a versatile parameter describing mechanical properties of materials thanks to application of two different measuring techniques [41-43]. Therefore, B is related to material ability to deform before breakage represented by ε_b as well as E' which is related to elasticity and fatigue properties measured in repetitive sinusoidal loading. Storage moduli of composite materials, applied for B calculations as per formulation (2), were determined in a torsion mode (G') during DMTA analysis at room temperature.

Brittleness values and data used for their calculations are presented in Table 3. Additional data concerning pure epoxy resin (EP) were gained from the literature and our previous studies [44,45]. Epoxy resin as a thermoset is characterized with high brittleness. Stiffness of all composite materials reinforced with basalt fibers allows to decrease brittleness in comparison to unmodified material. It should be noticed that incorporation of the lowest amount of basalt powder (2.5 wt%) results in a slight decrease in composite brittleness. Although higher amounts of the BP lead to an increase in composites' brittleness, it does not exclude them for a possible application. In accordance to data presented in Figure 6, this phenomenon may be related to lowered damping behavior of the 2.5BF composite in comparison to composites containing higher amounts of basalt powder. Low amounts of well dispersed particle-sized filler in hybrid composite systems, despite an increased stiffness, provide partial dissipation of mechanical load. Incorporation of additional low amounts of well dispersed particle shaped filler reduced brittleness of fiber reinforced composites.

Table 3. Brittleness of epoxy composites modified with BF and BP

Name	B [Pa·%/10^{10}]	$G'_{25°C}$ [GPa]	ε_B [%]
EP*	1.6	1.25	5
BF	0.89	2.97	3.79
2.5BF	0.88	3.4	3.35
5BF	1.3	2.39	3.21
10BF	1.04	2.9	3.31

*[43,44]

Thermogravimetry (TGA)

Thermogravimetric analysis is commonly used to determine decomposition processes of polymers in a wide range of temperatures. In nitrogen atmosphere, the composites are subjected to the pyrolysis process [46]. Whilst, investigation in the air atmosphere provides information on material resistance against oxidation. What is important, this method allows for obtaining information on thermal resistance of composites in conditions close to working conditions. The degradation process was described by such parameters as: 5 % weight loss temperature, residual mass and DTG peak temperature (Table 4).

Plots of weight loss vs. temperature, together with their derivatives indicated in air and nitrogen atmospheres, are presented in Figures 7 and 8. For all the materials investigated under inert atmosphere, a single step degradation process was observed. As shown in Figure 8, a two step decomposition process was visible for all the samples evaluated under air atmosphere. These two steps are primary degradation and combustion of char formed in the first step [47].

The highest thermal stability can be observed for the 2.5 BF sample. By increasing the powder content, the 5% weight loss decreases and reaches its minimum for the 10BF sample. This effect may be due to existence of active catalytic sites which influence polymer degradation. Moreover, during clay degradation a protonated silicate may be formed which catalyzes polymer degradation [48]. The first DTG peak corresponds to initiation of material decomposition which is useful in engineering applications when determining work temperature range [46]. The DTG peak average at 360°C (in nitrogen atmosphere) and 350°C (in air atmosphere) could result from an exothermic reaction caused by chain scission and resin decomposition into lower molecular weight products [49,50]. Therefore, rapid mass loss was observed in the TGA curves (Fig. 7 and 8). It should be underlined that basalt powder presence led to a decrease in DTG peak temperature values of the epoxy matrix. This might be a considerable advantage, especially when applying the material as a construction element. The same tendency was observed for the samples studied under air atmosphere.

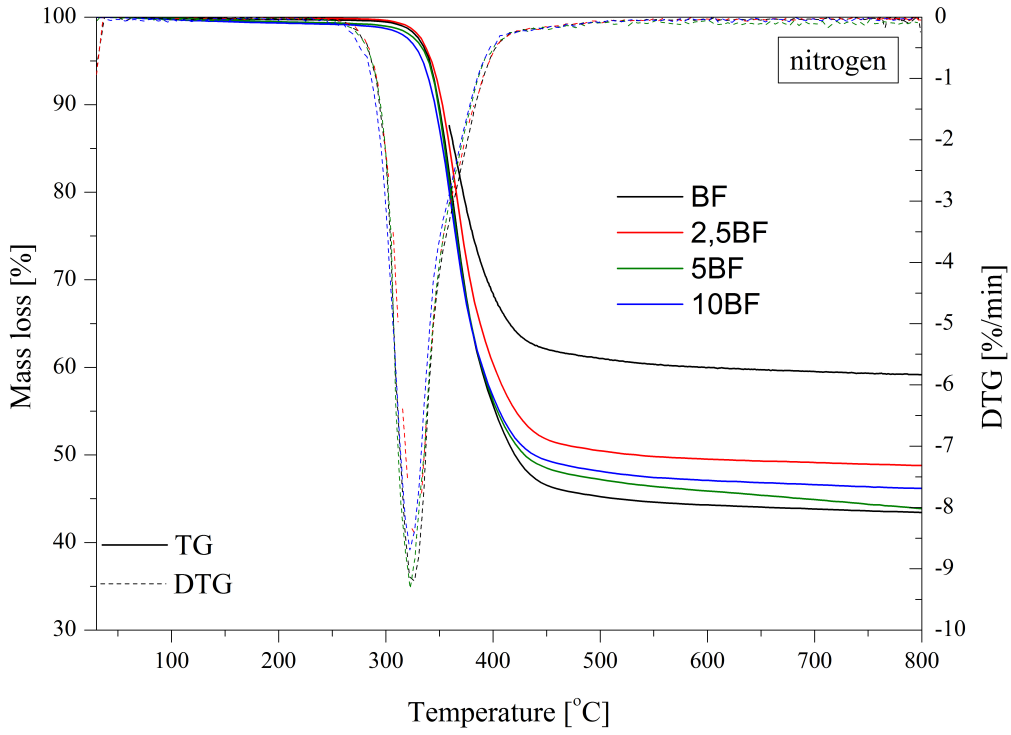

Fig.7. TGA and DTG curves investigated under nitrogen atmosphere

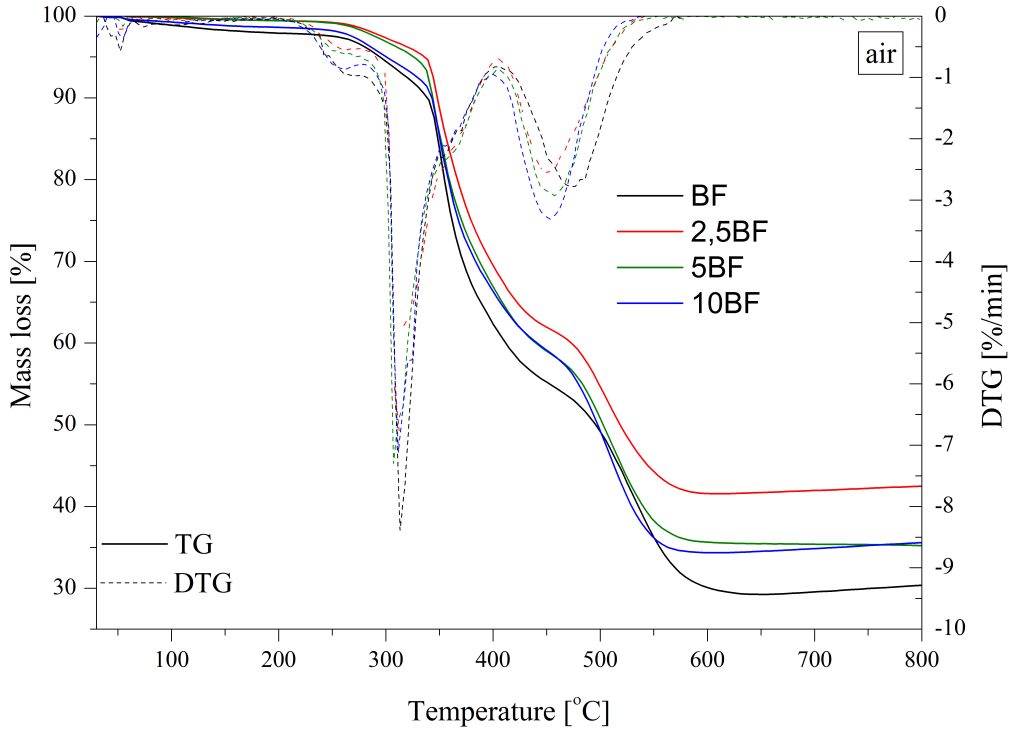

Fig.8. TGA and DTG curves investigated under air atmosphere

Table 4. TGA and DTG data of the composites investigated under nitrogen and air atmosphere

	Sample	5% Mass loss [°C]	Residual mass [%]	DTG
NITROGEN	BF	340.0	43.18	365.0°C; -9.2 %/min
	2,5BF	342.8	48.57	367.8°C; -8.4 %/min
	5BF	340.6	42.98	360.6°C; -9.3 %/min
	10ZBF	335.3	45.89	360.3°C; -8.6 %/min
AIR	BF	295.0	31.0	350.0°C; -8.39 %/min
	2,5BF	334.0	42.9	349.0°C; -6.76 %/min
	5BF	328.0	34.9	343.0°C; -7.30 %/min
	10ZBF	303,2	36.25	348.2°C; -7.11 %/min

Conclusions

It can be concluded that epoxy composites reinforced with basal fiber and modified with basalt powder indicate good thermomechanical properties. Hybrid effect, caused by an introduction of both powder and fibrous filler into epoxy matrix, was obtained. The introduction of basalt powder improves stiffness and thermal resistance of the composites Therefore, both elastic modulus values and storage modulus values of these materials increased. Complex modification of mechanical properties caused by hybridization of basalt fiber reinforced composites was observed. The most advantageous mechanical and thermomechanical properties for the sample containing 2.5 wt% of basalt powder were obtained, due to sufficient dispersion of basalt powder particles in epoxy matrix. Moreover, it was found that incorporation of low amounts (2.5 wt%) of basalt powder led to a decrease in composites' brittleness in comparison to unmodified epoxy composites. Introduction of higher amounts of the powder may cause formation of agglomerates (defects) in epoxy matrix. The new hybrid composites were more resistant to temperature changes than the reference sample what was proven during dynamic mechanical thermal analysis. It should be stressed that the presence of basalt powder retarded the degradation rate of epoxy matrix.

References

[1] Scarponi C, Sarasini F, Tirillò J, Lampani L, Valente T, Gaudenzi P. Low-velocity impact behaviour of hemp fibre reinforced bio-based epoxy laminates, Compos Part B Eng 2016, 91: 162–168. http://dx.doi.org/10.1016/j.compositesb.2016.01.048.

[2] Oliwa R, Heneczkowski M, Oleksy M. Epoxy composites for aviation industry, Polimery 2015, 60:167-178. http://dx.doi.org/10.14314/polimery.2015.167.

[3] Dwivedi UK, Trihotri M, Gupta SC, H Fozia, M Khan, Malik M. Effect of carbon nanotubes implantation on electrical properties of sisal fibre–epoxy composites, Compos Interface 2017, 24:111-123. http://dx.doi.org/10.1080/09276440.2016.1192314.

[4] Szolnoki B, Bocz K, Sóti PL, Bodzay B, Zimonyi E, Toldy A, Morlin B, Bujnowicz K, Wladyka-Przybylak M, Marosi G. Development of natural fibre reinforced flame retarded epoxy resin composites, Polym Degrad Stab 2015, 119: 68–76. http://dx.doi.org/10.1016/j.polymdegradstab.2015.04.028.

[5] Mittal V, Saini R, Sinha S. Natural fiber-mediated epoxy composites – A review, Compos Part B Eng 2016, 99: 425–435. http://dx.doi.org/10.1016/j.compositesb.2016.06.051.

[6] Fiore V, Di Bella G, Valenza A. Glass–basalt/epoxy hybrid composites for marine applications, Mater Des 2011, 32: 2091-2099. http://dx.doi.org/10.1016/j.matdes.2010.11.043.

[7] Fiore V, Scalici T, Di Bella G, Valenza A. A review on basalt fibre and its composites, Compos Part B Eng 2015, 74:74–94. https://doi.org/10.1016/j.compositesb.2014.12.034

[8] Czigány T. Trends in Fiber Reinforcements – the Future Belongs to Basalt Fiber, Express Polym Lett 2007, 1: 59. http://dx.doi.org/10.3144/expresspolymlett.2007.11.

[9] Wei B, Cao H, Song S. Environmental resistance and mechanical performance of basalt and glass fibres, Mater Sci Eng A-Struct 2010, 527: 4708-15. http://dx.doi.org/10.1016/j.msea.2010.04.021.

[10] Kim H. Enhancement of Thermal and Physical Properties of Epoxy Composite Reinforced with Basalt Fiber, Fiber Polym 2013, 14: 1311-1316. http://dx.doi.org/10.1007/s12221-013-1311-0.

[11] Lopresto V, Leone C De Iorio I. Mechanical characterisation of basalt fibre reinforced plastic, Compos Part B Eng 2011, 42:717-23. http://dx.doi.org/10.1016/j.compositesb.2011.01.030.

[12] Wei B, Song S, Cao H. Strengthening of basalt fibers with nano-SiO2–epoxy composite coating. Mater Des 2011, 32: 4180-4186. http://dx.doi.org/10.1016/j.matdes.2011.04.041.

[13] Wei B, Cao H, Song S. Surface modification and characterization of basalt fibers with hybrid sizings, Compos Part A Appl S 2011; 42: 22-29. http://dx.doi.org/10.1016/j.compositesa.2010.09.010.

[14] Kuzmin KL, Timoshkin IA, Gutnikov SI, Zhukovskaya ES, Lipatov YV, Lazoryak BI. Effect of silane/nano-silica on the mechanical properties of basalt fiber reinforced epoxy composites, Compos Interface 2017, 24:13-34. http://dx.doi.org/10.1080/09276440.2016.1182408

[15] Withers GJ, Yu Y, Khabashesku VN, Cercone L, Hadjiev VG, Souza JM, Davis DC. Improved mechanical properties of an epoxy glass–fiber composite reinforced with surface organomodified nanoclays, Compos Part B Eng 2015, 72, 175–182. http://dx.doi.org/10.1016/j.compositesb.2014.12.008.

[16] Mohanty A, Srivastava VK. Effect of alumina nanoparticles on the enhancement of impact and flexural properties of the short glass/carbon fiber reinforced epoxy based composites, Fiber Polym 2015, 16:188–195. http://dx.doi.org/10.1007/s12221-015-0188-5.

[17] Öztürk B, Arslan F, Öztürk S. Hot wear properties of ceramic and basalt fiber reinforced hybrid friction materials, Tribol Int 2007, 40, 37-48. http://dx.doi.org/10.1016/j.triboint.2006.01.027.

[18] Dhand V, Mittal G , Rhee K.Y, Park S-J, Huic D. A short review on basalt fiber reinforced polymer composites, Compos Part B Eng 2015, 73:166–180. https://doi.org/10.1016/ j. compositesb .2014.12.011

[19] Petrucci R, Santulli C, Puglia D, Nisini E, Sarasini F, Tirillò J, Torre L, Minak G, Kenny JM. Impact and post-impact damage characterisation of hybrid composite laminates based on basalt fibres in combination with flax, hemp and glass fibres manufactured by vacuum infusion, Compos Part B Eng 2015, 69:507–515. http://dx.doi.org/10.1016/j.compositesb.2014.10.031

[20] Petrucci R, Santulli C, Puglia D, Sarasini F, Torre L, Kenny JM. Mechanical characterisation of hybrid composite laminates based on basalt fibres in combination with flax, hemp and glass fibres manufactured by vacuum infusion, Mater Des 2013, 49: 728-735. http://dx.doi.org/10.1016/j.matdes.2013.02.014

[21] Fiore V, Scalici T, Calabrese L, Valenza A, Proverbio E. Effect of external basalt layers on durability behaviour of flax reinforced composites. Compos Part B Eng 2016, 84: 258-265. http://dx.doi.org/10.1016/j.compositesb.2015.08.087.

[22] Fiore V, Scalici T, Badagliacco D, Enea D, Alaimo G, Valenza A. Aging resistance of bio-epoxy jute-basalt hybrid composites as novel multilayer structures for cladding, Compos Struct 2017, 160:1319–1328. http://dx.doi.org/10.1016/j.compstruct.2016.11.025.

[23] Zivkovi I, Fragassa C, Pavlovi A, Brugo T. Influence of moisture absorption on the impact properties of flax, basalt and hybrid flax/basalt fiber reinforced green composites. Compos Part B Eng 2017, 111:148-164.

[24] Akinci A. Mechanical and morphological properties of basalt filled polymer matrix composites, Arch Mater Sci Eng 2009, 35: 29-32.

[25] Çalişkan M, Akinci A, Yilmaz Ş, Şen U. Assignment of mechanical properties of basalt-LDPE composite materials using experimental and computer aided simulation methods, Sci Res Essays 2011, 6:2315-2324. http://dx.doi.org/10.5897/SRE10.1106.

[26] Todic A, Nedeljkovic B, Cikara D, Ristovic I. Particulate basalt–polymer composites characteristics investigation. Mater Des 2011, 32:1677-1683. http://dx.doi.org/10.1016/j.matdes.2010.09.023.

[27] Akinci A, Yilmaz S, Sen U. Wear behavior of basalt filled low density polyethylene composites, Appl Compos Mater 2012, 19: 499-511. http://dx.doi.org/10.1007/s10443-011-9208-9.

[28] Subagia I.D.G.A, Tijing L.D., Kim Y., Kim C.S, Vist IV F.P., Shon H.K., Mechanical performance of multiscale basalt fiber–epoxy laminates containing tourmaline micro/nano particles, Compos Part B Eng 2014, 58, 611-617, http://doi.org/10.1016/j.compositesb .2013.10.034.

[29] Khosravi, H., Eslami-Farsani, R. Enhanced mechanical properties of unidirectional basalt fiber/epoxy composites using silane-modified Na+-montmorillonite nanoclay, Polym Test 2016, 55, 135-142, http://doi.org/10.1016/j.polymertesting.2016.08.011.

[30] Park, J.M., Subramanian, R.V., Interfacial shear strength and durability improvement by monomeric and polymeric silanes in basalt fiber/epoxy single-filament composite specimens, J Adhes Sci Technol 1991, 5, 6, 459-477. http://dx.doi.org/10.1163/156856191X00602.

[31] Liu, Q., Shaw, M.T., Shaw, M.T. Parnas, R.S., McDonnell, A.-M. Investigation of basalt fiber composite aging behavior for applications in transportation, Polym Compos 2006, 27, 475-483. http://dx.doi.org/10.1002/pc.20215.

[32] Jiang, Y.F., Liu, H.W., Jia, T.F., Improving mechanical properties of wood composites using basalt glass powder and basalt fiber, Adv Mater Res 2014, 1048, 400-403. http://dx.doi.org/10.4028/www.scientific.net/AMR.1048.400.

[33] Zhang L, Zhang G, Chang L, Wetzel B, Jim B, Wang Q. Distinct tribological mechanisms of silica nanoparticles in epoxy composites reinforced with carbon nanotubes,

carbon fibers and glass fibers, Tribol Int 2016, 104: 225–236. http://dx.doi.org/10.1016/j.triboint.2016.09.001

[34] Guan FL, Gui CX, Zhang HB, Jiang ZG, Jiang Y, Yu ZZ. Enhanced thermal conductivity and satisfactory flame retardancy of epoxy/alumina composites by combination with graphene nanoplatelets and magnesium hydroxide, Compos Part B Eng 2016, 98:134-140. http://dx.doi.org/10.1016/j.compositesb.2016.04.062.

[35] Bachtiar D., Sapuan S.M., Hamdan M.M., The effect of alkaline treatment on tensile properties of sugar palm fibre reinforced epoxy composites, Mater Design 2008, 29, 1285–1290. http://doi.org/10.1016/j.matdes.2007.09.006

[36] Sarasini F., Tirillò J., Ferrante L., Valente M., Valente T., Lampani L., Gaudenzi P., Cioffi S., Iannace S., Sorrentino L., Drop-weight impact behaviour of woven hybrid basalt–carbon/epoxy composites, Compos Part B Eng, 59, 2014, 204–220, http://doi.org/10.1016/j.compositesb.2013.12.006.

[37] Suresha B., Chandramohan G., Renukappa N.M., Siddaramaiah, Mechanical and Tribological Properties of Glass–Epoxy Composites with and Without Graphite Particulate Filler, J Appl Polym Sci 2007, 103, 2472–2480, http://doi.org/10.1002/app.25413.

[38] Marzocca AJ, Somoza A, Goyanes SN, Salgueiro W, König P. Characterization of free volume in particulate-filled epoxy resin by means of dynamic mechanical analysis and positron annihilation lifetime spectroscopy, Polym Int 2002, 51:1277–1284. http://dx.doi.org/10.1002/pi.1017.

[39] Reis PNB, Ferreira JAM, Zhang ZY, Benameur T, Richardson MOW. Impact response of Kevlar composites with nanoclay enhanced epoxy matrix, Compos Part B Eng 2013,46:7–14. http://dx.doi.org/10.1016/j.compositesb.2012.10.028.

[40] Fiore V, Di Bella G, Scalici T, Valenza A. Effect of Plasma Treatment on Mechanical and Thermal Properties of Marble Powder/Epoxy Composites, Polym Compos 2016, http://dx.doi.org/10.1002/pc.23937

[41] Brostow W, Hagg Lobland HE, Khoja S. Brittleness and toughness of polymers and other materials, Mater Lett 2015, 159: 478–480. http://dx.doi.org/10.1016/j.matlet.2015.07.047

[42] Brostow W, Hagg Lobland HE. Survey of relations of chemical constituents in polymer-based materials with brittleness and its associated properties, Chem Chem Technol 2016, 10: 595-600.

[43] Brostow W, Hagg Lobland HE, Narkis M. Sliding wear, viscoelasticity, and brittleness of polymers, J Mater Res 2006, 21: 2422-2428. http://doi.org/10.1557/JMR.2006.0300

[44] Kacperski M. Preliminary works on influence of modifier type on properties of epoxy/bentonite nanocomposites, Kompozyty(Composites) 2004, 4: 28-32.

[45] Chmielewska D, Sterzyński T, Dudziec B. Epoxy Compositions Cured with Aluminosilsesquioxanes: Thermomechanical Properties, J Appl Polym Sci, 2014, 131: 40672. http://doi.org/10.1002/app.40672

[46] Azwa Z.N., Yousif B.F., Characteristics of kenaf fibre/epoxy composites subjected to thermal degradation, Polym Degrad Stab 2013, 98, 2752 -2759, http://doi.org/10.1016 /j.polym degradstab.2013.10.008.

[47] Herbert W. Moeller, (J. Macan, M.Ivanković) Ch8 Influence of Epoxy amine Ratio on Degradation of Epoxy silica Hybrid Materials In Progress in Polymer Degradation and Stability Research, Nova Science Publisher, New York 2008

[48] Visakh P. M., Arao Yoshihiko, Thermal Degradation of Polymer Blends, Composites and Nanocomposites (Engineering Materials) Springer 2015th Edition, DOI 10.1007/978-3-319-09464-5

[49] Kandola B. K., Biswas B., Price D., Horrocks A. R. Studies on the effect of different levels of toughener and flame retardants on thermal stability of epoxy resin, Polym Degrad Stab 2010, 95, 144-152, http://doi.org/10.1016/j.polymdegradstab.2009.11.040.

[50] Grassie N, Guy MI, Tennent NH. Degradation of epoxy polymers: part 4ethermal degradation of bisphenol-A diglycidyl ether cured with ethylene diamine. Polym Degrad Stab 1986,14,125-37