Physico-chemical aspects of the use of cork in cementitious composites

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ABSTRACT

Various species of wood in the form chips, particles or fibres are added to cement to make composite materials for building applications. Most wood species are reported to retard the setting of cement and weaken its strength. Cork, which is the bark of *Quercus suber* trees, is not currently used for making such composites. It differs from other wood species in many aspects. A preliminary study conducted to assess the compatibility of cork with cement found that it is compatible with cement. This paper discusses the difference between the properties of cork and other woods and the advantages these properties bring to cementitious composites. Some physical and mechanical properties of cork cement composite materials are also presented.

Keywords: cork, wood, cement, composite, and cellular materials.

INTRODUCTION

Wood, in various forms, has been mixed with inorganic binders like cement, gypsum and magnesite, to make lightweight composite materials since the early part of the twentieth century. However, it appears that the commercial production of wood cement composite panels started in around 1965, when the health hazards associated with the use of asbestos became apparent (Coutts, 1988, Moslemi, 1989). Since then considerable research has been done in this area.

In general wood cement composites are of two types: wood particle-cement composites and wood fibre-reinforced cement products (Wolfe and Gjinolli, 1996). Wood particle-cement composites are mainly used in buildings as fire resistant and acoustic panels. Whereas wood fibre-reinforced cement products were developed primarily as asbestos substitutes in cement products by private companies (Moslemi, 1999). Unfortunately, unlike asbestos, wood contains various water and alkali soluble extractives, which cause inhibition of cement setting. In order to minimise this problem a range of strategies have been developed including: appropriate selection of wood species, addition of cure accelerators, cold and hot water extraction of woods and carbon dioxide injection. But there is very limited information available on the use of bark material of trees like cork in cement based composites. In this paper the properties of cork are reviewed and later the possible role of cork in cement based composites is discussed.

CORK

Cork is obtained from the bark of Cork Oak trees (*Quercus suber*), which are grown mainly in Portugal, Spain, and Algeria. Another oak, which produces cork, is *Quercus occidentalis.* Both species are alike differing only in their foliage and in the ripening season of their fruits (Hernandez-Olivares et al., 1999). More than 40 % of the world's cork oak forests are found in Portugal, which produces more than 50 % of the world's cork. Furthermore, the country imports cork and manufactures 70 % of the world's cork products (Carvalho et al., 1999). Cork is a lightweight, resilient, chemically stable and fire resistant material. It has very good thermal and sound insulation properties and it is impervious to liquids (Gibson and Ashby, 1999).

Structure of Cork

The cells of cork are roughly hexagonal on the tangential face and rectangular on the radial and axial faces (Gibson et al., 1981). The cork microcells are generally made of 14-sided polyhedrons, slotting in one against each other and filled with gases. The gases have not been analysed but are likely to be similar to air (Oliveira and Oliveira, 1991).

In order to confirm cell shape in the cork samples, a scanning electron microscope (SEM) was used. A SEM micrograph of cork is shown in Figure 1. Whilst looking at the section perpendicular to the radial direction, it was confirmed that these cells look like more or less closed hexagonal prisms. From other angles these hexagonal prisms were found to be stacked in rows parallel to the radial direction. Fortes and Rosa (1992) also reported similar observations. The structure, however, does not always show hexagonal sections. Gibson et al., (1981) reported that in some cases five, six, seven and eight sided figures were also observed. Nonetheless, the average number of sides per cell in section perpendicular to the radial direction was six. They further reported that most of the walls in the cells are corrugated. Fortes and Rosa (1992) attributed the corrugations of the cell wall to the growth stresses in the tree.

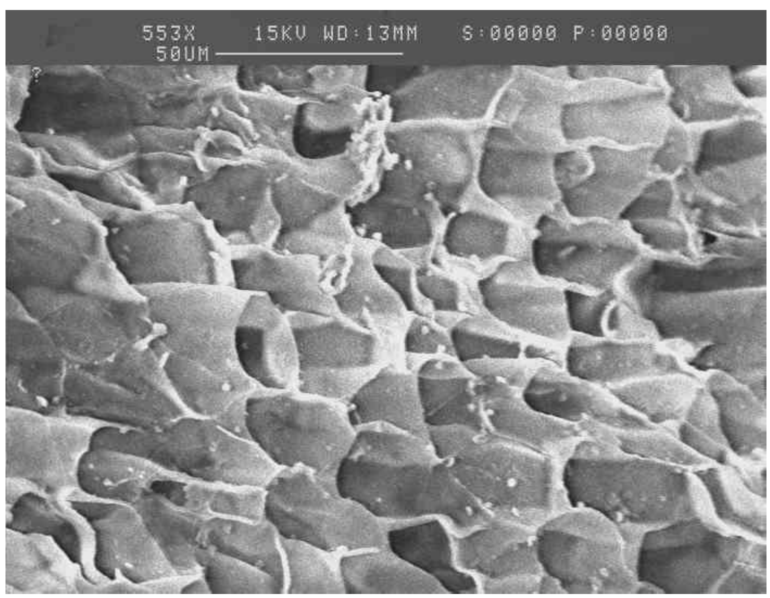

Figure 1: SEM micrograph of cork showing structure of cork cells

The density of cell wall material is found to be approximately 1150 kg/m^3. The mean density of cork is roughly 170 kg/m^3 and contains about 85 % voids (Gibson et al., 1981). The cells in cork are very small in size. It has been reported that there are about 30 to 42 million cells in a cubic centimetre cork (Oliveira and Oliveira, 1991). They are much smaller than those in normal foamed plastics, and comparable with those in microporus foams.

Mechanical Behaviour of Cork

Gibson and Ashby (1999) described the behaviour of cork under various load conditions. According to them when cork is loaded in compression, it deforms due to bending and buckling of its cell walls. This results in large recoverable strains of about 100 %. On the other hand, tensile deformation unfolds the corrugations and straightens the prism walls. About 5 % extension is possible in this way. Once straight, further application of tensile force stretches the cell walls and then breaks them, causing the cork to fail.

Typical mechanical properties of cork from various sources are given in Table 1. The Young's modulus along the prism axis is roughly one and half times that in the other two directions.

Chemical Composition of Cork

The chemical composition of cork is now well known although it varies slightly according to the findings of different research groups, which may be due to the different sources of the cork. The main characteristic of the chemical composition of cork is the presence of suberin as the main cell wall component. Suberin content in cork varies in the range of 35 % to 41 %. Cork also contains a high amount of extractives: waxes are associated with suberin in the suberin complex of the lamellated secondary wall and amount to approximately 5 %; tannins and other phenolic substances correspond to approximately 7 % of the cork material (Pereira, 1988).

The walls of cork cells are covered with layers of an unsaturated fatty acid (suberin) and waxes which make them impervious to air and water and resistant to attack by many acids (Graca and Pereira, 1997). In a recent study, conducted by Gil et al. (2000) using NMR techniques, it was verified that suberin is responsible for water the impermeability of cork.

Use of Cork

Cork is mainly used for wine bottle stoppers and has been used for this purpose since glass was popularised in the 16th century. About 30 % of the higher quality natural cork is used for this purpose (Oliveira et al., 1991). Nowadays, synthetic stoppering materials are replacing cork. Due to its flotation properties cork has been used for fishing floats and life belts, etc, for many years. It was also used for shoe insoles, but with the passage of time it has been largely replaced by modern materials like urethane foams, ' gels' , and plastics. Cork is still used for making notice boards and pottery stoppers (Gibson et al., 1981, Oliveira and Oliveira, 1991, Rosa and Fortes, 1991).

Table 1: Mechanical Properties of Cork

Property	Value	Reference
Tensile strength		
Tangential, at 9 % strain	1.1 ± 0.2 MPa	1
Tangential, at 7.5 ± 2.7 % strain	0.82 ± 0.18 MPa	2
Axial, at 9 % strain	1.1 ± 0.2 MPa	1
Axial, at 7.7 ± 2.7 % strain	0.70 ± 0.16 MPa	2
Radial, at 5 % strain	1.0 ± 0.2 MPa	1
Radial, at 18 ± 11.2 % strain	1.15 ± 0.1 MPa	2
Compressive strength		
Tangential and axial, at 6 % strain	0.7 ± 0.2 MPa	1
Tangential and axial, at 86.2 ± 0.9 % strain	12.5 MPa	3
Radial, at 5 % strain	1.0 ± 0.2 MPa	1
Radial, at 18 ± 11.2 % strain	1.15 ± 0.1 MPa	3
Young's modulus		
Tangential and axial	13 ± 5 MPa	1
Tangential	26.0 ± 4.4 MPa	2
Axial	24.2 ± 4.1 MPa	2
Radial	20 ± 7 MPa	1
Radial	38.1 ± 7.0 MPa	2
Poisson's ratio		
$\upsilon_{TA} = \upsilon_{AT}$	0.5 ± 0.05	1
$\upsilon_{TR} = \upsilon_{RT} = \upsilon_{AR} = \upsilon_{RA}$	0 ± 0.05	1
A = Axial, R = Radial and T = Tangential		

1.Gibson et al. (1981), 2. Rosa and Fortes (1991), 3. Rosa and Pereira (1994)

Table 2: Chemical Composition of Cork*

Component	Content (% wt.)
Ash	0.53 – 0.91
Total Extractives	14.1 - 16.9
Dichloromethane	6.3 - 7.9
Ethanol	4.5 - 5.8
Water	1.9 - 3.2
Suberin	35.2 -41.2
Insoluble lignin	19.5 - 21.0
Soluble lignin	1.2 - 1.6
Polysaccharides	15.7 - 21.3

*(Source: Pereira, 1988)

Currently cork is used for thermal insulators, acoustic insulators in submarines and recording studios, as seals between mating surfaces in woodwind instruments and internal combustion engines and as an energy absorbing medium in flooring, shoes and packaging (Gibson and Ashby, 1999). Flores et al. (1992) consolidated cork dust by heating under pressure without adding any binder for making panel products. They found that the tannin in cork provided sufficient bonding.

In the construction of buildings, cork is mainly used as a flooring material in various forms such as: tiles and sheets. It gives a slight springiness under foot. Its natural honeycomb structure allows it to slightly deform when a load is applied and gives it excellent heat and sound insulating properties. Carvalho (1996) used cork as a core material with gypsum board as facing material for making partition walls with various combinations and designs. He found its sound transmission class (STC) value to be up to 44 dB, which is more than the minimum required STC value 40 dB for partitions between rooms according to Portuguese Noise Code.

In addition to the above-mentioned applications, the chemical potential of cork has also recently been realised and research is in progress to exploit cork for the extraction of various chemicals. For example, Cordeiro et al. (1999) obtained suberin-based polyurethanes from cork.

A comparison of Cork and Wood

Considerable differences have been found between cork and wood. Moreover, cork granules can be considered as a lightweight aggregate rather than reinforcing fibres. The differences between cork and wood are discussed in the following paragraphs.

The most characteristic difference in chemical composition between cork and other wood species is its content of suberin, which is a polymer, made up of long chain aliphatic alcohols and acid monomers. Suberin is hydrophobic and when combined with waxes contributes significantly to the impermeability of cork (Pereira, 1988). The other main difference is cork's lower cellulose and hemicellulose content. Hemicellulose is known to retard the hydration of cement. Therefore, lesser amount of it would be beneficial from the cork-cement compatibility point of view.

Table 3: Comparison of chemical composition of cork and conventional wood fibres

Principal constituent (wt. %)	Wood[1]		Cork[2]
	Softwood	Hardwood	
Cellulose	40-45	45-50	9
Hemicellulose	20-30	20-35	~11
Lignin	26-34	22-30	22
Extractives	0-5	0-10	15-20
Suberin	---	----	40

1. Dinwoodie (1989)
2. Pereira (1988)

A comparison of various strength properties of wood and cork is presented in Table 4. It can be seen that the woods listed are stronger than cork. This may be due to the fact that wood is a cellulosic material containing fibre, whereas cork is a granular material and contains only 9 % cellulose in comparison to wood which contains (40 to 50) %.

Table 4: Comparison of the physical properties of cork and conventional wood*

Wood	Density (kg/m^3)	Tensile strength (MPa)		Compression strength (MPa)	
		Parallel	Perpend.	Parallel	Perpend.
Softwood					
Scots pine	510	110	--	47	5.5
Douglas Fir	545	138	209	50	6.9
Hardwood					
Ash	689	136	---	53	10.1
Beech	690	180	---	56	10.5
Cork	170	1.1 ± 0.2^a	1.0 ± 0.2^b	12.5^c	12.5^c

a = axial and tangential, at 9 % strain, b = radial, at 5 % strain, c = in all three directions at about 86 % strain

(* Source: Dinwoodie, 1989; Gibson et al., 1981; Rosa and Pereira, 1994)

Water absorption in cellular materials is directly related to the presence of open cells, and because the cells are so small in cork, each granule is mainly composed of closed cells. In addition, it has been reported by Gil et al., (2000) that cork cells are practically impervious to water. Moreover, with exception of the lamella, none of the cell walls in adjacent cork cells are connected, implying that there is no continuous path for diffusion along them (Rosa and Fortes, 1993).

CORK-CEMENT COMPOSITES (3C)

The cork producing industry generates large amounts of waste to the tune of about (20 to 25) % by weight of consumption of natural material (Cordeiro et al., 1999). Some of these wastes are burnt for process heat, while the remaining cork waste is used for land filling (McIlveen-Wright et al., 2000). Very limited information is available on the use of waste cork in cementitious composites,. Aziz et al. (1979) tested lightweight concrete made using the cork granules obtained from packing wastes of fruit stalls in Singapore. For cement:cork mixes of 1:1 to 1:3 by volume, they made lightweight concrete in the density range of (475 to 890) kg/m^3, which had compressive strengths in the range of (4.2 to 12.0) MPa and tensile strengths between (0.6 and 2.0) MPa. They did not report any compatibility problem between cement and cork. Henandez-Olivares et al. (1999) used waste cork granules with gypsum for making composite materials. They found good thermal insulation properties of the composite. Based on SEM examination of the bond between gypsum plaster and cork, they reported good compatibility between gypsum and cork. From these two papers it appears that the chemical compatibility between cork and cement was not tested, which is done generally in wood cement composites. However, Irle (2001) has done some preliminary work on cork-cement compatibility using a calorimetry technique. He did not report any compatibility problem between cork and cement.

In view of this a research study is underway at the Forest Products Research Centre (FPRC), Buckinghamshire Chilterns University College (UK) to explore the use of waste cork granules in cementitious composites.

Possible role of Cork in 3C

In cement-based composites, cracking mainly occurs due to volume changes , that occur in cement paste during hydration in the presence of restraints, and tensile stresses caused by applied loads. In the hardened cement gel, which is a framework of crystals of varying nature, micro-cracks are initially formed between needle shaped hydration products and also around the fine aggregates. At the tip of such cracks, only a small amount of energy is required to increase their length and if the energy input is continued the crack becomes larger and results in the separation of the solid body into two pieces. This is the reason of the failure of concrete specimens under compression by lateral tensile splitting (Brandt, 1995). However, cork granules can be advantageous due to their negligible Poisson's ratios in the tangential and axial directions with respect to the radial direction (Table 1). This implies that when the composite is loaded the cork granules exert very little lateral pressure, which will reduce the lateral splitting of composite.

The other advantage of using cork granules is that they contain several open cells at their surfaces. This facilitates good bonding with the cement paste, as can be seen in Figure 2.

If the aggregate present in the cement-based composite is stronger than the matrix, then any crack will propagate easily through the matrix and the material will fail without multiple fracture. However, if the aggregate is softer than the matrix, as is the case with most lightweight aggregates, cracks pass through the aggregate particles (Brandt, 1995) causing other granules to be stressed and in this way multiple fractures occur, which is important for increasing the toughness of the material. As can be seen in Figure 3, the 3C specimen fails after achieving much more deformation than the pure cement specimen. It is also evident from Figure 2, that after cracking of the cement paste the bond between cork cell and cement paste is intact and, therefore, cork granules significantly contribute in enhancement of deformation of the composite.

Since cork contains about 85 % air voids by volume, its addition to cement matrix would reduce the thermal conductivity and sound absorption of the composite with the added advantage of it being lightweight.

The problem with the use of cork is that it has very poor strength and a low resistance to high pH alkalis. But the lower strength at high deformation can be exploited for advantage in the use of 3C as crushable concrete in the stop barriers for moving vehicles. In such applications, the material should absorb large amounts of energy from the moving vehicles at lower stresses. It does not imply that 3C can not be used for structural purposes. 3C can be used as lightweight concrete and, if required, strength of 3C could be enhanced by the addition of synthetic fibres.

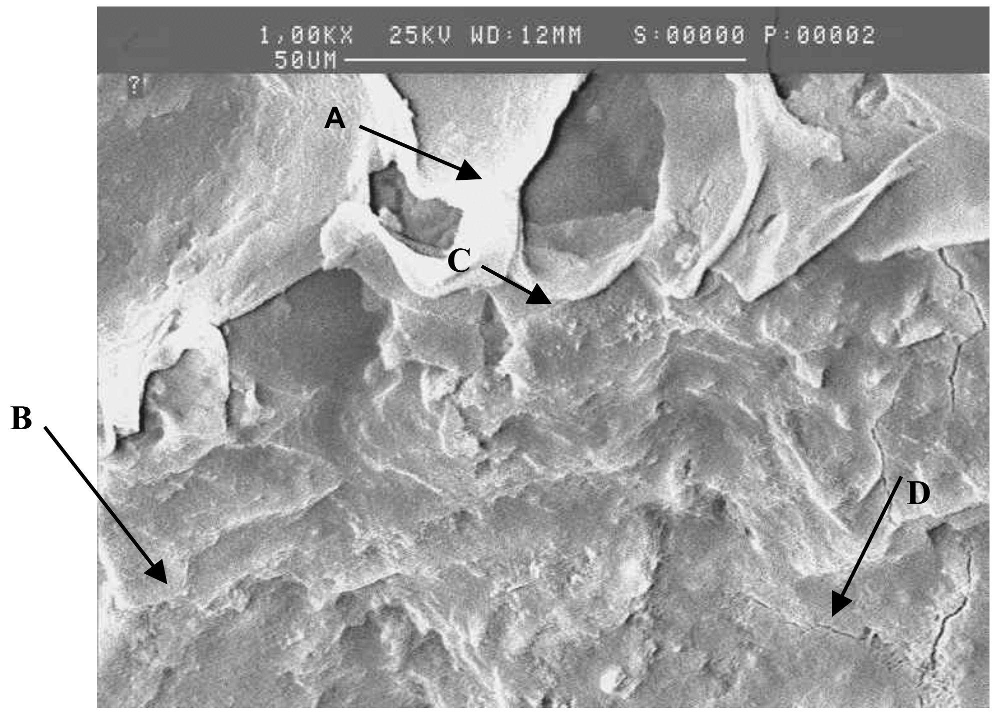

Figure 2: SEM Micrograph of fractured 3C specimen showing A: cork cell wall, B: hydrated cement paste, C: good bonding between cork cell wall and cement paste and D: crack in cement paste.

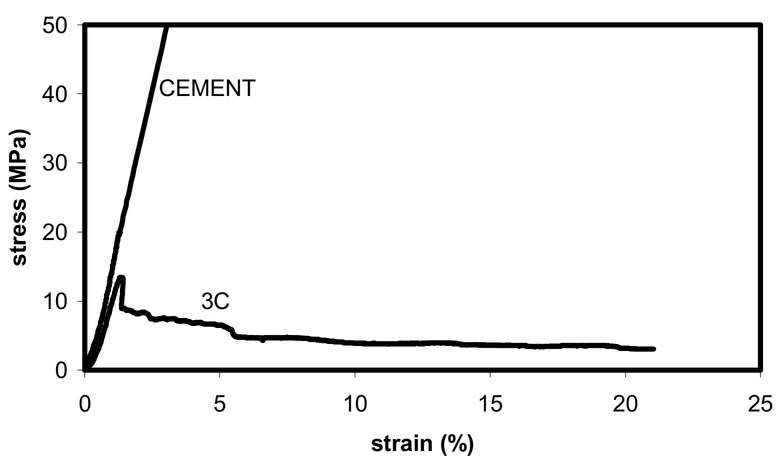

Figure 3: Stress-strain curve of cement paste and a 3C containing 5 % cork by weight.

CONCLUSION

Addition of wood particles to the cement matrix retards the hydration of cement, which adversely affects the production rate and strength of wood-cement composites. Cork seems to have better compatibility than wood with cement, mainly due to the presence of suberin and its relatively low water absorption. The preliminary studies on 3C show encouraging results. However, before cork can be used in practice, there is a need to do more research for gaining a broader insight into the behaviour of such composites.

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