

SHORT COMMUNICATIONS

Preparation and Properties of Conducting Polymer Blends of Polyaniline in Poly(vinyl formal) or Poly(methacrylic acid)

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Conducting polyaniline (PAn), with a bright future in application, has attracted considerable interest in recent years. But, up to now, commercial applications of it have been limited. One of the obstacles to practical use of PAn is its poor processability. With a rigid π -conjugated backbone molecular structure, PAn decomposes without melting when heated. Therefore, it is impossible to process it by conventional methods such as extrusion or injection molding. Also, few proper solvents have been found for PAn. Another hindrance is bad stability with air and water. So the search for means to improve processability and stability has been one of the most active aspects of studies for PAn. Among several proposed ways, the most effective is to synthesize polymer blends or polymer composites in which PAn is combined with inert polymers such as polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC), and so on. These polymer blends would possess good processability and stability in addition to novel conductivity. For this purpose, scientists have tried various things and yielded some positive results. Tang *et al.*¹ by vapor phase polymerization in which the oxidant containing insulating polymer is exposed to aniline vapor, obtained PAn/Nylon blend. Yang and Ruckenstein,² by emulsion method, in which PAn is coated onto the

surface of inert submicron thermoplastic polymer latex particles by *in-situ* polymerization, prepared PAn/PMMA and PAn/PS composites. Yamamoto *et al.*,³ by colloidal systems, in which an inert polymeric surfactant is coated on the outside of the sub-micron PAn particles through physical absorption, got PAn/PVA (PVA, poly(vinyl alcohol) composites. Heeger *et al.*⁴ synthesized PAn/PMMA blends which possess high electric conductivity and excellent optical quality.

This article reports a new way to prepare PAn/PVF (PVF, poly(vinyl formal)) and PAn/PMAC (PMAC, poly(methacrylic acid)) composites which contain pseudo-IPN system with a conjugated linear conducting PAn in a cross-linked PVF or PMAC matrix.

EXPERIMENTAL

First, adding HCl (0.2 mol l^{-1}) and varied concentrations of formaldehyde to aqueous solution of PVA (10 g l^{-1}) and stirring the solution for 2 hours at 40°C ; secondly, adding $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.2 mol l^{-1}) and aniline (0.2 mol l^{-1}) into the solution prepared in the first step and stirring for 24 hours at room temperature; thirdly, pouring the solution from the second step into a special beaker and drying it at room temperature for 36 hours, then at 100°C under N_2 atmosphere for 2 hours to get

free standing film, immersing the film successively in water and alcohol-ether (1:1 in volume) solvent for 48 and 36 hours respectively; finally, drying the film in vacuum at 40°C for 24 hours, we obtained a PAn/PVF film. The solution from the second step was heated to 100°C for 2 hours to precipitate the polymer blend. Washing the precipitate in 0.1 mol l⁻¹ HCl aqueous solution and alcohol-ether solvent and drying it in vacuum at 40°C for 48 hours, we got PAn/PVF composites.

By *in-situ* polymerization of aniline in aqueous solution of PMAC, PAn/PMAC composite was synthesized. An aqueous solution of methacrylic acid (0.5 mol l⁻¹) with (NH₄)₂S₂O₈ (0.2 mol l⁻¹) was stirred at 40°C for 4 hours. The reaction solution consisting of PMAC was allowed to cool to about 5°C. Aniline (0.5 mol l⁻¹) and (NH₄)₂S₂O₈ (0.3 mol l⁻¹) were added to the solution, and it was stirred at 5°C for 6 hours to get a dark blue solution which included PMAC and PAn. This dark blue solution was poured into ethanol-ether solvent to precipitate the polymer composite. After drying the precipitate at 50°C for 48 hours, we obtained a PAn/PMAC composite. With various molar ratios of aniline to methacrylic acid, we prepared several PAn/PMAC samples possessing different electrical properties.

Electron micrographs of PAn/PMAC and PAn/PVF were obtained using an SM-2000FT

scanning microscope. The specimen for SEM was prepared by fractured polymer samples under liquid nitrogen temperature. The machine was operated at 160 kV and the magnification in Figure 1 was 10,000 ×.

Thermal stability of PAn/PVF and PAn/PMAC was investigated by baking the composites in air atmosphere at 200°C. Conductivities of polymer blends at various baking times were measured and are shown in Figure 5.

Conductivity of blends was measured by compressed disc ($r=4$ mm; thickness = 1.5 mm) pressed under 600 kg cm⁻². A four-probe method and two-probe method were employed to measure conductivities of polymer blends, and an improved four-probe method⁵ was also used to determine conductivities of polymer films.

RESULTS AND DISCUSSIONS

SEM micrographs of PAn/PVF (aniline/PVA=0.2, in weight) and PAn/PMAC (aniline/methacrylic acid=0.2, in weight) are shown in Figure 1. The PAn component appears to have a continuous network morphology structure in PVF or PMAC matrix. This continuous network structure provides composites with conducting paths.

Figure 2 gives the relationship between the concentration of formaldehyde and conduc-



Figure 1. SEM of PAn/PVF (a) and PAn/PMAC (b), 10000 ×. The white section stands for the PAn component.

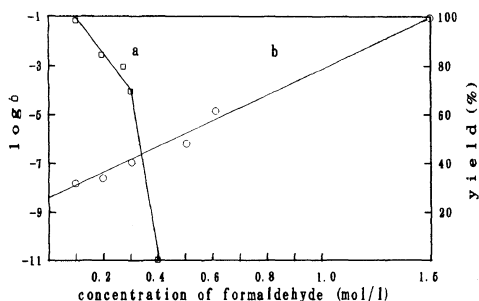


Figure 2. Conductivity (a) and yield (b) of PAn/PVF prepared with various formaldehyde concentrations and 0.5 mol l^{-1} aniline.

tivity (a) and yield (b) of PAn/PVF composites. The extreme sensitivity of PAn/PVF blends to concentrations of formaldehyde employed in preparing blends is shown in curve a. From the beginning of curve a, the conductivity decreases with increasing formaldehyde concentration. When the concentration rises to about 0.25 mol l^{-1} , the conductivity drops sharply and blend transforms from a conductor to insulator. This may be due to increasing formaldehyde concentration, with consequent increase in the volume of insulating PVF component in the composites. This leads to growth in the yield of PAn/PVF composite, as is illustrated in curve b of Figure 2. Thus, when the PVF component increases, PAn content in PAn/PVF decreases. When the insulating part rises to a critical value, the morphology of conducting component changes from a continuous network structure to an isolated domain. In other words, conducting paths in these composites are broken, which leads to transformation in electrical properties. This result is also illustrated clearly in Figure 3 in which the effect of weight ratios of aniline to PVA on the conductivity of PAn/PVF films, obtained under 0.1 mol l^{-1} formaldehyde, is shown. As may be seen in Figure 3, films synthesized with a lower aniline weight ratio (aniline/PVA < 0.2 , in weight) possess high resistivity, and composites synthesized with higher aniline weight ratio

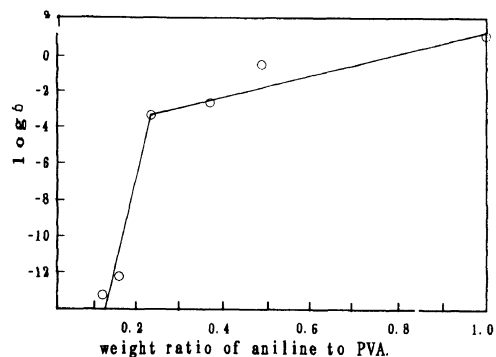


Figure 3. Conductivity of PAn/PVF films prepared at different weight ratios of aniline to PVA.

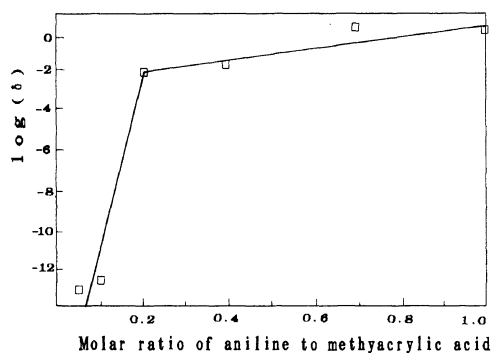


Figure 4. Relationship between the conductivity of PAn/PMAC and molar ratio of aniline to methacrylic acid.

(aniline/PVA > 0.2 , in weight) have high conductivity. The transformation from insulator to conductor takes place when aniline weight ratio nears 0.2.

Figure 4 gives the relationship between the molar ratio of aniline to methacrylic acid and conductivity of PAn/PMAC composites. As be shown in Figure 4, the conductivity rises with increasing molar ratio of aniline to methacrylic acid. The transformation from an insulator to conductor takes place as the aniline molar ratio nears 0.24.

The thermal stability for PAn and PAn/PMAC and PAn/PVF was investigated by baking at 200°C in air atmosphere. The conductivity of polymers for different baking periods is illustrated in Figure 4. PAn/PMAC gives a higher thermal stability than pure

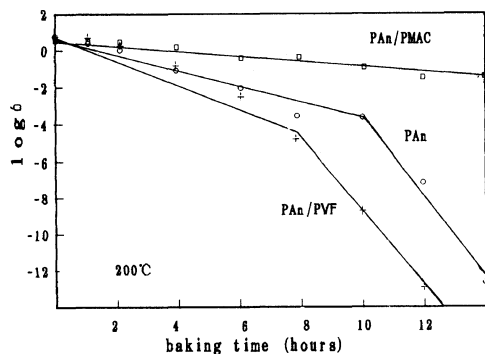


Figure 5. Conductivity of PAN and PAN/PMAC and PAN/PVF for different baking periods.

PAN and PAN/PVF do. This shows that the incorporation of PMAC with PAN provides a means to improve the thermal stability of PAN. In fact, the special molecular structure of PMAC possesses good thermal stability which prevents PAN/PMAC blends from oxidation and degradation. In other words, PAN/PMAC possesses both the conductivity of PAN and thermal stability of PMAC. But, surprisingly the thermal stability of PAN/PVF is bad and

even worse than that of pure PAN.

CONCLUSION

In conclusion, combining PAN with the proper amount of PVF or PMAC by *in-situ* polymerization may produce conducting PAN/PMAC and PAN/PVF composites. Conductivity is close to that of pure PAN. Compared with PAN and PAN/PVF, PAN/PMAC has the best thermal stability.

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