

# Poly-paper: a sustainable material for packaging, based on recycled paper and recyclable with paper

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## ABSTRACT

**Background:** Until now, environmental sustainability issues are almost entirely unsolved for packaging materials. With the final aim of finding materials with a single recycling channel, cellulose fiber/poly(vinyl)alcohol composites were investigated.

**Methods:** After extrusion and injection molding, samples of composite with different cellulose fiber content (30%, 50% and 70% w/w) were tested.

**Results:** Tensile mechanical tests exhibited an improvement in composite stiffness when the reinforcement content was increased together with a decrease in composite elongation. Solubility tests performed at room temperature and 45°C showed different behavior depending on the water-resistant film applied on the composite (50% cellulose fiber content). In particular, the uncoated composite showed complete solubility after 2 hours, whereas at the same time point, no solubility occurred when a non-water-soluble varnish was used.

**Conclusions:** The proposed composites, named Poly-paper, appear to warrant further investigation as highly sustainable packaging.

**Keywords:** Cellulose fiber, Composite, Polyvinyl alcohol, Solubility, Tensile strength

## Introduction

Popular packaging materials today involve unsolved environmental sustainability issues. The main reason is that packaging is, in most cases, made of multiple materials (corrugated board, polystyrene foam, polyethylene etc.), which are often disposed of unsorted. Consider the packaging of a TV set or any other home appliance: It includes corrugated board for the outer case, polystyrene foam for inner filling, bubble polyethylene wrap and sundry plastic parts. Each of these materials has a different recycling channel (often a complicated one, as in the case of polystyrene foam). Truly

sustainable packaging should have a single separate collection and recycling channel.

There is no doubt that taking effective steps in view of packaging sustainability will imply using a single material, or rather materials with different properties and functional performance but with the same recycling channel. The above considerations led to our interest in developing a composite material characterized by high environmental sustainability (1).

Paper and board can best satisfy these needs: recycling of corrugated board, newspapers and magazines has been customary for some time now, even before the term *recyclable* became so popular. Sustainability is ensured by the fact that recycling simply requires placing the discarded parts in the paper-and-board bins available close to our homes. However, recycling of our new material alongside the waste paper collected for recycling required using a water-soluble matrix. We chose polyvinyl alcohol (PVA), a polymer-based material produced without diverting fertile lands from agriculture, capable of melting in water and forming nontoxic composites (2, 3). We called this material poly-paper. Poor resistance to water due to the water-soluble matrix is obviously not an issue in this case, because the resistance of Poly-paper to water (which varies according to temperature) is anyway greater than that of corrugated board.

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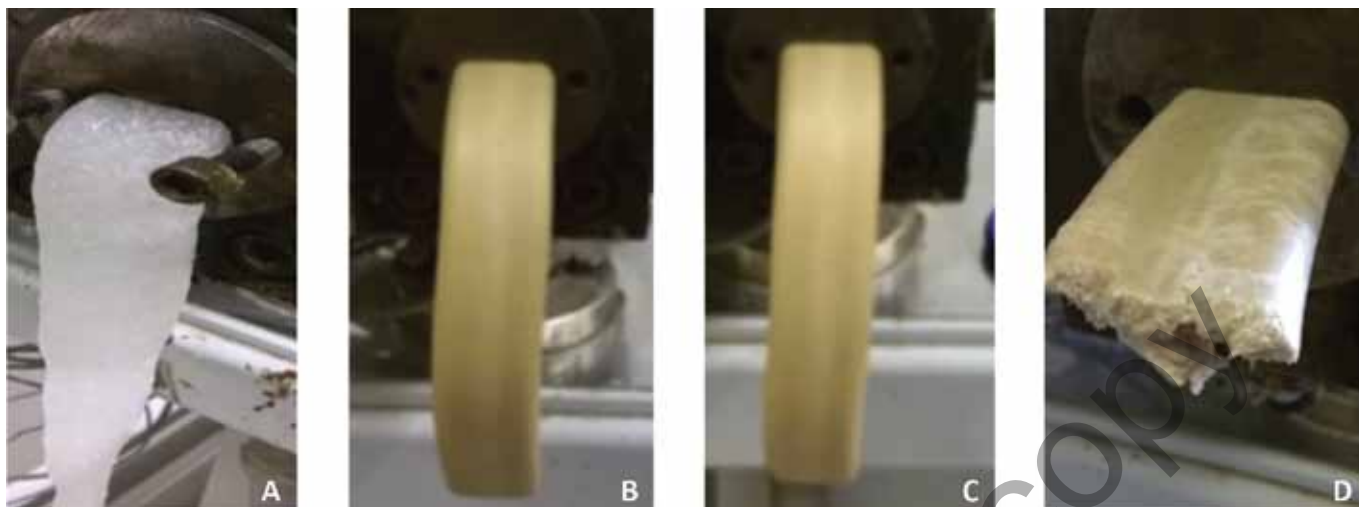
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**Fig. 1** - Extrusion tests on: (A) modified polyvinyl alcohol (PVA) alone, (B) modified PVA + 30% cellulose fibers, (C) modified PVA + 50% cellulose fibers, (D) modified PVA + 70% cellulose fibers.

A study by Zhang et al (4) focused on the influence of the chemomechanical treatments of cellulose on the physico-chemical properties of a cellulose/PVA composite material with 23% cellulose. The improvement of tensile strength and elongation has been shown to be a function of the decrease of the size of cellulose fibers, and was correlated with the combined expansion of the specific surface area of the latter, due to the increase of the grinding cycles that cellulose fibers undergo before mixing and extrusion with PVA.

In a study by Kaushik et al (5), cellulose fibers were added to a thermoplastic starch matrix (TPS), and mechanical properties were shown to improve as a function of the increase of the cellulose nanofibers, at a maximum demonstrated 15% rate. Huda et al (6, 7) showed that recycled newspaper fibers can be used as reinforcements in poly(lactic acid) (PLA) and polypropylene (PP) in place of talc. In a different paper, Huda et al (8) postulated the use of recycled newspaper fibers as a replacement for glass fibers. The economic and environmental advantages of using newspaper-derived fiber were outlined. In a recent study, Serrano et al (9) demonstrated the technical feasibility of the use of newspaper fibers over glass fibers for the production of products such as doors, windows, furniture and automotive interior parts.

The aim of the present study was to investigate novel formulations using significantly higher rates of cellulose to ensure easy recycling in water of the biocomposite. Furthermore, another purpose of the work was to assess the feasibility of the developed formulation to be used as a novel soluble material, Poly-paper, for processing using the fused deposition modeling technique.

## Materials and methods

The polymer selected as matrix was an experimental formulation based on water-soluble PVA with degree of hydrolysis between 75% and 90%, average molecular weight ( $M_w$ ) between 75 and 150 kDa and a polydispersity index

( $M_w/M_n$ ) between 2.5 and 4.3. The cellulose fibers selected as reinforcement had dimensions lower than 45  $\mu\text{m}$  (>45  $\mu\text{m}$  0%-0.1%), and bulk density in the range of 232-248 g/L. All materials were vacuum dried at 50°C for 48 hours prior to processing.

## Specimen preparation

Composites were melt blended in a corotating twin-screw extruder (Lab-Compounder KETSE 20/40D EC; Brabender, Duisburg, Germany). The extruder line was equipped with a side feeder (MT1-12; Brabender) to feed powder directly into the melt and a volumetric feeder (DRS28) to feed the pellet into the extruder barrel. The sequence of compounding was as follows: modified PVA pellets were fed through the input hopper with the volumetric feeder; finally the cellulose was dosed from the extruder opening side with the side feeder. The temperature pattern of the extruder was 190°C-190°C-195°C-195°C-190°C-190°C-180°C from input to output zones. The composites were pelletized from the extruded filament, to be processed by injection molding. Composites pellets were dried (24 hours at 50°C under vacuum) before injection molding. From all composites, pellet dog bone specimens with dimensions according to ASTM D638 were fabricated using a 12 mL microinjection molder (DSM Xplorer) at 190°C melt temperature and 60°C mold temperature with injection and holding pressure of 16 bar. The specimens were allowed to cool in the mold for 5 minutes before extraction. This allowed us to obtain homogeneous and strong postextrusion materials with cellulose fiber rates ranging from 30% to 50% (Fig. 1B, C). As shown, without fibers, the post-extrusion modified PVA only matrix had a thin texture (Fig. 1A), and became unsubstantial with 70% cellulose fibers (Fig. 1D).

The possibility to obtain filaments by extrusion was finally explored by checking, with positive results (data not shown), whether the material could be used to produce pellets (Fig. 2) in view of injection molding.



Fig. 2 - Poly-paper pellets obtained by extrusion.

### Experimental characterization techniques

Thermal stability of cellulose fibers was studied using a TGA-500 V6.7 instrument (TA Instrument), coupled with TA Instrument Explorer operating software. The analyses were performed under dynamic heating conditions, from 50°C to 800°C under nitrogen flow (60 ml/min), at a heating rate of 10°C/min, using about 2 mg of sample. Data recorded show the thermal behavior of cellulose fibers in terms of weight loss percentage increasing the test temperature.

The morphology of the dried cellulose fibers was observed by EVO Scanning Electron Microscope (Zeiss, Cambridge, UK) at room temperature. The fibers were stuck on the sample stub. The samples were gold sputtered up to a thickness of 20 nm by means of a Emitech K-550 sputter coater (Emitech, Ashford, Kent, UK). An accelerating voltage of 15 kV was used to collect the micrographs. The surface of the tensile-fractured specimens was also analysed after gold sputtering. The same observation conditions used for the dry fibers were used to analyze composite samples.

Tensile properties of the injection molded specimens were measured by using an Instron 5985 universal testing machine, equipped with a load cell of 10 kN in accordance to ASTM D638 standard. The tensile specimens had a length, width and thickness of narrow section of 165, 13 and 3.2 mm, respectively. These dimensions are in accordance with specimen Type I as reported in the ASTM D638 standard. Five specimens were

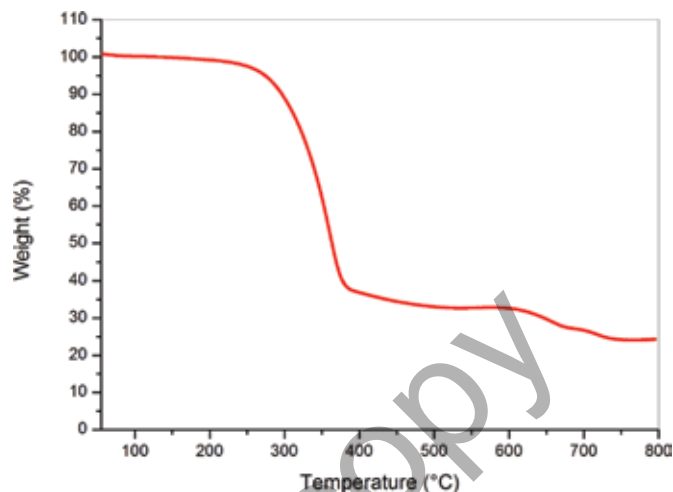


Fig. 3 - Thermogravimetric analysis curve for the cellulose fibers.

tested for each composite, with a constant speed of 5 mm/min, while compliance correction was used. System control and data analysis were performed using Instron's Blue Hill software.

The ability of the composite material (with 50% cellulose fiber) to melt by soaking with water was then evaluated by simulating maceration conditions. Briefly, tests were performed on specimens (40 × 40 × 5 mm), both at room temperature and at 45°C. Some specimens were superficially coated with a varnish film to check for possible water resistance of the material in view of specific applications.

## Results and discussion

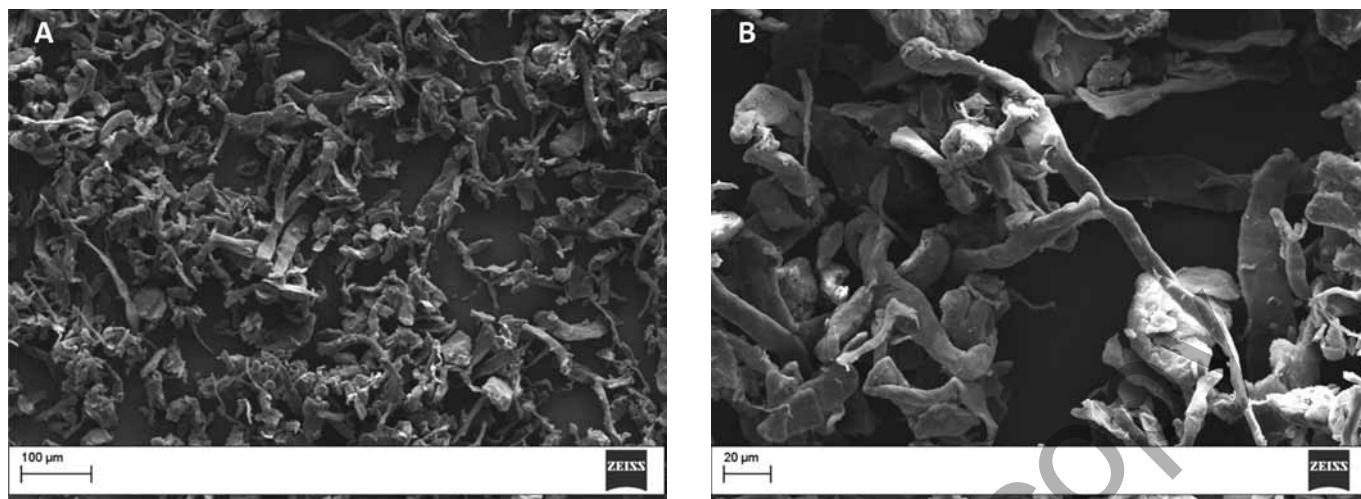
### Characterization of cellulose fibers

Thermal stability of the cellulose fibers was investigated by thermogravimetric analysis (TGA) under nitrogen flow. In Figure 3, the TGA result for dried cellulose fiber is reported. The TGA curve showed 3 thermal degradation steps ranging from 200°C to 800°C. In particular, the first degradation step at 267°C was due to the degradation of cellulosic substances, such as hemicellulose and cellulose. The second degradation (T = 383°C) of the decomposition was related to the degradation of noncellulosic materials in the fibers, while, the final degradation steps between 620°C and 800°C were due to minor components in the fibers. The residual char accounted for 19% of the initial weight. The thermal stability of the cellulose fibers up to 267°C ensured the processability of the composites up to 195°C which was the maximum selected temperature in the extruder for compounding.

The morphology of the cellulose fiber obtained by the paper recycling process was investigated with SEM (Fig. 4). The recycled paper appeared in a fibrillary form, with fibers ranging from 50 to 200 μm. The surface of the fibrils appeared rough probably due to the recycling method used.

### Tensile properties of the composites

The tensile properties of the modified PVA/cellulose composites were compared with neat modified PVA. The stress-strain



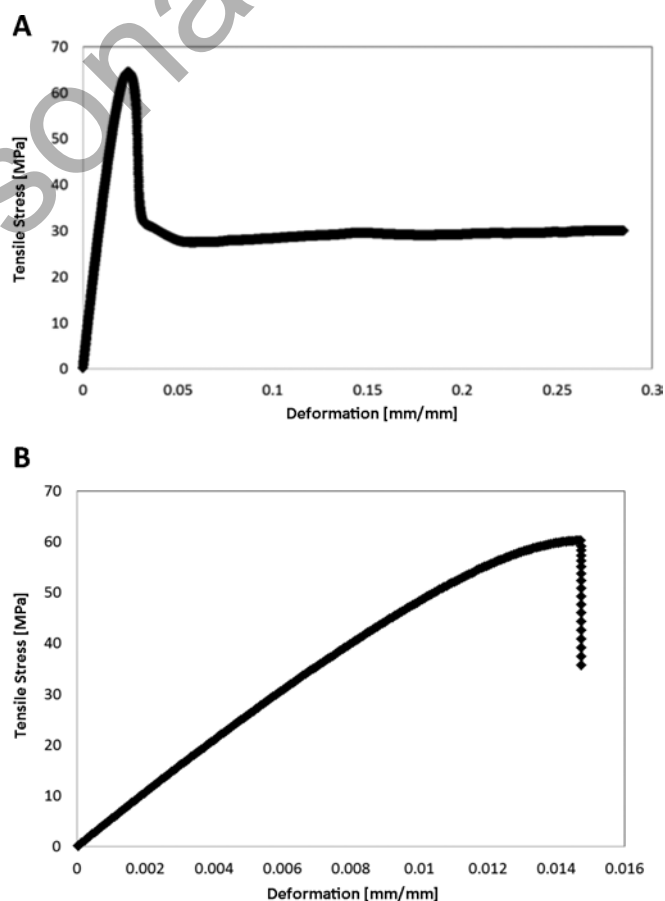
**Fig. 4** - SEM images of the dried cellulose fiber from recycled paper: (A)  $\times 300$  magnification (scale bar:  $100\ \mu\text{m}$ ); (B)  $\times 1,000$  magnification (scale bar:  $20\ \mu\text{m}$ ).

curves of the neat modified PVA and of the composites are reported in Figure 5. The stress–strain curves showed a necking extension for the neat modified PVA sample. The yield stress for the composites decreased slightly with increasing the cellulose fiber content. The tensile modulus showed sharp increases with tensile modulus varying from 3.57 to 5.19 and 7.17 GPa, with an increase of 45% and 101% for the composites with 30 wt% and 50 wt% of cellulose, respectively (Tab. I). This indicates that the stress would be expected to be transferred from the polymer matrix to the stronger cellulose fiber, indicating also a good interfacial adhesion. Similar results were obtained by Huda et al (6) with the addition of 30 wt% recycled newspaper fibers to PLA. In addition, the mechanical properties here obtained were in the range of, or even higher than, those reported by Graupner for PLA-reinforced composites for use in the automotive sector (10). In addition, the use of natural or recyclable constituents makes the composites studied interesting as environmentally friendly materials (11).

The tensile-fractured surface of the specimens considered was analysed by SEM (Fig. 6). Neat PVA (Fig. 6A) showed a rough surface, confirming the mechanical data for a ductile behavior, while the surface appeared less rough for the sample modified with 30 wt% cellulose fibers (Fig. 6B). The fibers were covered by matrix in both of the samples at 30 wt% (Fig. 6B) and 50 wt% (Fig. 6C, D). However, in the sample with 50 wt% of fibers, the higher fiber volume fraction resulted in a more complex surface topology.

### Stability test

The stability tests showed that the composite material (Fig. 7) was completely dissolved within about 2 hours when uncoated (cellulose 50 wt% in Fig. 7) and coated with 2 different percentages (3.3% and 10%) of ketone-aldehyde resin. When the composite was coated with a varnish, either non-water-soluble or water-soluble, the coated composite specimens showed good stability up to the end of the test. The obtained results showed that if appropriately coated,



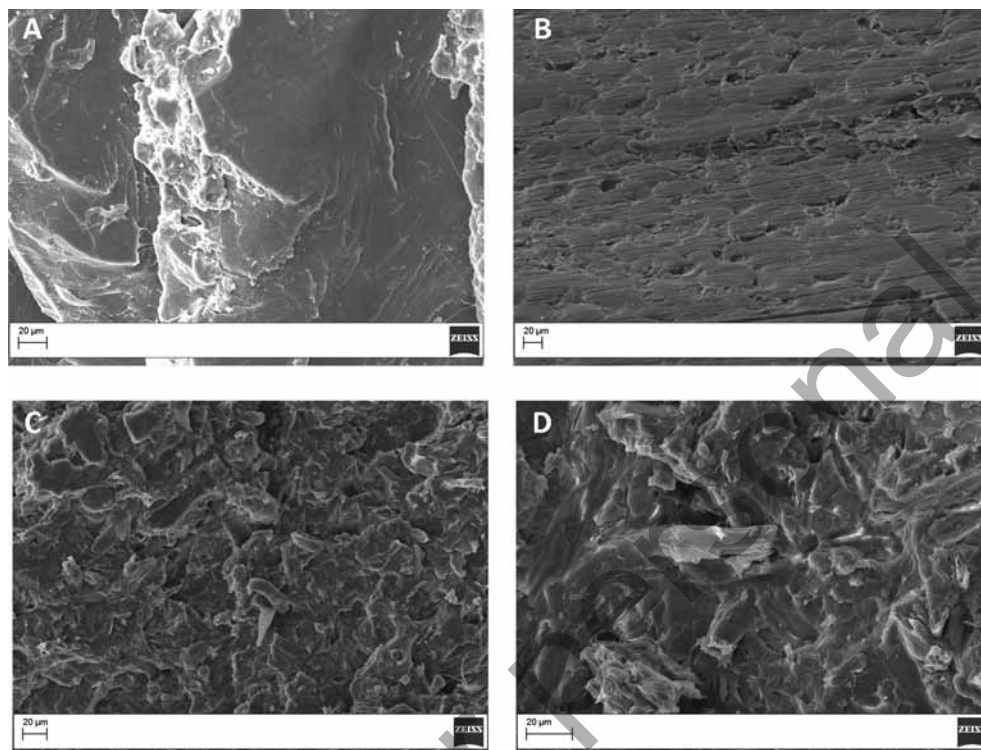
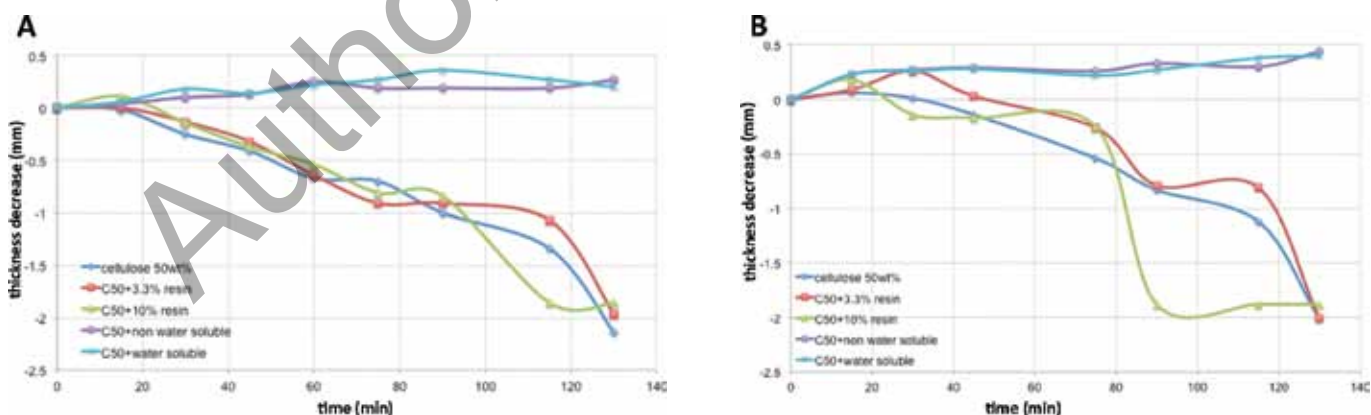
**Fig. 5** - Representative tensile stress–strain curves of the composites: neat polyvinyl alcohol (PVA) (A), and PVA/30 wt% cellulose fibers (B).

the composite can be stable for a longer time, hence it can be used also in an environment with a high percentage of humidity.

**TABLE I** - Mechanical parameters obtained in the tensile characterization test performed on the composites reinforced with different percentages of cellulose (30 and 50 wt%) compared with neat PVA (0 wt%)

Fibers	Yield stress (MPa)	Tensile modulus (GPa)	Strain to failure (%)
0 wt%	65.01 ± 0.57	3.57 ± 0.13	15.45 ± 11.28
30 wt%	58.10 ± 1.08	5.19 ± 0.09	1.49 ± 0.07
50 wt%	51.13 ± 9.46	7.17 ± 0.14	0.84 ± 0.19

PVA = polyvinyl alcohol.

**Fig. 6** - SEM images of the cross-section area of representative specimens after tensile tests: (A) neat polyvinyl alcohol (PVA; ×800 magnification); (B) 30 wt% cellulose/PVA composite (×700 magnification); (C) 50 wt% cellulose/PVA composite (×800 magnification); (D) 50 wt% cellulose/PVA composite (×1.3k magnification). Scale bar: 20 μm.**Fig. 7** - Solubility kinetics of the 50% cellulose fiber/PVA composite (C50) uncoated and coated with different percentages of ketone-aldehyde resin (3.3% and 10% resin), with non-water-soluble varnish and with water-soluble varnish: (A) at room temperature and (B) at 45°C.

## Conclusions

Once completed, the newly developed material (which is called Poly-paper) is expected to represent a significant

step toward the development of highly sustainable packaging, being a very stiff and strong material that can be shaped into complex forms and integrated with corrugated board for



inclusion in the recycling process of the board itself. Our findings resulted in the filing of a patent co-owned by the Milan Polytechnic and NextMaterials srl (12, 13).

### Disclosures

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Conflict of interest: None of the authors has any financial interest related to this study to disclose.

### References

1. Profaizer M, Barelli N, Del Curto B, Farè S, Tanzi MC, Cigada A. 3d-paper: a novel highly sustainable material for 3d printing. 10<sup>th</sup> international congress of INSTM, June 28-August 1, 2015 Favignana (TP), Italy.
2. De Merlis CC, Schoneker DR. Review of the oral toxicity of polyvinyl alcohol (PVA). *Food Chem Toxicol.* 2003;41(3):319-326.
3. Zhang SJ, Yu HQ. Radiation-induced degradation of polyvinyl alcohol in aqueous solutions. *Water Res.* 2004;38(2):309-316.
4. Zhang W, Yang X, Li C, Liang M, Lu C, Deng Y. Mechanochemical activation of cellulose and its thermoplastic polyvinyl alcohol ecomposites with enhanced physicochemical properties. *Carbohydr Polym.* 2011;83(1):257-263.
5. Kaushik A, Singh M, Verma G. Green nanocomposites based on thermoplastic starch and steam exploded cellulose nanofibrils from wheat straw. *Carbohydr Polym.* 2010;82(2):337-345.
6. Huda MS, Mohanty AK, Drzal LT, Schut E, Misra M. Green composites from recycled cellulose and poly(lactic acid): physico-mechanical and morphological properties evaluation. *J Mater Sci.* 2005;40(16):4221-4229.
7. Huda SM, Drzal LT, Misra M, Mohanty AK, Williams K, Mielewski DF. A study on biocomposites from recycled newspaper fiber and poly(lactic acid). *Ind Eng Chem Res.* 2005;44(15):5593-5601.
8. Huda SM, Drzal LT, Mohanty AK, Misra M. Chopped glass and recycled newspaper as reinforcement fibers in injection molded poly(lactic acid) (PLA) composites: A comparative study. *Compos Sci Technol.* 2006;66(11-12):1813-1824.
9. Serrano A, Espinach FX, Tresserras J, Pellicer N, Alcalá M, Mutje P. Study on the technical feasibility of replacing glass fibers by old newspaper recycled fibers as polypropylene reinforcement. *J Clean Prod.* 2014;65:489-496.
10. Graupner N, Herrmann AS, Müssig J. Natural and man-made dellulose fibre-reinforced poly(lactic acid) (PLA) composites: an overview about mechanical characteristics and application areas. *Compos Part A-Appl S.* 2009;40(6-7):810-821.
11. La Rosa AD, Cozzo G, Latteri A, Mancini G, Recca A, Cicala G. A comparative life cycle assessment of a composite component for automotive. *Chem Eng Trans.* 2013;32:1723-1728.
12. Cigada A, Profaizer M, Del Curto B, et al. Materiale composito ad alta sostenibilità ambientale Italian patent application No. 102015000028276, Application June 26, 2015.
13. Cigada A, Profaizer M, Del Curto B, et al. Highly environmentally sustainable composite material, PCT IB2016/053777, Application June 26, 2016.