

# The Thermal-Electrical Properties of Polyvinyl Alcohol/AgNO<sub>3</sub> Films

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**ABSTRACT:** In this article, one cast technique to fabricate 20–40 wt %AgNO<sub>3</sub>-doped polyvinyl alcohol (PVA) composite films of which electrical resistance sharply dropped (4–5 order) in a certain temperature range was reported. The phase, structure thermal, and electrical resistivity properties of films at different heat treatment temperatures were studied by X-ray diffraction (XRD), scanning electrical microscopy (SEM) and differential scanning calorimetry (DSC). The results showed that all the AgNO<sub>3</sub> (20–40 wt %) doped PVA films presented an exothermic peak at 182°C. And the temperature of exothermic peak kept constant for various contents of AgNO<sub>3</sub>. Meanwhile, the phase composition of the films was greatly affected by the heat treatment temperature. Ag particles

were generated during the heat treatment process, and the content of Ag particles increased with increasing the temperature. The resistivity of PVA/AgNO<sub>3</sub> films decreased with increasing the temperature. And a sharp decrease appeared at 155–165°C due to the generation and contact of a mass of Ag particles at this temperature. The thermal-electrical results suggested the applicability of these materials in temperature sensor, for example, critical temperature resistor thermistor. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 813–818, 2011

**Key words:** electrical resistivity; thermal; polyvinyl alcohol; AgNO<sub>3</sub>

## INTRODUCTION

Researchers have paid much attention to polymers in an attempt to synthesize organic polymers alternate to conventional inorganic materials.<sup>1</sup> The introduction of metal nanoparticles into polymer, can be achieved either by electrospinning polymer solutions containing the metal nanoparticles or by reducing metal salts or complexes in electrospun polymer nanofibers.<sup>2</sup> Various types of semiconducting organic polymers have excellent electrical properties. And to develop easily processed organic semiconductors, a method has been proposed using polymers as a base, which can be easily processed and modified.<sup>3</sup> Polyvinyl alcohol (PVA) is a polymer which has been studied intensively because of its good film forming and physical properties, water solubility, biocompatibility, processability, and good chemical resistance. These properties have led to its broad use and can be improved or modified by importing other composites.<sup>4</sup>

Recently, several reports have proposed a polymer prepared by silver nitrate mixed with PVA. The point of these reports attempted to create nanoparticles on morphology such as producing one-dimensional nanostructured metal material, controlling the shapes and particle sizes of noble metal nanoparticles.<sup>5</sup> A lot of methods were proposed to synthesize metal nanoparticles, such as thermal radiation,<sup>6–8</sup> ultraviolet irradiation<sup>5,9</sup> and gamma irradiation.<sup>10,11</sup> Among which thermal radiation was the easy one. However, the study related to electrical conductivity through thermal radiation has rarely been reported. Uma Devi et al. and Tawansi et al. have reported the electrical resistivity of AgNO<sub>3</sub> contained polymer would normally be classified as insulators possessing specific resistivity of the order 10<sup>7</sup>Ω·cm or greater.<sup>12,13</sup>

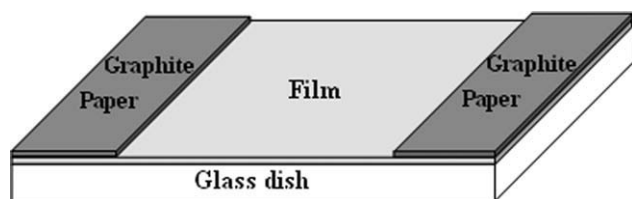
In this study, a thermal radiation technique for preparation of Ag particles from AgNO<sub>3</sub>-doped PVA composites films was reported. The Ag particles can be formed through the thermal radiation. And the electrical resistivity of the PVA/AgNO<sub>3</sub> composites can drop by several orders of magnitude in a given temperature range.

## EXPERIMENT

PVA with  $M_w = 74800$  and 99% hydrolyzed granule (Sinopharm Chemical Reagent, China), analytic-purity AgNO<sub>3</sub> (Sinopharm Chemical Reagent, China) were used as starting materials. The films of PVA

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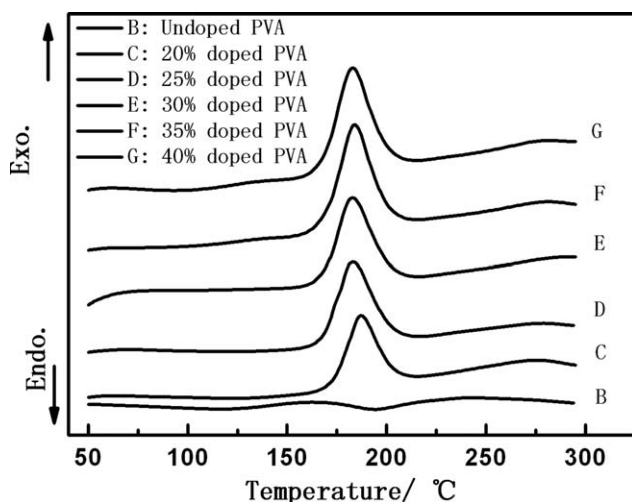
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**Figure 1** Schematic diagram of the film for conductivity measurement.

doped with different amounts of  $\text{AgNO}_3$  were prepared by a casting method.<sup>3,13,14</sup> The PVA and silver nitrate were completely dissolved in distilled water respectively. And then mixed uniformly. The viscous solutions were casted on a glass plate and dried at room temperature for 24 h. And then all the samples were put into air oven held at  $60^\circ\text{C}$  for 48 h to remove the solvent. Samples for the electrical resistance measurement were prepared by pasting two pieces of graphite paper of  $\sim 200\ \mu\text{m}$  thick on the two ends of film after the solution casting on the glass plates, as showed in Figure 1. The samples were subjected to the similar heat treatment as the previous one. The thickness of the obtained films ranged from 0.1 to 0.2 mm, and the amounts of  $\text{AgNO}_3$  in the PVA/ $\text{AgNO}_3$  films were 20, 25, 30, 35, and 40 wt %

The thermal analysis for the  $\text{AgNO}_3$ -PVA films were performed by TG/ differential scanning calorimetry (DSC) (SDT Q600, TA) in atmospherical ambience with a heating rate  $10^\circ\text{C}/\text{min}$  and temperature range of 50 to  $300^\circ\text{C}$ . The phases of the films with different heating treatment temperatures were analyzed with X-ray diffraction using Cu K $\alpha$  radiation at 40 kV and 25 mA. Morphology of film surface was observed by scanning electrical microscopy (SEM) (VEGAI XMU, Tescan, Czech Republic). The



**Figure 2** DSC curves for  $\text{AgNO}_3$ -doped PVA films with different amounts of  $\text{AgNO}_3$ .

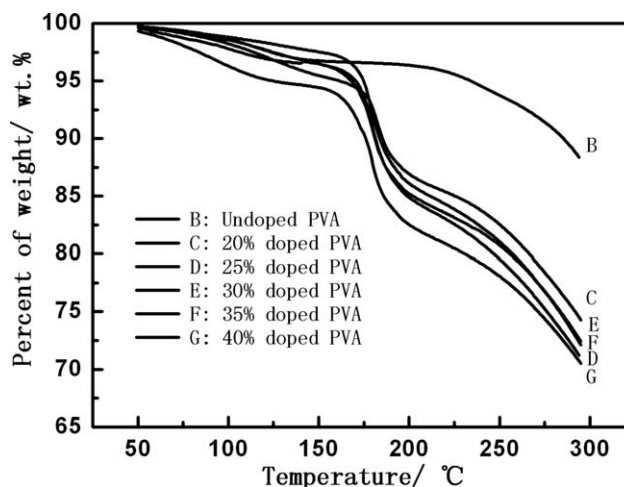
electrical resistance was measured by Fluke8846 digital multimeter using two-probe technique with a heating rate of  $3^\circ\text{C}/\text{min}$  from 25 to  $175^\circ\text{C}$ .

## RESULTS AND DISCUSSION

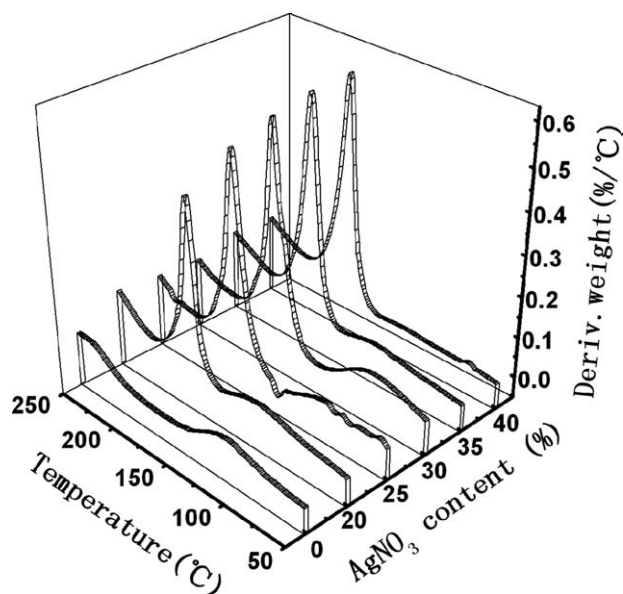
### Thermal analysis

The DSC thermograms of PVA films doped with different mass amounts of  $\text{AgNO}_3$  from 20 to 40 wt % are demonstrated in Figure 2. One exothermic peak is presented at about  $182^\circ\text{C}$  for all  $\text{AgNO}_3$ -doped PVA materials. It is well known that the thermal properties of original PVA film have the following characteristic temperatures, the glass transition temperature ( $T_g$ ):  $78^\circ\text{C}$ , the  $\alpha$ -relaxation temperature ( $T_\alpha$ ):  $110^\circ\text{C}$ , the melting temperature ( $T_m$ ):  $190^\circ\text{C}$  and the decomposition temperature ( $T_d$ ):  $270^\circ\text{C}$ .<sup>15</sup> The DSC results exhibited the exothermic peak at  $182^\circ\text{C}$  for the  $\text{AgNO}_3$ -doped PVA films and the constant exothermic temperature with increasing the amount of  $\text{AgNO}_3$  doping. The previous study reported that the value of  $T_\alpha$  shifted toward higher temperature and intensity increased with increasing the  $\text{AgNO}_3$  content,<sup>3</sup> but from the DSC results we know that the temperature of exothermic peak was the same for various additions (20–40 wt %) of  $\text{AgNO}_3$ -doped PVA films, so the exothermic peak at  $182^\circ\text{C}$  is correlated with the decomposition of the PVA phase or the PVA- $\text{Ag}^+$  chelate but not the exothermic peak of  $T_\alpha$ .

The thermogravimetry analysis (TGA) measurements of the pure PVA and PVA/ $\text{AgNO}_3$  are shown in Figure 3. Three main weight loss regions for all  $\text{AgNO}_3$ -doped PVA are revealed. The first region, at temperature of  $50$ – $155^\circ\text{C}$ , is due to the evaporation of physically weak and chemically strong bound  $\text{H}_2\text{O}$ <sup>16</sup>, and the weight loss of the films is about 2.3–



**Figure 3** TG curves for  $\text{AgNO}_3$ -doped PVA films with different amounts of  $\text{AgNO}_3$ .



**Figure 4** Derivative curves of TG for  $\text{AgNO}_3$ -doped PVA films with different amounts of  $\text{AgNO}_3$ .

5.7 wt %. The second fast degradation region, at temperature of 155–210°C appeared due to the degradation of the chain of the PVA- $\text{Ag}^+$  chelate and the total weight loss corresponding to this stage is about 10.3–13.4 wt %. The third stage at around 210–300°C, occurred due to the transfer of pure PVA as well as  $\text{AgNO}_3$ -doped PVA films to adjacent chains via interchain reactions and decomposing,<sup>17</sup> and the total weight loss about 11.2–29.1 wt % at 300°C.

The decomposition data of the TGA results showed that the weight loss of  $\text{AgNO}_3$ -doped PVA is much more than the pure PVA. These results agree with the results of the DSC. Therefore, it is concluded that some of PVA- $\text{Ag}^+$  chelate decompose during the heat treatment of  $\text{AgNO}_3$ -doped PVA films, especially during the temperature range of 155–210°C.

Figure 4 presents derivative thermogravimetric (DTG) curves of the  $\text{AgNO}_3$ -doped PVA films with different amounts of  $\text{AgNO}_3$ . The temperature of DTG peaks for all the  $\text{AgNO}_3$ -doped PVA almost is about 180°C. From the TG and DTG results, it shows that under the same heating condition, the weight loss and the height of the DTG peaks increased with increasing the amount of  $\text{AgNO}_3$  doping. Therefore, the thermal decomposition of PVA- $\text{Ag}^+$  chelate is significantly affected by the amount of  $\text{AgNO}_3$  doping.

#### X-ray diffraction analysis

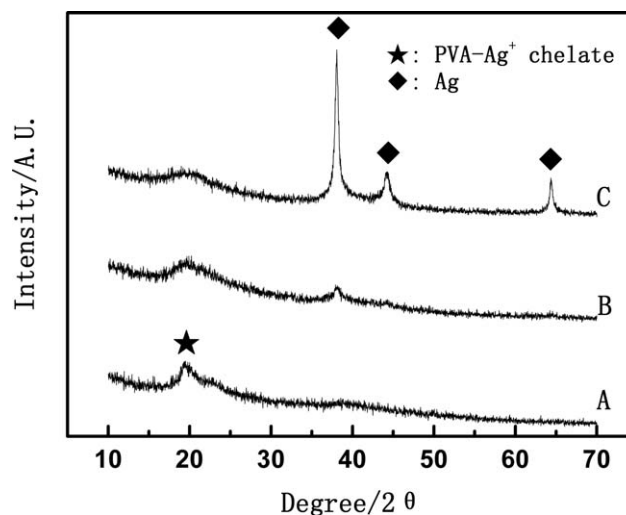
The XRD spectrum of PVA films doped with 35 wt %  $\text{AgNO}_3$  heated at 120°C, 155°C, and 165°C for 10 min are shown in Figure 5. A peak around at

$2\theta = 20^\circ$ , corresponding to the (101) plane of PVA semicrystalline structure,<sup>18</sup> is noticed for all films heated at different temperatures. However, the peak intensity of the 35 wt %  $\text{AgNO}_3$ -doped PVA film decreased with increasing the temperature. One peak is clearly observed at around  $2\theta = 38^\circ$  in Figure 5(B) for 35 wt %  $\text{AgNO}_3$ -doped PVA film heated at 155°C for 10 min. In Figure 5(C), three distinct XRD peaks at  $2\theta$  values of 38.2°, 44.3°, and 64.4° represent the (111), (200), and (220) crystalline planes of the FCC silver. These results indicate that amount of silver particles increased during heat treatment at 155–165°C.

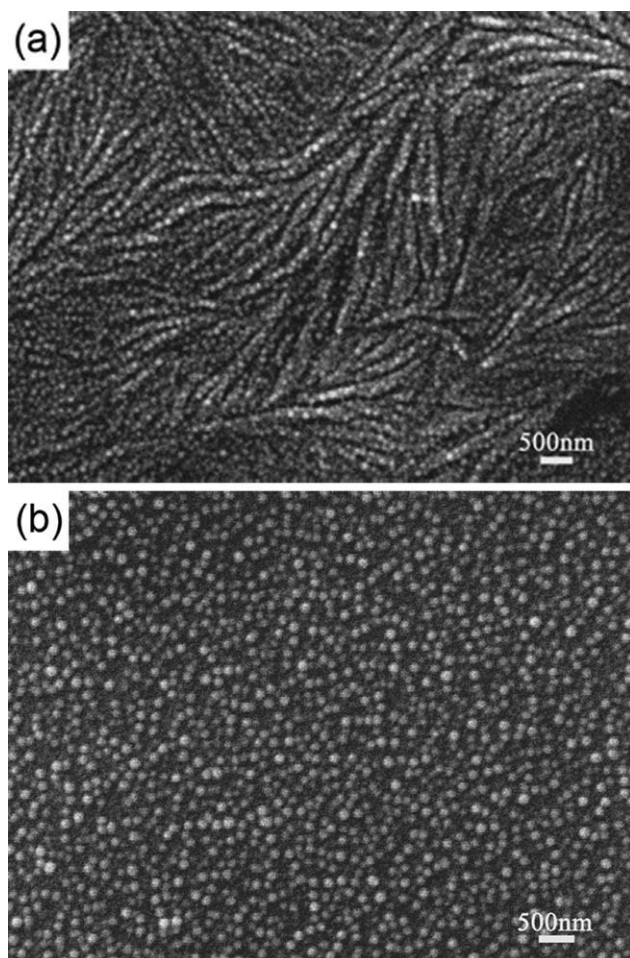
As compared with the results of DSC (Fig. 2) and TG (Fig. 3), it was found that the Ag particles generated during 155–210°C where the highest exothermic peak was 182°C. The XRD spectra indicated that the silver phase was presented after heat treatment at 155–165°C. The above results were well in agreement with each other.

#### SEM analysis

The typical SEM images of the 20 wt % and 40 wt %  $\text{AgNO}_3$ -doped PVA films heated at 155°C for 10 min are shown in Figure 6. As shown in Figure 6(a), a dendritic peculiar texture containing long fibrils is noticed for the micrograph for the 20 wt %  $\text{AgNO}_3$ -doped PVA film. From Figure 6(b), it is observed that the morphology of Ag particles is spherical and the average size is about 150 nm. These micrographs imply that there is a drastic influence of  $\text{AgNO}_3$  content on the structural morphology of PVA films. In the 20 wt %  $\text{AgNO}_3$ -doped PVA film, the continuous Ag particles are formed and then stuck to grow the dendritic structures by diffusion. Zhou et al. also observed the dendritic structures in 3%  $\text{AgNO}_3$ -



**Figure 5** XRD spectrum for 35 wt %  $\text{AgNO}_3$ -doped PVA films at different temperature treated for 10 min (A) 120°C, (B) 155°C, and (C) 165°C.

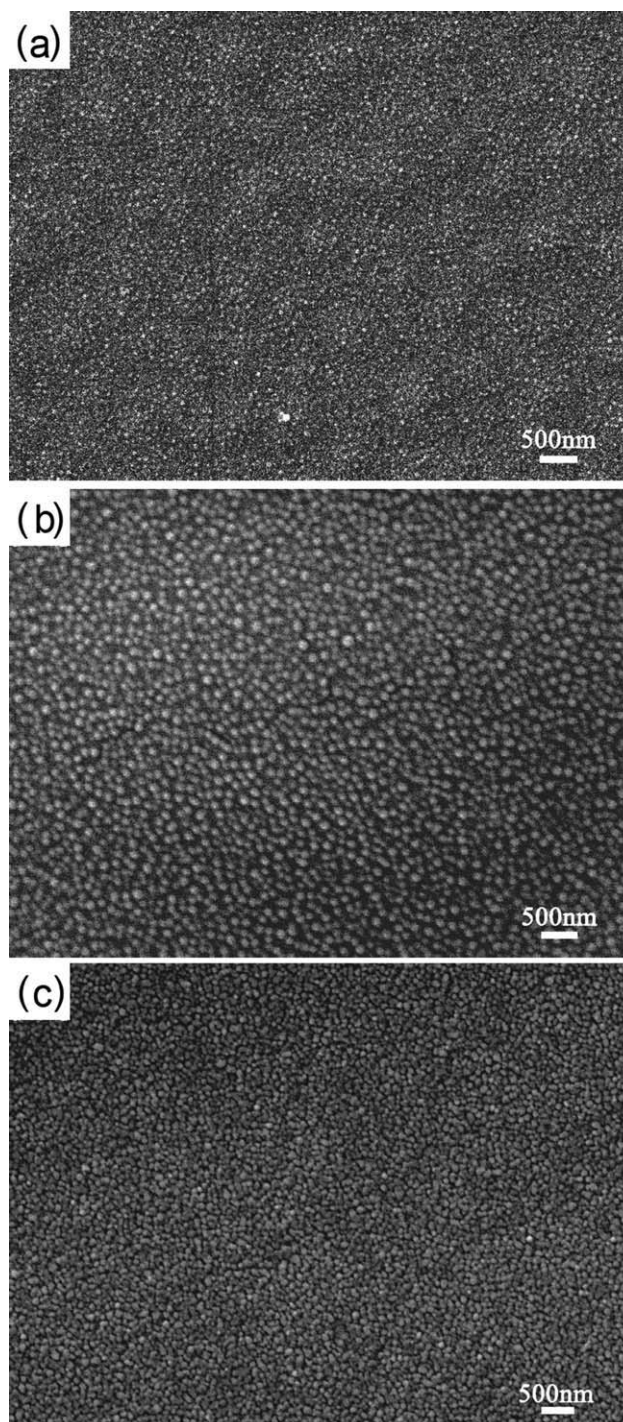


**Figure 6** SEM micrographs for  $\text{AgNO}_3$ -doped PVA films heat treated at  $155^\circ\text{C}$  for 10 min filled with different fraction of  $\text{AgNO}_3$  (a) 20% and (b) 40%.

doped PVA by UV-reduction method.<sup>5</sup> However, growth of the Ag particles into the dendritic structures does not occur in 40 wt %  $\text{AgNO}_3$ -doped PVA films. We believe that when the content of Ag particles reaches to a certain value, they may be favorable for the aggregation and growth into the dendritic structures, whereas the growth occurred in all direction when the content exceeds some values. The effect of the content of  $\text{AgNO}_3$ -doped PVA on the structures needs to be investigated further.

SEM images of 35 wt %  $\text{AgNO}_3$ -doped PVA heated at  $120^\circ\text{C}$ ,  $155^\circ\text{C}$  and  $165^\circ\text{C}$  for 10 min are shown in Figure 7(a–c), respectively. It is seen in photographs (a) and (b) of Figure 7 that the average sizes of silver particles are  $\sim 80$  and  $\sim 150$  nm, respectively. It is assumed that these silver nanoparticles are generated during the thermal process. All the Ag particles are sphere shaped and their sizes increase with increasing heat treatment temperature. However, the average size of silver particles in Figure 7(c) is similar to that in Figure 7(b). We propose a mechanism to explain the similar sizes of silver

particles in Figure 7(b,c), when the heat treatment temperature is above a certain value, the value which was indicated by Jin et al. was  $T_g$  value of the PVA ( $110^\circ\text{C}$ ),<sup>2</sup> all the  $\text{Ag}^+$  ions are transferred to Ag nanoparticles and that PVA act as a stabilizer of Ag nanoparticles. From Figure 7(c), it is also observed that large numbers of silver particles are generated and joined together. From these SEM results, it is



**Figure 7** SEM micrographs for 35 wt %  $\text{AgNO}_3$ -doped PVA films at different temperatures heated for 10 min (a)  $120^\circ\text{C}$ , (b)  $155^\circ\text{C}$ , and (c)  $165^\circ\text{C}$ .

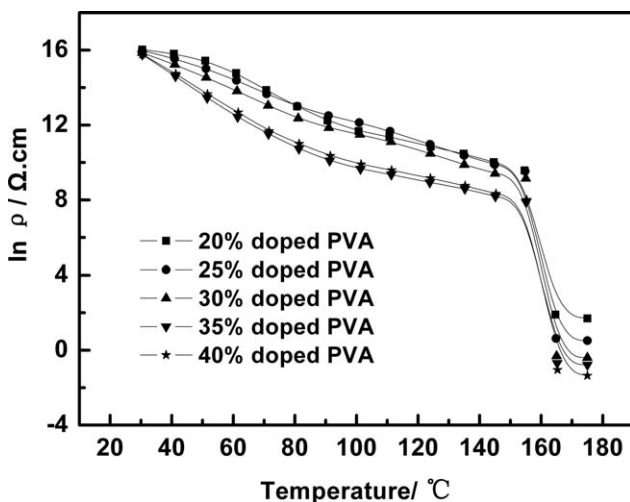


Figure 8  $\ln \rho$  against  $T$  plots for  $\text{AgNO}_3$  filled PVA films for different contents of  $\text{AgNO}_3$ .

clearly revealed that the amount of silver particles increased with increasing heat treatment temperature.

**Electrical measurement**

The electrical resistance for the 20, 25, 30, 35, and 40 wt %  $\text{AgNO}_3$ -doped PVA are  $9.2 \times 10^8 \Omega$ ,  $8.8 \times 10^8 \Omega$ ,  $7.7 \times 10^8 \Omega$ ,  $7.1 \times 10^8 \Omega$  and  $7.0 \times 10^8 \Omega$  respectively at room temperature. The room-temperature resistance decrease continuously with increasing  $\text{AgNO}_3$  amount. Figure 8 showed the  $\ln \rho$  (the logarithm of the electrical resistivity) vs.  $T$  (absolute temperature) plot for PVA filled with various contents of  $\text{AgNO}_3$ .

It is seen in Figure 8 that the resistivity decreased with increasing temperature. The rates differ in different temperature regions, so two regions are exhibited. The decrease rate of the resistivity dependence on temperature is moderate in low-temperature range (25–155°C), and sharply increased in high-temperature range from 155–175°C. This suggests that the conduction mechanisms are different in these two temperature ranges.

In the low temperature range (25–155°C), previous study reported that the double bond  $\text{C}=\text{C}$  and the deformation in the benzene ring, may evidence the formation of polarons and/or bipolarons in the polymeric matrix. Therefore the DC electrical resistivity can be discussed and interpreted on the base of the phonon-assisted hopping of charge carriers between polarons and/or bipolarons bound state as in polystyrene. The electrical resistivity can be expressed as<sup>1,19</sup>:

$$\rho = [kT/Ae^2\gamma(T)(R_0^2/\xi)][(Y_p + Y_{bp})^2/Y_p Y_{bp}] \times \exp(2BR_0/\xi) \quad (1)$$

where  $k$  is Boltzmann’s constant,  $A$  and  $B$  are constant,  $A = 0.45$ ,  $B = 1.39$ ,  $Y_p$ ,  $Y_{bp}$  the concentration of polarons and/or bipolarons, respectively, and  $R_0 = (\frac{3}{4}\pi C_{imp})^{1/3}$  the typical separation between impurities whose concentration is  $C_{imp}$ ,  $\xi = (\xi_{||}\xi_{\perp}^2)^{1/3}$  the average decay length of a polaron and/or bipolaron wave function,  $\xi_{||}$  and  $\xi_{\perp}$  the decay lengths parallel and perpendicular to the polymer chain, respectively. The electronic transition rate between polaron and bipolaron state can be estimated using the following equation:

$$\gamma(T) = \gamma_0(T/300k)^{n+1} \quad (2)$$

where  $n$  is a constant  $\sim 10$ , and the prefactor  $\gamma_0$  is evaluated by Kivelson and found to be  $1.2 \times 10^{17} \text{ s}^{-1}$ .<sup>20</sup> The complete details of this model were described elsewhere.<sup>13,19,20</sup> So the electrical resistivity can be expressed as:

$$\rho = [300k^{n+2}/\gamma_0 Ae^2 T^n (R_0^2/\xi)][(Y_p + Y_{bp})^2/Y_p Y_{bp}] \times \exp(2BR_0/\xi) \quad (3)$$

From formula (3), it indicates of a reciprocal relationship between the resistivity and the temperature ( $T^n$ ) in low temperature range.

From Figure 8, it is observed that the electrical resistivity of PVA/ $\text{AgNO}_3$  films dropped sharply from 155 to 165°C. The sharp decrease of electrical resistivity was attributed to the generated of Ag during the 155–165°C. As shown in Figure 5, many Ag nanoparticles were generated in the temperature range from 155–165°C. Meanwhile, an amount of Ag nanoparticles formed during the heat treatment were observed in Figure 7(c) also. Several Ag particles on the films surface joined together, so the electrical conduction mechanisms could be interpreted by the electrical conduction mechanism of Ag metal. The resistance for the 20, 25, 30, 35, and 40 wt %  $\text{AgNO}_3$ -doped PVA films at 175°C are 670, 188, 73, 51, and 35  $\Omega$ , respectively, and this result agrees with the TG (Fig. 3) and DTG (Fig. 4) as mentioned above that the weight loss and the height of the DTG peaks increased with increasing the amount of  $\text{AgNO}_3$  doping. Under the same thermal condition, the amount and speed of reducing Ag nanoparticles are increase with increasing the amount of  $\text{AgNO}_3$  doping. So the resistances of  $\text{AgNO}_3$ -doped PVA films are decreased with more electric Ag particles generated.

**CONCLUSIONS**

A casting method for preparing PVA/ $\text{AgNO}_3$  films was presented. The incorporation of  $\text{AgNO}_3$  (20–40 wt %) into the PVA polymer induced significant

changes in the thermal property of PVA films. All the AgNO<sub>3</sub>-doped PVA films presented an exothermic peak exactly at 182°C. XRD and SEM studies showed Ag particles aggregation on the surface of films. The amount of the silver particles increased with increasing heat treatment temperature, and large numbers of silver particles generated and joined together on the surface of films after heat treatment for 10 min at 165°C. Electrical resistivity-thermal results showed that the resistivity of the PVA/AgNO<sub>3</sub> films decreased with increasing temperature and dropped several (4–5) order of magnitude from 155 to 165°C. The behavior of resistivity decreased sharply in a certain temperature range of AgNO<sub>3</sub>-doped PVA films could be used as a new temperature alarm technique.

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