Evaluation of the Thermal Stability of Poly (O-phenylenediamine) (PoPD) by Thermogravimetric Analysis (TGA)

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Abstract: The poly (o-phenylenediamine) (PoPD) was synthesized from the monomer o-phenylenediamine in hydrochloric acid (HCl) using potassium dichromate as an oxidant by chemical oxidation method. The prepared PoPD sample was characterized by thermogravimetric analyzer (TGA) and scanning electron microscopy (SEM). The thermogravimetric analysis (TGA) results showed that a weight loss occurred. The weight loss as a result of the thermal energy applied to the polymer sample is 9.649mg which is 85.0% of the original polymer sample. The point of the greatest rate of change on the weight loss curve (point of inflection) is found to be 275°C and is the peak temperature of the degradation of the PoPD. SEM analysis showed that the PoPD sample has particle sizes ranging from 200µm-50µm at 360 magnification, 500µm-50µm at 1000 magnification, 200µm-50µm at 1550 magnification and 500µm-150µm at 2000 magnification which revealed more unevenly dispersed particles of the poly (o-phenylenediamine) polymer at different magnifications. Therefore poly (o-phenylenediamine) has different particle sizes and is also thermally stable at a higher temperature of 150°C.

Keywords: Thermal Stability, PoPD, TGA, SEM

1. Introduction

The discovery of conductive polymers has led to new technology. When interesting properties of material are observed in the laboratory, efforts are made to understand their mechanisms, which lead to the fine control of the fabrication process of this new and potentially important material [1]. Conducting polymers have been a popular area of investigation because of their potential application areas. Polymerization of a conducting polymer may be performed with chemical or electrochemical [2] methods. Different chemical oxidizing agents such as potassium dichromate [3, 4], potassium iodate, [5], hydrogen peroxide [6], Ferric chloride or ammonium persulphate [7] can be used. Polymers have been extensively studied as new materials for electronic and optoelectronic applications. The demands made on electronic components are constantly increasing. Aniline is

an important member of intrinsically conducting polymer. Phenylenediamine belong to aniline derivatives and PoPD shows different properties when compared to aniline [8]. Among the conducting polymers, PoPD, a highly aromatic polymer containing 2,3-diaminophenazine or quinoxaline repeating unit has received significant attention because it can be utilized in many fields [9]. The derivatives of polyaniline are found applications in different fields like removal of heavy metals from industrial effluents, anticorrosive agents [10], electromagnetic shielding and in optics [11-15]. Thermogravimetric analysis (TGA) of PoPD nanofibers possess good thermal stability [9]. A TGA can be used for material characterization through analysis of characteristic decomposition patterns. It is an especially useful technique for the study of polymeric materials. Thus a TGA is a method of thermal analysis in which the mass of a sample is measured over time as the temperature changes. It

can be used to evaluate the thermal stability of a material. TGA also gives the upper use temperature of a material beyond which the material will begin to degrade. Most polymers melt or degrade before 200°C. However, there is a class of thermally stable polymers that are able to withstand temperature of at least 300°C in air and 500°C in inert gases without structural changes or strength loss, which can be analyzed by TGA [16, 17]. In this work, TGA was used to analyze the thermal stability of PoPD using chemical oxidation technique. TGA curve was plotted to determine the inflection point useful for in-depth interpretations as well as differential thermal analysis (DTA). The scanning electron microscopy (SEM) which is the most versatile one available is used for the examination analysis of the microstructure morphology of the PoPD. ImageJ for microscopic image analysis is used to determine the average particle size from micrograph images [18].

2. Experimental

2.1. Materials

The (o-phenylenediamine) (oPD) used in this work was procured from Quallkems. The potassium dichromate ($K_2Cr_2O_7$) was procured from Kermel. The concentrated Hydrochloric (HCl) acid was procured from Sigma Aldrich, Oceanic chemicals Nig. Ltd.

2.2. Synthesis of PoPD

1.622g of (o-phenylenediamine) (oPD) was added to 50ml of 0.1M of HCl. The solution was heated and stirred for about 5 minutes. The temperature of the solution was brought down to 20°C. Then 50ml of potassium dichromate ($K_2Cr_2O_7$) was used as the oxidizing agent and was prepared by dissolving 4.413g of $K_2Cr_2O_7$ in 50ml of 0.1M of HCl. The dissolved $K_2Cr_2O_7$ was set to drop bit by bit (dropwise) with the help of a burette with a flow rate of 1.43ml/min. The solution was left for 24hrs. Then, the poly (o-phenylenediamine) was collected after filtration and repeated washing with distilled water and allowed to dry at a temperature of 50°C.

2.3. Sample Characterization

The prepared PoPD sample was characterized with TGA and SEM.

3. Results

3.1. Thermogravimetric Analyzer (TGA)

Thermogravimetric analyzer (TGA) measures the amount of weight change of a material, either as a function of increasing temperature or isothermally as a function of time, in an atmosphere of Nitrogen, Helium, air, other gas or in vacuum. Figure 1 shows the thermogram of the poly (o-phenylenediamine) with sample weight of 11.352mg.

Figure 1. Thermogram (TGA) of PoPD sample.

Figure 2 shows the time derivatives of the weight loss against temperature.

Figure 2. Derivative Thermogram (DTA) of PoPD sample.

The combination of TGA and DTA of sample is shown in figure 3.

Figure 3. Thermogram (TGA) and Derivative Thermogram (DTA) of PoPD sample.

3.2. Scanning Electron Microscope (SEM) Images Analysis

Figure 4. SEM Image of PoPD at 360 magnification.

Figure 5. SEM Image of PoPD at 1000 magnification.

Figure 6. SEM Image of PoPD at 1550 magnification.

Figure 7. SEM Image of PoPD at 2000 magnification.

4. Discussion

4.1. Thermogravimetric Analysis (TGA)

The descending TGA thermal curve shown in figure 1 indicates that weight loss occurred due to application of heat to the powder polymer sample. The temperature of the heat applied ranged from 45.00°C to 950.00°C at 10.00°C/min with Nitrogen as atmospheric condition. Beyond 572°C the sample shows no further degradation. The thermogram in figure 1 gives the various stages that lead to the thermal degradation of the synthesized polymer. The thermogram provide quantitative information such as loss of water (%), loss of solvents (%), pyrolysis (thermal decomposition), oxidation, and weight of ash or residual (%). The summary of the thermal degradation process is shown in table 1.

From table 1, the weight percentage of moisture content (water and other solvent) removed from the actual weight of the synthesized poly (o-phenylenediamine) within the onset temperature (T_{onset}) of 150°C and offset temperature of 200°C is given in the first stage. 8.0% which is equivalent to 0.908 mg of the actual sample used for the TGA analysis was lost. The second stage involves thermal decomposition (pyrolysis) of the sample with an onset temperature of 200°C and offset temperature of 470°C. The percentage weight loss in this stage is 85.0% which is equal to 9.649 mg of the original sample. The third stage which contain residual in form of charcoals has an onset temperature of 470°C and offset temperature of 572°C. Percentage weight of the residual remaining is 7.0% which represents 0.795 mg. Therefore, the weight loss as a result of the thermal energy applied to the polymer sample is 9.649 mg which represents about 85% of the original polymer sample. The temperature of the onset of thermal degradation was observed at 200°C while the offset temperature of thermal degradation is found to be 470°C.

At any given temperature in figure 2, the rate of weight loss is a function of the amount of original material remaining, the nature and relative amount of degradation product (residue) present. The peak temperature of the derivative indicates the point of greatest rate of change on the

weight loss curve shown in figure 4.13. This is known as point of inflection and is the most sensitive point at the temperature axis. This corresponds to the point at which the curve is changing direction at the greatest rate which can also be regarded as the peak degradation temperature. The peak

temperature of degradation of the PoPD is found to be 275°C. Figure 4.15 shows both the thermogram and the derivative of the thermogram. The derivative of weight loss is measured in percentage of weight loss per minute.

Table 1. Analysis of the stages on weight loss in the thermogram of PoPD powder.

Stages	Change in weight (%)	Loss of mass (mg)	Temperature change= $T_{offset} - T_{onset}$ (°C)
1 st (loss of water)	$W_1 - W_2 = 100 - 92 = 8.0$	$\frac{8.0}{100} \times 11.352 = 0.908$	200 - 150 = 50
2 nd (Pyrolysis or Thermal decomposition)	$W_2 - W_3 = 92 - 7 = 85.0$	$\frac{85}{100} \times 11.352 = 9.649$	470.0 - 200.0 = 270
3 rd (Residual)	$W_3 - W_0 = 7 - 0 = 7$	$\frac{7}{100} \times 11.352 = 0.795$	572 - 470 = 102

4.2. Scanning Electron Microscopy (SEM) Analysis

For poly (o-phenylenediamine) at 360 magnification (Figure 4), SEM analysis showed that the sample had particle sizes ranging from 200µm-50µm. Uneven masses littered the surface of the sample were observed at a lower magnification.

For poly (o-phenylenediamine) at 1000 magnification (Figure 5), SEM analysis showed that the sample had particle sizes ranging from 500µm-50µm. Uneven masses littered the surface of the sample were observed at a lower magnification.

For poly (o-phenylenediamine) at 1550 magnification (Figure 6), SEM analysis showed that the sample had particle sizes ranging from 200µm-50µm. Uneven masses littered the surface of the sample were observed at a higher magnification.

For poly (o-phenylenediamine) at 2000 magnification (Figure 7), SEM analysis showed that the sample had particle sizes ranging from 500µm-150µm. Uneven masses littered the surface with a very large mass of the sample were observed at a higher magnification.

Therefore the poly (o-phenylenediamine) sample has different particle sizes at different magnifications.

5. Conclusion

The synthesis of poly o-phenylenediamine in HCl medium with potassium dichromate as an oxidizing agent using chemical method was successfully achieved. Thermogravimetric analysis (TGA) was used to determine the thermal properties (stability) of the prepared PoPD. The thermogravimetric analysis (TGA) results showed that a weight loss occurred. It shows a weight loss of moisture content of 8.0% (0.908mg) of actual sample used and a weight loss (thermal decomposition or pyrolysis) of 85.0% (9.649mg) of the original sample with the percentage weight of the remaining residual of 7.0% (0.795mg). The weight loss as a result of the thermal energy applied to the polymer sample is 9.649mg which is 85.0% of the original polymer sample. The polymer sample has a thermal stability of 150°C and the point of the greatest rate of change on the weight loss curve (point of inflection) is found to be 275°C which is the peak temperature of the degradation of the PoPD. Also the

PoPD has different particle sizes ranging from 500µm-50µm at different magnifications from SEM images.

6. Recommendations

Having successfully polymerized PoPD using potassium dichromate by chemical oxidation method the following recommendations are made for further studies;

- The use of other oxidizing agents other than potassium dichromate for the synthesis of PoPD.
- The use of electropolymerization method in different acid medium with different substrates.

Contributions

- Determination of the thermal stability of the PoPD.
- Determination of the point of inflection of the PoPD.

Conflict of Interest

The authors declare that there is no conflict of interests regarding the publication of the paper.

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