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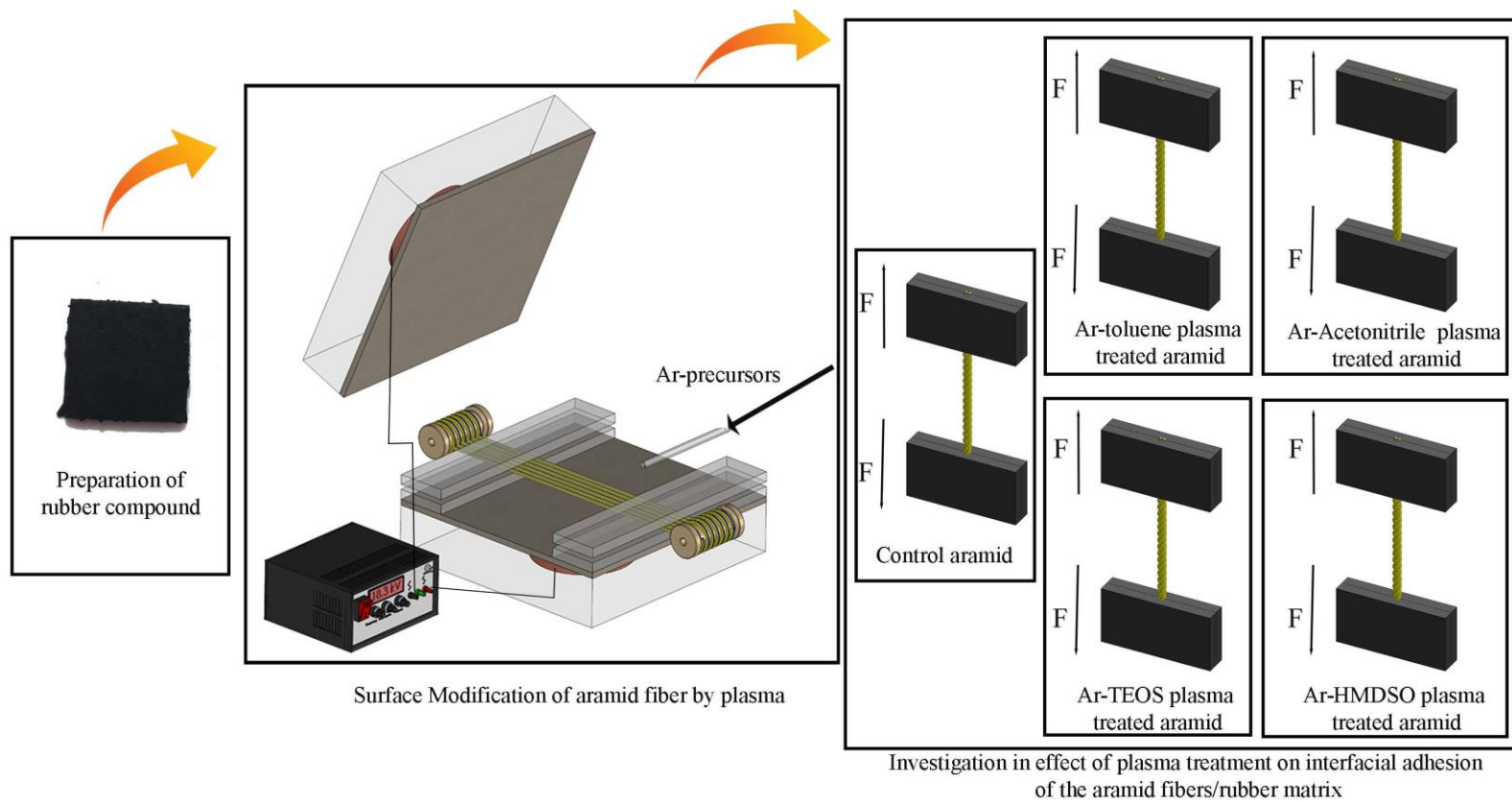
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### Graphical Abstract

1 A promising method for promoting interfacial adhesion of aramid/rubber  
2 composite using atmospheric pressure plasma surface modification

3  
4 Ehsan Shakerinasab<sup>1\*</sup>, Ensieh Poshtkouhian Bavi<sup>2</sup>, Cristina Balagna<sup>3</sup>, Monica Ferraris<sup>3</sup>

5  
6 1. Department of Atomic and Molecular Physics, Faculty of Science, University of Mazandaran,  
7 Babolsar, Iran

8 2. Department of Physics, University of North Texas, Denton, Texas 76203, USA

9 3. Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli, Abruzzi 24,  
10 Turin, Italy

11 \* **Corresponding Author:** E.Shn1400@gmail.com

12  
13 **Abstract**

14 Today, aramid fibers are well known as a high-performance and ideal material for reinforcement  
15 purposes in rubber product manufacturing including hoses, tires, cables, and conveyors  
16 composites. However, surface modification of aramid fiber is necessary to solve poor interfacial  
17 adhesion between aramid fibers and the rubber matrix. Accordingly, in the present study, the effect  
18 of the surface modification of aramid fibers using atmospheric pressure plasma treatment with  
19 different precursors on adhesion to the rubber matrix was investigated. For that, the plasma coating  
20 was conducted using argon as the main working gas, and toluene, acetonitrile, tetraethyl  
21 orthosilicate (TEOS), and hexamethyldisiloxane (HMDSO) as liquid precursors. The physical-  
22 chemical characterization of the layer confirmed the successful deposition of amorphous carbon,  
23 amorphous nitride-carbon, SiO<sub>2</sub>, and Polydimethylsiloxane (PDMS)-like coating layers on the  
24 surface of aramid fibers by using toluene, acetonitrile, TEOS, and HMDSO as precursors  
25 respectively. Overall, the result showed that the plasma surface modifications with acetonitrile  
26 precursor leads to the increase in interfacial adhesion of aramid/rubber composite, while retaining  
27 the tensile strength, and flame resistance properties of aramid as original fibers. Notably, the results  
28 of this study confirm the potential use of atmospheric pressure plasma for surface modification of  
29 aramid yarn to produce functional aramid for use in rubber composites.

30 **Keywords:** aramid fiber, rubber matrix, composites, plasma

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### **Highlights**

- The plasma-coated aramid using HMDSO, TEOS, toluene, and acetonitrile precursors was prepared, and its effect on the tensile properties of aramid fiber as well as interfacial adhesion between aramid/rubber composite was investigated.
- The positive effect of atmospheric pressure plasma coating using HMDSO precursor on the tensile properties of aramid fiber was revealed.
- The positive effect of atmospheric pressure plasma coating using toluene and acetonitrile on the interfacial adhesion between aramid/rubber composite was revealed.
- The positive effect of atmospheric pressure plasma coating using TEOS precursor on the flam resistance property of aramid fiber was revealed.
- This study provides valuable insights into the effect of the different plasma-coated organosilicon and hydrocarbon precursors on the interfacial adhesion between aramid/rubber composite.

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### **1. Introduction**

52 Nowadays, aramid fibers are well known as a high-performance material in various fields and  
53 industries, because of their promising properties including high mechanical strength, flame  
54 resistance properties, high tenacity, lightweight, and so on. Also in the composite field, aramid  
55 fiber is well known as reinforcement material for production of high-performance composites  
56 One of the important reinforcement applications of aramid fibers in high-performance composites  
57 productions is for rubber products manufacturing including hoses, tires, cables, and conveyors in  
58 the rubber manufacturing industry. This is because of the light weight of the aramid fibers followed  
59 by high specific strength, high specific modulus, and low density [1].  
60 However, the poor compatibility between aramid fibers and rubber matrixes, which is due to the  
61 chemical inertness, high crystallinity, and high smooth surface properties of aramid fibers  
62 restricted its application in the rubber industry. Thus, currently, the whole potential of the aramid  
63 fiber is not yet utilized [2-4].

64 Different surface modification techniques have been developed to promote the adhesion between  
65 aramid fiber and rubber matrix [5-11]. These methods include the coating method[12], chemical  
66 grafting[13], surface construction of nanostructures[14-16], and plasma treatment[17-19]. The  
67 purpose of all of them is to increase the surface roughness and improve the surface chemical  
68 activity, which will result in excellent mechanical interlocking and chemical bonding between  
69 aramid fiber and matrix [20]. *Zhang et al.* investigate the effects of the surface coating of aramid  
70 fiber with graphene/aramid to enhance interfacial adhesion to rubber matrix. The results of this  
71 study show the enhancement in interfacial adhesion of aramid fibers to rubber composite followed  
72 by maintaining the mechanical properties [2]. *Yang et al.* investigate the effect of the grafting  
73 hyperbranched polysiloxane of aramid fibers in increase adhesion to rubber matrix. The results  
74 show that this surface modification method can increase the interfacial adhesion of aramid fibers  
75 to rubbers matrix [6].

76 Among the different methods for surface modification of aramid fiber to improve its surface  
77 activity, the atmospheric pressure plasma is a known as a promising powerful approach [21, 22].  
78 The process is single-step, cost-effective, simple, and environmentally friendly that can be  
79 operated at room temperature. Non-thermal plasma processing is a dry approach that does not  
80 require large quantities of toxic chemical materials and water during the treatment process. Also,  
81 the process is a surface modification approach. It means that, by the plasma processing, only the  
82 surface properties of the samples are treated while bulk properties remain unchanged [23, 24]. So,  
83 the plasma processing can be used as a powerful approach for surface modification of aramid fiber  
84 to enhance interfacial adhesion of fibers to rubber matrix for composite production. However, the  
85 potential use of plasma processing for surface modification of aramid for rubber composite  
86 application was rarely investigated. Also, the effect of atmospheric pressure plasma coating on  
87 interfacial adhesion of aramid/rubber composite is not investigated before.

88 In the current study, we investigated the effect of the atmospheric pressure plasma coating with  
89 different precursors for surface modification of aramid fiber to increase the adhesion to rubber  
90 matrix. More precisely, in the first step, conventional atmospheric pressure dielectric barrier  
91 discharge (DBD) plasma with argon as the working gas and four different liquid precursors were  
92 used to surface modification of aramid fibers. In the second step, a rubber matrix with pre-defined  
93 precursors was fabricated. In the final step, a rubber matrix aramid composite was fabricated and

94 the effect of the plasma surface modification of aramid fiber on adhesion to aramid to rubber matrix  
95 was investigated.

96 Besides, the effect of the plasma treatment with different precursors on the formation of different  
97 chemical structures on the surface of aramid yarn was fully investigated. Regarding results about  
98 the plasma treatment of aramid fibers by different precursors, different surface chemical structures  
99 form on the surface of aramid fibers that induce different functionality to it. Overall, this process  
100 can improve the mechanical strength and of the fibers. Moreover, based on the achieved results,  
101 the plasma surface modification of aramid fibers can lead to the adhesion of aramid fiber to rubber  
102 matrix. This makes it suitable for reinforcement and flame resistance applications in different  
103 industries.

104 In summary, in this study, the application and advantage of using atmospheric pressure DBD  
105 plasma for surface modification of aramid fibers for rubber application was investigated and  
106 proved. The results promise the use of atmospheric pressure plasma for textile industries and  
107 joining application.

108 **2. Materials and Methods**

109 **2.1 Plasma surface coating on aramid fiber**

110 In this work, a conventional atmospheric pressure dielectric barrier discharge (DBD) plasma was  
111 employed as a plasma source for the surface treatment of aramid fibers. The upper and lower  
112 electrodes of the DBD system are cylindrical with a diameter of 5 cm, and both of its covered with  
113 0.5 mm thickness PTFE dielectric. Also, the ignition gap is fixed at 4 mm.

114 An argon gas with a purity of 99.9 was used as the feed gas for the ignition of the plasma. The  
115 feed gas goes through liquid precursors, during its pass to the ignition gap, including tetraethyl  
116 orthosilicate (TEOS), hexamethyldisiloxane (HMDSO), toluene, and acetonitrile to insert  
117 organosilicon and hydrocarbon precursors into the system.

118 For the treatment of aramid fibers, the fiber was inserted between the two electrodes by winding  
119 the device at an adjustable speed, and exited from the other sides. The plasma conditions and  
120 experimental parameters for the treatment of the fibers are listed in the Table1.

121 It should be noted that, before the treatment, the substrates were ultrasonically cleaned with  
122 acetone 99%, ethanol 99%, and deionized water respectively, each one for 10 min, and dried under  
123 atmospheric pressure.

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**Table1.** Plasma deposition condition on aramid fiber

Sample name	Deposition time (min)	Ar flow rate ( $\frac{L}{min}$ )	Plasma power (W)
Pristine aramid fiber	10	1.5	26
Ar/TEOS coated aramid fiber	10	1.5	26
Ar/HMDSO coated aramid fiber	10	1.5	26
Ar/toluene coated aramid fiber	10	1.5	26
A/acetonitrile coated aramid fiber	10	1.5	26

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## 2.2 Preparation of aramid/rubber composite

130 The rubber compounds were prepared by mixing the ingredients according to the rubber formula  
131 detailed in Table 1 in an internal mixer device (50 cc, Brabender, Germany). For this purpose, in  
132 the first step Styrene Butadiene Rubber 1520 and Standard 10 Malaysian rubber were mixed for 1  
133 min in an internal mixer. In step two, Antioxidant 4020 (6PPD), zinc oxide, coumarone indene  
134 resin, stearic acid, Adhesive (RS) and Accelerant (CZ) were mixed for 5 min; in step three, carbon  
135 black, white carbon black and Aromatic oil 840 were added to mix for 3 min; and finally, in step  
136 four, sulphur and rubber adhesive (RA) were mixed for 1 min. All the tests were performed at 80  
137 C.

138 After the preparations of the rubber composite, the mixture is compressed into rubber sheets with  
139 a 5 mm diameter by two roll mills. Afterward, two sheets were placed in the mold and the aramid  
140 was embedded between them. The mold was pressed at 140 °C for 45 min under 20 MP pressure.  
141 The process is schematically presented in Fig 1a.

142

**Table 2.** the rubber compounding materials

Ingredients	Parts per hundreds of rubbers (Pehr)
1 Styrene Butadiene Rubber 1520	70
2 Standard 10 Malaysian rubber	30
3 Carbon black N330	25

4	Aromatic oil 840	10
5	White carbon black	10
6	Coumarone-indene resin	10
7	Zinc oxide	5
8	Antioxidant 4020(6PPD)	4
9	Stearic acid	2
10	Accelerant (CZ)	1.5
11	Sulphur	1
12	Adhesive (RA)	1
13	Adhesive (RS)	1
	Total	170.5

143

### 144 **2.3 Physical and Chemical Characterizations**

145 First, the morphological characterization of the sample was performed by Field-emission scanning  
 146 electron microscopy (FE-SEM) method. The test was assessed by a ZEISS Field Emission SEM  
 147 device equipped with dispersive X-ray spectroscopy (EDS) and Map analysis.

148 Then, the chemical characterization was performed by Fourier transforms infrared (FTIR), Raman  
 149 spectroscopy, X-ray diffraction (XRD) analysis, and X-ray photoelectron spectroscopy (XPS).  
 150 The FTIR analysis was performed using the attenuated total reflectance (ATR) mode of Thermo-  
 151 Nicolet Avatar 380 FTIR spectrometer in the range of 4000-600cm<sup>-1</sup>. XRD analysis was  
 152 conducted using Philips PW1730 an X-ray diffractometer in the range of 10-85 °C with the step  
 153 of 0.05 °s. We used the radiation source of Cu K $\alpha$  in 1.542 Å wavelength. The Raman spectra  
 154 were performed by TakRam N1-Raman analyzer in 532 nm excitation wavelength. XPS analysis  
 155 was conducted by Phi 5000 Versa Probe<sup>TM</sup> XPS device.

156 Finally, thermal analysis was performed by Thermo-gravimetric analysis (TGA). TGA was  
 157 performed to investigate the thermal decomposition of the uncoated and plasma-coated aramid  
 158 fiber using NETZSCH's STA 2500 instrument. The temperature range was 30–800 °C and the  
 159 heating rate was 10 °C/min. The experiment was carried out in the ambient atmosphere.

### 160 **2.4 Mechanical Performance**

161 The effect of the plasma surface coating by different precursors on the mechanical performance of  
 162 aramid fiber was investigated using a breaking strength test. For that, a Micro 350, Shirley  
 163 universal testing machine with a gauge length of 500 mm was conducted.

164 Before the test, a TSH006 TST counts denier textile reeling length measuring instrument was used  
 165 to measure the denier of the fibers. The specific stress was calculated by converting the denier unit  
 166 to tex and using the equation below.

$$\text{Specific Stress (Force per unit linear density)} = \frac{\text{Maximum force required for fiber breakdowns}}{\text{fiber tex}} \left( \frac{\text{N}}{\text{tex}} \right)$$

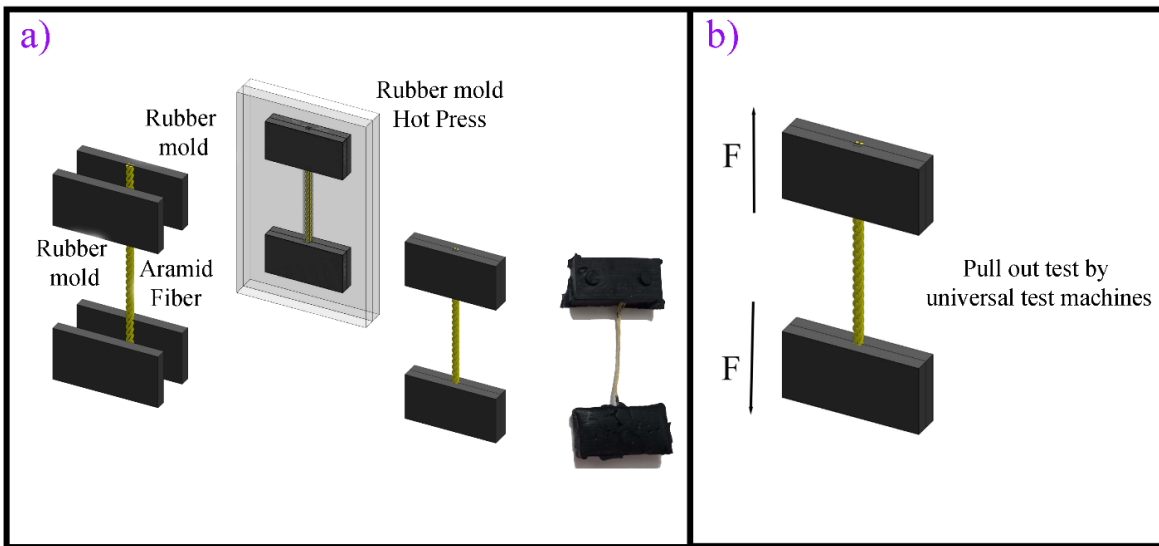
Denier = Weight per gram of 9000 meter or 9 km of yarn

Tex = Weight per gram of 1000 meter or 1 km of yarn

167 Finally, the specific stress versus strain diagram was used for comparing uncoated and plasma-  
 168 coated aramid fiber by different precursors.

### 169 2.5 Pull out test

170 The interfacial adhesion of aramid yarn to rubber matrix was investigated by the pull-out test. For  
 171 this purpose, the pull-out test was conducted on previously produced aramid/rubber composite. we  
 172 used of Shirley micro X350 universal testing machine with an adjusted speed of 3 mm per minute.  
 173 The process is schematically displayed in Fig 1b. The analysis was performed on 10 repeats to  
 174 ensure accuracy, and the average amount of maximum pull-out force was calculated.



175  
 176 **Fig 1.** a) schematics of the process for aramid rubber compound production b) Structure of pull-out test  
 177

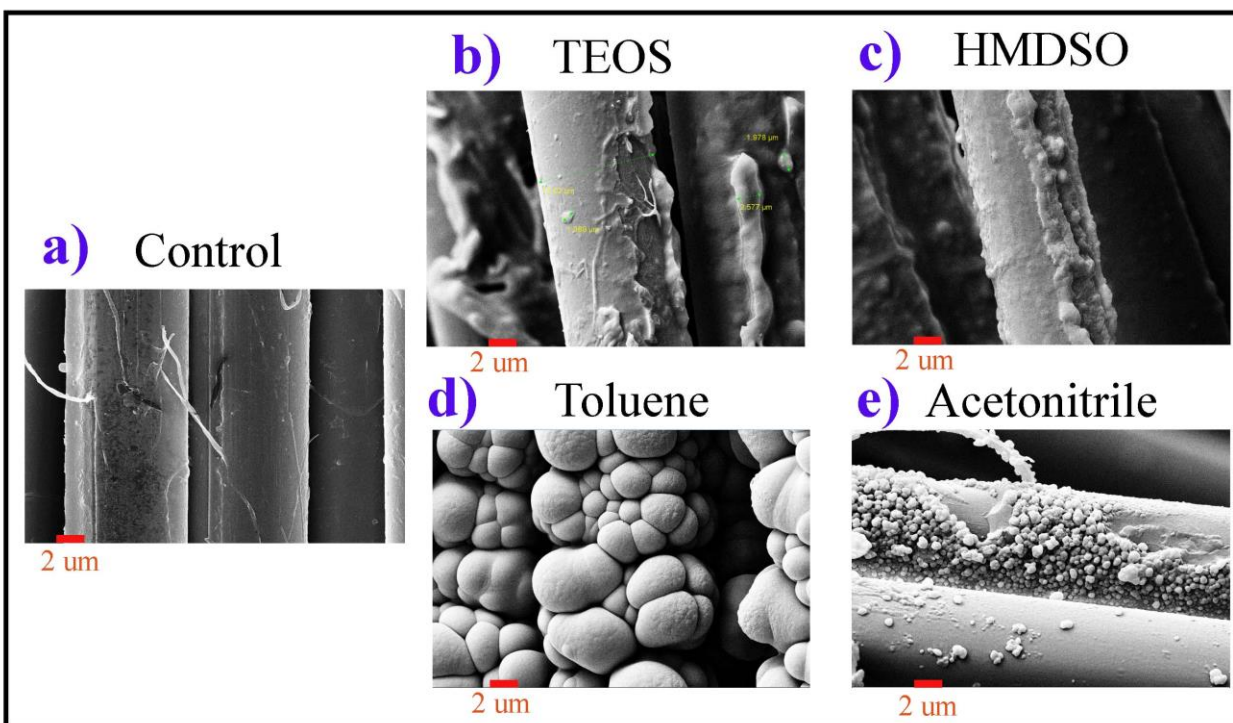
## 178 3. Results and discussions

### 179 3.1 Structural characterization

180 Fig 2 shows the FESEM images of uncoated and plasma-coated aramid fibers. As can be seen in  
 181 the figure, the uncoated aramid fibers show a completely smooth surface without any striations

182 and longitudinal markings on its surface. In contrast, plasma surface coated aramid fiber by  
183 different precursors shows completely different structures. Based on the results, the plasma  
184 treatment with different precursors lead to the formation of nanostructures with different  
185 configurations on the surface of the aramid.

186 Also, based on the results, a nano-sphere particle layer entirely covered the surfaces of the aramid  
187 by plasma surface coating with hydrocarbon precursors, while, the treatments by organosilicon  
188 precursors lead to forming a thick nearly smooth layer on the surfaces. However, the diameter of  
189 the nanosphere formed on the surface of toluene-coated aramid is very higher than that of  
190 acetonitrile-coated fiber. The first is at around 100 nm and the second at 2  $\mu\text{m}$ . This result is may  
191 be related to the easier degradation of toluene in plasma[25].



192  
193 **Fig 2.** FESEM images of a) uncoated and plasma-coated aramid fiber using b) TEOS c) HMDSO d)  
194 toluene e) Acetonitrile precursors at 2 $\mu\text{m}$  magnification  
195

### 196 3.2 Chemical structures and compositions

197 The ATR-FTIR analysis was employed to measure the changes in chemical structure of aramid  
198 fiber after the plasma coating (Fig. 3). It should be noted that, all spectra normalized based on the  
199 band at 820  $\text{cm}^{-1}$ . This bond is related to out-of-plane bending of the C-H of aromatic ring in the  
200 backbone structure of the aramid fiber, which is a main characteristic peak of the aramid. Also,

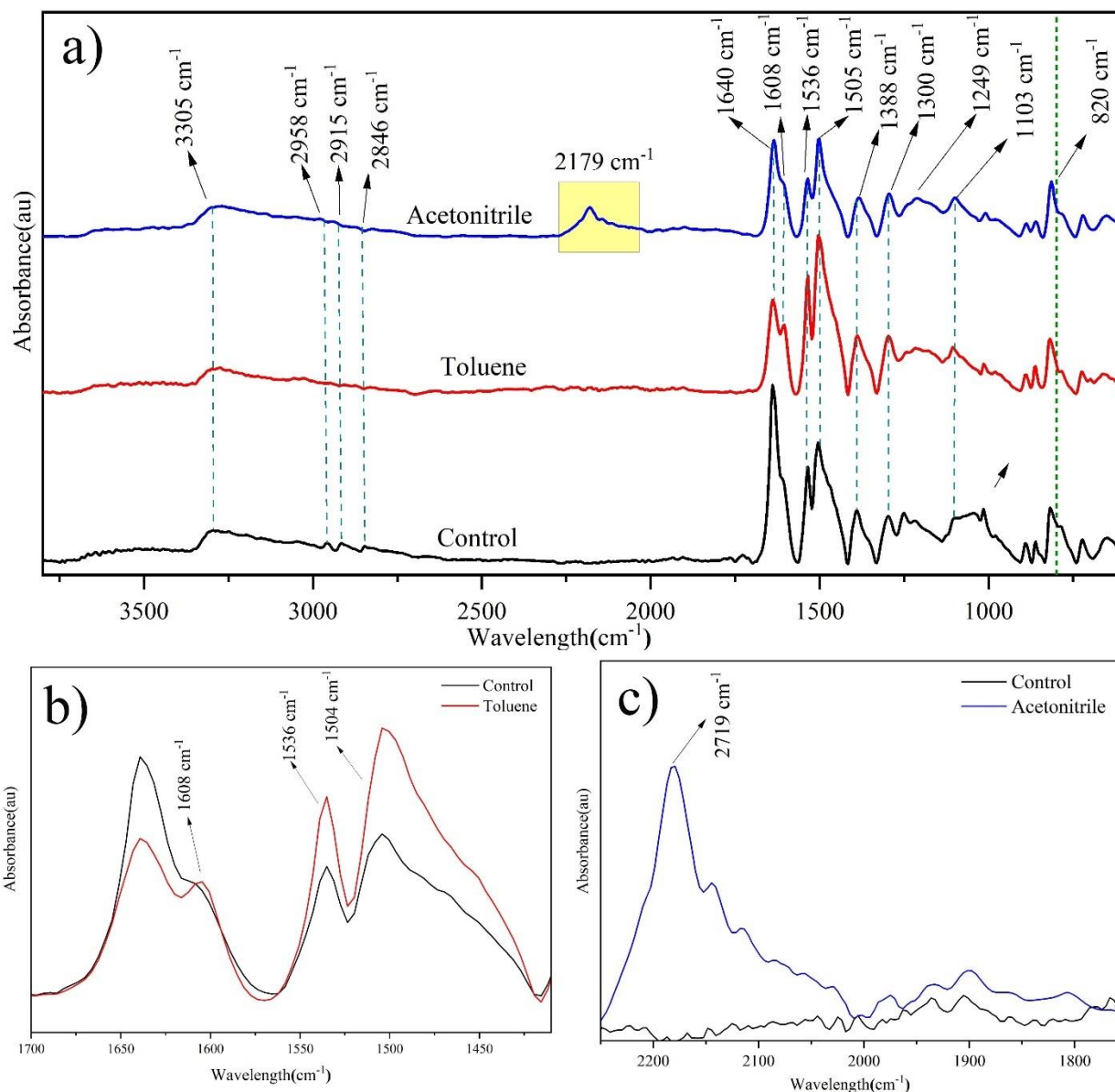
201 the intensity of this peak does not have considerable variations upon the treatment of the aramid  
202 fiber [26].

203 The full-length spectrum of uncoated and plasma coated aramid fibers using toluene, and  
204 acetonitrile precursors displayed in Fig 3a. As can be seen in this figure, these samples display  
205 similar spectra and similar bonds comparing to uncoated aramid fibers. The main chemical bond  
206 of uncoated aramid fiber is listed in Table 3. This bands are included the aromatic C-H out of  
207 plane bends, -C-N stretching (primary amine), -NH- and C-C vibration, Amide III (C-N stretching,  
208 -NH- bending), C-C vibrational in benzene skeleton, Amid II (C-N stretching, N-H bending),  
209 amide I band (C=O Stretching), C-H stretching, amid A (N-H stretching) and N-H stretching at  
210 818, 1103, 1249, 1300, 1388, 1505, 1536, 1640, 2846, 2915, 2958, and 3305  $\text{cm}^{-1}$ , respectively  
211 [8, 27]. However, based on the plasma treatment with different precursors, some changes happened  
212 in band intensity and position and some new chemical bonds appeared.

213 Fig. 3b, c shows the FTIR spectrum of uncoated and plasma-coated aramid fiber by toluene and  
214 acetonitrile precursors, respectively. As can be seen from the results, after the plasma depositions  
215 by toluene precursors, one shoulder peak was added at the position of 1608  $\text{cm}^{-1}$  as depicted in Fig  
216 3b. This peak is related to C=C stretching groups. Also, the peaks at 1504  $\text{cm}^{-1}$  and 1535  $\text{cm}^{-1}$  grew  
217 upon the plasma treatments by toluene precursors which indicates the formation of C-H stretching  
218 bonds on the surface of the aramid yarns. The results indicate in deposition of amorphous carbon-  
219 containing groups on the surface of aramid fibers [28, 29].

220 Also, based on plasma treatment by acetonitrile precursors, one broad peak with high intensity  
221 appeared between 2200 to 2400  $\text{cm}^{-1}$  with a center of 2179  $\text{cm}^{-1}$  as depicted in Fig. 3c. This peak  
222 is characteristic of the C=N stretching mode bond, which arises from the electron decomposition  
223 of acetonitrile in plasma and deposition of the C=N group. The results indicated in the deposition  
224 of amorphous carbon nitride groups on the surface of aramid fibers [30-33].

225



226  
 227 **Fig 3.** (a) Full-range FTIR spectra of the uncoated and plasma-coated aramid fiber with toluene and  
 228 acetonitrile precursors (b) overlay view of plasma coated sample with toluene precursor within the ranges  
 229 of 1420 to 1700  $\text{cm}^{-1}$ , (c) overlay view of plasma coated sample with acetonitrile precursor within the  
 230 ranges of 1720 to 2250  $\text{cm}^{-1}$   
 231

232 **Table 3.** The FTIR chemical band of the uncoated and plasma-coated aramid fiber [8, 27]

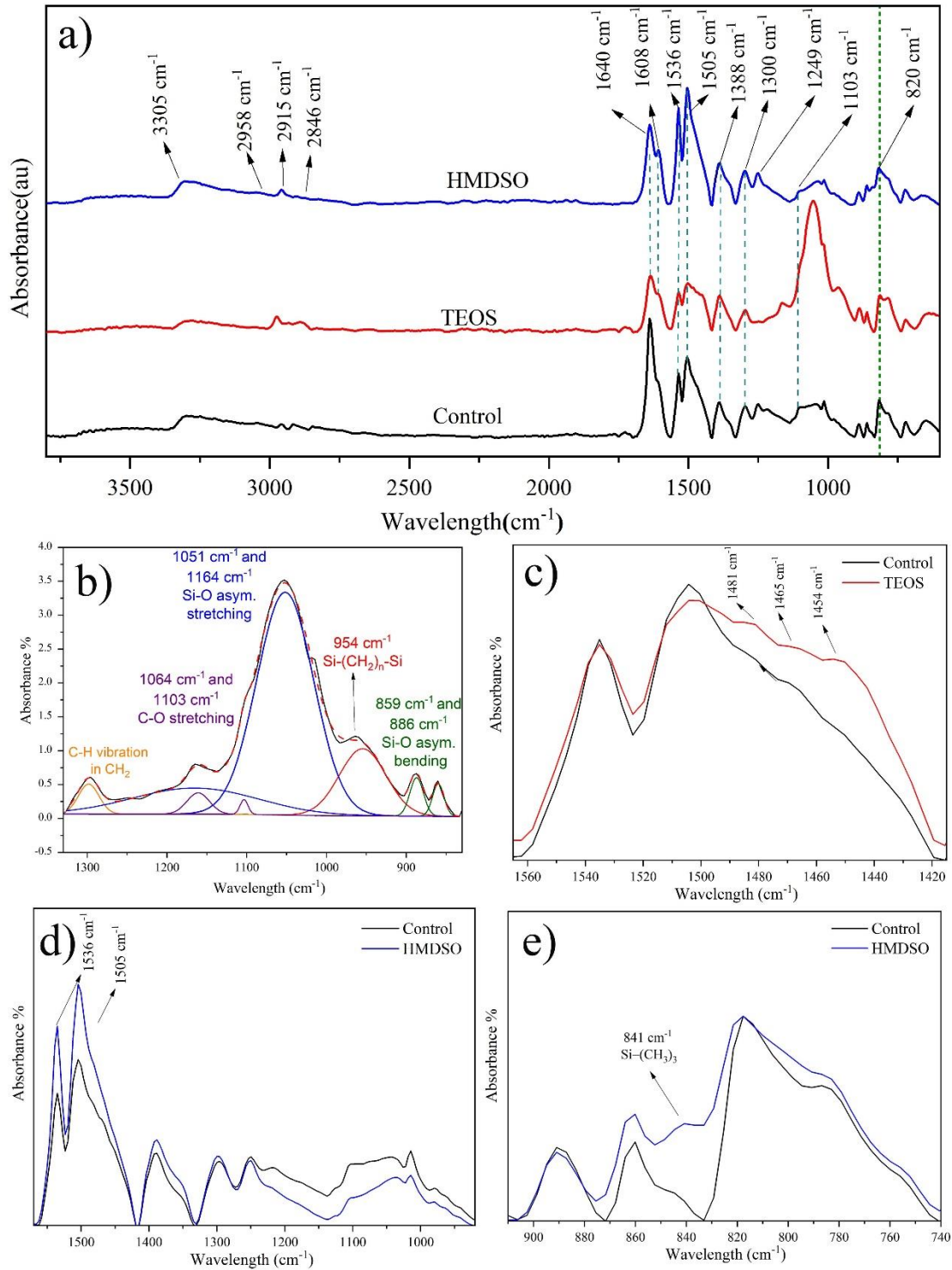
Wavelength ( $\text{cm}^{-1}$ )	Assignments
818	Aromatic C-H out of plan bends
1103	-C-N stretching (primary amine), -NH- and C-C vibration

1249	Amide III (C-N stretching, -NH- bending)
1300	
1388	C-C vibrational in benzene skeleton
1505	
1536	Amid II (C-N stretching, N-H bending)
1640	Amide I band (C=O Stretching)
2846	C-H stretching
2915	
2958	
3305	Amid A (N-H stretching)

233

234 Fig 4a shows the FTIR spectrum of uncoated and plasma-coated aramid fiber by TEOS and  
235 HMDSO precursors. As can be seen from the results, after the plasma depositions by TEOS  
236 precursors, the peak between 830 to 1330  $\text{cm}^{-1}$  incrementally grew. These peaks with a center of  
237 1051  $\text{cm}^{-1}$  are the characteristic peak of Si-O-Si groups. For further investigation, a Gaussian fit  
238 was performed in the range of 830 to 1330  $\text{cm}^{-1}$  shown in Fig. 4b. The corresponding peaks were  
239 detailed in Table 4. Based on the results, the deconvoluted spectrum contains Si-O asymmetrical  
240 bending, Si-(CH<sub>2</sub>)<sub>n</sub>-Si, Si-O asymmetrical stretching, C-O stretching, Si-O asymmetrical  
241 stretching, and C-H vibration in CH<sub>2</sub> bonds at 859.8, 886.93, 954.53, 1051.7, 1103.3, 1160.7,  
242 1164.81, and 1298.16  $\text{cm}^{-1}$ , respectively. Also, as can be seen in Fig 4c three peaks at 1454, 1465,  
243 and 1481  $\text{cm}^{-1}$  appeared which is the characteristic peak of C=C stretching bonds. All the results  
244 indicated the formation of a SiO<sub>2</sub> layer on the surface of the aramid fibers [32, 34-36].  
245 Finally, plasma coating with HMDSO precursors leads to the intense change in the FTIR spectrum  
246 that is indicated in Fig 4d-e. The main changes depicted in Fig 4d plasma coated spectrum with  
247 HMDSO precursor included the growth of peak at 1504, and 1535  $\text{cm}^{-1}$  related to C-H stretching  
248 bonds. Also, one shoulder peak was added at the position of 841  $\text{cm}^{-1}$  as depicted in Fig 4b. This  
249 peak is related Si-(CH<sub>3</sub>)<sub>3</sub> groups. The results indicate the formation of SiC film on the surface of  
250 aramid fibers by the plasma treatment. [37, 38].

251



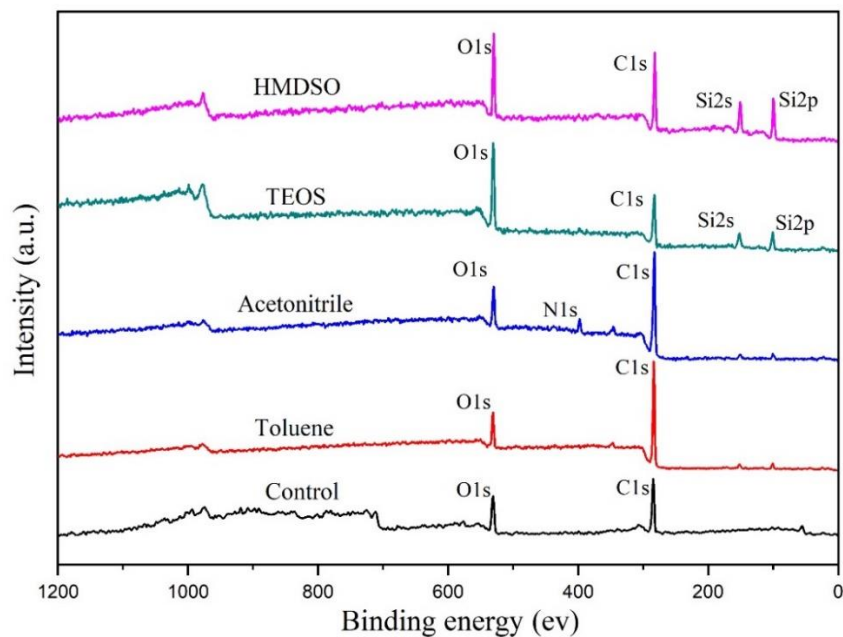
**Fig 4.** (a) Full-range FTIR spectra of the uncoated and plasma-coated aramid fiber with TEOS and HMDSO precursors, overlay view of plasma coated sample with TEOS precursor within the ranges of b) 830 to 1330 cm<sup>-1</sup> c) 1410 to 1570 cm<sup>-1</sup>, overlay view of plasma coated sample with HMDSO precursor within the ranges of d) 920 to 1570 cm<sup>-1</sup> e) 740 to 920 cm<sup>-1</sup>

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258 **Table 4.** Peak assignment of Gaussian fitting curves for FTIR spectrum of plasma coated sample with  
 259 TEOS precursor in the range of 830 to 1330  $\text{cm}^{-1}$  [32, 34-36].

Vibrational mode	Wavenumber ( $\text{cm}^{-1}$ )	Integration area	FWHM	Peak intensity
Si-O asymmetrical bending	859.9	8.5	16.9	0.48
Si-O asymmetrical bending	886.9	12.1	20.1	0.57
Si-(CH <sub>2</sub> ) <sub>n</sub> -Si	954.5	72.8	68.9	0.99
Si-O asymmetrical stretching	1051.7	294.2	84.1	3.28
C-O stretching	1103.4	2.7	11.6	0.22
C-O stretching	1160.8	11.1	33.2	0.31
Si-O asymmetrical stretching	1164.8	74.4	184.8	0.38
C-H vibration in CH <sub>2</sub>	1298.2	14.1	30.3	0.44

260  
 261 To acquire additional insight into the deposited layer, an XPS analysis was performed on the  
 262 samples surface. The survey spectrum of the uncoated and plasma-coated aramid fiber is depicted  
 263 in Fig 5. The results indicate the present of carbon, oxygen, nitrogen, and silicon atoms in different  
 264 samples whose composition and elemental ratios are presented in Table 5.



265  
 266 **Fig 5.** XPS survey spectrum of uncoated and plasma coated aramid fiber with different precursors.  
 267

268 **Table 5.** Atomic ratio of the carbon, oxygen, nitrogen, and silicon elements of the uncoated and plasma-  
 269 coated aramid fiber

	C	O	N	Si <sub>2</sub> S	Si <sub>2</sub> P	C/O	C/N	Si/C	Si/O
	(%)	(%)	(%)	(%)	(%)				
Control	57.24	38.69	4.06	0.00	0.00	1.48	14.08	0.00	0.00
Toluene	73.96	24.41	1.63	0.00	0.00	3.03	45.37	0.00	0.00
Acetonitrile	63.29	25.95	10.76	0.00	0.00	2.44	5.88	0.00	0.00
TEOS	45.96	28.62	4.81	9.34	11.26	1.61	9.55	0.45	0.72
HMDSO	33.85	31.70	4.09	12.14	18.49	1.07	8.28	0.90	0.97

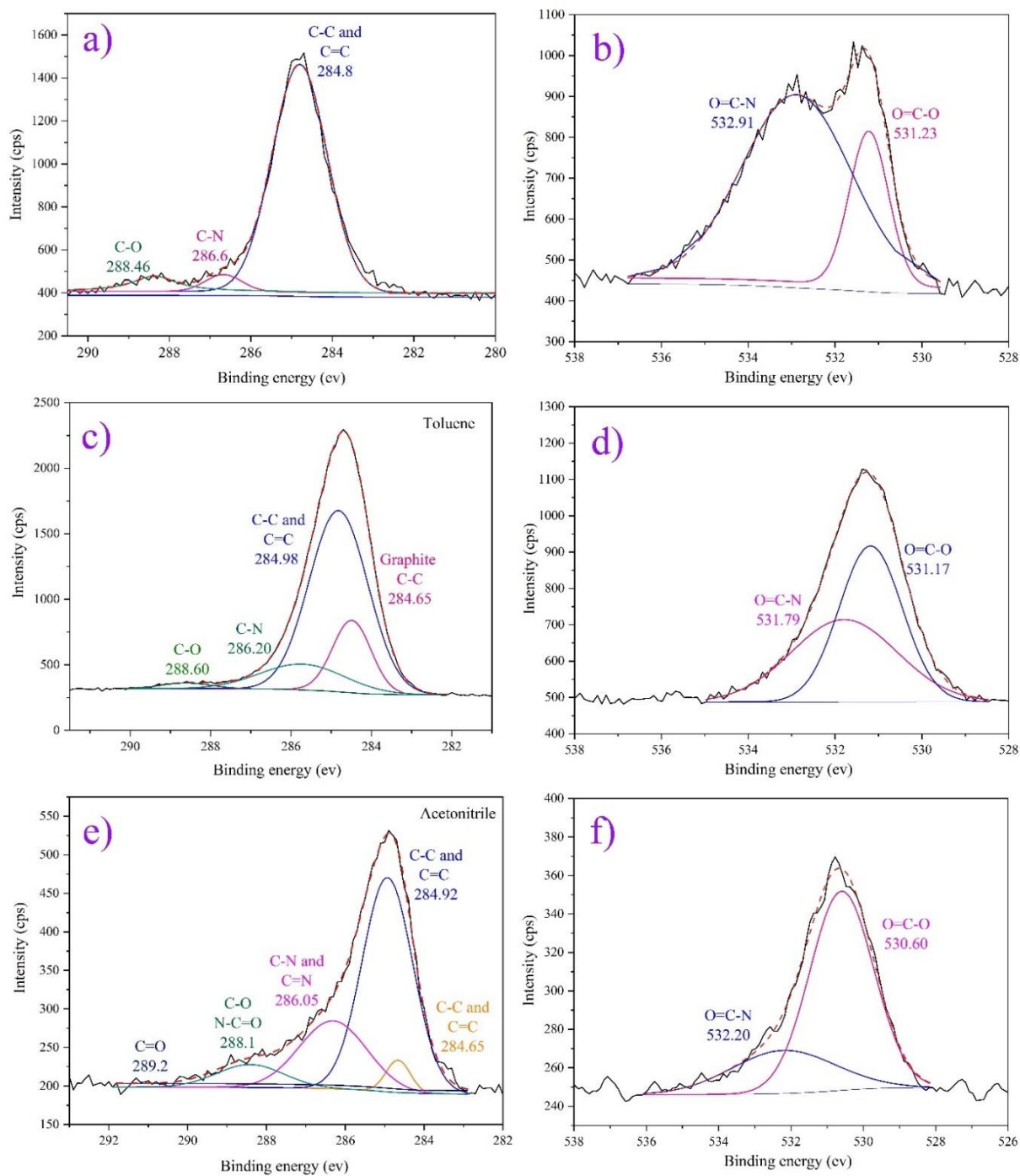
270  
 271 Comparing the plasma-coated samples with uncoated one for toluene precursors, the plasma  
 272 deposition with toluene precursors leads to the obvious increase in the C/O and C/N atomic ratio  
 273 which suggests the formation of a new carbon-containing group on the surface of aramid fibers.  
 274 For more investigation, a Gaussian fit was performed on the C1s and O1s spectrum of uncoated  
 275 and plasma-coated aramid fibers depicted in Fig. 6 and 7.

276 As can be seen from Fig 6a, the C1s curve fitted spectrum of uncoated aramid fibers included the  
 277 three peaks at 284.97 eV, 286.6 eV, and 288.46 eV which is related to C–C and C=C bonds, C-N  
 278 bonds, and C-O bonds, respectively. Also, the O1s spectrums depicted in Fig 7, show two  
 279 characteristic peaks of aramid fibers at 531.23 eV and 532.91 eV that are dedicated to O=C–O and  
 280 O=C–N structures, respectively [39-42].

281 Fig 6c and d show the curve-fitted spectrum of plasma-coated aramid fiber by toluene precursor.  
 282 As can be seen from C1s spectra, after the plasma treatment with toluene precursor one extra peak  
 283 appeared at 284.55 eV. This peak is mainly related to graphite-like structures. Also, the O1s  
 284 Spectra of plasma-coated aramid fiber with toluene precursor, similar to the pristine aramid fibers  
 285 shows the characteristic peaks of 531.17, and 531.79 related to the O=C–O and O=C–N follow  
 286 decreasing in the intensity of O=C–N peak. The results indicate in deposition of diamond-like  
 287 carbon coating on the surface of aramid fibers [43-47].

288 The survey spectrum of plasma-coated aramid fibers with acetonitrile precursor shows an increase  
 289 in the C/O atomic ratio and a decrease in the C/N atomic ratio which suggest the formation of new  
 290 carbon nitride on the surface of aramid fibers. Fig 6cand d show the spectrum of plasma-coated  
 291 aramid fiber by acetonitrile precursor. As can be seen from C1s spectra, similar to the plasma-

292 coated sample with toluene precursors, one extra peak appeared at 284.65 eV which relates to the  
293 graphite-like structures induced by plasma deposition. Besides, the results show the increment in  
294 C-N, C=N at 286.05 eV, and N-C=O peaks at 288.1 eV. Furthermore, the O1s Spectra of plasma-  
295 coated aramid fiber with acetonitrile precursor shows the characteristic peaks of 530.60 eV, and  
296 532.20 eV related to the O=C-O and O=C-N. The results indicate the deposition of the amorphous  
297 nitride carbon layer on the surface of aramid fibers [39, 40, 43].



298

299 **Fig 6.** Curve fitted spectra for a) C1s spectra of uncoated aramid fiber, b) O1s spectra of uncoated aramid  
 300 fiber, c) C1s spectra of plasma coated aramid fiber with toluene precursor, d) O1s spectra of plasma  
 301 coated aramid fiber with toluene precursor, e) C1s spectra of plasma coated aramid fiber with acetonitrile  
 302 precursor, f) O1s spectra of plasma coated aramid fiber with acetonitrile precursor

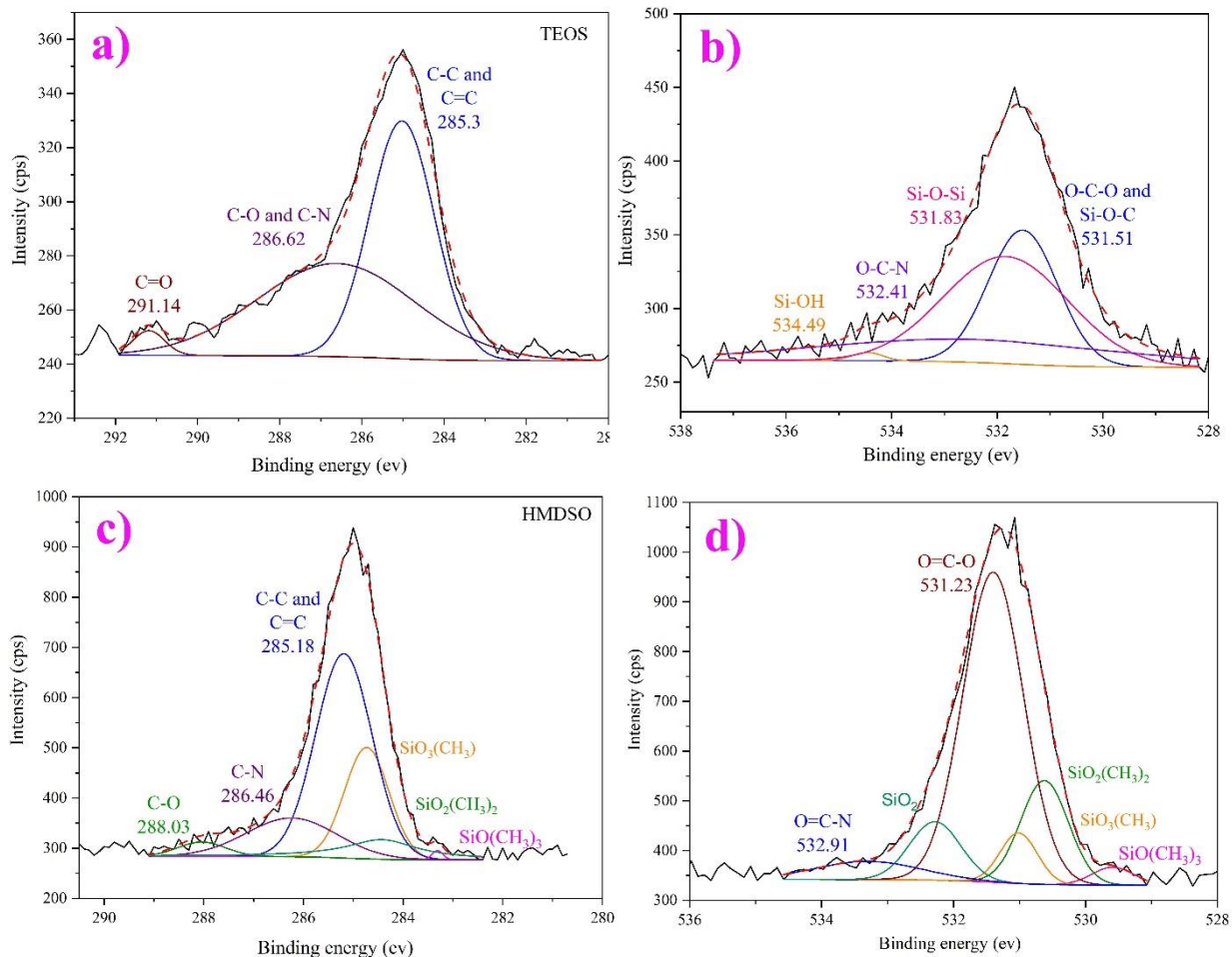
303

304 The survey spectrum of plasma-coated aramid fibers with TEOS precursors shows the formation  
305 of new silicon-containing groups on the surface of aramid fibers. Fig 7a, and 6b shows the curve-  
306 fitted spectrum of plasma-coated aramid fiber by TEOS precursor. Based on the results, in the C1s  
307 spectrum, we have one increase in the intensity of the peak located at 286.2 eV related to C-O and  
308 C-N structures. Furthermore, two new peaks add at the location of 531.59 eV and 534.49 eV related  
309 to the Si-O-C and O-C-O groups. the results indicate in the formation of new SiO layers on the  
310 surface of aramid fibers [48, 49].

311 Also, the survey spectrum of plasma-coated aramid fibers with HMDSO precursors shows the  
312 formation of new silicon-containing groups on the surface of aramid fibers. Fig 6c, and 6d show  
313 the curve fitted spectrum of plasma-coated aramid fiber by HMDSO precursor. As can be seen  
314 from C1s, and O1s spectrums, the fitting method consisted of four structures of silicon, including  
315  $\text{SiO}_2$ ,  $\text{SiO}_3(\text{CH}_3)$ ,  $\text{SiO}_2(\text{CH}_3)_2$ , and  $\text{SiO}(\text{CH}_3)_3$ , as abundantly available in many literatures [35-39]  
316 The results indicated fabrication of PDMS like layer on the surface of aramid fiber followed by a  
317 crosslinking process of organosilicon polymer chains during plasma coating on the surfaces [50].  
318 All the results of the XPS analysis confirmed the results of FTIR.

319

320



321 **Fig 7.** Curve fitted spectra for a) C1s spectra of plasma coated aramid fiber with TEOS precursor, b) O1s  
 322 spectra of plasma coated aramid fiber with TEOS precursor., c) C1s spectra of plasma coated aramid fiber  
 323 with HMDSO precursor, d) O1s spectra of plasma coated aramid fiber with HMDSO precursor  
 324  
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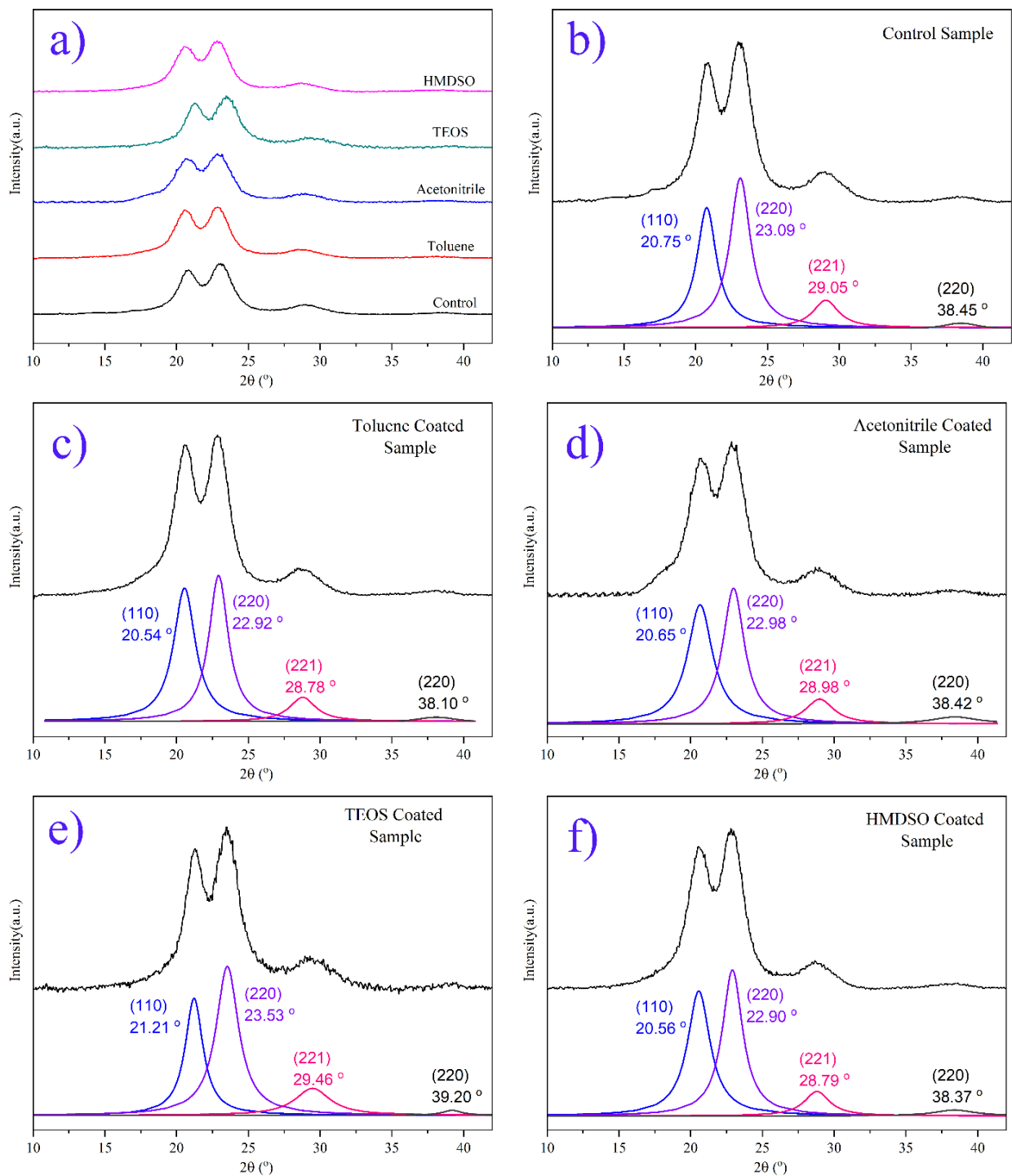
326 Further investigation in chemical structures of the sample was investigated by EDS analysis. The  
 327 results are depicted in Table 6. As can be seen from the results, the plasma coating with toluene  
 328 precursor leads to the increase in the weight percentage of C element on the surface from 79.3 %  
 329 to 96.6 %. This shows the good deposition of carbon chemical groups on the surfaces. On contrary,  
 330 the plasma coating with acetonitrile precursors leads to an increase in nitrogen groups based on  
 331 the chemical formula and structures of acetonitrile  $C_2H_3N$ .

332 For the plasma coating with organosilicon precursors, a new silicon element appeared on the  
 333 surface of the aramid sample after the plasma treatment which indicated well deposition of a layer  
 334 on the surfaces. All the results confirmed the FTIR and XPS results.  
 335

336 **Table 6.** weight percentage of the carbon, oxygen, nitrogen, and silicon elements of the uncoated and  
 337 plasma-coated aramid fiber

	C (%)	O (%)	N (%)	Si (%)	C/O	C/N	Si/C	Si/O	Si/O
Control	79.3	14.7	6	0	5.39	13.22	0	0	0
Toluene	96.6	2.9	0.5	0	33.31	193.20	0	0	0
Acetonitrile	77.9	14.4	7.7	0	5.41	10.12	0	0	0
TEOS	69.3	16.7	8.8	5.2	4.15	7.88	0.08	0.31	0.59
HMDSO	72.8	15	7.2	5.1	4.85	10.11	0.07	0.34	0.71

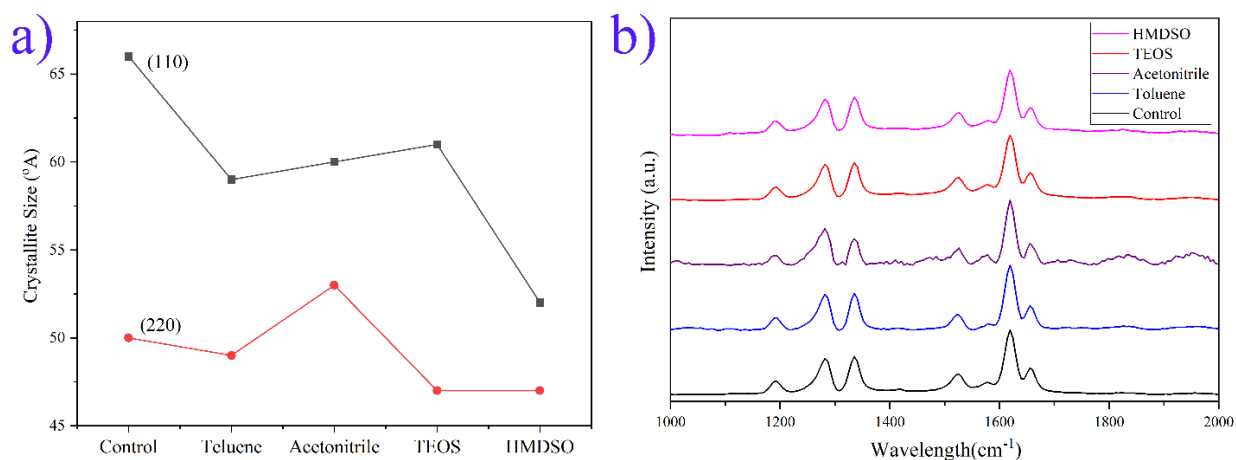
338  
 339 The XRD analysis was performed to investigate the effects of the plasma coating with different  
 340 precursors on the crystal structure of the fiber. The XRD diagram and corresponding fitting curve  
 341 results of the uncoated and plasma-coated aramid fibers are shown in Fig. 8(a-f).  
 342 Based on the results, The aramid fibers exhibited four strong peaks centered at 20.75°, 23.09°,  
 343 29.05° and 38.45° associated with the crystal planes (110), (200), (211) and (220) [7, 9-12]. As  
 344 can be seen from Fig 8a, The XRD patterns of the samples are very similar to each other, this is  
 345 indicating in the point that no new crystal structure formed on the surface of the aramid fibers after  
 346 the plasma coating.



347  
 348 **Fig 8.** a) XRD analysis peaks and corresponding fitting results for b) control sample and the fibers coated  
 349 with c) toluene d) Acetonitrile e) TEOS f) HMDSO precursors  
 350

351 The crystallite size of two strong peaks of aramid fiber including the (110) and (200) planes for  
 352 the uncoated and plasma-coated aramid fibers with different precursors depicted in Figure 9a. As

353 can be seen from the results, the crystallite sizes of the (110) and (200) planes have been decreased  
 354 with plasma coating with all precursors. These decreases can be related to the inducing defects in  
 355 the crystal planes as a result of the plasma surface coating on aramid fiber.  
 356 Additional investigation into the chemical structures of aramid fiber after plasma coating with  
 357 different precursors was performed by Raman spectroscopy. The results are depicted in Fig 9b. It  
 358 should be noted that all the spectrums were baseline corrected and normalized by the band at 1610  
 359  $\text{cm}^{-1}$ . This bond is related to the C-C stretching vibrations which are characteristic of aramid fiber  
 360 and doesn't main changes base on the fiber treatments. Based on the results, not any difference  
 361 can be seen in the Raman spectrum of uncoated and plasma-coated aramid fibers with different  
 362 precursors. This is due to the high level of crystallinity of the aramid fibers that make it difficult  
 363 to change in the Raman spectrum of aramid fibers.



364  
 365 **Fig 9.** a) Crystallite sizes of (110), and (220) plans and Raman spectra of uncoated and plasma-coated  
 366 sample with different precursors  
 367

### 368 3.3 Thermal Decomposition Analysis

369 Fig 10 shows the thermal decomposition curves of uncoated and plasma-coated fiber using toluene,  
 370 acetonitrile, TEOS, and HMDSO precursors. Also, Table 7 detailed the residual percentage of  
 371 fibers in different temperatures. As can be seen from the table, uncoated aramid fiber shows  
 372 exhibited a weight loss of 99.77% between 0 and 800 $^{\circ}\text{C}$ , which is related to the decomposition of  
 373 partial dihydroxylation and alkoxide aramid fiber.

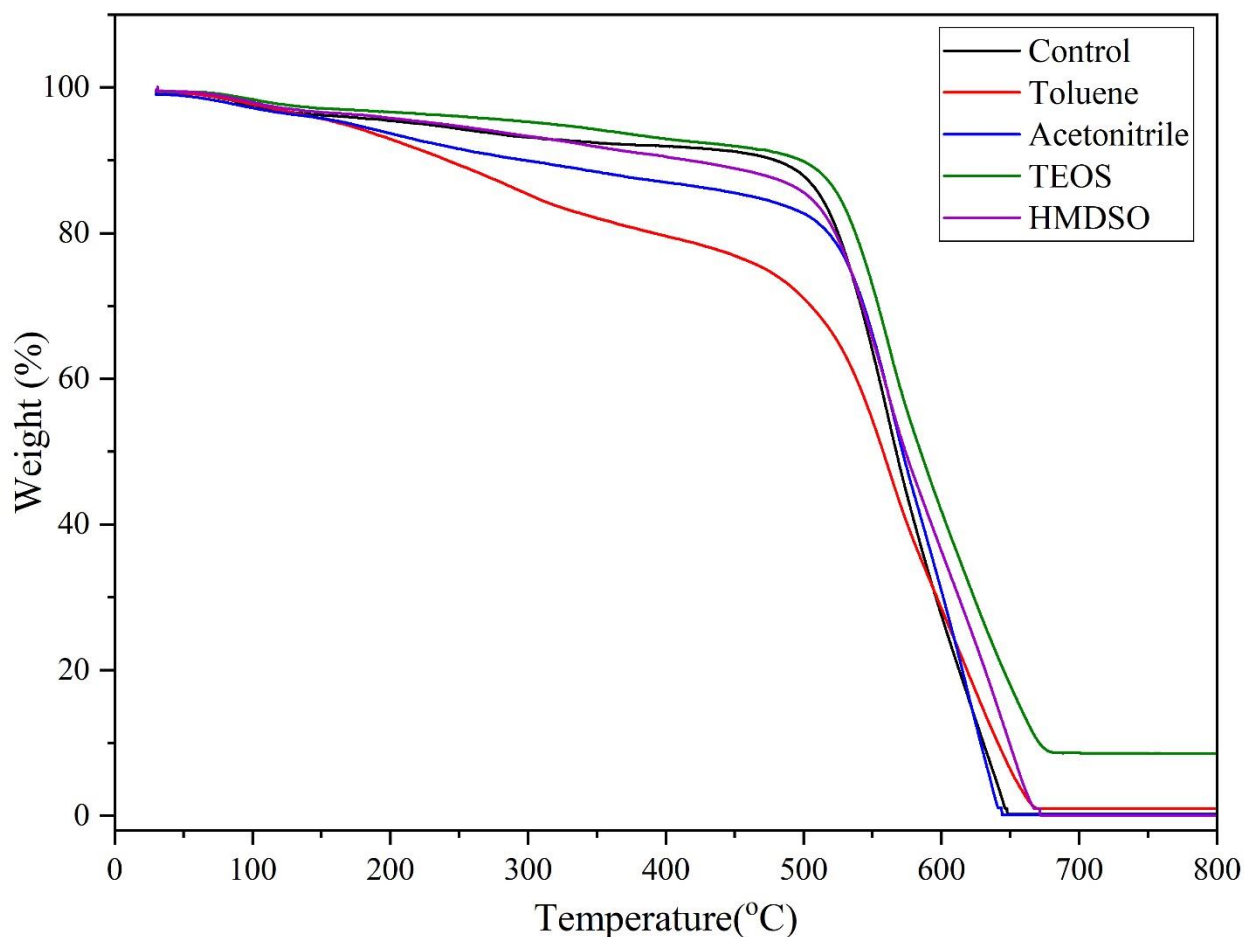
374 Compared with it, the weight loss between 0 to 800  $^{\circ}\text{C}$  for plasma-coated samples with toluene,  
 375 acetonitrile, TEOS, and HMDSO precursors are 99.00, 99.88, 92.50, and 99.82 % respectively.

376 The TG curve of plasma-coated samples with HMDSO, and TEOS precursors shows more stability  
377 compared to plasma-coated samples with acetonitrile and toluene precursors. For the plasma-  
378 coated sample with HMDSO, and acetonitrile precursors, the weight loss in different temperatures  
379 was not significantly different with uncoated fiber.

380 Also, for the plasma-coated sample with TEOS precursor, the weight loss between 0 to 800 °C is  
381 92.50, which is increased by 5.27% compared with the uncoated aramid fiber. Accordingly, it can  
382 be said that the plasma-coated sample with TEOS precursors has a positive effect on the thermal  
383 decomposition of aramid fiber.

384 However, based on the results, the plasma coating with hydrocarbon precursors including toluene  
385 and acetonitrile led to more weight loss in the range of 0 to 800 °C. The reason is may due to the  
386 more thermal stability of Si-O-Si bonds compared to C-C, C-N, and C-O [6, 51].

387



388

389 **Fig 10.** Thermal decomposition curves of uncoated and the plasma-coated fiber using with toluene,  
390 Acetonitrile, TEOS, HMDSO precursors

391  
392

**Table 2.** Residual Percentage of uncoated and the plasma-coated fiber using with toluene, Acetonitrile, TEOS, HMDSO precursors in different temperatures

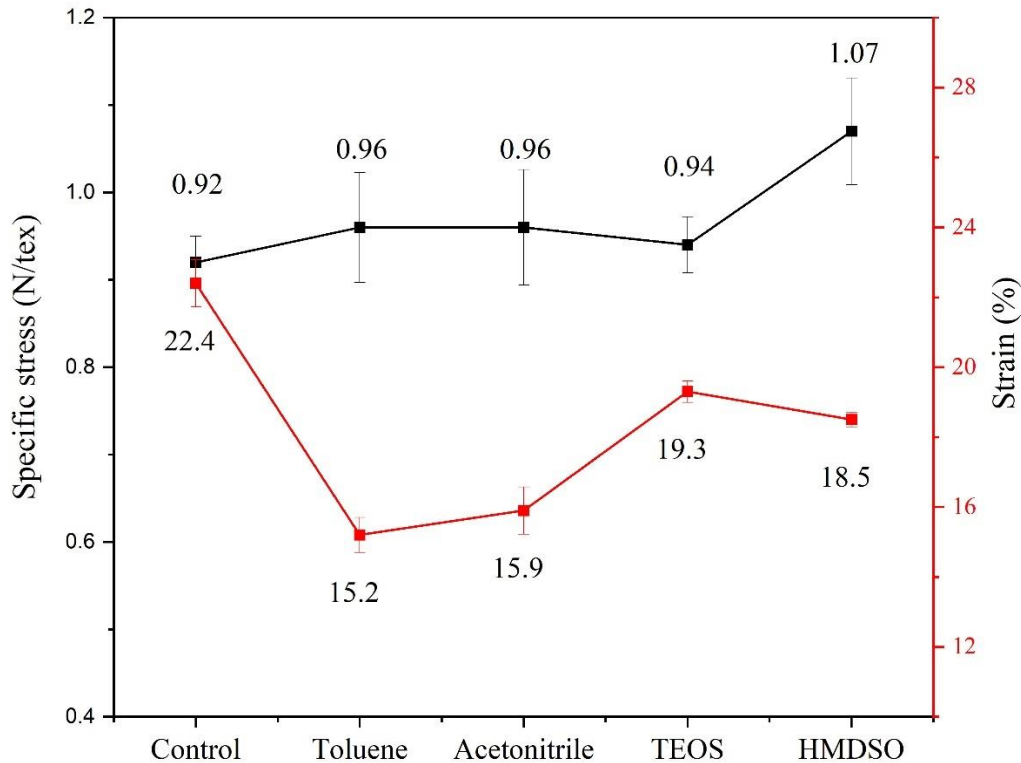
Residual percentage (%)	210 °C	400 °C	520 °C	800 °C	Weigh loss between 0 to 800 °C
Control	95.24	91.92	82.23	0.23	99.77
TEOS	96.52	92.94	86.70	8.50	92.50
HMDSO	95.58	92.94	81.10	0.18	99.82
Acetonitrile	93.23	87.96	80.21	0.12	99.88
Toluene	92.23	79.61	66.50	1.00	99.00

393

### 394 **3.3 Mechanical Properties**

395 The effect of the plasma surface modification using different precursors on the breaking strength  
396 of the aramid fiber was investigated by tensile test. The results depict in Fig. 11 and the same  
397 breaking strength is observed for uncoated and plasma-coated aramid fibers using toluene,  
398 acetonitrile, and TEOS precursors. This suggests that no damage was induced on the aramid fibers  
399 by the plasma surface modification with these types of precursors and plasma apparatus. On the  
400 contrary, the plasma surface modifications with HMDSO precursors lead to an increase in the  
401 mechanical strength of the sample. This increment may be ascribed to the uniform deposition of  
402 Si groups on the surface of the aramid fibers followed by some deposition between adjacent fibers  
403 that leads to the interlinking of fibers (Figure S5).

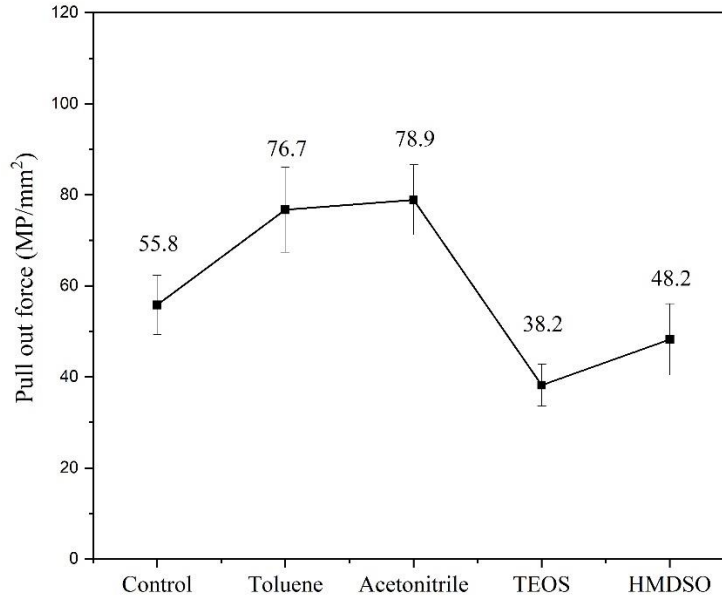
404



**Fig 11.** Specific Stress and strain curve of un coated and plasma- coated aramid fibers using toluene, acetonitrile, TEOS, and HMDSO

### 3.4 Interfacial adhesion of aramid/rubber composite

The pull-out test was performed to investigate the effects of the plasma treatments with different precursors on the interfacial adhesion of aramid/rubber composite. The results are depicted in Fig. 12. As can be seen from the results, by the plasma surface modification with hydrocarbon precursors including toluene and acetonitrile, we have an increment in aramid/rubber interfacial adhesion. The increment in interfacial adhesion aramid/rubber composite by DLC-based coating is maybe related to the generation of C=C bond on the surface of the aramid fibers, which directly chemical bond with the aramid and rubber matrix. Moreover, the formation of a nano-sphere particle on the surface of aramid fibers by plasma surface modification using hydrocarbon precursors (proved by FE-SEM analysis), increases the surface roughness followed by increment in surface area between aramid rubber that these two kinds of layers benefit the interfacial locking effect [52, 53].



421

422 **Fig 12.** Pull out Force for uncoated and plasma-coated aramid fibers using toluene, acetonitrile, TEOS,  
 423 and HMDSO

424 **4. Discussion on results**

425 Herein we briefed the results of some peer studies related to enhancing the adhesion effect between  
 426 aramid fibers and rubber matrix with different methods in Table 4. As can be seen from the table,  
 427 by comparing the results of this study with previous ones performed by a different method, it could  
 428 be concluded that the atmospheric pressure plasma can be used as a promising method for  
 429 enhancing the adhesion effect between aramid fibers and the rubber matrix.

430

431 **Table 8.** Briefed results of some peer studies related to enhance adhesion effect between aramid fibers  
 432 and rubber matrix

Author and publication data	Article title	Brief of the article	Pull out test
Current study	-	In the present study, the effect of the surface modification of aramid fibers using atmospheric pressure plasma treatment with different precursors on adhesion to the rubber matrix was investigated. For that, the plasma coating was conducted using argon as the main working gas, and toluene, acetonitrile, TEOS, and HMDSO as liquid precursors.	The results of the pull-out test show that the pull-out force between aramid fiber and rubber matrix was increased by 43% for plasma coated sample using acetonitrile precursor.
Zhang et al, 2022[54]	Mussel-inspired environmentally friendly dipping system for aramid fiber and its interfacial adhesive mechanism with rubber	In this study, a new dipping system was used for improving interfacial adhesion between aramid and rubber matrix. For this purpose, a network structure was prepared by water-soluble polyethyleneimine and pyrogallol acid and then	Based on the results of the pull-out test, the pull-out force between modified aramid fiber and rubber reached 147 N. The results show that the pull-out force

		was mixed with rubber latex to prepare the dipping solution.	with this method is comparable with the level of a traditional resorcinol-formaldehyde-latex dipping system(154 N) while using harmful resorcinol and formaldehyde was avoided.
Yin et al, 2022[55]	Surface construction of ANF/CNT onto aramid fibers to enhance interfacial adhesion and provide real-time monitoring of deformation	In this study, functional groups such as hydroxyl and amino groups were introduced on the surface of aramid fiber by tannic acid and polyethyleneimine. Then, to prepare a surface-coated fiber, the modified aramid fiber was impregnated in the aramid nanofiber/carbon nanotube aqueous dispersion.	The results of this study shows that, compared to raw aramid fiber, the pull-out force of the coated one is increased by 126.4%.
Fang et al, 2022 [56]	Biomimetic surface modification of UHMWPE fibers to enhance interfacial adhesion with rubber matrix via constructing polydopamine functionalization platform and then depositing zinc oxide nanoparticles	In this study, a biomimetic surface modification method was used to enhance the interfacial adhesion between ultrahigh molecular weight polyethylene (UHMWPE) fibers and rubber matrix. The method consists of constructing a polydopamine functionalization platform and then depositing zinc oxide nanoparticles.	The results of the pull-out test show that the pull-out force of the UHMWPE and rubber matrix was increased to 34.3 N. This is equal to an 84.57% increase in interfacial adhesion between UHMWPE fibers and rubber matrix.
Zhang et al, 2021 [2]	Surface Coating of Aramid Fiber by a Graphene/Aramid Nanofiber Hybrid Material to Enhance Interfacial Adhesion with Rubber Matrix	In this study, a novel method of constructing nanostructures on the surface of aramid fiber through the $\pi-\pi^*$ interaction between the aramid nanofiber, graphene, and the graphene/aramid nanofiber dispersion in water. For this purpose, a layer was deposited on the surface of aramid fiber by immersion in an alkaline solution of tannic acid and polyethyleneimine, a tannic acid/polyethyleneimine. Then, the modified aramid fiber was impregnated with the graphene/aramid nanofiber dispersion to construct surface nanostructures on the surface of the aramid fiber.	The results of the pull-out test shows that the pull-out force of the aramid fiber and rubber matrix was increased by 84.7%, for the best sample.
Fang et al, 2021 [57]	Polydopamine and Mercapto Functionalized 3D Carbon Nano-Material Hybrids Synergistically Modifying Aramid Fibers for Adhesion Improvement	In this study, surface coating on the surface of aramid fiber was performed based on polydopamine, mercapto functionalized graphene oxide, and carbon nanotube. For that, firstly, graphene oxide, and carbon nanotube were assembled through $\pi-\pi$ conjugation. Then, the assembled graphene oxide/carbon nanotube hybrids were performed by dehydration condensation reaction between the hydroxyls of graphene oxide and the silanol groups of the coupling agent. Finally, the substance was grafted on the surface of aramid fibers. Also, before grafting the aramid fiber was modified by polydopamine.	The results of this study show that the pull-out force between coated aramid fiber and the rubber matrix was increased by 110.95% compared to the uncoated one.

Zhang et al, 2021[58]	Enhanced interfacial adhesion of aramid fiber reinforced rubber composites through bio-inspired surface modification and aramid nanofiber coating	In this study, at first, a surface coating on aramid fiber was performed with an alkaline solution of tannic acid and polyethyleneimine which led to the introduction of functional groups such as hydroxyl and amino groups on the surface of aramid fiber. Then, to improve the interfacial adhesion between the aramid fiber and the rubber, the construction of nanostructure on the surface of modified aramid fiber was performed by an aramid nanofiber coating.	The results show that compared to raw aramid fiber, the interfacial adhesion of aramid fiber coated with aramid nanofiber was increased by 43.1% after 7 deposited cycles. Also, the results show that the mechanical properties of the fibers remain almost unchanged.
Zhang et al 2021 [59]	Nondestructive Grafting of ZnO on the Surface of Aramid Fibers Followed by Silane Grafting to Improve its Interfacial Adhesion Property with Rubber	In this study, a new method was used based on nondestructive grafting of zinc oxide onto a fiber surface followed by silane grafting. For this purpose, at first tannic acid and polyethyleneimine were used to form functional groups on the surface of aramid fibers. Then, by a hydrothermal reduction process, zinc oxide nanowires were deposited on the surface of modified aramid fibers. Finally, a polysulfide functionalized silane was grafted on the surface of the coated fiber.	The results of this study show that compared to uncoated aramid fiber, the interfacial adhesion between the modified fibers and rubber increased by 57%. Also, the results show that the breaking strength of aramid fibers does not change by the growth process of zinc oxide nanowires.
Yang et al, 2019 [5]	A Novel Method for Deposition of Multi-Walled Carbon Nanotubes onto Poly(p-Phenylene Terephthalamide) Fibers to Enhance Interfacial Adhesion with Rubber Matrix	In this study, a novel surface coating method was employed based on the deposition of multi-walled carbon nanotubes on the surface of PPTA to increase the interfacial adhesion between PPTA fiber and rubber matrix. The method was composed of the introduction of epoxy groups on the PPTA fibers, the carboxylation of MWCNTs, and the ring-opening reaction between the carboxyl and epoxy groups.	The results of this study shows that, compared to raw PPTA fiber, the pull-out force of the coated one is increased by 46.3%.
Wang et al, 2019 [7]	Enhanced adhesion property of aramid fibers by polyphenol-metal iron complexation and silane grafting	In this study, a green method has been used for surface coating on aramid fiber aiming to enhance their adhesion property with rubber matrix. For that, surface coating on aramid fiber was performed by polyphenol-metal by complexation between Fe(III) ions and tannic acid, followed by silane grafting.	The results of this study shows that, compared to raw aramid fiber, the pull-out force of the coated one is increased by 73.6%.
Yang et al, 2019 [60]	Surface modification of Poly(p-phenylene terephthalamide) fibers by polydopamine-polyethyleneimine/graphene oxide multilayer films to enhance interfacial adhesion with rubber matrix	In this study, a new surface coating method was employed based on graft polyethyleneimine-polydopamine/graphene oxide multilayer coating on the surface of PPTA fiber to increase the interfacial adhesion between PPTA fiber and rubber matrix.	The results of the pull-out test shows that the pull-out force of the aramid fiber and rubber matrix was increased by 78.1%, for the best sample.
Yang et al, 2019 [61]	Enhancing the interfacial adhesion with rubber matrix by grafting polydopamine-carbon nanotubes onto poly (p-phenylene terephthalamide) fibers	In this study, the interfacial adhesion between poly(p-phenylene terephthalamide) (PPTA) and rubber matrix was increased via aminated carbon nanotube deposition on the surface of PPTA fiber by combining the biomimetic modification of dopamine.	The results of this study shows that, compared to raw PPTA fiber, the pull-out force of the coated one is increased by 59.7%.
Kanbargi and Lesser 2017 [62]	Improving adhesion between aramid fibers and natural rubber through	In this article, a new method was employed to enhance the interfacial adhesion between PPTA fibers and natural rubber. For that, PPTA fiber	The results of this study shows that, compared to raw PPTA fiber, the pull-out

	morphological and synthetic modification of the fibers	underwent the pretreatment with two methods including a mechanical pretreatment and a microwave pretreatment. Then, the pretreated PPTA fibers were treated with coupling agents in the presence of supercritical carbon dioxide.	force of the coated one is increased by 100%.
Paolo et al, 2017 [63]	Microwave induced hierarchical nanostructures on aramid fibers and their influence on adhesion properties in a rubber matrix	In this study, a microwave-assisted surface modification of aramid fiber was used to improve adhesion between aramid fiber and rubber matrix. For that, the carbon evaporator method was employed to deposit a thin film of carbon onto the aramid fiber surface. Then microwave radiation was used to create hierarchical structures to the surface of aramid fiber.	The results of this study shows that, compared to raw aramid fiber, the bundle pull-out force of the coated one is increased by 259%.
Sa et al, 2015 [64]	Improved adhesion properties of poly-p-phenyleneterephthamide fibers with a rubber matrix via UV-initiated grafting modification	In this study, surface modification of PPTA was performed by ultraviolet irradiation-induced graft polymerization to enhance adhesion between PPTA fiber and rubber matrix. Also, resorcinol-formaldehyde-latex (REF) dipping was employed to further enhance in interfacial adhesion between PPTA fibers with the rubber matrix.	The results of this study show that, compared to raw PPTA fiber, the pull-out force of the coated one is increased by 53.7 % and 80.1% by grafted PPTA fibers and grafting PPTA fibers followed by RFL dipping respectively.

433

434 **5. Conclusion**

435 In this study, the potential use of atmospheric pressure plasma for the production of aramid/rubber  
436 composites with promoted surface adhesion was investigated. For this purpose, a conventional  
437 atmospheric pressure plasma device was used to modify the surface of aramid fibers. For this  
438 purpose, argon was used as the main gas for the generation of plasma, and toluene, acetonitrile,  
439 TEOS, and HMDSO were used as liquid precursors. The surface modifications were performed  
440 under equal conditions for all samples.

441 Based on the results, the physical-chemical characterization of the aramid fibers before and after  
442 the plasma surface modifications confirmed the successful deposition of amorphous carbon,  
443 amorphous Nitride-carbon, SiO<sub>2</sub>, and PDMS-like coating layers on the surface of aramid fibers by  
444 plasma surface modification using toluene, acetonitrile, TEOS, and HMDSO, respectively.

445 The pull-out test of coated aramid fiber indicated a 38%, and 43% increase in adhesion strength  
446 between toluene and acetonitrile aramid fiber and rubber materix respectively. The tensile test  
447 showed a 16% increase in the breaking strength of plasma-coated aramid fiber with HMDSO  
448 precursor, while no significant change was observed for plasma coating using toluene, acetonitrile,  
449 and TEOS precursors. The fire-retardancy test showed that the plasma-coated sample with  
450 HMDSO, and acetonitrile precursors, dose not any significantly different in weight loss at different

451 temperatures compared to uncoated fiber while for plasma coating with TEOS precursor, a 5.27%  
452 increase was detected.

453 So, the atmospheric plasma coating using acetonitrile precursors can be considered as a promising  
454 method for increasing adhesion between aramid fiber and rubber matrix for composite application.  
455 This method can lead to the promotion of interfacial adhesion of aramid/rubber while retaining the  
456 tensile strength, and flame resistance properties of aramid as original fibers. The method is simple,  
457 single-step, cost-effective, and environmentally friendly which has great potential for use in the  
458 rubber industry. Moreover, the operation is done at atmospheric pressure, which not only has no  
459 need for vacuum equipment but also has the potential for a continuous surface modification  
460 approach of aramid fiber.

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