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Ultimate use of Cork – Unorthodox and innovative applications

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Abstract

In this survey the untraditional practical applications of cork is presented. High-quality goods with improved performances have been developed by those who came up with creative ideas and develop them. From several types of industries to private entrepreneurs, cork has been calling the attention of many creative minds over the last decade. From surfboards or designer clothes to an outstanding work of art made from cork has proved that this natural material becomes a noble feedstock not only for those who appreciate a good beverage and high-performance materials but also for those who look for sustainable products from natural sources. A general overview of cork composition, origin, and industry is also briefly disclosed.

Keywords: cork; application; innovation; properties; materials; sustainable.

1. Introduction

The tree Quercus suber L., commonly known as a cork-oak tree, is widespread in western Mediterranean region (Figure 1), with higher prevalence in Portugal and Spain [1,2]. The bark of this oak tree is considered to be a source of an environmentally friendly and sustainable raw material, called cork [1].
The cork is harvested with the preservation of the tree, being its bark stripped without cutting it down. Thus, the tree can continue to live, growing and producing new barks for following extractions. These extractions are conducted every 9–14 years, with the improvement of corks quality, until the tree is approximately 200 years old [1].
Cork forests are extremely well adapted to Europe's southern semi-arid regions, preventing desertification and being the perfect habitat for many animal and plant species [3]. With more than sixty percent, Iberian Peninsula possesses the major cork tree area being Portugal the country that the biggest "Montado" area 34% (Figure 1).

The world's foremost producer of cork is the European Union. According to APCOR, Portugal produces almost 50 % of all cork (Figure 2b) and holds up to nearly 70 % of the cork industry market (Figure 2a) [4].

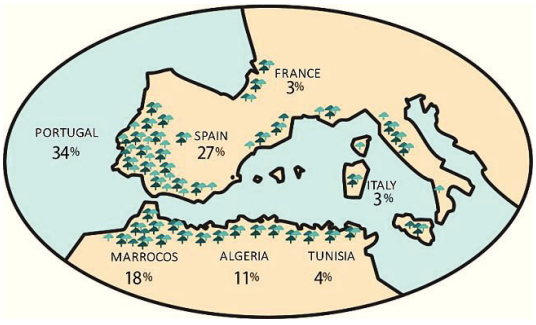

Fig. 1. World's distribution of Cork forest (adapted from APCOR).

Cork-based materials, durable products, are believed to play a role in the contribution to decreasing the amount of carbon dioxide in the atmosphere since they are considered to be "carbon neutral" [5]. The derived residues or by-products are classified mostly based on size, density (which is also related to the presence of woody parts) and moisture. An important amount of these residues is sent to granulation

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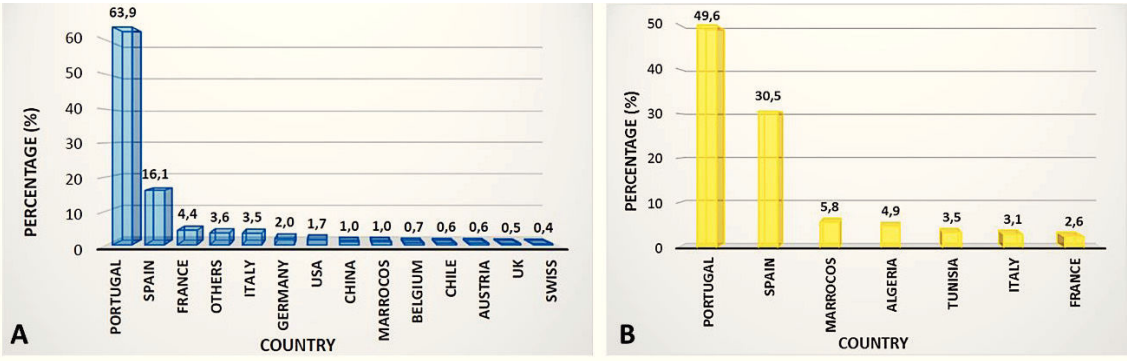

Fig. 2. A – Market share of cork industry; B – Production Share of cork (data source : APCOR).

originating granules used in a variety applications, mainly cork agglomerates, composites, cork pavement, insulation panels, lightweight structures and agglomerated wine closures among others [2,5-16]. On the other hand, the transforming industry generates a residue considered problematic, obtained from multiple production phases, including granulation: this is the so-called "cork dust" a substantial fraction of the total amount of wastes with no commercial value. As the name suggests, cork dust includes small size particles, usually a size too small (<0.5 mm) for any possible reuse, due to its high surface. According to the Portuguese standards NP-114 and NP-273 it has dimensions below 0.25 mm [17]. Even when used for agglomerates, the inclusion of the dust is only possible in small amounts, therefore not incorporating significant volumes compared to the production. Several efforts have been made to reuse the "cork dust". Currently, it is mostly applied as fuel for burning in furnaces: either in the cork industry or even in the ceramic industry, because it presents a high calorific value, which is between 18.9 and 29.3 MJ/kg [17].

In this brief survey, besides a short description of cork properties and characteristics, a summary of some of the most innovative applications of cork that overstepped from the usual ones (i.e., agglomerated composites, floor or wall .covering) will be described.

2. Cork characterization and properties

In this section, an overview of the cork composition, characterization and properties will be presented. For a more detailed data regarding this subjected surveys like those from Pereira [18] or Silva et al. [2] should be perused.

Cork, possessing a variable chemical profile dependent on geographic, climate and soil, genetic origin, and tree properties, is mainly, composed of suberin, lignin, polysaccharides (cellulose and hemicellulose), extractables (40%, 22%, 18%, 15%, respectively) and others minority compounds [2,19-21]. It is also worth mentioning that cork as a natural material has a strong similarity to the lignocellulosic material, like wood, despite its distinct chemical and structural character.

Regarding its unique cellular structure, corks pentagonal or hexagonal shape cells are the base of its most important features. As described by Duarte and Bordado, cork cells are filled with a gas mixture conferring cork the capability of resistance to compressibility, recovering it primitive shape after compression [21].

The high interest of the use of Cork in the most diverse forms and applications is bonded to its peculiar properties. Weighing about 0.16 grams per cubic centimeter this vegetal tissue can be compressed to around half its thickness without losing any flexibility, recovering its full shape and volume afterward. Possessing a Poisson's ratio of nearly zero, cork can adapt to temperature and pressures variations. Due to its great elasticity when one side is compressed the other is not affected, leading to its diverse applications [2]. Cork is also an excellent thermal and acoustic insulator due to its low conductivity to heat, noise, and vibration. Those properties result from the encapsulated of gaseous components in corks closed cells. Suberin and waxy components enclosed in the cell walls makes cork impermeable to liquids and gasses enabling it to age without decaying. Spite its soft feel to the touch, cork is embodied of an excellent resistance to impact or friction. This resistance is even higher than other hard surfaces, mostly thanks to its honeycomb structure. Since cork does not absorb any dust or other fine solids and has a stable composition over the years, it does not cause allergies not affecting, thus, those who suffer from asthma [17,21-24].

3. Applications and innovation

Due to its remarkable properties, cork has been seen as valuable and noble material since ancient times. Cork stoppers, agglomerated boards for wall and floors coverings, are the main applications that everyone can identify as soon as they think about cork. Those applications are the most well-known and implemented on the market. In fact, the manufacture of closures is the most relevant activity of the cork industrial sector but only uses about 25 % of the original raw material [4,18].

The amount of published works focused on cork has increased over the 15 years, according to ISI Web of Knowledge, from 124 at the beginning of the millennium to 277 in 2014. The collected data clearly indicates that interest of scientific community on this great raw material has been growing over the years (Source: ISI WoK; Topic: Cork, Science, and Technology) (Figure 3).

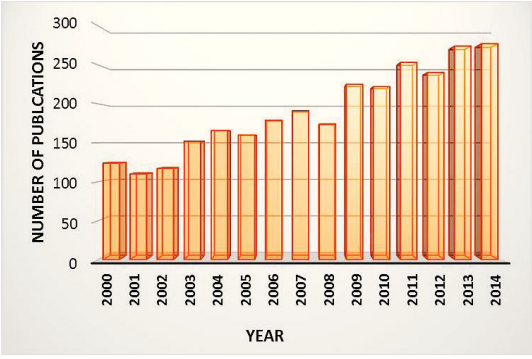

Fig. 3. Number of scientific publications from 2000 to September 2015.

In addition, to the traditional/conventional or more visible applications that take advantages of cork properties (i.e. stoppers, agglomerated boards) more creative ideas have appeared throughout the years. In fact, over the last years, innovative solutions for cork have been published. Lately, cork by-products, have been investigated as a source of biomass for acid liquefaction using polyhydric alcohols under conventional and ultrasounds-assisted methods [25,26]. This waste, proved to be suitable for the production of biomaterials based on the polyols obtained from its liquefaction [6,27].

New applications of cork for sports, filters, pharmacology, fashion, architecture amongst others have been developed and became part of our daily routine.

As a result of a significant investment in R&D, new products and applications for cork have been disclosed leading to a high input of innovation and high technology into an antique industry. New attractive products with improved qualities and performances have been designed and created. Though some of the applications discussed in this review have already been disclosed in other surveys [3,5,21,28], in the next sections, an overview of the most significant and exciting applications will be presented.

3.1. Chemicals

3.1.1. Polyols from Cork liquefaction

To access highly functionalized chemicals thermochemical liquefaction of cork has been exploited over the last years and the studies conducted have been presented [25,26].

Soares et al. have shown that it is possible to convert cork powder into useful polyols via sulfuric acid catalyzed liquefaction in the presence of polyethylene glycol and glycerol at 150 °C [25]. On the other hand, Mateus et al. have conducted a study where ultrasounds were applied to cork liquefaction and compared with the conventional method. As solvents 2-ethylhexanol and diethylene glycol were used since it leads to a less viscous products and catalyst p-toluene glycol afforded less residue at the end of the liquefaction reaction [26].

For both studies hydroxyl number and acid numbers were investigated, indicating that the polyols obtained are suitable to be used as substituents of those manufactured from petroleum sources.

3.1.1.1. Foams

Gama et al. disclosed the studies for the formulation of novel bio-based polyurethane foams produced from polyols derived from acid-liquefied cork. The bio-chemicals obtained from cork liquefaction led materials with low density and thermal conductivity, which allows to conclude that it is possible to convert cork into added-value raw materials for the formulation of new materials with adequate properties for insulation purposes [6].

3.1.1.2. Adhesives

A new type of adhesive was developed for the aqueous extraction of liquefied cork mixture. A two-

component natural polymeric water-based glue was formulated by the addition of the aqueous fraction obtained from the liquefied cork liquefied to distilled water, Desmodur DA-L and cork powder. The published results have demonstrated that the performance of the resulting bonded materials is quite the same as those glued with conventional epoxy or wood adhesives [27]. This novel adhesive is a sustainable alternative to those derived from petroleum sources.

3.1.2. Chemicals with pharmacological interest

Besides its physical properties, cork offers more beneficial properties than those usually related to its intrinsic properties. The chemical profile of oak bark has also been studied. [2,21,29,30] The pharmacological potential associated with cork is often due to its low molecular weight components [2]. Herein the most significant biological activities of some of the cork chemical constituents are briefly discussed.

As referred in section 1 cork transforming industry generates large amounts of problematic residues obtained from multiple production phases, cork powder [31]. Nevertheless, this by-product can be used as a potential source of low molecular weight compounds with biological activity (Table 1). Compounds such as friedelin and friedelin derivatives, triterpenes, have been already studied [32-34]. The biological activity associated to this compounds are anti-inflammatory [35], anti-carcinogenic [33,36], antioxidant, antihistaminic, antiulcer [33] and anticancer effects [36]. Another compound with triterpenes backbones, triterpenoids, obtained from cork by-products, have been screened by Moiteiro et al. disclosing very promising pesticidal activities [31].

Alongside with the triterpenes and triterpenes derivatives others compounds are also found within the chemical profile of cork. Some of them are sterols and polyphenolic and phenolic derivatives that are well known for its significant biological activity.

Sterols scaffolds can reduce significantly problems associated with cholesterol [37] as well as a role in the prevention of cancer proliferation [38]. On the other hand, polyphenolic compounds (i.e., flavonoids, as an example) can act as antioxidants [39] or be used in the in cancer chemoprevention [40].

These studies demonstrate that cork can be a natural alternative to access, towards the transformation of flat valuable raw materials into attractive molecules with excellent health benefits, not dependent on non-sustainable sources such as petroleum, for pharmaceutical, cosmetic, food, and plastics industries [2,21,30].

Table 1. Potential biological activity of compounds identified on cork.

Compounds	Potential Biological Activity	Ref.
Triterpenes derivatives	Pesticidal effect	[21,31]
	Antioxidant	[21,33]
	Antistaminic	[21,33]
	Antiulcer	[21,32,33]
	Anti-inflammatory	[21,35]
	Anticancer effects	[21,33,36]
Sterols problems	Reduce cholesterol	[21,37]
	Cancer proliferation	[21,38]
Polyphenols	Antioxidants	[21,30,39]
	Cancer chemoprevention	[21,40]

3.2. Sports

3.2.1. Natural synthetic grass infill

Cork granules have been widely used in the flooring industry. However, a new application in artificial grass sports fields was found. This natural infill is 100% environment-friendly and non-toxic since cork is an organic, recyclable, and sustainable product. Its unique closed cell structure makes it a resilient to moisture, shock absorbent, and little thermal conductor. The infill is placed in between the pile providing lawn's natural appearance and the needed elasticity and bouncing properties to allow the blades of synthetic grass to stand straight. The infill prevents the surface wearing in a non-uniform manner. Usually, the infills were cushioned by the use of rubber granules obtained from recycled tires with all sorts of impurities and associated toxicity. The number of synthetic lawns has widely grown over the last years. The high maintenance cost due to the lack water and its cost, the regular soil fertilization and the climate changes associated with the limited resistance of natural grass makes the use of natural grass almost impossible nowadays. Hence, the artificial lawns with cork infills are becoming more and more common [41].

3.2.2. *Sports boards, boats, and kayaks*

Surfboards containing cork are now a reality. There are already several surfboards being tailored with cork or cork-based composites (Figure 4a).
The inclusion of cork can reduce the use of thermoplastics resulting in a more environmentally friendly, ecological and sustainable product. Cork's mechanical properties such as elasticity, thermal and impact resistance embody the board with the right stiffness without compromising its flexibility assuring a great performance [42].
Taking advantages of the superior strength in high impact areas of their Cork/PVC sandwich material, Cork manufacturing industries together with surfboard companies have developed new surfboards. The composites products of a Portuguese company have been selected for the development of a new technology of internal impact absorption for their windsurf boards. By placing a piece of the sandwich-type composite into the laminated structure of the board, the impact and shear strength resistance is drastically improved. This material is referenced as "green foam" is an excellent shock absorber, preventing thus, the delamination from the blank and acts as an internal mattress for the heels of the surfer. This property leads to better vibration damping, better comfort and increases the life of the board [43,44].
Another Surf Board company taking advantage of this high-quality natural product created a carbon-cork composite board with an exposed cork surface, leaving aside the usual fiberglass covering shell, resulting in higher adherence of the surfer to its boards allowing a wax-free surf experience [45].
Alongside with the new surfboards, cork composite is also being used to manufacture boats. The intrinsic cork elasticity makes it very easy to bend into a mold and allows resin pass through very easily and homogeneously. The prototype developed in Politecnico di Milano proved that this material could face high speed and waves without any damage at all. Cork composites sheets can be cut to be printed before its assembly into the boat mold. Properties such as shock, impact and slamming resistance allow the cork core to retain its original thickness. Under the effect of high disturbing frequency created by an engine or the pounding of the waves, cork-sandwich composites dissipate the energy out of the system leading to a damping far better than others made with rigid foams [46].
Other companies have also been working on another type of boards such as skater boards one-hand surfboards and, also, on surfboards following the market tendency to incorporate natural materials into their products improving the performance, quality, and sustainability of the commercialized goods [4].
A well-known Portuguese brand of handmade kayaks has already manufactured some winning models made with cork composites for world class players who won many gold and silver medals at the 2008 Olympics (Figure 4c). This straightforward material does not rot and offers the lightness and stiffness needed for the construction for a racing kayak. The easy trimming and assembly of these composites, and also the possibility to increase its curing temperature and to reduce the time in the oven, leads to gains regarding productivity. Moreover, the cork ability to bend and adapt to the mold decreases resin quantity, reducing the panel weight and cost [47].

3.2.3. *Horseshoes*

A new type of horseshoes, called Dynamic, without metallic layers was developed by a Portuguese company. This product can be used in horse riding or equestrian competitions. In fact, this lightweight and comfortable product was specially designed to be shock absorbent and most fitted for racehorses. It is five layers *sandwich type* material. The assembly of cork composites and basalt fiber combines the best of nature with modern technology [48,49].

3.3. *Filtration activated carbon and absorbent*

The use of cork for filtration systems has been already largely reviewed [21,50,51], although here are described the recent and remarkable developments in this area.

3.3.1. *Sorption applications*

The search for solutions to treat effluents, new sorbents of natural origin, such as cork is being investigated and becoming a reliable alternative to those in use [52]. In fact, cork low valuable by-products are faced as a source of a new type for the development of sorbents of contaminants [2,53]. Those worthless cork wastes have already been reported as an alternative to expensive and non-regenerable materials, such as activated alumina, activated carbon, or polymer resins for the absorptive treatment of waters contaminated with heavy metals [54-56].

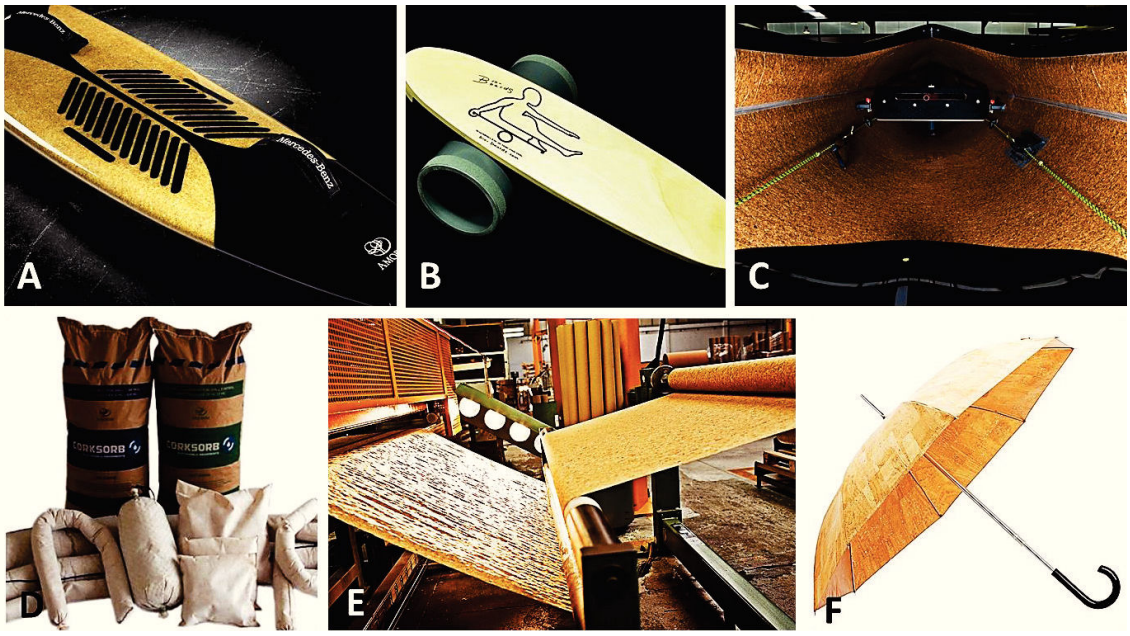

Fig. 4. Cork applications, A – Surfboard, B – Skateboard, C – Kayak, D – Corksorb, E – Fabric manufacturing, F – Umbrella (images source: APCOR)

3.3.2. *Activated carbon*

Activated carbon is widely used in gas and water purification, medicine, effluents treatment and many other applications. Despite its versatility, activated carbons, plays a significant role in medicine where, for example, they are is used for the treatment of poisonings and overdoses. The use of cork for the production of activated carbon has been exploited. The results demonstrated the efficiency of the obtained products. The afforded activated carbon presented different adsorption properties but with similar micropore volume to the current commercial activated carbons, which indicates the potential of cork to produce new high-quality products. The unique structure and chemical composition of cork can lead to new adsorption products with different but excellent performance when compared to those that are already well established (e.g., bentonites, diatomites, or zeolites) [16,21,57-60]. The efforts to investigate cork as a precursor of adsorbents for the removal of pharmaceutical compounds, such as paracetamol, iopamidol, isoprofen, caffeine are still being conducted. Lately, Mestre et al. have patented and published studies regarding the preparation and activation of activated carbon from this renewable and environmentally friendly biomass, granules of expanded corkboard [59,60].

3.3.3. *Cork as an absorber*

Cork is known to be a hydrophobic possessing affinity for organic compounds. Taking advantage of those properties, a product called CORKSORB was developed. The produce such product cork is selected and heat treated with no addition of additives, to afford the best performance to sorb oils and organic compounds. The resulting treated product possesses a high affinity for hydrocarbons, and the sorbent effect is almost instantaneous, cork cells absorb the oil and retain it [61]. A great advantage of these products, besides being 100% natural, relies on the fact that organic compounds can be absorbed without the absorption of water. When saturated the float above water making them suitable to deal with all kind of organic leakages. On-shore/Off-shore oil, and drilling companies, airports, mines, petrol stations, fire departments, truck fleet, refineries, industry and factories, dams, ports, harbors, and marinas can use this product. In the case of an oil spill the activate cork can by sprayed over the leakage avoiding its spreading by absorbing it, preventing, thus, major natural catastrophes (Figure 4d) [62].

3.4. *Fashion and art*

Is this section a brief reference to the use of cork as raw material for others products besides those which involved a higher research and development. The use

of cork to these purposes clearly indicates the versatile nature of this outstanding raw-material, which possesses a much higher economic value than that involved in the ancient and simple cork closure manufacturing.

Cork have become a precious material and regarded as raw materials for the fabrication of added-valuable products. From haute couture shoes to designer clothes, cork is being used as raw-material to enrich those goods, attracting customers who seek for not only for high quality/exclusive products but also goods from natural sources. The fabrics needed to manufacture commodities from cork consist in two steps. First of all the cork is cut into extremely thin laminated sheets of natural or agglomerated cork being than bonded over a cloth or other flexible support or paper. The latter process reveals the texture and patterns of cork (Figure 4e). These fabrics are produced in a wide variety of patterns and are applied to several products [63,64]. A Portuguese company was the pioneer, in 2003, when presented an umbrella made of cork (Figure 4f) re-inventing, thus, the use of cork fabrics. Afterward, the world has embraced this unique material that is now disseminated all over the world and widely used in the fashion industry. Nowadays public figures use cork products demonstrating the cork is not an old material but an innovative and up to date tendency [65,66].

4. Conclusions

This brief survey is focused on the innovative applications not promptly related to cork such as water sports board, fashion industry, chemicals, amongst others. A wide variety of applications has been disclosed demonstrating that the use of this valuable natural material is far from being exhausted. In fact, there are still quite many applications yet to be discovered and studied. Despite the efforts and resources that the scientific community has assigned to cork industry, there is still much work left to be done. Every year the studies related to cork applications have increased, and it is expected that this tendency will be maintained over the next decades, and hopefully new products will be developed.

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