

Solid State Grafting Copolymerization of Acrylamide onto Poly(Vinyl Alcohol) Initiated by Redox System

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ABSTRACT: A solid state grafting copolymerization of acrylamide (AM) onto poly(vinyl alcohol) (PVA) was conducted with ammonium persulfate and sodium bisulfite redox system as initiators. Before the reaction the PVA powder and required amount of AM were mixed evenly, and sprayed with water to swell the PVA powder and to dissolve AM. Then the swollen PVA powder was sprayed with the redox solution, and the reaction temperature was controlled at a temperature between 30°C and 80°C for 120 min. The grafting percentage and efficiency were determined as functions of monomer/PVA ratio, initiator concentration and reaction temperature. The structure and performance of the graft copolymers were confirmed by FTIR-ATR, XRD, ¹³C NMR, and thermogravimetric analysis, together with mechanical property and apparent viscosity measurements. It has been confirmed that grafting copolymerization of AM onto PVA initiated by this redox system occurred with higher grafting percentage and efficiency in the solid state. The thermal stability and water-solubility of grafted PVA were found to be better than those of unmodified PVA. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2013**, *000*, 39938.

KEYWORDS: swelling; grafting; hydrophilic modification; solid state; redox initiation

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INTRODUCTION

Poly(vinyl alcohol) (PVA) is a well-known water-soluble, biodegradable, and semi-crystalline polymer, which had been produced industrially by hydrolysis of poly(vinyl acetate). The presence of its hydroxyl groups on PVA backbone makes it possible to react with appropriate reagents under certain conditions.^{1–3} As the ever-increasing demand of different technical fields for suitable performance of PVA, there is requirement for subtle differences in chemical structure of PVA derivatives. Graft copolymerization is one of important techniques employed by polymer chemists for modifying the chemical and physical properties of a polymer.⁴ For example, a modified PVA possesses a hydrophilic backbone of PVA and hydrophobic branched chains after being grafted by vinyl monomers,⁵ which can serve as an amphiphilic compatibility-reagent between a hydrophobic polymer and a hydrophilic polymer.

A wide range of monomers has been successfully grafted to PVA in aqueous medium^{6–9} and initiated by ceric ammonium nitrate,^{10–14} potassium persulfate,^{15,16} and supernormal valence transition-metals.^{17,18} In an aqueous medium, the production efficiency could be limited severely by PVA concentration due to its solution viscosity. As the modification process finished, the product, if necessary, can be separated from the solution, dried and crushed. These processes usually consume a large amount of

water and energy. Fortunately, a known solid state reaction has been developed for a few post-modification processes of PVA, which is a useful technique for designing materials with a wide variety of properties.^{19,20} The advantages of the solid state modification include a short process and inexpensive equipment,^{21,22} implying to be economic, effective, energy-saving, and easy to operate.

This study relates to a modified PVA and its preparation by free radical grafting in a solid state process. Acrylamide has been selected as a monomer for improving physical and chemical properties of PVA, especially for hydrophilicity. A water-soluble redox system was used to initiate the graft copolymerization. As a result, a PVA-graft-polyacrylamide copolymer with higher thermal stability and solubility at low temperature can be produced by the practically energy-saving process.

EXPERIMENTAL

Materials

PVA1799 powder was supplied by Sichuan Vinylon Co. (Chongqing, China), with an average polymerization degree 1700 and alcoholysis degree 99.0 mol %. Analytically pure reagents of acrylamide (AM) fine powder, ammonium persulfate (APS) and sodium bisulfite (SB) were supplied by Kelong Chemical Reagent Co. (Chengdu, China). Absolute ethyl

alcohol, ethanediol, and acetic acid with analytical grade were used to remove the unreacted monomer and homopolymer from the copolymer samples.²³ Distilled water was used in all of the experiments.

General Method of the Graft Copolymerization in Solid State

A known amount of the original PVA powder and required amount of AM were mixed evenly in a vessel, which were sprayed with a limited amount of distilled water while stirring constantly for 60 min at 30°C to swell the PVA powder and to dissolve AM. Quantitative ammonium persulfate (APS) and sodium bisulfite (SB) were dissolved in water, respectively, mixed and then sprayed into the vessel under stirring. The mass ratio of APS to SB was restricted at 1 : 2 in the initiator mixture solution, and the total amount of water added in the reaction system was controlled to 16% based on dry weight of PVA. Then the temperature was raised to a temperature ranging from 30 to 80°C to initiate the grafting reaction and maintained at the temperature for 120 min with stirring. The graft copolymerization was performed under conditions of different monomer mass, initiator concentrations and temperatures, respectively. After that, the resultant was collected from the reaction vessel and dried in a vacuum oven at 50°C, weighed as W_1 . The homopolymer and unreacted monomer were removed from the crude graft copolymer by immersing it in a mixture of ethanediol and acetic acid (3 : 2, v/v) for 24 h, filtrated and followed by solvent extraction with the same solvent mixture in a Soxhlet apparatus²³ for 8 h at temperature 210°C. After washed with acetone and filtrated, the copolymer was then dried under vacuum at 50°C and weighed as W_2 .

Grafting Parameters Determination

Grafting percentage (G_p) and grafting efficiency (G_e) were used to evaluate the graft copolymerization.

$$G_p = \frac{W_2 - W_0}{W_0} \times 100\% \quad (1)$$

$$G_e = \frac{W_2 - W_0}{W_1 - W_0} \times 100\% \quad (2)$$

where W_0 denotes the weight of PVA, W_1 the weight of crude graft copolymer, and W_2 the weight of pure graft copolymer.

Film-Forming Process and Mechanical Property Measurement

Aqueous solutions (4 wt %) of PVA samples before and after grafting were cooked at 95°C for 50 min, severally. Each of the cooked solutions in 60 mL volume was spread out with a syringe onto a 210 mm × 150 mm of glass dish paved with a polyester film of the same size, which rested on a leveled surface in ambient condition until the casting film was dried. The dried PVA film (about 0.1 mm thickness) was separated from the polyester film and equilibrated further in a desiccator with controlled RH 68 % (over a saturated solution of CuCl_2) at room temperature for 3 days.

As the film was equilibrated, the exact thickness of the film was measured using a centesimal thickness tester (trade name: CH-10-AT; made by Shanghai Liuling Instrument Co., Shanghai, China). For every sample, ten data were recorded and the average thickness was taken. The tensile performance of PVA films were determined using a tensile testing equipment (trade

name: YG061; made by Laizhou Electron Instrument Co., Laizhou, China) with a clamping distance of 100 mm and stretching speed of 100 mm/min. For each set of data, 10 samples were tested, and the average values with the standard deviation were calculated.

Structure Characterization

FTIR spectra of the cast films were recorded by attenuated total reflection (ATR) method in FTS3000 FTIR Spectrum Scanner (Hercules). After dried over P_2O_5 powder, each film was allowed to contact intimately with the surface of the ATR crystal. The spectra data were collected over 32 consecutive scans with a resolution of 4 cm^{-1} at room temperature.

X-ray patterns of PVA granules before and after grafting were analyzed using an X-ray diffractometer (XRD D/max IIIA; Rigaku Co., Japan) with Cu radiation at a voltage of 40 kV and an electric current 30 mA. The samples were scanned between $2\theta = 5 \sim 40^\circ$ with a scanning speed of $0.5^\circ/\text{min}$.

Spectra of ^{13}C NMR was recorded by Bruker AV II-600 spectrometer (Bruker Corporation, Switzerland). It was operated at a frequency of 400 MHz with 256 numbers of scans, using deuterium oxide (D_2O) as the solvent.

Thermal Analysis, Apparent Viscosity, and Water-Solubility Testing

Thermogravimetric analysis (TGA) was performed with a TA Instruments (Netzsch TG 209F1, Germany) thermogravimetric analyzer under nitrogen atmosphere from 30 to 600°C at a heating rate of $10^\circ\text{C}/\text{min}$.

The viscosity of the grafted PVA and original PVA of 4 wt % aqueous solutions was tested by using a NDJ-79 rotational viscometer (Shanghai Analysis Instrument Co., Shanghai, China) in a constant temperature water bath at $20 \pm 0.5^\circ\text{C}$. The data presented are average of the three tests.

The test for water-solubility was carried out as follows: The sample (grafted or original PVA) 3 g, accurate to 0.0001 g, was dissolved in 100 mL of distilled water in a flask in water bath at a constant temperature ($T_s = 30\text{--}100^\circ\text{C}$) for 1 h with magnetic stirring. The resultant solution was transferred into a 100 mL volumetric flask, together with the undissolved PVA residues, and the flask was full-scaled with water. The upper solution of 25 mL was taken out after standing and equilibrium, and dried at 102°C to a constant weight. The water solubility $S\%$ was calculated according to eq. (3):

$$S\% = \frac{4w_1}{w_0} \times 100\% \quad (3)$$

where w_1 denotes the weight of dissolved sample; w_0 denotes the weight of analyzed sample.

RESULTS AND DISCUSSION

Effect of Grafting Conditions on the Grafting Copolymerization

The solid state modification method used in the article is for a chemical conversion or reaction of a polymer in the forms of film,¹⁶ granules,¹⁹ particles,²⁰ or powders,¹³ which is characterized by a host polymer in solid state as a feature. In the process,

a reactive guest reagent is sometimes carried by water or organic solvents to contact and react molecularly with the host polymer. The solvent amount is always limited to allow the polymer swelling and to carry the guest reagent into the host matrix, and is not enough to dissolve the polymer solids during the modification process.¹³ In our experiment, the pre-mixed PVA powder and AM monomer were sprayed with water in a required time, and then was sprayed with a redox initiator (ammonium persulfate and sodium bisulfite). The effects of monomer/PVA ratio (wt/wt), redox initiator/PVA concentration (wt %) and temperature on the graft copolymerization were investigated after the reaction time 2 h.

Monomer/PVA Ratio. The effect of monomer/PVA ratio on the grafting is shown in Figure 1. The G_p and G_e went up with an increase in the monomer/PVA ratio and then decreased as the ratio exceeded 0.7, when the other reaction conditions were kept unchanged. As the AM/PVA mass ratio was 0.7 under the reaction conditions, the G_p and G_e reached up to 64.6 and 93.9%, respectively. The high efficiency means low homopolymer formed in the solid-state grafting copolymerization. This may be due to relatively closer contact of AM monomer with PVA macromolecules in solid-state, in comparison with conventional solution grafting copolymerization, especially when the monomer/PVA ratio was lower than 0.7. The availability of monomer molecules in the proximity of PVA, together with hydrophilic nature of both the AM and PVA, could be the reason of higher G_e associated with the solid-state grafting copolymerization. With a further increase in the AM/PVA ratio over 0.7, however, both the G_p and G_e significantly decreased. This suggests that the probability of homopolymerization reaction was more than the graft copolymerization.

Initiator/PVA Concentration. The results obtained by changing the initiator concentration for the graft polymerization are presented in Figure 2. It is observed that the G_p and G_e went up with an increase in the initiator concentration, and then slightly dropped. This happened because an increasing amount of radicals could attack both the AM monomer and the PVA backbone directly, which initiated the graft copolymerization

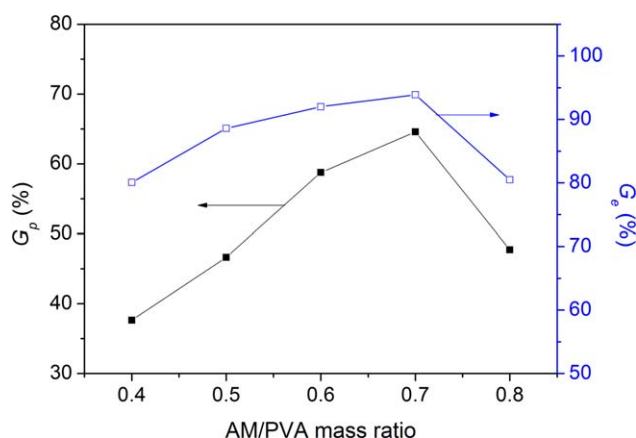


Figure 1. Effect of monomer/PVA ratio on the grafting copolymerization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

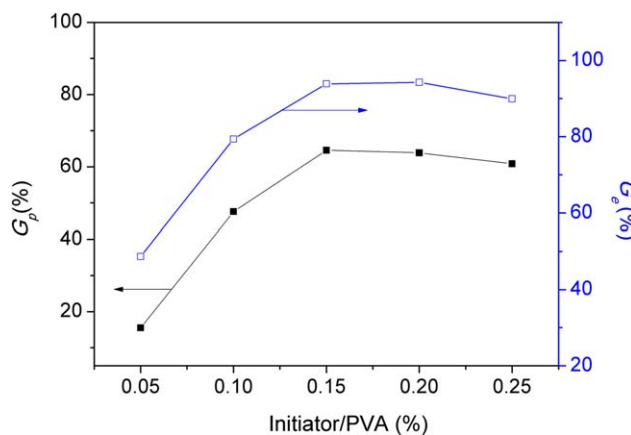


Figure 2. Effects of initiator/PVA ratio on the grafting copolymerization. The conditions: monomer/PVA = 70%; temperature = 60°C; time = 2 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

between PVA and AM. As a result, G_p and G_e grew. The G_e can be up to 94.3% when the redox initiator/PVA concentration was 0.15 wt % under the reaction conditions. Nevertheless, in the presence of excess initiator, more free radicals of polymer or monomer generated and participated in chain termination and homopolymerization.¹⁶ This resulted in a decrease in the grafting percentage and efficiency accordingly.

Temperature. At a fixed reaction condition, the relationship between reaction temperature and the result of grafting copolymerization was investigated as shown in Figure 3. The G_p and G_e showed an uptrend first with increasing temperature up to 60–70°C and then followed by a downward trend. The favorable effect of temperature on grafting could be ascribed to diffusion enhancement of monomer and initiator molecules into the PVA matrix, resulting in the increase of grafted propagation onto PVA. The decrease in the G_p and G_e above a certain temperature (70°C) can be attributed to more free radicals generated in favor of higher rate of termination of the growing chain.¹⁶

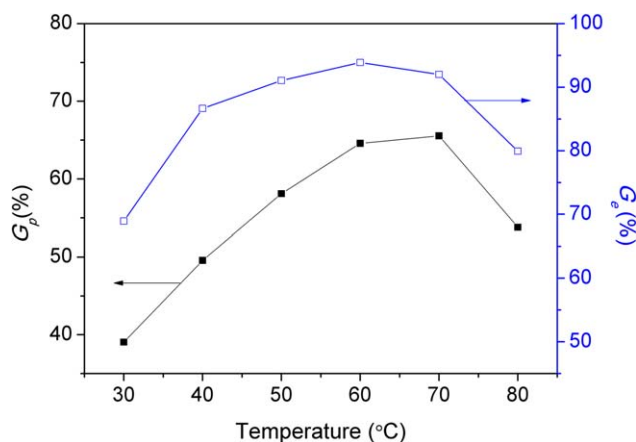


Figure 3. Effect of temperature on the grafting copolymerization. The conditions: initiator/PVA ratio = 0.15%; monomer/PVA = 0.7; time = 2 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

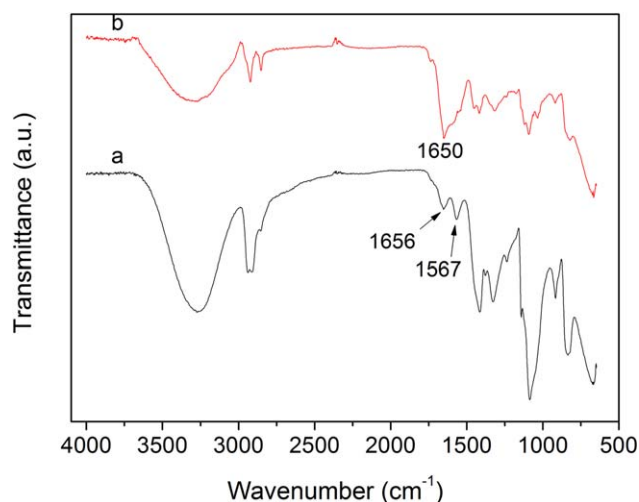


Figure 4. FTIR ATR spectra of (a) original PVA and (b) PVA-g-PAM ($G_p = 64.6\%$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Characterization of the Graft Copolymer

FTIR Spectroscopy. The IR spectra of original PVA and purified PVA-g-PAM ($G_p = 64.6\%$) are shown in Figure 4. Compared with the original PVA, the grafted product had a weaker and wider absorption band about 3300 cm^{-1} that corresponds to association of amide and hydroxyl groups, and a stronger absorption band at 1650 cm^{-1} ($\nu_{\text{C=O}}$) is characteristic of amide groups. It is evidence that the final product was obviously a graft copolymer of PVA-g-PAM.

Crystallization Analysis. The X-ray diffraction patterns of original PVA and PVA-g-PAM ($G_p = 64.6\%$) were measured and are shown in Figure 5. The original PVA has a typical crystalline structure with diffraction peaks at 2θ 11.3° , 19.3° , and 22.0° . It was observed that diffraction peaks were weakened after the graft copolymerization at the corresponding 2θ angles, especially that the peak at 11.3° almost disappeared and the peak at 19.3° obviously weakened. It suggests that the graft branched chain of

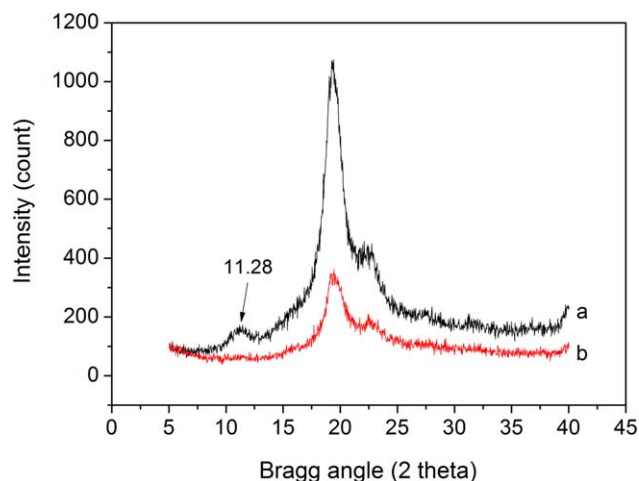


Figure 5. X-ray diffraction patterns of (a) original PVA and (b) PVA-g-PAM ($G_p = 64.6\%$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PAM can loosen the crystal structure of PVA. The crystallinity values calculated by the software of MDI Jade 5.0 decreased from the original PVA 50.5% to the PVA-g-PAM 10.4% due to the destruction of the ordered packing.

^{13}C NMR Spectroscopy. The ^{13}C NMR spectra of PVA and PVA-g-PAM ($G_p = 64.6\%$) were shown in Figure 6, which give the characteristic chemical shifts of carbon in polymers. The labels of the C atoms were shown in Figure 7 for a speculative chemical structure of graft copolymer of PVA-g-PAM. In the PVA spectrum in Figure 6, the chemical shifts of methylene and methine carbons in the polymer backbone appeared at about 45 ppm (a) and 65 ppm (b).¹⁵ Besides the two peaks, the PVA-g-PAM gives extra peaks at about 34.4 (e), 41.7 (d), and 179.7 (c) ppm corresponding to the CH_2 , CH , and C=O groups of polyacrylamide branched chains.^{15,24,25} This confirms unequivocally the grafting of PAM to PVA.

For the grafting sites of PAM on PVA chain, Aminabhavi and Naik²⁶ considered alkoxy radicals on PVA as the grafting sites in the presence of Ce^{4+} as the initiator, in which the hydrogen radical is abstracted from the hydroxyl group of the PVA substrate. Whereas in the case of persulfates as initiators for grafting copolymerization of PVA, sulfate radical is readily generated from homolytic cleavage of persulfate and then the sulfate radical can abstract hydrogen atom from the methine carbon atom of PVA.^{15,16,24} A grafting copolymerization may occur at varied active centers of PVA with different initiating system. Because of the complexity of radical grafting copolymerization, the real reaction mechanism remains still unknown.

In our graft copolymerization with APS and SB as redox initiators, such radicals, as $\text{SO}_4^{\cdot-}$, HO , and $\text{HSO}_3^{\cdot-}$, can be generated.^{16,27,28} This may be a more complex initiation of grafting copolymerization. Based on these free radicals and their random initiation, we proposed a mechanism involving both the polymeric alkoxy radicals and methine carbon radicals, as shown in Figure 7.

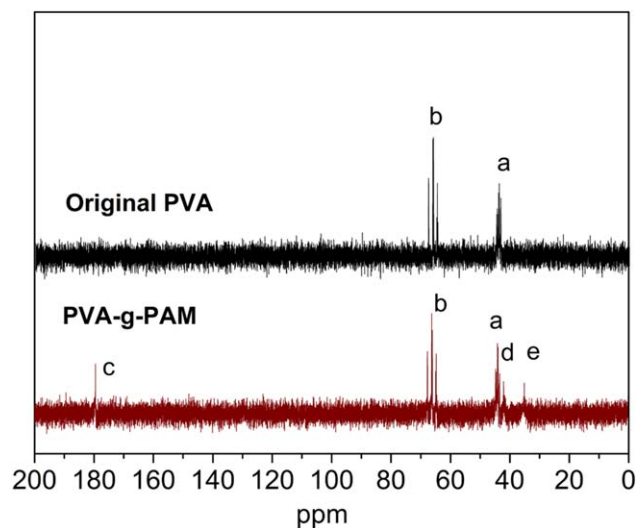


Figure 6. ^{13}C NMR spectra of (a) original PVA; (b) PVA-g-PAM ($G_p = 64.6\%$) in D_2O . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

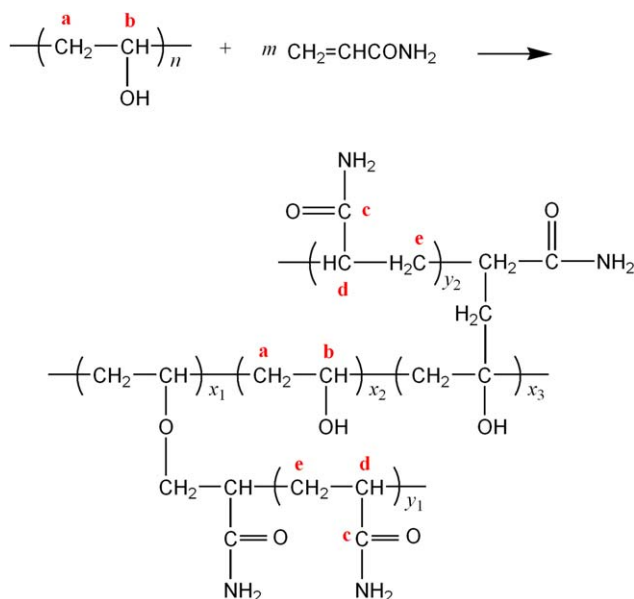


Figure 7. Schematic illustration of PVA-g-PAM initiated by redox system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Properties of the Graft Copolymer

Thermal Behavior. The effect of grafting on the thermal stability of the prepared copolymers was studied by using TGA and the curves of original and grafted PVA were shown in Figure 8. All weight retentions at the corresponding temperatures were measured. Both original and grafted PVA had a slight weight loss in the early stage of thermal analysis, which could be assigned to the loss of moisture, the trapped and adsorbed water by PVA.^{29,30} The original PVA showed roughly two steps of thermal degradation in the whole range of testing temperature. The one step was from 240.4 to 288.6°C with weight loss 60.6% corresponding to dehydration of PVA chains and formation of polyene structure, and the other step from 411 to 520°C with weight loss 23.5% was relative to degradation of the polyene chains.³⁰

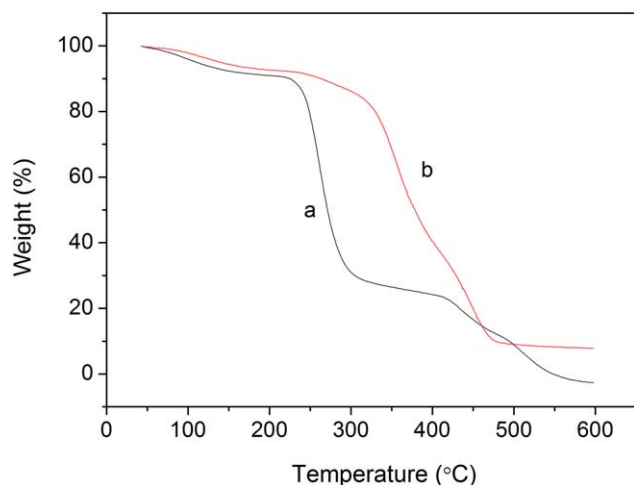


Figure 8. The TGA curve of (a) original PVA; (b) PVA-g-PAM ($G_p = 64.6\%$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For the grafted PVA, however, the two degradation steps seemed to be one compression step from a higher beginning of degradation temperature 282.4–466.7°C, relative to 75.2% of weight loss. Both the higher beginning temperature and less total weight loss means that the grafted PVA are more thermally stable than the original PVA. This is consistent with observations of Demchenko's group³⁰ and Abdel-Razik's group.³¹ The main reason for this has been claimed to be the result of cooperative hydrogen bonding between the main and graft chains and then cross-linking before the thermal decomposition.³⁰

Water Solubility. In general, solubility of a soluble polymer depends on largely on its molecular weight and crystallinity. The water-solubility testing of a series of grafted PVAs having different grafting percentages were carried out. The solubility curves of grafted PVAs in 30–90°C of water were shown in Figure 9. From these curves, it can be found that the water-solubility of the PVA-g-PAM resultants increased with increase of the grafting percentage, also with dissolving temperature. All of the grafted products showed better solubility than the original PVA at the dissolving temperature between 30 and 70°C. However, the solubility of grafted products was lower than the original PVA when the dissolution temperature was at 80°C or above, and some insoluble residues left were observed for the graft products at the end of the testing. That may be resulted from the formation of cross-linking accompanied by the grafting copolymerization.

For the original PVA, there was a quick dissolving temperature range 60–80°C, supposedly relative to the glass transition temperature of PVA and decrystallization of PVA by water. The PVA-g-PAMs with lower grafting percentage experienced a similar dissolution pattern with the original PVA. In contrast, the modified PVA products with higher grafting percentage 58.1% or above showed no any special quick dissolving temperature range. This effect may be explained by more hydrophilic grafted chains of polyacrylamide on PVA as the G_p increased, which

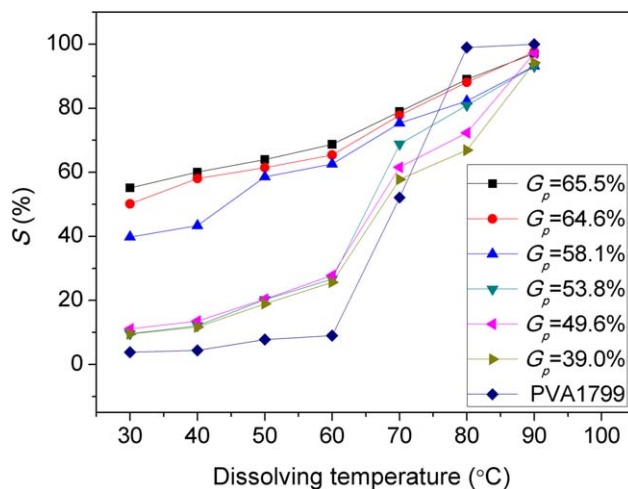


Figure 9. The relationship between solubility and dissolving temperature for the original PVA and PVA-g-PAM with different grafting percentages. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Mechanical Properties of Films and Apparent Viscosity of 4% Solution

Sample	Grafting percentage (%)	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)	Apparent viscosity (mPa s)
PVA-g-PAM	39.0	30.2 ± 1.2	205.9 ± 7.7	12.8 ± 0.6	12.5 ± 0.5
	49.6	29.5 ± 1.4	205.8 ± 8.2	18.8 ± 0.5	9.2 ± 0.2
	53.8	23.9 ± 1.1	196.5 ± 7.6	20.0 ± 0.4	8.2 ± 0.2
	58.1	27.3 ± 1.1	201.0 ± 8.3	15.6 ± 0.4	7.0 ± 0.5
	64.6	28.6 ± 1.2	192.5 ± 7.5	19.4 ± 0.4	6.8 ± 0.2
	65.5	28.7 ± 1.1	195.4 ± 8.8	21.1 ± 0.5	5.0 ± 0.5
Original PVA	-	35.2 ± 1.7	220.3 ± 10.2	12.4 ± 0.6	30.0 ± 0.5

can effectively reduce the crystalline of PVA during the grafting copolymerization.

Mechanical Properties and Apparent Viscosity of the Samples.

Tensile properties, such as tensile strength, elongation at break, and Young's modulus, were presented for all grafted PVA and original PVA films in Table I. The apparent viscosity was decreased with the increasing of the grafting percentage. These may arise from oxidation and a cleavage of C–C bond during the graft copolymer reaction, in which the PVA experienced a oxidative degradation process.²² However, the tensile strength of grafted PVA films showed a tendency of first decreasing and then increasing with the increasing of grafting percentage. The initiate decrease in tensile strength of the PVA-g-PAM could be due to reduction of molecular weight of PVA backbone, as indicated in lower viscosity. While for the increase in tensile strength of the copolymer with higher G_p , intermolecular interactions of the PVA-g-PAM in the amorphous region may be a critical factor. The branched PAM chains could enhance hydrogen bonding between acetylamino in the branched PAM chain and hydroxyl in PVA owing to hydrogen bond cooperativity, in comparison with that between hydroxyl pairs of the original PVA.^{30,32}

Also, it was found from Table I that the Young's modulus of grafted PVA films had an increase against the decrease of the tensile strength with the increase of G_p up to 53.8%, the reason for which could also be the hydrogen bonding between the branched PAM chain and the backbone PVA. The affecting factors behind this phenomenon possibly include molecular weight (both backbone and graft chain), grafting percentage, grafting density,³³ chemical cross-linking,³⁴ or their combination. Young's modulus of a polymer is the initial response to stress, closely relative to interaction of polymer chains; while the tensile strength is mainly related to the molecular weight. Small changes in chemical structure and/or physical bonding will lead to different variation trends of the tensile strength and Young's modulus, although they are interdependent features for a polymer.

CONCLUSIONS

Hydrophilic modification of PVA can be realized in solid state by radical graft copolymerization of AM onto PVA with persulfate ammonium and sodium bisulfate redox system as initiators. IR and ¹³C NMR demonstrated the formation of graft copolymer. The crystallinity of PVA-g-PAM decreased due to the graft reaction. The result of TGA indicated that the grafted copoly-

mer had more thermally stable than the original PVA. All the grafted products showed better solubility in water than the original PVA between 30 and 70°C. The tensile strength of grafted PVA films and the apparent viscosity of grafted PVA solution were decreased. The modification process had advantages to be economic, effective, energy-saving, and easy to operate.

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