# Investigation of the Properties of Polyacrylamide–Polyaniline Composite and Its Application as a Battery Electrode

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## SYNOPSIS

The composite films of polyacrylamide and polyaniline were prepared by polymerizing aniline using ammonium persulfate as an initiator in an aqueous solution containing polyacrylamide. A film was then cast from this solution. The structural, dynamic mechanical, electrical, and thermal properties of these films have been studied. The infrared spectrum shows the presence of polyacrylamide as well as polyaniline in the composite film. The thermal analysis shows that the composite degrades slower than does the polyacrylamide alone. The dynamic mechanical analysis indicates that there is an increase in the glass transition temperature after the composite formation. The electrical conductivity has been found to increase by more than eight orders of magnitude. These composite films have also been suitably used as electrodes in secondary batteries. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Ever since Mac Diarmid et al.[1] investigated polyaniline as an electrically conducting polymer, many papers have appeared on polyaniline. The electrical properties of polyaniline can be controlled suitably by charge-transfer doping or by protonation. Polyaniline can be synthesized by both electrochemical and chemical oxidative polymerization,[2] although not many papers deal with chemically polymerized polyaniline. Pron et al.[3] reported the chemical polymerization of aniline using different oxidizing agents. Armes and Miller[4] reported the polymerization of aniline at 20°C using ammonium persulfate as the oxidant.

The main disadvantages of conducting polymers are their poor processibility, mechanical properties, and environmental stability. Therefore, attempts have been made to form composites that have good electrical properties with improved mechanical strength.[5,6] Polypyrrole composites with poly(vinyl chloride), methyl cellulose, and methyl methacrylate have been reported using electrochemical as well as chemically oxidative polymerization of pyrrole.[7-10] In the present article, we have investigated the structural, thermal, electrical, and dynamic mechanical properties of a polyacrylamide and polyaniline composite. Its probable application as a battery electrode has also been investigated.

## EXPERIMENTAL

All the chemicals used were of AR grade. Aniline was distilled under reduced pressure before use. The polyacrylamide was prepared by polymerizing acrylamide using titanium chelate. The detailed procedure has been given elsewhere.[11] One hundred grams of 10% w/w aqueous solution of polyacrylamide thus prepared was taken. Five milliliters of $1.5M$ HCl solution containing 2 mL aniline was added to it. The temperature of this flask was maintained at 0°C. To this flask, 5 mL of $1.5M$ HCl solution containing ammonium persulfate was added dropwise with constant stirring, maintaining the temperature at 0°C. With the oxidation of aniline being highly exothermic, proper care was taken to maintain the temperature. The aniline/ammonium
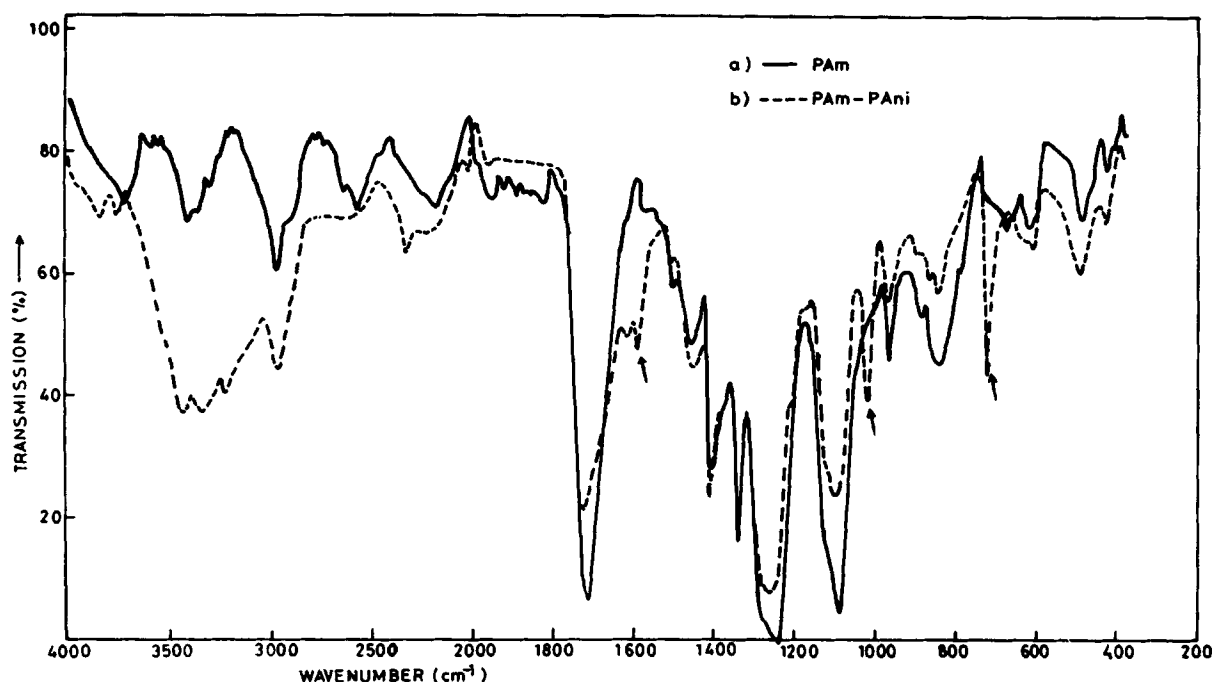
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**Figure 1**   Infrared spectra of (a) polyacrylamide and (b) polyacrylamide–polyaniline composite.

persulfate molar ratio was kept at 2. The addition was done over 1 h and it was kept at 0°C for a further 3 h. The detailed procedure is described elsewhere.[12]

After 4 h, the flask was taken out of the temperature bath. A dark bluish green color was seen in the polyacrylamide solution. A film of an approximate thickness of 100 microns was cast from this solution. This film was washed first with methanol and then with diethyl ether and dried under vacuum. This film was then used for further investigation. A similar film of polyacrylamide alone was cast for comparative study. The polyaniline content in the composite was varied between 1 and 20%.

The chemical compositions of the films were studied using a Perkin-Elmer 397 IR spectrometer. The dynamic mechanical properties of the films were studied using a Rheovibron DDV-II (Toyo Baldwin Co.) operating at a frequency of 11 Hz. A sample of size 0.5 × 4 cm was held between a pair of chucks in a temperature-controlled chamber. The sample was heated at the rate of 3°C/min, and dynamic force and tan $\delta$ values were measured. These measurements were done initially at increments of 5°C and later at increments of 3°C in the regions of greater change. The electrical conductivity was measured in sandwiched configuration as discussed elsewhere.[13,14] The thermal properties of the materials were studied using a Stanton Redcroft DTA/

TGA instrument Model STA 780 at a rate of heating 5°/min. The morphology of the films was studied using a SEM Philips Model 515.

## RESULTS AND DISCUSSION

The infrared spectra were taken by coating a thin layer of the polymer on polyethylene film and keeping a blank polyethylene film in the reference beam. This facilitated having better-resolved peaks. Figure 1(a) shows the infrared spectrum of polyacrylamide alone and Figure 1(b) shows its composite with polyaniline in which the polyaniline content is around 2%. The composite shows additional peaks at 1600, 1495, 1285, 1040, and 750 $cm^{-1}$. These peaks have been attributed to polyaniline.[15] The presence of these additional peaks in the composite film shows that a polyacrylamide–polyaniline blend has been formed.

Figures 2 and 3 show the differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of polyacrylamide and its composite with polyaniline. The differential thermal analysis for polyacrylamide shows an endothermic peak at 232°C, whereas for the composite, it has shifted to 242°C. This peak has been attributed to the melting of polyacrylamide.[11] From the thermogravimetric
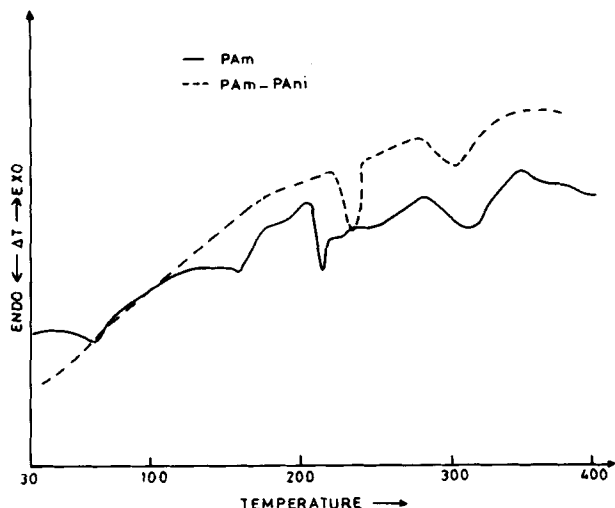
**Figure 2** Differential thermal analysis of polyacrylamide and its composite with polyaniline.



**Figure 4** Dynamic mechanical analysis of polyacrylamide and its composite with polyaniline.

analysis, we can see that the polyacrylamide loses more than 20% weight up to 250°C and, afterward, it loses weight at a still faster rate. The thermogravimetric analysis of the composite shows that it has lost only 10% of its weight up to 250°C, and even up to 300°C, it has retained more than 70% of its weight. Thus, the composite has a higher melting point and is thermally more stable than is polyacrylamide alone.

The dynamic mechanical analysis of the samples were carried out on a viscoelastometer at a frequency of 11 Hz. Figure 4 shows the plot of tan $\delta$ values vs. temperature. For polyacrylamide, we can see two peaks, respectively, at 48 and 135°C. The first
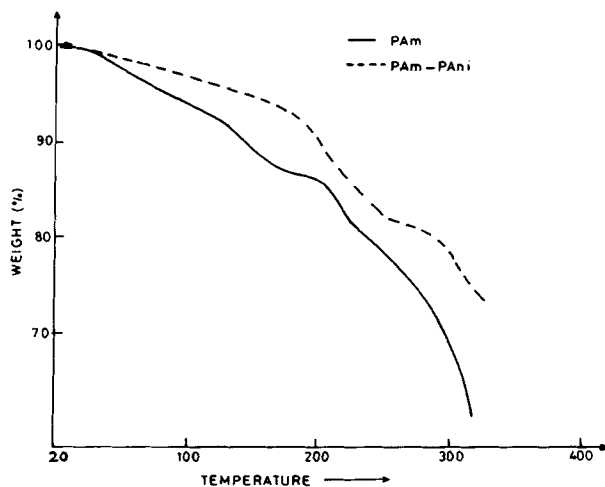
smaller peak is a $\beta$ transition peak, which can be attributed to the motion of part of a chain or its side groups.[16] Here, it is due to —$CONH_2$ groups. The second peak can be associated with the glass transition.[16] In the case of the composite, the first peak has reduced appreciably, suggesting that the side-chain motion is hindered when aniline polymerizes within the structure, making the movement of amide groups difficult. Also, the glass transition temperature for the composite has increased by about 10°C (145°C).

The electrical conductivities of the samples were analyzed in a sandwiched configuration. The conductivity of the polyacrylamide alone was lower than
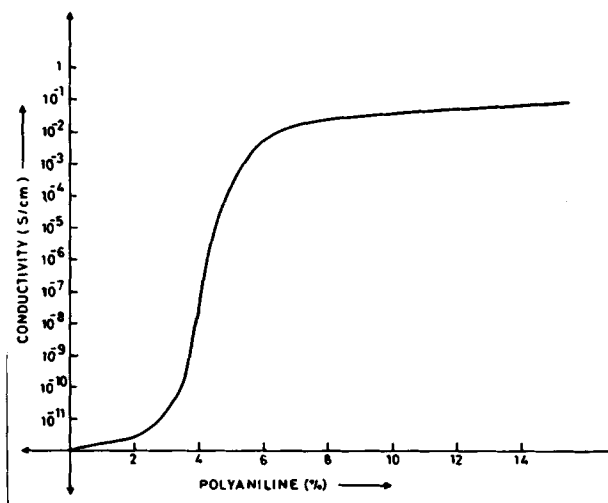


**Figure 3** Thermogravimetric analysis of polyacrylamide and its composite with polyaniline.



**Figure 5** Variation of conductivity of the composite with polyaniline content.
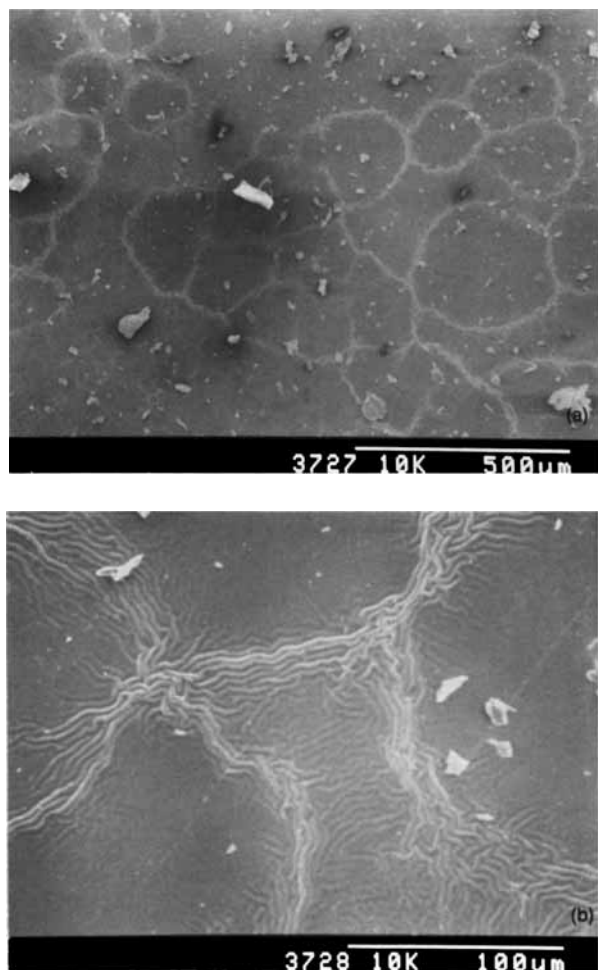
**Figure 6** (a) Micrograph of polyacrylamide–polyaniline composite film. Note typical ringlike network. (b) Same as (a), but at a higher magnification. Note the wrinkled wavy network.

$10^{-10}$ S/cm. The conductivity of the polyacrylamide–polyaniline composite was found to increase with polyaniline, and with 12% polyaniline, it was found to be $5.13 \times 10^{-2}$ S/cm. Further increase in the polyaniline content was not found to have an appreciable effect on the conductivity. Figure 5 shows the variation of conductivity with polyaniline content in the composite.

To understand the changes occurring in the conductivity, it was thought of interest to investigate the morphological features, in particular, the distribution of polyaniline in polyacrylamide. A scanning electron microscope was used for the purpose and photographs were obtained for various surfaces and sections of the film. A typical photomicrograph depicting the distribution of polyaniline is shown in

Figure 6(a) and (b). It can be seen that polyaniline forms a typical ringlike network [Fig. 6(a)]. At higher magnification [Fig. 6(b)], the ring reveals a wrinkled wavy network. It has a fibril-like appearance, having an average width of 2.5 microns and length of 40 microns. The rings are of various sizes and are not necessarily interconnected. Thus, the distribution of polyaniline in the host polymer is not even. The progressive increase in the polyaniline content gives rise only to such a structure and not to a homogenous distribution. The limiting value observed in the conductivity data is possibly due to such uneven distribution.

The composite film (5 × 1 cm) was washed with methanol and dried under vacuum. This was used as the test electrode without further treatment. An iron plate (surface area 5 cm²) was used as the other electrode. The electrodes were mounted in a simple beaker-type cell with no separator, containing 50 mL of $1M$ $FeCl_3$ solution. The discharging was conducted under a constant load of 2 kOhms. The charging was carried out using an external dc source. The current during charging was kept at 20 $\mu A/cm^2$.

The composite film acted as the anode and the iron plate acted as the cathode during discharge. The $V_{oc}$ was 0.73 V and $I_{sc}$ was 85 $\mu A/cm^2$. The discharge was stopped when the voltage reached 0.3 V. A typical charge–discharge curve is shown in Figure 7. The battery was rechargeable and several cycles were demonstrated. Table I shows $V_{oc}$, current density, and power density values for the different battery systems.
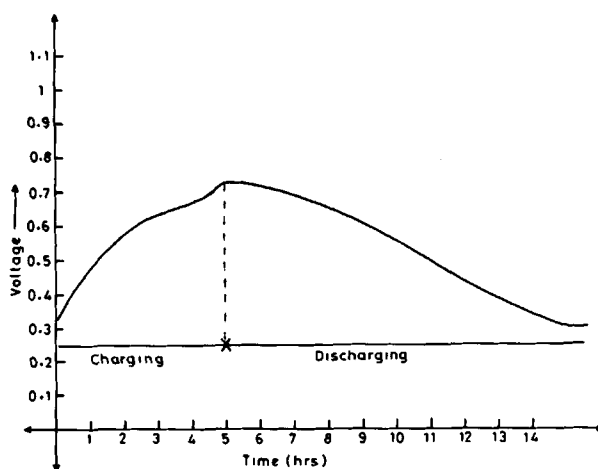


**Figure 7** Variation of voltage during a charge–discharge cycle of a secondary battery having polyacrylamide–polyaniline as the anode.

**Table I**   $V_{oc}$, $I_{sc}$, Current Density, and Power Density for Different Battery Systems

| Battery System | $V_{oc}$ (volts) | $I_{sc}$ ($\mu A/cm^2$) | $A$ (h/kg) | $W$ (h/kg) |
|---|---|---|---|---|
| PAm–PAni/ZnCl$_2$/Zn | 0.58 | 62 | 89.5 | 51.9 |
| PAm—PAni/CuCl$_2$/Cu | 0.76 | 78 | 106.7 | 81.1 |
| PAm–PAni/AlCl$_3$/Al | 0.84 | 89 | 124.3 | 104.4 |
| PAm—PAni/FeCl$_3$/Fe | 0.73 | 85 | 109.4 | 79.9 |

## CONCLUSION

The above studies indicate that the composite of polyaniline can be suitably prepared with polyacrylamide to obtain a free-standing and electrically conducting film. These films are quite stable up to 250°C. The composite formation is at the molecular level. The composite can be suitably used as an electrode in a rechargeable battery operating in a cheaper aqueous medium.

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