Silk Grafting with Methacrylic Monomers: Process Optimization and Comparison

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ABSTRACT: The process of silk weighting with methacrylamide (MAA) initiated by ammonium persulfate was studied to optimize the operating conditions to obtain high yields of grafted monomer. The influence of MAA concentration, liquor ratio, concentration of initiator, contact and heating time, acidification, and swelling agents were considered, and optimum operating conditions were outlined. Moreover, various monomethacrylates and dimethacrylates were grafted onto silk as alternative to methacrylamide. Most of these showed graft yields higher than MAA in the same operating conditions and some were found suitable for silk weighting since the weighted fibers show soft hand and good dyeing behavior. DSC and TGA analyses of grafted silk enabled to evaluate the influence of various monomers on the thermal behavior of the weighted fibers. Moreover, on the basis of DSC data, a correlation between the calculated enthalpy of grafted polyMAA and monomer content was studied. The molecular structure of silk grafted with methacrylic monomers was finally characterized by FTIR analysis. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 4039–4046, 2007

Key words: proteins; graft copolymers; thermal properties; FTIR

INTRODUCTION

Grafting of vinyl monomers onto silk has been introduced as a powerful alternative to mineral weighting. However this procedure has taken importance not only as weighting process but also as finishing operation to improve the properties of the fiber. In fact, silk fabrics treated with these monomers show significant improvements in crease recovery, wash and wear, dimensional stability, resistance to abrasion, photo-yellowing and staining.[1–3] Moreover, if the treatment does not make only a surface coating, typical properties of silk as luster and smoothness are not damaged, while dyeing affinity and fastness can be improved.

The reaction needs a radical initiator as hydrogen peroxide, persulfates,[4] redox systems involving metal salts,[5–7] or radiations.[8–10] Many works on silk grafting have been developed using various vinyl monomers: styrene,[11] acrylamide,[2] methacrylamide,[3,4,10,12–20] N(n-butoxymethyl)methacrylamide,[21,22] methacrylonitrile,[23,24] vinyltrimethoxysilane[25] and several methacrylates: methyl-,[4–8,20,24,26–29] ethyl-,[24] isopropyl-,[10] n-butyl-,[30] benzyl-,[31] glycidyl-,[2] 2-hydroxyethyl-,[3,4,9,10,18,19,32] ethoxyethyl-methacrylate.[33] Methacrylamide (MAA), however, is the monomer most used in industry because

it gives products with soft hand, crease recovery (up to 30% weighting), and increased hygroscopicity.[14,18]

Grafting occurs in amorphous regions of the fiber owing steric and chemical reasons: reagent diffusion, availability of reactive groups, etc. Crystalline regions of fibroin are not involved in this reaction as shown by the unchanged pattern of X-ray diffraction. Bire-fringence values demonstrate that grafting affects the molecular orientation of the chains, since the orientation degree decreases as weighting increases. Moreover, the viscoelastic behavior of the silk is also affected by grafting.[16] The most relevant morphology modification is the cross-sectional area increase of the fibers, which induces dark tones after dyeing.[13]

In this work a typical process of silk weighting with MAA was studied to optimize the operating conditions to obtain high yields of grafted monomer. In fact, MAA tends to homopolymerize also during the reaction and the resulting oligomers are released in the weighting bath. Then these products are washed off from the treated material by rinsing. This loss is economically expensive and contributes to increase the organic load of wastewaters. Moreover, other methacrylate monomers were considered and the results were compared with those obtained with MAA. Some monomers were already experimented in silk weighting, as n-butyl- and 2-hydroxyethyl-methacrylate, whereas the other monomethacrylates were not until now proposed for this use. Moreover difunctional monomers such as diethyleneglycol- and polyethyleneglycol-dimethacrylates were successfully

applied to graft silk fibers and significant wet crease recovery was achieved.[34] Some of them were tested also in this work since higher values of reactivity and graft yield than those obtained with monomethacrylates should be expected.

EXPERIMENTAL

Materials

Degummed and purged silk yarn, with a titer of 20–22 decitex (mass in g per 10,000 m), four-ply, was kindly supplied by Filtex–Como (Italy). This was dried for 2 h at 100°C and kept in desiccator. MAA was the commercial product provided by Röhm Italia (Garbagnate, Italy).

2-hydroxyethylmethacrylate (HEMA), *n*-butylmethacrylate (BMA), 2-ethylhexylmethacrylate (EHMA), triethyleneglycol-monoethylether-methacrylate (TEGEEMA), and ethyleneglycol- dimethacrylate (EGDMA) were supplied by Aldrich (Milan, Italy).

Triethyleneglycol-dimethacrylate (TEGDMA) and polyethyleneglycol-dimethacrylates (PEGDMA) were supplied by Kyoeisha Chemical (Japan). The latter were selected on the basis of the average molecular weight of the corresponding PEG as PEG200DMA, PEG400DMA, and PEG600DMA.

Tergitol NP14 was a nonionic surfactant from Union Carbide. Ammonium persulfate (APS) used as radical initiator and the other chemicals were analytical grade reagents.

Weighting operations

A first series of laboratory experiments was carried out on silk samples of 0.5 g in sealed test tubes plunged in heating bath. These were shaken by an oscillating plane. Weighting baths were introduced according to a liquor ratio in the range from 1 : 40 to 1 : 10. Temperature was increased up to 70°C in about 20 min and kept at 70°C for 60 min. Then the bath was cooled at 60°C in 15 min. The silk samples were taken off and washed three times for 10 min each at 70°C with a nonionic surfactant solution (2.0 g/L of Tergitol NP14). Finally the samples were thoroughly rinsed with distilled water at room temperature, dried in an oven at 100°C for 2 h, and cooled to room temperature in a desiccator until a constant weight. Weight increase was always referred to dried samples.

The weight gain was calculated as:

$$\text{Weight gain (\%)} = \frac{w - w_0}{w_0} \times 100 \qquad (1)$$

where w is the weight of grafted silk and w_0 the weight of original silk.

Moreover the graft yield was calculated as:

$$\text{Graft yield (\%)} = \frac{w - w_0}{w_m} \times 100 \qquad (2)$$

where w_m is the weight of monomer introduced into the bath.

Once the optimum operating conditions were defined, a small hank of yarn (20 g) was treated in a glass cylindrical reactor equipped with water jacket and mechanical stirrer. The hank was tied up to the stirrer shaft. The volume of this reactor enables to work with 300 mL of bath (liquor ratio 1 : 15). The jacket was connected to circulating heating bath and the same temperature program as above was applied. These samples were used for dyeing tests.

Dyeing tests and fastness evaluation

Yarn samples were dyed with acid as well as premetallized dyes in laboratory dyeing apparatus (liquor ratio 1 : 25) according to the procedure required by the specific dyeing recipe. After rinsing and drying the samples were subjected to color evaluation by a reflectance spectrophotometer.

The fastness to water, perspiration, and rubbing were assessed according to the standard procedures and color degradation and discharge were evaluated against the gray scales. Light fastness however was tested by Xenotest and evaluated against the blue wool scale.

DSC, TGA, and FTIR analyses

The DSC analyses were carried out by a Mettler TA 3000 Calorimeter equipped with a Mod. 20 DSC cell. Samples of about 5 mg of yarn were sealed in the standard aluminum pans of 40 µL and submitted to DSC analysis in the range from 50 to 400°C at the heating rate of 10°C/min under nitrogen flux. The data were processed on a personal computer with the aid of the Mettler TA 70 Graphware. Mettler TGA 851 was used for thermogravimetric determinations in the same operating conditions as DSC and the results were treated by means of the Star SW 8.10 software. FTIR analyses were performed on a Mattson Genesys II spectrometer on KBr pellets.

RESULTS AND DISCUSSION

Weighting with MAA: Effect of liquor ratio, APS, and MAA concentration

At first, the weighting bath composition was selected according to industrial practice: 60% MAA over weight fiber (o.w.f.), pH from 2.5 to 3 due to formic acid addition (2–4 mL/L of 99% formic acid), 0.2 g/L of Tergitol NP14 as wetting agent. Three parameters

were taken into account as variables: liquor ratio, APS, and MAA concentration. The results of graft yield showed a linear dependence on liquor ratio, which can allow to calculate a theoretical liquor ratio of 1 : 8.4 for obtaining 100% of grafted MAA with APS concentration of 4% o.w.f. This value however is not currently achieved in yarn dyeing machines used for silk weighting, which allow a liquor ratio of about 1 : 13, corresponding in this case to an expected yield of 60%.

A linear dependence of graft yield on APS concentration was also observed, but this trend was found strongly affected by the liquor ratio, since at the same APS concentration the yield increases three times by changing the liquor ratio from 1 : 40 to 1 : 20. However, at 1 : 20 liquor ratio and APS concentration higher than 4% o.w.f., the yield asymptotically tends to 50% and an APS concentration of 4% o.w.f. seems to be sufficient to assure the optimum yield.

Moreover, even a linear dependence of the yield on MAA concentration, at a given APS concentration and liquor ratio, was found. This effect and the influence of the liquor ratio can be justified by increasing the monomer concentration, which promotes its diffusion into the fiber.

Weighting with MAA: Effect of contact and heating time

In the previous runs, silk was introduced into weighting bath and immediately subjected to heating program with a final isothermal step at 70°C for 60 min. Since the diffusion of MAA should occur before the reaction, some tests were carried out by varying the contact time with the bath at room temperature, and then the samples were subjected to the usual heating program. The results are reported in Table I and show that a prolonged contact time of the silk with the acidified bath before heating improves the graft yield. Nevertheless this procedure is not acceptable for industry.

Therefore, to minimize this time a preheating step of the silk alone in nonionic surfactant acidified solution was introduced. MAA and APS solutions were

TABLE I
Effect of Contact Time with Bath at Room Temperature on the Graft Yield

Contact time (h)	Formic acid concentration (M)	Graft yield (%)
1	0.05	55.7
3	0.05	59.3
6	0.05	74.0
20	0.05	100
20	–	90.0

Bath: MAA 60% o.w.f., APS 4% o.w.f., Tergitol NP14 0.2 g/L, liquor ratio 1 : 15.

TABLE II
Effect of Preheating Time of Silk on the Graft Yield

Preheating time (h)	Temperature (°C)	Formic acid concentration (M)	Graft yield (%)
1	50	–	69.0
1	50	0.05	71.0
1	70	0.05	75.3
1	70	0.10	75.3
2	70	0.10	73.7
3	70	0.10	83.7
1	90	0.05	65.6
–	90[a]	–	46.0

Preheating bath: Tergitol NP14 0.2 g/L and formic acid. Weighting bath: MAA 60% o.w.f., APS 4% o.w.f., liquor ratio 1 : 15.
[a] Weighting process carried out at 90°C for 1 h instead of 70°C for 1 h.

then added and the thermal treatment was completed at 70°C for 60 min. The results are reported in Table II and show that the swelling effect of temperature can improve the yield, since after 1 h at 70°C the resulting value is higher than that found with 6 h at room temperature. In any case a significant improvement is reached at 3 h of preheating, while temperature exceeding 70°C is not advantageous.

Moreover, the influence of the reaction time was studied by varying the length of the isothermal step at 70°C and a linear increasing trend is observed up to 90 min then the yield becomes constant for longer time.

Weighting with MAA: Effect of nature and concentration of acid

Formic acid is often used for acidifying the weighting bath. It is known however that oxyacids show some affinity towards proteins. Therefore common oxya-

TABLE III
Influence of Nature and Concentration of Acid on Graft Yield

Acid	Acid concentration (M)	pH of the bath	Graft yield (%)
None	–	5.30	57.0
Formic	0.05	3.06	63.6
	0.10	2.35	68.3
Glycolic	0.05	2.63	74.3
	0.10	2.36	73.0
	0.15	2.24	66.3
Tartaric	0.03	2.35	68.7
	0.05	2.23	77.7
	0.10	1.91	70.3
	0.15	1.74	65.0
Citric	0.10	2.41	62.4
Sulfuric	–	2.00	64.7
	–	2.25	68.3
	–	2.50	71.7

Bath: MAA 60% o.w.f., APS 4% o.w.f., Tergitol NP14 0.2 g/L, liquor ratio 1 : 15.

TABLE IV
Graft Yields with Monomethacrylates

Monomer	Concentration of Tergitol NP14 (g/L)	Monomer concentration (% o.w.f.)	Graft yield (%)	
			APS 2% o.w.f.	APS 4% o.w.f.
HEMA	0.2	20	70.0	86.0
		40	68.0	99.0
		60	80.3	81.6
BMA	1.0	20	100	100
		40	59.5	100
		60	79.2	90.6
EHMA	1.0	20	33.9	55.4
		40	17.9	25.7
		60	35.2	69.9
TEGEEMA	0.2	20	75.9	78.0
		40	67.4	82.6
		60	70.9	81.9

cids as glycolic, tartaric, and citric were compared with formic and sulfuric acid to elucidate a potential influence of nature and concentration of acid on the graft yield. Oxyacid concentrations were chosen according to formic acid molarities already experimented, while sulfuric acid was added to achieve pH in the range from 2.0 to 2.5. The results are compared in Table III at the same MAA content (60% o.w.f.): glycolic and tartaric acids give higher yields than formic acid at $0.05M$ concentration and higher acidity levels are not useful. With citric acid however, a concentration of $0.10M$ is required for attaining satisfactory results. At the same pH values, sulfuric acid gives yields slightly lower than those found with glycolic and tartaric acids.

Weighting with MAA: Effect of swelling agents and optimum operating conditions

Since a prolonged heating step of silk alone improves the graft yield and this effect can be due to the fiber swelling, the action of swelling agents of proteins as N-methylurea and urea was tested. The results showed the improving effect of these additives with a maximum corresponding to 20% o.w.f. In this case the additive was added directly into the weighting bath, without a previous contact time.

In conclusion, the following operating conditions could assure optimal graft yields:

- liquor ratio lower than 1 : 15 if enabled by the weighting apparatus;
- APS concentration not lower than 4% o.w.f.;
- isothermal heating time of 90 min at 70°C;
- glycolic or tartaric acid to adjust pH of the weighting bath in the range from 2.2 to 2.5;
- swelling action onto silk achieved by addition of swelling agents, as urea or N-methylurea, at 20% o.w.f.

Weighting with monomethacrylates: HEMA, BMA, EHMA, TEGEEMA

HEMA and TEGEEMA, being readily water soluble, were tested according to the procedure already followed with MAA: liquor ratio 1 : 15, monomer concentration in the range from 20 to 60% o.w.f., APS 2, and 4% o.w.f., Tergitol NP14 0.2 g/L as wetting agent, pH about 2.5 by formic acid addition, thermal program with isothermal step at 70°C for 60 min. BMA and EHMA, however, required 1 g/L of Tergitol for making stable emulsions and a previous mixing step with silk to soak the fibers before adding APS. The results are compared in Table IV and show that the graft yields with APS concentration of 4% o.w.f. are higher in any case. Among these monomers, EHMA yields lower weight increase, whereas the others attain weighting levels of the same order as MAA or higher, as in the case of BMA. However the samples HEMA-grafted are stiff, as already reported in literature,[32] unlike those treated with BMA and TEGEEMA, which have softer hand.

Weighting with dimethacrylates: EGDMA, TEGDMA, PEGDMA

The dimethacrylates chosen for weighting tests have the same molecular pattern and differ only in the length of the intermediate ethoxy chain as follows:
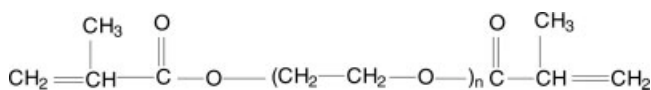
where $n = 1$ for EGDMA, $n = 3$ for TEGDMA, n average = 200 for PEG200DMA, and so on.

Increasing length of the ethoxy chain, the monomers become progressively more viscous and PEG600DMA

TABLE V
Graft Yields with Dimethacrylates

Monomer	Concentration of Tergitol NP14 (g/L)	Monomer concentration (% o.w.f.)	Graft yield (%)	
			APS 2% o.w.f.	APS 4% o.w.f.
EGDMA	0.2	20	30.3	86.5
		40	60.6	67.9
		60	34.2	54.1
TEGDMA	1.0	20	100	–
		40	100	100
		60	83.7	96.2
PEG200DMA	1.0	20	83.2	95.5
		40	71.2	86.5
		60	71.6	72.3
PEG400DMA	1.0	20	82.7	100
		40	88.9	98.2
		60	90.8	87.0
PEG600DMA	1.0	20	75.9	89.0
		40	65.7	58.0
		60	63.8	44.1

is a greasy solid. Therefore they were tested in the same conditions of monomethacrylates with 0.2 g/L of Tergitol NP14 for EGDMA only, being less viscous, and 1.0 g/L for the others with a previous mixing step.

The results are compared in Table V and some trends are similar to those observed with monomethacrylates, since at APS concentration of 4% o.w.f. the yields are generally higher, but tend to decrease by increasing the monomer concentration. TEGDMA shows better values than EGDMA, while PEG400DMA results the best among PEGDMA oligomers. In Figure 1, weight gain is plotted versus monomer concentration of PEGDMA. A linear increase is observed up to 40% of PEG200DMA and PEG400DMA, while with more than 20% of PEG600DMA the curve approaches asymptotically the value of 26% of weight gain. This trend suggests a saturation effect of the silk due to the highe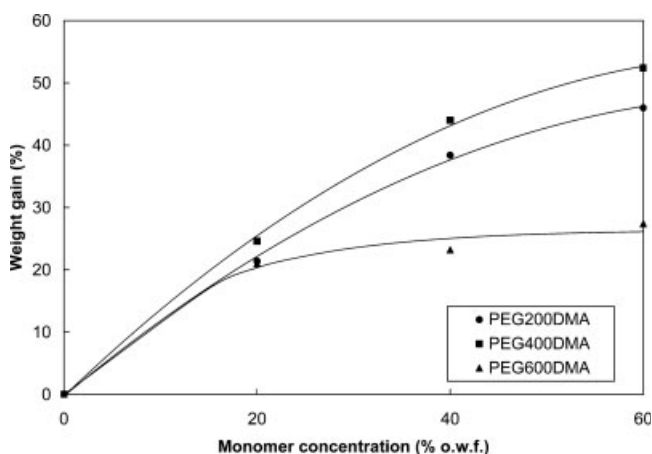r molecular weight of the monomer. Then the graft yield is lowered as the monomer concentration increases. However PEG400DMA and PEG600DMA yielded products with softer hand. These differences can be ascribed to a flexibilizing effect of the ethoxy chain, which increases as the length is growing. In all the cases various amounts of solid homopolymers were found in the grafting solutions.

Comparison between the methacrylic monomers

The comparison between the different methacrylic monomers, at the same conditions (APS 4% o.w.f., monomer 40, and 60% o.w.f.; liquor ratio 1 : 15) is reported in Figure 2. It is evident that monomers showing higher weight gain are HEMA, BMA, TEGEEMA, TEGDMA, and PEG400DMA, but TEGEEMA and dimethacrylates gave coatings tending to break off from the fiber surface in form of scales, hence seem to be less useful for weighting than HEMA and BMA.
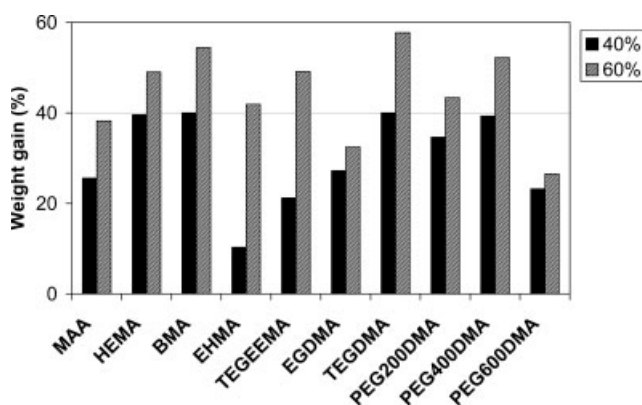

Figure 1 Influence of monomer concentration on weight gain of PEGDMA-grafted silk. APS 4% o.w.f. Liquor ratio 1 : 15. pH 2.5.

Figure 2 Comparison between weight gains obtained by grafting of various methacrylic monomers onto silk at 40 and 60% o.w.f. APS 4% o.w.f. Liquor ratio 1 : 15. pH 2.5.

With both of these monomers, small hanks of silk yarn were grafted and used for dyeing tests, which showed good results, i.e., acceptable color differences with respect to MAA-grafted silk control. Moreover, HEMA and BMA-grafted silk, after dyeing, showed water, perspiration, and rubbing fastness slightly lower than MAA-grafted samples (about one degree of the gray scales). The light fastness was the same in any case.

Thermal analysis of grafted silk

Samples of silk obtained by various grafting tests were subjected to DSC measurements. Figure 3 shows some DSC curves of MAA-grafted silk fibers with different weight gains. According to literature data,[1,14] the untreated control sample showed a single endothermic peak at about 325°C, attributed to the thermal decomposition of silk fibroin with oriented β-configuration. MAA-grafted silk exhibited an endothermic peak at around 280°C, in addition to the above. The area of the former became lower with increasing weight gain, and the latter accordingly increased. The endothermic peak registered below 300°C, can be attributed to the thermal decomposition of the MAA polymer grafted within the fiber matrix. These peaks are partially overlapped, but a calculation of the total enthalpy (ΔH_{tot}) contribution of the grafted MAA ($\Delta H_{polyMAA}$) was performed on the basis of the following equation:

$$\Delta H_{polyMAA} = \Delta H_{tot} - \frac{100 - MAA\ (\%)}{100} \times \Delta H_{silk} \quad (3)$$

where MAA (%) is the percent of MAA grafted onto the sample and ΔH_{silk} the enthalpy of untreated silk. ΔH_{tot} and ΔH_{silk} were obtained by integration of DSC thermograms, while MAA (%) was calculated from weight gain:
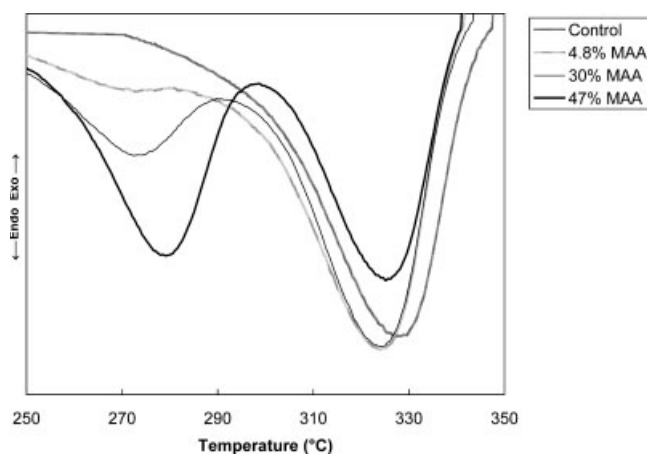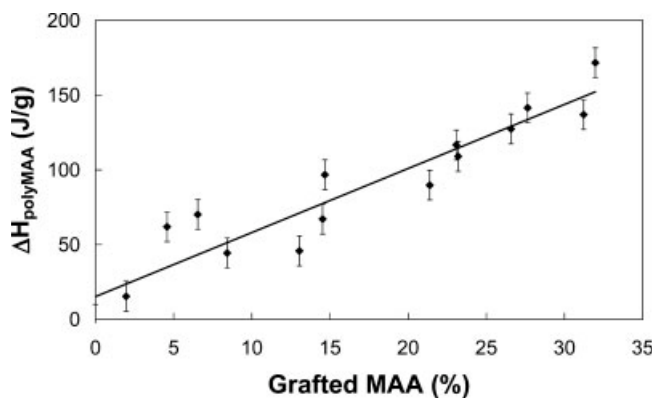

Figure 4 DSC analysis of MAA-grafted silk: correlation between the enthalpies calculated for polyMAA and content of grafted MAA.

$$MAA\ (\%) = \frac{Weight\ gain\ (\%)}{100 + Weight\ gain\ (\%)} \times 100 \quad (4)$$

The values of $\Delta H_{polyMAA}$ calculated using eq. (3) were plotted versus MAA (%), and showed a satisfactory linear correlation, as reported in Figure 4. This result confirms that the polyMAA does not affect the molecular structure of fibroin, because both thermal effects are substantially independent.[14] Moreover the reported calculation could provide a basis for a rapid method of evaluation of grafted MAA in weighted silk.

According to literature data,[14] TGA curves showed that the weight retention in the range 100–400°C of MAA-grafted samples up to 70% weight gain was roughly similar to that of the untreated fiber (about 58% at 350°C) without substantial modification of the thermal stability. However the derivative curves showed two peaks: the major at about 325°C and the
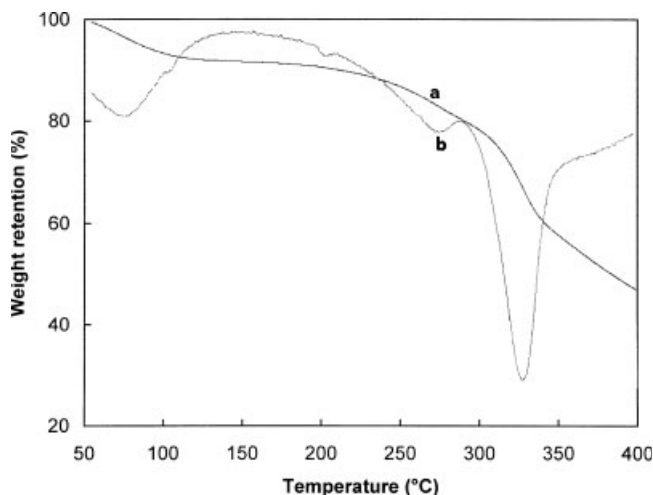

Figure 3 DSC curves of MAA-grafted silk with various weight gains.

Figure 5 TGA analysis of MAA-grafted silk with 47% weight gain (a: weight retention curve; b: derivative curve).

TABLE VI
Results of TGA Analyses on Silk Grafted with Various Methacrylates

Monomer	Weight gain (%)	Weight retention at 300°C (%)	Peak of derivative curve (°C)	Weight retention at 350°C (%)
Untreated Silk	–	82	327	58
HEMA	49	80	330	50
BMA	57	82	334	42
PEG400DMA	52	78	323	47
TEGDMA	50	77	326	43

smaller at about 280°, as reported in Figure 5. The latter can be attributed to the degradation of grafted polyMAA, while the former is similar to that observed in the untreated sample, which is due to the thermal degradation of the fiber, confirming the DSC results.

Unlike MAA-grafted silk, DSC analyses of the fibers weighted with the other methacrylic monomers showed only the endothermic peak of decomposition of fibroin, confirming the results observed by some authors with HEMA and ethoxyethylmethacrylate.[9,32,33] Similarly, TGA curves displayed only one inflection point in the range from 200 to 400°C, but the thermal stability was differently affected by the monomer type, as illustrated in Table VI. In the case of HEMA and BMA, unlike dimethacrylates, the peak of the derivative curve is shifted to higher temperature than untreated fiber, showing a moderate increase of thermal stability. However the degradation process seems to be faster for all the grafted samples, as shown by the weight retention values at 350°C.

FTIR analysis of grafted silk

To characterize the molecular structure of silk grafted with methacrylates the FTIR spectra were compared. According to literature data,[1,20] grafted silk should show characteristic absorption bands of fibroin with β-sheet structure at 1660 cm^{-1} (amide I), 1520 cm^{-1} (amide II), 1260, and 1231 cm^{-1} (amide III), while some peaks due to grafted monomers could be evidenced in addition.

Spectra of silk grafted with BMA and EHMA confirmed these assumptions without any significant difference with respect to the control silk, while HEMA-grafted silk exhibited only a minor shoulder at 1724 cm^{-1} in addition to the absorption bands of the fiber, according to Tsukada et al.[32] The spectra of MAA-grafted silk reported in Figure 6 show weak additional bands at 1385 and 1200 cm^{-1}, attributed to polyMAA.[1] In this case a satisfactory linear correlation between absorbance of the peak at 1200 cm^{-1} and MAA (%) was verified, as reported in Figure 7.

Stronger monomer features were found in the spectra of silk grafted with TEGEEMA and dimethacrylates over 50% weight gain, as reported in Figure 8. In the spectra of silk grafted with TEGEEMA, PEG400DMA, and TEGDMA, a strong peak was observed at about 1110 cm^{-1}, attributable to PEG aliphatic ether absorption, unlike the spectrum of EGDMA-grafted fiber, which showed only the peak at 1160 cm^{-1} already present in the spectrum of untreated silk. This difference is justified since in EGDMA the ether group is lacking. Moreover, in the spectra of silk grafted with TEGDMA and EGDMA the strong absorption at 1730 cm^{-1} can be attributed to the ester group derived from methacrylic acid.
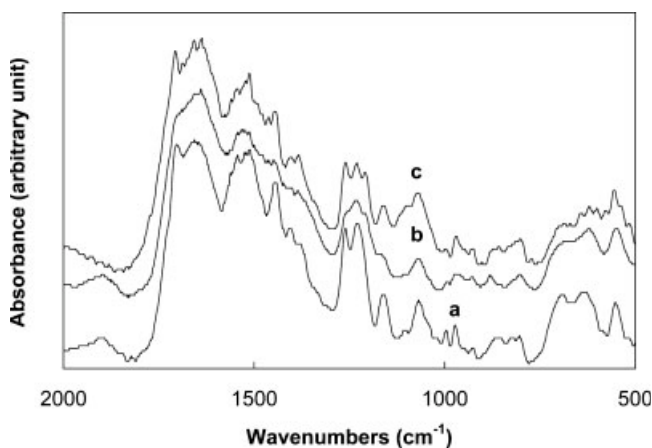

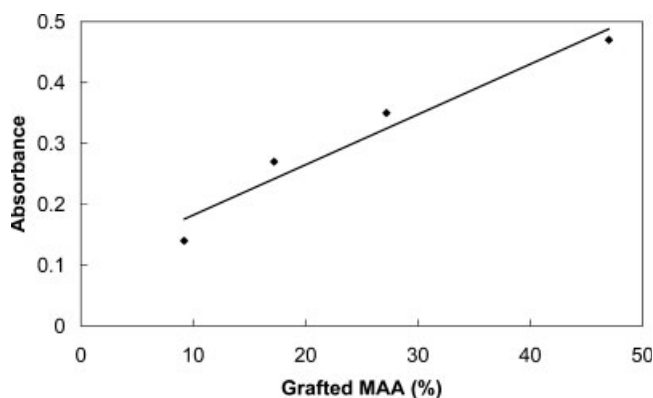**Figure 6** FTIR spectra of MAA-grafted silk with various weight gains (a: control; b: 27%; c: 47%).

Figure 7 Correlation between the absorbance of the peak at 1200 cm^{-1} and content of grafted MAA. The spectra were scaled to the peak at 1660 cm^{-1}.
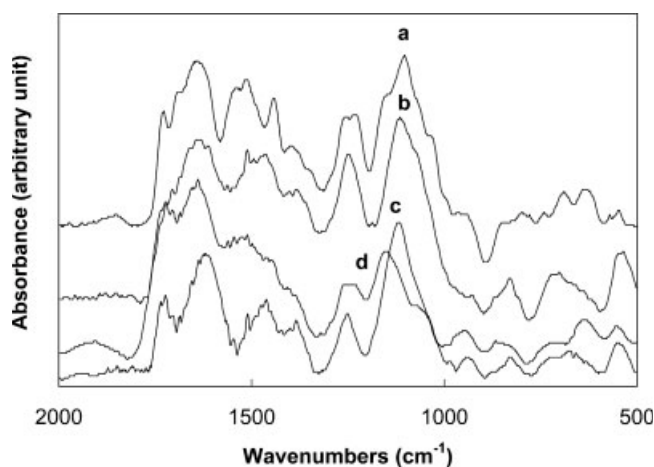
Figure 8 FTIR spectra of silk grafted with TEGEEMA and dimethacrylates (a: TEGEEMA 50%; b: PEG400DMA 55%; c: TEGDMA 61%; d: EGDMA 43%).

In conclusion, FTIR analysis of grafted silk confirmed that the structural pattern of fibroin was not substantially modified, but in the spectra of silk weighted with TEGEEMA and dimethacrylates the overlap of strong bands because the monomer could mask some minor features related to crystallinity and orientation of fibroin.[18]

CONCLUSIONS

In this work the operating conditions of weighting silk yarn with MAA were thoroughly investigated with the aim to improve the graft yield. The influence of MAA concentration, liquor ratio, APS concentration, contact and heating time, acidification, and swelling agents were considered and optimum operating conditions were outlined. Moreover, some monomethacrylates and dimethacrylates were grafted onto silk as alternative to MAA. Most of these monomers showed graft yields higher than MAA in the same operating conditions, but only HEMA and BMA are suitable for silk weighting since the weighted products have good dyeing behavior.

DSC analyses of MAA-grafted silk were performed to evaluate the influence of grafted monomer on the thermal behavior of the weighted fibers and a satisfactory linear correlation between the calculated enthalpy of polyMAA and monomer content was found. Thermal stability of grafted silk was checked by TGA, which confirmed the results of DSC analyses and showed a moderate increase of thermal stability for samples weighted with HEMA and BMA. The molecular structure of grafted silk was further investigated by FTIR analysis, which confirmed the structural pattern of fibroin with some peaks in addition due to grafted monomers.

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