

Biochar as a processing additive in poly(butylene adipate-co-terephthalate) (PBAT)

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Abstract: Poly (butylene adipate-co-terephthalate) (PBAT) is a promising alternative to non-biodegradable plastics in agricultural applications. However, it is usually blended with other materials to find a balance of strength, cost, and biodegradability. There is a need to understand the role of additives and fillers that can enhance both performance and biodegradability. Recently, biochar, a material known for its soil amendment qualities, has been proposed as a plastic filler. This study explores the effects and interactions of a commercial wood-based biochar (BC) as an additive within PBAT and compares it to a benchmark made with calcium carbonate (CaCO₃), a traditional filler. Mechanical, thermal, rheological, and morphological testing was performed on films manufactured through a blown-film process containing 0.5% weight of additives. Both BC and CaCO₃ were found to increase the flexibility and processability without affecting the complex viscosity. The strain at break increased by a factor of 2 and 1.3 for CaCO₃ and BC, respectively. On the other hand, CaCO₃ increased friction and blocking by factors of 1.7 and 4 respectively, while BC increased friction by a factor of 1.3 without affecting blocking. Moreover, thermal analysis suggests that only BC promotes crystallization. Additional films were prepared where BC initial particle size and loading (5 wt.%) was varied. Changing the particle size showed no significant changes in both tensile strength and rheology, suggesting that additional milling can be obviated. At 5 wt.% BC, lower mechanical properties were observed, but no blocking was detected, and friction was unaffected. An interaction was observed when using both BC (5 wt.%) and CaCO₃ (0.5 wt.%) together, improving flexibility and processing properties of PBAT.

Keywords: biochar, bio-plastics, PBAT, waste utilization, plastic film, calcium carbonate

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Introduction

Growing population and economic development require the use of agricultural mulching films as they are cheap, easy to use, increase crop yield, diminishes the use of pesticides and herbicides, and increases food quality [1, 2]. The major setback is the disposal of the films, as it generates an additional cost to growers who must collect it after each harvest and send it to landfill or incineration increasing the environmental impact [1]. The conventional plastic used for mulching is low-density polyethylene (LDPE), due to its low price and excellent mechanical performance. Biodegradable plastic films appear to be an option, but they need to achieve the properties needed for the agricultural application [1, 3–5]. Biodegradable plastic films are known to have lesser mechanical properties as compared to traditional fossil-based films and usually harder to manufacture [6]. Multiple biodegradable mulching films labeled as biodegradable are commercially available, but their biodegradability is slow and thus the polymer will remain in the soil for many years before breaking down fully [4].

Poly (butylene adipate-co-terephthalate) (PBAT) is a biodegradable polymer that has attracted attention of industry and academia due to its degradability, ductility and good processability [3, 4, 6–10]. Additionally, due to its high elongation at break, it is a promising alternative to replace conventional plastics in agricultural applications as it is soil degradable [11]. However, it has found a reluctant market mainly due to high cost [12, 13] and less than ideal mechanical properties [13]. Additives (less than 5% weight), fillers (more than 5% weight) or mixing with other polymers, usually polylactic acid (PLA) which hinders degradability, are needed to improve these properties. Nevertheless, traditional additives are not always effective for PBAT [14–16]. There is a need to understand the role of additives and fillers that can enhance both performance and biodegradability

Biochar (BC), a product of thermochemical conversion of organic waste, has been proven to have a wide range of applications [17]. BC can be used as a filler in plastics; for example, it has been shown to affect plastic surface properties [18] and can perform in certain cases as a reinforcement [19–23]. However, the positive effect of biochar in the polymeric matrix depends on the synergy of the specific matrix with the specific biochar [24, 25]. Botta and collaborators explored the effects of a commercial birch and beech wood biochar in PBAT films in large amounts, 5 wt.% 10 wt.% and 20 wt.%. This wood-based biochar showed good adhesion with the matrix up to a certain point: The 10% BC-filled sample showed an increase of the elastic modulus and elongation at break but the 20 wt.% did not. Therefore, recommending the 5 wt.% and 10 wt.% loadings for open-air applications [26], incorporating biochar within additive proportions (<<5wt.%) has not, to our knowledge, been explored in the current literature. Friction properties like blocking and slipping are critical for film processing. These are connected to surface properties, giving room to biochars to be used as an industrial additive for plastic films.

Calcium carbonate (CaCO_3) is a traditional, inexpensive, and environmentally friendly mineral filler and processing agent in polymers. CaCO_3 is commonly used in polyolefin compounds (e.g. LDPE) but is also used in other polymer formulations (e.g. polyesters). It aids the process in multiple ways, one of them being avoiding a phenomenon called blocking, that is the unintended adhesion between the plastic layers of the film during manufacturing [27]. In industry, it is usually added, between 1000 ppm to 4000 ppm (0.1 wt.%-0.4 wt.%) [27, 28], as an anti-blocking additive and reinforcement [27–29]. Recent literature investigated the effect of large amounts (up to 40 wt.%) of CaCO_3 in PBAT was examined; in addition to reducing costs it was also shown that the mechanical properties can be enhanced using this filler [30]. Additionally, CaCO_3 was seen to delay degradation in aquatic environment and weathering in PBAT [12, 30, 31]. Zhang and al. explored the use of high loadings to reduce the cost of PBAT and found a loss of elongation at break and of tensile strength in both machine and cross direction due to agglomeration and poor interfacial adhesion of CaCO_3 with PBAT. However, a recovery of properties was achieved with coating of the CaCO_3 with a silane coupling agent [30]. For CaCO_3 to be an effective filler agent, preprocessing [13] or additional additives [10, 12] are needed. Despite these problems, a patent from 2020 shows that usage, in smaller but still significant amounts, of CaCO_3 in PBAT rich films is of interest for industry [32]. This and an additional patent of the same year, explicitly show the need of anti-blocking and slipping agents [32, 33]. As mentioned before CaCO_3 is known to help with these effects. There is a need to understand the effects of CaCO_3 in additive proportions, in PBAT.

This work explores the use of wood-based biochar as an additive agent on raw PBAT and compared to a benchmark made with CaCO_3 . The sample manufacturing mimics traditional industry processes incorporating additives through a masterbatch. Comparing and understanding the effects of BC as an additive for plastic films can expand BC market and applications in the plastic industry. Raw PBAT was chosen over a mix of polymers (PLA/PBAT) more often used in industry, as the PLA would hinder the biodegradation (glass transition temperature higher than ambient temperatures) [4]. Understanding better what are the interactions and effects of additives on thermomechanical properties can yield to industrial use of these additives that could lower costs and improve properties of PBAT.

Methods

Materials

The recycled wood biochar used in this study was supplied from a commercial vendor, Aries Clean Energy (Franklin, Tennessee, USA). It was characterized by Soil Control Lab (Watsonville, California, USA) based on an International Biochar Initiative protocol commonly used for biochar intended for soil amendment applications [34, 35]. The key properties of the biochar for the plastic filling application [21, 24] are shown in Table 1.

Table 1. Principal characteristics of the used biochar based on the report of Soil Control Lab

Moisture [%wet wt]	Bulk Density [kg/m^3]	Organic Carbon [%dry wt]	Surface Area [m^2/g dry]	pH	Hydrogen/Carbon [molar ratio]
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2.7	128.1	88.7	288	9.86	0.39-0.70
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Another important characteristic is the particle size distribution: 99% of particles were reported to be in the range of 1 mm to 16 mm. A small sample of biochar was milled by the supplier and used to assess effects of particle size on the films.

The calcium carbonate was supplied by OMYA Inc. (Cincinnati, Ohio, USA), purity reported to be >99.5%. PBAT (EcoWorld®) was supplied by Jinhui Zhaolong High Technology Co. (Shanxi Province, P.R. China) with a melt flow index of 4.8 ± 0.4 g/10min (190°C, 2.16kg).

Masterbatch preparations

The masterbatches of PBAT containing 50 wt.% of either BC or CaCO₃ were prepared using an internal shear mixer (CWB Brabender Intelli-torque Plasticorder torque rheometer with a 60-cc 3-piece mixing head), with conditions of 170°C at 60 rpm for 5 min. The samples were then processed in a heated press (Carver 4391) with a pressure of 3 tons for 3 min at 180°C, and then cooled by running cold water through the platens. Samples were then cut into small pieces and mixed with the raw polymer pellets by hand prior to blown film processing.

Blown Film process

All processing was performed on a laboratory scale three-layer blown film line manufactured by Labtech Engineering Co. Thailand (Model LF-400-COEX). The equipment utilizes three single screw extruders feeding into a co-extrusion annular die with a 50 mm outside diameter and a gap of 0.8 mm. The extruders have a barrel diameter of 20.0 mm with an L/D = 30. For this work only one extruder was used at 15 rpm, with temperatures set of 180 °C; 180°C; 175°C ; 170°C and 160°C from feed to the die to achieve a melting temperature of 170°C. The blow-up ratio (BUR) was maintained between 1.8 and 2.5 so the film thickness was kept under 100 microns; this led to a draw-down ratio (DDR) between 3.5 and 6. The ratio between rollers was maintained between 2 and 3 to avoid slipping of the film. The mixing ratios of the masterbatches and the raw PBAT was 1:99 so the additive concentration was 5000 ppm or 0.5 wt.%, a typical loading for a processing additive.

Three additional films were made to further explore the effect of grinding the biochar and increasing the load content to 5 wt.%. A new masterbatch was made with ground BC and then used to make a film at 0.5 wt.% concentration, labeled as PBAT-Gr-BC. A second film was made with a content of 5 wt.% BC, depicted as PBAT-5%-BC. The third film manufactured had a content of 5 wt.% BC and 0.5 wt.% of CaCO₃ and is showed as PBAT-5%-BC-CaCO₃. These results will be discussed in the section *Additional Formulations*.

Characterization techniques

Fourier transform infrared (FTIR, Frontier PerkinElmer) spectroscopy was used to characterize the samples. Measurements were made in triplicate for each sample over wavelengths ranging from 600 to 4000 cm⁻¹, using attenuated total reflectance (ATR) spectroscopy. 16 spectra were averaged with a resolution of 4 cm⁻¹. Peak identification was made later in Python® using the SciPy® module.

Thermogravimetric analysis (TGA, TA Instruments Model 550 Discovery series) measurements were used to assess the thermal behavior of the films, with masses between 5 and 10 mg, and a heating rate of 10 °C /min to 550 °C. This was done with a nitrogen flow for the balance purge of 25 ml/min and for the mass purge of 35 ml/min. The samples were analyzed in triplicate.

Scanning electron microscopy (SEM, Vega 3 SEM/Xflash EDX Tescan-Bruker) was applied with a beam intensity of 10 keV. SEM images were obtained by first sputtering (gold/palladium) all samples for 90 s. Images were taken at 50x, 200x, 1000x and 5000x magnification.

Tensile testing was performed using a Universal Testing Machine 5542 Instron following ASTM D882-18. Blocking force was measured using two standards; the first ASTM D903-98 also used a Universal Testing Machine

5542 Instron and the second ASTM D3354-21 used a Universal Testing Machine 3365 Instron. Lastly, coefficient of friction (COF) measurements was made with a Testing Machine Inc machine for COF (Model: 32-07) following ASTM D1894. The reported values are based on at least five tested samples.

Differential scanning calorimetry (DSC, TA Instruments Model 250 Discovery series) measurements were made, with all samples tested in triplicate, with masses between 5 and 10 mg and a cell purge of nitrogen at a rate of 50 ml/min. A DSC heat/cold/heat cycle was performed, where samples were heated to 230°C, cooled to -50°C and heated a second time, all at a rate of 10°C/min. To calculate the degree of crystallization χ_c , equation 1 was used

$$\chi_c = \frac{\Delta H_m / (1 - filler)}{\Delta H_{100\%}} * 100 \quad (1)$$

where ΔH_m is the melting enthalpy, *filler* is the filler content, $\Delta H_{100\%}$ is the melting enthalpy of a 100% crystalline polymer and has a value of 114 J g⁻¹ for PBAT [36]. The temperature ranges used to calculate enthalpies and glass transitions were consistent throughout all samples.

Melt flow indexes were measured using a Tinius Olsen Plastometer (MP600) following ASTM D1238 procedure A.

Rheological analysis was performed using a hybrid rheometer (TA Instruments Discovery DHR-2) equipped with an advanced Peltier plate for temperature control and an 8mm flat plate geometry. Measurements were conducted using a gap of 1000 μ m and a frequency range of 0.01-100 Hz at 180°C. The strain amplitude, 0.4%, was chosen based on an amplitude sweep that confirmed that it measurements were made in the linear viscoelastic range.

All statistical analysis presented in this work is the result of a one-way analysis of variance (ANOVA) in the Minitab[®] software.

Results

Material characterization

FTIR and SEM were used to analyze the BC and the CaCO₃ before compounding (Figure 1). The interpretation of the peaks can be found in literature for both the calcium carbonate [37] and a wood-based biochar [38, 39]. Briefly, the CaCO₃ spectra shows peaks that can be assigned to calcite at 2513 cm⁻¹ and 1796 cm⁻¹. The carbonate (CO₃²⁻) asymmetric stretching can be assigned to the broadest and more intense peak at peak 1393 cm⁻¹. The asymmetric stretching of CO₃²⁻ can be assigned to 872 cm⁻¹ and 848 cm⁻¹. Lastly, the symmetric bending of the same group corresponds to the peak at 712 cm⁻¹. For the BC, the strong baseline in absorption at low wavelengths indicates a high fraction of carbon in a graphitic nature [39]. This aligns with Table 1, as 88% carbon content is relatively high. The small alteration in the region 2200-2084 cm⁻¹ is probably due to atmospheric background but may also relate to Si-H stretching [38]. Figure 1 also shows the drastic difference in the particle size of the two fillers. As mentioned before, the BC has a particle size mostly above 1 mm, whereas CaCO₃ is in the limit of nanoparticles, on the order of tens to hundreds of nanometers.

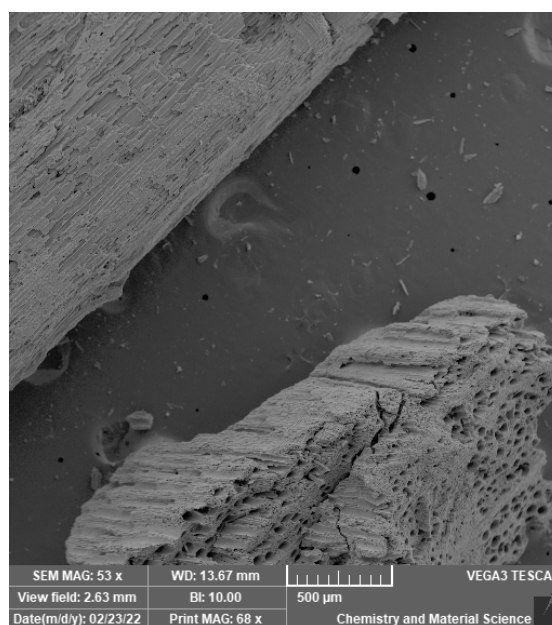
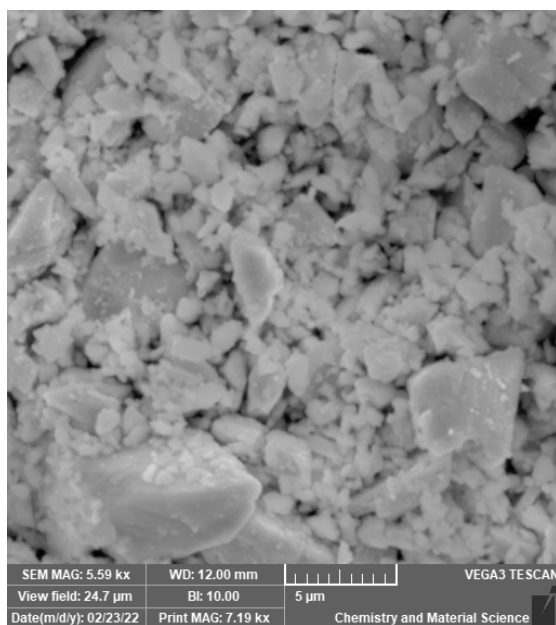
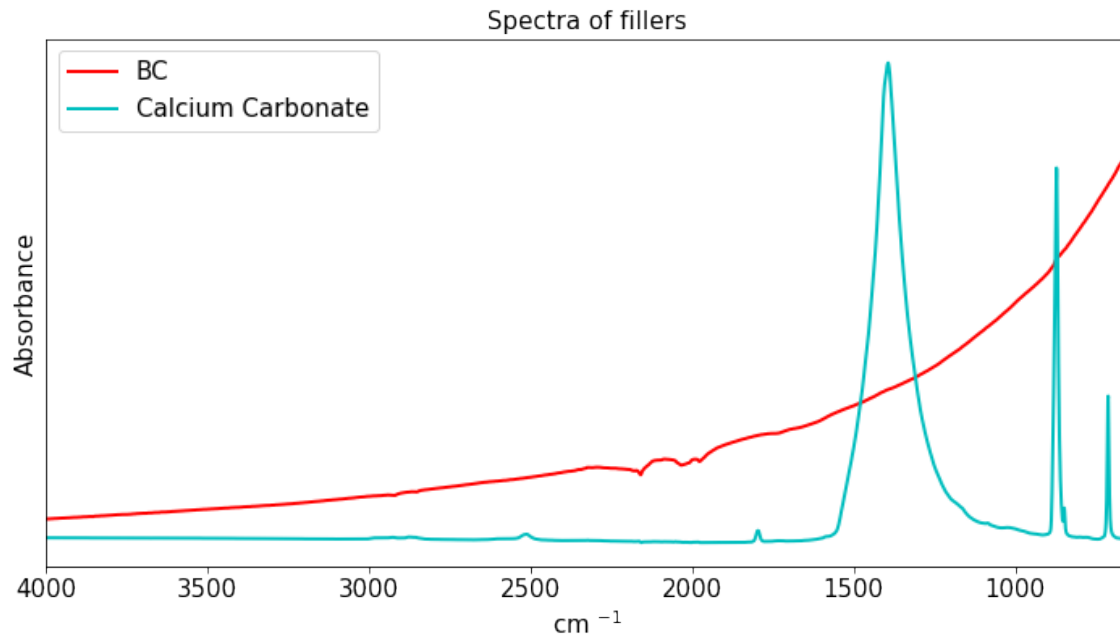


Figure 1. (Top) FTIR spectra of CaCO_3 and wood-based BC, indicating how the two fillers are chemically different. (Bottom left) SEM image at 5590x of the CaCO_3 filler. (Bottom right) SEM images at 53x of the BC filler.

Mechanical and processing results

Figures 2 and 3 show the effect of the additives on the mechanical properties of the films. The process of blown film leads to an orientation of the polymeric chains; if this orientation is pronounced it reflects strongly in the properties [40, 41]. Based on the processing values of the blown film process, a higher DDR than the BUR, there is a strong orientation of the chains in the machine direction. The properties displayed by Figures 2 and 3 for the films reflect this orientation.

Figure 2 shows an increase of more than 100% in machine direction elongation due to the added CaCO_3 . Figure 3 shows an increase of more than 100% in machine direction elongation for the CaCO_3 containing film, accompanied with a 25% decrease in tensile strength. On the other hand, the BC increases film elongation by 30% (p-

value = 0.047) but shows a 20% decrease in tensile strength. In the cross direction, we see a diminishing tensile strength of the PBAT with BC but not a significant one for the PBAT with CaCO₃. In this respect, CaCO₃ exhibits an excellent effect as an additive for flexibility.

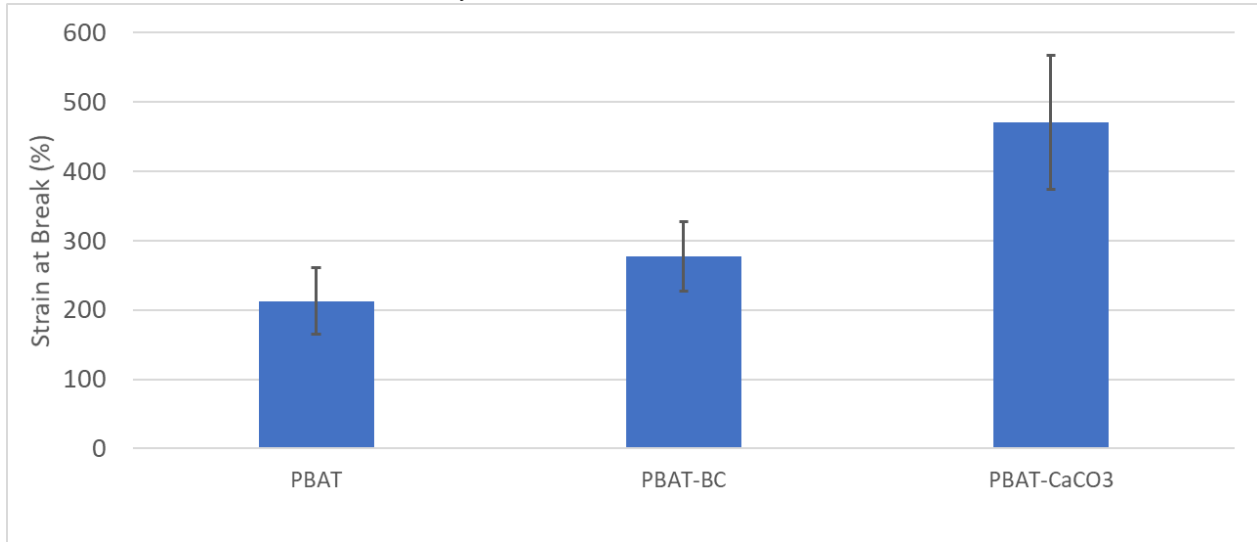


Figure 2. Effect of additives on the elongation break in the machine direction of the films; the cross direction elongation of all samples went beyond the limits of the instrument (550%) and did not break.

However, Figures 4 and 5 show that CaCO₃ has strong effects on friction and blocking properties of the film. Figure 4 demonstrates a difference of the effect on the friction of the film based on the additive. Figure 5 shows the effect of the additives on the blocking properties of the films. The statistical analysis of the data for standard ASTM

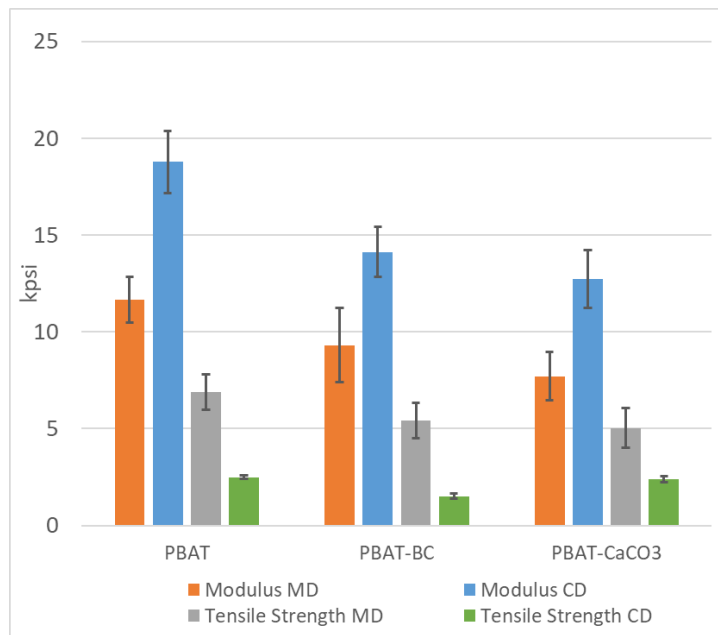


Figure 3. Effects of the additives on the mechanical properties of the films.

This would create a polarity within the CaCO₃ film contributing to the increase in adhesion. This reaction would also increase the molecular weight of the chains, as it connects different chains together [42–44].

D903-98, shows that PBAT-CaCO₃ and PBAT-BC have indistinguishable means. However, a trend is seen suggesting a stronger effect of CaCO₃ on the blocking of the films. This trend is confirmed by standard ASTM D3354-21 under which all means are different with a p-value lower than 0.01. Another result of this standard is that the PBAT-BC shows no effect or even a diminished blocking. The additives BC and CaCO₃ both increase the friction of the PBAT films, with CaCO₃ having a significantly stronger effect. This difference in particle size is one possible cause. Changing the surface of contact to an irregular surface could increase the friction while diminishing the blocking. SEM measurements to assess the surface morphology were made in the following section. An explanation of this result may be the polarity created between layer by the Ca²⁺ and CO₃²⁻ issued from an interaction with the hydroxyls and carbonyls of the matrix [10].

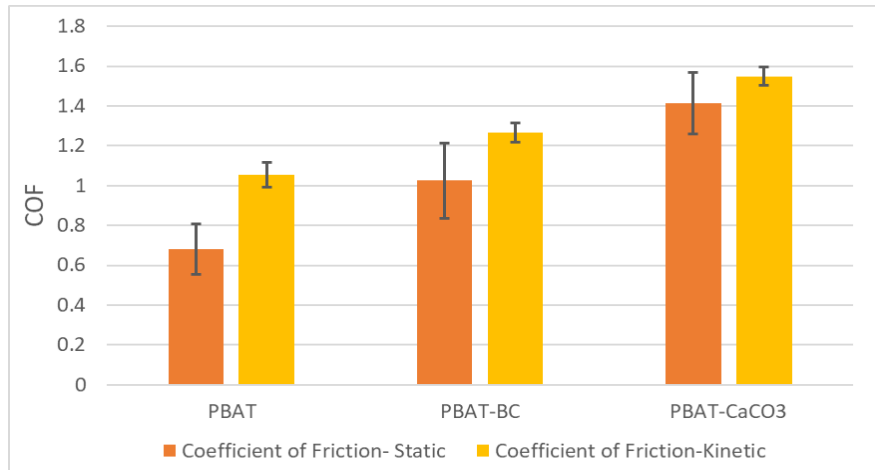


Figure 4. Effect of additives on the kinetic, and static, coefficients of friction following ASTM D1894. Significance differences, with a p-value under 0.01, are seen between all means.

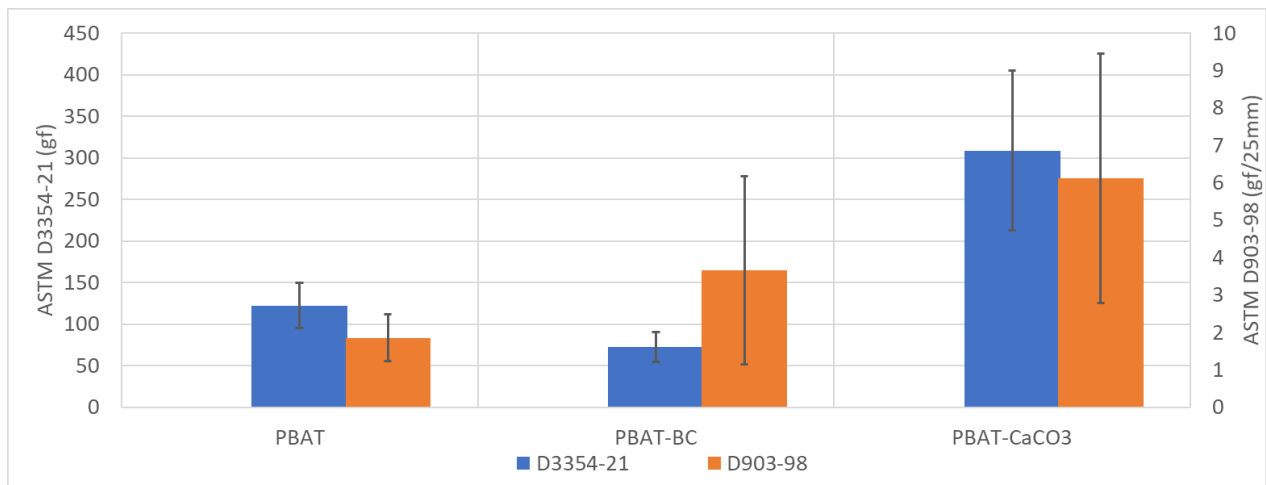


Figure 5. Effect of the additives on the blocking force of PBAT films, measured by two different standards. ASTM D3354 applies to the whole width of the film, including its defects; while D903 applies to a chosen, pristine sample of constant width.

Morphology characterization

Figure 7 shows the surface images of the plastic films at magnifications of 200x, 1000x and 5000x. 2a) shows surface asperities attributed to BC particles near/at the film surface. The low blocking for the BC containing film, seen in Figure 5, might be explained by the reduced surface contact area during blocking testing. It also explains the increase in friction as the surface becomes rougher. In contrast, CaCO₃ particles are three orders of magnitude smaller, making their presence in the matrix unnoticed. However, the increase in friction and blocking for the PBAT-CaCO₃ showed in Figures 4 and 5, is not originated by a surface modification but by a different interaction of the additive.

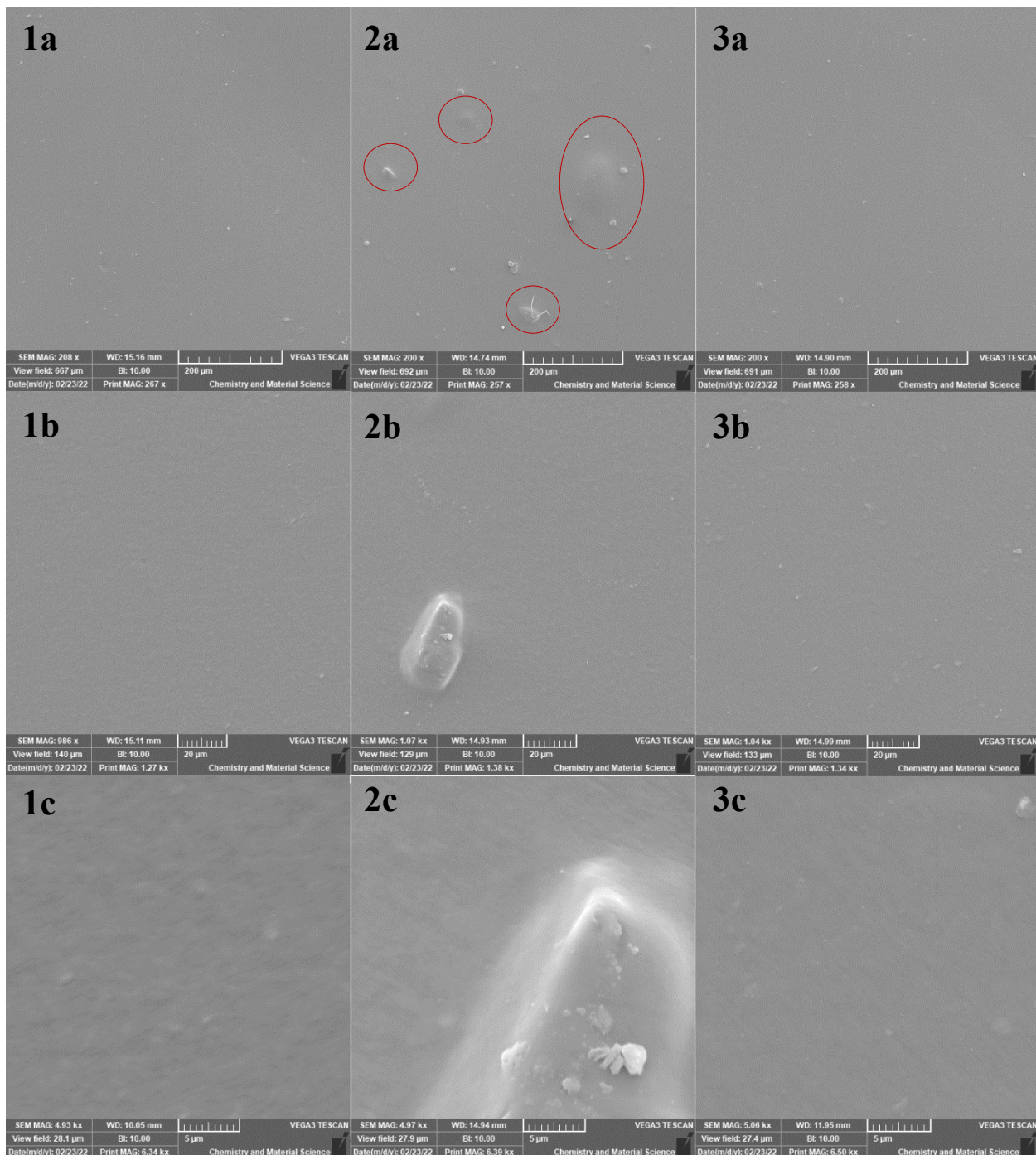


Figure 6. SEM images at magnifications **a.** 200x, **b.** 1000x and **c.** 5000x for **1.** raw PBAT ; **2.** PBAT-BC and **3.** PBAT-CaCO₃, (i.e., image 2c corresponds to PBAT-BC at 5000x). The difference on surface morphology appears to be a consequence of the particle size as shown in **2a** by the red ellipses.

Chemical characterization

Figure 8 show the FTIR spectra of the samples. These measurements were made on the surfaces of the films, finding little differences between the films. Table 2 shows the FTIR analysis based in literature [45, 46], completed with other PBT analysis [47, 48]. The ATR-FTIR demonstrates that chemical reactions that impose differences in chemical structure of the matrix did not occur. However, given the low concentration of loading, this does not preclude the

possibility that an interaction between polymer end-groups and CaCO_3 is occurring as the peaks are hardly identifiable when there is overlap on characteristic peaks (1393 cm^{-1} , 872 cm^{-1} and 712 cm^{-1}).

Table 2. FTIR analysis and bond correspondence of PBAT peaks.

Peak location (cm^{-1})	Possible correspondence	Source
2959	CH_2 asymmetric stretching	[45]
2870	C-H symmetric stretching	[46]
1710	C=O of the ester carbonyl, stretching vibration	[45, 46]
1570 and 1505	CH_2 in-plane vibration of the aromatic ring	[45]
1458	CH_3 asymmetric bending vibration	[47, 48]
1410	CH_2 out-of-plane bending	[45, 46]
1391	CH_2 wagging	[45]
1268	symmetric stretching vibrations of the C-O bond	[45]
1251	C-O-C asymmetric stretching.	[45]
1166	C-C asymmetric stretching, CH_3 asymmetric rocking and C-H wagging vibrations	[47, 48]
1118	in-plane aromatic ring vibrations	[47, 48]
1103	C-O wagging symmetric vibrations	[45, 46]
1018	in-plane aromatic ring vibrations	[45]
937	C-O symmetric stretching	[45]
873	Out-of-plane aromatic ring	[47, 48]
727	In-plane bending of the aromatic ring	[45, 46]

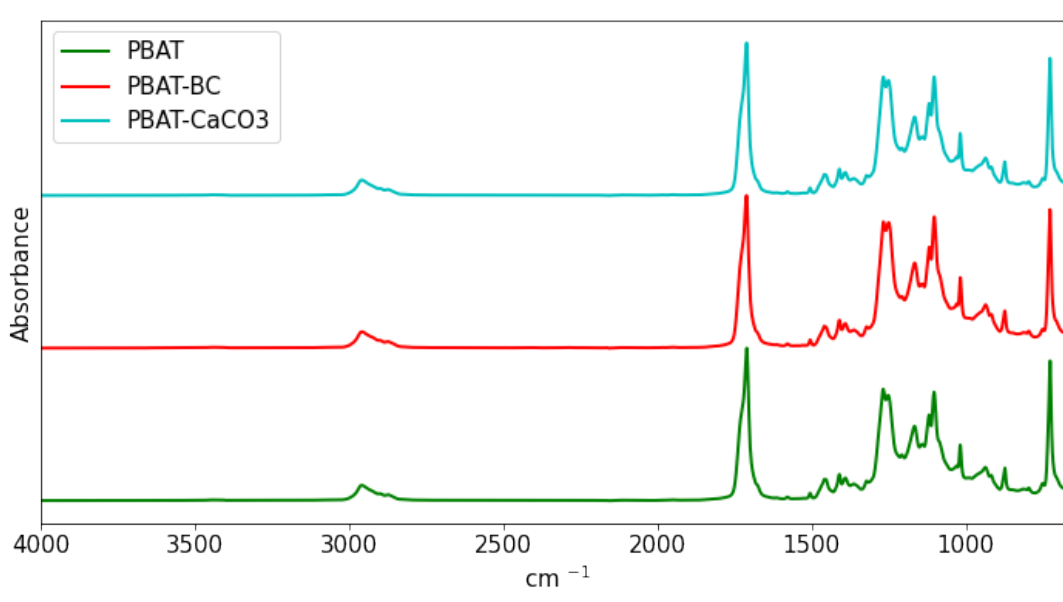


Figure 7. FTIR spectra of the PBAT (green), PBAT-BC (red) and PBAT- CaCO_3 (cyan).

Thermal characterization

DSC was used to characterize differences in the thermal behavior of the first heating informing the result of the blown film processing. DSC also informs, through cooling and second heating, on the kinetics of the polymer crystallization with the additive. Table 3 shows the results of the thermal measurements, showing little effect of the additives on the crystallization of the films. The curve shapes are depicted in the supplemental information (SI) figures A1 and A2. Nevertheless, there is a statistical difference in the effect of BC additive on the crystallization behavior of the polymer. These results suggest that this wood-based biochar is acting like a nucleation agent for the PBAT, as the crystallinity degree of the second heating is slightly higher than that of plain PBAT and PBAT containing CaCO₃. Also, an increase in the onset temperature of degradation is observed for the BC containing film.

Table 3. Thermal analysis, where statistical differences (p-value<0.05) are depicted by a different letter

	DSC-1st Heat			DSC-2nd Heat				DSC-Cooling			TGA
	T _m (°C)	ΔH _m (J/g)	χ _c (%)	T _g (°C)	T _m (°C)	ΔH _m (J/g)	χ _c (%)	ΔH _c (J/g)	T _g (°C)	T _c (°C)	T _{offset} (°C)
PBAT	122.3 ± 0.4	12.9 ± 0.7	11.3 ± 0.7 ^a	-31.3 ± 0.3 ^a	124.8 ± 0.1	10.0 ± 0.2	8.8 ± 0.2 ^b	15.1 ± 0.3	-34.6 ± 0.3 ^a	78.6 ± 1.4 ^b	367.2 ± 1.2 ^a
PBAT BC 0.5%	123.1 ± 0.4	13.9 ± 0.5	12.2 ± 0.5 ^a	-31.6 ± 0.3 ^a	124.2 ± 0.2	10.8 ± 0.1	9.5 ± 0.1 ^a	15.7 ± 0.2	-34.1 ± 0.2 ^a	76.3 ± 0.2 ^a	368.0 ± 2.0 ^a
PBAT CaCO ₃	122.5 ± 0.2	13.3 ± 0.3	11.7 ± 0.3 ^a	-31.6 ± 0.5 ^a	124.9 ± 0.4	9.8 ± 0.1	8.7 ± 0.1 ^b	15.0 ± 0.2	-34.2 ± 0.3 ^a	79.3 ± 1.4 ^b	369.1 ± 2.7 ^a

Rheological characterization

Figure 8 shows melt flow index (MFI) measurements on the films after processing. An increase of the flow after processing is usual as there is an inherent degradation in the processing. PBAT-BC and PBAT-CaCO₃ have a higher MFI at the same conditions when the intuitive result would be a lower MFI as the additive would hinder flow.

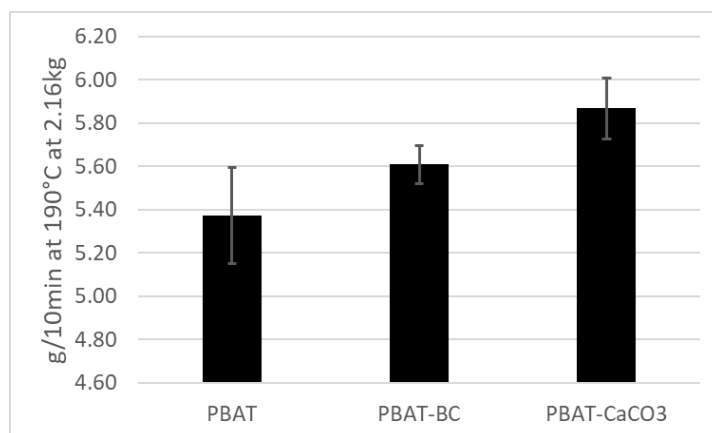


Figure 8. MFI measurements for the processed films. All values are statistically different with a p-value<0.05

Figure 9 shows viscosity measurements at 180°C and displays similar viscosity for the samples, contrasting with the MFI data. The additives in this work appeared to assist the flow of the polymer through the MFI die without affecting the rheology of the polymer, performing a similar role as lubricants. The similarity in viscosities of the added polymers (BC and CaCO₃) with the plain PBAT is explained by the low loadings considered in this study.

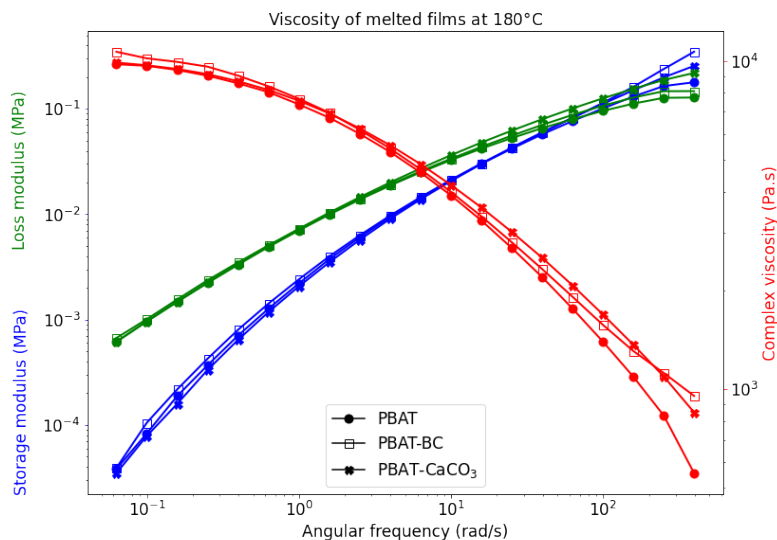


Figure 9. Frequency sweep at 180°C for samples of raw PBAT film, PBAT-BC and PBAT-CaCO₃.

Additional formulations

Particle size can affect ratios of functional groups and chemical reactivity of the BC [38], leading to a slightly more defined FTIR spectra of the BC as seen in Figure A3. However, it was still hardly possible to assign individual peaks to functional groups. Figure 10 shows the impact of the additive concentration on the mechanical properties where it also shows the relatively minor impact of particle size. A statistical difference (p -value <0.01) for tensile strength in the cross direction is observed, where a smaller particle size displays a higher strength. This can suggest that a smaller size allows a slightly better adhesion to the matrix as the surface area increased [24]. As expected, additional BC content affects strongly both mechanical properties and strain at break. However, an improvement of mechanical properties was recorded for the PBAT-5%-BC-CaCO₃ material compared to the PBAT-5%BC.

Figure 11 displays the strain at break of the machine direction of these films. Evidencing, again, an increase of mechanical properties by the addition of CaCO₃ in the 5 wt. % BC film. Figure 11 shows a trend, suggesting that the particle size does not affect positively the elongation at break, despite the lack of statistical difference (p -value = 0.06). However, the PBAT-5%-BC displays a negligible blocking or peeling strength by the tested standards, and a slightly lower friction as shown by Figure A4 and this is also true for the PBAT-5%-BC-CaCO₃. Confirmation that the change in blocking is a consequence of the surface change can be seen in Figure A5.

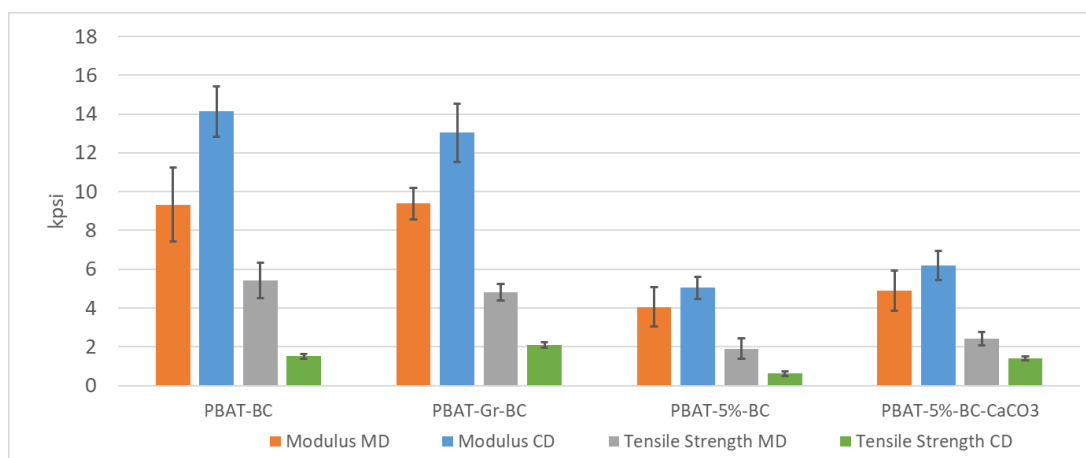


Figure 10. Mechanical properties of the additional films.

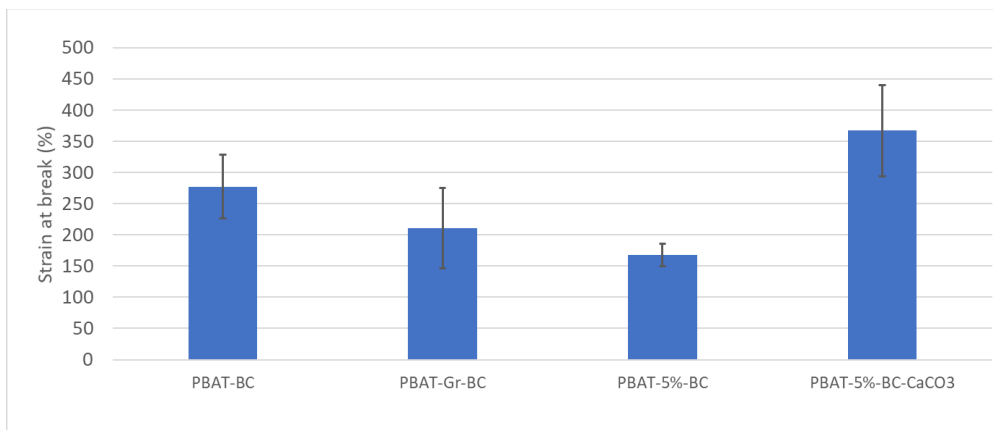


Figure 11. Machine direction strain at break of the additional films with variances on the biochar additives used, the cross direction elongation of all samples went beyond the limits of the instrument (550%) and did not break.

DSC, TGA and FTIR analysis were made and presented in Table A1 and Figures A6-A9. As shown, no significant differences in crystallization or thermal stability is noted. A slightly higher crystallization temperature of the 5% loading of BC in PBAT film suggests that the higher loading of BC is making the nucleation, and thereafter crystallization, easier than with 0.5 wt.%. However, the same sample shows less overall crystallization. Additionally, the high load of BC appears to affect the thermal stability as shown in Figure A9, but it is not a statistically significant difference. Figure 12 shows the impact of the variations of the BC additive on the MFI of the additional PBAT films. The difference in flow related to the initial particle size of the BC, does not suggest that particle size is the cause of the high impact of CaCO₃ as the smaller sized BC flows less than the ungrounded sample. However, the size of the grounded BC is still significantly larger than the CaCO₃. Another result is that there is not a clear and statistically significant (p-value=0.26) variation of the flow by the addition of 10 times more biochar. This suggests that there is not a strong impact on the viscosity of the polymer making it ideal for high filling, nevertheless it is important to recall that MFI results can overlap different effects. Finally, the addition of 0.5 wt.% of CaCO₃ to the high filled BC sample allows the polymer to flow more, reinforcing the same observation in Figure 8. Calcium carbonate is indifferent of the added BC and appears to act as a lubricant allowing a higher flow.

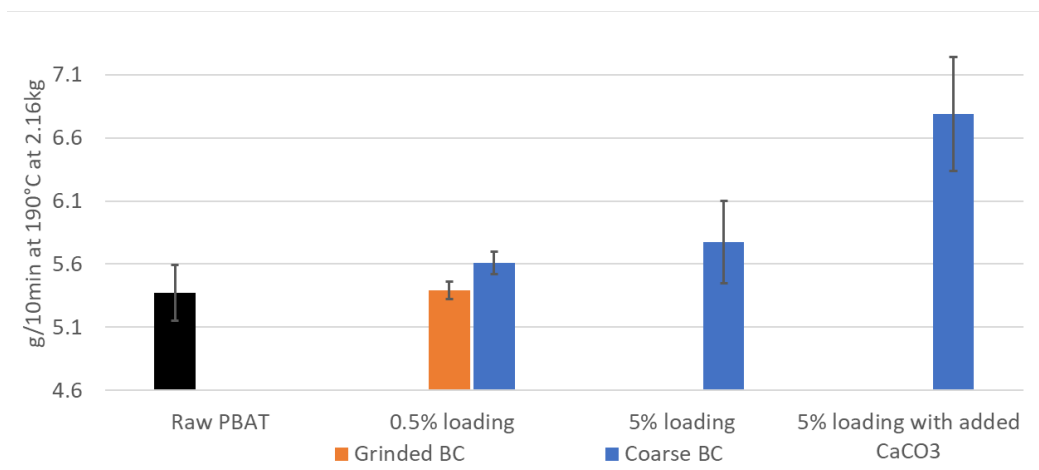


Figure 12. Melt flow index of the additional samples with PBAT for comparison.

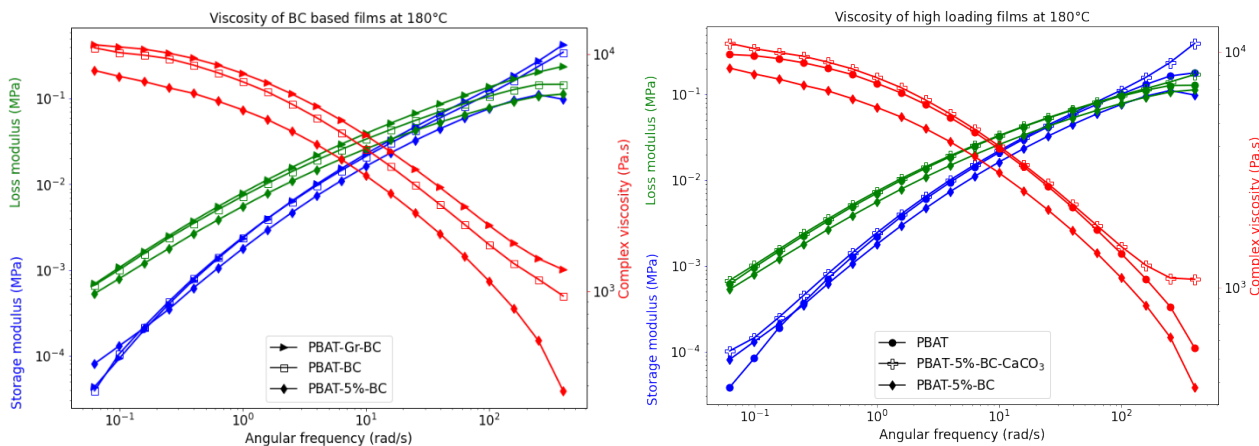


Figure 13. Viscosity measurements at 180°C of (left) the BC sample compared to the grounded BC and the 5% loaded BC sample. (right) The neat PBAT film compared to the 5% loaded BC sample and the 5% loaded BC with 0.5% CaCO₃.

Direct measurements of viscosity at 180°C of the additional samples are shown in Figure 13. The sample with 5 wt.% BC sample exhibits a decreased viscosity, in the same range of reported literature [26], nevertheless adding 0.5 wt.% of CaCO₃ increased viscosity to PBAT levels without diminishing the MFI (Figure 12). However, this increase in viscosity is not seen for the PBAT-CaCO₃ sample in Figure 9, therefore a synergy with the BC appeared to allow the calcium carbonate to have this effect. Additional insight is needed to understand the interactions of these materials, and the limits of each of them within the PBAT matrix.

Conclusions

This work explored the use of two inexpensive, environmentally friendly additives (CaCO₃ and wood-based commercial biochar) for PBAT in blown film manufacture incorporated using a masterbatch targeting a final concentration of 0.5 wt.%. A sample was prepared with ground BC to assess the effect of particle size. The combined effect of using BC and CaCO₃ was evaluated at high loadings of BC (i.e., 5 wt.%). Thermal, mechanical, morphological, and rheological analysis were performed on the resulting films.

The addition of calcium carbonate showed an impact on mechanical properties, more specifically an increase in the strain at break. On the other hand, an increase in friction and blocking were observed when adding CaCO₃, which can lead to a handling issue downstream. Biochar showed a similar but milder effect on PBAT's mechanical and processing properties. Additionally, the BC used in this work slightly enhanced crystallization. Particle size did not play a significant role on the analyzed properties, allowing to avoid the additional milling step.

Films with a higher loading of BC, 5 wt.%, and a combination of high BC loading (5 wt.%) with 0.5 wt.% CaCO₃ were tested. Additional loading reduced mechanical properties of the film. However, no blocking and a diminished friction was detected at high loadings of BC as the plastic surface became highly irregular. It appeared that the high loading of BC lowered the viscosity of the film. When added 0.5 wt.% of CaCO₃ the film improved mechanical properties, showed higher viscosity without the blocking and friction downfall showed for the sole addition of CaCO₃. However, this growth in viscosity did not translate to a lower melt flow index but in a considerably higher one, suggesting that the additives analyzed in this work can be used to increase flow without hindering viscosity. The addition of these materials allows a 5 wt.% loading of biochar to reduce cost with an addition of calcium carbonate to mitigate the loss of mechanical properties of the PBAT.

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