

## MICROWAVE IRRADIATION TECHNIQUE TO ENHANCE PROTEIN FIBRE PROPERTIES

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### Abstract

*Microwave irradiation technique was used for the chemical modification and grafting of protein fibrous materials, such as domestic silk (*Bombyx mori*), tussah silk (*Antheraea pernyi*), and wool fibres. Epoxide compounds Denacol EX810 and EX313 reacted effectively with the protein substrates. As alkali catalysts, sodium hydroxide was more effective than sodium thiocyanate. The optimum concentration was 0.25 w%. Weight gain values up to 8% were attained with 10-15 min irradiation time at 200W power. Graft-copolymerisation of vinyl monomers onto protein fibres resulted in variable weight gains, depending on the kind of fibre, the grafting monomer used, and the concentration of the padding solution. For example, after grafting with iso-propyl methacrylate (IPMA), the weight gain of fibrous proteins took place in the following order: *Bombyx mori* silk > tussah silk > wool. *Bombyx mori* silk gained more weight with IPMA than with 2-hydroxyethyl methacrylate (HEMA) or methacrylamide (MAA). The weight gain of *Bombyx mori* silk with HEMA significantly increased when the initial monomer concentration was raised to 400% owf, reaching a maximum value of 40%. The tensile properties of the protein fibres grafted with IPMA, MAA, and HEMA remained unchanged or slightly improved compared to the reference fibres. Fibres modified with epoxides showed a drop in tensile performance. The surface morphology of fibres treated with epoxide compounds or graft-copolymerised with vinyl monomers was almost unaffected, with the exception of HEMA-grafted fibres, which showed the presence of homopolymer deposited onto the surface at a weight gain exceeding 20%.*

### Key words:

*graft-copolymerisation, protein fibres, microwave irradiation, chemical modification, weight gain*

### Introduction

During the past three decades there has been an intensive academic and technological interest in the chemical modification [20] and grafting [4] of silk fibres. Silk fibres are grafted with various types of grafting monomers, such as methacrylamide (MAA) [18] and 2-hydroxyethylmethacrylate (HEMA) [17]. Grafting treatment effectively increases silk weight and improves the textile performances of silk, such as dimensional stability, anti-photoyellowing and colour fastness, etc. Chemical modification also alters fibre composition and properties [20]. This technique refers to modification of the material in an organic solvent (dimethyl formamide or dimethyl sulphoxide), with reactive agents such as epoxide compounds [14] and dibasic acid anhydrides [15,16]. These modifying agents react selectively with the basic, acidic, and hydroxyl-amino acid residues. Researchers face the key challenge of improving the performance of silk by grafting and chemical modifications while keeping its inherent properties intact.

The application of graft-copolymerisation techniques is currently confined to the textile field. However, silk is becoming an attractive multifunctional material for both textile and non-textile uses. Applications in the biotechnological and biomedical fields have already been reported for specific tasks such as

enzyme immobilization and sutures [5-11]. Both grafted and chemically modified silk fibres exhibit desirable characteristics, and appear potentially suitable for diverse applications.

Conventional grafting and chemical modification techniques require significant time and energy. The temperature is incrementally increased from room to reactive temperature, usually around 70-85°C, over approximately 45 min, and then kept constant for about 1-4 hours according to the required purposes. High temperature and long reaction time may have adverse effects on the fibre's intrinsic properties such as tensile performance, handle, and appearance. A novel approach intended to overcome these drawbacks has long been a matter of research. As an example, we demonstrated the viability of silk modification with epoxide compounds by the pad/batch method, and determined the optimum reaction conditions including NaOH concentration and reaction temperature [19]. In the pad/batch technique, the epoxide compound reacts at a significantly low temperature (as low as 40°C) for 24 hrs in a shielded polyethylene bag. The reactivity of target amino acid residues did not significantly differ from the results of conventional epoxide treatment at an elevated temperature. However, this system could be further improved by reducing the reaction's time span and cost.

The application of microwave (MW) techniques within the textile industry, although somewhat slow and still rather limited, is finding its way into numerous uses in production plants [1]. MW technology uses electromagnetic waves that pass through material and cause its molecules to oscillate. MW energy is not absorbed to any degree by non-polar materials, while polar water molecules held within a polymeric matrix do absorb energy very efficiently, thus becoming heated. The main MW functionalities provided for the industry are heating, drying, conditioning, bleaching, dyeing, finishing, and sterilising. Applications have been developed for knit, woven, non-woven and laundering industrial facilities. The most important advantages offered by MW technology are increased throughput and productivity, higher energy efficiency of processes, savings of energy, improved quality of textile goods. MW irradiation has also been proposed as an effective method for controlling insect pests in museums and for de-infestation of contaminated fabrics of artistic and historical interest [12].

The goal of the current research is to develop new and effective techniques for grafting and chemical modification of protein fibres by using MW irradiation. After using epoxide compounds, isopropyl methacrylate (IPMA) and popular grafting monomers such as HEMA and MAA, the optimum conditions for grafting and modification were determined. Finally, the physical and morphological properties of the fibres modified and grafted in this way were compared with those obtained by conventional modification and grafting techniques. Despite significant development in conventional grafting and chemical modification techniques, a simple and effective system is of interest from the standpoints of energy conservation and cost effectiveness. This research reveals an effective technique for replacing conventional high-energy reaction systems.

## **Experimental**

### **Materials**

*Bombyx mori* silk fibroin (Bm-SF) fibres were degummed with an aqueous solution of 0.7% Marseille soap (w/v) at 98°C for 1hr. The yarn was thoroughly rinsed several times with running water, and then dried at room temperature before being used as grafting substrates. Wild tussah silk fibroin fibres from *Antheraea pernyi* (Ap-SF) silkworm were used as grafting and chemical modification substrates after removing sericin by alkaline degumming. Wool (Wo) fibres, were cleaned by an acetone/ethanol mixture system in a Soxhlet extractor for 12 hrs, then rinsed with distilled water, dried to a constant weight and conditioned in air at room temperature.

2-hydroxyethyl methacrylate (HEMA) and methacrylamide (MAA), purchased from Wako Pure Chemical Industries, Ltd were used without further purification. Isopropyl methacrylate (IPMA) was purchased from Mitsubishi Rayon. The epoxide compounds Denacol EX810 (ethylene glycol diglycidyl ether) and EX 313 (glycerol polyglycidyl ether, mixture of di- and tri-substituted glycerol) were purchased from Nagase Chemtechs Co. Ltd (Tatsuno City, Hyōdo, Japan) and used without further purification.

Conventional graft-copolymerisation of vinyl monomers and chemical modification with epoxides were performed as reported elsewhere [4,20].

For MW-assisted reaction of epoxide compounds, fibres (300 mg) were preliminarily immersed into an aqueous solution (20ml) of EX313 or EX810 (12-26 w%), containing NaOH (up to 0.33 w%), and isopropyl alcohol (15 w%). Samples were then padded to an approximate 100% wet pick-up, sealed in a polyethylene bag to prevent solvent evaporation, and irradiated in a MW oven (Mitsubishi Electronic), at 200W power, for differing reaction times, up to 20 min. At the end of the reaction, the samples were washed with boiling acetone for 30 min to remove any unreacted monomer and oligomer, thoroughly rinsed with distilled water, and finally dried at room temperature.

For MW-assisted graft-copolymerisation, fibres (258 mg) were immersed for approximately 5 min, at room temperature, into an aqueous solution (20ml) containing differing amounts of grafting monomer (up to 400% owf) and 2.1 w% ammonium persulphate (APS). The pH was adjusted to 3 with formic acid. Padding conditions, MW irradiation parameters, and after-treatments were the same as for reaction with epoxides.

### **Measurements**

The percentage of the fibres' weight gain and the reaction efficiency were calculated as follows:

$$\text{Weight gain (\%)} = [(W_2 - W_1) / W_1] \times 100 \quad [A]$$

$$\text{Efficiency (\%)} = (W_2 - W_1) / W_3 \times 100 \quad [B]$$

where  $W_1$ ,  $W_2$ , and  $W_3$  denote the weight of the original sample, that of the same sample after grafting or chemical modification, and that of the grafting or chemical modification agent, respectively.

Equilibrium moisture regain was determined under standard testing conditions at 20°C and 65% relative humidity (RH).

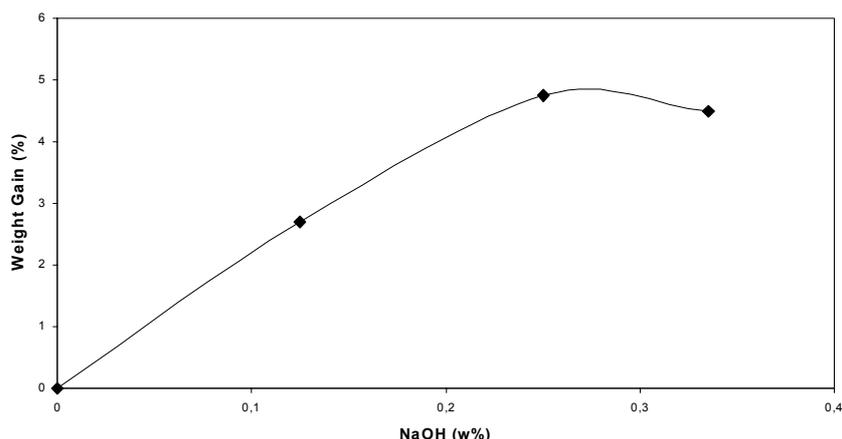
Tensile properties were measured with an automatic tensile testing machine (Tensilon UTM-II, Toyo Baldwin Co, Ltd.) under standard testing conditions. Each value is the average of 20 measurements. The constant drawing rate of the sample is 10 min/min, the load at full scale is 500g, the sample length is 10cm, the chart speed is 200 mm/min and the strain rate is 40 mm/min.

Surface morphology was examined with a Stereoscan 440 (LEO Electronic Microscopy Ltd.) scanning electron microscope at 10 kV acceleration voltage, after gold coating.

## **Results and Discussions**

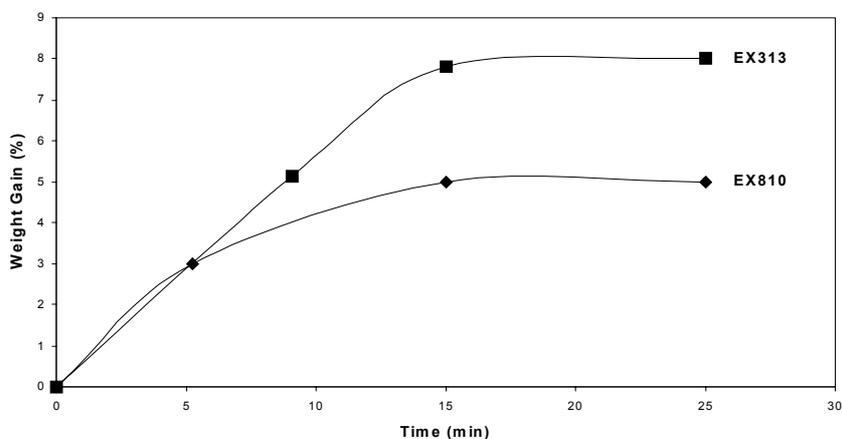
### **Chemical modification with epoxide compounds**

The optimum conditions of irradiation time and alkali concentration were determined for chemical modification of Bm-SF with epoxide compounds. Two commercial epoxides, Denacol EX810 and EX313, were used as modifying agents. It has been reported that the preliminary treatment of protein fibres with alkaline salts exerts a catalytic action and is conducive to enhancing the reactivity of epoxides [13]. NaSCN has often been used as a catalyst to promote the reaction of epoxides with protein fibres. Preliminary tests showed that NaOH was more effective than NaSCN in increasing the weight gain in the MW radiation system used in the present study (data not shown). However, there is a potential risk that alkali affects the physical properties of fibres. Hence, the optimum NaOH concentration was determined in order to maximise the reaction yield and to prevent the mechanical deterioration of fibres. Figure 1 shows that the weight gain of Bm-SF fibres with EX810 as the modifying agent increased with the increase in concentration of NaOH in the padding solution until 0.25 w%, and then remained almost constant, or decreased slightly. These results confirm that a mild concentration of NaOH of 0.2-0.25 w% is preferable for the MW-assisted chemical modification of silk.



**Figure 1.** Weight gain of Bm-SF with the epoxide compound EX810 (12 w%) as a function of the NaOH concentration in the reaction system. EX810 concentration: 12 w%; wet pick-up: 100%; MW power: 200W; reaction time: 15 min

The kinetics of the reaction of epoxides EX810 and EX313 with Bm-SF fibres was studied as a function of MW irradiation time. As shown in Figure 2, the weight gain increased gradually within 15 min of irradiation time, and then reached a plateau at about 5% and 8% weight gain for EX810 and EX313 respectively. Equilibrium was attained in a relatively short reaction time, whose span is restricted to only 15 min. Moreover, both epoxides displayed similar values of optimum irradiation time. The higher weight gain obtained with EX313 is mainly attributable to the slightly higher initial concentration of the modifying agent (18 w% for EX313 and 12 w% for EX810). The higher the epoxide concentration in the padding solution, the higher the uptake of the epoxide onto the fibres, and so the higher the yield of the reaction.



**Figure 2.** Weight gain of Bm-SF with the epoxide compounds EX313 (18 w%) and EX810 (12 w%) as a function of the irradiation time. NaOH concentration: 0.25 w%; wet pick-up: 100%; MW power: 200W

It is interesting to compare the reaction efficiency of epoxide compounds used under conventional and MW-assisted reaction conditions. Table I shows that in the conventional reaction system, the efficiency after 1 h of reaction was quite low, reaching about 12-13%. On the other hand, in the MW-assisted reaction system, where the amount of modifying agent available for the reaction is only that absorbed during padding, the efficiency doubled after only 5 min and was about 3.5 times higher at 25 min of reaction time. These results are of key interest with regard to developing more effective reaction systems for the chemical modification of silk fibres.

**Table 1.** Reaction efficiency of the MW-assisted modification and grafting systems (fibre: Bm-SF)

Epoxide compounds and grafting monomers	Reaction system	Reaction time (min)	Weight gain (%)	Efficiency (%)
EX810	MW	5	3.0	26
		25	5.0	41
	Conventional <sup>(1)</sup>	60	12.3	12
EX313	MW	5	3.0	27
		25	8.0	49
	Conventional <sup>(1)</sup>	60	13.1	14
HEMA	MW	20	32.0	95
	Conventional <sup>(2)</sup>	60	48.0	80
MAA	MW	10	3.5	48
	Conventional <sup>(2)</sup>	60	33.0	54

<sup>(1)</sup>Reaction conditions: padding with NaSCN 8.1g/l; 5 w% epoxide in tetrachloroethylene; material-to-liquor ratio 1:20; temperature: 75°C. <sup>(2)</sup>Reaction conditions: 60% owf monomer; pH 3; 1.8 w% APS; material-to-liquor ratio 1:15; temperature: 80°C.

The MW-assisted reaction system was used for the chemical modification of other protein fibres, such as tussah silk (Ap-SF) and wool (Wo). In preliminary experiments with EX313 as the modifying agent, Ap-SF and Wo fibres showed weight gain values of 3.0% and 7.3% respectively after 8 min of reaction time, under a MW irradiation power of 200 W. The weight gain of the different protein fibres with EX313 took place in the following order: Wo  $\cong$  Bm-SF > Ap-SF. It is interesting to note that Ap-SF exhibited a lower reactivity towards the epoxide compound than Bm-SF, in good agreement with previously reported results [3,19]. In fact, when the two kinds of fibres were treated with ethylene glycol diglycidyl ether by the pad-batch method, which implies a preliminary padding step followed by batching for several hours, during which time the reaction develops, the weight gain of Bm-SF was twice as high as that attained by Ap-SF.

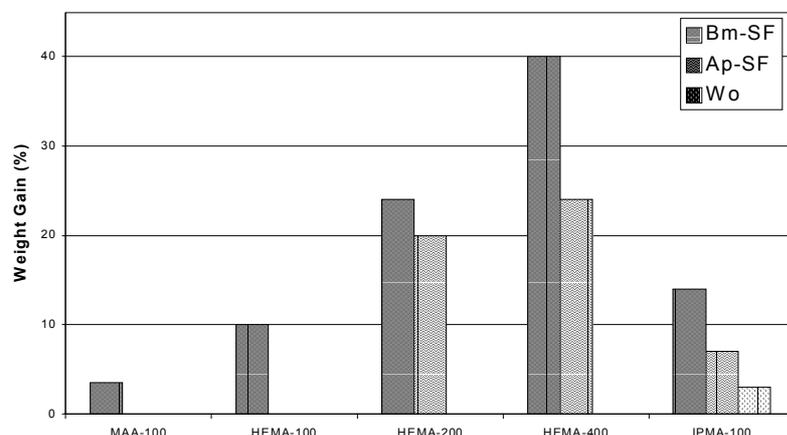
### Graft-copolymerisation with vinyl monomers

Bm-SF, Ap-SF, and Wo fibres were graft-copolymerised with different vinyl monomers, i.e. HEMA, MAA, and IPMA. The results obtained are summarised in Figure 3. The Bm-SF/HEMA grafting system resulted in higher weight gain values, which reached a maximum of 40%. In particular, the higher the monomer concentration in the padding solution, the higher the yield of the reaction, in good agreement with the previously discussed results on epoxides. The amount of monomer available for the reaction is that absorbed by the fibres during the padding step. Hence, this parameter is expected to play a critical role in the MW reaction system. Moreover, the properties of the fibre substrate subjected to grafting have to be carefully considered as well. In fact, Ap-SF also attained noticeable weight gain values with HEMA. However, the increase in the monomer concentration from 200% to 400% owf in the padding solution did not result in a parallel increase of weight gain as in the case of Bm-SF, suggesting that under experimental conditions the adopted Ap-SF fibres had already reached an equilibrium.

The dependence of the yield of the grafting reaction on the properties of the fibre substrate is further confirmed by the results of IPMA grafting. By using the same experimental conditions, the yield of grafting was in the following order: Bm-SF > Ap-SF > Wo. It appears that MW irradiation is specially and significantly effective for Bm-SF fibre compared with Ap-SF and Wo.

MAA and HEMA are particularly interesting as grafting agents because they are extensively used on an industrial scale for Bm-SF fibre weighting [4]. MAA is mainly used because it offers several advantages over other vinyl monomers. It is hygroscopic in nature, and it allows weighting of silk over a wide range of weight gain values, without the drawbacks often encountered with other grafting agents, i.e. solution and/or surface homopolymerisation. Moreover, MAA-grafted silk fibres maintain the typical silk-like handle and drape, exhibit improved comfort owing to the increased hygroscopicity,

and their easy-care properties (oil repellency, rub resistance, dimensional stability, washing and rubbing fastness, etc.) are significantly improved. For these reasons we considered that it would be of interest to test the performance of MAA under the conditions of the MW grafting technique. As shown in Figure 3, by using the same monomer concentration in the padding solution, MAA resulted in lower grafting yield than HEMA. These preliminary results seem to suggest that the MW grafting system is less effective than the conventional one when MAA is used as the grafting agent. Further studies are needed, aiming at optimising the MW grafting technique with MAA in order to attain a level of efficiency adequate for industrial application.



**Figure 3.** Weight gain of various protein fibres grafted with different vinyl monomers. The number in the sample label indicate the concentration of the grafting agent (expressed as w%) in the padding solution. Wet pick-up: 100%; MW power: 200W; reaction time: 15 min

In conventional grafting, the weight gain attained for Bm-SF fibres is usually around 30-80%, while the maximum weight gain value allowed by the MW irradiation technique was 40% with HEMA, even at a very high monomer concentration of 400% owf in the padding solution. Although the grafting efficiency was high (see: Table I), the relatively low weight gain attained could be a drawback for the industrial implementation of this innovative grafting technique. To overcome these drawbacks, further optimisation of the grafting conditions is needed. Additionally, suitable processing procedures could be implemented, such as to carry out repeating padding/MW curing steps in order to enhance the grafting yield up to the desired level.

### **Tensile properties**

Tensile properties of fibres are an important measure of the significance of grafting and chemical modification, since they are sensitive to the changes induced by these treatments. Table II lists the results of strength, elongation at break, and the energy of Bm-SF, Ap-SF, and Wo fibres treated with different epoxides and grafting agents by using the MW irradiation technique. Referring to the tensile properties of protein fibres grafted with different vinyl monomers, the values of strength remained almost unchanged or tended to increase, elongation at break decreased slightly, and the values of energy changed accordingly. It is interesting to note that the above changes were almost independent of the kinds of fibre and grafting agent used. These results suggest that the tensile properties of grafted protein fibres were not significantly affected by the treatment conditions of the MW irradiation technique.

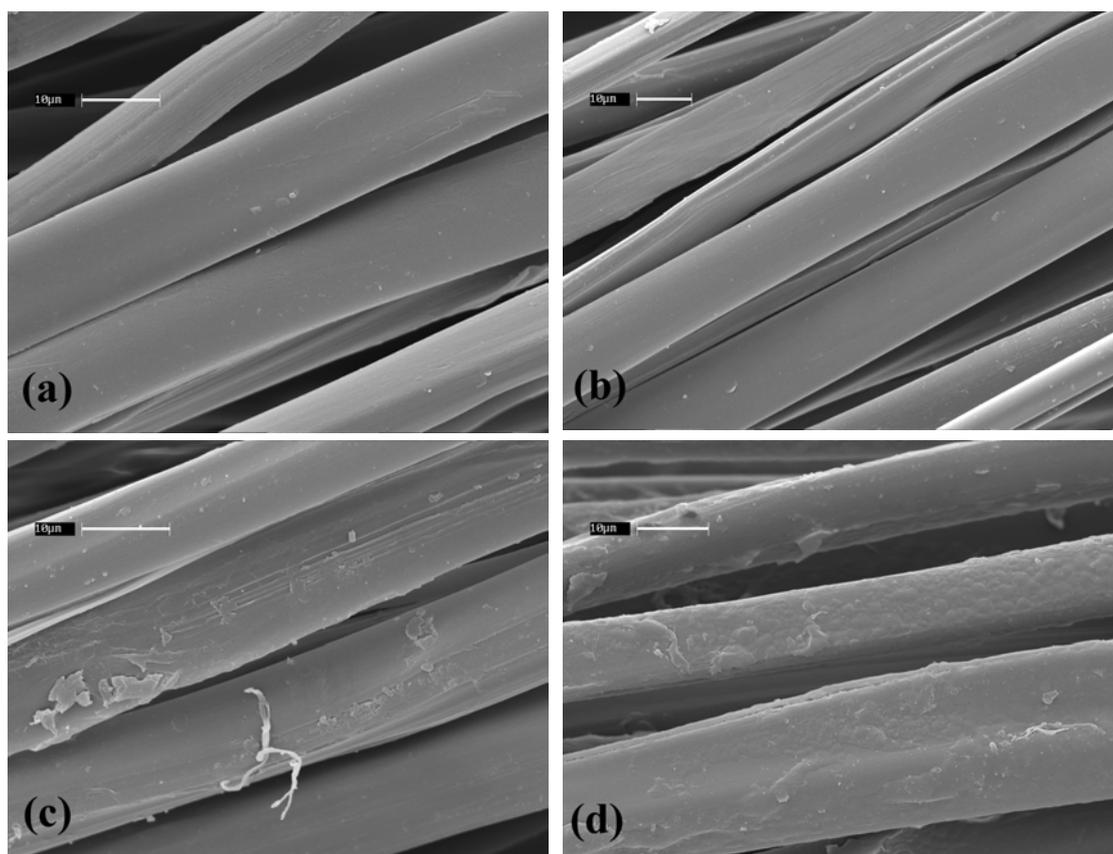
With reference to the tensile properties of the fibre samples subjected to epoxide reaction, the data listed in Table II is indicative of a drop of strength and elongation, irrespective of the type of fibre and weight gain. This effect could be partly attributed to the strong alkaline reaction of the padding solution used to impregnate the fibres. The sharp increase in the local fibre temperature during MW curing probably enhanced the hydrolytic attack of alkali towards the sensitive protein fibres, causing the observed drop of the tensile properties. These observations are of chief importance because they highlight the need for further improvements to the MW-assisted chemical modification technique. These may entail the substitution of NaOH with another salt of a better performance, as regards the balance between the strength of the alkaline reaction and of the catalytic activity.

**Table 2.** Tensile properties of protein fibres grafted or chemically modified by the MW irradiation technique

Sample	Weight gain (%)	Breaking load (gf)	Elongation (%)	Energy (gf x mm)
Bm-SF control	=	423 ± 2.9	18.0 ± 1.2	2138 ± 351
Bm-SF HEMA	10	479 ± 14.4	17.0 ± 0.7	3190 ± 365
Bm-SF HEMA	24	453 ± 18.3	17.6 ± 0.7	2849 ± 316
Bm-SF MAA	3.5	487 ± 13.2	18.1 ± 0.6	3352 ± 317
Bm-SF EX313	1.8	379 ± 47.0	14.9 ± 2.6	1952 ± 111
Ap-SF control	=	182 ± 7.3	31.8 ± 0.8	1901 ± 163
Ap-SF HEMA	20	230 ± 7.2	26.8 ± 0.7	2081 ± 103
Ap-SF IPMA	7	225 ± 10.5	29.1 ± 0.8	2099 ± 139
Ap-SF EX313	3	177 ± 13.0	26.5 ± 1.5	1753 ± 286
Wo control	=	272 ± 3.3	28.8 ± 2.8	4110 ± 770
Wo IPMA	3	273 ± 19.2	25.0 ± 3.3	3636 ± 386
Wo EX313	7.3	209 ± 20.0	16.0 ± 2.7	2676 ± 701

### **Surface morphology**

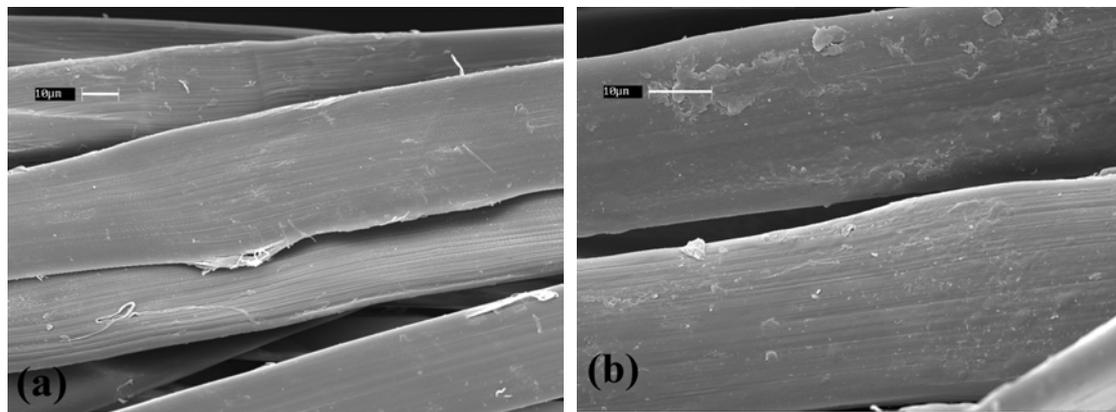
The surface morphology of Bm-SF fibres grafted or chemically modified by using the MW technique is shown in Figure 4. Below 10% weight gain, the fibres did not display any significant difference compared to the control sample (Figure 4(a) and 4(b)).



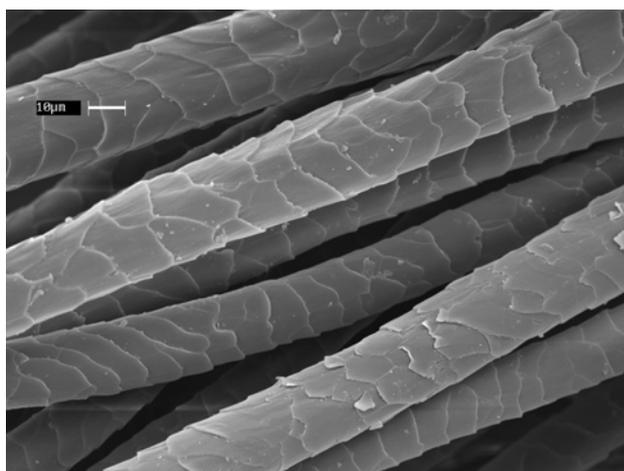
**Figure 4.** SEM pictures of Bm-SF fibers grafted or modified by the MW technique: (a) EX313, 1.8% w.g.; (b) MAA, 3% w.g.; (c) IPMA, 14% w.g.; (d) HEMA, 24% w.g

The surface was smooth and clean, irrespective of the kind of vinyl monomer or epoxide compound used. Increasing the weight gain above 10%, localised deposits of foreign matters appeared on the

fibre surface (Figure 4(c)). HEMA grafted Bm-SF fibres with weight gain higher than 20% displayed the presence of homopolymer deposition randomly distributed onto the fibre surface (Figure 4(d)). This is a well-known phenomenon which has also been observed in conventional grafting, especially when the weight gain exceeded 50% [2]. Similar features were detected on Ap-SF fibres grafted with HEMA, as shown in Figure 5(b). Wool grafted with IPMA showed no significant change in the characteristic morphological features of the fibre surface (Figure 6).



**Figure 5.** SEM pictures of Ap-SF grafted by the MW technique: (a) IPMA, 7% w.g.; (b) HEMA, 20% w.g



**Figure 6.** SEM picture of wool fibres grafted with IPMA, 3% w.g

## Conclusions

By using the MW irradiation technique, silk and wool fibres were effectively grafted or chemically modified with a range of vinyl monomers and epoxide compounds. The tensile properties and surface morphology of protein fibres graft-copolymerised with different vinyl monomers demonstrated that there was no significant deterioration of the intrinsic fibre properties, even at high weight gains. Fibres modified with epoxides showed a drop in the tensile performance, mostly attributable to the alkaline pre-treatment with the catalyst. In general, the properties of the fibres treated under the MW-assisted procedure are similar or even better than those of the fibres grafted or modified by using the conventional technique.<sup>1,2</sup> This is probably due to the significantly shorter reaction time, usually less than twenty minutes, which is one of the most important modification features of the MW irradiation technique, because it reduces the extent of the physico-chemical stresses to which the fibres are exposed during the conventional batch treatments.

Considering the shortcomings, the weight gain is usually lower than that obtained by conventional techniques. Further studies are necessary to optimise the procedures for grafting or chemical

modification by MW irradiation. However, these drawbacks could be overcome by improving the modification technique and by further optimising the reaction conditions and protocol.

The MW irradiation technique is an effective method, highly advantageous in terms of energy conservation, time consumption and cost effectiveness.<sup>16</sup> It is a promising technique for the replacement of the conventional grafting and chemical modification techniques currently applied onto protein fibres, because MW-assisted irradiation methods ensure increased throughput and productivity, as well as better quality of the textile goods.

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