Preparation of organic polymer/inorganic oxide conductive composites

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Preparation of conductive composites based on organic conducting polymer and inorganic oxide has been described. The composite materials thus prepared have been characterized by a wide range of experimental techniques including elemental analysis, density measurement, UV-vis and IR spectroscopy, X-ray and sedimentometry. Even after incorporating insulating silica, the composites exhibit electrical conductivity comparable to that of the conventional semiconductors. In contrast to the bulk polymer, the composites show relatively superior environmental stability when exposed to ambient atmosphere. The composites have been further characterized for their surface area; in this connection, adsorption of methylene blue on a composite matrix has been examined.

Electrically conducting organic polymers with \( \pi \)-conjugated system have been studied extensively for a variety of applications including electrochromic displays, batteries, solar energy conversion etc. Among the polymers studied, polyaniline (PANI) is considered to be a unique one that can be synthesized either chemically or electrochemically as a bulk powder or film, respectively. Although these materials are recognized to be highly promising for technological applications, their intractable and unprocessable nature and lack of superior environmental and electrochemical stabilities make their practical utilization limited. However, for the effective and wider practical use of these polymers, significant improvement of material properties and processability is required. Preparation of composites of conducting polymers could be a potential solution to the processability problem of conducting polymers as well as to enhance the material properties with desirable physical and mechanical characteristics. One way of making these composites involves synthesizing the conductive polymer inside the matrices of conventional polymers using chemical\(^5,6\) as well as electrochemical\(^6,14\) polymerization. In addition, studies pertaining to the chemical preparation of conducting polymer composites without involving any insulating polymer have also been reported\(^15,17\). In this approach, monomer is polymerized in the presence of inorganic oxide nanoparticles which act as a high surface area colloidal substrate for the precipitating polymer nuclei leading to the formation of polymer-inorganic oxide nanocomposite. These studies were focused solely on the processability problem of the polymers, although the use of costly commercially purchased nanoparticles, such as LUDOX (colloidal silica, 40% suspension in water) is considered to be a great constrain in dealing with this method.

In the present work, an attempt has been made to prepare organic polymer/silica conductive composites as an alternative new materials to the bulk polymers. The composites thus prepared were also characterized in terms of physical, chemical, optical and electrical properties.

Materials and Methods
All the chemicals (purchased either from E. Merck, Germany or BDH Ltd., England) used in this work were of AR grade and used as received unless stated otherwise. The monomers - aniline, \( o \)-toluidine and 2-chloroaniline were distilled twice under nitrogen atmosphere before use. The solutions used throughout the experiments were prepared using doubly distilled water except for the ultraviolet-visible (UV-vis) measurements where solution of the samples were made in dimethylformamide (DMF). Aqueous colloidal silica suspension was prepared in the laboratory just by beating a mixture of silica particles (SiO\(_2\) powder, 325 mesh) and distilled water with a homogenizer for 2 hours. The resulting dispersion
was then allowed to settle for the next 2 hours. Relatively bigger silica particles were sedimented and the smaller ones remain in the system and are dispersed well. The colloidal suspension was then decanted and used as such in the polyaniline/silica (PANI/silica), poly-o-toluidine/silica (CH$_3$PANI/silica) and poly-2-chloroaniline/silica (Cl-PANI/silica) composites preparation. In a typical preparation, 2.5 ml of monomer, 5 ml of HCl and 3.0 g of (NH$_4$)$_2$S$_2$O$_8$ were added to 400 ml of colloidal silica suspension at room temperature. The reaction yielded a deep green colloidal product within few seconds. The reaction mixture was stirred occasionally and left overnight for the completion of polymerization. The colloidal mixture was then sedimented by centrifugation. The resulting dark green sediment was redispersed in distilled water in an ultrasonic bath. The centrifugation-redispersion cycle was repeated several times in distilled water to remove free silica particles and soluble by-products and finally the cycle was repeated in an acid solution containing 5 ml of HCl in 400 ml of distilled water. The solid mass was then dried at 40°C under vacuum in a controlled heating vacuum oven (Gellencamp, England). The dried mass was ground to powder and passed through 100 mesh sieve prior to storing under vacuum for characterization.

Hydrofluorization method was employed to analyze the silica content of the composites. For this purpose, 1 g of the sample was treated with 10 ml of HF and 1 ml of concentrated H$_2$SO$_4$. Density measurements were carried out in a Pycnometer (Micromeritics Multivolume Auto Pycnometer, Model no. 1305, USA) following the conventional standard method. Sedimentation method was employed for the determination of particle size of the studied composites. For this purpose, the composite samples were dispersed in water and dispersion of known density and viscosity were obtained. The dispersion was then introduced into the sample holder of micromeritics sedigraph (Model no. 5100, USA). Data for particle size was made available from the computer interfaced with sedigraph. Optical microscopic analysis of the samples was performed in an optical microscope (SWIFTMASTER II, Swift Instruments, Inc, Japan) coupled with a very high precision canon camera. Infrared (IR) spectra of the samples were recorded on a IR spectrophotometer (IR-470, Shimadzu, Japan) while a double beam spectrophotometer (UV-160, Shimadzu, Japan) was employed for the UV-vis spectral analysis of the sample solutions in DMF. X-ray diffraction pattern were recorded on an automatic X-ray diffractometer (JDX-8P, JEOL Ltd., Japan) using Mo(Kr) radiation of wavelength 1.54 Å. Conventional two-point probe method was employed for measuring compressed pellet d.c. conductivities of the composites and bulk polymer. Resistance for each samples was read directly from an auto ranging microvolt (Keithley 197A, USA) equipment and, thus, specific conductance for the samples was calculated. Adsorption of methylene blue, C$_{16}$H$_{18}$ClN$_3$.3H$_2$O, (MB) on PANI/silica composite was studied spectroscopically. A typical experiment for the adsorption of MB on the composite and the bulk polymer matrices was done in the following way: A known weight of the adsorbent was taken in each of the 8 bottles with stopper. Water (0.5 ml) was taken in each bottle and was soaked overnight. Then 25.0 ml of 3.0 × 10$^{-5}$ MB solution was added. The bottles were shaken in a thermostated shaker maintained at 30°C. After a definite interval of time a bottle was withdrawn. The supernatant was centrifuged. The concentration of the clear solution was obtained spectroscopically by measuring absorbance at 664 nm, the $\lambda_{max}$ of MB. Solutions in other bottles were analyzed in the same way.

Results and Discussion

When the monomers aniline, o-toluidine or 2-chloroaniline are polymerized from an aqueous suspension of silica, colloidal PANI/silica, CH$_3$PANI/silica or Cl-PANI/silica particles of composite nature are produced. In this synthesis, the precipitating polymer gets adsorbed as an insoluble thin layer onto the high surface area silica substrate particles. The outer layer of the polymer is nonsolvated and acts as a binder, effectively gluing the silica particles together, leading to the formation of polymer/silica composite. Most of the colloidal silica has a negative charge. Since PANI, CH$_3$PANI and Cl-PANI are polycations, the attractive electrostatic interaction may play certain role in the formation of polymer/silica composites. The results of chemical analysis and densities of the synthesized composites are shown in Table 1. Each value presented in the Table is an average of at least three measurements. The results show that silica content in the composites is approximately 40% in all the samples. Although monomer with different functional group were used in the synthesis, it seems that the substituent group does not influence the silica content of the resulting
polymers/silica matrices. Measured densities of the composites are also presented in Table 1. The density of the PANI/silica composite is found to be higher than that of the bulk PANI. This result appears to be reasonable if one consider the incorporation of silica particles into the polymer matrix. The observed data are consistent with those in previous reports. The synthesized composites were also characterized by optical microscope. A wide distribution of white images was seen in the microstructure of the composites while that of bulk polymer did not exhibit such images. The observed white images in the microstructure of the composites may reflect the presence of silica particles in the matrix.

IR spectra of the composites clearly revealed absorption bands attributable to both the bulk polymers and silica component. A typical IR spectrum for PANI/silica is shown in Fig. 1. This spectrum is essentially identical to that of bulk PANI reported elsewhere except for the appearance of the peak at 1109 cm\(^{-1}\) which may be attributed to the presence of silica.

Particle size distribution for the composites synthesized were determined by sedimentometry method. Owing to the relatively large density difference between water (0.99 g cm\(^{-3}\)) and polymer/silica particles (Table 1), this technique yielded better weight average particle size distribution. Figure 2 shows typical results of measurements for PANI/silica. The graphical presentation of the mass frequency percent shows that the particle size varies in a range 1-40 \(\mu\)m. This is rather a broad range and similar features were observed with the other composites studied. Typical UV-vis spectrum of PANI/silica in DMF is presented in Fig. 3. The possible electronic processes that can take place under UV-vis irradiation on the sample are manifested as peaks in the spectrum. The result depicted in Fig. 3 is similar to that of a doped conducting polymer films reported elsewhere suggesting the peak observed at around 305 nm for the interband \(\pi-\pi^*\) (valence band to conduction band) transition while the peak at around 601 nm for the transition in the mid gap state formed by the polaron and bipolaron that are considered to be responsible for the polymer conductivity. However, the observed spectra of the polymer/silica samples are essentially identical to that of the corresponding bulk polymer. This finding suggests that optical properties of the bulk polymer changes hardly even after incorporating silica particles into the matrix.

The bulk polymer and polymer/silica composites studied were examined for their structural analysis in the powdered state using wide angle X-ray diffraction. A typical scattering pattern as a function

<table>
<thead>
<tr>
<th>Name of the sample</th>
<th>Silica content (%)</th>
<th>Density (g cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI</td>
<td></td>
<td>1.46</td>
</tr>
<tr>
<td>PANI/silica</td>
<td>40.36</td>
<td>1.62</td>
</tr>
<tr>
<td>CH(_2)-PANI/silica</td>
<td>38.92</td>
<td>1.61</td>
</tr>
<tr>
<td>CI-PANI/silica</td>
<td>39.78</td>
<td>1.60</td>
</tr>
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of the Bragg angle, 2θ for PANI/silica is shown in Fig. 4. It can be seen from the result that the sample shows only diffuse scattering, i.e., the exhibited pattern consists of amorphous peaks. Further, the diffraction patterns of the composites are exactly identical to those of bulk polymers suggesting that silica particles have no influence on the structure of the matrix and hence the diffraction patterns of the composites studied are mostly dominated by the response made by the polymer component alone. Indeed, most of the conducting polymers are reported to be extremely poorly crystalline.

Compressed pellet d.c. conductivities of the samples PANI, PANI/silica, CH$_3$-PANI/silica and Cl-PANI/silica measured by a conventional two-point probe method were found to be $1 \times 10^{-1}$, $2.1 \times 10^{-2}$, $2.3 \times 10^{-3}$ and $2.4 \times 10^{-5}$ S cm$^{-1}$, respectively. The observed conductance of PANI sample prepared chemically with ($\text{NH}_4$)$_2$S$_2$O$_8$ seems to be consistent with the previous finding. The result also shows significantly lower conductance for the polymer/silica composites than that of the bulk PANI. Presumably, this is due to the interparticle contact resistance arising from the incorporation of insulating silica into the matrix. However, even the conductance of the polymer/silica samples is few order of magnitude lower than the bulk PANI: their conductivities still correspond to the range of the semiconductor conductivity ($10^{-1}$ to $10^{-6}$ S cm$^{-1}$). Since electrical behaviour of the composites seems to be controlled by the polymer component, the mechanism of conduction in these composites is expected to be similar to those of the bulk polymer. The macroscopic conductivity has been interpreted as a result of anisotropic three-dimensional variable range hopping in a network of rods with metallic behaviour.

Fig. 5 represents the change in conductivities of the bulk PANI and polymer/silica composite samples when exposed to ambient atmosphere. The result shows that conductivities of all samples decay with time. In general, it can be seen that conductivity change is rather faster in the initial several hours. However, the magnitude of decay seems to be different for different samples. The conductance of bulk PANI seems to decay very sharply and decreases by more than three order of magnitude while conductance of the polymer/silica composites is found to be decayed only by an order of magnitude which is much smaller compared to that of bulk PANI. Evidently, the present findings suggest instability of all the samples studied although mechanism for the deactivation of the samples has not been investigated further in the present work. Chowdhury et al. also reported a decrease in the work function and electrical conductivity of doped poly(3-methylthiophene) film when exposed to air. However, the present result clearly suggests a better stability for the polymer/silica composites than that of the bulk.
polymer when exposed to air. The effect of ambient atmosphere on the above samples were further investigated by measuring weight change for per gram of the samples at different exposure time. The result is shown in Fig. 6. The weight of all the studied samples seems to increase when exposed to ambient atmosphere. The increase in weight may arise from the absorption of moisture. In fact, it has already been found that conducting polymer can absorb water as much as 40% of its mass\(^{20}\). It can be seen from the result that PANI (curve-a) exhibits higher affinity for moisture absorption compared to that of composites (curve-b, c and d) examined. However, all the samples show a saturation of moisture absorption within a couple of hour and the weight change remains almost constant at least for 24 hours. It is worth mentioning that the sample with a higher affinity for moisture absorption shows a greater deactivation of electrical property (curve-a, Fig. 5). The present result, thus, seems to show a good correlation between deactivation of electrical property and moisture absorption affinity of the samples. On exposure to air, the sample probably absorbs water to cause protonation or even degradation of the polymer by converting imine (=N-) form to amine (-NH-) or any other degraded structure, i.e., converting a higher conductive state to a lower one.

PANI/silica composite was examined by Micromeritics Sedigraph for its surface area. The result predicted a surface area as high as 3.2 m\(^2\)/g. The observed surface area of the composite matrix made us interested to study adsorption process on it. For this purpose, adsorption of MB on PANI/silica was attempted. Adsorption was followed spectroscopically by the change in concentration of MB at different time interval. Figure 7 shows the change in concentration of MB with time soon after charging it individually to bulk PANI (curve-a) and PANI/silica (curve-b). It can be seen from the result that as soon as the MB solution charged to the absorbents, a decrease in its concentration was observed. The concentration decay seems to be very sharp on the PANI/silica matrix. The decrease of MB concentration appears to be rather faster in the initial few minutes and gradually reached to constant value with the lapse of time. Silica particles have a net negative surface charge. Since MB is in the cationic form, so adsorption of MB on PANI/silica is quite likely, although adsorption of MB on the bulk PANI, even negligible, is not understandable at present. However, adsorption of MB on PANI/silica (curve-b) seems to be several times higher than that for bulk PANI. This observation suggests that such organic polymer/inorganic oxide composite particles might be an interesting new substrate for surface application.
Conclusion

Chemical polymerization of the monomers from an aqueous colloidal suspension of silica represents a simple route for the preparation of organic polymer/silica conductive composites. Even after incorporating the insulating silica particles, the composites thus prepared show electrical conductivity that correspond to the range of the conventional semiconductors. Spectral and structural properties of the polymer/silica composites seem to be controlled by the polymer component of the matrix. On exposure to ambient atmosphere, both the bulk polymer and polymer/silica composites show degradation in their electrical properties. The extent of degradation is less for the polymer/silica composites compared to that of the bulk polymer. Conductive polymer/silica composites exhibit reasonably higher surface area and can be used as an effective substrate for adsorption process.

References
4  See, for example, the conference proceedings of the ICSM'88, Aldissi M, ed, Synth Met, 27-29 (1989) and refs therein.
8  Mandal T K & Mandal B M, Synth Met, 80 (1996) 93.