Disclosure of Invention

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Control of Interface Properties between Fiber/Cement Using Plasma Treatment

Objective

The objective of this invention is to control interface properties, particularly bond strength (τ) and interface toughness (T_i), between synthetic fibers and cement based matrix. It is found that, with an optimum plasma treatment of fibers, as demonstrated using polyethylene fibers, τ can be increased by a factor of 6 and T_i can be increased by as much as 7 times, compared to the virgin non-plasma treated fibers. For fiber reinforced cement based composites, their practical applications are usually hindered by (1) low τ leading to insignificant changes in composite properties, when low fiber dosage (usually < 1 volume percent) is used, and (2) high cost and processing difficulties, when high fiber dosage (usually > 10 volume percent) is used. Much improved interface properties are essential to creating high performance fiber reinforced cement based composites which possess high strength and high ductility, requiring fiber volume fraction less than 2% for low cost and easy processing. In this new invention, a novel plasma treatment is developed as to significantly enhance bond strength (related to composite strength), interface toughness (related to composite ductility and composite toughness), or both of synthetic fibers. Thus, this invention can be used to tailor desirable interface properties of any given fiber systems to provide cost-effective high performance fiber reinforced cement based composites.

Background Review

During the past decades, numerous civil engineering structures such as buildings and bridges were carefully studied and designed. In particular, the structural elements of tall buildings must respond to the heavy vertical forces of gravity and significant horizontal forces of wind or seismic action. Therefore, the materials which make up the building are of ultimate importance. They not only provide the integrity of the buildings, but also determine their structural performance. The taller the structure, the more it becomes critical to engineer the properties for the performance requirements of the structure. This is driven by optimization of structural components which may vary from location to location even in the same structure, and by minimization of cost.

Consequently, high strength concretes have been developed and used in construction of tall buildings. However, the brittle nature of high strength concretes (hence leading to a catastrophic structure failure) hinders a widespread acceptance by structure design engineers. Although steel confinement may partially help, the steel confinement itself can hamper a proper placement of concrete in situ, and be vulnerable to corrosion attack. Alternatively, it is well known that fiber reinforcement in an ordinary fiber reinforced concrete (FRC) can improve significantly the toughness of the brittle matrix. However, insufficient bond properties between most synthetic fibers and cement matrix lead to little or no improvements in strength or ductility, unless a very high dosage of fibers is used (larger than 10 volume percent). The latter situation creates two major problems, i.e. high material cost and difficulties in processing using conventional equipments. Thus, a significant cost increase results. At present, ordinary FRCs (fiber volume fraction < 0.5%) are mainly used for control of shrinkage cracks as a secondary reinforcement. It should be noted that a combination of ductility and strength is essential for high rise structures constructed in earthquake zones. In these applications, regular reinforced concretes are not capable of serving their designed function as exemplified in the tragic collapse of numerous buildings in the Kobe earthquake, Japan, 1995.

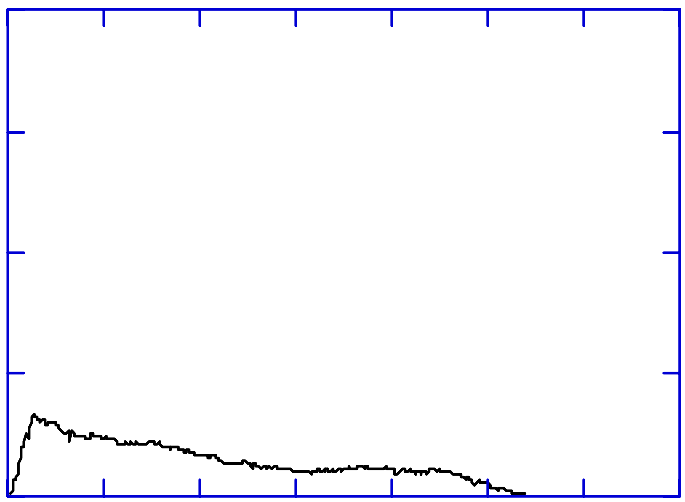
Recently, advances in micromechanics modeling of fiber reinforced cement based composites have created a "ductile" cement composite, Engineered Cementitious Composites (ECC), at the University of Michigan. ECCs have a strain capacity of 2 order of magnitude higher and toughness of 3 order of magnitude higher than that of normal concrete with only 2 volume percent fiber reinforcement. This achievement was made possible by using our micromechanical model which provides a quantitative linkage between micromechanical parameters such as properties of fiber, matrix, and interface, and composite properties, as a design tool. A minimum fiber quantity, critical fiber volume fraction (V_f^{crit}), is found essential to ensuring transition from a brittle to a ductile failure. V_f^{crit} is strongly dependent on interface properties (τ and T_i) and fiber aspect ratio (L_f/d_f, ratio of fiber length to fiber diameter). The latter L_f/d_f, in turn, is bound by a lower limit, $(L_f/d_f)_{limit}$, with τ in the denominator. Thus, a high τ is both critically favorable to significantly reduced V_f^{crit} and $(L_f/d_f)_{limit}$, leading to high performance fiber reinforced concrete (high strength, high toughness, and high ductility, yet low fiber content) which is processable with conventional construction equipments, hence minimum cost increase. This condition is decisively dependent on how to control the interface properties (τ and T_i).

Polymeric fibers (being lightweight and corrosion resistance) have the unique characteristics of poor interfacial bond strength (τ) with cementitious matrix and weak lateral strength resulting in surface abrasion (related to interface toughness, T_i). The need for enhancing interface bond properties is especially important for the design of high performance cement based products. For these value-added products, a wide range of applications such as in buildings, bridges, thin section panels, or pavements, is expected, and better interfacial bond strength is necessary to exploit the improved fiber property in the performance of the composite. This invention is directed towards developing methodology of interface (between fiber and matrix) property control by plasma treatment in order to optimize composite performance and cost efficiency on the basis of sound scientific understanding.

Plasma Treatment

A plasma is an ionized gas which received high ionization energy from an electromagnetic field. It consists of a mixture of electrons, ions, and radicals. These high energy particles can interact with a solid surface and produce the following effect : (1) abstraction of species from the surface, (2) rearrangement of surface bonds, and (3) grafting of molecular groups to the surface. In the case of fiber surface modification, the main mechanism is the removal of hydrogen atoms from the polymer backbone followed by the replacement with polar groups. The presence of polar or functional groups on the fiber surface enhances the reactivity with the matrix, thus promoting excellent adhesion. Since one can select optimum gas chemistry and operating conditions, plasma treatment can be applied to a wide range of fiber types.

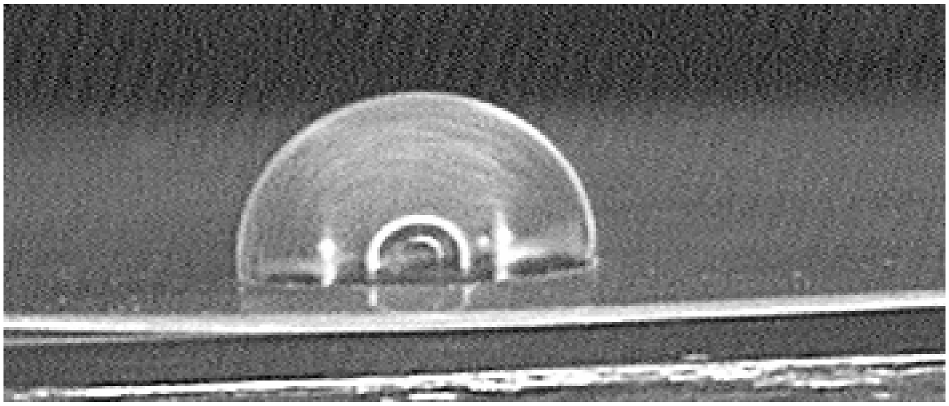
In order to demonstrate the working principle of this invention, an extensive study of plasma treatment of polyethylene fibers (chosen as an example) on bond property has been carried out at the ACE-MRL. A typical pull-out curve of single virgin and plasma treated fibers from cement matrix are shown in Figure 1. With the optimum treatment conditions, a six-fold increase in bond strength and seven-fold increase in interface toughness have been achieved (see next section and Table 1). In addition, a significant improvement of surface energy (related to wettability of fiber) was attained. High surface energy is associated with low contact angle. As shown in Figure 2, the contact angle of a polyethylene film can be dramatically reduced from 90^0 to 28^0.



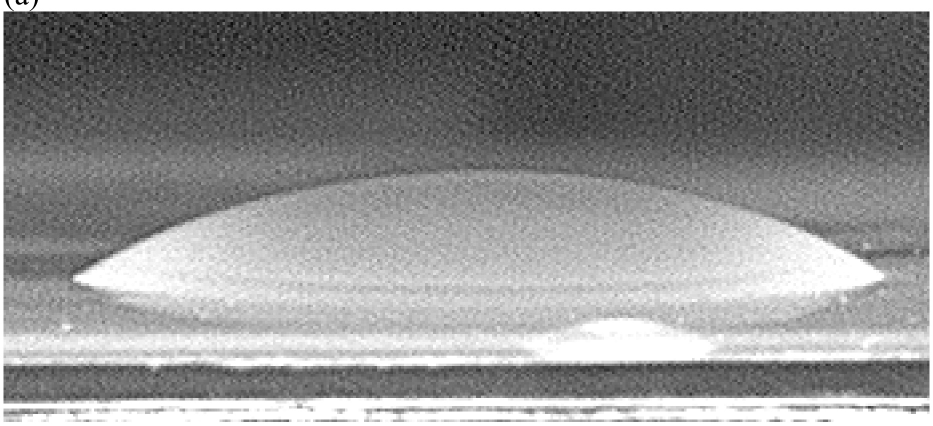
(a)

(b)

Figure 1: Typical pull-out curves of (a) virgin (b) plasma treated polyethylene fibers.



(a)



(b)

Figure 2: Contact angle measurement (a) untreated PE film, θ=90 (b) air plasma treated PE film with 300 watt for 1 minute, θ=27.5.

A comparison of maximum improvements of interfacial property (bond strength and interface toughness) by various plasma treatment conditions can be found in Table 1, together with the optimum conditions. It is clearly shown that high power plasma is more effective in modifying fiber surface leading to improved bond strength with the exception of ammonia plasma. Very high chemical bonds can be achieved with more aggressive gases containing oxygen, however, at the expense of interface toughness. Under this category, high power air plasma might be more desirable than oxygen plasma due to its easy process and low cost. Energy dissipation ability can be another important consideration for composite design, since very high composite toughness might outweigh strength requirement for some applications. In this regard, high power argon plasma demonstrates the highest improvement in interface toughness as well as high bond strength with a 5 minute treatment. When the treatment time is increased to 10 minute, a transition from frictional bond to chemical bond takes place, and results in lower energy consumption. Prolonged treatment with ammonia plasma leads to adverse result for both power levels used in this study. It is also suggested from the wettability study that the choice of functional group added onto fiber surface be the dominant factor for enhanced interfacial property, whereas wettability might be secondary.

Table 1: Maximum improvements of interfacial property by various plasma treatments.

Gas Type	Bond, τ/τ_0	Toughness, T_i/T_{i0}	Power Level (watt)	Optimum Time (min)
Argon	3.5	4.9	100	10
	4.5	6.9	300	5
Ammonia	3.7	3.6	100	1
	2.8	3.8	300	1
Oxygen	4.0	5.4	100	10
	6.3	1.3	300	10
Air	4.0	3.8	100	10
	6.0	0.7	300	10

τ: bond strength, T_i: interface toughness, τ_0 and T_{i0}: refers to the control.

To further demonstrate the versatility of this invention, a limited study on plasma treatment of polypropylene fibers was also conducted. As shown in Figure 3, significant toughness improvement was achieved with Argon plasma treatment, whereas initial frictional bond was marginally increased with a greatly enhanced slip-hardening leading to much improved "apparent" frictional bonds. It should be noted that the current plasma treatment of polypropylene fibers was not yet optimized. A much greater improvement in both bond strength and toughness can be expected with a well tuned plasma treatment.

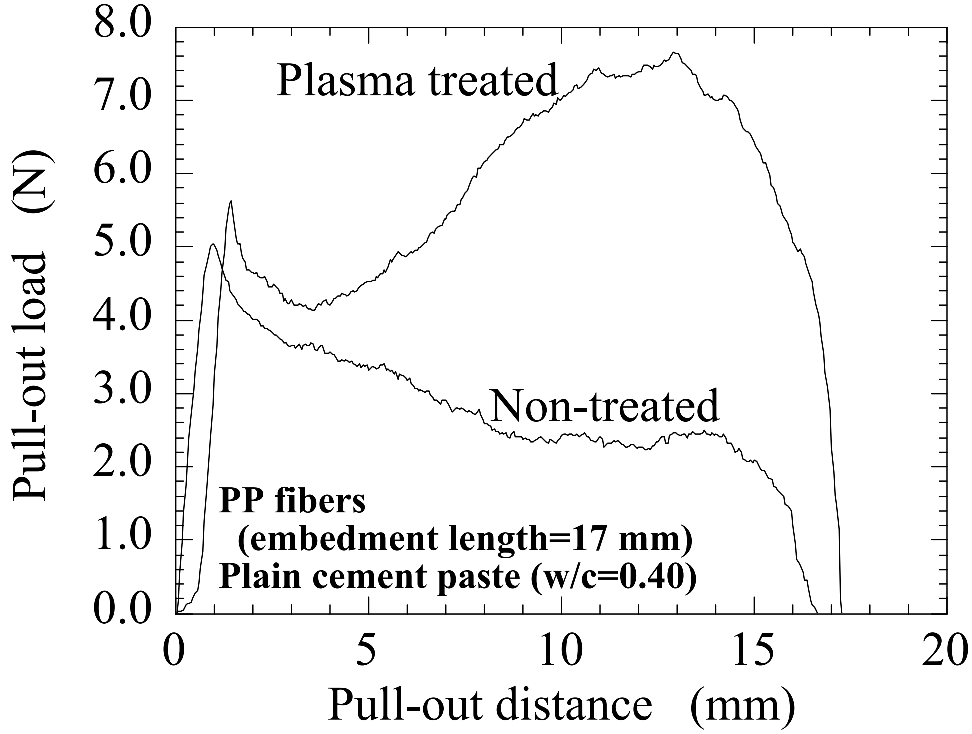


Figure 3: Pull-out curves of polypropylene fibers with and without Ar plasma treatment.

Summary

A fiber surface modification methodology of improving interface properties between fiber/cement using plasma technique has been successfully developed in our laboratory. High bond strength (τ), high interface toughness (T_i), or both can be achieved with optimum plasma treatment conditions, as already illustrated with polyethylene and polypropylene fibers. The significance of such interface tailoring on composite properties can be predicted through micromechanics models. Optimum combinations of fiber geometric parameters (fiber aspect ratio) and interface properties as suggested from the model predictions, can then be used as feedback criterion for optimization of plasma treatment. This performance driven design approach (PDDA) is currently being pursued at the ACE-MRL. The key elements of the PDDA is the ability of interface properties control as described in this new invention. A recent US patent search on plasma, fiber, concrete, and civil did not discover any existing patents on interface properties control by plasma treatment. The closest finding is a process involving fiber coating using plasma techniques.