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Improving the interfacial properties of para aramid fibers by surface treatment via plasma jet method in atmospheric pressure

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Abstract. Various methods have been used by the researchers in order to improve the interfacial adhesion of para aramid fibers. In the present research, poly para-phenylene terephthalamide (PPTA) fibers were treated by an innovative method through the utilization of plasma jet in atmospheric pressure using a mixture of oxygen and argon as inlet gases. The effect of the volume ratio of O₂/Ar and the treatment time were investigated on the interfacial properties of the fibers via SEM, AFM, ATR-FTIR analyses, and moisture sorption as well as the mechanical tests. SEM images demonstrated significant effect on the surface morphology of the fibers. In addition, ATR-FTIR spectra resulted in the creation of COOH, NH₂, and OH groups on the surface of fibers. The increase in the surface functionality led to an improvement in the surface adhesion of the fibers, as observed from the pull-out tests (a maximum of 31% improvement) and moisture sorption tests (a maximum of 54% improvement). According to the results of the tensile and pull-out tests via the design expert software, the optimum condition predicted that using atmospheric pressure plasma jet employing O₂/Ar volume ratio of 45.54/54.46% for 20 min results the best adhesion between the fibers and resin.

1 Introduction

High-performance engineering products such as composites require materials with excellent properties [1,2]. Poly para-phenylene terephthalamide fibers are one of the best candidates to reinforce composite materials due to their excellent properties such as high mechanical, thermal, chemical, and oxidative resistance, and also, since they possess a low density [1–4]. They have excellent mechanical properties, due to a high crystallinity and a smooth chemically-inert surface. The PPTA fibers, nevertheless, have poor interfacial adhesion to most resins [1–5]. To improve the interfacial adhesion of the PPTA fibers, many comprehensive studies have been performed on different methods including chemical and physical surface treatments that are presented in Table 1.

Chemical treatments such as grafting [6,7], coating [8,9], roughening the surface and etching [10,11], and using different solvents [12,13] can improve the interfacial adhesion. However, these processes have many limitations for practical and industrial applications because of multistep reactions, high cost of equipment, complicated reaction conditions, toxicity of materials, recycling wastewater, and solvent systems. Also, they have low efficiency on the mechanical properties of the fibers [1].

Physical treatments include heat treatment and modification of surface using radiation [14–22]. UV

irradiation is relatively powerful in modifying the surface of the PPTA fibers. Xing and Ding reported that after 156 h of UV irradiation, the PPTA fibers were completely destroyed [21]. It should be mentioned that generally the UV irradiation method needs a high level of control over the process parameters and the intensity of UV-ray. Additionally, our team studied the application of UV for denim discoloration [23].

Another physical method is plasma treatment that is more attractive in comparison with the other methods, because plasma modification can improve the surface quality of the PPTA fibers without any significant alteration of their bulk properties [4,24–28]. This method is possible in two pressure levels: low and atmospheric.

Low pressure plasma has been broadly used for surface modification in laboratory and industrial applications. This type of plasma requires achieving a low pressure as well as high vacuum, and it is not a continuous process. Therefore, it requires a long time and a high amount of energy [26]. In comparison to the low-pressure plasma, atmospheric pressure plasma technique (APPT) has many advantages such as: no need to expensive vacuum equipment, the ability to produce uniform and steady plasma so that it is possible as a continuous process with a good efficiency. Consequently, it can be considered as a reliable method for the surface modification of fibers. This technique is coming to attention for modifying the surface of polymeric fibers [3,29]. However, only a few studies have been done to modify the surface of the PPTA fibers using APPT [4,25,26,29,30].

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Table 1. Methods for the surface modification of the PPTA fibers.

Method	Description	References
Grafting	Addition of chemically functionalized sites on the surface of the fibers	[6,7,31–38]
Coating	Applying a layer with chemically active groups on the surface of the fibers	[2,8,9,39–43]
Chemical treatment (CT)	Fibers chemically roughening and functionalizing as the results of surface and bulk destruction	[12,13,44,45]
Usage of solvents (such as H ₂ SO ₄ & etc.)	Improving surface roughness and functionalizing by the usage of etching	[10,11,24,46–64]
Other chemicals (such as H ₂ O ₂ , KMnO ₄ & etc.)	Surface roughening, functionalization and activation through plasma irradiation	[4,5,65–70]
Low pressure plasma (LPP)	Controllable surface roughening and activation by plasma irradiation	[25,26,29,30]
Atmospheric pressure plasma (APP)	Surface activation and destruction by irradiation	[18,21]
UV-ray	Activation and destruction of fibers by irradiation	[19,20,22]
γ -ray	Usage of ultrasonic waves to improve surface roughness	[14]
Ultrasonic	Improving physical entanglement of fibers to resins	[15]
Texturizing	Including controlled heating to improve surface roughness	[16]
Heat treatment	Utilization of cooling process with different rates to improve roughness	[17]
Cryogenic treatment	The enhancement of the fibers' interfacial properties by irradiation and coating or coating and improving surface properties of the coated layer by plasma irradiation	[27,71–75]
LPP and chemicals	Surface functionalization using irradiation to achieve a coated layer by more adhesion or coating and enhancing the properties of the coated layer by plasma irradiation	[28]
Combination of CT and PT	APP and chemicals	

Atmospheric pressure plasma jet (APPJ) produces homogeneous plasma, and it can be used for surfaces with any geometry [76]. This technique is very applicable for the industrial surface treatment due to its unique properties [77]. Furthermore, the usage of APPJ technique can simultaneously treat both sides of the fabrics, which is necessary for an effective treatment [78]. In previous researches, APPJ technique has been used for the surface modification of cotton [79–81], wool [78], polyester [82], and Twaron fibers [83].

In the present research, poly para-phenylene terephthalamide (PPTA) fibers were treated by an innovative method through the utilization of plasma jet in atmospheric pressure using a mixture of oxygen and argon as inlet gases. Various methods have been used by the researchers in order to improve the interfacial adhesion of para aramid fibers. Atmospheric pressure plasma jet (APPJ) as a type of radiation which is applied on the solid state materials, produces homogeneous plasma, and it can be used for surfaces with any geometry. This technique is very applicable for the industrial surface treatment due to its unique properties.

For the modification of the PPTA fibers, oxygen has been investigated for application as the inlet gas to produce plasma [66–68]. Employing plasma technique for treating the surface of the fibers can produce a large number of oxygen atoms and other active chemicals [83]. In addition, the mixture of oxygen and argon has been applied to modify other types of the aramid fibers (PBO fibers). As studies reveal, compared to pure gas plasma treatment, the gas mixture can activate more chemical groups on the surface of the fibers, and thus, the wettability is increased [84].

Su et al. have found that the obtained surface roughness using oxygen plasma treatment depends on the treatment time and the supplied power [68]. Furthermore, the increase in the surface roughness has an important role in the enhancement of the mechanical properties of the composites. A higher roughness of the fibers' surface results in more mechanical interlocking between the fibers and resin [25,54,68].

In the present research, plasma treatment time and O₂/Ar (as inlet gases) volumetric ratio have been used in APPJ technique for treating the surface of a type of the PPTA fibers (Kevlar 49) as well as investigating the surface adhesion of the treated fibers with an unsaturated polyester resin.

2 Material and methods

2.1 Materials

Kevlar 49 yarns (LISO, Shanghai Lishuo Composite Material Technology, China) were the aramid fibers used in the present research. Oxygen and argon as inlet gases for plasma generation (Persia gas company, Iran) and acetone (Merck, Germany) were used. Unsaturated polyester resin and methyl ethyl ketone peroxide (MEKP) hardener (Aekyung Chemical Company, South Korea) were also applied.

Table 2. Characteristics of the surface-treated Kevlar yarn sample.

Sample	O ₂ /Ar (V/V %)	Time (min)
Untreated	–	0.0
(25/75-10)	25/75	10.0
(50/50-10)	50/50	10.0
(75/25-10)	75/25	10.0
(25/75-20)	25/75	20.0
(50/50-20)	50/50	20.0
(75/25-20)	75/25	20.0

2.2 Plasma treatment

Atmospheric Pressure Plasma Jet (APPJ, Kavosh Yaran Company, ACPJ-16AR model, Iran) was applied for surface modification of the PPTA fibers. The distance between the nozzle and surface of the fibers was fixed at 5 mm, the used power was set to 1000 W, and the rate of treatment was 4 m/min. The process parameters for the surface modification of the yarn samples are presented in Table 2.

Scanning electron microscope (EM3200 KYKY, China) was used to investigate the surface morphology of the PPTA fibers. The samples were coated with gold using a gold sputter coater (SBC-12, KYKY, China) before SEM experiments.

Atomic force microscopy (Multi mode (Full plus), Ara research, Iran) was employed to investigate the surface roughness of the PPTA fibers. The images were acquired from a 5 μm × 5 μm scan area on each sample. The roughness of the fiber surface was characterized by mean-square roughness (Rq) and arithmetic-mean roughness (Ra) which were calculated by the software of this device.

Tensile strength of the yarns was measured according to ASTM D 2256–02 test method via tensile strength machine (1446–60 tensile tester machine, Zwick, Germany). Pull-out test was performed at the rate of 0.5 mm/min for all samples by tensile strength instrument, and the application of the force was continued until the first rupture of the samples. This method was explained in literature reviews [48]. To prepare each sample for analyzing pull-out force, first of all, yarns were washed at 25 °C with acetone to remove any impurities from their surface. Then, the yarns were placed in an oven for 5 h at 110 °C. One end of the Kevlar yarns (20 cm in length) were vertically placed at the bottom of a mold (2.5 × 2.5 × 2.5 cm³). Then, the unsaturated polyester resin was mixed with MEKP with the optimum weight ratio (1% w/w MEKP/resin) provided by the manufacturer. After pouring the mixture of the resin and hardener into the mold, it was sealed by a plate to prevent air and dust contamination during the 24 h of curing. Then, the mold was pressed with a load of approximately 10 kN for 2 h at 80 °C for post-curing in order to remove air voids and improve the crosslinking of the matrix and yarns.

Crystal structure of the PPTA fibers was evaluated by XRD analysis using an XPert-MPD X-ray diffractometer (Philips Company, Netherlands) with Cu – K α targets with 2 mm slits at a scanning rate of $0.05^\circ 2\theta (s-1)$, 2θ range: $5-50^\circ$, applying 40 kV and 30 mA.

To investigate the chemical changes produced by APPJ treatment, ATR-FTIR analysis was performed on untreated and treated the PPTA fibers using a Bomem-MB 100 (Hartmann & Braun, Canada) spectrometer at ambient temperature and humidity (24°C , RH 65%). The wavelength was used in range of $800-3800\text{ cm}^{-1}$ with 8 cm^{-1} resolution and 16 scans were performed for each sample.

Moisture sorption was measured for each sample, before and after the plasma treatment, for 50 h, at 24°C temperature and 65% relative humidity, in order to investigate the effect of APPJ treatment on the wettability of the PPTA fibers [85].

Response Surface Methodology (RSM) is a statistical method for evaluation of the relation between input variables and output responses. The basic idea of this method is using a set of experiments to predict the optimum response. X_1 and X_2 were coded, respectively according to two input parameters consisting of Oxygen concentration in three levels (25%, 50%, and 75%) and time of plasma treatment in two levels (10 min and 20 min). Defined responses for this study are tensile strength and pull-out force of the fibers. RSM method was used in order to evaluate the effect of input parameters on tensile strength of fibers.

In RSM method, to achieve the best adjusting model for the data, the coded values were calculated by equation (1). Where X_i is coded value of input parameter c_i , and c_h and c_l refer to high and low level, respectively.

$$X_i = (c_i - [c_h + c_l]/2)/([c_h - c_l]/2). \quad (1)$$

The standard form of the second-order equation (quadratic model) which was significantly adjusted with the data was presented in equation (2), where Y is response (tensile strength or pull-out force), A is Oxygen ratio as inlet gas and B is time of treatment, $\beta_0-\beta_5$ are unknown coefficient of data. To have regression analysis according to the experimental data, the Design Expert software was used.

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 AB + \beta_4 A^2 + \beta_5 B^2. \quad (2)$$

3 Results and discussion

3.1 Experimental results

The surface morphology of the PPTA fibers after plasma treatment is generally complicated and it is especially dependent on the process parameters [5]. Untreated Kevlar fibers have a completely smooth surface (Fig. 1a). For sample (25/75-10) blisters and fibrillated ribbons appeared on the fibers' surface (Fig. 1b). Su et al. reported similar blisters after oxygen plasma treatment of the fibers using APPT [68].

After treatment of the fibers with calcium chloride as a solvent and heat treatment, similar changes in morphologies were observed [54,86]. It can be stated that APPJ has an aggressive effect, because the mentioned morphology is created under the minimum values of process parameters.

Furthermore, the fibers fibrillation resulted in the ribbons which were observed on the fibers' surface [87]. According to the previous researches and studies, the use of oxygen in the low pressure plasma technique is very effective in modifying the PPTA fibers [87], and with more oxygen volume ratio, the surface etching was increased as it is clear in Figure 1c (sample (50/50-10)). According to reports, the appeared roughness in morphology such as globular microstructures and tracks on the surface of the PPTA fibers can help to improve the mechanical interlocking between the fibers and resins [4,25,68]. As the ratio of oxygen increased, (75% volumetric ratio), it is demonstrated that an external layer of the fibers' surface was removed (sample (75/25-10)). The mentioned morphology can be the result of the inner morphology of the PPTA fibers [87] and observed applying the other methods, particularly low pressure plasma on the PPTA fibers [32,48,68]. As shown in Figure 1e (sample (25/75-20)), many bulges and ruts can be observed on the fibers' surface when the treatment time was doubled. Also, it seems that the ribbons which were fibrillated and separated from the fibers are adhered to the longitudinal surface. This phenomenon might be related to the applied plasma conditions. Therefore, sample (50/50-20), fibrillar structure by more rough surface and ribbons can be observed clearly on the surface of the fibers (Fig. 1f). In addition, tracks are observed through the longitudinal surface of the PPTA fibers, which is similar to the reported results by Su et al. [68]. For sample (75/25-20), APPJ technique causes complete fibrillation, sharp cracks and fragments inside the fibrillated structure (Fig. 1g) [88]. In previous reports, the similar morphology has been achieved via cryogenic treatment [17] as well as 156-hours irradiation of UV [21]. Although, it was believed that the plasma treatment is not a powerful method for surface modification of the PPTA fibers [26], but, in the present study, it is proved that APPJ technique can be one of the most powerful methods for surface modification of the PPTA fibers that causes such results.

As it was explained as well as the results of AFM analysis presents in Table 3 and Figure 2, APPJ treatment can increase the surface roughness of the fibers noticeably. In comparison to the untreated samples, the values of Ra and Rq increase 31.6% and 25.2% respectively for sample (50/50-10). It should also be mentioned that, by improvement at process parameters including volume ratio of oxygen and treatment time, the values of Ra and Rq have been improved to 69.4% and 8.3% respectively (sample (50/50-20)). Also for sample (75/25-20), through more improvements at both process parameters, compared to sample (50/50-20), the values of Ra and Rq decreased 21.6% and 26.6%. The reason might relate to over-degradation that causes some decrease in the roughness which can be observed in SEM image in Figure 1g. Therefore, it seems that the process parameters of sample

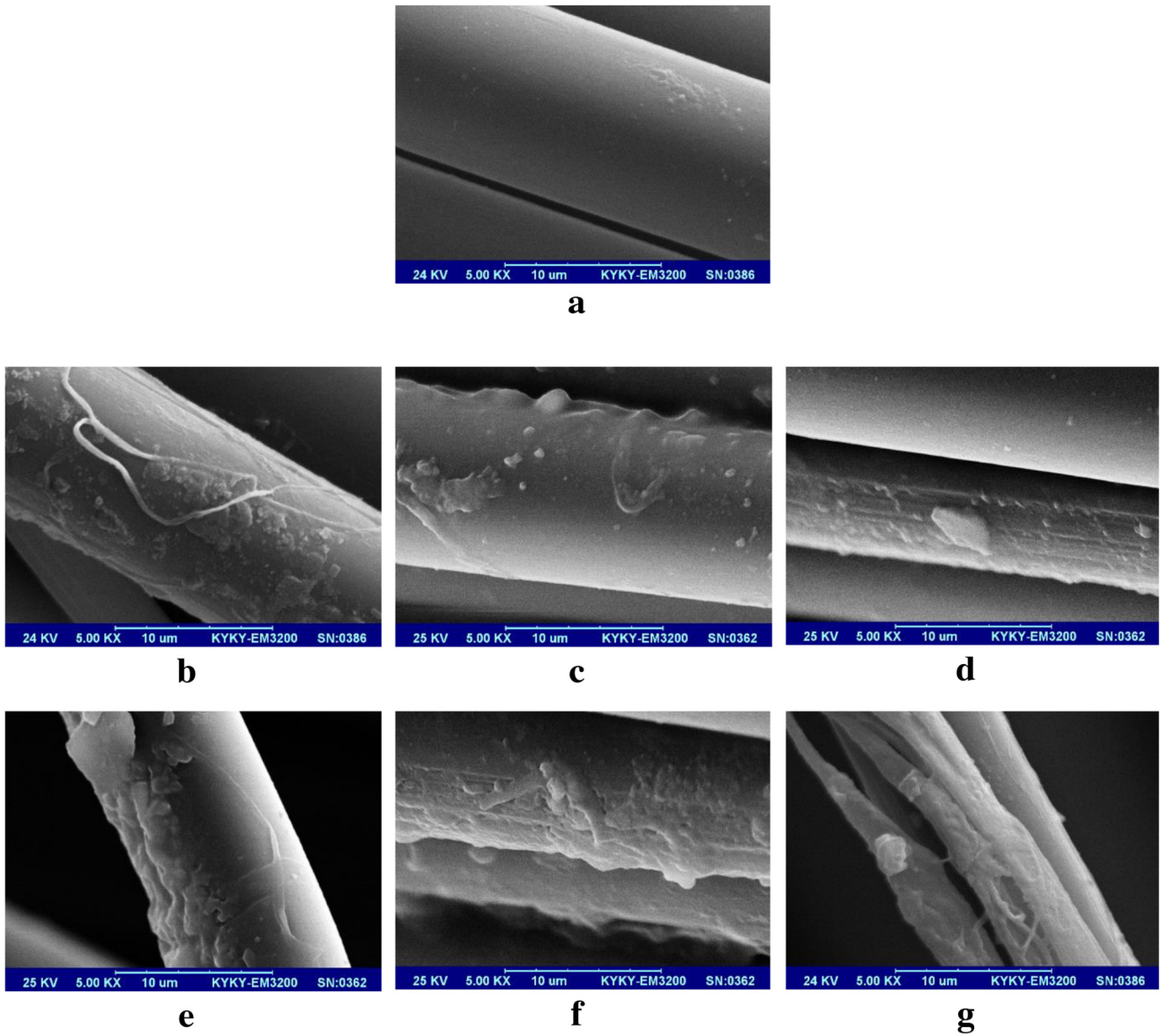


Fig. 1. SEM micrographs of: (a) untreated sample, (b) sample (25/75-10), (c) sample (50/50-10), (d) sample (75/25-10), (e) sample (25/75-20), (f) sample (50/50-20), (g) sample (75/25-20).

Table 3. AFM analysis results.

Sample	R_a	R_q
Untreated	141.6	105.7
Sample (50/50-10)	186.3	132.3
Sample (50/50-20)	239.9	196.9
Sample (75/25-20)	188.1	144.59

(50/50-20) can be regarded as the near optimum parameters to achieve an appropriate surface roughness on the PPTA fibers.

The PPTA fibers are consisted of a mixture of linear macromolecules so that a high crystallinity and orientation

can be demonstrated [89]. As observed in Figure 3, the diffraction peaks are cleared at $2\theta = 20.07^\circ$, 22.70° and 38.1° that are respectively related to the crystal planes (110), (200), and (310) of the Kevlar fibers, which are adapted with reports [19,45,49,89,90]. In contrast to the treated samples, the diffraction peak related to the crystal plane (310) cannot be detected for the untreated sample, but both of the process parameters raised, the crystal plane (310) growth in addition, the intensity of peaks related to planes (110) and (200) were increased compared to the untreated samples. This result indicates an improvement in the crystallinity of the PPTA fibers. For plasma treated samples, the diffraction peaks are sharper and narrower in widths which are related to reduce in amorphous backgrounds and enhancement in crystallinity [49]. This can be the result of the increase in the number of hydrogen bonds

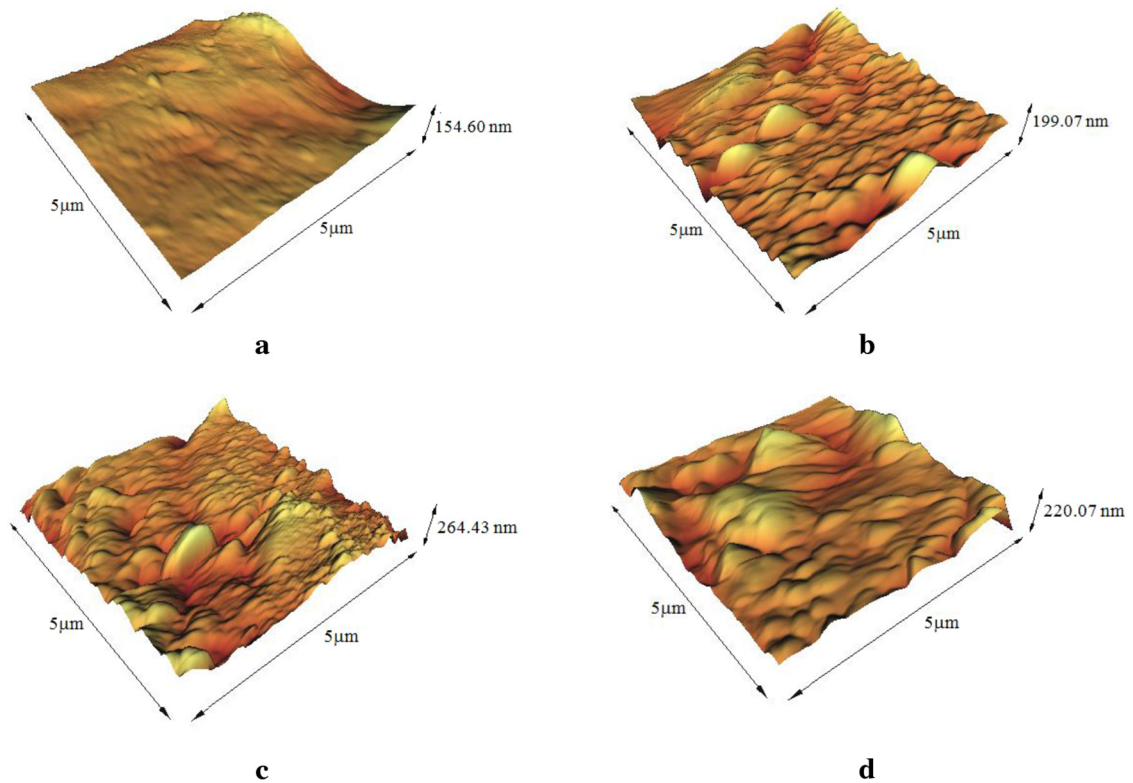


Fig. 2. AFM micrographs: (a) untreated sample, (b) sample (50/50-10), (c) sample (50/50-20), (d) sample (75/25-20).

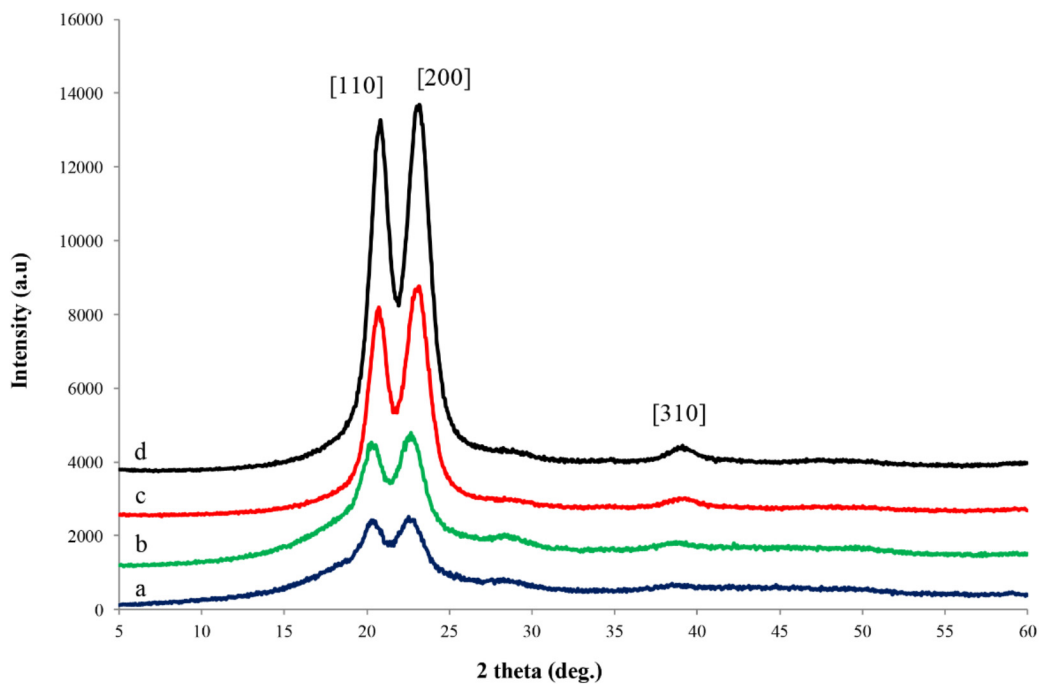


Fig. 3. XRD patterns of: (a) untreated sample, (b) sample (50/50-10), (c) sample (50/50-20), (d) sample (75/25-20).

in aramid polymeric chains [87]. The high plasma temperature and the crosslinking improvement lead to enhancement in crystallinity and orientation [54,90].

In order to investigate the probable chemical alteration of the fibers after plasma treatment,

ATR-FTIR spectroscopy was performed on the samples. As it is presented in Figure 4, the peak at 821 cm^{-1} is related to para substitution of the ring, which is not presented for untreated sample. Su et al. also reported this peak at 818 cm^{-1} [68].

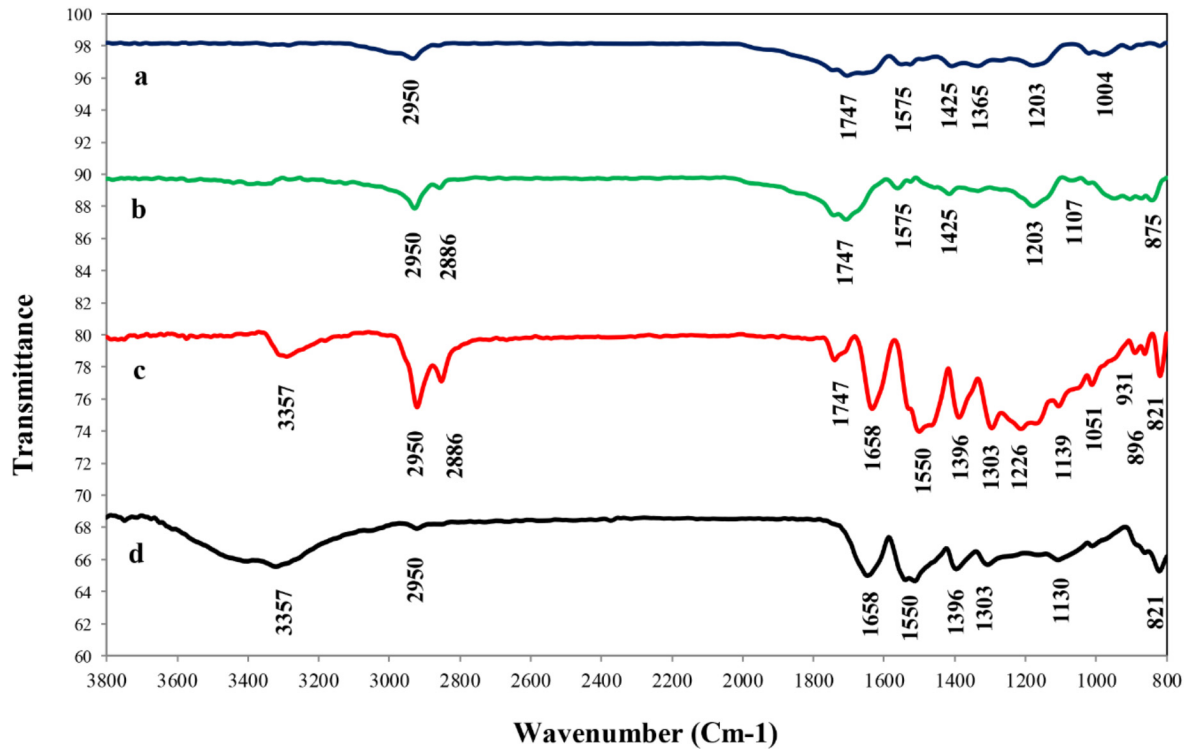


Fig. 4. ATR-FTIR spectra: (a) untreated sample, (b) sample (50/50-10), (c) sample (50/50-20), (d) sample (75/25-20).

The intensity of this peak has significantly increased in sample (50/50-20) and decreased in sample (75/25-20). The peak at 1575 cm^{-1} for untreated sample is attributed to amine I groups. The attributed peak of amine I for treated samples is shifted and presented in 1658 cm^{-1} . The intensity of the mentioned peak is decreased for sample (50/50-20) compared to the sample (50/50-10). This indicates the decomposition of the aromatic rings and the surface amide groups. In sample (50/50-20), the appeared peak at 1747 cm^{-1} belongs to carbonyl groups. The intensity of carbonyl peak has been maximized for sample (50/50-20), and after that, it has been reduced while increasing O_2/Ar volume ratio to 75/25%. By applying plasma treatment, the number of CONH groups has been decreased, and new functional groups have been formed.

Stretching vibrations of methylene and methyl groups are presented in peaks at 2886 and 2950 cm^{-1} . These peaks have also been observed as air and He were employed as inlet gases in low pressure plasma technique as well as atmospheric pressure plasma technique [4,73]. The peak at 2886 cm^{-1} which is appeared in treated samples related to carbonaceous contaminants on the surface of the PPTA fibers and Inagaki et al. reported the same results after oxygen plasma at low pressure [75]. Guo et al. attributed these peaks as the criteria of sizing agent existence on the surface of original PPTA fibers [4]. Moreover, changing in intensity of peak at 1550 cm^{-1} , which is assigned to C=C groups indicates decomposition of the surface aromatic rings of the PPTA fibers after plasma treatment. The peak at 3357 cm^{-1} is related to OH groups which demonstrate an enhancement of wettability in plasma-treated samples

specimens. Sample (50/50-20) exhibits the highest intensity of the hydroxyl peak among the others. In sample (75/25-20) according to extensive degradation (that is also clear in Fig. 1g), the intensity of hydroxyl peak was decreased. The amounts of hydroxyl groups on the surface of the PPTA fibers indicate the surface wettability of the fibers with the resin, and therefore, the sample (50/50-20) has the optimum conditions and is the best modified.

The peaks appearing at around 1000 cm^{-1} related to $-\text{CH}=\text{CH}_2$ and the peaks around 1300 cm^{-1} demonstrate the oxidation of NH_2 groups and creation of NO_2 on the surface of the PPTA fibers. The peaks at around 1100 cm^{-1} are related to C-O which also demonstrates the surface oxidation of the PPTA fibers. Inagaki et al. reported that the peaks at 1190 and 1410 cm^{-1} are related to C-O-C and C-O groups after treatment by oxygen plasma [75].

There are 4 possible chemical reaction sites on the surface of the PPTA fibers which are mentioned in Figure 5. Due to the interaction between the PPTA molecules and the photons generated by the plasma, chain break can occur at second position. The chemical reactions between the PPTA molecules and active species present in the oxygen plasma bulk generate carboxylic groups at chain ends [26,29]:

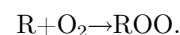
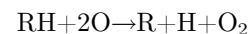


Figure 5 shows the proposed mechanism of hydroxyl groups in the PPTA molecules. Position 1 is a suitable potential site for generating free radicals by photons

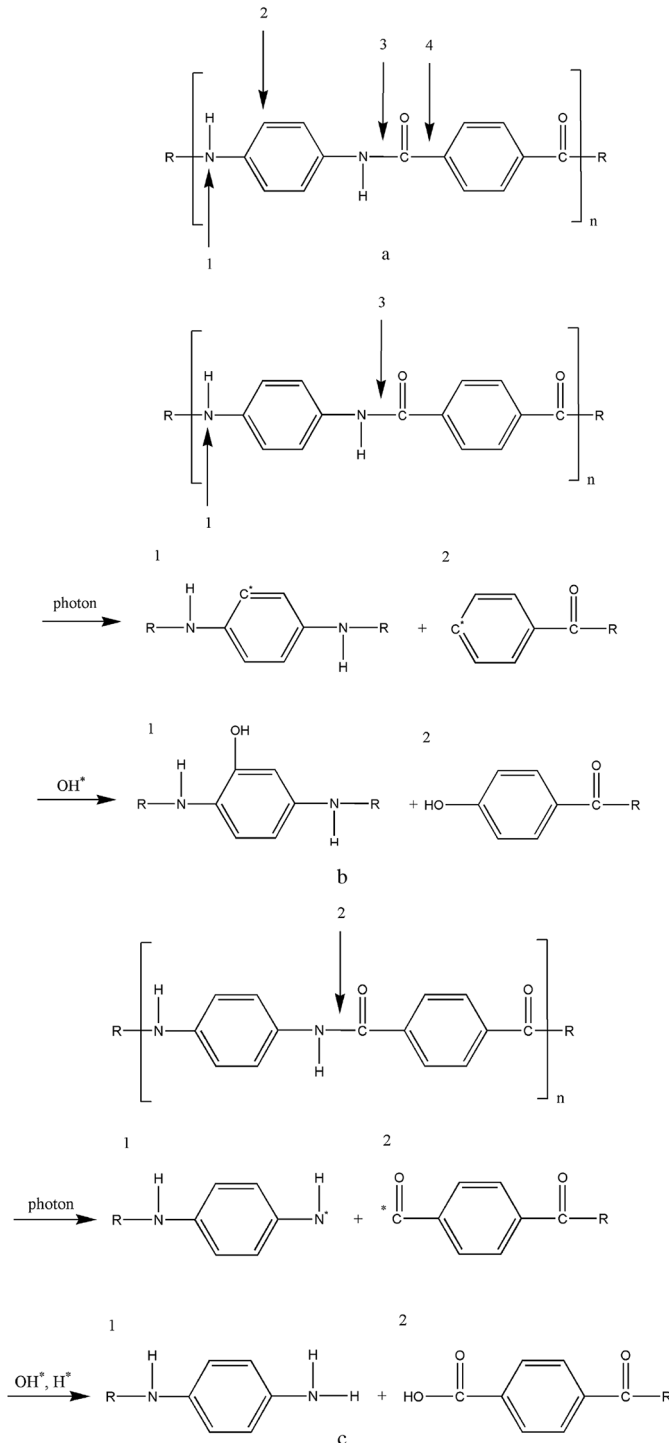


Fig. 5. Kevlar chemical reactions during plasma treatment: (a) possible reaction sites (1,2,3,4) in the PPTA molecules, (b) the proposed reaction mechanism for $-OH$ group generation at positions 1 and 3 in Kevlar Molecular Structure, (c) possible chain scission and reactions at position 2 in Kevlar Molecular Structures [30].

(UV-ray). Chain break and formation of radicals could occur simultaneously at position 3. The OH groups can be produced by reactions with oxygen radicals (O) in the

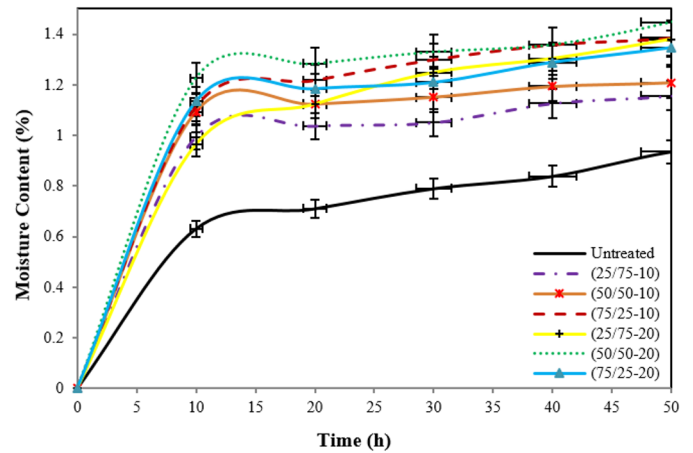
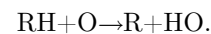
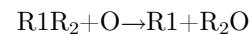
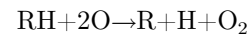
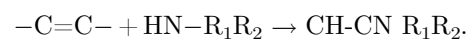
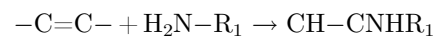
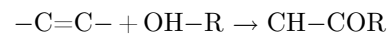


Fig. 6. Moisture sorption results based on time.

plasma [26], as presented in the below:



In the literature reviews the following mechanism reactions were suggested for the enhancement of adhesion between the PPTA fibers and unsaturated polyester resin via covalent reactions:



In addition to the above mechanisms, it can be mentioned that the creation of hydrogen bonds between hydroxyl, amine, carbonyl and carboxyl groups (on the surface of the plasma-treated fibers) and unsaturated polyester resin can contribute to the enhancement of adhesion.

A sufficient wettability is required to achieve a proper adhesion between the PPTA fibers and the matrix resin. As shown in Figure 6, the moisture sorption of the fibers has significantly increased by applying APPJ technique for the modification of the PPTA fibers, which also means a higher wettability for the PPTA fibers. This is related to the enhancement of functionality as a result of the generation of polar groups such as hydroxyl, carboxyl, etc. on the surface of the fibers. All of the treated samples showed a significant increase in wettability compared to untreated ones. Among all samples, sample (50/50-20) number 5 illustrated the highest moisture sorption (54% improvement in comparison to the untreated sample). Because of the extensive destruction of sample (75/25-20) sample 6, a noticeable decrease in moisture sorption is observed. Generally, enhancement in intensity of hydroxyl peak of the ATR-FTIR spectra for the treated samples in

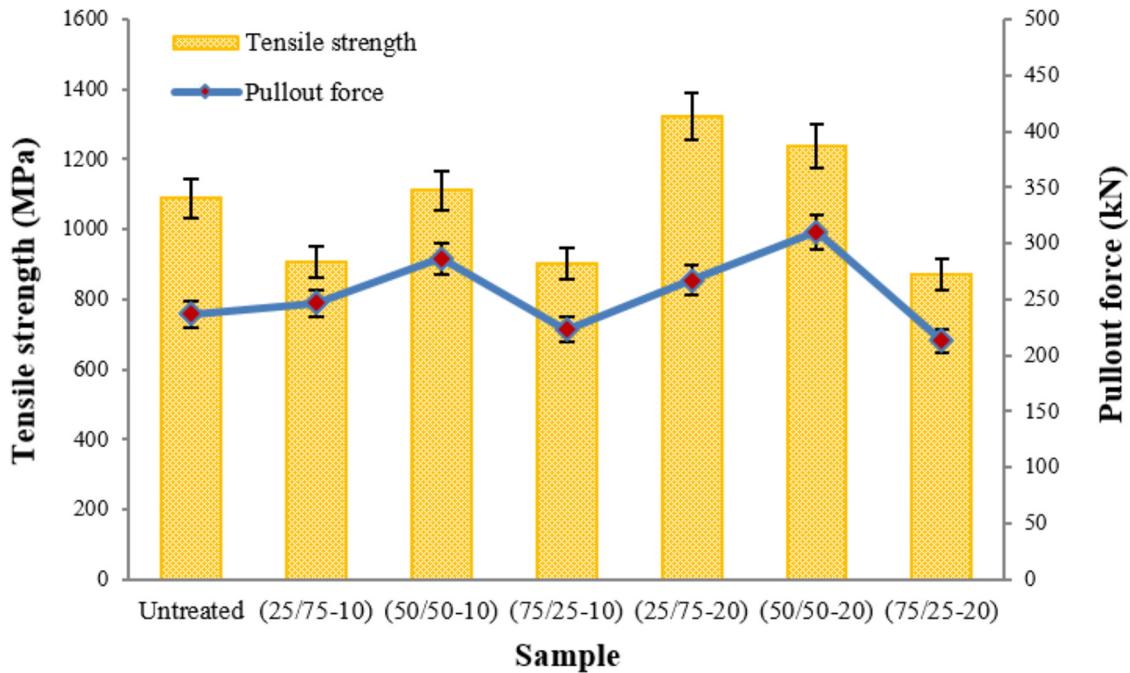


Fig. 7. Tensile strength and Pull-out force tests results.

comparison to the untreated ones can be the best proof for the wettability enhancement of the plasma treated PPTA fibers.

The results of the mechanical tests on the PPTA fibers is illustrated in Figure 7. Multiple variables can affect the tensile strength of the plasma-treated PPTA fibers, including crystallinity [49], crystal orientation [54], hydrogen bonds between aramid and polymeric chains, and also, the formation of crosslinks that cause improvement in crystallinity [87]. When the volume ratio of oxygen raised up to 50%, tensile strength increased in comparison with the untreated sample, but increasing the oxygen ratio to 75% decreased the tensile, and this decrease is maximized in sample (75/25-10) sample 3 when both time and oxygen ratio are maximum. In contrast, tensile strength has generally improved with increase in time of plasma treatment. As shown in Figure 7, at constant oxygen/argon volume ratio, when treatment time is increased from 10 to 20 min, compared to sample (25/75-10) samples 1 and sample (50/50-10) 2, the value of tensile strength is improved significantly for sample (25/75-20) samples 4 and sample (50/50-20) 5 respectively. However, the tensile strength of sample (75/25-20) sample 6 is lower than sample (75/25-10) 3 which is probably due to the extensive degradation of sample (75/25-20) sample 6 as a result of the high oxygen concentration in the applied plasma treatment. According to obtained results, it can be observed that there is an optimum value for each parameter of plasma treatment process that causes improvement in adhesion properties as well as mechanical properties. Increasing the process parameters beyond their optimum value causes opposite effects on the tensile of the PPTA fibers. Furthermore, it can be concluded

that oxygen can also modify the surface of the PPTA fibers especially in long time treatment.

Figure 7, also illustrates the results of pull-out test. For sample (25/75-10) sample 1, the adhesion between resin and the surface of the fibers was improved by plasma treatment, due to the enhancement in surface roughness, better interlocking, and chemical surface interactions between the PPTA fibers and resin. For sample (50/50-10) sample 2, pull-out force has improved as well as tensile strength. There is a decrease in the pull-out result of sample (75/25-10) sample 3, and the most reasonable explanation can be expressed by the results of SEM analysis which demonstrate extensive degradation in the fibers according to volume ratio of oxygen up to 75%. By increasing the time of treatment up to 20 minutes, pull-out force is increased. The highest pull-out force is related to sample (50/50-20) sample 5 (31% improvement compared to the untreated) similar to the results in the previous sections. It should be mentioned that there is an optimum condition for this sample. So, it is concluded that the high surface roughness, suitable physical interlocking, surface functionality and the enhancement in crystallinity are the main factors contributed to the increase in the pull-out force.

Finally, it can be stated that the surface adhesion between the PPTA fibers and unsaturated polyester resin, which was evaluated by pull-out force, depends on the surface morphology, roughness, and chemistry as well as crystallinity of the fibers. Oxygen is one of the effective used gases as plasma inlet for the surface modification of the PPTA fibers that can be a proper choice to produce functional or polar groups such as hydroxyl, carboxyl, etc. on the surface of the fibers, and effectively perform

Table 4. Coefficients of the model for tensile strength of the plasma treated PPTA fibers in coded form.

Variables	Coefficient	Value
	β_0	+1047.90
A	β_1	+255.55
B	β_2	+281.18
AB	β_3	-333.43
A_2	β_4	-391.60
B_2	β_5	0
R_2		0.9918

surface etching or roughness. In the present research, increasing the O₂/Ar volume ratio up to 50% leads to more functionality according to ATR-FTIR and moisture sorption results; but, using 75% volume ratio leads to less functionality (sample (75/25-20) sample 6) because of over-degradation of the structure of the PPTA fibers, and decreasing in surface roughness (AFM analysis) which causes decrease in pull-out force. Also, by increasing the time of plasma treatment from 10 to 20 min in comparing sample (50/50-10) sample 2 with sample (50/50-20) 5, a notable improvement in roughness was observed, due to more functionality as well as the creation of a significant amount of hydroxyl groups. These factors can help to improve adhesion between the PPTA fibers and unsaturated polyester resin. Finally, it can be observed that the increase in treatment time results more degradation in fibers and the increase in the volume ratio of oxygen/argon has a notable effect on the improvement of the adhesion between the PPTA fibers and polyester resin.

3.2 Response surface methodology

Response Surface Methodology (RSM) was applied to evaluate the correlation between output and input parameters. In RSM model, R_2 was obtained by regression analysis method which explained the degree of conformity with the model. Each parameter has its effect on response factor and as the R_2 is near to 1 the model is suitable.

According to the analysis of the results in Table 4, equation (3) is the fitted quadratic eq. for tensile strength of the plasma treated PPTA fibers, Where R_1 is tensile strength of the fibers, A is Oxygen ratio as inlet gas and B is the time of treatment, β_0 to β_5 are unknown coefficient of data.

$$R_1 = +1047.90 + 255.55 A + 281.18 B - 333.43 AB - 391.60 A^2. \quad (3)$$

In Table 4 the coefficient value for each parameter in equation (3) was determined. Figure 8 shows the contour and 3D plot of tensile strength of the plasma-treated PPTA fibers as a function of oxygen ratio and the time of plasma treatment as input parameters. As it is also clear in

Figure 8, when the oxygen ratio in inlet gas is increased up to 50%, the tensile strength is also increased; but, further increase up to 75% reduced the tensile strength, and thus, there is an optimum ratio for oxygen in this study. And it is mentioned, in advance, that increasing the oxygen ratio from optimum conditions results in degradation in the structure of the fibers. Therefore, the tensile strength of the fibers faces reduction.

There is another study related to the effect of oxygen ratio and time of plasma treatment on pull-out force of the fibers. The Table 5 shows the coefficient of equation (4) which expresses the relation of input parameters with pull-out force of fibers as response.

$$R_2 = +283.24 + 74.11 A + 18.99 B - 22.57 AB - 137.87 A^2. \quad (4)$$

Figure 9 shows that as it was mentioned, when the oxygen ratio in inlet gas increased up to 50%, the pull-out force increased, but further increase up to 75% resulted in the reduction of the tensile strength, and so, there is an optimum oxygen ratio. The other point is that when the time of the treatment increased up to 20 min, the pull-out force results were better. The same happens to tensile strength results which are shown in Figure 8. Therefore, increasing time up to 20 min has positive impact on both tensile strength and pull-out force.

3.3 Optimization of the results

According to the results of samples, it is possible to find out and predict the optimized condition for producing the best sample. Therefore, to determine the optimized sample, optimization criteria were defined as maximum tensile strength as well as pull-out force. These are desirable according to the final usage of the samples as composites. The predicted optimized conditions of production setting and related contours are presented in Table 6 and Figure 10 respectively.

4 Conclusion

In the present research, a number of innovative points have been considered that include using atmospheric pressure, jet of plasma, and the combination of inlet gases as plasma atmosphere. Atmospheric pressure plasma jet (APPJ) technique was performed to modify the surface of the PPTA fibers in order to enhance their adhesion to unsaturated polyester resins. The studied parameters were oxygen/argon volume ratio and the time of plasma treatment. The results indicated notable changes in the surface morphology and functionality of the PPTA fibers. With increasing the volume ratio of oxygen, the degradation also increased to the extent that at 20 min of treatment time, the treated fibers with the highest concentration of Oxygen were almost completely destroyed. By increasing the amount of oxygen and the duration of plasma treatment, the outer layer of the PPTA fibers was removed. With an increase in the treatment time, the crystallinity of the PPTA fibers and the surface function-

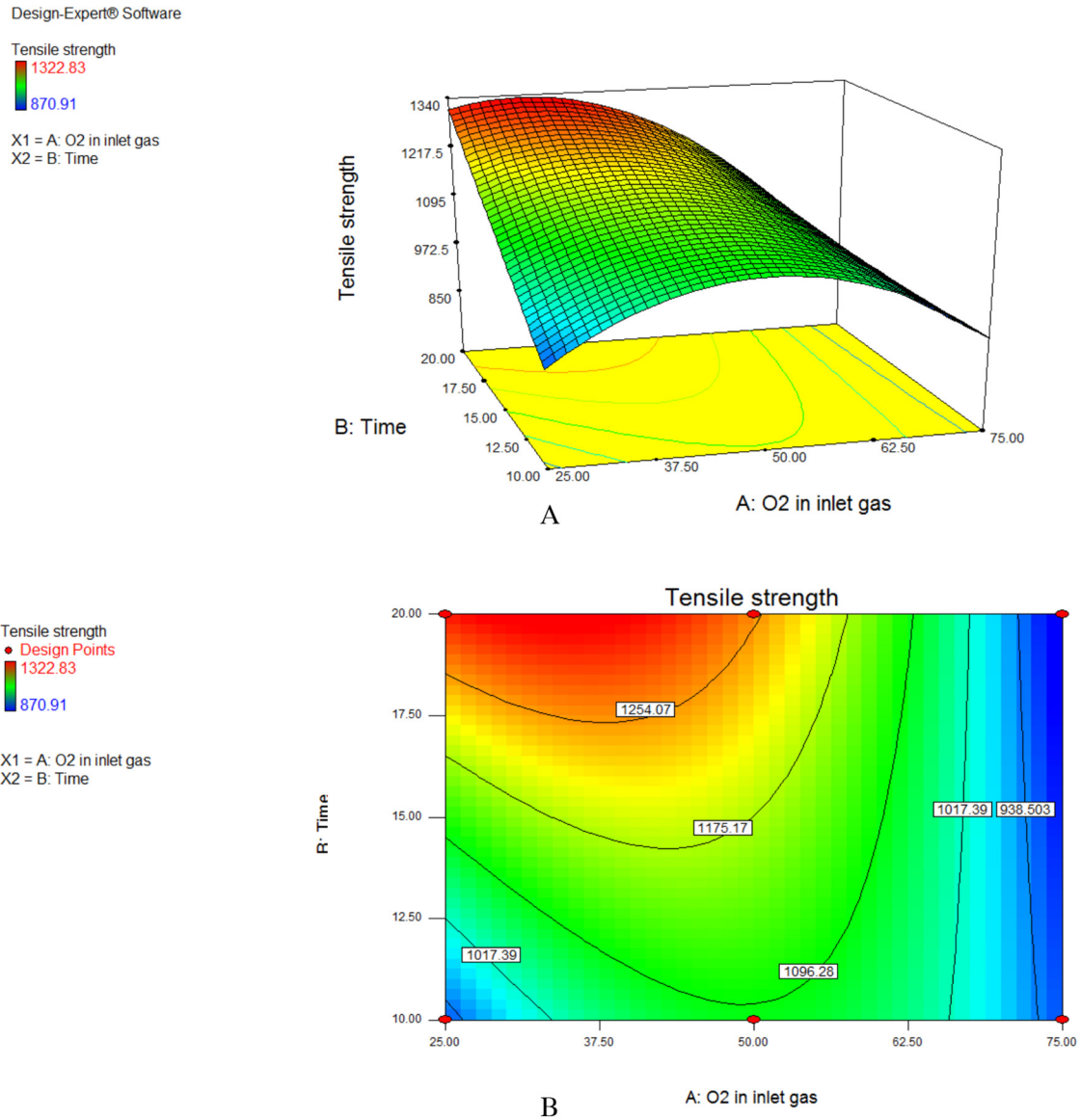


Fig. 8. 3D plot and contour of tensile strength of the plasma treated PPTA fibers (a) 3D plots (b) contours.

Table 5. Coefficients of the model for pull-out force of the plasma treated PPTA fibers in coded form.

Variables	Coefficient	Value
	β_0	+283.24
A	β_1	+74.11
B	β_2	+18.99
AB	β_3	-22.57
A_2	β_4	-137.87
B_2	β_5	0
R_2		0.9835

ality were also affected significantly. The enhancement in the surface roughness and functionality led to a better surface adhesion of the PPTA fibers to unsaturated polyester resin. Moreover, according to SEM, AFM, ATR-FTIR moisture sorption, and the mechanical results revealed that, although the plasma technique is effective on the surface of the PPTA fibers as well as bulk properties, the optimum condition of the treatment should be concerned too, because this method can reduce the mechanical properties which are important factors for the produced composites. Our study on the achieved data and optimizing them, suggests that the surface modification of the PPTA fibers with the use of atmospheric pressure plasma jet and the employment of O₂/Ar volume ratio of 45.54/54.46 for 20 min results in the best adhesion

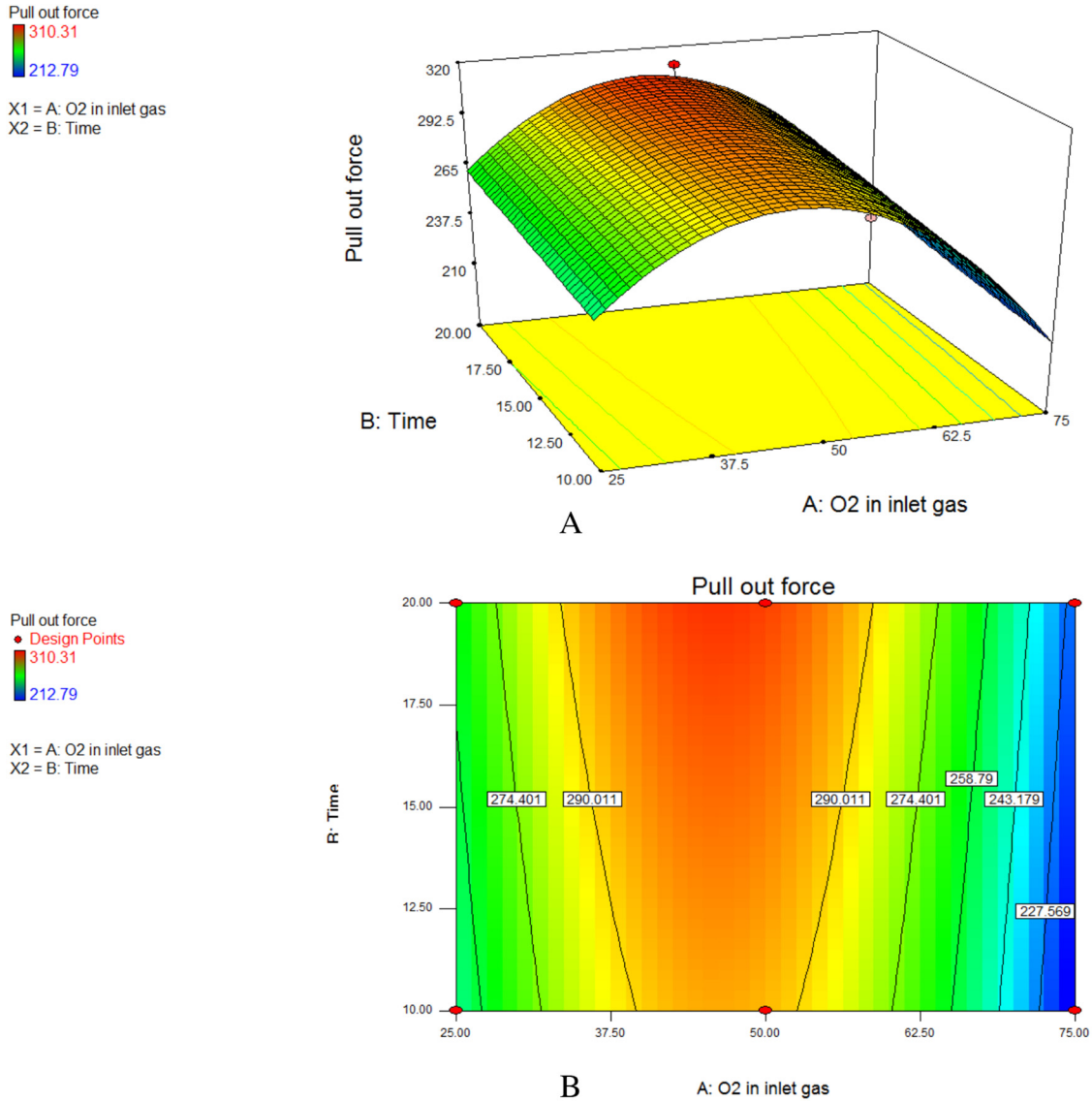


Fig. 9. 3D plot and contour of pull-out force of the plasma treated PPTA fibers (a) 3D plots (b) contours.

Table 6. Production parameters of prediction of optimized sample.

Oxygen ratio as inlet gas (%)	Time of treatment (min)	Tensile force (MPa)	Pull-out force (kN)	Desireability
40.54	20	1320.19	305.504	0.972

between the fibers and resin according to tensile strength and pull-out force results.

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Author contribution statement

In the present study, the statistical part as well as the estimation of the optimization has been done by Dr. Rahimi. Having provided the plasma treated samples and SEM images, Mr. Ebrahimi’s significant role in the

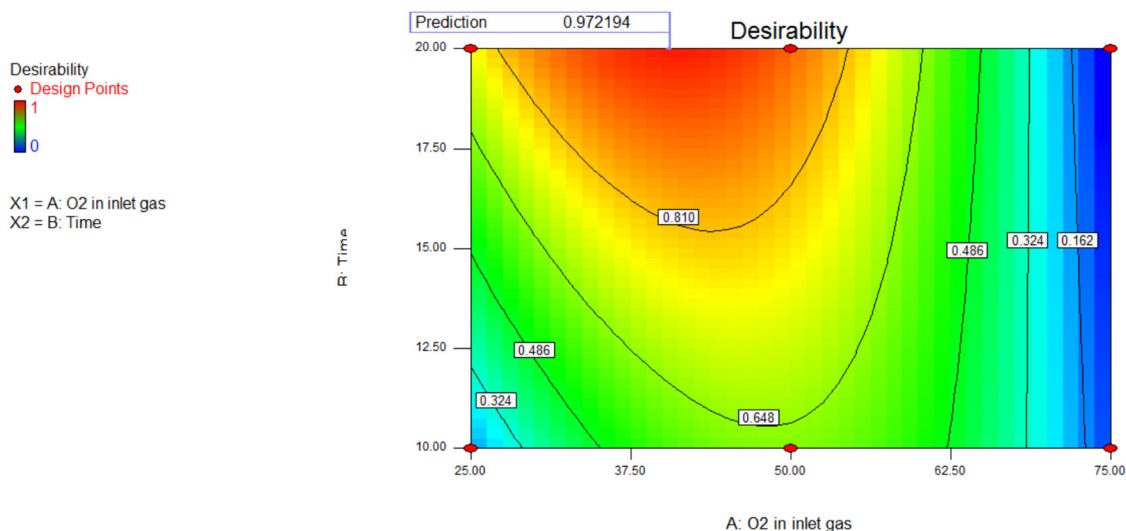


Fig. 10. Contour plot related to the optimized sample.

preparation of the curves is quite important. The preparation of the plasma treated samples for the tests, the collection of the data and tracing (drawing) charts and curves, the composition of the passage of the article, and the analysis of the data have all been accomplished by Mr. Sarafpour.

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