

GRAFTING OF ETHYLENE GLYCOL DIMETHACRYLATE ONTO SILK IN AQUEOUS ALCOHOLIC SOLUTION

Guo-qiang Chen^{a*}, Tie-ling Xing^a, Cai-rong Huang^a and Xiang Zhou^b

^a Silk Research Institute, Suzhou University, Suzhou 215021, China

^b College of Chemistry & Chemical Engineering, Dong Hua University, Shanghai 200051, China

Abstract The grafting of ethylene glycol dimethacrylate (EGDMA) onto silk in aqueous alcohol systems using potassium persulfate (KPS) in the presence of air was investigated. Effects of grafting conditions, such as concentrations of monomer, initiator and formic acid, temperature and time, on the graft yield were determined. The optimum graft conditions were found to be: $T = 80^{\circ}\text{C}$, $t = 30$ min, $[\text{KPS}] = 1.85\%$ [on the weight of monomer (owm)]; $[\text{formic acid}] = 0.2\%$ (V/V); $[\text{EGDMA}] = 80\%$ [on the weight of fiber (owf)]. The activation energy of grafting at $50\text{--}80^{\circ}\text{C}$ was found to be 71.31 kJ/mol for EGDMA. Grafting equations were also evaluated. The graft yield value can be regulated by the concentration of monomer. The graft copolymerization of EGDMA onto silk is effective in improving the crease-proofing of silk fabrics.

Keywords Silk, Grafting ethylene glycol dimethacrylate

INTRODUCTION

Silk has a distinguished position for its outstanding properties, such as equilibrium recovery, heat retention, hand, luster, comfort, brilliant color shades obtained by dyeing and printing, and so on. However, to make it more useful in its field of application, further improvement of its physiochemical properties is necessary. In recent years many attempts have been made to improve silk fiber or fabric properties by graft copolymerization techniques^[1], although their application on an industrial scale is still confined to certain articles such as necktie yarn and fabric, borders and embroidery. With the many kinds of vinyl monomers, epoxides and other modifying agents available^[2, 3], these techniques are powerful methods. Among the vinyl monomers methyl methacrylate^[4], methacrylamide^[5], 2-hydroxyethyl methacrylate^[6], methacrylonitrile^[7] and styrene (St)^[8] have been extensively studied. According to the kind of vinyl monomer used and to the grafting conditions adopted, the physical and mechanical properties as well as the structural characteristics of silk fiber may undergo drastic changes.

St was used at first as a grafting agent for silk fibers. St-grafted silk fibers have appreciable bulkiness and fullness of hand as well as a significant improvement in crease recovery^[8]. Due to their increased hydrophobicity, St-grafted silk fibers show, however, affinity towards disperse dyes and are suitable for heat-transfer printing^[8]. However, the use of St monomer for silk grafting entails some negative consequences due to its strong hydrophobic properties, to the hard hand and to the problems of air pollution during industrial application. To overcome these drawbacks, selection of new monomers or reagents has been attempted.

Chemical modification of silk with epoxies was introduced by Tanaka and Shiozaki^[9, 10] at the beginning of the 1970s. This technique was developed for improving some inferior properties of silk fabrics, such as crease recovery in either dry or wet state^[11–13], light resistance and color fastness to washing. Tsukada *et al.*^[14, 15] studied the effect of epoxide modification by analyzing the mechanical properties related to the hand and structure of silk

* Corresponding author: Guo-qiang Chen (陈国强), E-mail: uugqchen@public1.sz.js.cn

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fabrics treated with ethylene glycol diglycidyl ether.

Among the chemical modification techniques, the graft-copolymerization of vinyl monomers and the reaction with epoxides have been studied since the beginning of the 1970s. However, most researchers focused on the study of new modifying agents. Currently, some researchers are interested in the use of bifunctional vinyl monomers for silk grafting. Kato^[16] developed a new grafting technique using polyethylene glycol dimethacrylate (PEDGMA) as grafting agent and analyzed the optimum grafting conditions. He found that the crease recovery of grafted silk fabrics in the wet state was significantly improved.

However, there are no studies in the literature concerning ethylene glycol dimethacrylate (EGDMA) grafting onto silk by using potassium persulfate (KPS) in aqueous alcoholic solution. This work reports the grafting of EGDMA onto silk by using KSP in aqueous alcoholic solution. Also, changes in the crease recovery of the products were studied.

EXPERIMENTAL

Materials and Reagents

Degummed silk fiber (21/22D) or silk fabric (plain weave, 80 g/m²) was used as the grafting substrate. EGDMA monomer, purchased from Suzhou Anli Chemicals Company Ltd., was used. Other reagents were of laboratory reagent grade.

Grafting Procedure

A weighed amount of silk fiber or silk fabric was immersed in aqueous alcoholic solution [(alcohol/water = 1/7 (V/V)) at definite pH (adjusted with formic acid), containing the required amounts of KPS and EGDMA. A silk material-to-liquor ratio of 1:30 was maintained. The temperature was raised to 50–90 °C and was then maintained constant for the required time in a constant temperature and vibrational water kettle. At the end of the reaction the silk was soaked for 30 min at 60 °C in water which contained 0.5 g/L OS [poly(oxyethylene octylphenyl ether)], then rinsed with water at least three times and dried at 105 °C for 2 h. Samples were placed in a desiccator over silica gel before measurements. Then the samples were weighed and measured.

Test Methods

The graft yield G and rate of graft polymerization R_g were calculated according to the following formulas:

$$G(\%) = (W_2 - W_1) \times 100 / W_1 \quad (1)$$

$$R_g (\text{MolS}^{-1} \text{L}^{-1}) = (W_2 - W_1) / \text{VTM} \quad (2)$$

where W_2 is the weight of grafted sample, W_1 the weight of original sample, V the volume of the reaction mixture, T the reaction time, and M the molecular mass of the EGDMA.

Crease angles were measured by a method similar to that specified by American Association of Textile Chemists and Colourists (AATCC), Test Method 66-1990.

RESULTS AND DISCUSSION

In the present work, silk was grafted with EGDMA using KPS initiator. KPS is soluble in both water and alcohol, whereas EGDMA is insoluble in water and needs a small amount of alcohol to facilitate its dissolution. To obtain maximum grafting, the parameters of graft copolymerization, such as the time and temperature of the reaction, concentration of the initiator, formic acid and EGDMA were optimized.

In grafting systems like the one in this study, it is inevitable that homopolymer of the monomer will be formed in the graft polymerization medium. The common method for the removal of homopolymer from the fiber is by extracting the homopolymer with an appropriate solvent. For the grafting of vinyl monomers, the most common solvents used for the extraction of homopolymer are acetone^[17, 18] and benzene^[19, 20]. In the present work it was found that the weight of grafted sample was not decreased after it was Soxhlet-extracted with acetone and benzene, respectively, for 8 h. It is believed that the polymerization reaction is mainly a grafting process. So, the

increase in weight of the original sample after the grafting procedure was taken as the graft yield.

Effect of Reaction Temperature, Time and Overall Energy of Activation, E_a

Figure 1 shows the effect of reaction temperature and time on the grafting by keeping the concentration of EGDMA at 80% with respect to the weight of the fiber and the concentration of KPS at 1.85% with respect to the weight of the monomer. It can be clearly seen that the graft yield increases with increasing temperature up to 80°C and beyond this limit it decreases. The initial increasing trend can be ascribed to the greater activation. As pointed out by Arai and Negishi^[21, 22] in similar work (methyl methacrylate grafted silk), the mobility of the grafted polymer chain end was controlled by the segmental mobility of the backbone polymer. Owing to the high stability of silk fiber backbone chains, the mobility of the graft copolymer radicals would be greatly restricted. As a consequence, increasing the temperature will thus greatly increase the mobility of the graft copolymer radicals. Furthermore, at higher temperature, the diffusion of monomer into silk fiber is also enhanced. As a result of this, an initial increasing trend can be seen.

However, when the temperature is higher than 80°C, the combination rates of radicals will increase and the graft yield will decrease. The increase in temperature will enhance the ease of free radical formation, increase the mobility of monomer and initiator, raise the rate of diffusion of monomer and initiator from the solution phase to fiber phase and change the balance of competition between graft copolymerization and homopolymerization, etc.

The initial rates of grafting (R_g) were calculated at the experimental temperatures (50–80°C). Figure 2 is an Arrhenius plot of the initial rate of graft versus the reciprocal of temperature over the temperature range of 50 to 80°C. From the slope of the plot, the overall activation energy (E_a) for grafting is found to be 71.31 kJ/mol.

On the other hand, it can be seen from Fig. 1 that with the increase of reaction time, graft yields increase until 30 min and then become relatively constant with further increase of reaction time. A similar trend has been reported in the system of acrylonitrile grafting to silk fiber^[23]. This phenomenon may be explained by the decrease in monomer concentration as the reaction time increases.

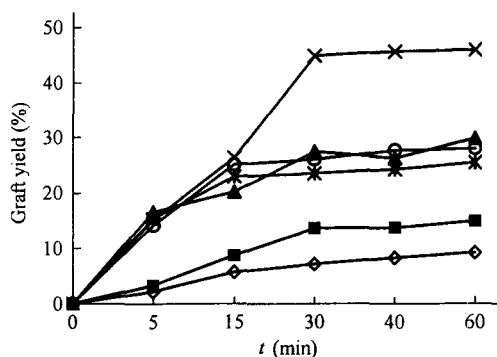


Fig. 1 Effect of graft temperature on graft yield: KPS, 1.85% (with respect to the weight of monomer) EGDMA, 80% (with respect to the weight of fiber); formic acid, 0.2% (V/V)

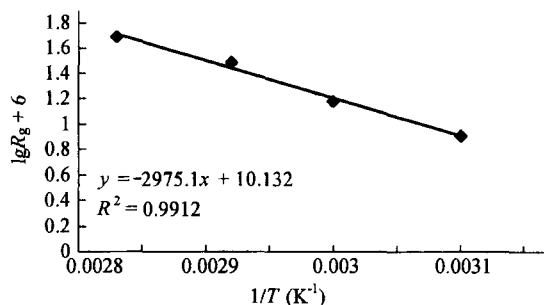


Fig. 2 Arrhenius plot of the initial rate of graft versus the reciprocal of temperature over the temperature range of 50 to 80°C for grafting EGDMA onto silk

Effect of Monomer and Initiator Concentrations

The effect of the variation of monomer concentration on the graft yield was evaluated by changing the concentration of EGDMA in the range of 10%–120% (with respect to the weight of fiber) while keeping the concentrations of all other reagents constant (Fig. 3). It is clear that the graft yield is directly related to the EGDMA concentration up to 80%. As the monomer concentration increases above this value, there is a substantial reduction in the graft yield. Hence, 80% is the optimal concentration for achieving maximum graft yield.

The decrease of graft yield at higher EGDMA concentration could be attributed to the probable absorption

of monomer onto silk fiber, which impedes the diffusion of initiator inside the fibers and thereby lowers the graft yield. Homopolymerization prevails over polymerization with silk fibers at higher EGDMA concentrations, so the graft yield decreases.

The effect of different concentrations of KPS on the graft yield is presented in Fig. 4. It is evident that graft yield rapidly increases to an initiator concentration of 1.85% (with respect to the weight of monomer), and then slightly decreases at higher KPS concentrations. As the concentration of KPS increases, many silk macroradicals will be formed through the interaction of free radicals with the groups present in the silk main chain that initiate grafting so as to increase the graft yield. However, when the concentration of KPS is higher than 1.85%, further increase in initiator concentration will result in the following effects: 1) abundant free radicals, as well as homopolymer macroradicals, are formed in the solution that might terminate the growing chain; 2) the free radicals formed on the main chain of silk might be oxidized, thus terminating the reactive sites; and 3) the graft copolymerization and homopolymerization is of a matter of "competition," which depends on the direct attack of free radicals on silk or on EGDMA monomer. Hence a higher concentration of initiator will result in the production of more homopolymer macroradicals and homopolymer, thus reducing the graft yield.

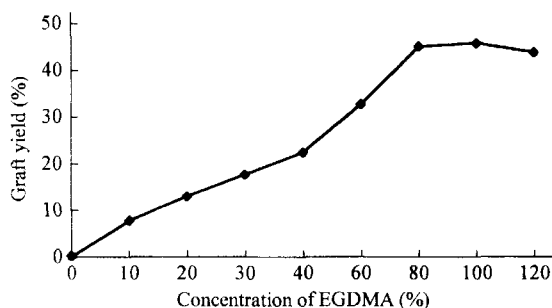


Fig. 3 Graft yield versus concentration of EGDMA:KPS, 1.85% (with respect to the weight of monomer), formic acid, 0.2% (V/V); temperature, 80 °C; time, 30 min

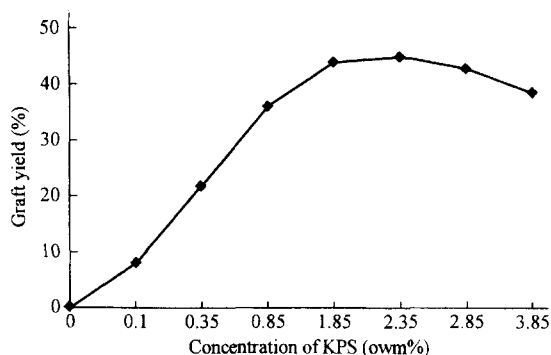


Fig. 4 Graft yield versus concentration of KPS: EGDMA, 80% (with respect to the weight of fiber), formic acid, 0.2% (V/V); temperature, 80 °C; time, 30 min

Effect of Formic Acid Concentration

Results are presented in Fig. 5 showing the effect of formic acid concentration on grafting. It is observed that the percent grafting is found to be optimum at 0.2% (V/V) and then it is decreased gradually as the acid concentration is increased. When formic acid concentration is 0.2% (V/V), the pH value of this solution is about 3.0. An optimum pH is needed for the reaction, and maximum rates will be obtained at pH 3.0 for this system. It is well known that silk swells in acid. Because of the swelling of silk fiber, the diffusion of reactants and reactive species into its matrix may be made easier. As the diffusion of monomer and radicals was facilitated, grafting could also be accelerated at pH values around 3.0. And further increasing the acid concentration, that is lowering the pH, probably hinders swelling and facilitates the dissolution by hydrolysis of grafted polymer chains, thus decreasing the rate of grafting at higher acid concentrations.

Kinetics of Grafting

In a grafting system similar to ours, the relation of the rate of grafting (R_g) with the monomer and initiator concentrations can be written as

$$R_g = k[\text{Monomer}]^m[\text{initiator}]^n$$

Here, m and n can be experimentally determined. The slope of the $\lg R_g$ versus $\lg[\text{KPS}]$ graph plotted from the data given in Fig. 4 by changing the concentration of KPS from 0.1% to 1.85% (with respect to the weight of

monomer) showed that the rate of grafting could be proportional to the 0.58 power of KPS concentration (Fig. 6). Likewise, the initial rate of grafting was determined by changing the concentration of EGDMA from 10% to 80% (with respect to the weight of fiber) (Fig. 3). From Fig. 7, it can be seen that R_g is proportional to the 0.82 power of EGDMA concentration. Therefore, the grafting rate of EGDMA onto silk fibers using KPS in alcohol aqueous solution can be written as

$$R_g = k[\text{Monomer}]^{0.82}[\text{initiator}]^{0.58}$$

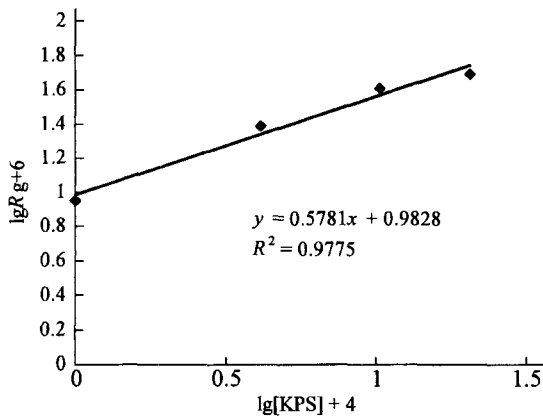


Fig. 5 Graft yield versus concentration of formic acid: EGDMA, 80%; KSP, 1.85%; temperature, 80°C; time, 30 min

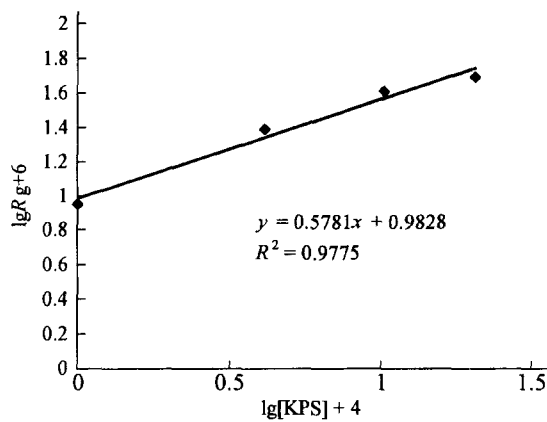


Fig. 6 A plot of $\lg R_g$ versus $\lg[\text{KPS}]$

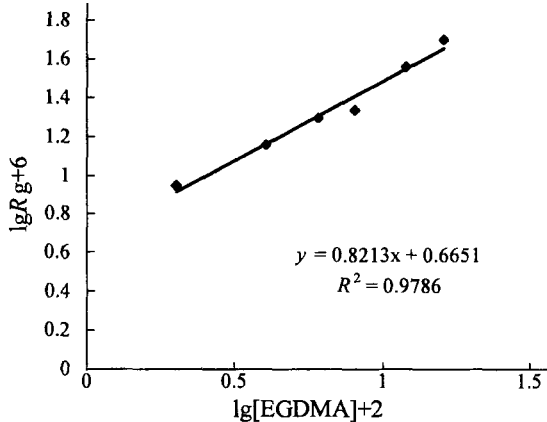


Fig. 7 A plot of $\lg R_g$ versus $\lg[\text{EGDMA}]$

Effect of Crease-Proofing

The graft copolymerization of EGDMA onto silk will modify the properties of the fabric. The crease recovery behavior of silk grafted with EGDMA with respect to the graft yield is given in Table 1. This graft copolymerization is effective in improving the crease-proofing of silk fabrics, even if with different rate and extent of grafting. When the graft yield was 30.8%, the wet and dry crease angles were 261.1 and 300.6 respectively as compared with 197.3 and 242.5 on ungrafted sample. This increase in crease recovery should be mainly attributed to the EGDMA introduced into the silk fiber. Other fabric properties were also measured. Light fastness, acid resistance and alkali resistance were also with improved with no loss in fiber strength observed.

Table 1. Crease angles of silk fabric grafted with EGDMA

Graft yield (%)	Crease angle (W+F) ^a	
	Dry	Wet
0 (Ungrafted)	242.5	197.3
5.1	258.1	241.3
14.8	273.4	247.4
30.8	300.6	261.1

^a Warp + Filling

CONCLUSION

The results reported in the present study show that EGDMA can be grafted onto the silk. Some reaction conditions, such as temperature, time, concentration of EGDMA and initiators, formic acid, will affect the grafting reaction. The graft copolymerization of EGDMA onto silk can improve the crease-proofing of silk fabrics.

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