GLOBULAR-STRUCTURED POLYANILINE THIN FILMS ON POLYETHYLENE TEREPHTHALATE SUBSTRATE

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ABSTRACT: *In this study, we investigated the effects of the monomer-oxidant ratio on the morphology of polyaniline (PANI) films deposited onto a polyethylene terephthalate (PET) substrate. The films were synthesized via the in-situ polymerization technique in aqueous solutions of hydrochloric acid, using potassium dichromate as the oxidant. The scanning electron micrograph reveals the presence of globular microstructures within the films. At a low monomer-oxidant ratio, aggregates with diameters of 5-10 μm form, along with nanorods, resulting in overall structural heterogeneity. On the other hand, films deposited at a high monomer-oxidant ratio exhibit remarkable uniformity, homogeneity, and enhanced PANI growth on the substrate. The globules possess an average diameter of 8.6-14 μm. This distinctive morphology holds promise in electronic and chemical sensing, due to the abundant presence of conducting islands in the form of granules.*

1. INTRODUCTION

Semiconductors have attracted significant interest from researchers due to their wide array of applications, such as electronic devices, photocatalysis, and sensors [1-5]. Polyaniline (PANI) is an organic semiconducting polymer that can exhibit both n-type and p-type behavior depending on its doping state and conditions. It consists of repeating units composed of either benzenoid or quinonoid units, or a combination of both types in varying proportions. PANI has a remarkable electrical conductivity, pH-responsive characteristics and environmental stability, and it is cost-effective and can be easily synthesized [6].

Polyaniline can exist as a powder, colloidal, or film form. Its growth is affected by various factors and can produce various morphologies. For instance, researchers investigated the self-organization of granular polyaniline precipitate and film, and template-assisted PANI nanofibers using Ammonium persulfate (APS; $(NH_4)_2S_2O_8$) as an oxidant [7, 8]. In two other papers, colloidally-dispersed polyaniline, and PANI-biomolecule nanotubes were synthesized using the same oxidant [9, 10]. Researchers have also investigated how the polymerization temperature affects the morphology of PANI using APS as oxidant. They obtained plate-like, granulated, and cauliflower-like nanostructures for selected temperatures [11]. The formation of PANI films is significantly influenced by polymer-interphase interactions. For instance, polyaniline films with globular nanostructures were also synthesized on a glass substrate using hydrochloric acid (HCl) dopant and potassium dichromate ($K_2Cr_2O_7$) as oxidant [12]. On the other hand, researchers obtained non-uniform flake-like PANI structures on glass using the same oxidant and Dodecylbenzene sulfonic acid (DBSA) dopant, but obtained a fibrous structure for APS [13]. PANI fibers were also deposited on Polyethylene terephthalate (PET) substrates using APS and HCl as oxidant and dopant, respectively [14].

However, even with the extensive research on polyaniline and their composites, there appears to be a gap in the literature regarding the morphology of PANI films in various substrates using potassium dichromate ($K_2Cr_2O_7$) as oxidant. In this study, we synthesized PANI films on PET through an *in-situ* chemical oxidative polymerization method. Furthermore, we investigated the influence of the reaction conditions, such as the monomer-oxidant ratio, on the film's morphology.

2. METHODOLOGY

2.1 Preparation of the substrate

Polyethylene terephthalate (PET) substrates with adhesive tape on one side were successively washed in acetone, ethanol, and 1.0 M hydrochloric acid (HCl). Acetone eliminates oils and organic substances from the glass, while ethanol and HCl remove residual acetone and various oxides, respectively.

2.2 Synthesis of polyaniline film and characterization

Polyaniline (PANI) films were synthesized on PET substrates through an *in-situ* polymerization process of aniline in an acidic environment, using potassium dichromate ($K_2Cr_2O_7$) as the oxidizing agent. To initiate the polymerization, the PET substrates were immersed in a solution containing aniline (3.01 mL) and $K_2Cr_2O_7$ (3.24 g), both separately dissolved in 2.0 M HCl. The resulting mixture had a monomer-to-oxidant ratio of 3.0. The steps were repeated for mixtures with molar ratios of 2.4 and 1.8, using 2.39 mL and 1.79 mL of aniline solutions, respectively. After 30 minutes, the samples were removed and subsequently washed with water and 1.0 M HCl, and air-dried for 24 hours. The synthesized PANI films were characterized using a Scanning Electron Microscope-EDS (JEOL) at different magnifications to investigate the morphology of the films.

3. RESULTS AND DISCUSSION

The SEM micrographs of the polyaniline films deposited on the PET substrate with varying monomer-oxidant ratios are shown in Figure 1. For PANI films prepared with an M/O ratio of 1.8, the films contain irregular-shaped nanostructures along with clusters of globular structures (approximately 5-10 μm in diameter) and nanorods (Figures 1a-1b). The presence of these irregularly shaped nanostructures strongly indicates a series of PANI precipitate adsorption or a secondary nucleation growth process, due to the high oxidant concentration [15, 16].

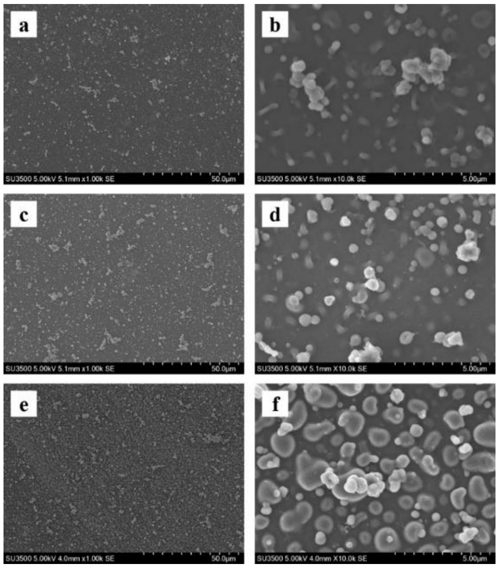

Figure 1. SEM micrographs of polyaniline films grown on PET substrates at various monomer-oxidant ratios: 1.8 (a-b), 2.4 (c-d), and 3.0 (e-f), with magnifications of 1,000× and 10,000×.

On the other hand, Figures 1c-1d show the SEM micrographs of the PANI film with an M/O ratio of 2.4. The film surface is dominated by globular morphology, with an average diameter of 8.6 µm, and irregular-shaped aggregates up to 100 µm in length. These aggregates may also be a result of overgrowth. The excess oxidant permits further protonation of the present oligomers in the solution, leading to the formation of new phenazine nucleates [16, 17]. This, in turn, promotes a secondary nucleation process for PANI growth [15].

Lastly, Figures 1e-1f present SEM micrographs of PANI films with an M/O ratio of 3.0. The film surface is covered with dense and uniformly distributed globular morphology. The resulting granular morphology also exhibits a uniform shape and size, with an average diameter of 14 µm. It is worth noting that PANI films with a M/O ratio of 3.0 exhibit higher PANI growth on the surface of the PET substrate compared to PANI films with monomer-oxidant ratios of 1.8 and 2.4. This observation aligns with findings reported in the literature, which highlight an increase in PANI growth in relation to the monomer-oxidant ratio [18]. This morphology exhibits promising potential for electronic and sensing applications, due to the wide arrays of conducting islands in the form of granules. The deposition of PANI films is influenced by the hydrophilicity of the substrate surface. In the case of PET, which has a hydrophobic surface, the process begins with the adsorption of hydrophobic phenazine during the induction period [19]. This adsorption occurs uniformly on the surface of PET, as illustrated in Figure 2.

The adsorbed phenazine nucleates serve as initiation sites for the PANI chain, enabling perpendicular growth from the surface and resulting in the formation of one-dimensional nanostructures [19].

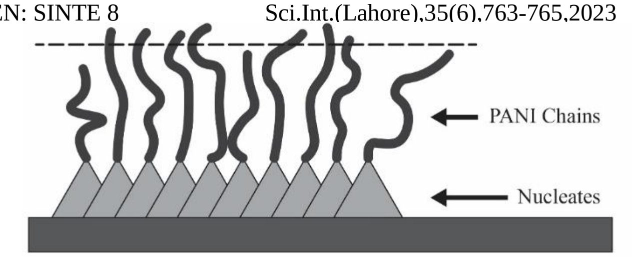

Figure 2. Formation of a polyaniline film on a hydrophobic surface [19].

The ionic strength of the medium, which is determined by the amount of the aniline monomer present, also influences the morphology of the PANI films. For the M/O ratio of 1.8, the concentration of nucleates is low, resulting in a prolonged induction period. This extended period allows for more time for the phenazine-containing oligomers to organize [20]. On the other hand, for M/O ratios of 2.4 and 3.0, where the monomer concentration is high, the globular morphology emerges due to the chaotic organization of the nucleates. This disorderly arrangement of nucleates is a consequence of both the increased ionic strength of the medium and the reduced solubility of the nucleates [20].

4. CONCLUSION

Polyaniline (PANI) films were successfully synthesized on a polyethylene terephthalate (PET) substrate via chemical oxidative polymerization using potassium dichromate ($K_2Cr_2O_7$) as the oxidant. The surface morphology of the films reveals globular microstructures. Films with a monomer-oxidant (M/O) ratio of 3.0 exhibited high PANI growth with a uniform shape and size. This morphology exhibits promising potential for electronic and sensing applications.

5. ACKNOWLEDGEMENTS

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