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Preparation of Wool-*g*-Glycidyl Methacrylate with a Constructed –SH Groups/Ammonium Persulfate Redox System and Characterization

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To explore suitable synthesis parameters of efficient graft copolymerization on wool, the disulfide bonds in wool chains were reduced to sulfhydryl groups by the treatment of thioglycolic acid to wool, and then wool-*g*-poly(glycidyl methacrylate) was prepared by graft copolymerization of wool with glycidyl methacrylate by building a redox system between sulfhydryl groups and ammonium persulfate. The wool-*g*-poly(glycidyl methacrylate) was characterized by the analyses of Fourier transform infrared spectroscopy, scanning electron microscopy, thermogravimetric and x-ray diffraction. Influences of molar concentrations of monomer and initiator as well as reaction temperature on grafting ratios were investigated. The experimental results showed that the sulfhydryl groups/ammonium persulfate redox system built could effectively initiate graft polymerization of lipophilic glycidyl methacrylate on the wool surface in an aqueous medium. The suitable process parameters of graft copolymerization were: 0.6 mmol/L molar concentration of glycidyl methacrylate, 3.0 mmol/L molar concentration of ammonium persulfate, and reaction temperature of 50 °C. At the suitable parameters, the grafting ratio of wool-*g*-poly(glycidyl methacrylate) showed a maximum value of 195.8 %, indicating an efficient graft copolymerization was achieved. The copolymerization could reduce the degree of crystallinity of wool. The wool-*g*-poly(glycidyl methacrylate) had higher thermal stability than raw wool at a temperature of below 406 °C by performing the thermogravimetric analysis. Based on the results, we successfully built new sulfhydryl groups on the wool/ammonium persulfate redox system, prepared the wool-*g*-poly(glycidyl methacrylate), and this work will lay an important foundation for the application of wool-*g*-poly(glycidyl methacrylate) in the textile field.

Keywords: wool, sulfhydryl, redox system, glycidyl methacrylate, graft copolymerization.

1. INTRODUCTION

It is well known that biomass materials such as cellulose material [1, 2] and wool possess the advantages of renewability and biodegradability. Glycidyl methacrylate (GMA) contains epoxy groups that can easily react with –COOH, –OH, and $–NH_2$ [3, 4]. The ring-open reaction of the epoxy groups in GMA polymers can not only be applied in gene therapy [5], enzyme immobilization [6], but also be employed to prepare chelating materials and adsorbents [7] for the solid phase extraction, separation, and purification of biological macromolecules [8], environmental treatment, and chromatographic fixation [9]. Therefore, it will fulfill the high-valued utilization of wool through grafting PGMA branches onto the wool surface.

Commonly, surface grafting methods of wool can be divided into two types, i.e., “grafting to” and “grafting from” [10, 11]. The grafting ratio of the product obtained by the method of “grafting from” is higher than that of “grafting to”. In the “grafting from”, when the active sites introduced on the wool surface are polymerizable double bonds [12], it is also known as the method of “grafting through”, which is easily and widely used, but it also has a certain limitation. The “grafting from” method that holds higher grafting efficiency due to the introduction of the initiating groups on the wool surface, is called “surface-initiated grafting”. Various active grafting methods are also included in this grafting method [13]. However, the reaction conditions of active graft polymerization are strict, resulting in a limited application. It needs vigorous development to the “surface-initiated grafting” method that can introduce free radicals onto the wool surface.

Based on the structure characteristic of the –S–S–, –S–S– in the wool molecules can be reduced into –SH by thioglycolic acid. By the strong reduction of the –SH groups, an aqueous oxidation-reduction initiation system between –SH groups and ammonium persulfate (APS) was constructed for efficiently initiating lipophilic GMA onto the wool surface in an aqueous medium. As a result, a grafted copolymer of wool (wool-*g*-PGMA) was prepared by graft copolymerization of wool with GMA at its surface using the –SH groups/APS redox system in an aqueous medium. Nowadays, no study about the process parameters for preparing the wool-*g*-PGMA using APS/–SH groups redox system at wool surface. Therefore, the aim of this work is to reveal the effect of process parameters such as molar concentrations of GMA and APS as well as reaction temperature on the grafting ratio of wool-*g*-PGMA. In addition, the wool-*g*-PGMA samples were characterized by the analyses of Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM),

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thermogravimetric (TG), and x-ray diffraction (XRD). The results of this work can provide a new idea for the grafting modification of wool and offer a new reference for preparing grafted copolymer of wool with a high grafting ratio. In addition, the preparation of wool-*g*-PGMA may be expected to promote the application of wool in producing the wool-based non-woven fabric through enhancing the adhesion between wool and PGMA adhesive in the textile field.

2. EXPERIMENTAL DETAILS

2.1. Materials and reagents

Wool was supplied by Hebei Refined Cashmere Co. Ltd. (Hebei, China). Glycidyl methacrylate (GMA) and thioglycolic acid were chemical pure reagents and supplied by Aladdin Industrial Corporation (Shanghai, China). The chemically pure chemicals such as anhydrous ethanol, acetone, and sodium dodecylbenzene sulfonate were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The ammonium persulfate (APS) and N, N-dimethylformamide (DMF) were purchased from Wuxi Yasheng Chemical Co. Ltd. (Jiangsu, China).

2.2. Preparation of wool-*g*-PGMA

Degreasing treatment of wool: Wool (1 g) and anhydrous ethanol (70 mL) were added into a 150 mL conical flask. After the bottle was sealed, the mixture was mechanically stirred at 70 °C for 6 h. Then, the mixture was washed with distilled water 3 times and oven-dried to a constant weight at 105 °C for obtaining the degreased wool.

Preparation of sulfhydrylated wool [14]: The degreased wool, DMF (70 mL), thioglycolic acid (1.29 g), and sodium dodecylbenzene sulfonate (0.06 g), were added into a 150 mL conical flask. After the nitrogen had been inlet for 15 min, the flask was sealed and the reaction was kept at 60 °C for 10 h under continuous oscillation. Finally, the product was washed with DMF and distilled water 3 times, respectively, followed by freeze-dried in vacuum for 15 h to obtain the sulfhydrylated wool.

Preparation of wool-*g*-PGMA: The sulfhydrylated wool, distilled water (20 mL), and a certain amount of GMA were added into a 100 mL conical flask. The flask was sealed after the addition of the nitrogen (15 min). After the reaction system had been heated to a set temperature, APS aqueous solution (20 mL) was added into the flask during three intervals of 30 min. Then, the reaction was maintained for 12 h at a set temperature. The product was extracted with acetone for 24 h using Soxhlet's extractor, washed with ethanol-distilled water 3 times, and oven-dried at 105 °C to obtain dried wool-*g*-PGMA.

2.3. Measurement of grafting ratio

The grafting ratio (*GR*, %) of wool-*g*-PGMA was calculated according to the literature [14] using the Eq. 1:

$$GR = \frac{W_2 - W_1}{W_1} \times 100\% , \tag{1}$$

where W_1 and W_2 denote the weights of dried sulfhydrylated wool and wool-*g*-PGMA, respectively.

2.4. Characterization

An IRPrestige-21 Fourier transform infrared (FTIR) spectrometer (Shimadzu Co., Japan) was employed to collect the spectra of wool, sulfhydrylated wool and wool-*g*-PGMA samples using KBr pellets at the wavenumber range of 500 – 4000 cm^{-1} for investigating the change in the chemical structure of wool before and after the graft copolymerization.

An S-4800 scanning electron microscope (SEM, Hitachi Limited, Japan) was employed to investigate the surface morphology of the wool and wool-*g*-PGMA samples. Before determination, the samples were coated with a thin layer of gold [15].

X-ray diffraction (XRD) patterns of the samples were recorded on a D8 X-ray diffractometer (Bruker, German). The patterns were recorded using a wavelength of 0.154 nm CuKα radiation at 40 kV and 30 mA with the scattering angle (2θ) range of 5° to 40°. The degree of crystallinity (X_c, %) was calculated according to Soest's method [16] using the Eq. 2:

$$X_c = \frac{A_c}{A_t} \times 100\% , \tag{2}$$

where A_c and A_t refer to the crystalline area and the total area in the X-ray diffractogram, respectively.

Thermogravimetric (TG) analyses of wool and wool-*g*-PGMA samples were performed using a DTG-60H (Shimadzu Corporation, Japan) under the protection of nitrogen atmosphere with a flow rate of 20 mL/min and a heating rate of 10 °C/min.

3. RESULTS AND DISCUSSION

3.1. Validation of active sites at the wool surface

The surface-initiated grafting method refers to the introduction of the active sites on the surface of the matrix and subsequently introducing the grafted branches into the sites of the matrix surface [17]. Active sites include polymerizable double bonds and initiating groups [18]. To confirm the types of active sites in the graft polymerization of this work, the controlled experiments of preparing wool-*g*-PGMA samples are performed, as shown in Table 1.

Table 1. Validation of the active sites at the wool surface

Groups	I	II	III	IV	V	VI
Dry mass of wool, g	1.000	1.000	1.000	1.000	1.000	1.000
Mass of GMA, g	2.558	2.563	2.567	2.560	2.558	2.563
Amount of APS solution, mL	10	10	10	0	0	0
Dry mass of wool after graft copolymerization, g	2.831	2.912	2.873	0.974	0.962	0.969

The graft copolymerization in the groups (I, II and III) contained the addition of APS solution (3.0 mmol/L) used as the initiator, whereas the copolymerization in the experiments (IV, V and VI, as contrast) did not contain the addition of APS. The experimental results showed that dry mass of wool after graft copolymerization in the groups (I, II, and III) had an obvious increase, whereas the mass in the groups [IV, V, and VI, without adding the initiator (APS)] had no increase. These observations revealed that the -SH groups and APS constructed the redox system and fulfilled the graft polymerization of wool and GMA, and the polymerization was not initiated without adding the initiator (APS) in the reaction system.

The preparation process of initiating graft polymerization of GMA on the wool surface by –SH groups/APS redox system is shown in Fig. 1.

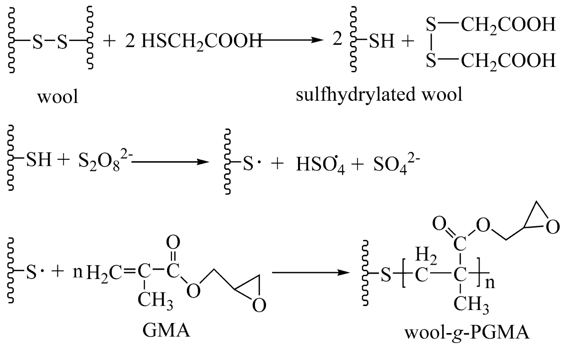

Fig. 1. Graft copolymerization of wool with GMA using the -SH groups/APS redox system built

The disulfide bonds on the wool molecules are reduced into the –SH groups by the treatment of thioglycolic acid to wool. The –SH groups can constitute a redox system with the APS in an aqueous medium. The –SH groups cause the decomposition of APS to produce sulfate free radicals at a lower temperature, meanwhile, the hydrogen atoms on the –SH groups of the wool surface are transferred to the sulfate free radicals. As a result, many sulfur free radicals are formed on the wool surface, which directly initiates the graft copolymerization of GMA on the wool surface, introducing grafted PGMA branches onto the wool surface and forming the wool-*g*-PGMA samples with high grafting ratios.

3.2. Influence of main process parameters on graft copolymerization

Fig. 2 shows the influence of molar concentration of APS on the grafting ratio of GMA. As observed, with the increase in the concentration, the grafting ratio consistently increased, reached its maximum value of 195.8 % as the concentration of APS was 3.0 mmol/L, and then decreased to 132.7 % at the 4.0 mmol/L concentration of APS. The increase in the molar concentration of APS implies the increases in the amounts of the sulfate free radicals produced by the decomposition of APS in the solution. The increased sulfate free radicals will adsorb more hydrogen atoms from the sulfhydryl groups on the wool surface, so that the numbers of sulfur free radicals produced on the wool surface obviously increase, thereby producing an increased grafting ratio. When the concentration of the APS exceeds 3.0 mmol/L, a larger number of sulfur free radicals is generated on the wool surface, which may lead to the acceleration in the homopolymerization [14]. The accelerated homopolymerization may disturb the graft polymerization of GMA on the wool surface. In addition, the participation of some free radicals in the termination reaction of graft polymerization may also be raised after the concentration exceeds 3.0 mmol/L, resulting in a reduced grafting ratio as the concentration exceeds 3.0 mmol/L. Therefore, the suitable concentration of the APS is 3.0 mmol/L.

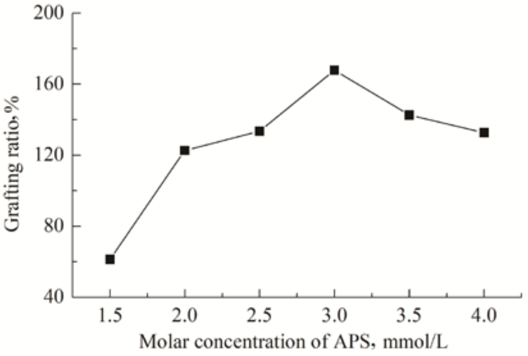

Fig. 2. Influence of molar concentration of APS on grafting ratio

When the other conditions were fixed, the influence of molar concentration of GMA on the grafting ratio is shown in Fig. 3. With the increase in the concentration, the grafting ratio gradually increased from 3.0 % to 216.6 %. Under a fixed amount of APS, with the increase in the concentration of GMA, it will increase the probability of the reaction between GMA molecules and the sulfur radicals on the surfaces of the sulfhydrylated wool fibers, thereby inducing an accelerated graft polymerization of GMA on the wool surfaces and leading to an increased grafting ratio [16]. Nevertheless, when the concentration of GMA exceeded 0.6 mmol/L, we found that there had an obvious formation of the homopolymer (PGMA) on the surface of the wool. Accordingly, based on the experimental phenomenon, the suitable concentration of GMA was 0.6 mmol/L.

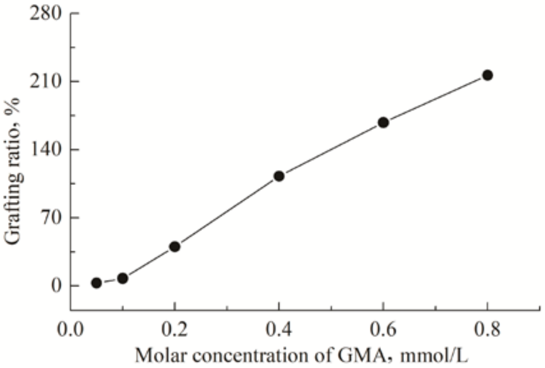

Fig. 3. Influence of molar concentration of GMA on grafting ratio

When the molar concentrations of APS and GMA were 3.0 mmol/L and 0.6 mmol/L, respectively, the influence of reaction temperature on the graft copolymerization of GMA on the surface of wool was investigated, as shown in Fig. 4. It could be seen that the grafting ratio of GMA was dependent on the reaction temperature. In the temperature range of 15 – 70 ºC, the grafting ratio gradually increased, reached its maximum value of 195.8 % when the temperature was 50 ºC, and then decreased. When the temperature was lower than 50 ºC, the decomposition rate of the APS increased as the temperature raised, leading to an increased grafting ratio. However, as the temperature was more than 50 ºC, the decomposition rate of the APS would increase rapidly, which might result in an increase in the homopolymerization of GMA due to the obvious increases in the amounts of free radicals in the reaction system. For this reason, a reduced grafting ratio could be expected as the temperature exceeded 50 ºC. Accordingly, we concluded that the appropriate reaction temperature under the given process conditions was 50 ºC.

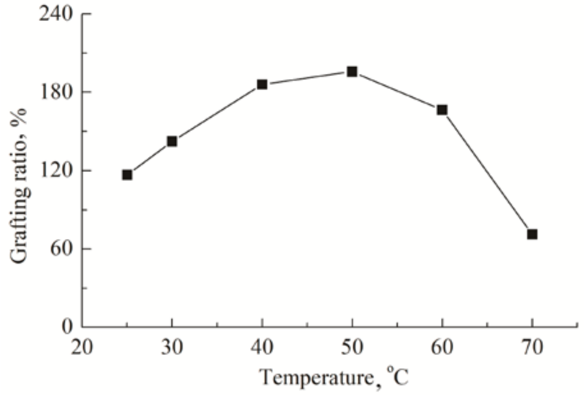

Fig. 4. Influence of reaction temperature on grafting ratio

As a result, the suitable process parameters of graft polymerization were: GMA concentration of 0.6 mmol/L, APS concentration of 3.0 mmol/L, and reaction temperature of 50 ℃. The grafting ratio of wool-*g*-PGMA showed a maximum value of 195.8 % observed from Fig. 4. At the suitable process parameters mentioned above, wool-*g*-PGMA samples with grafting ratios of 50.5 % and 137.0 % were prepared for the following characterizations.

Fig. 5 shows the FTIR spectra of raw wool, sulfhydrylated wool and wool-*g*-PGMA samples. The peaks that appeared at 2960 cm^{-1}, 2956 cm^{-1} and 2953 cm^{-1} corresponded to the characteristic absorption peak of the C–H [19]. And the peaks at 1644 cm^{-1}, 1542 cm^{-1}, and 1390 cm^{-1} corresponded to the amide I band (C=O telescopic vibration peak), the amide II band (N–H expansion vibration peak), the amide III band (C–N telescopic vibration peak), respectively [20]. In addition, a new peak appeared at 2560 cm^{-1} in the spectra of sulfhydrylated wool (Fig. 5 b), which belongs to the characteristic peak of sulfhydryl groups [21] and indicates the successful introduction of the sulfhydryl groups on the wool surfaces. There was no sign of this bond in the spectrum of the wool-*g*-PGMA (Fig. 5 c), and there were two new peaks that appeared at the wavenumbers of 1728 cm^{-1} and 906 cm^{-1}. The peak at 1728 cm^{-1} corresponded to the characteristic absorption band of C=O [22] in the PGMA branches. The other one appeared at 906 cm^{-1}, which indicated the asymmetric absorption vibration of the epoxy groups [23, 24]. The two new peaks demonstrated the successful grafting of the PGMA branches on the wool surface.

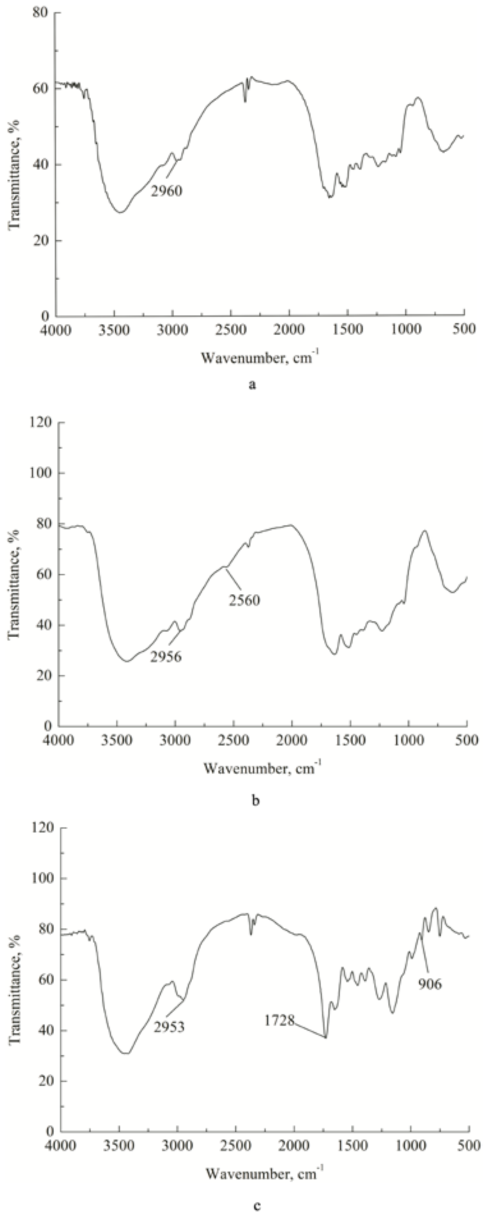

Fig. 5. FTIR spectra: a – raw wool; b – sulfhydrylated wool; c – wool-*g*-PGMA with *GR* = 137.0 %

Fig. 6 presents the SEM images of the raw wool and wool-*g*-PGMA samples. As observed, raw wool (Fig. 6 a) had smooth surfaces and clear scale layers, whereas some new substances covered on the surfaces of the wool-*g*-PGMA samples (Fig. 6 b and c), which induced a rough surface morphology. By using the –SH groups/APS redox system, a large number of PGMA branches was grafted onto the wool surfaces by performing the graft polymerization of GMA monomer with the sulfhydrylated wool, thereby generating a rough surface morphology of the wool-*g*-PGMA samples.

XRD patterns of raw wool and wool-*g*-PGMA samples with the grafting ratios of 50.5 % and 137.0 % are depicted in Fig. 7. It could be seen that there was no difference in the crystal configuration of the wool before and after grafting. Both raw wool and wool-*g*-PGMA samples appeared the diffraction peaks at about 9.0° and 19° (2θ). The strong diffraction peak appeared at about 9.0° corresponded to the common diffraction peaks of αcrystallization and β-crystallization [25], while the strong diffraction peak at about 19° corresponded to the peak of β-crystallization [26].

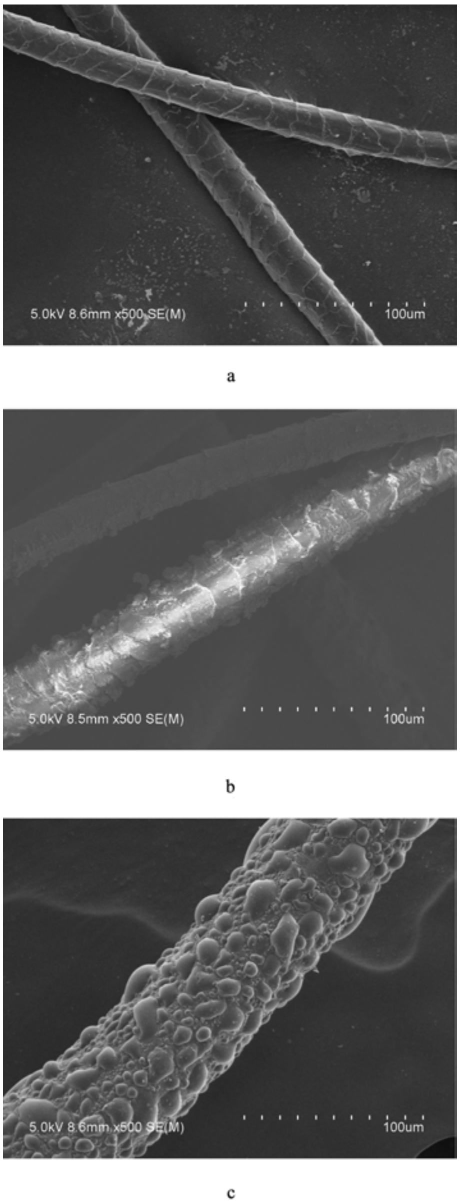

Fig. 6. SEM images (×500): a – raw wool; b – wool-*g*-PGMA samples with *GR*% = 50.5 %; c – wool-*g*-PGMA samples with *GR* = 137.0 %

In addition, it could be seen that the peak intensity at about 9.0° diminished, whereas the intensity at about 19° enhanced after graft copolymerization. Compared with that of the wool-*g*-PGMA sample (*GR* = 50.5 %), the peak intensity at about 9.0° of the wool-*g*-PGMA (*GR* = 137.0 %) weakened, while an increased peak intensity at about 19° was exhibited. The degrees of crystallinity were 33.3 %, 25.4 %, and 18.1 % for the raw wool and wool-*g*-PGMA samples with the grafting ratios of 50.5 % and 137 %, respectively, which implied the graft polymerization was able to reduce the degree of crystallinity of wool. The reduction of the degree of crystallinity is probably attributed that the graft polymerization destroys the scale layer of wool fiber and thus lowers the α-degree of crystallinity of wool.

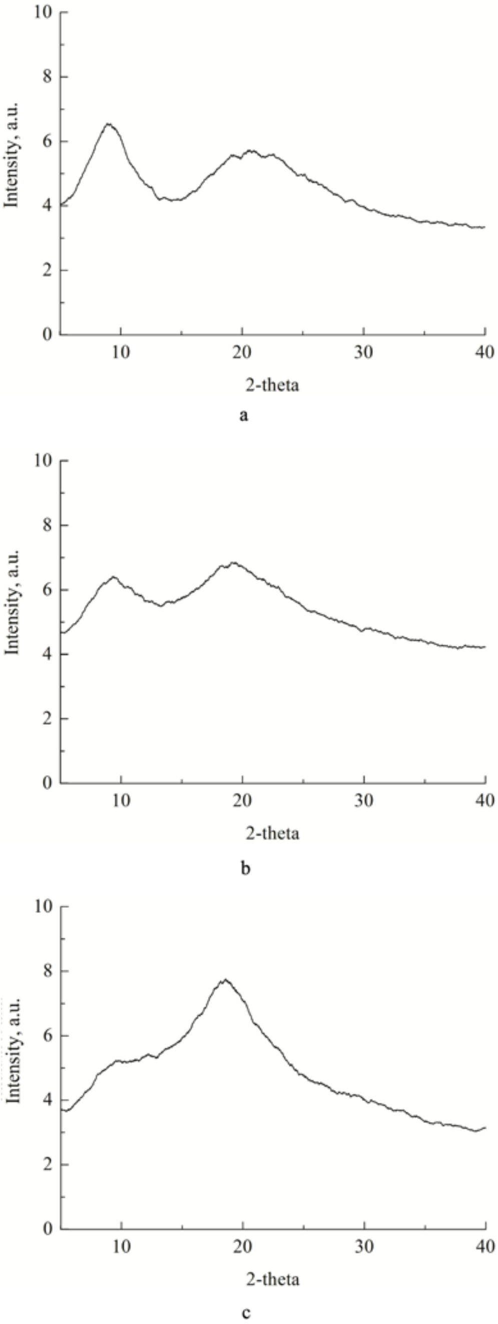

Fig. 7. XRD patterns: a – raw wool; b – wool-*g*-PGMA samples with *GR*% = 50.5 %; c – wool-*g*-PGMA samples with *GR* = 137.0 %

TG curves of raw wool and wool-*g*-PGMA samples are shown in Fig. 8. For the raw wool, it began to decompose at approximately 216 °C, and had a 10 % of weight loss before 230 °C due to the evaporation of water. When the temperature was 800 °C, there was 13 % of the residual weight. For the wool-*g*-PGMA samples, their initial decomposition temperatures showed a slight difference with the raw wool, and there were 8.5 % and 5.6 % of residual weight at 800 °C for the samples with the grafting ratios of 50.5 % and 137.0 %, respectively. Although the residual weight of raw wool was higher than that of wool-*g*-PGMA samples at 800 °C, it could be observed that the residual weight of wool-*g*-PGMA samples was higher than that of raw wool as the temperature was lower than 406 °C, indicating that the wool-*g*-PGMA samples had greater thermal stability in this temperature range by comparison with raw wool.

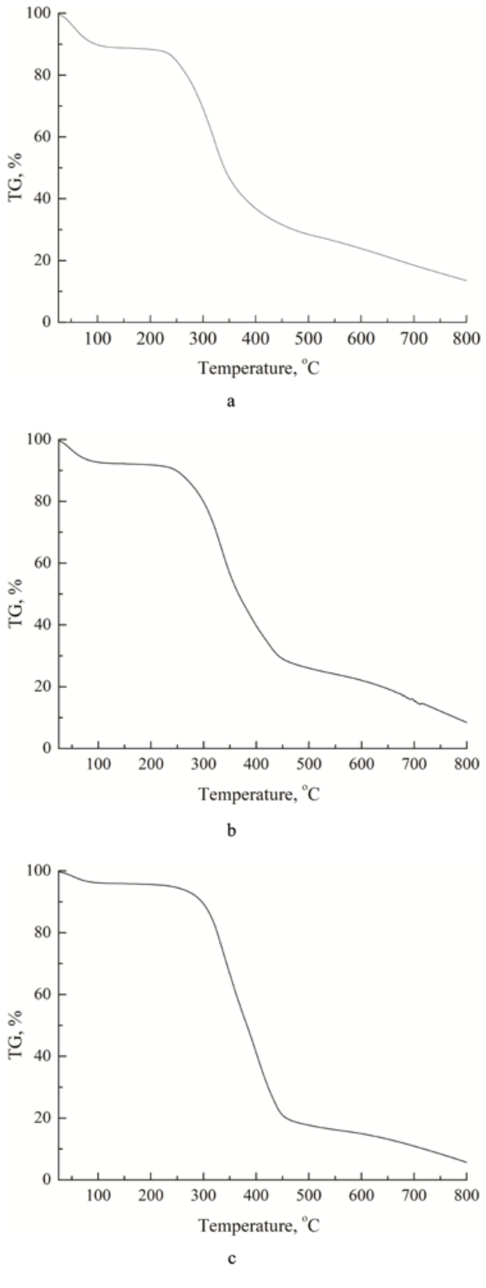

Fig. 8. TG analyses: a – raw wool; b – wool-*g*-PGMA samples with *GR*% = 50.5 %; c – wool-*g*-PGMA samples with *GR* = 137.0 %

There were two probable explanations for the increased thermal stability of grafted wool. The thermal stability of the carbon-carbon bonds in the PGMA branches was higher than that of the peptide bonds of wool. Additionally, the cross-linking between grafted branches that might occur during the grafting reaction favored increasing the thermal stability.

4. CONCLUSIONS

Wool was modified by thioglycolic acid for reducing the –S–S– existed on the surface of wool to –SH. By the strong reduction of the –SH groups, an aqueous redox system between –SH groups and APS was constructed, and then an efficient graft copolymerization of lipophilic GMA monomer with the wool was realized, and the wool-*g*-PGMA with high grafting ratios were obtained. Based on the experimental results, the optimum monomer concentration, initiator concentration, and reaction temperature of graft copolymerization were 0.6 mmol/L, 3.0 mmol/L, and 50 °C, respectively. At the suitable parameters, wool-*g*-PGMA with the highest grafting ratio of 195.8 % was obtained, which indicated that an efficient graft copolymerization by the –SH groups/APS redox system in an aqueous medium was achieved. The successful preparation of wool-*g*-PGMA was demonstrated by FITR analysis. Compared with raw wool, rough surface morphologies for the wool-*g*-PGMA samples were observed through the SEM technique. The XRD analysis exhibited that graft copolymerization of wool with GMA was able to reduce the degree of crystallinity of wool, and increasing the grafting ratio favored the reduction of the crystallinity. The TG analysis showed that thermal stabilities of wool-*g*-PGMA samples were higher than raw wool as the temperature was lower than 406 °C. The optimization of synthesis parameters and characterization for wool-*g*-PGMA will lay important foundations for efficient graft copolymerization of natural fibers and the preparation of wool-based non-woven fabric through enhancing the adhesion between wool and PGMA adhesive in the textile field.

Acknowledgments

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