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Multiple cracking response of plasma treated polyethylene fiber reinforced cementitious composites under flexural loading

Kamile Tosun *, Burak Felekoğlu [1], Bülent Baradan [2]

Department of Civil Engineering, Dokuz Eylul University, İzmir, Turkey

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ABSTRACT

The effects of low frequency cold plasma treatments on the microstructure and chemistry of Polyethylene (PE) have been investigated. PE plates and fibers were exposed to plasmas of argon and oxygen gases. The surface wettabilities of plasma-treated plates were monitored. Possible physical changes on fiber surfaces were observed by a scanning electron microscope (SEM) at micrometer scale and by an atomic force microscope (AFM) at nanometer scale after this process. The effects of plasma treatment on surface chemistry of PE fibers have been analyzed by using an X-ray photoemission spectroscope (XPS). The fibers modified by plasma treatments were used in prismatic cementitious composites. The flexural performance of samples were characterized at two different ages (28 days and 8 months). Results showed that plasma treatment caused significant modifications on fibers' surface structure and composites' performance. Proper plasma treatment conditions significantly leads to improvement of multiple cracking behavior of fiber reinforced composites.

1. Introduction

Fiber reinforcement is a preferred way of improving the toughness and reducing the cracking susceptibility of cementitious composites [1,2]. High-strength polyvinyl alcohol (PVA) and polyethylene (PE) fibers can be accepted as favorable examples of polymeric fibers for fiber reinforced composite (FRC) production. Among these fibers, PE fibers can be produced with variable densities and called as high density polyethylene (HDPE), ultra high molecular weight polyethylene (UHMWPE) depending on fibers' manufacturing procedure and polymerization degree [3].

Commercial examples of ultrahigh molecular weight polyethylene (Spectra®, Dyneema®) fibers have been previously produced with excellent tensile and shear strength properties and intensively being used in special applications like weapon armors, high strength ropes, etc. These fibers were recently employed in FRC applications, and found significantly effective in terms of toughness improvement. It was also reported that incorporation of PE fibers at dosages in the order of 1–1.5% by volume resulted with composites presenting multiple cracking behavior [4–6]. Furthermore, significant strength and toughness improvements were recently reported when PE fibers used in hybrid fiber applications with steel fibers [7–9]. Despite their high-performance in cementitious composites, the activated capacity of high-strength PE fibers limited due to their surface structure. These polyolefin group fibers have smooth and hydrophobic surface that may be susceptible to slipping when used as reinforcement in cementitious composites. Their potential can be further improved and activated if the surface structure of PE fibers properly changed and optimized by means of chemical bonding and mechanical interlocking capacity.

Cold plasma treatment can be a suitable pre-processing method to modify the surface properties of PE fibers without causing any significant change in their bulk properties [10–12]. Unlike other wet chemical etching methods, cold plasma treatment is an environmentally friendly alternative for polymer surface modification purposes. While the selection of plasma composition brings the controlled application of treatment, if appropriate gas composition is selected, no problematic waste will be disposed to nature after the treatment. A comprehensive literature survey on the comparison of cold plasma treatment of polymers can be found in Morent et al. [13]. The main changes on polymer surface by the application of cold plasma treatment can be listed as plasma deposition or polymerization, surface energy change due to additional bonding or bond breaking and physical etching [13,14]. All these modifications can be observed instantaneously. The resultant effect depends on the competition between etching and redeposition rate. If etching is more significant than redeposition, the resultant situation called plasma etching. If redeposition is dominant, plasma polymerization takes place [14–16]. While the former is usually observed in gas plasmas, the latter can be seen mostly in case of monomer plasma applications. In this study, gas plasma treatments have been implemented and the dominant

* Corresponding author. Tel.: +90 232 4127059.
E-mail addresses: kamile.tosun@deu.edu.tr (K. Tosun), burak.felekoglu@deu.edu.tr (B. Felekoğlu), bulent.baradan@deu.edu.tr (B. Baradan).
[1] Tel.: +90 232 4127041.
[2] Tel.: +90 232 4127011.

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Table 1
Composite mixture proportions.

Cement (kg/m^3)	Water (kg/m^3)	Limestone powder (kg/m^3)	Superplasticizer (by weight of cement %)	PE fibers (by total volume %)
854	380	854	1	1

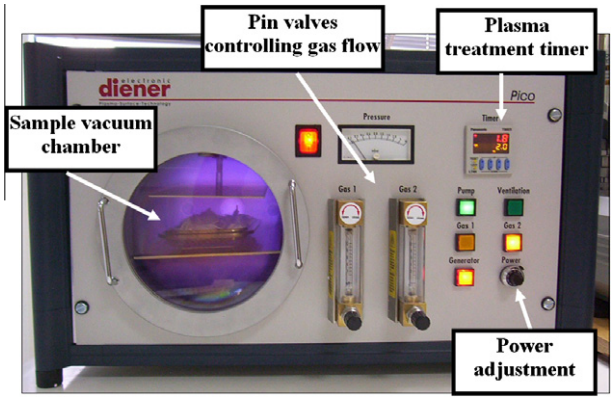


Fig. 1. Low frequency (LF: 40 kHz) plasma generator (0–200 W).

Table 2
Plasma conditions of fibers used in composite preparations.

Argon plasma	Oxygen plasma
Untreated (PE00–0)	
60 W, 8 min (PE60-A8)	60 W, 8 min (PE60-O8)
120 W, 2 min (PE120-A2)	120 W, 2 min (PE120-O2)
180 W, 2 min (PE180-A2)	180 W, 2 min (PE180-O2)
180 W, 30 min (PE180-A30)	180 W, 30 min (PE180-O30)

modification on the surfaces may be related to etching rather than redeposition.

The effects of low frequency cold plasma treatments on the microstructure and chemistry of Polyethylene (PE) surfaces have been investigated in the first stage of this study. PE plates and fibers were exposed to plasmas of argon and oxygen gases at different power levels and periods. The surface wettabilities of plates were monitored by means of static contact angle measurements. Possible physical changes on fiber surfaces were observed by a scanning electron microscope (SEM) at micrometer scale and by an atomic force microscope (AFM) at nanometer scale after this process. The effects of plasma treatment on surface chemistry of PE fibers have been analyzed a X-ray photoemission spectroscope (XPS). In the second stage, tests have been carried on four selected plasma conditions (60 W, 8 min – 120 W, 2 min – 180 W, 2 min and 180 W, 30 min argon and oxygen plasma) based on different surface modification degrees. The fibers modified by different plasma treatments were used in $40 \times 40 \times 160$ mm prismatic cementitious composites (notched and unnotched). The flexural performance of FRCs was characterized based on first cracking and flexural strength values, and toughness properties at two different ages (28 days and 8 months). A total of 108 prismatic samples (four series, 27 for each set) were tested.

2. Experimental studies

2.1. Materials and composite mixture proportions

Ultrahigh molecular weight PE fibers with a density of 0.97 g/cm^3 and elongation capacity of 3.8% were chosen for the production of FRC. The diameters of these fibers were within the region of 18–20 μm. They were the products of a hot (145 °C) stretching method. This method permits the alignment of more than 95% of polymer chain molecules along the fiber length. The crystallinity of PE fibers increases up to 85% by the application of special

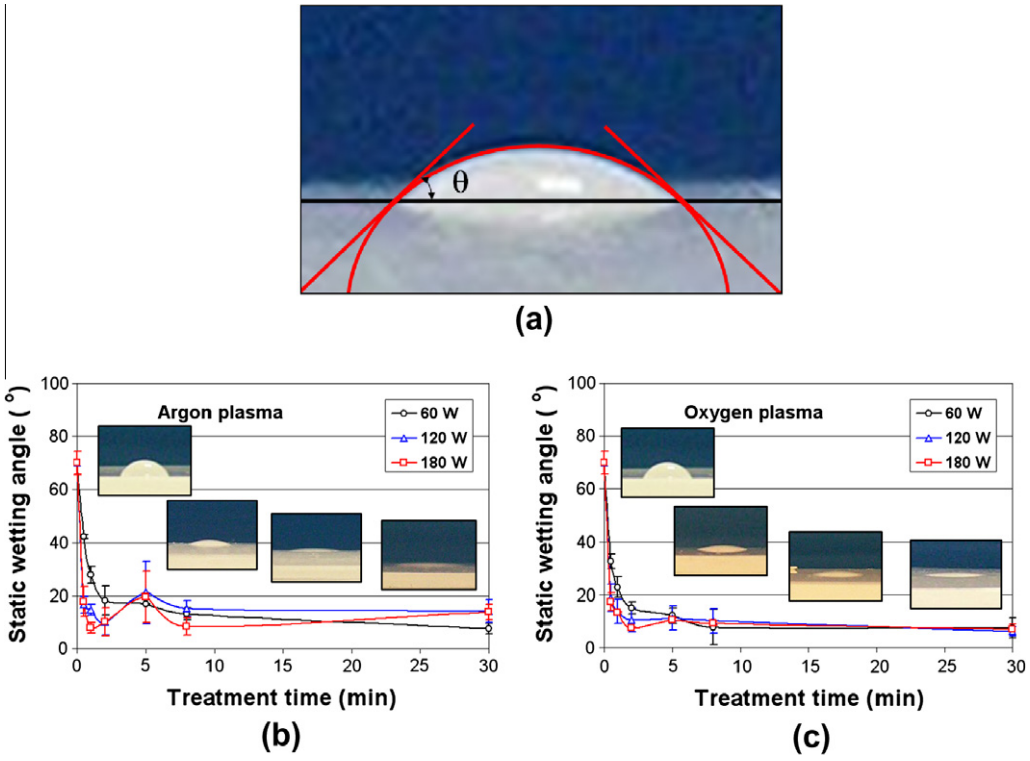


Fig. 2. Method of wetting angle measurement (a), wetting angle-treatment time relationships of PE plates after argon (b) and oxygen (c) plasma treatments.

mechanical alignment and heat treatment methods. Parallel to the improvement of crystal structure, mechanical and elastic properties of fiber also increases [16]. Modulus of elasticity and tensile strength of PE fibers procured from manufacturer were 107 GPa and 3400 MPa, respectively. The ultrahigh mechanical properties of these fibers may be attributed to the alignment process explained above.

Matrix ingredients were composed of CEM I 42.5R type cement, limestone powder, water and a polycarboxylate based superplasticizer. Maximum particle size of the matrix was limited to 100 μm in order to maintain homogeneous dispersion of the fibers. In a previous study where the same mixture ingredients employed, matrix mixture proportions and fiber dosage were optimized considering workability, fiber dispersion homogeneity and surface finishing [17]. The selected matrix mixture proportions are presented in Table 1.

2.2. Plasma treatment methodology

In order to modify surface morphology and convert the hydrophobic structure of PE surfaces to hydrophilic, argon and oxygen gas plasmas have been chosen. A low frequency (LF: 40 kHz) plasma generator with adjustable power (P = 0–200 W) and exposure time have been used for this purpose (Fig. 1). Recent studies showed that plasmas of argon and oxygen were capable of increasing the surface energy and roughness of polymers [15,18]. The same plasma treatment has been employed at 60, 120 and 180 W of power with 2–30 min of exposure periods [19]. At the end of plasma process, vacuum chamber was ventilated by argon gas in order to stabilize the free radicals formed on the surface of treated samples [20]. Some of the plasma conditions were selected for further testing based on wettability results. The selected plasma combinations considering different surface modification degrees are listed in Table 2.

2.3. Surface characterization of fibers

The effects of plasma treatment on microstructure and chemistry of PE surfaces were investigated by using four different analyses techniques. The surface wettabilities of plates were monitored by means of static contact angle measurements. At the same time possible physical changes on fiber surfaces were observed by SEM at micrometer scale and by AFM at nanometer scale. The effects of plasma treatment on surface chemistry and molecular bond structure have also been monitored by XPS analysis.

2.3.1. Static wetting angle measurements

In order to characterize the changes in the surface structure of PE due to plasma treatment, static wetting angle measurements have been conducted on PE plate surfaces. Deionised water of 5 μl was dropped on the surface of PE plates. The static wetting angle between PE surface and water drop was measured with a 0.1° accuracy. At least three measurements have been performed for each case. Photos of each dropping after 5 s have been taken with a high resolution camera and contact angles have been measured according to ASTM D724 [21]. A sample image used in contact angle measurement is presented in Fig. 2a.

2.3.2. SEM observations

Surface morphologies of the untreated and treated PE fibers were observed by a JEOL JSM 40 model scanning electron microscope (SEM) operating with an accelerating voltage of 5 kV. Prior to SEM analysis, the fibers were affixed to a standard sample stub by double-sided carbon conductive tape. A thin film of Au was sputtered over all samples by a plasma coater prior to imaging to prevent surface charging.

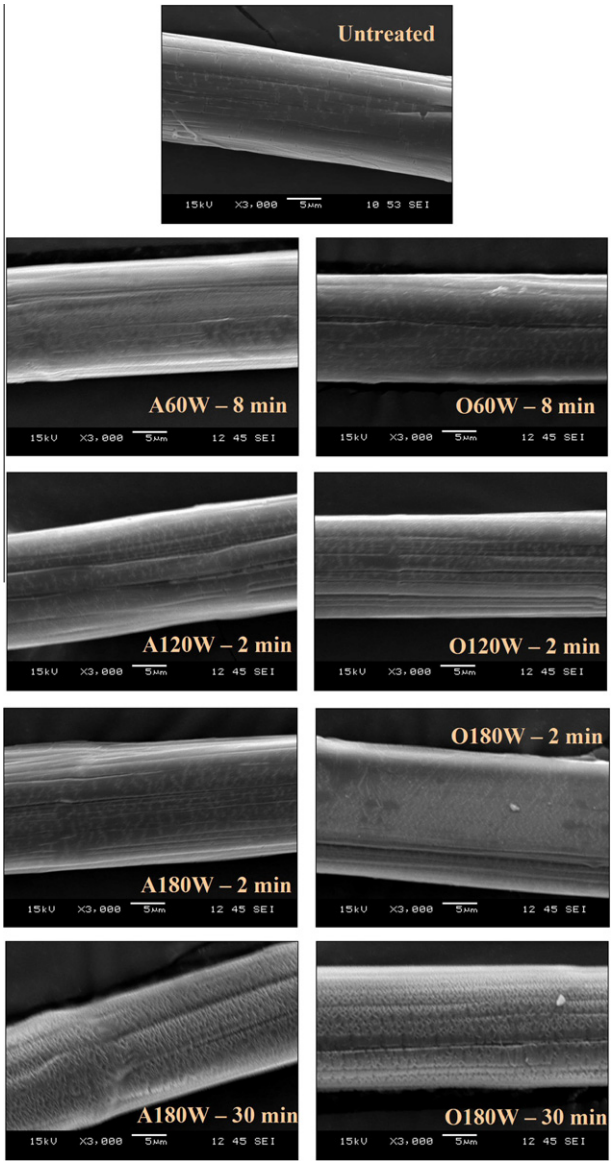


Fig. 3. Effect of plasma treatment on surface morphology of fibers (SEM images at 3000× magnification).

2.3.3. Nanostructure characterization by AFM and roughness analysis

Physical condition of PE fiber surfaces were investigated by using a Digital Instruments Nanoscope-IV AFM at scanning probe mode. Scanning probe microscopy has enabled to image surfaces at the nanometer scale. The 3D visualization of PE fiber surfaces has been obtained and surface nano-roughness Rms (Root-mean-square) values have been calculated by using Nanoscope 5.30r1 software [22]. At least three random points of untreated and treated fibers with a 5 μm square area were scanned.

2.3.4. XPS analysis

The variations on the top-surface (1–10 nm depth according to [23,24]) atomic elemental composition and bonding structure due to plasma exposure have been investigated by using X-ray photoelectron spectroscopy (XPS). Experiments were carried out on a ESCA system (SPECS) with Mg–K radiation. Fibers were initially pressed to a self-adhesive surface before transferring into the analyzer chamber. The whole spectra (1200 eV at 0.60 eV resolutions) and the narrow spectra of C1s (280–290 eV at 0.10 eV resolutions) were both recorded. The C1s envelope has been analyzed and

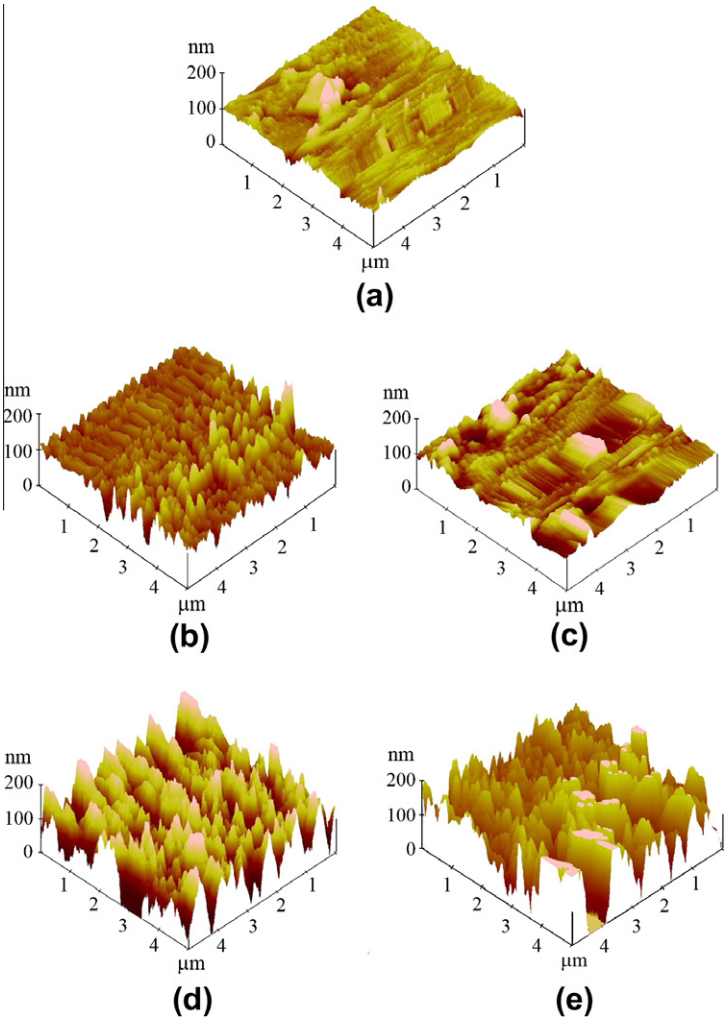


Fig. 4. 3D visualization of fiber surfaces at nanometric scale; (a) PE00-0, (b)PE60-A8, (c) PE60-O8, (d) PE180-A30, (e) PE180-O30.

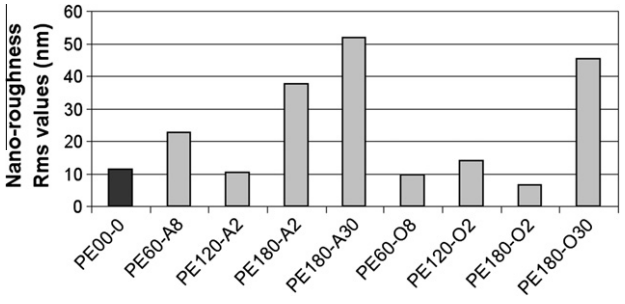


Fig. 5. The Rms nano-roughness values determined from AFM images.

peak-fitted after subtraction of a Shirley background using a Gaussian–Lorenzian peak shapes obtained from the XPS-Peak41 software.

2.4. Composite preparation and flexural strength tests

Prismatic samples of 40 × 40 × 160 mm were prepared with control (non-treated) and plasma treated fiber reinforced matrices. Matrix mixture proportions and fiber dosage were kept constant for all composites. Samples were demolded 1 day after preparation and cured in lime-saturated water at 20 °C prior to testing period. After 28 days and 8 months of curing, prismatic samples were left to drying for 1 day and subjected to center-point flexural loading test according to ASTM C348 with a more sophisticated deflection controlled loading mode [25]. Center-point loading test was performed with a close loop deflection controlled. The span was 130 mm and mid-span deflection rate was kept constant for all samples (0.2 mm/min). Mid-span deflection up to 4.5 mm was measured by using an encoder. Six samples have been prepared for each mix at each testing age. Three of them were tested as of their original form and three of the samples were notched. The notch dimensions were 2 mm deep and 1 mm width. The aim of notching was to initiate the cracking exactly from the center of the span. Load–deflection curves of each unnotched and notched sample were drawn. The first cracking strength and deflection, flexural strength and deflection values at maximum load have been determined by using load–deflection curves. The first cracking load and maximum load points on the average of three deflection curves for each condition were used in the calculations. Determination methodology of first cracking load and deflection can be found in [17]. Flexural toughness values for 1.3 mm deflection (span/100) were also calculated from the area under these curves.

3. Results and discussion

3.1. Wetting angle results

Wetting angle degrees of PE plates exposed to argon and oxygen gas plasmas at variable powers (60–120 and 180 W) and exposure

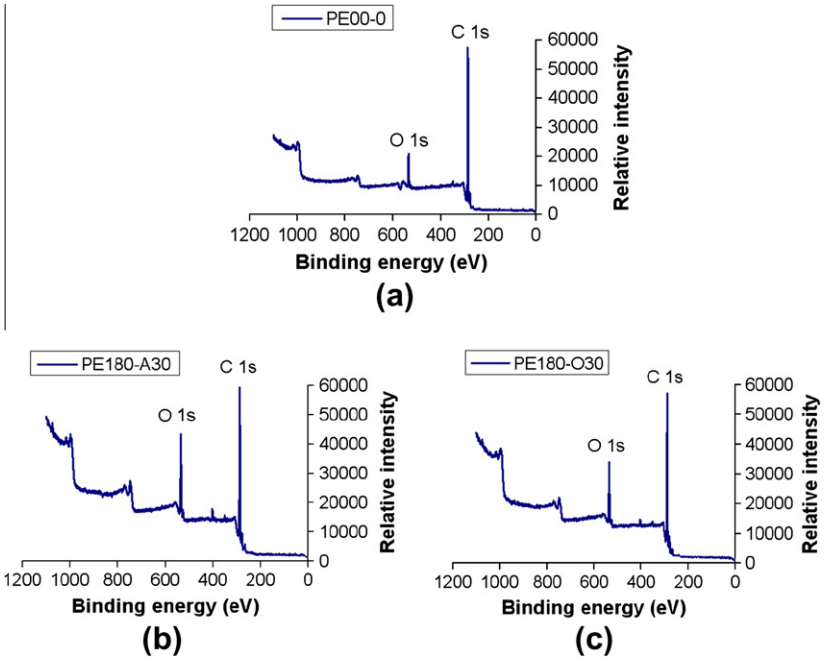


Fig. 6. XPS spectra of untreated (a), 180 W 30 min argon plasma treated (b) and 180 W 30 min oxygen plasma treated (c) fibers.

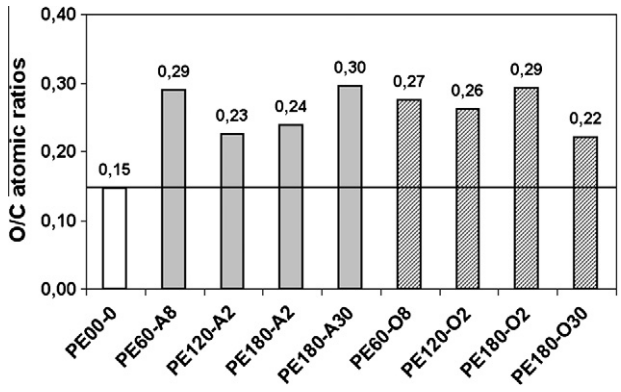


Fig. 7. Effect of plasma treatment on the O/C atomic ratios of fiber surfaces.

times have been presented in Fig. 2b and c. The images on the graphs were taken from the plates exposed to 0, 5, 8 and 30 min of plasma treatment at 60 W, respectively. Both plasma gases significantly decreased the static wetting angle values. Parallel to plasma exposure time increase the wetting angle values balanced an equilibrium degree. The wetting angles on the plates exposed to oxygen plasma decreased down to 6.1–7.3° from 69.9° during 30 min exposure period. On the other hand, argon plasma exposure decreased the wetting angle values to 7.6–14.1° at the same exposure period. Results showed that, oxygen plasma is slightly more effective in terms of wetting angle reduction. The effectiveness of oxygen plasma treatment on improving contact angle between polyethylene surfaces and water was previously reported by [26,27].

3.2. SEM investigations

The effect of plasma treatment on the surface morphology of PE fibers can be observed on SEM images captured at 3000× magnification (Fig. 3). As the plasma power and exposure time increase white staining started to form on the surface of samples. These formations can be accepted as an evidence of physical pitting and deterioration of the surface. Argon plasma was found more effective in terms of physical surface modification compared to oxygen plasma treatment in case of short plasma treatment times. The untreated (control) specimen was relatively smooth compared to most of the plasma treated samples. Additionally, longer exposure times increased the intensity of white staining on the surface. It should be noted that, in the case of long plasma exposure periods, excessive surface roughness may cause susceptibility against tearing when fibers are subjected to tensile forces.

3.3. AFM analysis and surface roughness results

In order to visualize the nano-roughness differences, vertical scale was adjusted to measure ±100 nm of depth (Fig. 4). The nano-roughness of plasma treated PE fiber surfaces was generally greater than control fibers. Visual investigations indicated that, the effect of plasma exposure conditions on nano-surface morphology is distinctive. Parallel to power and exposure time increase, the nano-roughness values were improved at nanometric-scale. Intrater et al. [28] reported similar findings for oxygen and Švorčík et al. [29] for argon plasma treatment in the case of PE surfaces.

The average Rms nano-roughness values of fibers are presented in Fig. 5. The Rms value of untreated PE fibers was 11.4 nm. In the case of argon plasma treatment, the nano-roughness values started to increase with the increasing plasma power and exposure time. The Rms values increased up to 51.8 nm at 180 W, 30 min of argon plasma application. The effect of oxygen plasma treatment on surface nano-roughness was relatively ineffective at short plasma exposure times. However, in case of 180 W, 30 min of oxygen plasma application significantly improved the nano-roughness of PE fibers (Rms = 45.3 nm). It can be said that, argon plasma is more effective compared to oxygen plasma treatment at nanometer scale. Longer plasma exposure periods are necessary to produce required nano-roughness values for oxygen plasma treatments.

3.4. XPS analysis and surface chemistry variations by plasma treatment

XPS analysis results have been evaluated by using complete (general spectra) and partial scan (resolved spectra) results

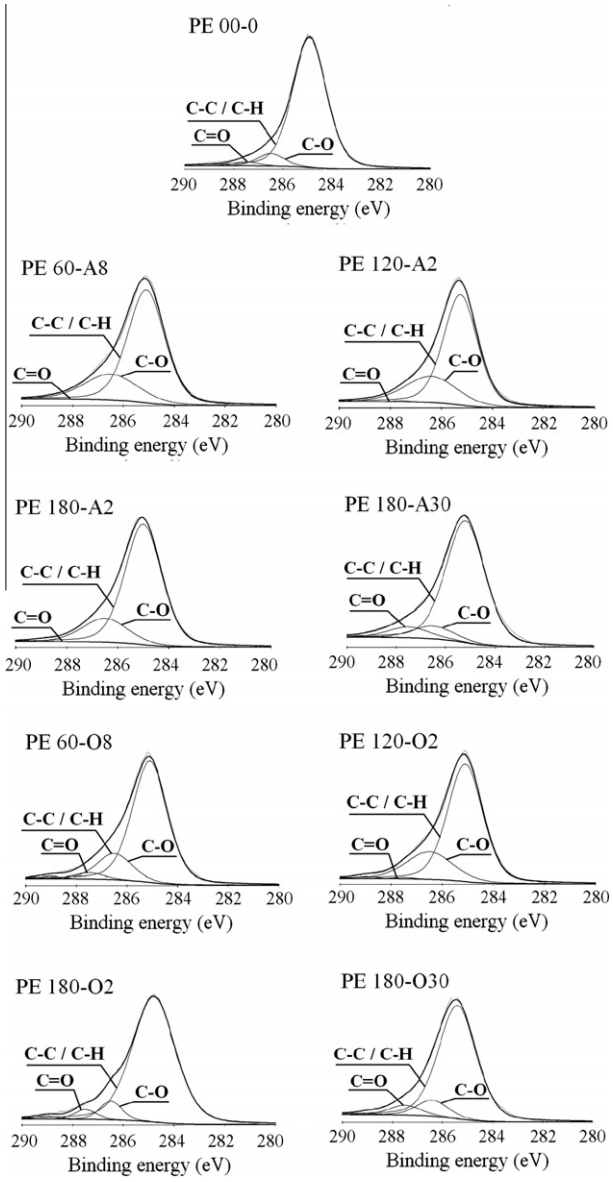


Fig. 8. High-resolution XPS spectra of C1s peaks of untreated and plasma treated fibers.

separately. The general spectra of untreated and treated fibers have been presented in Fig. 6. Note that, spectra of the highest plasma power and exposure time are given for comparison. There are two obvious peaks, the peak at 531.6 eV corresponding to O1s and the peak at 285 eV corresponding to C1s. It is clear that, the height of these peaks were modified by plasma treatment. The O/C atomic ratios of fibers presented in Fig. 7 also indicate a change in the atomic structure on the surface of plasma treated fibers. The O/C ratios increased from 0.15 to 0.22–0.30 by plasma treatment.

The atomic ratio variations may give an idea about the role of plasma treatment on surface modification. However, the formation of any new functional groups on the polymer surface can only be characterized by using partial scan results. High-resolution partial XPS analyses of C1s peaks (Fig. 6) have been applied in order to investigate the principal functional group formations over PE surfaces by plasma treatment. The resolved C1s spectrums at binding energy levels of 280–290 eV are shown in Fig. 8. The concentration of each chemical component with C1s has been calculated by deconvolution. The peak position intervals and types of functional groups proposed by [30–34] were used for this purpose (Table 3). The C—C/C—H percentage on the surface of fibers decreased from 90.7% to 72.9% by the application of 120 W argon plasma for 2 min. At the same time, the C—O percentage increased from 7.1% to 26.5% (Table 3). The results indicate that, plasma treatment cleave the C—C/C—H bonds and incorporate oxygen-containing functional groups into the molecular chain of PE surfaces. Similar results were recently reported by [34] for PP surfaces. The types and contents of oxygen-containing groups are different in different plasma treatment conditions. As the plasma power increases, higher amounts of high energy oxidized functional groups (C═O, O═C—O) are introduced on PE fiber surfaces. Deconvoluted peaks and peak area percentages are presented in Fig. 8. Table 3 shows that plasma treatment decreases the ratio of C—C/C—H groups and increases the oxidized functional group (C—O, C—O(H), C═O, O═C—O. . .) ratios at the same time.

It should be noted that in case of argon plasma treatment, oxidized functional groups may form over the PE fiber surfaces [23]. Theoretically, oxygen content is expected to be very low. Residual chamber contaminations may escape from the material surfaces in the chamber and can react with the polymer during the plasma treatment even in the case of argon gas [29,35].

3.5. Flexural performance of fiber reinforced unnotched and notched composites at 28 days

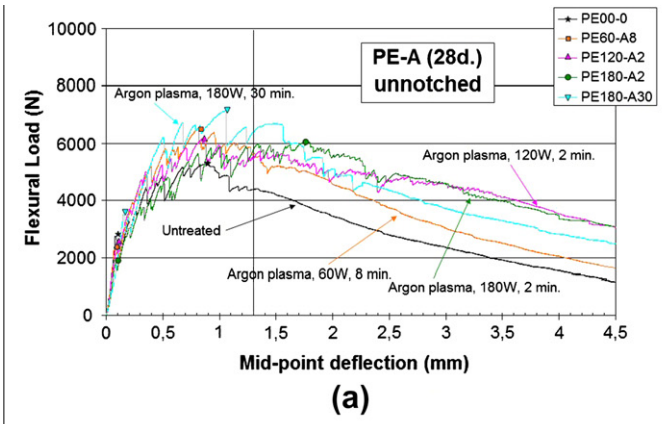
The load–deflection curves of unnotched and notched PE fiber reinforced composites tested at 28 days are presented in Figs. 9 and 10, respectively. For each plasma condition, first crack and maximum load values are marked on the curves. Additionally, first cracking and flexural strength, deflection values at these strength and toughness values of samples have been calculated and listed in Table 4. The samples photographed in Figs. 9 and 10 were loaded up to the mid-point deflection of 4.5 mm. After this deflection value the load has been removed.

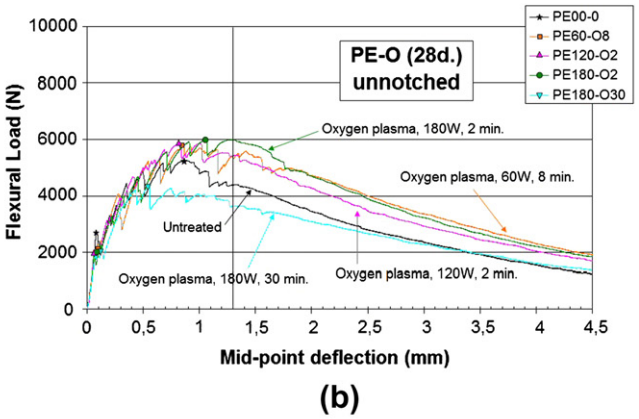
The effect of argon plasma treatment on the load–deflection performances of unnotched composites at 28 days is shown in Fig. 9a. As a general tendency, increasing plasma power and exposure time shifted the load deflection curves upwards. Argon plasma treatment increased the flexural strength and toughness values. Improvements were in the range of 15–35% and 4–27%, respectively. The best performance was obtained from 30 min of argon plasma treatment at 180 W (Table 4). All unnotched composites exhibited multiple cracking behavior regardless of the type of plasma treatment. However, there was a significant increase in the number of visible cracks around the mid-point by plasma treatment. While the unnotched control sample exhibited 5–6 visible cracks, the number of cracks were in the range of 15–20 when argon plasma treated PE fibers were used (Fig. 9c). As can be seen from the tail of load–deflection curves (4.5 mm mid-point deflection at the end of test procedure), the load carrying capacity of the composites at high deflection values was also improved by argon plasma treatment (Fig. 9a). The increase in the density of visible cracks and improvement in the load carrying capacity of fibers after cracking indicated that there is a fiber–matrix interaction enhancement by plasma treatment. Mechanical interlocking improvement between the matrix and argon plasma treated fibers improved the load bridging and distributing capacity of PE fibers [36,37].

The load deflection curves of samples prepared by using oxygen plasma treated fibers at 28 days are presented in Fig. 9b. At this testing age oxygen plasma treatment was found less effective compared to argon plasma treatment in terms of flexural performance improvement. The highest power and treatment time combination (180 W, 30 min) reduced the performance of unnotched composites and the load–deflection curve shifted downwards compared

Table 3
The binding energy peak point interval and percent peak area of XPS C1s core level spectra of plasma treated PE fibers.

Peak number	Peak point binding energy interval (eV)	Possible groups	Untreated PE	PE60-A8	PE120-A2	PE180-A2	PE180-A30	PE60-O8	PE120-O2	PE180-O2	PE180-O30
C_0	284.8–285.2	C—C/C—H	**90.7**	74.7	72.9	79.7	82.2	78.5	75.2	88.5	83.2
C_1	286.3–286.7	C—O or C—O(H) (hydroxyl groups)	7.1	25.3	**26.5**	19.8	9.4	16.9	23.4	6.7	9.9
C_2	287.5–288.0	C=O or O—C—O (carbonyl groups)	2.2	0.0	0.5	0.0	**7.9**	3.6	0.6	3.5	6.1
C_3	289.0–289.4	O=C—O(H) or O=C—O—C	0.0	0.0	0.1	0.5	0.5	1.0	0.8	**1.2**	0.9





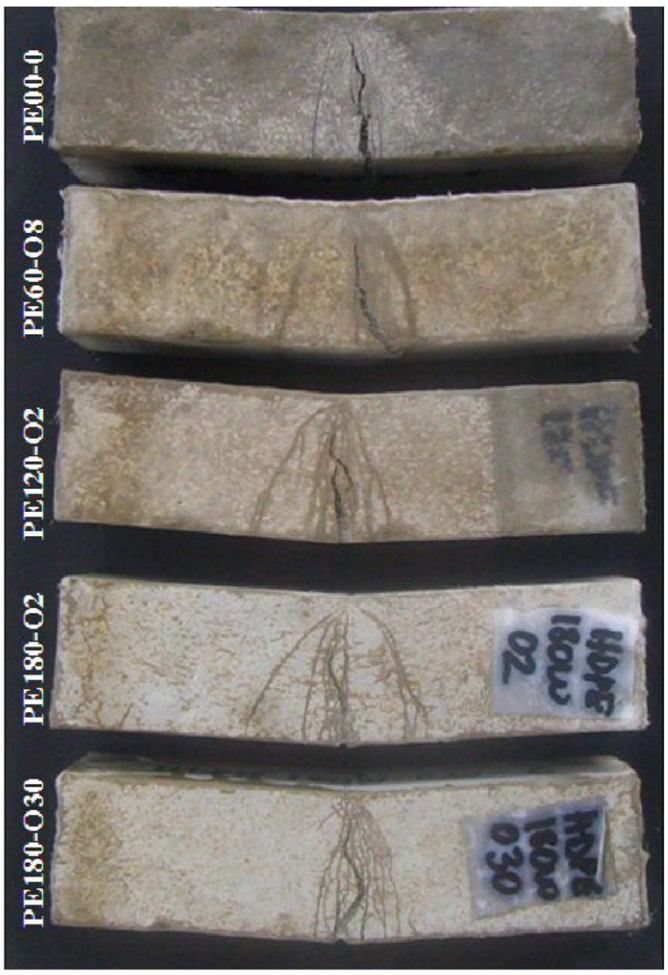


Fig. 9. The load–deflection curves and photographs of PE fiber reinforced unnotched composites at 28 days: (a and c) incorporating argon plasma treated fibers, (b and d) incorporating oxygen plasma treated fibers.

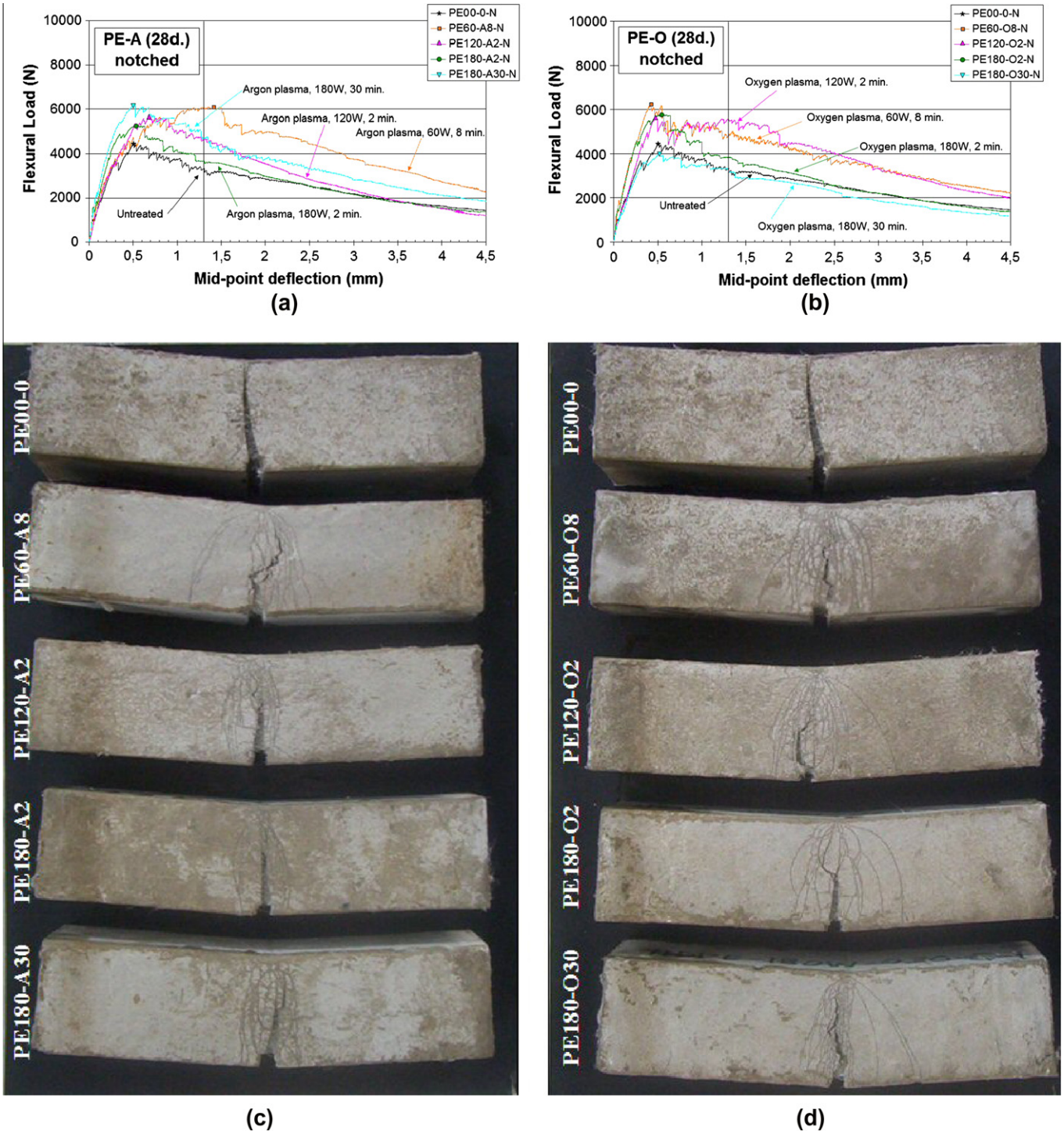


Fig. 10. The load–deflection curves and photographs of PE fiber reinforced notched composites at 28 days: (a and c) incorporating argon plasma treated fibers, (b and d) incorporating oxygen plasma treated fibers.

to composites prepared with the control fibers. However, composites including PE fibers subjected to shorter oxygen plasma exposure periods exhibited better performance. The numbers of visible cracks in the case of oxygen plasma treatment were also comparatively lower than argon plasma treated samples (Fig. 9d). From these results it can be concluded that, excessive oxygen plasma treatment may cause adhesion problems for PE fibers.

It should be noted that there is always performance variability from the view point of adhesion behavior of polymeric fiber reinforced cementitious composites due to the heterogeneous nature of matrix phase. A large range of behaviors can be observed even at the single pull-out tests [38]. For this reason it is hard to differentiate the effect of any slight fiber modification on mechanical performance of composites. However, if the magnitude of modification is significant enough, there may be a performance enhancement or reduction as observed in this study.

The load deflection curves of notched composites tested at 28 days are presented in Fig. 10a showed that argon plasma treatment improved flexural performance of the composites despite the formation of a notch at the center. The flexural strength values of

Table 4
The 28 days flexural test results of unnotched and notched samples.

PE 28 days	Unnotched samples					Notched samples		
	First cracking strength (MPa)	Deflection at first cracking load (mm)	Flexural strength (MPa)	Deflection at maximum load (mm)	Flexural toughness (at 1.3 mm) (N mm)	Notched flexural strength (MPa)	Deflection at maximum load (mm)	Flexural toughness (at 1.3 mm) (N mm)
PE00-0	8.4	0.080	16.1	0.87	5450	15.8	0.509	4403
PE60-A8	7.0	0.068	19.9	0.819	6540	21.5	1.492	5890
PE120-A2	7.6	0.087	18.6	0.849	6190	20.2	0.68	5640
PE180-A2	5.5	0.083	18.4	1.75	5680	18.6	0.635	5280
PE180-A30	10.6	0.150	21.8	1.062	6940	21.9	0.524	6450
PE60-O8	6.3	0.063	17.6	0.861	5800	22.1	0.421	6200
PE120-O2	6.4	0.064	17.9	0.83	5990	20.4	0.476	5840
PE180-O2	6.0	0.063	18.4	1.057	5920	20.3	0.573	5630
PE180-O30	6.1	0.074	13.2	0.56	4580	14.1	0.516	4130

[a] Strength and toughness values have been calculated by using average load–deflection curve data.

notched samples have increased from 15.8 MPa up to 21.9 MPa by 180 W, 30 min argon plasma treatment (Table 4). In accordance with the results of unnotched samples, the flexural toughness values were also improved up to 46% by argon plasma treatment conditions. Multiple cracking responses of the composites are also still evident and the numbers of cracks are significantly higher than the control composites (Fig. 10b). As seen in Fig. 10b, crack density around the notches is higher for samples incorporating plasma treated fibers.

In the case of oxygen plasma treatment, the flexural responses of notched composites were comparatively similar with the unnotched ones (Fig. 10c). Longer exposure times reduced the performance of composites in terms of flexural strength and toughness while the proper oxygen plasma treatment times were beneficial (Table 4). It should also be noted that, the crack density around the notch also significantly increased by oxygen plasma treatment (Fig. 10d). The first cracking was forced to appear at the mid-point of samples by notching. A weaker and smaller cross-section at this area, results with the formation and propagation of a single crack in the case of classic cementitious composites. However, if the strength and mechanical interlocking capacity of fibers are sufficient enough to distribute the load at the interface of the first crack, new cracks may form at the other sections of the composite. The multiple cracking behavior may be observed despite the formation of a short notch (a fault in practice) at the most stressed area of the composites.

Test results of notched samples indicated that, flexural performance of the composites incorporating plasma treated fibers (except the fibers exposed to excessive oxygen plasma) is less prone to faults. The formation of a fault in a most stressed cross section (notch) did not cause any significant performance loss (flexural strength and toughness) due to the improved load bridging and distributing capacity of plasma treated PE fibers.

3.6. Flexural performance of fiber reinforced unnotched and notched composites at later ages (8 months)

In a recent study it is reported that, the modified PE surfaces may undergo a time dependent hydrophobic recovery after plasma treatment [23]. In that study, PE surfaces aged at ambient air conditions. In order to understand if there is any degradation on the surface modification of fibers embedded in cementitious matrix within time, the effectiveness of plasma treatment as a function of time has been investigated in this section. For this purpose, the same flexural tests presented in previous section were performed on samples produced from the same batches after 8 months of curing period in water to facilitate the further hydration of cement. The load–deflection curves of unnotched and notched PE fiber reinforced composites are presented in Figs. 11 and 12, respectively. For each plasma condition, the first cracking strength, deflection at first crack, flexural strength, deflection values at maximum load and toughness values of samples have been computed and listed in Table 5.

The load–deflection curves of argon plasma treated fibers tested at 8 months are presented in Fig. 11a. The load–deflection curves shifted upwards and their general performance was better compared to 28 days values. The maximum flexural load values were in the order of 5000–7000 N at 28 days, these values increased to 6000–8000 N after 8 months (Fig. 11a). The flexural strength and toughness values of untreated fiber reinforced control specimen were 18.1 MPa and 6020 N mm respectively (Table 5). These values were increased to 24.4 MPa and 7376 N mm in case of 120 W 2 min argon plasma treated fibers usage.

Test results obtained from oxygen plasma treated fiber reinforced composites at 8 months were found parallel to the results of 28 days (Fig. 11b). Similarly, excessive oxygen plasma treatment periods caused performance loss as in the case of 28 days. Other oxygen plasma treatment conditions were found very effective in flexure strength improvement. If PE fibers subjected to 60 W oxygen plasma for 8 min are used in composite preparation, the flexural strength and toughness values reached to 24.0 MPa and 7188 N mm, respectively (Table 5).

In general, it seems that matrix aging significantly improved fiber–matrix interaction and multiple cracking behavior of unnotched samples. In practice, aging increases the brittleness of cementitious matrices [10]. Furthermore, the load carrying capacity at a definite deflection value and deflection at maximum load have been increased with aging. This is mainly due to the reduction of pore volume of matrix by the formation of new hydration products. While the deflection values at maximum load were usually less then 1 mm for 28 days old samples, these deflection values increased to 1–2 mm for 8 months old samples (Fig. 11a and b). The photographs of composites captured after each test showed that there is a significant increase in the number and distributed area of visible cracks with aging (Fig. 11c and d). Composites incorporating untreated fibers exhibited 10–15 visible cracks, however, depending on the treatment condition, the number of visible cracks increased to ~30 by plasma modification. The visible crack formations on the samples also showed that, aging and plasma treatment enlarged the scattering area of cracks throughout the PE fiber reinforced composites.

The flexural test results of 8 months old notched samples incorporating argon and oxygen plasma treated fibers have been presented in Fig. 12a and b, respectively. The multiple cracking

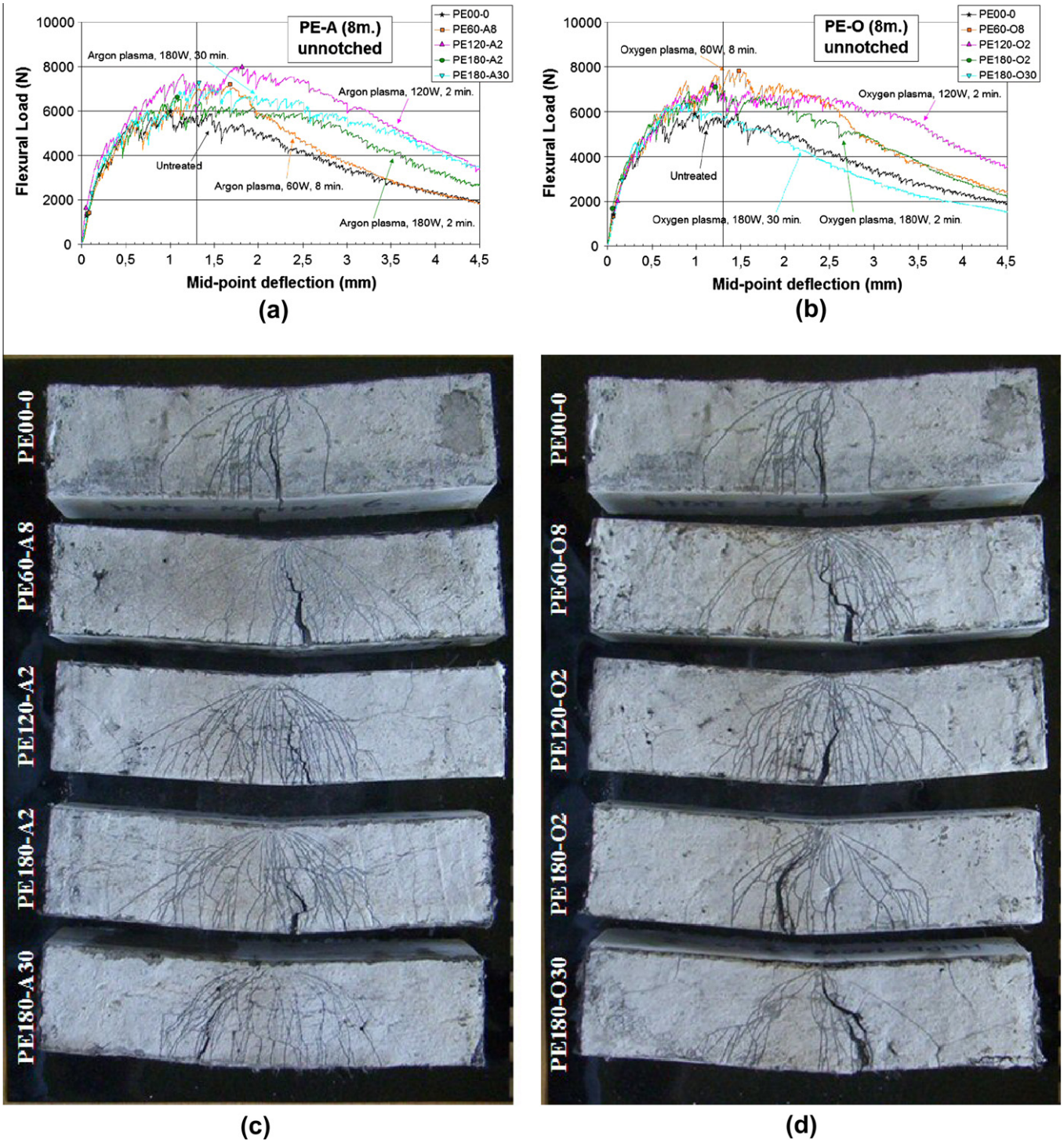


Fig. 11. The load–deflection curves and photographs of PE fiber reinforced unnotched composites at 8 months: (a and c) incorporating argon plasma treated fibers, (b and d) incorporating oxygen plasma treated fibers.

behavior is still significant despite the presence of a notch at the mid-span (Fig. 12c and d). The highest flexural strength and toughness improvements by argon plasma treatment have been obtained from notched samples of 120 W, 2 min and 180 W, 30 min plasma conditions (Table 5). However, the application of argon plasma treatment was not as effective as oxygen plasma treatment at 8 months. Oxygen plasma treatment at 120 W, 2 min increased the flexural strength and toughness values of notched composites to 27.2 MPa and 7776 N mm, respectively. In the case of notched samples, the effectiveness of plasma treatment and interaction between fiber and matrix seems more related to the matrix structure. It can be concluded that brittle matrix at 8 months is more vulnerable to faults compared to the younger one (28 days) in case of argon plasma treatment.

The improvements in the polyethylene surface bonding capacity with cementitious matrices by plasma treatment were also reported in the recent studies [10–12]. This improvement can be attributed to the superposed effect of plasma treatment generated polar surface functionalities (chemical factors) and surface roughness by micro- and nano-etching (physical factors) [24,39–42].

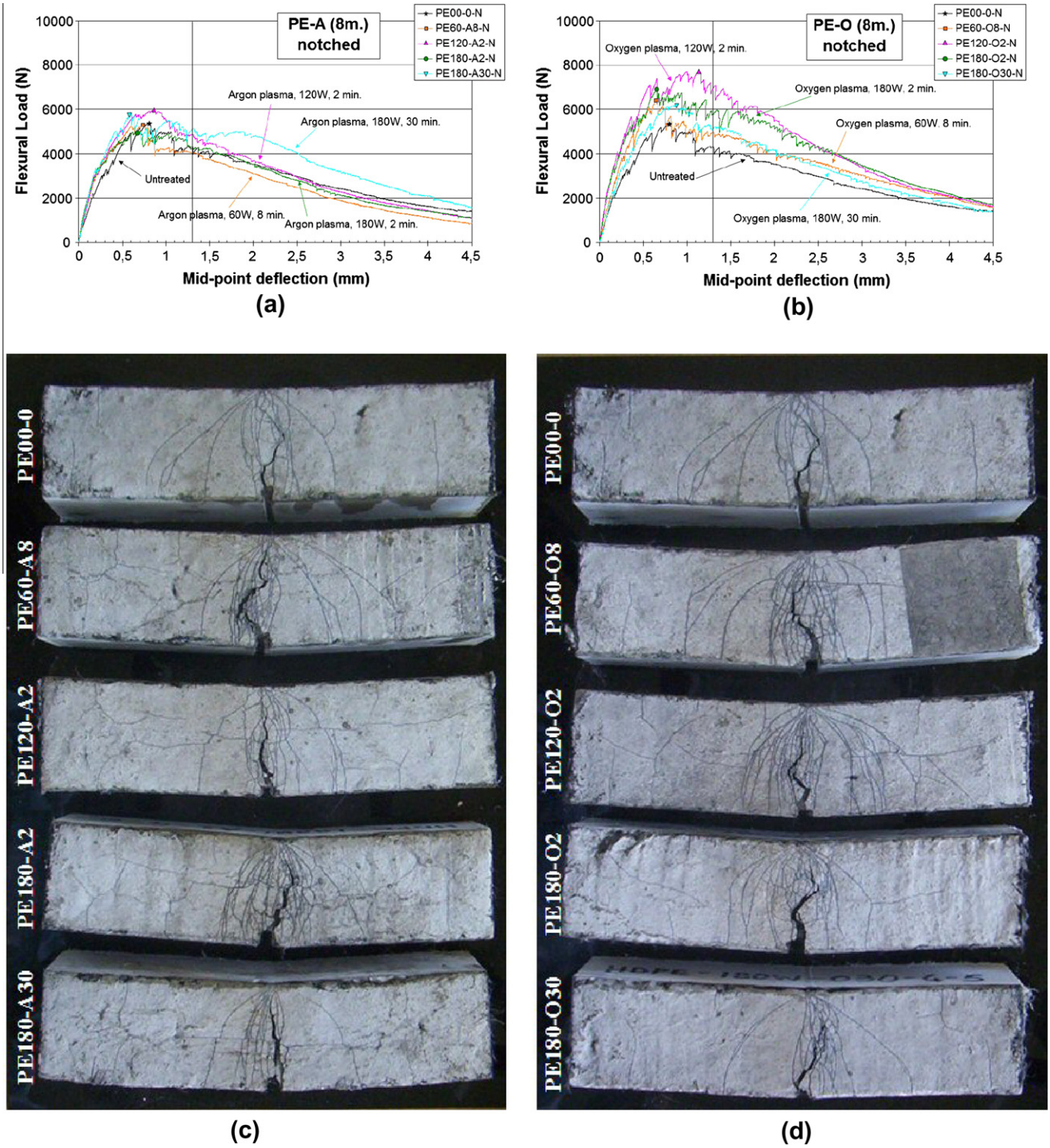


Fig. 12. The load–deflection curves and photographs of PE fiber reinforced notched composites at 8 months: (a and c) incorporating argon plasma treated fibers, (b and d) incorporating oxygen plasma treated fibers.

However, the magnitude of improvement cannot be quantitatively differentiated as chemical or physical.

4. Conclusions

The effects of argon and oxygen plasma treatment on the surface structure of PE fibers and on the performance of these fibers in a cementitious composite have been extensively investigated by different complementary techniques. The results of this two-stage experimental study can be summarized as follows:

1. Both argon and oxygen plasma treatments significantly decreased the wetting angle values of PE surfaces. The conversion of modified hydrophobic surface to hydrophilic by plasma exposure showed that there is a change in surface chemistry and structure at variable magnitudes depending on the type of plasma generating gas, power and exposure time.

Table 5
The 8 months flexural test results of unnotched and notched samples.

PE 8 months	Unnotched samples					Notched samples		
	First cracking strength (MPa)	Deflection at first cracking load (mm)	Flexural strength (MPa)	Deflection at maximum load (mm)	Flexural toughness (at 1.3 mm) (N mm)	Notched flexural strength (MPa)	Deflection at maximum load (mm)	Notched flexural toughness (at 1.3 mm) (N mm)
PE00-0	4.4	0.067	18.1	0.998	6020	19.0	0.817	5198
PE60-A8	4.9	0.089	22.0	1.679	6189	18.7	0.754	5214
PE120-A2	5.2	0.054	24.4	1.812	7376	21.0	0.876	5937
PE180-A2	4.8	0.085	20.2	1.087	6365	17.7	0.710	5308
PE180-A30	6.3	0.103	22.1	1.325	6722	20.8	0.603	5954
PE60-O8	4.2	0.056	24.0	1.49	7188	22.6	0.645	6102
PE120-O2	6.3	0.106	22.1	1.225	6899	27.2	1.148	7776
PE180-O2	5.3	0.061	21.8	1.228	6961	24.5	0.654	7072
PE180-O30	7.3	0.136	19.1	0.907	6470	22.0	0.889	5977

[a] Strength and toughness values have been calculated by using average load–deflection curve data.

2. SEM and AFM investigations showed that the physical surface etching effect of plasma treatment can be characterized at both micro and nano-scales. At micro-scale, parallel to the increase in power and exposure time, white staining gradually started to form on the surface of samples. These formations can be accepted as an evidence of the physical pitting and deterioration of surface. Longer exposure times at high plasma power (180 W, 30 min) increased the intensity of white staining on the surface. Nano-scale pitting formation on the surface of PE fibers due to plasma treatment can be quantified by Rms values calculated by using AFM images. The Rms values increased up to 51.8 nm at 180 W, 30 min of argon plasma application. The effect of oxygen plasma treatment on surface nano-morphology was relatively ineffective at short plasma exposure times. However; 180 W, 30 min of oxygen plasma application significantly improved the nano-roughness of PE fibers (Rms = 45.3 nm).
3. General XPS analysis revealed that the atomic O/C ratios of PE surfaces (1–10 nm depths) increased from 0.15 to 0.22–0.30 by plasma application. Modified fiber surfaces rich in oxygen atom give some clues about the formation of any new functional groups over the polymer top-surfaces. Results derived from the high-resolution partial XPS analysis of C1s peaks proved that, plasma treatment decreased the ratio of C—C/C—H groups and increase the oxidized functional groups (C—O, C—O(H), C═O, O═C—O...) ratio simultaneously.
4. The flexural performance of composites incorporating plasma treated PE fibers was significantly different from the untreated fiber reinforced ones. In most cases, increasing plasma power and exposure time shifted the load deflection curves of composites upwards both at 28 days and 8 months of testing. The flexural strength and toughness values were also improved by plasma treatment. Improvements by the application of argon plasma were in the range of 15–35% and 4–27% at 28 days and 12–35% and 3–23% at 8 months respectively. The crack density and distribution of cracks around the stress zone have increased. However, excessive oxygen plasma treatment (180 W, 30 min) caused adhesion problems for PE fibers when used in cementitious composites. Longer exposure times at higher plasma powers which cause excessive surface etching of PE fibers, may not always bring flexural performance improvement. Plasma power and exposure time optimization is necessary to certify the effectiveness of plasma application.
5. Test results of notched samples indicated that, the flexural performance of composites incorporating plasma treated fibers (except the fibers exposed to excessive oxygen plasma) is less prone to faults. The formation of a fault (notch) in cross section did not cause any significant performance loss (flexural strength and toughness) due to the improved load bridging and distributing capacity of PE fibers by plasma treatment. Furthermore, multiple cracking responses of composites are still evident and numbers of visible cracks were significantly higher than composite incorporating untreated PE fibers. The multiple cracking behavior can be observed despite the formation of a notch (a fault in practice) at the maximum stressed area of these composites.
6. In general, it seems that matrix aging improved fiber–matrix interaction behavior. Also argon plasma treatment further improved this property. In practice, aging increase the brittleness of cementitious matrices. However, in the case of plasma treated PE fiber reinforced composites, no significant changes were observed in the 8-month flexural strength and toughness values compared to the 28-day results. The load carrying capacity at a definite deflection value and deflection at maximum load were also increased with the aging. While the deflection values at maximum load were usually less than 1 mm for 28-day samples, the same values reached to 1–2 mm after 8 months.
7. As a general consideration physical etching effect of plasma treatment seems more dominant compared to the changes in surface chemistry from the view point of multiple cracking effectiveness of cementitious composites. However, further studies are needed to generalize such a conclusion.

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