

# Silk Grafting with Methacrylamide: A Near-Infrared Spectroscopy Study

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**ABSTRACT:** The grafting of methacrylamide (MAA) onto silk has taken importance not only as weighting process but also as finishing operation to improve the properties of the silk fibers. It was confirmed that the MAA monomer concentration, the initiator amount, and the liquor ratio are the major parameters affecting the yield of the reaction. Varying these parameters, a large number of samples, i.e., silk yarns with different grafting yields and exhaust grafting baths with different residual MAA concentrations, were obtained. Near infrared (NIR) spectroscopy was used for the quantitative determination of MAA in silk yarns and MAA in exhaust baths after grafting. A correlation between silk yarns grafting yield and NIR spectra of MAA grafted yarns was obtained. This correla-

tion shows a coefficient of determination ( $R^2$ ) of 0.96 and a standard error of calibration (SEC) of 8.37 w/w for a mean value (M) of 31.82% w/w. A second correlation between MAA in exhaust grafting baths and NIR spectra was obtained. This correlation shows a  $R^2$  of 0.95 and a SEC of 2.93 g/L for a M of 17.16 g/L. Previous correlations were improved using silk samples cleaned by extraction of sizing agents and detergents which could interfere with MAA grafting and modify absorption spectra of bath solutions. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 253–262, 2011

**Key words:** near infrared spectroscopy; silk; grafting; methacrylamide; process control

## INTRODUCTION

The graft-copolymerization of vinyl monomers onto silk fibers has been originally introduced in the 60s as an alternative to the traditional mineral weighting technique with tin-phosphate-silicate, a method used for decades to increase silk weight to compensate for the loss resulting from degumming.<sup>1</sup> Silk grafting is carried out by the free radical initiation method. The primary step involves diffusion of chemicals inside the fiber matrix and formation of free radical sites on the backbone of the silk fibroin chains. This can be achieved by chemical (redox systems, such as persulfates and various metal complexes) or physical methods (UV,  $\gamma$  irradiation, photo-initiation, etc.). Then, the fibroin macroradicals can react with the monomer leading to propagation of a grafted polymer chain. Homopolymer can be formed as well by interaction of the initiating free radicals with the monomer molecules. Thus, formation of both grafted and homopolymer chains within the silk fiber matrix is likely to occur during grafting.

The range of vinyl monomers applied onto silk fibers is very large, but only MAA has been successfully transferred to the industrial scale.<sup>1,2</sup> Various vinyl monomers are effective in conferring the desired weight increase and bulkiness to silk, but the grafted polymer often entail some negative consequences on silk fibers, such as an excessive hydrophobicity, electrostatic charge, stiffness, decreased dye uptake, which impair the intrinsic fiber properties. On the other hand, MAA leaves the typical silk handle and drape unchanged, while increasing hydrophilicity, comfort, and easy-care properties of MAA-grafted silk fibers. MAA grafting is typically carried out on degummed silk yarn by using package dyeing machines. The yarn is immersed in a solution containing the grafting agent, emulsified by means of nonionic surfactant. The silk/MAA weight ratio can be varied according to the desired grafting yield. An amount of MAA of about 60–70% w/w on the weight of silk is used to achieve a weight increase of 15–20% over the pair, meaning that the degumming weight loss is fully recovered (pair) and the weight of silk is further increased of 15–20%. Then the initiator, usually ammonium persulfate (APS), is added in an amount of about 4% on the weight of MAA. The material-to-liquor ratio is 1 : 20 or lower. The temperature is increased from room

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temperature to about 75°C and maintained constant for about 1 h. At the end of the cycle, the silk yarn is thoroughly washed to remove unreacted monomers, oligomers, and the homopolymer formed in solution. MAA-grafted silk yarn finds application in different articles such as neckties, borders, and embroidery.

In this study, we propose NIR spectroscopy as a tool to investigate the grafting yield of silk and the MAA amount in grafting baths.

In the textile field, NIR spectroscopy has been found to be a useful technique to characterize raw materials, finished textile products, textile coatings and to control textile process. Different applications have been proposed: the determination of reducing sugars and maturity of cotton fibers, the degree of mercerization of cotton fabrics, the polyester amount in polyester/cotton blends, the moisture content and the heat-set temperature of nylon, etc.<sup>3</sup> NIR spectroscopy has also been used for the determination of some characteristics of raw wool such as fineness, yield, medullation, grease, and moisture,<sup>4-11</sup> and more recently for the determination of moisture content and dichloromethane extractable matters in wool combed slivers.<sup>12</sup>

Recently, NIR spectroscopy acquired interest in the environmental field in the study of chemical, biological, and physical parameters concerning water quality and in the monitoring of industrial water effluents. De Medeiros et al.<sup>13</sup> proposed a screening analysis using NIR spectroscopy of river seston downstream of a textile industry effluent. Sousa et al.<sup>14</sup> proposed a method for the determination of chemical oxygen demand (COD) in a domestic wastewater treatment plant using NIR spectroscopy measurements of seston collected from wastewater samples by filtration. Suehara et al.<sup>15</sup> verified the potential application of NIR spectroscopy to measure oil (carbon source of microorganism) and urea (nitrogen source) concentrations and solids content (indicator of growth inhibition of microorganism) to monitor, prepare and maintain the optimal biodegradation conditions of wastewater discharged from a biodiesel fuel production process.

In a recent study, we proposed the use of NIR spectroscopy as a tool that can rapidly determine the degumming loss of silk and the amount of sericin peptides accumulated in the degumming bath, in view of implementing an on-line system to control the entire degumming process, from the original material to the final product, including the sericin content in the effluents.<sup>16</sup> The results obtained from lab-scale models, i.e., silk fabrics and sericin solutions, showed correlation values from satisfactory to very good between chemical and spectroscopic (NIR) parameters, thus confirming the powerfulness of NIR spectroscopy as a tool to control the degumming

process and opening the way to its implementation on industrial scale.

In the context of another industry-driven research project aimed at innovating current technology of silk grafting in terms of novel grafting agents and process automation, the possibility of using NIR spectroscopy for the on-line control of key process parameters was investigated. A large number of MAA-grafted silk samples covering a range of grafting yield values up to 150% w/w was prepared and subjected to NIR analysis to study the correlation between grafting yield and spectroscopic parameters. Exhaust grafting baths obtained from the same grafting experiments with a concentration of MAA monomer, oligomer, and homopolymer up to 50 g/L were also analyzed by NIR with the aim of both on-line controlling the kinetics of the grafting process and determining the concentration of MAA by-products in the waste water.

## EXPERIMENTAL

### Materials

Degummed silk yarn (size: 7.25 Tex) was kindly provided by Ambrogio Pessina srl Tintoria Filati (Montano Lucino, Como, Italy). MAA was the commercial product provided by Röhm Italia, (Garbagnate, Milano, Italy). Formic acid (Sigma), APS (Fluka) and the other chemicals were analytical grade reagents.

### Grafting silk yarn with MAA

Grafting experiments were carried out on lab-scale machines. A Linitest Heraeus (URAI S.p.A., Assago, Italy) and a beaker dyeing apparatus Labomat Type BFA12 (Werner Mathis AG, Oberhasli, Switzerland) were used throughout the study. The beaker dyeing machine allowed a more precise control of the temperature ramp used in the grafting cycle.

Silk skeins (1–10 g) were prepared and used for grafting. Before grafting, the initial dry weight of silk samples was always determined by oven drying at 105°C for 2 h. In some experiments, the silk yarn was preliminarily extracted with petroleum ether and ethyl alcohol. The nature of residual foreign substances remaining in the yarn after degumming (mainly residues of surfactants and sizing agents) was also determined.

The grafting solution was prepared by adding the required amounts of MAA (0–200% w/w on the weight of silk), formic acid (final pH: 2.5–3), radical initiator APS (1–6% w/w on the weight of MAA) into the test tubes. The material-to-liquor ratio was varied from 1 : 40 to 1 : 20. The silk was immersed in the grafting solution and the temperature was raised to 75°C in about 30 min and kept at 75°C for

50 min. At the end of the grafting cycle, the silk samples were taken off and washed with water at 50°C for 10 min and then extracted with acetone for 30 min. Finally, the samples were thoroughly rinsed with distilled water at room temperature, oven dried at 105°C for 2 h, and cooled to room temperature in a desiccator until a constant weight.

The grafting yield and the grafting efficiency were calculated as follows:

$$\text{Grafting yield (\% w/w)} = [(W - W_0)/W_0] \times 100 \quad (1)$$

$$\text{Grafting efficiency (\% w/w)} = [(W - W_0)/W_m] \times 100 \quad (2)$$

where  $W$  is the final dry weight of grafted silk,  $W_0$  is the initial dry weight of silk, and  $W_m$  is the weight of the monomer MAA used for the reaction.

The amount of MAA in exhaust grafting baths was calculated as difference between the initial weight of the monomer introduced into the bath and the amount of monomer grafted onto silk and expressed as g/L with respect to the bath volume.

For preliminary tests, blank solutions consisting of grafting solutions reacted in test tube for the previously reported time and temperature without silk were also prepared.

### FTIR measurements

Fourier transform infrared (FTIR) spectra of sericin and a dried exhaust baths were collected in the region between 4000 and 600  $\text{cm}^{-1}$  by a Nexus Thermo Nicolet Spectrometer using the attenuated total reflectance (ATR) technique.

### NIR measurements: Spectra acquisition and calibration

A spectrometer FT-NIR (PerkinElmer, model Spectrum IdentCheck, Monza, Italy) equipped with integrating sphere (IdentCheck Reflectance Accessory, ICRA) for reflectance was used. For each spectrum, 64 scans were recorded at a resolution of 8  $\text{cm}^{-1}$  in the spectral region between 10,000 and 3700  $\text{cm}^{-1}$ . One spectrum for each sample was acquired.

For silk yarn spectra acquisition, each sample, weighing around 1.0 g, was placed on the ICRA accessory and made to adhere with the pressure of a weight. A set of 85 yarn samples with different grafting yield were used for the calibration, a second set of 16 yarn samples previously extracted to remove residual sizing agents and detergents were used for a further calibration. The measurements were carried out at room temperature and relative humidity.

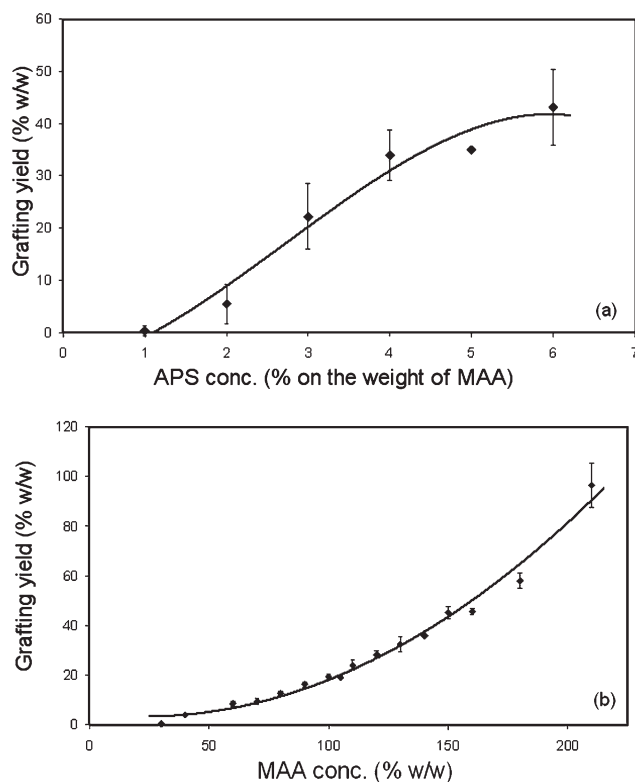
The NIR spectra of exhaust grafting baths were acquired in transmittance mode. A Petri plate with

sample solution and a transmittance mirror was placed on the measurement window.<sup>17</sup> The mirror creates a sample layer of defined thickness (0.5 mm) and reflects the beam back to the integrating sphere. NIR spectra were acquired at a constant temperature of 23°C. A set of 39 exhaust grafting baths with different amounts of MAA by-products were used for a first calibration. A second set of 14 exhaust grafting baths obtained using preliminarily extracted silk yarn samples was used for a second calibration.

The data were processed by means of Spectrum Quant+ (PerkinElmer) software package supplied with the instrument, and the partial least square 1 (PLS1) algorithms was used for all calibrations except for grafting yield in silk yarns, where principal component regression (PCR) algorithm was used. The grafting yield (% w/w) and the amount of MAA in exhaust grafting baths (g/L) were associated with the spectra of the respective samples, and the respective correlations were obtained. The entire spectral region of acquisition was used for all calibrations. A full cross-type evaluation process was used, excluding each standard in turn from the calibration, performing the calibration and then predicting the excluded sample using the calibration.

In the determination of grafting yield for validation purposes, 20 grafted silk yarn samples were removed randomly from the 85 original samples. Calibration was made using the remaining 65 samples. The set of 20 samples was used for method validation. This method was repeated 20 times, randomly changing the 20 samples used for calibration and validation each time. 400 predicted data of grafting yield were obtained and correlated with respective data obtained from the grafting yield equation. A similar validation process was carried out with data from the amount of MAA by-products in exhaust grafting baths. In this case, due to the lower number of samples used for the calibration (39 samples obtained with 4% w/w initiator, a material to liquor ratio of 1 : 40 and using the lab scale machine Linitest Heraeus), a set of 15 samples was removed from the original calibration and used 20 times for validation, changing each time the samples used for calibration and for validation. In this case, 300 predicted data of MAA concentration in exhaust grafting baths were obtained and correlated with respective reference data.

The principal statistics used to assess the quality of the NIR results were the coefficient of determination of the calibration ( $R^2$ ) and the coefficient of determination of the validation ( $r^2$ ). The standard error of calibration (SEC) and the standard error of prediction (SEP) and the ratio between standard deviation in original data set and the standard error of calibration (which is a cross validation calibration) SD/SEC.



**Figure 1** Dependence of grafting yield on (a) APS concentration in the reaction bath ( $R^2 = 0.971$ , grafting conditions: 70% w/w MAA on the weight of silk, material-to-liquor ratio 1 : 20) and on (b) MAA concentration in the reaction bath ( $R^2 = 0.9848$ , grafting conditions: 4% w/w APS on the weight of MAA; material-to-liquor ratio 1 : 40). Grafting experiments were carried out in triplicate, error bars represent standard deviation of measurements.

## RESULTS AND DISCUSSION

### Grafting MAA onto silk yarn

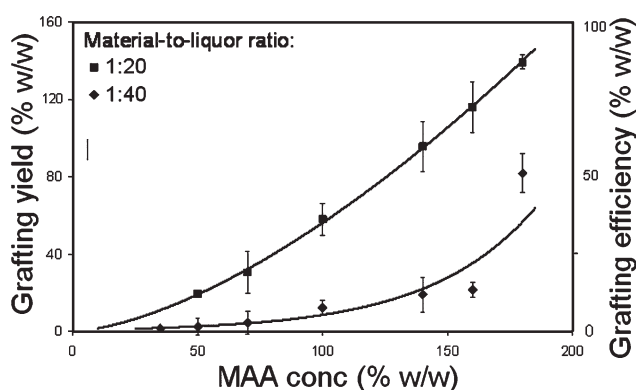
The graft-copolymerization of MAA onto silk fibers has been extensively investigated.<sup>1</sup> It is well known that key parameters affecting the yield of reaction are: the concentration of monomer and initiator and the liquor ratio. Other parameters, such as the temperature/time diagram, the circulation of the bath with respect of the fiber material, the level of agitation, the heating and contact time, the presence of surfactants or swelling agents, etc., are likely to affect the kinetics of the graft-copolymerization reaction by influencing the diffusion of monomer and initiator into the fiber and the initiation/propagation/termination steps of the reaction. Starting from this knowledge base, a series of grafting experiments was planned and carried out with the aim to prepare samples, i.e., MAA-grafted silk yarns and exhaust grafting baths containing MAA homopolymer by-products, for the subsequent NIR measurements.

The monomer/initiator weight ratio has a great effect on the yield of silk grafting with MAA. As

shown in Figure 1(a), the grafting yield increased almost linearly up to an APS concentration of 4% w/w on the weight of MAA, then tending to a plateau. These results are in good agreement with others previously reported.<sup>2</sup>

The silk/monomer weight ratio is another important parameter affecting the yield of grafting. Figure 1(b) shows that the grafting yield of grafted silk fibers increased gradually with increasing the concentration of MAA in the reaction bath, the other parameters being constant. Grafting yield values higher than 100% w/w were obtained under the reaction conditions used in this set of experiments, meaning that the initial weight of silk was more than doubled. Interestingly, such a large amount of MAA polymer was fully grafted inside the fibers. No traces of MAA polymer were found at the fiber surface, as demonstrated by the smooth and clean appearance of the fibers observed under the microscope (data not shown).

The grafting yield and grafting efficiency are strongly influenced by the material-to-liquor ratio. To maximize the yield of graft-copolymerization of MAA onto silk fibers with respect to homopolymerization in solution, the material-to-liquor ratio must be kept as low as possible. The plots of Figure 2 show that by changing this parameter from 1 : 40 to 1 : 20, both grafting yield and grafting efficiency increased sharply over the entire range of MAA concentration examined. At the highest MAA concentration of 180% w/w, the grafting efficiency increased from about 50% w/w to more than 85% w/w as the material-to-liquor ratio was decreased from 1 : 40 to 1 : 20.



**Figure 2** Behavior of grafting yield and grafting efficiency as a function of MAA concentration in the reaction bath at two different material-to-liquor ratios. ( $R^2 = 0.9984$  for material to liquor ratio 1 : 20 –  $R^2 = 0.9514$  for material to liquor ratio 1 : 40). APS concentration: 4% w/w APS on the weight of MAA. Grafting experiments were carried out in triplicate in the beaker dyeing apparatus Labomat Type BFA12. Error bars represent standard deviation of measurements.



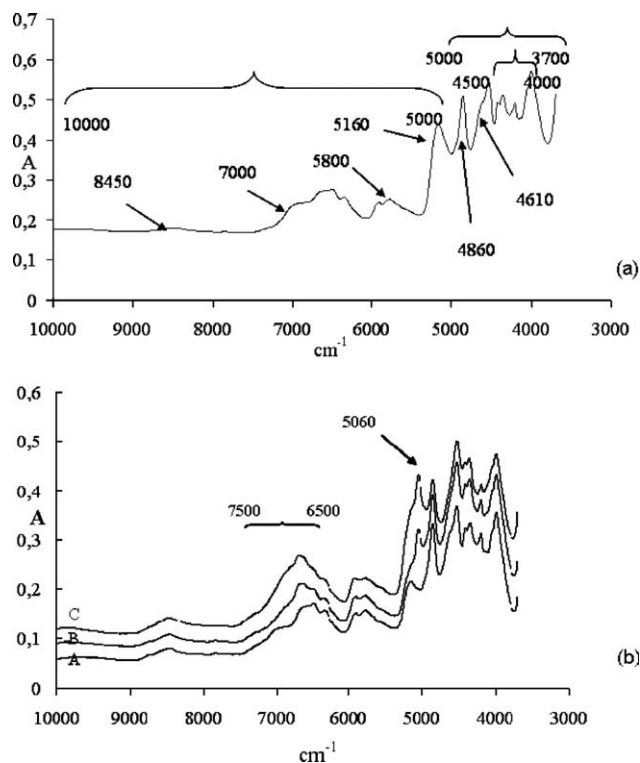
The grafting experiments performed in this study allowed preparing a large number of samples, comprising MAA-grafted silk yarns and the corresponding exhaust grafting baths, covering a wide range of grafting yield values, up to 150% w/w, and amounts of MAA by-products in solution up to 50 g/L. Typical grafting processes carried out at the industrial scale allow achieving grafting yield values of 50–60% w/w, while the content of residual MAA by-products in the waste water can be estimated to be about 10–15 g/L. These values fall within the ranges defined by the lab scale samples prepared in this study.

### NIR spectra of pure silk fibroin yarn, grafted yarn, and exhaust grafting baths

The absorption bands in the NIR region (13,000–4000  $\text{cm}^{-1}$ ) are the results of overtones or combination of overtones originating in the fundamental mid-range (4000–600  $\text{cm}^{-1}$ ) infrared region of the spectrum. These absorption bands are generally severely overlapped, difficult to resolve and, once resolved, difficult to interpret.<sup>18</sup> The bonds involved are usually R-H (C–H, O–H, N–H, S–H, etc.). The NIR spectra are generally used for quantitative purposes. In the quantitative approach, statistical connection between spectral data and a known sample characteristic can be found by means of chemiometric analysis.

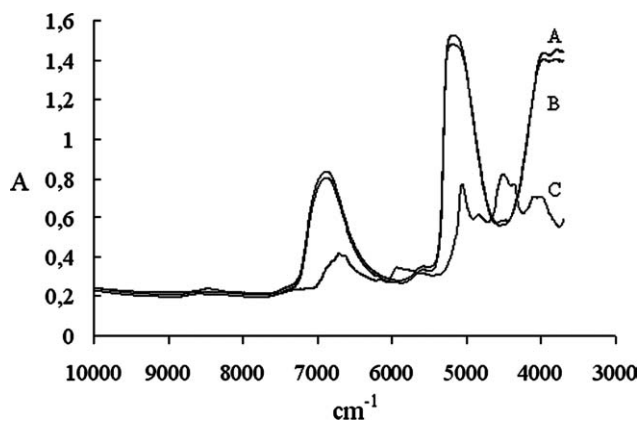
Figure 3a shows a spectrum in the near infrared field of a degummed silk fibroin yarn. The characteristic broad absorption bands of a protein can be seen: the weak intensity band at about 8450  $\text{cm}^{-1}$  is due to protein backbone, the shoulder at 7000  $\text{cm}^{-1}$  is assigned to the first overtone of O–H stretching vibration of water and the band at 5160  $\text{cm}^{-1}$  is assigned to a combination of the O–H stretch and the H–O–H bending vibration of the hydroxyl group from water. The doublet at about 5800  $\text{cm}^{-1}$  is the overtone of the C–H stretch of protein side chains. The bands between 5000 and 3700  $\text{cm}^{-1}$  give information about the protein-type structure of silk fibroin. In particular, the strong band at 4860  $\text{cm}^{-1}$  is assignable to amide A–amide II combination and a partly broad feature at 4610  $\text{cm}^{-1}$  is assignable to amide B–amide II combination.<sup>19</sup> Moreover, the region between 4500 and 4000  $\text{cm}^{-1}$  is influenced by different C–H combination bands of the amino acid composition in proteins, and it is very sensitive to the nature of side chains of proteins.<sup>16,19,20</sup>

Figure 3(b) compares the spectra of untreated silk fibroin yarn and those of grafted silk yarn with 58% w/w and 103% w/w grafting yield values. The main differences can be observed in the region between 7500 and 6500  $\text{cm}^{-1}$  and in the region around 5060  $\text{cm}^{-1}$ , where a new peak appears. The higher the grafting yields the more intense the peak.



**Figure 3** (a) NIR spectrum of degummed silk fibroin yarn. (b) NIR spectra of silk fibroin yarn with different grafting yield (A = 0% w/w, B = 58% w/w, C = 103% w/w).

Primary amines, which are present in poly-MAA, show a double peak assignable to the first overtones of asymmetric and symmetric N–H stretching in the region around 6600  $\text{cm}^{-1}$ . Moreover, they show a first combination band in the region around 5000  $\text{cm}^{-1}$  due to the N–H stretching modes and the deformation of the N–H<sub>2</sub> group.<sup>21</sup> Therefore, the absorption band at 5060  $\text{cm}^{-1}$  in grafted silk is reasonably attributable to primary amine combination, while the first overtone of primary amine contributes to spectrum modification in the region between 7500 and 6500  $\text{cm}^{-1}$ . Other poly-MAA absorptions arising from methyl group (CH<sub>3</sub> combination around 4400  $\text{cm}^{-1}$  and first overtone of the C–H stretching mode around 5850  $\text{cm}^{-1}$ ) are hidden by silk fibroin absorptions.<sup>22</sup> It is worth to note that the absorptions of hydroxyl group from water falling in the regions around 7000 and 5160  $\text{cm}^{-1}$  increase with increasing the grafting yield. In effect MAA-grafted silk fibers exhibit a marked increase of moisture content and the increased hygroscopicity has been recognized to improve the comfort of silk fabrics. As shown in a previous work,<sup>23</sup> the moisture content in grafted fibers increases almost linearly in the low grafting yield range and then shows a tendency to attain a saturation value at higher grafting yields. The non-linear trend of moisture content with respect to



**Figure 4** NIR spectra of exhaust baths with different concentrations of MAA ( $A = 50.0$  g/L,  $B = 0$  g/L), and NIR spectrum of a dehydrated exhaust bath (C).

grafting yield might be a factor able to affect the accuracy of NIR calibration.

Other differences between grafted and ungrafted fibroin yarn spectra are associated with changes in the optical reading which occurs in a nonlinear fashion throughout the NIR spectrum. MAA grafting induces an increase of the transversal dimension of the silk filaments proportional to grafting yield in a wide range of MAA grafting.<sup>1</sup> From Figure 3(b), it can be noticed that as the filament diameter becomes larger due to increasing grafting yield, the spectra shift upward. This spectral behavior, imputable to filament dimensions that affects the diffuse light scattering at all wavelengths, but not to the same degree,<sup>24</sup> in most cases is an anomaly, which must be corrected using mathematical spectra pretreatment (such as derivative or multivariate spectral correction (MSC)). In this case, this behavior associates with the characteristic under investigation, so it contributes to the correlation.

As regard to the secondary structure of silk fibers, the similarity between grafted and ungrafted silk yarn in the region between  $5000$  and  $4500$   $\text{cm}^{-1}$  confirmed that the secondary structure of silk remains unchanged after MAA grafting, so the grafting preferentially occurs in the amorphous domains of the fibroin filaments.<sup>25</sup>

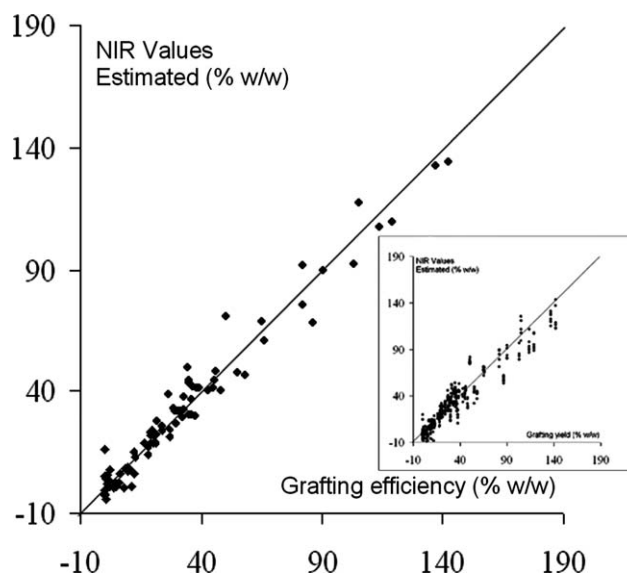
The NIR spectra of MAA exhaust baths (Fig. 4) are characterized by the broad bands assigned to hydroxyl group of water (first overtone of O—H stretching vibration and H—O—H bending vibration, respectively). Only a small absorption around  $4490$   $\text{cm}^{-1}$  that falls in the region of C—H combination bands can be observed. The water bands hide absorptions of poly-MAA by-products that appear only after dehydration. We can see the first overtone of the primary amine around  $6600$   $\text{cm}^{-1}$ , the primary amine combination near  $5000$   $\text{cm}^{-1}$ , the first overtone of the C—H stretching vibration near  $5900$   $\text{cm}^{-1}$ , the

C—H combination around  $4400$   $\text{cm}^{-1}$ . In the spectrum of dried exhaust bath the broadening of bands around  $7000$   $\text{cm}^{-1}$  suggests the presence of residual water.<sup>22</sup>

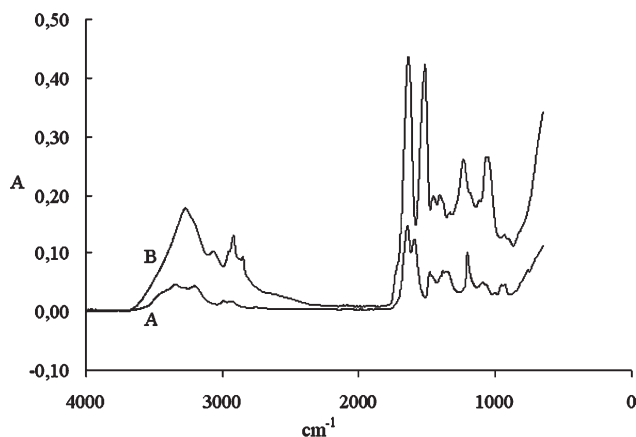
#### NIR analysis of silk grafting yield after MAA grafting

Silk samples with different grafting yield obtained by varying the MAA and APS concentration and the material to liquor ratio in grafting baths were subjected to NIR analysis.

Figure 5 shows the correlation obtained between the calculated values of grafting yield and values estimated by NIR spectra from respective samples. The results were obtained with the PCR algorithm in the spectral region between  $10,000$  and  $3700$   $\text{cm}^{-1}$ . The correlation shows a  $R^2$  of  $0.96$  and SEC of  $8.37\%$  w/w for an average grafting yield of  $31.82\%$  w/w. The grafting yield range is from  $0.1\%$  w/w to  $150\%$  w/w. To validate the results,  $400$  predicted data of silk grafting yield were used and correlated with reference data from respective samples. The correlation obtained shows an  $r^2$  of  $0.91$  and SEP of  $12.10\%$  w/w (detail in Fig. 5). In accordance with other authors,<sup>26,27</sup> the accuracy of the calibration was evaluated based on the coefficient of determination  $R^2$  for predicted versus measured grafting yield in cross validation, and based on the ratio of standard deviation in the original data set (SD) to standard error of cross validation. Literature data show that a  $R^2$  above  $0.90$  and a ratio SD/SEC above  $3.0$  indicate that a prediction is classified as good or excellent. In



**Figure 5** Grafting yield of silk yarn samples. Known values ( $x$ -axis) versus NIR estimated values ( $y$ -axis). SEC =  $8.37\%$  w/w;  $M = 31.82\%$  w/w;  $R^2 = 0.96$ . Detail in the figure: verification of the correlation ( $r^2 = 0.91$ , SEP =  $12.10\%$  w/w).



**Figure 6** Spectra in the medium infrared field of (A) dehydrated exhaust grafting bath, (B) silk sericin.

this case both  $R^2$  and SD/SEC are above these values. In particular SD/SEC was calculated as 3.87, being the SD of the data set 32.41% w/w.

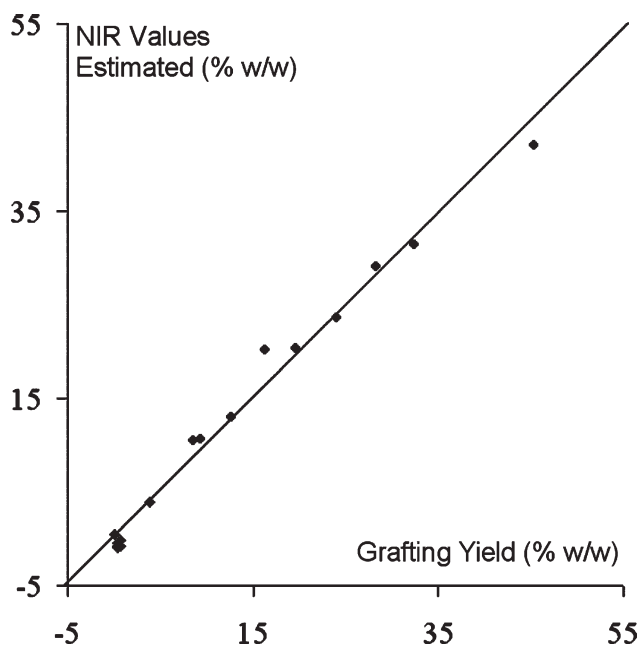
Although the aforementioned correlation between calculated and NIR estimated grafting yield values can be considered satisfactory for practical uses, it can be affected by some sources of error that are here briefly discussed. As previously mentioned, the moisture content of grafted silk yarn increases with grafting but not in a linear mode over all the range of grafting yield, being proportional to the amount of grafted MAA at low grafting yield, then tending to a saturation value at higher grafting yield. Moreover, silk yarns obtained from industrial degumming may contain residues of sizing agents used in previous processing steps (doubling and twisting), whose amount is strongly influenced by the chemical products used and by the processing conditions, and may be in the range of 1–2% o.w.f. but sometimes even higher, i.e., up to 4% o.w.f. Their presence may interfere with the grafting process in terms of both kinetics and yield, and with the spectroscopic characteristics of the exhaust grafting baths. Another potential source of error would be the release of protein materials (more likely residual sericin remaining after degumming) into the grafting bath during grafting. Among these potential sources of error for the NIR approach to the control of the grafting process, the presence of protein materials in the exhaust grafting baths can be excluded because protein absorption bands are absent in the mid infrared field spectra of dehydrated exhaust grafting baths, where only the absorptions of poly-MAA are visible (Fig. 6).<sup>28</sup>

The potential effect of moisture content and residual sizing agents was addressed with a specific test. Starting from the aforementioned assumptions, silk yarn samples were extracted before grafting with a solvent mixture able to remove residual sizing agents and detergents remaining on silk after degumming. Extracts were found to be prevalently composed of

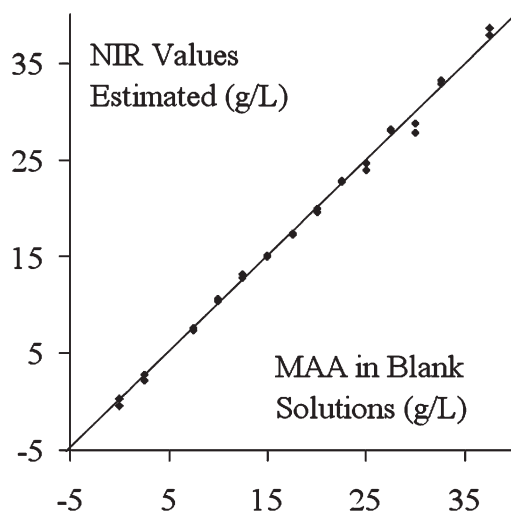
fatty acid esters and non ionic surfactants as resulting from absorption spectra measured in the mid infrared field (data not shown). Afterwards, grafting with MAA was performed and 16 samples of MAA grafted silk yarn with grafting yield up to 50% w/w, a range where there is a linear relation between grafting yield and moisture content increase, were selected and analyzed by NIR. The correlation obtained using grafted silk yarn samples preliminarily extracted shows a  $R^2$  of 0.99 and a SEC of 2.30% w/w for an average silk grafting yield of 12.66% w/w (Fig. 7). The ratio SD/SEC was calculated as 6.03 being the SD of original data set equal to 13.88% w/w. The improvement in accuracy of the correlation confirms that the two variables considered, both moisture content and residual sizing agents, are able to affect the results of NIR measurements, although not to such an extent to make the NIR approach to predict the MAA content of grafted silk yarns useless, as demonstrated by the results of Figure 5. Actually, the removal of residual sizing agents is unfeasible on an industrial level because any extraction process will prolong the processing cycle with an overload in terms of processing costs.

#### NIR analysis of MAA by-products concentration in exhaust grafting baths

The determination of MAA in exhaust baths is an important topic because the loss of polymerized MAA in baths is economically expensive and contributes to increase the organic load of wastewaters.



**Figure 7** Grafting yield of samples previously extracted with solvent. Known values (x-axis) versus NIR estimated values (y-axis). SEC = 2.30% w/w; M = 12.66% w/w;  $R^2$  = 0.99.



**Figure 8** Amount of MAA by-products in blank solutions. Known values (*x*-axis) versus NIR estimated values (*y*-axis). SEC = 1.00 g/L; *M* = 18.44 g/L;  $R^2 = 0.995$ .

As shown by exhaust baths spectra (Fig. 4) main absorptions arise from hydroxyl group of water. Water associates with ions, organic monomers, and polymers by hydrogen bonds, therefore water absorptions bands are influenced by effects of solutes on water molecule vibrations. The modifications of water absorptions seem to be in relation to hydration potential of respective solutes, in other words the NIR spectrum is easily affected by conditions surrounding water molecules. The hydrogen bonds are relatively weak, therefore the light absorbance energy will be very sensitive to ion strength, to aggregation and formation of gel-like structures in solution and to the presence of other ions and molecules.<sup>29</sup>

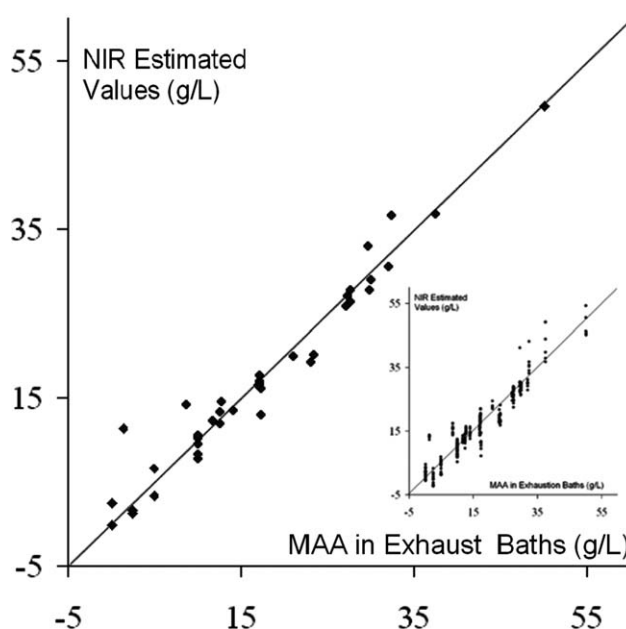
To investigate the potential of the NIR approach to characterize the exhaust grafting baths obtained from a MAA grafting process, preliminary tests were carried out with blank solutions prepared by incubating various amounts of MAA and APS (4% w/w on the weight of MAA) at pH 2.5–3.0 into test tubes without silk yarn, and then performing the grafting reaction cycle under the required experimental conditions of temperature and time. The correlation obtained between known amount of polymerized MAA in blank solutions and the respective NIR spectra was very promising and shows a  $R^2$  of 0.995, the SEC was determined to be 1.00 g/L for an MAA polymerized concentration in blank solutions of 18.44 g/L (Fig. 8).

In the exhaust grafting baths obtained by laboratory experiments carried out in the presence of silk yarn, the amount and characteristics of poly-MAA by-products recovered at the end of grafting depend on the operating conditions used, as discussed in previous paragraphs, which are able to influence the

yield of grafting, the amount and the degree of polymerization of MAA homopolymer in solution and so the interaction between the polymer in solution and water. For these reasons, it has been decided to make a selection among the overall exhaust baths available and to choose only those obtained under reproducible conditions, i.e., keeping the initiator/MAA ratio and the material to liquor ratio constant and changing only the amount of MAA in the reaction system. Therefore, 39 grafting exhaust baths obtained using an initiator/MAA ratio of 4% w/w, a material to liquor ratio of 1 : 40 and the lab-scale machine Linitest Heraeus were used for the calibration.

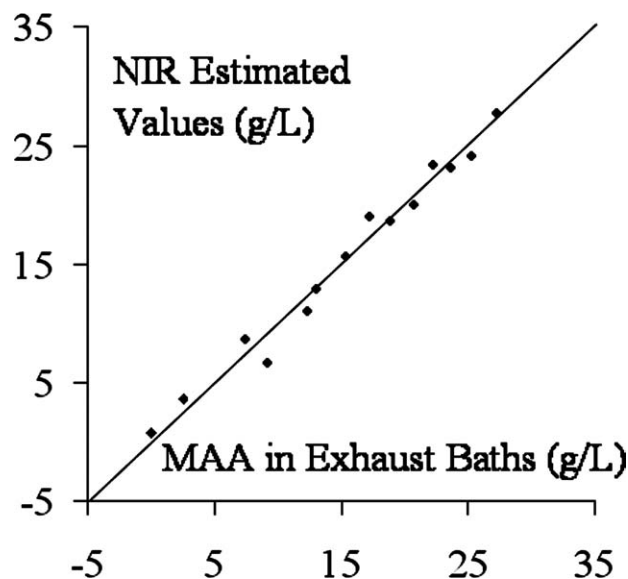
Figure 9 compares the measured amount of MAA in exhaust grafting baths with the amount predicted by NIR analysis. The correlation shows a  $R^2$  of 0.95 and a SEC of 2.93 g/L for an average MAA concentration in exhaust baths of 17.16 g/L. For validation purposes, the previous correlation was verified using 300 predicted data of MAA in exhaust baths compared to reference data from respective samples. An  $r^2$  of 0.89 and a SEP of 3.71 g/L were found (detail in Fig. 9).

As calculated for grafting yield, the accuracy of the calibration was evaluated based on the coefficient of determination  $R^2$  for predicted versus measured amount of MAA in exhaust grafting baths in cross validation, and based on the ratio of standard deviation in the original data set (SD) to standard error of calibration. A  $R^2$  of 0.95 and a SD/SEC of



**Figure 9** Amount of MAA by-products in exhaust grafting baths. Known values (*x*-axis) versus NIR estimated values (*y*-axis). SEC = 2.93 g/L; *M* = 17.16 g/L;  $R^2 = 0.95$ . Detail in the figure: verification of the correlation ( $r^2 = 0.89$ , SEP = 3.71 g/L).





**Figure 10** MAA by-products in exhaust grafting baths of silk samples previously extracted with solvent. Known values ( $x$ -axis) versus NIR estimated values ( $y$ -axis). SEC = 1.7 g/L;  $M = 15.35$  g/L;  $R^2 = 0.98$ .

3.89 (the SD of the data set was found to be 11.42 g/L) show that the prediction can be considered good.

However, to improve the results previously obtained, we tried to eliminate any possible interference in the aqueous environment. So, a different set of experiments was carried out using the exhaust grafting baths obtained from the grafting experiments where silk yarn was preliminarily extracted to remove residual sizing agents (see previous paragraph). Only two exhaust grafting baths where the initiator/MAA ratio was different from 4% w/w were excluded. Then the calculated amounts of MAA in exhaust grafting baths were correlated with the NIR spectra of the respective samples. The correlation previously obtained was improved and an  $R^2$  value of 0.98 and SEC value of 1.7 g/L for an average MAA amount in exhaust grafting baths of 15.35 g/L were obtained (Fig. 10). The ratio SD/SEC was calculated as 4.93 being the SD of original data set equal to 8.38 g/L. These results confirm that foreign substances carried by the silk yarn and released into the grafting bath may affect the accuracy of NIR measurements, although their influence remains within acceptable limits, at least judging from the results here reported from lab-scale trials. These parameters can be carefully controlled in view of scaling up the NIR approach to the control of the grafting process at pilot and industrial level.

## CONCLUSIONS

In this study, degummed silk yarn was grafted with different amount of MAA. The possibility of measuring the grafting yield of silk yarn and the amount

of MAA by-products in exhaust grafting baths was then investigated using NIR spectroscopy.

The first correlation, which is related to the quantitative estimation of grafting yield of grafted silk yarn, shows a coefficient of determination ( $R^2$ ) of 0.96 and a SEC of 8.37% w/w for a mean value ( $M$ ) of 31.82% w/w. The second correlation related to the quantitative determination of MAA by-products in exhaust grafting baths shows a  $R^2$  of 0.95 and a SEC of 2.93 g/L for a  $M$  of 17.16 g/L. These two correlations were improved when silk yarn was preliminarily cleaned by extracting residual sizing agents and detergents before grafting experiments.

The lab-scale results reported in this study may open up new opportunities for the implementation of an on-line system for the control of the grafting process and of the processing effluents.

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