**Effect of incorporation of microstructured carbonized cellulose on surface and mechanical properties of epoxy composites**

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**Abstract**

In this study, we reported the use of cellulose derived micro-structured biochars for the production of reinforced plastics. Cellulose nanocrystals and wasted cotton fibers were used as cellulose template structures and converted into carbonaceous materials under pyrolytic conditions. Biochars particles were produced with the shape of deformed spheres or rods and dispersed into an epoxy matrix with a loading ranging from 1 wt.% to 10 wt.%. Biochar-based composites showed remarkably elongation properties of up to 8.2 % using 2 wt.% of carbonized cellulose nanocrystals and a very low friction coefficient of 0.22 using 10 wt.% of carbonized cotton fibers.

**Highlights**

* Carbon spheres and carbon rods were produced through pyrolytic conversion of cellulose nanocrystals and wasted cotton fibers.
* Mechanical properties of carbon spheres and carbon rods epoxy composites were studied showing the differences induced by the particle shapes.
* An ultimate tensile strength improvement of 57% was reached using 5 wt.% of carbonized cellulose nanocrystals.
* A maximum elongation improvement of 100% was reached using 2 wt.% of carbonized cellulose nanocrystals.
* A friction coefficient reduction of 61 % was reached using 10 wt.% of carbonized cotton fibers.

**Keywords:** Microscopy, Mechanical Properties, Composite, Resins, Thermosets

**1.Introduction**

Nowadays, carbon additives are massively used for the production of reinforced plastics[1-3](#_ENREF_1). Every year, the worldwide market requires an increased amount of carbon containing composites for a lot of applications ranging from automotive[4](#_ENREF_4),[5](#_ENREF_5) to aerospace[6](#_ENREF_6),[7](#_ENREF_7) sector. Among all polymeric matrix, epoxy resins represent an interesting compounds class due to their impressive properties[8](#_ENREF_8),[9](#_ENREF_9). Actually, carbon fibers are the most used filler for reinforced plastics production[10](#_ENREF_10) but a wide range of carbonaceous materials have been used for epoxy composites synthesis[11-13](#_ENREF_11). Driven by the environmentally policies[14](#_ENREF_14), the use of eco-friendly and waste derived filler has been intensively explored[15-17](#_ENREF_15). Among all the green carbonaceous fillers, biochar has gained a lot of attention due to its eco-friendly production and promising properties[18](#_ENREF_18),[19](#_ENREF_19). The beneficial effects of biochar addition to epoxy composites has reported by many studies[20](#_ENREF_20),[21](#_ENREF_21). Giorcelli et al.[21-23](#_ENREF_21) reported the use of high thermal treated biochar for the production of conductive epoxy composite while other studies reported the improvement of mechanical properties of biochar containing reinforced plastics[24-26](#_ENREF_24). Recently, Bartoli et al.[27](#_ENREF_27) described the influence of biochar surface structures on brittleness or ductility of epoxy materials showing how smooth surface could enhance the maximum elongation. Nonetheless, a comprehensive explanation of biochar-polymer interactions is quite challenging due to all the particle properties (*i.e.* porosity, shape, residual groups, surface area)[28](#_ENREF_28). A reasonable approach is represented by the study of a simplified system containing particles with a simply well known shape, the same residual groups and without high structured surfaces. A promising case of study could be represented by the comparison of spheres[29](#_ENREF_29) and rods[30](#_ENREF_30) particles. As reported by Bartoli et al.[31](#_ENREF_31), carbon spheres can be produced by pyrolytic treatment of cellulose nanocrystals (CNCs)[32-34](#_ENREF_32) while carbon rods can be obtained by the same process using wasted cotton fibers (CFs)[35](#_ENREF_35). Additionally, these materials are both composed by cellulose and pyrolytic reactivity and biochar residual groups are the same using the same pyrolytic conditions[36-38](#_ENREF_36).

In this work, we studied the effect of biochar spheres and rods produced from carbonization of CNCs or CFs on the mechanical and superficial properties of epoxy resin composites. The interaction between filler and polymeric matrix was evaluated through tensile, tribological and hardness test using a filler concentration of 1 wt.%, 2 wt.%, 5 wt.% and 10 wt.%. Furthermore, field emission scanning microcopy was used to study the interfacial interactions between carbonaceous particles and resin after fracture.

**2.Materials and methods**

*2.1Materials*

CNCs were purchased from Alberta-Pacific Forest Industries (Batch COMP170823-H) and used as received without any purification. CF were recovered from waste cotton cloths.

Two components BFA diglycidyl resin was purchased from CORES (Cores epoxy resin, LPL). The curing agent was a mix of primary amines and a catalyst (DMP-30)

*2.2 Pyrolysis*

Pyrolysis experiments were carried out using 25 g of CNC or CF. Feedstock was introduced into a quartz reactor. The reactor was sealed and a flux of argon was used to remove the initial residual atmosphere. The argon flux (4 mL/min) was kept constant during the pyrolytic run to drag out the gas released by the thermal degradation reactions. The heating rate was set at 50°C/min with a set high treatment temperature respectively of 400°C. The system was kept at the maximum temperature for 30 min and cooled down at room temperature. Carbonized CFs were pulverized for 10 min using a mechanical blender prior the utilization as composite filler while CNCs were used without further purification.

*2.3. Methods*

Morphology of CNCs and CFs were investigated using a Field Emission Scanning Electrical microscopy (FE‐SEM, Zeis SupraTM 40).

Biochar-based composites were dispersed into the epoxy monomer using a tip ultrasonicator apparatus (Sonics Vibra-cell) for 15 minutes. Ultrasounds were pulsed with cycles of 20 s alternating between pauses of 10 s to allow a better heat diffusion.

After the addition of the curing agent, the mixture was further ultrasonicated for 2 minutes and left into the appropriated moulds for 16 h at room temperature. A final thermal curing was performed using a ventilated oven (I.S.C.O. Srl “The scientific manufacturer”) at 70°C for 6h.

Biochar containing composites were produced in dog-bone shape according with ASTM 638 procedure. Composites bulk properties were investigate using a tensile testing machine (MTS Q-test10), a reciprocating tribometer (Anton-Paar Pin-on-Disk TribometerTRB) and a microindetometer (INNOVATEST, Nemesis 9000).

Surface properties were investigate using a reciprocating tribometer (Anton-Paar Pin-on-Disk Tribometer TRB) equipped with a polished steel sphere (AISI 420) 6 mm in diameter and with a microindetometer (INNOVATEST, Nemesis 9000) equipped with a pyramidal tip (Vickers) applying a nominal force of 0.1 N.

Data were analysed using homemade software compiled using Matlab®. Average values of at least three samples were reported.

Thermogravimetric-Differential Thermal Analysis TG-DTA (STA 409, Netzsch, Selb, Germany) was performed on neat resin and biochar based composites in the temperature range 35–600 °C with a heating ramp of 10 °C/min under nitrogen.

**3.Results**

*3.1 Microstructured carbonized cellulose characterization*

CNCs and CFs were pyrolyzed at 400°C using a heating rate of 50°C/min in Ar atmosphere. The biochars recovered after pyrolysis were preliminary analyzed through FE-SEM technique and captures are shown in Figure 1.

**INSERT FIGURE 1 HERE**

Pyrolyzed CNCs are characterized by deformed spherical shapes with an average diameter ranging from 2 m to 10 m (Figure 1 a). As previously reported[31](#_ENREF_31), small defects can be identified on the surface due to the pyrolysis of volatile organic matters release from the particles inner core during the cracking process (Figure 1 b).

Carbonized CFs showed a twisted rods shape (Figure 1 c) with an average length ranging from 30 m to 50 m and an average diameter around 2-5 m (Figure 1 d). As reported by Pravin et al.[35](#_ENREF_35), some of CFs presented a hole that could collapse as shown in Figure 1 d creating a ribbon-like structure. This phenomenon was not so massive and carbonized CFs could be reasonably assumed as rod-like.

Surface residual groups on carbonized CFs and CNCs were investigated though FT-IR spectroscopy (ATR mode) and spectra are shown in Figure 2.

**INSERT FIGURE 2 HERE**

Pristine CF and pristine CNCs spectra (Figure 2 a-b) showed a broad band between 3600 and 3300 cm-1 due to the presence of hydroxylic groups (O-H), signals of saturated C-H at 2900-2850 cm-1, CH2 at 1426 cm-1 due to the C6 of glucose structure and a bands envelopment between 900 cm-1 and 1100 cm-1 due to the CH2 and C-O. Pristine CFs showed a medium intesity peak at 1232 cm-1 due to C-O at to of etheric functionalities of glycosidic bonds.

Spectra of both carbonized CFs and CNCs at 400°C (Figure 2 c-d) did not show any bands at 3600 or 2850 cm-1 according to the pyrolytic degradation of cellulose chains[*39*](#_ENREF_39). In the spectrum of carbonized CNCs, some residual groups could be detected such as ketonic (1580 cm-1, C=O) and carboxylic (C=O at 1700 cm-1 andO-H at 1436 cm-1) functionalities together with ethers (C-O at 1228 cm-1 and C-O at 1119 cm-1). In the spectrum of carbonized CFs, a broad envelopment of bands was present in the region between 1000 cm-1 to 1500 cm-1 due the more degradated structures. This was reasonably due to the low crystallinity degree of CFs compared with CNCs that promoted a faster pyrolytic cracking with lower residual functionalities.

*3.2 Epoxy composites characterization*

*3.2.1 Thermogravimetrical analysis*

Thermogravimetrical analysis (TGA) of neat resin and biochar based composites are shown in Figure 3.

**INSERT FIGURE 3 HERE**

Neat resin showed a 5 wt.% loss at 184°C reasonably due to loss of the additives of the mixture (such as benzyl acohol and fatty acids)[40](#_ENREF_40) and a further degradation step at 330°C imputable to degradation of alkyl chains of polymeric structure[41](#_ENREF_41). TGA curves of the biochar-based composites showed very homogenous trends proving a negligible effect of carbonized CNCs and CFs on thermal stability of the related composites.

*3.2.2 Bulk properties*

Dog-bone samples were produced according to the methods above described using a filler concentration of 1 wt.%, 2 wt.%, 5 wt.% and 10 wt.% and analyzed trough stress test producing the curves reported in Figure 4 while the main mechanical properties are summarized in Figure 5.

**INSERT FIGURE 4 HERE**

**INSERT FIGURE 5 HERE**

Pure epoxy resin was characterized by a Young’s modulus (YM) of 1286 ± 185 MPa, an ultimate tensile strength (UTS) of 17.0 ± 1.4 MPa and a maximum elongation of 4.1 ± 0.1 %. Furthermore, the toughness values were attested of up to 0.57 ± 0.03 MJ/m3.

Composites containing carbonized CNCs showed a general improvement of maximum elongation even at low concentration elongation (8.7 ± 0.1 % with 2 wt%) reaching a maximum value of up to 8.2 ± 0.1 % with a concentration of 5 wt.%. Even at 10 wt.% loading, carbonized CNCs composites remained ductile with a elongation of 6.4 ± 0.1 %. YM values were not significantly different from neat resin while UTS was affected by the presence of CNCs. Using a filler loading of 1 wt.%, UTS was not significantly different from neat resin but a with an increment of up to 2 wt.% it reached 21.6± 0.9 MPa. A further increment to 5 wt.% induced a decrement to 19.7± 0.9 MPa while using a filler loading of 10 wt.% a value of 26.8 ± 0.6 MPa was achieved. Toughness values were higher than neat resin reaching a maximum value of 1.46 ± 0.08 MJ/m3 using a filler loading of 5 wt.%. Toughness increments are mainly due to the elongation magnification promoted by the addition of carbonaceous fillers.

Composites containing carbonized CFs showed a very similar behavior with an increment of maximum elongation of up to 7.8 ± 0.1 % using a filler loading of 2 wt.%. Further increments of filler induced a decrement of elongation down to 4.0 ± 0.9 % using a filler loading of 10 wt.% while UTS and YM values were generally comparable with those achieved using the same CNCs loads.

As shown in Figure 6, carbonized CNCs and CFs showed a different distribution into the polymeric matrix after the factures.

 **INSERT FIGURE 6 HERE**

Composites containing carbonized CNCs showed a diffuse cracks patters (Figure 6 a) that move all around the filler particles. On the interphases between polymer and biochar, a detachment could be noticed (Figure 5 b). Accordingly to the surface analysis and thermogravimetrical data, the interaction between particles and resin can be ascribed to the weak forces instead of chemical bonding. Furthermore, this phenomenon explained the great increment of the elongation observed that was due to the mobility of filler inside the matrix under external solicitations. This phenomenon contributed to the force redistribution inducing a ductility improvement[42](#_ENREF_42).

Carbonized CFs showed a very interesting and different behavior. After the stress-strain test rods reoriented themselves accordingly with the force applied (Figure 6 c). Contrary to carbonized CNCs, carbonized CFs were more fragile and they can be disrupted by mechanical stress (Figure 6 d, black circle). Furthermore, the detachment between carbonized CFs and epoxy matrix was less relevant than in the case of carbonized CNCs. This was due to the high surface area of rods that induced a better interaction with the polymer but it could be imputable for the decreased of elongation at high filler loading. The movements of rods-like particles could induced an additional stress issue to the material reaching the fracture point earlier than sphere like material.

*3.2.3 Surface properties*

Use of carbonaceous materials as solid lubricants is a well known and consolidate practice in many engineering sectors[43-45](#_ENREF_43). Furthermore, addition of biochar has been proved as a reasonable approach to reduce the friction coefficient[16](#_ENREF_16) in epoxy matrix.

Accordingly, composites surface properties were investigated using a tribometer determining the friction coefficients (Figure 7).

**INSERT FIGURE 7 HERE**

Using both carbonized CNCs and CFs friction coefficients decreased with the increment of filler. At low filler concentrations, friction coefficients were higher than neat resin (0.56± 0.3) with values around 0.7. Using carbonized CNCs, a filler amount of 2 wt.% was sufficient to induce a decrement of friction coefficient down to 0.48 ± 0.01 reaching a minimum of 0.37 ± 0.04 using a filler loading of 10 wt.%.

Carbonized CFs were less performant till a loading of 10 wt.% when the friction coefficient decreased down to 0.22 ± 0.05.

The reduction of friction coefficient due to the addition of biochar was due to the formation of regions with an increased filler concentration. This increment was due to the removal of epoxy matrix due to the stress applied and induced the formation of carbon rich layer that act as solid lubricants[46-49](#_ENREF_46).

Composites micro-hardness was also tested and results are shown in Figure 8.

**INSERT FIGURE 8 HERE**

Hardness data were in good agreement with UTS showing values generally lower than neat epoxy resin. An exception was represented by the composite containing 10 wt.% of carbonized CNCs. In this case hardness was higher than resin (13.5 ± 0.1 HV0.1) reaching a value of up to 16.8 ± 0.1 HV0.1.

According with the data collected, we hypothesized that using a high filler loading carbonized CF could interact as shown in Figure 9.

**INSERT FIGURE 9 HERE**

Using concentration up to 10 wt.% carbonized CNCs still acted as rigid spheres but CFs can assembled themselves forming a net-like structure. This diffuse structure could lead to a decrement of maximum elongation due to the multiple solicitations of CFs that reoriented themselves according to the deformation applied. At the same time, the very same structure improved the lubricant effect of carbonaceous filler due to its reduced mobility.

**4.Conclusions**

In this study, spherical and cylindrical biochar particles were used for demonstrate the influence of particle shape on the mechanical properties of epoxy resin composites.

Tensile stress tests showed how both spheres and rods particles induced an increment of maximum elongation achieving a magnification of 100% using 2 wt.% of carbonized CNCs. Composites YM and UTS values were generally comparable with neat resin with exception of composite containing 5 wt.% of carbonized CNCs when UTS was increased of 57%. Furthermore, data clearly evidenced the great increment of toughness that increased from 0.56 ± 0.03 MJ/m3 to 1.46 ± 0.08 MJ/m3 using 2 wt.% of carbonized CNCs. While the addition of biochar was detrimental for composite hardness, it improved the friction coefficient reaching a value of 0.22 ± 0.05 wt.% of carbonized CFs.

The different of mechanical properties observed could ascribed to the different interaction surface that change with particle shape as clearly emerged from FE-SEM of composites. Summing up, spheres promoted more complex fracture patterns while rods seemed to rearrange themselves in the same direct of the deformation. Both fillers are characterized by a good mobility into the polymeric matrix guaranteed a general improvement of elongation.

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