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Article

Lamination of Cast Hemp Paper with Bio-Based Plastics for Sustainable Packaging: Structure-Thermomechanical Properties Relationship and Biodegradation Studies

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Abstract: Composite laminate recycling and waste disposal routes remain a burden to existing systems, requiring special treatment and separation. The inclusion of a plastic layer is important for several key properties that are required for food safety, which in turn has made these products exceptionally hard to substitute in food packaging. Yet, the continued use of non-degradable commodity plastics is unsustainable. In this research, we compare the four most promising biodegradable and bio-based plastics that could replace non-degradable plastics in laminates. Polyhydroxyalkanoate (PHA), polylactic acid (PLA), polybutylene succinate (PBS), and polybutylene succinate adipate (PBSA) were applied as a direct melt coating on porous cast hemp papers, and the final composite was compressed under three different loads: 0.5 MT, 1.5 MT, and 3.0 MT. To promote sustainable agriculture waste management, we opted to use cast paper made from ground hemp stalks. The formation of the composite structure was examined with scanning electron microscopy (SEM), while surface wetting on the paper side of the laminate was performed to understand structural changes induced by polymer impregnation into the paper layer. Mechanical performance properties were investigated with tensile and peel tests, and suitability for an extended range of temperatures was examined with dynamical mechanical analysis. An increase in compression pressure yielded up to a two-fold improvement in elastic modulus and tensile strength, while thermomechanical analysis revealed that the polymer's transition into a viscoelastic state significantly affected the laminate's storage modulus values. Biodegradation was performed in a controlled compost at 58 °C, resulting in full degradation within 40 to 80 days, with PLA and PHA laminates showing 40 and 50 days, respectively. Produced bioplastic laminates have a tremendous potential to replace polyolefin laminates in packaging applications.

Keywords: polyhydroxyalkanoate; polylactic acid; polybutylene succinate; polybutylene succinate adipate; multi-layer composites

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1. Introduction

Food packaging and other consumer goods account for 30% of all polymer-based packaging. Food packaging is designed to prevent food deterioration and degradation, allowing the product to remain and retain the benefits of processing by extending shelf life and maintaining the quality and safety of food provided to consumers [1]. The incompatibility of different plastics and food remains makes recycling recovered packaging waste problematic [2]. This is especially prevalent with laminates. Separating laminated materials from plastics is challenging, limiting the number of packaging materials that may be recycled using modern sorting systems [3–5]. Globally, approximately 80% of produced plastic waste has been accumulated in landfills or in the natural environment [6].

Thus, organizations such as European Bioplastics have proposed a revision of the European Union waste framework to recognize the role of bioplastics, especially biodegradable ones [7,8]. Within this framework, key points include reducing waste generation and simplifying waste collection. In this research, the focus is on often overlooked materials, i.e., biodegradable laminates, to fill the gap in the literature and compare performance between various bioplastics.

Laminated plastic materials (laminates) are used in various industrial applications, including food packaging, furniture, and disposables [9]. However, most commercial laminates are produced from synthetic polymers derived from fossil fuels, which leaves a significant environmental impact due to the sheer number of produced consumer goods [10]. To substitute plastic packaging, laminated cardboard and papers have been introduced and presented as green alternatives, which unfortunately are not due to the presence of a non-degradable layer of polyethylene (PE) or polypropylene (PP). Widely popular plastic cups have been substituted with laminated paper cups, and similarly, various small vegetable and fruit trays have been introduced to appear greener. Likewise, one of the world's most popular milk and beverage packaging is the well-known TetraPak®, which is similarly laminated and contains plastic. All these laminates contain a small amount of plastic that makes them almost completely non-degradable in nature, but worst of all, they are hard to recycle and reuse, thus requiring special facilities or incineration plants.

The negative impact of nondegradable composites on the environment has sparked a revolutionary transition to eco-materials and biocomposites. Unfortunately, high safety and quality standards for materials such as food packaging limit the available and feasible alternatives. Various biodegradable polymers have been presented as promising alternatives for packaging materials, and some are now in use [11]. Bio-based and compostable plastics such as polylactic acid (PLA), polyhydroxyalkanoates (PHA), polybutylene succinate adipate (PBSA), and polybutylene succinate (PBS) have emerged as alternatives to existing commodity plastics [12,13]. Additionally, studies have demonstrated that thin biodegradable plastic films can attain outstanding barrier properties, but they often require the application of additives such as cellulose [14] or nanoclay [15] or specialized techniques such as electron beam-mediated cross-linking [16]. While many studies have focused on using biodegradable polymers such as PLA and PBS to replace non-biodegradable polymer matrices for direct plastic packaging [17–19], there are still relatively few studies that focus on laminates.

PLA is the most produced biodegradable plastic [20]. As a result, the cost of the material has fallen due to advancements in manufacturing technology, and it has found many applications, including ingarments, food packaging, coffee cups, and fibers [21,22]. PHA is a unique group of bioplastics fully produced by microorganisms. By using this unconventional route, the properties of PHA can be tuned. Currently, commercial forms of PHA consist of polymers produced from short-chain monomers, which yield polymers such as polyhydroxybutyrate (PHB). As a result, PHAs have relatively similar physical properties to those of PLA [23]. The most notable difference includes PHA's ability to degrade in the water environment, which makes it a superior material regarding reduced environmental impacts [24–26]. Both PLA- and PHA-based plastics undergo glass transition above 60 °C, showing similar mechanical performance with relatively high elastic modulus (above 2 GPa) and low strain values. This lack of ductility is a significant drawback if these polymers are used to replace flexible PE and PP, which are the most produced and used plastics, in addition to being commonly used in laminates. As a result, the biodegradable plastic portfolio has been expanded to include plastics that are like PE and PP. These include bioplastics such as PBS, PBSA, and various similar copolymers [27]. While PBS and PBSA production volumes are relatively low [3], various studies have estimated that with an increase in production they could become competitive with PLA [28,29]. PBS is already applied in various products, including films, foamed sheets, expanded foam, blown bottles, and other throwaway items [17]. PBS and PBSA are more compatible with hot press techniques because they have lower melting temperatures (80–120 °C) than PLA and PHA (170–185 °C) [30].

Hervy et al. studied multi-layer bacterial cellulose nanopaper/PLA laminates to characterize mechanical response and create high-performance composite materials [31]. The tensile moduli of the laminates were from 12.4–13.6 GPa with bacterial cellulose content of 65–72 vol.%, thus demonstrating good compatibility between PLA and cellulose. Bacterial cellulose nanopaper/PLA laminates were studied to understand the influence of paper grammage on mechanical properties [32]. Authors demonstrated that even low grammage of nanopaper shows good mechanical properties, thus enabling more environmentally friendly solutions by reducing the time needed for the dewatering step. Dilkes-Hoffman et al. showed that thermoplastic starch (TPS) film barrier properties were enhanced with PHA coating [33]. The prepared laminate showed that even after several weeks of storage, the moisture content in the TPS layer remains significantly lower compared to uncoated TPS. Melendez-Rodriguez et al. demonstrated that cellulose nanocrystals can be incorporated into multi-layer PHA films to obtain high-oxygen-barrier properties [34]. The authors reported that 1 µm of the cellulose nanocrystal interlayer reduced the oxygen permeance by 71% to 86%. PBS was investigated as a coating for paperboard food packaging [1]. Authors demonstrated that PBS is a suitable replacement for plastics used in convenience ready-to-eat food packaging that undergoes microwave reheat conditions.

With this article, we take an opportunity to bring attention to biodegradable plastic and cellulose laminates, a much-needed replacement for conventional plastics to solve existing waste disposal problems. Using hemp fibers, a cast paper was prepared and a melt coating with compression was used to obtain laminates. A selection of the most promising bio-based and biodegradable bioplastics was used in the lamination process. A comparison of PBS, PBSA, PLA, and PHA laminates prepared with three different compression pressures is presented. Analysis of mechanical, thermomechanical, and structural properties is carried out, and biodegradability is evaluated in the composting conditions. With this comparison, we hope to improve on the existing literature while also filling a gap for less studied biodegradable plastics by highlighting their advantages.

2. Materials and Methods

2.1. Materials

Polyhydroxyalkanoate (PHA) grade PHI 002 was purchased from Nature Plast. PHA is 100% bio-based, recyclable, industrially compostable according to the ASTM D6400, and suitable for injection molding. PHA melting temperature is in the range of 170–176 °C, melt flow index 5–10 g/10 min (2.16 kg at 190 °C), and density 1.23 g/cm^3. Polylactic acid (PLA) with trademark Ingeo™ and grade 6201D produced by NatureWorks LLC is 100% bio-based and compostable resin targeted for fiber production. It is characterized by a melting temperature of around 170 °C, a melt flow index of 15–30 g/10 min (210 °C, ASTM D1238), and a density of 1.24 g/cm^3. Polybutylene succinate (PBS) with trademark BioPBS™ grade FZ71PB® is 50% bio-based (from bio-based succinic acid), composable, and suitable for injection molding and lamination. It has an inherent melting point of 115 °C, a melt flow index of 22 g/10 min (2.16 kg at 190 °C), and a density of 1.26 g/cm^3. It is made from bio-based succinic acid and 1,4-butanediol polymerization. Polybutylene succinate adipate (PBSA) with trademark BioPBS™ grade has a bio-based content of around 30–50% and is compostable. PBSA is suitable for blown and cast film extrusion. It has a melting point of 84 °C, melt flow index of 4 g/10 min (2.16 kg at 190 °C), and density of 1.24 g/cm^3. All selected polymers are thermoplastic.

For the preparation of the paper, *Santhica 27* variety locally obtained hemp stalks were used. Kraft lignin, beechwood xylan grade, and sodium hydroxide (NaOH) were purchased from Merk KGaA and used as received.

2.2. Hemp Paper Preparation

The hemp paper preparation procedure was adopted from our previous study [35]. Hemp stalks were processed in a Retsch SM300 cutting mill using two grinding cycles with a sieve size of 4.00 mm and 0.25 mm. Retsch ZM200 with a sieve size of 0.12 mm was used to further reduce the size of hemp fibers. The mills were manually fed throughout the process, with the rotation speed set to 1500 rpm. The obtained hemp fibers were characterized with optical microscopy (Figure S1a) and showed a length of around 30–60 µm and a width of 6–14 µm.

An amount of 26.7 g of hemp powder was dispersed in water (100 mL) using an ultrasonic sonotrode Hielscher UIS250V (Teltow, Germany). Kraft lignin was dispersed in water, heated to 80 °C, then pH was adjusted to 10 by adding NaOH, and in the last step filtered to obtain 15 g of 2 wt% homogeneous dispersion. Three grams of xylan was dissolved in 27 mL of water, and heated to 80 °C to obtain the final solution. Prepared dispersions were combined with xylan solution and stirred for 2 h followed by homogenization with an ultrasonic sonotrode. The obtained solution was then cast into the tray. The simplified scheme of the process is shown in Figure 1a. The hemp paper (paper) was obtained after the water evaporated (3 days, 22 °C, 45% humidity). After drying, a cast paper was cut into 10 × 10 cm square-shaped samples. The thickness of cellulose paper reached 800 µm.

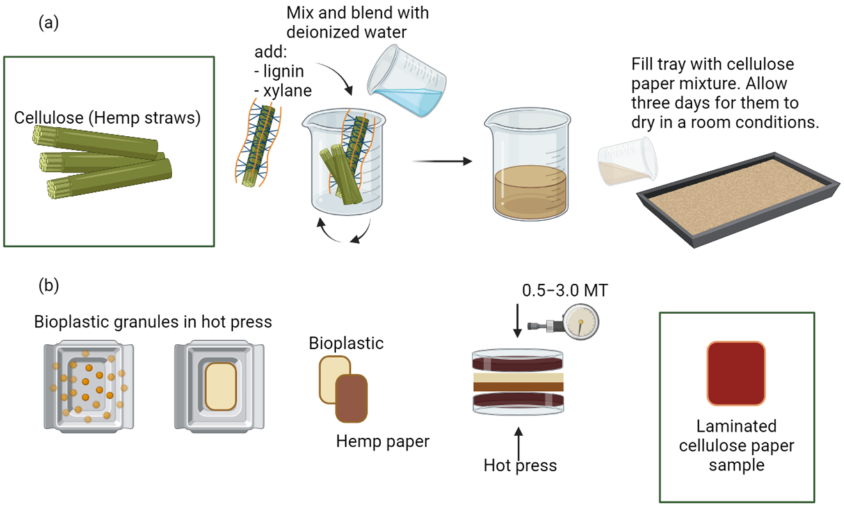

Figure 1. Scheme of (**a**) hemp paper preparation, (**b**) paper lamination process.

2.3. Cellulose Paper Lamination

PBSA, PBS, PLA, and PHA granules were dried for 24 h at 60 °C in a vacuum oven J.P. Select (Barcelona, Spain). After drying, the granules were molded into 180 µm thick films that matched the dimensions of the paper (10 × 10 cm). The hot press heating plates were set at 110 °C for PBSA, 130 °C for PBS, 180 °C for PLA, and 190 °C for PHA. The granules were preheated for 2 min, then pressed for 3 min under 3 MT (metric tons) pressure. The sample films were rapidly cooled to room temperature.

The obtained films were combined with previously prepared cast paper and pressed together. The hot plates were set at 85 °C for PBSA, 120 °C for PBS, 175 °C for PLA, and 180 °C for PHA. The laminate samples of cellulose paper were positioned at the bottom and bioplastic films at the top, then they were preheated for 2 min before being squeezed for 3 min. The applied pressure was set to 0.5, 1.5, and 3.0 MT. For all experiments, the thickness of the obtained specimens was around 400 µm. As a result of pressure, the excess polymer was squeezed out of the mold and the remaining bioplastic formed a 100 µm thick layer (obtained from the weight), while the paper formed a 300 µm thick layer. The prepared laminates are abbreviated and summarized below in Table 1. The simplified scheme of laminate preparation is presented in Figure 1b. For adhesion tests, Teflon films were inserted between paper and bioplastic to separate the layers.

Table 1. The prepared laminates.

Sample	Lamination Pressure, MT
cPBSA0.5	0.5
cPBSA1.5	1.5
cPBSA3.0	3.0
cPBS0.5	0.5
cPBS1.5	1.5
cPBS3.0	3.0
cPLA0.5	0.5
cPLA1.5	1.5
cPLA3.0	3.0
cPHA0.5	0.5
cPHA1.5	1.5
cPHA3.0	3.0

2.4. Characterization Methods

The Tinius Olsen model 25ST (Horsham, PA, USA) was used to measure tensile properties. The experiment used a 5 kN load cell with a testing crosshead speed of 1 mm/min. Five parallel measurements were recorded for each composite at 21 °C and 45% relative humidity. A peel test was performed using the same parameters.

A laboratory balance test was carried out to characterize biodegradation in composting conditions. Compost soil (swamp peat) with a pH of 6.5 was acquired from a local distributor Biolan Baltic (Pärnu, Estonia). The aerobic conditions were maintained at 58 °C and 55% soil humidity. A 58 °C temperature was selected for comparison to tests carried out according to ISO 14855, ISO 20200, and ASTM D 6400 standards for bacterial-based biodegradation. Laminates with thickness of 400 µm were cut into squares (25 mm × 25 mm), which were encased between sieves and deposited in the soil at a depth of 1.5 cm using closed plastic containers. For each sample, six parallel specimens were put together. Three samples were recovered every 5 days, dried in a vacuum oven at 60 °C for 4 h, weighed, photographed, and inserted back into the soil. Tests were carried out till it was impossible to separate laminates from the soil (up to 80 days).

In liquid nitrogen, the fracture surface morphology of nanocomposites was obtained. Images were obtained using the scanning electron microscope NovaNano SEM 650 (Hillsboro, OR, USA). The specimens were attached to standard aluminum pin stubs with electrically conductive double-sided carbon tape, and the image was generated with a 5 kV acceleration voltage.

The Mettler DMA/SDTA861e (Columbus, OH, USA) was used for dynamic mechanical analysis (DMA) of laminates and experiments were performed in tension mode. Specimens of 8.50 mm in length, 4.00 mm in width, and 0.40 mm in thickness were measured. The analysis employed a temperature range of −70 to 90 °C with a heating rate of 3 °C/min, an applied force of 10 N, an elongation of 10 µm, and a frequency of 1 Hz.

The contact angle of the laminates was measured using the sessile drop method with a Theta Lite optical tensiometer Attension® (Beijing, China). Around 1 µL of water was deposited on the surface of the specimen, and the contact angle was recorded for 10 s by measuring 12 frames per second. The measurements were recorded at 20 °C. The shape of a liquid droplet is ideally defined by the liquid's surface tension. The high-resolution camera captures a comprehensive droplet profile at the intersection and helps record it over time, allowing the contact angle to be studied afterward.

The geometry of hemp fibers was measured using images obtained with an optical microscope, Leica DMR (Leica Microsystems) (Wetzlar, Germany) at 10× magnification. The fiber length and diameter were calculated using Leica Image Suite™ and Fiji software. 100 measurements were recorded, and statistical analysis was applied to determine fiber length and diameter.

The rheological behavior of the bioplastics was investigated with Anton Paar SmartPave 102 (Graz, Austria) by utilizing a 25 mm plate-and plate configuration to carry out oscillatory shear tests at lamination temperatures. Complex viscosity was determined at a shear range of 0.1–1000 rad/s. The shear strain was increased logarithmically and nonlinearly to avoid reasonable signal intensities. The strain amplitude was fixed at 5%. The temperatures for the rheometer were set at 85 °C for PBSA, 120 °C for PBS, 175 °C for PLA, and 180 °C for PHA.

3. Results and Discussion

3.1. Structure Analysis

The scanning electron microscopy (SEM) micrographs of laminates are shown in Figure 2. Samples are between 400 and 450 µm thick. All bioplastics show good adhesion to hemp fibers, and no clear boundary layer between layers can be seen. Bioplastics form about a 100 µm thick layer above paper. It can be seen that in the case of cPBS1.5, a more uneven layer of polymer is formed and hemp fibers are mixed into it, while the other three bioplastics form a more uniform polymer layer. This could be attributed to the relatively higher viscosity of the selected PBS grade. The paper layer shows random fiber distribution, with some voids, but the overall structure of the paper shows a relatively dense structure. In the case of PLA, some defects can be observed in the middle of the paper layer, indicating some random formation of agglomerates. Except for cPLA1.5, it can be seen that bioplastics have an impregnated paper layer for at least 50 µm, thus forming a transition layer of laminate, which consists of polymer, impregnated layer, and paper. Polymer adhesion with cellulose has been extensively studied and reviewed [36]. Hydrophilic groups enhance the adhesion to cellulose, and in our case, all selected bioplastics are polyesters, thus enabling hydrogen bond formation between ester groups and hydroxyl groups. Some researchers have studied and shown good layer adhesion in SEM for bioplastics such as PHA [34] and PLA [31].

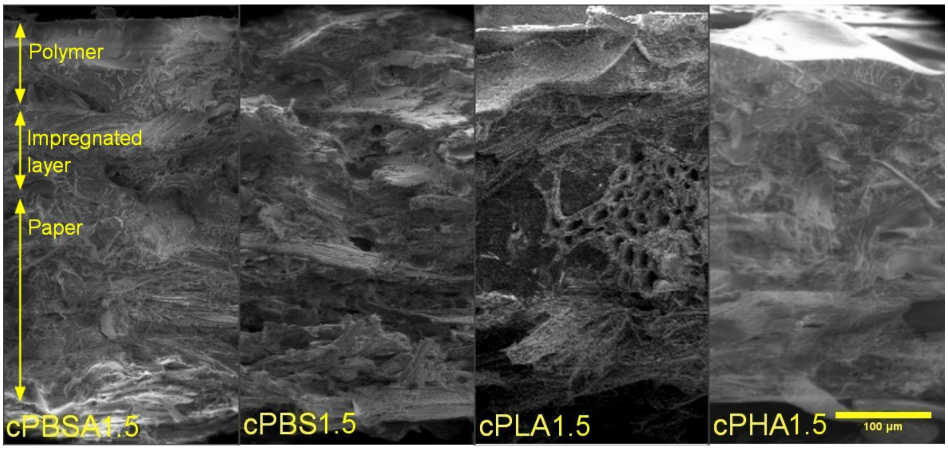

Figure 2. SEM micrographs for laminates prepared with 1.5 MT pressure.

To further understand the layer formation process, the polymer's complex viscosity was measured at lamination temperature (Figure 3). It can be seen that laminates, which show distinct paper and polymer layers, have lower complex viscosity, while higher viscosity yields more impregnated composites. However, viscosity is not the only property of a polymer that influences the polymer's interaction with a substrate. Polymer branching, surface groups, additives, surface tension, and density could be responsible for this observation. In this case, our selected polymer density was in the range of 1.23 to 1.26 g/cm^3, thus indicating that the structure of polymers could be responsible for boundary layer formation during the lamination process.

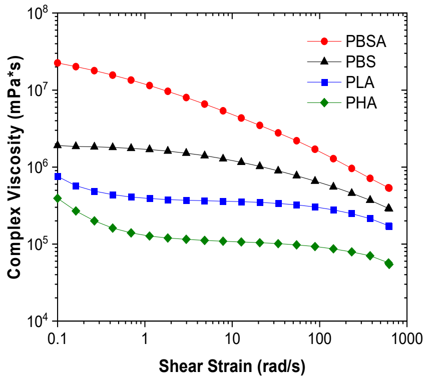

Figure 3. Bioplastic complex viscosity measured at lamination temperature.

To further understand the bioplastic lamination and impregnation processes, the contact angle was determined on the paper side of the laminates. Figure 4a shows contact angles after 4 s, while Figure 4b shows how the initial contact angle changes for up to 10 s. The water showed higher affinity towards laminates prepared with lower pressure. At 0.5 MT, the laminate paper layer shows a wetting angle of 20 ± 5°. With an increase in hot press pressure to 1.5 MT, the minimum wetting angle is 40° for cPLA1.5 but the maximum reaches 90° for cPBSA1.5. A higher wetting angle on the cellulose paper side shows changes from lamination to impregnation composite effect. The scatter of data is somewhat reduced with higher pressure showing a value distribution between 63° and 83°. In this case, we can look at two effects that could be reducing the hydrophilic nature of the surface. First, SEM already showed signs of polymer impregnation into the paper layer, and second, densification of the fiber structure could result in a denser structure, which absorbs water slower. The change in initial contact angle reflects how water is absorbed. In this case, all samples at 0.5 MT pressure show a continued decrease in contact angle. This trend is only partly observed at 1.5 MT, where PBSA and PBS show stabilization of contact angle values after the initial drop. However, for 3.0 MT, only cPHA3.0 shows a continuous drop in contact angle value.

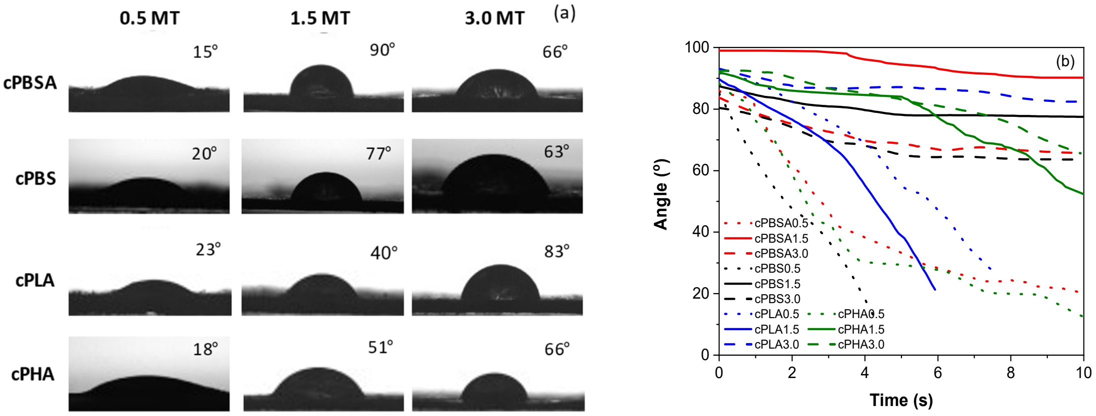

Figure 4. (**a**) Pictures of contact angles for laminates measured on the paper side and (**b**) contact angle vs. time for laminates measured on the paper side.

3.2. Mechanical Properties

The elastic modulus, tensile strength, and elongation at break for laminates prepared with different bioplastics and pressures are shown in Figure 5a–c, while representative stress–strain curves for 1.5 MT samples are presented in Figure 3. It can be seen that an increase in lamination pressure generally increased elastic modulus and tensile strength, but for elongation values of laminates prepared with 3.0 MT there was a sharp drop in recorded values except for cPLA3.0. All laminates show a 2-fold improvement in elastic modulus values when comparing 0.5 MT and 3.0 MT pressure samples. While for tensile strength generally, the highest values were achieved with 1.5 MT pressure. The drastic changes in tensile characteristics could be explained by significant structural changes induced by applied pressure during the lamination process. As observed in SEM, 1.5 MT is enough to promote thermoplastic polymer's impregnation into paper. Thus, it could be concluded that 0.5 MT mainly formed laminates, 1.5 MT induced some impregnation, and 3.0 MT strongly disrupted the structure of the paper and impregnated composites instead of laminating them. Elastic modulus and tensile strength favor impregnated composites, as stress can be distributed more evenly, while in laminates, only the most durable layer is mostly responsible for load bearing. The decrease in mechanical properties (mainly elongation) observable for laminates prepared with 3.0 MT could be explained by the strongly disrupted original structure of the paper. The slippage between fibers was limited and local defects were introduced, thus promoting the concentration of stress and early composite failure.

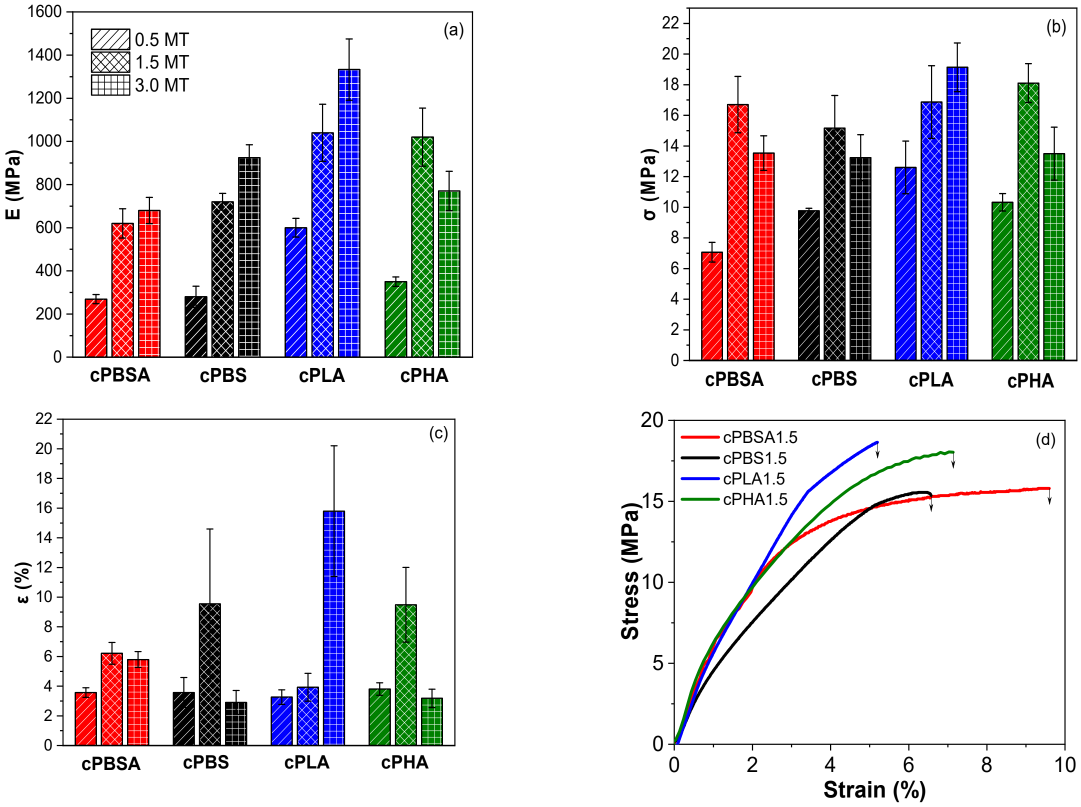

Figure 5. (**a**) Elastic modulus, (**b**) tensile strength, (**c**) elongation at break, and (**d**) representative stress–strain curves for laminates prepared with 1.5 MT pressure.

The characteristics of bioplastics were partly transferred to laminates as the polymer layer only forms about 25 vol% and 20 wt% of the laminate, while the rest is formed from hemp fibers. PBS and PBSA are known as relatively soft and ductile materials, while PLA and PHA possess high elastic modulus but are also known to be brittle. All stress–strain curves (Figure 5d) show a clear yield point, but only cPBS1.5 shows a pronounced plastic deformation region. Moreover, the upper limits of tensile strength values achieved for most bioplastics are very similar, indicating that they were limited by paper, not bioplastic. PBSA laminates showed the lowest elastic modulus, as expected, and similarly, PLA ones showed the highest. However, surprisingly, PBS and PHA laminates showed very similar performances. In addition, it is known that an increase in paper density would yield higher mechanical performance, and cellulose poses much higher mechanical properties than selected bioplastics [37]. This is mainly related to cellulose's self-adhesion due to an increase in contact surface and hydrogen bonding. Thus, the increase in mechanical properties should also be attributed to densification caused by pressure, while cast paper pressed under low pressure can recover its porosity, especially with the effect of room humidity [38].

Figure 6a shows the experimental peel test stress–strain curves for laminate strips. One grip was used to secure bioplastic while the other grip fixed paper. This setup was used to test the adhesion between layers by employing tension. It was possible to test cPBS1.5 and cPBSA1.5, but cPLA1.5 and cPHA1.5 laminates had a brittle failure of the bioplastic layer during the insertion into the grips. The results show that cPBSA1.5 and cPBS1.5 had relatively similar performance, showing almost equal maximum stress values, which stem from the paper layer failure. The scatter of data is observed for both strain and stress regions, which could be the result of inherited defects in the paper layer. Strain values are within the range of values measured in the tensile test, thus indicating that layer separation did not occur fully, thus limiting the obtainable data. The pictures of laminates presented in Figure 6b reveal a color shift introduced by more crystalline PBS and PHA, which show a significantly lighter brown color, while cPLA1.5 and cPBSA1.5 are much closer to the initial paper's dark brown color.

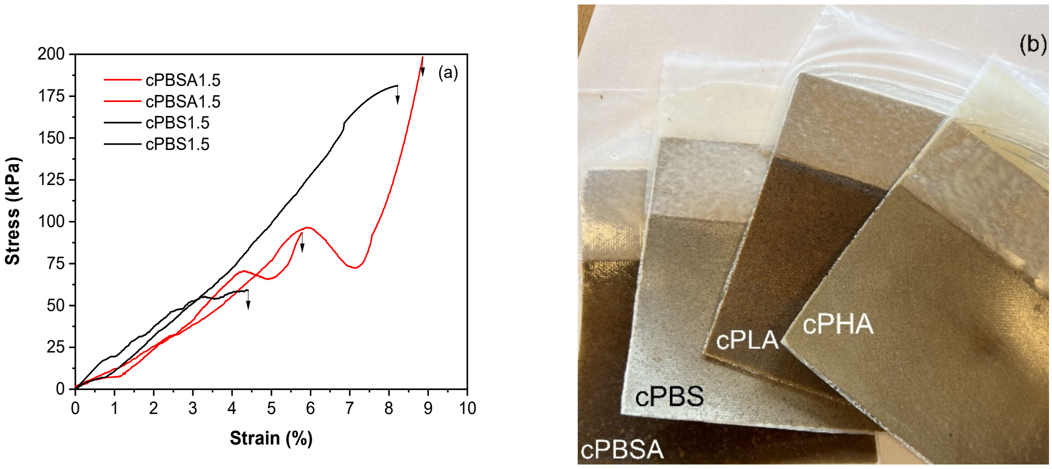

Figure 6. (**a**) Experimental adhesion peel test stress–strain curves for cPBSA1.5 and cPBS1.5 showing the highest and lowest measured values (**b**) picture of prepared laminates for peel test.

Packaging materials are often used in a relatively broad temperature range. To characterize laminate thermomechanical properties, storage modulus (E′) and tanδ were measured (Figure 7a,b). Storage modulus can be considered relatively similar to elastic modulus values obtained from tensile tests. As can be seen, the general trend is very similar at room temperature (20 °C). cPHA1.5 shows the highest values, while cPBSA1.5 and cPBS1.5 are almost equal with the lowest values that are around 2.1-fold lower compared to cPHA1.5. The general trend of storage modulus is to decrease with an increase in temperature, while a sharp drop in properties happens at the glass transition region where the polymer layer transitions into a viscoelastic state. The glass transition temperature (T_g) can be determined from the tanδ peak. This shows that T_g is −31 °C, −19 °C, and 62 °C for cPBSA1.5, cPBS1.5, and cPLA1.5, respectively. However, in the case of cPHA1.5, there is no clear glass transition peak and a broad region can be attributed to structural changes, starting from around 30 °C and going up to 90 °C. This could be related to the mixed composition of different monomers in the PHA structure. As a result, PBSA and PBS laminates show viscoelastic properties at room temperature and are more ductile, while PLA and PHA promote more rigid and brittle structures in laminates. After the glass transition, cPLA1.5 shows a sharp drop in elastic modulus values, which drop significantly below cPBSA1.5 and cPBS1.5. This further indicates the structural differences between laminates, as the impregnated layer in the middle promoted load distribution in the composite's structure. When PBSA starts to melt, nearing 85 °C, cPBSA1.5 experiences a sharp drop in properties. cPHA1.5 did not fully undergo the glass transition and remained with an exceptionally high storage modulus value of 1711 MPa at 90 °C.

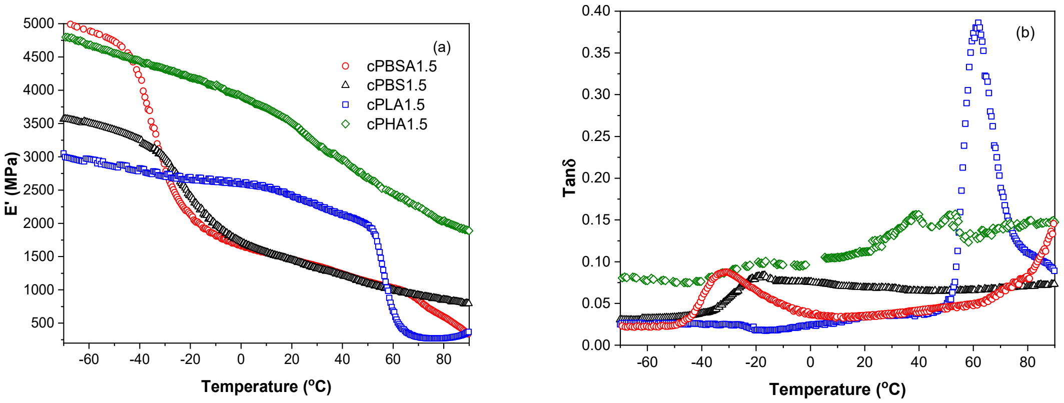

Figure 7. (**a**) Storage modulus and (**b**) tanδ curves for laminates cPBSA1.5, cPBS1.5, cPLA1.5, and cPHA1.5.

3.3. Biodegradation in Composting Conditions

Biodegradation is influenced by many factors, such as microbial activity, soil moisture content, temperature, the pH of the environment, exposed surface area, the composition and molecular weight of the polymer, and crystallinity [23,39]. Bioplastics need to have high-performance properties during use, which limits their degradability. While they are biodegradable, they do not meet various standards set for biodegradable materials, and manufacturers present them as compostable or industrially compostable, which allows them to degrade from 30 days up to half a year depending on specific conditions. However, if they are left in the environment degradation could take years [40,41]. In our case, we tried to replicate degradation conditions close to commonly studied ones in the literature by using samples with a polymer thickness of around 100 µm (total sample thickness of around 400 µm), a temperature of 58 °C, and high soil water content. Hemp fibers mainly consist of cellulose, which is hydrophilic, so water and microorganisms can easily penetrate the paper layer and reach polymer from both sides. Thus, the biodegradation of laminates should be mainly dependent on the polymer's composition.

Figure 8 shows the visual changes in cPBSA1.5, cPBS1.5, cPLA1.5, and cPHA1.5 laminates during the biodegradation process, while Figure 9 reflects the recorded mass loss during the biodegradation process. From the 10th to the 30th day, laminates lose their ductility and become frail and discolored. The surface area shows the first brown discoloration marks after 5–10 days. The most noticeable change is after 20 days when biodegradation specimens turn darker. Small cracks were observed, as well as an increase in surface texture (roughness). Finally, between the 30th and 75th-day laminates are inextricably linked to the soil and become hard to distinguish, marking the end of the observable biodegradation process. When no particles could be separated from the soil, the final degradation time was registered. For cPLA1.5 and cPHA1.5, it took significantly less time to degrade when compared to cPBSA1.5 and cPBS1.5, which needed around 30 to 40 days longer.

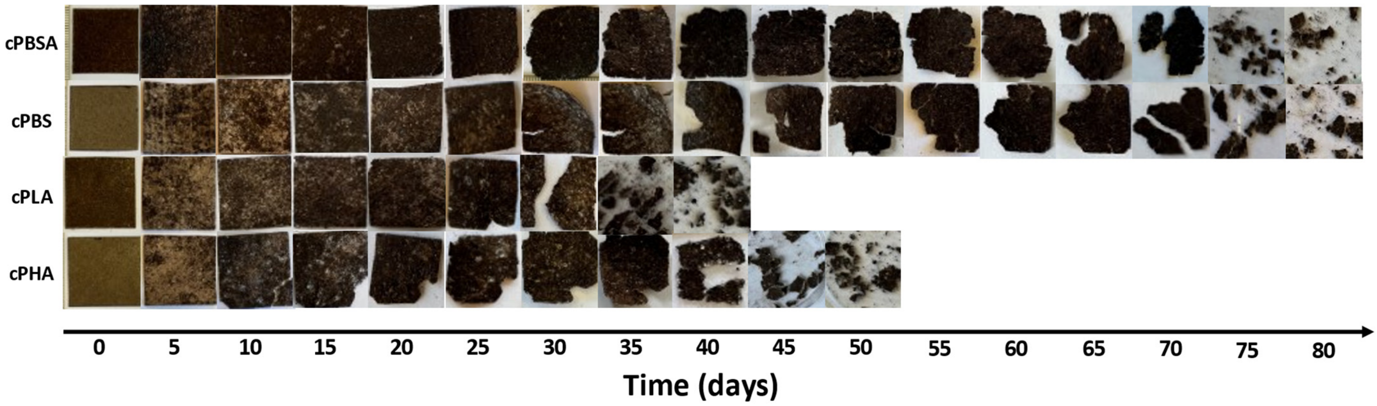

Figure 8. Photos of cPBSA1.5, cPBS1.5, cPLA1.5, and cPHA1.5 laminates during the biodegradation process in the composting conditions.

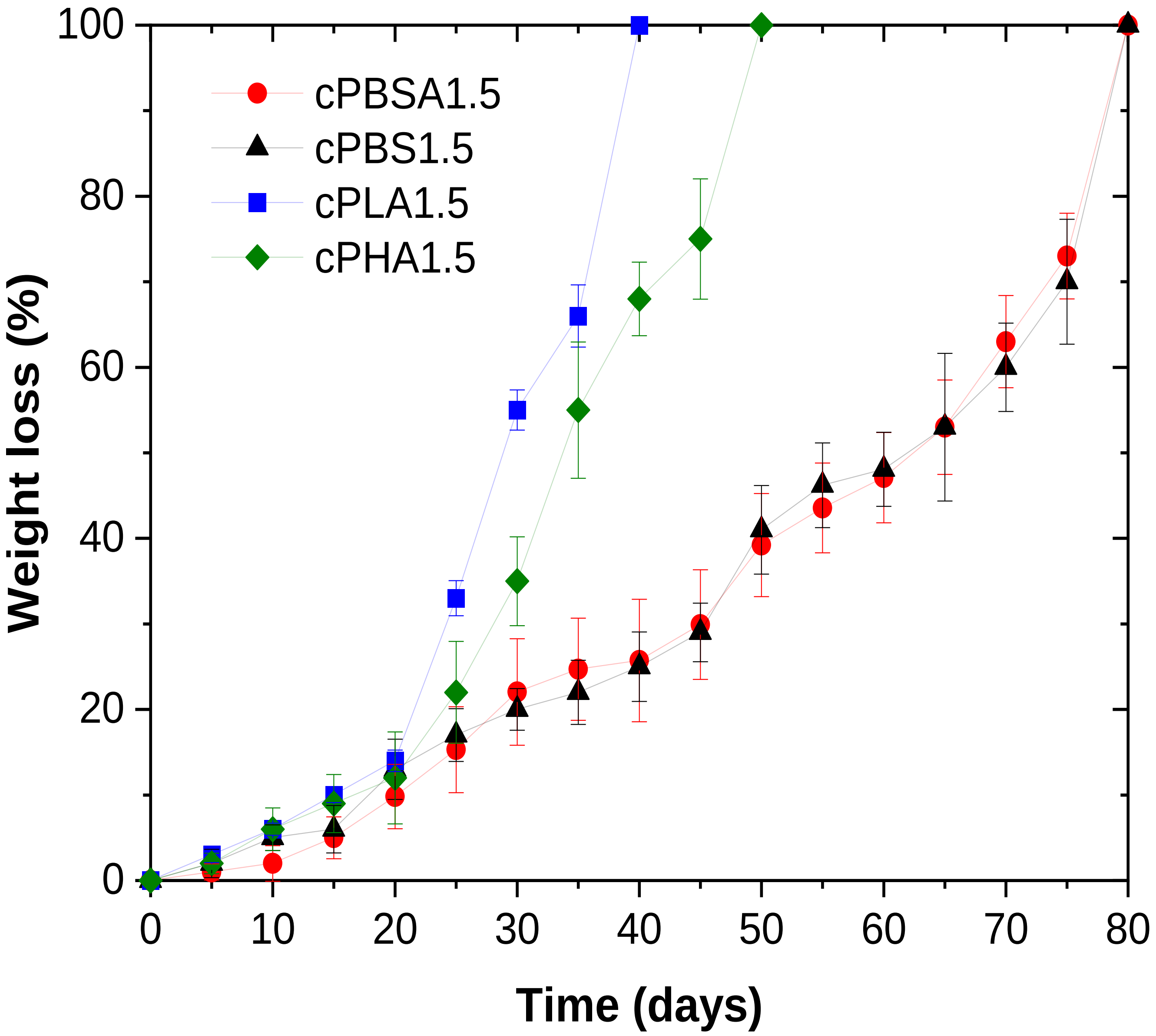

Figure 9. Cumulative weight loss of cPBSA1.5, cPBSA1.5, cPLA1.5, and cPHA1.5 laminates during biodegradation process.

Plastic sheets containing 85 wt% PHA and 15 wt% TPS with a thickness of up to 3.5 mm were shown to degrade in 12 weeks (84 days) at 40 °C in composting conditions [42]. Kunioka et al. showed that PLA powder degraded and lost 90% of mass after 20 days in a controlled compost at 58 °C [43]. In addition, authors compared it to cellulose, which degraded slower and only lost about 60% of mass. Evolved CO_2 from controlled compost at 58 °C has shown that PBS loses about 80% of its weight in 70 days [44], while gravimetric tests indicate mass loss of approximately 80% at 80 days [45]. Puchalski et al. studied tensile test dumbbell specimen degradation in compost at 58 °C and compared PBSA and PBS [3]. The thickness of specimens makes results hard to compare to other tests that use powders or films, but the authors demonstrated that PBSA degraded faster than PBS. Samantaray et al. reviewed and compared various results of biodegradation studies for different biodegradable plastics [46]. In a broad overview, the authors showed that generally, PLA is the fastest to degrade of our selected plastics, followed by PHA. PHA composition plays a significant role in degradation time, with neat PHB showing the highest degradation rate. The authors also indicated that PBS is significantly slower to degrade compared to other bioplastics and that PBSA degrades faster than PBS.

The data in the literature indicate that cellulose biodegradation could be slower than that of PLA and PHA, which explains the sharp rise in degradation speed after the 20th day for cPLA1.5 and cPHA1.5. Thus, cellulose is the one crumbling away and rapidly losing molecular weight, which shows as the final degradation time for laminates. While for cPBS1.5 and cPBSA1.5, degradation is more gradual as layers that contain polymer and cellulose impregnated with polymer degrade much slower.

4. Conclusions

This work demonstrates the compatibility of PBSA, PBS, PHA, and PLA bioplastics for the preparation of biodegradable composite laminates. By applying desired pressure on the porous cast paper, impregnation and excellent layer adhesion can be achieved. SEM images combined with contact angle analysis indicate that PBSA and PBS are much more likely to impregnate the paper at lower compression pressure. The complex viscosity of bioplastics indicates that other polymer properties, e.g., surface tension, play a significant role in the impregnation process. While the peel test showed that for specimens prepared with 1.5 MT pressure, layer separation did not occur. A tensile test showed that up to a two-fold improvement in elastic modulus and tensile strength can be achieved with an increase in compression pressure from 0.5 MT to 3.0 MT. PLA laminates yielded the highest elastic modulus. In the case of tensile strength and elongation at break, all polymers showed similar performance. The increase in tensile properties observed at higher compression pressure could be related to the densification of the paper structure, resulting from self-adhesion of cellulose fibers as well as polymer impregnation. Dynamical mechanical analysis showed that elastic modulus exhibits strong dependance on selected polymer as glassy PLA and PHA showed significantly higher energy-storing capabilities in temperatures above −20 °C. Storage modulus values favored PHA in the case of tested 1.5 MT laminates. Biodegradation studies in composting conditions showed that PLA and PHA seem to degrade even faster than cellulose (hemp fibers), which resulted in rapid degradation above 20–25 days with complete designation at 40 and 50 days for cPLA1.5 and cPHA1.5, respectively. cPBSA1.5 and cPBS1.5 demonstrated much more gradual degradation and decomposed within 80 days.

Production costs of all bioplastics have seen a gradual decrease with an increase in yearly production volumes. Despite this, they remain more costly alternatives to commonly used commodity plastics. This could be offset by exploiting more of the zero-burden resources obtained from agricultural waste to prepare low environmental impact papers. With an emerging alternative to PLA, there is a chance to adapt biodegradable composites to meet the needs of specific applications. Considering the presented results, bioplastics are very promising materials for paper laminate production in a variety of food packaging applications.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/jcs6090246/s1, Figure S1: (a) Optical microscope micrographs of the microcellulose powder (b) histograms with measured width and length data.

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