Physical Properties of PVA/PSSNa Blends

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ABSTRACT: Blends of conductive polymers with conventional nonconductive ones have, together, the virtues of good electroconductivity and good mechanical properties, whose prospect for electronic industrial application is very good. We prepared poly(vinyl alcohol) (PVA)–sodium poly-styrene–sulfonate (PSSNa) blends through aqueous solution casting; the films are flexible and transparent, with electroconductivity that could reach 10^{-5} S/cm. The dependence of the electroconductivity on the weight fraction of PSSNa was found to follow the percolation theory. A general discussion is given on the factors that could influence the percolation threshold and the exponent. The films are stable in a 30% KOH solution and keep their conductivity after 10 days' exposure. Some mechanical properties are measured and the best mixing ratio is obtained for future use. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 79–87, 2003

Key words: conducting polymer; blends; PVA; percolation; SEM

INTRODUCTION

Inherently insulating polymers can be made conductive by two ways: One is to add inorganic conductive particles, such as metal powder, carbon black powder, or their fibers to a resin[1–4]; the other is to make a polymer blend composed of a conductive polymer and an insulating resin. The latter has aroused much attention in recent years because the function of a conductive polymer is much richer than are inorganic fillers[5] and the two polymer composites can be mixed more thoroughly than in the former method. Polyaniline (PANI) has been one of the most intensively studied conductive polymers in the past decade,[6–15] but, unfortunately, it cannot resist deprotonation in basic media, which has a disastrous effect on the conductivity of PANI-based blends because only the protonated form of PANI is conductive. Furthermore, its solubility is very poor: To process it with other polymer composites, one has to use large quantities of a poisonous solvent such as *m*-cresol and xylene, which limits its industrial use. In modern technology, there exists a strong demand for materials that combine the flexibility of plastics with stable electronic conductivity and good transparency in the visible part of the spectrum.[16] Moreover, environmental consideration has also become more important than usual. Polyelectrolytes have shown their superiority in these aspects. Owning to such a consideration, we chose sodium polystyrene–sulfonate (PSSNA) as the conductive composite to blend with poly(vinyl alcohol) (PVA). PVA is widely used in adhesives, coatings, and textiles; furthermore, it is water soluble and does no harm to the environment, but its blend with polyelectrolytes to make a conductive polymer has been seldom reported in the literature.

In this article, we mixed the two polymers in different ratios using water-solution blending and prepared their transparent films. Electrical conductivities under different mixing proportions were studied in an attempt to understand the mechanism of conduction in such systems. The results show that it is characteristic of a percolation system, which is also proved by the SEM photos of the freeze-fractured surface. Some mechanical properties of these blends were also studied to evaluate their potential for use in industrial applications.

EXPERIMENTAL

The polymers used in this study were the following: PSSNA, average molecular weight 7000 (Aldrich, Geel, Belgium), and PVA-124, average molecular weight 6000 (Sumitomo, Osaka, Japan).

PVA was dissolved in enough distilled water to make a dilute solution of about 2 wt %. Then, this solution was mixed in various ratios with PSSNa in powder form; after that, the mixture was carefully homogenized by vigorous stirring for 24 h at the temperature of 50°C. The clear solution was subsequently cast onto a glass plate and water was slowly evaporated at 30–40°C, yielding flexible and transparent films (samples having 40 and 50% PSSNa show a milk-white color). Their thickness ranged from 30 to

60 μm. Their electrical impedance spectrums were measured on an EG&G-M273 electrochemical analyzer. Two parallel stainless discs (16 mm in diameter) were used as electrodes; the input frequency range was between 500,000 and 0.01 Hz and the alternating current amplitude was 5 mV. The electroconductivity of pure PVA film and the sample containing 10% PSSNa were measured by the four-probe method because their resistance exceeds the working magnitude. The tensile tests were carried out on an Instron 4466 strain–stress analyzer at the rate of 10 mm/min. The freeze-fractured surface of the blend was studied using a Hitachi X-650 scanning electron microscope.

RESULTS AND DISCUSSION

Percolation theory

In general, a solid polymer electrolyte has a geometrical capacitance C_b and a bulk resistance R_b in parallel with it. These elements produce a Nyquist semicircle in an impedance complex plane, where R_b is the diameter of the semicircle, while CPE refers to the interfacial capacitance between the electrode and the film sample (Fig. 1). Normally, a partial semicircle with center below the Z_{re} axis by an angle $\alpha\pi/2$ is observed due to microscopic inhomogeneity or non-Debye capacitance.

The impedance spectrums of the PSSNa–PVA blends are shown in Figure 2. In this experiment, only a part of the above curve is observed because of the narrow range of the applied frequencies. The low-frequency intercept of the simulated semicircle with the real axis is suggested to be the estimation of the bulk resistance R_b of the sample. For samples which only have part of the semicircle, two methods can be used to calculate R_b: One is to simulate the semicircle from part of the points on its curve, and the other is to estimate R_b from the intercept of the CPE line with the imaginary axis; both methods are supported by M273 software. From Figure 2(2–4), R_b is calculated by both methods (see Table I); as the differences are less than 7%, we regard the method of the CPE line fit as a reasonable estimation of R_b. In Figure 2(5), R_b is calculated from the intercept of the CPE line on the Zim axis, because only the CPE line is visible in the working frequency ranges. The electroconductivity σ of the samples is calculated from eq. (1):

$$\sigma = d/(R_b \times S) \tag{1}$$

in which d is the thickness of the sample and S is the area of the electrode. The electrical conductivity of the PSSNa/PVA conductive blends as a function of the PSSNa weight fraction is illustrated in Figure 3. Obviously, the electrical conductivity of the composites increases dramatically before the PSSNa concentration
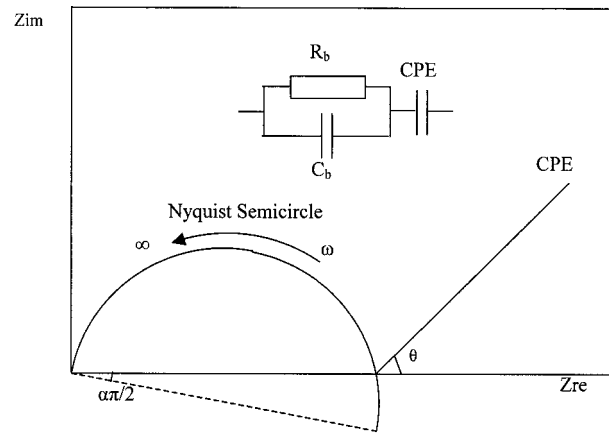

Figure 1 Schematic impedance loci and equivalent circuit of a cell composed of a polymer electrolyte sandwiched between two blocking electrodes.

reaches the percolation threshold at approximately a 0.2 weight fraction. Among the many theoretical models used to explain the conductive behavior of conductive polymer blends, percolation theory is the most commonly accepted one. We fit the data of conductivity versus the PSSNa content in Table I to the scaling law of percolation theory as follows:

$$\alpha(f) = c(f - f_p)^t \tag{2}$$

in which $\alpha(f)$ represents the electrical conductivity of the composites; c is a constant; t, the critical exponent; f, the volume fraction of the conductive phase; and f_p, the volume fraction of the conductive polymer at the percolation threshold. For practical reasons, we use the weight fraction instead of the volume fraction in the calculation, because the densities of the two components are very close and the change can be neglected. The data in this system fit the scaling law of percolation well (Fig. 4). From the slope and the intercept of the straight line, the values of t and c can de determined. The results of the parameters of c and t calculated from computer simulation are listed in Table II.

The blend system yields a value of 20–23% for f_p, 1.11–1.28 for t, and 8.35×10^{-8} to 1.72×10^{-7} for c. This value of the exponent is smaller than are some of the results observed in polyaniline blends,[6,8,9] reported from 1.6 to 3.0. Most of them are blends with brittle polymers such as poly(methyl methacrylate), polystyrene, and cellulose, but small values such as 1.2 and 1.3 were also observed by some authors and they attributed them to the thermally induced hopping between disconnected parts of the percolating network.[10,11] In electrolytes, electrons are transferred through ions instead of the conjugated double-bond passage, so they are not as efficient as the latter and they are more easily affected by the residual water or
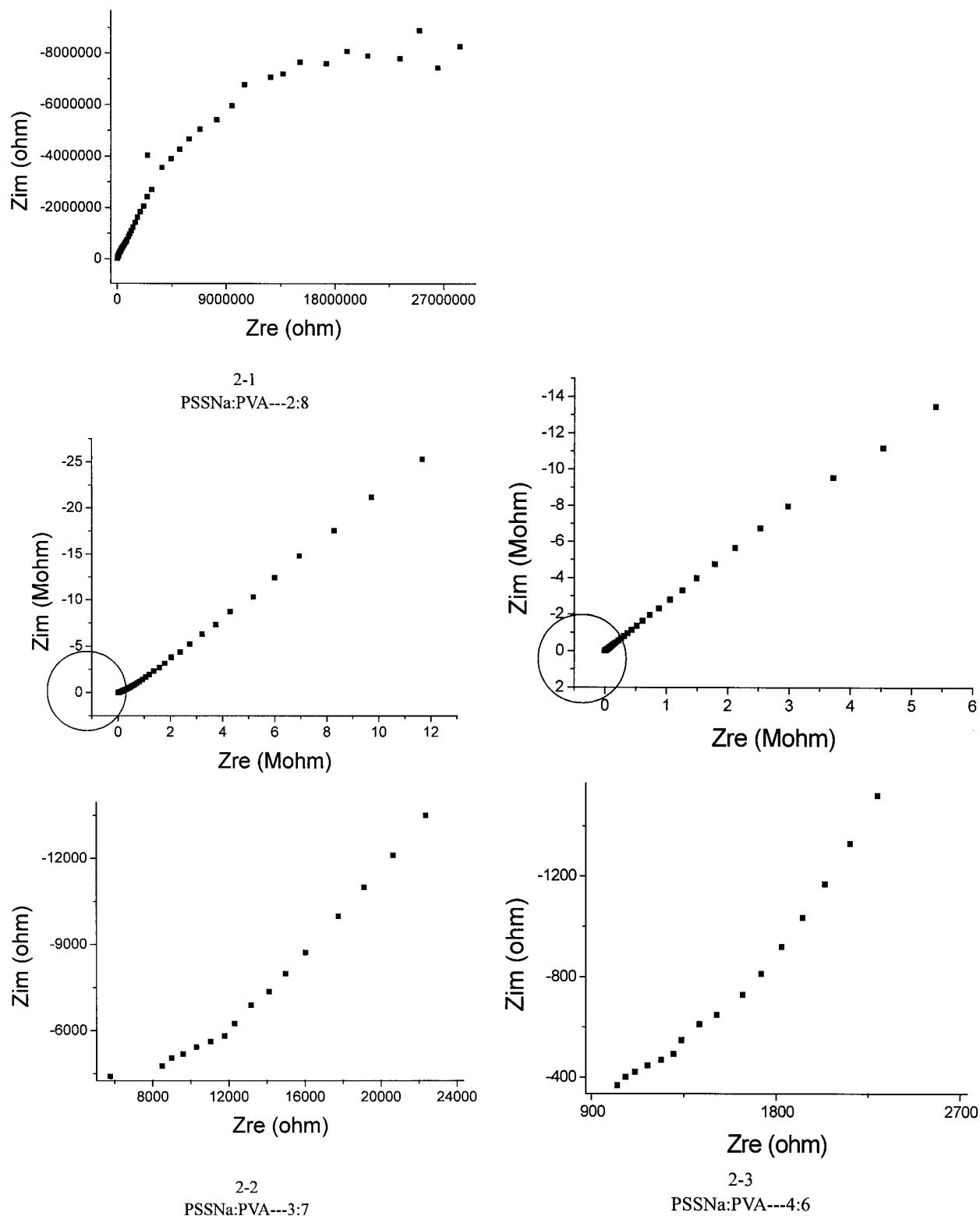
Figure 2 Impedance spectrums of different weight ratios of PSSNa:PVA. The graphs at the high-frequency range are enlarged in the bottom figures: (1) PSSNa:PVA, 2:8; (2) PSSNa:PVA, 3:7; (3) PSSNa:PVA, 4:6; (4) PSSNa:PVA, 5:5; (5) PSSNa:PVA, 6:4 to 10:0.

salt. Furthermore, the phase separation structure is more complex than is the hard-core model. These reasons may deflect t from the theoretical value 2.0.[17]

In this experiment, the percolation threshold is higher than that of some PANI-based blends systems,[6–10,12] which is less than 10%, but is comparable to most CB-
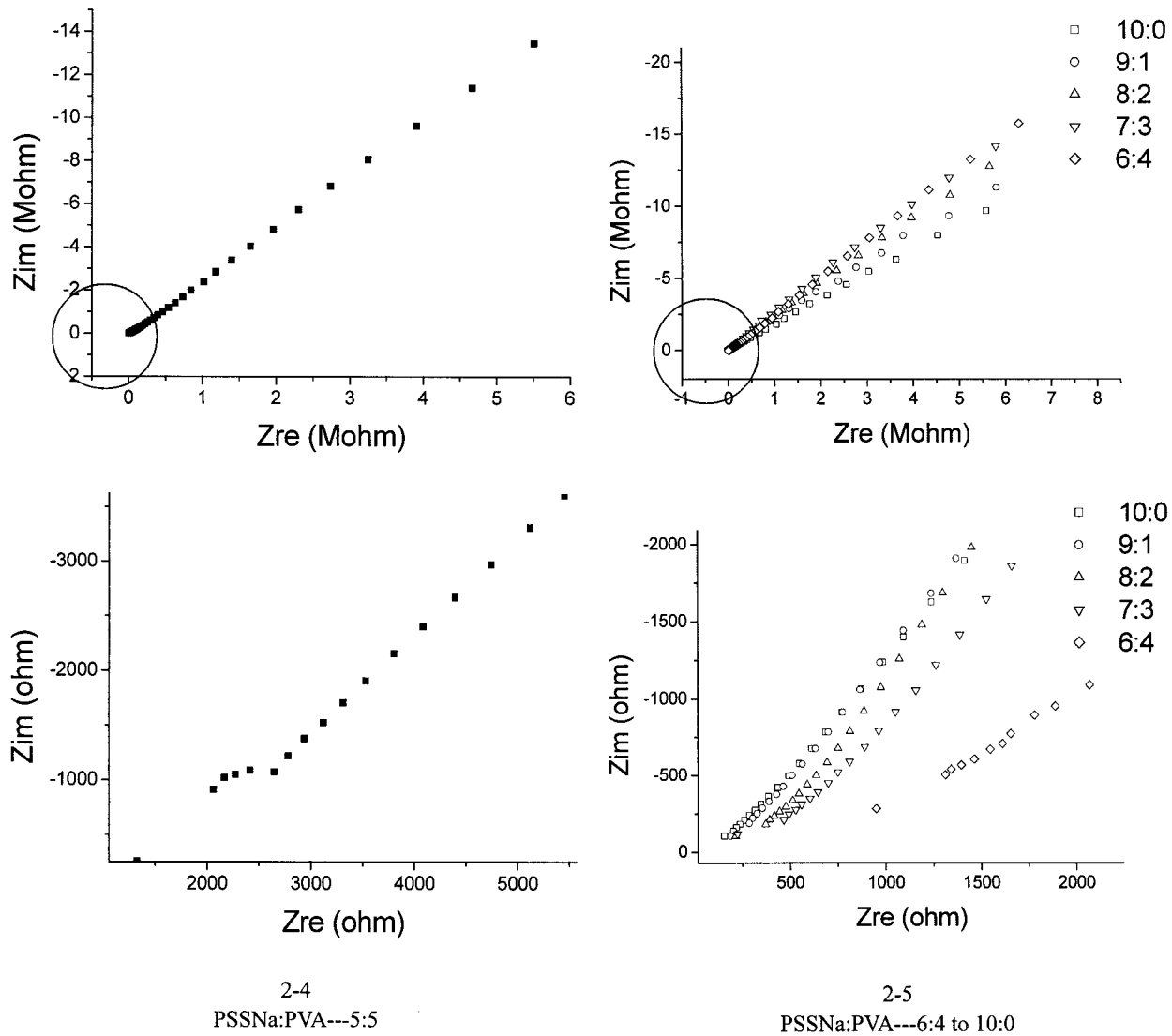
2-4
PSSNa:PVA---5:5

2-5
PSSNa:PVA---6:4 to 10:0

Figure 2 (*Continued from the previous page*)

TABLE I
Change of Electroconductivity of the Blends with an Increasing of PSSNa Content

PSSNa (wt %)	R_b (ohm)	Conductivity (S/cm)
0	1.71×10^9 (four-probe method)	1.89E-12
10	8.72×10^8 (four-probe method)	3.09E-12
20	1.97×10^6 (semicircle fit)	3.19E-10
30	4.00×10^3 (semicircle fit); 4.02×10^3 (line fit)	1.69E-6
40	2.55×10^3 (semicircle fit); 2.40×10^3 (line fit)	3.59E-6
50	1.78×10^3 (semicircle fit); 1.74×10^3 (line fit)	5.75E-6
60	1.12×10^3 (line fit)	8.53E-6
70	3.10×10^2 (line fit)	1.41E-5
80	2.64×10^2 (line fit)	1.59E-5
90	1.74×10^2 (line fit)	1.99E-5
100	1.08×10^2 (line fit)	2.09E-5

filled polymer composites,[2,4] which has been reported to be 15–25%. The value of the thresholds varies considerably between different systems. Low thresholds were observed in blends of conducting polymer nanostructures[7,9] and carbon black composites containing certain kinds of polymers such as poly(vinylidene fluoride),[3] where $f_p < 5\%$, were reported. In Ref. 18, it was concluded that, in an idealized fractal structure, f_p decreases greatly with decreasing of the particle diameter from 10 to 0.5 μm. Forming a loose network for the charge carriers to proceed is also a key point for getting low threshold blends. In this system, the SEM photos show that the phase-separation conditions are complex. In a low PSSNa concentration (10%), the PSSNa phase forms seemingly interconnected branch-shaped domains in the host matrix of PVA, but the conductivity is barely improved. This may mean that, for the polyelectrolyte blend system, a loose network of a conductive phase is required but may not necessarily lead to a great change
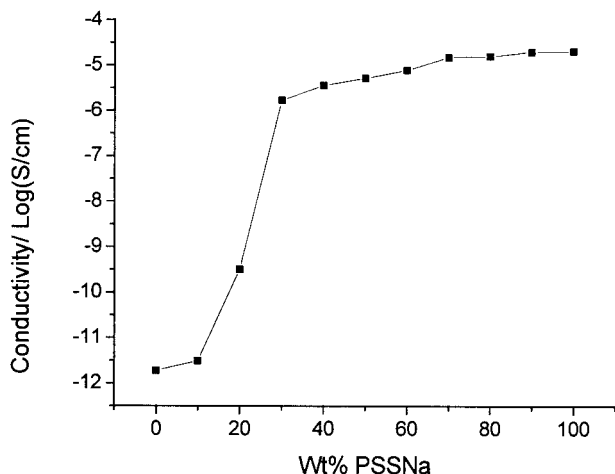
Figure 3 Change of electroconductivity of the blends with increasing PSSNa content.

of conductivity. Because the direction of the electron-transfer passages is disordered, a large part of them are perpendicular to the film surface, which increased the difficulty of electron transfer and made the percolation threshold to increase. For this condition, a perpendicular electric field applied during the formation of the film may lead to a decrease of the percolation threshold. On the other hand, a thermal dynamic study of the casting procedure—from a homogeneous solution to phase-separated clusters—would provide clues for questions such as whether there is a minimum threshold, what molecular weight is the best for achieving an interpenetrated network, and what temperature is good for evaporating water. Levon et al.[19] pointed out one possible way to make a blend with a conductive polymer content lower than the threshold conductive, that is, to make the conductive polymer percolate in its rich phase while the conductive polymer-rich phase percolates in its minor phase, and have put forward an equilibrium dynamics
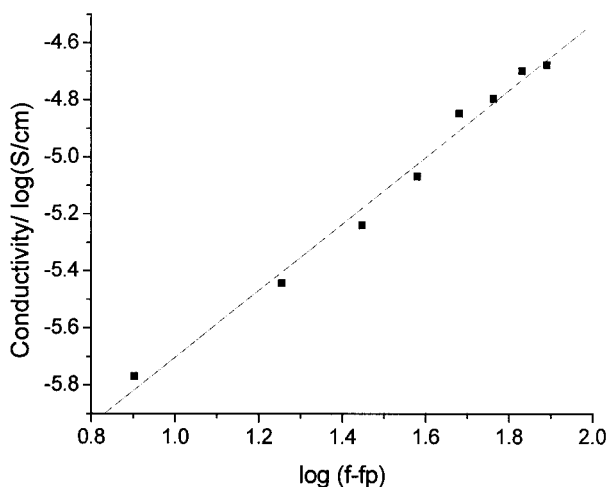
TABLE II
Scaling Law Parameters Calculated for PSSNa–PVA Blends

f_p (wt %)	t	R_t (correlation coefficient)	c	R_c (correlation coefficient)
20	1.28	0.948	8.35×10^{-8}	0.917
21	1.22	0.947	1.06×10^{-7}	0.916
22	1.17	0.945	1.34×10^{-7}	0.913
23	1.11	0.943	1.72×10^{-7}	0.910

equation according to their model, but they did not give applicable factors, which would form the multiple percolation. Takeno et al.[20] found that it is common for a polymer mixture in off-critical conditions to form a co-existence structure, with the minority phase forming interconnected droplets in the sheetlike percolating structure of the rich phase, which hints to us that polymer behavior in a metastable state is important for obtaining multiple percolation.

Basic media resistance

One of the weakest points of many highly conductive polymers such as polypyrrole and polyaniline is their tendency to deprotonate. Because only the protonated form is conductive, their conductivity will decrease quickly in basic media. Juvin et al.[6] studied the conductivity of a PANI-based blend with different dopants such as camphorsulfonic acid and poly(alkylene phosphate) in a pH 9 buffer solution. The resistance of most samples increased 10^5 times in 4–8 days, which shows that its resistance to basic media is weak. In our experiment, we exposed the PSSNa-based blend sample containing 30% PSSNa (because it shows good mechanical properties and conductivity, as is discussed under Mechanical Properties) and the sample with 60% PSSNa (because it shows good compatability of the two components, as is discussed under Morphology) in a 30% KOH solution for 10 days, dried them in a vacuum afterward, and measured their electroconductivity. The results are listed in Table III, which shows that the conductivity of the two samples does not change and they are stable in highly basic media, which is a reasonable character owning to the

Figure 4 $\log_{10}$–$\log_{10}$ plot of conductivity versus $(f - f_c)$.

TABLE III
Changing of Conductivity Versus the Length of Time Exposed in KOH Solution

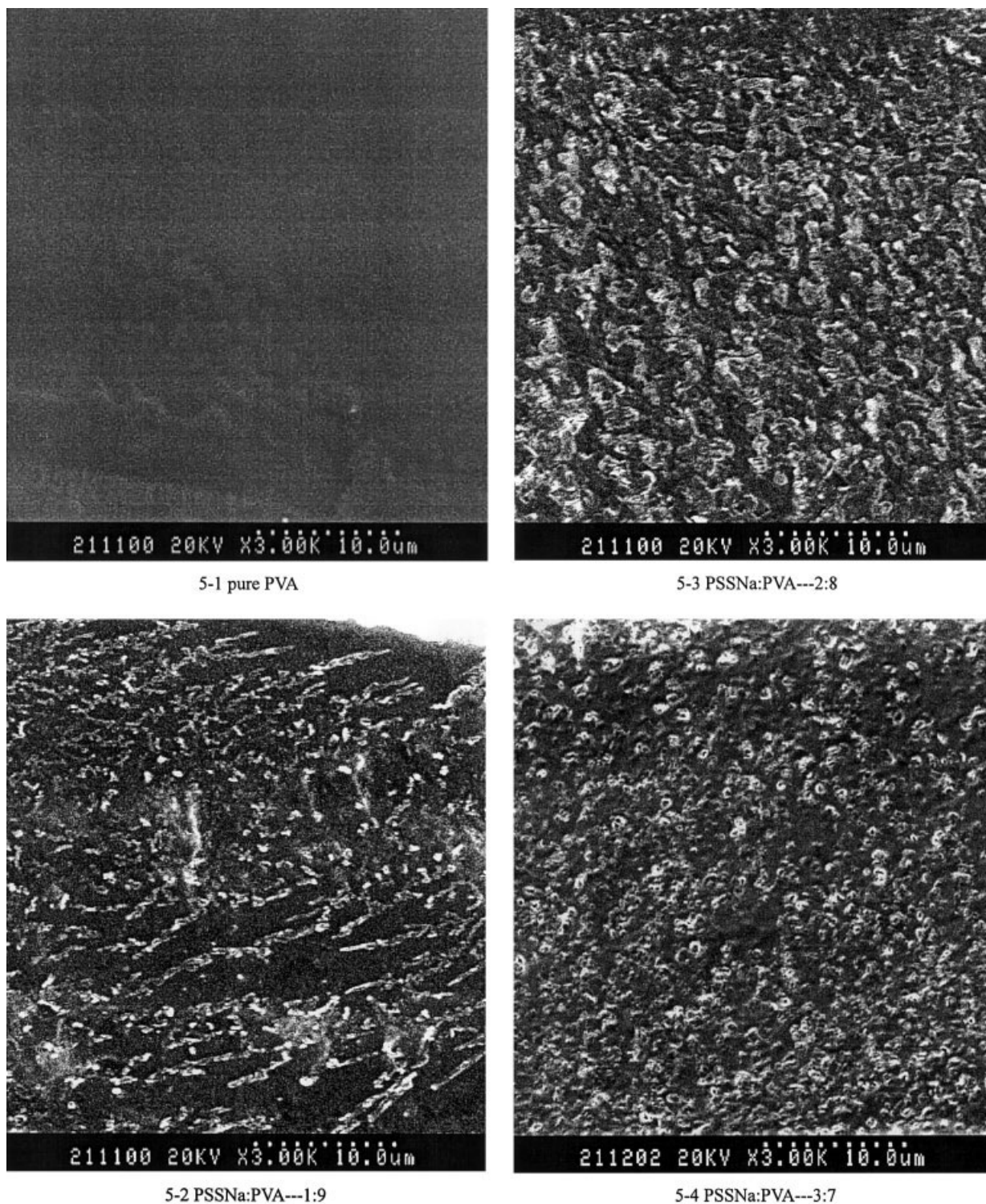|	Days					
	0	2	4	6	8	10
PSSNa Percent			Conductivity $(10^{-6}$ S/cm)			
30%	1.69	1.72	1.71	1.78	1.75	1.76
60%	8.53	8.64	8.69	8.65	8.71	8.70

Figure 5 Freeze-fractured surfaces of the PSSNa–PVA blends (weight fraction): (1) pure PVA; (2) PSSNa:PVA, 1:9, the film surface is parallel to the bottom line of the photo; (3) PSSNa:PVA, 2:8; (4) PSSNa:PVA, 3:7; (5) PSSNa:PVA, 4:6; (6) PSSNa:PVA, 5:5; (7) PSSNa:PVA, 6:4; (8) PSSNa:PVA, 7:3; (9) PSSNa:PVA, 8:2; (10) PSSNa:PVA, 9:1.

nature of the polyelectrolyte. Also, they do not swell in highly basic media. So, the blends are promising for use in a conductive adhesive, a high-energy cell, and other aspects where basic media is required.

Morphology

Micrographs of the PSSNA /PVA blends are shown in Figure 5. Figure 5(1) shows the freeze-fractured sur-

5-5 PSSNa:PVA---4:6

5-7 PSSNa:PVA---6:4
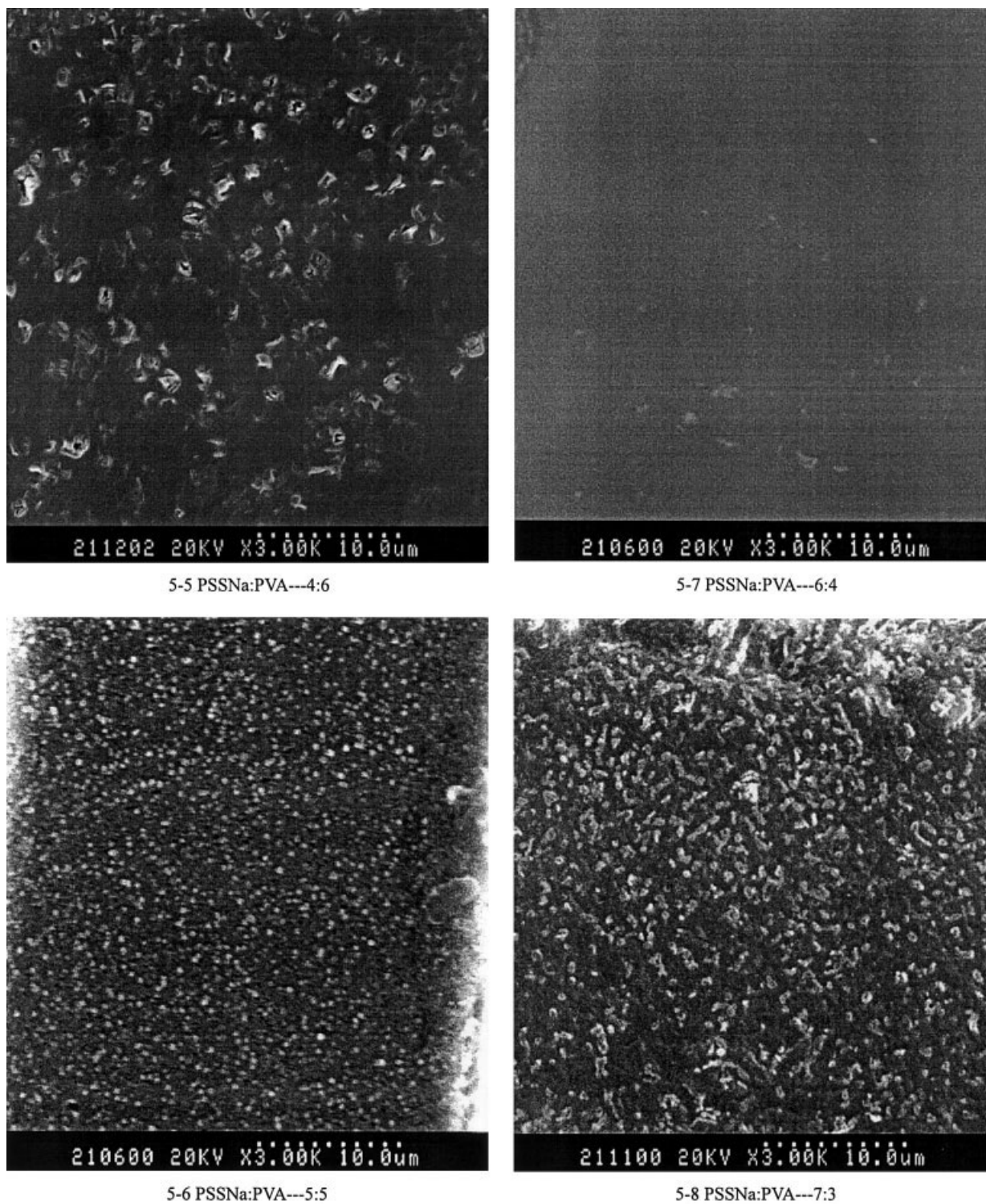

5-6 PSSNa:PVA---5:5

5-8 PSSNa:PVA---7:3

Figure 5 (*Continued from the previous page*)

face of pure PVA as a comparative figure. In Figure 5(2), it is clear that a two-phase structure is present and PSSNa forms a branch-shaped minor phase in the PVA base. Its distribution is uniform but contributes little to increasing the conductivity of the whole material. We owe it to the disorder of the passages' direction and the lower efficiency of the electron-transport property of the polyelectrolyte compared to PANI. In Figure 5(3), the phase-separation status is not clear but the increasing of the PSSNa content made the surface very rough and the conductivity increased 10^2 times, which shows that more direct and larger electron-transfer passages begin to form in the material. Figure 5(4–5) shows that the PSSNa phase began to
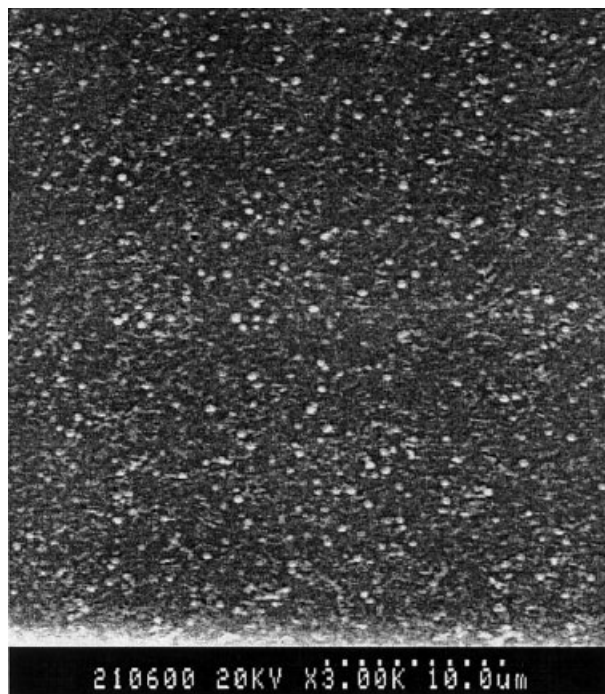
5-9 PSSNa:PVA---8:2
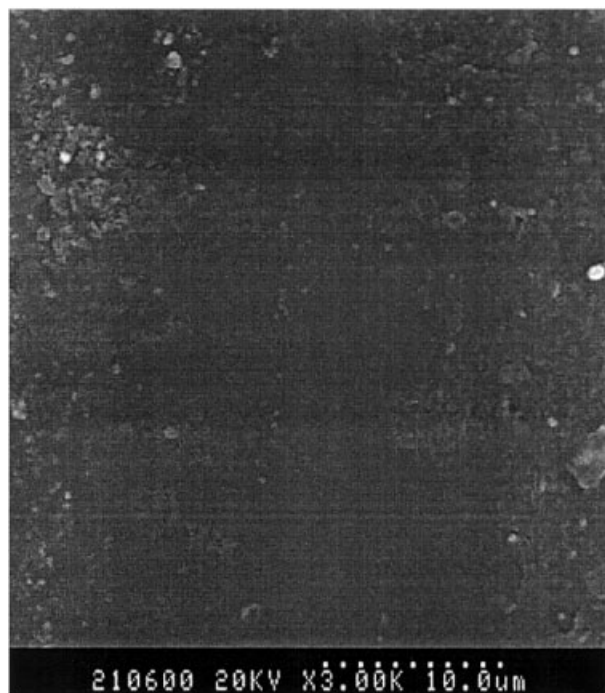
5-10 PSSNa:PVA---9:1

Figure 5 (*Continued from the previous page*)

form spherical particles; although they seem to be isolated [especially in Fig. 5(5)], the conductivity jumped 10^4 times. This shows that part of the PSSNa is dissolved into the PVA phase and forms an interconnected network between the isolated PSSNa particles and makes the conductivity not greatly affected by the shape of the PSSNa phase. In Figure 5(6), the two

phases mix more uniformly and the sizes of the PSSNa particles become 200–500 nm. Until Figure 5(7), the two phases nearly become one phase in micrometer scale, which shows that at the point PSSNa:PVA 6:4 the two composites mix most thoroughly. They are interpenetrated or yield a metastable network structure due to viscoelastic stress between the macromolecules. Figure 5(8) shows that the PSSNa phase becomes the matrix phase while PVA is dispersed in it, appearing as white blocks in the photo.

Mechanical properties

We examined the mechanical properties of the film samples by a tensile test; the results are listed in Table IV, from which we can see that the adding of PSSNa has a great influence upon the mechanical properties of the PVA–PSSNa blends. The sample containing 10% PSSNa shows an obvious decrease of the modulus and strain at maximum load and an autobreak, while the broken strain does not change much. This reveals that the PSSNa and PVA phases do not show special polymer–polymer interactions due to the nature of their chemical structure. PSSNa is very hard and brittle, which tends to form weak points in blend materials while the PVA phase acts as the flexible part, which will elongate at the applied stress and prevent the little weak points from getting big and to break easily. Compared with the SEM photo of Figure 5(2), we could see that the branched chains of the PSSNa phase tend to be parallel to the film surface. Although they will decrease the overall strength, they will not easily expand when the direction of stress is also parallel to the film surface, so the broken strain does not change much. With an increase of the PSSNa content from 10 to 30%, the stress at maximum load and autobreak decreases to about 50% of those of the bare sample, while the broken strain decreases less rapidly, with the 30% sample still retaining nearly 70% of the PVA sample. The brittleness of the PSSNa phase, a part of which will break under the given stress, and the PVA phase will be the main factor that contributes to the broken stress or maximum stress, so with an increasing of the PSSNa content the stress will decrease greatly. On the other hand, the SEM photos of Figure 5(3,4) show that the distribution of PSSNa at the PVA matrix is uniform, that the PSSNa particles are as small as 1 μm, and that the part of the PSSNa is dissolved in the matrix, as was discussed under Morphology, so the PVA phase is still the chief factor that contributes to the broken strain and retains a large part of the value of PVA. The sample containing 40% PSSNa shows a relatively larger decrease of broken strain than that of the former samples. We owe this to the larger size and relatively more irregular dispersing of the PSSNa particles in the PVA matrix than in the former samples. When the PSSNa content increases to

TABLE IV
Change of Some Mechanical Parameters with the PSSNa Content

PSSNa (Wt %)	Modulus (Young's) (MPa)	Stress at maximum load (MPa)	Strain at Maximum load (mm/mm)	Stress at break (MPa)	Strain at break (mm/mm)
0	190.5	58.22	7.892%	53.41	39.47%
10	103.8	42.28	6.490%	38.93	37.14%
20	814.4	32.67	6.736%	27.45	32.91%
30	761.8	30.07	5.543%	23.19	27.32%
40	553.6	26.13	4.122%	17.68	17.66%
50	394.0	22.04	3.864%	13.23	12.73%
60	77.00	20.10	2.961%	8.051	4.257%

Elongation speed, 5 mm/min; humidity, 60%; temperature, 24°C.

50 and 60%, the mechanical properties of the blends become weak and brittle. The ratios of maximum stress/broken stress become much larger than before, which shows that PVA no longer forms a good interconnected phase. The weak points of the PSSNa phase will easily expand to hollow belts after the level-off point of the stress–strain curve. Although the blend containing 60% PSSNa shows the best compatibility, the mechanical properties of the film samples are almost completely destroyed because PSSNa has become the dominant phase, as shown in Figure 5(7), and contribute greatly to its stretching behavior. From Table IV, we conclude that the best usage of PSSNa is 30%, which retains approximately one-third of the modulus, two-thirds of the broken strain, and one-half of the broken stress compared with PVA, while its electroconductivity increases 10^6 times from the nonconductive polymer. One way to improve the mechanical properties lies in increasing polymer–polymer interactions. Using polystyrene sulfonate acid to blend with PVA may improve their interaction and lead to a stronger conductive material.

CONCLUSIONS

To summarize, we prepared PSSNa–PVA blends using water-solution casting; the films are flexible and transparent. The addition of PSSNa improves the conductivity by 10^7 times and reaches 10^5 S/cm. From percolation theory simulation, we obtained the percolation threshold, which ranges from 20 to 23 wt %, while t ranges from 1.28 to 1.11. In addition, we examined the resistance of a PSSNa-based blend to basic media in a 30 wt % KOH solution and compared the results to the PANI-based blends. We found that it is stable in highly basic media and the electroconductivity remains unchanged.

From freeze-fractured SEM photos, we found that, for samples of a low concentration of PSSNa, the conductive polymer phase is separated from the nonconductive phase. With an increase of the PSSNa content,

the PSSNa phase slowly dissolves in the PVA phase and forms a interconnected structure until the cocontinuous phase structure is formed. The results from the tensile test show that the addition of PSSNa decreased the mechanical properties rapidly and the best ratio for applicable use is below 30%.

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