Cork biomass biocomposites: Lightweight and sustainable materials

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17.1 Introduction

Nature has produced a huge number of natural fibers with high potential to reinforce the properties of many composites [1–3]. When compared with most synthetic fibers, natural fibers are low cost, are easier to handle, have appropriate specific mechanical properties, have low density, and require only around 20%–40% of the production energy. Using natural materials increases energy efficiency while promoting the concept of sustainability [1,4,5]. These are some reasons that have led to reduce the use of petroleum-based nonbiodegradable composites and focus the attention on the development of bio-based composite materials in which at least one component is from renewable resources [6]. Lignocellulosic polymer composites are generally engineering materials in which polymer (obtained from natural/petroleum resources) is used as matrix and the lignocellulosic component (most commonly natural fibers) is from renewable resources and acts as reinforcement to provide the desired characteristics in the resulting composite material. Depending on its source, the lignocellulosic fraction can be used in the form of fibers or particles. In terms of reinforcement, typically the word leads to the increase of the mechanical performance; however, in the field and more particularly in this chapter, it will be also considered when the increase of a specific property of the resulting composite material is achieved. Thus, the reduction of the density (i.e., lightweight material) or the improvement of the thermal properties of the composite is also considered reinforcement.

The cork industry is mostly represented in the southeast European zone, where 60% of the world's *Quercus suber* L. plantation area is established. Research and development on cork and cork by-products is of high concern for knowledge transfer, which is essential in the cork industry's strategy and valorization, promoting the development of new materials. Cork-polymer composite (CPC) is one of the most promising fields in cork technology to produce new materials based on sustainable development. Cork combined with polymer matrices, such as thermoplastics, thermosetting, and bio-based polymeric matrices, can result in sustainable products for different sectors of application with economic and environmental benefits. Thus, different melt-based technologies such as extrusion, pultrusion (i.e., palltruder), injection molding, compression molding, and its combination are employed to obtain the final composite

Lignocellulosic Fibre and Biomass-Based Composite Materials. http://dx.doi.org/10.1016/B978-0-08-100959-8.00017-2

materials. The main drawback with the use of natural-based components such as lignocellulosic materials in polymeric composites is their hydrophilicity due to the high surface concentration of hydroxyl group, which leads to poor interface and moisture resistance. Thus, it is possible to employ different reinforcement strategies that improve the lignocellulosic-matrix compatibility via (i) the structure of the matrix, by employing coupling agents [7–9], and (ii) the use of natural fibers combined with cork (i.e., hybrid composites) [10–12] or by chemically modifying the fiber surface [13,14]. Indeed, all of these strategies lead to cork-based composites with improved mechanical properties. In the literature, the use of the main chemical components of cork (i.e., suberin and lignin) as bio-based coupling agents through a reactive extrusion process to improve polymer-cork interfacial bonding was successfully proposed [15]. Moreover, cork also offers economic and environmental advantages over traditional inorganic reinforcements and fillers.

The combination of cork with polymeric matrices results in a significant added value to cork-based materials, with high potential for a wide range of innovative applications in different areas, including civil construction, transports, aeronautics, naval construction, and furniture [5].

17.2 Cork material

17.2.1 Structure and chemical composition

Cork is a cellular material composed of empty closed polygonal cells with a size of, ~20–40 µm that are oriented in the radial direction of the tree. Polygons with faces in the range between 4 and 9 have been observed, the most common ones being pentagons, hexagons, and heptagons. In the nonradial directions (i.e., tangential and axial ones), its cells present a rectangular shape within the same size range, where the long axis is coincident with the radial direction of the tree (Fig. 17.1) [16–18]. The thickness

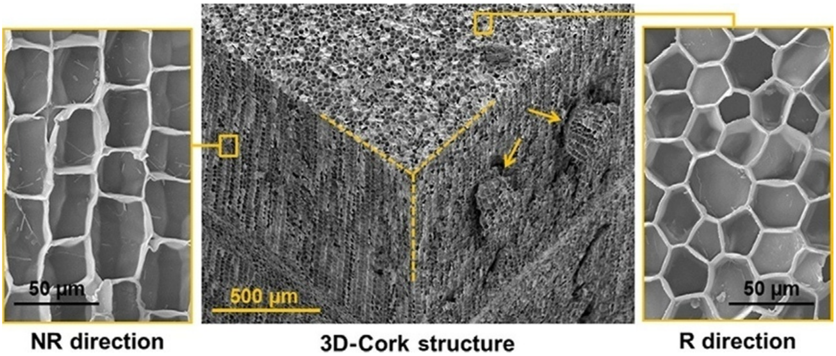

Fig. 17.1 Cork morphology obtained by scanning electron microscopy showing in detail the nonradial direction (NR) and radial direction (R).
Reproduced with permission from Fernandes EM, Correlo VM, Mano JF, Reis RL. Cork-polymer biocomposites: mechanical, structural and thermal properties. Mater Des 2015;82:282–9.

of the cell wall is ~1–2 μm in all directions. In addition to this structure, cork also presents a series of lenticular channels that are oriented in the radial direction of the tree used to transfer oxygen, carbon dioxide, and water from/to the environment, through cork to/from the inner part of the tree [19]. Their number can vary significantly, and its presence is typically associated with the corks' quality; while a higher number of lenticels usually produce a lower density structure, the presence of a lower number of lenticels and more corrugated cell walls produces cork with a higher density.

While the microscopic structure and morphology of cork are important characteristics that define most of its properties, its chemical composition is also important to consider. As any natural material, cork also presents a wide chemical variability that is affected by the region where the tree is planted [20] and the meteorologic conditions that the tree was subject during the formation of its bark, that is, cork [21]. We can divide the chemical constituents of cork into suberin, lignin, polysaccharides, and extractives [16,18,20]. Suberin is a polyester-based structure (Fig. 17.2A) [18,22] and is the most abundant component in cork (contributing to between 33% and 50% of cork) [16,20,23]; lignin is a polyether and is the second most relevant component (Fig. 17.2B) [24], accounting between 13% and 29% of cork [16,20,25,26]; the polysaccharide fraction (composed of cellulose and hemicellulose) is usually present in cork at a percentage between 6% and 25% [16,20]; the extractive fraction is highly variable (present at a percentage between 8% and 24%) and is regarded as the precursor of suberin, lignin, and polysaccharides, and it is usually composed of phenolic and polyphenolic compounds, terpenes, condensed tannins, and waxes, among other chemical structures [16,20,27–30].

Cork components have been fractionated from cork powder biomass and tested for a series of applications that range from pharmaceuticals and cosmetics (e.g., friedelin and polyphenols) [31,32] to polymer synthesis [33–36], adsorbents [37], and antibacterial films [38].

17.2.2 Properties and environmental sustainability

The empty closed cell morphology of cork entraps air in the inner part of the cells that is not expelled during compression creating an elastic response under mechanical pressure. This organization is also one of the main responsibilities for the high recovery rates of cork [39] and its near-zero Poisson coefficient [40].

These properties are the basis of the generalized use of cork as stoppers for wine bottles. In this case, its capacity to limit the oxygen exchange to levels appropriate for wine aging and not to promote its extended oxidation has also been a key factor to maintain cork as the best choice for stoppers [41]. Stoppers are still the most widespread and important application for cork; however, there are a series of other uses that exploit corks' properties and generate materials and products that are unique, such as floorings, wall coverings, and acoustic and thermal insulation panels, among others [16,18]. Industries develop these materials with cork due to its capacity to absorb the impact (due to its elasticity and recovery), to reduce the propagation of acoustic waves, and to limit the heat exchange throughout the closed cell structure. These materials are highly competitive in terms of performance when compared with synthetic ones.

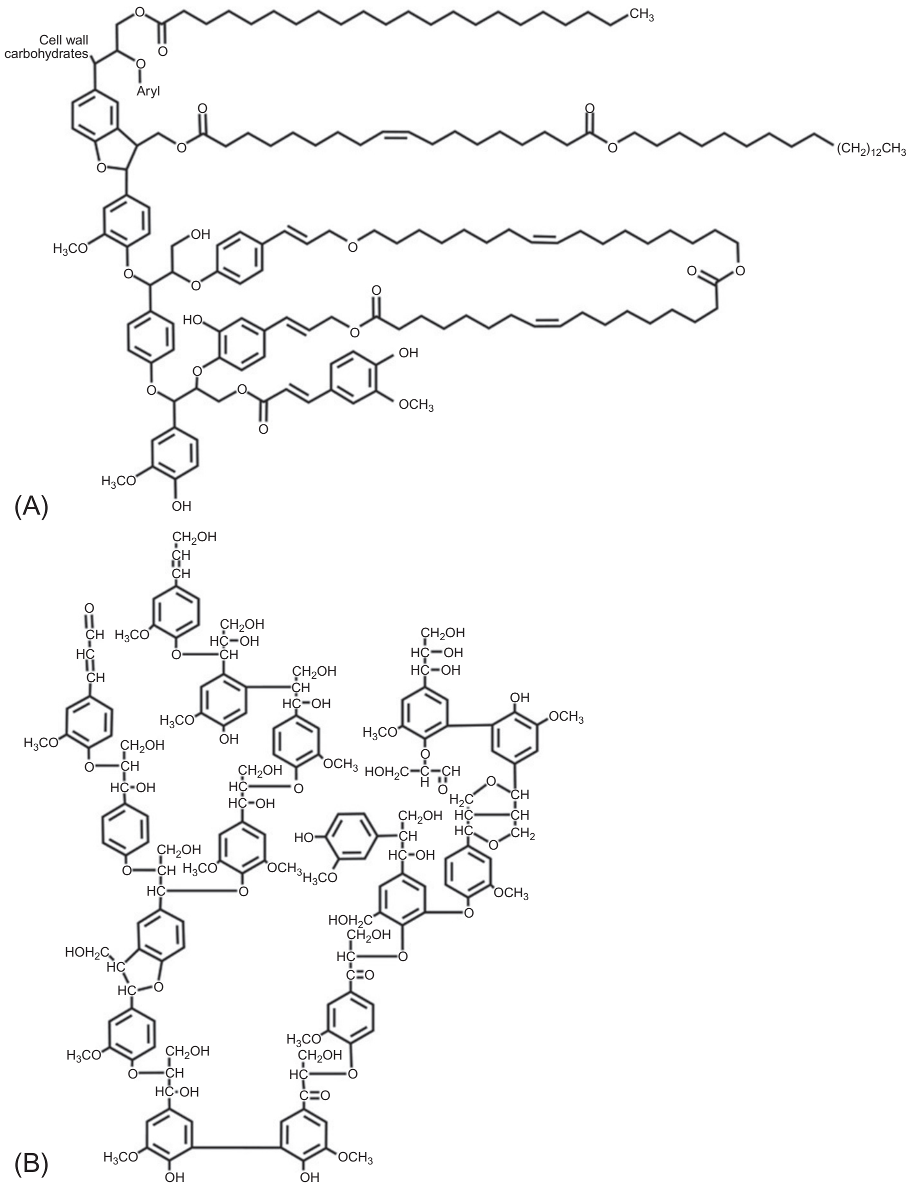

Fig. 17.2 Chemical structure of (A) suberin and (B) lignin, two of the main chemical components of cork.

Based on Cordeiro NMA, Belgacem MN, Silvestre AJD, Gandini A, Neto CP. Cork suberin as a new source of chemicals: 2. Crystallinity, thermal and rheological properties. Bioresour Technol 1998;63:153–8; Adler E. Lignin chemistry—past, present and future. Wood Sci Technol 1977;11:169–218.

In addition to technical performance, cork has the major advantage of being a renewable natural material, whose harvesting does not harm the tree and, in fact, promotes its regeneration. The first cork harvesting is executed after 25 years of the cork oak plantation and, afterward, systematically every 9 years [42]. While being natural and renewable are appealing characteristics, the condition for harvesting is one of its major industrial limitations: the large timeframe between harvestings (and the large space needed between trees in their plantations that reduces the density of trees) limits the availability of this raw material for processing purposes.

In an environmental perspective, its sustainability is supported by the abovementioned characteristics; in particular, the fact that the tree is not harmed during harvesting (contrary to wood) allowing the existence of plantations composed of trees during their whole natural life cycle contributes to a significant carbon sequestration. The maintenance of the cork oak plantation is supported by the industrial value of cork. However, the environmental benefits go beyond the tree itself: the natural environment within the cork oak plantations is of enormous natural richness, being the regions where protected species (e.g., eagles and falcons) can find a secure place to proliferate.

17.3 Cork composites

Composites are heterogeneous materials having two or more solid phases, which are in intimate contact with each other on a microscopic scale [43]. According to the standard ASTM D 3878, composite material is defined as a substance consisting of two or more materials, insoluble in one another, which are combined to form a useful engineering material possessing properties different than the ones shown by the individual constituents [44]. Thus, this chapter does not explore, for instance, the potential of cork sandwich structures, cork agglomerates, and expanded cork (also known as black agglomerated) that is used as an insulation product.

Cork is one of the finest natural materials with high acoustic insulation properties due to its porous structure. In addition, cork presents high water resistance due to its hydrophobic nature that can be seen as a relevant advantage when compared with other lignocellulosic materials, such as wood.

Research involving cork and cork by-products combined with thermoplastics and, more recently, with bio-based matrices has been conducted, preferably using extrusion-based systems to obtain the final product or to obtain cork composite pellets that are further used in injection molding or compression molding. As for other lignocellulosic composites, the final properties of these cork composites are dependent of the processing conditions. Thus, the properties of a cork composite can be tailored for a specific application by varying the compounding process, amount and cork particle size, chemical or surface treatment and type, and the amount of coupling agent. Studies conducted with different CPC formulations have shown the potential of this natural-based product on the development of sustainable composites with improved characteristics in terms of low water absorption (WA), fire resistance, impact resistance, and insulation properties.

17.3.1 Chemical modification and use of adhesion promoters

A proper integration of the cork filler in the composite matrix is governed by the interfacial compatibility between both materials. When combining cork with apolar thermoplastics, the interfacial regions are the weakest sections in the composite structure [45,46]. However, there are a series of chemical treatments that can be performed to the disperse phase, the polymeric phase, or in both to improve the stability of the composite and enhance the interfacial bonding between the filler and the matrix. In relation to the cork biomass, these treatments include mercerization, grafting, and plasma treatment, among other approaches that have been also used for the optimization of wood- and fiber-based composite formulations [45,47–50]. Under these methodologies, composites prepared through the compounding of polypropylene (PP) with mercerized cork (using sodium hydroxide at concentrations ranging from 0.01 to 0.1 M) did not present an improvement in the mechanical performance [13]. The same authors also suggested the silanization and the use of compatibilizers, such as maleic anhydride (MA) modified PP, to improve the mechanical properties of the cork-PP composites. Both strategies resulted in composites with 15% higher tensile modulus (with silanized cork) and 33% higher flexural modulus (using the MA modified PP as adhesion promoter) when compared with PP alone [13]. The use of MA modified polymers has been also tested with high-density polyethylene (HDPE). In this case, the use of MA-HDPE as an additive during the processing of cork-HDPE composites improved both its tensile modulus and strength [15]. This functionalization strategy also reduced the WA of the cork-HDPE composites in a range between 33% and 66% during the first 15 days of immersion [15]. The hexanoylation of cork particles has been also tested to improve the interfacial bonding between cork and polycaprolactone (PCL). This modification increased the tensile modulus of the cork-PCL composites up to 50% [14].

There is a set of other modification methodologies that have been used specifically on cork, namely, the extraction of its water-soluble fraction [51], which generates a modified cork biomass that, combined with PP, yields composites with an improved tensile modulus (up to 7% higher) when compared with cork-PP composites prepared with untreated cork. A series of water extraction timeframes have been tested, and cork with only 1 h of treatment revealed to be the most appropriate, while in higher timeframes, a reduced increment of the mechanical performance was observed [51].

Reactive extrusion has been also tested in the preparation of functionalized CPCs. While this methodology has been used also in the preparation of wood-based composite systems, to our knowledge, the exploitation of the cork components as functionalization agents has been restricted to cork-based composites. Cork components, such as suberin and lignin, have been tested as promoters of adhesion between the cork and polymeric phases, such as HDPE and low-density polyethylene (LDPE) [15,52]. Suberin acted as plasticizer agent with antioxidant benefits for the polyethylene (PE) composites, while lignin works as a coupling agent, increasing both tensile modulus and strength and improved the thermal stability [15]. In addition, chemically modified suberin (extracted from birchbark) has been also tested as functionalization agent (under this methodology) to promote the adhesion between cork and LDPE. The results indicate an increment of the tensile strength and maximum strain and a reduction of the elastic modulus of the cork-LDPE functionalized composite [52]. The results confirmed the suitability of these components to improve the mechanical performance of the composites and the interfacial bonding between the disperse phase (cork) and the matrix (thermoplastic).

17.3.2 Processing and properties

17.3.2.1 Cork-polymer composites

Polyolefins, like PE and PP, are two of the most commonly used polymers with a wide range of applications. Polyolefins are one of the preferred choices among the commercial polymers because of their excellent combination of chemical and physical properties along with low cost, superior processability, and good recyclability [53].

The cork industry produces considerable amounts of cork powders resulting from the final stages of cork processing stages or resulting from existing cork products, such as cork flooring products typically with density ranging from 157 to 400 $\mathrm{kg\,m^{-3}}$ [7]. Usually, these powders are burned and are used to heat boilers in industrial processes. The previously referred thermoplastic matrices (i.e., HDPE and PP) were combined with cork biomass using melt-based technologies such as pultrusion to obtain the composite pellets and further compression molding to obtain boards with appropriate dimensional stability [7,8]. These works used high amount of cork powder (i.e., 50 wt%) from different origins combined with different thermoplastic materials that can be transformed into a highly valued composite products as shown in Fig. 17.3. The cork-based composite pellets showed lower density as compared with the used thermoplastic matrices, indicating the potential to obtain lightweight composites. The morphology of the surface fractures indicated a good dispersion of the cork and a good adhesion between both phases, preferably in the presence of low amounts of coupling agent based on MA [7]. Further work compared the properties of the developed CPC with commercially available products, namely, medium-density fiberboard (MDF) and high-density fiberboard (HDF). It was found that the CPCs have good dimensional stability, lower water uptake, better acoustic insulation performance at high frequencies, and similar behavior in terms of hardness and fire resistance when compared with both MDF and HDF. While the mechanical strength was lower compared with both commercial materials (i.e., MDF and HDF), it was also observed that the addition of cork improved the flexural modulus, impact resistance, and hardness on the developed CPC [8]. In a recent work, cork biomass was combined with polyvinyl chloride (PVC) in different concentrations as a recycling strategy [54]. It was found that the incorporation of coupling agent based on maleic anhydride (PVC-g-MA) enabled the elimination of the adverse effect of cork biomass, improving the tensile strength. Thus, using cork biomass combined with high-consumption thermoplastic matrices resulted in a composite material to be considered and applied in the design of flooring and building strategies to achieve greater strength and rigidity for specific applications.

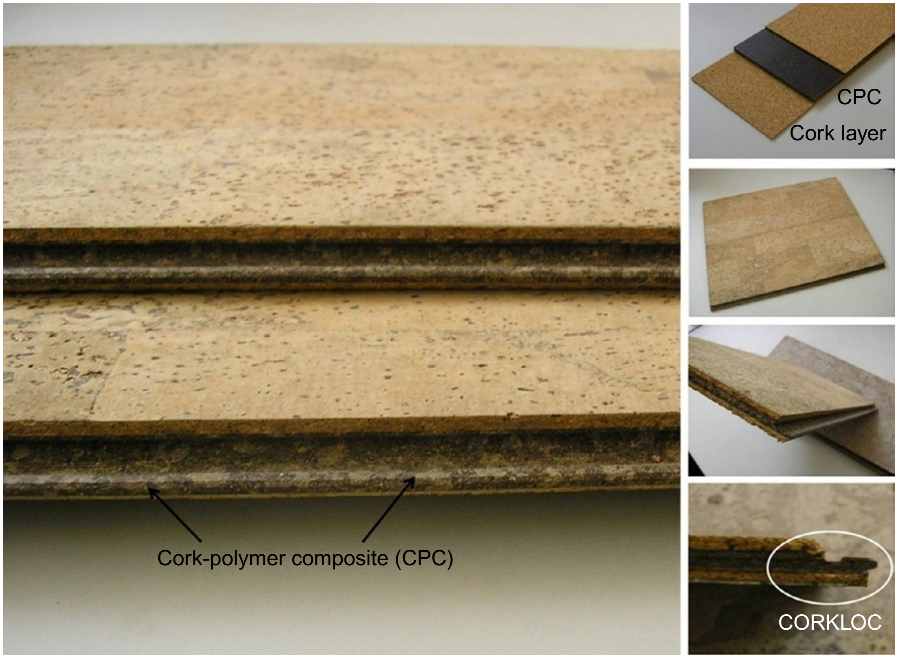

Fig. 17.3 Prototype of a laminated flooring system using cork-polymer composite (CPC) as underlay.
Reproduced with permission from Fernandes EM. New functionalization—reinforcement strategies for cork plastics composites: opening a wide range of innovative applications for cork based products [Doctoral thesis]. University of Minho, Portugal; 2013.

The production of lignocellulosic composites through melt-based technologies is strongly limited by the available range of temperatures and processing times that do not promote the degradation of the lignocellulosic part. In fact, at temperatures around 180–200°C, it is observed a significant thermal degradation of cellulose and the residence of the melt for long periods of time at these temperatures decreases the mechanical properties of the final composite. Therefore, the processing of these composites must be limited to temperatures at lower range of degradation and for limited processing times, avoiding significant damage to the lignocellulosic fraction and reduced composite performance [4,55]. The moisture content at a given relative humidity also can have a great effect on the biological performance of a composite made from natural fibers. Cork, as a material of hydrophobic nature, presents a low moisture content. This is a clear advantage in comparison to wood, that due to its high-water absorption capacity can compromise the integrity of the wood-based composites [56].

The particle size of the cork biomass is another important factor to be considered when compounding it with polymeric matrices. Cork particles and powder were compounded with PP by twin-screw extrusion and further processed by injection or compression molding [57]. The cork composites revealed good distribution and dispersion with interesting esthetic characteristics. Low cork content (5 wt%) reinforces the stiffness of the PP. The addition of PP-g-MA up to 8 wt% promotes an increase on the tensile strength. The PP-cork composites presented reduced WA, and in general, the tensile properties of the PP-cork composites were not significantly affected after the WA tests. Moreover, the WA was found to increase with the increment of cork content and was reduced with the use of a coupling agent based on MA. It was also found that cork acts as nucleating agent and promotes antioxidant protection to the PP matrix [57–59]. The addition of low cork content improves the thermal resistance, while increasing the bio-based component increases the composite density and its thermal conductivity. In terms of processing, the addition of cork to the thermoplastic matrix reduces considerably the viscosity and consequently the melt flow index (MFI), while the addition of the coupling agent (based on MA) to the polyolefin-cork system promotes opposite effect improving the mixability [57]. The rheological properties of PP-cork composites for injection molding were recently studied keeping the same matrix/cork weight ratio and varying the cork particle size distribution [9]. Rheological analyses showed that all composites exhibited non-Newtonian, pseudoplastic behavior. Related to neat PP, cork incorporation led to a clear viscosity increase. This increase is more significant in the CPC with the lowest cork particle size. On the other hand, the addition of coupling agent results in a decrease of CPC viscosity, in accordance with other study that reports MFI tests [57].

Polymers from renewable resources have attracted an increasing attention, predominantly due to two major reasons: firstly, environmental concerns and secondly, the fact that our petroleum resources are limited [60]. More recently, CPC materials were produced using bio-based polyester matrices such as synthetic polymers from natural monomers, named poly(lactic acid) (PLA) and poly(L-lactic acid) (PLLA); polymers from microbial fermentation, such as polyhydroxybutyrate-co-hydroxyvalerate (PHBV); and biodegradable polyesters, such as poly(caprolactone) (PCL) and starch-poly(caprolactone) (SPCL), starch being a natural polymer starch [14,61,62]. In all cases, the biocomposites showed a good dispersion of cork biomass and a strong interfacial adhesion between the cork particles and the polymeric matrices. Moreover, combining melt mixing or extrusion followed by injection molding processes reduces significantly the composite density by the use of cork biomass [14,61]. Thus, by using this strategy, it was possible to obtain lightweight cork biocomposite materials.

Fig. 17.4 shows a possible application as biodegradable caps for wine bottles [61], obtained by two melt-based steps: extrusion to produce the bio-based cork composite pellets and injection molding, the last process being used for the formation of parts with excellent dimensional accuracy. In this work, it combined different biodegradable aliphatic polyesters (i.e., PLLA, PHBV, PCL, and SPCL) with cork at 30 wt%. Some of the presented solutions in Fig. 17.4 resulted in 100% renewable material. Thus, the combination of cork with bio-based polymeric matrices can generate composites of 100% natural origin that are fully biodegradable. These materials are highly relevant for eco-friendly applications, where sustainability plays a relevant role. In this study, the cork biocomposites were engineered to satisfy acceptable stiffness, strength, and in-service durability while maintaining the tendency for rapid out-of-service biodegradation [56,61].

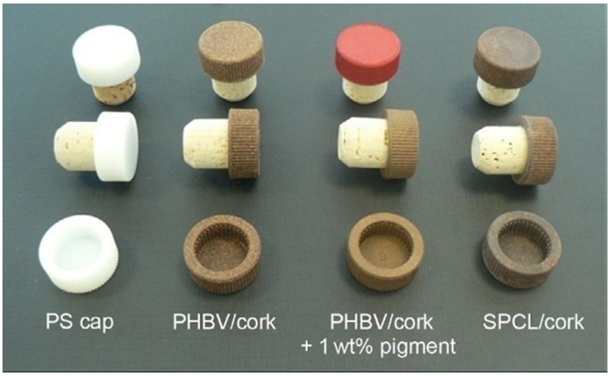

Fig. 17.4 Commercial stopper using a polystyrene (PS) cap for wine bottles and prototype of cap solutions based on cork and bio-based polyester obtained by injection molding. Based on Fernandes EM, Correlo VM, Mano JF, Reis RL. Cork-polymer biocomposites: mechanical, structural and thermal properties. Mater Des 2015;82:282–9.

17.3.2.2 Hybrid CPCs

Hybrid composites are one of the emerging fields in polymer science that brings attention for its application in various sectors ranging from automobile to the construction industry [63]. The incorporation of two or more fibers into a single polymer matrix leads to the development of hybrid composites. Hybridization can improve the mechanical properties of single fiber-reinforced polymer composite [43]. The mechanical properties of lignocellulosic composite depend upon reinforcement, matrix, and adhesion between them, and the failure of any parameter may cause the failure of others.

Maximum hybrid results are obtained when the fibers are highly strain compatible [64]. The properties of the hybrid system consisting of two components can be predicted by the rule of mixtures [64,65], as presented in Eq. (17.1):

$$P_{\mathrm{H}} = P_1V_1 + P_2V_2 \tag{17.1}$$

where P_{H} is the property to be investigated, P_1 the corresponding property of the first system, and P_2 the corresponding property of the second system. V_1 and V_2 are the relative hybrid volume fractions of the first and second system and $V_1+V_2=1$.

In literature, relevant references can be found referring to the potential and the principal challenges of this reinforcing strategy [1,43,63,66]. Hybrid composites formulated with two different types of lignocellulosic fibers are not common. However, they present an environmental advantage compared to composites that are constituted by the more widespread combination of natural and synthetic fibers [63].

The mechanical properties of cork biomass are much lower when compared with the common lignocellulosic fibers; however, the combination of cork biomass with natural fibers will result in a composite higher stiffness and higher natural component in the final solution. Cork-based composites have been reinforced with different short natural fibers (i.e., coconut, wood, and sisal fiber) and synthetic fibers (i.e., glass fiber) to improve the mechanical performance under tensile, impact, and bending loads [10,12,67]. These hybrid cork-based composites were produced using HDPE as matrix and applying twin-screw extrusion followed by compression molding. In those works, it used a cork ratio of 40–50 wt%. This reinforcement strategy showed that the lignocellulosic-matrix interaction was improved via (a) the use of the natural fibers, (b) by modifying the fiber's surface, (c) via the matrix, or (d) by employing coupling agents resulting in composites with considerably higher mechanical properties.

Hybrid CPCs using HDPE as matrix were combined with short sisal fibers [10]. It investigated the use of chemical fiber treatment and the addition of a coupling agent on the composite formulation that contains 40 wt% of cork biomass. Sisal fibers were modified using alkali treatment, and the FTIR analysis revealed some lignin and wax from the fiber surface promoting a cleaner fiber surface to interact with the matrix. Moreover, X-ray diffraction revealed a small increase on the crystallinity, confirming the surface modification of the sisal fibers. Mechanical tests indicated some loss on the fiber's mechanical performance in terms of maximum strength after treatment, probably due to the reduction of the fiber thickness and some removal of the hemicelluloses and lignin. The mechanical properties of those hybrid composites under flexural load showed a reinforcement of the matrix in terms of stiffness and strength that was achieved mainly after alkali treatment to the sisal fibers in combination with the low amount of the used coupling agent, as present in Fig. 17.5 (formulation CPC6).

The flexural properties using alkali-treated sisal fibers with coupling agent show an increase of 33% in flexural modulus and an increase of 98% in the strength when

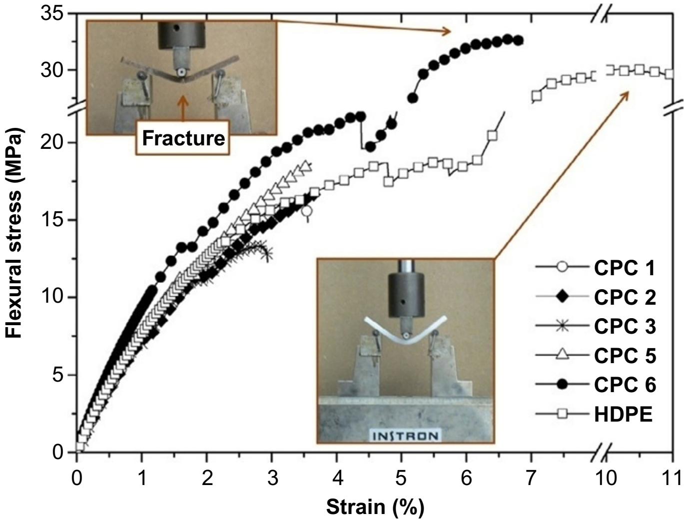

Fig. 17.5 Flexural stress-strain curves of the developed CPCs (40–60 wt%) reinforced with sisal fibers and comparison with the HDPE matrix.
Reproduced with permission from Fernandes EM, Mano JF, Reis RL. Hybrid cork-polymer composites containing sisal fibre: morphology, effect of the fibre treatment on the mechanical properties and tensile failure prediction. Compos Struct 2013;105:153–62.

compared with unreinforced cork composites. The alkali treatment leads to higher mechanical properties of the composites since cellulose has higher mechanical performance than lignin and increases the specific surface area leading to a better interaction with the matrix [10]. Higher mechanical properties were obtained by using short wood fibers also in the presence of a coupling agent based on MA [12]. Typically, under those reinforcement strategies, the high strain of the matrix is considerably reduced by the incorporation of a high content of lignocellulosic component (i.e., cork biomass and/or natural fibers). Moreover, mathematical models, such as Weibull function, were applied to predict the mechanical properties of the CPC composite safety limits, being in agreement with the mechanical tests.

The morphology of the hybrid composite fractures after mechanical testing can elucidate the importance in improving fiber-matrix interaction, as shown in Fig. 17.6. In this case, coconut fiber was used to reinforce the CPCs [67]. Fig. 17.6A shows a lack of adhesion between coconut fibers (10 wt%) and the cork-polymer phases, clearly observed in the presence of voids, while Fig. 17.6B shows a good interfacial adhesion between the coconut fibers and the polymeric matrix. In this last case, the fracture of the coconut fiber occurred preferentially at the same level of the composite fracture. Generally, coupling agents are molecules that present two functions: (i) the first is to react with the hydroxyl groups of cork and of cellulosic fibers and (ii) the second is to react with functional groups of the matrix. The expected result is the reduction on the number of these groups that contribute to the lowering of these hydrophilic characters, promoting the compatibility between the matrix and the natural component.

Indeed, different natural fibers (i.e., short and long fibers) should be tested, and the cork surface modification attempted to promote cork-matrix compatibility. A deeper understanding of the complex nature of cork and natural fibers and their surface properties is still needed in order to take advantage of this complex system. Using materials

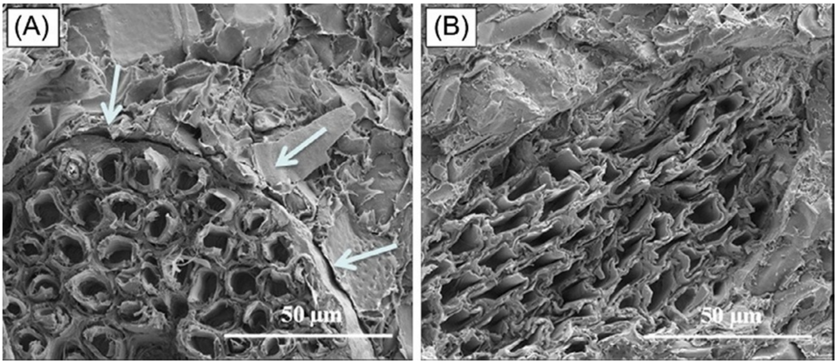

Fig. 17.6 SEM micrographs of CPC fracture after tensile tests at a magnification of 2400×; CPC reinforced with 10 wt% coconut fiber (A); CPC reinforced with 10 wt% coconut fiber with 2 wt% of coupling agent (B).

Based on Fernandes EM, Correlo VM, Mano JF, Reis RL. Novel cork-polymer composites reinforced with short natural coconut fibres: effect of fibre loading and coupling agent addition. Compos Sci Technol 2013;78:56–62.

like natural-based composites that reduce construction waste and increase energy efficiency would provide a solution to immediate infrastructure needs while promoting the concept of sustainability.

17.3.2.3 Cork rubber composites

Cork composites with rubber are made by mixing and binding cork granules with natural or synthetic rubber, where they combine the properties of the two materials [68]. Cork, as cellular material, presents high compressibility and recovery characteristics with a near-zero Poisson coefficient [16,68], while rubber shows higher lateral expansion under compression load and small recovery after deformation. Moreover, the low mechanical resistance of cork is compensated by the rubber component that acts as matrix.

Regarding the processing, the cork and rubber particles present low particle sizes and are thoroughly mixed with cross-linking agents and catalysts, among other additives, such as antioxidant agents and color masterbatches. The mixture is then homogenized and repeatedly roll pressed to obtain a homogenous past that is further injected or compression molded before the temperature induced the cross-linking polymerization [68]. In this area, different rubber types can be used to provide different properties (nitrile, neoprene, natural rubber, and synthetic rubber), and these can be combined with different cork particle sizes to impart the composite with properties relevant for different applications.

Cork rubber composites are mainly used as: gaskets and sealing devices for the automotive industry; vibration and acoustic insulation panels; energy absorption devices; footwear; specific gaskets for electric transformers; and nonslip materials. Thus, the dielectric properties of the material are highly relevant and were addressed, for instance, in a study of isotactic PP nitrile rubber blends [69]. The effect of the addition of fillers on the dielectric properties was investigated for different fillers and their concentrations. It was found that the fillers affect the dielectric properties: the silica filler induced an increase of the dissipation factor, whereas cork biomass induced a reverse trend for concentrations higher than 10 wt%. Moreover, in the design of these composites, it is important to consider changes with the temperature. The literature indicates modification of the dielectric properties of cork, which occurs as a consequence of heating above 60°C [70]. It was suggested that the modification of the dielectric properties arises from desorption, induced by heating or evacuation, of water molecules absorbed in the cork structure. The performance of different cork rubber gaskets to seal combustion engines was also investigated. The study showed that cork rubber composites have adequate sealing properties for gasoline and blends of gasoline with ethanol [71].

Cork-polyurethane composites are rubber-like materials that result from the combination of cork particles with a polyurethane gel. It has its potential use in products such as comfort enhancement devices, for instance, in shoe systems, and vibration damping. Thus, computer-aided engineering tools have been applied to predict the mechanical response of these cork rubberlike materials and its suitability for particular loading case scenarios [72,73]. These studies revealed that the cork-polyurethane gel composite materials are mechanically characterized by a nonlinear elastic behavior at large deformations (hyperelastic behavior) and a dissipative behavior evidenced by the hysteretic effect that occurs during loading-unloading cycles. The effect of the cork filler on the mechanical properties of the polyurethane elastomeric bearing materials for passive isolation was also conducted [74]. It was shown that the addition of cork filler into polyurethane composites yields an increase in stiffness and a decrease in the elongation at break. The developed polyurethane-cork composite materials presented better damping properties and were proposed to be used as a bearing pad for acoustic and vibratory isolation for railway and underground lines.

17.3.3 Industrial applications

Cork biomass is a lightweight natural material from renewable resources. The incorporation of cork in polymers through melt-based technologies has become an effective approach to develop new sustainable materials promoting added value to cork biomass. In the last two decades, applications of CPC products have been developed, the use of gaskets for the automotive industry being one of the most relevant applications. In the last decade, a series of lignocellulosic-based composites were developed for decking applications, industrial insulation systems, handles in tools, among others. Some of these representative examples are shown in Fig. 17.7.

The partnership between companies, Pallmann, Wacker, and Amorim Group, resulted in a product containing cork biomass and polymer using the constituents in powder form [75]. It is highlighted that by applying different polymeric matrices, it is possible to obtain a range of cork composite materials from rigid to highly flexible formulations. Fig. 17.7A presents a machine known as a double-belt press, which has been used to bond the cork layers to wafer-thin slate sheets under high pressure and temperatures of roughly 180°C.

A composition of a composite product composed of 60% of cork mixed with 40% of VINNEX powder was applied as slate-cork flooring. As it was pointed out before, the difference in terms of volume between the constituents is very high, a challenge in terms of processing in this area of application. The natural cork and VINNEX powder binder are blended together to form homogenized pellets as presented in Fig. 17.7B that can be used in a further melt-based process [76,77]. The Thermofix Technology Center GmbH presented a hybrid composite solution based on 30% cork biomass (i.e., cork flour), 30% of coconut fiber, and 40% polyvinyl acetate (PVAc) polymer [78]. Similar to the previous product, the mixture is melt compounded and granulated. The resulting particles are dispersed on a press and consolidated under heat and mild pressure to give a composite board. The resulting board can be used for indoor applications, that is, wall covering or floor covering systems.

A different CPC material produced by the company Greenfiber Tech, known as SmartComposite (see Fig. 17.7C) obtained by extrusion, is also highly representative of the potential of this area. This product not only presents some similarities to wood plastic composites) but also intends to compete to the oriented strand board products that are the most-used sheathing and subflooring material. This CPC is composed by a PP matrix compounded with two different types of natural fibers/particles, being

Fig. 17.7 Representative applications of CPC: (A) cork-slate sheets, (B) CPC pellets for melt-based processes, (C) terrace decking, (D) cork gaskets for automotive, and (E) hand tools. Reproduced from Wacker Chemie AG (photos A and B); Greenfiber Tech (photo C); Manufactures Cusell, SL (photo D); and Muller Kunststoffe (photo E).

one of them cork. The resulting products are envisaged for outdoor furniture, terrace decking and naval construction, siding, structural elements, and shoe industry components [5,79]. The new formulations show significantly enhanced properties regarding swelling, water uptake, and density. For special applications, the good fire resistance of cork can be also an advantage [80].

As highlighted before, cork is a lightweight and stable material with water resistance and good insulation properties. Cork rubber gaskets combine the properties of those constituents and can be manufactured with different filler rubbers, such as (i) styrene butadiene rubber (SBR) cork for oils and low-pressure applications; (ii) nitrile rubber (NBR) cork for oils, fuels, and gases; and (iii) neoprene cork that generally combines the weather and oil resistance of the polymer with the resilience of the cork. This blend has become widely used where low-cost, low-pressure gaskets are required for electric transformers, (iv) silicone cork for use with special oils in the automotive and electric industries, and (v) nitrile cork that gives very good oil and fuel-resistant gasket material, which is widely used in the automotive and general engineering industries. There are different designs and colors of these types of cork rubber gaskets as presented in Fig. 17.7D [81,82].

A partnership between Hexpol, Muller Kunststoffe, and Elasto resulted in a product named lifocork that can be obtained using thermoplastic processing methods [83], and one of those potential uses is shown in Fig. 17.7E. Lifocork can be processed using both standard injection molding equipments and under two-component molding machines. It is also referred an excellent bond to thermoplastic elastomer (TPE), PP, and PE matrices. Other processing methods include extrusion or thermoforming with a double-belt press system. Possible uses are pointed for handles and grips, trays, boxes, and plant pots and toys. It is also possible to make foamed parts from Lifocork, therefore giving lightweight parts. In this case, its uses are envisaged to give a damping, shock absorbent effect, ideal for orthopedic shoe lifts and inserts. In all industrial applications, the use of standard masterbatches, such as pigments, opens even more design possibilities in the development of CPC solutions.

The interest in additive manufacturing techniques also called 3D printing has been growing in different fields of application. Additive manufacturing is the process of joining materials to make objects from computer-aided design model data, usually layer upon layer using an extrusion head, and allows to replicate complex architectures. A recent example in this area is called EasyCork [84], which is a lightweight filament composed of PLA and filled with ~30 wt% of cork that can be used in fused deposition modeling equipments. This composite filament allows to obtain 3D printing objects with cork-like esthetics and cork-like properties.

17.4 Conclusions and future trends

The uses of CPCs obtained through melt-based technologies and its principal properties, last developments, and industrial applications in different fields as lightweight and sustainable materials were discussed in this chapter. The use of lignocellulosic material, such as natural fibers and cork biomass in industrial applications, provides challenges for researcher to develop suitable techniques that are able to produce good quality CPC materials. Some of the recent interests in this area include the production of lightweight bio-based CPCs and the potential of low-molecular-weight fractions from cork (i.e., extractives) as antioxidant stabilizers in polymers, already with some promising results. The findings reported in these previous studies showed that the general properties of CPCs reveal the required (i) dimension stability with reduced water absorption; (ii) homogeneous distribution and dispersion of the cork particles in the polymer matrix; (iii) improved fire resistance to the polymeric matrix promoted by cork and good thermal and acoustic insulation properties, compared with MDF and HDF; and (iv) an interesting range of mechanical properties potentiating the application in different areas. The potential application of these composites in the construction sector may include flooring and floor frames, wall covers, electric protection systems, and outdoor applications such as decking, tables, chairs, benches, and trash bins for gardens. As it was pointed out before, some companies are effectively exploring the potential of the CPC materials creating added value to cork biomass.

Research in CPCs ranges from fundamental studies to applied and/or oriented ones. Since cork biomass presents different chemical composition, as compared with other lignocellulosic materials, it lacks more knowledge on the chemistry of those composites to take advantage of the unique characteristics of this natural material. It is also important to look similar areas of application and find efficient manufacturing systems to produce structural CPCs and strategies to produce complex parts. For some applications, there is a need to develop appropriate mathematical modeling and computational simulation concepts to support the structural optimization and the failure prevention of the new design solutions. In terms of manufacturing using melt-based technologies, more understanding should be helpful in the rheological properties of the different cork-polymer compositions, preferably monitoring them under in-line conditions. It is also expected to see the production of lightweight CPCs using foaming strategies, by utilizing either physical or chemical blowing agents. The combination of cork with different polymeric matrices answers to specific challenges of their indoor or outdoor uses; thus, the UV and weather resistance should be considered and strategies to improve fire resistance. The use of nondestructive characterization techniques to address the mechanical behavior, such as full-field measurements or other relevant information of those composite structures, will be of interest in this field. Life cycle assessment methodologies for companies should also be conducted to evaluate the potential of these developments, in particular considering the forest feedstock supply chains to fulfill the future demand of forest biomass.

The future outlook for development in the field of lignocellulosic polymer composites and particularly of CPC materials is promising due to their inherent eco-friendly potential, low density, insulation, and esthetics, among other advantages. Challenges still exist in the CPC field and will tend to increase the interest of researchers and product designers in seeking for new routes to effectively use their solutions and to overcome the drawbacks on cork composite materials in different respective fields of application.

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References

[1] Faruk O, Bledzki AK, Fink HP, Sain M. Biocomposites reinforced with natural fibers: 2000–2010. Prog Polym Sci 2012;37:1552–96.

[2] Gurunathan T, Mohanty S, Nayak SK. A review of the recent developments in biocomposites based on natural fibres and their application perspectives. Compos Part A Appl Sci Manuf 2015;77:1–25.

[3] Fernandes EM, Mano JF, Reis RL. Polyethylene composites with lignocellulosic material. Polyethylene-based blends, composites and nanocomposites. Hoboken, NJ, USA: John Wiley & Sons, Inc.; 2015. p. 117–61.

[4] Dittenber DB, GangaRao HVS. Critical review of recent publications on use of natural composites in infrastructure. Compos Part A Appl Sci Manuf 2012;43:1419–29.

[5] Gil L. New cork-based materials and applications. Materials 2015;8:625–37.

[6] Thakur MK, Rana AK, Thakur VK. Lignocellulosic polymer composites: a brief overview. Lignocellulosic polymer composites. Hoboken, NJ, USA: John Wiley & Sons, Inc.; 2014. p. 1–15.

[7] Fernandes EM, Correlo VM, Chagas JAM, Mano JF, Reis RL. Cork based composites using polyolefin's as matrix: morphology and mechanical performance. Compos Sci Technol 2010;70:2310–8.

[8] Fernandes EM, Correlo VM, Chagas JAM, Mano JF, Reis RL. Properties of new cork-polymer composites: advantages and drawbacks as compared with commercially available fibreboard materials. Compos Struct 2011;93:3120–9.

[9] da Silva SPM, Lima PS, Oliveira JM. Rheological behaviour of cork-polymer composites for injection moulding. Compos Part B Eng 2016;90:172–8.

[10] Fernandes EM, Mano JF, Reis RL. Hybrid cork-polymer composites containing sisal fibre: morphology, effect of the fibre treatment on the mechanical properties and tensile failure prediction. Compos Struct 2013;105:153–62.

[11] Fernandes EM, Correlo VM, Mano JF, Reis RL. Natural fibres as reinforcement strategy on cork-polymer composites. In: Pinto AMP, Pouzada AS, editors. Advanced materials forum Vi, Pts 1 and 2. Stafa-Zurich: Trans Tech Publications Ltd; 2013. p. 373–8.

[12] Fernandes EM, Correlo VM, Chagas JAM, Reis RL. Fibre-reinforced cork-based composites. WO 2011014085 A2. Amorim Revestimentos; 2011.

[13] Ben Abdallah F, Ben Cheikh R, Baklouti M, Denchev Z, Cunha AM. Effect of surface treatment in cork reinforced composites. J Polym Res 2010;17:519–28.

[14] Vilela C, Sousa AF, Freire CSR, Silvestre AJD, Neto CP. Novel sustainable composites prepared from cork residues and biopolymers. Biomass Bioenergy 2013;55:148–55.

[15] Fernandes EM, Aroso IM, Mano JF, Covas JA, Reis RL. Functionalized cork-polymer composites (CPC) by reactive extrusion using suberin and lignin from cork as coupling agents. Compos Part B Eng 2014;67:371–80.

[16] Silva SP, Sabino MA, Fernandes EM, Correlo VM, Boesel LF, Reis RL. Cork: properties, capabilities and application. Int Mater Rev 2005;50:345–65.

[17] Pereira H, Rosa ME, Fortes MA. The cellular structure of cork from *Quercus suber* L. IAWA Bull 1987;8:213–7.

[18] Gil L, Moiteiro C. Cork. Ullmann's encyclopedia of industrial chemistry. Weinheim: Wiley-VCH; 2002.

[19] Groh B, Hubner C, Lendzian KJ. Water and oxygen permeance of phellems isolated from trees: the role of waxes and lenticels. Planta 2002;215:794–801.

[20] Pereira H. Chemical composition and variability of cork from *Quercus suber* L. Wood Sci Technol 1988;22:211–8.

[21] Caritat A, Gutiérrez E, Molinas M. Influence of weather on cork-ring width. Tree Physiol 2000;20:893–900.

[22] Cordeiro NMA, Belgacem MN, Silvestre AJD, Gandini A, Neto CP. Cork suberin as a new source of chemicals: 2. Crystallinity, thermal and rheological properties. Bioresour Technol 1998;63:153–8.

[23] Cordeiro NMA, Belgacem MN, Silvestre AJD, Neto CP, Gandini A. Cork suberin as a new source of chemicals: 1. Isolation and chemical characterization of its composition. Int J Biol Macromol 1998;22:71–80.

[24] Adler E. Lignin chemistry—past, present and future. Wood Sci Technol 1977;11:169–218.

[25] Neto CP. Isolation and characterization of a lignin-like polymer of the cork of *Quercus suber* L. Holzforschung 1996;50:563–8.

[26] Marques AV, Pereira H, Meier D, Faix O. Quantitative analysis of cork (*Quercus suber* L.) and milled cork lignin by FTIR spectroscopy, analytical pyrolysis, and total hydrolysis. Holzforschung 1994;48:43–50.

[27] Sousa AF, Pinto PCRO, Silvestre AJD, Neto CP. Triterpenic and other lipophilic components from industrial cork byproducts. J Agric Food Chem 2006;54:6888–93.

[28] Santos SAO, Pinto PCRO, Silvestre AJD, Neto CP. Chemical composition and antioxidant activity of phenolic extracts of cork from *Quercus suber* L. Ind Crop Prod 2010;31:521–6.

[29] Santos SAO, Villaverde JJ, Sousa AF, Coelho JFJ, Neto CP, Silvestre AJD. Phenolic composition and antioxidant activity of industrial cork by-products. Ind Crop Prod 2013;47:262–9.

[30] Araujo AR, Pereira DM, Aroso IM, Santos T, Batista MT, Cerqueira MT, et al. Cork extracts reduce UV-mediated DNA fragmentation and cell death. RSC Adv 2015;5:96151–7.

[31] Moiteiro C, Manta C, Justino F, Tavares R, Curto MJM, Pedro M, et al. Hemisynthetic secofriedelane triterpenes with inhibitory activity against the growth of human tumor cell lines in vitro. J Nat Prod 2004;67:1193–6.

[32] Moiteiro C, Justino F, Tavares R, Marcelo-Curto MJ, Florencio MH. Synthetic secofriedeline and friedelane derivatives as inhibitors of human lymphocyte proliferation and growth of human cancer lines in vitro. J Nat Prod 2001;64:1273–7.

[33] Evtiouguina M, Barros AM, Cruz-Pinto JJ, Neto CP, Belgacem MN, Gandini A. Oxypropylation of cork and the use of the ensuing polyols in polyurethane formulations. Biomacromolecules 2002;3:57–62.

[34] Evtiouguina M, Gandini A, Neto CP, Belgacem NM. Urethanes and polyurethanes based on oxypropylated cork: 1. Appraisal and reactivity of products. Polym Int 2001;50:1150–5.

[35] Cordeiro NMA, Belgacem MN, Gandini A, Neto CP. Urethanes and polyurethanes from suberin 2: synthesis and characterization. Ind Crop Prod 1999;10:1–10.

[36] Cordeiro NMA, Belgacem MN, Gandini A, Neto CP. Urethanes and polyurethanes from suberin: 1. Kinetic study. Ind Crop Prod 1997;6:163–7.

[37] Mestre AS, Pires RA, Aroso I, Fernandes EM, Pinto ML, Reis RL, et al. Activated carbons prepared from industrial pre-treated cork: sustainable adsorbents for pharmaceutical compounds removal. Chem Eng J 2014;253:408–17.

[38] Garcia H, Ferreira R, Martins C, Sousa AF, Freire CSR, Silvestre AJD, et al. Ex situ reconstitution of the plant biopolyester suberin as a film. Biomacromolecules 2014;15:1806–13.

[39] Rosa ME, Fortes MA. Rate effects on the compression and recovery of dimensions of cork. J Mater Sci 1988;23:879–85.

[40] Fortes MA, Nogueira MT. The Poisson effect in cork. Mater Sci Eng 1989;A122:227–32.

[41] Karbowiak T, Gougeon RD, Alinc JB, Brachais L, Debeaufort F, Voilley A, et al. Wine oxidation and the role of cork. Crit Rev Food Sci 2010;50:20–52.

[42] Costa A, Oliveira AC. Variation in cork production of the cork oak between two consecutive cork harvests. Forestry 2001;74:337–46.

[43] Gupta MK, Srivastava RK. Mechanical properties of hybrid fibers-reinforced polymer composite: a review. Polym-Plast Technol Eng 2016;55:626–42.

[44] ASTM D 3878-04a. Standard terminology for composite materials; 2004.

[45] Zhou YH, Fan MZ, Chen LH. Interface and bonding mechanisms of plant fibre composites: an overview. Compos Part B Eng 2016;101:31–45.

[46] Kalia S, Kaith BS, Kaur I. Pretreatments of natural fibers and their application as reinforcing material in polymer composites—a review. Polym Eng Sci 2009;49:1253–72.

[47] Csikos A, Faludi G, Domjan A, Renner K, Moczo J, Pukanszky B. Modification of interfacial adhesion with a functionalized polymer in PLA/wood composites. Eur Polym J 2015;68:592–600.

[48] Cabane E, Keplinger T, Merk V, Hass P, Burgert I. Renewable and functional wood materials by grafting polymerization within cell walls. Chemsuschem 2014;7:1020–5.

[49] Altun Y, Dogan M, Bayramli E. Comparative study of maleated and glycidyl methacrylate functionalized terpolymers as compatibilizers for low-density polyethylene-wood flour composites. J Appl Polym Sci 2013;127:1010–6.

[50] Cantero G, Arbelaiz A, Mugika F, Valea A, Mondragon I. Mechanical behavior of wood/polypropylene composites: effects of fibre treatments and ageing processes. J Reinf Plast Compos 2003;22:37–50.

[51] Ben Abdallah F, Ben Cheikh R, Baklouti M, Denchev Z, Cunha AM. Characterization of composite materials based on PP-cork blends. J Reinf Plast Compos 2006;25: 1499–506.

[52] Fernandes EM, Aroso I, Pires RA, Correlo VM, Pitkänen P, Koskimies S, et al. Improvement on the mechanical properties of cork composites using suberin as coupling agent through a reactive extrusion process. Annu Tech Conf 2011;1:611–5.

[53] Chung TC. Functionalization of polyolefins. Massachusetts: Academic Press; 2002.

[54] Boulahia H, Zerizer A, Touati Z, Sesbou A. Recycling the cork powder in a PVC-based composite material: combined effect on physico-mechanical and thermal properties. Int Polym Process 2016;31:346–55.

[55] Fuqua MA, Huo S, Ulven CA. Natural fiber reinforced composites. Polym Rev 2012;52:259–320.

[56] Fernandes EM. New functionalization—reinforcement strategies for cork plastics composites: opening a wide range of innovative applications for cork based products [Doctoral thesis]. Portugal: University of Minho; 2013.

[57] Fernandes EM, Correlo VM, Mano JF, Reis RL. Polypropylene-based cork-polymer composites: processing parameters and properties. Compos Part B Eng 2014;66:210–23.

[58] Aroso IM, Fernandes EM, Pires RA, Mano JF, Reis RL. Cork extractives exhibit thermo-oxidative protection properties in polypropylene-cork composites and as direct additives for polypropylene. Polym Degrad Stab 2015;116:45–52.

[59] da Silva SPM, Lima PS, Oliveira JM. Non-isothermal crystallization kinetics of cork-polymer composites for injection molding. J Appl Polym Sci 2016;133:44124.

[60] Yu L, Dean K, Li L. Polymer blends and composites from renewable resources. Prog Polym Sci 2006;31:576–602.

[61] Fernandes EM, Correlo VM, Mano JF, Reis RL. Cork-polymer biocomposites: mechanical, structural and thermal properties. Mater Des 2015;82:282–9.

[62] Fernandes EM, Correlo VM, Mano JF, Reis RL. Innovative bio-based composites comprising cork and biodegradable polyester. In: Ferreira AJM, editor. 16th international conference on composite structures (ICCS16). Porto: FEUP; 2011.

[63] Jawaid M, Khalil H. Cellulosic/synthetic fibre reinforced polymer hybrid composites: a review. Carbohydr Polym 2011;86:1–18.

[64] Sreekala MS, George J, Kumaran MG, Thomas S. The mechanical performance of hybrid phenol-formaldehyde-based composites reinforced with glass and oil palm fibres. Compos Sci Technol 2002;62:339–53.

[65] Thwe MM, Liao K. Durability of bamboo-glass fiber reinforced polymer matrix hybrid composites. Compos Sci Technol 2003;63:375–87.

[66] Nunna S, Chandra PR, Shrivastava S, Jalan AK. A review on mechanical behavior of natural fiber based hybrid composites. J Reinf Plast Compos 2012;31:759–69.

[67] Fernandes EM, Correlo VM, Mano JF, Reis RL. Novel cork-polymer composites reinforced with short natural coconut fibres: effect of fibre loading and coupling agent addition. Compos Sci Technol 2013;78:56–62.

[68] Cork PH. Biology, production and uses. 1st ed. Radarweg, Amsterdam, Netherlands: Elsevier Science; 2007.

[69] George S, Varughese KT, Thomas S. Dielectric properties of isotactic polypropylene nitrile rubber blends: Effects of blend ratio, filler addition, and dynamic vulcanization. J Appl Polym Sci 1999;73:255–70.

[70] Dionísio MSC, Correia NT, Mano JF, Moura Ramos JJ, Fernandes AC, Saramago B. Absorbed water in the cork structure. A study by thermally stimulated currents, dielectric relaxation spectroscopy, isothermal depolarization experiments and differential scanning calorimetry. J Mater Sci 1995;30:4394–400.

[71] Gil P, Fernandes J, Neves MM, Reis L. Suitability of cork rubber gaskets in gasoline-ethanol blends. In: Rosa LG, Margarido F, editors. Advanced materials forum V, Pt 1 and 2. Stafa-Zurich: Trans Tech Publications Ltd; 2010. p. 266–72.

[72] Antunes PJ, Dias GR, Coelho AT, Rebelo E, Pereira T. Hyperelastic analysis of cork-polyurethane gel composites. London: Taylor & Francis Ltd; 2008.

[73] Antunes PJ, Dias GR, Coelho AT, Rebelo F, Pereira T. Hyperelastic modelling of cork-polyurethane gel composites: non-linear FEA Implementation in 3D foot model. In: Marques AT, Silva AF, Baptista APM, Sa C, Alves F, Malheiros LF, et al., editors. Advanced materials forum IV. Stafa-Zurich: Trans Tech Publications Ltd; 2008. p. 700–5.

[74] Oprea S. Effects of fillers on polyurethane resin-based polyurethane elastomeric bearing materials for passive isolation. J Compos Mater 2008;42:2673–85.

[75] Cork polymer composites: materials based on cork waiste, http://www.haute-innovation.com/en/magazine/sustainabilty/cork-polymer-composites.html [Accessed September 2016].

[76] http://www.wacker.com/cms/en/press_media/press_service/feature_service/feature-detail_25026.jsp [Accessed September 2016].

[77] A special bond: polymeric binding powder fuses cork and slate to form natural stone flooring that is warm underfoot, http://www.wacker.com/cms/media/en/documents/feature-pdf/kork_naturstein.pdf [Accessed September 2016].

[78] CPC Cork Polymer Composite, http://www.archello.com/en/product/cpc-cork-polymer-composite [Accessed September 2016].

[79] Gil L. Cork: sustainability and new applications. Front Mater 2015;1.

[80] Santos J, Haider A. SmartComposite®—a new composite generation. In: Sixth WPC & NFC conference, cologne, wood and natural fibre composites, Germany; 2015.

[81] http://www.washersandgaskets.com/en/257039/Cork-and-cork/rubber-gaskets-.htm [Accessed September 2016].

[82] http://www.british-gaskets.co.uk/product/cork/ [Accessed September 2016].

[83] Lifocork, http://www.hexpoltpe.com/en/lifocork.htm [Accessed September 2016].

[84] EasyCork™, http://www.formfutura.com/easycork/ [Accessed November 2016].