

## Conductive Composite Films Prepared Using Undoped Polyaniline and Poly(methyl methacrylate)

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**ABSTRACT:** In this study, undoped polyaniline–poly(methyl methacrylate) films were cast from solutions containing different amounts of soluble part of undoped polyaniline and poly(methyl methacrylate) in dimethylformamide. The films contained undoped polyaniline up to 60% since the solubility of undoped polyaniline in dimethylformamide was 1.14 g/100 mL. The conductivity of undoped polyaniline–poly(methyl methacrylate) films were investigated after being redoped in some acids such as oxalic, nitric, and hydrochloric acids. When the films doped with hydrochloric acid was kept in air, the conductivity decreased gradually by 32%. Their temperature sensor behavior was examined in the range of –15 to 120 °C. The characterization of films was performed by conductivity measurement, FT-IR, UV, and TGA techniques.

**KEY WORDS** Polyaniline / Conductive Film / Poly(methyl methacrylate) / Composite /

Polyaniline (PAN) is one of the intrinsically conducting polymers (ICPs). Its doped form is insoluble in common organic solvents and decomposes before it melts.<sup>1</sup> That is why it is not always possible to cast into different forms. The chemical polymerization gives a powdered PAN.<sup>2–4</sup> The electrochemical polymerization of aniline gives a film on the electrode with very poor mechanical properties. The PAN film formed on the electrode surface after the electrolysis can not be peeled off in a freestanding form.<sup>5–7</sup>

There are various methods to improve the mechanical properties of polyaniline. One of them is preparation of the composites or blends of polyaniline with an insulating polymer having better mechanical properties.<sup>8–13</sup> The preparation of conductive films can be carried out by both the electrochemical and chemical ways. In the electrochemical method the surface of the electrode is covered with an insulating polymer in advance and then this electrode is used as a working electrode in the electrochemical oxidation of aniline.<sup>14–16</sup> In the chemical method the polymerization of aniline is carried out in a solution of an insulating polymer and the resulting mixture is cast into films on a smooth surface such as glass in order to obtain polyaniline-insulating polymer conducting film.<sup>8,12</sup> In an alternative method, conductive PAN is directly mixed with a solution of an insulating polymer and films are cast from the solution. However, in this method it is not possible to control the homogeneity of the conducting PAN particles in the film.<sup>10,17,18</sup>

PAN doped with specific dopant ions can be soluble to a certain extent in some organic solvents

such as dimethylsulphoxide, dimethylformamide and *N*-methylpyrrolidone.<sup>19–21</sup> It is also reported that the solubility of undoped PAN is higher in these solvents than that of the conductive form.<sup>22–24</sup>

This study deals with a new method of preparation of PAN-insulating polymer films. In this method, soluble parts of undoped PAN in DMF and poly(methyl methacrylate) were mixed together in DMF and the mixture was cast into undoped films. Undoped films obtained by this way were doped with various acids in order to convert them into conductive PAN–poly(methyl methacrylate) films. These films were characterized by means of conductivity measurement, FT-IR, UV-vis, and TGA techniques.

### EXPERIMENTAL

#### Materials

Aniline was distilled under vacuum. Poly(methyl methacrylate) (PMMA) with a viscosity average molecular weight of 150000 was synthesized by solution polymerization using benzoyl peroxide. Other chemicals were used as purchased from Merck Co.

#### Procedures

Aniline was polymerized in 1.0 M oxalic acid solution with  $K_2Cr_2O_7$  at 25 °C. The aniline/oxidant mole ratio was 6/1. The mixture was allowed to react for 24 h. PAN doped with oxalic acid precipitated in the final stage of the polymerization was filtered and the polymer was washed with water. The conductive PAN sample was treated with 3.0 M  $NH_3$  solution for 8 h.

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PAn being freed from the dopant was filtered and washed with excess water and dried.

The undoped PAn sample was added to excess DMF and stirred at room temperature for 4 h. The insoluble part of the PAn was filtered. The filtrate was kept in air to remove the solvent, which left undoped PAn soluble in DMF. These parts of undoped PAn were used to obtain undoped PAn-PMMA films containing undoped PAn at different ratios in DMF.

The films were prepared by mixing the solutions containing prescribed amounts of the undoped PAn and the PMMA (0.5%) in DMF. The mixtures were dropped on glass plates ( $1.5 \times 1.5 \text{ cm}^2$ ) and dried at room temperature for 24 h in ambient atmosphere and then in vacuum at  $50^\circ\text{C}$  for 12 h. The films with different thickness were obtained by changing the amount of the solution put on the glass plate. The thickness of the films was determined by the use of a micrometer with sensitivity of 0.01 mm by taking average of the thickness at 5 different points.

#### Measurements

The conductivity of the samples was measured by the use of four-probe technique. FT-IR spectra of the doped and undoped PAn-PMMA films and pure polymers were taken with KBr pellets by using a Matson 1000 FT-IR spectrometer. UV-vis spectra were obtained by the use of Shimadzu 160 A spectrophotometer. Thermogravimetric analysis was carried out by using a Linseis Model thermal analyzer under He atmosphere with a flow rate of  $10 \text{ mL min}^{-1}$  at a heating rate of  $10^\circ\text{C min}^{-1}$ .

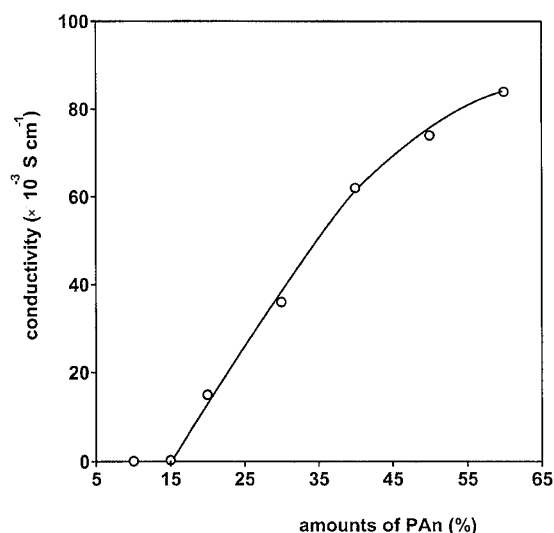
Temperature dependence of the resistance was measured in a temperature range of  $-15$  to  $+120^\circ\text{C}$ . The film attached to a copper wire using a conducting Ag paint was placed in a temperature-controlled chamber with a heating rate of  $3^\circ\text{C min}^{-1}$ . The resistance of the conducting PAn-PMMA film was recorded as a function of temperature.

## RESULTS AND DISCUSSION

#### Conductivity of Composite Films

PMMA, which is soluble in DMF, was used as the insulating polymer since undoped PAn is partly soluble in DMF. The solubilities of oxalic acid in the doped and undoped PAn are  $0.008 \text{ g/100 mL}$  and  $1.14 \text{ g/100 mL}$ , respectively. The films containing the undoped PAn up to 60% were prepared due to limitation of the solubility of undoped PAn in DMF.

The PAn-PMMA film containing 60% undoped PAn was easily peeled off the glass surface. The comparison of this film with the ones containing lower amount of



**Figure 1.** Effect of PAn content on conductivity at  $25^\circ\text{C}$  for PAn-PMMA films doped with 2.0 M HCl, for 1 h. Film thickness was 0.07 mm.

undoped PAn showed no significant difference in durability.

The undoped PAn-PMMA films were redoped by keeping them in 1.0 M aqueous oxalic acid for an hour. Dark blue color of undoped PAn-PMMA films changed into dark green, which is characteristic of conductive PAn. The conductivity of the doped film containing 60% PAn was found to be  $1.3 \times 10^{-5} \text{ S cm}^{-1}$ . The conductivity values of films having undoped PAn lower than 60% were out of measurement limit ( $10^{-6} \text{ S cm}^{-1}$ ) in our laboratory conditions. Similarly the doping process of the film containing 60% undoped PAn with  $\text{HNO}_3$  resulted in a conductivity value of  $5.6 \times 10^{-5} \text{ S cm}^{-1}$ .

High conductivity values were observed by doping of films in 2.0 M HCl. As seen from Figure 1 the films containing 10–60% undoped PAn after the doping treatment gave conductivity values in the range of  $0.05 \times 10^{-3}$  to  $8.5 \times 10^{-3} \text{ S cm}^{-1}$ . The conductivity of the PAn-PMMA film increased with the amount of PAn they contain. The conductivity of pure PAn doped in 2 M HCl was  $0.25 \text{ S cm}^{-1}$ . The conductive form of PAn-PMMA film was redoped in 3.0 M NaOH.

Table I shows the dependence of conductivity of films on HCl concentration employed in doping process. The experiments were carried out on films containing 60% undoped PAn. It was found that the conductivity of the film increased with the dopant concentration and then leveled off as mentioned in numerous studies.<sup>25,26</sup>

The conductivity of the films is affected by the diffusion capability of the dopant ions into the film. Therefore waiting period in HCl and the thickness of the film is of great importance for homogenous distribution of

**Table I.** Effect of concentration of HCl used as dopant on the conductivity of HCl doped PAN-PMMA film containing 60% undoped PAN

[HCl] (mol L <sup>-1</sup> )	Conductivity (10 <sup>-3</sup> S cm <sup>-1</sup> )
0.5	0.9
1.0	3.7
1.5	5.8
2.0	8.5
2.5	8.2
3.0	8.7

Thickness, 0.07 mm; temperature, 25 °C; doping period, 1 h.

**Table II.** Effects of film thickness and doping period in 2.0 M HCl on the conductivity of PAN-PMMA film containing 60% PAN

Time (min)	Conductivity (10 <sup>-3</sup> S cm <sup>-1</sup> )			
	0.05 mm	0.07 mm	0.09 mm	0.12 mm
5	0.45	2.2	2.6	1.7
10	0.56	3.6	3.5	2.8
30	0.62	6.3	5.2	4.5
60	0.96	8.5	6.8	6.0
120	1.02	8.8	8.1	7.5

Temperature, 25 °C; [HCl], 2.0 M.

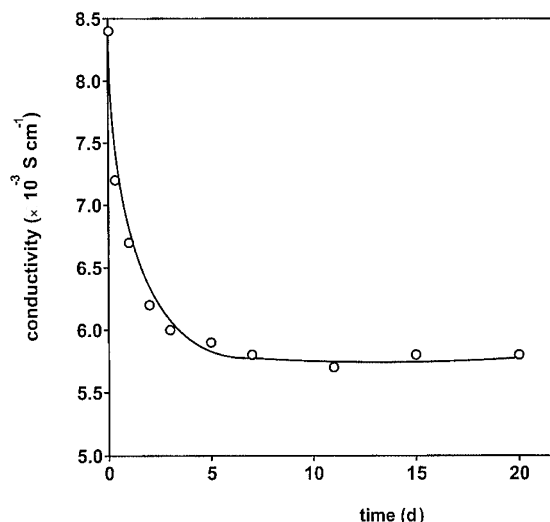
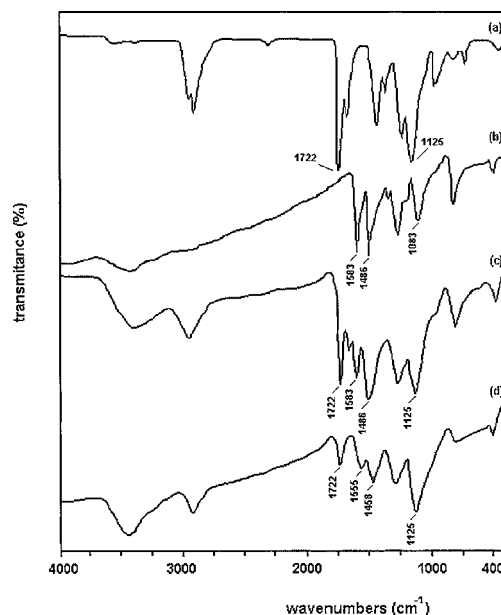
the dopant ions. In order to investigate these effects the films containing 60% undoped PAN with varying thickness were kept in 2.0 M HCl for different periods. The conductivities of samples were given in Table II.

The film reached to a certain conductivity value within five minutes and the conductivity increased with the doping period. In the films with thickness of 0.05 and 0.07 mm the conductivity reached equilibrium after one hour. The doping period of two hours in films with thickness of 0.09 and 0.12 mm gave higher conductivity values than that those obtained with a doping period of one hour. Therefore even a period of two hours is not sufficient in these films for attaining equilibrium distribution of the ions in the films.

Figure 2 shows the effect of waiting period in air upon the conductivity of film. This experiment was carried out using PAN-PMMA film doped in 2.0 M HCl for one hour. The conductivity of the film was decreased with time and remained constant at  $5.8 \times 10^{-3}$  S cm<sup>-1</sup> after 6 d. The decrease in conductivity in this period was approximately 32%.

#### FT-IR Spectra

Figure 3 shows the FT-IR spectra of (a) PMMA, (b) conductive PAN, (c) undoped, and (d) conductive PAN-PMMA films. Among these films, conductive films were prepared by doping with HCl. The C=O band observed at 1722 cm<sup>-1</sup> in PMMA and the bands observed at 1486 and 1569 cm<sup>-1</sup> belonging to the C-N and C=N bands of benzenoid and quinoid units<sup>27</sup> in doped PAN

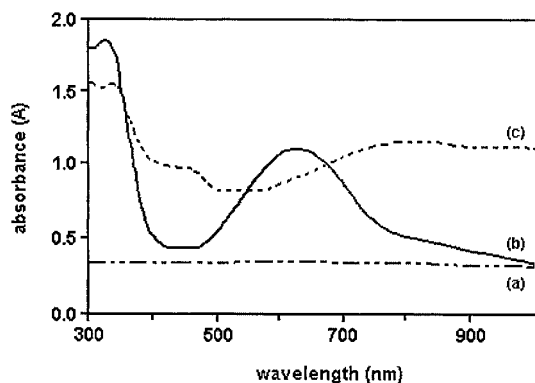
**Figure 2.** Effect of waiting period in air upon the conductivity of PAN-PMMA films doped with 2.0 M HCl. The thickness of film was 0.07 mm.**Figure 3.** FT-IR spectra of (a) PMMA, (b) doped PAN, (c) undoped PAN-PMMA film, and (d) doped PAN-PMMA film.

are clearly seen in the doped PAN-PMMA film.

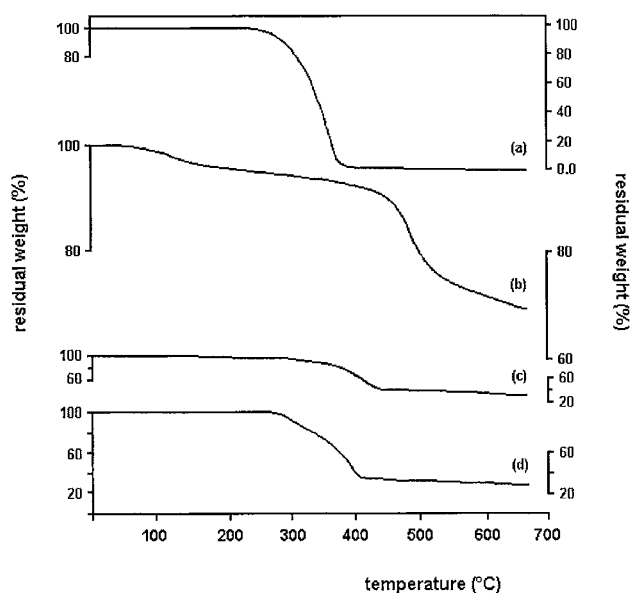
The bands observed at 1500 and 1583 cm<sup>-1</sup> in the undoped PAN-PMMA film (spectrum c) shift to 1486 and 1569 cm<sup>-1</sup> in the conductive film (spectrum d), respectively. This shift corresponds to benzenoid-quinoid ring transitions.<sup>28</sup> Also the intensity of peak at 1150 cm<sup>-1</sup>, which is characteristic to conductive PAN (spectrum b), decreases in the undoped PAN-PMMA film (c) and appears in an intensive and broader fashion in the conductive PAN-PMMA film (d). This conductivity band corresponds to charge delocalization on the PAN chains.<sup>29</sup>

#### UV-vis Spectra

The UV-vis spectra taken by the use of the undoped



**Figure 4.** UV-vis spectra of (a) PMMA film, (b) undoped PAN-PMMA film, and (c) PAN-PMMA film doped with 2.0 M HCl.

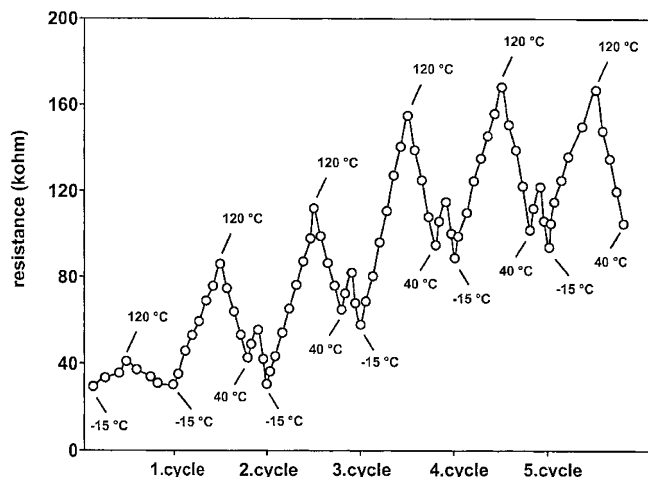


**Figure 5.** TGA thermograms of (a) PMMA, (b) doped PAN, (c) undoped PAN-PMMA film, and (d) PAN-PMMA doped with 2.0 M HCl.

PAN-PMMA film peeled off from the glass surface are shown in Figure 4. The band at 630 nm observed in the undoped PAN-PMMA film (b) is due to a  $\pi$ - $\pi^*$  transition of quinone-imine groups.<sup>30</sup> This band disappears in the conductive PAN-PMMA film (c) and two new bands appear at 456 and 800 nm which are related to the  $\pi$ - $\pi^*$  transitions of quinone-iminium ions and the presence of localized cation radicals, respectively.<sup>30-32</sup>

#### TGA

Figure 5 shows the thermograms of PMMA, doped PAN, undoped and doped PAN-PMMA films taken in a temperature range of 20 °C to 680 °C. It is observed that the weight loss of pure PMMA (a) starts at 270 °C and loses all its weight at 680 °C. The first weight loss of doped PAN gives range of 100–300 °C due to removal of water and dopant molecules.<sup>26</sup> The second weight loss starting at 300 °C corresponds to the degradation of the PAN chain and it loses 58% of its total weight



**Figure 6.** Temperature dependence of the resistance of conductive PAN-PMMA film in the range from -15 °C to 120 °C.

at 680 °C (b). On the other hand, the weight losses of the undoped PAN-PMMA and doped PAN-PMMA films are 76% and 85% at 680 °C, respectively (c and d). These data indicate that both the undoped and doped PAN-PMMA films have higher thermal stability than PMMA and lower thermal stability than doped PAN.

#### Thermal Sensor Properties

Figure 6 shows the change in the resistance of the doped PAN-PMMA film with the temperature. The curve in Figure 6 was obtained by heating the film from -15 to +120 °C and then cooling down to -15 °C. The resistance of doped PAN-PMMA film increased during the heating process. However the resistance decreased in the range from 120 °C to 40 °C, increased in the range from 40 °C to 10 °C and decreased again below 10 °C during the cooling process. The results of five heating and cooling cycles revealed that the doped PAN-PMMA film gave a reversible response against the temperature.

#### CONCLUSION

In this study, conductive PAN-PMMA films having excellent mechanical strength were prepared using a new method. Firstly, ternary solutions of undoped PAN and PMMA in DMF were cast into films and then these films were doped with acids such as oxalic acid, HNO<sub>3</sub> and HCl to obtain conductive PAN-PMMA films. Due to the soluble part of undoped PAN was used these films were highly homogenous. The dopants were removed to be remarkable by treating with NaOH. Films having the highest conductivity were obtained by doping with HCl. It was found that undoped and doped PAN-PMMA films have higher thermal stability than PMMA and lower thermal stability than doped PAN.

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