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Effect of Ar^+ Ion Irradiation of Polymeric Fiber on Interface and Mechanical Properties of Cementitious Composites

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ABSTRACT

The values of fracture energy and mechanical flexural strength of Fiber Reinforced Cement (FRC) with polypropylene (PP) fiber modified by Ion Assisted Reaction (IAR), by which functional groups were grafted on the surface of PP fiber, was improved about 2 times as those of fracture energy and flexural strength of cement reinforced by untreated PP fiber. PP fiber was irradiated in O_2 environment by Ar^+ ion. The contact angle of PP treated by IAR decreased largely when compared with untreated PP. From this result, we expected that surface energy and interfacial adhesion force of treated PP fiber increased. The strain hardening occurred in the strain-stress curve of FRC including PP treated by IAR when compared with that of FRC with untreated PP. These enhanced mechanical properties might be due to strong interaction between hydrophilic group on modified PP fiber and hydroxyl group in cement matrix. This hydrophilic group on surface modified PP fiber was confirmed by XPS analysis. We clearly observed hydration products that were fixed at modified PP fiber due to the strong adhesion force of interface in cement reinforced modified PP by SEM (Scanning Electron Microscopy) study.

Key words* : *Ion Assisted Reaction (IAR), PP fiber, Hydrophilic group, Adhesion force, Fracture energy

1. Introduction

Since cement has advantageous properties such as cheapness, easy forming and certain strength in short period. And it is the most widely used materials in the construction field. However, the tensile strength of cement is only about 10% of its compressive strength and the crack of cement composite would be occurred when subjected to tensile stress.[3] Therefore, many studies have been conducted in order to increase tensile strength and fracture resistance so one of the methods of improving these mechanical properties of cement is introduction of steel or polymeric fiber as reinforcement of cement. In the case of Steel-Reinforced Cement (SRC), steel in cement matrix is easily corroded when exposed to acid or base environments, resulting in deteriorating mechanical properties such as tensile strength and fracture resistance.[2] In order to overcome the corrosion problem of SRC, polymeric fiber, which is chemically stable under corrosion environments, could be used for reinforcing cement.

Recently, many attempts have been made to improve tensile strength of cement by using polymeric fiber such as polypropylene (PP).[1-3] These studies[3,4] have been focused on the enhancement of bonding strength between polymeric fiber and cement matrix, which leads to the improvements of tensile strength of Fiber Reinforced Cement (FRC). Since the surface of PP is very hydrophobic, it is difficult to obtain high bonding strength between untreated PP fiber and cement matrix. Therefore, it is required to modify the surface of PP fiber for high bonding strength, and as surface treatment, there are chemical treatment such as surface-active agents, chemical oxidation by acid or base, etc.[4] As surface modification technique of polymer, Ion Assisted Reaction (IAR) process has recently been developed by Koh and his co-workers.[8]

IAR treatment introduced oxygen gas near the polymer surface during energetic Ar^+ ion irradiation. Breaking of low bonding energy of polymer chains by IAR caused the hydrophilic groups formation by the interaction between unstable chains and oxygen gas.[8] Therefore, when compared with various treatments, IAR had advantage of using of low energetic ions not to change bulk properties of polymer.[8]

The aims of this study were to prove the enhancement of mechanical properties such as strength and fracture energy of FRC with fiber treated by IAR and this improvement was confirmed the development of bonding strength between cement and PP fiber by inecreasing of surface energy, adhesion force, and interfacial microstructure and formation of hydrophilic group on surface modified PP fiber.

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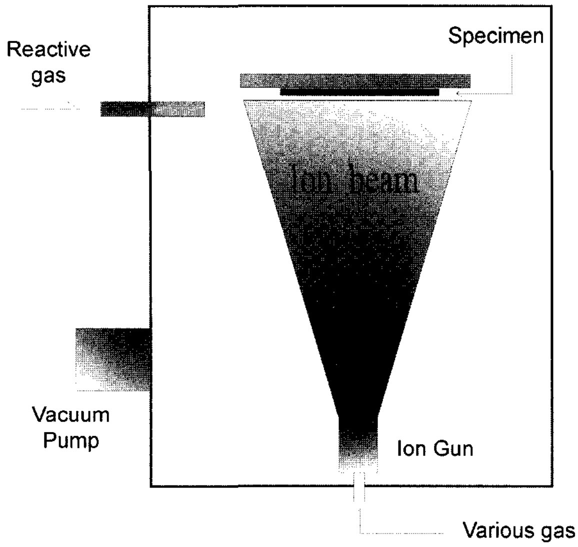

Fig. 1. Schematic view of IAR (Ion Assisted Reaction).

2. Experimental Procedure

Surface of PP fiber is treated by Ion Assisted Reaction (IAR) with ion dose quantities, in which ion beams were generated from cold hollow cathode type ion source of a 5-cm diameter attached in the chamber as shown in Fig. 1. The base pressure was 5×10^{-5} Torr and the working pressure was about 1.0×10^{-4} Torr during IAR treatment. Experimental apparatus was represented in detail on the previous studies.[8] Amounts of ions were controlled from 5×10^{14} to 1×10^{17} ions/cm^2. The flow rates of Ar for the ionized beam and oxygen gas as reactive gas were 4 and 8 sccm respectively. The contact angle of specimen surface was measured by contact anglometer (Cam Micro, Tantec). After measuring the two contact angles of water and formamide, surface energy, i.e. the sum of the polar force and the dispersion force, was calculated. When we used formamide and another polar liquid for calculating surface energy, the value of surface energy is the same and, therefore, there is no particular reason for only using formamide. From the measuring contact angles, the polar force and the dispersion force were calculated using the Owens method.[5] Owens method is used in each case for 2 different liquids. An average is taken of the surface tension values obtained. The interfacial tension of each phase can be broken down into a polar and a disperse component.

In order to measure the contact angle of modified PP surface, the sheet of PP were used the same materials as PP fiber. We measured the adhesion force between cement matrix and PP sheet by pull-off adhesion tester (hand-operated PosiTest). The tester measures the force required to pull a specified test diameter (10 mm) of cement matrix coating away from its sheets using hydraulic pressure.

Ordinary Portland Cement (OPC) and polymeric fibers and sheets were used in this study. Three fiber strings (diameter : 0.4 mm, length : 30 mm) were used for each test. Fiber was placed in the middle of cement matrix and the size ($40 \times 10 \times 20$) of steel mold was used for preparing rectangular shape of specimen. The volume fraction of three fibers in sample was 0.4%.

According to these processing, we prepared rectangular parallelepiped specimen for 3-point flexure test and flexural strength measurement.[9] In accordance with the change of strain we determined stress in 3-point flexure test. Loading speed maintained at 0.5 m/min during testing. After testing, we can obtain the strain versus stress curve and load. And we can calculate the values of flexural strength ($\sigma = 3PL/2d^2w$, where P : load, L : length, d : thickness, w : width) were averaged from 5 sample-testing results. Fracture energy was calculated as the area under the test curve between the starting point of the test and the break point.[6] By using of diamond cutter, the specimen was cut in longitudinal section for observing interfacial microstructure by means of Scanning Electron Microscopy (SEM).

3. Results and Discussion

Fig. 2 shows the change of contact angle for water on untreated and treated PP by IAR as a function of irradiating ion dose that is varied from 5×10^{14} ions/cm^2 to 1×10^{17} ions/cm^2. When compared with the contact angle of untreated PP, the contact angle of surface modified PP decreased rapidly and reached constant value as ion dose quantities increased. The value of contact angles shows difference with changing ion dose and this difference may be due to change of surface roughness by energetic ion irradiation.[8] The change of contact angle explains that some chemical reaction would be occurred on surface modified PP. The decrease of contact angle shown in Fig. 2 was due to the for-

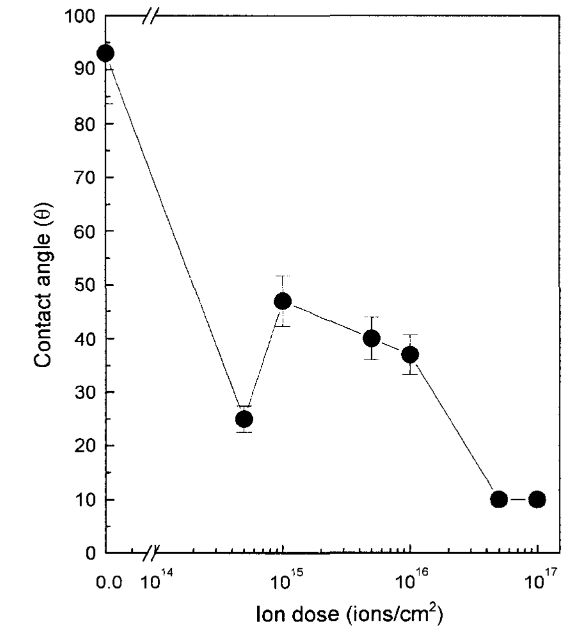

Fig. 2. Values of contact angle with water for PP treated at different ion doses.

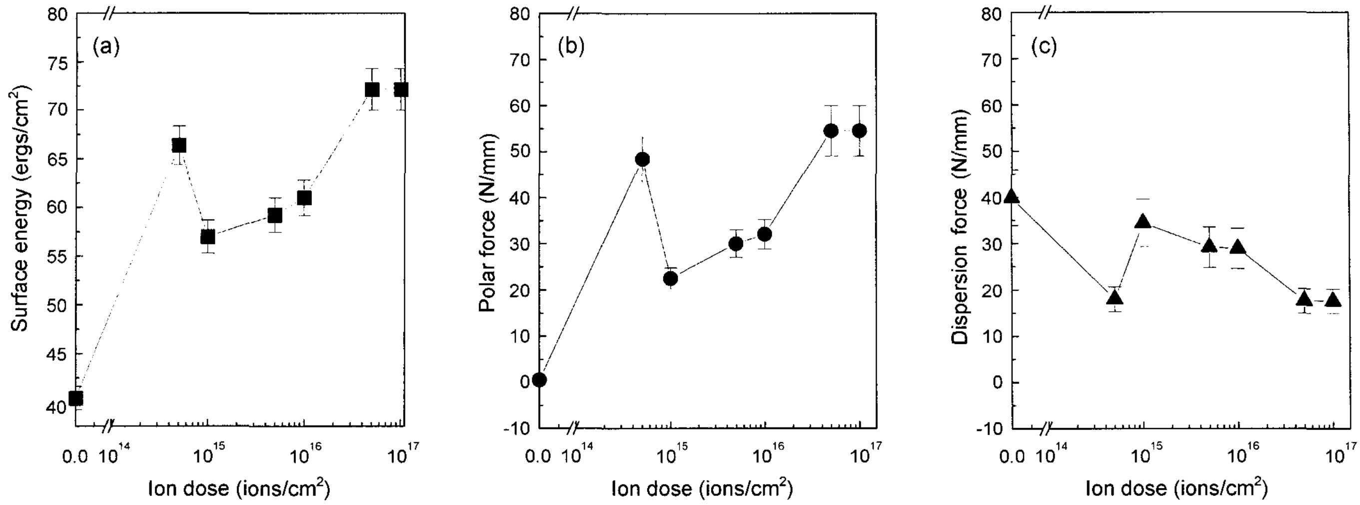

Fig. 3. Change of (a) surface energy, (b) polar force, and (c) dispersion for PP surface as a function of ion dose.

mation of hydrophilic groups by two-step reaction.[8]

Contact angles are closely related to surface energy. And we also measured the change of surface energy due to formation of hydrophilic groups by using two polar liquids, distilled water and formamide as shown in Fig. 3. The change of surface energy (a) was similar with that of polar force (b). It is well known that surface energy is closely related to the wettability and consists of dispersion (c) and polar force. IAR effectively increases the polar force of surface energy by dipole-dipole interaction of hydrogen bond between the newly hydrophilic group and water.[8] The large increase of surface energy can be explained directly by means of dominant increase of polar force of the surface energy that treated PP by IAR. And it is also expected that the adhesion force between cement matrix and modified PP fiber would be enhanced by the increase of surface energy.

In order to investigate the change of chemical state and hydrophilic formation on surface modified PP, XPS analysis performed. Fig. 4 shows the C 1s core level spectra of the untreated PP and the modified PP. Fig. 4(a) shows the C 1s peak of untreated PP in which C-C peak is only located at 284.6 eV. But, in the C 1s peak of modified PP (Fig. 4(b)), C-O and C = O peaks are located at 286.1 and 287.7 eV. Through XPS analysis, it is well supported that the increase of polar force on modified PP surface is due to the formation of new hydrophilic group, especially C = O bond by a chemical reaction of unstable chains and oxygen.[8]

Fig. 5 shows the O 1s core level spectra of the untreated PP and the modified PP. The peak of modified PP at 532 eV in Fig. 5(b) has been assigned to carbonyl group. On the other hand, the very small peak of untreated PP at 532 eV as shown in Fig. 5(a) appeared. This intensity increase of O 1s peak indicated that the creation of hydrophilic oxygen which should be generated by the reaction between the bombarded polymer chain and oxygen gas.[7]

Fig. 6(a) and (b) show microstructures of interface between cement matrix and PP fiber in FRC with modified PP and untreated PP. As shown in Fig. 6, particles would be

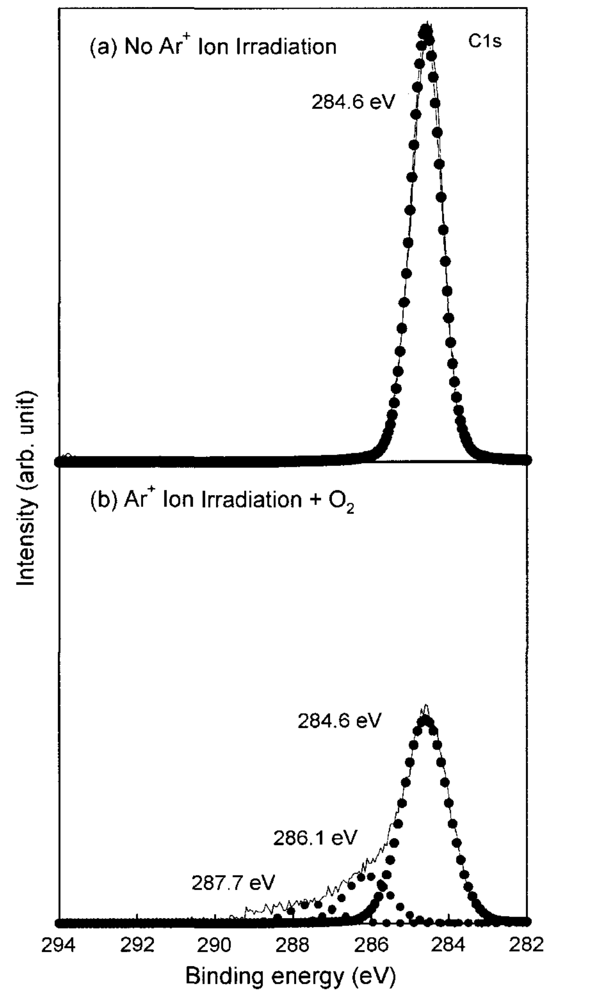

Fig. 4. Evolutions of C1s spectra of the PP surface : before (a) Ar^+ ion irradiation (solid line) and after (b) Ar^+ ion irradiation with O_2 (circle dotted line).

formed on the interface between cement matrix and PP modified. These particles might be considered to be hydra-

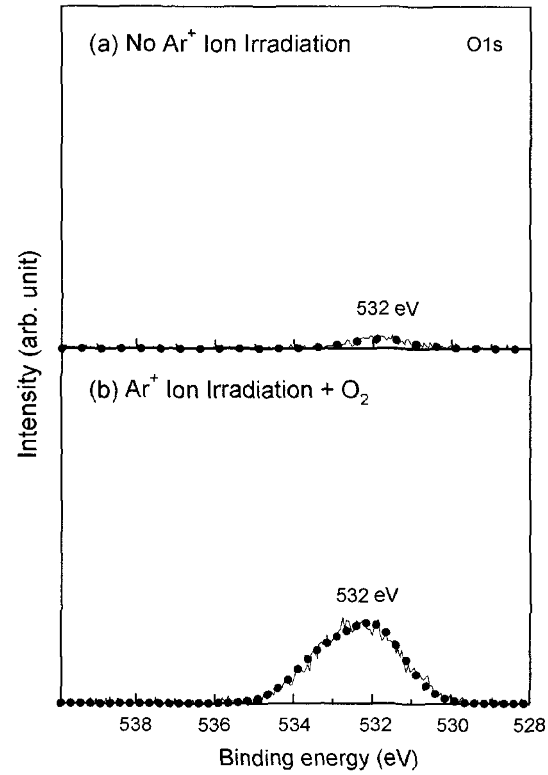

Fig. 5. Evolutions of O1s spectra of the PP surface : before (a) Ar^+ ion irradiation (solid line) and after (b) Ar^+ ion irradiation with O_2 (circle dotted line).

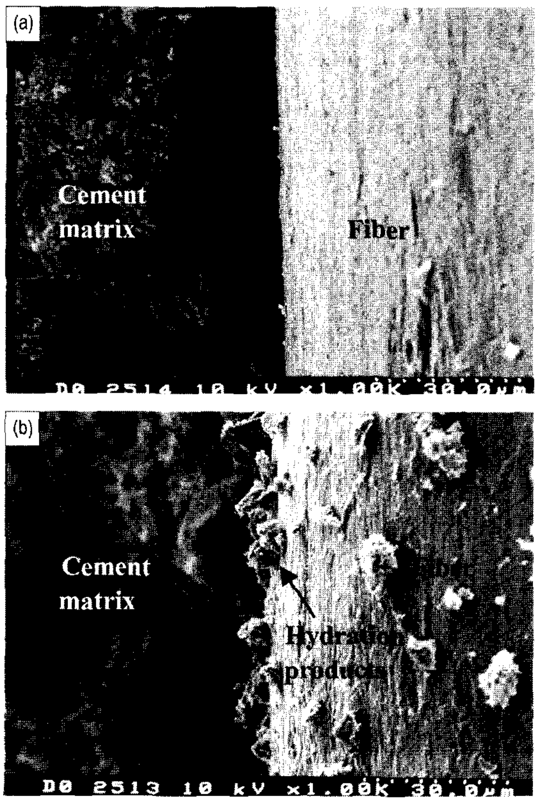

Fig. 6. SEM images of interface between cement and fiber of FRC with untreated PP (a) and modified PP (b).

Table 1. The Values of Adhesion Force between Cement Matrix and Untreated and Modified PP and the Flexural Strength and Fracture Energy of FRC with Untreated and PP Modified Fiber by IAR

	Adhesion force (N)	Flexural strength (N/m^2)	Fracture energy (J)
Untreated	0.025	78	175
Modified	0.25	115	350

tion products that would be known to consist of C-S-H ($CaO \cdot SiO_2 \cdot H_2O$), $Ca(OH)_2$.[13] These particles may be strongly attached to PP fiber treated by IAR due to interface bonding force improvement between hydration products in cement matrix and hydrophilic groups of modified PP fiber. However, in the case of untreated PP fiber, the particles of interface between cement matrix and untreated PP fiber was not found because of absence of hydrophilic groups to interact with hydration products in cement matrix. From these results, we confirmed the adhesion force improvement between cement matrix and modified PP fiber by microstructure analysis of SEM.

Table 1 shows the change percentage of adhesion force, flexural strength and fracture energy for FRC with untreated and modified PP. When compared with the adhesion force values of untreated PP, the adhesion force of modified PP increased from 0.025 to 0.25 N. These improvements of adhesion force directly related to the development of mechanical properties. Therefore, when compared with FRC using untreated PP, cement reinforced modified PP shows that the flexural strength and fracture energy were improved because of strong adhesion force between cement matrix and PP fiber treated by IAR. The reduction in crack propagation due to the increase in adhesion force could improve mechanical properties. The values of flexural strength and fracture energy of cement reinforced modified PP were about 2 times as those of FRC with untreated PP and rate increase of 70% from the flexural strength value which is reported by N. Segre *et al.*[6] The reasons for the difference between the value of adhesion force and flexural strength & fracture energy might be considered that another effect, for example micro pore and defect present in cement matrix, have influenced the mechanical properties of FRC. From these results, we confirmed improvement of bonding strength between cement matrix and PP fiber and expected that strain hardening will be developed.

Fig. 7 shows the strain-stress curve of cement reinforced by untreated and modified PP. For both samples, up to 10000 Pa, initial stress constantly increased as strain increased. However, the yield strength of FRC with modified PP fiber was 18095 Pa, which is very higher value than that of FRC with untreated PP fiber. After yield point, strain-hardening development, at which stress was constant despite strain increased, was shown in cement reinforced by modified PP. This phenomenon was related to the adhesion force between cement matrix and modified PP fiber to hinder crack propa-

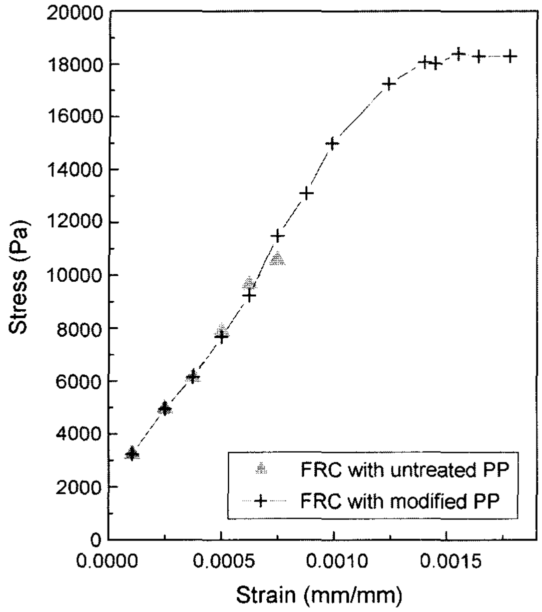

Fig. 7. Strain-stress curve of FRC with surface modified PP and untreated PP fiber.

gation. Fiber reduced the path of crack propagation.[10-12] Therefore, crack propagation route in FRC decided by interface bonding strength between cement and fiber.[13-15] Finally, modified PP fiber stopped crack from propagating in interface between modified PP and cement matrix because modified PP fiber could be fixed at cement matrix due to strong adhesion force between modified PP fiber and cement matrix. Althoug the strain that applied to FRC with modified PP fiber increased, the final fracture of FRC by breaking of modified PP fiber in cement matrix was not happened.

4. Conclusions

IAR treatment of PP fiber improved the mechanical properties of fiber-reinforced cement with PP treated by IAR. Enhancement of mechanical performance of fiber-reinforced cement by IAR treatment can be attributed to the strong bonding force between cement and modified PP fiber. This result related to the surface change of PP fiber modified by IAR. This treatment converted from hydrophobic nature of the PP fiber surface to hydrophilic. And this change of surface property was confirmed by variations of contact angle, surface energy, and XPS analysis of PP fiber treated by IA.

REFERENCES

1. J. R. Brown, P. J. C. Chappell, and Z. Mathys, "Plasma Surface Modification of Advanced Organic Fibers," *J. Mater. Sci.*, **27** 3167-73 (1996).
2. A. E. Naaman and J. R. Homrich, "Tensile Stress Properties of Sifcon," *ACI Mater. J.*, **86** [3] 244-51 (1989).
3. Z. F. Li, A. N. Natravali, and W. Sachse, "Ammonia Plasma Treatment of Ultra High Strength Polyethylene Fibers for Improved Adhesion to Epoxy Resin," *J. Mater. Sci.*, **27** 4625-36 (1992).
4. C. Zhang, V. S. Gopalaratnam, and H. K. Yasuda, "Plasma Treatment of Polymeric Fibers for Improved Performance in Cement Matrices," *J. Appl. Polym. Sci.*, **76** 1985-92 (2000).
5. D. K. Owens and R. C. Wendt, "Estimation of the Surface Free Energy of Polymers," *J. Appl. Polym. Sci.*, **13** 1741-52 (1969).
6. N. Segre, E. Tonella, and I. Joekes, "Evaluation of the Stability of Polypropylene Fibers in Environments Aggressive to Cement-Based Materials," *Cem. Conc. Res.*, **28** 75-87 (1998).
7. S. C. Choi, S. Han, W. K. Choi, H.-J. Jung, and S. K. Koh, "Hydrophilic Group Formation on Hydrocarbon Polypropylene and Polystyrene by Ion Assisted Reaction in an O_2 Environment," *Nucl. Instr. and Meth. B.*, **152** 291-301 (1999).
8. J. S. Cho, Y.-W. Beag, S. Han, K.-H. Kim, J. Cho, S.-K. Koh, "Hydrophilic Surface Formation on Materials and Its Application," *Surf. and Coat. Tech.*, **128-129** 66-70 (2000).
9. Standard Test Method for Flexural Strength of Hydraulic Cement Mortars ASTM C 348 95.
10. D. B. Marshall, B. N. Cox, and A. G. Evans, "The Mechanics of Matrix Cracking in Brittle-Matrix Fiber Composites," *Acta Metall.*, **33** [11] 2013-20 (1985).
11. M. A. Sanjuan and A. Moragues, "Polypropylene-Fiber-Reinforced Mortar Mixes : Optimization to Control Plastic Shrinkage," *Com. Sci. & Tech.*, **57** 655-62 (1996).
12. D. J. Hannant, "Fiber Reinforcement in the Cement and Concrete Industry," *Mater. Sci. & Tech.*, **11** 853-61 (1995).
13. A. Bentur and M. D. Cohen, "The Microstructure of the Steel Fiber-Cement Interface," *J. Mater. Sci.*, **20** 3610-20 (1985).
14. Y. W. Chan, "Fiber/Cement Bond Property Modification in Relation to Interfacial Microstructure"; Ph. D. Thesis Department of Civil and Environmental Engineering, The University of Michigan, Ann Arbor, MI, 1994.
15. D. N. Hild and P. Schwartz, "Plasma Treated Ultra-High Strength Polyethylene Fibers. Part II : Mechanical Properties of PMMA Composites," *J. Adhes. Sci. Tech.*, **6** 897-921 (1992).