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Synthesized of conductive polyaniline by solution polymerization technique

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Abstract

Polyanilines (PANIs) have been synthesized by the emulsifier free polymerization process utilized Ammonium Persulphate (APS) as an initiator at room temperature (28 °C). The complete reaction of polymerization process was indicated by increasing viscosity from 20 mPa.s to 180 mPa.s. A particle size formation also was observed during the polymerization process. Both indicators occurred due to a proceeding progress of polymer molecule chain. Hence, the formation of polymer particle is confirmed. In addition, temperature test indicated that there was an increase in temperature from 28 °C in the first 120 minutes to 52 °C after 8 hrs progressing time. Evidently, an increment in the temperature was due to an increase of reaction rates. The present of synthesized PANI was then confirmed by their respective FTIR spectrum. It is concluded that PANI has successfully synthesized by the emulsifier free polymerization process. The electrical conductivity value of PANI is driven by protonic acids. This value shown significant increase from 17.5 μS/cm as pure PANI to 3600, 1520 and 920 μS/cm after the addition of photonic acids of HClO₄, H₂SO₄ and HCl.

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1. Introduction

Interest in the conductive polymers is increasing due to the expansion of their area of practice applications¹. Conductive polymers can be used in modern technology applications like in new electronic devices not the exception as materials for protecting the electromagnetic irradiation like Radar Absorbing Materials and

Electromagnetic Interference Shielding^{2,3}. When conductive Polyaniline is used as a matrix for metals or oxide particles making a composite system, some exciting physical and chemical properties can be anticipated to emerge from the system. Polyaniline properties are determined by the regular structure of polymer chains. The latter could be formed in various dimensions and morphologies. Hence, structure of fibers, plates and granules^{4, 5} are possible, which are all depending on the way how Polyaniline is synthesized. It was reported in the previous work that conductive Polyaniline has been obtained by the addition of precursors in which the protonation process of Emeraldine base by three different protonic acids increased the electrical conductivity value⁶. Hence, it is very important to develop methods of controlled synthesis of Polyaniline giving polymers with predetermined properties. This paper reports some results of conductive Polyaniline synthesized by a polymerization technique. It obtained higher conductivity value after additional photonic acid as doping agent. The value increase from 17.5 $\mu\text{S}/\text{cm}$ before additional doping agent to 3600, 1520 and 920 $\mu\text{S}/\text{cm}$ after doped by HClO_4 , H_2SO_4 and HCl respectively⁶.

2. Experimental method

Two different solutions named respectively solution A and B were prepared. Solution A was made of 60 gr aniline monomer mixed homogeneously with 750 gr Hydrochloric acid (HCl). Whereas the solution B was made of 75 gram Ammonium Persulphate (APS) and 750 gr HCl led to 1.5 Molar solutions. Feeding process was carried out in the control manner in which the solution A was introduced into solution B with a flow rate of ± 2 ml/minute at room temperature by keeping the agitation for 8 hours. The feeding process has ended up with a result of blackish green precipitant of PANI-ES. It is Polyaniline (emeraldine) salt based is deprotonated using weak base as alkaline medium to form Polyaniline (emeraldine) base (PANI-EB). Cleaning and washing process by water and methanol are required. The next step was a deprotonation process in which powders of PANI-ES dissolved into a NH_4OH with a 0.1 M solution. The completion of deprotonation process was about 15 hrs indicated by the appearance of the blackish blue of the solution. The deposit was then filtered and washed by NH_4OH 0.1 M and Tetra Hydro Furan (THF) and to be dried in vacuum desiccators for 60 hours. Purging gas N_2 was required before the drying process. The final step was re-protonation of PANI-EB in which 0.22 moles of PANI-EB and 80 ml each protonic acid were placed in the reactor and keep mixing them for 10 hours which resulted in a blackish green color precipitant (PANI-ES). During polymerization process, some parameters are determined such as viscosity by Viscosimeter, particle size by Mastersizer Particle Size Analyzer and thermometer is put in the reactor to control temperature during process. The final characterization is using FTIR Spectrophotometer Shimadzu to ensure that the polymerization reaction has been complete.

3. Result and discussion

Changing properties of viscosity and particle size from the liquid during polymerization reaction are plotted in Fig. 1. The result shown in Figure 1a) indicated that there is a viscosity increase of the solution during the polymerization process. Initially, the viscosity of pure aniline monomer was only 80 mPa.s. No changes in the viscosity value, at least in the first 30 minutes of polymerization time. However, when the APS solution was gradually introduced, the viscosity is progressively increased and the level off to 180 mPa.s as the highest value. The steady value of the solution with a final viscosity of 180 mPa.s indicates that there must be no more reactions in progress. The changing in viscosity indicated that there must be molecules changing during the polymerization reaction along with a propagation process that's taken place which result in longer polymer molecule chains. Hence, the solution contains long molecule chains will have higher viscosity value⁷. The other basic parameter of a polymer to define a reaction is the particle size. According to report of Paine⁸, a particle growth of polymers will happen during polymerization reaction. A monomer containing solution usually is a clear liquid and hence the size of the particles must be zero. This is different with a polymer which has a certain particle size.

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