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Layer by Layer-functionalized rice husk particles: a novel and sustainable solution for particleboard production.

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Abstract

Rice husk particles from agro-wastes have been treated with a Layer by Layer (LbL) deposition of polyelectrolytes and further assembled to prepare a bio-based particle board. The all polymer system employed uses a branched polyethyleneimine combined with a polyacrylic acid. The two polyelectrolytes show a super-linear growth as demonstrated by infrared spectroscopy. A schematic description of the mechanism behind the LbL deposition on rice husk particles is proposed and discussed on the basis of electron microscopy observations. The mechanical properties of the prepared LbL-joined particle boards are evaluated and related to the unique structure and intermolecular ionic interaction occurring between the assembled polyelectrolytes. Only 2 BLs allow for the preparation of a free-standing/self-supporting material. Boards assembled with 3 and 4 BL-coated particles yielded impressive storage moduli of 1.7 and 2.2 GPa, respectively, as measured by dynamic mechanical analyses performed at different temperatures and relative humidities. When tested by three points bending mechanical tests the same materials showed an elastic moduli up to 3.2 GPa and a tensile strengths up to 12 MPa. The presented results demonstrate that the LbL functionalization of agro-waste particles represents an attractive, functional and sustainable solution for the production of mechanically strong particleboards.

Keywords: rice husk; Layer by Layer; polyelectrolytes; thermo-mechanical properties; natural boards

1. Introduction

In recent years the materials science field has been focusing more and more towards the production of ecological and sustainable materials with the aim of minimizing resource consumption, pollution release and our growing awareness of the need for a functional circular chemistry. In particular, the disposal of solid wastes generated from agricultural or industrial production represents an area of growing concerns due to the increased waste volumes related to population/urbanization growth and rising standards of living. The reuse of such wastes rather than their disposal appears to be a sustainable and appealing solution. [1] An excellent example of this is the use of raw materials derived from agro-wastes for the preparation of fiberboards and particleboards to be used as walls, ceilings, furniture panels and doors also showing how the value of a low value raw material can be significantly improved. [1][2] In our current contribution, agro-waste fibers or particles are assembled together in the final material using a thin, tailored nanostructured adhesive that serves as continuous matrix in the final material. The way this task is accomplished is strictly related to a detailed control of the composition, morphology and mechanical properties of the interfacial layers between the nanostructured adhesive and filler particles in order to control the adhesion between the modified particles and to significantly improve the properties of the final materials. Up to now, the most commonly used binders or adhesives are formaldehyde-based resins [3] that present a huge drawback due to documented toxicity during their preparation and final use.[4] Recently, attempts to replace these synthetic solutions with new bio-based binders such as soybean protein or starch have been reported opening up new possibilities for this class of materials. [5] [6] It is thus apparent that the search for new, advanced and functional adhesive solutions is of both scientific and industrial interest.

To circumvent many of the problems associated with joining agro-waste particles together into valuable products we propose the use of the Layer by Layer assembly technique (LbL) as

a functional and sustainable approach for the production of particleboards made of LbL-functionalized agricultural wastes. To this aim, rice husk (RHK) particles have been LbL-treated and then assembled, without the use of an additional binder, in boards. This is schematically described in **Figure 1**.

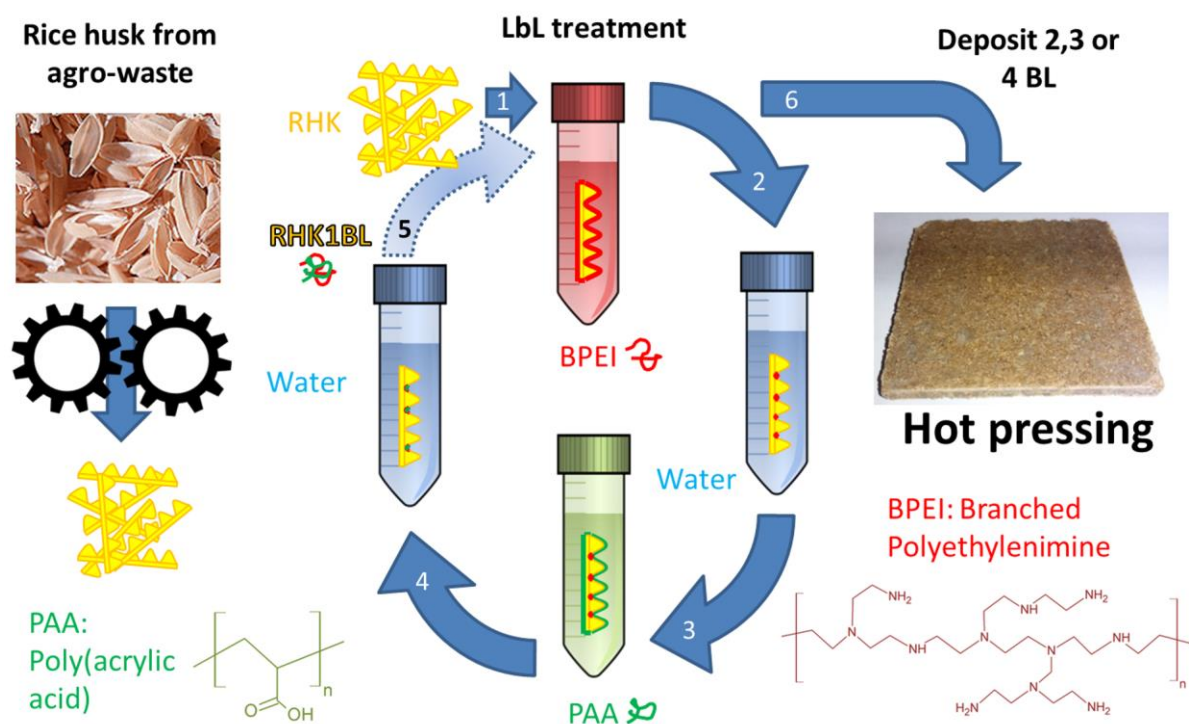


Figure 1 Schematic representation of the LbL approach has been adopted to tailor the adhesion between agro-waste particles: rice husk particles are recovered from agricultural waste, cleaned and LbL coated in order to deposit a functional nanostructured coating capable of allowing their assembly into a strong and durable particleboard.

The LbL technique represents a functional and versatile method for the step-by-step modification of solid surfaces.[7] The most common application of this technique relies on the electrostatic interaction between oppositely charged species (polyelectrolytes or nanoparticles) in aqueous medium emanating from the gain in free energy due to the release of counter-ions upon complex formation.[8] During the assembly, the substrate is alternately placed into contact with a solution/suspension containing either positively or negatively

charged species. Each step deposits, in an entropy-driven process,[9] [10] a layer containing the selected reagents (as shown in **Figure 1**). By alternating the adsorption of positively and negatively charged species it is thus possible to assemble structures in which the selected components are held together by strong electrostatic interactions occurring at the molecular scale. The properties of the deposited layer (e.g. thickness, morphology,...) vastly depend on many parameters such as the chemistry of employed species, [11] [12] [13] temperature, [14] pH and the ionic strength. [15, 16] The versatility to control the properties of the adsorbed layers, has paved the way for the use of LbL in many application fields such as gas barrier coatings,[17] [18] [19] flame retardancy, [20] [21] [22] dielectric properties [23] and antimicrobial treatments. [24] [25]

During recent years the LbL has been adopted for the deposition of nanostructured multilayers on colloids or micron scale objects such as fibers. [26] [27] [28] [29] [30] [31] In the present work, the LbL has been used for depositing functional coatings on agro-waste rice husk; an all-polymer system consisting of branched polyethylenimine (BPEI) and poly(acrylic acid) (PAA) has been selected due to the good adhesion properties imparted by BPEI and the super-linear growth regime of the BPEI/PAA system that allows to deposit thick film using comparably few deposition steps.[32] The coating serves as continuous coverage of the treated particles which subsequently forms a continuous binder/matrix when the coated rice husk particles are pressed together into self-sustained and mechanically strong particleboards. Wood is the main material employed in conventional particleboards but the use of alternative raw products has become important due to the depletion of forest resources in certain areas of the world. RHK has the same basic components as wood (i.e. cellulose, hemicellulose and lignin) with an additional content of silica and presents the undeniable advantages of being more resistant to biological attacks and having better dimensional stability when exposed to moisture than wood. [33] Additionally, the LbL approach allows for the deposition of multi-

functional nanostructured coatings (different properties can be imparted by selecting the components) using ambient application conditions (room temperature and pressure) in an eco-friendly way (water at near neutral pH is the main solvent and concentrations are typically ≤ 1 wt.-%) which can be used to tune the properties of the particle boards to fit a certain end-use application.

In our present work the LbL growth of the selected polyelectrolytes has been followed by using infrared spectroscopy analysis of treated Si wafers while the coating build-up on RHK surface has been evaluated by scanning electron microscopy observations. A very low number of BLs (3-4 BL, 15-20 % -wt) is needed in order to completely cover the RHK particles and allow their assembly in free-standing and mechanically strong particleboards, as evaluated by dynamic mechanical thermal analysis (DMTA) and three points bending tests. This study opens the way and makes it possible to more systematically design of LbL-coated particles for the production of functional materials with reduced environmental impact.

2. Materials and methods

2.1 Materials

Rice husk was kindly supplied by S.P. S.p.A. (Stroppiana (VC), Italy) Branched poly(ethylene imine) (BPEI, Mw $\sim 25,000$ by Laser Scattering, Mn $\sim 10,000$ by Gel Permeation Chromatography, as reported in the material datasheet) and poly(acrylic acid) (PAA, solution average Mw $\sim 100,000$, 35 wt.-% in water) were purchased from Sigma Aldrich (Milwaukee, WI). BPEI and PAA were dissolved in 18.2 M Ω deionized water supplied by a Q20 Millipore system (Milano, Italy) and kept under magnetic stirring overnight before use. BPEI solution had a solid content of 0.5 wt.-%, while PAA was at 1 wt.-%; the pH was kept unmodified: 10 and 3 for BPEI and PAA solution, respectively.

2.2. Layer by layer build-up on silicon wafers

Si wafers were alternately dipped into solutions of positively charged (BPEI) and negatively charged (PAA) polyelectrolytes in order to deposit a coating consisting of a bi-layer repetitive unit. After each adsorption step, the substrate was washed by static dipping in deionized water and then dried by compressed air. The dipping time was set to 3 min for both the adsorption and rinsing step.

2.3 Layer by layer formation on rice husk particles

Before the LbL treatment, rice husk particles were washed with deionized water. 5 g of RHK were placed in a 50 ml centrifuge tube, kept under stirring in deionized water for 2 min and then centrifuged at 4400 rpm for 1 min using a Eppendorf Centrifuge 5702 (Milano, Italy) in order to remove the supernatant and collect the precipitated RHK particles. This process was repeated two times. Then, the LbL-functionalization was carried out, as schematically shown in **Figure 1**. The wet particles, collected after centrifugation, were re-suspended, by pouring 45 ml of the BPEI or PAA solution inside the tube, and kept under stirring for 2 min. The suspension was then centrifuged for 1 min as described above and the supernatant removed. After each adsorption step the collected particles were washed with deionized water for 2 min and then centrifuged again using the same conditions as reported earlier. The process was repeated until 2, 3 and 4 BL were deposited. The samples are hereafter coded as a function of the bi-layer number deposited on the surface (i.e. the RHK sample covered by one bilayer was coded as RHK1BL). The materials collected at the end of the deposition cycles were either used as coated particles for characterization or used for the production of the particleboards as described below.

2.4 Rice husk particle assembly

Particleboards made with LbL coated rice husk particles were produced by hot pressing using a Collin P200T table-top platen press (Ebersberg, Germany).

The wet particles retrieved after LbL assembly were spread in the specimen mold and pressed with an increasing temperature from 110 to 140°C for 6 min, as reported in **Figure S2** (Supporting Information). During that time the mold was continuously opened and closed to degas water vapor. At the end of this process, a final pressure of 10 MPa was maintained for 1 min. Subsequently, the mold was cooled till room temperature and the sample (50x50x3 mm³) removed.

2.5 Evaluation of LbL coating content

A gravimetric method was employed to evaluate the final amount of LbL coating in the assembled particleboards. 1±0.1g of the final boards and reference RHK were thermally treated in a muffle furnace at 800°C for 1 h (in air) in order to remove the organic content. The residues collected at the end of the test were comprised of white silica powder which percentage is characteristic for the reference RHK. By evaluating the difference between the reference and LbL coated RHK the coating content has been calculated using the following equation:

$$coating\ content\ \% = \left(1 - \frac{\%residue\ from\ LbL\ coated\ RHK}{\%residue\ from\ reference\ RHK}\right) * 100$$

2.6 Specimen preparation for analysis

All the specimens used for DMTA (10x50x3 mm³), thermogravimetric analyses and scanning electron observations were prepared by cutting the corresponding board obtained by compression molding. For the water absorption, the 50x50x3 mm³ specimens were directly used.

2.7 Characterization techniques

Fourier Transform InfraRed spectroscopy: the growth of the LbL assembly was monitored using a Frontier FT-IR/FIR spectrophotometer (16 scans and 4 cm⁻¹ resolution, Perkin Elmer). IR spectra were acquired after each deposition step.

Scanning Electron Microscopy: the particle surface morphology was studied using a Field Emission Scanning Electron Microscopy (FE-SEM) on a ZEISS, FEG MERLIN model. The neat and treated particles were directly attached to the sample holders and chrome metallized prior to FE-SEM imaging. The cross section morphology of the prepared boards was studied using a LEO-1450VP Scanning Electron Microscope - SEM - (beam voltage: 20 kV). The samples were obtained by cutting 3 mm thick specimen. These pieces were pinned up to conductive adhesive tapes and gold-metallized.

Thermal stability: thermogravimetric analysis (TGA) was carried out both in nitrogen and in air, from 50 to 800°C with a heating rate of 10°C/min, using a TA Q500 thermo balance (TA Instruments) (experimental error: ± 0.5 wt.-%, $\pm 1^\circ\text{C}$). The samples (ca. 10 mg) were placed in open alumina pans and fluxed with nitrogen or air (gas flow: 60 ml/min). $T_{10\%}$ (temperature, at which 10% weight loss occurs), T_{\max} (temperature, at which maximum weight loss rate is achieved) and the mass of the final residues at 800°C were evaluated.

Water absorption properties: water content at different relative humidity was calculated with progressive weight control on compression mold samples (50x50x3 mm³) until constant weight was reached. These results were expressed as percentage of weight increase with respect to the weight in initial dry condition. The water absorption was assessed by measuring the weight of the specimens after 2 h and 24 h of immersion in water following the ABNT NBR 18810 and EN317 standards.

Thermo-mechanical analysis: Dynamic mechanical thermal analysis (DMTA) were performed using a DMA Q800 (TA Instruments) in single cantilever configuration. The following experimental conditions were adopted: temperature range from 30 to 120 °C in air, heating rate of 3 °C/min, 1 Hz frequency and 0.05% of oscillation amplitude in strain-controlled mode. The storage modulus (E') and $\tan\delta$ curve were measured. For each

formulation, the test was repeated two times and the experimental error was calculated as standard deviation for all the measured parameters.

Mechanical Analysis: Three point bending tests were performed at room temperature ($23\pm1^{\circ}\text{C}$) by using a Zwick Roell Z100 machine equipped with a loading cell of 5 kN. The tests were carried out with a span of 45 mm with a loading speed of 2 mm/min. The specimen was placed on two supports with a radius of 5 mm, and the actuator with the same radius applied a force in the middle of the two supports.

Three specimens were used for each formulation and the average values and corresponding standard deviations were calculated. These tests provided the Young's modulus values (E) and maximum tensile strength (σ) of the materials.

Prior to the three-point bending mechanical tests, all the samples were conditioned at $23\pm1^{\circ}\text{C}$ and 50% R.H., in a climate-controlled chamber Binder BFK240 for a minimum of 3 days, until reaching constant weight.

3. Results and Discussion

3.1 Coating growth and assembly on rice husk particles

The LbL assembly of BPEI and PAA on silica has been monitored by FTIR in order to evaluate the growth regime of employed polyelectrolytes at the selected deposition conditions. Then, FE-SEM observations have been employed in order to evaluate the coating deposition on rice husk particles.

3.1.1 Coating growth by FT-IR

The coating growth has been assessed by FT-IR spectroscopy on Si wafers. First of all, the spectrum of each layer constituent has been registered (**Figure S2** in Supporting Information). BPEI shows characteristic signals at 1640 cm^{-1} (NH_3^+ asymmetric stretching), 1570 cm^{-1} (NH_2 deformation bending and NH_3^+ asymmetric stretching), 1475 cm^{-1} (NH deformation bending and NH_3^+ symmetric stretching) as well as CH_2 signals at 1410 and 1310 cm^{-1} (CH_2 deformation and twisting bending).[34] Weak signals in the range $1180\text{-}975\text{ cm}^{-1}$ are ascribed to C-N stretching vibration. [34] PAA spectrum yields signals at 1720 cm^{-1} (C=O stretching), 1455 cm^{-1} (CH_2 deformation bending) and 1415 and 1255 cm^{-1} (C-O stretching coupled with O-H bending).[35] The LbL assembly of BPEI and PAA as monitored by FT-IR spectroscopy is shown in **Figure 2**.

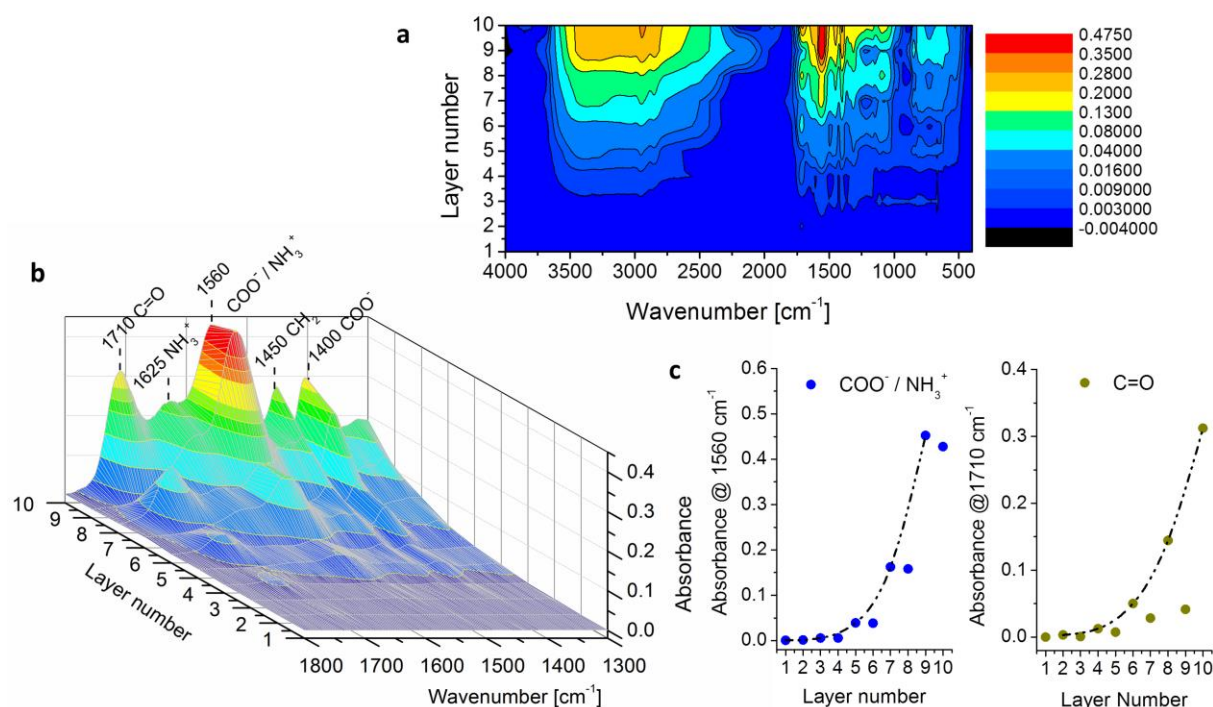


Figure 2 Coating growth by infrared spectroscopy of BPEI and PAA on silica : a) intensity surface plot as a function of each deposited layer (even numbers refer to BPEI adsorption, odd numbers to PAA), b) 3D projection of restricted IR region between 1300 and 1800 cm^{-1} and c) intensities of signals at 1560 and 1710 cm^{-1} as a function of layer number.

When the BPEI and PAA are LbL assembled they yield a steady coating growth with signals that increase in intensity after each deposition step (**Figures 2a** and **2b**). Characteristic signals of both components are found at 1710 cm^{-1} (C-O stretching), 1625 cm^{-1} (NH_3^+ asymmetric stretching), 1560 cm^{-1} (NH_3^+ and COO^- asymmetric stretching), 1450 cm^{-1} (CH_2 deformation) and 1400 cm^{-1} (COO^- symmetric stretching and CH_2 twisting). Of particular interest is the behavior of PAA C=O and COO^- signals; indeed, the intensity of the former increases at each PAA adsorption step and it is significantly reduced after BPEI adsorption (*compare* intensity of signal at 1710 cm^{-1} at odd and even numbers in **Figure 2c**). On the other hand, COO^- signal (1560 cm^{-1}) increases at each BPEI adsorption and remains almost constant after PAA deposition, as shown in **Figure 2c**. This can be easily explained by considering that the

degree of ionization of PAA carboxyl groups is strongly pH dependent.[36] Indeed, during PAA adsorption step, the pH of its solution is acidic (pH 3-4) and the ionization degree is low (below 5%), thus most of the carboxyl groups of the adsorbed PAA exist in the non-ionized COOH form, yielding an IR peak at 1710 cm^{-1} . Conversely, during BPEI adsorption, the adsorbed PAA is exposed to basic pH values (pH = 9-10), which triggers the dissociation of non-ionized carboxyl groups into COO^- with a subsequent increase of related IR band (1560 cm^{-1}) and hence a strong decrease of the COOH signal (1710 cm^{-1}).[37] [38]

Finally, the intensity vs. layer number plots of signals at 1560 and 1710 cm^{-1} (**Figure 2c**) clearly point out the super-linear growth regime of this BPEI/PAA assembly. This is in accordance with literature values where BPEI and PAA were LbL assembled in similar pH conditions, although at different concentrations, yielding highly interdiffused coatings.[32] Such super-linear growth is very useful as it allows for the deposition of thick coatings containing even at low BL numbers, thus matching the requirements for being adopted as efficient surface modification tool for RHK particles.

3.1.2 Morphology of coating on rice husk particles

It is well known that RHK is characterized by different surface morphologies: the outer surface is uneven with evenly distributed globular protrusions while the inner one is smoother with few defects (**Figure S3**). [5, 33, 39] Such difference is normally ascribed to the different functions of the two surfaces and is the result of the nature engineering process that provided RHK with a thick, lignified and heavily silicified outer shell capable of withstanding harsh environmental conditions.[40] As far as the surface composition is concerned, it is possible to find, in different proportions depending on the surface considered, polar functional groups such as C-OH characteristic of cellulose, hemicellulose and lignin or Si-OH characteristic silica. [39] Indeed, elemental analyses performed in previous works demonstrated the presence of silica within the entire thickness of RHK but with higher concentration in the outer part. ⁵ [40] [41] The different morphology is kept after grinding RHK into particles having dimensions ranging from 10 to 1000 μm as demonstrated by FE-SEM observation (**Figures S3a** and **3b**). **Figure S3** reports a schematic representation of RHK particles morphology and composition, such features will be considered for a proper understanding of both the LbL assembly and the following board production.

RHK particles were LbL-treated following the procedure described in the materials and method section depositing 2, 3 or 4 BL. Then, LbL-coated particles have been imaged by FE-SEM microscopy in order to investigate the changes in surface morphology imparted by the LbL deposition. **Figure 3** reports collected micrographs and a schematic description of the LbL deposition growth on RHK particles.

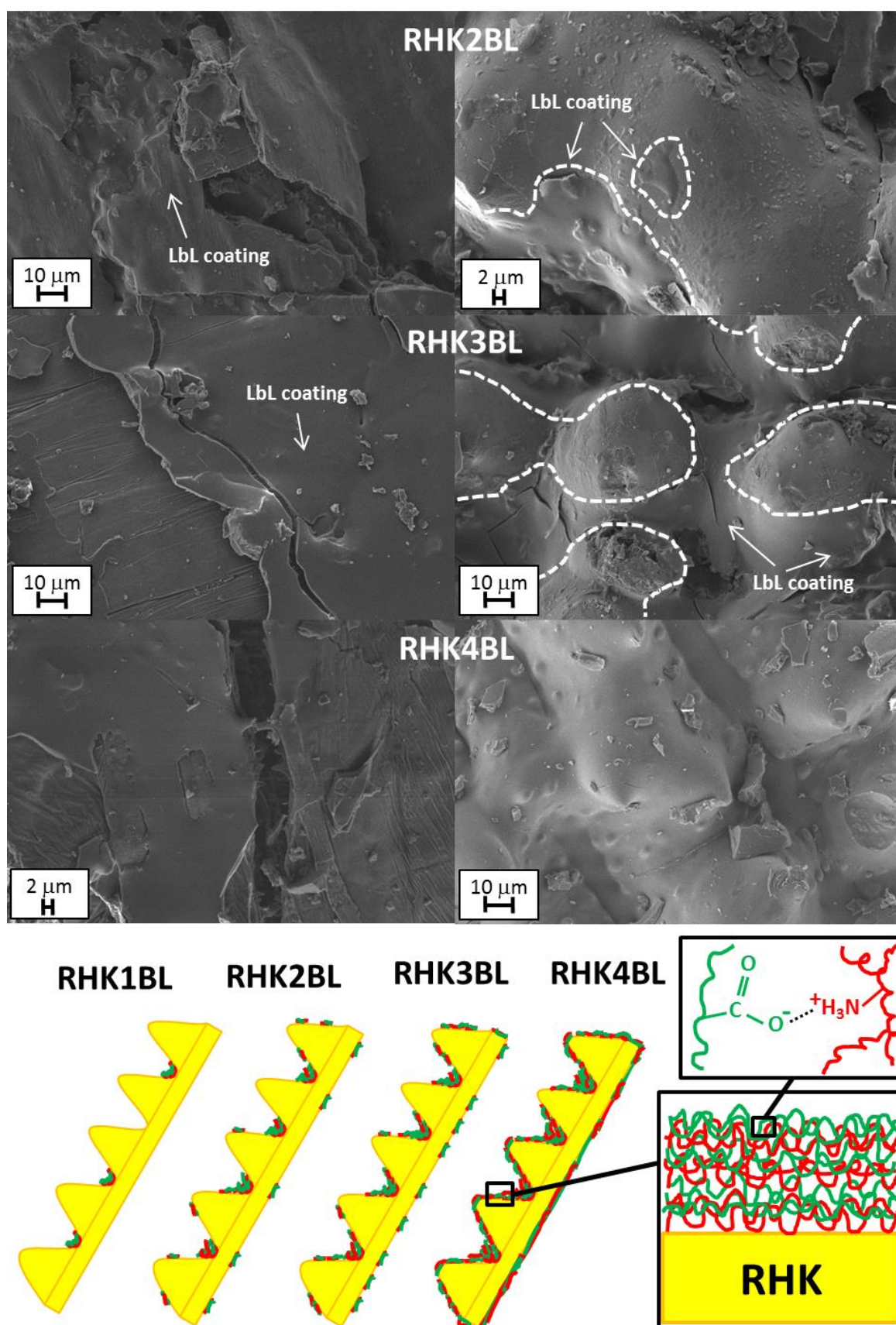


Figure 3 FE-SEM magnifications of inner (left) and outer (right) part of coated RHK particles and a schematic LbL deposition description.

1 BL sample was not significantly different in comparison with pristine RHK because the amount of coating is not enough to be detected with the SEM methodology. After the deposition of 2 BL, the outer highly undulated surface clearly shows a change in morphology with the formation of smooth regions (as marked in **Figure 3**) that are mainly found in the valleys between the protrusions and are ascribed to the deposited LbL coating.

On the other hand, the inner surface seemed to be not altered by the deposition as the presence of the coating is more difficult to detect. Indeed, here only small portions of the surface present a smooth morphology similar to that already observed on the outer surface.

By increasing the BL number, the coverage of the outer surface is gradually increased. At 3 BL, signs of the LbL treatment are not only pointed out in the valleys but also on the protrusions leaving only the top uncovered (*see* RHK3BL in **Figure 3**). Moreover, the inner surface is now partially covered by the deposited layers, as evidenced by a very smooth surface in contrast with the typical fibrous alignment of the unmodified RHK particles, which is only visible in some uncoated regions.

Finally, the fourth BL was able to completely cover the conical protrusions in the outer surface and completely fill the valleys. Indeed, as reported in **Figure 3** for RHK4BL, the protrusions are less evident than the previous samples. The inner surface of RHK is quite completely covered by the coating. On the basis of the observed morphologies, it is possible to prepare a schematic description of the LbL deposition on RHK particles. The LbL formation follows an island growth procedure likely ascribed to the RHK surfaces that are naturally uneven and partially damaged due to the grinding process (*see* **Figure S3 c and d**). These defects provide preferential adsorption spots for the polyelectrolytes during the first deposition steps; subsequently, by increasing the BL number, the so-formed islands grow both in thickness and radius. In this way the initial and separated islands increase in shape and spread on the surface until coalesce into a more complete coverage of the surface. The valleys

on the outer surface act as preferential site for coating deposition during the first BL. From there, the coating can grow until it completely covers the entire protrusion. The inner surface shows a similar behavior but the formation of islands and their subsequently coalescence takes place at a reduced growth with respect to the outer surface. Indeed, for this latter surface the coating appears to be thicker. Nevertheless, the proposed LbL deposition can be considered very efficient as only 4 BL are needed to completely cover the particles with highly interpenetrated polyelectrolyte coatings as schematically depicted in **Figure 3**. Such fast growth and coating spread upon the surface of RHK can be certainly related to the super-linear growth exhibited by BPEI and PAA. There is no direct explanation to the island growth mechanism for these solid substrates but the island growth process has been used to explain the super-linear growth of LbLs which is accordance with the present results. [42] Thus, on the basis of observed morphology and the proposed LbL growth mechanism it can be concluded that the surface morphology rather than surface chemistry plays a predominant role in promoting the LbL formation and growth. The wet particles coated with 2, 3 and 4 BL were assembled in the final materials with a compression molding machine (**Figure S1**). The resulting particleboards were characterized regarding morphology, thermal stability, water absorbance and the mechanical behavior point of view.

3.2 Morphological characterization of particleboards

The morphology of the particleboards has been investigated by SEM observations on cross sections in order to evaluate the ability of the LbL treatment to connect the particles in the assembled board. The collected cross section micrographs are reported in **Figure 4**.

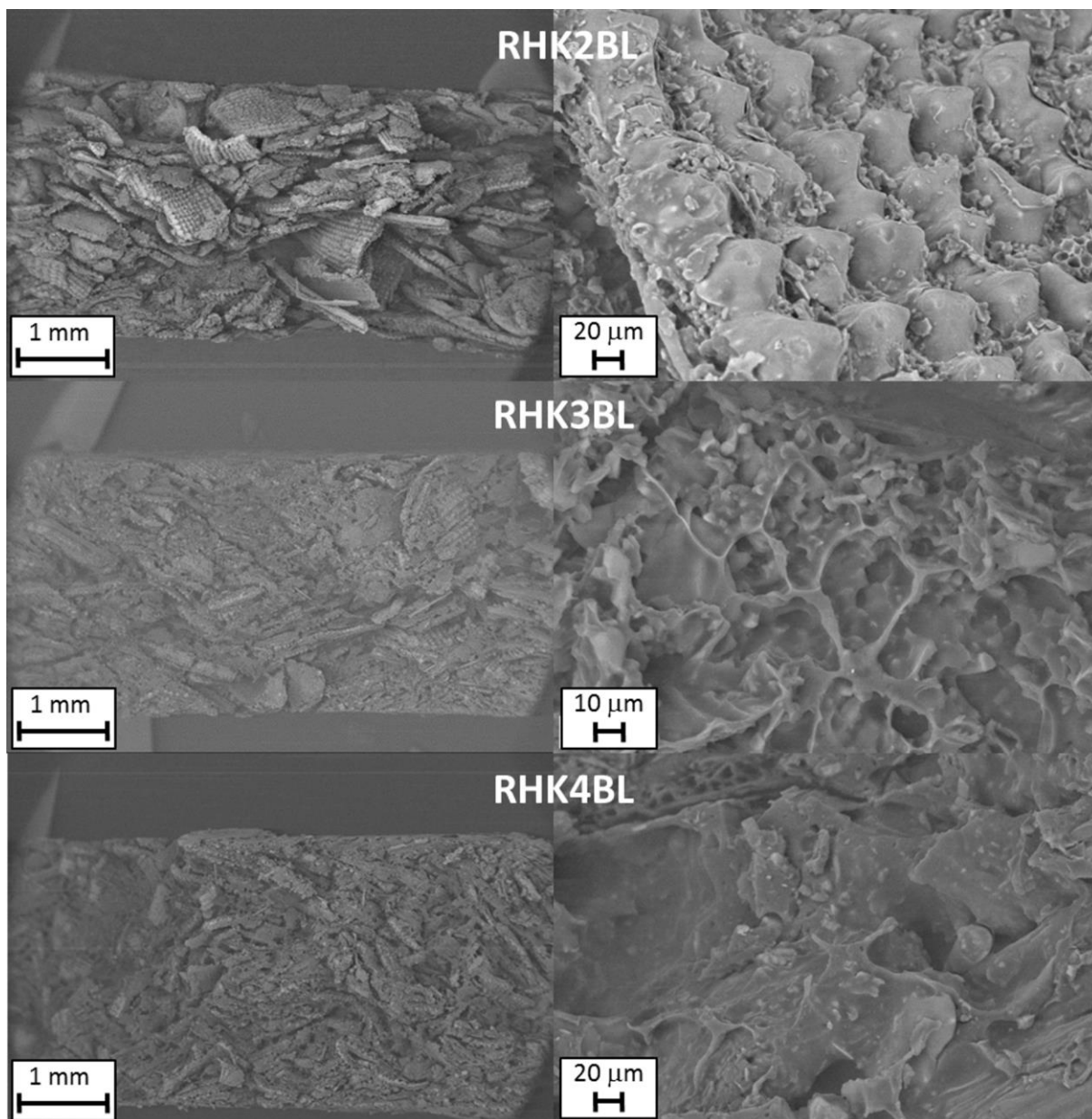


Figure 4 SEM micrographs of RHK2BL, RHK3BL and RHK4BL.

The RHK2BL sample shows a cross section in which the particles are packed together with many empty spaces in between them. In the points where there is a contact between the particles the LbL treatment can create few connections that might provide enough mechanical strength to maintain an overall integrity of the particle board. The RHK3BL sample has a completely different morphology. The particles are no longer isolated from each other but well interconnected by the LbL deposited polymers which is especially evident in the

micrograph with a higher magnification. The connection structure is not completely filled as empty spaces can still be detected. The RHK4BL is similar to the RHK3BL but with reduced internal cavities resembling a traditional composite with the filler surrounded by a continuous matrix made of LbL assembled BPEI/PAA. The minimum amount of LbL coating to hold together RHK particles has been evaluated as 4.5 % for RHK2BL; the more stable RHK3BL and RHK4BL are achieved with a deposited amount of 14.7 and 19.7%, respectively.

The apparent density of the samples has been calculated according to the EN 323 standard demonstrating a direct relationship between density and deposited BLs. Indeed, densities of 722, 882 and 1025 kg/m³ were found for RHK2BL, RHK3BL and RHK4BL, respectively. This is in accordance with SEM observations and provides a quantitative characterization of the cavities observed within the boards. According to the ANSI A208.1 standard, the calculated densities classify the prepared particleboards as high-density which is a very interesting results considering the few and very simple treatment steps.

3.3 Thermal characterization of particleboards

The thermal and thermo-oxidative stability of LbL treated RHK particleboards have been evaluated by means of thermogravimetric analyses. The aim is to evaluate whether the deposition of a LbL coating can modify the thermal and thermo-oxidative stability of the RHK, thus affecting the material behavior during particleboards preparation. The thermogravimetry (TG) and the derived curves (dTG) obtained under nitrogen and air are shown in **Figure 5**.

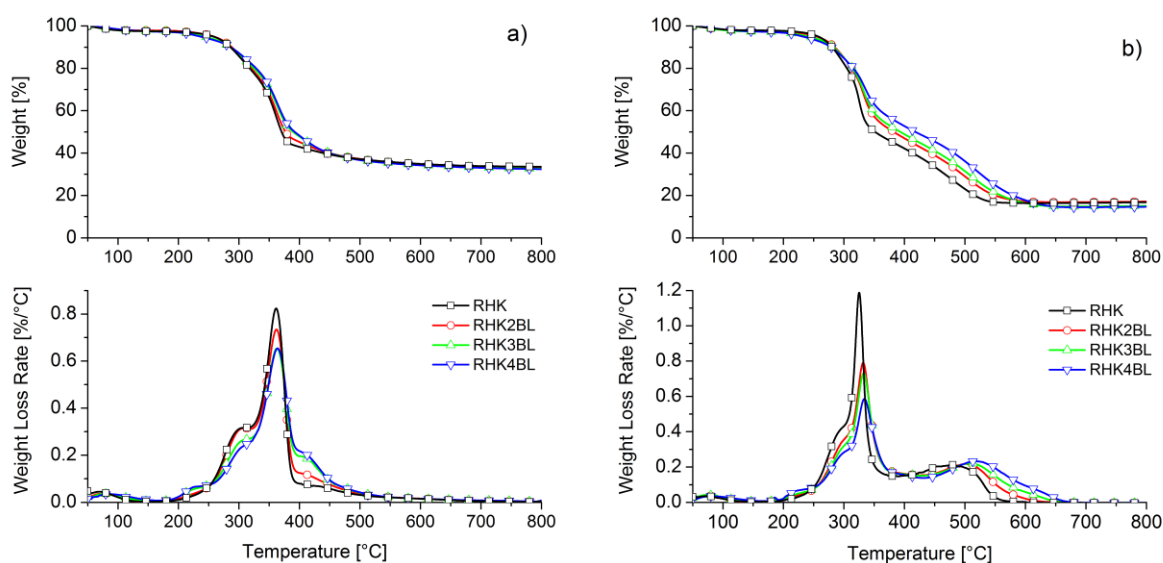


Figure 5. TG and dTG curves of neat and LbL-treated RHK in nitrogen (a) and air (b).

Table 1. Thermogravimetric data of untreated and treated LbL-particles

| Sample | Nitrogen | | | Air | | | |
|--------|------------------|------------------|---------|------------------|-------------------|-------------------|---------|
| | T _{10%} | T _{max} | Residue | T _{10%} | T _{max1} | T _{max2} | Residue |
| | [°C] | [°C] | [%] | [°C] | [°C] | [°C] | [%] |
| RHK | 275 | 361 | 33 | 274 | 325 | 482 | 17 |
| RHK2BL | 288 | 362 | 33 | 284 | 331 | 500 | 17 |
| RHK3BL | 286 | 363 | 32 | 282 | 332 | 509 | 15 |
| RHK4BL | 286 | 364 | 32 | 279 | 334 | 519 | 15 |

As usually occurs for ligno-cellulosic compounds, RHK thermal decomposition takes place between 200 and 400°C and account for around 50% of the total weight loss, as reported in TG and dTG curves. An initial weight loss occurring in between 100-150°C is related to removal of firmly adsorbed water (about 5% of the total weight) and is present in both neat and LbL-modified samples. The first degradation step (15%) takes place at around 305°C and

it is due to the depolymerization of hemicelluloses and amorphous cellulose to volatile fragments. [5] The second and main degradation step occurs at 352°C and is associated to crystalline cellulose (25% of the total weight loss). The degradation of lignin is found within the above mentioned steps as it normally shows a wide range of degradation temperatures. The residue at 800°C is mostly composed of carbonaceous products from the cellulose and lignin degradation and the inorganic silica fraction originally present in RHK, and accounts for about 33% of the original weight, in agreement with earlier investigations. [5]

The deposition of a LbL coating on RHK particles does not affect its thermal degradation that still occurs in two steps; however, the temperatures at which such degradation starts and reach the maximum are shifted to higher values as demonstrated by $T_{10\%}$ and T_{\max} reported in **Table 1**.

This could be ascribed to the removal of low molecular weight waxes and fatty acids during the LbL deposition as a consequence of the acid and basic pH of PAA and BPEI solution, respectively. Such low molecular weight components are likely to have limited thermal stability and would start to degrade earlier with respect to the other RHK components.

The final residue shows a 1% reduction with respect to neat RHK. This is ascribed to the deposited BPEI/PAA layers that degrade together with the RHK organic part. It is noteworthy that treated all LbL-treated RHK were as stable as the original RHK up to over 200°C, which is higher than the temperature used in the production of particleboards (140°C). Thus, no thermal degradation of coated RHK during processing operations is expected.

The thermal degradation was also performed under oxidative atmosphere (**Figure 4b**). In air the decomposition mechanism of the organic components does not significantly change but occurs at lower temperatures with respect to what happens in nitrogen (*compare* $T_{10\%}$ values in nitrogen and air listed in **Table 1**). The organic char produced during the above mentioned degradation steps is then oxidized between 380 and 600°C, leaving a residue which is made

almost exclusively of silica. This residue is 17% for neat RHK and is decreased to 15% for RHK3BL and RHK4BL due to the presence of the organic LbL coating. Once again as observed in nitrogen, the effect of the LbL deposition is to delay the thermal degradation and, in these latter measurements, the oxidation of the RHK organic components, as clearly noticeable from $T_{\max 1}$ and $T_{\max 2}$ values reported in **Table 1**. Surprisingly, the delay in char oxidation is found proportional to the deposited BL number reaching a maximum $\Delta T=37^{\circ}\text{C}$ with 4BL.

3.4 Water adsorption and absorption of particleboards

As already discussed in a previous paper, [43] [44] it is very important to assess the effects of humid environments on these bio-based materials as water adsorption can be rapid and large and will dramatically change the properties of produced particleboards. Water adsorption/absorption tests have been performed by exposing prepared particleboards to controlled humid environments (50 and 75% R.H at 23°C) or by immersion in water (2 or 24 hours at 28°C). Collected results are reported in **Table 2**. The data clearly show that the water absorption is significantly affected by the relative humidity, and slightly raised by increasing the BL number. However, the water content for all the samples is still under the limit of the EN 322 norm that fixes a weight gain threshold at 13% for a relative humidity of 65% and a temperature of 20°C , which are less severe demanding than the 23°C and 75% R.H. adopted here. The results here presented are comparable with what already reported in literature for natural particleboards using either starch (weight gain: 6,7%) or urea-formaldehyde (weight gain: 8.29-8.75%) as binder. [44] [45]

The water absorption was also measured after 2 h and 24 h immersion in water. As reported in **Table 2**, the water uptake values are very similar regardless of the deposited BL number (15 and 30% weight gain were measured after 2 h and 24 h, respectively). No visual change in shape (specimen warping or deformation) was observed at the end of the test. Such findings

stress that water absorption due to water immersion is not affected by the deposited coatings but is rather mainly depending on hygroscopic nature of the RHK.

In a previous research, [45] particleboards produced with wood, bamboo and rice straw with urea-formaldehyde adhesive showed a comparable water absorption after 2h (10-23%) and higher value after 24 h of immersion in water (43-72%).

Table 2. Water absorption data of particleboards

| Sample | Water content after exposure at 23°C | | Water content after | Water content after |
|--------|--------------------------------------|--------------|----------------------------|-----------------------------|
| | 50% R.H. [%] | 75% R.H. [%] | 2 h immersion at 28 °C [%] | 24 h immersion at 28 °C [%] |
| RHK2BL | 7.5±0.1 | 10.5±0.1 | 15.2±2.0 | 34.2±2.0 |
| RHK3BL | 7.9±0.1 | 11.8±0.1 | 15.5±2.0 | 31.2±2.0 |
| RHK4BL | 7.9±0.1 | 12.6±0.1 | 14.8±2.0 | 36.7±2.0 |

3.5 Thermo-mechanical properties of particleboards

In order to evaluate the practical application of the prepared particle boards, the mechanical properties of prepared particleboards were evaluated. To this aim, DMTA analyses in bending configuration were carried out at different relative humidity in the temperature range from 30 to 100°C to clarify the dependence of these two factors. The collected storage modulus (E') results as a function of temperature are shown in **Figure 6** and the data at 30°C listed in **Table 3**. Moreover, the EN 310 standard test was applied on the 3 BL and 4 BL specimens with a dynamometer in tree point bending configuration are also shown. This last test is useful to assess the suitability of the materials for a practical application. The modulus of elasticity (E) and the bending strength (σ) deduced from these tests are also summarised in **Table 3**.

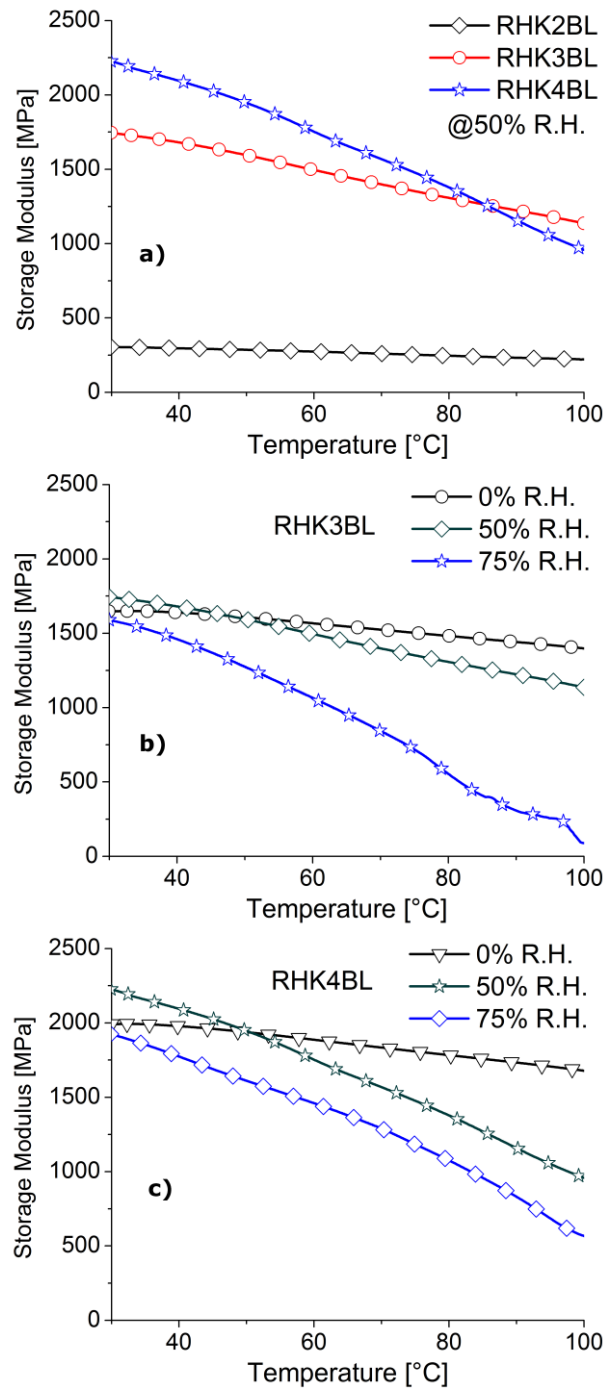


Figure 6 Storage modulus as a function of temperature for a particle board at 50% R.H. (a) and at different R.H. conditions for 3 BL (b) and for 4 BL (c).

Table 3. Data collected by DMTA and three point bending.

| Sample | E' at 30°C, DMTA | | | Three point bending | |
|--------|------------------|----------|----------|---------------------|-----------------------|
| | 0% R.H. | 50% R.H. | 75% R.H. | E at 23°C, | σ max at 23°C, |
| | [MPa] | [MPa] | [MPa] | 50% R.H. [Mpa] | 50% R.H. [Mpa] |
| RHK2BL | 176* | 305* | 210* | - | - |
| RHK3BL | 1650* | 1740* | 1590* | 2309±400 | 8.9±2.1 |
| RHK4BL | 2030* | 2220* | 1920* | 3201±614 | 12.0±2.6 |

* standard deviation = $\pm 10\%$

First, the storage modulus of particleboards has been evaluated at 50% relative humidity that represents an ordinary condition of testing. The resulting E' modulus reaches values around 300, 1700 and 2200 MPa at 30°C for RHK2BL, RHK3BL and RHK4BL, respectively.

By increasing the temperature, E' is obviously reduced; surprisingly, samples treated with 3 and 4 BL are able to maintain a modulus over 1.0 GPa up to 100°C. These values support the removal of voids with the LbL treatment as observed in the SEM micrographs (*see Figure 4*). The results also show that the very low modulus of RHK2BL is dramatically increased with the addition of more BLs that progressively fill the spaces between particles. In this way, the E' values reached by 3 BL and 4 BL are normally suitable for applications where high mechanical properties are required. Such finding demonstrates the high efficiency of the selected LbL assembly in binding the RHK particle together and providing strong mechanical properties with very few deposited layers. Indeed, E' moduli at 30°C of RHK3BL and RHK4BL are greater than what found in a previous work with 40 wt.% of starch as binder (1300 MPa). [44] The main reasons for the observed properties are identified in the documented super-linear growth and the strong intermolecular ionic interaction occurring

between BPEI and PAA. Indeed, the highly interpenetrated BPEI-PAA coating results in a high density of ionic bonds between the two polyelectrolyte polar groups (see **Figure 3**).

However, humidity levels higher than 50% R.H. could represent a problem.[43] [44] For this reason, a deeper analysis on the influence of different humidity conditions has been conducted on 3 and 4 BL samples. DMTA tests have been performed for samples conditioned to equilibrium at 23°C and 0 or 75% R.H. and compared with the one obtained after conditioning at 23°C and 50% R.H. The storage moduli obtained are reported in **Figures 6b** and **6c** for 3 BL and 4 BL, respectively. The maximum value of E' at 30°C for every sample is reached at 50% R.H.; however, dry specimens are able to maintain high modulus values at temperatures above 50°C. Increasing the relative humidity to 75%, the modulus is only slightly reduced at 30°C while it drops as the temperature increases due to the plasticizing effect of the combination of temperature and water. The fact that high modulus values are maintained within a wide range of R.H. is very important because it allows the use of these materials in wide range of applications where mechanical properties are required. RHK4BL is the composite that is able to better maintain the properties at different relative humidity in addition to being the most rigid material.

In order to provide a comparison with commercially available materials, the materials with the best DMTA performances (RHK3BL and RHK4BL) were tested according to the EN 312 standard. This test provides the use of a dynamometer in three point bending configuration and gives the modulus of elasticity (E), the strength of break (σ). Average modulus of 2309 and 3201 Mpa and strength of 8.9 and 12.0 MPa were found for RHK3BL and RHK4BL boards, respectively. The calculated standard deviations are around 20%. This is a value normally ascribed to the heterogeneity of particle dimension, as reported in **Figure S3**. It is worth mentioning that such high standard deviation could be reduced when scaling up the

dimensions of the samples, thus limiting the possibility of defects and ensuring the consistency and uniformity of the manufacturing process.

Previous research [44] with the same filler but starch as binder yielded a lower flexural modulus (1300 ± 300 MPa) and a slightly higher maximum strength (16 ± 2 MPa). Conversely, conventional RHK particleboards made with urea-formaldehyde obtained lower modulus (1.9-2.3 GPa) and lower strength (8.3-11.2 MPa). [46]

The calculated mechanical properties can be compared to the ones recommended by the EN 312 standard for particleboards type P2 (thicknesses from 3 to 4 mm) to be used in interior fitments (including furniture) in dry conditions. Both boards satisfy the requirements of 1800 MPa for modulus, while only the RHK4BL approaches the recommended tensile strength of 13 MPa. It is worth mentioning that, different from other polymer processing technologies where the matrix accounts for 40-50%, [47] [48] [33] the proposed approach allow for the production of particleboards containing up to 80% of RHK. This can be considered an additional advantage as more RHK could be recycled and employed in functional materials.

4. Conclusions

The LbL deposition of branched poly(ethyleneimine) coupled with poly(acrylic acid) has been presented as an easy and efficient approach for the surface functionalization of rice husk recovered from agro-wastes. The typical natural morphology of RHK particles was found to play an important role during the LbL deposition that was promoted on the uneven outer surface rather than on the smooth internal one. The LbL-functionalized RHK particles have been successfully employed for the production of free-standing particleboards by simple hot pressing. 2 BL-coated particles (4.7 wt.%) already allow for the preparation of a free-standing material but only the 3 (14.7 wt.%) and 4 BL (19.7 wt.%) yielded the mechanical properties needed for structural applications (e.g. ceilings, furniture panels and doors). The best

performance of 3.2 GPa and a tensile strength of 12 MPa can be achieved with 4BL treated RHK. DMT analyses demonstrated that good mechanical properties can be maintained up to 100°C and 75% R.H. These impressive results, achieved with a very low BL number, have been ascribed to both the super-linear growth and the strong intermolecular ionic interactions exhibited by the BPEI/PAA nanostructured assembly.

In conclusion, the LbL deposition can be considered as an efficient surface modification tool for agro-waste particles with the possibility of tuning the process in order to include different properties (i.e. mechanical resistance, fire retardancy, etc.). Furthermore, the materials obtained in this paper can be considered eco-friendly: firstly, for the re-use of an agro-waste such as rice husk (or other agro-waste particles, e.g hemp, straw etc.) and secondly for the green nature of the LbL approach that is performed in room conditions using water as solvent and with low solution concentrations (≤ 1 wt.-%). Finally, all the results reported in this paper indicate that particleboards obtained from LbL-functionalized agro-wastes have a promising sustainable potential for industrial applications with reduced environmental impact.

Supplementary material. IR spectra of neat branched poly(ethylene imine) and poly(acrylic acid), snapshots of the particleboards production and FESEM observation of uncoated rice husk particles are supplied as Supporting Information.

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TOC graphics

