



Spectroscopic investigations and electrical properties of PVA/PVP blend filled with different concentrations of nickel chloride

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ABSTRACT

Films of PVA/PVP blend (50/50) filled with different concentrations of NiCl₂ were prepared by casting method. The prepared films were investigated by different techniques. XRD scans demonstrated that the peak intensity at $2\theta \approx 20^\circ$ decreased and the band width increased with increase in the concentrations of NiCl₂ content, which implied decrease in the degree of crystallization and hence causes increase in the amorphous region. UV–vis analysis revealed that the values of the optical band gap are affected with increase in NiCl₂ content. This indicates the formation of charge transfer complexes between the polymer blend and the filler. The rise of conductivity is significant with increased concentration of NiCl₂ filler; this reveals an increase in degree of amorphosity. AC conductivity (σ_{ac}) behavior of all the prepared films was investigated over the frequency range 42 Hz–5 MHz and under different isothermal stabilization in the temperature range 313–393 K. It suggests that the hopping mechanism might be playing an important role in the conduction process in high frequency region. The dielectric behavior was analyzed using dielectric permittivity (ϵ' , ϵ'') dielectric loss tangent ($\tan \delta$) and electric modulus (M''). The decrease in dielectric permittivity was observed with increase in the concentration of NiCl₂ filler. This suggests the role of NiCl₂ as filler to improve the electrical conductivity of PVA/PVP blend.

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1. Introduction

Polymer blend is one of the most important contemporary ways for the development of new polymeric materials and it is a useful technique for designing materials with a wide variety of properties [1].

Polyvinylpyrrolidone (PVP) deserves a special attention among the conjugated polymers because of its good environmental stability, easy processability, moderate electrical conductivity, and rich physics in charge transport mechanism. The local modification of the chemical structure induces drastic changes in electronic properties [2].

Polyvinylalcohol (PVA) has different internal structures, which may be considered as amorphous or semicrystalline. The semicrystalline structure of PVA showed an important feature rather than of amorphous one. This is because semicrystalline PVA leads to the formation of both crystalline and amorphous regions.

Although some works have been reported on the charge carrier transport and optical properties of doped polymers, very little work is available on PVA/PVP films. PVA/PVP is a potential material having good charge storage capacity and dopant-dependent electrical and optical properties.

Polymeric materials have special interest because, in combination with suitable metal salts, they give complexes that are useful

for the development of advanced high energy electrochemical devices, electrochemical display devices, and photo electrochemical cells with ease of fabrication into thin films of desirable sizes.

NiCl₂ is used in polymers for a variety of reasons: cost reduction, improved processing, density control, optical effect, thermal conductivity, control of thermal expansion, electrical properties, magnetic properties, flame retardation, hardness, etc. [R.N. Rothon, Particulate Fillers for Polymers, Summery, 1st Ed., Chen Tec., UK, 2002].

The composite materials consisting of conducting medium in the insulating polymer matrix provide satisfactory mechanical as well as electrical properties. Both PVP and PVA are water-soluble and miscible in all proportions. The structural, optical, and electrical properties of blends can be suitably modified by the addition of the fillers depending on their reactivity with the host matrix [3]. In this work, the author spots light on the structural and electrical properties of PVA/PVP (50/50) blend and their complexes' films filled with different concentrations of NiCl₂ to use the final product in some technical application.

2. Experimental work

Polyvinylalcohol (PVA) from Merck, Germany, has molecular weight 14,000 and polyvinylpyrrolidone (PVP) from Aldrich Chemical Co. Ltd., England, were used as received. Equal quantities of PVA and

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PVP (50/50) by weight to weight (wt%) was added to doubly distilled water with stirring the solution at 70 °C to complete dissolution. Required quantity (0, 1, 2.5, 5, 10, and 20 wt%) of NiCl₂ was also dissolved in doubly distilled water and added to the polymeric solution with continuous stirring. Then we have the prepared samples for 24 h to eliminate bubbles. The solution was poured onto cleaned petri dishes and dried in oven at 70 °C for 4 days to ensure removal of the solvent traces. After drying, the films were peeled from petri dishes and kept in vacuum desiccators until use. The thickness of the obtained films was in the range 7–90 μm for the IR measurement and 100–150 μm for other measurements.

X-ray diffraction scans were obtained using DIANO corporation US equipped Cu-K radiation ($\lambda = 1.540 \text{ \AA}$), the tube was operated at 30 kV, Bragg's angle (θ) of 550. Ultraviolet and visible (UV–vis) absorption spectra were measured in the wavelength region of 200–500 nm using a spectrophotometer (V-570 UV/VIS/NIR, JASCO, Japan). FT-IR absorption spectra were carried out using the single beam Fourier transform-infrared spectrometer (FT-IR-430, JASCO, Japan). FT-IR spectra of the samples were obtained in the spectral range of 4000–500 cm^{-1} . AC electrical properties have been studied using a programmable automatic Model Hioki 3531Z Hitester, analyzing their dependence on temperature and frequency.

Resistance (R), capacitance (C), and dielectric loss tangent ($\tan \delta$) have been measured in the frequency range 42 Hz–5 MHz and in the temperature range 313–393 K. Samples in the form of rectangular plates and coated with silver paste were used in AC measurements for good contact. All measurements were carried out in a specially designed cell.

The real part of AC conductivity $\sigma_{ac}(\omega)$ is calculated from

$$\sigma_{ac}(\omega) = \frac{L}{aR} \quad (1)$$

where L is the thickness of the sample (m), a is the cross-sectional area (m^2), and R is the resistance (Ω).

The real part of dielectric constant (ϵ') is calculated using

$$C = \epsilon' \frac{a}{L} \quad (2)$$

where C is the capacitance of the sample (F), L is the thickness of sample (m), and ϵ_0 is the permittivity of free space $= 8.854 \times 10^{-12} \text{ F m}^{-1}$. The error in these measurements does not exceed $\pm 0.2\%$.

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 1 represents the X-ray diffraction scans of pure PVA/PVP (50/50) blend and PVA/PVP blend filled with different concentrations of NiCl₂ filler. The figure shows the main peak centered at about $2\theta \approx 20^\circ$, revealing the semicrystalline nature of the blend, because it contains crystalline and amorphous structure. This peak corresponds to (1 1 0), which is consistent with the values in the standard card (JCPDS file no. 41-1049). On the other hand two typical peaks at $2\theta \approx 10.3^\circ$ and 19.4° were observed for pure PVP, as reported in Refs. [4,5]. For the filled samples, it can be seen that the peak intensity at $2\theta \approx 20^\circ$ decreased and the width of the peak increased with increase in the concentrations of NiCl₂; this is because the interaction between the blend and the filler leads to decrease in intermolecular interaction between the polymers blend chains, which implied decrease in the degree of crystallization and hence increase in the amorphous region [6]. This tends to increase conductivity and will be confirmed for DC and AC conductivity. This behavior demonstrates the complexation between the filler and the polymers blend, which takes place in the polymeric network.

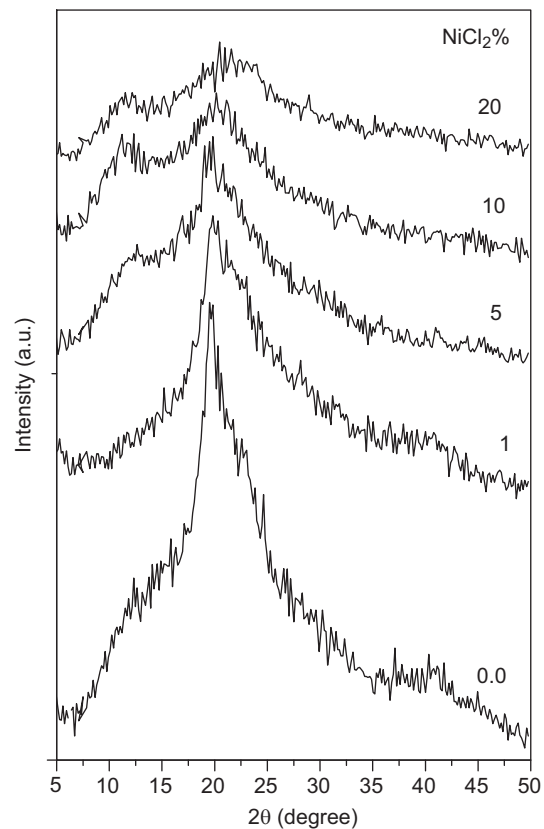


Fig. 1. X-ray diffraction scans of pure PVA/PVP blend and PVA/PVP blend filled with different concentrations of NiCl₂.

3.2. Ultraviolet and visible analysis

UV–vis spectra were observed as shown in Fig. 2 of the present system. With increase in the NiCl₂ content, these shifts indicate the complexation between the NiCl₂ and the polymer blend, which is due to the optical energy gap variation [7].

The figure shows absorption bands in the range 207–230 nm and are assigned to localized $n \rightarrow \pi^*$ transitions [8]. In other words, the absorption band was observed as a shoulder at about 275 nm may be attributed to $\pi \rightarrow \pi^*$, which comes from unsaturated bonds (C=O and/or C=C), mainly C=O [9].

3.2.1. Determination of optical energy band gap (E_g)

The study of optical absorption gives information about the band structure of the polymer. Davis and Shalliday [10] reported that near the fundamental band edge, indirect transitions occur and can be observed by plotting $(\alpha h\nu)^{1/2}$ as a function of photon energy ($h\nu$). The analysis of Thutupalli and Tomlin [11] is based on the following relation:

$$(\alpha h\nu)^{1/2} = B(h\nu - E_g) \quad (3)$$

where $h\nu$ is the photon energy, E_g is the band energy gap, B is constant, and α is the absorption coefficient. The absorption coefficient (α) can be determined as a function of frequency using the formula [12]:

$$\alpha = 2.303 \frac{A}{d} \quad (4)$$

where A is the absorbance and d is the thickness of the sample under investigation. By plotting $(\alpha h\nu)^{1/2}$ versus photon energy (h), each linear portion indicates a band energy gap (E_g). It is well noticed that the curves are characterized by the presence of an exponentially decay tail at low energy [12].

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