

Investigation of Electrical and Optical Properties of Polyvinyl Acetate Doped with Some Polymers

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ABSTRACT: Polyglycerol (PG) and polytriethanolamine (PTEA) have been prepared. The electrical resistivity (ρ) and the optical absorption of polyvinylacetate (PVAc) doped with polyglycerol (PG), polyaniline (PA), and polytriethanolamine (PTEA) have been studied. It was found that the conduction was mainly ionic in the temperature range from 20 to 120°C. The resistivity decreased with the increase of the dopant concentration. The optical absorption spectra were

determined in the wavelength range 400–2500 nm. The analysis of the absorption spectra showed that the intensity of the bands is remarkably affected by the dopant concentration. The optical energy gap of pure PVAc and the samples containing different dopants were estimated. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1558–1563, 2002

Key words: optics; X-ray; activation energy

INTRODUCTION

Traditionally organic substances, including organic polymers, are insulators.^{1,2} During the past 15 years, however, a new class of organic polymers has been devised with remarkable ability to conduct electrical current. The conductivity of intrinsically insulating polymers can be enhanced by about 10–15 orders of magnitude into the metallic or semiconducting range by doping of electron donors or acceptors. Complexes between molecules acting as electron donors and molecules acting as electron acceptors have been studied extensively.³ Some kinds of polymers that can give semiconducting properties are polyvinylalcohol and polyvinylacetate. Examples for polyvinyl alcohols that are semiconductors are those doped with CoCl_2 , NiCl_2 , and other transitional metal halides.^{4–6} Research work on the electrical and optical properties of polyvinyl acetate is rare.⁷ However, as it is well known, polyvinylacetate can be easily hydrolyzed to polyvinylalcohol.

In this work the electrical conductivity and the optical absorption of polyvinylacetate was measured. Its electrical conductivity was found to increase when it was doped with polyaniline (AP), polyglycerol (PG), or with polytriethanolamine (PTEA), which were prepared at the laboratory.

EXPERIMENTAL

Polyvinylacetate (PVAc)

PVAc produced by K.C.K. emulsion polymers Ltd., has the following specification, nonvolatile content, 49–51% viscosity at 25°C, 40,000–110,000 cps, specific gravity at 0°C, 1.0 g cm.

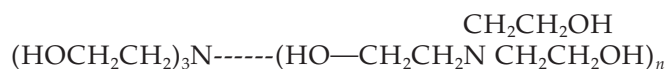
Polyaniline, was used with average molecular weight 60,000, highly soluble in organic solvents, and has good thermal stability.

Preparation of PTEA and PG

Polytriethanolamine (PTEA)

PTEA was prepared by reacting triethanolamine 1 mol with 0.04 mol sodium hydroxide as a catalyst in a three-neck round-bottomed flask equipped with a refluxing condenser, a stirrer, and a thermometer.⁸ The catalyst was added while stirring, then the triethanolamine was heated at 140–160°C until the viscosity of the formed polymer become 12.6 cp.

The reaction can be illustrated as shown below



where $n = 3.9$.

PTEA has yellow color, the density at 20°C is 1.1872, the viscosity is 16.6, the average molecular weight is 578.5, and the PH is 10.73.

Polyglycerol (PG)

PG was synthesized⁹ by treating 100 mL of glycerol with 2.2 g of sodium hydroxide as a dehydrating

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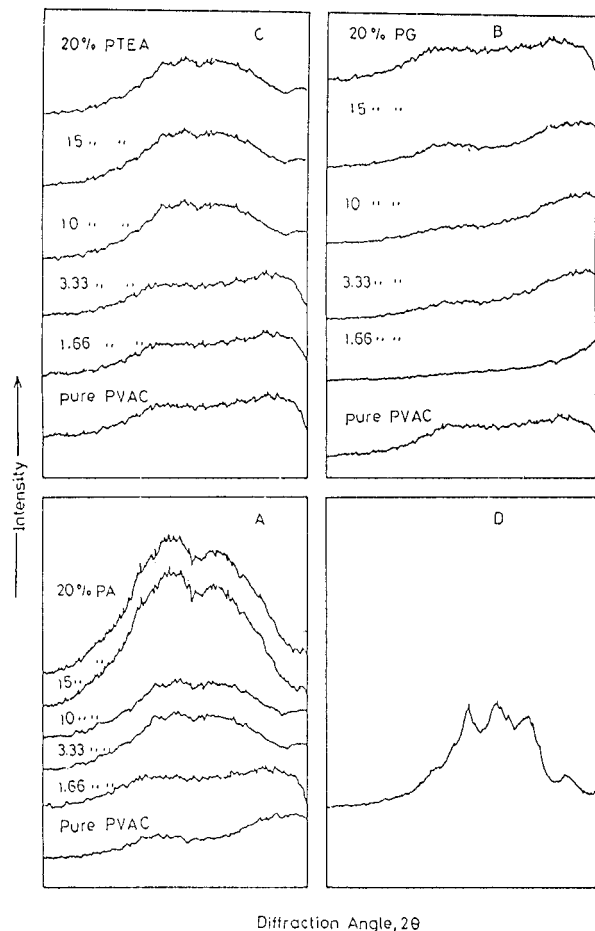
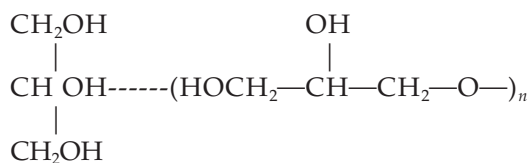


Figure 1 XRD Patterns for PVAc doped with PA, PG, and PTEA at different concentrations and (D) for PA powder.

agent. The reaction mixture was refluxed slowly for 30 min at 260°C and then allowed to cool. The reaction can be illustrated as follows:



PG has yellow color, and its molecular weight was 340. The concentration of PVAc that was used as the matrix was 30 g. The dopants had the following percentages: 1.66, 3.33, 5, 10, 15, and 20 wt %.

The structure of the samples was characterised using X-ray diffractometer (Philips PW 1130/00).

The optical absorption measurements were made using spectrophotometer model UV VIS NIR 3101 PC from Shimadzu. Absorbance measurements covered the range 400–2200 nm with an accuracy better than 3% in nearly all of measured spectra.

The resistances of the polymers were obtained directly using a Keithley 6517 A electrometer in the

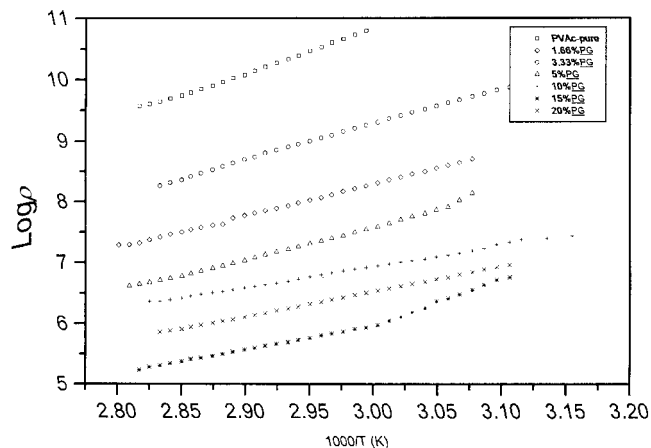


Figure 2 Log ρ vs. $1000/T$ for PVAc with different content of PG.

temperature range between room temperature and 120°C.

RESULTS AND DISCUSSION

Structural

X-ray diffraction patterns of PVAc doped with PA, PG, and PTEA at concentrations 1.66, 3.33, 10, 15, and 20 wt % are shown in Figure 1(A)–(C), respectively. The X-ray diffraction pattern of pure PA powder shows four diffraction peaks [Fig. 1(D)]. The X-ray diffraction pattern exhibits a broad amorphous diffraction hump for pure PVAc and PVAc doped with PG and PTEA as shown in Figure 1(B) and (C). In the case of PVAc doped with PA, only two diffraction peaks are observed. Disappearance of the other two peaks of PA shows that strong interaction complexation between PVAc and PA took place.¹⁰

Electrical resistivity

The electric resistivity (ρ) of PVAc was found to be:

$$3.72 \times 10^9 \Omega \text{ cm at } 70^\circ\text{C}$$

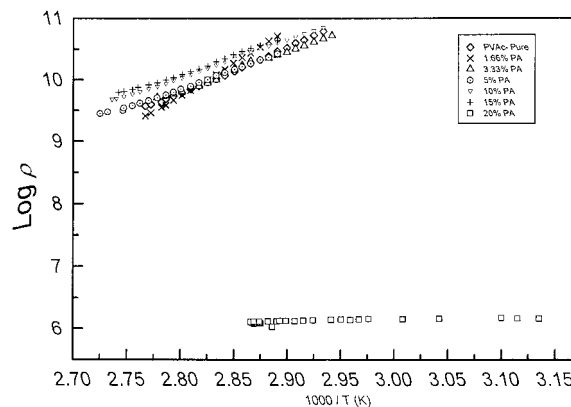


Figure 3 Log ρ vs. $1000/T$ for PVAc doped with different contents of PA.

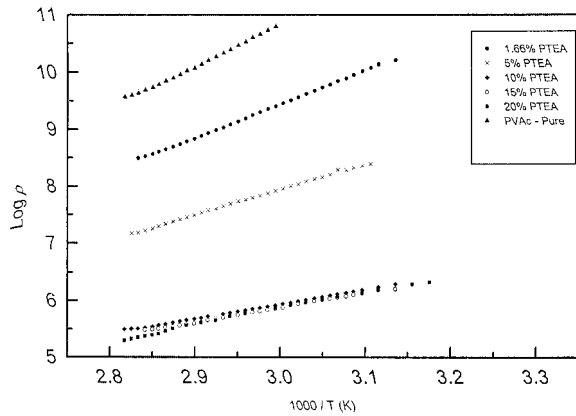


Figure 4 Log ρ vs. $1000/T$ for PVAc doped with different contents of PTEA.

and $4.56 \times 10^{10} \Omega \text{ cm}$ at 55°C

These values are in the range of semiconductors. The relation between $\log \rho$ and $1/T$ is linear as shown in Figure 2, which is a typical relation for semiconductors.

When PVAc was doped with 1.66, 3.33, 5, 10, 15, and 20 wt % of PG, it was found that ρ decreases heavily with increasing the concentraion of PG. When the concentration of PG was 15 wt % ρ was found to be:

$$\rho = 2.376 \times 10^5 \Omega \text{ cm at } 80^\circ\text{C}$$

$$\text{while } \rho = 6.715 \times 10^6 \Omega \text{ cm at } 40^\circ\text{C}$$

PG in this case will act as an electron electron donor. It releases electrons that combine with the polyvinyle acetate (electron acceptor).⁸

When PG was 20 wt % ρ was found to be:

$$\rho = 7.211 \times 10^5 \Omega \text{ cm at } 80^\circ\text{C}$$

$$\text{and } \rho = 9.885 \times 10^6 \Omega \text{ cm at } 40^\circ\text{C}$$

When PVAc was doped with 1.66, 3.33, 5, 10, 15, and 20 wt % of PA the resistivity decreases with the increase of polyaniline content. The greatest decrease in ρ at the concentration of the dopant was 3.33 wt %, while the PVAc doped with 15 and 20 wt % PA increase the resistivity as shown in Figure 3. In this case the highest ionization on polyaniline salt takes place at 3.33 wt % of PA and ρ has the values:

$$\rho = 9.977 \times 10^5 \Omega \text{ cm at } 70^\circ\text{C}$$

$$\text{and } \rho = 1.393 \times 10^6 \Omega \text{ cm at } 45^\circ\text{C}$$

In PA the nitrogen atom will carry a positive charge and acts as an electron donor.⁸ The PVAc is the electron acceptor.

The PTEA is also an electron donor when it was used as a dopant with PVAc. The PTEA concentration was 1.66, 3.33, 5, 10, and 15 wt % (Fig. 4).

The highest decrease in ρ occures when the concentration of the dopant was 15 wt %. In this case:

$$\rho = 3.258 \times 10^5 \Omega \text{ cm at } 75^\circ\text{C}$$

$$\text{and } \rho = 1.538 \times 10^6 \Omega \text{ cm at } 45^\circ\text{C}$$

The relation between $\log \rho$ and $1/T$ is linear, as shown in Figure 4.

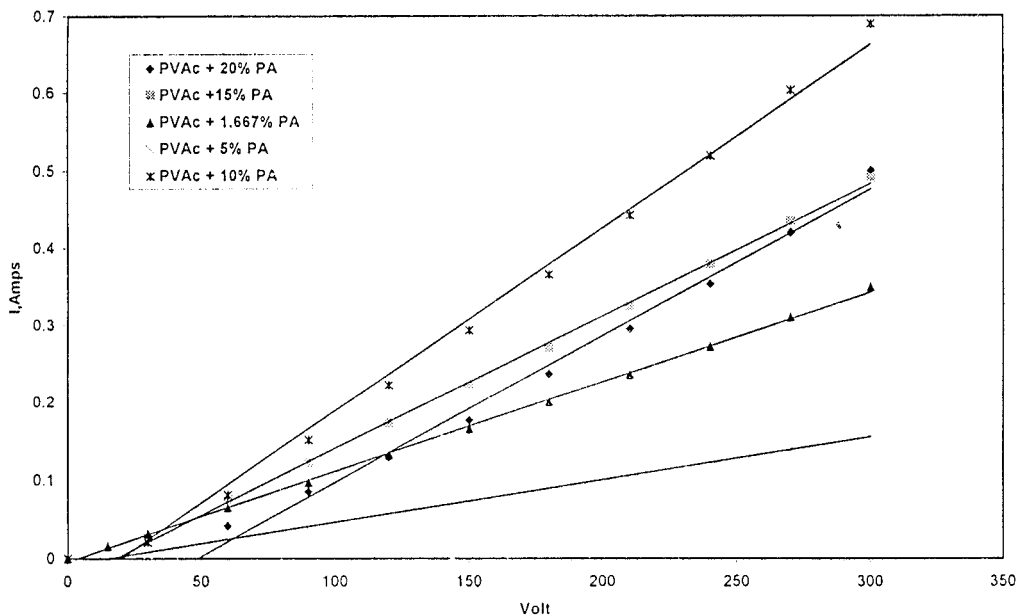


Figure 5 The voltage vs. the current in amperes for PVAc + different concentrations of PA.

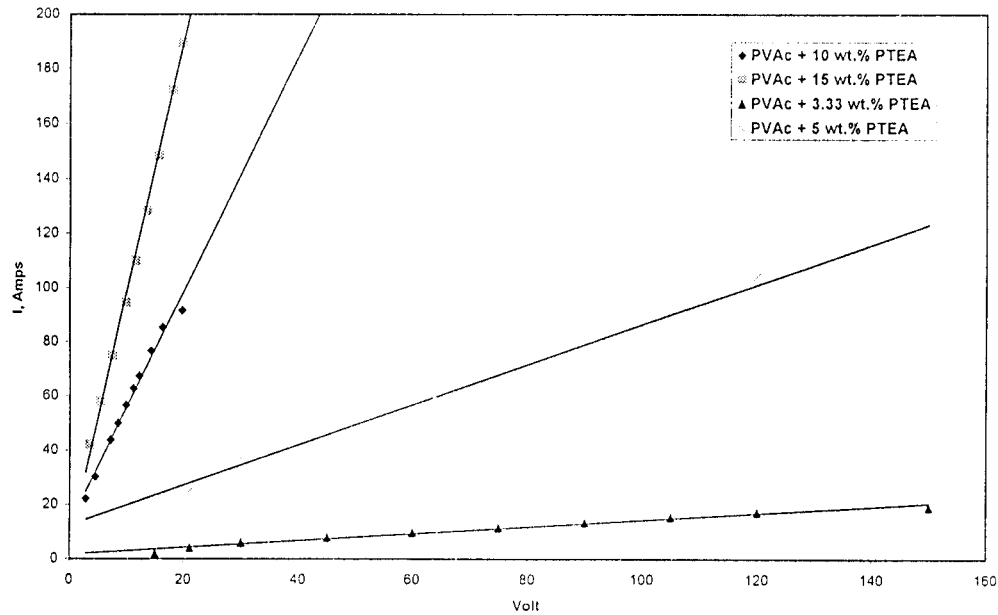


Figure 6 The voltage vs. the current in amperes for PVAc + different concentrations of PTEA.

All the relations between the electric current and the voltage were linear, i.e., it is an Ohmic relation as shown in Figures 5, 6, and 7.

Optical propertie

The optical characterization of semiconducting polymers is usually carried out by either preparing a transparent thin films or making a solution of the polymer transparent to the incident radiation. The optical absorption method is a tool for studying the optically induced transition and for determining the energy gap in crystalline and noncrystalline materials. The absorption spectra in the lower energy part (IR) region are useful to study the atomic vibrations, while the

higher energy parts (UV) region of the spectrum manifest the electronic states in the atoms.

The absorption spectra of all samples are consistent with a strong interband transition characteristic of direct gap semiconductors.

The PVAc doped with PG, PTEA, and PA introduce additional absorption in the energy gap, but appears to leave the principal interband transition intact, suggesting little change in the basic band structure.¹¹

The absorption peaks correspond to various levels in the energy gap for PVAc doped with PG, PA, and PTEA were observed as shown in Figures 8, 9, and 10, respectively.

Figure 8 presents the results of the measurements of the optical absorption in PVAc doped with 1.66, 5, 10,

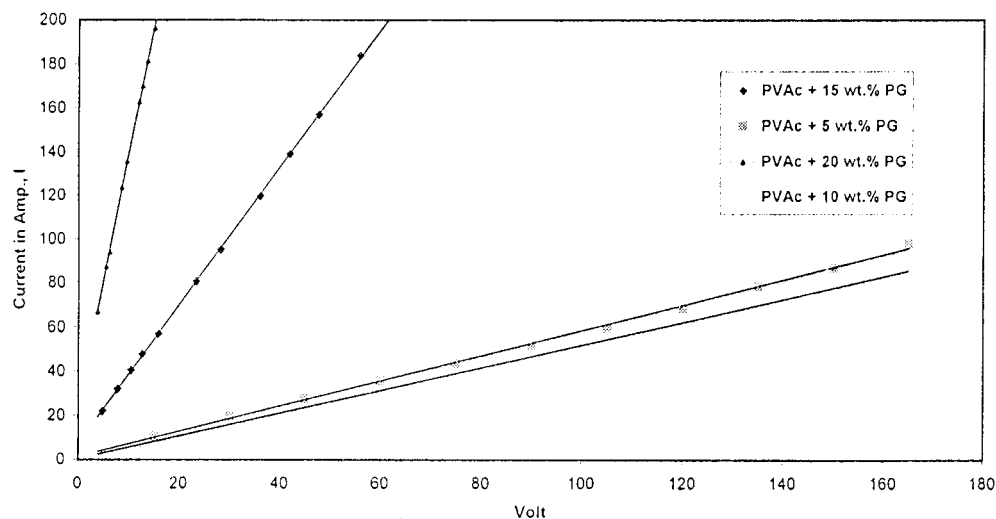


Figure 7 The voltage vs. the current in amperes for PVAc + different concentrations of PG.

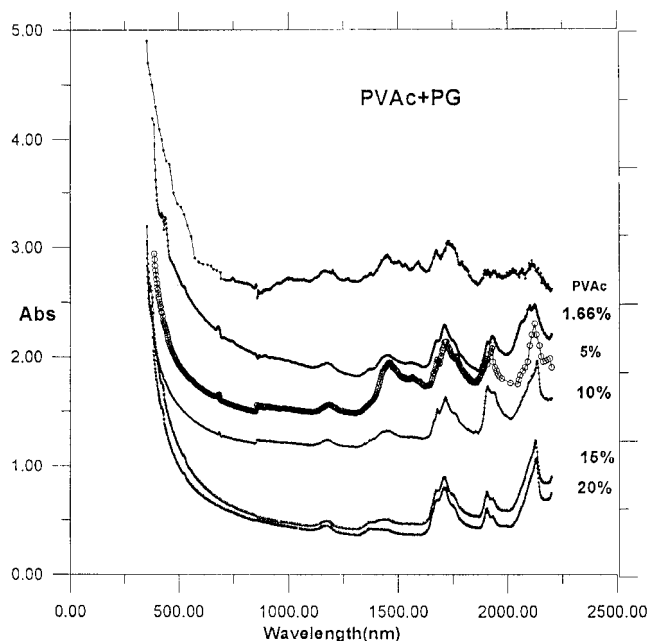


Figure 8 Optical absorption vs. wavelength (nm) for PVAc doped with 1.66, 5, 10, 15, and 20 wt % PG.

15, and 20 wt % PG at the wavelength range from 400 to 2200 nm at room temperature. Four bands were observed, characterizing the different optical transition of the dopant. All samples show nearly the same absorption peaks position at optical bands 0.885, 0.728, 0.655, and 0.59 eV.

In the case of 15 wt % and 20 wt % PG dopant, the absorption peak at 1500 nm disappeared while the other peaks enhanced with increasing PG content. The

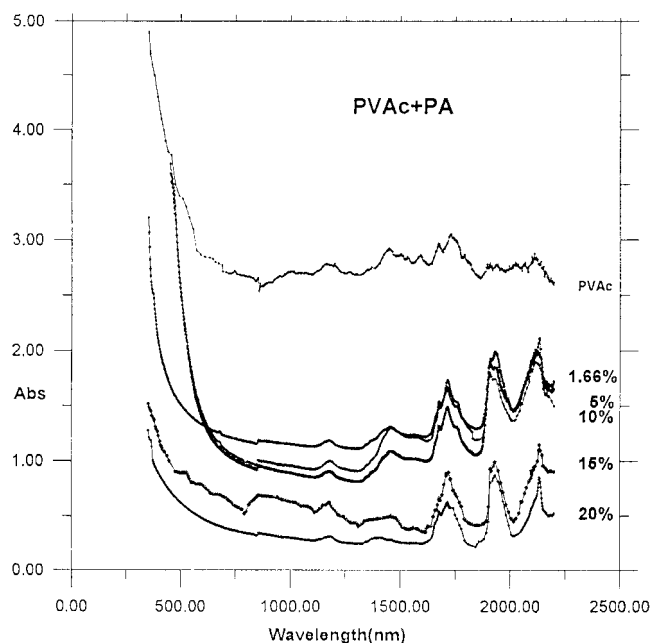


Figure 9 Optical absorption vs. wavelength (nm) for PVAc dopant with 1.66, 5, 10, 15, and 20 wt % PA.

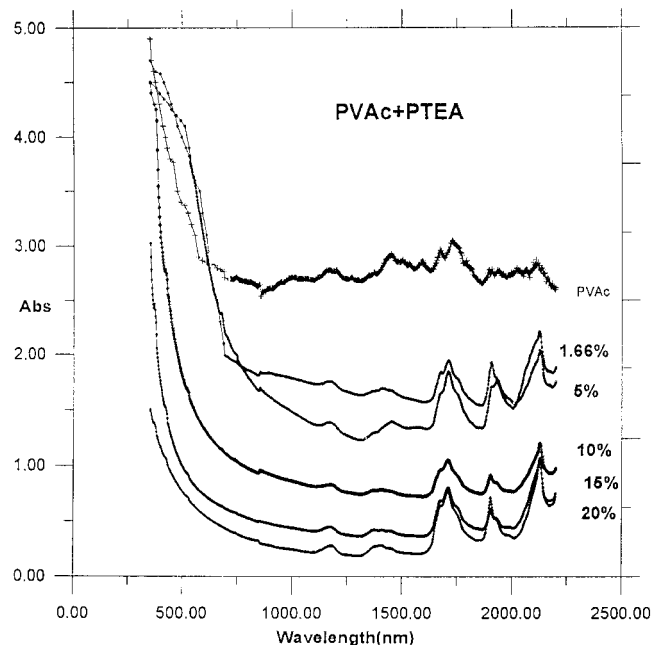


Figure 10 Optical absorption vs. wavelength (nm) PVAc doped with 1.66, 5, 10, 15, and 20 wt % PTEA.

disappearance of the absorption peaks is attributed to the structural change due to the effect of doping.

From Figure 9 it is clear that four energy bands were observed at 0.831, 0.728, 0.669, and 0.59 eV for the PVAc samples with 1.66, 5, and 10 wt % PA. The peak at 1500 nm disappeared in the samples with 15 wt % PA, while the other peaks become better shaped when the PA concentration increased. This may be due to the interband π - π transition in the conjugated polymer chain.¹²

Figure 10 shows the variation of optical absorption of PVAc doped with PTEA at wavelength in the range of 400–2200 nm. All samples at 1.66 up to 15 wt % PTEA have the same behavior, and have four peaks corresponding to the various energy bands, which have been estimated to be 0.885, 0.728, 0.669, and 0.59 eV, respectively.

From Figures 8, 9, and 10 it is concluded that the various dopants are responsible for most of the induced changes in the properties of the doped samples.

CONCLUSION

PVAc was doped with PG, PA, and PTEA. The two polymers PG and PTEA were prepared by chemical methods. The electrical resistivity and the optical absorption of PVAc doped with PG, PA, and PTEA have been studied. It was found that the conduction was mainly ionic in the temperature range from 20 to 120°C. The resistivity decreased with increasing the dopant content. Optical absorption spectra were obtained in the wavelength range from 400 to 2200 nm at room temperature.

Analysis of the optical absorption spectra revealed the existence of three energy bands. The values of the energy bands were affected by dopant concentration. It is concluded that there is no big difference in the effect of PG and PTEA dopant on the electrical and optical properties of the PVAc samples.

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