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Morphology of conductive polyaniline blended with poly(4-vinyl pyridine)

M.-C. Su, J.-L. Hong*

Institute of Materials Science and Engineering, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan, ROC

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Abstract

Strong methanesulfonic acid (MSA) was used as solvent to prepare blends of polyaniline (PAn) and poly(4-vinyl pyridine) of different compositions. Products obtained after removal of MSA were surveyed by scanning and transmission electron microscopes (SEM and TEM) to reveal their morphologies. The blend with 80 wt% of PAn showed an interesting elliptical flake morphology, in contrast to the spherical particle morphology observed for other blends. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyaniline; Poly(4-vinyl pyridine); Elliptical flake

1. Introduction

Polyaniline (PAn) [1] is the only conductive polymer whose electrical properties can be controlled by charge-transfer doping and/or protonation. To enhance processability and mechanical properties, blending of PAn with bulky organic sulfonic acids [2,3] and/or other polymers to make PAn composites [4,5] is commonly practiced. In one particular report [5], PAn doped with methanesulfonic acid (MSA) was blended with polyurethane, and its conductivity, charge transport and magnetic properties were studied. Here, the MSA used may simultaneously complex with both PAn and polyurethane through hydrogen-bonds.

Similar to PAn, poly(4- and 2-vinyl pyridine)s (P4VP and P2VP) had been previously used to complex with organic sulfonic acids through their pendant pyridinyl rings. The homogeneous complexes of PVPs and DBSA had been proved to exhibit liquid crystalline properties [6]. It was suggested that the pendant DBSA molecules, thus attached to the PVPs' main chains by H-bonds, can be aligned successfully either in the solid or in the solution state to construct the mesogenic units required for a thermotropic or a lyotropic liquid crystalline polymer. Another interesting point [7] about P4VP is its increase of DC conductivity (from 10^{-4} to 10^{-6} S/cm) when it was doped with mixtures of iodine and *p*-toluenesulfonic acid (PTSA). Here, PTSA is used as counter ion for the strong electron acceptor iodine dopant (Fig. 1). The charge transfer complex formed between PVP and iodine shows good stability by the addition of PTSA. Therefore, PTSA acted as a stabilizer and a plasticizer too.

To enhance the processability of PAn, we prepared blends of PAn and P4VP in the presence of the strong organic acid MSA. The choice of MSA as blending solvent was in view of its capability to hydrogen-bond to both PAn and P4VP. In addition, MSA is an efficient dopant for PAn as illustrated above [5]. Free standing films of different compositions of PAn and P4VP can be easily prepared through the use of the MSA solvent, and the relationship between the composition and the resulting morphology was thus evaluated.

2. Experimental

2.1. Materials

Emeraldine base (Aldrich, $M_w > 15{,}000$) and P4VP (Aldrich, $M_w \sim 60{,}000$) were used directly without any treatment. MSA (70 wt% aq. solution, Elf Atochem North American) was vacuum distilled twice and stored under nitrogen atmosphere.

2.2. Preparation of PAn/P4VP (PAn(MSA)/P4VP(MSA)) blends

The respective 5 wt% solutions of emeraldine base and P4VP in MSA were prepared beforehand. Desired quantities of the two solutions were drawn, and mixed thoroughly

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* Corresponding author. Tel.: +886-7-5252000 ext.4065; fax: +886-7-5254099.

E-mail address: jlhong@mail.nsysu.edu.tw (J.-L. Hong).

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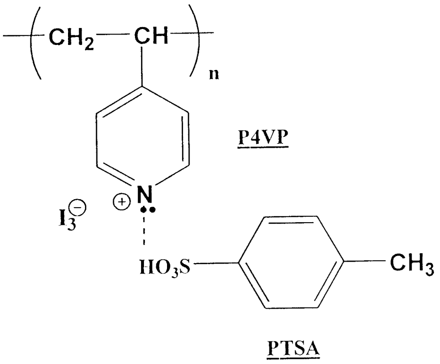

Fig. 1. Possible structure of charge transfer complex of P4VP/PTSA/I_2.

before vacuum distillation to yield dry PAn–P4VP films of different compositions. The resulting blends were named PAn(MSA)/P4VP(MSA)-*X*, where *X* stands for the molar percentage of the PAn component used in the preparation step.

2.3. Instrumentation

The fractured sample was coated with gold by vapor deposition using a Polaron SC502 vacuum sputter coater before examination. A Joel TEM-100S transmission electron microscope was further employed to survey the particle morphology in the blends. Two sample preparation methods were used. The first one used a sample film obtained after removal of the MSA solvent from the mixture solution. The sample film was then embedded in a cured epoxy resin, sectioned by ultromicrotome of Reichert Ultracut E, and then coated with carbon. The second one involves the suspension formed after dropping the mixture solution into ethanol. A copper mesh was used to dredge the suspension, and the whole set was vacuum dried before being coated with carbon with a Pelco CC-7A sputter machine. Conductivity was measured with a four-point method by a Keithley 237 model. Free standing films of thickness between 180 and 290 μm were prepared and their thickness was measured by scanning electron microscopy (SEM).

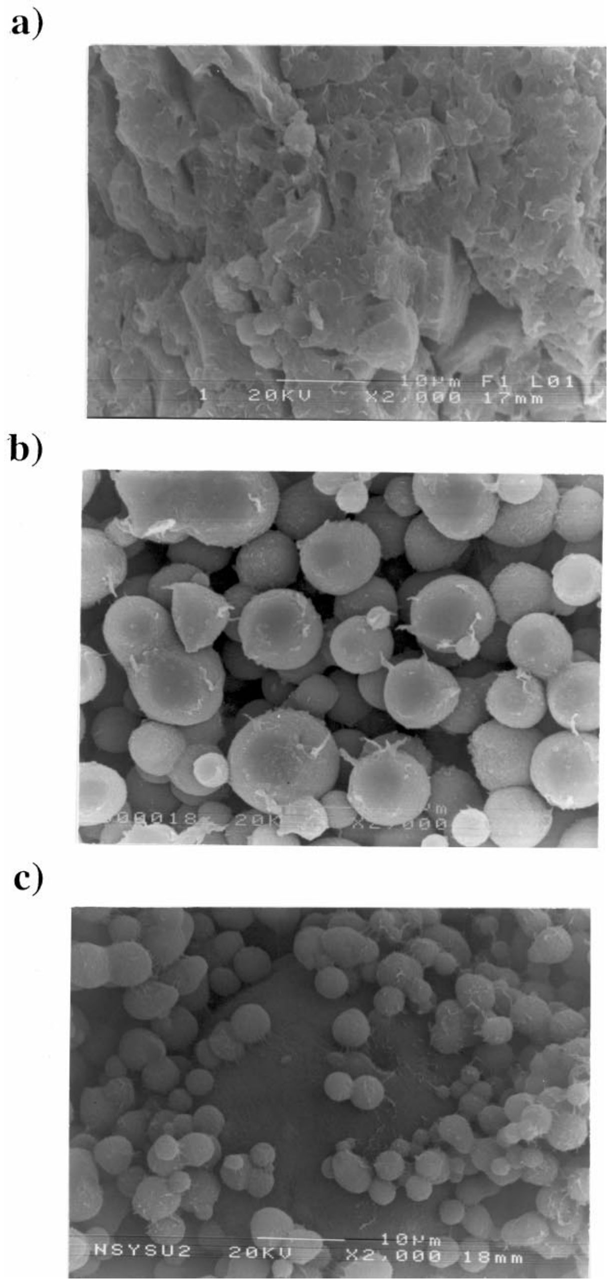

Fig. 2. Fractograph of a) PAn(MSA)/P4VP(MSA)-80, b) PAn(MSA)/P4VP(MSA)-60, and c) PAn(MSA)/P4VP(MSA)-50.

3. Results and discussion

Fracture surfaces of the PAn(MSA)/P4VP(MSA) blends were first examined by SEM. For PAn(MSA)/P4VP(MSA)-80, the fracture surface showed basically various chunks of different shapes and sizes (Fig. 2a), indicative of the brittle nature of the specimen. No second phase was visualized as judged from Fig. 2a; however, further inspection by transmission electron microscopy (TEM) gave different views. The fracture surfaces of PAn(MSA)/P4VP(MSA)-60 and PAn(MSA)/P4VP(MSA)-50 are full of spherical particles (Fig. 2b,c). For PAn(MSA)/P4VP(MSA)-60, most of the spheres have diameters in the ranges 4–10 μm (Fig. 2b), while some spheres of diameters less than 2 μm still existed. Careful examination revealed the presence of some elongated, broken whiskers attached to the surface of the spheres. These whiskers most likely originated from the fractured portions of a mechanically weaker phase, that is the P4VP phase. For PAn(MSA)/P4VP(MSA)-50, the spheres are more heterogeneous in size (Fig. 2c), with most of the spheres less than 5 μm but with the exception of one large sphere with a diameter more than 40 μm. Here also, we detected the whiskers attached to both the small and large spheres.

TEM provided us more detailed morphological information. Here, the products after removal of MSA solvent from

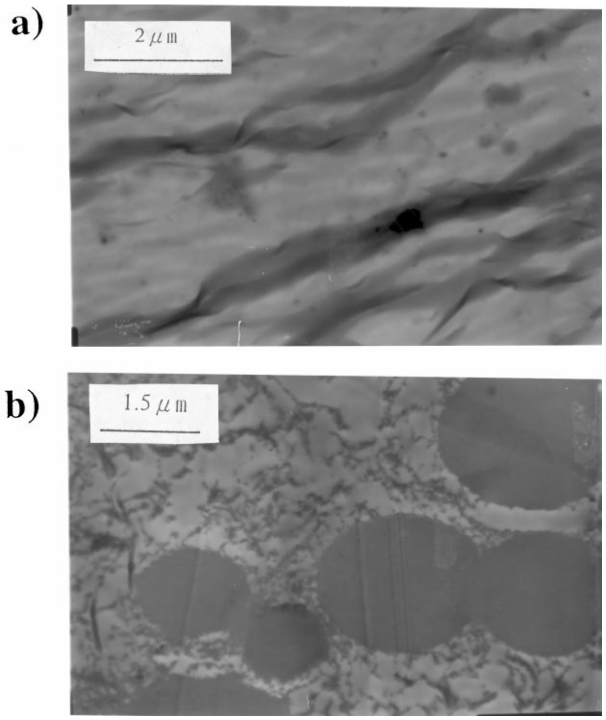

Fig. 3. TEM images of microtomed a) PAn(MSA)/P4VP(MSA)-80 and b) PAn(MSA)/P4VP(MSA)-50.

Fig. 4. TEM image of PAn(MSA)/P4VP(MSA)-80 sample prepared from the suspension solution.

the corresponding mixture solutions were microtomed and examined by TEM. Samples of PAn(MSA)/P4VP(MSA)-80 and -50 were surveyed first (Fig. 3a,b). With higher PAn content, PAn(MSA)/P4VP(MSA)-80 exhibited the presence of several large, dark stripes imposed on the light matrix phase. The sample preparation here used no staining agent and the carbon coating does not impart any electron contrast; therefore, the dark stripes in Fig. 3a should correspond to areas of higher electron density and most probably, PAn-rich domains with electron conductivity. The prevalence of dark stripes of a different shade may indicate the presence of certain layered structures. The microtomed sample of PAn(MSA)/P4VP(MSA)-50 was used to scrutinize the interior morphology of the spherical particles observed in SEM (cf. Fig. 2c). The corresponding TEM micrograph in Fig. 3c clearly demonstrates that the interior portions of the spheres are darker than the matrix phase, which suggests that the particle phase is mainly composed of the PAn component. However, the prevalence of the scattered dendrite-like structures in the matrix phase indicates the inclusion of some PAn in the PVP-rich phase.

Mixture solutions in MSA were poured into ethanol and the resulting suspensions were investigated by TEM. The TEM micrograph for PAn(MSA)/P4VP(MSA)-80 shows an interesting feature, in which several dark, elliptical flakes were scattered over the specimen (Fig. 4). These dark ellipsoids are basically thin flakes as suggested from the observation that the regions superimposed by two or three flakes are darker than other regions without overlapping. One of the dark needle-like profiles (indicated by an arrow) shows the flake nature of the morphology. Several morphologies, such as spherical particles, needle-shaped, and fibrilar structures had been reported for PAn composites prepared from different methods [8–10]. Until now, no such morphology has been mentioned.

The different morphologies shown in Figs. 3a and 4 are both for the same sample, PAn(MSA)/P4VP(MSA)-80; however, the sample preparations are different. The first preparation method involves the continuous removal of MSA from the 5 wt% solution of PAn and P4VP in MSA. During the solvent removal stage, domains with different degrees of phase separation were developing dependent on the residual MSA in the sample mixtures. Fig. 3a shows the existence of stripes of different lightness and shade, which indicates the prevalence of incomplete phase separation in the resulting domains. In contrast, the second preparation method involves instantaneous suspension formation upon dropping the homogeneous solution into the ethanol solvent. Different factors, including phase separation processes between the constitutive components and solvent, diffusion of the MSA solvent into the ethanol, possible liquid crystalline ordered phase, and the shear force experienced by the components, may control the final morphology. Among them, we first considered that this particular composition of PAn/P4VP-80 in MSA may be lyotropic in nature, which upon interaction of the shear force during suspension formation may generate the final elliptical flake morphology. However, the blackish green color of the PAn/P4VP solution prevented a clear identification of any birefringence under polarized light.

The conductivity of doped PAn (PAn(MSA)) and different blends was measured in this study. With the inclusion of 20 wt% P4VP, PAn(MSA)/P4VP(MSA)-80 has a conductivity of 1.1×10^{-1} S/cm, which is comparable to the pure doped PAn(MSA) (4.6×10^{-1} S/cm). A clear trend that the blend's conductivity decreases with increasing P4VP content is seen as the conductivity for PAn(MSA)/P4VP(MSA)-60 and -50 is 5.9×10^{-2} and 2.9×10^{-3} S/cm, respectively. No speculation on the relationship between morphology and conductivity is made at this moment since there are only a few data points available.

4. Conclusion

Free standing films can be prepared from solutions of PAn and P4VP in MSA with PAn content from 100 to 50 wt%. For blends with 80 wt% of PAn, an interesting elliptical flake morphology was observed, which is in contrast to the pure PAn(MSA) and blends of other compositions. For all samples prepared in this study, a conductivity ranging from 4.6×10^{-1} to 2.9×10^{-3} S/cm was detected.

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