Effect of BaTiO₃ Doping on the Vibrational Properties of PAni

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Abstract
Due to the advantages of material abundance and synthetic simplicity, polyaniline can be used as a high-capacity cathode material. However, its practical application in batteries has been hindered by poor electrochemical utilization and cycling instability. This paper reports the enhancement in the conductivity of the polymer (PAni) using the oxidation polymerization method. After successfully synthesis of PAni the vibrational properties have been analyzed by using FTIR. From experimental data, it has been observed that after doping of BaTiO₃ the carriers along the surface enhanced which increases vibration along with the fingerprint reason. The polymers showed less electrical conductivity than polyaniline. Unlike polyaniline, the presence of the nitro group caused higher frequency dependence of electrical conductivity. The FTIR bands at 1492, 1291 and 1147 cm^{-1} are corresponding to the polyaniline salt.

Keywords- Polymerization, FTIR, Conductivity.

1. Introduction

There is an explosive increase in the demand for composite materials in the last two decades, which are now available as materials with a unique combination of properties (Xu et al., 2013) Polyaniline (PAni) has been at the forefront of the global search for commercially viable conducting polymers because of its unique proton dopability, excellent redox recyclability, chemical stability, variable electrical conductivity (which can be varied by changing the pH at which it is prepared), low cost and ease of synthesis (Ram et al., 2020; Thomas et al., 2017; Tang et al., 2017). Thus, the composites based on conducting polymers

and insulating polymers have been studied as materials for industrial products, such as rechargeable batteries, conductive coatings, light-emitting diodes, gas sensors and antistatic materials (Kumar et al., 2020; Ram et al., 2019).

Copolymerization offers a way of improving the processibility of PAni. The properties of the poly (substituted anilines) like toluidine, anisidine, etc. depend on the type of substitution like electron-withdrawing, electron-donating groups, or less affecting groups like alkyl groups. The electron-withdrawing group decreases the electron density in aniline, the electron-donating group increases the electron density in the phenyl ring, whereas the alkyl group may not affect much to the electron density in aniline only some mild positive inductive effect (+I) may increase the electron density.

In the present work, we have focused on developing conducting polymer PAni using the oxidation polymerization method. We have considered polyaniline as the candidate material due to its superior electrical properties and stability. Polyaniline has been discovered by Runge (1834) and he named it aniline black (Letheby, 1862). Green and Woodhead (1912) discovered PAni Chain has a mixed oxidation state polymer composed of reduced benzenoid and oxidized quinoid units (Green and Woodhead, 1912). Epstein et al. (1987) discovered that the characteristic of PAni switches between a conductor and an insulator. Further to this work, the research on polyaniline attracted much attention from material scientists and the engineering community. Conductive polymers such as PAni remain of widespread interest (Heeger, 2001) providing an opportunity to address fundamental issues of importance to condensed matter physics, including, for example, the metal-insulator transition (Tzamalis et al., 2003), the Peierls instability and quantum decoherence (Cattena et al., 2010). The unique property of polyaniline alters its electrical properties on exposure to acidic and basic environments by forming a Lewis acid-base complex.

1.1 Mechanism of Polymerization
The polymerization of aniline proceeds via a radical propagation mechanism as shown in Figure 1.

The initial steps (1 and 2) are common to both methods, but slight differences appear in the initial product of the chain propagation step and product MN formation steps (3 and 4) (Gospodinova et al., 1998). Step 1 shows the Oxidation of monomer during polymerization of aniline and step 2 is generally known as Radical coupling and re-aromatization in which Radical coupling and re-aromatization of the polymer during polymerization of aniline. Step 3 is the chain propagation during polymerization of aniline and step 4 is oxidation and doping of the polymer during polymerization of aniline monomer.
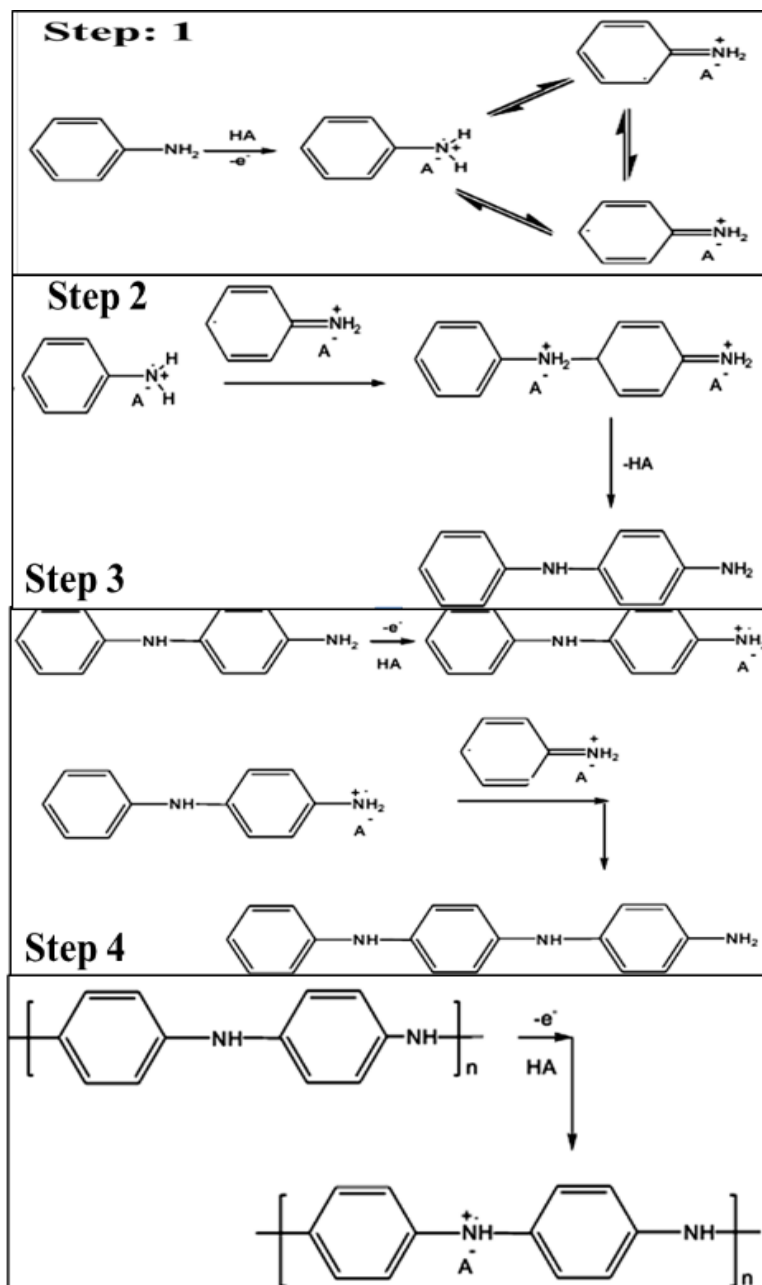
Figure 1. Mechanism for the polymerization of PAni.

1.2 Structure of Polyaniline

PAni has a mixed oxidation state of benzenoid and oxidized quinoid units (Shimano et al., 2001), PAni's average oxidation state is denoted as 1y whereby the value of y determines the existence of each of the three distinct PAni oxidation states (Wallace et al., 2009) as shown in Figure 2. Thus, PAni exists as fully reduced leucoemeraldine (LE) where 1-y = 0, half oxidized emeraldine base (EB) where 1-y= 0.5 and

fully oxidized pernigraniline (PE) where 1-y =1 (Green and Woodhead, 1912). The EB is the most useful form of PAni due to its high stability at room temperature for a long time; it is composed of three benzenoid units and one quinoid unit. Furthermore, EB can be doped in a non-redox reaction in an acidic medium which results in an emeraldine salt (ES). On the other hand, LE is easily oxidized while the PE is easily degraded (Huang and MacDiarmid, 1993).
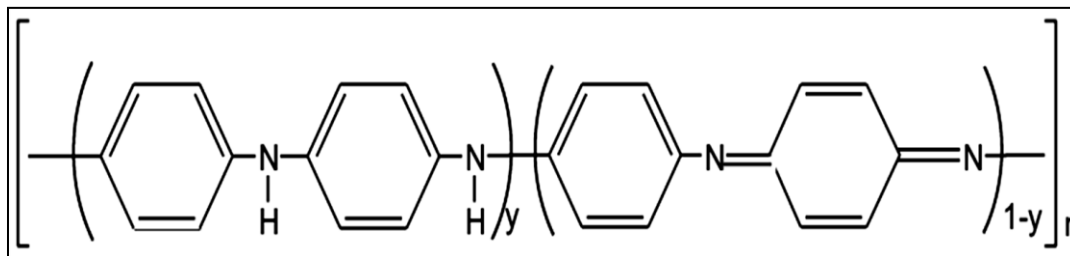

Figure 2. Different oxidation states of polyaniline (y = 1: leucoemeraldine, y = 0.5: emeraldine and y= 0: pernigraniline.

1.3 Conductivity Properties of PAni

The polyaniline chain can be formed by various combinations of the two repeating units known as the X and Y components of polyaniline as shown in the above figure (De Albuquerque et al., 2004). Due to this, PAni has many unique properties and electronic conduction mechanisms that distinguish it from the rest of the conducting polymers.

Among the various oxidation states that PAni can exist in, the one that can be doped to a highly conductive state is the moderately oxidized EB (Tzamalis et al., 2003). This form of PAni has a structure that consists of equal proportions of imine (=N–) and amines (–NH–) sites. Through protonic acid doping, imine sites are protonated by acids HA to the bipolaron (dication salt) form (Stafström et al., 1987). The bipolaron then undergoes a further rearrangement to form the delocalized polaron lattice which is a polysemiquinone radical-cation salt as shown in Figure 3 below.

The resulting emeraldine salt has conductivity on a semiconductor level of the order of 100 S/cm, which is many orders of magnitude higher than that of common polymers ($<10^{-9}$ S/cm) but lower than that of typical metals ($>10^4$ S/cm) (Bhadra et al., 2009). Only 1% of the charge carriers which are available in the ES salt contribute to its observed conductivity. If all the available charge carriers were to contribute, the resulting conductivity at room temperature would be $\sim 10^5$ S/cm, which is comparable to that of copper.
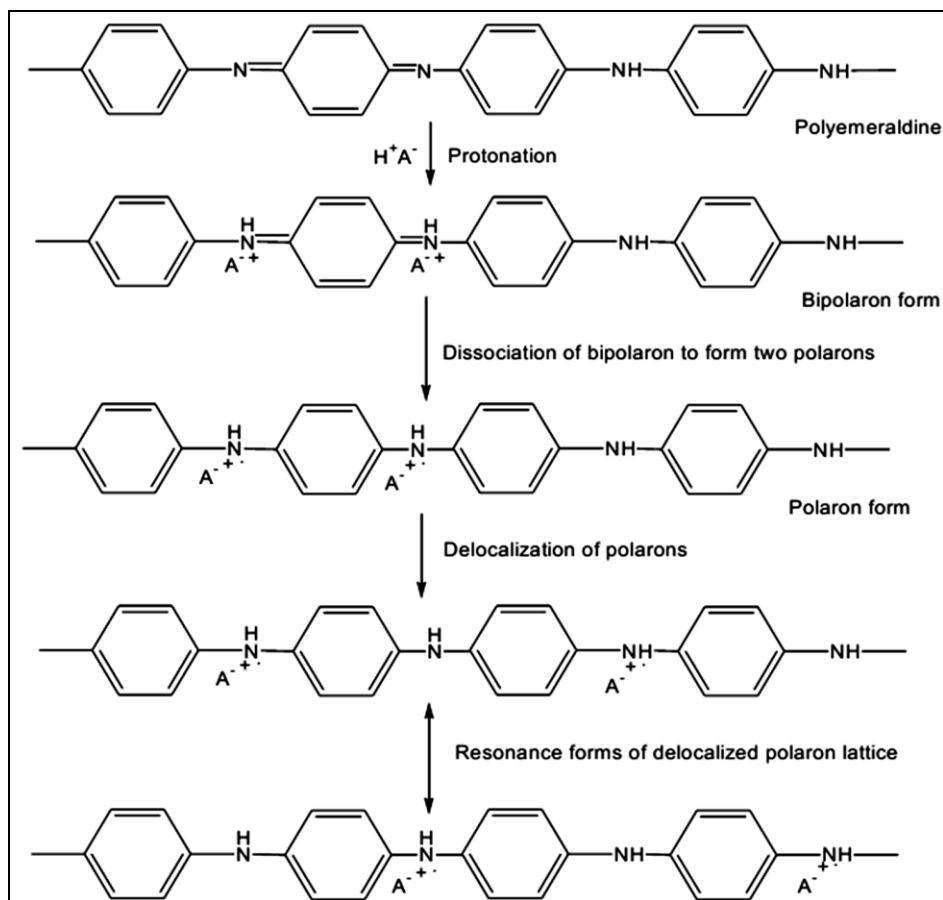
Figure 3. Doping of EB with protons to form the conducting emeraldine salt (PAni/HA) form of polyaniline (a polaron lattice).

2. Experimental Investigation

2.1 Synthesis of PAni using Oxidation Polymerization Method

The polyaniline has been prepared by using the oxidation polymerization method. In this method, 0.5 M of Aniline was dissolved in distilled water and stirred for 30 min. After dissolving 20 ml of Ammonium peroxysulphate has been added to the solution and again stirred for 30 min. The solution was kept at room temperature (19-25℃) and vigorously stirred for 1 hr. After stirring the solution was kept in the dust-free chamber for polymerization. The next day, the solution was filtered and washed with distilled water and acetone. The filtered nanomaterial was dried at 60 ℃ finally the PAni has been formed.

During the doping of BaTiO₃ nanoparticles in PAni, BaTiO₃ nanoparticles were first synthesized using the Co-precipitation method. After successful synthesis, BaTiO₃ nanoparticles are mixed with aniline during the polymerization process. In such a process, the PAni layer is completely covered with the BaTiO₃ nanoparticles and increases the conductivity of the material.

2.2 Results and Discussion

FTIR spectra of both PAni and doped copolymer, are shown in Figure 4 (a-d). The spectra of all the copolymers show the main bands in the region of 1492, 1294 and 1276 cm^{-1} corresponding to the ring-stretching vibrations of the quinoid and benzenoid rings of aniline and nitro aniline, respectively.

Furthermore, the quinoid peak appears split, while the benzenoid band is not split in the spectra. The quinoid band is sensitive to the structure, and hence, two bands at 1492 and 1560 cm^{-1} arising from quinoid stretching of aniline and nitro aniline ring segments are observed. A band near 1276 cm^{-1} is assigned to the C$=$N+ stretching adjacent to the quinoid structure while a medium intensity band at 1291 cm^{-1} is associated with C–N stretching vibration in the alternate units of quinoid–benzenoid–quinoid rings. The peaks at 1294 and 1247 cm^{-1} correspond to N–H bending and the symmetric component of the C–C (or C–N) stretching modes. Most of the bands of the copolymers are asymmetric and symmetric stretching modes of the nitro group of o-nitro aniline which occur at 1490 and 1294 cm^{-1}, respectively.

The band around 1130 cm^{-1} is attributed to the B–(NH$^+$)$=$Q structure which is formed during the protonation process. A band at 1130 cm^{-1} is assigned to the C–H in-plane bending. This confirms the presence of o-nitro aniline segments in the copolymer and also suggests an increase in the conjugation of the nitro group with the ring. The significant lowering of the frequencies can be related to the hydrogen bonds formed between the oxygen of the nitro group and the hydrogen of the amine group.

The bands at 1130 and 881 cm^{-1} can be attributed to the in-plane and out-of-plane C–H bending modes, respectively. The strong band at 1082 cm^{-1} in the base is much more intense and broader in the salt spectrum. In addition to the above peaks, the spectrum of the polyaniline exhibits peaks at 3253 cm^{-1} that could be attributed to NH$_2$ stretching mode and a band located at 1653 cm^{-1} related to the NH$_2$ bending vibration, while the peak at 881 cm^{-1} is attributed to NH$_2$ wagging. In addition, the peak at 1490 cm^{-1} confirms the presence of a protonated imine function, and the band characteristic of conducting protonated form is observed at 1247 cm^{-1}.
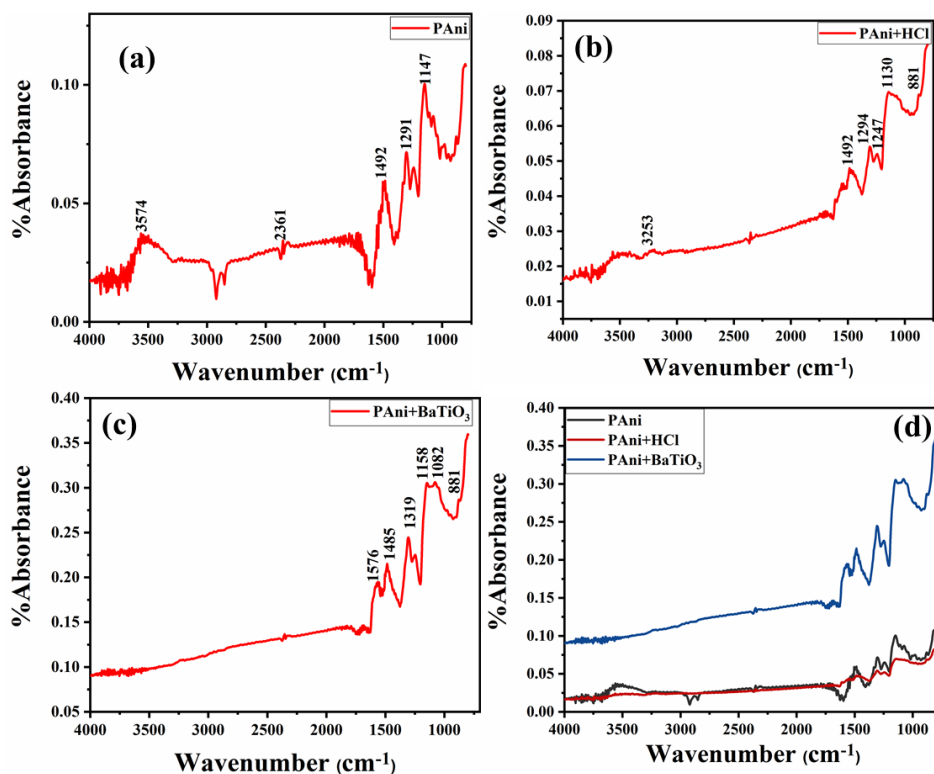

Figure 4. FTIR analysis of (a) PAni (b) PAni+HCl (c) PAni+BaTiO$_3$ (d) Comperetive data.

3. Conclusion and Future Scope

In this paper, the vibration property of PAni copolymer and doped polymer has been successfully analyzed by the FTIR spectrum. The oxidation polymerization method and characterization results reveal that the material is successfully synthesized and doped with BaTiO$_3$ during such a process. The characterization peak at 881 cm^{-1} is attributed to NH$_2$ wagging and at 1490 cm^{-1} confirms the presence of a protonated imine function which confirms the formation of PAni in this method. The conductivity of the material also increases during this process so it can be used in so many different kinds of applications.

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