Optical parameters and characterisation of polyaniline doped PVAc- PVC polymer composite systems

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Abstract:

The optical transmission and absorption spectra in (UV-VIS) have been recorded in the wavelength range 400-1000 nm for different compositions of polyaniline doped PVAc-PVC polymer composites. The optical parameters such as absorption coefficient (α), optical energy gap (E_{opt}), refractive index (n_0), optical dielectric constant ($\varepsilon^{'}$), measure of extent band tailing $(nB)^{-1} \simeq \Delta E$, constant B and ratio of carrier concentration to the effective mass (N/m^*) have been evaluated. The effects of composition of polymer blend on these parameters have been discussed and the nonlinear behavior for all the parameters are investigated. The X-ray diffractogram of all the polymer composites are homogenous and are of single phase. Infrared spectroscopy has been used for the identification of polymer structure.

Keywords : *Optical parameters, PVAc-PVC thin films, Non-linear behavior.*

Introduction:

Polymer composites have steadily gained growing importance during the past decade. A good amount of work has been reported on the conduction mechanism in polymeric materials. Deshmukh *et al*[1] (2005) reported electrical conduction in semiconducting PVC-PMMA thin film. Electrical properties constitute one of the most convenient and sensitive method for studying the polymer structure.[2]

Refractive index is an important optical parameter for the design of prisms, windows and optical fibers.[3] The study of optical absorption spectra in solids provides essential information about the band structure and the energy gap in the crystalline and non crystalline materials. Analysis of the absorption spectra in the lower energy part gives information about atomic vibrations while the higher energy part of the spectrum gives knowledge about the electronic state in the atom.[4]

In recent years there has been increasing interest in the size dependent electrical and optical properties of semiconductors.[5] In nano-crystallites, the electrons confined in a narrow potential will exhibit extra-ordinary characteristics in the optical and electrical properties.[6] When the width of such confining potential is very small i.e. of the order of few hundred angstroms quantum size effect arises[7]

During the last five years, the research on the growth of nano particles Pbs films has increased, for its technological applications in photo resistance, diode lasers, decorative coatings and optoelectronic devices (Wang *et al*[8]. Optical properties of polyaniline doped PVC-PMMA thin films have been investigated.[9] The effect of doping percentage of polyaniline on the optical parameters has been discussed and nonlinear behavior for all parameters has been investigated. Also Burghate *et al*[10] has studied the optical properties of PVC-PMMA polymer blends. Berman *et al*[11] reported structural and optical parameters of chemically prepared CdS non crystalline thin films. Optical Band gap in polyaniline doped PVC-PS bend have been investigated by Joshil.[12] The effect of doping percentage of polyaniline on these parameters have been discussed and non-linear behavior for all parameters have been investigated. PVC as proton donar and PVAc as a proton acceptor. Tager, have been selected for the present work. PVC-PVAc polymer composites doped with polyaniline (PANI) have been prepared for the study of optical parameters and Characterization.

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27

Experimental details:

2.1 Preparation of samples:

The polyvinylchloride (PVC) of standard grade product supplied by Polychem Industries, Mumbai and (PVAc) of standard grade were used for the study. The two polymers PVC (1.2g) and PVAc (0.3g) were taken in the ratio of 4:1 by weight and PANI of different weights 0.003g, 0.006g, 0.009g, 0.012g and 0.015g i.e. 0.2%, 0.4%, 0.6%, 0.8% and 1.0% respectively. The 1.2g PVC in 15ml of tetrahydorfuran (THF), 0.3G PVAc in 10 ml of tetrahydorfuran and PANI in 5ml of THF were dissolved separately. After allowing them to dissolve completely, all the three solutions were mixed together. The solution was heated at 60ºC for two hours to allow polymers to dissolve completely to yield clear solution. A glass plate (15cm x 15cm) thoroughly cleaned with hot water and then with acetone was used as a substrate. To achieve perfect leveling and uniformity in the thickness of the film, a pool of mercury was used in the plastic tray in which the glass plate was freely suspended. The solution was poured on the glass plate and allowed to spread uniformly in all directions on the substrate. The whole assembly was placed in a dust free chamber maintained at constant temperature (40ºC). In this way the film was prepared by isothermal evaporation technique.[14]The film was subjected to 12 hrs heating at constant temperature 50ºC and kept for another 12 hrs at room temperature to remove the traces of solvent. Finally, the film was removed from the glass plate. It was cut into small pieces of suitable size, which were washed with ethyl alcohol to remove the surface impurities. The X-ray powder diffractogram (XRD) of all the polymer composites sample is recorded by using a Philips (Holland) automated X-ray diffractometer at (RSIC-Nagpur). The XRD of only one sample is shown in fig . The main aim of the XRD study was to know the amorphousness of the sample. The absence of peak in the X-ray spectra confirmed the amorphous nature of the sample.

2.2 Thickness Measurements:

For measuring the thickness, micrometer screw gauge,[15]with least count 0.001cm (10um) was used. But for greater accuracy and resolution, a compound microscope in conjunction with an acculometer, which gives least count 13 and 3.3 um at the magnification 1:10 and 1:100, respectively was used. A small section of the sample was taken and mounted vertically to get a clear section view of the thickness. The film used for the present study is of thickness 60um.

2.3 Theory:

The absorbance A and transmittance t of samples were measured by means of CARY 2390 double beam automatic scanning spectrophotometer (at Regional Sophisticated Instrumentation Centre, Chennai) in the spectral range 400 – 1000nm at normal incidence. The spectral dependence of both A and t on doping percentage of PANI thin film is shown in fig 2.

The optical absorption coefficient, $\alpha(v)$, at a given frequency (v) is given by :

$$\alpha(v) = \frac{4\pi\sigma_{min}}{C\, n_0 \Delta E} \frac{(hv - E_{opt})^r}{hv} \dots\dots(1)$$

where σ_{min} is the extrapolated dc-conductivity at $T=0$, n_0 is the refractive index, C is the velocity of light, ΔE is a measure of the extent of band tailing, hv is the photon energy, $E_{opt}$is the optical gap, $r = \frac{1}{2}$ is a number which characterized the transition process, and

$$B = \frac{4\pi\sigma_{min}}{C\, n_0 \Delta E} = \text{Constant}$$

The reflectance was calculated wing the

$$t = (1 - R)^2 \exp(-A) \dots(2)$$

Where R is the reflectance, t is the transmittance and A is the absorbance. The relation between optical dielectric constant $\acute{\varepsilon}$ and the square of wavelength λ^2 is given by

$$\varepsilon' = n^2 = \left[\frac{1 + \sqrt{R}}{1 - \sqrt{R}}\right]^2$$

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28

$$\varepsilon'_\infty = \frac{e^2}{\pi C^2} \frac{N}{m^*} \lambda^2 \ldots\ldots(3)$$

where ε'_∞ is the infinitely high frequency dielectric constant, e is the electronic charge and $\frac{N}{m^*}$ is the ratio of carrier concentration to the effective mass.

Results and Discussion:

The results regarding the various optical parameters obtained for different samples are listed in Table. The plots of $(\alpha h\upsilon)^2$ as a function of $h\upsilon$. The observed behaviour suggests

Sample	Optical energy gap (E_{opt})eV	Dielectric constant at infinite frequency $(\varepsilon'\infty)$	Refractive index n_0	Constant B (cm⁻¹eV)	Ratio of carrier concentration to the effective mass (N/m^*) (cm⁻³)	$(n_0B)^{-1}$ (cm² eV⁻¹)
PP1	2.60	70.0	7.30	19.0×10^4	4.66×10^{21}	7.2×10^{-7}
PP2	2.63	82.3	8.05	50.8×10^4	5.7×10^{21}	2.44×10^{-7}
PP3	2.64	20.0	2.86	47.6×10^4	1.27×10^{21}	7.35×10^{-7}
PP4	2.65	84.7	7.97	100×10^4	8.56×10^{21}	1.25×10^{-7}
PP5	2.65	11.8	3.13	125×10^4	2.54×10^{21}	2.56×10^{-7}
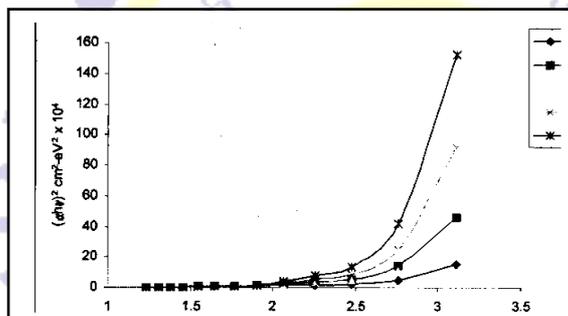
forbidden direct transition for amorphous material. The values of optical energy gap E_{opt} obtained from the extrapolation of the linear region and constant B from the slopes of the curves shown in fig.

The values obtained for E_{opt} are found to increase with percentage of PANI. The similar behaviour was observed by Burghate *et al.,* (1995). The optical energy gap, E_{opt} is found to be increase with increasing PANI%. The calculated values of (n0B)⊐ΔE, which is a measure of the extent of band tailing for the five different percentage of PANI samples are found to be nonlinear. Similar observations were found in $Ge_{20}Te_{80-x}Se_x$ thin films investigated by Shokr (1992).

The dielectric constant ε' versus λ^2 plots shown in Fig. 4 are linear. Verifying equ. 3, values of $\acute{\varepsilon}$ determined from the extrapolation of these plots to $\lambda^2 = 0$ and values of N/m* ratio of carrier concentration to effective mass are listed in Table as a function of film composition. The compositional dependence of the refractive index and dielectric constant is observed to be nonlinear for all samples such a nonlinear behavior is observed for amorphous materials as reported by Shoker (1992).   The value of refractive index n_0 we calculated from optical dielectric constant, ε' for all wave length λ^2. These values are found to be more or less same throughout the wavelength range (400 nm to 1000 nm). Therefore average value 01 n_0 are reported in this wavelength region. The average value of refractive index n_0 shows dependence on polyaniline (PANI) percentage.

The variation of $(n_0B)^{-1} \simeq \Delta$E the width of the tail of localized state with the normal forbidden gap and E_{opt} against PANI% is shown in fig 5. The optical energy gap, E_{opt} is found to be increase with increasing PANI% and $(n_0B)^{-1}$ is observed to be nonlinear with PANI %. The decreasing trend of the band tailing energy suggested that the presence of sharp localized states in the band gap. The ratio of

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29

carrier concentration to the effective mass N/m* has been calculated from the plots. $\acute{\epsilon}$ versus λ^2 fig. The value of N/m* for different samples are found to be of the order of 10^{21} cm^{-3} which are in agreement with the values reported by other workers (Shokr 1992;Burghate*et al* 1995;Sawarkar 2002).

It is not possible to calculate the degree of tailing of band edges without a detailed knowledge of the fluctuation potential. It is clear, however that the larger the fluctuation, the larger is the tailing. Thus the effective band gap becomes narrow in the disorder lattice. Tailing may extend deep in the forbidden zone and may execs result in the overlapping of the conduction and valence bands. The localization of discussed on the basis of speculative criterion, suggested that the localized and non-localized states are separated by a critical electron energy at which the electron mean free path and the electron wavelength as comparable.

Conclusions:

The optical gap (E_{opt}) is found to be increase with increasing PANI % and $(n_0B)^{-1}$ is observed to be nonlinear with PANI %. The refractive index (n_0) calculated in the region 400 nm to 1000 nm is found to be nonlinear with increasing content of PANI.

The ratio of carrier concentration to the effective mass (N/m*) is found to be of the order of 10^{21} (cm^{-3}). The linearity of the graph indicated the direct allowed transition Fig ----

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