

# Silk Grafting with Methacrylic and Epoxy Monomers: Thermal Process in Comparison with Ultraviolet Curing

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**ABSTRACT:** Silk grafting with methacrylic and epoxy monomers was studied with the aim to obtain high graft yields. With both monomer types optimum operating conditions of thermal grafting in water bath were established. In particular, three epoxy monomers were tested at various concentrations, at different temperatures and reaction times, with sodium chloride or sodium thiosulphate as catalysts. Optimum yields (76–82%) were found with Araldite DY-T for 2 h at 70°C with 3M sodium chloride. The results were compared with those obtained with the same monomers by UV curing, radical with methacrylates and cationic with the epoxy resin. The UV curing efficiency was tested by gel content determinations. Thermal and UV cured fibers were then subjected to measurements of fibroin solubility in ethanol–calcium chloride–water mixture to evaluate the crosslinking

degree. Except in the case of methacrylamide, radical UV curing yielded fibers more crosslinked than thermal treatment, or crosslinked to the same extent, whereas cationic UV curing showed lower crosslinking effects. The grafted fibers were characterized through DSC measurements and FTIR-ATR spectrometry. Finally, surface morphology of UV-cured samples was investigated through SEM analyses which showed that the better products could be obtained with UV curing at low add-on, mainly with dimethacrylates and Araldite DY-T, whereas the thermal grafting seems to be preferable for high add-on. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1019–1027, 2008

**Key words:** silk; proteins; fibers; graft copolymers; photopolymerization; radical polymerization

## INTRODUCTION

Silk grafting with organic monomers has taken importance not only as alternative to mineral weighting but also as finishing operation to improve properties of silk fabrics as hydrophilicity, crease recovery, dimensional stability, wash and wear, resistance to abrasion, photoyellowing and staining. For this purpose, various vinyl monomers were experimented, but methacrylamide, methyl- and 2-hydroxyethylmethacrylate have received more attention and methacrylamide is the monomer nowadays most used in industry because the products show soft hand, good crease recovery, increased hygroscopicity, and dyeing affinity. With these monomers the grafting reaction is carried out in water medium at about 70°C and needs radical initiators as hydrogen peroxide, persulfates, redox systems, or radiations.<sup>1–8</sup>

On the other hand, the salt-catalyzed reaction of epoxy compounds with silk fibers is known from many years, thanks to Shiozaki and Tanaka's

works.<sup>9–13</sup> Lysine, histidine, arginine, tyrosine, and serine residues of the fibroin have been found to react with epoxides to improve the fiber properties such as crease recovery, wash and wear and photodegradation resistance.<sup>12,14–17</sup> Effective catalysts for this reaction have found to be potassium thiocyanate, sodium thiosulfate, and sodium sulfite.<sup>12</sup> However, this reaction has attracted little commercial attention in silk finishing industry because it needs organic solvents as reaction media and long treatment times.<sup>18</sup> More recently these drawbacks have overcome by using alternative applications of epoxides such as pad-batch, pad-dry-steam, and pad-dry-bake.<sup>18,19</sup> Moreover, water soluble multifunctional and silicone-containing epoxides were synthesized to obtain fabrics with increased wet resiliency without hand worsening.<sup>20–26</sup>

To reduce the environmental impact, thermal processes for grafting silk fibers in water medium should be optimized to obtain high graft yields because unreacted monomers and oligomers strongly contribute to the organic load of wastewaters. For the same purpose, another grafting technique involving UV curing could be proposed, since this process does not need solvent and is carried out at room temperature with low-cost equipment,

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TABLE I  
Characteristics of Epoxy Monomers

	Araldite DY-0397	Araldite DY-3601	Araldite DY-T
Epoxy index (ISO 3001) (eq/kg)	8.00–8.50	2.47–2.60	7.80–8.2
Epoxy equivalent (ISO 3001) (g/eq)	118–125	385–405	122–128
Viscosity at 25°C (ISO 12058-1) (mPa s)	15–25	42–52	100–300
Density at 25°C (ISO 1675) (g/cm <sup>3</sup> )	1.08	1.03	1.12
Flash point (°C)	>156	>183	>100

hence it results commercially competitive with respect to conventional grafting methods. In UV curing, radical or cationic species are generated by the interaction of the UV light with a proper photoinitiator, which induces the curing reaction of reactive monomers and oligomers. UV curing technology is used in many industrial applications for coating of paper, plastic, metals, wood and glass surfaces because of low energy consumption, short start-up period, fast and reliable curing, low environmental pollution, curing at room temperature, and space saving.<sup>27</sup> In the field of textile finishing processes the radiation curing was proposed for pigment printing,<sup>28,29</sup> to realize coatings for shrink-resist wool,<sup>30,31</sup> and various functional finishes as flame retardant,<sup>32</sup> durable press<sup>33</sup> and water-repellency.<sup>34</sup> Only one limitation could arise from the fact that UV curing should be applied to fabrics while thermal grafting of silk can be applied also to yarns in common dyeing equipment. However UV curing of silk can be compared with microwave irradiation technique, recently proposed by Tsukada et al.,<sup>8</sup> and radiation grafting with electron beam.<sup>6,7</sup>

In a previous paper we have reported the optimum operating conditions of thermal silk grafting with several methacrylic monomers to obtain high graft yields.<sup>35</sup> As a continuation of this study, in the present work thermal silk grafting with epoxy monomers in water bath was first investigated, then UV curing process was studied with the aim to compare the results of both the processes. This comparison was made easier by the fact that some methacrylic monomers used in thermal silk grafting are suitable also for radical UV curing in inert atmosphere, while epoxy monomers can be UV-cured with a cationic photoinitiator in air. However in UV curing the use of selected chemical reagents, able to modify the fibrous substrate, can improve chemical and physical silk properties without strong add-on of polymer, unlike traditional weighting processes.

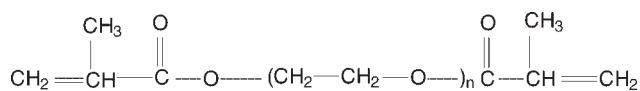
## EXPERIMENTAL

### Materials

Degummed and purged *Bombyx mori* silk yarn, with a titer of 20–22 decitex, four-ply, was kindly sup-

plied by Filtext-Como, Luisago (Como), Italy. The used fabrics were stockings knitted with the same yarn. These materials were dried for 2 h at 100°C and kept in desiccator.

Methacrylamide (MAA) was the commercial product provided by Röhm Italia (Garbagnate, Italy). The 2-hydroxyethylmethacrylate (HEMA) and ethylene-glycol-dimethacrylate (EGDMA) were supplied by Aldrich (Milan, Italy). Triethyleneglycol-dimethacrylate (TEGDMA) and polyethyleneglycol-dimethacrylates (PEG200DMA and PEG400DMA) were supplied by Kyoeisha Chemical (Japan). The dimethacrylates 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 and 400 for PEG200DMA and PEG400DMA, respectively.

The epoxy monomers chosen were: Araldite DY-0397 (diglycidylether of butanediol), Araldite DY-3601 (diglycidylether of polyoxypropylene glycol), and Araldite DY-T (triglycidylether of trimethylolpropane). All these monomers were supplied by Ciba Specialty Chemicals (Origgio, Italy) and their most important characteristics are summarized in Table I, while the structures are reported in Figure 1.

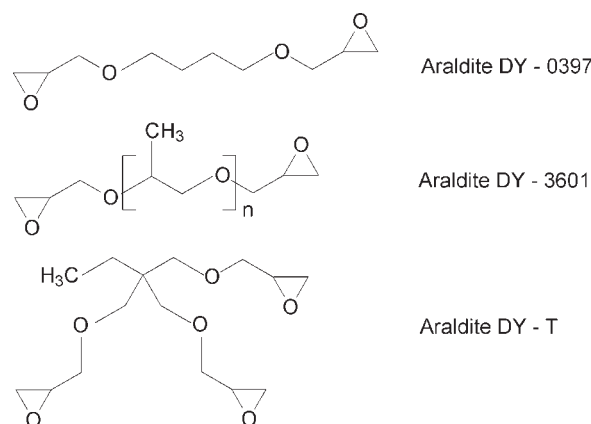


Figure 1 Structure of epoxy monomers.

Darocure 1173 (Ciba Specialty Chemicals) was used as radical photoinitiator, while Cyracure UVI 6974 (a mixture of sulfonium salt at 50 wt % in propylene carbonate gently given by Dow, Midland, MI) was used as cationic photoinitiator.

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

### Grafting operations by thermal treatment

Laboratory experiments of thermal treatment were carried out on silk yarn samples of 0.5 g in sealed test tubes plunged in heating bath. These were shaken by an oscillating plane. Grafting baths were introduced according to liquor ratio in the range 1 : 12 – 1 : 15, close to that enabled in yarn dyeing machines used for silk weighting. The soaking of silk yarn was favored by introduction of a nonionic surfactant into the bath (0.2–1.0 g/L of Tergitol NP14). In the case of methacrylic monomers, the pH was adjusted to 2.5 by formic or citric acid addition and APS was used as radical initiator, whereas in the case of epoxy monomers, salts as sodium chloride or thiosulfate were added as catalysts. Temperature was increased up to 70°C in about 20 min and kept at 70°C for different reaction times to obtain graft yields as high as possible. Then the silk samples were taken off and washed three times for 10 min each at 70°C with nonionic surfactant solution (2.0 g/L of Tergitol NP14) to remove monomers and oligomers physically adhering to silk fibers. Finally the samples were thoroughly rinsed with distilled water at room temperature, dried in oven at 100°C for 2 h, cooled to room temperature in a desiccator over silica gel for 30 min and weighted.

### UV curing

The formulation was first prepared by the dissolution of the photoinitiator in the liquid monomer in the proper amount (4% w/w) to produce a film on plastic substrate with each system considered. In some cases, to achieve a more homogeneous spread of the liquid mixture on fibers, surfactant aqueous solution (0.5 g/L of Tergitol NP14) was added. The formulation was then applied with a glass stick onto the surface of strips of silk fabrics having fixed dimensions of 5 × 2.5 cm<sup>2</sup>. In the case of water solutions, fabrics were then left in oven at 80°C for some minutes to evaporate water. The amount of resin put on the fabrics was adjusted according to the desired weight percentage.

The surface-coated fabrics were exposed to UV radiation using a medium-pressure mercury lamp with a light intensity on the fabric of about

20 mW/cm<sup>2</sup>, in a small box equipped with a quartz window and fluxed with nitrogen (oxygen content <20 ppm) in the case of radical UV curing. The required radiation dose was obtained by the adjustment of the distance of the sample from the lamp and the exposure time.

### Property measurements

For what concern the thermal process, the weight gain of silk, that is the add-on of polymer, was calculated as:

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

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

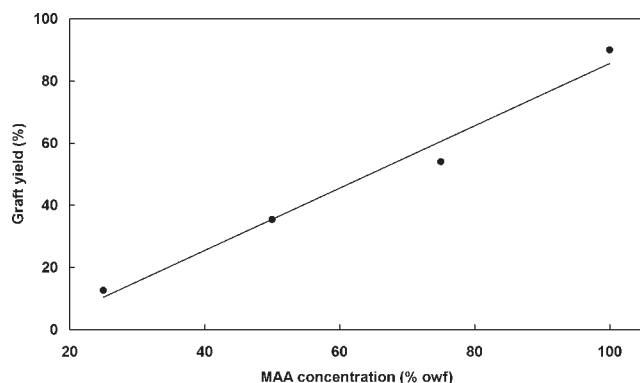
Moreover the graft yield was calculated as:

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

where  $w_m$  is the weight of monomer introduced into the bath. The weights were always referred to dried samples.

In the case of UV curing, the monomer and photoinitiator mixture should be absorbed by the fabric so the polymer structure does not form only a superficial coating but may penetrate inside the silk fibers. To test if UV radiation was effective even inside and the monomer was completely polymerized, the gel content was measured, according to the procedure commonly followed in many works on UV curing (ASTM method D2765-84).<sup>34,36</sup> This value was determined on the cured fabrics by measuring the weight loss after 24-h extraction with chloroform, at room temperature, followed by solvent evaporation in oven at 90°C for 1 h. The yield of the process was estimated by a comparison of the amount of the monomer polymerized on the textile with the initial weight of the monomer absorbed by the same. It might differ from the gel percentage if, particularly with diluted formulations, a part of monomer is lost by evaporation with water and in the radiation room.

The solubility of the silk fibroin in a solvent mixture was evaluated according to the method proposed by Cai et al.<sup>26</sup> Silk samples (about 2 mg) were boiled in a mixture of C<sub>2</sub>H<sub>5</sub>OH : CaCl<sub>2</sub> : H<sub>2</sub>O = 2 : 1 : 8 molar ratio for 30 min. In these conditions the silk fibroin is completely solubilized and the solution is stable at pH above its isoelectric point (3.8–3.9).<sup>37</sup> Two absorption bands at 212 and 278 nm in the UV spectra of silk solutions were attributed to tyrosine, phenylalanine and tryptophan aminoacid residues. A calibration line was constructed by dissolving



**Figure 2** Yield of grafted MAA versus MAA concentration, with 1 : 12.5 liquor ratio, 2.6% owf APS in 0.1M citric acid.

known amounts of the control silk into the solvent mixture and measuring the absorption band at 212 nm with an Unicam UV 2 Spectrophotometer. The solubility rates (ratio between the mass of the solubilized silk and the original mass of silk in the grafted samples) were evaluated by comparison of the absorption band intensity of the treated silk with the calibration line.

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  $\mu$ L 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. FTIR-ATR analyses were performed on a Nicolet FTIR 5700 spectrophotometer equipped with a Smart Orbit ATR single bounce accessory mounting a diamond crystal. Each spectrum was collected on film or directly on a single yarn by cumulating 128 scans, at 4  $\text{cm}^{-1}$  resolution and gain 8, in the wavelength range 4000–600  $\text{cm}^{-1}$ .

The surface morphology of the fabrics was examined by Scanning Electron Microscopy (SEM) on a Leica Electron Optics 135 VP SEM, with an acceleration voltage of 15 kV, current probe of 400 pA and working distance of 20 mm. The samples were mounted on aluminum specimen stubs with double-sided adhesive tape and sputter-coated with gold in rarefied argon using an Emitech K550 Sputter Coater with a current of 20 mA for 180 s.

## RESULTS AND DISCUSSION

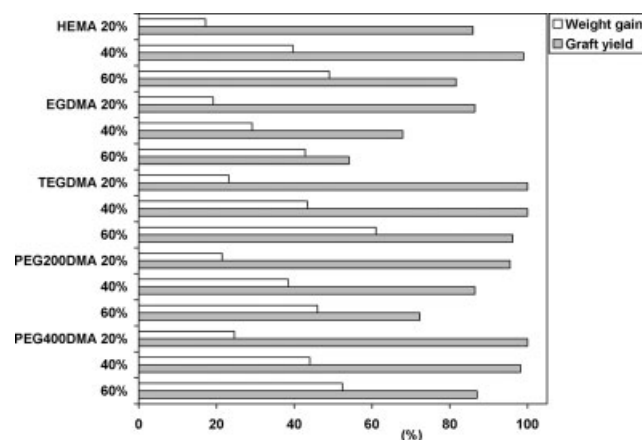
### Thermal process optimization of silk grafting with methacrylic monomers

The optimum operating conditions of thermal silk grafting with MAA and several methacrylic monomers were reported in the previous paper.<sup>35</sup> Among

these, MAA, HEMA and dimethacrylates, which resulted suitable also for UV curing, are recalled here. In grafting with MAA, liquor ratio, concentration of APS, monomer and acid strongly affect the graft yield. This, with a liquor ratio of 1 : 12.5 and 2.6% owf APS in 0.1M citric acid, was found linearly increasing with the monomer concentration, as observed in Figure 2. Hence a yield of 90% was achieved only with 100% owf MAA. Better results were obtained with HEMA and dimethacrylates at lower monomer concentrations and these are compared in Figure 3. TEGDMA shows the highest yields, very close to 100% and practically unaffected by the concentration, followed by PEG400DMA and PEG200DMA with slightly lower values decreasing as the monomer concentration increases. This trend is more pronounced with EGDMA which shows even lower yields, from 87 to 54%, ascribable to the shortening of the ethoxy chain with a consequent decrease of molecular flexibility.

### Thermal process optimization of silk grafting with epoxy monomers

At first, different concentrations of the epoxy monomers were tested at 1 : 15 constant liquor ratio with the temperature program previously reported. The results are shown in Table II. In the case of monomer concentration of 100% owf the reaction time at 70°C was extended up to 5 h to evidence a possible dependence of graft yield on this variable. With all the monomers higher yield values were obtained decreasing the concentration and in the presence of sodium chloride 1M as catalyst. A further increase was generally observed prolonging the reaction time and the highest yield was achieved with Araldite DY-T at 100% owf after 4 h, but lower values were found after 5 h. Higher temperature (80°C) was



**Figure 3** Weight gain and graft yield of silk with various methacrylic monomers (% owf monomer concentration), 4% owf APS, liquor ratio 1 : 15, pH 2.5.



**TABLE II**  
Graft Yields with Epoxy Monomers

Monomer	Monomer concentration (% owf)	Catalyst	Graft yield (%) with reaction time			
			2 h	3 h	4 h	5 h
Araldite DY-0397	150	None	3.3	–	–	–
	150	NaCl 1M	4.4	–	–	–
	100	NaCl 1M	15.1	21.2	51.9	27.1
Araldite DY-3601	50	NaCl 1M	28.4	–	–	–
	150	None	18.6	–	–	–
	150	NaCl 1M	26.6	–	–	–
	100	NaCl 1M	38.2	59.2	22.5	22.8
Araldite DY-T	50	NaCl 1M	68.5	–	–	–
	150	None	8.0	–	–	–
	150	NaCl 1M	14.6	–	–	–
	100	NaCl 1M	46.6	59.6	75.2	52.8
	50	NaCl 1M	59.8	–	–	–

tested, but without substantial improvement. In Table III the results obtained with Araldite DY-T, at 70°C for 2 h, varying sodium chloride concentration are compared with those obtained using sodium thiosulfate. The latter catalyst showed graft yields slightly lower than sodium chloride and in both cases an improvement was observed increasing the catalyst concentration.

In conclusion, the highest graft yields (76–82%) were obtained with Araldite DY-T in the concentration range from 20 to 60% owf in the presence of NaCl 3M at 70°C for 2 h. These results might be justified by the higher reactivity of the trifunctional structure with respect to the other epoxides. Therefore Araldite DY-T alone was chosen as model epoxy monomer for comparison of thermal silk grafting with UV curing.

### Silk grafting by UV curing

Methacrylic monomers as MAA, HEMA, EGDMA, TEGDMA, PEG200DMA, and PEG400DMA mixed with 4% Darocure 1173 were found suitable to yield solid films after irradiation with UV lamp for 45 s under nitrogen atmosphere. The same result was achieved with Araldite DY-T subjected to cationic photopolymerization in the presence of 4% Cyracur-eUVI 6974 for 75 s of curing in air.

Then the same formulations were applied to silk fabric and the results of weighting, percent gel and yield are reported in Table IV. The higher yields ( $\geq 79\%$ ) and gel percentages ( $\geq 85\%$ ) were shown in the adopted conditions by PEGDMA and Araldite DY-T. HEMA, EGDMA, and TEGDMA showed slightly lower values, whereas the results obtained with MAA were poor satisfactory even at low weight percentage. The efficiency values reported for silk grafting of epoxides with microwave irradiation technique<sup>3</sup> were much lower than those found

in UV curing of Araldite DY-T, whereas in the case of MAA and HEMA the yields were higher with microwave irradiation, but at longer reaction times (10 and 20 min).

### Crosslinking reactions onto silk fibroin

The solubility rates of silk fibroin in solvent mixture (C<sub>2</sub>H<sub>5</sub>OH : CaCl<sub>2</sub> : H<sub>2</sub>O = 2 : 1 : 8 molar ratio) are very useful to evaluate the occurrence of crosslinking reactions.<sup>27</sup> The results of some tests on various samples grafted either by thermal treatment or UV curing are reported in Table V.

In silk grafted with MAA, the solubility of fibroin was found high in any case and complete below 17% weight gain, without evidence of crosslinking. Even in thermal grafting with HEMA the solubility was high, whereas in UV curing the value at the same add-on was much lower, suggesting the presence of a significant crosslinkage. EGDMA showed lower solubility rates than monomethacrylates and decreasing with weight gain, without apparent differences between thermal and UV curing. However TEGDMA seems a more efficient crosslinking agent, particularly in UV curing. With PEGDMA the

**TABLE III**  
Weight Gains and Graft Yields with Araldite DY-T and Various Catalysts at 70°C and 2 h Reaction Time

Monomer concentration (% owf)	Catalyst	Weight gain (%)	Graft yield (%)
20	NaCl 3M	16.4	82.0
40	NaCl 3M	31.0	77.5
60	NaCl 2M	40.4	67.3
60	NaCl 3M	45.6	76.0
60	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> 1M	18.6	31.0
60	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> 2M	40.0	66.7
60	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> 3M	42.8	71.3

**TABLE IV**  
**Results of Silk Grafting by UV Curing**

Monomer	Irradiation time <sup>a</sup> (s)	Weight gain (%)	Gel content (%)	Graft yield (%)
MAA	45	16.9	41.1	15.0
HEMA	45	14.6	79.8	70.2
EGDMA	45	10.7	90.0	61.2
TEGDMA	45	12.9	76.8	64.3
PEG200DMA	45	50.3	91.6	86.7
PEG400DMA	45	26.0	89.8	79.4
Araldite DY-T	75	27.6	85.8	80.5
Araldite DY-T	75	37.4	96.8	84.9

<sup>a</sup> On each side of the fabric.

solubility was further lowered and at about 50% add-on the fibroin became fully insoluble. Even in this case UV curing yielded more crosslinked fibers. Finally, Araldite DY-T was found the most powerful crosslinking agent, even at low add-on, in thermal process, as it might be expected because of its tri-functional structure. In UV curing, however, Araldite DY-T showed higher solubility rates in dependence on the polymer add-on, which could indicate lower crosslinking effects than the grafting ones, due to the different curing mechanism.

In conclusion, on the basis of these results, a decreasing order of crosslinking power of the tested monomers in thermal process could be suggested as:

Araldite DY-T > PEGDMA > TEGDMA  
> EGDMA > HEMA > MAA

In any case, radical UV curing yielded fibers more crosslinked than thermal treatment, or crosslinked to

the same extent, whereas cationic UV curing showed lower crosslinking effects.

#### Thermal analysis and FTIR spectra

The comparison between DSC thermograms of 17% MAA-grafted samples thermal and UV cured is reported in Figure 4. The UV cured sample showed only the endothermic peak of decomposition of fibroin at about 325°C, whereas the thermal grafted fibers exhibited an additional endothermic peak at around 280°C attributed to thermal decomposition of poly-MAA.<sup>35</sup> This result is in agreement with the low crosslinkage yielded by the solubility rate and suggests that in UV curing MAA grafting prevails on homopolymerization.

DSC thermograms of silk grafted at low add-on with the other methacrylic monomers by UV curing are compared in Figure 5 and show the peak due to fibroin practically without differences, as observed

**TABLE V**  
**Solubility Rates of Silk Fibroin in Solvent Mixture (C<sub>2</sub>H<sub>5</sub>OH : CaCl<sub>2</sub> : H<sub>2</sub>O = 2 : 1 : 8 Molar Ratio) After 30-min Boiling**

Monomer	Treatment	Weight gain (%)	Solubility rate (%)
MAA	Thermal	7.0	100
	UV curing	16.9	100
	Thermal	25.8	90.6
HEMA	Thermal	14.0	85.0
	UV curing	14.6	39.6
EGDMA	Thermal	6.0	79.5
	UV curing	10.7	48.8
	Thermal	19.2	16.0
TEGDMA	UV curing	12.9	68.6
	Thermal	25.2	71.4
PEG200DMA	UV curing	50.3	0
PEG400DMA	Thermal	24.6	47.6
	UV curing	26.0	14.0
	Thermal	52.0	0
Araldite DY-T	Thermal	16.4	0
	UV curing	27.6	48.7
	Thermal	31.0	0
	UV curing	37.4	6.4
	Thermal	45.6	0

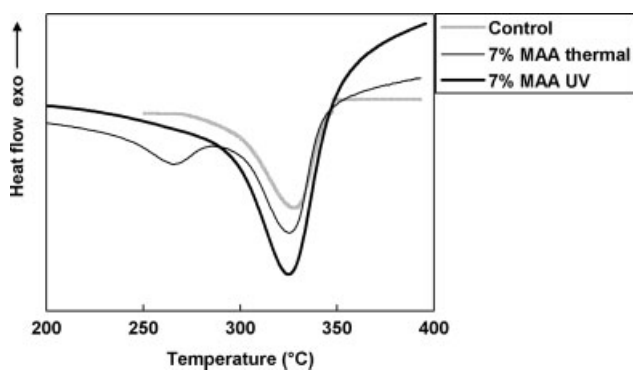


Figure 4 DSC thermograms of MAA-grafted silk.

in thermal grafting.<sup>35</sup> Finally thermal or UV cured epoxy-grafted fibers show also the same peak, but slightly broader and more asymmetric compared with that of the control silk, as can be seen in Figure 6. This is more evident in the thermal-grafted sample, in agreement with the results of solubility rate indicating a more extended crosslinkage. In fact, shifting and broadening of the decomposition peak was observed in silk fibers treated with other epoxides.<sup>15,16,26</sup>

FTIR-ATR spectra of silk grafted with methacrylic monomers by UV curing are very similar to those shown by thermal grafted products and reported in the previous paper.<sup>35</sup> However in Figure 7 the spectra of two silk samples grafted with Araldite DY-T, one thermal treated and the other UV cured, are compared with that of film of UV cured Araldite. In the latter, a strong peak at  $1077\text{ cm}^{-1}$  is observed, which can be attributed to the ethoxy group. In the other spectra this band is overlapped to the typical absorption bands of silk fibroin:  $1630\text{ cm}^{-1}$  (amide I),  $1520\text{ cm}^{-1}$  (amide II),  $1265\text{ cm}^{-1}$  (amide III), and its intensity is increased by increasing the polymer add-on. In any case thermal or UV cured samples showed similar spectra.

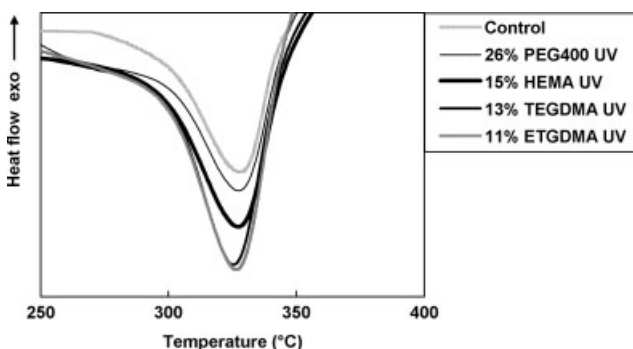


Figure 5 DSC thermograms of silk UV-grafted with methacrylic monomers.

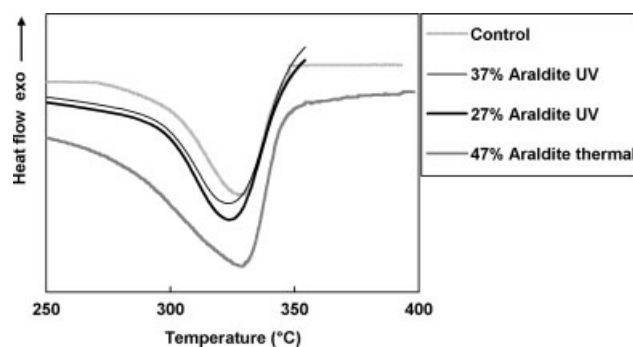


Figure 6 DSC thermograms of silk grafted with Araldite DY-T.

### SEM analysis

Surface examination by SEM analysis was focused on UV cured fabrics to evidence the morphology of the polymer-grafted fibers. In Figure 8 the comparison between untreated silk and samples grafted with EGDMA and TEGDMA shows fibers individually sized rather than glued in a polymeric matrix, whereas with HEMA the coating is less regular and homopolymer segregation becomes evident, despite a low add-on of the same order (11–15%). However in Figure 9 the comparison of the SEM images of silk grafted with high add-on of Araldite DY-T shows that the UV cured fibers with 37.4% of resin appear to be glued together in a polymeric coating, whereas those thermally weighted are well distinguishable, in agreement with an individual sizing, despite the higher add-on (45.6%). The same effect was observed also with UV cured dimethacrylates at high add-on (about 50%) and could be justified by

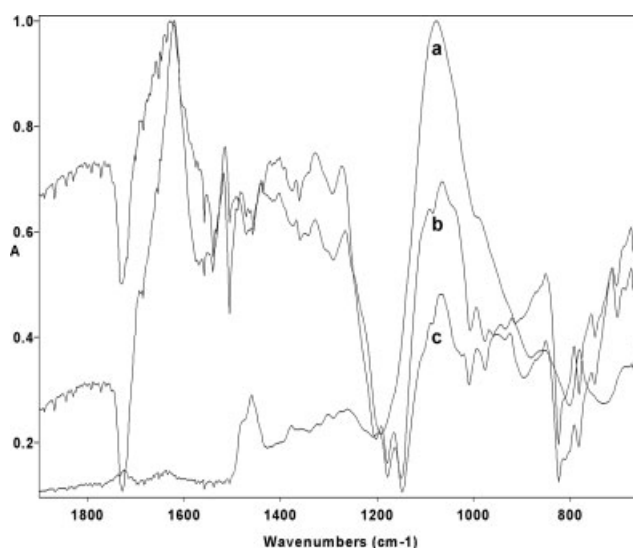
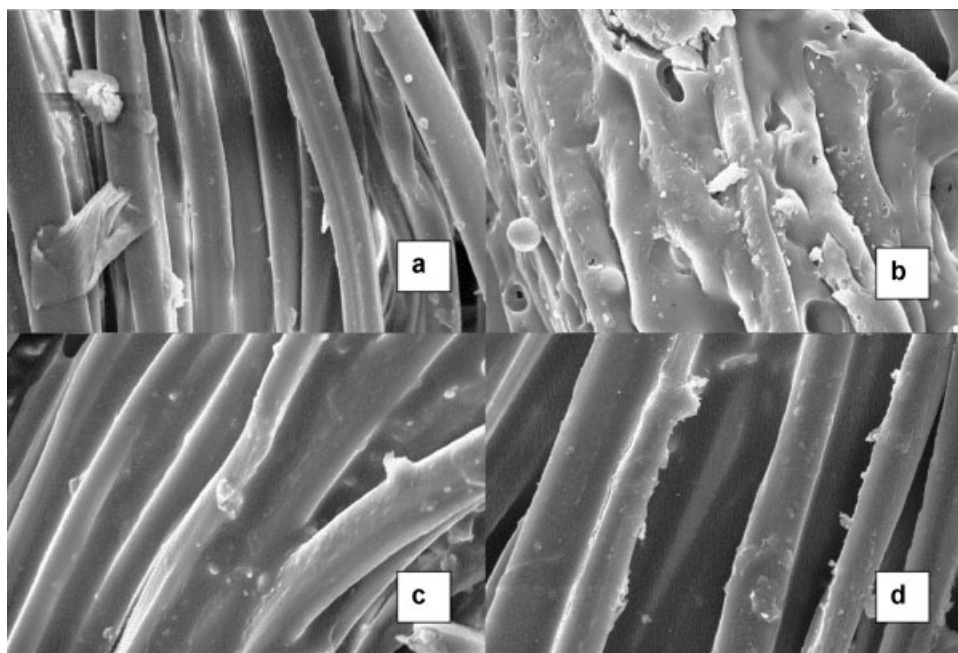


Figure 7 FTIR-ATR spectra of (a) film of UV cured Araldite DY-T, (b) silk thermal-grafted with 45.6% Araldite DY-T, (c) silk UV-grafted with 27.6% Araldite DY-T.



**Figure 8** SEM images (1000 $\times$ ) of silk samples (a) untreated, (b) UV-grafted with 14.6% HEMA, (c) UV-grafted with 12.6% EGDMA, (d) UV-grafted with 12.9% TEGDMA.

the different grafting mechanism: in water solution at 70°C for 2 h the monomer is able to diffuse inside the fibers before the reaction, whereas in the case of UV curing the impregnation of a concentrated resin solution followed by a rapid drying cannot allow the penetration into the fibers, hence the curing is running preferentially on the surface.

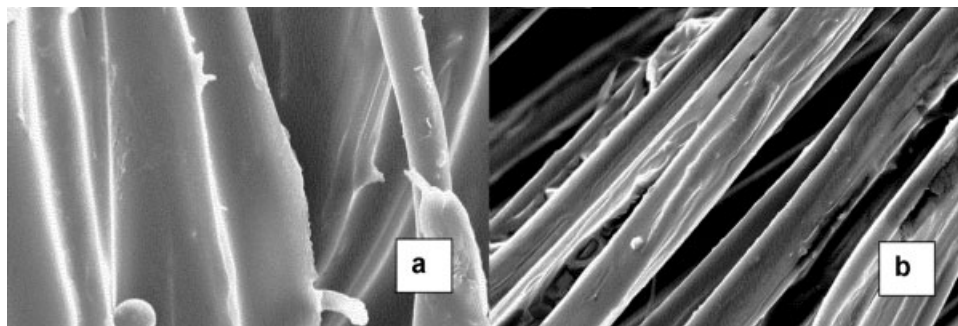
### CONCLUSIONS

Operating conditions of grafting silk fibers with MAA, HEMA and dimethacrylates were established to obtain high graft yields in thermal treatment. Grafting with epoxy monomers in water medium was then studied and the influence of monomer concentration, temperature, reaction time and catalyst were considered. Optimum yields (76–82%) were

found with Araldite DY-T for 2 h at 70°C with NaCl 3M as catalyst.

The same monomers were grafted on silk fabric by UV curing in the presence of suitable photoinitiators. High yield and gel content were shown by HEMA and dimethacrylates in radical UV curing, whereas the results obtained with MAA were poor satisfactory. Even Araldite DY-T subjected to cationic UV curing gave good results.

The crosslinking power of the various monomers was investigated on the basis of the solubility rate of the silk fibroin in grafted fibers and a classification of the monomers relating to the effect of crosslinkage in thermal grafting was suggested. In radical UV curing the same or higher crosslinkage effects were shown, whereas in cationic UV curing of epoxide these were lower. Some typical morphological



**Figure 9** SEM images (1000 $\times$ ) of silk samples (a) UV-grafted with 27.6% Araldite DY-T, (b) thermal-grafted with 45.6% Araldite DY-T.



features of UV cured fibers arose mainly from the results of the SEM analysis which showed a gluing effect rather than an individual sizing at high polymer add-on and with HEMA even at low weighting. In conclusion, with UV curing the better products could be obtained at low add-on, mainly with dimethacrylates and an epoxy monomer such as Araldite DY-T, whereas the thermal grafting seems to be preferable for high add-on.

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