Journal of Scientific & Innovative Research

Calculation of particle size distribution of polyaniline salts using imageJ

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Abstract

The detailed analysis of particle size distribution is desirable in several technical fields that ma-nipulate granular/particulate materials including size reduction. This article describes the mani-pulation of scanning electron micrographs (SEM) of polyaniline (PANI) salts using ImageJ soft-ware. The PANI salts were prepared by two servable methods i.e. emulsion polymerizations and inverse emulsion polymerizations.[1,2] The effects of these synthesis routs on the particles shape and size distributions of the PANI salts were evaluated. Slight differences in the particle shapes were observed for these PANI salts. The polymer synthesized by inverse emulsion polymerization method showed smaller size than the one prepared by emulsion polymerization method. This type of computer based image processing methods provide better solutions to practical measurement and size distribution analysis as compared to the time consuming and vague manual means.

Keywords: Polyaniline salts, Emulsion/inverse emulsion polymerizations, SEM, ImageJ software, Size distribution.

Introduction

It is well known that polyaniline (PANI) is an interesting polymer for technical applications due to its good stability in the environment and reasonable conductivity, high redox reversibility, and easy transformation in colored films.[3] Accordingly, many applications of PANI have been proposed such as rechargeable batteries[4], capacitors[5], corrosion protections of metals[6, 7], actuator[8] and sensors[9]. PANI can be synthesized by chemical or electrochemical oxidation of aniline by which PANI is obtain as a green powder or thin film on electrode, respectively. The main goal of chemical polymerization route is to enhance two crucial parameters of this polymer i.e. the yield and solubility. In this case the successful strategies include the synthesis of substi-tuted PANIs[10-13], copolymerization of ani¬line with substituted anilines[14] and syn-thesis of PANI by emulsion/inverse emulsion po¬lymerization techniques[15-17]. In case of synthesis of substituted PANIs or copolymers the solubility improves at the expense of electrical conductivity.[17] Therefore, among these methods emulsion/inverse emulsion polymerization pathways are more interesting for improving its solubility and electrical conductivity simulta-neously.[17] This type of oxidation route is also fruitful for preparation of PANI with a variety of morphology.

Kinlen *et al.*[18] developed an emulsion process for the synthesis of PANI. The process entailed formation of emulsion particles with a mean hydrodynamic diameter of 150 nm and consisted of a water-soluble organic solvent (e.g. 2-butoxyethanol), a water-insoluble organic acid (e.g., di-nonylnaphthalenesulfonic acid), aniline and water. They obtained needle-like structures of the synthesized PANI. Li *et al.*[19] prepared HCl and dodecyl benzene sulfonic acid (DBSA) doped PANI by using solution and emulsion polymerization processes. The HCl-doped polyaniline consisted of granular particles in size of 200-500 nm while the DBSA-doped polyanilines consisted of long fibrils in length of 1500-2000 nm and in diameter of 100–200 nm. Ram and Palaniappan[20] developed a process for preparation of polyaniline salts such as

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polyaniline-sulfate, polyaniline-nitrate and polyaniline-hydrochloride by emulsion polymerization pathway. The polyaniline salts and bases prepared in this study showed aggregated granular form, with moderate degree of crystallinity. Palaniappan and John[21] synthesized a novel polyaniline–fluoroboric acid–dodecylhydrogensulfate (PANI–HBF4–DHS) salt via emulsion polymerization pathway. The scanning electron micrograph (SEM) of PANI–HBF4–DHS showed aggregated granular morphology. Shreepathi and Holze[22] developed a new inverse emulsion protocol for the synthesis of polyaniline (PANI). Benzoyl peroxide was used as the oxidizing agent and toluene + 2-propanol-water was used as the solvent. SEM pictures revealed that PANI flakes were formed during layer-by-layer stacking of the polymer. High-resolution SEM micrographs revealed that morphology of PANI was strongly influenced by the mole ratio of DBSA/ aniline in the feed. PANI prepared at 5:1 DBSA/aniline exhibited fibrillar morphology. When the ratio of DBSA to aniline was increased to 7:1 and 10:1, morphology changed to porous network and compact film, respectively. Kim *et al*.[23] synthesized dodecylbenzene-sulfonic acid (DBSA)-doped polyaniline (PANI) by emulsion polymerization, where DBSA was used as both an emulsifier and a dopant. The results indicated that PANI particles had an irregular and plate-like structure with a particle size distribution. Yang and Weng[24] prepared PANI via an inverse emulsion polymerization path using ammonium peroxydisulfate as oxidant and DBSA as surfactant and dopant simultaneously. They got nice fibrillar morphology of PANI with approximately length of 20µm and diameter of 1 µm. Suckeveriene *et al*.[25] described an ultrasonically assisted in situ interfacial dynamic inverse emulsion polymerization process of aniline. The prepared PANI exhibited a smooth surface with numerous voids ranging in size. Wang *et al*.[26] successfully prepared polyaniline nanofibers by emulsion polymerization. They used fumaric acid as a dopant. Fumaric acid-doped PANI mostly existed in the form of interconnected and entangled nanofibers, showing its flexibility. PANI nanofibers with the diameter of about 150 nm and different lengths showed the coarse surface with a dense array of PANI nodules with a diameter of 50 nm.

We also successfully developed two novel methods, i.e. emulsion polymerization[1] and inverse emulsion polymerization[2], for the synthesis of processable polyaniline salts with high solubility and electrical conductivity. The purpose of the present study was to analyze and compare the mor-phology and particle size distribution of these polymers in details.

Materials and Method

Materials and Chemicals

All chemicals were of analytical grade. Aniline (Riedel-de Häen) was distilled under reduced pressure and stored in a refrigerator. H2SO4 (Riedel-de Häen), Chloroform (Scharlau), Dodecyl Benzene Sulfonic Acid, DBSA, (Aldrich), Ammonium persulfate (Riedel-de Häen), Benzoyl peroxide (Merck), 2-Propanol (Merck) were used as received. Water (Milipore) was used for solution preparation.

Synthesis of Polyaniline Salts

Polyaniline (PANI) salts were prepared by the following two reported methods.[1, 2]

Method A: Emulsion Polymerization

0.10 M DBSA was added to 50 mL of chloroform under constant stirring. To this mixture aniline (0.01) was added. This was followed by the drop wise addition of 25 mL of H2SO4 (0.5 M) and 25 mL of ammonium per¬sulfate (0.05 M) in order to get a milky white emulsion. The content of the round-bottom flask gradually turned green and the stirring was continued for 24 hours. Then this reaction was stopped, the organic phase was separated and washed re¬peatedly with deionised water followed by acetone to precipitate out the pure polymer. The green precipitate having PANI salt was dried overnight in an oven at 60 ℃. The synthesized polymer was labelled as PANI 1.

Method B: Inverse Emulsion Polymerization

0.29 mol of chloroform was taken in a 100 mL round bottom flask. Then benzoyl peroxide (1.25 mmol) was added to it under mechanical stirring. To the above solution of 2-butanol (0.13 mol), DBSA (3.73 mmol), and aniline (0.97 mmol) were added. To the resulting mixture 0.28 mol of deionized water (Millipore) was added to form a milky white emulsion. The mixture turned green in 5 hours and the reaction was allowed to proceed for 24 hours. In the end the organic phase containing PANI salt was separated and washed four times with acetone. After thorough washing, a dark green highly concentrated PANI salt was obtained. Then it was dried at room temperature for 24 hours in a petri dish. Then few 5 mL of acetone was added to it and PANI salt was separated by filtration and dried. The synthesized polymer was labelled as PANI 2.

Characterizations

Morphological features of particles were analyzed with a scanning electron mi¬croscope (JSM-5910, JEOL). In every case, the sample was made by mounting a little amount of the given powder on an aluminum stub using double-coated conducting carbon adhesive tape. Samples were coated with gold through using auto fine coater [JEOL, JFC-1600] for the duration of 30 sec. The working distance was kept 10 mm from the sample to electron gun tip and the accelerat-ing voltage was adjusted to 15 kV.

Image Analysis

The SEM images of PANI salts were analyzed with ImageJ software. ImageJ can read/analyze images in many formats such GIF, TIFF, DICOM, PEG, BMP, JPEG and FITS. In the present study JPEG images were used. ImageJ can calculate area and pixel value statistics of user de-fined selections.

Firstly, pixel values of the images were converted into micrometer unit using the scale factor. Before using this command, the straight line selection tool was used to make a line selection that corresponded to known distance. Then original SEM Images were converted into binary images after unwanted parts of the images were cropped without disturbing the main particles in the im-ages to eliminate any bad light effects at the edges of the images. It is assumed that the binary images have black objects and white background. These images were then converted into "Mask" As the particles in the SEM images (Figure 1) are touching/ overlapping each other, "Watershed" was did to separate/clarify the particles. Then the size of the particles was calculated by setting measuring parameters.

Results and Discussions

Morphology of PANI salts

The morphologies PANI salts were analyzed by scanning electron microscopy (SEM) and their photographs are shown in Figure 1. It demonstrates that all the particles of PANI salts are highly aggregated and irregularly shaped.
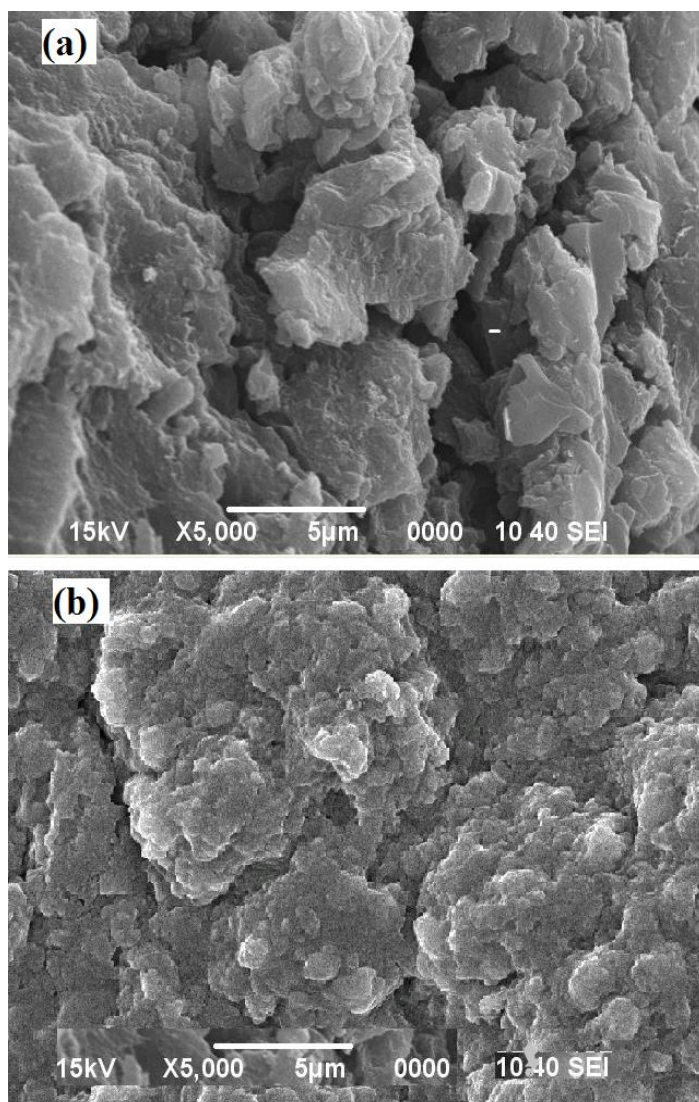

Figure 1: Scanning electron micrographs of (a) PANI 1 and (b) PANI 2

The size distribution of the particles of these PANI salts was further investigated in details by using Imagj software. This is because in addition to other desirable properties like solubility, electrical conductivity and thermal stability, the knowledge of size distribution of particulate materials is also very crucial. The size of the particles can influence a wide range of the material properties such as reaction rates, dissolution rates, easily ingredients mixing, surface properties and mechanical properties. Therefore, the detailed study of size distribution of PANI salts was carried out. The results of Imagj were analyzed and we categorized the particles in 10 bins based on which size range they fall under. The results are displayed in Table 1. The total number of particles in the image of PANI 1 is 519. The mean, mode, minimum and maximum sizes of the particles were found to be $105 \mu m^2$, 10 (375) μm^2, 10 μm^2 and 1000 μm^2, respectively.

Table 1: Particle size distribution of PANI 1

Number of bin	Size of particles (μm^2)	Number of particles
1	10	375
2	109	74
3	208	38
4	307	8
5	406	4
6	505	6
7	604	7
8	703	3
9	802	2
10	901	2

In case of PANI 2 we also categorized the particles in 10 bins based on their sizes and results are presented in Table 2. The total number of particles in the image of PANI 2 is 3864. The mean, mode, minimum and maximum sizes of the particles were found to be $13 \mu m^2$, 1 (3258) μm^2, 1 μm^2 and 250 μm^2, respectively.

Table 2: Particle size distribution of PANI 2

Number of bin	Size of particles (μm^2)	Number of particles
1	1	3258
2	25	296
3	50	156
4	75	60
5	100	30
6	125	23
7	150	13
8	175	16
9	200	8
10	225	4

By comparing these parameters of size/ size distribution, it was found that the overall size of PANI 2 is smaller than PANI 1. The difference in results of these PANI samples is due to the synthesis pathways. Therefore, it can be inferred from these results that as compared to emulsion polymerization, inverse

emulsion polymerization is more fruitful for production of PANI with reduced size. The reduced sizes of the particles of PANI 2 enhances its various properties such surface area, reactivity, dissolution and stability in suspension which are desirable in various technologies like catalysis, paint, etc.

Conclusions

ImageJ, an image processing software, was used for the evaluation and comparison of particles size distribution of polyaniline (PANI) salts. The processable PANI salts were synthesized by emulsion polymerization and inverse emulsion polymerization pathways. It was found that the synthesis route did not have any major effect on the shape of the particles of the PANI salts. However, an overall increasing trend in the particle size of PANI 1 (prepared by emulsion polymerization) was observed as compared to PANI 2 (prepared by inverse emulsion polymerization).

Acknowledgement

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