Conducting polymer nanocomposites with extremely low percolation threshold*

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Abstract. This article gives a brief review of our work on conducting polyaniline nanocomposites which exhibit extremely low percolation threshold, ca. ~ 0.03 vol.%. The nanocomposites are essentially blends of nanoparticles of HCl doped polyaniline (PANI) with conventional polymers. The nanoparticles (< 20 nm) were prepared by sonicating a suspension of sterically stabilized colloidal PANI particles in solutions of conventional polymers. The sonication process breaks down the stable colloid particles into nanoparticles. The latter are unstable and they aggregate fractally to yield nanocomposites with extremely low percolation threshold.

Keywords. Polyaniline; conducting polymers; blends; nanocomposites; nanoparticles; percolation threshold.

1. Introduction

Conducting polymers (CP) are important emerging materials with the potential of varied applications e.g. in static charge dissipation, electromagnetic shielding, LED displays, gas sensors, biosensors, pressure sensors, corrosion protection of metals and semiconductors, transistors, light weight batteries, etc (Ellis 1986; Garnier 1989). However, many of the conducting polymers are difficult to process because of their insolubility and infusibility. Blending with commodity plastics provides a means of overcoming processing difficulties since the blend can be processed as the matrix polymer. Furthermore, blending reduces the cost of the materials. The cost of the neat materials may be prohibitively high. In this respect lower the CP loading, cheaper will be the blend. Also, blends with low CP loading can be transparent. This property is technologically attractive because it opens up the possibility of using the transparent conducting blends as electrode materials in liquid crystal display devices. They may also find application as hole injecting materials in flexible polymeric LEDs (Heeger *et al* 1992) and as antistatic coating on microelectronic components. However, blends constituted of randomly dispersed conducting polymer particles fillers in a non-conductive matrix can reach percolation threshold (f_p) at a composition of about 16 vol.% of CP according to the percolation theory (Zallen 1983). Below this critical concentration the blend is an insulator but the conductivity increases sharply at f_p due to the first development of connectivity between the particles in three-dimension

which provides the conducting pathway for the electrical charge carriers. With further increase in concentration of CP more such conducting paths are formed and the conductivity increases. However, the above mentioned concentration is high enough to make the blend non-transparent and cost-ineffective.

Recently, we have used nanoparticles of CPs as particulate fillers in conventional polymers and achieved percolation at extremely low CP concentration ca. 0.03 vol% (Banerjee and Mandal 1995a, b). The fractal aggregation of the unstable nanoparticles has made possible achieving this remarkable result. Our result for polyaniline nanoparticle blends will be presented here.

2. Experimental

Dispersions of polyaniline in water were prepared using the method of oxidative dispersion polymerization of aniline at $\sim 0^\circ\text{C}$ in acidic aqueous (1.2 M HCl) medium using ammonium persulfate (APS) initiator oxidant and poly(vinyl methyl ether) (PVME) as polymeric stabilizer (Banerjee *et al* 1994, 1995). The oblong shaped particles (250×190 nm) were isolated by centrifugation and purified by way of redispersion in aqueous HCl followed by centrifugation. For the preparation of the blends the PANI particles as prepared by the above mentioned method were suspended in solutions of conventional polymers in THF, acetone, water etc depending on the solubility of the polymers. The suspension was then placed in a sonicating bath for periods ranging from 1 to 2 h. The resultant dispersions were then cast into films which were formed on evaporation of the

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solvent. The blend films thus obtained were dried in vacuum at room temperature (Banerjee and Mandal 1995a, b).

The conductivity of the films was measured by the usual four-probe method. For transmission electron microscopy (TEM), the blend film was cast over carbon coated copper grids from suitably diluted dispersions and examined using a JEOL JEM 100CT electron microscope.

3. Nanoparticles of polyaniline

The polyaniline colloid particles prepared as mentioned above have one remarkable property in that they undergo disintegration when suspension of the particles is sonicated (figure 1). Figure 1a shows the original PANI particles (250×190 nm) and figure 1b shows that the

particles have been reduced to sizes less than 20 nm following sonication.

4. Blends of polyaniline nanoparticles with conventional polymers

4.1 Electrical conductivity

The electrical conductivity of the blends of the nanoparticles of PANI with conventional polymers when plotted against PANI concentration does not exhibit any well defined percolation threshold as is shown in figure 2 for polyaniline-poly (vinyl alcohol) (PANI-PVA) blends. However, an estimate of the percolation threshold may be obtained by fitting the data used in figure 2 to the scaling law of percolation theory which is as follows (Zallen 1983)

$$\sigma = C(f - f_p)^t,$$

where C is a constant, t the critical exponent, f the volume fraction of the filler particles (here PANI), the subscript p signifying percolation threshold. The fitting is shown in figure 3 which yields a value of 3.6×10^{-4} for f_p and 1.96 for t . For blends using other polymer materials similar f_p and t values were obtained as shown

Figure 1. TEM images of PANI-HCl colloid particles: (a) prior to sonication and (b) 1.5 h after sonication (reprinted with permission from Banerjee and Mandal 1995a; © 1995 American Chemical Society).

Figure 2. Plot of log electrical conductivity vs PANI concentration in PANI-PVA blend films. The inset shows an enlarged view for the low PANI concentration region (reprinted with permission from Banerjee and Mandal 1995a; © 1995 American Chemical Society).

in table 1. The f_p values are extremely low in comparison to the values of 0.16 predicted by the percolation theory for percolation in three dimension of spherical conducting particles in an insulating matrix.

Previously, Reghu *et al* (1994) reported conducting polyaniline blends which also have very low f_p (ca. $f_p = 3 \times 10^{-3}$). In contrast to the present method those blends were prepared by the solution blending method. However, in order to make PANI soluble the dopant anion was changed from Cl^- to camphor sulphonate (CSA) (Yang *et al* 1993). The dispersed PANI-CSA phase in the blends were shown with the help of TEM to have a fractal structure. The latter was presumed to result from the self-assembly of PANI-CSA molecules during liquid-liquid phase separation which occurs on the evaporation of solvent from the solutions of the blends (Reghu *et al* 1993).

Table 1. f_p and t data for various blends of PANI-HCl with conventional polymers.*

Matrix	$10^4 f_p$	t
PVC	4.02	1.87
PS	4.19	1.91
PVAc	3.18	1.94
PMMA	2.14	1.89
PVA	3.60	1.96

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Figure 3. Plot of $\log$ conductivity vs $\log (w - w_c)$ where w is the wt% of PANI in the blends and w_c that at percolation threshold (reprinted with permission from Banerjee and Mandal 1995a; © 1995 American Chemical Society).

4.2 Morphology of the dispersed PANI phase

In order to find out the origin of the low f_p in the present blends the morphology of the dispersed PANI phase was studied with the help of TEM. Figures 4a-d show the bright field images of the PANI-PVA blend films containing respectively 0.035, 0.045, 0.05, and 0.5 wt% of PANI. The images show a fibrillar morphology of the dispersed phase. At the lowest PANI loading of 0.035% the PANI nanoparticles are formed to exist in isolated clusters. On increasing the PANI concentration to 0.045% the clusters appear to be weakly interconnected (figure 4b) which indicates that the system is near percolation. The structure is stringy and tenuous at this stage which is the characteristics of percolation threshold. As the PANI concentration is increased further to 0.05% the network becomes more dense. These results thus show that the percolation threshold is somewhere around 0.045% which is in very good agreement with the f_p determined from conductivity studies (figures 2 and 3).

On increasing PANI concentration still further to 0.5% the system is found to undergo self ordering generating a particular pattern for the network which is in the process of formation in figure 4d and near completion in figure 4e. This self-ordering is characteristic of fractal growth (Mandelbrot 1983; Peitgen and Richter 1986). The fractal dimension of the structure shown in figure 4e has been determined to be 1.78 (Mandal 1998). The low percolation threshold is attributed to the fractal growth of the dispersed phase. A fractal object grows faster than an Euclidian object since not every point which is defined by the Euclidian space is occupied in a fractal object.

4.3 Mode of aggregation of nanoparticles

As regards the cause behind the aggregation of the nanoparticles it may be noted that the nanoparticles as produced by the disintegration of the bigger particles do not have enough stabilizer to cover their surface. They are therefore unstable and it is well known that unstable colloid particles undergo fractal aggregation (Forrest and Witten 1979; Weitz and Oliveria 1984; Lin *et al* 1990). For example, Weitz and Oliveria (1984) found that stabilized gold sols containing particles of ~ 14.5 nm dia. undergo fractal aggregation to form aggregates which have a fractal dimension of ~ 1.75 . In the present case for the structure shown in figure 4e, we determined a fractal dimension of 1.78 (Mandal 1997).

5. Conclusion

This study shows that polyaniline nanoparticles can be produced through the disintegration of sterically stabilized

Figure 4. TEM images of PANI-PVA blend films containing different amounts of PANI (in wt%) (a) 0.035%, (b) 0.045%, (c) 0.05%, (d) 0.5% and (e) 0.5%, but from a different region of the same film as was used for part (d) (reprinted with permission from Banerjee and Mandal 1995a; © 1995 American Chemical Society).

polyaniline colloid particles with the help of ultrasound. Nanoparticles produced *in situ* in solutions of conventional polymers undergo fractal aggregation such that the blends exhibit extremely low percolation threshold ($\sim 3 \times 10^{-4}$ volume fraction).

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