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BIOSHOES4ALL – INNOVATIVE GREEN MATERIALS, PROCESSES AND PRODUCTS

MARIA J. FERREIRA*, VERA PINTO, PATRICIA COSTA, ADRIANA SOARES AND BIOSHOES4ALL CONSORTIUM

CTCP – Portuguese Footwear Research and Technological Centre, Rua de Fundões,
*Devesa Velha, 3700–121 São João da Madeira, Portugal; *mjose.ferreira@ctcp.pt*

The bioeconomy covers sectors and systems that rely on biological resources such as animals, plants and derived biomass and includes industrial and economic sectors that use biological resources and processes to produce bio-based products. A bio-based footwear economy using renewable biological resources sustainably, to produce biomaterials will help the industry reduce dependence on non-renewable resources. It will also address global commitments associated with the United Nations 2030 Agenda for Sustainable Development and the Paris Agreement by ensuring sustainable consumption and production patterns, combating climate change and its impacts. In footwear, the materials used, and waste produced are in general the highest contributors to the total greenhouse gas emissions. Research and innovation are core to pursuing 2030 targets. The sector needs to develop and deploy the 'next generation' of sustainable materials and processes, including biological and plant-based materials and man-made bio-based materials. Seps in this direction are being taken within BioShoes4All project that is developing namely leathers tanned with pine tree bark, wet-white tanned leather "bisphenols free"; coated textiles with over 65% biological carbon; soling materials incorporating up to 80% bio content; recyclable physically expanded lightweight soles, and new concepts of footwear, all tuned using life cycle assessment (LCA) in order to reduce the fossil, carbon or environment footprint.

Keywords: Footwear, bioeconomy, environmental footprint.

INTRODUCTION

The world is facing challenges that invite the footwear sector to accelerate its efforts to be sustainable by adopting inclusive, green and digital sustainable solutions and business models. Fashion businesses need to be resilient and help minimize depletion of the planet's resources, greenhouse gas emissions, and climate change and prevent complex problems such as those posed by fossils overspend and hazardous substances. Globally regarding environmental issues footwear will benefit from tackling the products design, the impact of materials, production and distribution processes, recycling, and water, fossil resources and land usage. At consumption level, it calls for durable long-lasting goods, repair, reuse and circularity.

There are many potential areas of intervention and significant research and innovation needs to be done. Firm steps are being accomplished within BioShoes4All. It includes five areas of intervention: Biomaterials, Ecological Footwear, Circular Economy, Advanced Production Technologies, Training and Promotion (Figure 1), and it is developing new leathers, bio-based materials, recycled materials, traceability tools, production systems, footwear concepts and business models.

The project comprises 50 companies covering the whole footwear value chain including leather, polymers, soles, software, production equipment, leather goods, footwear and retail representation and leadership, plus 20 R&D bodies with complementary capabilities, coordinated by the CTCP, led by the Portuguese Footwear Cluster (Figure 2), and cofinanced by Next Generation EU and the Portuguese Recovery and Resilience Plan.

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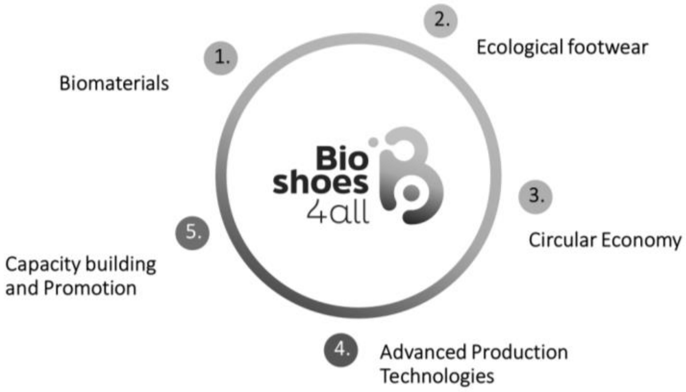

Figure 1. BioSoes4All main areas of research and intervention

Figure 2. BioSoes4All consortium and cofinancing

OBJECTIVES, METHODS AND RESULTS

Innovative Tannins and Leathers

Pine Tree Bark Tanned Leathers

Hides are biological *per se* but need to be chemically stabilized to be used in footwear. The stabilization process involves several steps being the tanning phase of the outmost importance. Tanning is done mainly using metals specially chromium, fossil derivatives, and to lesser extent using vegetable tannins, in many cases imported to Europe.

Chromium (III) tanning has been under scrutiny due to the possibility of oxidizing to chromium (VI) and hindering leather waste and post-consumer products recycling. In response to this concern, a great deal of research is carried out in recent years. BioShoes4All defined as target to develop up to 100% biological tanned leathers using local and agri-food, agro-industrial or forest biomass. Several possibilities were identified and are under study by leather and chemicals producers and R&D teams from ISEP, CTIC, UCP and CTCP.

These teams are working complementarily to identify useful biomass (e.g., composition, quantity), characterize, pretreat and extract tannins from different biomass (e.g., pine, olive, coffee), develop bioproducts that can effectively tan the hides, develop the tanning processes, develop leathers with adequate functional and organoleptic properties, and carry out the new materials life cycle analysis.

Interesting results are being obtained using *Pinus pinaster* pine tree bark (Figure 3). These vegetable tanned leathers present good surface appearance and tear resistance and retraction temperature values of over 100 N and 70° C, respectively. Industrial application tests indicate may be used to produce footwear and leather goods.

Figure 3. Leather tanned with Pinus pinaster bark modified extract

Wet-White Bisphenol 'Free' Leather

Bisphenols have become an important topic of discussion as regards leather and footwear. Bisphenols are a family of very similar synthetic organic chemicals with two hydroxyphenyl functional groups that allow polymerization reactions to form larger molecules. Each type is identified by a CAS number, including Bisphenol-A (CAS 80-05-7), Bisphenol-B (CAS 77-40-7), Bisphenol-F (CAS 620-92-8) and Bisphenol-S (CAS 80-09-1). According to the project partners knowledge, none of these bisphenols are used directly as raw materials in leather manufacturing processes. However, Bisphenol-F and Bisphenol-S may potentially be found in some condensed chemical products as unwanted by products of secondary reactions of their production processes. In the leather industry, these condensed chemicals, or syntans, are mainly used in pre-tanning and retanning processes to enhance important leather characteristics such as softness, tear resistance or whitening effect. For these reasons, replacing them while maintaining the leather's performance represents a challenge.

This challenge inspired the project R&D team, led by Indutan, a sheep and goat leather manufacturer, to develop durable and functional leathers with bisphenol levels below 500 ppm (parts per million). Exhaustive work to carefully test, review and develop new leather processing recipes, resulted in new leather products in the high added values range with low bisphenol F and bisphenol S values, which fulfil the required specifications. Two examples of the new leathers' properties are shown in Table 1. From the results obtained, can be appreciated the new leathers are very similar to those previously produced by the company, and are ready to be produced on an industrial scale.

Table 1. New wet-white leathers bisphenol ‘free’ indicative properties

Parameter	Base	New 1	New 2
Bisphenol F(mg/kg)	BQL	58	40
Bisphenol S(mg/kg)	>10000	69	16
Shrinkage temperature (ºC)	85	72	72
Leather “flower” strength - elongation (mm)	8.3	13.2	14.6
Leather “flower” load resistance (N)	165	328	446
Tear strength (N)	61	91	54
Elongation at break (%)	53	67	68
Tensile strength (N/mm^2)	19.3	37	18.6

BQL – Bellow quantification limit

Bio-Based Coated Textiles

In recent years the consumers demand for footwear made without leather has resulted in the search for biobased coated textiles which favor raw materials of biological origin. It is now possible to synthesize polyurethane coatings partly from raw materials of plant origin such as vegetable oils modified into polyols, which are then polymerized with reagents of fossil origin.

Portugal is one of the largest producers of olive oil and the actual olive stone represents an abundant biomass estimated to be 60,000 tons per year and currently without any other use other than burning to create energy. This has contributed to it being chosen by Monteiro Fabrics as a bio-filler to be incorporated into bio coating formulations. The ORIGIN material created within the BioShoes4All project is the result of the development of a BioTPU and water-based formulation containing olive stones applied to a cotton fibre textile base. Some relevant physical and mechanical characteristics are shown in Table 2 and fulfil the specifications for shoe uppers. It also has a proven 72% bio-based carbon content in accordance with ASTM D6866-22 Method B.

Table 2. ORIGIN olive composite physic-mechanical properties

Parameter		Specifications fashion shoes	Results
Tensile Strength (N/mm)	T	> 10	11.3
	TR	> 5	6.6
Elongation at break (%)	T	> 50	62.7
	TR	> 100	115.6
Tear strength (N)	T	> 25	29.4
	TR	> 20	26.2
Adhesion to the coating (N/5cm)	T	> 1	1.19

T – Warp, TR – Weft

The company, together with local partners, is also valorizing chestnuts byproducts. These biomaterials are crushed and ground into a fine powder and turned into an innovative material. The PEEL collection incorporates 60% plant-based materials including chestnut waste, organic cotton and natural oils, and 40% PVC. The material allows customers to create products without having to choose between cost, performance, aesthetics or sustainability. It is a technologically viable product, ready to be produced on a large scale and without compromising its performance.

Technical requirements for use in cemented footwear are all met including high Bally flex resistance (150000 cycles), Martindale abrasion (400000 cycles), resistance to friction (Crockmeter), among others. Peel’s 65% bio-based carbon content has been verified in accordance with ASTM D6866-22 Method B. Additionally, the material Life Cycle

Assessment (LCA) made by CTCP based in the EU footwear draft Product Environmental Footprint (PEF) methodology indicates a reduction of 19% in fossils resources used and a reduction of 9% of its carbon footprint (Figure 4; LCA from raw material extraction to PEEL production).

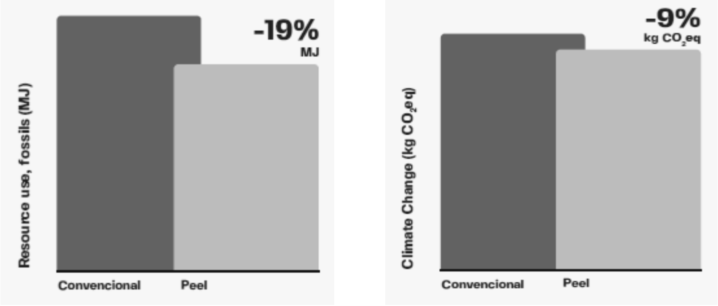

Figure 4. Biobased coated textile fossils resources and carbon footprint reduction

Bio and Ecosoles

BioPVC

The sustainability of materials has achieved unprecedented importance, particularly in the search for biobased and/or recyclable approaches. This is motivating BioShoes4All project partners to develop materials with high biobased content, that can be processed by injection molding to produce flexible and recyclable soles and complete footwear. One example is the LCR Coblex bioPVC incorporating bio plasticizers and additives claiming up to/more than 80% biobased content and the same level of performance of conventional materials, in terms of hardness, density, and flexion and abrasion resistances (Table 3). Additionally, the material LCA made by CTCP indicates a reduction of 36% in fossils resources used (LCA from raw material extraction to BioPVC pellets).

Table 3. BioPVC physical properties

Parameter	Specification	Results
Hardness (ISO 868, Shore (A))	60 - 65	63 - 64
Density (ISO 2781-met A, g/cm^3)	1.18 - 1.22	1.19-1.2
Abrasion resistance (ISO 20871, mm^3)	<250	106 - 115
Ross flex resistance (BS5131-Part 2.1, mm)	<0.4	0.0

E-blast "Super Critical" Physical Foaming TPU Material

An innovative approach is proposed by ALOFT that implemented after a detailed research and development with national and international partners, to the best of our knowledge, the first system used in the footwear and allied trade sectors in Europe to produce footwear components by E-blast "Super Critical" physical foaming process (N2). The preliminary LCA analysis of E-Blast TPU done by CTCP indicates a Carbon footprint reduction of 75% comparing to standard compact TPU (Figure 5). Comparing to usual PU foam the new material has the advantage of being thermoplastic thus more easily recyclable and having no residues from chemical foaming agents in the final products. Physical tests are being carried out to verify the material properties after grind/injection cycles.

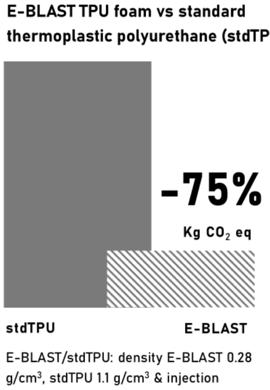

Figure 5. E-blast “Super Critical” foamed TPU carbon footprint reduction

BioShoes

BioShoes4All partners are developing concepts of footwear based in ecodesign approaches and new materials aiming to reduce products footprints based in the EU draft footwear Product Environmental Footprint (PEF) methodology. The PEF method assesses 16 impact categories (Table 4), covering climate change, acid rain, human toxicity, and particulate matter as well as impacts due to the use of water, land, and resources.

Table 4. Footwear environmental footprint impact categories assessed

EF Impact Category	Impact category Indicator	Unit
Climate change, total + fossil + biogenic + land use and land use change	Radiative forcing as global warming potential (GWP100)	kg CO_2-eq
Ozone depletion	Ozone Depletion Potential (ODP)	kg CFC-11-eq
Human toxicity, cancer	Comparative Toxic Units for humans	CTUh
Human toxicity, non-cancer	Comparative Toxic Units for humans	CTUh
Particulate matter	Impact on human health	disease incidence
Ionising radiation, human health	Human exposure efficiency relative to U235	kBq U235-eq
Photochemical ozone formation, human health	Tropospheric ozone concentration increase	kg NMVOC-eq
Acidification	Accumulated Exceedance (AE)	mol H+-eq
Eutrophication, terrestrial	Accumulated Exceedance (AE)	mol N -eq
Eutrophication, freshwater	Nutrients reaching freshwater end compartment (P)	kg P-eq
Eutrophication, marine	Nutrients reaching marine end compartment (N)	kg N-eq
Ecotoxicity, freshwater	Comparative Toxic Unit for ecosystems	CTUe
Land use	Soil quality index and others	Dimensionless
Water use	User deprivation potential	m3 world eq
Resource use, minerals and metals	Abiotic resource depletion	kg Sb eq
Resource use, fossils	Abiotic resource depletion – fossil fuels, ADP	MJ

As shown in one example in Table 5, frequently, most relevant impact categories include “Climate change”; “Fossil resources use”; and “Minerals/metals resources use”.

Table 5. Footwear most relevant impact categories, stages and process (example)

Impact category	% Contribution	Life cycle stage	% Contribution	Component	% Contribution
Climate change	24,0%	Raw materials in final product	55,5%	Outsole	22,3%
				Insole	8,0%
				Interlayer	7,8%
				Insock	6,9%
				Upper	3,5%
		Raw materials that go to waste	3,0%	Interlayer	1,4%
		Waste	19,8%	Waste	15,7%
		End of Life	7,3%	Transport	3,8%
				Solid waste	3,2%
Resource use, fossils	16,8%	Raw materials in final product	68,0%	Outsole	35,1%
				Insole	9,9%
				Insock	7,5%
				Interlayer	5,6%
		Waste	15,4%	Waste	12,0%
		Raw materials that go to waste	2,8%	Interlayer	1,3%
Resource use, minerals and metals	16,1%	Waste	90,9%	Waste	84,0%

The data obtained (Table 5) also details the environmental impact associated to the product “Life cycle stage” and “Materials, components and/or processes”, giving indications to make changes to reduce the products PEF. Among these, “Climate Change” is often chosen to present and discuss the environmental impact of shoe models. Figure 6 presents the results of the Climate Change impact category, Global Warming Potential indicator (GWP100), in kg CO_2 eq, calculated for an example pair of footwear before and after redesign. Within this study was possible to reduce the selected model carbon footprint (kg CO_2 eq) up to 36% considering the more sustainable version.

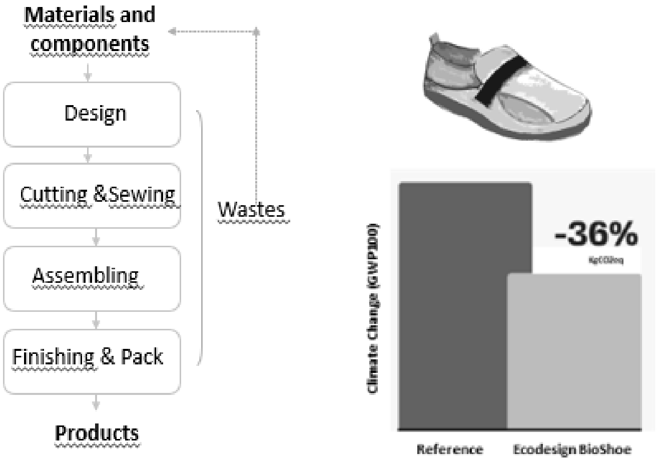

Figure 6. Redesigned footwear and carbon footprint reduction

CONCLUSIONS AND FUTURE WORK

The world is facing challenges that invite the footwear sector to accelerate its efforts to be sustainable by adopting inclusive, green and digital sustainable solutions and business models. Fashion businesses need to be resilient and help minimize depletion of the planet's resources, greenhouse gas emissions, and climate change and prevent complex problems such as those posed by fossils overspend and hazardous substances.

BioShoes4All is researching and deploying sustainable solutions for the footwear value chain. Globally regarding environmental issues the sector benefit from using bioeconomy renewable resources and adopting circular business models, tackling the products design, the impact of materials, production and distribution processes, recycling, and water, fossil resources and land usage. At consumption level, it calls for durable long-lasting goods, repair, reuse and circularity.

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For more information see the websites recuperarportugal.gov.pt. #ContruirOFuturo & https://bioshoesforall.pt/