Chapter 3

Effect of radiofrequency argon plasma treatment on physico-chemical properties of muga silk fibre

3.1 Introduction

Extensive research has been carried out on the radio-frequency (RF) plasma treatment of natural muga silk fibres by modifying their wetting, dyeing, and printing properties along with tensile properties; shrink resistance; flame retardance; anti-bacterial properties; biocompatibility; hydrophilicity and hydrophobicity [1-5]. RF plasma treatment is a dry and clean process and does not suffer from any environmental and health concerns. It has a major advantage over the conventional wet chemical process in terms of reduction of waste and pollution problems and conservation of chemicals, water, energy, and time [6, 7]. RF plasma treatment on silk fibres with non-polymerizable precursors, such as inert gases, only influences their outermost surfaces by increasing or decreasing the surface roughness up to few-nanometre skin depth [8-17].

Plasma treatment is also beneficial to remove the contaminants like pollutants, oxide layer, etc. from the silk surface and also etching the weakly bonded components from the fibres surface [18-20]. The objective of this part of work is to study the surface modification of muga silk fibres by improving their tensile strength and hydrophobicity using Ar plasma treatment without altering their bulk properties. Moreover, the plasma discharge characteristics are investigated at different plasma conditions to understand the effect of the fundamental plasma parameters on the properties of the muga fibre. The performances of virgin and plasma treated muga silk fibres have been evaluated using various characterization techniques.

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3.2 RF Ar plasma discharge characteristics

3.2.1 Measurement of plasma parameters

In the present study, the plasma parameters of the Ar discharge are measured using self-compensated planar Langmuir probe and emissive probe. The self-compensated probe is used to minimize the perturbation effects of the RF voltage across the probe sheath. The Langmuir probe (probe tip diameter of 0.6 cm) is used to evaluate electron temperature ($T_e$) and plasma density (electron density, $n_e$ and ion density, $n_i$). The electron temperature is calculated from the current-voltage (I-V) characteristics obtained from the Langmuir probe.

The plasma potential of the Ar discharge is evaluated by the self-compensated emissive probe using inflection point method. The emissive probe is constructed using a 5 mm long, 0.1 mm diameter thoriated tungsten wire. The probe is heated by a half-wave DC voltage source (0-5 V). During all measurements reported here, both the probe tips are kept 3 cm above the RF electrode. The variation in plasma parameters at various discharge conditions is presented in Table 3.1.

**Table 3.1** Ar plasma discharge characteristics at various RF powers (10-30 W)

| RF power (W) | Ar Plasma characteristics |  |  |  |  |  |  |
|--------------|---------------------------|---|---|---|---|---|
|              | $T_e$ (eV) | $n_e$ ($\times 10^8$ cm$^{-3}$) | $n_i$ ($\times 10^8$ cm$^{-3}$) | Plasma potential ($V_p$) | DC self bias voltage ($V_B$) | Ion energy (qV) |
| 10           | 6.4          | 3.6 | 3.7 | 16.0 | – 26 | q $\times$ 42.0 |
| 20           | 6.7          | 3.9 | 4.0 | 16.9 | – 50 | q $\times$ 66.9 |
| 30           | 6.9          | 4.2 | 4.1 | 17.8 | – 74 | q $\times$ 91.8 |

As revealed from the data given in Table 3.1, the electron temperature and plasma density (electron and ion density) increase with the increase of RF power. This is simply attributed to the fact that when the RF power is raised more dissipation of power occurs in the plasma and this eventually leads to the increase in electron energy (or electron temperature). An increase in electron energy will enhance the ionization rate of the Ar atoms and hence plasma density is also increased with the increase of RF power. During Ar plasma treatment, the DC self-bias voltage ($V_B$) that is developed on the substrates is
observed to be increased from -26 to -74 V with increasing RF power. The DC self-bias voltage is measured using a digital voltmeter connected to the RF electrode through a high impedance \( R_L = 1.35 \times 10^5 \Omega \) inductor. However, the plasma potential \( V_p \) remains almost constant irrespective of the increase in RF power. With the knowledge of DC self-bias voltage and plasma potential the maximum energy gained by ions as they travel through the sheath to the substrate is calculated according to the following relation:

\[
E_{\text{max}} = q (V_p - V_B) \quad (3.1)
\]

where \( q \) is the ion charge. The variation in the ion energy at RF power range of 10–30 W is presented in Table 3.1 which shows an increase in ion energy with RF power. In the present work, the ion energy cannot be quantified as the types and charges of the ionized species formed near the plasma sheath are not known.

### 3.3 Chemical properties of virgin and Ar plasma treated muga silk

#### 3.3.1 Fourier transform infra-red (FTIR) analysis

Figure 3.1 represents the FT-IR spectra of the untreated and Ar plasma treated muga fibres at the RF power range of 10-30 W (treatment time of 10 min) and the assignments of the peaks are listed in Table 3.2. The IR absorption bands displayed all the characteristic functional groups present in different amino acids.

![FTIR spectra of the virgin and Ar plasma treated muga fibres](image)

**Figure 3.1** FTIR spectra of the virgin and Ar plasma treated muga fibres at the RF power range of 10-30 W and treatment time of 10 minutes.
In the present investigation, the treated muga fibres exhibit similar chemical composition irrespective of the increase in treatment time. However, the increase in RF power seems to affect the chemical composition of the treated fibres. As observed from Figure 3.1, the intensity of the band at 1448 and 2928 cm\(^{-1}\) is higher for untreated fibre than all the plasma treated muga fibres. Interestingly the FT-IR spectra of the plasma treated fibres show the absence of the band at 800 cm\(^{-1}\) which is observed to be appeared in the spectrum of virgin fibre. This may be attributed to the breakage of the H-bonded amide I and amide V groups due energetic ion bombardment on the surfaces of the fibres.

**Table 3.2** Assignment of the peaks detected in FTIR spectra of virgin and Ar plasma treated muga fibres in the RF power range of 10–30 W (treatment time: 10 min).

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Assignments of functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3406</td>
<td>N-H stretching/OH stretching</td>
</tr>
<tr>
<td>3070</td>
<td>Amide II</td>
</tr>
<tr>
<td>2928</td>
<td>N-H stretching (Amide I)</td>
</tr>
<tr>
<td>2852</td>
<td>C-H stretching</td>
</tr>
<tr>
<td>1645</td>
<td>Amino acid band 1 (Amide I)</td>
</tr>
<tr>
<td>1539</td>
<td>N-H in-plane bending, C-N stretching (amide II)</td>
</tr>
<tr>
<td>1448</td>
<td>CH(_4) group frequency of Ala.</td>
</tr>
<tr>
<td>1387</td>
<td>-CH(_3) deformation</td>
</tr>
<tr>
<td>1315</td>
<td>Gem-distributed ((=\text{C}=\text{CH}_2)) C-H stretching</td>
</tr>
<tr>
<td>1231</td>
<td>C-H stretching, N-H in-plane bending (amide III)</td>
</tr>
<tr>
<td>1161</td>
<td>O-H bending</td>
</tr>
<tr>
<td>1048</td>
<td>Gly-Ala sequence</td>
</tr>
<tr>
<td>964</td>
<td>N-H rocking</td>
</tr>
<tr>
<td>800</td>
<td>N-H out of plane bending (amide V)</td>
</tr>
<tr>
<td>680</td>
<td>N-C=O in-plane bending (amide IV)</td>
</tr>
<tr>
<td>543</td>
<td>N-C=O out of plane bending (amide VI)</td>
</tr>
</tbody>
</table>

On the contrary a new and weak absorption peak at 1308 cm\(^{-1}\) appears in the FT-IR spectra of the plasma treated fibres. It is further observed from Figure 3.1 that the intensity of the absorption band at 680 cm\(^{-1}\) increase for the fibre treated at lower RF power (10 W) and after that it decreases with increase in RF power. It is assumed that
some of the destroyed H-bonded amide I and amide V groups takes part in bond formation process of amide IV group. This possibly results in an increase in the absorption intensity of the band (680 cm$^{-1}$) at RF power of 10 W. At RF power >10 W, the energy of the ions is sufficiently high enough to destroy the amide IV groups thereby leading to a decrease in absorption peak intensity. More observable variation in absorption peak intensity is shown by the spectra of the fibres treated at RF power of 30 W. As seen from Figure 3.1 the intensities of the absorption bands at 1161, 1231 and 1539 cm$^{-1}$ considerably decrease as compared to those treated at lower RF powers (10-20 W). It is apparent that at higher RF power of 30 W, the energy of the impinging ions is sufficiently high enough to destroy the chemical structure of the fibres. The above findings indicate that at lower RF power (10 W) the ions do not possess sufficient energy to influence the chemical composition of the muga fibres whereas at higher RF power (30 W) the energy of ions significantly alters the chemical structure of the fibres.

3.3.2 Reaction mechanism

Muga silk fibre is a protein (fibrous polypeptide) polymer consisting of 18 amino acids [6]. As compared to mulberry silk, muga silk contains higher percentage of alanine, glycine and serine contents. Due to the presence in large amount, these three amino acid groups can easily form their derivatives in the fibrous polypeptide polymer under suitable chemical condition. Unlike the conventional chemical treatment, the interaction of RF Ar plasma with the different types of amino acid groups is very complex due to simultaneous occurrence of various chemical reactions at the surface of the muga fibre. However, in the present work the possible reaction phenomenon is proposed, by considering the three major amino acid groups (alanine, glycine and serine) present in muga silk, with the help of living radical polymerization mechanism. In the reaction mechanism the main initiating species as Ar ions and electron,

$$\text{Ar} \rightarrow \text{Ar}^+ + e$$  \hspace{1cm} (3.2)

Step 1:

\[
\begin{align*}
\text{CO-CHCH}_2\text{NH}_2 \xrightarrow{\text{Ar plasma}} & \text{CO-\daggerCH}_3\text{NH}_2 \\
\text{CO-CH}_2\text{NH} \xrightarrow{\text{Ar plasma}} & \text{CO-\daggerCH}_2\text{NH} \\
\text{CO-CHCH}_2\text{OH-NH} \xrightarrow{\text{Ar plasma}} & \text{CO-\daggerCH}_2\text{OH-NH} \\
\end{align*}
\]

\hspace{1cm} \text{(Monoradicals)} \hspace{1cm} (3.3)
Step 2:
The monoradicals so formed have certain probabilities to undergo cross termination with the formation of dimers \((P_r, P'_r\text{ and } P''_r)\). The dimers may then produce diradicals under the Ar plasma environment. These diradicals then again undergo cross-termination to produce the trimer and also the tetramer. This process will go on to produce various protein subunits which later recombine to form complex macromolecular structure in the form of oligomers and/or hetero-oligomers. This reaction is similar to Michael Szwarc living radical polymerisation. The reaction will stop once the plasma is withdrawn.

\[
\begin{align*}
R\cdot + R\cdot & \rightarrow P_r \\
\vdots & \\
R_1\cdot + R_1\cdot & \rightarrow P'_r \\
R_2\cdot + R_2\cdot & \rightarrow P''_r
\end{align*}
\]

(3.4)

3.3.3 X-ray photoelectron spectroscopy (XPS)
Figure 3.2 shows the XPS survey spectra of virgin and Ar plasma treated muga fibres at various RF powers (10-30 W) and treated for 10 minutes. The variation in atomic concentration of the virgin as well as the Ar plasma treated fibres is shown in Figures 3.3 (a)-(c). It is revealed from Figures 3.3 (a)-(c) that the fibre treated at 10 W exhibits similar variation in atomic composition than that of the virgin fibre, irrespective of the increase in treatment time.

At RF power of 20 W and lower treatment time (5-10 min), the treated fibres show relatively higher carbon content Figure 3.3(a) and lower oxygen content Figure 3.3(b), as compared to the virgin and other treated fibres. Above treatment time of 10 min, the fibres show a gradual decrease in carbon content and increase in oxygen content. The variation in nitrogen content follows the similar trend as that of oxygen as the treatment time is increased from 5 to 20 min. From these findings, it is apparent that with increasing treatment time from 5 to 10 min, the impinging ion energy is responsible for the cleavage of peptide chain as well as the breakdown of side chain groups of amino acid, mainly glycine \((\text{---NH---CH---CO---})\) and alanine \((\text{---NH---CH---CO---})\),
which are the major constituents of muga fibre. Similar observation has already been made in case of UV/ozone-irradiated Bombyx mori silk fibroin.

**Figure 3.2** XPS spectra of virgin and Ar plasma treated muga fibres at various RF powers (10 - 30 W) and treated for 10 minutes.
The breakage of the amino acid groups and peptide chain scission may contribute to the removal of loosely bonded fibroin region through the formation of various volatile products (CO, OH, CO₂ etc) which subsequently lead to a decrease in oxygen and nitrogen contents in the fibres. Above the treatment time of 10 minutes, the prolonged ion bombardment on the substrates creates severe peptide chain scission as well the breakage of the amino acid groups and this possibly lowers the carbon content in the fibres through the formation of more volatile products. Besides this may lead to the
formation of free radicals at the surfaces of the fibres and on exposure to atmosphere these free radicals readily react with atmospheric oxygen and nitrogen and/or water vapor thereby increasing oxygen and nitrogen contents in the fibres. With increase in RF power (30 W) and treatment time (5 – 20 minutes), more and more free radicals are generated at the surfaces which contribute to the increase in oxygen and nitrogen contents in the fibres.

In order to have greater insight into the surface chemistry of the fibres, the curve fitting of C1 peaks for all the samples is performed. The deconvoluted C1s peaks for the virgin and plasma treated fibres are shown in Figures 3.4 (a)-(d). As observed from Figures 3.4 (a) – (d), the C1 peak has been fitted with six peaks corresponding to C-N (283.9 eV), C-C/C-H/C=N (284.9 eV), C-O/C-O-C (286.6 eV), O=C-N/C=O/O-C-O (288.7 eV), O-C=O/COOH/COOR (289.5 eV) and OCOO (291.7 eV) units.
Figure 3.4 Deconvoluted C1s peaks of (a) virgin muga fibre and plasma treated samples at 10 minutes and RF power of (b) 10, (c) 20 and (d) 30W.

The details of C1 Peak fitting are given in the Table 3.3. It is observed from Table 3.3 that the functional composition in the fibres treated at 10 W and treatment time range of 5-20 minutes is almost similar to that of the virgin one. This indicates that at RF power of 10 W, the impinging ion energy is insufficient to alter the surface chemistry of the fibre even an increase in treatment time from 5 to 20 minutes. With increase in RF power (20 W) and treatment time (5-10 minutes), the functional units C-O/C-O-C, C-C/C-H/C=N and OCOO increase while the C-N, O=C-N/C=O/O-C-O and O-C=O/COOH/COOR units decrease as compared to the fibres treated at lower RF power (10 W). With further increase in treatment time (from 15-20 minutes), the
O=C-N/C=O/O-C-O, O-C=O/COOH/COOR and OCOO units increase while the C-O/C-O-C and C-C/C-H/C=N units decrease at the fibres. This attributed to the degradation in the chemical structure of the fibres due to prolonged energetic ion bombardment. At higher RF power (30 W) and increase in treatment time, the ion energy is sufficiently high enough to destroy the peptide bond and side chain of amino acid groups through sputtering and thereby leading to a severe loss of C-N, C-O/C-O-C and C-C/C-H/C=N units. It is apparent that ion bombardment to the sample promotes the chemical interaction of the nearby atoms at the surface of the fibre through momentum transfer which eventually leads to the change in its surface chemistry. Besides at such higher RF power more and more free radicals are formed at the surfaces of the fibres which possibly contribute to the increase in O=C-N/C=O/O-C-O and OCOO units in the fibres.

**Table 3.3** Summary of the curve fitting of C1s peaks of virgin and plasma treated muga fibres at various treatment conditions.

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>Treatment time (mins)</th>
<th>Functional composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C-N</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>5.7</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>5.0</td>
</tr>
<tr>
<td>20</td>
<td>5</td>
<td>3.8</td>
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<tr>
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<td>3.0</td>
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<td>5</td>
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<tr>
<td></td>
<td>10</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>1.2</td>
</tr>
</tbody>
</table>
3.4 Surface morphology of virgin and Ar plasma treated muga silk fibre

3.4.1 Scanning electron microscopy (SEM) and EDX analysis

The SEM micrographs of virgin and Ar plasma treated muga fibres are shown in Figures 3.5 (a)-(h). Figure 3.5 (a) shows smooth surface of virgin muga silk fibre with fewer defects. This confirms the presence of thin layer of sericin remained even after the chemical degumming process. In between the fibroins some kind of flaws are present for untreated muga silk fibre. At RF power of 10 W, the variation in treatment time does not seem to bring any significant change in surface morphology of the fibres with respect to virgin one (Figures 3.5 (b)-3.5 (c)). This is may be due to the fact that the impinging ion energy on the substrate (at RF power of 10 W and within treatment time of 5-20 minutes) is not sufficient enough to change the surface morphology of the treated fibre. From this finding it can be concluded that the last and final layer of sericin has good adhesion to fibres surface and to remove it impinging ions with high energy may be beneficial. As expected, At RF power of 20 W and treatment time of 5 minutes (Figure 3.5 (d)), slight surface roughness is introduced on the fibre due to the ion sputtering effect on the substrate. However, the fibre treated for 10 minutes shows relatively smooth surface (Figure 3.5 (e)) as compared to that treated for 5 minutes. This is attributed to the efficient removal of fibroin region through the peptide bond scission and breakage of side chain of amino acid residues, which is well revealed from XPS analysis.
At higher RF power of 30 W, extensive surface degradation can be observed on the fibres' surfaces when the treatment time is increased from 5 to 20 minutes. It is apparent that at such higher RF power (30 W) the ions acquire sufficiently high energy to sputter
the fibres thereby causing extensive damage to the peptide bond and side chain of amino acid groups and this results in much more surface degradation to the fibres in the form of micro pits and voids (Figure 3.5 (g) and 3.5 (h)). From these discussions it is revealed that above a critical plasma discharge parameter value the ions acquire sufficiently high energy to sputter the fibre surface while below that critical value the energy of the ions is too low to produce any observable change in the surface morphologies of the fibres. The observed crystals on the fibre surface are attributed to calcium oxalate (Ca$_2$C$_2$O$_4$) deposits, a typical contaminant left by the silkworm on silk surface during spinning (excrements) processes [21-23]. The presence of calcium oxalate (CaC$_2$O$_4$) is confirmed after the EDX analysis. The effect of Ar plasma treatment on muga silk fibre surface is presented in Table 3.4.

**Table 3.4** Elemental percentage of C, N, O and Ca in virgin and Ar plasma treated muga silk fibre at various RF power and treatment time (10-30 W).

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>Treatment time (minutes)</th>
<th>Elemental percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>0</td>
<td>0 (untreated)</td>
<td>63.0</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>62.8</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>63.1</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>63.2</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>63.4</td>
</tr>
<tr>
<td>20</td>
<td>5</td>
<td>63.1</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>63.5</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>64.8</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>63.8</td>
</tr>
<tr>
<td>30</td>
<td>5</td>
<td>58.4</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>58.2</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>54.8</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>55.6</td>
</tr>
</tbody>
</table>

Untreated muga silk yarn has highest percentage of C with the presence of N and O. Calcium (Ca) is also present in bulk amount. After the Ar plasma treatment at various parameters it is observed that no significant variation in the elemental percentage of C, N and Ca contents for lower treatment time (5-15 minutes) and RF power (10 W). Ar
plasma treatment at these parameters results in lowering the percentage of O, due to the removal of sericin layer. At RF power of 20 W with higher treatment time (except 5 minutes) some changes are observed. Constituent elements percentage are remained with heavy lose in Ca percentage. With increased treatment time at same RF power O content is found to be decreases, possibly due to the removal of several other polar functional groups from the side chain of macromolecule structure. Lowering in Ca contents reveals the removal of calcium oxalates from the surface due to ion bombardment effect. At further increased RF power (30 W), lowering in C and N content is observed with Increment in O content. As evident from SEM images at higher RF power, due to energetic ion bombardment savoir surface degradation takes place results in etched out the fibroin surface.

3.4.2 Atomic force microscopy (AFM)

Figures 3.6 (a)-(d) show the 3 dimensional AFM micrographs of the virgin and Ar plasma treated fibres for treatment times of 5, 10 and 20 minutes.

![AFM micrographs](image)

**Figure 3.6** AFM micrographs of the (a) virgin and plasma treated muga fibres at treatment time of (b) 5, (c) 10 and (d) 20 minutes.
AFM characterization is carried out in some of the samples prepared in optimized parameter. It is revealed from Figures 3.6 (b)-(d) that the RF Ar plasma treatment on the muga fibres affects their surface roughness within the nm-scale range. The small root mean square (rms) value for virgin fibre is due to the fine fibril structures of the fibre. These fibril structures are formed during the fibre extraction process [24, 25]. For lower treatment time of 5 minutes maximum rms roughness (34.02 nm) is observed due to the incorporation of pits and craters all over the fibre surface (Figure 3.6 (b)). At treatment time of 10 minutes, the rms roughness value of the treated fibre is observed to be decreased and this finding agrees well with the results drawn from the analyses of SEM micrographs. Further increase in treatment time (15-20 minutes) leads to the non-uniform distribution of surface roughness and hence rms roughness value gets decreased.

3.5 Wide angle X-ray diffraction (WAXD)

Figure 3.7 (a)-3.7 (b) shows the XRD patterns of the virgin and plasma treated fibres at various RF power (10-30W) for same treatment time of 10 minutes and also with variation in treatment times (5-20 minutes) at RF power of 20W. The XRD patterns reveal the coexistence of both α-phase and β-phase in the muga fibres. From Figures 3.7 (a) and (b), two sharp diffraction peaks is observed at scattering angles (2θ) of 16.5° and 20.2° with corresponding crystalline spacing’s of 5.3 and 4.4Å respectively [8, 33]. Appearance of the peak at 20.2° represents the highly ordered crystalline region of anti-parallel β-sheet of macromolecular structure of the muga silk and 16.5° suggest the random coil α-helix conformation. The presence of the minor peaks at 14.7°, 24.40, 26.4°, 28.2 and 29.9 are attributable to calcium oxalate (CaC₂O₄) present on the surface of the fibres, a typical contaminant left by the silkworm on silk surface during excrements [8, 26, 27].

The appearance of the two broad peaks at 33.0° and 38.8° corresponds to the existence of parallel β-sheet structure in the fibres. From Figure 3.7 (a) it is evident that Ar plasma treatment effects the crystalline structure of muga silk may be due to the etching/ removal of some amorphous constituents of the fibre and subsequently re-arrangement of the crystalline regions in such a way that the treated fibres show more crystalline nature. Similarly XRD pattern for treated silk with variation in their treatment time at same RF power of 20 minutes are presented in Figure 3.7 (b).
Figure 3.7 (a) XRD patterns for Ar plasma treated muga silk fibre at various RF power and treatment time of 10 minutes and (b) different treatment time at RF power of 20W.

The relatively higher value of intensity of the peak at 16.64° indicates more crystallinity of the fibres treated at 10-20 minutes than that of the virgin one. It is observed that the shapes and intensities of the peaks corresponding to α-phase remains same for both virgin and plasma treated fibres thereby indicating that Ar plasma treatment has little effect on the α-sheet structure in the amorphous region. On the other hand at lower
treatment time (5-10 minutes) the crystallinity of the fibre increases due to increase in the intensity of the major peak at 16.5° and becomes enhanced at treatment time of 10 minutes. With further increase in treatment time (15-20 minutes) the intensities of the peaks at 16.6° and 20.1° decrease thereby indicating lowering in crystallinity of the fibres. This is may be attributed to the destruction in complex macromolecular structure containing peptide bond and side chain groups of amino acid by prolonged energetic ion bombardment to the substrates. The molecular rearrangement of the macromolecule in glycine and alanine unit and also the formation of oligomer/hetero-oligomer at the surface of muga fibre due to impinging energy of the ions lead to increase the silk crystallinity [23].

3.6 Physical properties of untreated and RF Ar plasma treated muga silk fibre

3.6.1 Mechanical strength
The variation of tensile strength of the virgin and Ar plasma treated muga fibres as a function of treatment time is shown in Figure 3.8.

**Figure 3.8** Variation in tensile strength (gm/den) of the virgin and Ar plasma treated muga fibres as a function of treatment time (minutes).
The tensile strength of virgin muga fibre is evaluated to be 3.81 gm/den. At lower RF power of 10 W, no significant variation in tensile strength of the treated fibres can be observed. This is possibly attributed to similar surface chemistry of the treated fibres as compared to the virgin one which is well revealed from XPS analysis. For muga fibres treated at 20 W, tenacity reaches a maximum value of 4.5 gm/den at treatment time of 10 minutes and after that it decreases with further increase in treatment time (from 15 to 20 minutes). The higher value of tenacity at 10 minutes is attributed to the presence of highest percentage of carbon content and also the increase in more C-O/C-O-C and C-C/C-H/C=N units at the surfaces of the fibres. The decrease in carbon content and C-O/C-O-C and C-C/C-H/C=N units are the possible reasons for lowering the tensile strength of the fibres treated for longer times (15 - 20 minutes). Moreover increase in oxygen content and the O=C-N/C=O/O-C-O, O-C=O/COOH/COOR and OCOO units may also contribute to a decrease in the fibres’ tensile strength. At higher RF power (30 W) the tensile strength of the fibres gradually decreases with the increase in treatment time. This may be contributed due to increase in oxygen content and decrease in C-N, C-O/C-O-C and C-C/C-H/C=N units in the fibres. The tensile strength of the fibres treated at 30 W and treatment time of 5-20 minutes lies well below that of the virgin one.

The observed tensile strength behavior of treated muga fibres can further be explained from stress concentration effect induced by Ar plasma treatment [27]. As observed from SEM micrographs (Figures 3.5 (b)-3.5 (c)) the energy of the impinging ions on the substrate does not seem to introduce significant surface roughness or defect on the fibres thereby making the stress concentration effect almost independent of the treatment time. These results in nearly similar variation of tensile strength of the muga fibres treated at RF power of 10 W and within the treatment time range of 5-20 minutes. At RF power of 20 W and in the treatment time of 5 minutes, the impinging ions on the fibres produce defect in the form of irregularities (micro pits and voids) through the cleavage of peptide bond and side chain of amino acid residues. This may have concentration effect on the fibre thus leading to a decrease in the fibre tensile strength (Figure 3.5 (d)). At treatment time of 10 minutes the removal of more weakly bonded fibroin region possibly smoothen the surface of the fibre, thereby inducing less defects than that of the fibre treated for 5 minutes (Figure 3.5 (e)). The minimization the stress concentration effect due to less defects thus probably leads to a higher value for fibre’s
tensile strength (maximum in this case) [27]. With higher treatment time, much more destruction in the chemical structure and subsequent increase in surface defects takes place by prolonged energetic ion bombardment and this can be associated with lowering in tensile strength in the fibres (Figure 3.5 (f)). At RF power of 30 W, the ions acquire sufficiently high energy to bombard the substrate leading to a severe damage on the surface chemical structure of the fibre even at lower treatment time which is well revealed from XPS analysis. This incorporates more surface defect in the fibre (Figures 3.5 (g) – 3.5 (h)) with higher treatment time and consequently leads to the decrease in the tensile strength of the fibres.

3.6.2 Water contact angle

The variation in water contact angle on the virgin and plasma treated muga fibres as a function of treatment time is shown in Figure 3.9. The water contact angle for virgin muga fibre is measured to be 100°. No significant variation in water contact angle on the fibres, treated at 10 W, can be observed within the treatment time range of 5-20 minutes. Maximum water contact angle of 115° is observed for the muga fibre treated for 5 minutes and at RF power of 20 W. This is due to the increase in carbon content as well as the C-C/C-H/C=N and C-O/C-O-C units in the fibres. Not only the lowering in oxygen content and O=C-N/C=O/O-C-O and O-C=O/COOH/COOR units may also contribute to the increase in water contact angle on the fibres. The water contact angle on the treated fibres remains almost same as the treatment time is increased from 5-10 minutes. This is attributed to the almost similar variation in atomic concentration and functional composition of the fibres as revealed from XPS analysis. With further increase in treatment time (from 15 to 20 minutes) the water contact angle decreases by ~ 30° thereby indicating more increase in surface roughness due to energetic ion bombardment on the substrates for longer time. The decrease in water contact angle on the fibre surface above 10 minutes of treatment time can be correlated with the decrease in carbon content and C-C/C-H/C=N units in the fibres. An increase in oxygen content and the O=C-N/C=O/O-C-O and OCOO units also apparently contribute to the decrease in water contact angle on the fibres. At higher RF power of 30 W, the water contact angle is observed to be further decreased with increase in treatment time and this may be attributed to the growth of more surface roughness on the surface of the fibre caused
by energetic ion bombardment to the substrates. The variation in water contact angle of
the fibres treated at 30 W can be well corroborated with the XPS results.

It is important to mention that along with enhanced water contact angle Ar plasma
muga silk fibre are also able to exhibit the “lotus effect”. The lotus effect refers to the
very high water repellence (superhydrophobicity) exhibited by the leaves of the lotus
flower (*Nelumbo*). Dirt particles are picked up by water droplets due to a complex
micro- and nanoscopic architecture of the surface, which minimizes adhesion. In similar
manners as evident from AFM analysis due to the formation of nano-patterns on fibre
surface after Ar plasma treated muga silk fibre has increases the water contact angle
with self-cleaning behaviour of the fibre.

![Figure 3.9](image.png)

**Figure 3.9** Variation in water contact angles on the virgin and Ar plasma treated muga
fibres as a function of treatment time.

### 3.7 Thermal properties of virgin and Ar plasma treated muga fibre

#### 3.7.1 Differential scanning calorimetry (DSC)

Figure 3.10 shows the DSC thermograms of virgin and Ar plasma treated (10 minutes)
muga fibres at various RF powers (10 – 30 W). All the plots presented in Figure 3.10
show similar DSC thermograms thereby indicating that the variation in plasma
discharge parameters have less significant effect on the thermal behavior of the fibres. The first broad endotherm below 100$^\circ$C is due to the evaporation of water. The thermal stability of virgin and Ar plasma treated muga fibres remains almost same and unchanged up to 206$^\circ$C.

![Figure 3.10](image)

**Figure 3.10** DSC thermograms of virgin and Ar plasma treated muga fibres in the RF power range of 10-30 W (treatment time: 10 minutes)

As revealed from Figure 3.10, two minor and broad shoulder peaks appear at 231$^\circ$C and 297$^\circ$C and this can be related to the molecular motion of the fibroin chains in the fibres [17]. It is assumed that the water molecules adsorbed in the fibres probably restrict the alignment of the fibroin chain molecules. On removal of these water molecules from the fibres above 100$^\circ$C (Figure 3.11), the restricted force being withdrawn, the molecular chains are free to rearrange within the fibres. This explanation may find good agreement with the results obtained for some plant fibres [20]. The prominent endothermic peak at 362$^\circ$C is attributed to the thermal decomposition of muga fibres.

### 3.7.2 Thermogravimetric analysis (TGA) analysis

The thermal behaviour of the virgin and Ar plasma treated muga fibres are further studied by TGA. The thermograms of virgin and plasma treated muga fibres (treatment time 10 minutes) at RF power range of 10-30 W and the corresponding differential thermagrams (DTGA) are shown in Figures 3.11 (a) and 3.11 (b). All the Ar plasma
treated fibres exhibit almost similar thermal stability irrespective of the change in RF power and treatment time. From Figures 3.11 (a) and 3.11 (b) no significant variation in the weight loss of the treated fibres from the virgin one can be observed within the temperature range of 33-850°C. As observed from the plot presented in Figure 3.11 (b), each of the thermogram is accompanied with four steps of weight loss. The thermal behaviour of the virgin and Ar plasma treated muga fibres data are summarized in Table 3.5. The results obtained from Table 3.5 indicate that all the endotherms attributed in the DSC records are accompanied by the weight loss steps as shown in Figure 3.12 (b).

![Graph](image1)

**Figure 3.11** (a) TGA and (b) DTGA curves of virgin and Ar plasma treated muga fibres in the RF power range of 10-30 W and treatment time of 10 minutes.
Table 3.5 Thermal behavior of virgin and Ar plasma treated muga fibres (treatment time: 10 minutes) at in the RF power range of 10-30 W.

<table>
<thead>
<tr>
<th>RF power (W)</th>
<th>First step</th>
<th>Second step</th>
<th>Third step</th>
<th>Fourth step</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (virgin)</td>
<td>2.9/(39-117)</td>
<td>2.7/(117-269)</td>
<td>15.2/(269-333)</td>
<td>44.8/(333-846)</td>
</tr>
<tr>
<td>10</td>
<td>3.6/(35-130)</td>
<td>3.6/(130-261)</td>
<td>14.9/(261-329)</td>
<td>45.7/(329-846)</td>
</tr>
<tr>
<td>20</td>
<td>3.0/(37-128)</td>
<td>3.5/(128-263)</td>
<td>15.1/(263-330)</td>
<td>46.2/(330-846)</td>
</tr>
<tr>
<td>30</td>
<td>3.6/(36-121)</td>
<td>3.1/(121-260)</td>
<td>15.9/(260-334)</td>
<td>45.3/(334-846)</td>
</tr>
</tbody>
</table>

The occurrence of the first weight loss step is attributed to the removal of absorbed water while the fourth step weight loss is due to decomposition stage as stated earlier from the DSC results. The DTGA curves reveal that in the temperature region (333-846°C) for decomposition, the virgin muga fibre show slightly more thermal stability (370°C) than all the plasma treated fibres (366°C). From the above findings it is apparent that Ar plasma treatment within the RF power range of 10-30 W and treatment time of 5-20 minutes does not much affect the thermal stability of the fibres.

3.8 Conclusion

Studies of Ar plasma discharge characteristics reveal an increase in electron temperature and plasma density with increasing RF power. Plasma potential is observed to remain almost same irrespective of the increase in RF power. The thermal behavior of the treated fibres remains unaffected by the variation in treatment time and RF power. Significant change in the chemical structure of the plasma treated fibres can be observed at higher RF power (30 W). As revealed from XPS analysis, the peptide bond scission and the breakage of side chain of amino acid groups caused by impinging ion energy contribute to the variation in atomic concentration and functional composition in the treated fibres and subsequently affect the tensile strength and hydrophobicity of the fibres. At critical RF power of 20 W and lower treatment time (5-10 minutes), the plasma treated fibres exhibit enhanced tensile strength and hydrophobicity and this may be attributed to the higher carbon content in the fibre and low stress concentration effect on the fibre induced by smoother surface structure. Besides, the presence of more carbon containing functional (C=O/C=O-C and C-C/C=H/C=N) units at the surfaces may
also enhance the observed tensile strength and hydrophobicity of the fibres. Higher RF power and treatment time results in severe destruction of the peptide bond and side chain of amino acid groups and hence results in incorporation of more surface roughness and stress concentration effect thereby deteriorating the observed properties of the fibres. Moreover, incorporation of more oxygen and oxygen containing functional (O=\cdot N/C=O/O-C-O, O-C=O/COOH/COOR and OCOO) units is also observed to be responsible for decrease in the tensile strength and hydrophobicity of the fibres. The results indicate that in the present Ar plasma discharge conditions, the muga fibre can find efficient application in textile industries in terms of weaving and decorative purposes.
References