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Influence of Carbon Fibers Addition on Selected Properties of Microwave-Cured Moulding Sand Bonded with BioCo2 Binder

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Abstract

It was found that the addition of carbon fibers (CFs) does not affect the crosslinking process in the microwave radiation (800 W, 2.45 GHz) of the BioCo2 binder, which is a water solution of poly(acrylic acid) and dextrin (PAA/D). It has influence on BioCo2 thermal properties. The CFs addition improves the thermostability of a binder and leads to the reduction of gas products quantity generated in the temperature range of 300-1100°C (TG-DTG, Py-GC/MS). Moreover, it causes the emission of harmful decomposition products such as benzene, toluene, xylene and styrene to be registered in a higher temperatures (above 700°C). BioCo2 binder without CFs addition is characterized by the emission of these substances in the lower temperature range. This indicates the positive effect of carbon fibers presence on the amount of released harmful products.

The selected technological tests (permeability, friability, bending strength, tensile strength) have shown that the moulding sand with the 0.3 parts by weight carbon fibers addition displays the worst properties. The addition of 0.1 parts by weight of CFs is sufficient to obtain a beneficial effect on the analyzed moulding sands properties. The reduction of harmful substances at the higher temperatures can also be observed.

Keywords: Carbon fiber, Polymer binder, Thermostability, Moulding sand

1. Introduction

Carbon Fibers (CFs) are mainly obtained from polyacrylonitrile, cellulose, asphalt, mesophase pitch (residue from the distillation of coal tars) or phenolic resin. Their properties mostly depends on the production method. They are characterized by good thermal and chemical resistance. One of the most important criteria for selecting the type of fibers as a reinforcing phase in composites, including polymer matrix, is their work temperature [1,2]. In comparison with glass and aramid

fibers, the CFs properties do not change in a non-oxidizing atmosphere up to 2000°C. The main advantages of carbon fibers used to reinforce a polymer matrix are: low density, good thermal and electrical conductivity and low coefficient of friction in case of the friction materials. In addition, these fibers have the ability to dampen vibrations and low absorption of X-ray radiation [3, 4]. Moreover, the application potential of CFs increase constantly due to its chemical structure of the surface and the type and amount of functional groups appearing on it. The presence of functional groups on the carbon fibers surface determines such properties as: ion-exchange, oxidation-reducing, catalytic

properties and level of adhesion of fibers to polymers in polymer matrix composites [5]. The fibers containing carboxylic, sulfonic, phosphate or amino groups are known. As a ceramic material, the disadvantages of CFs include fragility and relatively high price [6, 7].

Carbon fibers based on cellulose fibers were first investigated by Thomas Edison as long ago as 1880. He used them as filaments in his incandescent lamp prototype [8]. In recent years, carbon fibers have been increasingly used as reinforcing elements of polymer matrix composites in the plastics, construction and automotive industries. Carbon Fiber Reinforced Polymers (CFRP) are e.g. used to manufacture yachts and boats masts, bicycle frames, surfboards or arrowheads. CFs are also part of heat-resistant and non-flammable fabrics as well as electrically heated fabrics and orthopedic splints in the medical industry [9, 10].

Taking into account the properties of carbon fibers and their wide range of applications, research has been undertaken to determine the effect of CFs on selected properties of moulding sands bonded in microwave radiation with BioCo binders. In recent years, research at the field of modifications, including reinforcing of polymer binders from the BioCo group, have been carried out at the Faculty of Foundry Engineering AGH. BioCo aqueous polymer binders contain acrylic polymers (poly(acrylic acid), poly(sodium acrylate)) and modified polysaccharides (dextrin, carboxymethyl starch). The curing process can be carried out physically as a result of microwave radiation or chemically through calcium cations or glutaraldehyde [11–13]. BioCo binders are completely biodegradable in the water environment and in the soil. The products of their biological and thermal degradation have no harmful effect on environment. During the technological process, they do not emit toxic products of the thermal decomposition [14]. Therefore, the attention of researchers was also directed to acquiring knowledge about determining the effect of carbon fiber additive on thermostability of BioCo binders, which is important in the process of binder processing itself, as well as is important from the point of view of environmental protection [14–17]. Recent works have indicated that the silicate additive increases the thermostability of the BioCo3 binder, while its amount does not influence on the increase of the emissions of organic products of destruction. It was found that during the decomposition of the BioCo binder with the addition of silicate, the compounds from the aromatic hydrocarbons group are generated in the third temperature range (420–838°C). At the temperature of 838°C, benzene and toluene were detected among the decomposition products. Moreover, the silicate addition introduced into moulding sand bonded with BioCo3 binder in the microwave radiation field leads to the creation of the network of hydrogen bonds with its participation, which are mainly responsible for maintaining the cross-linked structures in the binder-mineral matrix system. As a result of microwave curing process in the presence of Poraver, the mechanical properties of moulding sand are improved (R_m^u) [18].

In this study, the results of structural tests (FTIR - Fourier transform infrared spectral analysis) of the BioCo2 polymer binder, being an aqueous solution of poly(acrylic acid) and dextrin (PAA/D) with the CFs addition uncured and microwave cured (800 W, 2.45 GHz) were investigated.

This research was also carried out to determine the effect of carbon fibers addition on the thermal properties of the BioCo2 binder, including the identification of the degradation products

during the thermal destruction process (TG-DTG - thermogravimetry, Py-GC/MS - pyrolytic gas chromatography with mass spectrometry). Moreover, the effect of CFs additive on selected technological properties of moulding sand bonded with BioCo2 binder were investigated. Microwave cured BioCo2 bonded moulding sands with the addition of carbon fiber were prepared, followed by a cycle of technological tests: permeability (P^u), friability (S^u), tensile and bending strength (R_m^u , R_g^u).

It should be noticed that the introduction of carbon additives, such as graphite, resin compositions, into moulding sands is often purposive. For example, in mass technology with bentonite, they are introduced in order to improve the quality of castings [19–21]. Therefore, the authors plan in the next stage of works to make casts from a selected grade of cast iron using the moulds obtained from the moulding sands bonded with BioCo2 binder with the addition of carbon fibers and determine their quality. The obtained results will be the subject of another publication in this regard.

2. Methodology

2.1. Materials

The following materials were used in the study:

- Polymer binder BioCo2,
- Carbon fibers (ground, Primson Composites). The carbon fibers were made from polyacrylonitrile. Properties of CFs: specific surface area 4.6 m²/g, arithmetic mean of fiber size 22.28 μm, density 1.40 g/cm³, Young's Modulus approx. 420 GPa, tensile strength approx. 2500 MPa,
- Mineral matrix, silica grain sand (Sibelco Poland), main fraction: 0.20/0.16/0.32 mm (PN-85/H-11001), density 2.5–2.8 kg/dm³, bulk density 1.4–1.6 kg/dm³.

2.2. Preparation of binder samples

The BioCo2 binder was prepared in the form of an aqueous solution of a two-component polymer composition: a 40% solution of poly(acrylic acid) (BASF) and dextrin (Fluka). The polymer components were mixed using a mechanical stirrer in a weight ratio of 1:1 at the room temperature. The mixing time was 30 min.

For structural and thermoanalytic tests, the BioCo2 binder samples without and with the carbon fibers addition were prepared. The carbon fibers were introduced into the prepared binder and then the whole was mixed at the room temperature for 30 min using the mechanical stirrer. The weight ratio of carbon fibers to binder was 1:10 (fibers : binder).

The cross-linking process of the BioCo2 binder samples without and with the addition of carbon fibers was carried out in the microwave radiation field (2.45GHz, 800W) using Samsung MS23F301TAS device. The temperature in the microwave device was about 100°C. The curing process of 20 g weight samples was carried out within 60 seconds.

2.3. Moulding sand preparation

Three moulding sands of different carbon content: 0.0 (without additive), 0.1, 0.3 part by weight were prepared. Each of them was obtained by mixing in a LM-type mixer: 100 parts by weight of quartz sand, 3 parts by weight of polymer binder BioCo2 and the appropriate amount of CFs. The molding sand was prepared by mixing the following materials, according to that order: 1. The matrix, 2. The BioCo binder, 3. The carbon fiber. Total mixing time of each compound was 3 min. In order to precisely spread the binder between the matrix grains an R-1 mechanical agitator (DANLAB, 1,000 rpm) was used. The vibration frequency of the device was constant at 50 Hz. Prepared mixtures were used for the formation of normalized samples for the determination of characteristic moulding sand properties.

2.4. Preparing and curing samples

Three types of shapes of standard laboratory samples: cylindrical to determine permeability and wear resistance, octal to set down tensile strength and oblong to measure bending strength, were prepared. All of the samples were compacted by triple hitting of standard laboratory rammer (LU type) weighing 6.667 kg. Normalized samples were cured in the microwave radiation field (2.45 GHz, 800 W) in the microwave device Samsung MS23F301TAS. The temperature inside the device was about 100°C. The curing process was carried out by 180 s. The prepared specimens were stored in the laboratory with an air humidity of about 42% and a temperature within the range of 23-24°C.

2.5. Examinations

Fourier transform infrared spectroscopy (FTIR)

The structural tests were performed by using the transmission technique (with KBr pellets) with the use of a Digilab Excalibur FTS 3000 Mx spectrometer with the DTGS detector. The spectrum was recorded within an infrared radiation range of 4000–400 cm^{-1} , with a power of resolution of 4 cm^{-1} . Interferograms consisted of 32 sample scans, which were averaged over one spectrum. The preparation of the materials for the FTIR technique required mixing 200 mg of pure and dry potassium bromide with an adequate amount of the researched sample (2 mg). The pellets received by compressing the prepared mixtures in a hydraulic press at 200 bar for 1 min were then placed in the measuring chamber of the spectrometer. The obtained spectrum of each sample was compared with the background spectrum (KBr).

Thermal analysis

The thermal examinations (thermogravimetry TG-DTG) were performed by using Thermal Analyzer produced by Jota. The temperature range of test was 20-1000°C and a heating rate was of 10°C/min in oxygen atmosphere.

Pyrolysis gas-chromatography/mass spectrometry

Pyrolysis gas-chromatography/mass spectrometry (Py-GC/MS) was used to determine the emission level of gaseous products during the thermal degradation of the tested material. In the pyrolysis gas chromatography (Py-GC/MS) method, the following instrumentation was used: the pyrolyzer "Py" Pyroprobe 5000 (CDS Analytical Inc.), the gas chromatograph "GC" Focus GC (Thermo Scientific), coupled with the mass spectrometer (MS) Focus ISQ (Thermo Scientific). The study is based on transforming a solid sample (2–3 mg) into gas by heating in an atmosphere of inert gas (helium) in a pyrolyzer, which is accompanied by thermal decomposition. The obtained mixture of compounds (pyrolysate) is separated on a chromatographic column in a chromatograph. The gas chromatography "GC" conditions were as follow: an initial temperature of 40°C (3 min hold) was raised at 3°C/min to 100°C (3 min hold) and then at 20°C/min to 250°C (3 min hold) using constant helium flow of 1 cm^3/min during the whole analysis. The temperature of the split injector was 250°C and the split ratio was 1:30. The transfer line temperature was 250°C. The EI ion source temperature was kept at 250°C. The ionization occurred with a kinetic energy of the impacting electrons of 70 eV. The gas products were identified based on the mass spectral library NIST MS Search 2.0 Libera (Chemmm. SW, Version 2.0, Fairfield, CA, USA).

Permeability determination

Permeability (P) was performed by the fast method in electrical apparatus type LPiR1. The permeability values were expressed in the SI unit $10^{-8} \text{ m}^2/\text{Pa}\cdot\text{s}$. The permeability was determined for microwave-cured cylindrical samples after 24 hours of the storage (PN-80/H-11072).

Friability determination

Friability was determined by means of a special apparatus (Huta Stalowa Wola production). A normalized cylindrical-shaped sample after a preweighing (Q_1) was placed in the jaws of the device so it was in a horizontal position. The steel shots striking a rotating sample caused attrition of its top layer. In the end the sample was reweighed (Q_2). Due to the expected high abrasion of the tested moulding sands, only half of the recommended weight of steel shots (i.e., 875 g) was used in measurements. Friability (S) in % was calculated based on formula (1):

$$S^u = \frac{Q_1 - Q_2}{Q_1} \cdot 100\% \quad (1)$$

where:

Q_1 – mass of the sample before the test, g;

Q_2 – mass of the sample after the test, g.

The wear resistance was examined after 24 hours of the storage.

The cylindrical-shaped samples were subjected to friability tests after 24 hours from curing in the microwave field. The results were averaged from three measurements of a sample.

Strength testing

All the strength properties were performed using the universal strength testing machine LRu-2c (Multiserw Morek). Depending on the tested property, 8-shaped (tensile strength)

or oblong-shaped (bending strength) sample was placed in the measuring machine. The measurement range was (0-130 N/m²) for R_m^u and (0-860 N/m²) for R_g^u . The results were registered on the scale of the machine. The tests were examined after 1, 4, and 24 h of sample storage in accordance with PN-83H-11073/EN.

3. Results and discussion

3.1. Studies on FTIR Spectra and Py-GC/MS

FTIR spectra of BioCo2 polymer binder uncured and cured in microwave field (with and without the carbon addition) have been shown in Fig. 1.

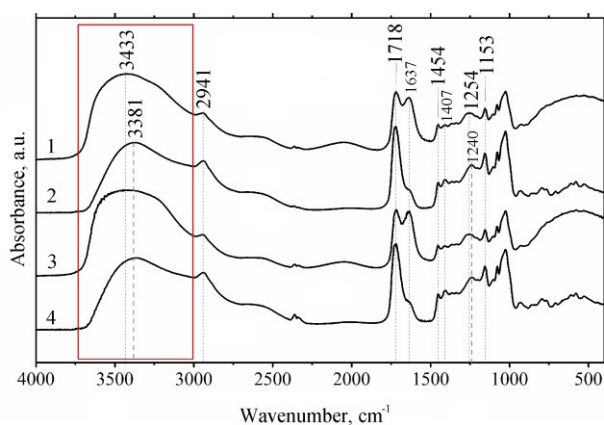


Fig. 1. IR spectra of the BioCo2 binder: 1 - uncured, 2 - microwave cured, 3 - uncured with CFs addition, 4 - microwave cured with CFs addition

As a result of microwave radiation, the solvent water evaporated from the binder samples, which is indicated by the changes in the intensity of bands in the range of wave number 3800-3000 cm⁻¹ (spectra 1 and 2, 3 and 4). There is a visible reduction in the maximum intensity and a shift to lower wave numbers. The bands have not disappeared completely, which is the result of the curing process of BioCo2 binder associated with the formation of hydrogen bonds (spectra 2 and 4). The band in the region of 2941 cm⁻¹ refers to C-H stretching vibrations present in the polymers structure.

Intensive adsorption band at 1718 cm⁻¹ corresponding to C=O vibrations occurs in all FTIR spectra, but under the influence of curing agent there is a noticeable increase in its intensity. Band in the wave number 1637 cm⁻¹, which corresponds to the bending vibrations of OH groups from water present in the liquid BioCo2 binder, disappears almost completely after cross-linking. This indicates effective evaporation of the solvent water. The band related to symmetric shearing vibrations $\delta(\text{CH}_2)_n$ is recorded at all IR spectra in the wave number range of 1450 cm⁻¹. The changes in shape and shifts to lower wave numbers of the band ~1250 cm⁻¹ are related to the participation of the groups C-OH and C=O in the process of curing. The bands related to vibrations of CH (-CH₂ group and -CH) remain almost the same (~1150 cm⁻¹).

It was not found that the presence of CFs in the system, before and after cross-linking, caused structural changes of the pure BioCo2 polymer binder, which can be captured using the FTIR technique.

No changes in the intensity of characteristic bands on IR spectra were recorded (spectrum 1 and 3). All shifts in the position of the maxima of these bands are within the limits of the method sensitivity (± 4 cm⁻¹). The factor causing the structural changes in the binders was microwave radiation, but for both microwave cured samples almost identical changes in the IR spectra were recorded (spectra 2 and 4).

Identified bands on IR spectra for a BioCo2 polymer binder without or with carbon fibers addition, in liquid (uncured) and solid (cured) state, are summarized in Table 1.

Table 1.

Characteristic bands in the IR spectra of polymer binder BioCo2

Sample				Assignment	Remarks
1	2	3	4		
Wavenumber, cm ⁻¹					
3439	3381	3439	3381	v-OH	Band of free OH group (water)
				O-H...O-H	Hydrogen bond
				O-H...O=H	
2941	2941	2941	2941	v-C-H	Stretching vibrations asymmetric and symmetric
1718	1718	1718	1718	ν_s -C=O	Stretching vibrations of carbonyl group in PAA
1637	1638	1637	1638	δ -OH	Bending vibrations
1454	1454	1454	1454	$\delta(\text{CH}_2)_n$	Bending vibrations
1407	1407	1407	1407		
1254	1240	1254	1241	C-O	Stretching vibrations
				C-O-H	Deforming vibrations
1153	1154	1153	1155	C-CH ₂	Twisting vibrations

The samples of BioCo2 binder without and with the addition of carbon fibers were then directed to thermoanalytical tests (TG-DTG, Py-GC/MS). In an oxidizing atmosphere, decomposition of cross-linked polymer binder BioCo2 with CFs occurs with four weight losses (Fig. 2 a,b). In total, four mass loss steps of 34.9% and 62.4% were observed. The maximal mass loss steps were observed at the temperatures 232°C, 332°C, 488°C and ~730°C which can be seen from the DTG signal. A sample actually completely decomposes to the temperature of 1000°C (remaining sample mass 2.7%).

The addition of carbon fibers changes the thermal characteristics of the BioCo2 polymer binder (Fig. 2b). Three weight losses can be seen on the TG curve (7.6%, 27.3%, 58.3%). Less thermal effects can be seen in the lower temperature range. Finally, the total loss of sample mass in a given temperature range was 93.2%. This means that the addition of carbon fibers has increased the thermal stability of the BioCo2 binder.

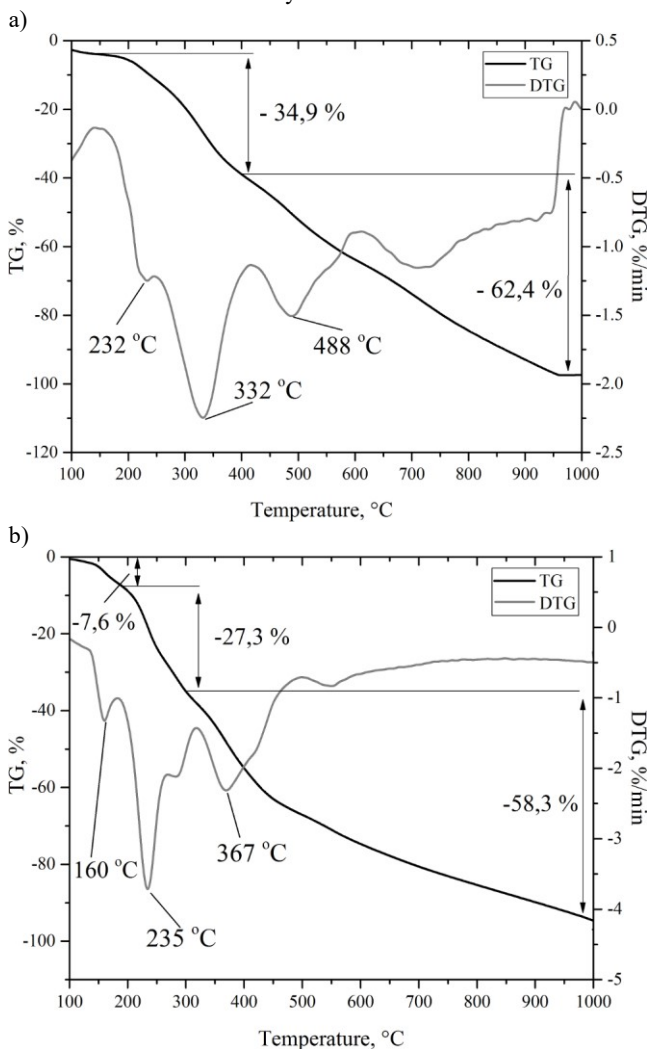


Fig. 2. TG-DTG curves of polymer binder BioCo2: a) without CFs, b) with CFs in an oxidizing atmosphere

For prepared samples of BioCo2 binder without and with the carbon fibers addition, qualitative thermoanalysis was also carried out using the pyrolysis-gas chromatography-mass spectrometry technique. For each of the samples, measurements were taken successively at temperatures of: 300°C, 450°C, 700°C and 1100°C (Fig. 3 and 4). The temperature values in which the measurements were made were correlated with the results of the TG-DTG. Fig. 3 presents the GC/MS chromatograms registered for the BioCo2 binder without carbon fibers.

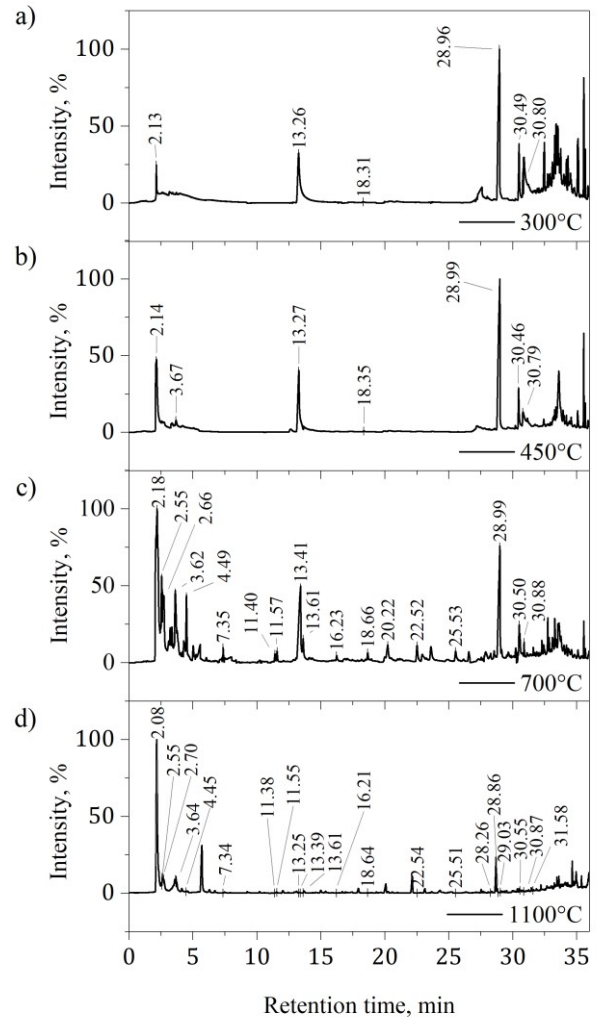


Fig. 3. Chromatograms GC/MS obtained for artwork polymer binder BioCo2 without CFs treated with temperature: a) 300°C, b) 450°C, c) 700°C, d) 1100°C

Table 2 summarizes the identified compounds generated from the BioCo2 polymeric binder.

Table 2.

Py-GC/MS results for the BioCo2 binder without CFs additive

Name	No. CAS	M_w^*	Retention time R_T , min			
			300°C	450°C	700°C	1100°C
Carbon dioxide	124-38-9	44	2.13	2.14	2.18	2.08
1,3-Cyclopentadiene	542-92-7	66	-	-	2.66	2.70
Furan	110-00-9	68	-	-	2.55	2.55
Methyl vinyl ketone	78-94-4	70	-	3.67	3.62	3.64
Benzene	71-43-2	78	-	-	4.49	4.45
Toluene	108-88-3	92	-	-	7.35	7.34
Furfural	98-01-1	96	13.26	13.27	13.41	13.25
Phenylethyne	536-74-3	102	-	-	-	13.39
Styrene	100-42-5	104	-	-	13.61	13.61
Ethylbenzene	100-41-4	106	-	-	11.40	11.38
m-Xylene	108-38-3	106	-	-	11.57	11.55
Indene	95-13-6	116	-	-	22.52	22.54
2-methylstyrene	611-15-4	118	-	-	18.66	18.64
2,3-Benzofuran	271-89-6	118	-	-	20.22	20.21
m-Ethyltoluene	620-14-4	120	-	-	16.23	16.21
2,4-Dihydroxy-2,5-dimethyl-3(2H)-furan-3-one	10230-62-3	144	18.31	18.35	-	-
7-methylbenzofuran	17059-52-8	132	-	-	25.53	25.51
1H-Indene,1-methylene-	2471-84-3	128	-	-	-	28.26
Naphthalene	91-20-3	128	-	-	-	29.03
Lewoglukozan	37112-31-5	126	28.96	28.99	28.99	28.86
2-Furan	67-47-0	126	30.80	30.79	30.88	30.87
1,4:3,6-Dianhydro-r-d-glucopyranose	n/a	144	30.49	30.46	30.50	30.55
Biphenyl	92-52-4	154	-	-	31.57	31.58

* M_w - molecular weight, u

Fig. 4 shows the GC/MS chromatograms obtained for the BioCo2 binder with carbon fibers addition.

Analysis of the obtained results of Py-GC/MS showed that the increase in temperature caused an increase in the number of decomposition products of both the BioCo2 binder with and without addition of carbon fibers. Most of the decomposition products of the BioCo2 binder without CFs were identified at 700°C (Fig. 3, Table 2).

The presence of a CFs in the binder promoted the reduction of the binder degradation products produced at temperatures: 300°C, 450°C, 700°C and 1100°C (Fig. 4, Table 3). Moreover, the addition of carbon fibers caused that harmful decomposition products, such as benzene or styrene, were recorded at a higher temperature compared to the BioCo2 binder without CFs addition (Tables 2 and 3).

Table 3.

Py-GC/MS results for the BioCo2 binder with CFs additive.

Name	No. CAS	M_w^*	Retention time R_T , min			
			300°C	450°C	700°C	1100°C
Carbon dioxide	124-38-9	44	2.15	2.19	2.17	2.13
1,3-Cyclopentadiene	542-92-7	66	-	-	2.78	2.77
Furan	110-00-9	68	-	-	2.59	2.58
Methyl vinyl ketone	78-94-4	70	-	3.67	3.62	3.64
2-Butanone	78-93-3	72	-	-	3.69	3.70
Benzene	71-43-2	78	-	-	-	4.53
Toluene	108-88-3	92	-	-	-	7.40
Furfural	98-01-1	96	-	-	-	13.43
Styrene	100-42-5	104	-	-	-	13.62
Ethylbenzene	100-41-4	106	-	-	11.40	11.38
m-Xylene	108-38-3	106	-	-	11.57	11.55
Indene	95-13-6	116	-	-	-	22.53
Levogluconone	37112-31-5	126	28.79	28.82	28.82	28.80
Naphthalene	91-20-3	128	-	-	-	28.99

* M_w - molecular weight, u

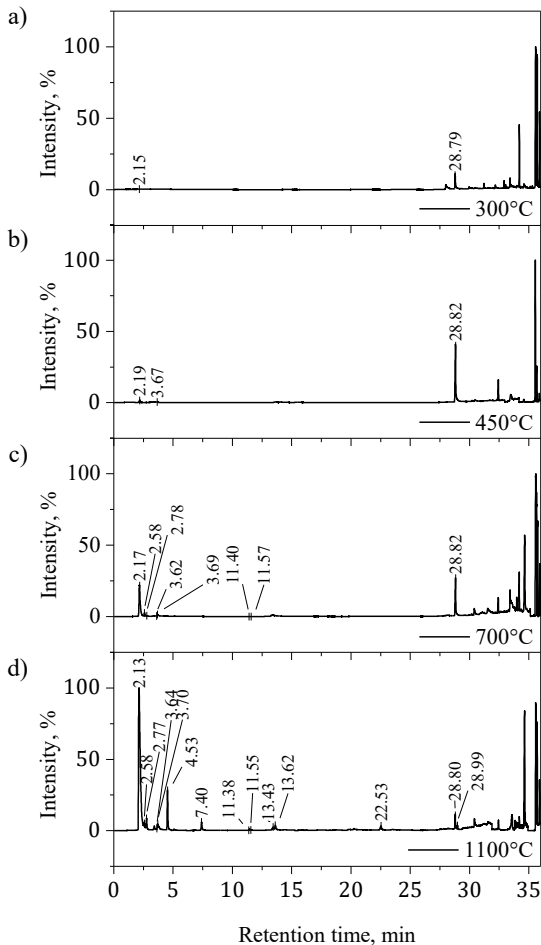


Fig. 4. Chromatograms GC/MS obtained for artwork polymer binder BioCo2 with CFs treated with temperature: a) 300°C, b) 450°C, c) 700°C, d) 1100°C

3.2. Technological tests

Permeability and friability

Fig. 5 illustrates the effect of carbon additive on permeability P^u and friability S^u of moulding sands bonded with BioCo2 polymer binder depending on its content, after 24 h from curing in the microwave field.

According to the results, the worst properties were obtained by the moulding sand with a 0.3 parts by weight of carbon fibers. Its permeability was in the range of $316 \times 10^{-8} \text{ m}^2/\text{Pa}\cdot\text{s}$, and the friability was 19.55% (Fig. 5). Thus, the content of CFs in the amount of 0.3 parts by weight is too big in terms of improving the technological properties of moulding sand bonded with BioCo2 and cured in the microwave field. The highest permeability value of $400 \times 10^{-8} \text{ m}^2/\text{Pa}\cdot\text{s}$ with the lowest friability value of 13.99% were obtained by the moulding sand with a 0.1 parts by weight of carbon fibers addition. Therefore, 0.1 parts by weight of CFs is the optimum amount having an advantageous effect on the properties of the moulding sand.

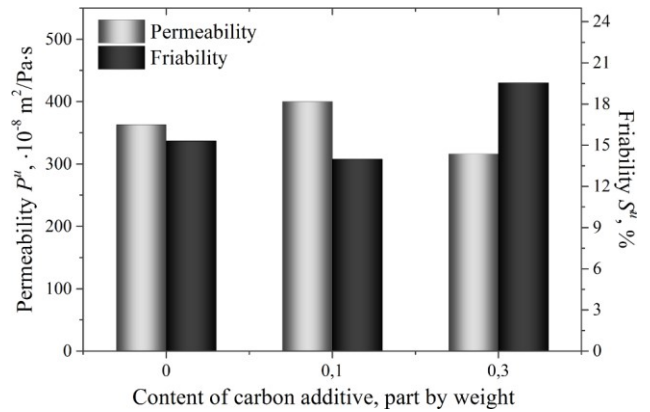


Fig. 5. Results of permeability and friability tests of microwave cured, and then stored for 24 hours moulding sands bonded with BioCo2 binder depending on the content of CFs: 0 (without addition), 0.1 and 0.3 parts by weight

The small amount of the additive of carbon fibers to the system may change the course of the thermal degradation process of the BioCo binder in moulding sand. It is possible that reducing conditions are created, which increases thermostability and reduces emissions. The second concept is related to the adsorption of the resulting gaseous products on the surface of the fibers. It should be noted, however, that the emission level of harmful compounds in the BioCo bound moulding sands is low (compared to organic resins used in technology), and it was found that the addition of carbon fibers reduces emissions.

Explanation of the mechanism requires more extensive research and deeper analysis (eg. conjugated methods TG-MS, TG-IR), which will be the subject of a new publication.

Strength testing

Moulding sands bonded only with the polymer binder BioCo2 and with the same binder, but in the presence of CFs (0.1 and 0.3 parts by weight) after 1, 2, and 24 h from curing in the microwave radiation field were subjected to tests of tensile R_m^u and bending R_g^u strength. The results are illustrated in Fig. 6 and 7.

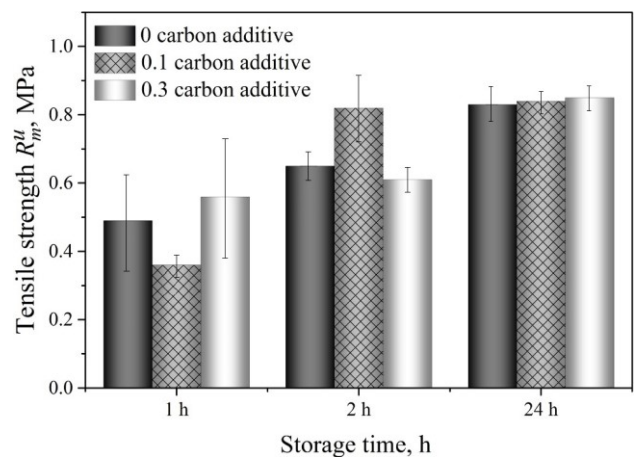


Fig. 6. Tensile strength of moulding sands after 1, 2 and 24 h from curing in the microwave field depending on the content of carbon fibers: 0 (without added), 0.1 and 0.3 parts by weight

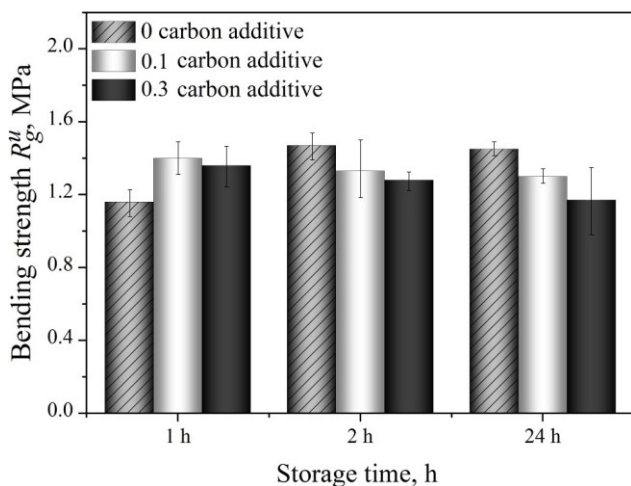


Fig. 7. Bending strength of moulding sands after 1, 2 and 24 h from curing in the microwave field depending on the content of carbon fibers: 0 (without added), 0.1 and 0.3 parts by weight

The tensile strength of all three types of moulding sands was the lowest when the test was carried out after 1 h from curing samples in the microwave field, with the highest value achieved by a sample with an addition of 0.3 parts by weight carbon fibers (0.56 MPa). After 2 h from the cross-linking, the best properties showed a sample containing 0.1 parts by weight of CFs. Its tensile strength was equal to 0.82 MPa. The same sample obtained the highest, but similar value (0.84 MPa) after 24 h of storage. A moulding sand without a carbon fibers addition, as well as moulding sand bonded with BioCo2 binder with 0.3 parts by weight of CFs also showed the highest tensile strength after 24 h from the curing with microwave radiation. The values of their strength were successively 0.83 and 0.85 MPa (Fig. 6).

Fig. 7 shows the results of the bending strength test, based on which it can be concluded that the moulding sand without the carbon fibers addition after 1 h (1.16 MPa) from curing, had the worst strength, while it achieved the highest values after 2 h (1.47 MPa) and 24 h (1.45 MPa) from cross-linking in the microwave field. Moulding sand with 0.1 parts by weight of CFs had the best bending strength after 1 h (1.40 MPa) from curing, after 2 h and 24 h was respectively 1.33 MPa and 1.30 MPa. Sample with carbon fibers addition in the amount of 0.3 parts by weight reached the lowest strength values of 2 (1.28 MPa) and 24 h (1.17 MPa) of all tested samples.

The observed differences in variations in tensile and bending strength over 24 hours of storage after curing may be associated with the statistical distribution of carbon fibers in the prepared molding sand, which may be important for the process of its strengthening.

4. Conclusions

The performed investigations indicate that the carbon fibers does not affect the course of the curing process of the BioCo2 binder, but has an influence on its thermal properties. The addition of the determined amount of carbon fibers increases the thermal stability of the binder and reduces the quantity of gas products generated in the temperature range of 300-1100°C. It is

also noteworthy that thanks to the addition of carbon fibers, the harmful decomposition products, such as benzene, toluene, xylene and styrene, were registered in a higher temperature range (above 700°C). The emission of these substances for BioCo2 binder without CFs addition, was observed in the lower temperature range. This means that the addition of carbon fibers inhibits the release of harmful substances.

In addition, the obtained results of selected technological tests (permeability, friability, tensile strength and bending strength) allow to notice that the worst properties are obtained by mass with the addition of 0.3 parts by weight of carbon fibers. The addition of 0.1 parts by weight of CFs is sufficient to obtain a beneficial effect on the analyzed moulding sands properties.

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