Sustainable Biocomposites from Pyrolyzed Grass and Toughened Polypropylene: Structure–Property Relationships

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ABSTRACT: A novel class of injection-molded, toughened biocomposites was engineered from pyrolyzed miscanthus-based biocarbon, poly(octene ethylene) elastomer, and polypropylene (PP). The elastomer and biocarbon were added to the PP matrix at 30 and 20 wt %, respectively. The particle size of the biocarbon varied within two main ranges: <20 and 106–125 μm. The morphology and adhesion between the filler and the matrix were controlled by the addition of maleic anhydride grafted PP (MAPP). The composites were melt-blended and then injection-molded to tensile, flexural, and impact bars. The results showed that although the morphology of the composite is almost independent of particle size it is greatly dependent on the addition of MAPP. Two completely different morphologies, separate dispersion and encapsulated filler particles, were obtained in the presence and absence of MAPP, which was verified by atomic force and scanning electron microscopies. Model calculations based on a modified Kerner equation showed that the encapsulated filler content decreased from 64 to 8% by the addition of MAPP, which caused a major improvement in the stiffness and strength of the composites. Despite having a different morphology caused by the compatibilizer, composites with smaller particles exhibited better strength and modulus and lower impact toughness compared to those with a larger particle size. Results suggest that the failure mechanisms are mainly controlled by the local fracturing of biocarbon particles, which was more pronounced when the particle size was larger.

INTRODUCTION

Particulate-filled polypropylene (PP)-based composites are one of the main categories of polymer composites that have been researched and utilized in academia and industry over the last few decades. The properties of these composites are usually determined by their two main constituents, namely, a hard particulate filler and a rubber phase. Through proper selection of the filler and rubber phase, a diverse range of properties can be obtained. This flexibility in their properties combined with their affordable price has allowed these composites to pass the stringent requirements of the automotive industry; thus, they have become a central material for many of the interior and exterior parts of a car. However, because of sustainability issues, such as greenhouse gas (GHG) emission and the advent of natural fillers, a significant amount of research has been focused on replacing traditional mineral- or petroleum-based fillers with biobased fillers. In the U.S., a new corporate average fuel economy (CAFE) standard has been set in response to increasing GHG emissions, which requires vehicles to have better fuel economy. This can be achieved through weight reduction by utilizing materials with lower densities. Biobased fillers, having a naturally lower density compared to that of mineral ones, can provide the added benefit of being lighter weight. Therefore, replacing mineral-based fillers with biobased ones not only alleviates the sustainability issues but also may provide an improvement in properties, such as density, in which mineral-filled composites have reached their limits. Moreover, replacing a portion of petroleum-based matrices with biobased fillers will provide further sustainability for currently used petroleum-based composites.

Although replacing mineral fillers with natural materials seems to be a simple solution to the density problem, it creates a lot of challenges with regard to producing composites with comparable mechanical properties. Normal composites exist on either end of a spectrum in which they have either high stiffness and low impact toughness or high impact toughness and low stiffness. The main challenge is to keep the balance between stiffness and toughness in the final composites because there is a trade-off between these two properties. Besides the inherent properties of the filler and rubber constituents, one important factor that affects the properties of a multicomponent system consisting of two or more polymeric phases and filler is the morphology of phases within the composites. Earlier studies on multicomponent PP composites...
revealed that two main structures are commonly generated when the constituents are mixed together. The first is that the filler particles and the rubber phase (being dispersed in the PP matrix) separate from each other, and the second is that the rubber partially or fully encapsulates the filler particles. Several studies on CaCO₃, BaSO₄, and other forms of filled, toughened PP showed that the final structure is determined by adhesion between the components and the external shear forces experienced during the melt mixing process. Different morphologies can be produced by changing the particle size and/or modifying the chemical nature of the particle’s surface or the polymer. Hammer et al. investigated the effect of different particle sizes of BaSO₄ in PP/ethylene propylene rubber (EPR) composites. Their results suggested that a smaller particle size (up to 0.7 µm) may provide better impact toughness in the case of an encapsulated structure.

Several studies were also conducted on particulate lignocellulosic filler composites. These studies, which are focused mainly on wood flour as a renewable filler, magnify the dissimilar failure mechanisms between lignocellulosic-based fillers and mineral fillers. For example, the effect of particle size when using wood flour was investigated in a PP/ethylene propylene diene (EPDM) system, and unlike the results of Hammer et al., composites with larger wood particles showed better impact toughness. The main differences between lignocellulosic and traditional mineral fillers are particle size and the integrity of the particles themselves. While mineral fillers are usually available in micrometer and submicrometer sizes, the original particle size of lignocellulosic-based fillers can be quite large. Therefore, it is of practical importance to determine how small the particles should be to perform in a manner that is desirable. Furthermore, traditional fillers such as talc, silica, CaCO₃, and BaSO₄ hardly break during impact or under a tensile load, whereas filler breakage is very common in lignocellulosic-based fillers such as wood. This particle failure changes the status of the local stress in the composite and produces a different failure mechanism in composites with lignocellulosic-based fillers.

Besides wood flour, biocarbon is another biobased particulate filler that has been the focus of interest in recent years. The density of biocarbon is reported to be in the range 1.34–1.96 g/cm³, which is considerably lower than that of mineral fillers and therefore can be used to reduce the weight of the final composite. Although biocarbon has been used in several polymeric matrices, the structure–property relationships of a ternary composite (thermoplastic, elastomer, and a hard filler system) have not been studied. In this work, the effect of biocarbon particle size and the addition of a functionalized PP-based compatibilizer on the structure and properties of the resulting biocomposites has been investigated. Changes in the thermal and mechanical properties were related to the structural differences and compared to currently available theories for multicomponent PP-based composites.

### RESULTS AND DISCUSSION

#### Particle Characterization

Particle Characterization. Scanning electron microscopy (SEM) images of biocarbons in the two particle size ranges described are shown in Figure 1. Because mechanical sieving was used to separate the particles, any particle that has a cross-sectional area within the range of openings in the sieve would be trapped between the sieves. Therefore, particles of a greater length may have been trapped between the designated sieves. The overall shape of the particles was irregular, with a tendency to have an aspect ratio greater than 1. This correlates well with the findings of Nagarajan et al. on the size fractionation of miscanthus-based biocarbon.

The thermal degradation of these biocarbons is depicted in Figure 2. It appeared that <20 µm particles had almost half of the ash content as that of the 106–125 µm particles (Table 1). The ash mainly consisted of silica (Figure S2) and is believed to originate from the epidermis of the plant material. Therefore, the lower ash content of the smaller particles can be correlated to the lower grindability of their mineral content.

#### Composite Characterization

Strength and Stiffness. The mechanical properties of the PP/POE (base blend), PP/POE with MAPP, and biocarbon-based biocomposites with and without compatibilizer are presented in Figures 3 and 7. In all of the blends and composites, the tensile strength was determined from the yield point of the stress–strain curve and hence is equal to the tensile stress at yield. A few important characteristics of the biocomposites can be observed by comparing the tensile or maximum flexural stress of the samples. First, the addition of biocarbon resulted in a reduction in the tensile strength compared to that of the base blend. Second, the addition of MAPP to the PP/POE binary blend...
reduced its tensile strength, but when MAPP was added to the composites, the tensile strength of the composite systems improved. In general, the tensile strength is strongly dependent on the transfer of stress between the particles and the matrix.\textsuperscript{30} Strength analysis showed that the addition of biocarbon, regardless of the two particle size ranges tested, reduced the tensile strength, which suggests that the particles were poorly bonded to the matrix. However, when a compatibilizer was added, this transfer became more efficient and hence the strength improved significantly. This suggests that MAPP acts as a compatibilizer and promotes adhesion between the filler particles and the matrix. Similarly, Renner et al.\textsuperscript{31} found that the application of MAPP results in an improvement of the adhesive force from about 100 mJ/m\textsuperscript{2} to nearly 1000 mJ/m\textsuperscript{2} in PP/\textit{CaCO\textsubscript{3}} and PP/glass bead composites.

The tensile strength of smaller particle composites was higher both with and without MAPP compared to that of larger particle composites. In general, this behavior can be related to the higher total surface area available with smaller particles. The increase in tensile strength with decreasing particle size (or increasing surface area) indicates that a more efficient stress transfer mechanism is involved, especially when MAPP is added to the composites.\textsuperscript{30} It can be observed that compatibilized smaller particles had a tensile strength almost equal to that of the base binary blend. This is an additional evidence indicating that the observed improvement is directly related to the interaction of PP with the surface of the particles.

To obtain an estimate of interfacial interactions, a semiempirical model developed by Turcsányi et al.\textsuperscript{32} was used. This model relates the changes in the yield strength of a composite to the properties of the interface.

\[
\sigma_{yc} = \sigma_{ym} \frac{1 - \varphi}{1 + 2.5 \varphi} \exp(B\varphi)
\]

where \(\sigma_{yc}\), \(\sigma_{ym}\) and \(\varphi\) are the yield strength of the composite, the yield strength of the matrix, and the filler volume fraction, respectively. Parameter \(B\) is related to the load-bearing capacity of the particles, which depends on the interface strength and the filler's size and contact area.\textsuperscript{33} Table 2 shows the \(B\) values for the uncompatibilized and MAPP-compatibilized biocarbon composites. The addition of MAPP caused a similar improvement in the \(B\) value for particles in both size ranges, which can be related to the improvement of the interface, as suggested by microscopy. The \(B\) value is slightly higher for smaller particles, which agrees with the well-established trend that smaller particles have bigger values because of their higher specific surface area.\textsuperscript{32}

Besides being an important structural characteristic of materials, the stiffness of a ternary composite offers valuable information about its internal structure. It has been established that, unlike the tensile stress at yield, an improvement in the

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
biocarbon & medium volatile matter & combustible material & ash content \\
(\textmu m) & (wt \%) & (wt \%) & (wt \%) \\
\hline
106–125 & 23.3 ± 0.54 & 65.2 ± 0.08 & 11.5 ± 0.46 \\
<20 & 28.5 ± 2.57 & 65.2 ± 2.46 & 6.3 ± 0.11 \\
\hline
\end{tabular}
\caption{Compositional Analysis of Biocarbons with Different Particle Sizes\textsuperscript{4}}
\end{table}
adhesion strength between a filler and matrix does not change the value of the elastic modulus.\textsuperscript{14,30} However, in this system, the addition of MAPP increased the modulus values for both small and large particles even though the addition of MAPP alone decreased the tensile modulus of the PP/POE blend (Figure 3). This indicates that other mechanisms are also involved when MAPP is added to the system, which changes the structure of the composite profoundly. In ternary composites where both rubber and hard filler were added to the matrix, either the filler and rubber are dispersed separately in the matrix or the rubber phase tends to fully or partially encapsulate the hard filler particles.\textsuperscript{11–13} Dubnikova et al.\textsuperscript{11} observed that the relative modulus (ratio of the composite modulus to the binary blend of PP and rubber) of the composites remains unchanged through the addition of fillers in the case of rubber encapsulation of filler particles. However, in the case of a separate dispersion, the modulus increased with the addition of filler. As can be observed from the composites without the compatibilizer, the modulus remained statistically insignificant. This is in good agreement with the findings of Dubnikova et al.\textsuperscript{11} Therefore, the only way that the addition of MAPP could have improved the modulus of the system is to limit the encapsulation of the biocarbon particles. This phenomenon can be confirmed through SEM images of etched, cryofractured surfaces. As can be seen from Figures 4 and 5, after etching the rubber phase from the uncompatibilized composites, all of the biocarbon particles were surrounded by voids representing the etched rubber phase.

On the other hand, the interphase between the biocarbon particles and the matrix in the compatibilized samples is free of any visible voids in most of the detected particles. This suggests that the rubber is more dispersed in the PP phase rather than encapsulating the particles, hence confirming the change in morphology that was expected from the stiffness analysis above. High-resolution AFM scans of the biocarbon interface in the presence and absence of MAPP are shown in Figure 6. In both images, the green color represents the phase with the lowest modulus, which is the POE phase. The blue and pink colors represent stiffer phases, which are PP, MAPP, and biocarbon particles. As can be observed from Figure 6a, biocarbon particles in the compatibilized composites are surrounded mainly by the blue phases, whereas in the case of the uncompatibilized composite (Figure 6b), the interphase mostly consists of the green phase. This confirms the SEM observation that rubber is dispersed separately from biocarbon in the presence of MAPP.

Since microscopy images are qualitative, they do not provide the right measure to evaluate the extent of encapsulation. A modified Kerner equation\textsuperscript{34} has been shown to provide a proper estimate to describe the effects of fillers on the modulus of ternary composites.\textsuperscript{35–37} The theoretical modulus will be calculated from eq 2

\[
E_c = E_b \left(1 + A B \psi \right) \frac{1}{1 - B \psi \phi_f}
\]

where quantities \( A, B, \) and \( \psi \) are defined as

\[
B = \left( \frac{E_h}{E_b} - 1 \right) \left( \frac{E_b}{E_h} + A \right)
\]

\[
A = K_e - 1
\]

\[
\psi = 1 + \left[(1 - V_f)/V_f^2\right] \phi_f
\]

In eqs 2–5, subscripts b and f denote binary blend and filler, respectively, and \( K_e, V_f, \) and \( \phi \) are the Einstein coefficient, maximum volume fraction, and volume fraction, respectively.
The value of \( K_e \) was estimated to be 2.6 for rod-shaped particles with a length over diameter ratio of 2.5 according to estimates from SEM images (Figure 1).\(^{34}\) The maximum volume fraction of fillers was 0.64 based on the random close packing of hard spheres.\(^{38}\) Although the particles may not be of a uniform spherical shape, the values should be very close for both sizes; therefore, choosing a rough estimate will not change the conclusions. The modulus for biocarbon was converted from Derjaguin, Muller, and Toporov (DMT) modulus values measured by AFM for miscanthus biocarbon in a previous study.\(^{28}\) The extent of encapsulation is presented in Table 3.

The calculated amount of embedded filler is the difference between the actual filler volume fraction (13.8%) and the filler volume fraction that will result in a similar theoretical value of the measured modulus based on eq 1. It can be seen from these calculations that in the presence of MAPP the dominant structure is a separate dispersion of phases. The addition of MAPP caused a greater improvement in the tensile modulus of the smaller particle size composites compared to the larger particle size composites. The same trend can be observed from the flexural modulus data. However, it is known that particle size on the microscale level has little influence on the elastic modulus of a composite.\(^{30}\) Taking encapsulation theory into consideration, the balance between the adhesion strength and shear stress determines the extent of encapsulation.\(^{17}\) Therefore, smaller particles, which have a higher adhesion strength, should have a greater extent of encapsulation than larger ones.\(^{16}\) On the basis of this theory, after the addition of a compatibilizer and a separate dispersion of phases, the moduli of both the large and small particle size systems should be similar or even higher in the case with larger particles. The unexpected lower modulus of the large particle size composite can be attributed to the presence of holes (Figures 1 and 4) within the structure of large biocarbon particles (originating from the lumen structure of miscanthus grass). These holes, which were absent in the smaller particles (Figure 1), can produce voids in the final composites that reduce the final modulus values.\(^{39}\) This caused an artificial inflation of the embedded filler value in Table 3 for the large particle composite. In general, the calculated modulus values for smaller particles look more reasonable when compared to the SEM images (Figure 4). Nevertheless, the differences observed between the measured moduli of the larger and smaller particles in the separate dispersion morphology may not be of practical significance.

The notched Izod impact strength is plotted against biocarbon particle size in Figure 7. Additionally, the effect of MAPP is also shown in this figure. In all cases, the impact toughness was greatly reduced compared to that of the base binary blend. The changes in the extent of encapsulation of the particles caused significant differences in the impact strength of the composites. Molnár et al.\(^{37}\) showed that although the extent of encapsulation affects the impact resistance of PP/ethylene propylene rubber and BaSO\(_4\) composites, encapsulation alone cannot explain the variation in the impact resistance.
SEM images of the impact fracture surfaces in the presence and absence of MAPP (panels a and b in Figures 4 and 5) provide some useful information regarding the fracture mechanism. In the absence of MAPP, a lot of particles can be seen in the fractured surface in both the small and large particle composites. This suggests that the impact path either went through the particle interface or fractured the particles themselves. On the other hand, in the presence of MAPP, a lower number of particles can be observed in the fractured surface, which suggests that the fracture path went mainly through the toughened matrix. This suggests that in the case where many particles are observable in the fracture surface, the particle interfaces were the weak points of the system, which caused the considerable loss of impact toughness. The addition of MAPP replaces this defective interface with a stronger interphase, which results in an impact improvement for both particle size ranges.

Although the two series of composites (with large and small particles) had similar impact strengths in the encapsulated structure, the impact strength showed a larger improvement in composites with larger particles after the addition of MAPP. It has been reported that fracture and/or debonding of large wood flour particles (160 μm) plays an important role in the local deformation process of MAPP-compatablized PP/EPDM/wood composites. Likewise, impact results of Keledi et al. on PP/EPDM/wood composites revealed that debonding is the main micromechanical deformation mechanism taking place during the impact fracture of these ternary composites. The larger particles have less surface area; therefore, debonding can happen more easily in comparison with small particles. Consequently, more debonding is expected to occur in composites with larger particles. Additionally, the fracture of particles requires that energy is expended, which is also expected to be greater for larger particles since smaller ones may not even break (fewer holes exist in the smaller particles). The sum of all of these energies together can further improve the impact toughness of larger particles over smaller ones. Figure 4a shows that even in the presence of MAPP a significant number of broken large biocarbon particles are observable, which confirms the above idea and contributes to their higher impact toughness compared to that of the smaller particle size composites.

The effect of MAPP addition and morphology changes in the tan δ shift of the base blend and biocomposites are shown in Figure 8. Two tan δ peaks were observed around 13 and −40 °C, corresponding to the glass transition temperatures \( T_g \) of PP and POE, respectively. In both uncompatibilized biocomposites, the location of the tan δ peaks for PP and POE did not change from that for the base blend. However, when MAPP was added to the biocomposites, the \( T_g \) of PP shifted to a higher temperature, suggesting that more PP chains were immobilized. On the other hand, the \( T_g \) of POE was shifted to a lower temperature, which indicates that POE chains were more mobile. Premphet et al. observed this in PP/POE/CaCO₃ composites. These changes were more pronounced for smaller particle size composites. These observations are in good accord with the morphological changes caused by the addition of MAPP and the theoretical calculations of the extent of encapsulation (Table 3).

The DSC crystallization exotherms of the PP/POE blend and the composite systems are depicted in Figure 9. It is evident that despite the differences in their structures, the composite samples shifted the crystallization peak of PP toward higher temperatures. This effect is more pronounced in the case with larger biocarbon particles.

However, no significant difference was observed in the crystallinity of the samples. The higher ash content (11.5 wt %) in the larger particle size range compared to the smaller range (6.3 wt %) could be the reason for the nucleating behavior of the composites with a larger particle size. As shown in Figure S2, the ash mainly consists of silica. It has been shown that SiO₂ can increase the crystallization temperature of isotactic PP. A positive shift in the crystallization temperature has been observed by Das et al. in PP pine wood biocarbon composites (13 wt %).

### CONCLUSIONS

In summary, the results presented in this work show that the properties of the composites are less dependent on the particle size of the biocarbon in the encapsulated morphology because the rubber phase masks the properties of the filler by intervening in the load transfer between PP and the biocarbon, whereas in the separate dispersion (with compatibilizer) the properties of the composites strongly changed with the size of the particles. In the separate dispersion morphology, the smaller particles provide better stiffness and strength, whereas the larger ones were more efficient in terms of impact...
toughness. The addition of MAPP can significantly change the structure of the PP/POE/biocarbon composites. The encapsulated morphology, which is the result of an uncompatibilized mixture, possesses low stiffness and toughness values in the ternary systems, which limits the application of such composites. The addition of the compatibilizer caused a simultaneous improvement in the stiffness and toughness of the system caused by the separate dispersion of the phases. This yields a composite with a better stiffness—toughness balance, which widens the application of such biocomposites. These composites benefit from having lower densities and more biobased content as compared to common mineral-filled composites. This study investigates the mechanism governing the interaction between the compatibilizer and biocarbon, laying the foundation for understanding the reinforcing mechanism of such materials. The use of renewable fillers like biocarbon is still in its infancy, and more fundamental studies are required to reveal the underlying mechanisms.

■ EXPERIMENTAL SECTION

In this study, miscanthus biocarbon (BC), which was hammer milled to ∼400 μm (1/64 in.), was received from Competitive Green Technologies, Leamington, ON, Canada. This biocarbon was produced through a slow pyrolysis process at ∼630 °C. In this process, after a predrying cycle, 300 kg of the chopped miscanthus grass was conveyed through the pyrolysis chamber using an auger system, which took 15 min from entrance to exit. The whole chamber was set at the above-mentioned temperatures. The functionalities are still present, as evident from the FTIR spectra (Figure S1).

Injection molding grade PP pellets (trade name 1335Z) were from Pinnacle Polymers LLC, LA, USA. The melt flow index (MFI) at 230 °C/2.16 kg and the density of PP were 35 g/10 min and 0.9 g/cm³ according to the material’s datasheet, respectively. The polyolefin elastomer used was an ethylene-octene copolymer (POE), a product of Dow Chemical Company (trade name Engage 8137), in the form of pellets. The MFI at 190 °C/2.16 kg and the density of POE were 13 g/10 min and 0.866 g/cm³, respectively. A maleic anhydride grafted PP (MAPP) copolymer was added to produce preferential adhesion between the particles and PP. The grafting PP (MAPP) copolymer was added to produce a composite with a better stiffness, toughness balance, which widens the application of such biocomposites. The encapsulation of the PP/POE/biocarbon composites. The encapsulation of the PP/POE/biocarbon composites.

Figure 10. Schematic of the sieve setup on a Ro-Tap sieve shaker.

All formulations were melt processed at 190 °C, at a screw speed of 100 rpm (co-rotating), for a period of 120 s in a DSM Xplore micro compounder with a length over diameter ratio (L/D) of 18 (DSM Xplore, The Netherlands) and then transferred to a DSM Xplore 12 cc injection molding machine to make the test specimens. The injection, packing, and holding pressures and duration were 4, 8, and 8 bar and 4, 6, and 10 s, respectively. The temperature of the mold was kept constant at 40 °C during all injections. Table 4 shows all of the formulations and corresponding designations used in this study.

Table 4. Sample Designation and Formulation of Unfilled and Biocarbon-Filled Composites

| title           | elastomer content* (wt %) | MAPP content* (wt %) | filler content | filler size (μm) |
|----------------|--------------------------|----------------------|---------------|-----------------|
| PP/POE         | 30                       | 0                    | 0             | 0               |
| PP/POE with MAPP | 30                    | 5                    | 0             | 0               |
| small (<25 μm) | 30                       | 0                    | 20            | 13.8            | <20            |
| small with MAPP | 30                       | 5                    | 20            | 13.8            | <20            |
| large (106–125 μm) | 30                       | 0                    | 20            | 13.8            | 106–125         |
| large with MAPP | 30                       | 5                    | 20            | 13.8            | 106–125         |

*With respect to total matrix weight.

Thermal behavior of the samples was analyzed with a DSC Q200 (TA Instruments, USA) under a nitrogen flow at a rate of 50 mL/min. Flat pieces of about 10 mg were shaved from the core portion of an untested impact bar and used for the analysis. Sample were heated to 220 °C at a rate of 10 °C/min, subsequently cooled to −50 °C with a 5 °C/min ramp, and then reheated to 220 °C at a 10 °C/min heating rate. Average values of the melting temperature (T_m), crystallization temperature (T_c), and crystallization enthalpy (H_c) were determined from at least two separate samples. For calculating the crystallinity of the PP phase, the specific melting enthalpy used for 100% crystalline polypropylene was considered to be 209 J/g.26
Thermogravimetric analysis (TGA) and ash content measurement were carried out in a thermogravimetric analyzer (TA Q400, TA Instruments, USA) according to ASTM E1131-08. These tests studied the weight loss profile in a three-step process starting with a nitrogen atmosphere and then switching to an oxidative environment. During the first step, the biocarbon was kept at 110 °C for 15 min under nitrogen purge to remove moisture and highly volatile compounds. At this point, the sample weight was reset to 100% so that the TGA curve represents only the medium and nonvolatile portion of the samples. In the second step, the temperature was set to reach 950 °C with a 50 °C/min ramp rate and then remained isothermal for another 15 min. In the third step, the gas was switched to air and the material underwent a 10 min isothermal cycle at 950 °C. The results were produced in duplicates.

Viscoelastic behavior of the samples was investigated using a DMA Q800 (TA Instruments, USA) in dual cantilever mode. The samples were tested by heating from −110 to 150 °C with a 3 °C/min ramp rate, a 1 Hz frequency, and a 0.1% strain (equal to 40 μm amplitude, tested to be within the linear viscoelastic range). The results were generated in duplicates.

Tensile properties of the composites were measured by Instron universal testing machine (Norwood, MA). Type IV specimens were tested as per the ASTM D638-14 protocol with a test speed of 50 mm/min at room temperature and with 50% relative humidity. Flexural properties were measured as per ASTM D790-15 (procedure B), with a crosshead speed of 14 mm/min and a span length of 52 mm. The impact strength of the samples was measured in accordance with ASTM D256-10. The impact tests were conducted on a TMI monitor impact tester (Testing Machine Inc. DE, USA) with 5 ft lb pendulum at room temperature. Five replicates were tested for each of the mechanical tests.

The biocarbon particles and the fracture surface morphologies were observed by SEM (Phenom ProX, Phenom World BV, Netherlands) equipped with a backscattering electron. A Cressington sputter coater 108 was used to gold coat the composite samples for 15 s under an argon atmosphere. Impact testing was performed using a vacuum oven before gold coating.

To observe the interface of the biocarbon and matrix, high-resolution AFM was performed. All samples were polished using an ultra microtome (Leica Ultracut, Leica, Wetzlar, Germany) before the scans. The scans were performed using a TAP525 probe to obtain modulus mapping of the samples. Details of the analysis and calibration are reported elsewhere.27,28

**ASSOCIATED CONTENT**

## Supporting Information

Representation of The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00122.

Fourier transform infrared spectrum of biocarbon (Figure S1); particle elemental composition using energy-dispersive X-ray spectroscopy (Figure S2) (PDF)

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**Notes**

The authors declare no competing financial interest.

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