

## EFFECT OF POLYVINYL ALCOHOL ON STRUCTURAL AND DIELECTRICAL PROPERTIES OF POLYANILINE

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In this paper, we have synthesized polyaniline (PAni) composite with poly vinyl alcohol (PVA) having various ratio of PVA by chemical polymerization method. For structural investigation, the prepared composites have been characterized by using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and thermo gravimetric (TG) analysis. The XRD pattern reflects the amorphous nature of all composites. Strong structural bands formation has been observed in FTIR spectra and also the inter-linking of PAni and PVA in these composites. The SEM pictures exhibit that composites are having grain size ranging from 40-90 nm. TG analysis shows that (PAni-PVA) composites are thermally stable up to 180 °C. Moreover, dielectric properties of composites have been measured by LCR meter in the frequency range of 1Hz to 3GHz. The dielectric constant ( $\epsilon$ ) has an inverse relation with the frequency. Interestingly, the ac conductivity displays plateau like behavior in low frequency region and shows dielectric dispersion in high frequency range for all composites.

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*Keywords:* Polyaniline (PAni), Poly vinyl alcohol (PVA), Polymerization, Composite, Dielectric constant ( $\epsilon$ )

### 1. Introduction

In modern days, the entire world moves from non-renewable energy resources (fossil fuels) to renewable energy resources like solar energy, wind energy etc. In the past, solar energy conversion devices are made from inorganic semiconductors like silicon and germanium, but this trend was totally changed after the invention of organic semiconductors. The organic semiconductors are classified into two major classes. One is monomer and the other is polymer. Monomers are low weight molecular compounds on the other hand polymers are made from long conjugated chains. Polymers are produced from monomers through polymerization. By chemical reactions, monomers form together two types of chains. One is linear chain and the other is three-dimensional chain. Polymers have three-dimensional chains; do not show electrical conductivity, these are insulators. Conjugated polymers are organic compounds show electrical conductivity; their conductivity can be controlled by doping process. During last two decades, these conducting polymers have received much attention due to its poly-aromatic backbone and ease of their availability. Polyaniline, polythiophene, polypyrrole etc. are renowned conducting polymers [1]. Conjugated polymers and its composites have numerous applications in basic sciences as well as in electronics. Heterogeneous substances consisting of two or more materials called composite. A composite does not lose the properties of individual existing material. It enhances the characteristics of each material. That is why; composite polymers are used rather than homogeneous polymers due to their splendid properties in electronic devices [2]. Polyaniline is one of the most optimistic conducting polymers due to its glamorous properties, high thermal stability, low resistivity [3], environmental stability and can be synthesized easily by various

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techniques [4, 5]. Poly vinyl alcohol (PVA) being a biodegradable synthetic polymer, acquires unique attention because of its high transparency, very good flexibility, anti-electrostatic properties, chemical resistance, capability of film forming and broad commercial availability. Earlier workers reported characterization and synthesis of polyaniline with polyvinyl alcohol composites [6, 7]. These properties of PAni-PVA composites enhance their industrial uses and utilizes in preparing un-harmful materials for better environment [8, 9]. Poly acetylene, polyaniline and poly vinyl alcohol are polymers that have gained much attention by many researchers, due to their interesting applications like optical devices [10] and rechargeable batteries [11]. In present work, aniline monomer has been polymerized. In this polymerization process ammonium per sulfate (oxidizing agent) and hydrochloric acid (HCl) as an inorganic acidic medium has been used to prepare (PAni- PVA) composites. In this regard the structural properties of this polymer and its composites have been pointed out by X-Ray diffraction (XRD) to observe any possible structural variation. Thermal analysis of (PAni-PVA) composites was determined through thermogravimetric analysis (TGA). Surface morphology of these composites were investigated by scanning electron microscopy (SEM). Some peaks of these composites have been seen by FTIR which also reflects some structural distortion. Dielectric properties were investigated through LCR meter and the obtained results were compared with pure PAni and (PAni-PVA) composites and their co-relation has been discussed in the light of the possible structure distortion.

## 2. Experiment

To prepare the composites of polyaniline with poly vinyl alcohol, using different ratios of (PVA) as 0.5, 1.0 and 1.5 grams were taken to obtain 3 different samples. Initially, a scaled beaker was taken and pours 6 ml aniline monomer in it then adds 60 ml deionized water and 6 ml hydrochloric acid (HCl). Place the beaker on a magnetic stirrer for half an hour to stir it vigorously, pour 0.5, 1.0 and 1.5 grams (PVA) in a beaker after weighing by electronic weight to obtain different samples, respectively in the presence of 6.125 gram oxidizing agent ammonium per sulfate (APS) under continuous stirring at room temperature. On appearing deep greenish blue color, the reaction was stopped. Kept the composites at very low temperature 0 °C to 4 °C for 24 hours so that polymerization occurs. To remove the acid and reagents from the composites, wash it with deionized water many times until the residual material becomes colorless, and then dry the composites on sunlight for four hours. For simplicity, we will further define the composite as (PAni-PVA) with 0.5% (P05), PVA with 1.0% (P1) and PVA 1.5% (P15).

Marble mortar and pestle was used for grinding the samples, so that an unwanted material cannot mix with pure polyaniline and its composite samples during grinding process. Moreover, Surface morphology was investigated by SEM using Hitachi (Japan SU 3500). In this research work, TG analysis was used to investigate PAni/PVA composite in powder form, range of temp 40°C to 500°C at the rate of 10°C/min by the instrument Netzschsta 409, switch the gas to nitrogen at 20.0 ml/min. Structure of composites are investigated by X pert PRO diffract meter, which is operated at (40.10<sup>3</sup> V) potential and (30.10<sup>-3</sup> A) current, Cu-K<sub>α</sub> radiation source having wavelength 1.5Å was used. Diffraction pattern of samples have been recoded, ranging from 2 degrees to 80 degrees with step size 0.02 degree. Perkin Elmer Spectrum One (FT-IR) (p/n Q0315) was used to measure the infrared response of composites. Bands formations show the poly crystalline and amorphous nature of the prepared samples. Impedance analyzer IM 7583 frequency range 1Hz to 3GHz with 0.5ms test speed has been used in present research work to examine the precise measurement dielectric material.

## 3. Results and discussion

Fig. 1 shows the XRD pattern of the composites. Diffractogram images show amorphous nature of composites. P05 composite exhibits a broad diffraction peak at  $2\theta$  value of 25° corresponding to (200) plane. For P1, sharp peak appearing for  $2\theta$  value of around 25° are ascribed to the periodicity perpendicular to the polyaniline chain. By increasing the concentration of PVA in composite decreased intensity in peaks, it may bring disorder in the chains packing of polyaniline during chemical polymerization of aniline with in the PVA matrix [12].

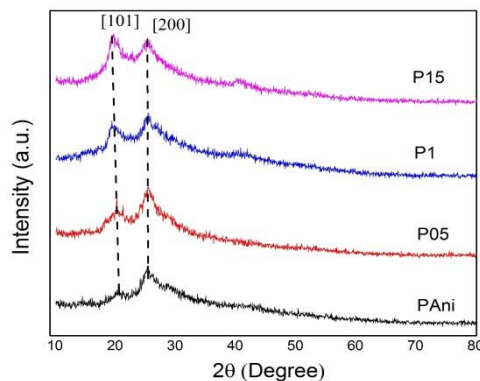


Fig. 1. XRD Pattern of (PAni-PVA) Composites

Grain size of (PAni-PVA) composite has been observed by SEM analysis and its ranging from 40 nm to 90 nm as shown in Fig. 2. An interesting phenomenon occurs in Fig. 2(c), while increasing the ratio of PVA, rod shape, spherical nanoparticles start appearing. This clearly shows that particle size agglomeration decreases with increasing PVA content. Increase of PVA facilitates regular shape and alignment of the nanoparticles as the interaction with increasing number of PVA molecules (capping) hinders aggregate formation and inhomogeneity. This reflects the increase of order with the increase of PVA content [13]. In Fig. 2(a), grain size of nano particle of PAni is about 90 nm. The size of grain in Fig. 2 (b) composite sample of P05 is about 70 nm. Similarly, the size of grain decreases with the increase in PVA concentration. In Fig. 2(c) shape of grains like sphere in P1 composite having sizes 40 nm. Furthermore increase in the concentration of PVA grain size increases, about 45 nm, which can be seen in Fig. 2(d). This shows that increase the concentration of PVA beyond the certain limit produce disorder in the polyaniline chain and grain cluster is seen also.

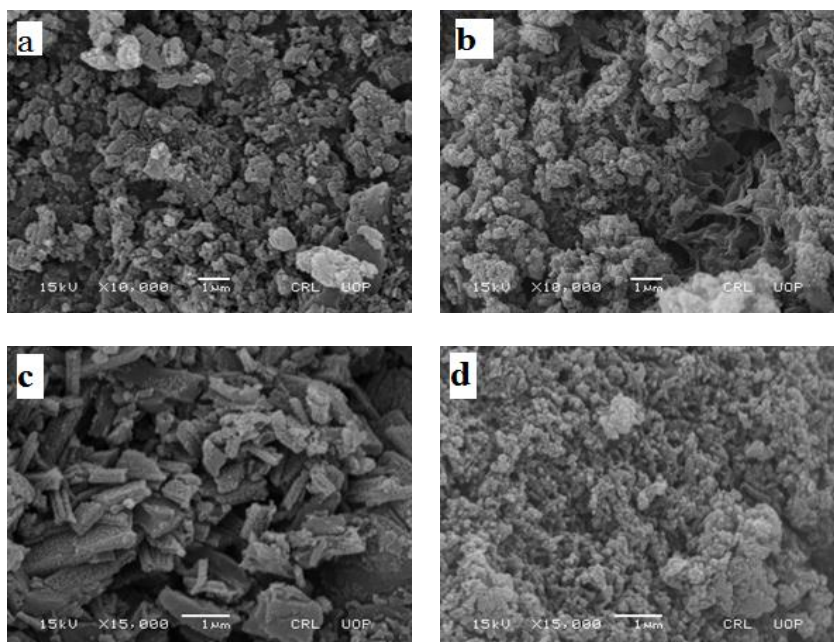


Fig. 2. SEM images of (PAni-PVA) Composites (a) PAni, (b) P05, (c) P1, (d) P15.

Fig. 3(a) shows IR spectrum of PAni which exhibits some characteristics bands as observed at 1574, 1483, 1302, 1132, 825, 587, 519  $\text{cm}^{-1}$ . Fig. 3(b) indicates IR spectrum of P05 and the characteristics bands are observed at 1609, 1495, 1325, 1086, 836, 531  $\text{cm}^{-1}$ . In Fig.3(c),

characteristic bands of P1 are detected at 1574, 1495, 1302, 1132, 803, 598, 507  $\text{cm}^{-1}$ . Fig. 3(d) shows the IR characteristic bands of P15 at 1597, 1472, 1325, 1132, 621, 530  $\text{cm}^{-1}$  [14, 15]. In the spectrum of PANi, the peaks at 1574  $\text{cm}^{-1}$  corresponds to C=N stretching vibration of Quinone ring and 1483  $\text{cm}^{-1}$  is attributed with C=C stretching vibration of Quinone ring and benzene ring structure, respectively. Band observed at 1302  $\text{cm}^{-1}$  correspond to C-N stretching vibration due to polaron structure and the band at 1132  $\text{cm}^{-1}$  corresponds to C-H plane bending vibration. Synthesis of PANi was confirmed by benzoid and quinonoid ring stretching. The extra bands observed in Fig. 3(b) of P05 composite, which are not present in PANi. These extra bands indicate the cross-linking of (PANi-PVA) composite. The absorption band observed in Fig. 3(c) at 1495  $\text{cm}^{-1}$  (C-O stretch) and in Fig. 3(d) at 1132  $\text{cm}^{-1}$  (Ph-CH bends) [16], in this range absorption is much stronger, so P15 indicates stronger cross-linking of PANi with PVA composites than P05 and P1. In the patterns of (PANi-PVA) composites some bands are observed at 1086, 973, 836, 803, 621, 598, 531, 530 and 507  $\text{cm}^{-1}$ . These bands indicate cross-linking of PANi with PVA composites. In FTIR spectrum of (PANi-PVA) composites, the bands lies below 1000  $\text{cm}^{-1}$  are the characteristics of mono substituted benzene ring [17].

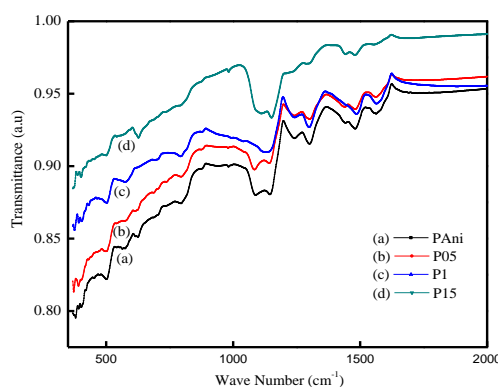


Fig. 3. FTIR Spectroscopic curves of (PANi-PVA) composites.

In Fig. 4 thermo gravimetric curve of PANi shows first step weight loss about 14% up to 96 °C. When temperature increases gradually deionized water releases in the form of moisture and the second stage weight loss 28% up to 187 °C is due to hydrochloric acid (HCl) which is chemically combined in the composition of pure polyaniline. TG curve shows the third stage of remarkable weight loss occur from 200 °C up to 500 °C is due to dehydration as well as degradation of (PANi) itself [18].

In Fig. 4 P05 composite curve shows the same pattern with slight difference as pure polyaniline. When PVA concentration increase TG curve indicates three steps of weight loss in P1, first stage at 112 °C weight loss 16% , second stage at 180 °C with composite sample weight loss about 32% and third stage of weight loss occurs in the range of about 180 °C up to 500 °C composite becomes carbonized. However, P15 composite elaborates different behavior of weight loss at various temperatures as compared to others composites ratio. From 150 °C to 250 °C release of doped material about 35% weight loss, secondly release of bound water and moisture in the range of 250 °C to 400 °C at weight loss 65%, third stage shows decomposition of composite from 400 °C to 500 °C with release of gases like carbon dioxide ( $\text{CO}_2$ ) and leaving the residue 30%. Investigation of all (PANi-PVA) composite graphs and thermal study indicates that (PANi-PVA) composites are thermally stable up to 180 °C. From TGA study, conjugated polymer composite samples of (PANi-PVA) can be easily utilized for fabrication of electronic devices [19, 20].

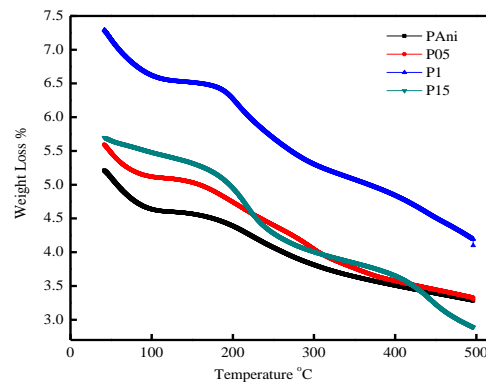


Fig. 4. Thermo Gravimetric (TG) Curves of (PAni-PVA) composites.

The Real part of permittivity ( $\epsilon'$ ), which impersonates the storage capability of electricity of an insulator or dielectric. It is frequency dependent property of composite materials. Dielectric constant ( $\epsilon$ ) versus log of frequency graph shows in Fig. 5, by increasing the value of frequency the value of  $\epsilon$  of the composite material decreases. Perhaps ac electric field does not followed by high frequency dipoles that indicate dispersion behavior of dipole. At low frequency range the increasing value of  $\epsilon$  indicates the interfacial and ionic polarization. In present research work (PAni-PVA) composites exhibits similar behavior as discussed above.

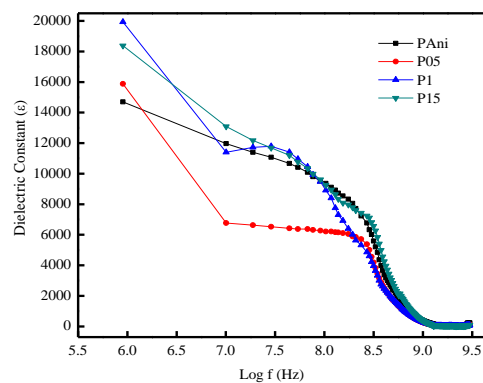


Fig. 5. Dielectric Constant versus Log f (Hz) of (PAni-PVA) composites.

Imaginary part of relative permittivity of dielectric ( $\epsilon''$ ) and is called dielectric loss ( $\tan \delta$ ) or energy loss is shown in Fig. 6. It is frequency dependent property of composite materials. The  $\tan \delta$  for (PAni-PVA) composites show the same behavior in all concentration of PVA. It can be seen from Fig.6, dielectric loss has high value at low frequencies and low value at higher frequencies. Further it is observed that dielectric loss shows same trend of decreasing nature with the increase in applied frequency as found in real dielectric constant. The value of dielectric loss is always lesser than the real dielectric constant [21], as we also observed.

According to linear response theory ( $\epsilon'$ ) and ( $\epsilon''$ ) both the quantities are not independent of each other and are related by the Kramers- Konig relations:

$$\epsilon'(\omega) = \epsilon'_{\infty} + \frac{1}{\pi} \oint \frac{\epsilon''(\omega')}{\omega' - \omega} d\omega'$$

$$\epsilon''(\omega) = \frac{1}{\pi} \oint \frac{\epsilon'(\omega')}{\omega' - \omega} d\omega'$$

Here  $\varepsilon'_{\infty}$  denotes the permittivity at high (optical) frequency.

Theory of dielectric relaxation is a special form of linear response theory: relates to relative permittivity  $\varepsilon^*(\omega)$  to the time correlation function  $\Phi(t)$  is defined as

$$\frac{\varepsilon^*(\omega) - \varepsilon'_{\infty}}{\varepsilon_{stat} - \varepsilon'_{\infty}} = \frac{1}{\pi(\varepsilon_{stat} - \varepsilon'_{\infty})} \int_{-\infty}^{\infty} \frac{-d\varepsilon(t)}{dt} e^{-i\omega t} dt$$

where  $\varepsilon_{stat}$  is the permittivity for  $\omega \rightarrow 0$  [22].

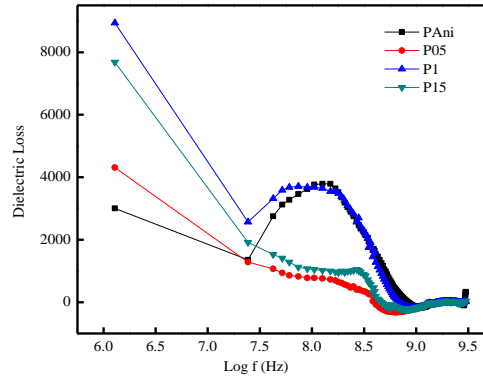


Fig. 6. Dielectric Loss versus Log f (Hz) of (PAni-PVA) composites.

Table 1. XRD, FTIR, grain size and ac conductivity for PAni and PAni-PVA composites.

Sample Name	XRD Peaks (2 $\theta$ )	FTIR Peaks (cm <sup>-1</sup> )	Grain Size (nm)	ac Conductivity S/cm log f = 9.3 Hz
Pure Polyaniline	14°, 21°, 25°	1574, 1302, 1132, 825, 519	90	45
PAni-PVA (1:0.5 gm.)	20°, 25°	1609, 1325, 1086, 836, 531	70	16
PAni-PVA (1:1 gm.)	19.5°, 25.27°	1574, 1302, 1132, 803, 507	40	09
PAni-PVA (1:1.5 gm.)	19.3°, 25.32°	1597, 1325, 1132, 621, 530	45	10

The electrical conduction in (PAni-PVA) composites takes place by polaron hopping mechanism. It simply means that the electron movement with its corresponding elastic distortion field causes an electrical conduction. Conductivity is a reciprocal of resistivity, which indicates charge carrier mechanism, so that the prepared sample is valid for manufacturing electronic devices or not. Conductivity of prepared sample carried out by the following formula after characterizing the sample result.

$$\sigma_{ac} = 2\pi f \varepsilon_0 \varepsilon' \tan \delta$$

Here f is the frequency at which sample was characterized, the range of frequency was 10<sup>6</sup> Hz to 10<sup>9</sup> Hz,  $\varepsilon_0 = 8.85 \times 10^{-12}$  F/m.

Fig. 7 shows variation of ac conductivity with frequency for doped and undoped samples of present material. Interestingly PAni has high ac conductivity as compared to other samples. P1 composite shows the value of conductivity about 9 S/cm at log f = 9.3 Hz, best result is obtained by this ratio. This fact indicates optimization of composite formation at this particular ratio. Results presented in Table 1 indicate that by increasing the concentration of PVA, ac conductivity decreases. Defects are produced in the present system by increasing the concentration of PVA doping beyond a certain limit which increase the resistivity of the sample. Present research work indicates that PVA is an insulator material and it also enhances the crystallinity of the composite.

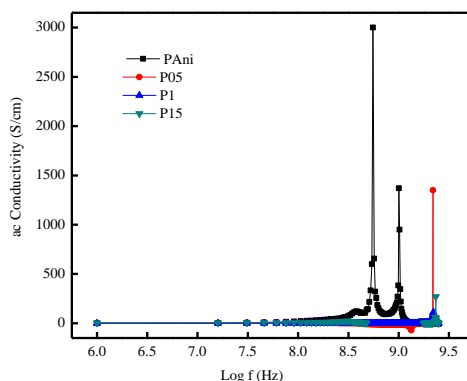


Fig. 7. ac Conductivity versus Logf (Hz) of (PAni-PVA) composites.

#### 4. Conclusions

Polyaniline and poly vinyl alcohol composite samples have been prepared by chemical polymerization method. XRD Pattern of the composite indicates the presence of PVA because of increase in the crystallinity. Inter-linking of PAni-PVA is seen by FTIR spectroscopy, band formation confirms that composite is well formed. TG curve indicates the stability of composite up to 180 °C. SEM images show that the grain sizes decreases with the increase of PVA concentration. The grain size decreases from 70 nm to 40 nm because of the dipoles free movement of (PAni-PVA) molecular chain. The variation of ac conductivity with frequency shows that the electrical conduction is mainly due to polaron hopping.

It was observed that pure polyaniline has high ac conductivity as compared to other samples. In dielectric constant, the values are high at low frequency due to Max Well Wagner interfacial polarization. In case of dielectric loss, the loss peak appears at the frequency of  $10^8$  Hz. Hence the present result indicates, conductivity find drops due to the presence of impurities/defects. It may be due to insulating nature of the PVA. ac conductivity decreases with the increase of PVA. The stability of the composite increases with the increasing amount of PVA while its conductivity decreases. In electronic materials it can be used as a humidity sensing, and for switching purpose.

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