Grafting of 2-Hydroxyethyl Methacrylate onto Silk by ATRP

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1. INTRODUCTION

As a textile fiber, silk exhibits many outstanding properties (handle, luster, dyeability, etc.) that distinguish it from other natural and synthetic fibers. Silk may be regarded not only as a textile fiber but also as biomedical materials for its' good biodegradability. However, for some applications, the properties of silk still need to be improved to meet the corresponding demands. For example, dimensional stability, wrinkle recovery and antimicrobial activity are other examples of properties that can be improved by chemical modification.

Some articles [1-3] reported silk grafting using 2-hydroxyethyl methacrylate (HEMA) as monomer by traditional grafting method. In this work, silk was grafted with hydrophilic HEMA through ATRP in water aqueous.The optimal grafting condition was studied and some characterization was done.

2. EXPERIMENTAL

The procedures of synthesis of the macroinitiator and surface-initiated ATRP, and characterization apparatus were provided in our previous articles of other monomer grafting [4,5].

The weight gain was calculated as:

$$\text{Weight gain } (\%)=(w_2-w_1)/w_1\times 100 \qquad (1)$$

where w_1 and w_2 denote the weight of S-Br and S-g-HEMA, respectively.

3. RESULTS AND DISCUSSION

The optimal grafting technic

Through single factor experiments, the effects of monomer concentration, the proportion of CuBr and PMDETA, grafting temperature and time on the silk grafting were discussed, and the optimal grafting technic was obtained: 0.225mol/L of HEMA monomer, 0.24 mmol of CuBr, n (PMDETA):n (CuBr) = 2:1, grafted under pH 8, at 80℃ for 6h.

FT-IR spectra

FT-IR analysis (Fig.1) was used to demonstrate the presence of polymer grafted onto the silk surface. There was no weight gain for the S-Br macroinitiator (0%sample). The spectra of the silk all showed the characteristic absorption peak of amide linkage at about 1650 and 1530 cm^{-1}. However, in the case of S-g-HEMA samples there were additional peaks of carbonyl of ester groups at about 1730 cm^{-1}, and the strength of peaks at about 1150 cm^{-1} arrtibuted to C-O stretching vibration of ester increased with increasing of weight gain. Thereby HEMA was confirmed to be grafted onto silk fabric.

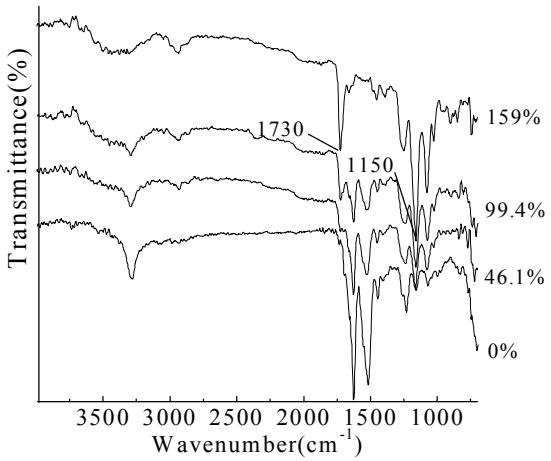

Fig.1. FT-IR of silk with different weight gain values.

Surface characteristics

Fig.2 shows the surface of the S-G-HEMA with different weight gain values. At low weight gain (<50%), the silk surface was similar to that of the untreated sample, while at higher gain (>100%) a thin polymeric film partly covered the fibers. As the weight gain further increased, the film became thicker attribute to the homopolymerization. And the homo-polymer was not too much. Because in ATRP grafting system, there was no initiator in the grafting solution, theoretically the monomer could only react with the macroinitiator.

Thermal properties

Figure 3 shows the DSC curves of silk with different weight gain values The control sample displayed an intense endothermic peak at 325℃, attributed to the thermal decomposition of silk with oriented β-sheet structure. New endothermic peaks appeared at about 230–250℃ and 415℃ in the curves

of S-g-HEMA, which were attributed to specific thermal transitions of poly(HEMA) chains (melting). The decomposition peak of silk in the grafted samples showed a tendency to move upwards with the increase of weight gain. Hence the effect of grafting HEMA onto silk was to make silk more thermally stable though the change was small.

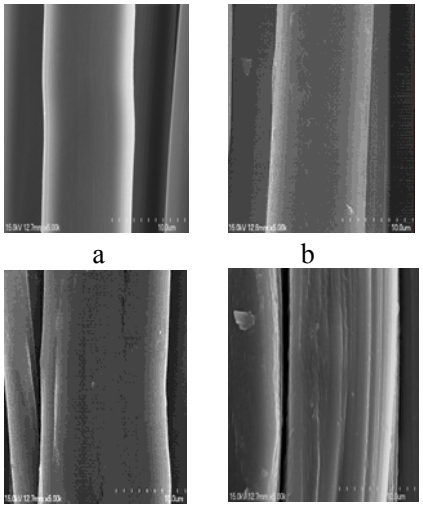

Fig.2. SEM photos of silk with different weight gain (a) 0%; (b) 46.1%; (c) 99.4%; (d) 159%.

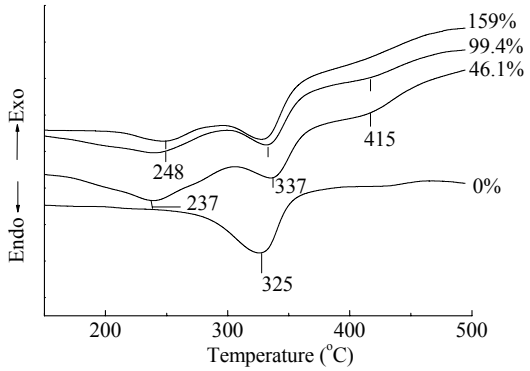

Fig.3. DSC curves of silk with different weight gain.

Crystalline Structure

In order to define the crystalline structure of the S-g-HEMA before and after grafting, X-ray diffraction was analyzed as shown in Fig. 4. The silk with different weight gain all exhibited a major X-ray diffraction peak at 20.5 degrees, corresponding to the crystalline spacing of 4.39 A, which is characteristic of silk with highly ordered β-structure. The position and intensity of the major X-ray diffraction peak did not change regardless of the introduction of HEMA. The results indicated that the crystalline structure with oriented β-crystals was not directly modified by the graft-copolymerization reaction by ATRP method. It was also reasonable to assume that the HEMA monomer was grafted into the amorphous region and not in the crystalline region.

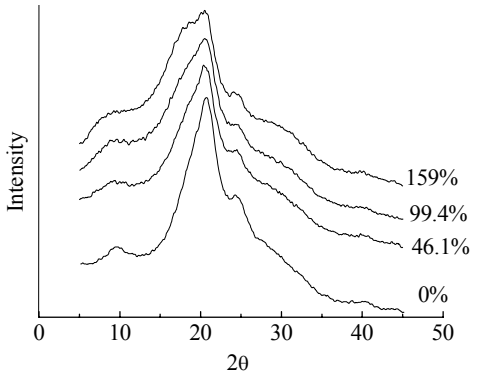

Fig.4. X-ray diffraction intensity cures of silk.

4. CONCLUSION

In conclusion, we have successfully developed a method for producing silk fibroin grafted HEMA using ATRP. The optimal grafting technology was obtained in this work. FT-IR characterization of the grafted silk demonstrated that HEMA had been grafted on the silk surface. X-ray diffraction curves showed that the crystalline structure of silk remained unchanged regardless of the HEMA grafting. And the described method affords a wide scale of grafting copolymers with HEMA on silk, which has potential application and properties.

5. ACKNOWLEDGEMENT

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