

Structural characterization of PMMA blended with chemically synthesized PANi

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ABSTRACT

In the present study, we discuss the synthesis of Polyaniline (PANi (ES)) and its composites with Poly-methylmethacrylate (PMMA). PANi doped with Dodecyl benzene sulfonic acid (DBSA) has been synthesized through chemical oxidation of aniline in presence of Ammonium persulphate (APS). Composites of PMMA and PANi have been formed by solution blending method using Chloroform as solvent. The X-ray and FTIR studies reveal the formation of inter-penetration network of PANi particles with the chain of the PMMA.

Keywords: Emeraldine salt (ES), PANi, solution blending, inter-penetration network.

INTRODUCTION

Organic conducting polymers having extended π -electron conjugation attracted the attention of various researchers because of their special electrical properties, morphology and crystallinity as compared to other conventional insulating polymers [1-2]. Also, they acquire importance over inorganic semiconductors in their application because of their high strength to weight ratio, toughness, low cost and ease of processing into films. Some of the potential devices based on these polymers are organic light emitting diodes (OLEDs), sensors, low power rechargeable batteries, super capacitors, photovoltaic cells and low dielectric materials in ICs [3-6]. These organic materials possess electrical conductivity comparable to metals and semiconductors with the possibility of controlling the conductivity by limiting the nature and degree of doping of protonic acids. The conducting polymer, polyacetylene, discovered by Shirakawa, Heeger and Macdiarmid [7] has electrical conductivity of the order of 10^5 S/cm [8] whereas conductivity of copper is 10^6 S/cm. Amongst the class of CPs, Polyaniline (PANi) is one of the most studied conducting polymers due to its controllable and relatively higher level of electrical conductivity coupled with excellent environmental stability, electro-optical properties, corrosion resistance, low cost raw materials and ease of synthesis in high yields [9-11]. Both chemical as well as electrochemical methods can be used to synthesize PANi. Chemical synthesis is preferably used because of its large yield [12]. However, the major drawback of chemically synthesized PANi is

its intractability, i.e., insolubility in common solvents and infusibility, which results in poor processibility [13-14]. Many promising approaches to circumvent these setbacks and turn PANi into a more tractable polymer have been developed over the years, either by counter-ion induced solubility or melting processibility [15]. In addition, the use of conducting polymer composites with common insulating polymers has arisen a new way of combining metal like electrical conductivity with mechanical properties of conventional polymers [16-17]. There has been reported work on the blending of PANi with a number of polymers including poly-styrene, poly-vinylchloride (PVC), poly-vinylalcohol (PVA) and poly-methylmethacrylate (PMMA) [18-21].

In the present work, we have chemically synthesized Dodecyl benzoic sulfonic acid (DBSA) doped PANi (Emeraldine Salt form) and its blends with PMMA. FTIR and XRD techniques have been described to corroborate the blending of PANi and PMMA.

MATERIALS AND METHODS

Aniline (99%), Ammonium per sulfate (APS), DBSA (70 wt % in 2-Propanol), PMMA (granules), Chloroform (Laboratory Reagent) were purchased from Sigma Aldrich and used as received. Double distilled water was used as solvent in chemical reaction and washing.

2.1 Synthesis of PANi

For the preparation of stable PANi doped with DBSA, the method given by Chen [22] was adopted. Briefly, PANi (ES) was synthesized by oxidative chemical polymerization of aniline in the presence of DBSA and APS, at a molar ratio of 1:1:1. DBSA here acts both as dopant as well as surfactant. The reaction was carried out at low temperature (0 to 5^oC) under constant magnetic stirring. At the end of reaction, a dark green mixture was found. This reaction mixture was then allowed to place in refrigerator and after 24 hours, this suspension was precipitated with acetone. The PANi-DBSA precipitates were filtered and washed with distilled water repeatedly until the pH of the filtrate became neutral. The collected product was dried in oven at 60^oC for 48 hrs to obtain a fine dark green powder of PANi.

2.2 Preparation of PANi-PMMA blends

For pure PMMA film, PMMA granules (0.5 gm) were dissolved in 15 ml of Chloroform at room temperature. PANi-PMMA blends were prepared by dissolving different amount of PANi powder (1% and 6% by weight) in PMMA-Chloroform solution under continuous stirring of 1 hour followed by ultra sonication for 40 minutes. The content of PMMA was kept constant for all samples. Films were prepared by casting this solution in glass Petri Dish and allowed to evaporate the solution at room temperature. After this, the films were peeled off from glass plate using doctor blade to obtain free standing films.

2.3 Characterization

Structure of PANi powder, pure PMMA and their blended films was analyzed using X-ray Diffraction (XRD) and Fourier Transform Infrared spectroscopic (FTIR) techniques.

RESULTS AND DISCUSSION

3.1. PANi powder

In order to congregate information about the structure, XRD and FTIR spectra of PANi-DBSA powder were studied. The X-ray pattern (figure 1) of PANi shows peaks at $2\theta = 15.86^{\circ}$, 19.85° , 25.12° and 26.89° which shows the semi crystalline structure of the PANi particles [6, 23].

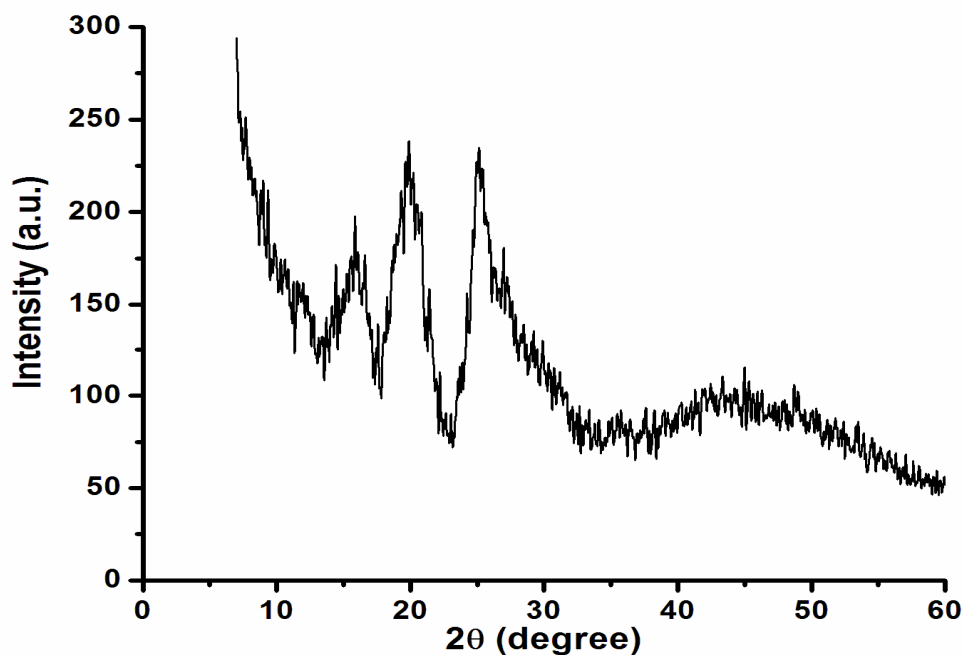


Figure 1. XRD pattern of DBSA doped PANi Powder

The FTIR spectrum of PANi, presented in figure 2, confirms the various bonds [24] present in PANi-DBSA structure. The peak around 3432 cm^{-1} is attributed to the N-H stretching vibrations, the 2921 cm^{-1} is due to CH stretching, the 1663 cm^{-1} and 1575 cm^{-1} assigned to bending mode of NH bond of quinoid (Q) and benzenoid (B) units respectively.

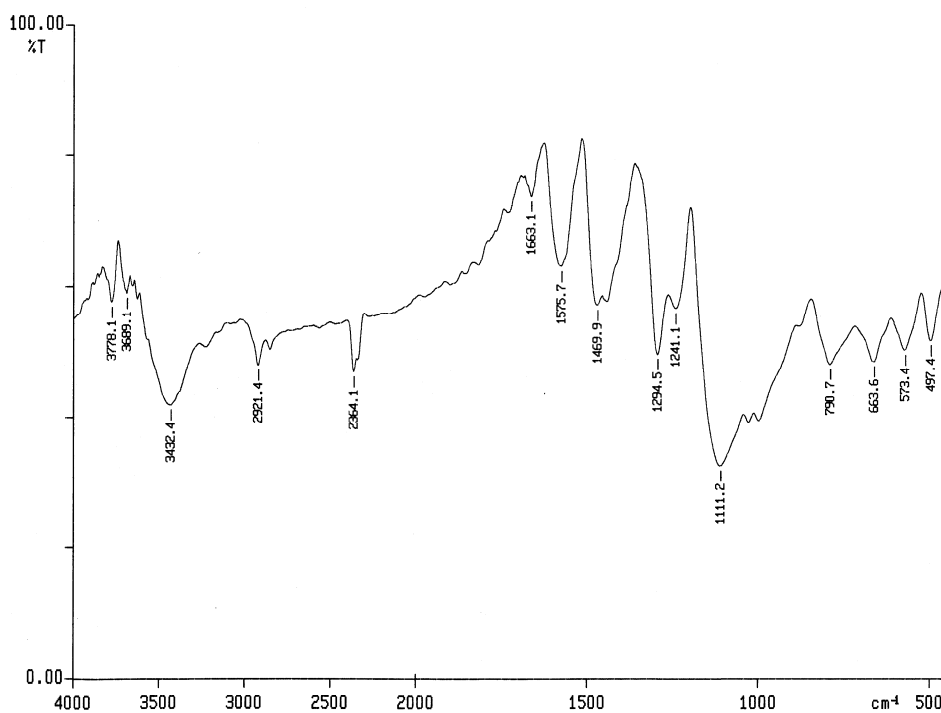


Figure 2. FTIR spectrum of DBSA doped PANi Powder.

The peaks at 1294 cm^{-1} and 1241 cm^{-1} are due to intrinsic C-N stretching and the region $490\text{-}790\text{ cm}^{-1}$ corresponds to B-NH-B vibration modes formed during doping reaction. Intense and broad peak at around 1111 cm^{-1} is attributed to B-N=Q units. This shows the presence of the positive charge present in the backbone chain, thus, confirms the emeraldine salt [ES] form of PANi [25].

3.2. Blends of PANi-PMMA

X-ray diffraction patterns of unblended PMMA and various PMMA-PAni blended films are presented in figure 3. It is apparent from this figure that X-ray pattern of PMMA matrix shows broad bands peaking at around $2\theta = 15.45^\circ$, 29.93° and 41.22° [26] indicating its amorphous nature.

The X-ray pattern of various PANi-PMMA blended films (figure 3) show the absence of the peaks which are present in PANi (figure 2) with the broadening of peak of PMMA indicating the amorphous nature of PANi-PMMA blended films. Thus, we can articulate that PANi, which is semi-crystalline in nature as confer earlier, when forms blend with PMMA loses its crystallinity. This amorphization of PANi-PMMA blends may be ascribed to the formation of inter-penetrating network between PANi and PMMA chains in which the local ordering of PANi chains is destructed [27].

The interpenetration of PANi and PMMA is further corroborated through the study of FTIR spectra of PANi-PMMA blended films. The structure of pure PMMA is primarily characterized by the 1736 cm^{-1} band shown in figure 4(a) assigned to free lateral C=O stretching [27].

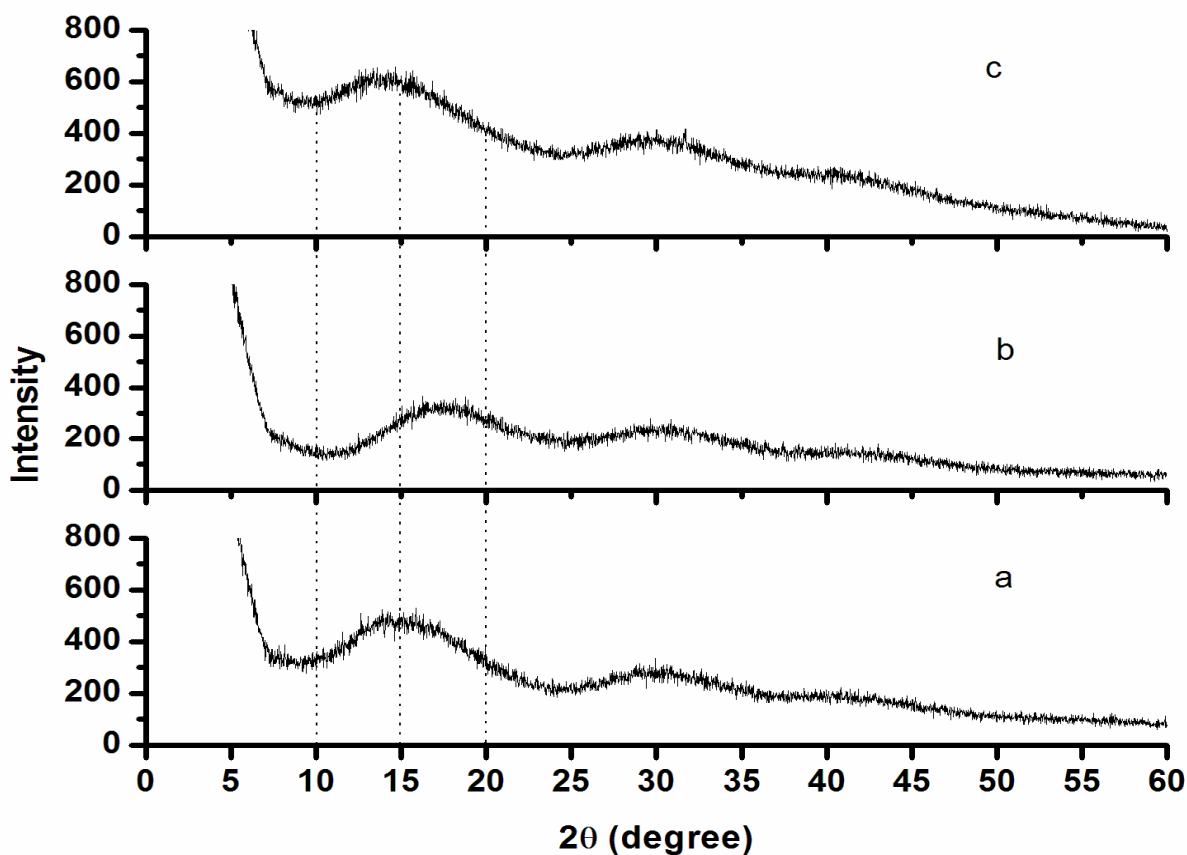


Figure 3. XRD Pattern of (a) pure PMMA (b) PANi+PMMA(1%) (c) PANi+PMMA(6%).

Other peaks in this figure at 2953 cm^{-1} and $990\text{-}627\text{ cm}^{-1}$ correspond to CH_3 symmetric stretching and bending respectively and peaks at $1490\text{-}1437\text{ cm}^{-1}$ are ascribed to O-CH_3 deformation, 1070 cm^{-1} to O-CH_2 stretching vibrations and 1196 cm^{-1} to C-O stretching vibrations [26].

In the blends of PANi with PMMA (figure 4(b) & 4(c)), the band assigned to carbonyl group (C=O) of PMMA at 1736 cm^{-1} (figure 4(a)) split into sharp peaks with slight shift towards the lower ($10\text{-}20\text{ cm}^{-1}$) wavenumber side with increasing concentration of PANi. In addition to this, the signature of quinoid ring (1475 cm^{-1}) of PANi observed in the absorption band of PMMA at $1490\text{-}1437\text{ cm}^{-1}$ which causes the slight shifting of peak towards lower wavenumber side with reduce in intensity as concentration of PANi increases overtaking the corresponding peak of NH bending vibration mode in PANi. These changes can be assigned to formation of hydrogen bonding between these groups because of H donation in NH group. This H bonding allows compatibility between PANi and polymers containing carbonyl group such as PMMA and enhances the formation of an inter-penetrating network of PANi and the matrix chain [10, 24]. Further, with increase in PANi concentration, we observe the compression and splitting of C-O band into multiple sharp peaks with reduced intensity, which shows the signature B-NH-B , B-N=Q (polaron bands) stretching vibrations of PANi in C-O absorption peak of PMMA [28].

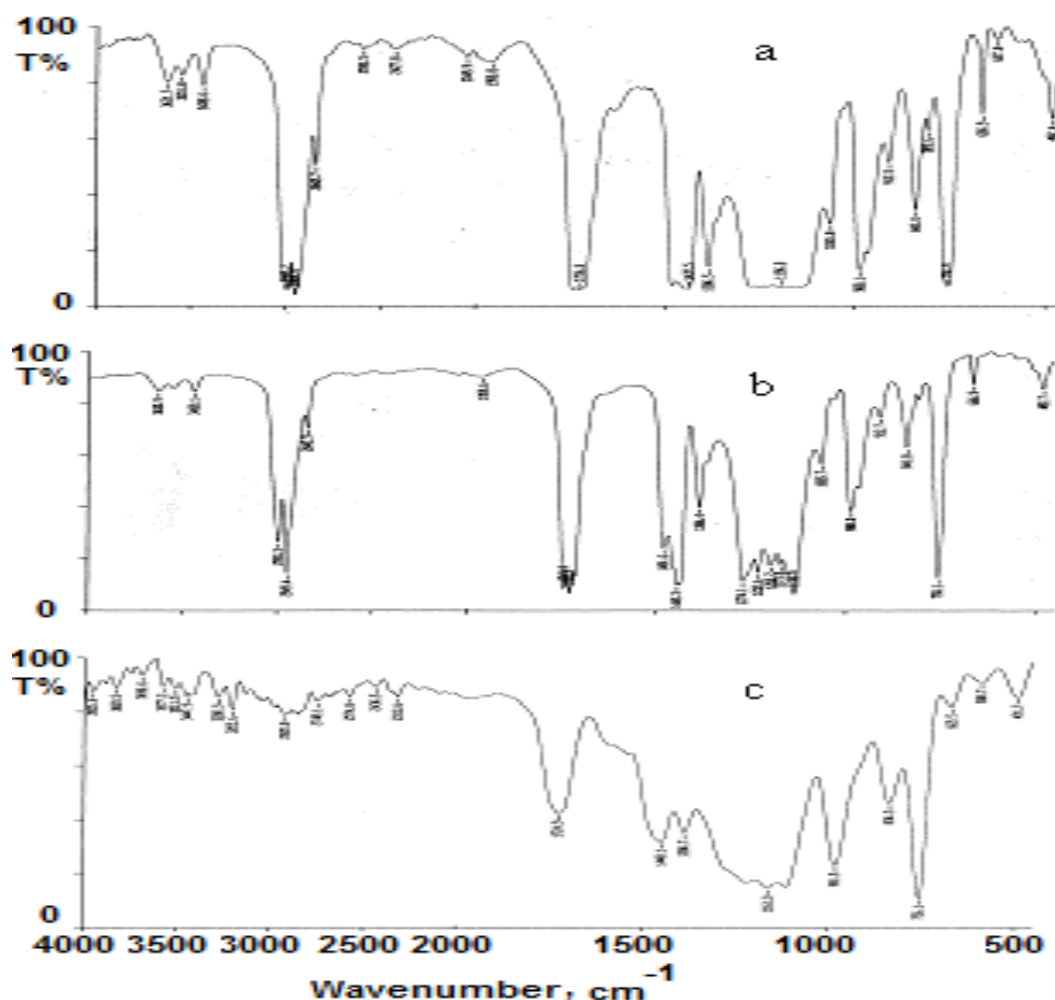


Figure 4. FTIR Spectrum of (a) Pure PMMA (b) PANi+PMMA(1%) (c) PANi+PMMA(6%).

Such studies are quite imperative to correlate the improvement in optical and electrical properties to the structural behaviour of conventional polymer on blending with varying concentration of PANi.

CONCLUSION

The PANi doped with DBSA, synthesized through chemical oxidative polymerization, has been found to be semi-crystalline in structure. After doping PANi (ES) in PMMA matrix, an inter-penetration network of PANi with the chain of the PMMA was formed as confirmed through XRD and FTIR spectroscopy.

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