Preparation of three-component conducting polymer composite using nucleate doping technique

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This paper reports a new route for the preparation of conducting network in insulating polymer matrix. In existing techniques solubility of conducting component is an essential condition. Reported technique facilitates making composite of conducting polymer, which is insoluble in normal solvents, with percolation threshold of 0.5 wt%. Mechanism of formation of the three component hybrid may be described as when silica which acted as seed is dispersed in insulating polymer, the in-situ polymerized conducting polymer having high aspect ratio is grown over the silica surface connecting each other and making a continuous network. The star like growth of the conducting polymer can be seen under optical microscope.

Keywords: Conducting polymer composite, DLA model, Percolation, Nucleate doping

Organic molecular materials, charge-transfer complexes and conducting polymers, offer a multidisciplinary challenge to chemists, physicists, material scientists and electronic engineers and have a great potential for commercialization. Organic materials cover full range of materials from insulators to superconductors, diamagnetic to ferromagnetic and optical to non-linear optical (NLO) properties. But the mechanical and processibility issues need considerable attention in these materials. Charge-transfer complexes are usually soluble in organic solvents, so they have better processibility but have very little mechanical strength. On contrary the conducting polymers are self sufficient on mechanical account but being almost insoluble practically unprocessible. A common solution to both the problem is making their composite with conventional polymers. Conventional polymers form matrix in which organic conductive fillers are embedded giving mechanical strength, retaining the electrical properties; at the same time processibility of insulating polymer can also be exploited for fabrication of devices.

Owing the potential of the composite material several methods have been proposed for the preparation of these materials. These include simple grinding, zone casting, two-step reticulate doping and electrochemical method; blending method; grafting reaction and two-phase synthesis.

Reticulate doping method is one of the best among these methods. In reticulate doping method, the microcrystals are grown during film casting. In appropriate conditions the crystallization of the charge-transfer complex leads to formation of a conductive network of crystallites in the bulk of polymer, which makes the film conductive at as low as 0.3 wt% level of loading, due to high aspect ratio. Tracz et al. have summarized main parameters controlling the charge-transfer complex crystallization in reticulate doping process. Reticulate doping is a good method for making composite, where both the components are easily soluble in same solvent, but this procedure cannot be used if either of the components is insoluble or are soluble in two different immiscible solvents.

In this paper, we report a new technique for preparing nucleate doped composite of conducting polymers which are not soluble in ordinary solvents) with high aspect ratio. In this method, we disperse silica in insulating polymer and let the conducting polymer grow over it. The silica acts as seed and the polymer having high aspect ratio was grown connecting each other and making a continuous network.

Experimental Procedure

Silica gel-G (TLC grade, Sulab’s chemical) was dispersed in PVA (S D Fine chemicals, Mol.wt (1,25,000)) (in triple distilled water) (2% w/v) with continuous stirring on magnetic stirrer so that silica
particle could uniformly distribute in solution. PANI/silica hybrid was prepared by simple chemical polymerization route. The aniline monomer was purchased from (Qualigen AR) and used after distillation. Aniline (0.05 M) in 0.5 M HCl was added to the silica gel dispersion and kept under continuous stirring in ice bath for one hour. Ammonium persulphate (0.05 M) (Qualigen) was added very slowly to start polymerization. After completion of polymerization the solution turned into violet color. Required amount of the solution was added in the petri dish and left for solvent evaporation at room temperature. The concentration of monomer and oxidant was kept low to slow down the rate and degree of polymerization so that polymerization could take place on the surface rather than in bulk. The samples for BET surface area measurement and SEM measurement were taken after one hour from the start of the polymerization and then the system was left for slow evaporation of the solvent. The solution slowly turned into gel and finally into thin film after complete evaporation of solvent. After around 4-5 days the resultant hybrid has shown well-dispersed structure of PANI over silica in poly (vinyl-alcohol) matrix having high aspect ratio. The composite thus formed have been characterized by various techniques. FTIR was recorded in KBr medium on Jasco 5300. TEM photos were taken using JEOL-JEM 100SX at 100 kV acceleration voltage, the samples for the TEM experiments were prepared by suspending dried samples in absolute ethanol. A drop of the sample suspension was allowed to dry on a copper grid (400 mesh) coated with a carbon film. SEM images were taken by employing FEI - Quata 200 at 5 kV acceleration voltage. Optical microscopies were done on Lietz Labour Lux-D with built-in-camera; BET surface area was measured on Micromeritics-Gemini 2375 surface area analyzer. XRD were recorded on Bruker X-ray diffractometer D8 using Cu-Kα radiation and the electrical measurements were done using LCZ meter-Keithley 3330. The contacts for electrical measurements were made by silver paint and the dimension of the sample was 1 cm × 1 cm × 0.1 cm.

Results and Discussion

The silica used in current study has irregular faces, which can be seen in the TEM image (Fig. 1). These faces acted as nucleating point for the growth of polyaniline (PANI), which could be seen in SEM images, taken just after start of polymerization (Fig. 2). In Fig. 2a, silica particles dispersed in poly (vinyl-alcohol) (PVA) matrix can be seen, whereas Fig. 2b shows coating of PANI over silica faces as a thinner lager. The dispersion of silica particles in poly (vinyl-alcohol) has been studied by Boisvert et al. in details. They observed nice microphase separation and well defined surface-to-surface distance within the silica clusters. These mono-dispersed silica particles act as nucleus for the growth of polyaniline in our experiment. When the monomer was added to the silica/PVA dispersion under continuous stirring the annilinium ion got adsorbed on the surface of silica particles which on further slow addition of oxidizing agent polymerization started leading to the formation of long chain of polyaniline. It can be seen apparently in SEM (Fig. 2b) images that nucleation started from different faces of silica. This was further confirmed by the BET surface area measurement. The surface area of bare silica was found to be 90.7 m²/g where as after PANI coating it was increased up to 106.10 m²/g.

The interaction between polyaniline and silica through hydrogen bonding has already been reported. Weak ineractions between silica and polyaniline has been confirmed by IR analysis. After 4-5 days star like morphology of PANI/silica hybrid growing in PVA matrix was observed, though they were fewer in number. When the sample was left for at least 10-15 days under slow evaporation the solution slowly tuned into thin film through the formation of gel. We observed many more prominent stars. The optical micrograph of the growth is given in
Fig. 3a shows the pattern of the growth on a single particle, whereas Fig. 3b shows the interconnectivity of the stars. These stars have very high aspect ratio (~12). The aspect ratio of an image describes the proportional relationship between its width and its height. The star-like morphology in silica/PANI hybrid is reported elsewhere. But those star structures were small enough so that they could be seen under TEM only. In the present study the PVA matrix provides support to the polyaniline for larger growth giving high aspect ratio. This growth in general can be explained on the basis of diffusion-limiting-aggregation (DLA). DLA has generated considerable interest in the percolation model. The model is quite simple, this starts with a seed, which is silica particle in the present case. Perhaps the success of this technique is because of the homogeneous dispersion of seed (silica) in PVA matrix. In absence of these seed particles the conducting seed generated in insulating polymer generally get aggregated at fewer places resulting in molecularly dispersed composite. Another particle is then allowed to walk at random (i.e. diffuse) from far away until it arrives at one of the site adjacent to the occupied site, and so forth. A large cluster may be formed in this way.

The assignment for the main IR peaks in silica, poly (vinyl-alcohol), polyaniline and the composite are given in Table 1. Bare silica shows bands and peaks between 800 cm\(^{-1}\) - 1200 cm\(^{-1}\) due to various symmetric and asymmetric vibrations of Si-O-Si. Another peak which was assign to silica is at 505 cm\(^{-1}\) due to Si-O-Si-O deformation. The peak at 3393 cm\(^{-1}\) in silica is assigned to the –OH stretching vibration.
which is due to adsorbed water. Poly (vinyl-alcohol) shows peaks at 1442 cm\(^{-1}\), 2930 cm\(^{-1}\) and 3415 cm\(^{-1}\). These peaks are assigned to C=H of vinyl group, C-H stretching vibration and –OH groups, respectively. The peaks at 1597 cm\(^{-1}\) and 1495 cm\(^{-1}\) in polyaniline are due to quinonoid and benzenoid forms, since conducting polyaniline is partially oxidized state having 50% quinonoid and 50% benzenoid structures. In the composite we can see all these peaks with a slight shifting in the vibrational band positions which may be due to weak interactions like hydrogen bonding and vander Waals forces etc, which hold the components of the composites together.

The XRD patterns of the pure polymer, silica, and the composite are given in Fig. 4. It is clear from the XRD patterns that, while polyaniline is amorphous, silica shows short range ordering. The peaks in \(2\theta = 20-30\) are already reported for silica. The XRD peaks matches well with hexagonal lattice reported for silica (PDF 12-708) having peaks at \(2\theta = 26.35\) (100%), 35.92 (10%), 41.68 (18%), 44.99 (12%) and 49.44 (60%). The composite shows reduced intensity of the peaks, which confirms the adherence of polyaniline over silica. Further it is clear from the IR and XRD data that the composite formed has only physical interactions and no chemical interaction exist between the components.

The electrical conductance of the composites was measured at three frequencies (1 kHz, 10 kHz & 100 kHz). The plot of specific conductance and loading of polyaniline is given in Fig. 5. The percolation threshold as low as 0.5 wt% (at all the three frequencies used in current investigation) of PANI (showing 4 order increase in conductance) has been observed in these composites. This is only slightly higher than 0.3 wt% measured in reticulate doping and significantly lower than other reported (mainly dispersion type) composites of PANI and PVA, where this data lies at about 24 wt%. Since the earlier reported PANI/PVA composites are molecular dispersion they don’t show typical percolation behavior, but the conductivity of those composites increases gradually with increased loading of PANI. Whereas in present case we see sudden increase of conductance at 0.5 wt% loading level and after that the plot shows a plateau. It can also be seen in Fig. 5

| Table 1— FTIR assignments of silica/PVA/PANI composite |
| Assignment | Silica | PVA | PANI | Composite |
| Si-O-Si, (stretch, sym) | 802 cm\(^{-1}\) | --- | --- | 800 cm\(^{-1}\) |
| Si-O-Si, (stretch, asym) | 1128 cm\(^{-1}\) | --- | --- | 1111 cm\(^{-1}\) |
| Si-O-Si-O deformation | 505 cm\(^{-1}\) | --- | --- | 464 cm\(^{-1}\) |
| Vinyl group (C=H), -OH, stretch | --- | 1442 cm\(^{-1}\) | --- | 1450 cm\(^{-1}\) |
| C-H stretch | --- | 2930 cm\(^{-1}\) | --- | 2920 cm\(^{-1}\) |
| Quinonoid imine (-C=N-), stretch | --- | --- | 1597 cm\(^{-1}\) | 1581 cm\(^{-1}\) |
| Benzenoid amine (-C-N-), Stretch | --- | --- | 1495 cm\(^{-1}\) | 1477 cm\(^{-1}\) |

Fig. 4— X-ray diffraction pattern of (a) polyaniline, (b) silica/ PVA/PANI composite and (c) silica gel

Fig. 5— Variation of specific conductance of silica/PVA/PANI composite as a function of loading of polyaniline at various frequencies (a) 1 kHz, (b) 10 kHz and (c) 100 kHz
that these composites show prominent frequency dependence of the conductivity. The conductance at lower frequency is less and it keeps on increasing gradually as the frequency increases. Frequency dependence of conductance shows the existence of the capacitive component, which exists due to charging of the heterojunctions. This confirms our assumption that individual stars grow and then connect each other to make continuous conducting network.

Conclusions

In conclusion we can say that a three-component nucleate doping method can easily be used for the fabrication of conducting composites of practically insoluble components, with low percolation threshold and better processibility. The success of proposed technique is because of the homogeneous dispersion of seed (silica) in PVA matrix. In absence of these seed particles the conducting seed generated in insulating polymer generally get aggregated at fewer places resulting in molecularly dispersed composite. Another particle is then allowed to walk at random (i.e. diffuse) from far away until it arrives at one of the lattice site adjacent to the occupied site, and so forth. A large cluster may be formed in this way. The present work demonstrated the superiority of the three-components composite over individual two-component composites.

References