(REFEREED RESEARCH)

AN ECOLOGICAL APPROACH FOR THE SURFACE MODIFICATION OF ARAMID FIBERS

ARAMİD LİFLERİNİN YÜZEY MODİFİKASYONU İÇİN EKOLOJİK BİR YAKLAŞIM

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ABSTRACT

Since aramid fibers have very high crystallization degree and high chemical inertness, the surface modification is needed to enhance the adhesion between fibers and matrix for the usage of composite applications. In the present study, para-aramid fibers were treated by atmospheric pressure plasma under various plasma powers to improve interfacial adhesion between aramid fiber and epoxy resin. The surface morphologies of untreated and treated fibers were investigated by scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy. Composite interfacial adhesion properties were determined by interlaminar shear strength (ILSS) using a short-beam bending test. Results indicated that argon plasma treatment was an effective method for improving interfacial adhesion between fiber and matrix with ecological treatment.

Keywords: Aramid, atmospheric plasma, surface modification

ÖZET

Aramid lifleri yüksek kristalizasyon derecesi ve kimyasal inertliği, nedeniyle kompozit uygulamalarında lif-matriks adhezyonunu arttırmak için yüzey modifikasyonu gerekmektedir. Bu çalışmada, para-aramid lifleri aramid lifi ve epoksi reçine arasındaki adhezyonu arttırmak için farklı güçlerde plazma işlemi görmüştür. İşlem gören ve görmeyen kumaşaların yüzey morfolojileri taramalı elektron miksroskobu (SEM) ve Fourier Transform Infrared Spektroskopisi (FTIR) ile incelenmiştir. Kompozit adhezyon özelikleri, tabakalararası kayma mukavemeti (ILSS) ile analiz edilmiştir. Sonuçlar, argon plazma işleminin lif ve matriks arasındaki adhezyonu arttırmak için etkili ekolojik bir yöntem olduğunu göstermiştir.

Anahtar Kelimeler: Aramid, atmosferik plazma, yüzey modifikasyonun

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INTRODUCTION

Usage of aramid fibers attracts more attention day by day because of the fiber's unique properties and variety of usage fields. Aramid fibers, with high performance organic fibrous material most widely used in various industrial applications, offer a relatively smooth and inert surface, which limits potential chemical and/or mechanical interactions with polymeric systems [1]. Aramid fiber is a linear chain macromolecule with high crystallization, high orientation, high strength, high specific modulus and high temperature-resistance [2]. With these outstanding mechanical and thermal properties, they are widely used in aviation, automobile, shipbuilding, civil engineering, sports and many new areas such as creating highly loaded textile structures and high-strength composites, including for occupational protection and rescue equipment in extreme situations [2,3].

Since aramid fibers combine high specific modulus, high strength with high thermal resistance, high chemical inertness and low electrical conductivity, they are very suitable as reinforcements in high-performance composite materials [2,3]. Therefore, these properties make aramid fibers one of the best fibers as reinforcement for composite industry [2].On the other hand, because of high crystalline structure, the surface of aramid fiber is chemically inert and smooth. Various approaches have been developed for the surface modification of aramid fibers such as chemical and physicochemical treatments to improve the interfacial adhesion between aramid fibers and matrices and roughness on the surface for composite usage areas [4].

Conventional chemical treatments, such as surface grafting, chemical etching, polymerization are energy, time, cost intensive and also have negative effects on mechanical properties and produce large amount of waste water, organic solvents, which leads the production process environmentally unfriendly. On the other side, physical/ physicochemical treatments would be more advantageous [3,4]. Plasma technology, as a physicochemical treatment, is emerging one of the most important methods. Plasma is a totally or partially ionized gas which contains radicals, ions, photons and other excited species. By means of atom, electron bombardment and UV radiation, some new polar functional groups occur on the fiber surface without altering bulk properties of material. Surface modification by plasma does not require the use of water and chemicals, resulting in a more economical and ecological processes [3,5]. Dielectric barrier discharges (DBD) is a low temperature plasma discharge technique, which could be used under atmosphere pressure without the vacuum device, and enables the large-scale industrialization. It has important advantages compared to vacuum plasma such as high efficiency, flexibility and continuous processes [5, 6].

The aim of this study is to modify the surface properties of para-aramid (Kevlar®) fiber by argon plasma treatments for a better adhesion between fiber and polymer. The expected property can lead better and more usage properties in composites. Different powers (100, 200 and 350 W) are applied while maintaining a constant exposure time during argon atmospheric plasma treatments. The surface morphologies are investigated by scanning electron microscopy (SEM), the effects of plasma treatment on fiber adhesion properties were determined by surface friction coefficient, and pull-out and fabric tensile tests.

Experimental

Materials

Para aramid fabric (Kevlar®) was received from Dost Kimya Company, Turkey. The plain weave fabric with mass per unit area 60 g/m^2, linear density of 215 tex and thickness of 0,08 mm was used as a substrate in the experiments. The epoxy system R 1040 (unmodified liquid epoxy) and hardener R 1048, both manufactured by Resoltech (France), were chosen as the matrix. The composition for the epoxy resin system is specified in the product data sheet from the manufacturer to be (by weight): R 1040 (78%) and R 1048 (22%).

Plasma treatment

A dielectric barrier discharge (DBD) plasma system operating under atmospheric condition was used. The detailed explanation of device was given in Ref [7]. This device can be operated with rectangular or cylindrical electrodes. In this study, four cylindrical electrode pairs with three power sections were used. Each electrode pairs were placed 4 cm apart from each other. The samples (10x40 cm^2) were placed between the electrodes and passed at 100, 200, 350 W for different time intervals of 120, 240 and 480 s. In all treatments argon (99.995 % purity) was used as process gas.

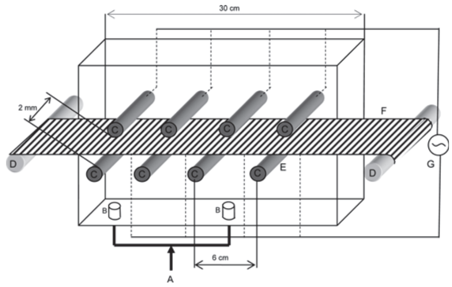

Figure 1. Laboratory scale atmospheric plasma device: A: Processing gas, B: Holes for gas entrance, C: Electrodes, D: Fabric wrapping mechanisms, E: Quartz, F: Fabric, and G: Electrical current.

Composite fabrication

The mixture of modified epoxy resin and hardener was applied onto the aramid fabric surface by means of hand lay-up technique. After that, five layers were used to fabricate laminates of 3.5mm thick. Thereafter, resulting material was compression molded at a pressure of 100 bars at room temperature for 100 min. The samples for the mechanical tests were prepared from these laminated composites according to ASTM standards.

Wettability test

To determine the wettability of fabrics, contact angle and drop tests were used for untreated and plasma treated fabrics. Contact angle measurements were made by distilled water. The equipment consists of a camera (PULNIX TM-765, UK), a computer and a monitor. The contact angles of water were measured with a sessile drop method. The images of each drop were captured by the camera connected with a computer-based image capture system. The captured images were viewed at the monitor [8].

The absorbency of fabrics was measured according to AATCC 79-1995 standard. For this aim, a drop of water was fallen from a fixed height onto the tight sample. The time required for the disappearance of water drop was recorded as wetting time [9].

Tensile test

Tensile tests were conducted by using a computer-controlled Shimadzu Autograph AG-IS Series universal testing machine, a 5-kN load cell. The tensile tests of the composites were performed according to the ASTM D-3039 standard, and the crosshead speed was 2 mm/min. System control and data analysis were preformed using Trapezium software. All mechanical tests were tested for 6 times to evaluate the repeatability.

Short Beam Shear Testing

The short beam shear test is used to calculate interlaminar shear strength (ILSS). ILSS values were determined by using a computer controlled Shimadzu AUTOGRAPH AGIS Series universal testing machine with cross-head speed of 1.3 mm/min in accordance with ASTM D2344 standard. A nominal 5:1 span to-depth ratio was used. Each specimens were width of 6.4 mm and length of 26.3 mm. The ILSS was calculated as follows:

$$ILSS = 0.75\left(\frac{P_{\max}}{bd}\right)$$

where ILSS is the maximum shear strength, Pmax was the applied load, *b* and *d* are the width and thickness of the specimen, respectively.

Surface observations

Changes on the untreated and plasma treated fabric surfaces were evaluated using scanning electron microscopy (Phillips XL-30S FEG scanning electron micro-scope). Scanning electron microscope (SEM) was operated at 2.5 kV. The surface of the fibers were coated with gold by means of a plasma sputtering apparatus. The aramid fibers were investigated at 5,000 magnification to observe the surface morphological changes caused by the plasma treatments.

Friction coefficient

To measure the kinetic friction coefficient of the fabric surface, the Frictorq instrument was used as described by Lima et al [10].

FTIR-ATR analysis

The Fourier transform infrared (FTIR) spectra of aramid fabrics were determined by means of a Perkin Elmer 100 FTIR spectrometer in the attenuated total reflectance (ATR) mode using a diamond ⁄ zinc selenide crystal. To provide a reproducible contact between the crystal faces and the fabric, a pressure of 80 kPa was applied to the crystal holder by means of a calibrated torque screw driver and an average of 10 scans were made using a resolution of 4 cm^{-1}.

RESULTS

Wettability

The contact angle values and images were given in Table 1 and Fig 2.After bombardment by argon plasma (350 W), there were physical and chemical changes on the surface of the fabric as shown by SEM and FTIR results as well.

On the fabric surface, the new polar side groups can be created in the microvoids of aramid after the plasma treatment. The side groups on the molecular chains could likely make the intermicrofibril space relatively large therefore more surface area or more bonding sites for water molecules occurs. Moreover, microvoids by plasma treatment could be penetrated and bonded to the matrix better than the untreated fabric. These results are consistent with the ILLS and pull out test results [11].

Table 1 shows that the wetting time decreases with duration of plasma treatment. 480 s plasma treated aramid fabric can be wetted very quickly as can be seen from contact angle images as well (Figure 2).

Table 1. Contact Angle and Wetting Time of Fabrics

Fabric	Mean Contact Angle (^{o})	Wetting Time (second)
Untreated	93.65	>300
120 s treated fabric	25.45	0.576
240 s treated fabric	23.63	0.192
480 s treated fabric	0	0.128

Atmospheric plasma treatments improved the surface of aramid fabrics. The plasma modification only affects a very thin, monomolecular top layer (app. 1000 A° of the surface). Lower contact angle means a higher amount of hydrophilic groups formed on the surface of the fabric and better wetting properties.

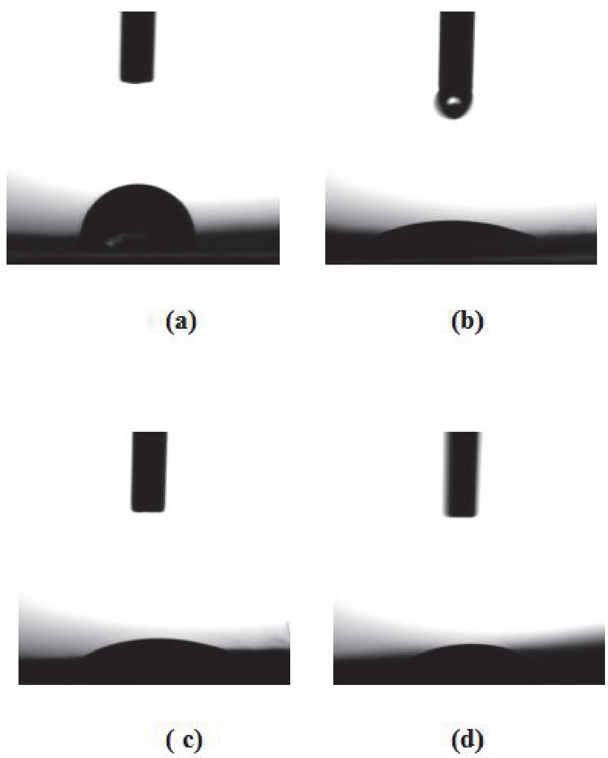

Figure 2. Contact angle images of a) Untreated b) 120 s treated c) 240 s treated d) 480 s treated aramid fabrics

The contact angle was significantly reduced from 93.65 to 25.45, 23.63 and 0 for 120 s, 240s and 480 s treatments respectively and gradually increased with increasing plasma treatment time [2].

SEM Analysis

The SEM images of untreated and treated fiber surfaces are shown in Figure 1. It is clearly apparent in the pictures that the untreated aramid fiber has a smoother surface. The microcracks and groves, because of the etching effect of plasma treatment, can be seen on the atmospheric plasma treated fiber surface [12].

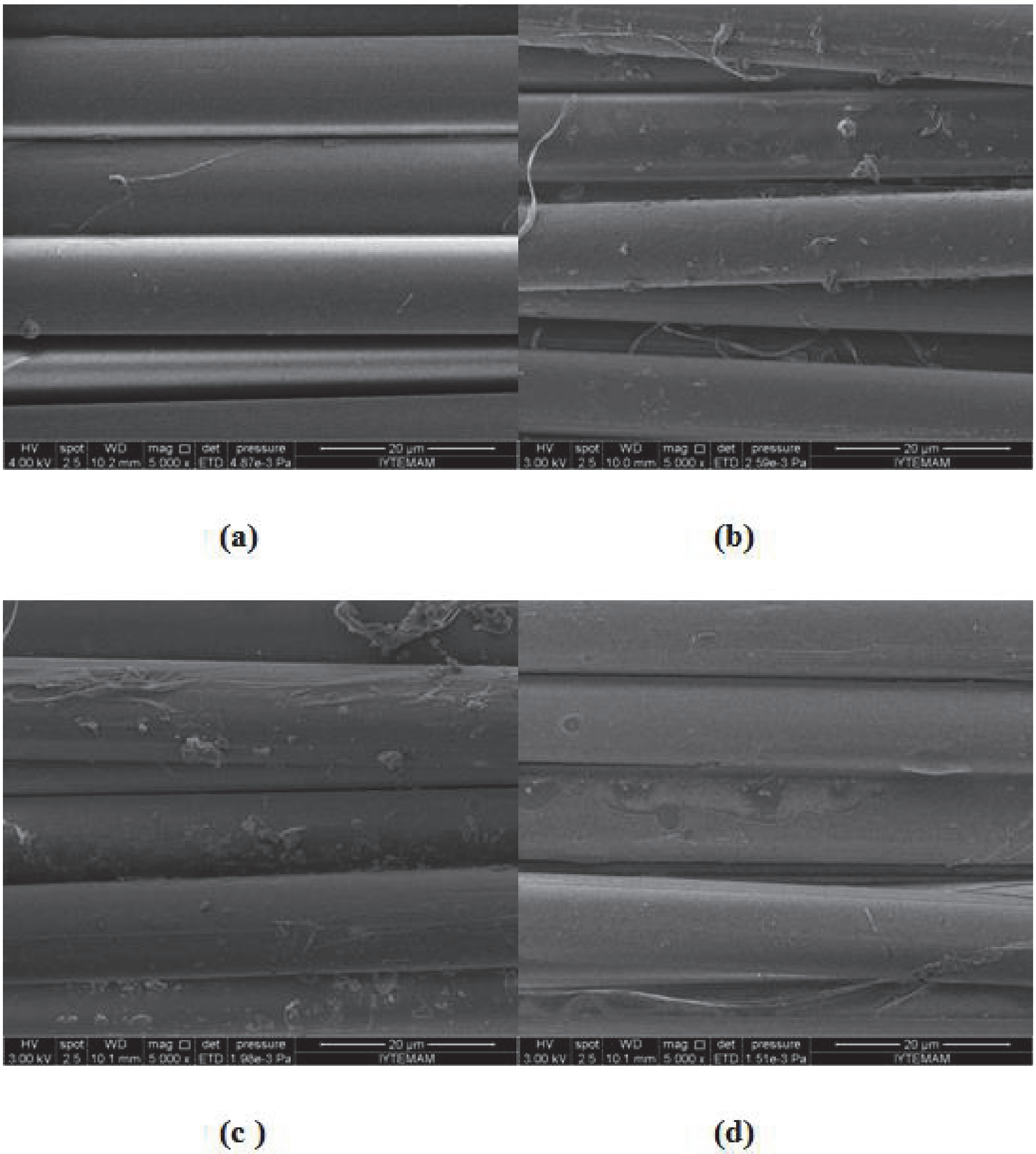

Figure 3. SEM images of a) Untreated b) 120 s treated c) 240 s treated d) 480 s treated aramid fabrics

Surface friction coefficient

Surface friction values indicate the roughness characteristic of the fabric surface. The friction coefficient values of aramid fabrics were given in Table 3. After plasma treatment, there was an obvious increase in roughness of plasma treated fabric surface in comparison with untreated one [13].

The surface friction coefficient of argon plasma treated fibers increased from 0, 2617 to 0, 4128. The values tend to increase with increasing of plasma duration because of the etching effect of the atmospheric plasma. Surface roughness and microcracks caused by ablation process were enhanced adhesive bonding by providing a mechanical interlocking effect [13].

Table 3. Surface Friction Coefficient Values of Fabrics

Sample	Surface Friction Coefficient (μ)
Untreated	0,2617
120 s treated	0,2879
240 s treated	0,2887
480 s treated	0,4128

Mechanical properties

It is well known that good mechanical properties of composites are largely controlled by the interface, which is usually required to be strong in polymer matrix composites, thus transferring load from the matrix to the fibers efficiently. The mechanical properties of the interface are characterized especially by the interlaminar shear strength [13,15].

Table 4 shows the ILSS of aramid fiber-reinforced epoxy composite as a function of exposure time. As can be seen from Table 4, the greatest value of ILSS was obtained at 350 W 480 s plasma treatments amongst all fabrics. The ILSS values increase to 39.45, 42.48 and 51.78 MPa after atmospheric argon plasma treatment for 120, 240 and 480s at 350 W, respectively.

Table 4. ILSS Values of Composites

Sample	ILSS (MPa)
Untreated	27,68
120 s treated	39,45
240 s treated	42,48
480 s treated	51,78

Table 5 and Figure 4 shows tensile strength and modulus of fabricated composites, respectively. Tensile strength of untreated aramid/epoxy composite was 454.85 MPa. After atmospheric argon plasma treatment, tensile strength of aramid/epoxy composites improved up to 19,4%. As can be seen from Table 5, the greatest tensile strength was obtained after 480 s plasma treatment.

Table 5. Tensile Strength Values of Composites

Sample	Tensile strength value (MPa)
Untreated	454,85
120 s treated	481,78
240 s treated	498,48
480 s treated	542,87

The mechanical results indicate that atmospheric argon plasma treatment improves the interfacial adhesion properties between the fiber and the matrix. Surface friction coefficient values were increased with the prolonged treatment time due to the etching effect of the atmospheric plasma. Therefore, the ILSS and tensile strength increasing can be explained by the increase of surface roughness of aramid fiber, which causes a better mechanical interlocking [13].

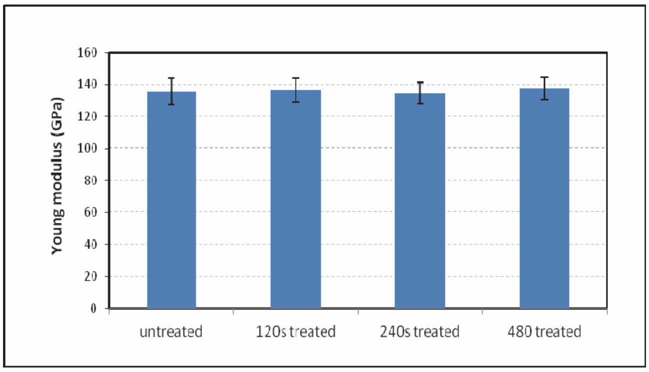

Figure 4. Young modulus of composites

As can be seen from Figure 4., tensile modulus of aramid/ polyester composites was not affected for each exposure time of plasma treatment.

FTIR analysis

FTIR measurements were performed on both the original and the atmospheric plasma treated fabrics. For all samples, the FTIR spectra in the range of 650–4000 cm^{-1} are depicted in Figure 5. Since plasma surface modification occurs only 10 nm surface while the depth of penetration of FTIR is approximately 1 μm, IR signatures are most likely dominated by the information from the unmodified bulk of polymer [16].

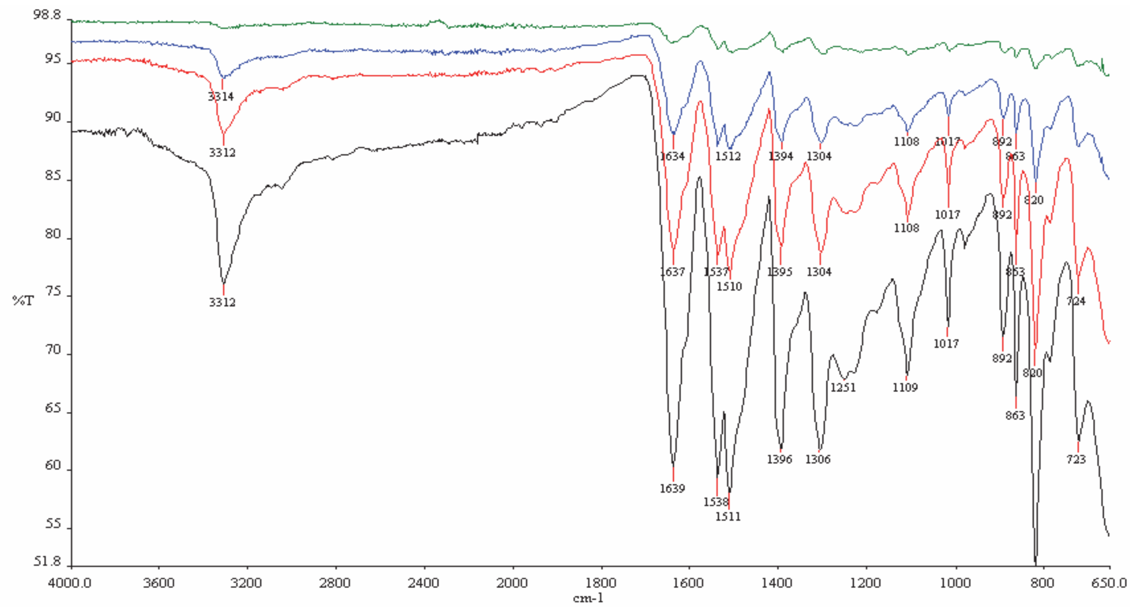

Figure 5. FTIR Spectra of untreated and plasma treated aramid fabrics

The peak at 3312 cm^{-1} is ascribed to the stretching vibration in an amide in trans with a bonded hydrogen. The wave numbers at 1637, 1534 and 1304 cm^{-1} are assigned to amide I(C¼O) in an amide stretching vibration for the hydrogen-bonded amide group, amide II (N-H deformation and C-N stretching coupled modes) and amide III (the C-N and N-H combined vibrations). The C¼C stretching vibration of the aromatic ring is 1510 cm^{-1}; 1017 cm^{-1} is assigned to in-plane C-H vibration, characteristic of para-substituted aromatic compounds, particularly polyaramids; 820 cm^{-1} is ascribed to be the out-of-plane C-H vibration of two adjacent hydrogens in an aromatic ring (para-substitution of the aromatic); 724 and 892 cm^{-1} are assigned to the out-of-plane N-H deformation modes. The FTIR spectrum profiles of these fibers are not significantly different from that of the original. A weak difference is noticed at the absorption peak located around 1251 cm^{-1}, which is assumed to be the C-N stretching and N-H deformation combined vibration in the associated state.

The peak at 3312 cm^{-1} corresponds N-H stretching vibrations in secondary amide which becomes weaker in the circumstance of 480 s treatment because the hydrogen bonds are destroyed by the plasma etching [17].

CONCLUSION

In this study, the surface of aramid fibers modified by argon plasma treatment under atmospheric conditions was investigated. The mechanical results indicate that atmospheric argon plasma treatment improves the interfacial adhesion properties between the fiber and the matrix. With the prolonged plasma treatment time, better mechanical interlocking was obtained due to the etching effect and surface roughness of aramid fiber. The improvement on surface roughness is illustrated by SEM images as well. By means of the microvoids occurred on the surface on the fibers after plasma treatment, it could be penetrated and bonded to the matrix better than the untreated fabric. The greatest value of ILSS was obtained at 350 W 480 s plasma treatments. Moreover, the tensile strength of composite increased by 19,3 % after plasma treatment. The enhancement on the chemical and physical properties by the atmospheric plasma provides the better wetting effect of treated fabrics compared to untreated ones. As can be seen from the results, plasma treatment has a great potential for the modification and functionalization of aramid fibers without affecting bulk properties of the fibers. It should be mentioned that this research was carried out at the laboratory scale. For the bulk production, a different set up and approach would be necessary in future.

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