

MODIFICATION OF SILK FIBER *via* EMULSION GRAFT COPOLYMERIZATION WITH FLUOROACRYLATE*

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Abstract 2,2,3,3,4,4,5,5-Octafluoropentyl acrylate was grafted onto silk fiber in a two-step heterogeneous system through the vinyl bonds of acryloyloxyethyl isocyanate modified on the silk. The grafted copolymer was analyzed by FTIR and WAXD, and the results revealed that the fluoroacrylate was successfully grafted onto silk fiber and the crystalline structure of silk fibroin with β -sheet structure was not changed after graft copolymerization. The FT-IR corrected method was used to simulate the grafting yield onto silk compared with the weight increasing method. The results obtained from these two methods were roughly consistent. The influence of the initiator concentration, monomer concentration, react time and temperature on the graft yield was also investigated. The experimental data of thermogravimetry (TG) and differential thermal analysis (DTA) showed that the thermal stability of the modified silk fibers was improved due to the introduction of fluoroacrylate. In comparison with the untreated silk fibers, the water repellence of the modified silk fibers was also improved.

Keywords: Graft copolymerization; Silk; Fluoroacrylate; Modification.

INTRODUCTION

Silk is a kind of traditional textile clothing materials with gorgeous appearance, comfortable wearing and function for health. However, silk have some disadvantages such as yellowing-tendency, shrinkage, poor wrinkle resistance and so on. To overcome the above-mentioned shortage of silk, many chemical modification works on silk have been developed over the worldwide^[1–5]. Among them, most investigations focused on graft modification initiated by free radicals^[6–14]. The monomers used for graft copolymerization include vinyl monomers (vinyl acetate, acrylonitrile, phenylethylene), methacrylate monomers (methyl methacrylate, 2-hydroxyethyl methacrylate, ethyl methacrylate), acrylamide monomers (acrylamide, methacrylamide, hydroxy methacrylamide) etc. In addition, other techniques also have been developed, such as γ -ray radiation grafting, plasma grafting and ultraviolet ray initiated grafting^[15]. There is a general agreement that the graft copolymerization with methacrylamide has advantages over other techniques. The graft copolymerization can improve the fluffiness and softness meanwhile not damages the whiteness and handle of silk.

As to our knowledge, there was no literature on the graft copolymerization of silk with fluoroacrylate. Due to the introduction of fluorine with low surface energy, silk fiber grafted with fluoroacrylate was expected to gain the higher water and oil repellence, chemical stability and thermal resistance. In the present work, fluoroacrylate was used for graft modification of silk fibers. The silk fibers were initially activated by treatment with C=C double bond compound. And then the pre-treated silk fibers were grafted using free radicals copolymerization to give the fluorine containing silk with high graft yield. The chemical structure of graft copolymer was analyzed and some physical properties were also investigated.

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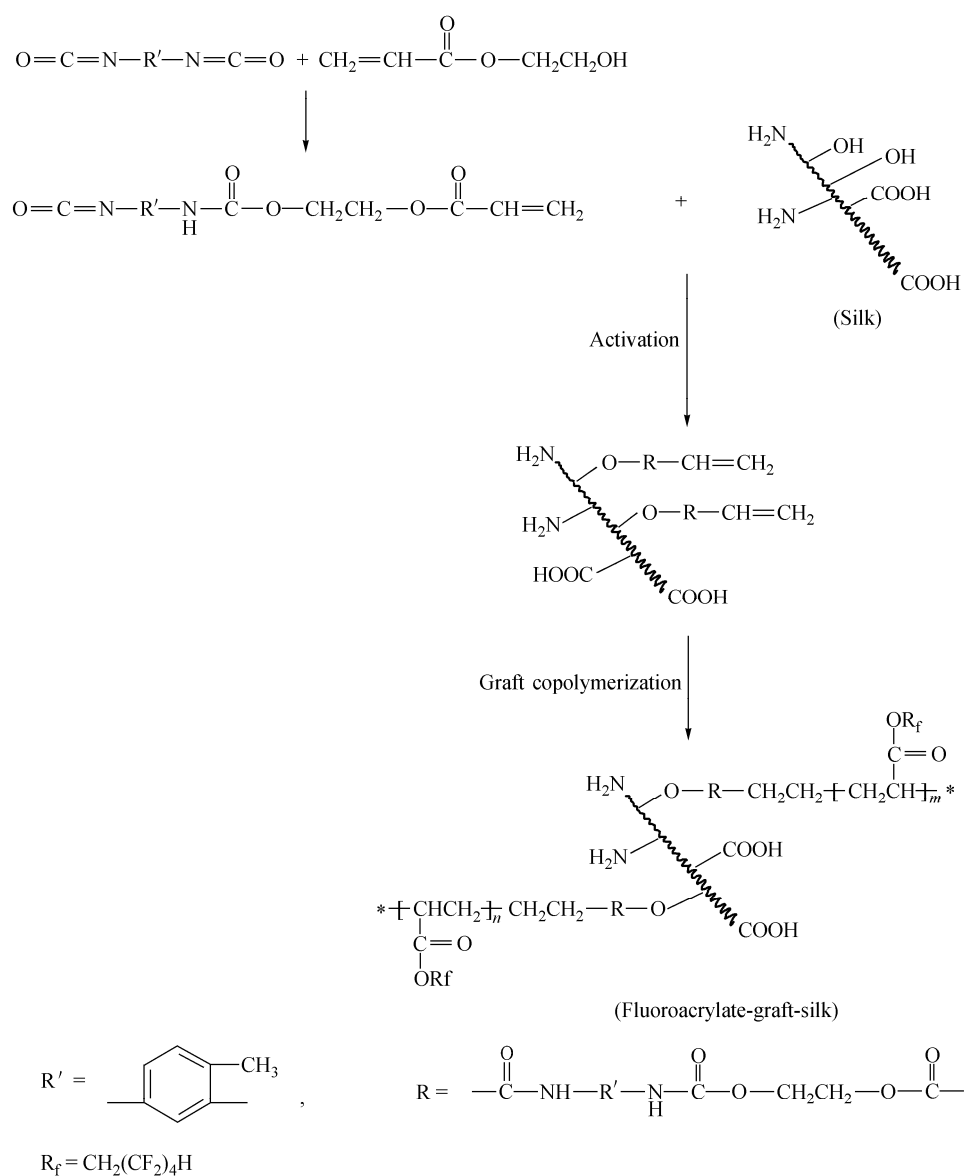
EXPERIMENTAL

Materials

Silk fibers: 21/22D silk fibers (degumming efficiency is 25%), Zhejiang Haoyunlai Printing and Dyeing Ltd. Co. 2,2,3,3,4,4,5,5-Octafluoropentyl acrylate was prepared in our laboratory. Fluorine containing emulsifier of ammonium fluoroalkyl phosphate (FSP) was purchased from Du Pont. Potassium persulfate and acetone were commercial reagents from Shanghai Reagent Factory, China. All the compounds were analytical grade reagents.

Activation Process of Silk

Silk was activated prior to the graft copolymerization. Some reactive groups on silk such as $-\text{OH}$ 、 $-\text{NH}_2$ and $-\text{COOH}$ can act as active reactive sites (Scheme 1)^[16]. By choosing diisocyanate as the bridge group, double bond was introduced into macromolecule side-chain of silk fiber. Isocyanate is so active that can react readily with hydroxy or amino group at mild reaction conditions. Therefore, in the present work, diisocyanate



Scheme 1 Modification of silk with fluoroacrylate

was chosen for bonding 2-hydroxyethyl methacrylate (HEMA) to silk. By initiating the activation double bond of methacrylate, graft copolymerization modification on silk with high graft yield was achieved. The synthesis route was shown in Scheme 1.

A three-necked round-bottom flask fitted with a condenser, a stirrer and thermometer was charged with 100 mL of anhydrous acetone, 100 mmol of toluene 2,4-diisocyanate, 3 mmol catalyst of di-*n*-butyltin dilaurate and 2 mmol hydroquinone. When the mixture was heated to 45–50°C, 100 mmol of HEMA was then slowly added to the reactor through a dropping funnel under a nitrogen atmosphere. After the addition of HEMA, the solution was kept at that temperature for another 1 h. Then 1 g dried silk fiber was introduced into the reactants and was treated at 45–50°C. After the desired reaction time, the silk fiber was taken out and washed successively with acetone, methanol and large amounts of distilled water. The silk fiber was weighed after drying.

Emulsion Preparation of Fluoroacrylate Monomer

The emulsion polymerization method was adopted in this paper, and water was used as medium of grafting polymerization since octafluoropentyl acrylate was not soluble in water. Therefore, it is required that the fluoroacrylate monomer was pre-emulsified by choosing suitable emulsifier to prepare an emulsion with excellent stability. This can assure the grafting procedure to be steady and controllable.

Emulsion ingredients were as following: 200 g of water, 16 g octafluoropentyl acrylate monomer, 0.8 g of Sorbitan monolaurate (SPAN-20), 0.8 g polyoxyethylenesorbitan monooleate (TWEEN-80) and 0.8 g ammonium fluoroalkyl phosphate (FSP) were emulsified at the stirring rate of 7000 r/min on an emulsification equipment, fluoroacrylate was emulsified for 20 min to give the pre-emulsion. The stability of the pre-emulsion was determined to be excellent, because no delamination was found when it was placed at room temperature for two weeks or at 85°C for 24 h. This property of the emulsion was considered to be fully competent for the following graft polymerization reaction condition.

Graft Copolymerization

50 mL of fluoroacrylate emulsion of predetermined concentration was placed into 250 mL tapered flask fitted in a temperature-controlled water bath. A certain amount of initiator potassium persulfate was added at certain temperature. 1 g activated silk fibers were transferred to the flask at material to liquor ratio 1:50. Then the reaction was kept for certain time at that temperature. Variation the concentration of fluoroacrylate emulsion from 8%, 16%, 20% to 32%, the graft modification silk was obtained and named as A, B, C and D.

Extraction Procedure

During the grafting process, graft copolymerization between activated silk and fluoroacrylate and formation of homo polymers from fluoroacrylate took place at the same time. The homo polymers adhering to the silk fibers will affect the handle of silk and be harmful for the finishing treatments. According to Soxhlet extraction method, mixed solvent of methanol/acetone (*V/V* = 2:1) was found to be the most effective solvent for removing homo polymers from the treated silk fibers completely. The extraction was fulfilled for 7–8 h at 85°C. Finally, modified silk fibers were dried and weighed.

Measurement of Water Absorbency

The water absorbency of untreated and grafted silk fibers was determined by immersing the fibers in distilled water for 3 h. The fibers were taken out and excess water was removed by putting the fibers between two filter papers under gentle pressure. The fibers were weighed, recorded as WET, and then dried in an oven at 65°C for 2 h and weighted (recorded as DRY). Water absorbency was expressed as water absorbance value (WAV) and was calculated as following:

$$\text{WAV (g/g)} = (\text{WET} - \text{DRY})/\text{DRY}$$

Characterization

FTIR

The ungrafted silk fibers (S) and grafted silk fibers with different graft yield were measured by Fourier transform infra-red (FT-IR) spectroscopy. IR transmittance was recorded on a Nicolet 5700 FT-IR spectrometer (Thermo Electron Corporation) equipped with a DTGS KBr detector and KBr beamsplitter. The test was carried out under dried air in the spectral region of 4000–400 cm^{-1} , with the number of sample scans 32 and resolution 4.0.

WAXD

The ungrafted silk fibers and grafted silk fibers with different graft yield were measured by wide-angle X-ray diffraction. The wide-angle X-ray diffraction measurements were performed on a Rigaku D/Max-IIIC diffractometer, operated at 40 kV, 30 mA with $\text{CuK}\alpha$ target. Scan from 5° to 45° and the scanning rate was $2^\circ/\text{min}$. The X-ray diffraction curves (2θ) of silk fibers were then obtained.

Thermal analysis

The ungrafted silk fibers and grafted silk fibers with different graft yield were measured by thermal analysis. The thermogravimetry (TG) and differential thermal analysis (DTA) measurements were performed on a Perkin Elmer Diamond TG/DTA instrument. The sample was under N_2 atmosphere at a flow rate of 20 mL/min. The temperature range was from 50°C to 650°C and heating rate was 10 K/min.

SEM

The ungrafted silk fibers and grafted silk fibers with different graft yield were performed on a Hitachi S-570 Scanning Electron Microscope (SEM). The magnification was 3000.

RESULTS AND DISCUSSION

Calculation of the Graft Yield Through Weight Increase

In the present work, the weight increase of silk is contributed to the side-chain gain of fluoropolyacrylate during the graft copolymerization. By weighting the silk sample before and after reaction, the graft yield was calculated as following^[17–19]:

$$\text{Graft yield} = (w - w_0)/w_0 \times 100\%$$

where w is the weight of grafted silk fibers and w_0 is the weight before treatment.

As a result, the graft yield of sample A, B, C and D was measured to be 28.0%, 59.7%, 88.8% and 116.2% respectively.

FTIR

The FTIR spectrograms of untreated silk and different graft copolymerized silks were shown in Fig. 1. In Fig. 1(a), all the specimens exhibited characteristic absorption bands of fibroin at 1650 cm^{-1} (amide I), 1540 cm^{-1} (amide II), 1230 cm^{-1} (amide III) and 699 cm^{-1} (amide IV). It was indicated that modified silk fibers still had β -sheet structure for fibroin. Two new bands at 1758 cm^{-1} and 1170 cm^{-1} which attributed to $\text{C}=\text{O}$ stretching vibration and $\text{C}-\text{F}$ bond stretching vibration, respectively, appeared for modified silk fibers. Additionally, for graft copolymers some other new peaks were found in fingerprint areas, which attributed to $\text{C}-\text{H}$ out-plane bending vibration of $-\text{CH}_2-$, $-\text{CH}_2-\text{CH}_2-$ groups. It revealed that the fluoroacrylate was successfully graft copolymerized onto silk. In Fig. 1(b), the narrower range of carbonyl band region was presented in order to compare the spectra of the grafted and non-grafted silk. It is clear that the spectrum of the non-grafted sample S present no absorbance at $1757\text{--}1759\text{ cm}^{-1}$, which was identified to be the absorbance of carbonyl groups of poly(2,2,3,3,4,4,5,5-octafluoropentyl acrylate).

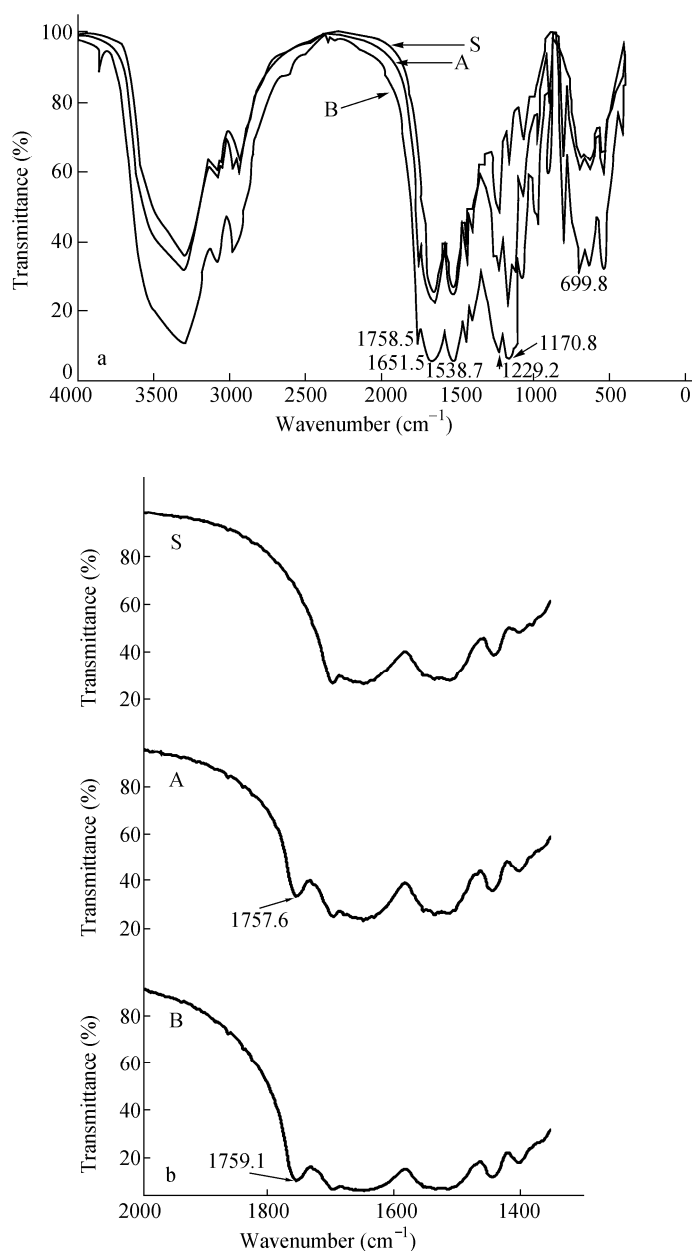


Fig. 1 FT-IR spectra of grafted and untreated silk fibers
(S) Untreated fibers; (A) Graft yield of 28.0%; (B) Graft yield of 59.7%

As the infrared spectra of treated silk exhibit characteristic bands of the C=O stretching vibration of aliphatic ester bond at 1758 cm^{-1} . This band was different from the C=O stretch vibration of the amide groups in the macromolecular main chain, and could be used to simulated the graft yield through the absorbance ratio of these two bands^[20].

Figure 2 showed the corrected areas of the two C=O absorbance peak in sample A, B, C and D. From the absorbance ratio of C=O in aliphatic ester and amide, the mass increase percent of these four sample was identified to be 48.7%, 78.7%, 103.0% and 138.0% respectively. The simulated result of graft yield from absorbance peak area corrected method by FT-IR was roughly consistent with the result from weight

increase calculation (see Fig. 3), and the datum from the former tech. were higher than the latter method, it is probably because of the migration of fluorinated group to the surface of polymer easily^[21, 22].

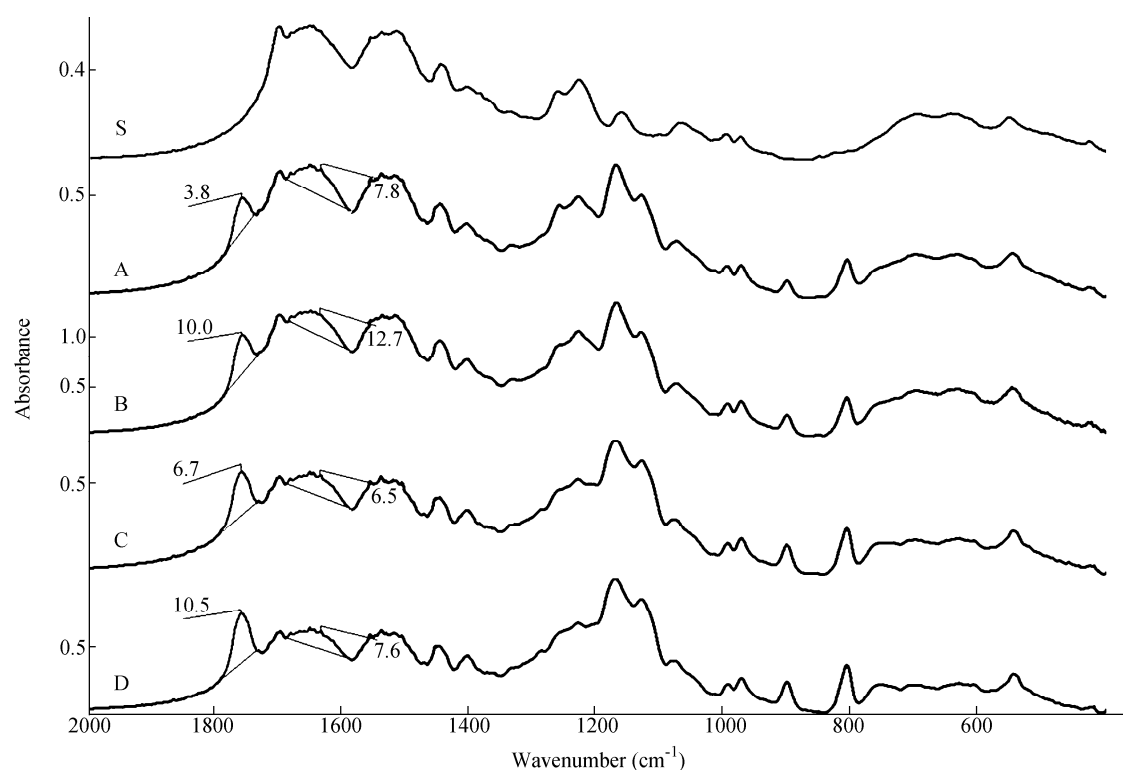


Fig. 2 C=O absorbance peak area simulation of grafted silk FT-IR spectrum (S) Untreated fibers; (A) Graft yield of 28.0%; (B) Graft yield of 59.7%; (C) Graft yield of 88.8%; (D) Graft yield of 116.2%

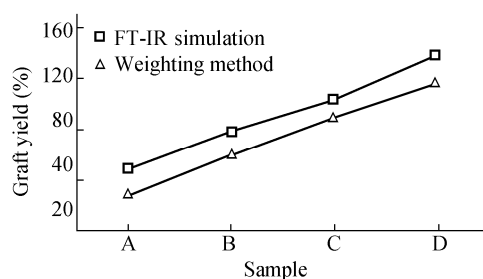


Fig. 3 Comparison of the weighting method of grafted yield with FT-IR simulation

WAXD

The structures of aggregation state of modified silk fibers with various graft yield and untreated fibers were studied by wide-angle X-ray diffraction. The WAXD patterns for all samples were shown in Fig. 4. As can be obviously seen, X-ray diffraction peaks of all samples were found at 20.05° (2θ), corresponding to the characteristic peak of oriented β -sheet structure of silk fibroin. It suggested that the crystalline structure of silk fibroin with β -sheet structure was not changed after graft copolymerization. Meanwhile, a new X-ray diffraction peak of grafted fibers was observed at $2\theta \approx 17.4^\circ$ and the intensity of diffraction peak increased with the increase of the grafted yield. It was probably because that another structure of oriented aggregation state appeared by macromolecules side-chain grafting onto silk fibers.

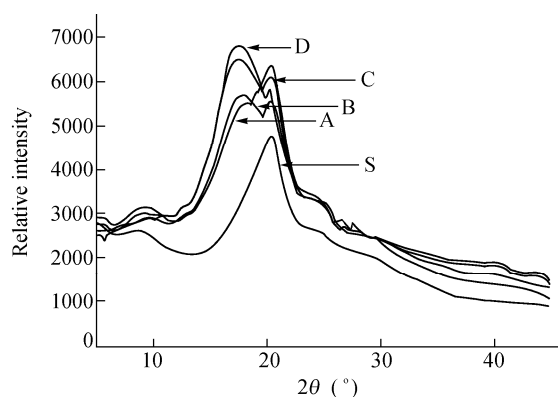


Fig. 4 X-ray diffraction patterns of grafted and untreated silk fibers
(S) Untreated fibers; (A) Graft yield of 28.0%; (B) Graft yield of 59.7%; (C) Graft yield of 88.8%; (D) Graft yield of 116.2%

SEM

The SEM micrographs of the surface of untreated and grafted fibers were shown in Fig. 5. As can be observed, the surface of modified silk fibers became rough compared with untreated fibers. Moreover, the greater the graft yield, the rougher the surface of grafted fibers.

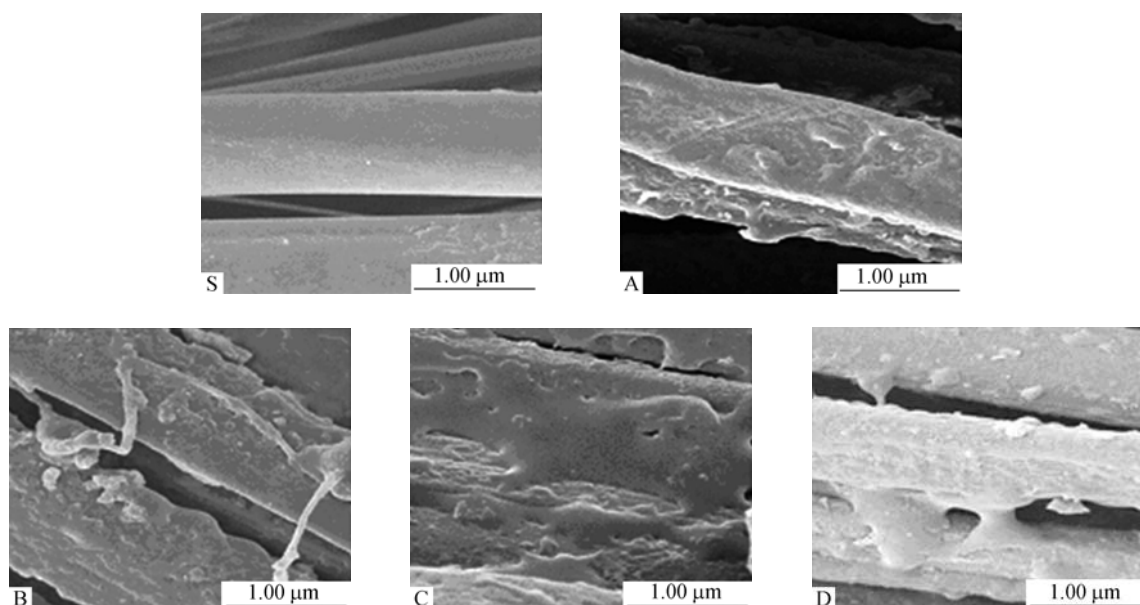


Fig. 5 SEM photos of untreated and grafted silk fibers with different graft yield
(S) Untreated fibers; (A) Graft yield of 28.0%; (B) Graft yield of 59.7%; (C) Graft yield of 88.8%; (D) Graft yield of 116.2%

Activation Processing

The silk fiber was activated treating by $\text{N}=\text{C}=\text{O}$ group containing methacrylate. The treating reagent was synthesized by addition reaction using tolylene-2,4-diisocyanate TDI and 2-hydroxyethyl methacrylate as materials. During the addition reaction of HEMA, FT-IR was applied to test its' $\text{HO}-$ absorbance at 3340 cm^{-1} , the absence of this absorbance peak was identified to be the end-point of the addition reaction. This resulted reactant was used as activation reagent followed by introducing silk fiber sample into it.

During the activation reaction under the reaction condition in Section "Activation Process of Silk", it can

be found that the weight gain of activated silk fiber increases with the increase of time exposure to mono $\text{N}=\text{C}=\text{O}$ reactants, and it reaches a constant value of 6% when the time was long than 6 h. So, the activation treatment condition was fixed at 45~50°C for 6 h and the weight gain of activated silk fiber was kept at 6%.

Effect of Initiator Concentration on the Graft Yield

Figure 6 showed the effect of initiator concentration on the graft yield. It was observed that the graft yield increased rapidly from 5.6% to 84% when initiator concentration varied from 0.485×10^{-3} mol/L to 0.971×10^{-3} mol/L. And then it gradually decreased with the further increase of the initiator. It was indicated that 0.485×10^{-3} mol/L of potassium persulfate was not enough to initiate the graft copolymerization completely, but excessive amount of initiator would result in the formation of homo polymers when the concentration of initiator was up to 1.942×10^{-3} mol/L. The by-products of homo polymers would overlay the surface of silk fibers and prevent further graft copolymerization reaction between fibers and monomer. Additionally, excessive amount of potassium persulfate would not be used in the graft modification because it would accelerate the oxidation of silk and led to a stiff handle of the fibers.

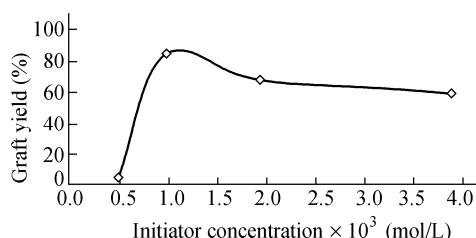


Fig. 6 Effect of initiator concentration on graft yield

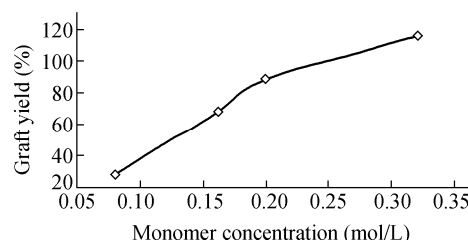


Fig. 7 Effect of monomer concentration on graft yield

Effect of the Monomer Concentration on the Graft Yield

The graft yield as a function of the monomer concentration was illustrated in Fig. 7. As can be seen, the graft yield increased obviously with the initial increase of the monomer concentration. And then the curves leveled off when the monomer concentration was higher than 0.201 mol/L. It can be concluded that the increase of the monomer concentration in emulsion might be beneficial for both graft copolymerization and homo polymerization. We speculated that homo polymer readily formed in the case of the excessive monomer, the surface of silk fibers was then overlayed by large amounts of homo polymers, which hindered the reaction between monomer and fibers.

Effect of Reaction Time on the Graft Yield

The effect of reaction time on the graft yield was presented in Fig. 8. It was found that the graft yield increased with the extension of the reaction time. The graft yield increased significantly to 85% when the reaction time was 40 min and was up to 96% in the case of 80 min.

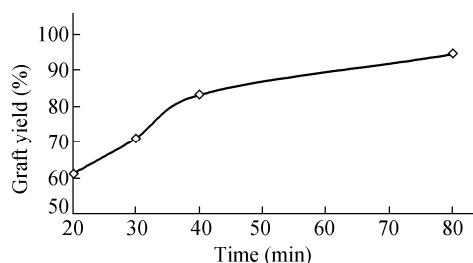


Fig. 8 Effect of reaction time on graft yield

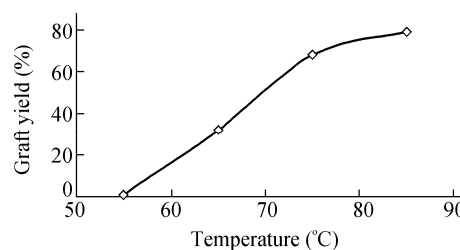


Fig. 9 Effect of reaction temperature on graft yield

Effect of Reaction Temperature on the Graft Yield

Figure 9 showed the effect of reaction temperature on the graft yield. The graft yield exhibited an increase tendency with the increase of reaction temperature. It was well known that the high temperature is beneficial for radical polymerization. Meanwhile, in our system the high temperature will lead to a great swollen extent of silk fibers, which is favorable for the graft co-polymerization. However, silk fibers are apt to be damaged under too high treating temperature, which will lead to ashing damage and affect the handle and following treatments.

Thermal Analysis

The thermal stability of untreated fiber and various modified silks were investigated by thermogravimetry (TG) and differential thermal analysis (DTA). The thermograms were shown in Fig. 10.

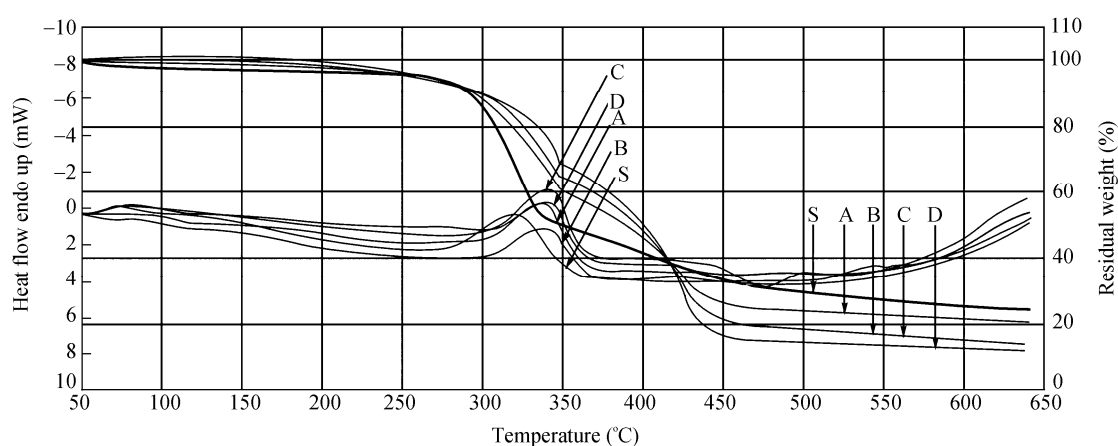


Fig. 10 TG and DTA curves of untreated and grafted silk fibers
(S) Untreated fibers; (A) Graft yield of 28.0%; (B) Graft yield of 59.7%; (C) Graft yield of 88.8%;
(D) Graft yield of 116.2%

As shown in DTA curves, only one obvious major endothermic peak, corresponding to the thermal decomposition of silk fibroin with β -sheet structure, was observed to be between 300°C and 330°C for untreated silk fibers. For grafted silk fibers the main decomposition endotherm occurred between 320°C and 360°C, and the peak temperature shifted toward higher temperature (339°C). It suggested that the graft copolymerization improved the thermal stability of silk. In addition, the decomposition peak temperature of grafted silk shifted toward the higher temperature with the increase of graft yield. As seen in TG curves, silk fibers showed a gradual tendency of two-step thermal weight loss between 300°C and 450°C with the increase of the graft yield. The tendency of the second step thermal weight loss became more obvious for silk fibers with higher graft yield. However, only one endothermic peak of grafted silk fibers was found to be between 300°C and 450°C in DTA curves and no endothermic peak of fluoroacrylate homo polymers was found.

Therefore, it could be concluded that the first step thermal weight loss of grafted silk fibers was mainly caused by untreated silk fibroin molecules, and the second step thermal weight loss was primarily caused by the grafted silk fibroin molecules^[10, 17]. Meanwhile, the temperature of maximal rate of thermal weight loss was gradually improved with the increase of graft yield during the period of two-step thermal weight loss.

Water Absorbency

The WAVs for the untreated silk fiber and the grafted silk fibers with various graft yields were listed in Table 1. It was found that all of grafted silk fibers displayed a lower WAVs in comparison with the untreated silk fiber. The WAVs also decreased with the graft yield increasing since the increment of the fluorine content resulted in a reduction of water absorbency. Therefore, the water repellence of the modified silk fibers was improved.

Table 1. WAVs of untreated and grafted silk fibers

Sample	Graft yield (wt%)	WAV (g/g)
Untreated silk fibers	—	2.61
Grafted fibers	44.56	1.94
	57.66	1.71
	70.7	1.04
	94.49	0.67

CONCLUSIONS

In this work, fluoroacrylate was successfully grafted onto silk fibers which were activated with acryloyloxyethyl isocyanate. The graft yield could be controlled by adjusting the initiator concentration, monomer concentration, react time and temperature. The thermal stability of grafted silk fibers was improved because of the introduction of fluoroacrylate macromolecule. The WAVs indicated that the hydrophobic nature of the silk fibers was improved due to the introduction of fluorine with low surface energy. This provides a new effective way to improve the water repellence of silk fibers.

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