Cement and Concrete Composites 89 (2018) 205–215

Contents lists available at ScienceDirect

Cement and Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Deterioration of bonding capacity of plasma-treated polymer fiber reinforcement

J. Trejbal [a], V. Nežerka [a], M. Somr [a, *], J. Fládr [a], Š. Potocký [b], A. Artemenko [b], P. Tesárek [a]

[a] Faculty of Civil Engineering, Czech Technical University in Prague, Thákurova 7, 166 29 Praha 6, Czech Republic
[b] Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, 162 00 Praha 6, Czech Republic

ARTICLE INFO

Article history:
Received 25 February 2017
Received in revised form
21 December 2017
Accepted 17 March 2018
Available online 19 March 2018

Keywords:
Polymer fiber reinforcement
Chemical bonding
Cold plasma treatment
Pull-out strength
Contact angle

ABSTRACT

Bonding between reinforcing fibers and a brittle cementitious matrix is the key ingredient for a ductile concrete production. Oxygen plasma treatment proved to be a promising technique for increasing the fiber surface adhesion to liquids, but a question about the stability of activated bonding when exposed to atmospheric conditions arises. We present a comprehensive study on deterioration of such treatment in time for different fibers commonly used as dispersed reinforcement. A microscopy investigation allowed to observe changes in the fiber surface morphology, while the changes in chemical bonds were detected by XPS analysis. To quantify the impact of plasma treatment and its deterioration, water contact angle measurements and pull-out tests were carried out. The results indicate that the exposure to atmospheric conditions has a negligible impact on fiber bonding, because surface roughening plays a major role. Therefore, fibers need not be incorporated into a concrete mix immediately after their treatment.

1. Introduction

Fiber-reinforced composite materials used in structural engineering are most frequently based on a combination of steel or polymer fibers and inorganic cementitious matrix that exhibits brittle behavior [1]. Discrete, randomly oriented, and uniformly distributed fibers prevent a complete loss of stress transfer across cracks after reaching ultimate matrix strength in tension. Hence, the character of a cementitious material changes from brittle to ductile [2], if designed properly. In engineering practice, the fiber reinforcement is the most frequently utilized for (i) elimination of excessive shrinkage cracking and crack opening, (ii) rendering the reinforced material ductile in tension, and (iii) production of strain-hardening composites.

Strain hardening of a properly designed fiber-reinforced composite allows a multiple cracking as opposed to failing by a single brittle crack [1]. As a consequence, the material retains a macroscopic integrity even after reaching ultimate tensile strength, and a reduced crack opening prevents a penetration of harmful chemical agents. As suggested by Marshall et al. [3], the fiber bridging over cracks in a brittle matrix has the dominant influence on whether the material exhibits multiple cracking. When a fiber-bridged crack opens, the process of fiber extraction from a matrix can be divided into two stages: fiber debonding and pull-out [4,5]. During the debonding stage, the fiber elastically deforms and the pull-out is restrained by chemical and mechanical bonding with the surrounding matrix. Once the embedded fiber becomes fully debonded, a bridging force generated by friction stress over the fiber-matrix contact area restrains the crack opening. The bridging force at both stages is fundamentally influenced by the fiber surface properties [6–8].

Because an inorganic cementitious matrix contains water, it was conjectured that a fiber surface wettability is an appropriate indicator of the fiber-matrix interfacial bond strength [9]. The limited adhesion of untreated polymer fibers to a cementitious matrix [10] results in easy debonding during fiber pull-out and weakening the interfacial zone due to a formation of micropores within the surrounding matrix [11].

Several strategies have been addressed to increase the fiber hydrophilicity, thus enhancing the interface strength. Cold plasma treatment appears to be the most suitable for its controllable outcomes [12–14], which is why plasma treatments have been quite extensively employed for a modification of polymer properties since 1980's, mostly in the textile industry to improve surface adhesion and dyeability of fabrics [15,16]. Unlike wet chemical treatment, the cold plasma technology can be considered eco-

* Corresponding author.
E-mail address: michael.somr@fsv.cvut.cz (M. Somr).

https://doi.org/10.1016/j.cemconcomp.2018.03.010
0958-9465/

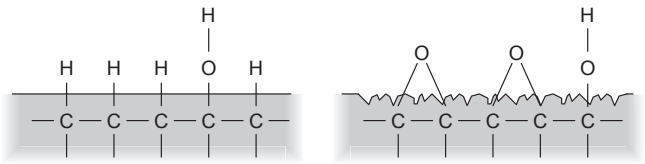

Fig. 1. Principle of the oxygen plasma treatment modification; polymer surface before (left) and after (right) the treatment.

friendly [17] and fast, and plasma-treated fibers do not exhibit an excessive brittleness as in the case of hot air or flame treatments. A mechanical indentation of the fiber surface significantly reduces the effective fiber cross-sectional area and consequently its tensile strength. Therefore, such technology cannot be considered for fibers of small diameters [8].

The effect of plasma treatment is twofold (Fig. 1): the ion beam bombardment renders the surface rough, while activation of polar groups on the polymer surface reduces the surface energy and promotes chemical bonding with a cementitious matrix [18–20]. A significant reduction of polymer surface energy caused by plasma treatment was reported by e.g., Öktem et al. [21] or Mittal [22]. Oxygen, or any noble gas, must be present during treatment in order to stabilize free radicals formed on a treated surface [23]. A few authors (e.g. [9,13,24]) reported that treatment in a duration of several seconds ensures sufficient surface modification, but the surface wettability was always tested immediately afterwards and not repeatedly in the long term.

Activation of chemical bonding cannot be considered permanent due to a reaction of the activated polar groups with airborne dust and air humidity [25]. Therefore, besides determination of an optimal treatment duration, the assessment of the bonding capacity deterioration is crucial for a successful implementation of the method in the construction industry. After a comprehensive literature review, we are not aware of any study focused on the issue of fiber bonding deterioration in fibers treated by cold oxygen plasma. The purpose of this paper is to fill that void and assess the rate at which the effect of plasma treatment decreases.

2. Tested fibers

The present study is focused on polymer macro fibers, i.e., those with a diameter larger than 0.1 mm and length exceeding 10 mm. These can substitute steel-fiber reinforcement, or even rebars and steel meshes. The tensile strength of such fibers is comparable to those made of steel, while their stiffness is up to 20 times lower. This can suppress the formation of shrinkage-induced cracking at the fiber-matrix interface [26,27], and therefore enhance the interfacial bond. In contrast to steel fibers, polymer-based ones can be used as concrete reinforcement with no special finishing or cover to prevent injuries caused by their sharp protruding ends. Polymer fibers are also less harmful to shotcreting machines and easy to distribute in a concrete mix [28].

Commonly available materials used in the construction industry were chosen for the study. However, the outcomes are not limited only to the studied fibers, since these are typical representatives of a broad range of available polymer fibers intended for reinforcement of cementitious materials.

2.1. Coated fibers

Bicomponent elliptic coated fibers (Fig. 2(a)) made of polyolefin are primarily produced as dispersed reinforcement to concrete. A compliant polymerous coating of a high-modulus high-strength core is declared to increase the adhesion between the fibers and the surrounding matrix. The bond is further enhanced through transverse folds in the surface. The coated fibers were selected to demonstrate whether the plasma treatment affects only the fiber surface, because a modification of the stiff load-bearing core would be translated into a reduction of the fiber tensile strength.[1]

2.2. Uncoated fibers

Flat and slightly twisted uncoated fibers (Fig. 2(b)) by a Czech manufacturer, made of a mixture of polypropylene (PP) and polyethylene (PE), were chosen as a cheaper alternative to the coated ones. The surface roughening by transverse folds is negligible, and there is no coating to support bonding with a cementitious matrix. The basic characteristics of both fiber types provided by their manufacturers are summarized in Table 1.

3. Impact of cold plasma treatment on fiber surface properties

The hydrophobic polymer fibers were subjected to a low-pressure oxygen cold plasma in order to increase their adhesion to a cementitious matrix. Treatment was accomplished in a vacuum chamber using an inductively coupled plasma device (Tesla VT 214). The fibers were exposed to plasma for different durations (5, 10, 30, 60, 120, 240, and 480 s) in order to determine the most suitable one that provides sufficient surface roughening without melting or excessive warping of the fibers. The process conditions were: 56 Pa gas pressure, 100 W RF power, and 50 sccm oxygen gas flow.

3.1. Weight loss

In order to assess a physical damage due to plasma treatment, the weight loss was measured on sets of fibers exposed to a different treatment duration using a high-sensitivity scale. It is obvious that plasma treatment causes weight loss (Fig. 3), which is more pronounced in the case of treatment durations exceeding 60 s. After 480 s, the coated and uncoated fibers lost 2.4% and 4.7% of their weight, respectively. This can be attributed to the ion bombardment resulting in a sputtering of the fiber surface. Moreover, the presence of oxygen with broken covalent bonds could cause oxidation of the material.

3.2. Microscopy investigation

A mechanical surface disruption was observed by a scanning electron microscope (SEM) Maia 3, Tescan. To eliminate surface charging, the investigated fibers were coated with a thin gold layer using plasma sputtering system (BOC Edward Scancoats Six). The sputtering process parameters were as follows: deposition time 40 s, sputtering voltage 1.3 kV and current 35 mA, and total gas pressure 26.6 Pa. The gold layer thickness was approximately 10 nm, as measured by a profilometer (Veeco DekTak 150). The surface images were acquired at 5 k× magnifications.

The surface of reference (untreated) fibers, both coated and uncoated, was smooth with rounded projections, (Fig. 4). After 30 s of plasma treatment, the surface of fibers was noticeably altered and longitudinal grooves emerged (Fig. 5). The surface of the fibers treated for 480 s was etched and scaly, and with residues of the coated polymerous coating (Fig. 6). This corresponds

[1] In this paper, the term tensile strength refers to the maximal tensile force a single fiber can withstand.