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Residual sisal fibers treated by methane cold plasma discharge for potential application in cement based material

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ABSTRACT

The use of residual sisal fiber is becoming more frequent as reinforcement element in organic or inorganic matrix due to its low cost, high abundance in some countries and constitutes a renewable material. However, a significant loss in the mechanical performance in long term has been observed in fiber-cement composites after natural aging. These alternative fibers can be utilized in a hybrid fiber-cement in order to decrease the content of traditionally used synthetic fibers. The objective of this work was to evaluate the potential of the methane cold plasma treatment of 10 min duration on structural and physical properties of the residual sisal fibers to mitigate the degradation mechanisms when applied to cementitious matrices. Moisture sensitivity evaluation by capacitance method, dielectric measurements, X-ray diffraction, Fourier transform infrared (FTIR), spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), atomic force microscopy (AFM), angle contact and pullout test were carried out in order to follow the effect of the proposed treatment. Besides, mechanical behavior of untreated and treated sisal fibers was evaluated before and after accelerated aging in cementitious solution at 60 °C by 72 h. The results obtained in all these tests confirmed the high potential of the methane cold plasma treatment to delay the degradation of the residual sisal fibers in the presence of a Portland cement environment and these fibers present the higher pullout load and shear stress than one untreated.

1. Introduction

In the past decades, related issues to environment and social development have been the challenge of different fields of the industry, as well as, the theme of several studies around the world. Thus, the construction industry, known for being an emergent sector with significant participation in the economy of developed and undeveloped countries, have to incorporate the sustainability in its production process, since the sector has as drawback the massive use of the natural resources (both renewable and non-renewable), waste generation and a high energy consumption (Ortiz et al., 2009; Pacheco-Torgal and Jalali, 2011). One way to minimize this backdrop is the replacement of the fossil fuel based fibers by vegetable fibers as reinforcement in products such as flat or corrugated roofing materials, water containers and cladding panels (Tonoli et al., 2013).

1.1. Sisal fiber

Lignocellulosic fibers have reached a remarkable importance as high specific strength materials, for a broad use in the composite materials. In view of the significant advantages provided by the lignocellulosic fibers, mainly due to low-cost production and large availability in nature, there is an increase in the potential use of these fibers in civil engineering (Pereira et al., 2013; Mármol et al., 2013). Moreover, the vegetable fibers come from renewable, have low density, and they are obtained with low energy consumption. Additionally, the creation of this new market could benefit the economy of the producing regions that are generally connected to products of low added value, such as cordage and packing industry. Tropical countries such as Brazil have an abundance of crops for fiber suppliers, many of which are located in underdeveloped or developing regions. The diversity of plants that can provide fiber generates numerous possibilities for production and application, such as sisal (*Agave sisalana*), which is easily available and can be produced even under arid climate conditions (Li et al., 2000). Further, the partial replacement of synthetic fibers (e.g.polypropylene,

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glass and polyvinyl alcohol) by sisal fibers as a reinforcement element has been of advantage for the fabrication of composite materials in the last years (Tonoli et al., 2011; Tan et al., 2012).

The use of sisal fiber is becoming more frequent, for example, in the toughening of cementitious composites (Gutiérrez et al., 2005; Tan et al., 2012). Besides, some residual sisal fibers commonly sold to the paper and matting industry, such as wadding, crude or cleaned, and also waste brushed or unbrushed, can be utilized for these purposes (Bledzki and Gassan, 1999; Satyanarayana et al., 2007).

However, significant losses in the mechanical performance in long term have been observed in sisal fiber-cement composites after natural or accelerated aging, due to the degradation mechanisms of the cellulose fibers in the cementitious environment (Toledo Filho et al., 2000; Savastano Jr. et al., 2005, 2009; Silva et al., 2011; Melo Filho et al., 2013). The degradation of the vegetable fiber is caused by the alkaline environment with pH > 12 (Toledo Filho et al., 2000). Some progressive degradation mechanisms may take place, such as the destruction of macromolecular chains during the partial alkaline hydrolysis of the cellulose, which causes their rupture and the consequent decrease in the degree of polymerization. This degradation occurs by the easy movement from the pore water towards the surface of the fibers. Another mechanism is the gradual filling of the inner cores of the vegetable fibers with the hydration products leading to the embrittlement of the fibers, reducing their mechanical performance (Melo Filho et al., 2013; Silva et al., 2011; Pavasars et al., 2003; Scrivener and Young, 1997). These mechanisms could affect some important physical properties of the material reinforced, such as adhesion toughness mechanisms and, consequently, mechanical properties (Bentur and Mindess, 2007). The volume stability of the fiber in a water based environment is also crucial in the conservation of the fiber-matrix adhesion Tonoli et al., 2009).

1.2. Methane cold plasma

The deposition of hydrophobic coatings on the surface of the fiber counteracts some degradation mechanisms such as the deposition of calcium hydroxide crystals in the interior of the fiber and the attack of other ions from cement suspension on the fiber surface. Recently some applications of plasma-based techniques to coating processes have made a significant progress to improve surface characteristics of the fiber materials (Kim et al., 2006). The surface treatment with cold plasma has been applied in the study of adhesion between several kinds of polymers or biopolymers through the modification of the surface free energy for efficient functionalizing (Mahlberg et al., 1998; Novak et al., 2008). The cold plasma treatment is a useful technique that utilizes ionized gas, at negative pressure, composed by a mixture of neutral species (atoms, molecules and free radicals), electrically charged species (electrons, positive and negative ions), photons, radicals, and excited molecules produced by electric discharge (Wielen and Ragauskas, 2004; Wielen et al., 2006; Gaiolas et al., 2008, 2009; Kalia et al., 2011; Costa et al., 2006). Although the surface property alterations obtained with cold plasma treatment are very complex, they offer an efficient and reliable mechanism to alter surface properties of materials without affecting the bulk properties of the treated substrate (Carlsson and Ström, 1991; Rolf and Sparavigna, 2010). For example, plasma species do not penetrate deeper than about 100×10^{-10} m from the surface which means that more than 99% of the bulk of a 10 μm thickness polypropylene film remains unchanged (Hua et al., 1997). The most important factor is that the substrate surface properties change significantly after a few minutes of plasma treatment. Plasma treatment of chemithermomechanical pulp resulted, as in the case of the pulp, in an increment in the quantity of tagged functionalities, which was seen mainly for carboxyl and carbonyl groups (Östenson et al., 2006). This has significant implications for the lignocellulosic fiber industry (Olaru et al., 2005; Wielen et al., 2005; Kalia et al., 2011; Anwer and Bhuiyan, 2012). Due to the physical process the treatment does not make use of water and chemicals and thus is considered quick and environmentally friendly without generating any contamination. Besides the operating costs are lower than some chemical treatments, such as those based on silanes (Shenton and Stevens, 2001; Indarto et al., 2005; Morent et al., 2008; Felekoglu et al., 2009; Navarro et al., 2009).

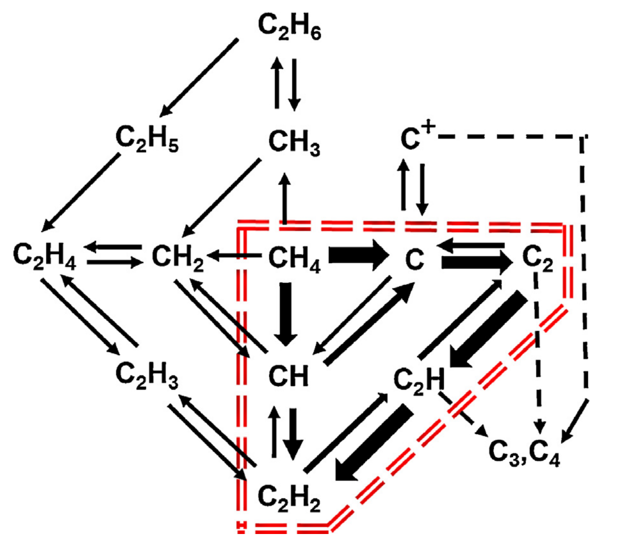

Fig. 1. Schematic diagram of the methane gas fragmentation of the methane gas produced in the cold plasma system.
Adapted from Kado et al.(2003).

Based on the outcomes of interactions with materials, cold plasmas can be classified into the broad categories like as plasma polymerization, plasma treatment, and plasma etching (Siow et al., 2006). When cold plasma is generated from a pure organic gas (e.g., methane) or mixed with other gases, a collision occurs between energetic electrons and gas molecules resulting in the formation of a series of reactive fragments, which are recombined to give rise to a solid polymeric material which is deposited on the surface to be treated, or just some functional groups can be grafted on the surface (Kim et al., 2006; Bozaci et al., 2013). This process is known as plasma polymerization. The plasma contains a variety of species including electrons with energies great enough to break molecular bonds from organic gas by collision (Kumar et al., 2010).

Fig. 1 shows a schematic diagram of possible fragments produced in the methane cold plasma for non-equilibrium (non-thermal) discharge. The highlighted region indicates the compound most likely to occur. The thickness of the arrows is correlated to the most probable reactions to occur, as well as, dash line arrows are related to lower probability reactions. Although the dehydrogenation of C_2H_6 rapidly produces C_2H_4 and C_2H_2, the contribution of that reaction path is small because the composition of C_2H_6 in the discharge region is very low due to the low CH_3 concentrations as highlighted in Fig. 1 (Kado et al., 2003). It is accepted that in non-thermal plasma systems, the formation of free radicals and ion-radicals is the decisive stage for the consecutive transformations of methane (Ghorbanzadeh et al., 2005).

1.3. Lignocellulosic fiber and methane cold plasma

Based on many XPS studies, the vegetable fiber surface has a series of functional groups that rise up, mainly, from lignin and extractives (C—C, C—H, C=O, O—C—O, COOH, COOC), as well as, from