

# Solid-State Grafting of Succinic Anhydride onto Poly(vinyl alcohol)

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**ABSTRACT:** The graft reaction of succinic anhydride onto poly(vinyl alcohol) (PVA) was catalyzed by *p*-toluenesulfonic acid monohydrate in solid state. The infrared spectra and <sup>1</sup>H-NMR spectra confirmed that succinic anhydride was successfully grafted onto PVA backbone. The influences of reaction temperature, reaction time, the amount of succinic anhydride, and the amount of catalyst on the graft reaction were studied. Uncrosslinked PVA graft copolymer with grafting degree up to about 6.5% could be obtained

under low reaction temperature, short reaction time, and low amount of catalyst, whereas crosslinked PVA with high gel content could be obtained under high reaction temperature, long reaction time, and high amount of catalyst. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 848–852, 2007

**Key words:** poly(vinyl alcohol); graft copolymers; succinic anhydride; solid state

## INTRODUCTION

Grafting reactions provide a potential route for significantly altering the chemical and/or physical properties of a substrate polymer to specific end uses.<sup>1</sup> Altering the chemical property of PVA is largely concerned by introducing carboxylic group, which also enables three-dimensional networks to be obtained in a further step. These PVA derivatives are of great interest in several industrial fields, such as temperature and pH sensitive hydrogels,<sup>2–4</sup> soft tissue replacement hydrogels,<sup>5</sup> water-ethanol mixture separation membrane,<sup>6–8</sup> heavy metal selective separation membrane,<sup>9</sup> superabsorbent polymers,<sup>10,11</sup> control release of biologically active compounds,<sup>12</sup> and polymeric catalytic membranes.<sup>13</sup>

Bodugoz et al.<sup>2</sup> grafted succinic and citric acid onto PVA by irradiation in water solution to prepare pH sensitivity hydrogels, and they also studied the affinity of grafted hydrogels for the adsorption of Ni<sup>2+</sup> and Co<sup>2+</sup> ions. Chiang et al.<sup>6,7</sup> grafted styrene-maleic anhydride hydrazine copolymer and poly(sodium salt styrene sulfonic acid-*co*-maleic acid) onto PVA by a condensation coupling reaction in dimethyl sulfoxide solution to prepare water-selective membrane for the pervaporation separation of water-ethanol mixture, respectively.

Solid-state grafting of functional monomer onto polypropylene has widely been reported,<sup>14</sup> but graft-

ing of succinic anhydride onto PVA in solid-state has rarely been reported in published articles so far. In this work, uncrosslinked PVA grafted with succinic anhydride or crosslinked PVA with high gel content could be obtained in solid-state graft reaction condition, which could avoid using solvent in solution graft reaction condition. The influences of various factors such as reaction temperature, reaction time, the amount of succinic anhydride, and the amount of catalyst on grafting degree and gel content were discussed.

## EXPERIMENTAL

### Material

PVA (Wan Wei, China) had a degree of hydrolysis of 99% and an average degree of polymerization of 1700. Succinic anhydride, *p*-toluenesulfonic acid monohydrate, and acetone were obtained from Shanghai Chemicals, and were used as received without further purification.

### Solid-state graft reaction

The solid-state graft reactions were carried out using a SK-160B two roll mills (Shanghai Rubber Machinery Works, China). The PVA and succinic anhydride were previously vacuum dried to constant weight at 80°C, respectively. In a typical reaction, precise amount of PVA (100.0 g), succinic anhydride (28.4 g), and catalyst (*p*-toluenesulfonic acid monohydrate, 3.0 g) were mixed in a tissue disintegrator, and then the mixture was put into the two-roll mills, which was already

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adjusted to the desired reaction temperature. The rough sample was taken out from the two-roll mills after desired reaction time, and then it was purified by the method explained in the following paragraph. The typical melting point of PVA is about 226°C,<sup>15</sup> whereas the reaction temperature of this grafting system is lower than 65°C, so the graft reaction takes place in solid state.

### Determination of gel content and grafting degree

The rough sample was extracted by distilled water using Soxhlet extraction. The crosslinked graft copolymer, which was dried to constant weight in vacuum oven at 80°C, remained in extractor, whereas the uncrosslinked graft copolymer, ungrafted succinic anhydride and catalyst were extracted from the rough sample by distilled water. The gel content (GC) of graft copolymer is given by

$$GC(\%) = \frac{m_2}{m_1} \times 100 \quad (1)$$

where  $m_1$  is the weight of rough sample (g) and  $m_2$  the weight of crosslinked graft copolymer (g).

The uncrosslinked graft copolymer was precipitated by pouring the water solution of uncrosslinked graft copolymer, ungrafted succinic anhydride, and catalyst into 10-fold volume of acetone with vigorous stirring, and then filtered after 2 h stirring. The percolate, which contained ungrafted succinic anhydride and catalyst, was collected and titrated by 0.1 mol/L sodium hydroxide (NaOH) ethanol solution using phenolphthaleine as indicator. The overall grafting degree (GD) is given by

$$GD(\%) = \frac{A - (V_1 - V_0) \times C \times 10^{-3} \times M}{m_0} \quad (2)$$

where  $A$  is the amount of succinic anhydride added in the reaction (g),  $V_0$  the amount of titration solution consumed by the percolate coming from the reaction where the succinic anhydride was not added, but the catalyst was added (mL),  $V_1$  = the amount of titration solution consumed by the percolate from certain reaction (mL),  $C$  = the mole concentration of titration solution (mol/L),  $m_0$  = the weight of PVA added in the reaction (g),  $M$  = molecular weight of succinic anhydride.

The uncrosslinked graft copolymer was dried to constant weight in a vacuum oven at 30°C. The grafting degree of uncrosslinked graft copolymer ( $GD_1$ ) was determined by dissolving 0.20 g sample in 40 mL distilled water, and then titrated by 0.1 mol/L NaOH ethanol solution using phenolphthaleine as indicator.  $GD_1$  was defined as the amount of acid grafted as a

percentage of PVA and calculated by the following equation:

$$GD_1(\%) = \frac{(V_1 - V_0) \times 10^{-3} \times C \times M}{m - (V_1 - V_0) \times 10^{-3} \times C \times M} \times 100 \quad (3)$$

where  $V_0$  = the amount of NaOH consumed by using pure PVA as reference (mL),  $V_1$  = the amount of NaOH consumed by grafted sample (mL),  $m$  = the weight of sample (g),  $C$ ,  $M$  is the same as eq. (2).

The grafting degree of crosslinked graft copolymer ( $GD_2$ ) is shown in eq. (7), which is calculated from eqs. (4–6).

$$m_0 \times \frac{GD}{100} = m_3 \times \frac{GD_1}{100} + m_4 \times \frac{GD_2}{100} \quad (4)$$

$$m_0 = m_3 + m_4 \quad (5)$$

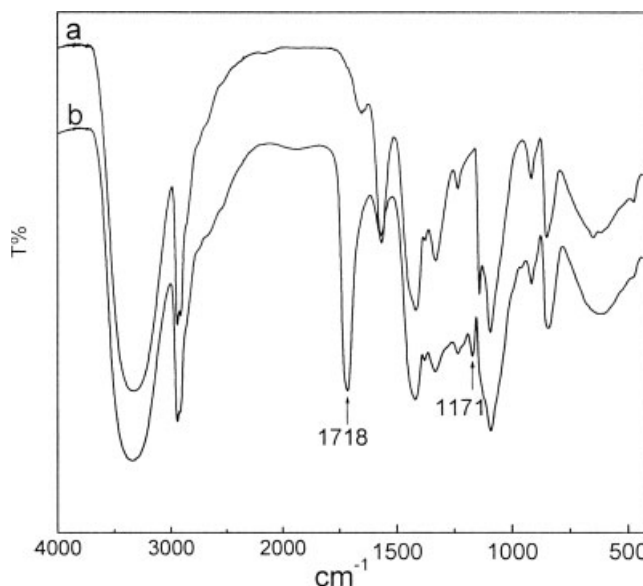
$$GC = \frac{m_4 + m_4 \times \frac{GD_2}{100}}{m_0 + m_0 \times \frac{GD}{100}} \times 100 \quad (6)$$

$$GD_2(\%) = \frac{100 \times (GD - GD_1) + (1 + 0.01GD) \times GD_1 \times GC}{GD_1 - GD + (1 + 0.01GD) \times GC} \quad (7)$$

where the  $m_0$ ,  $m_3$ , and  $m_4$  represent the PVA in total graft copolymer, uncrosslinked graft copolymer, and crosslinked graft copolymer, respectively.

### Characterization

Infrared spectroscopic information of PVA and uncrosslinked graft PVA was obtained using a Perkin



**Figure 1** Infrared spectra of PVA and uncrosslinked graft PVA (a) PVA; (b) uncrosslinked graft PVA.

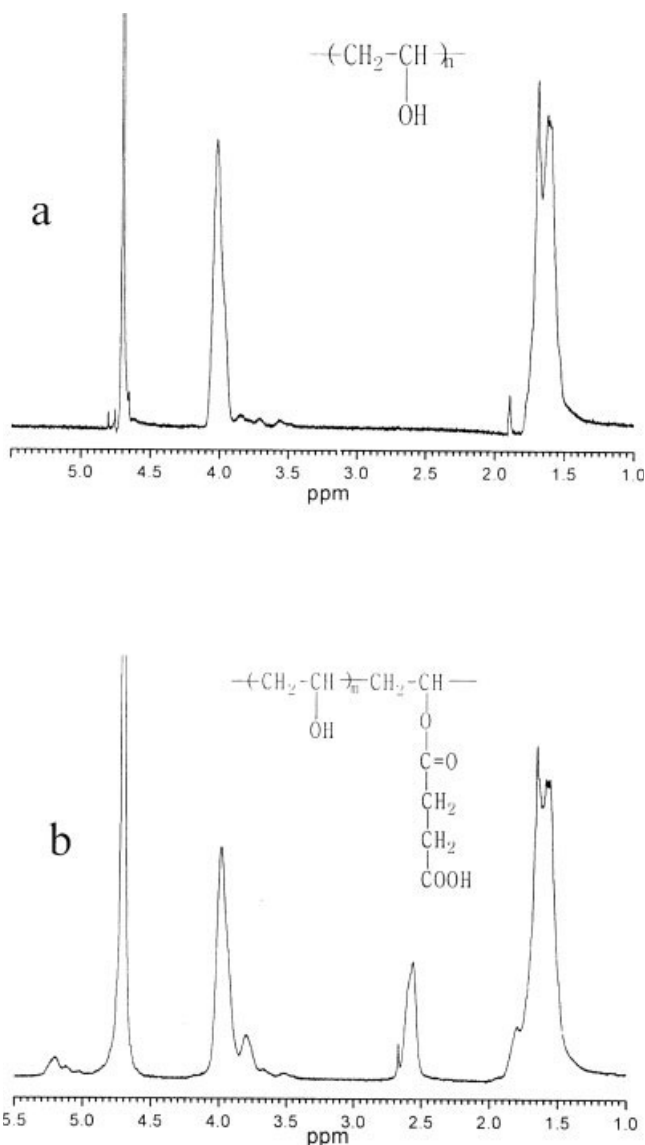
Elmer Paragon 1000 Fourier Transform Infrared spectrophotometer (FTIR). Samples were cast into films of 0.010–0.015 mm in thickness using distilled water as solvent. No significant changes were observed in FTIR spectrum of the grafted PVA after further purification, and this indicated that the purification procedure was effective.

The NMR spectra were recorded using Bruker AV400 spectrometer operating at a proton frequency of 400.13 MHz. The PVA and uncrosslinked graft PVA were dissolved in D<sub>2</sub>O.

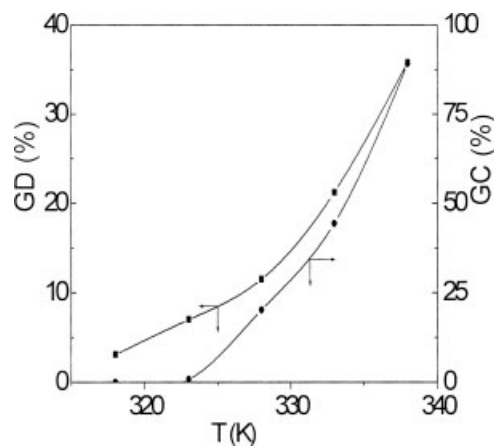
## RESULTS AND DISCUSSION

### Evidence of grafting

Figure 1 shows the infrared spectra of PVA and uncrosslinked graft PVA. The appearance of new ab-



**Figure 2** <sup>1</sup>H-NMR spectra of PVA and uncrosslinked graft PVA in D<sub>2</sub>O (a) PVA; (b) uncrosslinked graft PVA.



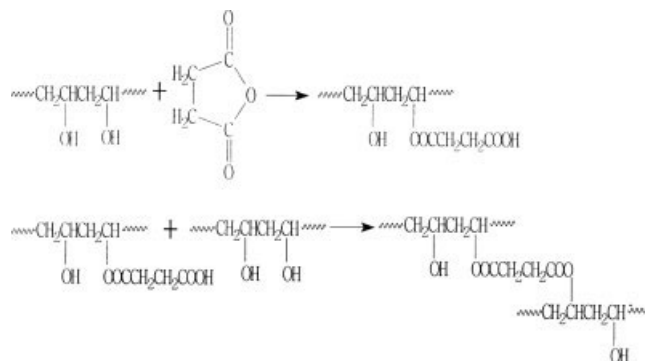
**Figure 3** Effect of reaction temperature on grafting degree and gel content: PVA = 100 g; succinic anhydride = 50 g; *p*-toluenesulfonic acid monohydrate = 2 g; reaction time = 10 min.

sorbance at 1718 and 1171 cm<sup>-1</sup> of grafted PVA indicates the introduction of C=O and C—O groups of succinic anhydride onto PVA.

Figure 2(b) shows the <sup>1</sup>H-NMR spectrum of uncrosslinked graft PVA taken in D<sub>2</sub>O. All the peaks, which have appeared in the PVA shown in Figure 2(a), have also appeared in the uncrosslinked graft PVA with a very little change in the chemical shift values. However, extra peaks appear at 2.6 ppm and 5.2 ppm corresponding to methylene protons of succinic anhydride and methine protons attached to —OCOCH<sub>2</sub>CH<sub>2</sub>COOH, respectively. This clearly confirms the grafting of succinic anhydride onto PVA.

### Effect of reaction temperature

The effect of reaction temperature on grafting degree and gel content is shown in Figure 3. The grafting degree and gel content increase with the increase in reaction temperature. The succinic anhydride reacting with PVA may be described as Scheme 1, and succinic anhydride reacts with hydroxy group of PVA through ring opening reaction to produce side carboxylic



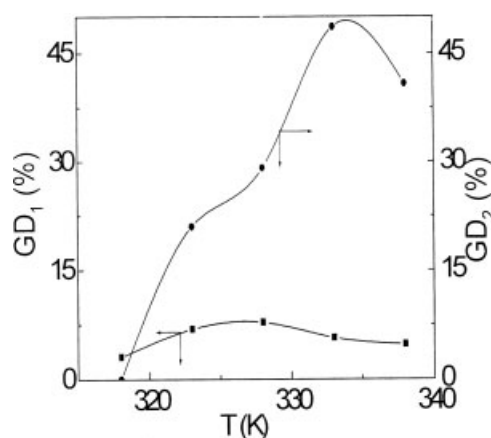
**Scheme 1**

group, which then may react with the inter and/or intra hydroxy group of PVA to generate crosslinked PVA. The rapid of succinic anhydride reacting with hydroxy group of PVA increases with increasing reaction temperature, so the grafting degree increases. The reaction of carboxylic group with hydroxy group is more difficult than that of anhydride group with hydroxy group, as a result, there observed no gel content at low temperature. The reaction rapid of carboxylic group with hydroxy group increased considerably when reaction temperature increased, so the gel content of grafting system increased with increasing reaction temperature.

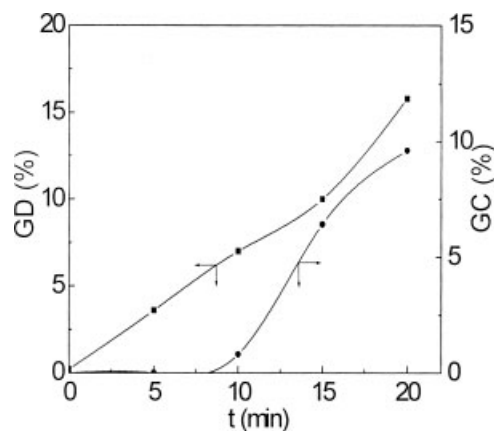
Figure 4 illustrates that the grafting degree of crosslinked graft copolymer ( $GD_2$ ) initially increases rapidly with increasing reaction temperature, but decreases when reaction temperature exceeds 333 K. On the other hand, the grafting degree of uncrosslinked graft copolymer ( $GD_1$ ) changes indistinctively. The grafting degree of crosslinked graft copolymer is much higher than that of uncrosslinked graft copolymer in most cases. The  $GD_1$  and  $GD_2$  decrease when reaction temperature exceeds 333 K may be due to volatilization of succinic anhydride at high temperature.

#### Effect of reaction time

Figure 5 shows the effect of reaction time on grafting degree and gel content. The grafting degree increases steadily with increasing reaction time, whereas the gel content is almost zero during the beginning of 5 min, and then it increases rapidly with increasing reaction time. There is considerable shearing strength, which may accelerate the reaction of carboxylic group with hydroxy group in Scheme 1, existing in this graft system. As a result, the crosslinking of PVA is remarkable when reaction time is long enough.



**Figure 4** Grafting degree versus reaction temperature. The reaction condition is the same as Figure 3.



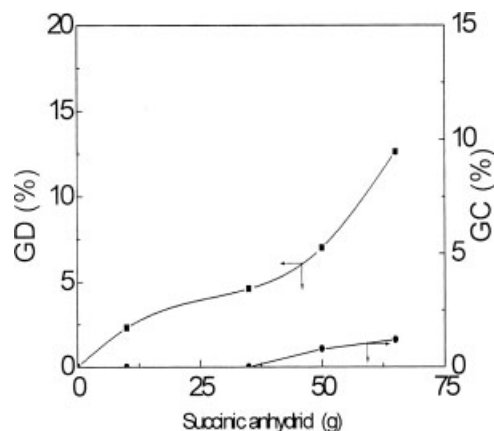
**Figure 5** Effect of reaction time on grafting degree and gel content: PVA = 100 g; succinic anhydride = 50 g; *p*-toluenesulfonic acid monohydrate = 2 g; reaction temperature = 323 K.

#### Effect of the amount of succinic anhydride

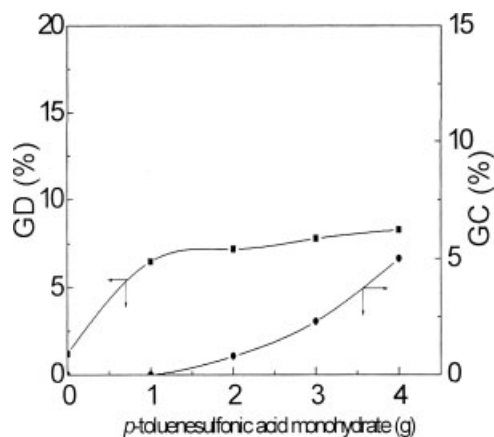
The influence of the amount of succinic anhydride on grafting degree and gel content is illustrated in Figure 6. The grafting degree increases initially slowly with the increasing amount of succinic anhydride, and then accelerates at about 35 g of succinic anhydride. The crosslinked PVA is rarely observed when succinic anhydride is less than 35 g; after that point, the gel content increases as the amount of succinic anhydride increases.

#### Effect of the amount of catalyst

Figure 7 shows the effect of the amount of catalyst on grafting degree and gel content. The grafting degree increases with increasing catalyst dosage, but levels off when catalyst dosage exceeds 1.0 g. Crosslinking of PVA does not take place when catalyst is less than 1.0 g, then the gel content increases with the increas-



**Figure 6** Effect of the amount of succinic anhydride on grafting degree and gel content: PVA = 100 g; *p*-toluenesulfonic acid monohydrate = 2 g; reaction time = 10 min; reaction temperature = 323 K.



**Figure 7** Effect of the amount of catalyst on grafting degree and gel content: PVA = 100 g; succinic anhydride = 50 g; reaction time = 10 min; reaction temperature = 323 K.

ing amount of catalyst, which accelerates the rapid of carboxylic group reacting with hydroxy group in Scheme 1.

### CONCLUSIONS

It is successful to graft succinic anhydride onto PVA by using *p*-toluenesulfonic acid monohydrate as catalyst in solid-state. One can obtain no crosslinked PVA graft copolymer with grafting degree up to about

6.5% under low reaction temperature, short reaction time, and low amount of catalyst, whereas one can obtain crosslinked PVA with high gel content under high reaction temperature, long reaction time, and high amount of catalyst.

### References

- Huang, N. J.; Sundberg, D. C. *J Polym Sci Part A: Polym Chem* 1995, 33, 2533.
- Bodugoz, H.; Pekel, N.; Guven, O. *Radiat Phys Chem* 1999, 55, 667.
- Nonaka, T.; Yoda, T.; Kurihara, S. *J Polym Sci Part A: Polym Chem* 1998, 36, 3097.
- Atta, A. M.; Arndt, K. F. *Polym Int* 2005, 54, 448.
- Jabbari, E.; Karbasi, S. *J Appl Polym Sci* 2004, 91, 2862.
- Chiang, W. Y.; Chen, C. L. *Polymer* 1998, 39, 2227.
- Chiang, W. Y.; Lin, Y. H. *J Appl Polym Sci* 2002, 86, 2854.
- Rhim, J. W.; Yeom, C. K.; Kim, S. W. *J Appl Polym Sci* 1998, 68, 1717.
- Abd El-Rehim, H. A.; Hegazy, E. A.; Ali, A. M. *J Appl Polym Sci* 2000, 76, 125.
- Ruiz, J.; Mantecon, A.; Cadiz, V. *J Appl Polym Sci* 2003, 88, 3026.
- Ruiz, J.; Mantecon, A.; Cadiz, V. *J Appl Polym Sci* 2001, 81, 1444.
- Mishra, S.; Panda, A.; Singh, B. C. *J Appl Polym Sci* 1999, 73, 677.
- Castanheiro, J. E.; Ramos, A. M.; Fonseca, I.; Vital, J. *Catal Today* 2003, 82, 187.
- Li, D.; Jia, D.; Zhou, P. *J Appl Polym Sci* 2004, 93, 420.
- Nishino, T.; Kani, S. C.; Gotoh, K.; Nakamae, K. *Polymer* 2002, 43, 2869.