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PLENARY INVITED PAPER

BASIC INTERFACIAL CHARACTERISTIC OF POLYETHYLENE FIBER/CEMENT COMPOSITES AND ITS MODIFICATION BY PLASMA

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ABSTRACT

The interfacial properties govern many important composite performance. These include all composite strengths, fracture energy, ductility, and energy absorption capacities. Most polymer fibers bond poorly to cementitious materials. Hence techniques to enhance interfacial bond strength has been a major research activity. In this paper, results of interfacial properties improvement by cold plasma treatment of polyethylene fibers are presented. A 6-fold increase in interfacial bond strength, and a 7-fold increase in toughness have been achieved with various plasma treatment conditions. In contrast to frictional bonds, chemical bonds are observed for the first time for the polyethylene/cement system in which a poor frictional bond of the magnitude less than 1.0 MPa is typically present. In addition to the discussion of the plasma effect on the interfacial properties, the single fiber pull-out behavior of the polyethylene fibers with respect to the speed of pull-out loads and the magnitude of the free lengths is described. This information is particularly relevant to the determination of the fiber debonding modes, whether strength base or fracture base. Finally, the effect of load precycling on the interfacial bond properties is highlighted.

INTRODUCTION

Most polymeric fibers have the unique characteristics of poor interfacial bond strength with cementitious matrix and weak lateral strength resulting in surface abrasion. The poor bonding characteristics is a severe limitation to the effective use of polymeric fibers in high performance cementitious composites. The need for enhancing interface bond properties is especially important for higher modulus higher strength polymeric fibers, which are being introduced

commercially at increasingly attractive prices. For these fibers, better interfacial bond strength is necessary to exploit the improved fiber property in the performance of the composite. Hence, the interfacial properties dictate composite performance. These include all composite strengths, fracture energy, ductility, and energy absorption capacities. Therefore, developing interface (between fiber and matrix) modification strategies in order to optimize composite performance and cost efficiency on the basis of sound scientific understanding is of great importance.

In this paper, some basic fiber pull-out behavior is briefly discussed, focusing on polyethylene fibers. This is followed by a summary of a comprehensive study on the optimal conditions of plasma treatment of polyethylene fibers on their interfacial property.

MATERIALS AND EXPERIMENTAL METHODS

Materials

Single fiber direct pull-out tests were conducted to evaluate interfacial bond properties. A cement paste with w/c ratio of 0.3 was used throughout. The compositions of the matrix is shown in Table 1. A high strength/high modulus polyethylene fiber (trade name Spectra 900 by Allied Signal, diameter of 38 μm) was employed.

Table 1: Matrix compositions.

Cement	Silica fume	Superplasticizer	water
1	0.1	0.01	0.3

In preparation of the test samples, specimens were demolded 24 hours after casting and were cured in a water tank till testing. Fiber pull-out tests were conducted at the age of 28 days. At least 6 specimens were tested for plasma treated and non-treated samples.

Single fiber pull-out tests

To evaluate fiber/matrix interface bond improvement by the plasma treatment, fiber pull-out tests were conducted by pulling individual fibers out of cement matrix bases. The test setup and specimen configuration of the fiber pull-out test are shown in Figure 1. A fiber sample is partially embedded in the specimen. The specimen is held by the loading fixture connected to a load cell. On the other end of the specimen, an aluminum plate is used to hold the protruding fiber such that no slip between the plate and the fiber may happen. The pull-out test is conducted using a uniaxial hydraulic MTS testing machine which applies a constant displacement rate to the fiber grip. A computer data acquisition system is employed to collect data during the tests, including the applied load P obtained from the load cell and the displacement of the fiber grip by measuring the cross-head movement. The displacement of the fiber protruded end u is obtained

by subtracting the elastic stretch of the fiber free length between the matrix base and the fiber grip from the measured cross-head displacement. The elastic stretch of the fiber free length at any given applied load, in turn, is calculated based on the initial fiber free length, fiber cross-sectional area, and fiber elastic modulus. In general, the interfacial bond properties are interpreted based on these P-u curves obtained from the pull-out tests.

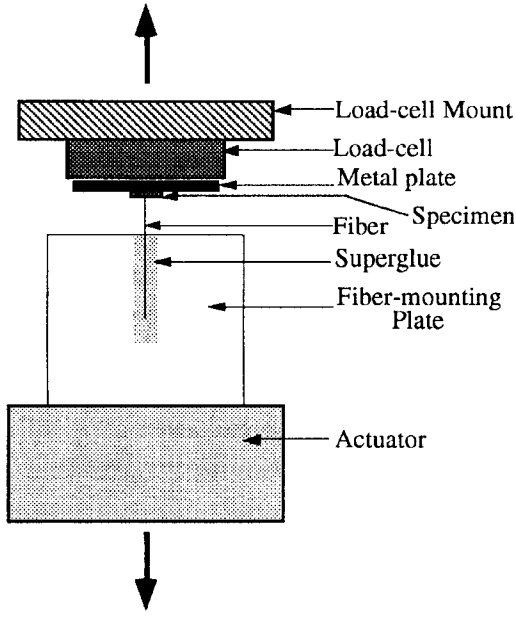

Figure 1: Single fiber pull-out test setup.

A standard fiber free length of 5 mm, fiber embedment length of 6 mm, and pull-out speed of 0.02 mm/sec were used throughout the study. The effect of a longer free length (50 mm) and various pull-out speed (from 0.002 to 0.2 mm/sec) on interfacial properties were also investigated. In addition to monotonic loading to complete fiber pull-out, 10 times precycling between 0 to 80% of the bend-over-point loads followed immediately by ramp to complete pull-out was also employed to examine such effect on bond properties. In the precycling tests, a longer embedment length of 12 mm was adopted to promote the slip-hardening phenomenon.

Plasma treatment

A plasma, taking into consideration the energy of the particles constituting it, is energically the fourth state of the matter, apart from the solid, liquid, and gas. A plasma generally consists of electrons, positive ions, molecules (or atoms), and molecular fragments (free radical). The charge density of ions, which is approximately equal to the density of the ions, is equal to the density of electrons (and is called plasma density), making the plasma electrically neutral.

Energy from an applied electric field is mainly received by the free electrons in the plasma due to their being extremely lightweight. They are accelerated and absorb large amount of energy. The electrons then transfer energy through collision with the molecules of the gas and cause their ionization and dissociation. Hence the mechanism for surface modification of polymer fibers in a gas plasma is the removal of hydrogen atoms from the polymer backbone followed by their replacement with polar groups. The presence of polar or functional chemical groups on the fiber surface enhances reactivity with the matrix, thus promoting excellent adhesion [1]. The selection of reaction gases and process conditions such as generator power and reactor pressure provides opportunities for tailoring fiber surface chemistry and reactivity most adequate for a given fiber/matrix.

Various processing conditions of plasma treatment have been conducted on a high strength/high modulus polyethylene fiber. This fiber has been successfully used to create high performance Engineered Cementitious Composites (ECCs) at the University of Michigan [2]. For evaluation of interfacial modification by plasma treatment on bonding property, continuous single polyethylene fibers were treated and tested on the single fiber level (single fiber pull-out test). A plasma treatment system manufactured by AIRCO/Plasma Science (Model PS 300) was used throughout this study.

Continuous fibers were treated by gas plasma in the abovementioned plasma treatment system. Four types of gas, i.e. Argon, Air, Ammonia, and Oxygen, was employed. Various power levels and treatment times (see Table 2) were used along with a fixed flow rate of 58 ml/min, and initial pressure of 100 mtorr. After the end of each treatment, the plasma chamber was flushed with the same type of gas for 30 seconds before the chamber was devacuumed to atmosphere pressure. This is to ensure that no contamination arises from the purging air. The process of plasma treatment was followed immediately by specimen casting.

Table 2: Plasma treatment conditions.

Gas	Power (Watt)	Time (min)
Air	100, 300	1, 5, 10
Ar	100, 300	1, 5, 10
NH_3	100, 300	1, 5, 10
O_2	100, 300	1, 5, 10

RESULTS AND DISCUSSIONS

Figure 2 shows typical pull-out curves from tests with the Spectra fibers. Generally, the pull-out curves include a near-linear portion, corresponding to the debonding process at the very

beginning, and a non-linear portion, which covers most of a pull-out curve, representing the pull-out process. The average initial frictional bonds are calculated from the load at full debonding which, in this case, refers to the onset of the nonlinear branch (bend-over-point, coincided with the maximum peak in Figure 2) of the pull-out curve divided by the initial fiber/matrix contact area, $\pi d_f l_f$, where l_f and d_f are fiber embedment length and fiber diameter, respectively. The total toughness was determined by the total area under the pull-out load vs. displacement (P-u) curves.

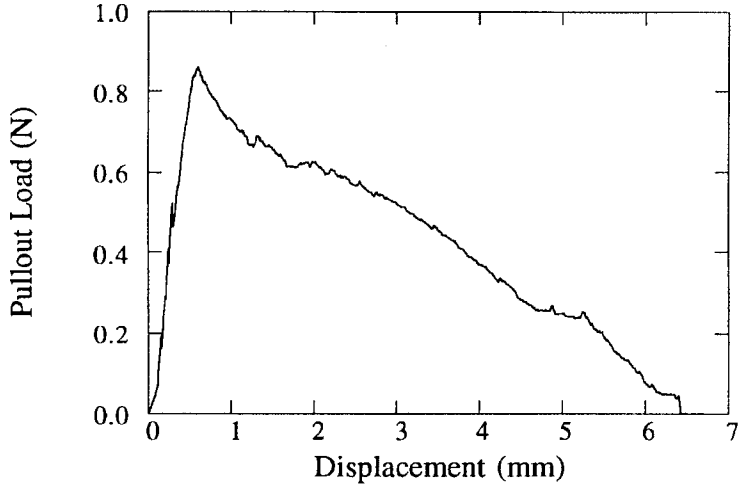

Figure 2: Typical pull-out (P-u) curve, l_f =6 mm.

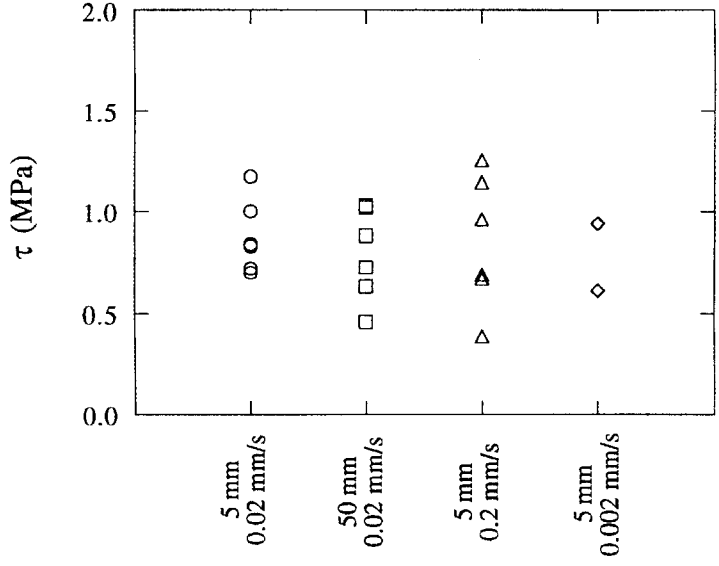

Figure 3: Effect of fiber free length and pull-out speed on frictional bonds.

Effect of free length

The apparent frictional bonds for two different free length (5 and 50 mm separately) specimens, together with the data for different testing speed, are shown in Figure 3. The independence of τ on the free length seems to suggest that the frictional debonding be governed by the strength-based criterion rather than the fracture-based criterion [3 - 5]. The fracture-based criterion would involve an elastic energy contribution from the fiber free length portion, suggesting an influence of the magnitude of the free length on the apparent bond strength. However, at present, there is no model predictions available taking this free length effect into account, making unequivocal comparisons difficult.

Effect of pull-out speed

As shown in Figure 3, the pull-out speed has little or no effect on the bond strength.

Effect of precycling

The effect of the 10 times precycling between 0 and 80% of the bend-over-point (BOP) loads are shown in Table 3. The τ_{max} is calculated based on the maximum peak loads which are the second peaks after the BOP and exceed the BOP values due to a severe slip-hardening for the specimens with a long embedment length (l_f =12 mm). Such profound slip-hardening phenomenon was not observed for the shorter embedment length specimens (l_f=6 mm).

Contrary to the steel fiber case where bond degradation after precycling was reported [6], the current study shows that precycling is actually beneficial to a softer fibers like polyethylene used in this study. Polymer fibers are more vulnerable to surface abrasion damage, whereas steel fibers tend to cause damage on the matrix side during load cycling [7].

Table 3: Comparison of interfacial properties obtained from monotonical and precycling tests.

	τ (MPa)	τ_{max} (MPa)	T (N-mm)
Monotonic	0.64	0.72	7.1
Precycling	0.73 (+14%)	0.88 (+22%)	8.6 (+21%)

values represent the average of 4 tests, () indicates % of changes.

Effect of plasma treatment

Detailed results of the plasma treatment will be published elsewhere [8]. Only a summary is given in this paper. With the Ar plasma treatment, the concave-downward shape of the descending nonlinear branch indicates slip-hardening behavior of fiber pull-out caused by the abrasion effect. The average frictional bond increases with pull-out distance. A more profound

abrasion damage might give rise to a second peak which is higher than the first peak in magnitude, as shown in Figure 4 (also in the above section). A significant increase in friction bonds and energy is achieved. In the case of the oxygen and air plasmas, a distinct interfacial failure mode was noticed. An immediate load drop after the peak follows by a descending branch (see Figure 5). This is typical characteristics of chemical bond (or elastic bond) failure. It is the first time that a true chemical bonding is achieved for a polyethylene/cement system. In fact, the bond strength was so strong that the embedment length of the fibers in the matrix has to be shortened from 6 mm to 3 mm in order to avoid fiber rupture. The total toughness of the 10-minute specimens was, however, significant lower than that of other treatment, although it should be noted that the embedment length was half of other specimens. Such a reduction in energy consumption ability is expected when a significant load drop occurs in the pull-out behavior of the 10 minute case.

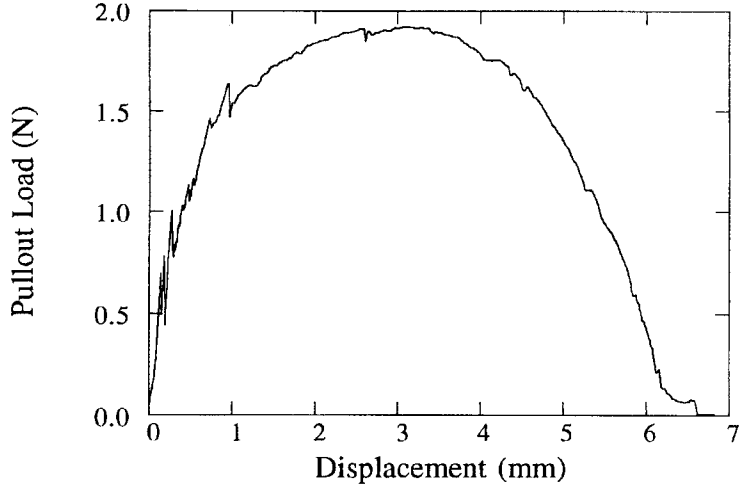

Figure 4: Typical pull-out curves of Ar plasma treated fibers with 300 watt power showing slip-hardening portion after the onset of complete debonding, l_f=6mm.

A comparison of maximum improvements of interfacial property (frictional bond and total toughness) by various plasma treatment conditions can be found in Table 4, together with the optimum conditions. It is clearly shown that high power plasma is more effective in modifying fiber surface chemistry, leading to improved bond strength, with the exception of the ammonia plasma. Very high chemical bonds can be achieved with more aggressive gases containing oxygen, however, at the expense of total 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 requirements for some applications. In

this regard, high power argon plasma exhibited the highest improvement in total toughness as well as high friction with a 5 min treatment. When the treatment time is increased to 10 min, a transition from frictional bond to chemical bond takes place, resulting in lower energy consumption. Prolonged treatment with ammonia plasma gave adverse results for both power levels used in this study. This phenomenon is not observed for other plasmas, and the reason is unknown.

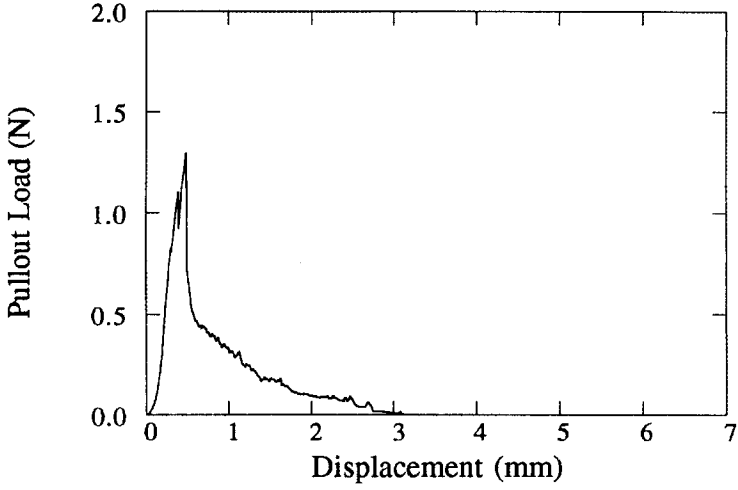

Figure 5: Typical pull-out curves of oxygen plasma treated fibers with 300 watt power, showing strong chemical debonding, treatment time=10 minute, l_f=3mm.

Table 4: Maximum improvement of interfacial property by various plasma treatments.

Gas Type	Power Level (watt)	Bond, τ/τ_0	Toughness, T/T_0	Optimum Time (min)
Argon	100	3.5	4.9	10
	300	4.5	6.9	5
Ammonia	100	3.7	3.6	1
	300	2.8	3.8	1
Oxygen	100	4.0	5.4	10
	300	6.3	1.3	10
Air	100	4.0	3.8	10
	300	6.0	0.7	10

τ: frictional bond, T: toughness, τ_0 and T_0: refers to the control.

CONCLUSIONS

With the optimum treatment conditions, a six-fold increase in bond strength or seven-fold increase in total toughness can be achieved separately. Furthermore, a distinct interfacial chemical bond, compared to a common frictional bond was observed for the first time in the polyethylene/cement systems. This finding represents a significant breakthrough for interface tailoring. This is because we can now truly *design* interfacial properties such as bond magnitude, post peak behavior, or slip hardening through fiber surface tailoring. This flexibility allows us greater freedom in satisfying various composite performance requirements, e.g. whether high bond strength leading to high composite strength or high energy capability leading to high composite toughness is the dominant factor for fiber surface modification. The choice is obviously dependent on individual applications.

The slip-hardening, beneficial to the interfacial bond properties and the composite properties, is found to be more profound when increasing the fiber embedment lengths or precycling 10 times between 0 to 80% of the BOP loads prior to complete fiber pull-out. The effect of the fiber free lengths and the fiber pull-out speed on the bond properties is found to be minimal.

ACKNOWLEDGMENT

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