Preparation of hemp-based biocomposites and their potential industrial application

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Abstract

Biocomposites are an emerging field in plastic industry. The incorporation of agri-food waste in conventional or biobased polymer matrices allows the industry to lessen its carbon footprint, while producing recyclable plastic products. In this work, hemp hurd, a byproduct of hemp fibre production process, was used as a filler to prepare novel compostable composites in two different loadings (22% and 32% w/w respectively).
Waste hemp hurds were selected due to their abundance and the lack of derived high-value products. Three different polymers were used, namely poly[(tetramethyleneadipate)-co-(tetramethyleneterephthalate)] (PBAT) and poly(tetramethylene succinate) (PBS) as compostable polymers and a polyethylene elastomer for comparison. The bare polymers and prepared blends were then characterized for their structure and morphology by XRD and FESEM, as well as for their wettability, thermal and mechanical properties (namely energy absorbed on impact and flexural modulus). Structural and morphological characterization unveiled the different interactions occurring between hemp and the polymer matrices, suggesting the major impact of the type of used polymer when compared with biomass loading percentages. Mechanical tests showed that both PBAT and PBS blends properties are comparable to those of the pure polymers (i.e. in the case of PBAT the flexural modulus of the pure polymer was 82.2 MPa while the hemp-loaded blends stood at around 50 MPa, whereas all PBS polymers and blends were 220 MPa, with no statistical difference between samples). These biomaterials have also similar thermal properties with respect to the bare polymers, underlining the promising potential as sustainable alternative to pure polymers.

Highlights

- Waste hemp hurds were used to load biodegradable polymers at different percentages;
- Hemp hurd-based biomaterials with excellent properties were prepared;
- Polymer flexural behaviour was maintained even after hemp addition;
- Polymer-hemp interactions for each polymeric matrix were elucidated;
- Hemp substitutes up to 32% w/w of polymer without affecting its properties;

Keywords
biocomposites, hemp hurds, circular economy, waste valorisation

1. Introduction

In the emerging context of circular bioeconomy, the use of plant-derived resources for developing novel biomaterials is gaining more interest for both academic and industrial sectors. Keeping in mind that annual worldwide plastic production amounts to more than 460 million tons, 90% of which are from fossil sources[1], this trend will play a crucial role in establishing sustainable waste management strategies and reducing the carbon footprint linked to the plastic industry. In line with this approach, various countries and international institutions have been taking actions to tackle plastic pollution. For instance, the European Union started to address the plastic packaging waste management in 1994[2] and redoubled its efforts in recent years, with initiatives such as the Zero Pollution Action Plan[3], for reducing the single use of plastics[4], promoting viable biodegradable alternatives and banning various microplastics-related applications[5,6].

Agricultural and agrifood-derived by-products are widely known to be cheap, abundant, and renewable. The addition of this copious waste to degradable biopolymers can enhance the sustainability properties of biomaterials, reduce the use of plastics, and contribute to the valorisation of agrifood waste. This concept will further contribute to the valorisation of biomasses for developing novel high-added value products, which can further be used for plenty of industrial applications such as automotive, aeronautics, construction, food packaging, interiors, among others. Various types of natural loading products, mainly sisal, coir, jute, wood, cotton, palm, hemp, and bamboo, have been extensively investigated and used for developing bio-based materials[7–10]. Among them, hemp bio-composites are currently emerging as a promising field of research[11,12].

Italy stands as the 5th hemp (*Cannabis sativa* L.) producer in Europe and 10th in the world, with nearly 5 million tons harvested yearly[13]. Hemp, also Known as “industrial hemp”, refers to cannabis cultivars that are mainly grown for agricultural production (e.g., seeds, fibres, oil and hurds). They are characterized by their low contents of the psychotropic substance Δ-9 tetrahydrocannabinol (THC), typically less than 1%[14]. Hemp stem processing is responsible for the generation of two materials, namely fibres and hurds. The physico-chemical and mechanical characteristics of such bio-products make them suitable candidates for application in various industrial sectors, in both forms. Hemp fibres are usually used as reinforcing biomaterials to manufacture isolation mats to be employed mainly in car interior panels and green buildings with thermoacoustic

insulation functions[15,16]. Hurds, which constitute around 65% of total weight of hemp, are widely used in hemp-lime products[17,18].

Along time, a considerable number of researchers have carried out studies aimed at investigating the potential use of hemp fibres for developing novel bio-composites and unlocking the effect of their loading on the characteristics of biomaterials. For example, Pappua et al[19]. manufactured hybrid fibre reinforced eco-friendly materials using sisal and hemp fibres with polylactic acid (PLA) employing melt processing and injection moulding techniques. The reported findings revealed that the mechanical properties of hybrid composites were improved compared to neat PLA. In a related note, Singh and colleagues prepared hemp fibre composites, containing 10%, 20% and 30% hemp fibres treated with 5% NaOH solution as reinforcement, and a mixture of virgin and recycled high density polyethylene (HDPE) as matrix using injection moulding[20]. Hemp fibre reinforced polyethylene composites were compared with specimens made of 100% fresh HDPE and mixture of virgin and recycled HDPE (50:50) in terms of tensile and flexural properties. The study found that increasing the hemp content from 10 to 30% resulted in a decline in the tensile strength of the hemp-based composite. The addition of hemp fibre to composites made of HDPE was also investigated by Lu and Oza[21]. Bourmaud et al.[22] conducted a study on the use of recycled polymers, demonstrating the technical benefits of using recycled materials instead of virgin ones. The study showed that recycled polypropylene and recycled polypropylene/hemp fibre composite can exhibit good mechanical properties after recycling.

Focusing the attention on hemp hurds, the available literature on their use is quite scarce and their potential is not fully uncovered. However, hemp plastic bio-composites may serve as a viable alternative to pure plastic or wood products for various industrial applications. Loading hemp hurd into polymer matrices has been shown to impart good mechanical, thermal, and acoustic properties to the resulting composite[23]. Sassoni et al.[18] reported a study on novel hemp-based composite materials designed for building applications. These materials, produced by bonding hemp hurds with a novel hybrid organic–inorganic binder, were characterized by both thermal insulation and physical-mechanical resistance. Another study investigated the effect of simulated recycling of HDPE up to six times and evaluated its suitability as a matrix for hemp hurd bio-composites[24]. The behaviour of the hemp plastic composites with less than 15% hemp

hurd powder resembled that of pure HDPE. However, when the composites contained more than 15% of the powder, the particles began to aggregate, resulting in a deterioration of properties. Further extensive information about hemp-based composites can be found in various review papers[12,16,25].

The aim of the present work is to contribute to the valorisation of hemp hurds with the goal of achieving zero agri-food waste and limiting the use of plastics in accordance with the United Nations Sustainable Development Goals (SDGs). To do so, different percentages of hemp hurds were used without any pretreatment to load different polymers. The chosen polymers were poly[(tetramethyleneadipate)-co-(tetramethyleneterephthalate)] (PBAT) and poly(tetramethylene succinate) (PBS) as novel biomaterials and an ethylene-octene elastomer as a well known polymer for comparison. The resulting materials were characterized after undergoing a pre-mixing step followed by compression moulding to correlate their mechanical properties with their structure and morphology.

2. Materials and Methods

2.1. Reagents and materials

Ethylene-octene elastomer (QUEO 0203, Borealis) was provided by GIMAC (Castronno, VA, Italy). PBAT and PBS polymers were issued by Novamont S.p.A. (Novara, Italy). PBS monomeric units are 1,4-butandiol and succinic acid, while PBAT is composed by 1,4-butandiol, adipic acid and terephthalic acid. Both PBS and PBAT are biodegradable and compostable according to UNI EN 13432 norm. Prior to usage, PBAT was oven dried overnight at 80°C in a laboratory oven.

Micronized hemp was provided by CHC-Chiaramonte Canapa Consapevole srls, Belmonte Mezzagno (Palermo, Italy) and sieved to mesh 70 (212 μm).

Calcium carbonate ($CaCO_3$) was purchased from Merck (Merck KGaA, Darmstadt, Germany). After sieving, hemp was dried at 45 °C in a laboratory oven upon reaching a 0.5 wt% moisture content and then stored in a tightly sealed container until usage.

2.2. Preparation of the samples

Hemp – polymer blends were prepared by melt-mixing, using a Brabender W50E apparatus (Plasti-Corder, Duisburg, Germany). The melting chamber was previously heated to a specific temperature for each polymer (namely 135 °C for elastomer and 160 °C for both PBS and PBAT). A mixture of polymer, hemp and $CaCO_3$ (as a compatibilizer) was poured in the melting chamber, and the components were allowed to mix for 2 minutes at 50 rpm. Preliminary tests were conducted to find the optimal amounts of hemp (based on visual and manual examination of the polymer after the mixing step, excluding quantities that resulted in poor incorporation). For each polymer, three different set of samples were prepared: pure polymer, polymer loaded with 22 wt% hemp and 5 wt% $CaCO_3$, and polymer loaded with 32 wt% hemp and 4,5 wt% $CaCO_3$ (all percentages are calculated on weight).

The obtained blends were manually cut, so to be in the adequate size for the compression molding and then compression-molded in a Collin P200T laboratory press (Maitenbeth, Germany). Each polymer was pressed at the same temperature used for the blend preparation for 3 minutes without applied pressure and then for 2 minutes with 50 bar pressure for elastomer and 100 bar for PBS and PBAT. Following this procedure, plates of the different blends were produced (**Figure 1**).

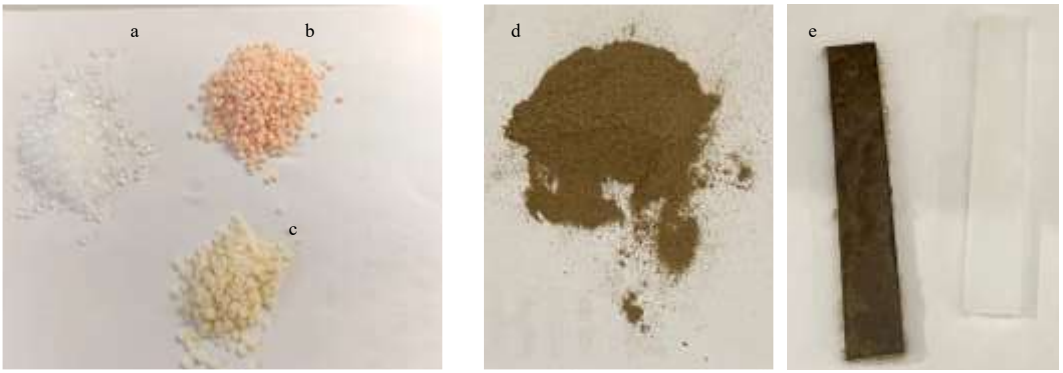

Figure 1. *Polymer, hemp and prepared specimens. a) Elastomer; b) PBAT; c) PBS; d) micronized hemp; e) loaded (left) and pure (right) elastomer.*

2.3. Morphological and structural characterization

Field emission scanning electron microscopy (FESEM) measurements were carried out using a TESCAN S9000G FESEM 3010 microscope (30 kV), equipped with a high

brightness Schottky emitter and Energy Dispersive X-ray Spectroscopy (EDS) analysis thanks to a Ultim Max Silicon Drift Detector (SDD, Oxford, Abingdon-on-Thames, UK). The samples were deposited on a stub that was coated with a conducting adhesive and inserted into the chamber in a fully motorized procedure. The samples were submitted to metallization with Cr (ca. 5 nm) to avoid any charging effect (Emitech K575X sputter coater). Images were acquired by using both secondary electrons (SE) and backscattered electrons (BSE) detectors. Both surface sides of the produced plates were analysed. Images of the cross-sections of hemp-loaded polymer blends were acquired after breaking the sample plates previously cooled by liquid nitrogen.

X-Ray Diffraction (XRD) patterns were collected by using a PW3050/60 X′ Pert PRO MPD diffractometer from PANalytical working in Bragg–Brentano geometry, using as a source the high-powered ceramic tube PW3373/10 LFF with a Cu anode (Cu $K_{\alpha 1}$ radiation $\lambda = 1.5406$ Å) equipped with a Ni filter to attenuate K_{β}. Scattered photons were collected by a real time multiple strip (RTMS) X′ celerator detector. Data were collected in the $5^{\circ} \leq 2\theta \leq 80^{\circ}$ angular range, with 0.02° 2θ steps.

2.4. Rheology

Rheological analyses were carried out with ARES TA Instrument rheometer (TA Instruments Inc., New Castle, DE, USA). The instrument was equipped with a parallel plate geometry having a diameter of 25 mm and a selected gap of 1 mm. The complex viscosity was measured with frequency scans from 100 to 0,1 rad/s at constant strain amplitude. The value was determined for each matrix by a strain sweep test, to fall in the linear viscoelastic region. For all the materials the test was performed under inert atmosphere.

The analysed samples were obtained with compression moulding and all the PBAT-based materials were dried overnight at 80 °C in vacuum oven before the test. In addition, the test's temperatures were properly selected. In particular, 135 °C for the elastomeric-based materials and 160 °C for PBS and PBAT and corresponding hemp-filled.

2.5. Contact angle

Contact angle measurements were taken on a Attention Theta Lite (Biolin Scientific, Västra Frölunda, Sweden) and data were elaborated by the OneAttension software on

Young-Laplace mode, with manual baseline correction. Instrument calibration was done with a stainless steel 4.0003 mm ball. Each measure was taken with 4 μL water drop at room temperature over 5 minutes observation, recording 0.51 FPS. Measurements were done in triplicate.

2.6. Thermal and mechanical properties

Thermal analyses were performed using a Differential Scanning calorimeter (DSC) 7 system (Perkin-Elmer, Connecticut, USA). For calibration, indium standard samples were used. Samples of 5–6 mg were weighed in aluminium pans and then heated at a rate of 10 ◦C/min in the 40–200 ◦C range under a nitrogen purge. An empty pan was used for reference.

Three-point bending tests were performed according to ASTM International D790[26] on a Instron 5966 machine (Instron, Norwood, MA, USA) equipped with a loading cell of 2 kN. Tests were carried out with a loading speed of 2 mm/min on 5mm radius supports distanced 33 cm. The specimen was placed on the supports and the actuator applied a force in the middle of the sample.

For each blend at least three specimens were used to obtain the Young modulus, and average values with the corresponding standard deviation were calculated.

Impact tests were carried out accordingly to ASTM D4812[27] on a Zwick Roell HIT25P (Zwick Roell Group, Ulm, Baden-Württemberg, Germany) equipped with a 5.4J pendulum. Samples were loaded on the supports and the pendulum was manually dropped. Unnotched samples were tested both at room temperature and, for specimens that didn't break in the aforementioned conditions, after freezing in liquid nitrogen. Each test was performed in triplicate and standard deviation was calculated.

3. Results and discussion

3.1. Morphology and structure of the hemp–polymer blends

FESEM measurements were carried out to investigate the morphology of the hemp–polymer blends employed to obtain the bio-composites. Surfaces and cross-sections were

234 analysed to unravel the hemp spatial distribution within the polymeric matrix and
235 therefore to obtain information on the polymer-biomass interaction occurring within the
236 materials depending on the nature of the polymer. FESEM representative images
237 collected on the hemp-elastomer blends are shown in **Figure 2**. In particular, the surface
238 of these samples appears smooth, and some ridges are observed by increasing the hemp
239 loading from 22 wt% to 32 wt% (**Figure 2a** and **b**). Moreover, the presence of embedded
240 $CaCO_3$ observed as particles with squared shape and bright contrast for both elastomer-
241 hemp blends is confirmed by EDS mapping analysis (**Figure SI-1**). The FESEM
242 representative images collected on the cross-sections barely revealed the presence of few
243 hemp fibres (shown in **Figure SI-2** and signalled by arrows in **Figure 2c** and **d**) which
244 likely unthreaded from the polymer and slip off upon fractionation to obtain the cross-
245 sections, leaving small micrometric holes in their place (dashed circles). These features
246 indicate that hemp is dispersed within the elastomeric matrix and likely not strongly
247 interacting with the polymer.
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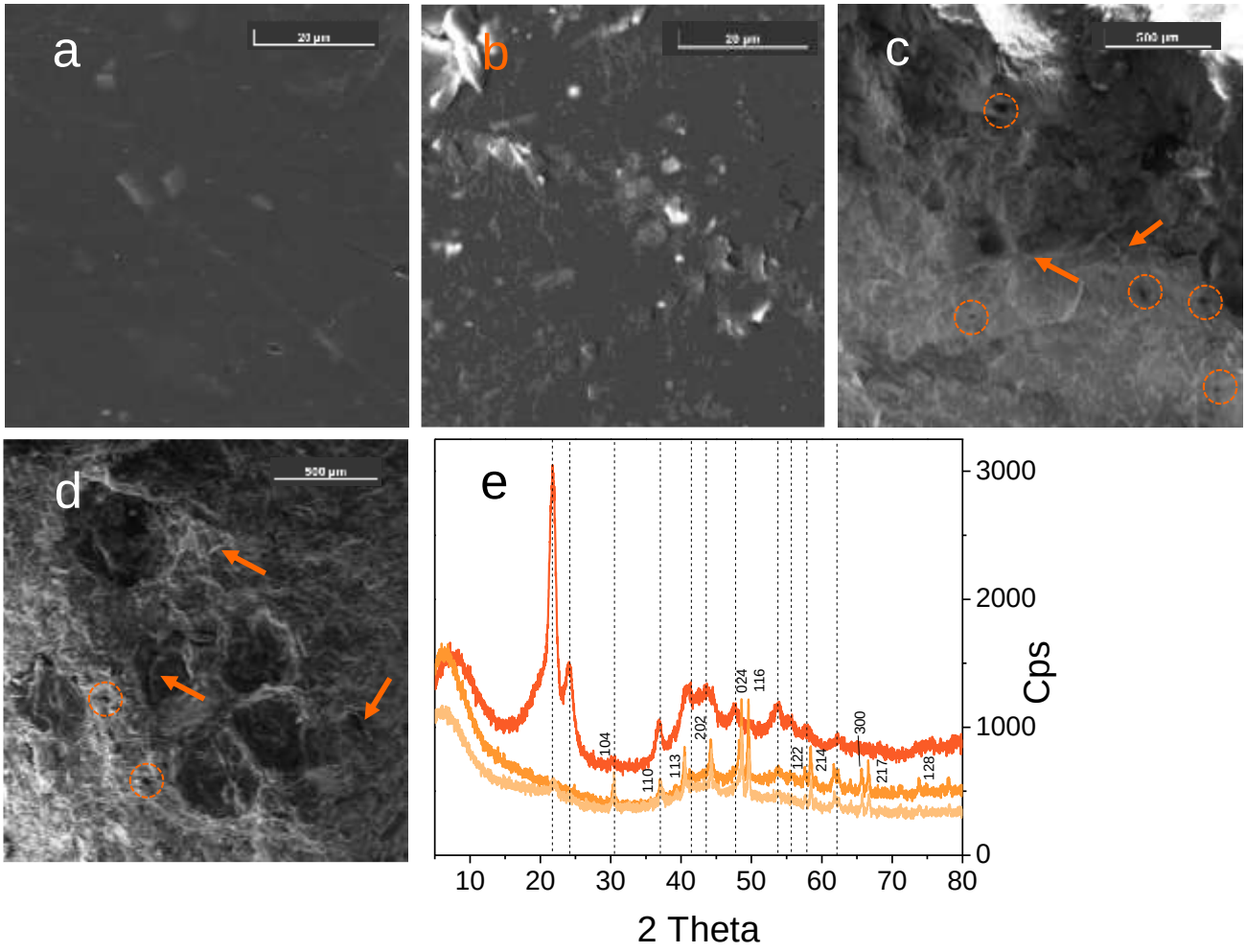

***Figure 2**. FESEM representative images of the hemp-polymer blends: surfaces of the bio-composite obtained from the elastomer loaded with 22 wt% (a) and 32 wt% hemp loading (b), cross section of the elastomer with 22 wt% (c) and 32 wt% hemp loading (d). Images taken with the SE detector at 15 keV. Instrumental magnification 4000× (a and b), 130000× (c and d). XRD patterns (e) of the bare elastomer (dark orange line), elastomer loaded with 22 wt% (orange line) and 32 wt% hemp loading (light orange line). Miller indexes for rhombohedral calcitecrystalline phase (black, 00-002-0623). The position of the peaks of the elastomer is pointed out by dashed lines.*

The XRD patterns of bare elastomer (dark orange line), elastomer loaded with 22 wt% (orange line) and 32 wt% hemp loading (light orange line) are shown in **Figure 2e**. The elastomer displays two characteristic peaks in the 20°-25° 2θ range. When hemp is introduced in the blends, only a small peak at 2θ around 37° is maintained, although greatly diminished in intensity, while the other peaks completely disappeared indicating deep structural changes induced by the presence of hemp. The indexed peaks are related to rhombohedral $CaCO_3$ (00-002-0623, calcite). $CaCO_3$ and bare hemp were also analysed by XRD as reference samples. As expected, the XRD pattern of $CaCO_3$ shows sharp and intense peaks which are proper of a highly crystalline compound (**Figure SI-**

3). These crystalline particles were observed in the FESEM images of the polymer blends, thus confirming the findings from FESEM and EDS analyses which showed the inclusion of inorganic particles inside the bio-composites. The XRD pattern of bare hemp reveals instead the presence of a broad and structured peak in the 15°-25° 2Theta range typical of both cellulose (00-003-0192) and amorphous lignin[28] components. Nevertheless, some kind of structural order is further put in evidence by several peaks in the 15°-48° 2 Theta range (15.3°, 21.9°, 24.8°, 27.0°, 28.5°, 29.7°, 30.5°, 36.3°, 38.5°, 40.1° and 47.5°), which reveals that hemp is not completely amorphous (**Figure SI-4**).

When considering the bio-composites produced with the PBS polymer, quite different features are observed. While elastomer/hemp surfaces appear smooth and flawless (**Figure 2a** and **b**), the surface of the bio-composite containing PBS is jagged, irregular and uneven (**Figure SI-5**), being however the morphology of the smooth regions quite similar to that observed for the elastomer hemp bio-composite, independently from the hemp loading (**Figure 3a**). First, by comparing the surfaces with the cross-sections, the appearance of the holes located on the external surface greatly differs from that related to the holes cross-sections. This feature allowed to ascribe the irregularities observed on the surface of the PBS-containing blends to moulding-derived artifacts, as also supported by the similar morphology of the bare PBS surface (**Figure SI-6**). The presence of protruding parts made up by hemp fibres, which are intimately coated by the PBS polymer was observed (**Figures 3c-e** and **Figure SI-6**). These fibres are reasonably formed during the breaking of the sample plates at low temperature and demonstrates the occurrence of polymer-biomass surface interactions. Such strong interaction could be attributed to the formation of hydrogen bonds between cellulose-hemicellulose on hemp and the PBS carbonyl groups. As a result, hemp fibres embedded in this polymer break simultaneously with the matrix and remain in place without slipping off as shown in **Figures 3c-e**. The XRD patterns of bare PBS and of the corresponding blends are shown in **Figure 3f**. Similarly to the elastomer-hemp blends, the peaks at 2Theta around 25° is observed only in the XRD pattern of the bare polymer (dark violet line).

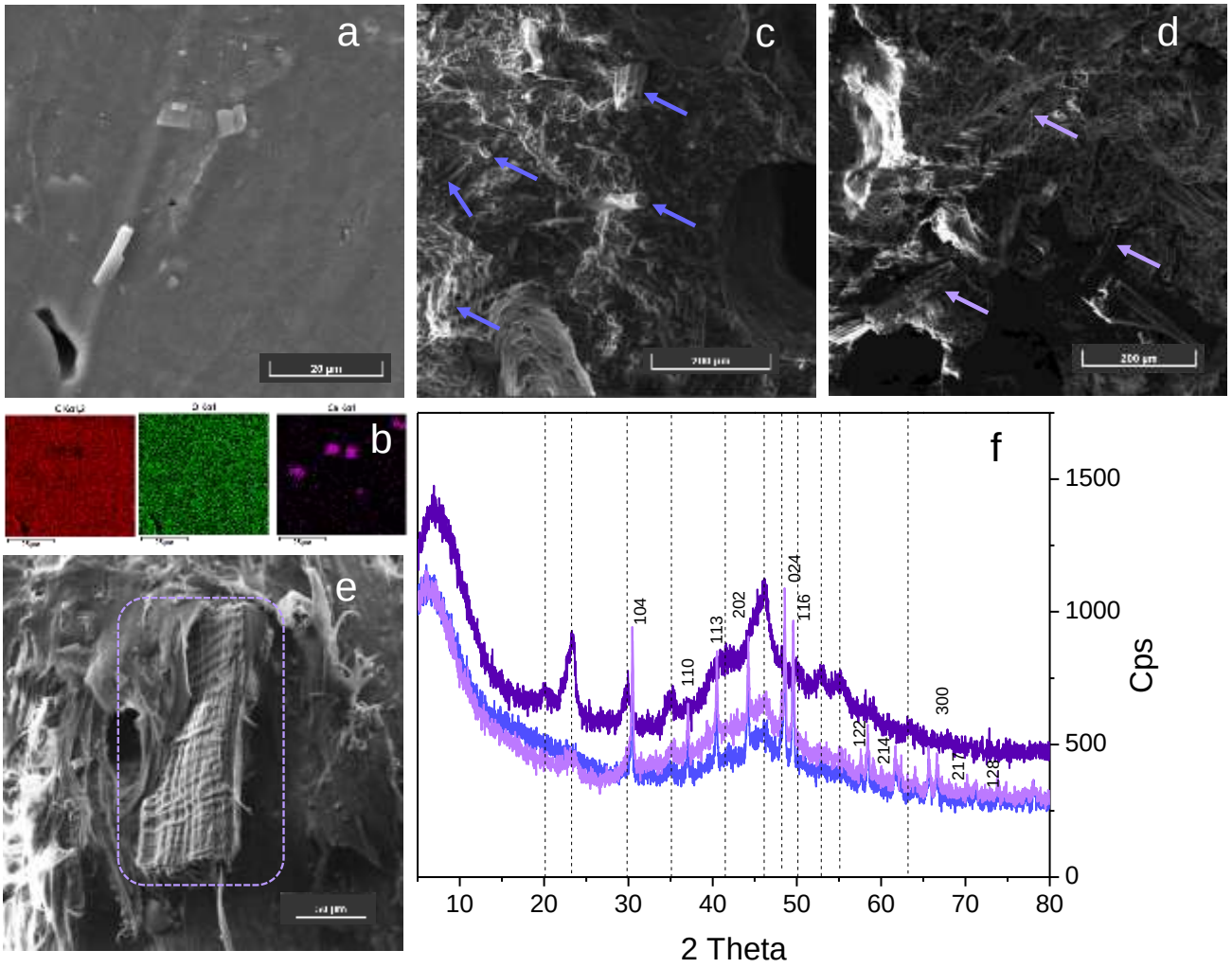

Figure 3. *FESEM representative images of the hemp-PBS blends: surface of the PBS-hemp bio-composite with 32 wt% hemp loading (a), EDS maps of the region shown in a) for C, O and Ca (b), cross sections of the bio-composite with 22 wt% (c and d) and 32 wt% hemp loading (e). Images taken with the SE detector at 15 keV. Instrumental magnification 4000× (a), 400× (c and d) and 1000× (e). XRD patterns (f) of bare PBS (dark violet line), PBS loaded with 22 wt% (violet line) and 32 wt% hemp loading (light violet line). Miller indexes for rhombohedral calcitecrystalline phase (black, 00-002-0623). The position of the peaks of PBS is pointed out by dashed lines.*

However, other peaks proper of PBS as those one at 30° and between 45°-50° are still present in the blend, although their intensity is lower with respect to that of pure PBS. Therefore, in this case hemp induced contained structural modification of the polymer. PBAT blends also exhibit smooth surfaces (**Figure 4a** and **b** and **Figure SI-8**) and the images collected on the cross-sections show protruding hemp fibres intimately embedded within the polymer (**Figures 4c-e**). Another particularity of these samples is the presence of hemp-void and hemp-rich areas, appearing with roundish shape and smoother surface (with respect to the other areas with higher rugosity) as those reported in **Figure 3c and**

e. This feature could be attributed to the nature of the employed polymer, being PBAT an aliphatic-aromatic copolymer. It can be hypothesized that while butandiol and adipic acid moieties, being mainly composed of carbon atoms with sp^3 hybridization, are less constrained within the polymeric structure, the carbon atoms of terephthalic acid are all hybridized sp^2, meaning that they all lie on the same plane.

Thus, spatial orientation of the PBAT polymer chains could be influenced by both degree of freedom and interaction among the aromatic rings of the terephthalic moieties, creating hydrophobic pockets which cannot bind the hemicellulose and cellulose hydroxyl groups. Conversely, the PBAT samples do not show any peaks of the original polymer after blending, and the hemp loading seems to have no effect on the entity of structural changes. Only signals typical of an amorphous nature can be observed. While hemp inclusion slightly modifies the broad peak in the 25-60° 2Theta range, its shape is not modified, and the blends seem to maintain the same amorphous character.

Therefore, the characterization by FESEM combined with EDS performed on the three samples (**Figures 2-4**) reveal the absence of hemp on the surfaces of the blends, independently from the hemp loading, whereas $CaCO_3$ crystals are randomly distributed. The analysis of the cross-sections put in evidence some differences in hemp distribution, depending on the nature of the polymer and likely resulting from different polymer-hemp interaction.

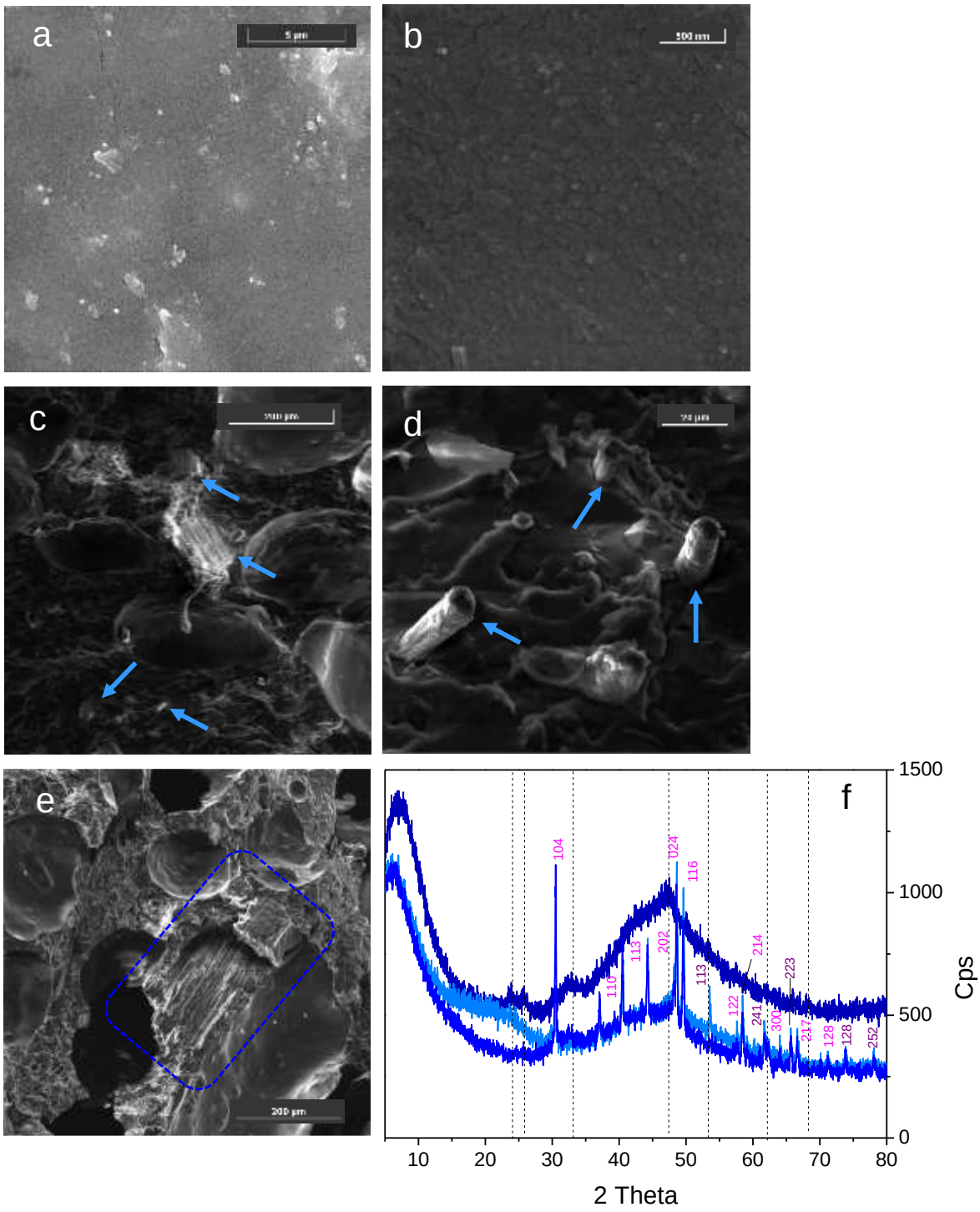

Figure 4. *FESEM representative images of the hemp-PBAT blends: surfaces of the PBAT-hemp bio-composite with 22 wt% hemp loading (a and b), cross sections of the bio-composite with 22 wt% (c and d) and 32 wt% hemp loading (e). Images taken with the SE detector at 15 keV. Instrumental magnification 15000× (a), 100000× (b), 400× (c and e) and 2500× (d). XRD patterns (f) of bare PBAT (dark blue line), PBAT loaded with 22 wt% (blue line) and 32 wt% hemp loading (light blue line). Miller indexes for rhombohedral calcite crystalline phase (pink, 00-002-0623) and Miller indexes for orthorhombic aragonite crystalline phases (wine, 00-001-0628). The position of the peaks of PBS is pointed out by dashed lines.*

3.2. Rheological analysis

Rheological analyses were carried out on all prepared composites and on pure polymers for comparison (**Figure 5**). As reported in **Figure 5a**, the pure elastomer has a non-Newtonian behaviour in all the frequency shift analysed. When considering the composites, the one with 22 wt% of hemp has a rheological behaviour comparable to that of the matrix. Thus, this hemp loading does not affect the rheological behaviour. On the other hand, the composite containing 32 wt% hemp shows an increase of the viscosity in all the frequency range. The increase in the complex viscosity is due to the addition of hemp in the composite[29,30].

The complex viscosity of PBS is reported in **Figure 5b**. The matrix shows Newtonian plateau at low frequencies, while at high values shear-thinning is appreciated. The composite with 22 wt% hemp has a higher viscosity when compared to the matrix. Also in this case, the Newtonian plateau and shear-thinning are observed at low and high frequency respectively. Lastly, for the material containing 32 wt% of hemp the increase of the viscosity in all the frequency range is observed, along with the disappearance of the Newtonian plateau. Thus, the increase in the viscosity value is correlated to the hemp content as expected from the literature[31,32]. In addition, non-Newtonian behaviour observed for the 32 wt% hemp load suggest the interaction of the filler with the matrix[32,33].

Figure 5c refers to PBAT. For the matrix is observed the Newtonian plateau at low frequencies and shear thinning at high frequencies. The introduction of 22 wt% of hemp increases the viscosity along all the range of frequencies considered, and the Newtonian plateau is appreciated at low values. The further increase in the hemp content does not increase the viscosity in the mid-high frequency region, while the non-Newtonian behaviour is appreciated at low values. The increase in the complex viscosity is related to the presence of the hemp[24,34]. In addition, also the non-Newtonian behaviour is due to the filler[24,35].

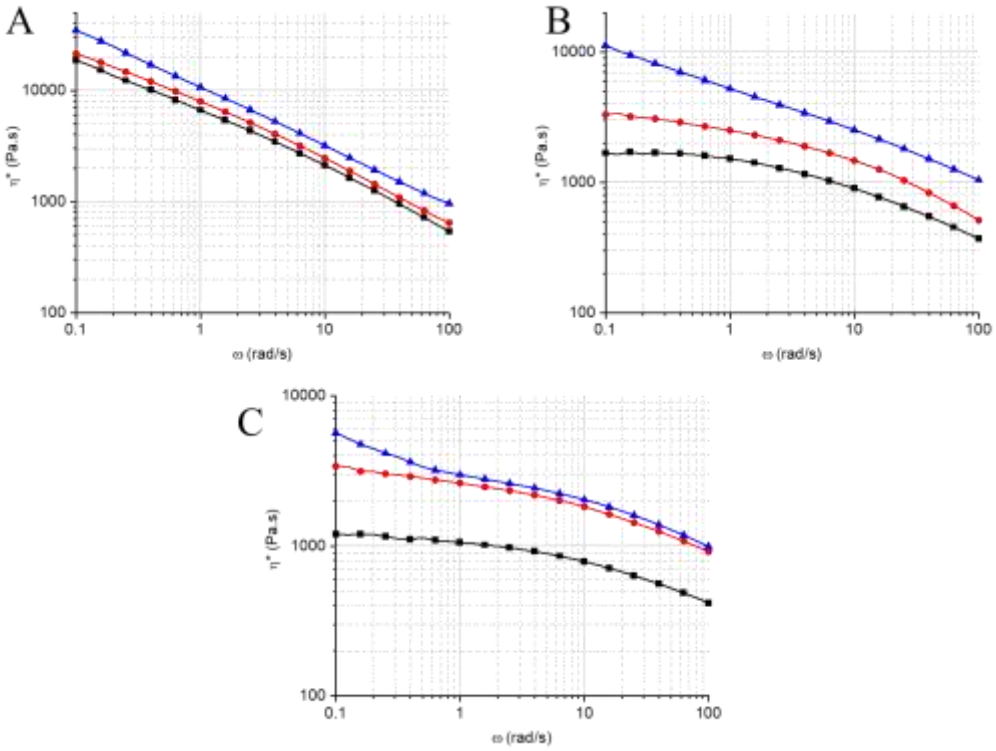

Figure 5. *Rheological behaviour of pure polymers and blends. Black lines represent pure polymers, red lines are for 22% hemp loading and blue lines refer to 32% hemp loading. a) Elastomer; b) PBS; c) PBAT.*

3.3. Wettability

Polymers and blends wettability have been evaluated through contact angle measurement and the results are shown in **Figure 6**.

Elastomer samples show a statistically significative difference only for the 32 wt% hemp loading, while the pure polymer and 22 wt% hemp loaded one have the same behaviour. Both loaded polymers could be considered hydrophobic by the standards of Vogler[36], while for the pure polymer much caution is needed regarding its possible hydrophobicity. PBS shows no statistically significant difference for all treated samples, showing a clear hydrophobic behaviour only for 32 wt% loaded blend.

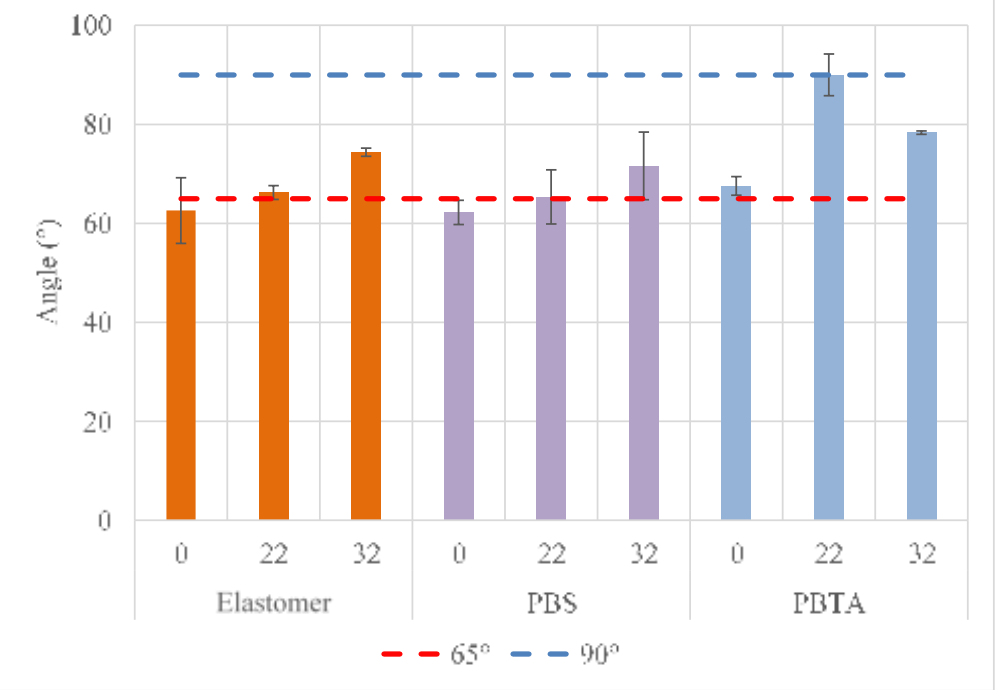

***Figure 6**. Contact angle for the different polymer blends. Numbers above polymer names specify the hemp loading. Green and red dashed lines show the commonly recognized hydrophobicity thresholds for polymers[36,37].*

By the same standards, both pure PBAT and its blends can be considered hydrophobic, and their behaviour is significantly changed by hemp addition.

While there are significant differences between some samples, these variations don't fundamentally change the actual polymers behaviour and their destination of use. So, while PBAT can be considered for water-resisting coating or similar usage, much caution should be exercised with the other tested samples.

3.4. Thermal analysis

Calorimetric analyses were conducted on both pure polymers and blends. The amorphous nature of PBAT, as signalled by XRD (**Figure 4f**), has been further confirmed by the wide peaks observed in the DSC measurements. The irregular shape of the peaks may be attributed to a heterogeneous crystal habit formation due to polymer chains spatial constraints and high filler amount (**Figure 7**).

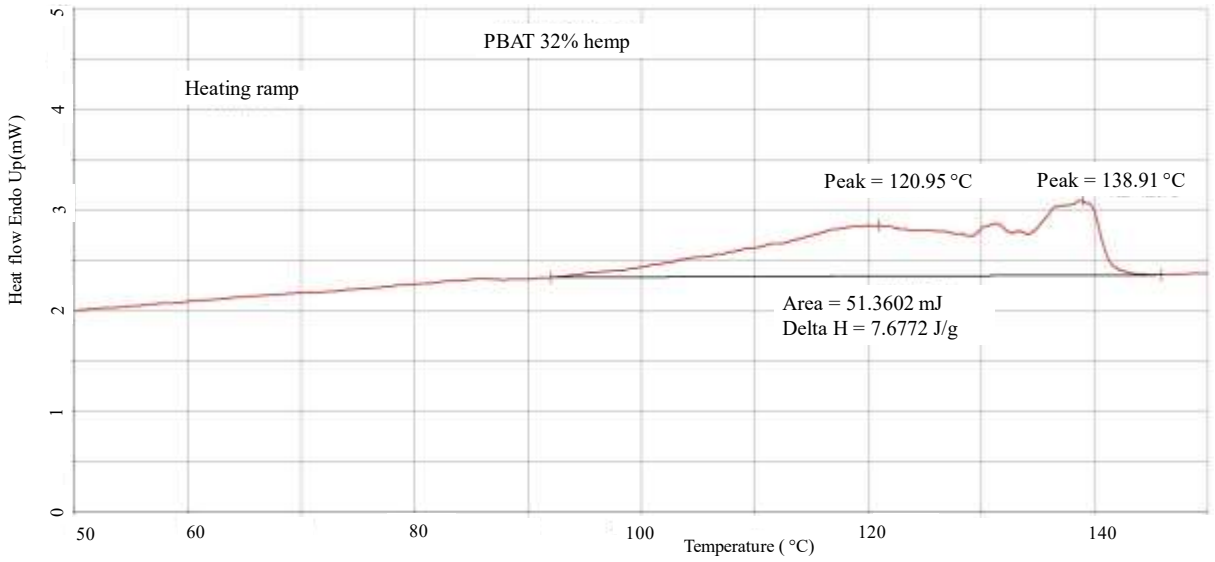

Figure 7. *DSC thermogram of PBAT loaded with 32% hemp.*

Elastomer and PBS instead present clear peaks. The results are summarized in **Table 1** and DSC thermograms can be found in **Figure SI-9-16**.

Table 1. ΔH_f and peak melting temperatures of studied polymers in DSC.

Polymer	Hemp Loading (wt%)	ΔH_f (J/g)	Peak T (°C)
Elastomer	0	30.6	102.5
	22	68.53	97.2
	32	58.34	96.9
PBS	0	64.7	114.0
	22	52.0	112.0
	32	54.0	110.7
PBAT	0	16.6	117.4
	22	7.2	120.7
	32	<11.3	120.9; 138.9

3.5. Mechanical properties

Samples mechanical properties have been investigated both for their resistance to impact and flexural behaviour. Samples were subjected to a 3-point bending test and their modulus was thus determined, as shown in **Figure 8**, which reports the values of flexural modulus for pristine matrixes and composites with the highest percentage of hemp content, equal to 32 wt %. It should be noted that the polymers were not broken under common test conditions.

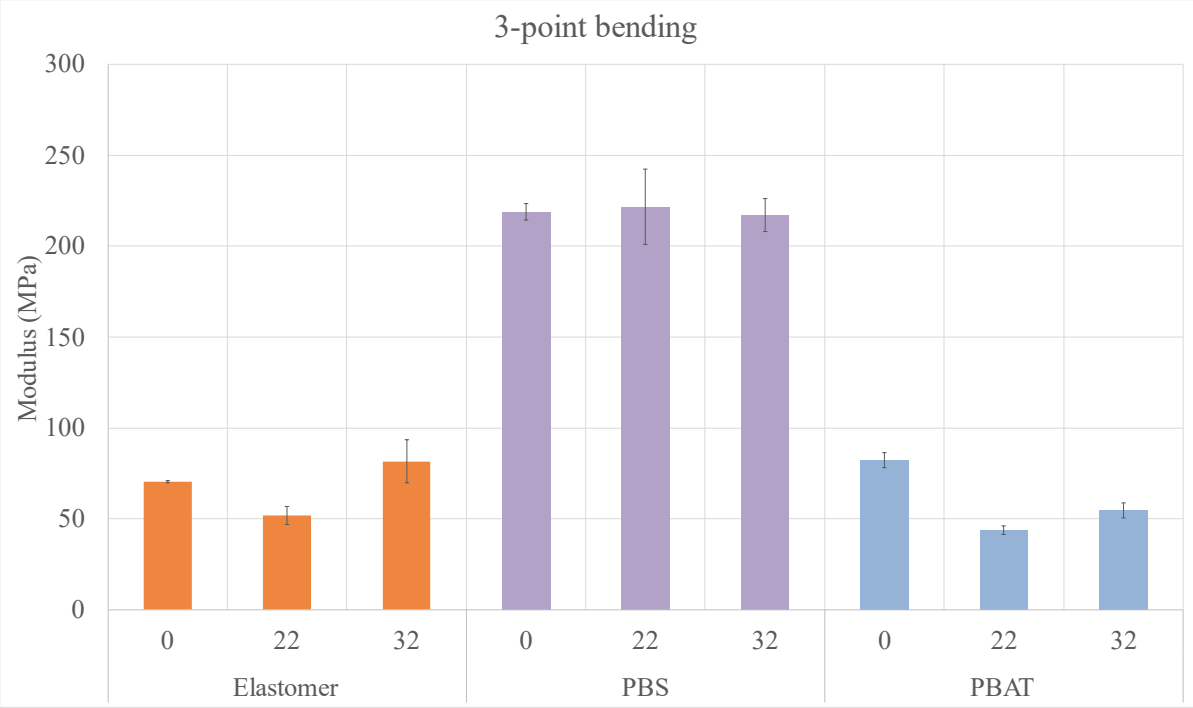

***Figure 8**. Modulus value for tested polymers and blends. Numbers above polymer names specify the hemp loading.*

The flexural modulus mildly increases thanks to the presence of hemp only in the case of the elastomer, while it remains almost constant for PBS and slightly diminishes for PBAT (**Figure 8**).

In literature, the improvement of mechanical characteristics related to presence of hemp into an elastomeric matrix is well-known [38–41]. On the contrary, PBS shows no statistically difference between pristine polymer and the hemp loaded one, while the reduction of the flexural modulus for PBAT is likely to be related to the decreasing of this property with

high fibre content, in particular with loading beyond a certain value due to particle agglomeration[42–44]. The most interesting finding is that the hemp addition to polymer matrices does not fundamentally change their behaviour: variations are on a small scale and the modulus maintains the same order of magnitude, meaning that hemp inclusion does not affect meaningfully the flexural behaviour of the tested polymers.

Impact test results are shown in **Figure 9**. All the polymers only yielded when frozen in liquid nitrogen.

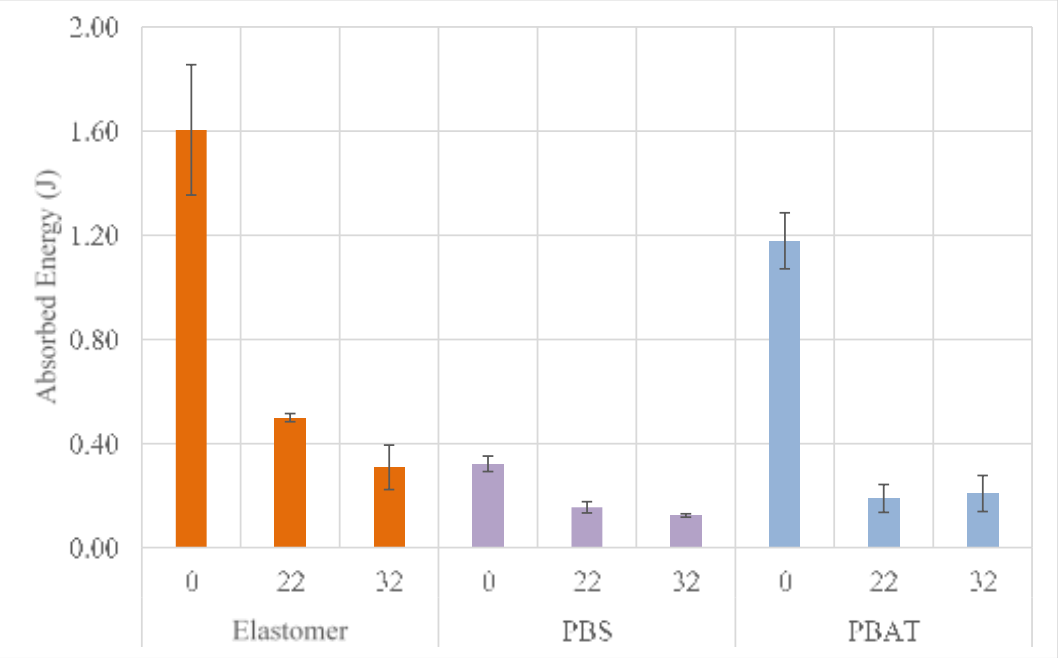

Figure 9. *Impact test results for pure polymers and loaded samples. Numbers above polymer names specify the hemp loading.*

All systems show a statistically significant difference between the pure polymer and the loaded one and higher loadings lead to lower absorbed energy. In particular, all matrixes show diminishing absorbed energy with increasing presence of hemp. As in flexural test results, the most important finding regards the order of impact resistance of tested samples: hemp inclusion change the fundamental behaviour of these matrixes, that is strengthened by the filler presence.

Hemp has a huge effect on impact strength values of elastomer[40] and the ones of PBAT, which are considerably reduced[33,44,45], while PBS shows slightly reduction of impact strength when hemp is present[46] and the differences of this mechanical characteristic between 22 wt% and 32 wt% is little[47,48]. In fact, several authors highlighted the decrease

of this mechanical property with increasing filler content when dealing with biodegradable matrixes[33,44,49], as well as the reduction of impact strength for the toughening of the overall composite[45,49,50].

4. Conclusions

In this study, one of the most abundant hemp byproducts, hemp hurds, was successfully blended with different polymeric matrices for preparing biobased composites. The preparation of such systems and complete structural, morphological, thermal and mechanical characterization were described. The detailed morphological (FESEM) and structural (XRD) characterization of the blends highlighted different polymer-hemp interactions depending on the nature of the polymer rather than the tested hemp loadings. Furthermore, mechanical analysis showed that hemp inclusion can maintain the fundamental properties of the materials in terms of both bending and impact tests, since the tested blends exhibited values within the same order of magnitude of pure polymers. PBAT systems with elastomeric behaviour compared with an elastomeric PE and PBS with stiffer behaviour were investigated. Interestingly, introducing up to 32 wt% waste biomass in the polymer did not significantly change the mechanical properties: flexural modulus of PBAT blends and pure polymer was 82.2 MPa for the pure polymer and around 50 MPa for both the 22 wt% and 32 wt wt% hemp-loaded blends, a small difference that doesn't change the common applications of this material, while no statistically significant difference was found between all tested PBS polymers and blends, which modulus stood at 220 MPa.

The proposed methodology in this work can greatly contribute to establishing a circular economy concept in the hemp industry, while reducing the carbon footprint in materials manufacturing processes. Furthermore, considering that two compostable polymers were used in this study, the developed biomaterials offer a cost-effective solution for plastic industries to partially replace polymers with agri-food byproducts while maintaining their main characteristics.

Following this process, other agri-food waste products can be investigated for incorporation into polymer matrices, advancing research into compostable, natural fibres-based blends and their industrial applications.

REFERENCES

1. *International Energy Agency, The Future of Petrochemicals. https://www.iea.org/reports/the-future-of-petrochemicals. Published in 2018. Accessed on 20 May 2024.*

2. *European Parliament and Council Directive 94/62/EC on Packaging and Packaging Waste*.; 1994.

3. *Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions Pathway to a Healthy Planet for All EU Action Plan: "Towards Zero Pollution for Air, Water and Soil."* Vol COM/2021/400 final.; 2021.

4. *Directive (EU) 2019/ of the European Parliament and of the Council of 5 June 2019 on the Reduction of the Impact of Certain Plastic Products on the Environment*.; 2019.

5. *Commission Regulation (EU) 2023/2055 Amending Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council Concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as Regards Synthetic Polymer Microparticles*.; 2023.

6. *Annex to the Commission Regulation (EU) 2023/2055 Amending Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council Concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as Regards Synthetic Polymer Microparticles*.; 2023.

7. Senthilkumar K, Saba N, Rajini N, et al. Mechanical properties evaluation of sisal fibre reinforced polymer composites: A review. *Constr Build Mater*. 2018;174:713-729. doi:10.1016/j.conbuildmat.2018.04.143

8. Pappu A, Patil V, Jain S, Mahindrakar A, Haque R, Thakur VK. Advances in industrial prospective of cellulosic macromolecules enriched banana biofibre resources: A review. *Int J Biol Macromol*. 2015;79:449-458. doi:10.1016/j.ijbiomac.2015.05.013

9. Pickering KL, Efendy MGA, Le TM. A review of recent developments in natural fibre composites and their mechanical performance. *Compos Part Appl Sci Manuf*. 2016;83:98-112. doi:10.1016/j.compositesa.2015.08.038

10. Thakur VK, Singha AS. Mechanical and Water Absorption Properties of Natural Fibers/Polymer Biocomposites. *Polym-Plast Technol Eng*. 2010;49(7):694-700. doi:10.1080/03602551003682067

11. Saradava BJ, Kathwadia AJ, Goraviyala AD, Joshi VK. Mechanical characterization of hemp fiber reinforced polyester composites. 2016;1(5).

12. Moscariello C, Matassa S, Esposito G, Papirio S. From residue to resource: The multifaceted environmental and bioeconomy potential of industrial hemp (Cannabis

sativa L.). *Resour Conserv Recycl*. 2021;175:105864. doi:10.1016/j.resconrec.2021.105864

13. FAOstat data on 2022 world hemp production. FAOstat. Accessed March 12, 2024. https://www.fao.org/faostat/en/#data/QCL

14. Johnson R. *Hemp as an Agricultural Commodity*. U.S. Congressional Research Service; 2014. https://crsreports.congress.gov/product/pdf/RL/RL32725

15. Li Z, Wang L, Wang X. Compressive and flexural properties of hemp fiber reinforced concrete. *Fibers Polym*. 2004;5(3):187-197. doi:10.1007/BF02902998

16. Ingrao C, Lo Giudice A, Bacenetti J, et al. Energy and environmental assessment of industrial hemp for building applications: A review. *Renew Sustain Energy Rev*. 2015;51:29-42. doi:10.1016/j.rser.2015.06.002

17. Ip K, Miller A. Life cycle greenhouse gas emissions of hemp–lime wall constructions in the UK. *Resour Conserv Recycl*. 2012;69:1-9. doi:10.1016/j.resconrec.2012.09.001

18. Sassoni E, Manzi S, Motori A, Montecchi M, Canti M. Novel sustainable hemp-based composites for application in the building industry: Physical, thermal and mechanical characterization. *Energy Build*. 2014;77:219-226. doi:10.1016/j.enbuild.2014.03.033

19. Pappu A, Pickering KL, Thakur VK. Manufacturing and characterization of sustainable hybrid composites using sisal and hemp fibres as reinforcement of poly (lactic acid) via injection moulding. *Ind Crops Prod*. 2019;137:260-269. doi:10.1016/j.indcrop.2019.05.040

20. Singh S, Deepak D, Aggarwal L, Gupta VK. Tensile and Flexural Behavior of Hemp Fiber Reinforced Virgin-recycled HDPE Matrix Composites. *Procedia Mater Sci*. 2014;6:1696-1702. doi:10.1016/j.mspro.2014.07.155

21. Lu N, Oza S. Thermal stability and thermo-mechanical properties of hemp-high density polyethylene composites: Effect of two different chemical modifications. *Compos Part B Eng*. 2013;44(1):484-490. doi:10.1016/j.compositesb.2012.03.024

22. Bourmaud A, Le Duigou A, Baley C. What is the technical and environmental interest in reusing a recycled polypropylene–hemp fibre composite? *Polym Degrad Stab*. 2011;96(10):1732-1739. doi:10.1016/j.polymdegradstab.2011.08.003

23. Stevulova N, Kidalova L, Cigasova J, Junak J, Sicakova A, Terpakova E. Lightweight Composites Containing Hemp Hurds. *Procedia Eng*. 2013;65:69-74. doi:10.1016/j.proeng.2013.09.013

24. Jubinville D, Sharifi J, Fayazfar H, Mekonnen TH. Hemp hurd filled PLA - PBAT blend biocomposites compatible with additive manufacturing processes: Fabrication, rheology, and material property investigations. *Polym Compos*. 2023;44(12):8946-8961. doi:10.1002/pc.27749

25. Müssig J, Amaducci S, Bourmaud A, Beaugrand J, Shah DU. Transdisciplinary top-down review of hemp fibre composites: From an advanced product design to crop variety selection. *Compos Part C Open Access*. 2020;2:100010. doi:10.1016/j.jcomc.2020.100010

26. *Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials*. ASTM International

27. D20 Committee. *Standard Test Method for Unnotched Cantilever Beam Impact Resistance of Plastics*. ASTM International https://www.astm.org/d4812-19e01.html

28. Gomide RAC, De Oliveira ACS, Rodrigues DAC, et al. Development and Characterization of Lignin Microparticles for Physical and Antioxidant Enhancement of Biodegradable Polymers. *J Polym Environ*. 2020;28(4):1326-1334. doi:10.1007/s10924-020-01685-z

29. DiKmen Küçük S, Tozluoğlu A, Güner Y, Arslan R, Sertkaya S. Nano-fibrillenmiş selüloz / EPDM kompozitlerin mekanik, reolojik ve yaşlanma özellikleri. *Artvin Çoruh Üniversitesi Orman Fakültesi Derg*. 2022;23(1):11-22. doi:10.17474/artvinofd.934238

30. Miedzianowska J, Masłowski M, Strzelec K. Thermoplastic Elastomeric Composites Filled with Lignocellulose Bioadditives. Part 1: Morphology, Processing, Thermal and Rheological Properties. *Materials*. 2020;13(7):1598. doi:10.3390/ma13071598

31. Arabeche K, Abdelmalek F, Delbreilh L, Zair L, Berrayah A. Physical and rheological properties of biodegradable poly(butylene succinate)/Alfa fiber composites. *J Thermoplast Compos Mater*. 2022;35(10):1709-1727. doi:10.1177/0892705720904098

32. Bhattacharjee SK, Chakraborty G, Kashyap SP, Gupta R, Katiyar V. Study of the Thermal, Mechanical and Melt Rheological Properties of Rice Straw Filled Poly (Butylene Succinate) Bio-composites Through Reactive Extrusion Process. *J Polym Environ*. 2021;29(5):1477-1488. doi:10.1007/s10924-020-01973-8

33. Yan Y, Dou Q. Effect of Peroxide on Compatibility, Microstructure, Rheology, Crystallization, and Mechanical Properties of PBS/Waxy Starch Composites. *Starch - Stärke*. 2021;73(3-4):2000184. doi:10.1002/star.202000184

34. Gupta A, Lolic L, Mekonnen TH. Reactive extrusion of highly filled, compatibilized, and sustainable PHBV/PBAT – Hemp residue biocomposite. *Compos Part Appl Sci Manuf*. 2022;156:106885. doi:10.1016/j.compositesa.2022.106885

35. Mohammadi M, Heuzey MC, Carreau PJ, Taguet A. Morphological and Rheological Properties of PLA, PBAT, and PLA/PBAT Blend Nanocomposites Containing CNCs. *Nanomaterials*. 2021;11(4):857. doi:10.3390/nano11040857

608 36. Vogler EA. Structure and reactivity of water at biomaterial surfaces. *Adv Colloid*
609 *Interface Sci*. 1998;74(1-3):69-117. doi:10.1016/S0001-8686(97)00040-7

610 37. Law KY. Definitions for Hydrophilicity, Hydrophobicity, and Superhydrophobicity:
611 Getting the Basics Right. *J Phys Chem Lett*. 2014;5(4):686-688.
612 doi:10.1021/jz402762h

613 38. Stelescu MD, Airinei A, Bargan A, et al. Mechanical Properties and Equilibrium
614 Swelling Characteristics of Some Polymer Composites Based on Ethylene
615 Propylene Diene Terpolymer (EPDM) Reinforced with Hemp Fibers. *Materials*.
616 2022;15(19):6838. doi:10.3390/ma15196838

617 39. Tutek K, Masek A. Hemp and Its Derivatives as a Universal Industrial Raw
618 Material (with Particular Emphasis on the Polymer Industry)—A Review.
619 *Materials*. 2022;15(7):2565. doi:10.3390/ma15072565

620 40. Wang J, Wu W, Wang W, Zhang J. Preparation and characterization of hemp hurd
621 powder filled SBR and EPDM elastomers. *J Polym Res*. 2011;18(5):1023-1032.
622 doi:10.1007/s10965-010-9503-4

623 41. Stelescu MD, Manaila E, Georgescu M, Nituica M. New Materials Based on
624 Ethylene Propylene Diene Terpolymer and Hemp Fibers Obtained by Green
625 Reactive Processing. *Materials*. 2020;13(9):2067. doi:10.3390/ma13092067

626 42. Rouison D, Sain M, Couturier M. Resin transfer molding of hemp fiber composites:
627 optimization of the process and mechanical properties of the materials. *Compos Sci*
628 *Technol*. 2006;66(7-8):895-906. doi:10.1016/j.compscitech.2005.07.040

629 43. Ho M po, Lau K tak, Wang H, Hui D. Improvement on the properties of polylactic
630 acid (PLA) using bamboo charcoal particles. *Compos Part B Eng*. 2015;81:14-25.
631 doi:10.1016/j.compositesb.2015.05.048

632 44. Sreekumar PA, Joseph K, Unnikrishnan G, Thomas S. A comparative study on
633 mechanical properties of sisal-leaf fibre-reinforced polyester composites prepared
634 by resin transfer and compression moulding techniques. *Compos Sci Technol*.
635 2007;67(3-4):453-461. doi:10.1016/j.compscitech.2006.08.025

636 45. Xiao X, Chevali VS, Song P, He D, Wang H. Polylactide/hemp hurd biocomposites
637 as sustainable 3D printing feedstock. *Compos Sci Technol*. 2019;184:107887.
638 doi:10.1016/j.compscitech.2019.107887

639 46. Dash BN, Nakamura M, Sahoo S, Kotaki M, Nakai A, Hamada H. Mechanical
640 Properties of Hemp Reinforced Poly(butylene succinate) Biocomposites. *J Biobased*
641 *Mater Bioenergy*. 2008;2(3):273-281. doi:10.1166/jbmb.2008.403

642 47. Dolza C, Gonga E, Fages E, Tejada-Oliveros R, Balart R, Quiles-Carrillo L. Green
643 Composites from Partially Bio-Based Poly(butylene succinate-co-adipate)-PBSA
644 and Short Hemp Fibers with Itaconic Acid-Derived Compatibilizers and
645 Plasticizers. *Polymers*. 2022;14(10):1968. doi:10.3390/polym14101968

646 48. Qu J ping, Tan B, Feng Y hong, Hu S xi. Mechanical Properties of Poly(Butylene
647 Succinate) Reinforced with Continuously Steam-Exploded Cotton Stalk Bast.
648 *Polym-Plast Technol Eng*. 2011;50(14):1405-1411.
649 doi:10.1080/03602559.2011.593081

650 49. Muthuraj R, Misra M, Mohanty AK. Biodegradable biocomposites from
651 poly(butylene adipate- *co* -terephthalate) and miscanthus: Preparation,
652 compatibilization, and performance evaluation. *J Appl Polym Sci*.
653 2017;134(43):45448. doi:10.1002/app.45448

654 50. Graupner N. Improvement of the Mechanical Properties of Biodegradable Hemp
655 Fiber Reinforced Poly(lactic acid) (PLA) Composites by the Admixture of Man-
656 made Cellulose Fibers. *J Compos Mater*. 2009;43(6):689-702.
657 doi:10.1177/0021998308100688

658