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ADDITIVES WEIGHT PERCENT DEPENDENCE MORPHOLOGY OF CONDUCTING POLYMER/METAL OXIDE NANOCOMPOSITES

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A B S T R A C T

Polyaniline Emeraldine salt (ES) and its composites with V2O5, ZnO, MgO metal oxides were synthesized by chemical oxidation route by taking various mass % of metal oxides with monomer in polymerization mixture using sulfuric acid as dopant and APS as oxidant. Morphological nano shape and size of these composites were examined by their SEM analysis.

1. Introduction

Potential applications of conducting polymers such as polyaniline (PANI), polypyrrole (PPY) and polythiophene (PTP) in batteries [1], electronic devices [2], displays, sensors [3], nanotubes or nanorods [4] and molecular electronics are well known. There are mainly two routes for the preparation of CPs: chemical and electrochemical polymerization [5]. Among various CPs, PANI is unique in nature from the viewpoint that its electrical behaviour in emeraldine salt dorm can be reversibly controlled by charge-transfer doping and by protonation and it has a good environmental stability. Numerous oxidant systems including transition metal salts were reported for the chemical polymerization of aniline (ANI) [5]. In particular, polymerization of aniline can be conventionally achieved by using $(NH_4)_2S_2O_8$as the oxidant system [6]. In continuation of works on new oxidant systems it was found that isopolymetallates of vanadium could act as the oxidant for the

polymerization of aniline [7]. In this context, it was observed that V2O5, ZnO, MgO could also act as the oxidants for the aqueous polymerization of ANI.

Several reports can also be found in the literature regarding the synthesis of PANI-metal oxide composites nanofibers, where the size, morphology and conducting properties of the PANI were greatly influenced by the addition of metal oxides such as iron oxide [8], graphene oxide. However, only very few reports can be found on the use of MgO on PANI. Therefore, an investigation of the effects of V2O5, ZnO and MgO on the size and morphology of high molecular weight sulphonated PANI nanofibers is needed, both because of lack of information in the field and in order to achieve the direct control of the diameter, surface morphology and the prevention of secondary growth and agglomeration of nanofibers during the growth process. The results may be promising for the preparation of new functional polymer, such as organic devices based on metal oxide-incorporating conducting polymer.

2. **Experimental**

2.1 ***Conducting Polymer synthesis***

Conductive polyaniline (PAni) was prepared from aniline sulphide monomer using sulphuric acid as dopant [9]. Oxidation of aniline by ammonium per sulphate (APS) yields polyaniline in or close to emeraldine form. The degree of oxidation may vary smoothly between fully reduced leucoemeraldine and completely oxidized pernigraniline [10] both reduced and oxidized forms can be protonated in the presence of acids [11].

2.2 ***Conducting polymer/Metal oxide nanocomposite synthesis***

The composites of PANI with V2O5, ZnO, MgO were synthesized by chemical oxidation method. The method was same as that of PANI, and

inorganic powder added in aqueous solution of aniline containing sulfuric acid as dopant before addition of oxidant, ammonium persulphate. The inorganic powders were added in pre- cooled (0-4^{o}C) 100-ml solution of 0.4 M aniline in 1M sulphuric acid by keeping various weight % of their with aniline monomer. The another solution of 100 ml precooled (0-4^{o}C) solution of 0.4 M ammonium persulphate in 1 M sulfuric acid was added to the former solution for 1 hour with constant stirring. After completion of the oxidant addition, stirring was continued for another 7 hours at 0-4^{0}c to ensure completion of the reaction. During polymerization, the sequence of colorations of the reaction mixture was light blue, blue green and finally greenish black precipitate. Dark green color ensures the formation of conductive PANI salt. The reaction mixture was kept overnight. Then precipitated emeraldine salt was filtered, washed with distilled water until the filtrate became colorless and finally with methanol and dried in oven at 70-80^{0}C for 8 hours.

3. Characterization by Scanning Electron Microscopy

3.1 *Morphology of PANI and PANI/Metal Oxide Nanocomposites*

Fig. 1 shows, SEM micrographs of PANI (a) and PANI/25% V_2O_5 (b), PANI/15% ZnO (c), PANI/25% ZnO (d) and PANI/20% MgO (e) composites nanofibers are clearly visible. Table 1 highlighted the effect of percent weight of metal oxide while the polymerization of aniline on morphology of resultant composites. The addition of V2O5, ZnO, MgO not only effects the size but also the surface morphological features of PANI micro sheets & nanofibers.

3.2 *The concentration of metal oxide and monomer*

The 25 wt % of ZnO in polyaniline composite has the morphology of honeycombed clews. This indicates that the morphology of high

molecular weight PANI is strongly dependent on the concentration of metal oxide [12]. It is found that with the increasing monomer, quantity of clews is decreasing gradually and the block precipitation of PANI appears, several PANI particles are also found. However, the clews will disappear if the concentration of aniline becomes higher. Concentration of aniline could only affect the quantities of honeycombed clews. However, the morphology of PANI was not affected by the molar ratio of aniline: oxidant and the concentration of H_2SO_4.

It is clear that the use of H_2SO_4 as dopant produced nanosheet-nanofiber network/cluster of high molecular weight PANI structure with the nanofibers having diameters 94.28 nm to 80.00 nm (Fig.1a). The sheets with diameter more than 0.5 μm and thickness ranging 30–80 nm are abundant in PANI SEM well agreed with report by [13]. Significant changes in morphology are seen in the PANi/MO composite prepared with H_2SO_4 dopant. In case of PANI/25% V_2O_5 (Fig.1b), nanosheet-nanofiber cluster of PANI is surrounded by microrodes of V_2O_5, PANI nanosheet bcomes more flat in size and shorten length of PANI nanofiber has been observed with diameter below 100 nm size. In the SEM of PANI/15% ZnO (Fig.1c) the PANI nanofibers agglomerated in the composites without PANI nanosheets. While the SEM of PANI/25% ZnO (Fig.1d) nanocomposite (NC) becomes like honeycomb with nanowires or cactus like with nanowires. It shows the agglomerated PANI nanofibers in NC having diameter up to 80 nm and particles up to 40 nm size are abundant. SEM of PANI/20% MgO (Fig.1e) shows the agglomerated PANI nanofibers of 113 nm to 63 nm widths in the NC

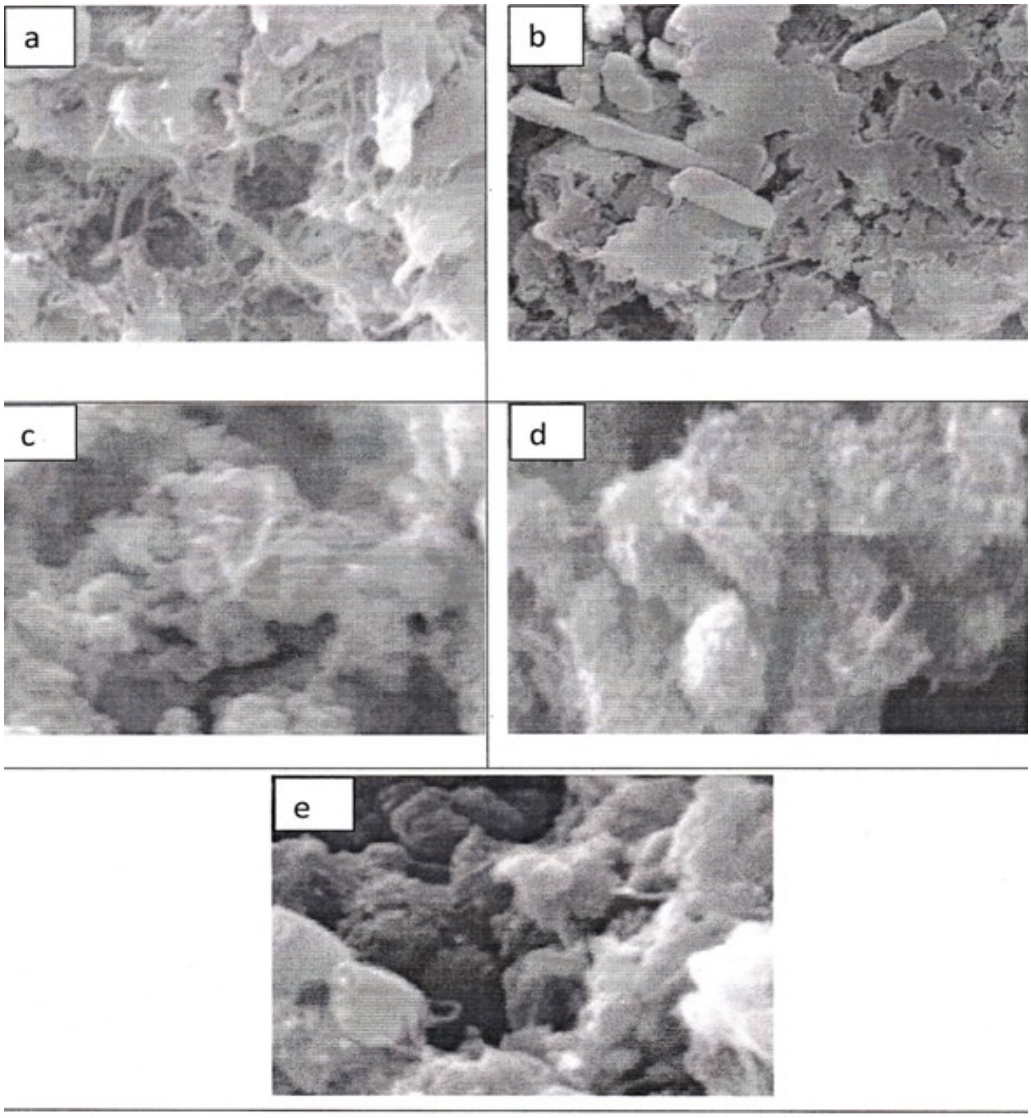

Figure1: SEM of sulphonated PANI salt (a), PANI/25% V_2O_5 (b), PANI/15% ZnO(c), PANI/25%ZnO (d) and PANI/20% MgO (e)

and adsorbed particles below 40 nm sizes are abundant on PANI nanosheets.

Nanofiber - nanosheet structure of high molecular weight PANI became agglomerated when the polymerization is carried out in existence of metal oxides. The average diameter of PANI nanofiber in PANI salt structures is varying in PANI/MO NCs with wt % of MO to monomer. The result is well agreed with as reported by [14]. Most remarkable

achievement in this study is the formation of nanoparticles up to 40 nm size.

Table: 1 – Morphology data with wt% of MOs

Sample	Type	Size
PANI	-Nanosheets (NSs) -Nano wires (NR)	NS thickness – below 100 nm NR-94.28 nm to 80.00 nm
V_2O_5(PURE)	-Microrodes (MR) Surrounded by NSs & NRs	MR- 723 to 569 nm
V_2O_5 (10%)	-MR Surrounded by NSs	MR- (460 nm x 0.29 μm) to (832 nm to 2.79 μm)
V_2O_5 (15%)	-MR Surrounded by NSs	MR-Below 500nm NR- below 100nm
V_2O_5 (20%)	-MR Surrounded by NSs & NRs	NR- below 100nm
V_2O_5 (25%)	-MR Surrounded by NSs & NRs	MR- (407nm x 2.35 μm) NR- below 100nm
V_2O_5 (30%)	- particle	Below 500 nm
V_2O_5 (35%)	- particle	Below 500 nm
ZnO (PURE)	- particle	172 to 197 nm
ZnO (15%)	- Reduced size of NS and NR - particle	Particle- Below 500nm
ZnO (20%)	-Reduced size of NS and NR -particle	Particle-Below 200nm
ZnO (25%)	-Honey comb with NRs -particles	NR-90 to 80 nm Particle-50 to 40 nm
ZnO (30%)	-Reduced size of NS -particle	Particle-Below 300nm
ZnO (35%)	-particle	Below 300nm
MgO(PURE)	-particle	Below 200nm
MgO (15%)	-Reduced size NS -Particle	Particle- micrometer
MgO (20%)	-Reduced size of NS -NR -particle	NR- 113 nm to 63.00 nm Particle- below 100 nm
MgO (25%)	-Reduced size of NS	Below 200nm
MgO (30%)	-particle	Below 200nm
MgO (35%)	-NSs	Thickness below 100nm

We observed that the use of simultaneously APS and V_2O_5 shows the regular nanosheets and nanofibers as in SEM of PANI. In this case, the joint addition of APS and V_2O_5 reduce the number of nucleation sites on the surface of nanofibers [8], therefore, allowing PANI to grow preferably into fibril direction to produce thinner fibers.

The SEM images shows the below 100 nm size glued particles of MgO, 172 nm size glued particles of ZnO and microrodes of V_2O_5. The length of fibers is shorter in all hybrids than in the pristine PANI and the diameter of fibers being more variable in the hybrids [15]. The image of the PANI/MO (15–25wt%) nanocomposite shows the shorter length and diameter of PANI nanofibers, and nanoparticles (MgO), microparticles (ZnO) and micro rodes (V_2O_5) are glueded into nanofibrous morphology of PANi (ES) and embedded within the netlike structure built by PANi chains. The result is well agreed with as reported by [16].

4. Conclusions

Change in the morphology of high molecular weight PANI emeraldine salt taken place by the addition of oxides like V2O5, ZnO and MgO. Length and diameter of PANI nanofibers significantly reduced in the PANI/MO NCs for 15 to 25 weight percent of MO to monomer. Disappearance of PANI nanosheets gives the high porous honey comb clews for 15% to 25% weight of ZnO in PANI/MO NCs. Reduced diameter of PANI nanofiber up to 63nm and reduced particle size below 40 nm has been remarkably observer in PANI/20% MgO. Concentration of metal oxides in PANI/MO nanocomposites had a significant impact on the morphology.

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