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Graft Polymerization of Native Chicken Feathers for Thermoplastic Applications

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ABSTRACT: Inexpensive and biodegradable thermoplastics were developed through graft polymerization of native chicken feather with methyl acrylate as a potential substitute for petroleum products. Poultry feathers are available in large quantities at a low price. However, natural chicken feathers have poor thermoplasticity, cannot be used to develop thermoplastic products, have very limited industrial applications, and are often considered as solid wastes. In this research, the effects of graft polymerization conditions, such as molar ratio of $NaHSO_3$ to $K_2S_2O_8$, initiator and monomer concentrations, pH, temperature and time of polymerization, on grafting parameters, that is, the conversion of monomer to polymer, grafting percentage, and grafting efficiency were evaluated. Methyl acrylate was found to be successfully grafted onto functional groups on the surfaces of the chicken feathers, and optimal graft polymerization conditions were also obtained. The feather-*g*-poly(methyl acrylate) developed showed good thermoplasticity, and feather films had substantially higher tensile properties than soy protein isolate and starch acetate films.

KEYWORDS: feathers, thermoplastics, grafting, films, biodegradable

INTRODUCTION

Thermoplastics have many advantages, such as being recyclable and easy to mold into various forms. Currently, thermoplastics are mainly derived from petroleum products. Although petroleum-based thermoplastic products have good performance properties, they have major limitations, such as poor biodegradability, increasing price, and decreasing availability. Therefore, it is necessary to develop various kinds of thermoplastics that are cheap, easily available, and environmentally friendly to replace those from petroleum products.

It is estimated that 3−4 billion pounds of feathers are generated as byproducts of the poultry industry in the United States every year.[1] In addition to their easy availability and low cost, feathers are also renewable and biodegradable. However, there is limited use of feathers for industrial applications, and most of the feathers are disposed as solid wastes in landfills. That is, the feathers take up precious land and cause a waste of keratin resources.[2]

Developing products from feathers will add value to feathers, reduce wastes disposed in landfills, and provide inexpensive polymers to develop various products. Efforts have been made to utilize feathers as animal feed, reinforcement in composites, and other products.[3−5] However, chicken feather still has little added value and is mostly used as an organic fertilizer or as an additive to animal feed.[6] In recent years, some investigators have aimed at expanding industrial applications of chicken feather and looked for physical and/or chemical modifications to turn feathers into thermoplastics. Some studies employed a large amount of plasticizer to blend with feathers to develop thermoplastics. Feather films that contained different amounts of glycerol (15−50 wt %) made by Barone et al. had values of elastic modulus of 40−500 MPa, stress at break of 6−15 MPa, and strain at break of 8−50%.[7] Schrooyen et al. blended carboxymethylated feather keratin with various amounts of glycerol (5− 47 wt %) and then prepared keratin films.[6] The values of elastic modulus, tensile strength, and breaking elongation of the modified keratin films were 150−350 MPa, 15−25 MPa, and 10−50%, respectively. To obtain higher tensile properties of feather films, especially higher elastic modulus, as well as make feathers less dependent on plasticizer, it is necessary to find an efficient and inexpensive way to modify native feathers and make them thermoplastic without or with less plasticizer.

Graft polymerization is an efficient chemical modification to develop thermoplastics. Graft polymerization introduces one or more kinds of polymers onto molecular chains of another polymer as a substrate.[8,9] Previous papers have shown that grafting makes many natural polymers thermoplastic, and the products developed from the grafted natural polymers have better mechanical properties than unmodified ones.[10,11]

A few attempts were made to modify keratin or feather fibers through graft polymerization. Sastry et al. prepared modified keratin as an important composition of fertilizers by grafting 2-hydroxyethyl methacrylate onto the molecular chains of keratin purified from feathers.[12] The weight ratio of 2-hydroxyethyl methacrylate to feather keratin was about 1.6, and grafting percentage was about 32%. Tsukada et al. grafted benzyl methacrylate monomers onto the molecular chains of wool keratin to enhance thermal stability and shrink resistance of wool fibers.[13] Martinez-Hernandez et al. studied the graft polymerization of

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feather with methyl methacrylate and reported that the grafted feather could be potentially used as a reinforcement in composites.[14,15] The weight ratio of methyl methacrylate to native feather was about 10.5, and grafting percentage was 80%. However, to the best of our knowledge, there are no reports on the preparation of thermoplastics by graft polymerization of native feathers. In addition, in the papers above, only grafting percentage (% grafting) was reported. Two other important grafting parameters, conversion of monomer to polymer (% monomer conversion) and grafting efficiency (% grafting efficiency), were not mentioned. It should be noted that % monomer conversion and % grafting efficiency indicate the amount of the monomer converted to polymer and the weight ratio of grafted branches grafted onto the backbone of substrate to the sum of grafted branches and ungrafted homopolymers, respectively. The two grafting parameters are both major factors that influence the cost of grafting. In this research, to reduce the cost, grafting conditions were optimized to obtain not only high % grafting but also high % monomer conversion and % grafting efficiency to develop grafted feathers with good thermoplasticity.

Graft polymerization can be initiated in three ways, that is, redox, oxidation, and radiation. Using a redox system is the most common method for the initiation of graft polymerization because free radicals can be generated efficiently under mild conditions. Some studies on grafted keratin indicated that preferred grafting sites were mercapto groups on cystine.[13] Later, the amino and hydroxyl groups on the molecular chains of keratin were also found to act as reactive groups.[16,17] In a redox system, persulfates are commonly used as oxidant. A redox system of persulfate exhibits high initiation efficiency and reproducibility. In addition, the temperature does not change drastically during graft polymerization in the redox system. Thus, the polymerization process can be easily controlled.[18] Moreover, persulfate is inexpensive and nontoxic. Common reductants for the redox system of persulfate are generally sodium bisulfite and ferrous ammonium sulfate, which are capable of substantially decreasing the activation energy of decomposition of persulfate.[19,20] Therefore, we adopted potassium persulfate and sodium bisulfite as oxidant and reductant, respectively, in this paper.

In the present study, methyl acrylate (MA) was grafted onto chicken feathers through a $K_2S_2O_8/NaHSO_3$ redox system to develop thermoplastics as previous studies had proved that poly(methyl acrylate) (PMA) showed good thermoplasticity.[21,22] Although PMA by itself is not biodegradable, Chen reported that starch-*g*-PMA showed good biodegradability and the presence of starch assisted microorganisms in attacking PMA when the % grafting was low.[21] In our research, graft polymerization conditions such as molar ratio of $K_2S_2O_8$ to $NaHSO_3$, initiator concentration, pH, polymerization temperature and time, and monomer concentration were varied to obtain high % monomer conversion, % grafting, and % grafting efficiency. Grafting vinyl monomer onto native feathers instead of keratin will not only reduce the cost involved in extracting keratin but also help to retain the unique structure of feathers for various applications.

MATERIALS AND METHODS

Materials. Native chicken feather fibers were supplied by Feather Fiber Corp. (Nixa, MO). The feather fibers were cleaned (washed and treated with ethanol) and ground in a Wiley mill. Methyl acrylate (99%) and paradioxybenzene (99%) purchased from Alfa Aesar were used as monomer and terminator, respectively. Potassium persulfate as oxidant (99%) and sodium bisulfite as reductant (99%) were supplied by Spectrum and J. T. Baker, respectively. All other reagents used were of analytical grade.

Reaction Mechanism. The section of chain initiation in Scheme 1 shows that free radicals are produced by redox reaction of $S_2O_8^{2-}$ and HSO_3^-. There were many pendant functional groups such as $-OH$, $-NH_2$, $-COOH$, and $-SH$ along the molecular chains of feather keratin. The active sites were formed on these groups, and thus monomers could be grafted onto these functional groups.

The section of chain propagation in Scheme 1 indicates the propagation of grafted branches during polymerization of feathers with monomers. The last section in Scheme 1 describes the detailed process of chain termination. Comparable mechanisms were reported by previous investigators on graft polymerization of different proteins.[23−25]

Graft Polymerization. Before grafting, chicken feathers were soaked by mixing with distilled water. Then, the mixture was transferred into a 500 mL four-neck flask. Dilute hydrochloric acid was added to adjust the feather dispersion to a desired pH (4.5−6.5). The flask was maintained at a specific temperature (40−70 °C) in a water bath. After the mixture was deoxygenated by the passing of nitrogen gas for approximately 30 min, the initiator including the oxidant ($K_2S_2O_8$) (2.5−10 wt %, to feather) and the reductant ($NaHSO_3$) (0.96−3.84 wt %, to feather) was dissolved in the proper amount of distilled water, respectively. The initiator solutions and MA monomer (10−60 wt %, to feather) were added continuously into the flask through three funnels. The addition was completed in 10−20 min, and the final weight ratio of feather to water was 1:18. The graft polymerization was carried out in a 500 mL four-neck flask under vigorous stirring using a mechanical stirrer (Talboys Engineering Corp., model T Line 134-1) at 1000 rpm under a nitrogen atmosphere for a predetermined time (1−5 h). Finally, 1 mL of 2% paradioxybenzene solution was added to terminate the polymerization. The product was neutralized to about pH 7.0, filtered, washed thoroughly with distilled water, and dried at 105 °C.

Determining Grafting Parameters. The amount of residual monomer (MA) remaining after reaction was determined by titrating the double bonds of residual monomer in the filtrate. % Monomer conversion was calculated using eq 1

$$\%\ \text{monomer conversion} = \frac{W_1 - W_2}{W_1} \times 100 \qquad (1)$$

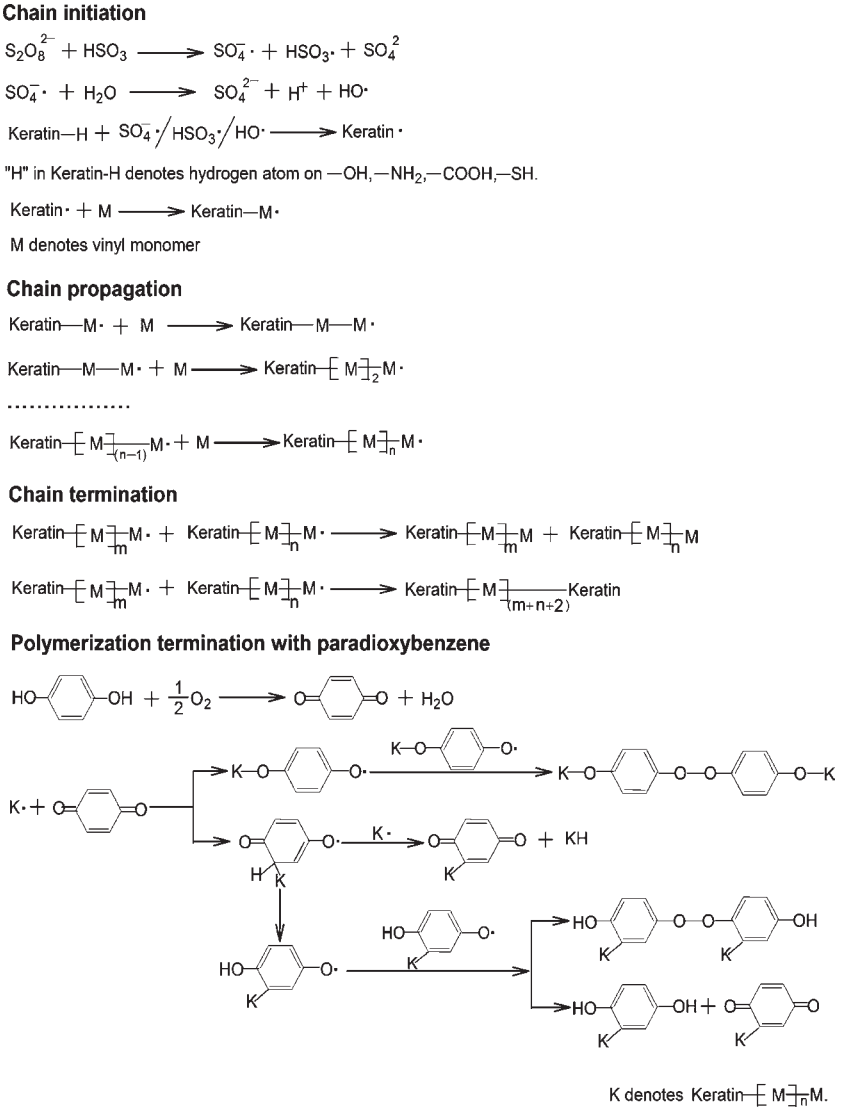
where W_1 and W_2 denoted the weight of the total and the residual monomer, respectively.

In our experiment, the grafted feathers with homopolymers, that is, PMA, were extracted by repeated refluxing in Soxhlet with acetone, which was a good solvent for PMA,[26] for 24 h to remove the homopolymers. The extraction method for the homopolymers using acetone has been reported by many investigators.[27−29] The feather-*g*-PMA product obtained was later dried at 105 °C for 4 h to remove acetone.

To ensure complete removal of the homopolymers (PMA), we extracted the grafted feathers with acetone for 24 and 48 h. The extractants obtained after 24 h showed characteristic peaks belonging to the homopolymers by FTIR. There was no residue in the solvent when the feathers were further extracted for another 24 h (total 48 h), indicating that all of the homopolymers were removed after 24 h of extraction. Also, the feathers obtained after 24 and 48 h of extraction had equal weight after being dried completely. In addition, a known quantity of ungrafted homopolymers was added into the feather and extracted with acetone for 24 h. The extracted feathers did not show any characteristic peak belonging to the homopolymers by FTIR. All of these tests showed that extraction with acetone for 24 h was able to completely extract the homopolymers.

In this paper, % grafting describes the weight percentage of PMA branches grafted onto functional groups on the surfaces of the feathers to the feathers and % grafting efficiency describes the weight percentage of

Scheme 1. Graft Polymerization of Feather Keratin with Vinyl Monomer through $NaHSO_3/K_2S_2O_8$ Redox System



PMA branches grafted onto functional groups on the surfaces of the feathers to the total PMA, including grafted PMA and ungrafted homopolymers. % Grafting and % grafting efficiency were determined using eqs 2−4

$$W_3 = W_b - W_a \quad (2)$$

$$\%\ \text{grafting} = \frac{W_1 - W_2 - W_3}{W_0} \times 100 \quad (3)$$

$$\%\ \text{grafting efficiency} = \frac{W_1 - W_2 - W_3}{W_1 - W_2} \times 100 = \frac{\%\ \text{grafting}}{\%\ \text{monomer conversion}} \times \frac{W_0}{W_1} \times 100 \quad (4)$$

where W_b and W_a were the weights of the products before and after the extraction, respectively, and W_3 and W_0 were the weights of the homopolymer and feathers, respectively.

Fourier Transform Infrared Spectrometry (FTIR). FTIR was used to verify the grafting of MA onto the feathers. The feather-*g*-PMA was extracted by acetone for 24 h, and the homopolymer (PMA) that adhered on the feather-*g*-PMA was removed completely. Measurements were taken on a Thermo Nicolet (Avatar 380) spectrophotometer through the diffuse reflectance technique with a spectral resolution of 32 cm^{-1} for 64 scans.

Proton Nuclear Magnetic Resonance (^{1}H NMR). Unmodified feather and feather-*g*-PMA were characterized by ^{1}H NMR in the deuterated DMSO solvent to confirm the successful grafting using an Avance 600 MHz Digital NMR spectrometer (Bruker Co. Ltd., Switzerland). The feather-*g*-PMA was extracted by acetone for 24 h, and the homopolymer on the feather-*g*-PMA was removed completely. A basic proton pulse sequence (zg30) was used with a relaxation delay of 1 s and an acquisition time of 3 s. Sixty-four scans were acquired to obtain an adequate signal-to-noise ratio. The concentration of each sample was about 1 wt % in the solvent.

Thermal Behavior. Thermal behaviors of unmodified feather and feather-*g*-PMA were studied using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The feather-*g*-PMA was extracted by acetone for 24 h, and the homopolymer on the feather-*g*-PMA was removed completely.

TGA was performed to determine the degradation temperature (T_d) of the unmodified and grafted samples using a Universal V4.4A (TA Instruments) thermogravimetric analyzer. About 10 mg of the sample

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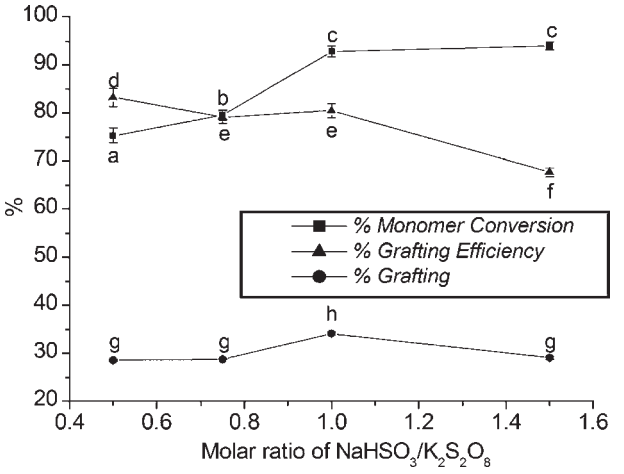

Figure 1. Effect of molar ratio of $NaHSO_3/K_2S_2O_8$ on grafting parameters. The grafting was carried out at 60 °C and pH 5.5 for 3 h. The concentration of $K_2S_2O_8$ was 0.010 mol/L, and the monomer concentration was 40 wt %, to feathers.

was heated at 10 °C/min in a temperature range of 30−600 °C under a nitrogen atmosphere.

A Mettler Toledo DSC 822^e thermal analyzer was used to obtain the DSC thermograms and determine the melting temperature (T_m) of the samples. The samples were completely dried at 105 °C for 4 h before DSC determination. The measurement was conducted by heating the samples from 25 to 180 °C with a heating rate of 40 °C/min under a nitrogen atmosphere.

Preparation of Feather Films. The unmodified and grafted feathers (with and without the homopolymer) were used to develop films. Glycerol (0, 10, 20, and 30 wt %, to grafted feathers with the homopolymer) was used as a plasticizer to improve the thermoplasticity of the grafted feathers. About 10 g of grafted feathers was placed between layers of aluminum foil and compression molded in a Carver press at 170 °C for 18 min at a pressure of 27.6 MPa. After compression molding, the films were removed and cooled under ambient conditions. Photographs of unmodified and grafted feathers (with and without the homopolymer) with glycerol (20%, on weight of the feathers) were taken using a digital camera.

Measurement on Mechanical Properties of Feather Films. The grafted feathers containing four levels of glycerol (0, 10, 20, and 30%) were cut into strips (80 mm × 15 mm) and conditioned at 65% relative humidity (RH) and 21 °C for 24 h before testing. Tensile strength, breaking elongation, and Young's modulus of the films were measured on a MTS (model Q Test 10; MTS Corp., Eden Prairie, MN) tensile tester equipped with a 50 N load cell. Five samples were tested for each condition, and the average ± one standard deviation was reported. Photographs of the feather films before and after grafting were collected using a digital camera.

Statistical Analysis. Each graft polymerization was repeated three times. The data were analyzed using SAS software (SAS Institute, Inc., Cary, NC). The confidence interval was set at 95%, and a p value of <0.05 was considered to be a statistically significant difference. In Figures 1−6, data points with the same small letter were not statistically significantly different from each other.

RESULTS AND DISCUSSION

Effect of Molar Ratio of $NaHSO_3/K_2S_2O_8$ on Grafting Parameters. Figure 1 shows the effect of the molar ratio of $NaHSO_3$ to $K_2S_2O_8$ on the graft polymerization of feathers with MA. The molar concentration of $K_2S_2O_8$ was kept constant.

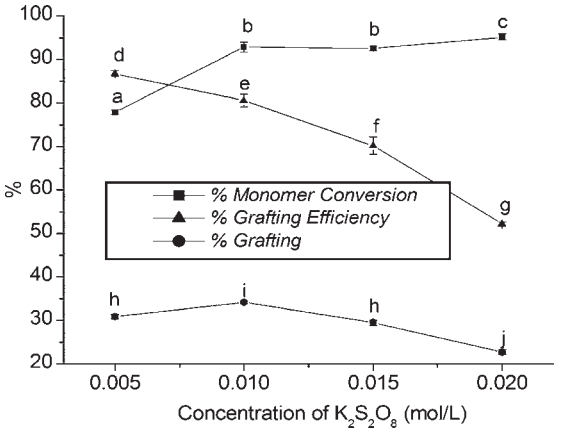

Figure 2. Effect of initiation concentration on grafting parameters. The grafting was carried out at 60 °C and pH 5.5 for 3 h. The molar ratio of $K_2S_2O_8/NaHSO_3$ was 1.0, and the monomer concentration was 40 wt %, to feathers.

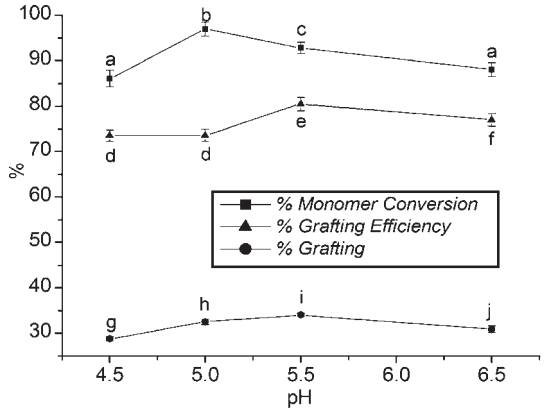

Figure 3. Effect of pH on grafting parameters. The grafting was carried out at 60 °C for 3 h. The molar ratio of $K_2S_2O_8/NaHSO_3$ was 1.0, and the concentration of $K_2S_2O_8$ was 0.010 mol/L. The monomer concentration was 40 wt %, to feathers.

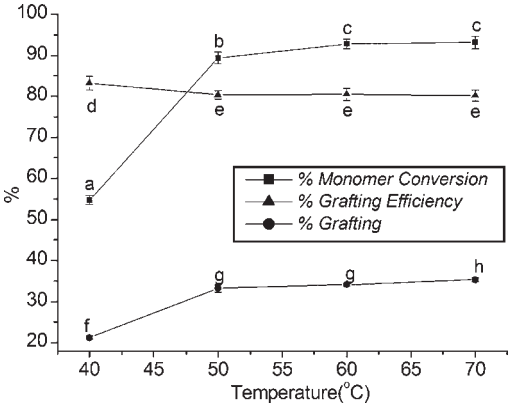

Figure 4. Effect of polymerization temperature on grafting parameters. The grafting was carried out at pH 5.5 for 3 h. The molar ratio of $K_2S_2O_8/NaHSO_3$ was 1.0, and the concentration of $K_2S_2O_8$ was 0.010 mol/L. The monomer concentration was 40 wt %, to feathers.

It can be observed that with the increase in molar ratio of $NaHSO_3$ to $K_2S_2O_8$, % monomer conversion initially increased.

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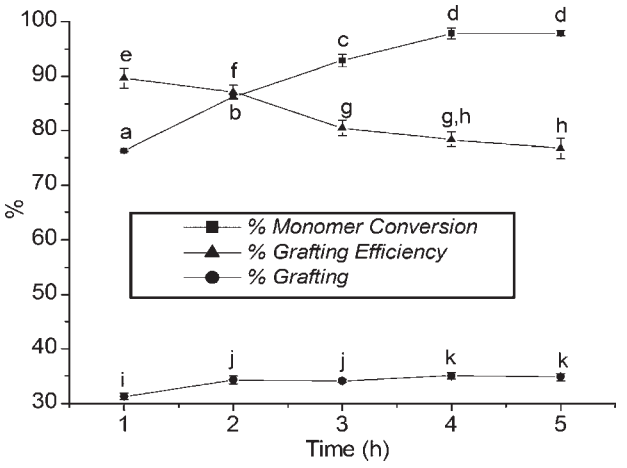

Figure 5. Effect of polymerization time on grafting parameters. The grafting was carried out at 60 °C and pH 5.5. The molar ratio of $K_2S_2O_8$/$NaHSO_3$ was 1.0, and the concentration of $K_2S_2O_8$ was 0.010 mol/L. The monomer concentration was 40 wt %, to feathers.

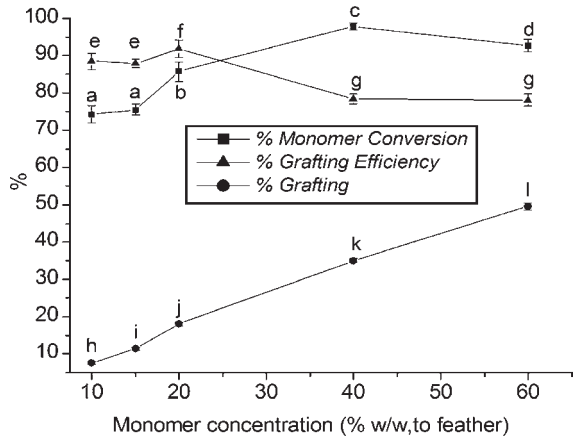

Figure 6. Effect of monomer concentration on grafting parameters. The grafting was carried out at 60 °C and pH 5.5 for 4 h. The molar ratio of $K_2S_2O_8$/$NaHSO_3$ was 1.0, and the concentration of $K_2S_2O_8$ was 0.010 mol/L.

Thereafter, the slight increase in the mean value of % monomer conversion with increasing molar ratio of $NaHSO_3$ to $K_2S_2O_8$ from 1.0 to 1.5 was not statistically significant as shown by the same letter, "c". % Grafting initially increased, reached the maximum when the ratio was 1.0, and then decreased. % Grafting efficiency continuously decreased and was reduced substantially when the ratio was above 1.0.

As seen from Scheme 1, redox reaction occurs between a molecule of bisulfite as reductant and a molecule of persulfate as oxidant, leading to the generation of free radicals. Therefore, when the molar ratio of $NaHSO_3$ to $K_2S_2O_8$ was <1.0, the increasing amount of $NaHSO_3$ could react with superfluous $K_2S_2O_8$ and generate more free radicals. The increase in the amount of free radicals favored both graft polymerization and homopolymerization. Therefore, both % grafting and % monomer conversion increased initially. From eq 4, it could be observed that % grafting efficiency was directly proportional to % grafting and was inversely proportional to % monomer conversion when the ratio of feathers to total monomer was kept constant. When the molar ratio increased from 0.5 to 1, the rate of increase in % grafting was lower than that of % monomer conversion due to homopolymerization among the monomers. As a result, % grafting efficiency decreased when the molar ratio ranged from 0.5 to 1.0.

When the molar ratio exceeded 1.0, an excessive amount of $NaHSO_3$ would function as a chain transfer agent.[30] As a result, the radicals on the propagating chains of PMA were likely to transfer to monomer or initiator. Hence, the propagation of the molecular chains of PMA was restrained. As for graft polymerization, the number of active sites on the surfaces of the chicken feathers was limited. Generation of every grafted branch on the backbones of the feather was based on active sites. Therefore, the number of grafted branches was also limited. Chain transfer caused by an excessive amount of $NaHSO_3$ would restrain the propagation of grafted branches and decrease their degree of polymerization (DP). Therefore, the total weight of grafted branches was reduced and % grafting decreased. As for homopolymerization, each monomer could be considered as a potential active site and thus the number of active sites of homopolymerization was much larger than that of active sites on the surfaces of the chicken feathers. Although chain transfer could decrease DP of PMA, the amount of homopolymer could still increase. Thus, the weight of homopolymer kept increasing even if the molar ratio of $NaHSO_3$ to $K_2S_2O_8$ was >1.0. Thus, % grafting efficiency sharply decreased when the molar ratio was >1.0. When the molar ratio reached 1.0, nearly all of the monomers (93%) were converted to polymers. Thus, the slight increase in the mean value of % monomer conversion was not statistically significant.

Effect of Initiator Concentration on Grafting Parameters. Figure 2 depicts the effect of initiator concentration on the grafting parameters. With the increase in the concentration of $K_2S_2O_8$, % monomer conversion increased substantially when the concentration ranged from 0.005 to 0.010 mol/L and then increased slightly. As for % grafting, it initially increased and then decreased after an optimum value of 0.010 mol/L. % Grafting efficiency continued to decrease with increasing initiator concentration from 0.005 to 0.020 mol/L.

As the concentration of initiator increased, more free radicals were generated. In general, enhancing the amount of free radicals contributes to increases in both graft polymerization and homopolymerization. Therefore, % grafting and % monomer conversion increased markedly when the concentration of $K_2S_2O_8$ ranged from 0.005 to 0.010 mol/L. However, the rate of the increase in % monomer conversion was higher than that of % grafting due to homopolymerization among the monomers. Therefore, % grafting efficiency decreased when the concentration of $K_2S_2O_8$ ranged from 0.005 to 0.010 mol/L.

When the concentration of $K_2S_2O_8$ was excessively high, $K_2S_2O_8$ not only reacted with $NaHSO_3$ in the redox but also oxidized the radicals on propagating chains of PMA.[15,20] Therefore, excessively high concentrations of $K_2S_2O_8$ would restrict the propagation of grafted branches and decrease their DP.[20] As was explained in the preceding section, when the number of grafted branches on the backbone of the feather was limited, the decrease in DP of grafted branches would lead to the decrease in % grafting. As for homopolymerization, the amount of homopolymer would still increase when the concentration of $K_2S_2O_8$ was high. Hence, the weight of homopolymer continued to increase when the concentration of $K_2S_2O_8$ was >0.010 mol/L. Therefore, there was still a decrease in % grafting efficiency. When the concentration of $K_2S_2O_8$ exceeded 0.010 mol/L,

nearly all of the monomers (93%) were converted to polymers. Thus, there was no substantial increase in % monomer conversion.

Effect of pH on Grafting Parameters. The effect of pH during the reaction on grafting parameters is depicted in Figure 3. With the increase in pH from 4.5 to 6.5, the three grafting parameters (% monomer conversion, % grafting, and % grafting efficiency) initially increased but decreased later. The reducing ability of $NaHSO_3$ should be more effective when the pH ranged from 5.0 to 6.0.[31] A pH range of 5.0−6.0 favored the redox reaction between $NaHSO_3$ and $K_2S_2O_8$ and helped to generate more free radicals. Therefore, the optimum values of all grafting parameters were obtained when the pH ranged from 5.0 to 5.5. Excessively high or low concentrations of H^+ decreased the reducing ability of $NaHSO_3$ and impeded the production of free radicals. Therefore, the decreased amount of free radicals led to the decreases in the grafting parameters.

Effect of Reaction Temperature and Time on Grafting Parameters. Effect of temperature on grafting parameters is studied by changing the reaction temperature from 40 to 70 °C as depicted in Figure 4. With the increase in temperature from 40 to 70 °C, % monomer conversion and % grafting both increased. As for % grafting efficiency, it initially decreased from 40 to 50 °C and then leveled off.

In general, the higher the reaction temperature is, the higher the rates of graft polymerization and homopolymerization become. Increases in the rates could be ascribed to the following reasons: the increase in temperature favored fast decomposition of the initiator and led to the generation of a greater number of free radicals at an early stage of the reaction; the mobility of free radicals and monomers would increase at higher temperature, leading to higher % monomer conversion and % grafting if reaction time was equal and inadequate. In Figure 4, % monomer conversion and % grafting both increased with the increase in temperature when the reaction time was 3 h. Hence, it was necessary to study the effect of reaction time on the grafting parameters.

Effects of reaction time on grafting parameters are shown in Figure 5. With the increase in reaction time ranging from 1 to 4 h, both % monomer conversion and % grafting increased but % grafting efficiency decreased. All of the grafting parameters leveled off after the reaction time exceeded 4 h.

Generally, the longer reaction time, the larger the amount of the monomer converted to polymers. At 4 h, almost all of the monomers (about 97%) were converted to polymers including both grafted branches and homopolymer. Thus, % monomer conversion and % grafting did not increase further.

Effect of Monomer Concentration on Grafting Parameters. Figure 6 shows the effect of monomer (MA) concentration on grafting. % Grafting increased continuously with the increase in the concentration of MA from 10 to 60%, whereas % monomer conversion initially increased, reached the maximum when the concentration of MA was 40%, and later decreased. As for % grafting efficiency, it increased when the concentration ranged from 10 to 20%, decreased after the concentration reached 20%, and then leveled off.

The initial increase in % monomer conversion is mainly due to the invariability of the equilibrium constant of polymerization. In general, higher monomer concentration helps to make polymerization including both graft polymerization and homopolymerization move toward the positive direction. In addition, increasing concentration of MA could increase the concentration of PMA, which included grafted branches and homopolymer. The increasing concentration of PMA led to a higher viscosity of the reaction system. The increased viscosity hindered chain termination, especially the coupling termination of growing PMA chains.[20] However, with the increase in the length of molecular chains of PMA, the entropy and stability of the reaction system increased. It would be more difficult for the molecular chains of PMA to become longer if the amount of MA exceeded 40%. Therefore, % monomer conversion began to decrease when the MA concentration reached 40%.

% Grafting in our study describes the weight percentage of PMA branches grafted onto feathers, to feathers. The higher the concentration of MA, the larger the amount of PMA branches formed. Because the amount of feather used was constant during grafting, % grafting kept increasing when the concentration of MA increased from 10 to 60%.

During the grafting process, graft polymerization and homopolymerization are a pair of competitive reactions. With the gradual occupation of active sites on the surfaces of the chicken feathers, it might be more probable for residual monomer in the reaction medium to take part in homopolymerization. Therefore, % grafting efficiency decreased when the monomer concentration was >20%. The aim of our investigation was to prepare a thermoplastic product through the grafting of native feathers using as little MA as possible to achieve high values of all grafting parameters. MA has a much higher price than feathers, and its polymer (PMA) is not biodegradable. Generally, higher monomer concentration will increase the amount of synthetic polymers, including grafted branches and homopolymers. The presence of higher amounts of synthetic polymers will decrease the biodegradability of the products.[21] In our investigation, using a 40% monomer concentration was enough to obtain thermoplastic grafted feathers with good mechanical properties. In addition, % monomer conversion was high (about 98%) when the monomer concentration was 40%. Hence, the monomer concentration is recommended to be 40% after overall considerations.

FTIR Analysis. FTIR spectra of unmodified feather and feather-*g*-PMA are shown in panels a and b of Figure 7, respectively. It could be observed that two peaks appeared at 1660 and 1550 cm^{-1} due to characteristic absorption bands of the amide I and amide II bands, respectively. The FTIR spectrum of feather-*g*-PMA showed a new characteristic absorption band of a carbonyl group of methyl ester at 1738 cm^{-1} in addition to the absorption bands of unmodified feather.[12] The peak at 1738 cm^{-1} confirmed the grafting of MA onto the feather.

^{1}H NMR Analysis. ^{1}H NMR spectra of unmodified feather and feather-*g*-PMA are shown in panels c and d of Figure 7, respectively. Compared to the spectrum of unmodified feather, new chemical linkages were found in feather-*g*-PMA. In Figure 7d, the protons of methyl ester ($-COOCH_3$) appeared at 3.5 ppm, and the grafting of MA onto the feather was confirmed.[32] PMA contained groups such as methylene ($-CH_2-$) and methine (>CH−). Therefore, the increases in peak intensities of the protons of $-CH_2-$ and >CH−, which appear at 1.4−2.3 ppm in Figure 7d, could be considered as additional proof of the grafting of MA onto the feather.[32]

Thermogravimetric Analysis. Panels a, b, and c of Figure 8 reveal the thermal degradation behavior of unmodified feather, grafted feathers without homopolymers, and grafted feathers with homopolymers, respectively. From TG and DTG curves, it could be observed that thermal degradation behaviors of grafted

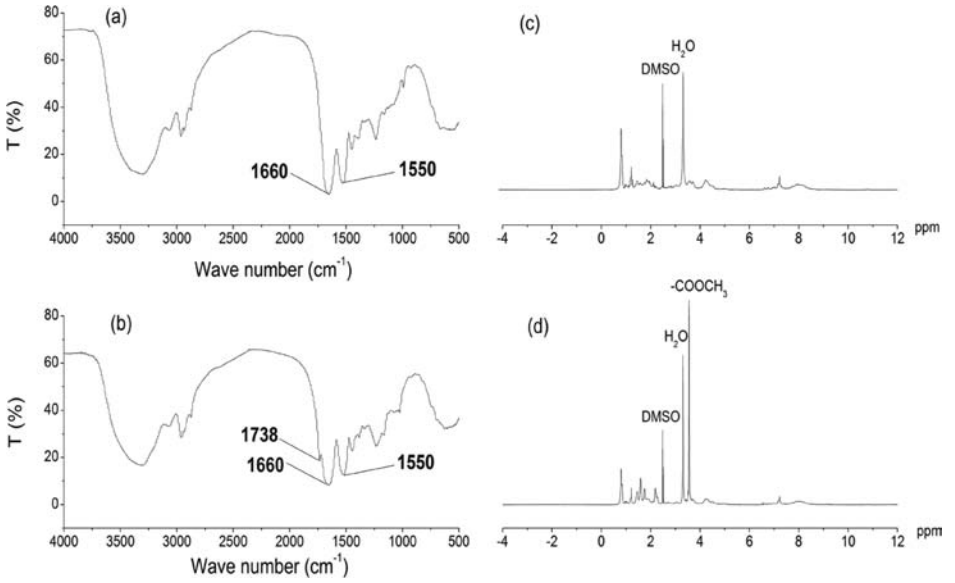

Figure 7. FTIR spectra of unmodified feather (a) and feather-*g*-PMA (b) and ^{1}H NMR spectra of unmodified feather (c) and feather-*g*-PMA (d). The grafting was carried out at 60 °C and pH 5.5 for 4 h. The molar ratio of $NaHSO_3/K_2S_2O_8$ was 1.0, and the concentration of $K_2S_2O_8$ was 0.010 mol/L. The monomer concentration was 40%. % Grafting = 35%.

feathers with and without homopolymers were very similar. The ratio of the homopolymers was only 6.7% (w/w, to the total weight of the grafted feathers with homopolymers), and at this low ratio, the homopolymers did not affect the thermal degradation of the feathers substantially. However, the thermal degradation temperature of the grafted feathers was higher than that of unmodified feathers, as seen in the figures. TG and DTG results show that the starting thermal degradation temperature of unmodified feathers is about 208 °C, whereas that of grafted feathers is about 228 °C. From the peaks of DTG curves, we could observe that the unmodified feathers lost weight the most quickly at about 320 °C, whereas the grafted feathers did at about 330 °C. There were two possible explanations for the improved thermal stability of grafted feathers. The thermal stability of the carbon−carbon bond of grafted branches (PMA) was higher than that of the peptide bond of feather keratin. In addition, mild cross-linking between grafted branches that might occur during the grafting helped to increase the thermal stability.

As seen in TG curves, about 67% of unmodified feathers was lost after heating to 600 °C, whereas 78% of grafted feathers without homopolymers was lost. Through the integration of the peaks of DTG curves, the weight loss percentages of unmodified feather and grafted feather without homopolymers at 600 °C were 71% and 81%, respectively, which were in agreement with TG results. The difference in weight loss between the unmodified and grafted feathers could be used to confirm % grafting of the sample. On the basis of the curve of unmodified feather, the residual amount of unmodified feather, which was decomposed after heating at 600 °C, should be 33%. Assuming that all of the grafted branches (35%) would have decomposed, the actual weight loss of the feather mathematically will be 78.5%, which is similar to the weight loss observed from the curve of grafted feather without homopolymers (78%). This shows that the % grafting achieved is 35%.

DSC Analysis. The DSC thermogram of unmodified feather and feather-*g*-PMA is shown in Figure 9. It could be observed that there was no endothermic peak for unmodified feather, indicating its poor thermoplasticity. The melting curve of feather-*g*-PMA has a broad endothermic peak around 120 °C that can be attributed to the melting of feather-*g*-PMA. The presence of the melting peak demonstrates that the thermoplasticity of the feathers was improved due to the grafting of PMA.

Thermoplastic Feather Films. Figure 10 shows the digital photographs of unmodified feather (1), modified feather with the homopolymer (2), and modified feather after the complete removal of the homopolymer (3) after compression molding. Due to the poor thermoplasticity of unmodified feathers (sample 1), compression molding at high temperature damages and chars the feathers as shown in Figure 10. The modified feathers melted well and became transparent thermoplastic films from fibers after compression molding, indicating good thermoplasticity of the modified feathers. Compared with sample 3, sample 2 was more homogeneous and transparent because the homopolymer (PMA) attaching on the surface helped to increase the thermoplasticity.

Tensile Properties of Feather Films. Table 1 shows the tensile properties of the films developed from grafted feathers containing various amounts of glycerol in comparison to films made from two common natural polymers, soy protein isolate (SPI) and starch acetate (SA). It could be observed that the tensile strength and Young's modulus decreased but breaking elongation increased with increasing amount of glycerol. The tensile strength of grafted feather films with 30% glycerol was only about 27% compared to that of the films without glycerol but with 13 times higher elongation. The modulus of the films also decreased substantially with increasing glycerol content. Glycerol plasticized the feathers and improved the thermoplasticity but decreased the tensile strength. Table 1 also shows the tensile properties of the films made from SPI and SA. It could be observed that, even with the concentration of 30% glycerol, the tensile strength of the feather films was about 10 and 11 times higher than that of SPI and SA films, respectively.

Without any glycerol, the tensile strength of feather films was about 5 and 4 times higher than that of SPI and SA films, respectively. However, the elongation of feather films was similar to that of SPI films but lower than that of SA films. The much

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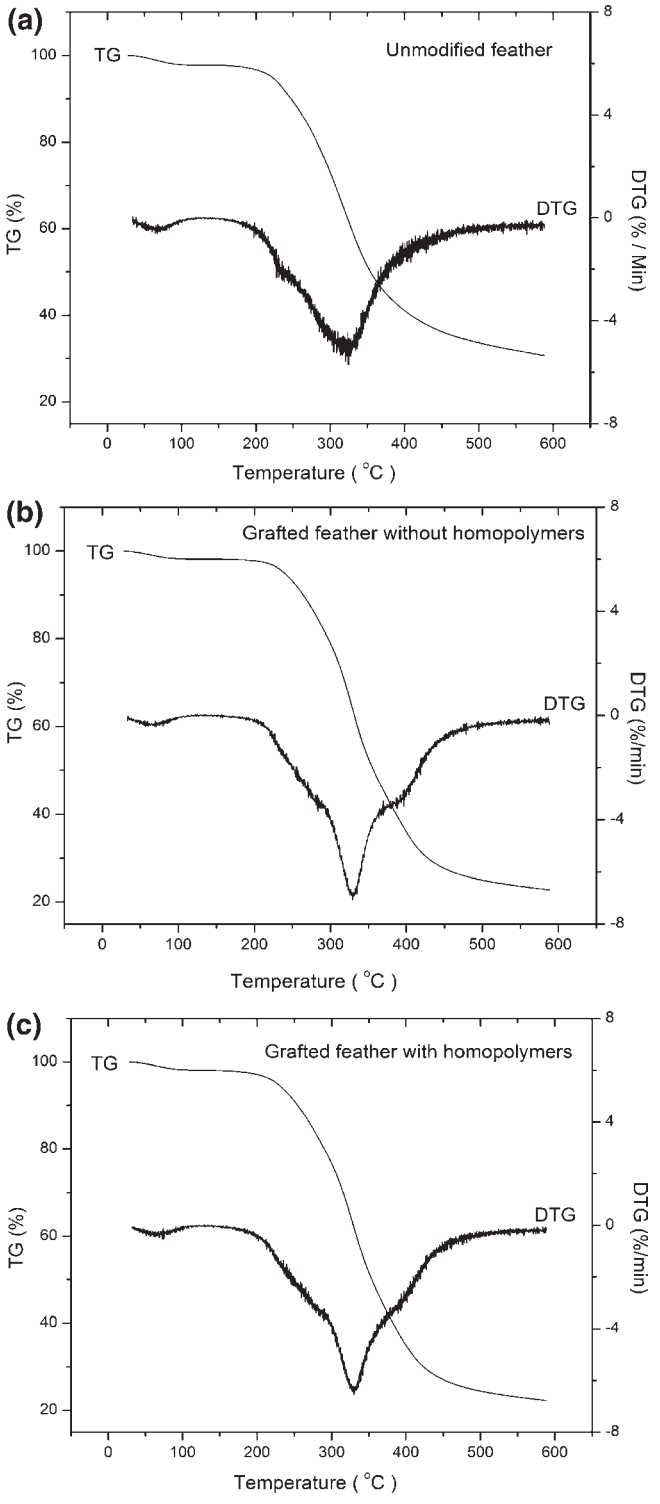

Figure 8. TGA and DTG thermograms of (a) unmodified feather, (b) grafted feather without homopolymers, and (c) grafted feather with homopolymers. The grafting was carried out under the same conditions as in the caption of Figure 7.

higher tensile strength of feather films without any glycerol compared to SPI and SA films might be due to the better thermoplasticity of the modified feather than SPI and SA and the higher tensile strength of feather keratin compared to soy protein and starch acetate. The higher tensile strength is also due

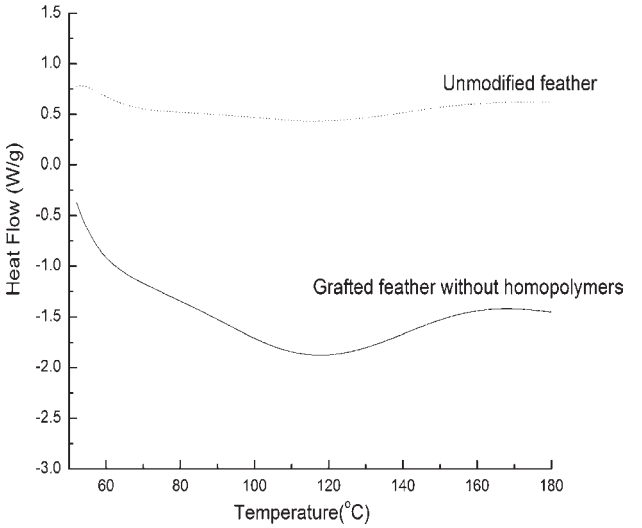

Figure 9. DSC spectra of unmodified feather and grafted feather without homopolymers. The grafting was carried out under the same conditions as in the caption of Figure 7.

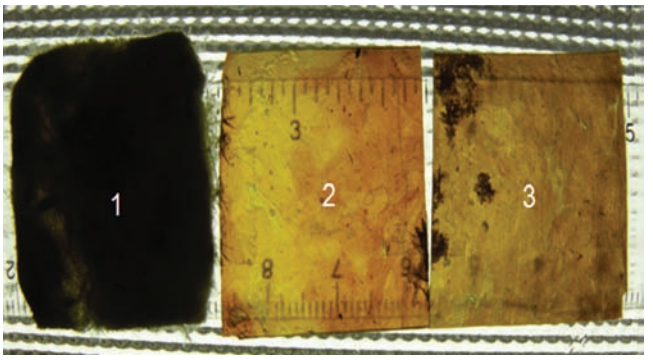

Figure 10. Digital photographs of films developed from unmodified feathers (1), grafted feathers with the homopolymer (2), and grafted feathers without the homopolymer (3). Glycerol (20 wt %, to feathers) was used as a plasticizer in the three samples. The grafting was carried out under the same conditions as in the caption of Figure 7.

to the presence of unmelted feathers that act as reinforcement in the film.

With no glycerol or low concentrations of glycerol (0−20%, to the weight of the feathers), some of the feathers do not melt during compression molding as seen in Figure 10. These unmelted feathers acted as reinforcement and provided higher strength and modulus. However, the unmelted feathers could also cause stress concentration and decrease the breaking elongation of the film. Adding more glycerol (30%, to the weight of the feathers) improved the thermoplasticity, and most feathers melted during compression molding, leading to a substantial increase in breaking elongation but decreases in tensile strength and modulus. By comparison of the properties of feather films with the SPI and SA, the thermoplastic feather films developed with different amounts of glycerol are expected to be suitable for various applications.

In conclusion, native chicken feathers can be made thermoplastic by grafting MA using a $K_2S_2O_8/NaHSO_3$ redox system. High % monomer conversion (97%), % grafting (35%), and % grafting efficiency (78%) were obtained when the grafting was

Table 1. Comparison of Tensile Properties of Grafted Feather Films with SPI and SA Films with Different Amounts of Glycerol

type of film	tensile strength (MPa)	breaking elongation (%)	Young's modulus (GPa)
0% glycerol−feather[a]	206.3 ± 15.7	1.1 ± 0.4	28.8 ± 0.7
10% glycerol−feather[a]	122.1 ± 8.4	1.6 ± 0.5	11.1 ± 0.6
20% glycerol−feather[a]	96.2 ± 9.6	3.0 ± 0.5	8.4 ± 0.2
30% glycerol−feather[a]	55.7 ± 9.0	14.2 ± 2.2	4.4 ± 0.2
0% glycerol−SPI through solvent-casting[b]	41.6	1.3	1.2
11% water−SPI through compression molding[c]	40 ± 6	4.0 ± 0.5	1.63 ± 0.03
20% glycerol−SPI[d]	15.8 ± 0.2	4.2 ± 1.4	
30% glycerol−SPI[d]	5.4 ± 0.2	96.5 ± 6.2	
0% glycerol−SA[e]	56.30 ± 7.59	1.97	
10% glycerol−SA[e]	20.45 ± 5.38	1.63	
20% glycerol−SA[e]	10.22 ± 1.32	2.37	
30% glycerol−SA[e]	4.98 ± 0.65	9.00	

[a] The grafting was carried out at 60 °C and pH 5.5 for 4 h. The molar ratio of $K_2S_2O_8$/$NaHSO_3$ was 1.0, and the concentration of $K_2S_2O_8$ was 0.010 mol/L. The monomer concentration was 40% (w/w, to feathers). % Grafting was 35%. The feather films were conditioned at 65% RH and 21 °C for 24 h before testing. [b] Data from Su et al. The SPI films were solvent-cast at 50 °C for 6 h. The films were conditioned at 43% RH and room temperature (20 °C) for 72 h before testing.[33] [c] Data from Paetau et al. The SPI films were prepared at 140 °C and 20.7 MPa for 6 min using a hot press. The films were conditioned at 50% RH for 40 ± 2 h before testing.[34] [d] Data from Cunningham et al. The SPI films were prepared at 150 °C and 10 MPa for 2 min using a Carver Laboratory Press. The films were conditioned at 50% RH and 25 °C for 24 h before testing.[35] [e] Data from Bonacucina et al. The SA films were cast through the evaporation of the solvent at room temperature (20 °C) for 48 h. The authors did not describe the equilibration conditions before testing.[36]

performed under optimum polymerization conditions. The grafted feathers were thermoplastic and had a broad melting peak around 120 °C. Both ^{1}H NMR and FTIR confirmed the grafting of MA onto the feathers. Compression-molded films developed from the grafted feathers had substantially higher tensile properties than SPI and SA films even at high glycerol concentrations. Grafting can be an effective and simple procedure to develop inexpensive thermoplastic products from poultry feathers.

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