ORIGINAL ARTICLE

Effect of solvents on properties of *Bombyx mori* silk grafted by methyl methacrylate (MMA) and methacrylamide (MAA)

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Abstract

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Mulberry silks were chemically modified in order to increase weight gain, resulting from degumming process using graft copolymerisation technique with vinyl monomers, i.e. MMA, MAA and MMA/MAA. Due to the appearance of PMMA homopolymer granules adhered on the MMA- and MMA/MAA-grafted silk surfaces resulting in surface roughness when silk was grafted by MMA in water, the influence of grafting solvents was examined, using different water/ethanol volume ratios of 100/0, 75/25, 50/50, 25/75 and 0/100. FTIR spectra of the grafted silks presented the absorption bands of the vinyl monomers used for the grafting process. In addition, high values of % polymer add-on were obtained for all of the grafted silks. It was also found that the suitable solvents were 25/75 water/ethanol for the silk grafted by MMA and MMA/MAA, and water for the silk grafted by MAA, in order to get the smooth grafted silk surface and high polymer add-on. Moreover, all the grafted silks showed slightly greater stiffness, as indicated by the increase of Young's modulus and the decrease of elongation.

Key words : grafting, silk, morphology, mechanical properties

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บทคัดย่อ

จุฑารัตน์ ปรัชญาวรากร และ วัฒนา คล้ายรัศมี

ผลของตัวทำละลายที่มีต่อสมบัติต่าง ๆ ของไหมต่อกิ่งโดยเมทิลเมทาไครเลท และเมทาไครลาไมด์

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นำไหมมาดัดแปรทางเคมีเพื่อเพิ่มน้ำหนักของไหมที่เป็นผลมาจากการลอกกาวด้วยเทคนิคของการต่อกิ่งโดยใช้ไวนิลมอนอเมอร์ คือ เมทิลเมทาไครเลท เมทาไครลาไมด์ และมอนอเมอร์ผสมระหว่างเมทิลเมทาไครเลทและเมทาไครลาไมด์ เนื่องจากลักษณะของพอลิเมทิลเมทาไครเลทที่ติดอยู่บนพื้นผิวของไหมทำให้เกิดความขรุขระของไหมที่ต่อกิ่งในน้ำด้วยเมทิลทาไครเลทและเมทิลเมทาไครเลทผสมเมทาไครลาไมด์ จึงได้ทำการศึกษาเกี่ยวกับผลของตัวทำละลายที่ใช้ในการต่อกิ่ง โดยใช้น้ำและเอทานอลที่อัตราส่วนต่าง ๆ กัน คือ 100/0 75/25 50/50 25/75 และ 0/100 อินฟราเรดสเปกทรัมของไหมต่อกิ่งแสดงถึงแถบการดูดกลืนที่เป็นลักษณะเฉพาะของมอนอเมอร์ที่นำมาใช้ในการต่อกิ่ง นอกจากนี้ร้อยละการเพิ่มขึ้นของพอลิเมอร์มีค่าที่สูงสำหรับทุกตัวอย่าง และยังพบว่าตัวทำละลายที่เหมาะสมสำหรับไหมต่อกิ่งด้วยเมทิลเมทาไครเลทและมอนอเมอร์ผสมระหว่างเมทิลเมทาไครเลทและเมทาไครลาไมด์ คือ น้ำผสมเอทานอลในอัตราส่วน 25/75 ส่วนไหมที่ต่อกิ่งด้วยเมทาไครลาไมด์ควรใช้น้ำเป็นตัวทำละลายเพื่อให้ได้ไหมที่มีพื้นผิวที่เรียบและมีค่าร้อยละการเพิ่มขึ้นของพอลิเมอร์ที่สูง นอกจากนี้ไหมต่อกิ่งแสดงถึงความแข็งที่เพิ่มขึ้นซึ่งพิจารณาได้จากการเพิ่มขึ้นเล็กน้อยของค่ามอดุลัสและการลดลงของค่าการดึงยืด

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Silk is composed of main polypeptide chains and side chains of amino acids, produced by silkworm. Mulberry silk (*Bombyx mori*) is one of the most precious raw materials from natural origin employed in manufacturing textile products. Over the centuries, silk has been highly valued as a textile fibre because of its qualities of unique luster, strength, excellent softness, comfortable to handle, etc. However, some textile performances, such as thermal stability, wash and wear characteristics, crease recovery, need to be improved in order to enlarge silk consumption and meet consumer requirements.

Chemical treatment can cause modification of the silk main polypeptide chains and side chains of amino acids, which in turn influence the fibre's chemical, physical and mechanical properties. In recent years, grafting technique has been regarded as a powerful tool to modify properties of silks since the technique maintains the silk structure and mechanical properties of the resulting silks (Das *et al*., 2001; Freddi *et al*., 1996; Kawahara *et al*., 1996 and 1997; Maji *et al*., 2002; Tsukada *et al*., 1988, 1991, 1992, 1998, 2001)

Grafting, involving the generation of reactive sites on the polymer followed by the addition of monomer and the propagation in a conventional manner, was originally introduced as an alternative to the traditional mineral weighting technique, to increase silk weight and compensate for the loss resulting from degumming. The physical and chemical properties of grafted-silk fibres depend not only on the extent of grafting and/or weight gain but also on the characteristics of the functional group carried by the monomer, which becomes an integral part of the silk fibre. Methacrylamide (MAA), methyl methacrylate (MMA) and 2-hydroxylethyl methacrylate (HEMA) have been widely applied for grafting silk fibres (Das *et al*., 2001; Freddi *et al*., 1996; Kawahara *et al*., 1996 and 1997; Maji *et al*., 2002; Tsukada *et al*., 1988, 1991, 1992, 1998, 2001). For MMA-grafted silk fibres, the wrinkle recovery was found to be improved (Das *et al*., 2001; Maji *et al*., 2002; Tsukada *et al*., 1991); however, uneven surface deposition of PMMA homopolymer or oligomer

was clearly detected when water was used as solvent, regardless of the usage of different types of initiators (Das *et al*., 2001; Maji *et al*., 2002; Tsukada *et al*., 1991). This appearance becomes a great obstacle for using the MMA-grafted silk in textile application.

In this article, in order to prevent the surface roughness appearance, we present the results of the graft copolymerisation of MMA and MAA onto *Bombyx mori* silk using water, ethanol and water/ethanol mixture. The influence of the grafting solvents on the % polymer add-on, IR characteristic absorption bands, morphologies and tensile properties of the MMA-, MAA- and MMA/MAA-grafted silks was investigated in detail.

Experimental

Materials

Raw silks (*Bombyx mori*) were obtained from Jim Thompson, Thailand. Reagent grade MAA and MMA momomers were purchased from Fluka, Co. Ltd. and MMA was washed with 5% sodium hydroxide solution for removing inhibitor before use. The initiator was ammonium persulfate (APS) from Fluka, Co. Ltd. Alkalies of sodium carbonate and sodium bicarbonate and Sandopan 60 as surfactant for silk degumming were obtained from Merck, Co. Ltd.

Degumming and Grafting

The silks were degummed in an aqueous solution containing 0.05 M sodium carbonate, 0.05 M sodium bicarbonate and Sandopan 60 for 30 min at 80ºC using material to liquid ratio of 1:30. Then, the degummed silks were dried using a vacuum oven at room temperature for 24 h. The degummed silks were then immersed in an aqueous solution consisting 0.8 M momomer and 0.05 M APS initiator for 30 min at the temperature of 80ºC under nitrogen atmosphere. The material-to-liquid ratio during the treatment was maintained at 1:100. Then, the silks were thoroughly rinsed with water for 3 times and finally vacuum-dried. It should be noted that the monomers were MAA, MMA and 50/50 MAA/MMA, and the effect of solvents i.e. water and ethanol of varied compositions (100/0, 75/25, 50/50, 25/75 and 0/100) was studied.

Percent polymer add-on was calculated from the increase in the mass of the fibres by using the equation,

$$\%\text{Polymer add}-\text{on}\ (\%) = \frac{W_2 - W_1}{W_1} \times 100$$

where W_1 and W_2 are the masses of the dry fibres before and after the graft treatment.

IR studies

FTIR spectra of silk samples were recorded on a Spectrum 2000 GX spectrometer (Perkin-Elmer) using KBr disk technique with a resolution of 4 cm^{-1} in a spectral range of 4000-650 cm^{-1} using 16 scans per sample.

Morphology

The surface morphologies of the degummed and grafted silks were observed using a LEO 1455 VP scanning electron microscope (SEM). The cryogenic fracture specimens of silk samples were sputter coated with a thin layer of gold to prevent electrical charging before the SEM observation.

Tensile Properties

The mechanical property measurements of silk samples in form of single yarn were carried out using a Universal Testing Machine (Lloyd Instrument) with 100 N load cell, crosshead speed of 30 mm/min and gauge length of 25 mm. A minimum of 20 specimens was tested to obtain average values of load at break, % elongation at break and Young's modulus. It should be noted that all mechanical tests were carried out at the temperature of 23±1ºC and relative humidity of 50±5%.

Moisture Regain

Moisture regains of ungrafted and grafted silks were determined by the percentage weight difference between wet and dried samples, according to ASTM D 2654-89a. The wet and dried silks were obtained from keeping the silks in the standard condition of 21ºC and 65% RH and then dried

at 105ºC until the constant weights were reached. The moisture regain was calculated with the following formula:

$$\text{Moisture regain } (\%) = \frac{W_w - W_d}{W_d} \times 100$$

where W_w and W_d are the weights of the wet and dry samples, respectively.

Results and Discussion

Silks can be grafted with MAA and MMA vinyl monomers that can be polymerised through free radicals. At the temperature of 80ºC, the APS initiator generates free radicals that lead to different free radicals not only from vinyl monomers but also from structural chains of silk fibroin. As a result, various chemical reactions can occur, i.e., polymerisations of the individual monomers, copolymerisation between the monomers and also grafting of monomers and macromonomers onto silk fibroins. A high weight gain, combined with a reduced level of homopolymerisation, is a prerequisite for the industrial application of grafting techniques.

IR Studies

The chemical modification of silk entails the incorporation into the protein substrate of chemical group characteristic of the modifying agent. It can be seen in Figure 1(a) that the IR spectrum of the degummed silk presents the fibroin absorption bands at 1510 and 1650 cm^{-1}, assigned for C=O stretching and N-H stretching of amide I and amide II, respectively. Other peak positions are located at 2926 and 3413 cm^{-1}, attributed to the C-H stretching and N-H stretching deformations, respectively.

For the grafted silks in water/ethanol solvent (25/75), new IR absorption bands of the MMA-grafted silk are presented in Figure 1(b) at the wavenumbers of 1146 and 1236 cm^{-1}, responsible for C-O stretching of ester group of PMMA. Another dominant peak at 1733 cm^{-1} is due to C=O stretching from PMMA molecule. Figure 1(c) illustrates the absorption bands at 1516 and 1636 cm^{-1}, assigned for C=O stretching and N-H bending of primary amide of PMAA. Besides, the silk grafted by MMA/MAA (Figure 1(d)) presents IR wavenumbers of the specific characteristic from the monomers used, i.e. 1156 and 1226 cm^{-1} from

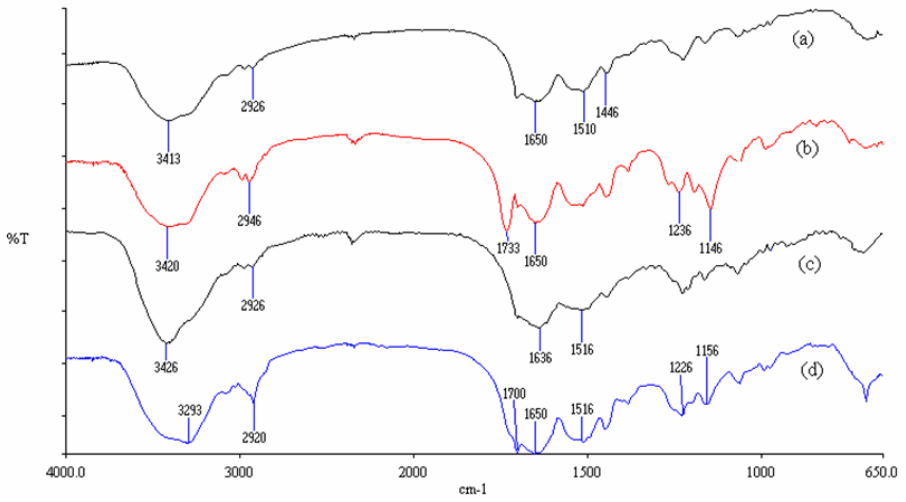

Figure 1. IR spectra of (a) degummed silk (b) MMA-grafted silk (c) MAA-grafted silk and (d) MMA/MAA-grafted silk. Note: The grafted silks were grafted using 25/75 water/ethanol.

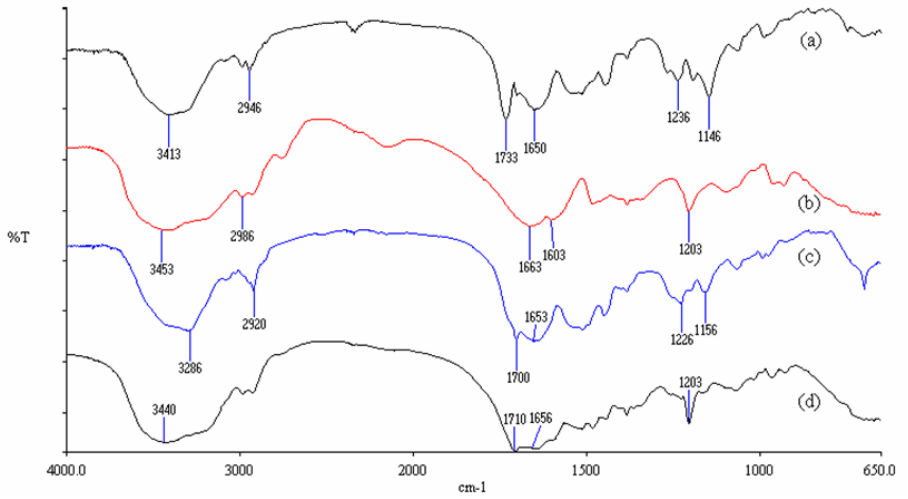

Figure 2. IR spectra of (a) silk grafted by MMA in ethanol (b) silk grafted by MAA in water (c) silk grafted by MMA/MAA in ethanol and (d) silk grafted by MMA/MAA in water.

MMA monomer and 1516 and 1650 cm^{-1} from MAA monomer.

When either water or ethanol is utilised as grating solvent, IR spectra of the grafted silks are represented in Figure 2. The MMA-grafted silk in Figure 2(a) using ethanol shows IR peak position at 1733 cm^{-1} (C=O stretching), 1236 and 1146 cm^{-1} (C-O stretching of PMMA); however, the MAA-grafted silk in water presents vibrations of C=O stretching and N-H stretching of amide I from PMAA at the wavenumbers of 1603 and 1663 cm^{-1}, respectively (Figure 2(b)).

Comparison between the MMA/MAA-grafted silk in ethanol (Figure 2(c)) and water (Figure 2(d)), reveals that grafting in ethanol shows more prominent peak positions at 1226 and 1156 cm^{-1} from PMMA than those of grafting in water (Figure 2(d)). Nevertheless, grafting in water presents dominant wavenumbers from PMAA vibrations at 1656 cm^{-1}. The results indicate that the solvent affects the IR absorption bands of the grafted silks.

% Polymer add-on

Table 1 shows % polymer add-on of the MMA, MAA and MMA/MAA-grafted silks using different water/ethanol ratios. The difference in % polymer add-on with two types of vinyl monomers,

Table 1. % Polymer add-on of the MMA-, MAA- and MMA/MAA-grafted silks using different ratios of water/ethanol.

Water/ethanol ratio	% Polymer add-on		
	MMA	MAA	MMA/MAA
100/0	135±5	145±5	44±5
75/25	116±7	92±7	38±4
50/50	86±10	45±7	35±5
25/75	54±3	33±5	36±5
0/100	60±3	25±7	41±5

i.e. MMA and MAA might be because of the chemical reactivity of the chemical structure of the used monomer towards silk. By comparison between the MMA- and MAA-grafted silks in water, it can be clearly seen in Table 1 that MMA monomer shows higher chemical reactivity toward graft copolymerisation than MAA monomers, except in 100% water. When the mixture of MMA and MAA monomers are used for grafting, it results in a significant drop in polymer weight gain of the MMA/MAA-grafted silk due to the reactive competition between MMA and MAA monomers during the grafting process.

For the silks grafted by MMA, water gives rise to higher % polymer add-on than does the ethanol solvent, suggesting that swelling ability of the MMA-grafted silk by water is more dominated than that of in ethanol. Unfortunately, higher polymer add-on brings about the rigidity of the MMA-grafted silk that is not suitable for textile products. Nevertheless, the lower value of % polymer add-on obtained from grafting by 25/75 and 0/100 water/ethanol, in turn, results in the silk softness, measuring from feeling touch.

Like MMA-grafted silk, the greatest % polymer add-on for the MAA-grated silk is found when water is used as solvent. The more the water used, the more the % polymer add-on obtained in the silk grafted by MAA, implying that water is a suitable solvent for MAA grafting. Besides, the MAA-grafted silk present soft surface, regardless of grafting solvent used in the system.

Comparable values of % polymer add-on for the MMA/MAA-grafted silks using different ratios of water/ethanol are obtained as shown in Table 1, indicating that grafting solvent is not the factor affected grafting ability for the silk grafted by MMA/MAA. Nevertheless, the use of 25/75 water/ethanol solvent brings about the grafted silk with smooth surface and moderate stiffness.

The variation of graft percentage with the use of different solvents could be due to the difference in capability of silk swelling ability and miscibility of monomer. The results suggest that good swelling ability is obtained for MMA and MAA using water, resulting in high % polymer add-on; nevertheless, high grafting ability of MMA leads to the formation of PMMA attached on the silk surface (see morphology section).

Morphology

A high weight gain, combined with a reduced level of homopolymerisation, is a prerequisite for the industrial application of grafting techniques. In fact, the presence of homopolymer attached to the silk surface may draw negative consequences on the physical properties and functional performances of silks. It can be seen in Figure 3(a) that the surface of the degummed silk is rather smooth.

However, the silk grafted by MMA in water (Figure 3(b)), causes PMMA homopolymer oligomers adhering on the surface of the silk leading to surface roughness; but, the silk grafted by MMA in ethanol (Figure 3(C)) leads to the smooth surface of the grafted silk. When (25/75) water/ethanol is used (Figure 3(d)), it can be clearly seen that PMMA granules are not presented on the MMA-grafted silk surface. The observed morphological micrographs suggest that grafting solvent greatly affects the surface characteristic of the MMA-grafted silk. Combining % polymer add-on (Table 1) and surface morphology (Figure 3), the results indicate that higher % polymer add-on may be due to the PMMA granules attaching on the silk surface.

For the MAA-grafted silk surface morphology, it can be seen in Figures 4(a) and 4(b) that the silks grafted in water or (25/75) water/ethanol mixture give rise to the smooth surface without the presence of PMAA oligomers, as in the case of PMMA grafted in water. It should be noticed that the greater silk diameter grafted by MAA is obtained when water is used, suggesting that water is applicable for the MAA-grafted silk.

When both MMA and MAA are utilised for grafting, the SEM micrographs in Figures 5(a) and 5(b) show that granules are evident from the MMA/MAA-grafted silk surface using water as a grafting solvent. The opposite effect is obtained when 25/75 water/ethanol is used; therefore, it can be suggested that the observed surface roughness mainly comes from PMMA oligomers.

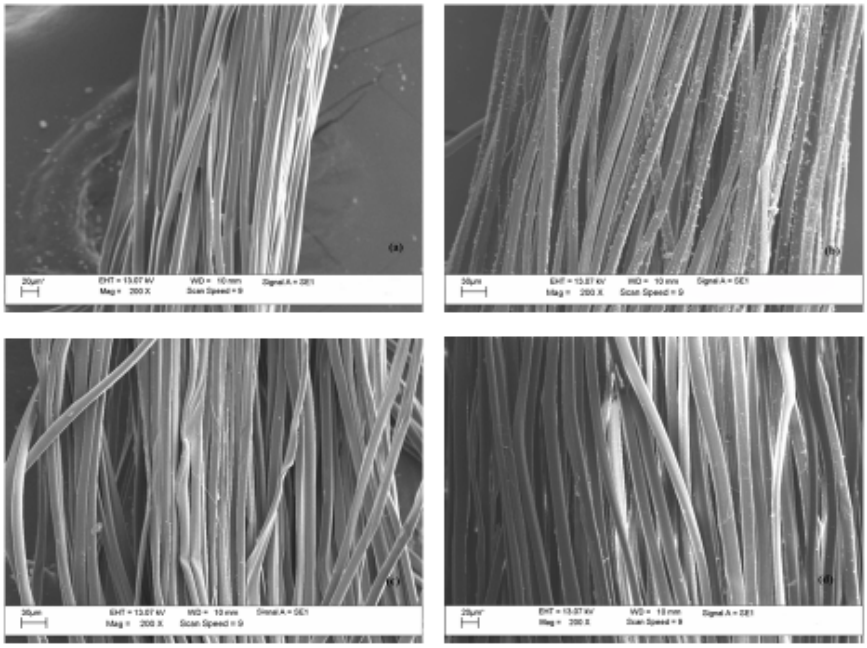

Figure 3. SEM micrographs for (a) degummed silk (b) silk grafted by MMA in water (c) silk grafted by MMA in ethanol and (d) silk grafted by MMA in 25/75 water/ethanol.

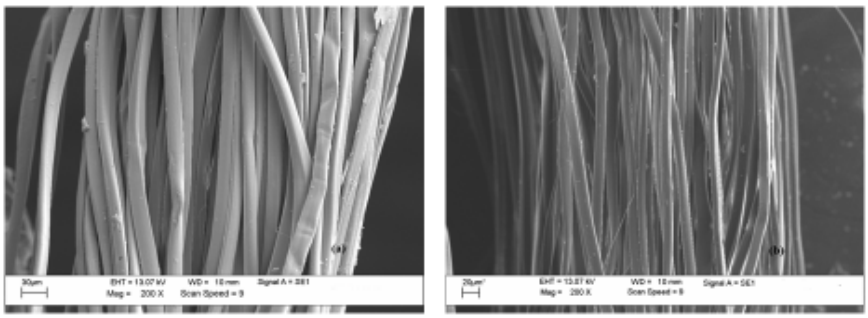

Figure 4. SEM micrographs for (a) silk grafted by MAA in water and (b) silk grafted by MAA in 25/75 water/ethanol.

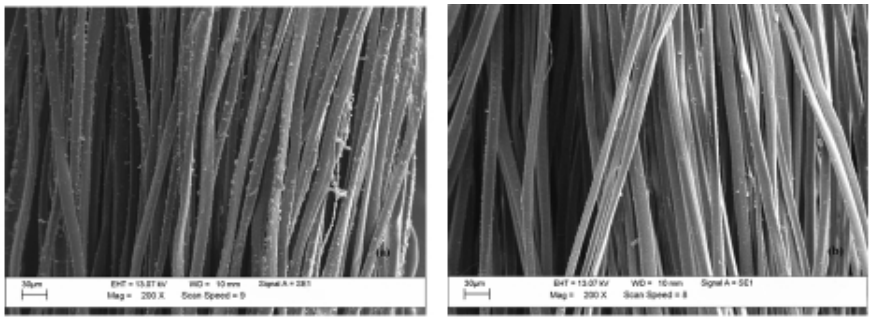

Figure 5. SEM micrographs for silk grafted by MMA/MAA (50/50) (a) in water and (b) in 25/75 water/ethanol.

Table 2. Tensile properties of the MMA-, MAA- and MMA/MAA-grafted silks using different ratios of water/ethanol.

Water/ethanol ratio	Load at break (N)[a,b]			Elongation at break (%)[a,c]			Young's modulus (MPa)[a,d]		
	MMA	MAA	MMA/MAA	MMA	MAA	MMA/MAA	MMA	MAA	MMA/MAA
Degummed silk		10.70			24.0			1.89	
100/0	9.19	9.73	9.35	20	22	24	2.93	2.50	3.15
75/25	9.10	9.96	9.30	20	22	24	2.77	2.80	2.74
50/50	9.78	9.34	9.63	21	21	24	2.59	2.59	2.68
25/75	9.89	9.32	9.46	23	19	24	2.71	2.62	2.80
0/100	9.25	9.10	9.72	22	22	20	2.56	3.00	2.10

[a] **The tensile property data were averaged from 20 measurements.**
[b, c and d] **presented the standard deviation of approximately ±0.20, ±1 and ±0.25, respectively.**

Table 3 Moisture regain of the MMA-, MAA- and MMA/MAA-grafted silks using different ratios of water/ethanol.

Water/ethanol ratio	Moisture regain		
	MMA	MAA	MMA/MAA
Degummed silk		5.80	
100/0	3.16	16.95	7.58
75/25	2.80	13.07	8.02
50/50	2.85	8.55	7.90
25/75	2.60	8.06	6.97
0/100	2.55	8.12	7.27

Tensile Properties

Tensile behaviour is an important parameter in the assessment of the properties and functional performances of textile fibres, e.g. maintenance, comfort and handle. Besides, the evaluation of the silk's tensile properties obtained from the grafting process is important to establish guidelines to decide grafting limits. Table 2 shows load at break, elongation at break and Young's modulus of the degummed, MMA-, MAA- and MMA/MAA-grafted silks. The tensile results appear that load at break for the degummed silks are greater than that of the grafted silks. Elongation of the silks grafted with MMA, MAA and MMA/MAA monomers tends to be slightly dropped, regardless of the grafting solvent. As grafting takes place in the amorphous region, it restricts chain mobility, thus causing decline in the load at break and elongation at break. It was observed that load at break and elongation at break of all the grafted silks were found to be more or less in the same order with the different solvents used for grafting. This is due to the fact that the solvents used are not true solvents for the silk and monomers but help in swelling.

On the other hand, the substantial deposition of polymer causes the silk stiffness, resulting in the increase in Young's modulus of the grafted silks. This may be attributed to the increased density of polar groups, which hinders segmental motion and inhibits elastic deformation. It should be mentioned that, regardless of the type of solvent, the softness of the grafted silks from the feeling test can still be obtained for all of the MAA- and MMA/MAA-grafted silks. In addition, the MMA-grafted silks are also presented soft surface with % polymer add-on less than 70%.

Moisture Regain

Water content is an important physical parameter that, together with other factors, can significantly influence the functional behaviour of silks. Moisture absorption of fibres depends not only on temperature and relative humidity but also on the basic chemical components, macromolecular structure and morphological structure of the fibres. The MMA- and MAA-grafted silk present lower and greater moisture regains than that of the ungrafted silk as presented in Table 3 due to more hydrophobicity of PMMA and more hydrophilicity of PMAA.

When the silk grafted by MMA/MAA is concerned, it appears that the grafted silk shows slightly greater moisture regain, compared with the degummed silk. It can also be detected that moisture regain is not dependent on different ratios of water/ethanol solvents for the MMA- and MMA/MAA-grafted silks; however, moisture regain for the silk grafted by MAA shows a dependence on the different solvent ratios. The results illustrate that higher values of moisture regain is reached for the higher composition of water used in the MAA graft copolymerisation; therefore, the lowest moisture regain is for the MAA-grafted silk using ethanol, possibly due to the lower % polymer add-on.

It can be concluded that solvents play an important role for grafting MMA, MAA and MMA/MAA vinyl monomers onto silks. Solvent might affect the swelling ability of the silk. Any change in silk swelling ability would be reflected on its behaviour towards grafting since the diffusion of monomer and initiator, availability of functional groups, etc., would depend to a considerable extent on the swelling properties of silk. The higher the ability of the solvent to swell the fibres, the lower the restriction to diffusion and the higher the reaction efficiency. Grafting by MAA in water and grafting by MMA and MMA/MAA in a mixture of 25/75 water/ethanol were favoured mainly due to the smooth surface appearance and moderate % polymer add-on, resulting in silk softness.

Conclusion

Silk properties were modified by graft co-polymerisation with MAA and/or MAA in relation of the types of solvent, i.e. ethanol and/or water. The increase in % polymer add-on was obtained in the range of 25-145%, regardless of the monomers and solvents. Higher polymer add-on resulted in the greater stiffness of the grafted silks. In order to remove the appearance of MMA oligomers attached to the MMA- and MMA/MAA-grafted silks, a mixture of water/ethanol was used. Grafting by MAA in water and grafting by MMA and MMA/MAA in a mixture of 25/75 water/ethanol were preferred. It was also found that moisture regain of the grafted silks was characterised by the monomers used for the grafting. A decline of elongation at break and an increase in Young's modulus were also observed.

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