Chapter-IV

The physico-chemical properties of grafted silk fibre *

4.1. Introduction

Graft copolymerization of vinyl monomer onto silk is one of the universal, effective and accessible methods for chemical modification of higher molecular weight compounds or for producing substantial modification of the physical, mechanical, and morphological properties of the fibres.\textsuperscript{1-4} The characterization of grafted products is an important aspect of graft copolymerization for better understanding of nature of grafting, surface morphology, area of applications as end products. The structural, thermal properties and morphological structure of grafted fibres have been characterized by X-ray diffraction, differential scanning calorimetry (DSC), thermogravimetry, water absorption measurements, scanning electron microscopy (SEM),\textsuperscript{5} tensile strength measurements, water absorption measurement etc. The physico-chemical properties of grafted silk fibres depend on the chemical characteristics of monomer used as well as on the extent of grafting and on the reaction conditions.\textsuperscript{4} The study of the effect of grafting of MMA onto silk fibres are interesting from the point of exploiting the modified fibres for textile and nontextile uses.

X-ray diffraction studies usually applied to monitor the effect on crystalline nature of grafted fibres. Tsukada et al.\textsuperscript{4} studied the X-ray diffrac-

* Part of result is accepted for publication in Bioresource Technology, 2005 (In press).
tion intensity curves of MMA-grafted silk fibres along untreated silk sample and finally concluded that the graft copolymerization reaction that occurred inside the fibre.

DSC and TGA thermograms indicate the thermal stability of grafted products and increasing in value shows the increase of thermal stability in compare with untreated fibres.

SEM technique elaborate the changes in surface topology brought about by different chemical treatment such as dewaxing, mercerization, grafting.¹

Water absorption measurements also contributes important conclusion in characterization of grafted fibres as moisture exerts a significant role on physical properties of hydrophilic polymers. For example, as moisture content increases from 0 to 20% by weight, $T_g$ of cellulose decreased by approximately 260°C.⁶

A tensile strength measurement indicates the mechanical stability of treated fibres. Mechanical study showed that intrinsic tensile properties of silk are influenced by grafting as a result of various physico-chemical and morphological changes.⁷

4.2. Characterization methods of grafted products

4.2.1. X-ray diffraction studies

X-ray diffraction studies were performed using an X-ray source with $CuK_α$ radiation ($\lambda = 1.54$ Å). The conditions for X-ray measurement were followed from standard literature available.⁸
4.2.2. Thermal analysis

Thermal analysis was carried out by the Perkin Elmer differential scanning calorimeter (DSC) and DSC thermograms were recorded at the heating rate of 10°C per minutes in the nitrogen environment.

TGA analysis of ungrafted and grafted silk fibres were carried out by Perkin Elmer thermal analyzer in the temperature range of 50-800°C at the heating rate of 10°C per minutes in the nitrogen environment.

4.2.3. Scanning electron microscopy (SEM)

The surface morphology of grafted and ungrafted fibre was investigated by a scanning election microscope (Hitachi S-415 A) operating at accelerating voltage:10-15kV, image mode: secondary electron image. The samples were coated with gold in a sputter coater under vacuum with a layer of 15-20 mm thick.

4.2.4. Tensile properties

The stress-strain behaviour of the grafted and ungrafted fibres under tension was evaluated by Zwick (Z010) Tensile Testing Machine (UTM) as per ASTM D 638 standard.9

The fibre samples were cut into 10 cm in length and care has been taken that each specimen free from abnormalities like cut edges, creases or wrinkles. The samples were selected randomly and conditioned at 25°C and 65% relative humidity (RH).10 The fibres were first clamped to the upper jaw, and then carefully clamped in the lower jaw. The gauge length and rate of extension were 50 mm and 10 mm/min, respectively. After carefully clamped
in the both jaws load was applied to the specimen until it breaks. An average of ten samples of each silk fibre was run under same conditions.

4.2.5. Water absorption measurements

The water absorption measurements of grafted and ungrafted silk fibres were compared with standard method.\textsuperscript{11, 12} The weight of the dry silk fibre was recorded before the sample were soaked in deionised water until an equilibrium weight was achieved at ambient environment. After that, determination of the water absorption by fibre was practiced by centrifuging the samples. The samples were placed on the strainer of a specially made centrifuge tube and centrifuged for 15 min. An arrangement was made so that the bottom of the tube to allow excess water to drain away from the sample. The centrifuge tube was sealed to ensure 100\% relative humidity to prevent desorption of water by the fibres. The samples were weight and this weight was considered as wet weight of fibre and the samples were then dried in a vacuum oven at $40 \pm 5^\circ C$ for 24 h. The dry weight was recorded and compared with the earlier one. The water sorbency was calculated in terms water retention value and expressed as follows

\[
WRV (g/l g) = \frac{\text{weight of silk fibre (wet)} - \text{weight of silk fibre (dry)}}{\text{weight of silk fibre (dry)}} \times 100
\]

where, WRV implies water retention value in gram of water per gram of dry sample. The average values were estimated from five replicate measurements for each specific sample, and results were reported.
4.2.6. Chemical resistance measurement

The chemical resistance of grafted and ungrafted fibres was measured using ASTM D 443-87 method. Each fibre was dipped in the respective chemical for 24 h and above (in some cases), then removed from the respective solvent and followed by washing in distilled water. The samples were weighed after drying in the oven at 40°C for 10 h and the loss/gain was calculated in terms of percentage.

4.3. Results and discussion

4.3.1. DSC thermograms

DSC thermograms of grafted (PMMA-g-silk, PAAm-g-silk) and ungrafted silk fibres are reported in Figures 4.1.(a), (b), (c). The DSC thermogram of ungrafted fibre shows one exotherm at 320°C possibly due to decomposition of fibre. The grafted product shows two exotherms at 330°C and 410°C possibly due to decomposition of grafted fibre. The shifting of initial decomposition temperature from 320°C to 330°C for grafted fibres.

Figure 4.1. (a): DSC thermograms of ungrafted silk
indicate the increased thermal stability of grafted fibre whereas the homopolymer (PMMA) alone shows exotherm around 360-380°C due to degradation. The result is similar when grafting was carried of with conventional initiator.

![Graph](image)

**Figure 4.1. (b):** DSC thermograms of 10.20 % MMA grafted silk

![Graph](image)

**Figure 4.1. (c):** DSC thermograms of 11.95 % AAm grafted silk

The DSC thermogram of grafted fibre (PAAm-g-silk) shows two exotherms at 330°C and 380°C. The shifting of exotherm is also observed as in the earlier case which indicates the improvement of thermal stability of grafted fibre.
4.3.2. **Thermal behaviour from TGA analysis**

The thermal behaviour of ungrafted and grafted silk fibres was analyzed with TGA. The TGA was performed at heating rate of 10°C per minute. TGA curves for ungrafted and grafted fibres are plotted in the Figures 4.2 (a), (b), (c).

![TGA curve](image)

**Figure 4.2 (a):** TGA curves for ungrafted silk fibre

The initial decomposition temperature noted for TGA thermogram for grafted and ungrafted fibre. The initial decomposition for ungrafted fibre was 306°C whereas 350°C and 370°C for MMA grafted and AAm grafted fibre respectively. This shows higher thermal stability of the grafted fibre.

In terms of weight loss values, grafted fibre showed 10% weight loss at 370°C (MMA grafted) and 350°C (AAm grafted) in compare with 337°C for ungrafted fibre. Similar trend was observed in other values of weight loss of fibres (Table 4.1), though AAm grafted showed unusual behaviour in the first phase of heating.
Figure 4.2 (b): TGA curves for MMA grafted silk fibre

Figure 4.2 (c): TGA curves for AAm grafted silk fibre
Table 4.1: Weight losses of ungrafted and grafted silk fibres at heating rate 10°C/minute

<table>
<thead>
<tr>
<th>Nature of silk</th>
<th>Weight loss (%) in different temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5%</td>
</tr>
<tr>
<td>Ungrafted</td>
<td>306</td>
</tr>
<tr>
<td>MMA grafted</td>
<td>350</td>
</tr>
<tr>
<td>AAm grafted</td>
<td>214</td>
</tr>
</tbody>
</table>

4.3.3. X-ray diffraction study

X-ray diffraction curves for ungrafted fibre and PMMA-grafted silk fibre with different amount of graft yield were recorded and represented in the Figure 4.3. The untreated silk fibre (curve a) showed a major X-ray diffraction peak at 20.5 degree. It has been observed from diffraction curve (curve b) of 10.20% PMMA-grafted silk that the position and intensity of the

![X-ray diffraction intensity curves](image)

Figure 4.3: X-ray diffraction intensity curves of the grafted silk fibres with various amounts of MMA grafted yield. (a) ungrafted silk, (b) 10.20% grafted silk, (c) 18.67% grafted silk
main diffraction peak did not change. Thus it suggested that the crystalline structure of silk fibre was not altered after grafting which was also confirmed from literatures available.\textsuperscript{5,15} Though a little change was notified in the grafted silk of higher graft yield (curve c).

4.3.4. SEM studies

The morphological studies of ungrafted and grafted silk (PMMA-\textsuperscript{g}-silk, PAAm-\textsuperscript{g}-silk) fibres were performed by scanning electron microscopy (SEM). The SEM micrographs of ungrafted and grafted fibre were shown in Figures 4.4 (a)-(h). As semiconductor-based photografting is likely to occur on the surface of the fibres hence grafting should leave its mark on the surface morphology of the fibres.\textsuperscript{13} The smooth and evenness of the fibre surface was observed in the micrograph of ungrafted fibre. The change in surface morphology after grafting with monomers was clearly revealed by the SEM micrograph as grafting affected the surface of silk fibres. The unevenness of surface resulted from deposition of polymer, which formed during graft copolymerization with monomers. The cracks in the surface of ungrafted fibre [Figure 4.4 (a)] are filled up by the monomer that uploaded during the graft copolymerization in grafted fibre [Figure 4.4 (c)]. The roughness of surface of the grafted fibre increased with increasing the percent grafting.

These results are quite similar with the works by Tsukada \textsuperscript{5} on the grafted fibres (PMMA loading silk), which demonstrating the presence of granules that appeared chemically bonded and/or physically adhered to the surface of the grafted silk fibres. However, the changes in thermal and
Figure 4.4: Scanning electron micrographs of MMA grafted silk fibres. Graft yield (%): a) 0; b) 10.20; c) 18.67; d) 24.59.
Figure 4.4: Scanning electron micrographs of AAm grafted silk fibres. Graft yield (%): e) 11.95; f) 16.38; g) 17.25; h) 26.47.
mechanical properties (as observed in earlier results) may support that grating is not merely a surface phenomenon.

4.3.5. Tensile strength measurements

The stress-strain curves for ungrafted and grafted fibres with MMA and AAm are shown in Figure 4.5. Grafting results in increase in yield point and slope of the stress-strain curve. The percentage of elongation at break has been increased from 7% to 12% for MMA grafted fibre (curve b) and 14% for AAm grafted fibre (curve c). The decrease in yield point for grafted fibre is observed as percent of grafting increases. Similar nature is also observed for AAm grafted fibre. On the other hand MMA grafted fibre shows high yield value but lower elongation at break than the AAm grafted fibre. In case of MMA grafted fibres, lower elongation at break is expected since

![Figure 4.5: Stress-strain curves for ungrafted and grafted fibres. (a) ungrafted silk fibre, (b) MMA-g-silk; 37.84% grafted, (c) MMA-g-silk, 48.45% grafted, (d) AAm-g-silk; 17.38% grafted, (e) AAm-g-silk; 26.47% grafted.](image-url)
flexibility of PMMA is lower than the PAAm uploaded fibre at room temperature. The increase in elongation at break for grafted fibre indicates that due to grafting many of intermolecular forces holding the chains together are broken, facilitating the slippage of molecules. Further, acrylic polymers except MMA have the $T_g$ value below room temperature and making the grafted polymer more easily extendable. This phenomenon is also reflected while comparing the slope of stress-strain curve. With grafting, slope is gradually decreased, i.e., modulus of elasticity is decreased.

4.3.6 Chemical resistance measurements

The effect of different chemicals on ungrafted and grafted silk fibres is reported in the Table 4.2. It was observed that on treating with acetic acid, NaOH, benzene and toluene, ungrafted and grafted silk fibres (PMMA-g-silk, 24.59% grafting; PAAm-g-silk, 26.47% grafting) lose their weight to some extent. In 60% NaOH solution the ungrafted silk fibre was dissolved but both types of grafted fibre showed resistance towards the alkali. It was also found that nitric acid couldn’t fully dissolve the grafted silk fibre even after 7 days.

Table 4.2: Effect of chemicals on weight of ungrafted and grafted fibres

<table>
<thead>
<tr>
<th>Chemical</th>
<th>% weight loss in dipping for 24 h</th>
<th>Ungrafted silk</th>
<th>PMMA-g-silk</th>
<th>PAAm-g-silk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>7.14</td>
<td>15.38</td>
<td>18.75</td>
<td></td>
</tr>
<tr>
<td>Conc. HCl</td>
<td>Dissolved</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60% NaOH</td>
<td>Dissolved</td>
<td>12.28</td>
<td>Slightly swollen</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>4.95</td>
<td>3.47</td>
<td>4.61</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>2.88</td>
<td>2.24</td>
<td>2.39</td>
<td></td>
</tr>
<tr>
<td>Conc. HNO₃</td>
<td>Dissolved</td>
<td>Slightly swollen</td>
<td>Partially dissolved</td>
<td></td>
</tr>
</tbody>
</table>

*a Data reported from the average of five experiments.*
On grafting overall improvement in chemical resistance was observed. The weight loss in every case was decreased in case of grafted fibres but methyl methacrylate grafted fibres showed better chemical resistance than acrylamide grafted fibres. It may be due to the nature of the hydrophobic side chains of the MMA polymer filled in the fibre.

4.3.6. Water sorbency measurements

The grafting of silk with PMMA has imparted the hydrophobic nature onto silk, which is evident from the water retention values of ungrafted and grafted silks (Table 4.3). As the grafting percentage increases, the WRV (water retention value) is decreased. The low rate of grafting (%) did not show much variation of water retention value from ungrafted silk. With the increase of grafting on silk, the surface was covered with PMMA, which made the surface more hydrophobic thereby, decreasing the water retention value.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grafting (%)</th>
<th>WRV (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ungrafted silk</td>
<td>-</td>
<td>3.2</td>
</tr>
<tr>
<td>Grafted silk</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.51</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>6.42</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>10.20</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>18.67</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>21.52</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>48.45</td>
<td>2.0</td>
</tr>
</tbody>
</table>

^a Data reported from the average of five experiments.
A similar trend was also observed for acrylamide grafted fibre. The result showed that WRV value of grafted silk decreased with the increase of grafting (Table 4.4). The decrease in the water retention value might be due to decrease in cohesive force of the highly swollen fibre.¹⁷,¹⁸

<table>
<thead>
<tr>
<th>Sample</th>
<th>Grafting (%)</th>
<th>WRV (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ungrafted silk</td>
<td>-</td>
<td>3.2</td>
</tr>
<tr>
<td>Grafted silk</td>
<td>4.56</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>11.95</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>16.23</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>26.23</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>26.47</td>
<td>2.0</td>
</tr>
</tbody>
</table>

⁻ Data reported from the average of five experiments.

4.4. Conclusion

The semiconductor-based photocatalyst in combination with additives (Et₃N and ethylene glycol) is showing as a promising initiator in graft copolymerization of methyl methacrylate and acrylamide onto silk fibres. SEM clearly illustrates the surface unevenness of grafted fibres. On grafting, increase in thermal stability is observed. Moreover, the grafted fibres have shown increase in chemical resistance, increase in elongation at break, decrease in slope of the stress-strain curve and decrease in water retention values in some extent.
References