

Analysis of biochar with different pyrolysis temperatures used as filler in epoxy resin composites

Original

Analysis of biochar with different pyrolysis temperatures used as filler in epoxy resin composites / Giorcelli, Mauro; Savi, Patrizia; Khan, AAMER ABBAS; Tagliaferro, Alberto. - In: BIOMASS & BIOENERGY. - ISSN 0961-9534. - ELETTRONICO. - (2019), pp. 1-13. [10.1016/j.biombioe.2019.01.007]

Availability:

This version is available at: 11583/2724878 since: 2020-07-10T14:54:06Z

Publisher:

Elsevier

Published

DOI:10.1016/j.biombioe.2019.01.007

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

Elsevier postprint/Author's Accepted Manuscript

© 2019. This manuscript version is made available under the CC-BY-NC-ND 4.0 license
<http://creativecommons.org/licenses/by-nc-nd/4.0/>. The final authenticated version is available online at:
<http://dx.doi.org/10.1016/j.biombioe.2019.01.007>

(Article begins on next page)

Analysis of biochar with different pyrolysis temperatures used as filler in epoxy resin composites

Mauro Giorcelli¹, Patrizia Savi², Aamer Khan^{1,3}, Alberto Tagliaferro^{1,4}

¹*Department of Applied Science and Technology (DISAT), Politecnico di Torino, 10129, Italy.*

²*Department of Electronic and Telecommunication (DET), Politecnico di Torino, 10129, Italy.*

³*Department of Textile Engineering, University of Engineering and Technology,
Lahore (Faisalabad Campus), Pakistan.*

⁴*Faculty of Science, University of Ontario Institute of Technology, Oshawa, Ontario, Canada.*

Biocomposites are composite materials formed by a matrix and a filler derived from natural biomass. The use of biomasses and other biogenic wastes in composites represent an eco-friendly way to use these natural fillers. Biochar is a solid material generated by pyrolysis of biomasses. It is characterized by high carbon content, and for this reason it can be considered a possible substitute for more expensive and/or less environment friendly carbon fillers in composites. Biochars produced at different pyrolysis temperatures are investigated in this work (Miscanthus). They were characterized as produced (morphology, elemental analysis, graphitization grade, DC electrical conductivity) and subsequently used as fillers in epoxy resin. The complex permittivity of composites was then investigated. The aim of this work is to predict the final electrical properties of the composite by an evaluation of biochars characteristics. Results on biochar characterization, in particular DC electrical conductivity, are in agreement with the electrical performances on final composites.

Keywords: biochar, composites, epoxy resin, FESEM, Raman, complex permittivity.

1. Introduction

In recent years, there has been an increased interest in composite materials, with a particular focus on polymer composites. As fillers, carbon materials are receiving a great attention due to their ability to enhance mechanical, electrical and thermal properties of final composites. Countless articles report advantage of carbonaceous particles used such as fillers in composites [1-3]. Among them carbon nanotubes are the most quoted [4], but one of the most important obstacles that impede their large scale application is their cost. Alternative materials with high carbon content and low cost are evaluated as possible substitutes. Research is looking into the possibility of using waste materials as possible feedstock to produce these carbon fillers. In particular, waste biomasses are attracting much interest for the production of carbon filler called biochar. Biochar is a carbonaceous product obtained from the pyrolysis of biomasses and other biogenic wastes [5-6]. During the production process pyrolysis parameters such as temperature, play a crucial role in controlling the yield as well as the properties of the final product [7]. Lower pyrolysis temperatures result in higher biochar yields, higher levels of volatile compounds emissions during the heat treatment and excellent cation-exchange capacity. Conversely, higher temperatures treatments generate an activated biochar with a greater extent of aromatic carbon, higher alkalinity, large specific surface area and extended microporosity [8]. Their graphitization grade increase with temperature.

Biochar, obtained by the pyrolysis of biomasses, has proved to be a possible alternative to other high cost carbon fillers because of its ability to improve mechanical, electrical and thermal properties of the final product. Biochar performances seem to be correlated to two main parameters: the feedstock and the pyrolysis temperature used to produce the biochar. For example, biochar derived from pine wood, produced at 500°C and then activated at 900°C, has been used in polypropylene composites in order to improve their mechanical properties [9]. This study also demonstrated that the flammability properties were not affected by the addition of biochar. In [10], date palm tree wastes, produced at 700°C and 900°C, were used to produce polypropylene (PP) composites and their electrical, mechanical, thermal and rheological properties were investigated. The results of this study indicated

1 that the composite electrical conductivity was enhanced by four orders of magnitudes on increasing
2 the biochar content from 0 to 15 wt.%. The tensile modulus of composites was found to be improved
3 when compared to the neat PP for all biochar loading. The thermal studies revealed that the
4 crystallinity of composite was reduced compared to neat PP and the rheological studies indicated poor
5 biochar-polypropylene interfacial interactions. Also soft polymers such as poly vinyl alcohol (PVA)
6 was used in combination with biochar for pressure sensor applications [11]. In this case, commercial
7 hardwood biochar was dispersed in PVA to produce sensors. The variation of electrical signal through
8 the composite was measured with relation to applied pressure. Results indicated that the increase in
9 biochar content from 8 to 12 wt.% significantly improved the conductivity and piezoresistive effect
10 of PVA/biochar sensors. In epoxy resin, biochar was used to improve mechanical and electrical
11 properties. For example, the elastic constant of epoxy resin and biochar composites was investigated
12 using ultrasonic pulse echo overlap method [12]. Pine cone char and china poplar char, obtained after
13 a 450°C pyrolysis process, were used to produce biochar to fill epoxy resin at 10, 20 and 30 wt.%. In
14 this case a general improvement of elastic properties of composites were obtained, but china poplar
15 char, at the same filler percentage, reported best result if compared with the pine cone char composite.
16 Electrical properties (permittivity and conductivity) coupled with mechanical properties (stress strain
17 curves, ultimate tensile strength and tensile toughness) in biochar, derived from maple wood, treated
18 up to 950°C, was used as filler in epoxy resin [13]. In this case, the biochar performances were
19 compared to those obtained using multi wall carbon nanotubes (MWCNTs). Biochar obtained results
20 comparable to the results from MWCNTs even if in different percentage.

21 In the light of these results, it seems that the type of biochar and its pyrolysis temperature could
22 influence the final composite performances, in particular electrical performances. Moreover, a pre
23 selection of the biochar to be used in composite could be an advantage to drive results in the desired
24 direction.

1 In this work, biochars derived from Miscanthus char (MIS) treated at different temperatures were
2 characterized before their application in composite preparation. Field Emission Scanning Electron
3 Microscopy (FESEM), Energy Dispersive X-ray (EDX), Raman and DC-conductivity performed on
4 biochar were used to predict the final electrical composites performance. Electrical characterization
5 of composites confirmed that a pre-screening of biochars is representative of the final results
6 obtained.

7 8 **2. Materials and methods**

9 10 **A. Biochars and their composites**

11 MIS samples were prepared by ICFAR (London Ontario CA) derived from residues miscanthus
12 (plant growing in southern Ontario). These residues were pyrolyzed at 650, 700 and 750 °C. After
13 that, biochars were activated by CO₂ process as described in detail in [14]. Briefly, this activation
14 process takes place switching the gas from Nitrogen to CO₂ when the maximum temperature is
15 reached. These biochars are identified here with the acronyms MIS650, MIS700 and MIS750. Epoxy
16 Resin (Cores LPL, Italy) is the polymer matrix used to produce samples for electrical characterization.

17 18 **B. FESEM – EDX- Particle size distribution**

19 In order to analyze the structure of the biochar particles, a FESEM analysis was performed with a
20 ZEISS SUPRATM 40 Field Emission Scanning Electron Microscope. The microscope was equipped
21 with an Energy Dispersive X-Ray detector (EDX, Oxford Inca Energy 450) that was used to explore
22 the elemental composition of biochars. The particle size distribution of raw materials was determined
23 by means of a laser granulometer (Fritsch Analyzette 22, Idar-Oberstein, Germany) after dispersion
24 in ethanol and sonication in an ultrasonic bath for 10 min.

25

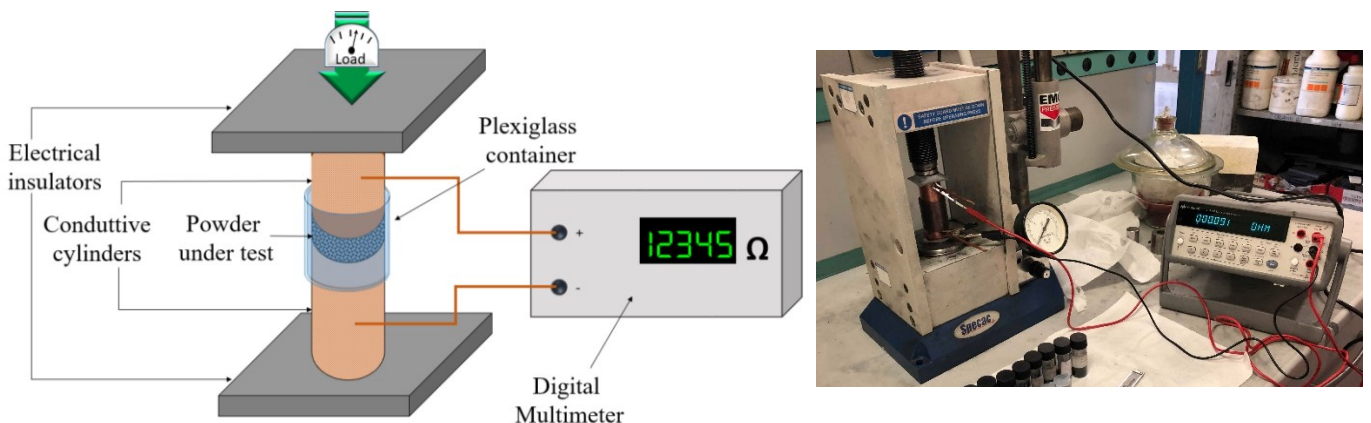
26

1 **C. Raman Characterization**

2 Raman spectroscopy was performed using a Renshaw Ramascope MicroRaman, equipped with an
3 Argon green laser (excitation at 514.5 nm at 50 mW). Measurements were taken at different points
4 for each sample, with a 50-x objective.

5 **D. Conductivity Measurements on biochar powder**

6 With the aim of predicting the electrical behaviour of the final composite, DC electrical
7 conductivity measurements of biochar powders were performed. The measurement set-up was
8 derived from [15] and is sketched in Figure 1. It is composed of two solid copper cylinders, 30 mm
9 in diameter and 5 cm in length, encapsulated in a hollow Plexiglas cylinder with a nominal inner
10 diameter of 30 mm. The inner diameter is slightly higher so that it is possible to force the copper rods
11 inside the Plexiglas cavity and the upper rod can slide inside the cylinder during the measurement.
12 This arrangement creates an internal chamber between the two cylinders, where the carbon powder
13 can be inserted. The electrical resistance of the powders was measured at increasing loads (up to 1400
14 bar) applied by a hydraulic press (Specac Atlas Manual Hydraulic Press 15T). Electrically insulating
15 sheets were placed between the conductive cylinders and the load surfaces. The resistance of the
16 carbon fillers was measured using an Agilent 34401A multimeter.



17

18 Fig. 1. Sketch of Measurement set-up for conductivity study of Biochar powders (left). Measurement set-up
19 for the DC conductivity (right).

20

1 The conductivity of the samples was calculated from the resistance using the relationship:

$$2 \quad \sigma = \left(\frac{R \cdot A}{L} \right)^{-1} \quad (1)$$

3 where σ is the powder conductivity (S/m), R is the powder resistance (Ω), A is the surface area (m^2)
4 of each copper electrode, and L is the distance (m) between the two copper electrodes. Normally the
5 values of the electrical conductivity change in relation to the pressure applied. This is due to the
6 compaction process of carbon powders. When pressure is increased, the voids between particles
7 decrease in volume and then the carbon particle structure collapses. Both phenomena create
8 conductivity value fluctuations. In this work, conductivity values obtained after 800 bar pressure are
9 averaged and their error bars are evaluated.

10

11 **E. Complex permittivity measurements**

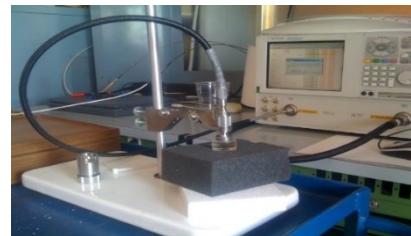
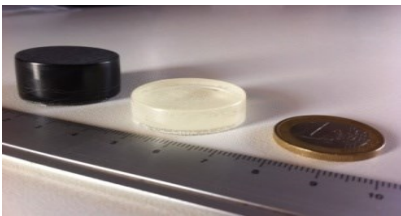
12 The complex permittivity [16] of the samples was measured using a commercial open-ended
13 coaxial sensor (Agilent 85070D) and a Network Analyzer (E8361A), (see Figure 2) [17-19]. The
14 main advantage of this sensor is that it requires samples of small dimensions (diameter around 20mm,
15 thickness around 10mm) compared to the free-space method, Thus, much smaller quantities of fillers
16 are necessary in the sample production. Moreover, it can be used from 200MHz to 20GHz.
17 Drawbacks are that the surface of the sample should be planar and flat in order to ensure a good
18 contact between the sensor and the surface. From the measurements of the imaginary part, the AC
19 conductivity was evaluated using a standard Drude model [16].

20 **F. Composite preparation**

21 Biochars treated with different temperatures (650, 700 and 750 °C) were used as fillers in
22 epoxy resin to prepare the composites for electrical characterization. Biochars (MIS650, MIS700,
23 MIS750), epoxy resin and curing agent were weighed in order to obtain a 1 to 5 ratio between biochar
24 and polymer. Biochar at 20 wt.% was selected as an optimum compromise to obtain a detectable
25 electrical signal for all the biochars prepared at the different temperatures and the possibility to

1 produce a manipulable composite. Liquid epoxy resin was delicately mixed for 20 minutes with
2 biochar in order to avoid the air bubble formation. Subsequently, Ultraturrax ® mixer was used for 5
3 minutes. This mixer is able to achieve appropriate dispersion of small size particles. The pre weighted
4 curing agent was added to the mixture and mechanical stirred for 10 minutes. The mixture was slowly
5 poured into cubic silicon moulds carefully avoiding the formation of air bubbles and later positioned
6 in a vacuum chamber for 20 minutes in order to remove any possible air bubbles. The final products
7 were cured in an oven for 4 hours at 50°C. After an overnight rest, the composites were delicately
8 removed from their silicon moulds. An example of samples is shown in Figure 5 (left panel).

9



10

11

12 Fig. 2. Sample for the permittivity measurements (left). Measurement set-up for the complex permittivity
13 measurements (right).

14

15

16 3. Results and Discussion

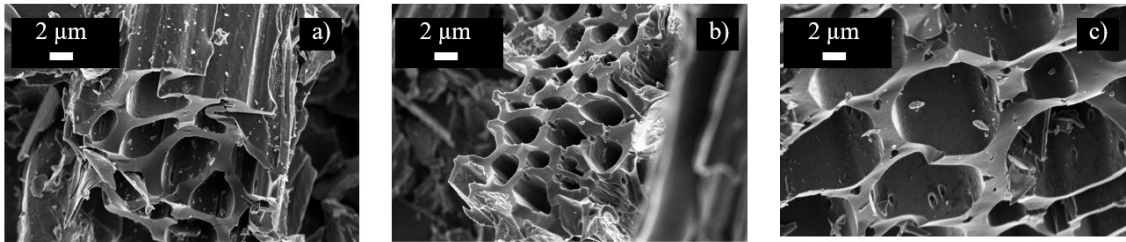
17

18 A. FESEM – EDX – Particle size distribution

19 FESEM, EDX and particle size distribution were performed on samples MIS650, MIS700 and
20 MIS750. Figure 3 displays some significant FESEM, while Table 1 shows EDX results. The FESEM
21 images evidence the variation of the porous biochar structure, where increasing the temperature
22 generates the wear of the thin walls of the biochar channels.

23 EDX analysis, performed on all biochars under study, show an increase of carbon content in
24 relation to the treatment temperature and a consequent decrease of other elements (O, Mg, Si, K, Ca).
25 In particular, MIS750 show a carbon content over 70 wt.% and traces of Sulfur.

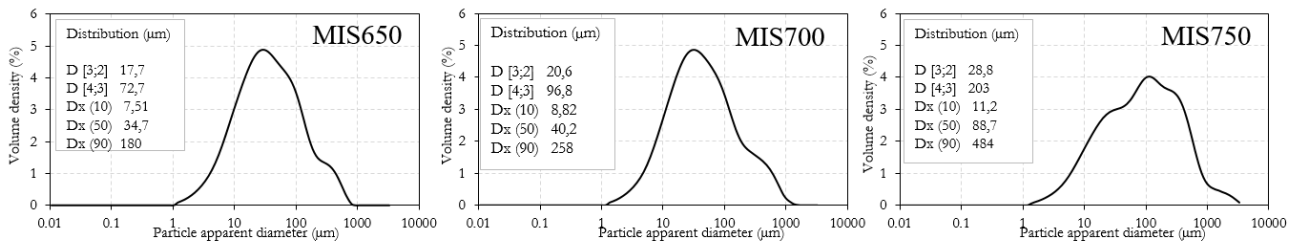
1 Particle size distribution (see Fig.4) show relatively fine powders for MIS650 and MIS700, with
 2 a d_{50} of about 35 and 40 μm respectively and d_{90} values in the range 180-260 μm . The particle size
 3 distribution of MIS750 is displayed at large values: the cumulative frequency distribution shows than
 4 50% and 90% of the particles are smaller that 90 and 500 μm , respectively.



5
 6 Fig. 3. FESEM images of a) MIS 650, b) MIS 700 and c) MIS 750 Biochars at 10kX magnifications.

Element	Wt.%		
	MIS650	MIS700	MIS750
C	54.98	67.48	71.46
O	32.62	21.51	20.48
Mg	0.76	0.82	0.26
Si	7.21	6.73	4.68
K	1.72	1.65	1.16
Ca	2.71	1.81	1.38
S	-	-	0.58
Total	100	100	100

7
 8 Table 1. EDX analysis of MIS 650, MIS 700 and MIS 750.

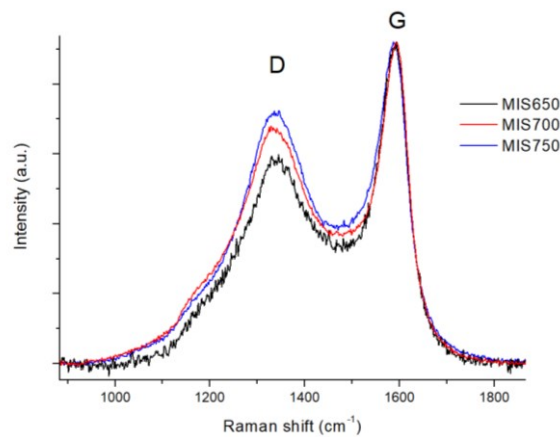


9 Fig. 4 Particle size distribution for MIS650, MIS700 and MIS750

10 **B. Raman Characterization**

11 Raman analyse were performed on all biochars, and their spectra are shown in Figure 4 5. Bands
 12 and signals on the Raman spectrum are related to the stretching of various bonds and lattice vibrations.
 13

1 For Raman spectra on carbon materials there are two main peaks: D and G [19]. The G peak
 2 (Tangential Mode, E_{2g}-mode) is positioned in the 1550-1615 cm⁻¹ range and corresponds to the
 3 stretching of carbon- carbon sp² bonds [21,22]. The D peak (breathing mode, A_{1g}-mode) is
 4 positioned in the 1300-1400 cm⁻¹ range and is related to the edge disorder in carbon structure [21,22].
 5 The ratio between the intensity of D and G peak (I_D/I_G) is used to evaluate the ratio between disordered
 6 and graphitized structures in the carbon material tested. The intensity of each peak is evaluated by
 7 fitting the peak with appropriated curves and calculating its area. This area takes into account peak
 8 intensity and its shape, with particular emphasis on its width. The fitting procedure performed on all
 9 the Raman spectra made it possible to calculate the I_D/I_G ratio and fill Table 2. This ratio is correlated
 10 to the graphitization of carbon material and its disorder grade [19, 23]. Increasing the pyrolysis
 11 temperature from 650 to 750°C it is possible to observe an increase of disorder as shown in Table 2
 12 where the I_D/I_G peak ratio increases [24].



13

14 Fig. 5. Raman characterization for MIS biochars in function of pyrolysis temperature.

15

Biochar	I_D/I_G
MIS650	1.73
MIS700	2.55
MIS750	2.95

16

Table 2. I_D/I_G ratio derived from the study of Raman spectra.

17

C. Conductivity Measurements on biochar powder

In order to predict the behaviour of the composites, a pre-screening of the biochar powder was performed. The conductivity values of biochar in powder in relation to pressure are reported in Figure 6. Their average values and error bar are listed in Table 3. Error bars represent the variation of conductivity during compression at loads exceeding ~800 bar. After this pressure the powder could be significantly compacted and voids between particles were minimized. After this pressure, if not sufficiently fine, the biochar structure was crushed by pressure and its conductivity tended to increase. This effect is relevant for MIS 700 and MIS750, where quite a rapid increase of conductivity can be observed after 800 bar. For MIS650, that has the smallest particle distribution, this effect was less relevant. Conversely, for MIS750, with the largest particle distribution, we observed an increase effect of pressure stress with a rapid increase of conductivity values. Due to the increase of treatment temperature the carbon structure changed as previously shown by the Raman analysis. The organic component of the biochar also decreased due to the temperature treatment. This allowed an increase of carbon content as shown by EDX analysis and as consequence we expected an increase of conductivity. These high conductivity values (up to 2.75+/-0.85 S/m for MIS750) could be explained by the fact that these samples were activated by the CO₂ process, which aids the conductivity of biochar.

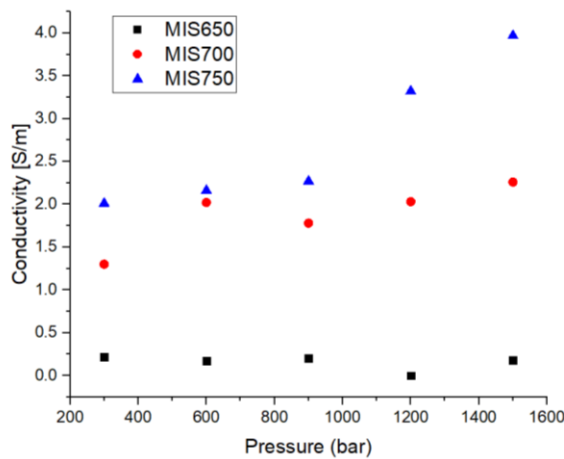


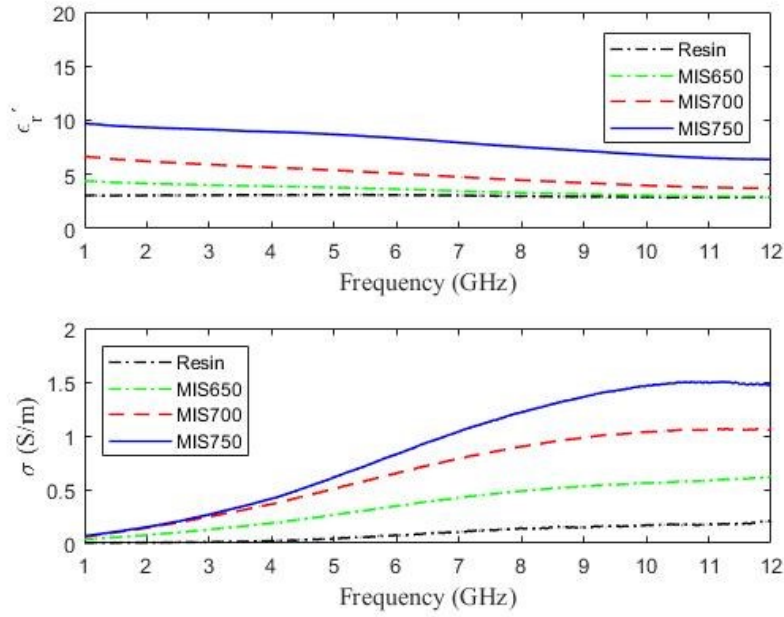
Fig. 6. Conductivity values of the various types of biochars.

Biochar	Conductivity (S/m)	
	Mean	Error bar
MIS650	0.20	0.14
MIS700	1.88	0.39
MIS750	2.75	0.85

Tab.3 Conductivity values and their error bar.

D. Complex permittivity measurements on composite

After an air/short/water calibration, ten measurements were done on each samples in order to check the homogeneity of the samples and overcome problems due to the flatness and roughness of the surface on which the probe is positioned. In Figure 7 the average values of the real part of permittivity and conductivity of composites filled with 20 wt.% of Miscanthus biochar is compared with a sample of pure epoxy resin in the frequency range 1-12 GHz. A percent error close to 15% was estimated on these measurements. The results of samples MIS650 and MIS700 may not be distinguishable. An increase in the value of the complex permittivity compared to the resin is always present but it is higher for the MIS750. This trend is in agreement with the higher DC conductivity observed for this Miscanthus Biochar (Fig. 4 6). At a frequency of 12 GHz, the conductivity increases from 0.1 S/m for the pure resin to ~1.5 S/m for the MIS750-based composite. The increased of the permittivity ~~real part~~ and conductivity could be correlated with the increase of the conductivity of the filler. As reported in Table 1, EDX analysis shown the increase of carbon content and decrease of other elements (O, Mg, Si, K, Ca, S) in the biochar with the increase of pyrolysis temperature. This behaviour has been observed also for DC conductivity of powders themselves.



1

2 Fig. 7. Permittivity real part (top) and conductivity (bottom) values for pure resin, and composites with 20
 3 wt.% of MIS (650,700,750).

4

5 4. Conclusions

6 In this work biochars derived from miscanthus (MIS) produced under different pyrolysis
 7 temperatures (650,700,750°C) and an activation process (CO₂) were analyzed by FESEM, EDX,
 8 Raman and DC conductivity. Subsequently, biochars were used as filler in Epoxy resin to create a
 9 composite. FESEM showed an organized structure for these samples (honeycomb structure). EDX
 10 analysis showed an increase of carbon in relation to the pyrolyzed temperature. Raman analysis
 11 showed the increase of disorder with the increase of pyrolysis temperature. DC-conductivity analysis
 12 showed an increase of conductivity in function of pyrolysis temperature (up to 2.75 S/m for MIS750)
 13 that could be correlated with their carbon content. Complex permittivity up to 12 GHz of composites
 14 containing 20 wt. % of biochars were measured. The composite electrical performances increase in
 15 agreement with the increase of biochar conductivity. In conclusion, Biochar has demonstrated its
 16 ability to modify the electrical properties of composite. For this reason, biochar could be an
 17 economical, eco-friendly alternative to more expensive carbon fillers.

18

1 Acknowledgements

2 The authors would like to thank Salvatore Guastella for FESEM analysis. ICFAR London
3 Ontario and in particular Douglas Matthew Cuthbertson, for the supply of Miscanthus biochar, Massimo
4 Rovere for Raman measurements and spectra fit and Andrea Marchisio for particle size analysis. This
5 work was partially supported by grant 685844 (project MODCOMP) in the framework of European
6 H2020 program.

7 References

- 8 [1] F.Qin, C.Brosseau, A review and analysis of microwave absorption in polymer composites filled with carbonaceous particles, *Journal of Applied*
9 *Physics* 111, 061301 (2012)
- 10 [2] S. Sankaran, K. Deshmukh, M.Basheer Ahamed, S.K. Khadheer Pasha, Recent advances in electromagnetic interference shielding properties of
11 metal and carbon filler reinforced flexible polymer composite: A review, *Composites Part A* 114 (2018) 49-71
- 12 [3] H. Wu, Multifunctional polymer composites containing inorganic nanoparticles and novel low-cost carbonaceous fillers, (2014)
13 Graduate theses dissertation 13708
- 14 [4] M.T. Byrne, Y.K. Guin'Ko, Recent advances in research on carbon nanotube – polymer composites, *Advanced Materials*, vol.
15 22, n. 15, pp. 1672-1688, 2012.
- 16 [5] S. Nanda, A.K. Dalai, F. Berruti, J.A. Kozinski, Biochar as an Exceptional Bioresource for Energy Carbon Sequestration,
17 *Agronomy Activated Carbon and Speciality Material, Waste Biomass Valor*, (2015) 1-35.
- 18 [6] K. Weber, P. Quicker, Properties of biochar, *Fuel* 2017, (2018) 240-261.
- 19 [7] A.V. Bridgwater, Review of fast pyrolysis of biomass and product upgrading, *Biomass and Bioenergy*. 38 (2012) 68-94.
- 20 [8] R. Wahi, Nur Fakhirah Qurratu'ain Zuhaidi, Y. Yusof, J. Jamel, D. Kanakaraju, Z. Ngaini, Chemically treated microwave-derived
21 biochar: An overview, *Biomass and Bioenergy*. 107 (2017) 411-421.
- 22 [9] S. Ikram, O. Das, D. Bhattacharyya, A parametric study of mechanical and flammability properties of biochar reinforced
23 polypropylene composites, *Composites: Part A*,91 (2016) 177-188.
- 24 [10] A. M. Poulouse, A. Y. Elnour, A. Anis, H. Shaikh, S.M. Al-Zahrani, J. George, M. I. Al-Wabel, A. R.Usman, Y. S.Ok, D. C.W.
25 Tsang, A. K. Sarmah, Date palm biochar-polymer composites: An investigation of electrical,mechanical, thermal and rheological
26 characteristics, *Science of the Total Environment* 619–620 (2018) 311–318
- 27 [11] Nan Nan1 and David B. DeVallance, Development of poly(vinyl alcohol)/wood-derived biochar composites for use in pressure
28 sensor applications, *J Mater Sci* (2017) 52: 8247-8257
- 29 [12] I. Oral, Determination of elastic constants of epoxy resin/biochar composites by ultrasonic pulse echo overlap method, *Polimer*
30 *composites*, 37 (9) (2016) 2907-2915
- 31 [13] A.A. Khan, P. Savi, S. Quaranta, M. Rovere, M. Giorcelli, A. Tagliaferro, C. Rosso, C. Jia, Low-Cost Carbon Fillers to Improve
32 Mechanical Properties and Conductivity of Epoxy Composites', *Polymers*. 9 (12) (2017) 642-654.
- 33 [14] S. Nanda, A.K. Dalai, F. Berruti, J.A. Kozinski, Biochar as an Exceptional Bioresource for Energy Carbon Sequestration,
34 *Agronomy Activated Carbon and Speciality Material, Waste Biomass Valor*, (2015) 1-35.
- 35 [15] R. S. Gabhi, D. W. Kirk, C. Q. Jia, Preliminary investigation of electrical conductivity of monolithic biochar, *Carbon*, 116, 435-
36 442.
- 37 [16] A. Ishimaru, *Electromagnetic wave Propagation, Radiation, and Scattering*, Prentice Hall, 1991.
- 38 [17] P. Savi, M. Miscuglio, M. Giorcelli, A. Tagliaferro, Analysis of microwave absorbing properties of Epoxy MWCNT composites,
39 *Progress in Electromagnetics Research Letters*. 44 (2014) 63-69.
- 40 [18] M. Giorcelli, P. Savi, M. Yasir, M. Hajj Yahya, A. Tagliaferro, Investigation of Epoxy Resin/MWCNT composites behaviour at
41 low frequency, *Journal of Material Research, Soft Nanomaterials Focus Issue*. 30 (1) (2015) 101-107.
- 42 [19] P. Savi, S. Puthoor Josè, A.A. Khan, M. Giorcelli, A. Tagliaferro, Biochar and Carbon Nanotubes as fillers in polymers: a
43 comparison, *IEEE MTT-S International Microwave Workshop Series on Advanced Materials and Processes*, Pavia, Italy,
44 September 20-22 (2017) 1-3.
- 45 [20] A. C. Ferrari; J. Robertson, Interpretation of Raman spectra of disordered and amorphous carbon, *Physical Review B (Condensed*
46 *Matter and Materials Physics)*, Volume 61, Issue 20, May 15, 2000, pp.14095-14107.
- 47 [21] J. Robertson, Diamond-like amorphous carbon, *Material Science and Engineering R* 37 (2002) 129-281
- 48 [22] A. Jorio, M. S. Dresselhaus, R. Saito, and G. Dresselhaus, *Raman Spectroscopy in Graphene Related Systems*, Wiley-VCH, Weinheim, Germany,
49 2011
- 50 [23] A. C. Ferrari; J. Robertson, Raman spectroscopy of amorphous, nanostructured, diamond-like carbon, and nanodiamond, *Phil.*
51 *Trans. R. Soc. Lond. A* (2004) 362, 2477–2512
- 52 [24] A. Burian, P.Daniel, S. Duber, J. Dore, Raman scattering studies of the graphitization process in anthracene and saccharose based
53 carbons, *Philosophical Magazine B*, 2001, vol. 81, No. 5, 525-540