

## Fiber/cement interface tailoring with plasma treatment

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### Abstract

A comprehensive study on the optimal conditions of plasma treatment of polyethylene fibers on their interfacial property with cement matrix is reported in this paper. Single fiber pullout tests were performed for bond property evaluation. With the optimal treatment conditions, a sixfold increase in bond strength or sevenfold increase in interfacial toughness can be achieved separately. Furthermore, a distinct interfacial chemical bond, compared to common frictional bond was observed for the first time in the polyethylene/cement systems. On the matrix side, matrix modifiers such as high alumina cement and PVA powder were also studied to examine their additional influence on the interface properties. Some preliminary results of the stability of plasma treatment are also reported in this paper. © 1999 Elsevier Science Ltd. All rights reserved.

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### 1. Introduction

Polymeric fibers (particularly hydrophobic) have the unique characteristics of poor interfacial bond strength with cementitious matrix and weak lateral strength resulting in surface abrasion during fiber pull-out from the matrix. The poor bonding characteristic 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.

After careful review of the literature, we do not find any study on the surface modification of polymer fibers by plasma in a cement-based composite. Nevertheless, there are abundant reports of such studies in polymer composites [1,2]. Bonding to polyethylene fibers has been studied considerably, especially in epoxy [3–6] and PMMA [7]. Next to polyethylene, carbon and aramid

fibers were also well studied [1,8,9]. Much effort has been focused on fiber surface modification, primarily by oxidative treatments such as chemical oxidation, corona treatment, and plasma treatment [4,5,10]. All of these modification techniques are directed towards improving interfacial strength and are employed with various degrees of success. The most significant improvement in adhesion has been accomplished with cold gas plasma [3].

Plasma is generated by exciting gas molecules with a source of electrical energy. When excited, electrons are stripped from the molecules, producing a mix of highly reactive disassociated molecules [3,11]. Hence the mechanism for surface modification of polymer fibers in 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 [3,12]. 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 matrix.

Various gases, ammonia, air, nitrogen, argon, and carbon dioxide have been employed in production of polyethylene/epoxy or polyethylene/PMMA composites [1,4–7]. In general, the interfacial bond strength can be readily doubled with only a few minutes' fiber exposure

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to plasma. Prolonged exposure does not improve the strength further. In addition to excellent adhesion, plasma treated fibers have also exhibited significantly enhanced pull-out energy in a single fiber pull-out test [7]. The enhanced interfacial properties are expected to be transferred to the composite performance. In different studies on composite properties, a fourfold increase in interlaminar shear strength of polyethylene/epoxy composites over untreated fiber was achieved with plasma surface treatment [3,6].

As to the effect of plasma treatment on the properties of the fibers, a minor reduction (less than 10%), if any, of the tensile strength of the fibers has been found under most treatment conditions [3,6,7,13]. A slight increase in tensile modulus of plasma treated fibers was observed by Kaplan et al. [3]. Cross-linking and chain scissions were generally cited as the main cause of changes in modulus and tensile strength. However, these effects are probably surface phenomenon, and are contained within a few hundred angstroms of the fiber surface [3,6]. The bulk properties, therefore, are not significantly affected. Certain evidence of roughening or micropitting of the fiber surface are reported, and it has been suggested that mechanical interlocking is also beneficial to interfacial bond strength [14]. Further, it was found that pit sizes might control the degree of improvement [15]. It should be also noted that an intensive plasma treatment (e.g. using O<sub>2</sub> and high power) could significantly reduce fiber strength [1,16].

Compared to polymer matrix composites, there is little research on fiber surface modification for the cementitious composites [17]. Motivated by the success of using plasma techniques for polymer composites, research tasks in this area have recently been carried out at the University of Michigan, and reported in this paper.

## 2. Single fiber pull-out tests

For evaluation of interfacial modification by plasma treatment on bond property, continuous single polyethylene fibers (tradename Spectra, diameter of 38 µm, modulus of 120 GPa) were treated and tested on the single fiber level (single fiber pull-out test). Four types of gas, i.e. Argon, Air, Ammonia, and Oxygen, were employed. Various powers level (100 and 300 W) and treatment times (1, 5, 10 min) were used along with a fixed flow rate of 58 ml/min, and initial pressure of 100 mTorr. The process of plasma treatment was followed immediately (within 30 min) by specimen casting. A cement paste with *w/c* ratio of 0.3 was used throughout this study. The compositions of the matrix are shown in Table 1. Detailed description of the specimen preparation and testing procedure can be found elsewhere [17]. The test setup is shown schematically in Fig. 1.

Table 1  
Matrix compositions

Cement	Silica fume	Superplasticizer	Water
1	0.1	0.01	0.3

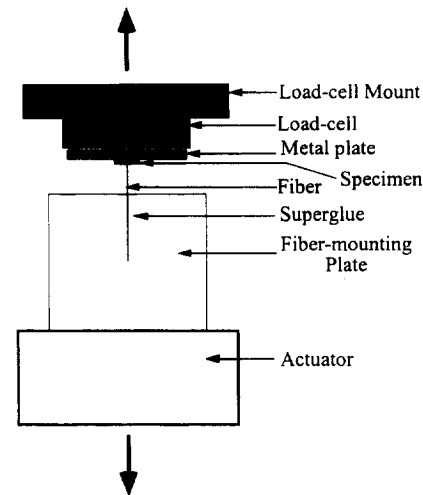


Fig. 1. Single fiber pull-out test setup.

## 3. Interfacial bond characteristics

### 3.1. Effect of fiber surface finish

For as-received polyethylene fibers, when treated with Ar gas in a trial test, a plasma color change occurred rapidly from regular orange color to light blue in the first minute of treatment. The light blue plasma is typically associated with oxygen. Therefore, it is hypothesized that some oxygen or oxide from the fibers was released during the treatment. The source of such oxygen probably comes from the (proprietary) finish of the fibers. Presumably, finish is applied during fiber spinning process to reduce friction damage. This hypothesis is supported by the fact that 20% oxygen was detected on the same polyethylene fiber surface from ESCA measurement [18]. It might be necessary to remove this finish before applying plasma for efficient fiber surface modification. Thus, fibers were soaked in a 1% solution of tribasic sodium phosphate ( $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ ) in distilled water for 10 min, and rinsed in acetone prior to plasma treatments. The use of such a solution was found satisfactory for the same kind of polyethylene fibers [12]. A much smoother fiber surface was obtained after the chemical treatment under SEM examination.

Fig. 2 shows typical pull-out curves from tests of untreated as-received and chemically cleaned Spectra fibers. Fibers have embedment length of 6 mm. Generally, the pull-out curves include a near-linear portion corresponding to the debonding process at the very

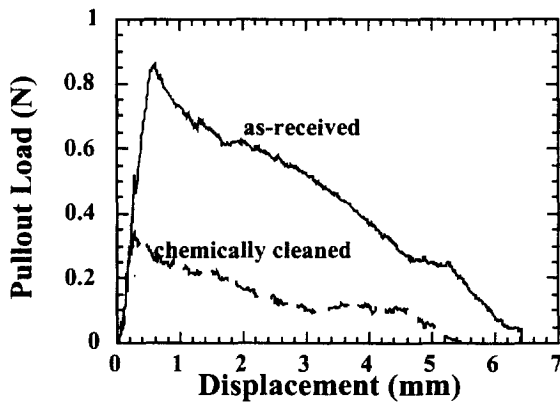


Fig. 2. Typical pull-out curves of as-received, and chemically cleaned (with tribasic sodium phosphate solution) fibers.

beginning and a non-linear portion, which covers most of a pull-out curve, representing the pull-out process.

Comparing the features of these pull-out curves in Fig. 2, it is obvious that the as received fiber sample has a much higher frictional bond and consumes much more energy than does the chemically cleaned fiber. Table 2 summarizes the initial frictional bonds and interfacial toughness from the results of a series of pull-out tests. The average initial frictional bonds are calculated from the load at full debonding which, in this case, refers to the onset of the non-linear branch of a 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 area under the pull-out load vs. displacement curves determined the interfacial toughness. As shown in Table 2, the mean of the frictional bond and interfacial toughness of the chemically cleaned Spectra fiber has been reduced by approximately 60% and 70%, from 1.07 to 0.45 MPa, and 3.22 to 0.98 N-mm, respectively. These results indicate that the fiber surface finish does have significant effect on interfacial bond property, although the exact finish information and mechanism are not known.

### 3.2. Effect of cement brands

Two kinds of Type I cement, A and B, were used to investigate the effect of different cement brands on interfacial bond property. The results are also summarized in Table 2, the mean of the frictional bond and inter-

facial toughness of the specimens made with cement A are slightly lower. However, the difference is considered insignificant, since the specimens with cement B show much higher variation.

### 3.3. Effect of plasma

#### 3.3.1. Ar, 100 Watt power

Plasma treatment is also a process of cleaning of fiber surface. Therefore it is expected to have similar effect on removing fiber surface finish as that of a chemical solution. The pull-out behavior of Ar plasma treated as-received fibers as well as chemically cleaned fibers (as described above) for 1 min were compared. It was found that the average of the initial frictional bonds and interfacial toughness of the Ar plasma treated chemically cleaned fibers are slightly reduced by 9% and 10% respectively, compared to that of Ar plasma treated as-received. These are consistent with the effect of fiber surface finish as described previously, since some residue of finish might still exist after the plasma treatment. For consistency, the control specimens hereinafter are referred to the chemically cleaned fibers, and all plasma treatment are performed on those fibers thus previously cleaned.

Typical pull-out curves of Ar plasma treated fibers with 100 W power are shown in Fig. 3. Two types of post peak behavior can be identified, i.e. a gradual descend immediately after the peak or slip-hardening prior

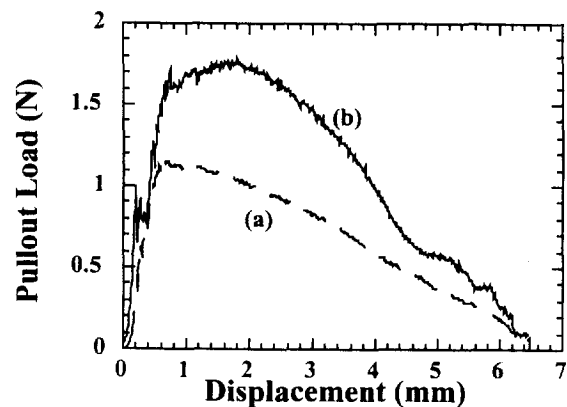


Fig. 3. Typical pull-out curves of Ar plasma treated fibers with 100 W power (a) descending branch immediately following the peak (b) slip-hardening portion after the onset of complete debonding.

Table 2  
Averaged interfacial properties of as-received and chemically cleaned fibers

	Interfacial bond (MPa)		Interfacial toughness (N mm)	
	Mean	Std deviation	Mean	Std deviation
As-received/Type A cement	1.07	0.09	3.22	0.31
Chemically cleaned/Type A cement	0.45	0.17	0.98	0.31
Chemically cleaned/Type B cement	0.55	0.23	1.39	0.81

Table 3  
Average treatment results of 100 W

	Treatment time (min)		
	1	5	10
Ar	1.43 (0.28)	1.63 (0.33)	1.78 (0.23)
	4.11 (1.70) <sup>a</sup>	5.52 (0.73)	5.92 (1.32)
Ammonia	1.89 (0.28)	1.77 (0.29)	1.74 (0.35)
	4.35 (0.91)	4.24 (1.49)	4.12 (1.18)
Oxygen	2.01 (0.22)	2.01 (0.31)	2.03 (0.24)
	5.15 (1.08)	6.13 (1.16)	6.50 (2.08)
Air	1.39 (0.36)	1.81 (0.39)	2.05 (0.23)
	4.18 (1.85)	4.13 (0.96)	4.04 (0.58)

<sup>a</sup> First number indicates average  $\tau$  in MPa, second number average interfacial toughness in N mm, ( ) indicates std. deviations.

to descending. The concave-downward shape of the descending non-linear branch indicates slip-hardening behavior of fiber pull-out caused by the abrasion effect. The average frictional bond increases with pull-out distance [19]. A more profound abrasion damage might give rise to a second peak which is higher than the first peak in magnitude, as shown in Fig. 3(b). This feature is general regardless of treatment time. As summarized in Table 3, it is clearly shown that a significant increase in friction bonds (2.8 times higher) and interfacial toughness (3.4 times higher) is achieved with only 1 min treatment time; thereafter moderate improvements are achieved with prolonged treatment.

### 3.3.2. Ar, 300 W power

With a high power plasma treatment, similar behavior as the low power treatment was observed. A summary is provided in Table 4. The improvement of frictional bond reaches its maximum with 5 min treatment; it represents a 4.5 times increase compared to the control. As for the 10 min specimens, slight reductions in bond strengths are found. The interfacial toughness has been increased by a factor of 7 when a 5 min exposure time was used compared to the control. The average of the interfacial toughness of the 10 min

Table 4  
Average treatment results of 300 W

	Treatment time (min)		
	1	5	10
Ar	1.48 (0.24)	2.30 (0.28)	1.81 (0.19)
	5.91 (1.19) <sup>a</sup>	8.39 (1.01)	5.61 (1.25)
Ammonia	1.45 (0.19)	1.39 (0.08)	0.98 (0.26)
	4.64 (1.06)	3.27 (0.78)	2.88 (1.89)
Oxygen	1.91 (0.31)	2.42 (0.41)	3.23 (0.86)
	5.00 (1.34)	5.04 (1.06)	1.29 (0.63) <sup>b</sup>
Air	1.88 (0.17)	1.86 (0.54)	3.07 (0.58)
	5.52 (1.25)	5.61 (1.20)	0.89 (0.61) <sup>b</sup>

<sup>a</sup> First number indicates average  $\tau$  in MPa, second number average interfacial toughness in N mm, ( ) indicates std. deviations.

<sup>b</sup> Embedment length = 3 mm.

specimens is 33% lower than that of the 5 min specimens. This is due to the presence of a slip-hardening portion of the load-displacement curves (e.g. Fig. 3(b)) in the 5 min specimens, but not in the 10 min specimens.

### 3.3.3. Ammonia, 100 W power

NH<sub>3</sub> plasma is more reactive than argon. With a 1 min treatment of fiber, an immediate load drop after the peak followed by a descending branch (see Fig. 4(a)) is observed. This is a typical characteristic of chemical bond (or elastic bond) failure [20]. When the exposure times were increased to 5 and 10 min, the chemical bonds disappear and the same type of frictional bonds as the control are present with a higher bond strength (3.5 times higher, see Fig. 4(b)). For consistency, the chemical bond strengths are calculated in an identical manner as the frictional bond described above. In addition to the change of the bonding characteristics, prolonged exposure times seems to degrade the bond strength (Table 3), on average, from 1.77 MPa (for 5 min treatment) to 1.74 MPa (for 10 min treatment). Similar trend was observed for the interfacial toughness. The reason for the degradation is not yet known.

### 3.3.4. Ammonia, 300 W power

When high power NH<sub>3</sub> plasma was used, a mixture of chemical bonds and frictional bonds was observed for all treatment times. As shown in Table 4, an even greater degree of degradation was noticed, not only with respect to prolonged exposure times, but also to the power level (compared with Table 3). The mean of the "apparent" initial frictional bond of the 1, 5, and 10 min specimens is 1.45, 1.39, and 0.98 MPa, respectively, vs. 0.51 MPa for the control. The corresponding interfacial toughness is 4.64, 3.27, and 2.88 N mm, vs. 1.21 N mm for the control.

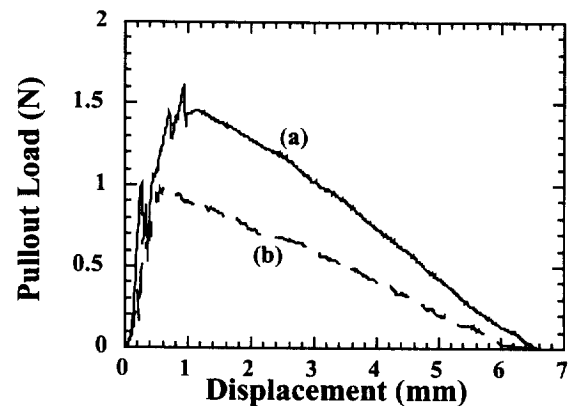


Fig. 4. Typical pull-out curves of ammonia plasma treated fibers with 100 W power (a) chemical debonding with 1 min treatment (b) frictional debonding with 5 and 10 min treatment.

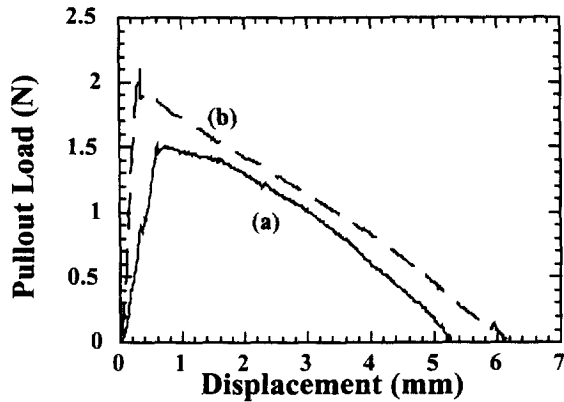


Fig. 5. Typical pull-out curves of oxygen plasma treated fibers with 100 W power, showing chemical debonding (a) treatment time = 1 min (b) treatment time = 5 min.

### 3.3.5. Oxygen, 100 W power

Chemical debonding was the dominant phenomenon for all the treatment times. More profound load drops after the peak were found when longer exposure times were used (as shown in Fig. 5). The apparent frictional bonds and interfacial toughness were slightly improved with increasing treatment times, representing roughly 4.0 times (from 0.5 to 2.0 MPa) and 6.0 times (from 1.2 to 6.1 N mm) higher than the control (see Table 3).

### 3.3.6. Oxygen, 300 W power

When high power of  $O_2$  plasma was used, very strong chemical bonds were achieved, exhibiting very high peak load and a large load drop in the pull-out load vs. displacement curves, especially for the 10 min treatment specimens (see Fig. 6). In fact, the chemical bond strength was so strong that the embedment length of the fibers in the matrix had to be shortened from 6 to 3 mm in order to avoid fiber rupture. The apparent frictional bonds were increased from 0.51 to 1.91, 2.42, and 3.23 MPa, respectively for the treatment times of 1, 5, and 10 min,

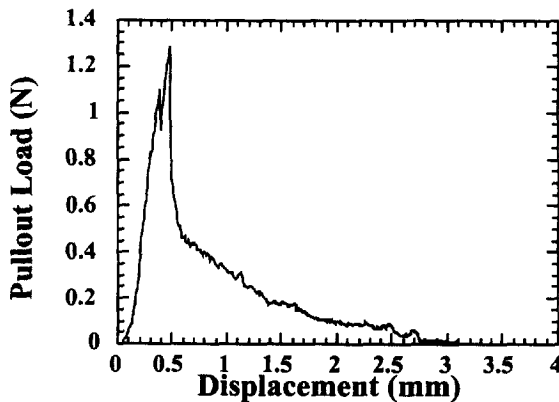


Fig. 6. Typical pull-out curves of oxygen plasma treated fibers with 300 W power, showing strong chemical debonding, treatment time = 10 min.

compared to the control (see Table 4). The latter represents a 6.3 times increase. The interfacial toughness of the 10 min specimens was, however, significantly lower than that of other treatment times (Table 4), 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 such as the 10 min case. The chemical bond, frictional bond and interface toughness may contribute in different manners to composite strength and composite toughness. An optimal combination of these interfacial parameters will depend on the particular application. As described above, we should have a systematic approach as how to engineer fiber surface so that optimal composite performance can be achieved.

### 3.3.7. Air, 100 W power

Regular air consists of oxygen and nitrogen, which might provide active sources for fiber surface modification. It is similar to the case of Ar plasma treatment, for which two types of post peak behavior were identified, i.e. a gradual descend immediately after the peak or slip-hardening prior to descending. This feature is general regardless of treatment time. As shown in Table 3, the mean of the initial frictional bonds of the 1, 5, and 10 min specimens are 2.7 times, 3.5 times, and 4.0 times higher than that of the control. The corresponding interfacial toughness is 3.4 times, 3.4 times, and 3.3 times higher than that of the control. It should be noted that the actual embedment length of the 10 min specimens is only 5 mm, compared to 6 mm for other specimens. Therefore, the actual interfacial toughness of the 10 min specimens is somewhat higher than the measured values. A higher scattering of the interfacial toughness data of the 1 min specimens is found, and can be attributed to a much profound slip-hardening behavior of the 1 min specimens, whereas the majority of the 5 and 10 min specimens show a descending branch immediately following the peak in the pull-out load vs. displacement curves.

### 3.3.8. Air, 300 W power

Similar to the case of  $O_2$  plasma treated specimens, strong chemical bonds were observed for all specimens with different treatment times. It is necessary again to shorten the embedment length of the 10 min specimens to avoid fiber rupture. A summary of the initial apparent frictional bonds and interfacial toughness is given in Table 4. The mean of the bond strength is 1.88, 1.86, and 3.07 MPa, respectively for the 1, 5, and 10 min specimens, vs. the control of 0.51 MPa. The latter represents a 602% increase. The interfacial toughness of the 10 min specimens was again significantly lower than that of other treatment times, although it should be noted that the embedment length was half of other specimens.

Table 5  
Maximum improvements of interfacial property by various plasma treatments

Gas type	Power level (W)	Bond, $\tau/\tau_0$	Toughness, $F/F_0$	Optimal 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 <sup>a</sup>	10
Air	100	4.0	3.8	10
	300	6.0	0.7 <sup>a</sup>	10

$\tau$ : frictional bond,  $F$ : interfacial toughness,  $\tau_0$  and  $F_0$ : refers to the control.

<sup>a</sup> Energy underestimated due to shorter embedment lengths.

A comparison of maximum improvements of interfacial property (frictional bond and interfacial toughness) by various plasma treatment conditions can be found in Table 5, together with the optimal conditions. It is clearly shown that high power plasma is more effective in modifying fiber surface leading to much 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 interfacial 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 interfacial toughness as well as high frictional bonds with a 5 min treatment. Prolonged treatment with ammonia plasma leads to adverse result for both power levels used in this study. This phenomenon is not observed for other plasma, and the reason is unknown.

#### 4. Additional effect of matrix modification

The optimal plasma treatment conditions were identified on the basis of the fiber pull-out behavior from the cement paste. Since ordinary plain cement was used in the study, an even greater degree of improvement in interfacial property might be achieved with a modified matrix. Therefore, the effect of addition of matrix modifiers for enhanced interfacial property with the optimally plasma treated fibers was further examined.

The matrix modifiers included high alumina cement and PVA powder. The former contains  $Al^{+++}$ , which might provide reactive sites for bonding with active functional groups on the fiber surface introduced by plasma treatment. A small quantity of PVA addition to the cement has been shown to have positive effect on bond strength between cement and steel fibers [21] or aggregate [22]. For comparisons, chemically cleaned

Spectra fibers without the plasma treatment and with a plasma treatment were both used in this study. The plasma treatment conditions included treatment duration of 10 min with Ar gas at 300 W.

##### 4.1. High alumina cement

A high alumina cement was used to replace ordinary Portland cement. The specimen preparation was identical to that with Portland cement. The results from the single fiber pull-out tests were summarized in Table 6. With the chemically cleaned fibers and the high alumina cement, both the interfacial bonds and interfacial toughness are comparable to those with the Portland cement. No differences were detected. When the plasma treated fibers were used in both Portland and high alumina cements, indistinguishable changes in both bond and interfacial toughness were again obtained, as shown in Table 6.

##### 4.2. Addition of PVA powder

A small amount of PVA powder (1.4% by weight to cement) was added to the mix following the standard preparation procedure. The interfacial bonds and interfacial toughness are shown in Table 6. With the chemically cleaned fibers, the addition of the PVA appears to improve both the bond and interfacial toughness, approaching those of the as-received fibers (see Table 2). The surface finish on the as-received fibers seems to provide similar affinity to cement as the PVA.

When the Ar plasma treated fibers were used, the interfacial bonds and interfacial toughness were similar to those with plain Portland and high alumina cements (see Table 6).

#### 5. Stability of plasma treatment

To determine the stability (shelf life) of fiber surface modifications by plasma treatment, fibers treated by two types of plasmas were stored in clean plastic bags

Table 6  
Effect of matrix modification

	Interfacial bond (MPa)		Interfacial toughness (N mm)	
	Mean	Std deviation	Mean	Std deviation
Chem cleaned/Portland cement	0.51	0.21	1.21	0.66
Chem cleaned/alumina cement	0.45	0.20	1.24	0.47
Chem cleaned/Portland + PVA	1.11	0.20	3.12	0.68
Plasma/Portland cement	1.81	0.19	5.61	1.25
Plasma/alumina cement	1.88	0.24	5.17	0.63
Plasma/Portland + PVA	1.86	0.21	4.95	1.67

and under laboratory conditions. The plasmas were chosen based on the previous tests, which showed significant improvement in either bond strength ( $O_2$  gas, 10 min, and 300 W) or in interfacial toughness (Ar, 10 min, 300 W). The storage time was 1 yr. After 1 yr, single fiber pull-out specimens were made with these fibers following the standard preparation procedure. The pull-out was performed at the age of 28 d of these specimens.

#### 5.1. Ar plasma treated fibers

The average frictional bond ( $\tau$ ) of the Ar plasma treated fibers is reduced by 45%, and the reduction in interfacial toughness is 70% after 1 yr storage in air (see Table 7). Rapid deterioration of surface modification is probably attributed to contamination, thus the storage environment is a very important consideration to maintain a plasma activated surface.

#### 5.2. $O_2$ plasma treated fibers

As shown in Table 7, the reduction in  $\tau$  is found to be 45%, whereas the reduction in interfacial toughness is 63% after 1 yr storage. Again, significant deterioration of the plasma surface modification after 1 yr storage in clean plastic bags and laboratory conditions is observed.

Although a significant aging effect on the interfacial properties was found, these preliminary data should be treated with caution. A recent study on the treatment life of plasma treated polystyrene stored in three different environments over a period of 1 yr showed that an

extreme variation is found from very unstable to very stable [23].

## 6. Conclusions

It is confirmed from the current study that plasma treatment can effectively modify the surface characteristics of polyethylene fibers used for reinforcing cementitious matrices. The resulting surface modifications can lead to significant improvement in the interfacial properties, the frictional bond and the interfacial toughness evaluated from the single fiber pull-out tests. With the optimal treatment conditions, a sixfold increase in bond strength or sevenfold increase in interfacial toughness, compared to the chemically cleaned fibers can be achieved separately.

Additional matrix modifications by addition of high alumina cement and PVA powder do not show any further improvement in bond properties. The stability of the current plasma treatment of the polyethylene fibers in relation to storage environment deserves attention to ensure suitability for industrial adoption.

The current finding represents an important step as to interface tailoring. This is because we can now truly *design* interface property such as bond magnitude, post peak behavior, or slip hardening through fiber surface tailoring. This flexibility allows us a greater freedom in satisfying various composite performance requirements, e.g. high chemical bonds can lead to very high first crack strength, whereas frictional bond with slip-hardening can consume enormous energy during fiber pullout process.

Table 7  
Stability of plasma treatment

	Interfacial bond (MPa)		Interfacial toughness (N mm)	
	Mean	Std deviation	Mean	Std deviation
Chem cleaned/Portland cement (fresh)	0.51	0.21	1.21	0.66
Ar Plasma/Portland cement (fresh)	1.81	0.19	5.61	1.25
Ar Plasma/Portland cement (after 1 yr)	0.99	0.20	1.68	1.21
$O_2$ Plasma/Portland cement (fresh)	3.23	0.86	1.29	0.63
$O_2$ Plasma/Portland cement (after 1 yr)	1.78	1.00	0.47	0.32

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