

OPTICAL AND ELECTRICAL PROPERTIES OF POLYVINYL-CHLORIDE (PVC) FILMS

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Abstract

The optical properties of the polyvinyl-chloride thin films were studied which include their absorbance, transmittance, reflectance spectra, band gap, and refractive index, before and after annealing at $T = 75^{\circ}C$ for 24 hours. The films were found to exhibit high transmittance, low absorbance and low reflectance in the visible, and near infrared region up to 1100nm. However, the absorbance of the films was found to be high in the ultra violet region with peak around 306nm. The dielectric constant ϵ' , dielectric loss ϵ'' , and *ac* conductivity of polyvinyl-chloride were obtained at different frequencies and temperatures. The experimental results show that ϵ' and ϵ'' decreased with increasing frequency, which indicates that the major contribution to the polarization comes from orientation polarization. The value of ϵ' increased with increasing temperature, which is due to great freedom of movement of the dipole molecular chains at high temperature.

(PVC) -

-

(PVC) -

.24 hours T=75°C

.1100nm

.306nm

- ϵ'' ϵ' ϵ'' ϵ'

for the provision of information about the band structure and energy gap in both crystalline and non-crystalline materials [1]. On the other hand the dielectric properties of polymeric films are of direct interest to both the basic studies of electrical conduction through such films, and

1. Introduction

Polymers, both in fiber and thin film form, continue to receive global attention. The study of optical absorption and particularly the absorption edge is a useful method for the investigation of optically induced transitions and

dielectric permittivity ϵ^* as a function of angular frequency of the measuring electric field ω can be represented as [8]

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) \quad (4)$$

The dielectric constant ϵ' of the PVC films is evaluated from the capacitance C measured using Programmable Automatic Precision LCR meter type PM6036 and from equation:

$$\epsilon' = \frac{C}{C_o} \quad \text{and} \quad C_o = \epsilon_o \frac{A}{d} \quad (5)$$

where C_o is the vacuum capacitance, ϵ_o is the vacuum permittivity, A is the effective cross-sectional area of the sample and d is its thickness.

The observed dielectric loss factor ϵ'' can be divided into

$$\epsilon''(\omega) = \epsilon''_{dp}(\omega) + \epsilon''_{dc}(\omega) + \epsilon''_{mw}(\omega) \quad (6)$$

where ϵ''_{dp} , ϵ''_{dc} , and ϵ''_{mw} are the losses associated with dipole orientation, dc conductance, and Maxwell-Wagner interfacial polarization, respectively. Maxwell-Wagner interfacial polarization occurs in heterogeneous system where the conductivity and permittivity of the constituent phase differ [9]. The dc conductance loss can be represented as

$$\epsilon''_{dc}(\omega) = \frac{\sigma_{dc}}{\epsilon_o \omega} \quad (7)$$

σ_{dc} is the dc -conductivity of the polymer sample that arises from the motion of charge carriers through the polymer. Then the loss tangent $\tan \delta$ can be determined using this equation:

$$\epsilon'' = \epsilon' \tan \delta \quad (8)$$

where δ is the phase angle between the electric field and the polarization of the dielectric.

4. Experimental detail

For optical properties measurements, thin film of thicknesses $d = 20 \mu m$ of pure Polyvinyl-chloride (PVC) supplied by Sigma-Aldrich Company has been deposited onto clean glass substrate by using rotation technique at room temperature; while for electrical properties, film of thicknesses $d = 32 \mu m$ were prepared using solution-cast technique. 50gm of polymer was dissolved in 8ml Tetrahydrofuran THF and stirred at room temperature for 1hr to make the solution homogeneous. This homogeneous solution is spread on glass dishes and allowed to

their application in capacitors for microelectronics [2]. The dielectric dispersion and absorption are the crucial quantities required in the design of any device. The study of dielectric loss as a function of temperature and frequency was used to characterize the molecular motion and dielectric relaxation behavior of the polymer [3]. The molecular orientation behaviour and the associated relaxation mechanisms of the polymers are not fully understood [4].

2. Optical measurement technique:

The optical absorption coefficient $\alpha(\omega)$ near the band edge in many amorphous semiconductors and insulators shows an exponential dependence on photon energy $\hbar\omega$ and obeys an empirical relation due to Urbach [5].

$$\alpha(\omega) = \alpha_o \exp(\hbar\omega / E_o) \quad (1)$$

where ω is the angular frequency of the radiation, α_o is a constant and E_o is related to width of the tails of localized states in the forbidden band gap. The absorption edge for direct and non-direct transitions, for most amorphous and semiconductors can be obtained in view of the models proposed by Tauc et al [6]:

$$\alpha(\omega) = B(\hbar\omega - E_{opt})^n / \hbar\omega \quad (2)$$

where B is a constant, E_{opt} is the optical energy band gap of the material, and $n=1/2, 3/2, 2,$ or $1/3$ for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions respectively [2]. A plot of $(\alpha\hbar\omega)^{1/n}$ versus $(\hbar\omega)$ often yields a reasonably good straight line fit to the absorption edge and the extrapolated $(\hbar\omega)$ at which $(\alpha\hbar\omega)^{1/n} = 0$ provides a convenient experimental benchmark for the optical band gap E_{opt} . Practically the optical absorption coefficient $\alpha(\omega)$ can be calculated from the relation [1]:

$$\alpha(\omega) = 1/d \ln(I_t / I_o) \quad (3)$$

where I_o and I_t are the intensities of the incident and transmitted beams respectively, corrected for any reflection at the first surface, and d is the thickness of the sample.

3. Dielectric Relaxation in Polymers

In an alternating ac field, the dielectric constant is a complex quantity ϵ^* , and is the combination of a real component, called the relative permittivity or dielectric constant ϵ' and an imaginary component called the dielectric loss or dissipation factor ϵ'' [7]. The complex

from the reflectance data R and absorption constant K using equation:

$$n = \left[\frac{4R}{(1-R)^2} - K^2 \right]^{\frac{1}{2}} - \frac{(R+1)}{(R-1)} \quad (9)$$

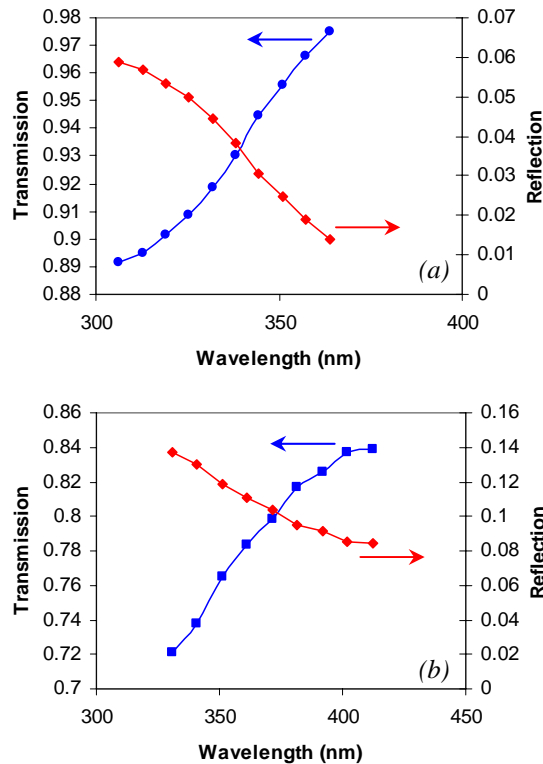


Figure 2: Transmission and Reflection as a function of wavelength for PVC (a) before and (b) after annealing.

The refractive indices over the exponential absorption region are shown in Figure 3.

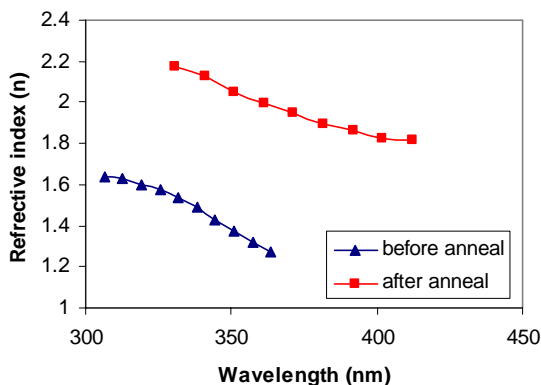


Figure 3: Refractive index as a function of wavelength for PVC before and after annealing.

The most satisfactory results were obtained by plotting the quantity $(\alpha\hbar\omega)^2$ as a function of photon energy $(\hbar\omega)$, for direct allowed transitions as shown in the Figure 4. However, the plots of quantity $(\alpha\hbar\omega)^{2/3}$ as a function of

evaporate the solvent slowly in air at room temperature.

Samples of radius 2.8cm were taken and silver was deposited on both surfaces of the film to ensure good contacts in electrical measurements. Silver coated samples were sandwiched between the two similar aluminum electrodes having a screw to avoid the parasite capacitance induced by the presence of air interstices at the interfaces between the sample and the electrodes [10]. The whole assembly was placed in a temperature controllable isolated chamber, the temperature was measured by Chromel-Alumel thermo-couple using a digital multimeter with an accuracy of $\pm 1^\circ\text{C}$.

5. Results and Discussion

5.1. Optical properties

The optical absorption spectra of Polyvinylchloride thin films were recorded at room temperature, by UV-VIS double beam spectrometer in the wave length range from 190 to 1100 nm. (Figure 1) shows the absorbance in arbitrary units as a function of the wavelength before and after annealing at $T= 75^\circ\text{C}$ for 24hours, for low wavelengths, in the UV region the absorption coefficient is decreasing exponentially. It is of interest to discuss the shift of the UV absorption band to longer wave lengths after annealing, this shift may be due to change in phase of the sample. When the crystalline becomes amorphous, one observes a shift in the absorption edge either towards lower or higher energies. No simple rule governing these changes has been suggested [11].

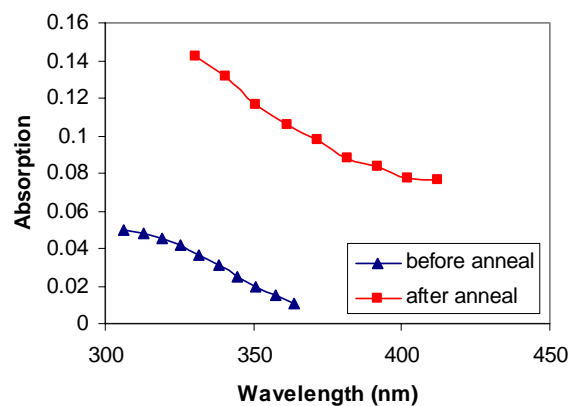


Figure 1: Optical absorption spectra for PVC before and after annealing.

The transmission and reflection for the PVC thin film before and after annealing are given in Figure 2. It was clear that the films exhibit high transmittance, low absorbance and low reflectance. The refractive index was determined

caused by the changes in the degree of crystallization, which is known to increase the width of the localized states, thus reduce the value of the optical gap. Such a change has been reported by others for different polymer compositions [13].

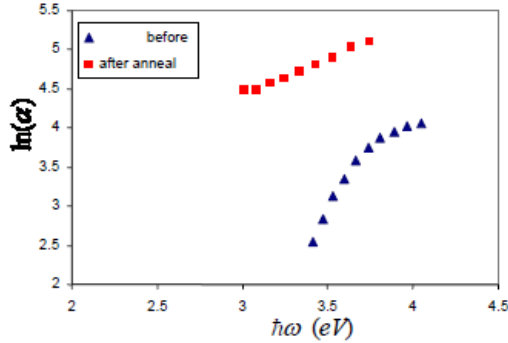


Figure 6: Variation of $\ln(\alpha)$ with photon energy ($\hbar\omega$) for PVC before and after annealing.

Table 1: Optical energy band and band tail for PVC before and after annealing.

	Before annealing	After annealing
E_{opt} direct allowed	3.56 eV	3.16 eV
E_{opt} direct forbidden	2.83 eV	2.41 eV
E_o band tail	0.0128 eV	0.3429 eV

5.2. Electrical properties

The evaluation of dielectric properties of the insulator film is carried out by measuring simultaneously the *ac* conductivity and capacitance of the film over a wide range of frequencies and three different temperatures (e.g. 40, 60 and 80°C), as shown in (Figure 7 and 8). There is sudden increase of *ac* -conductivity at frequency higher than (50KHz). The increase in *ac* -conductivity with frequency and a weak temperature dependence indicate that charge carriers are transported by hopping through defect sites along the chains [14]. These observations agreed with published data for different polymers and amorphous semiconductors [15-17].

The polarization of a dielectric is contributed by the ionic, electronic, and dipole polarization. The electric and ionic polarization occurs during a very short interval of time, but dipole polarization requires a relatively long time compared with that of ionic and electric polarization [2]. In the case of polar polymers, the dipole molecules cannot orient themselves in the lower temperature region. However, owing to thermal expansion, as the temperature

photon energy ($\hbar\omega$) also yields a good straight line fit, for direct forbidden transitions as shown in the Figure 5. All plots show straight lines with some deviations from linearity at the lower of α , which were suggested by Redfield and Afromowitz [12] as possibly due to imperfections in the material, but this region of the curve is still not fully understood.

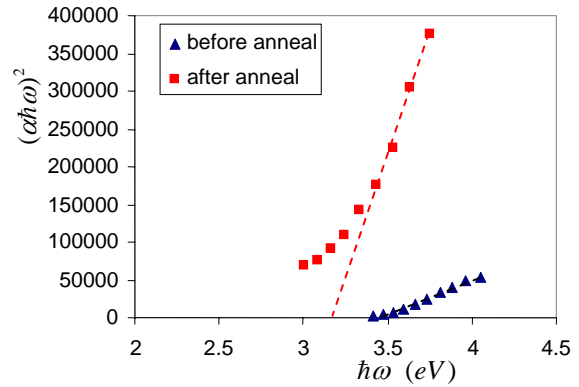


Figure 4: $(\alpha\hbar\omega)^2$ against ($\hbar\omega$) for PVC before and after annealing for direct allowed transitions.

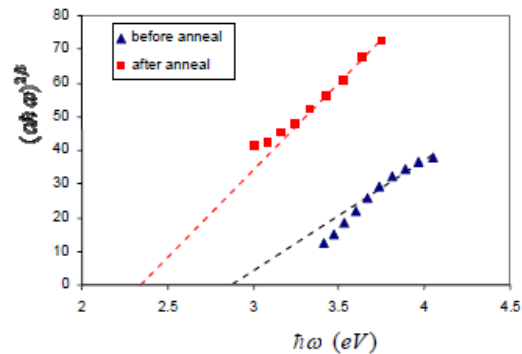


Figure 5: $(\alpha\hbar\omega)^{2/3}$ against ($\hbar\omega$) for PVC before and after annealing for direct forbidden transitions.

The Urbach plot is presented in Figure 6. in which the absorption coefficient is plotted as a function of ($\hbar\omega$). The values of E_o were determined using equation (1).

The values of absorption edge for direct allowed and forbidden transitions, and width tails localized states in the band gap E_o for unannealed and annealed samples are tabulated in table (1).

It is clear that the optical energy gap E_{opt} decreases after annealing, but on the other hand the width of the band tails of the localized state shift towards higher energies which range from 0.0128 eV to 0.3429 eV after annealing. This was attributed to the increase in the disorder

factor ε'' can be observed in the frequency range 1-20 KHz and finally reaches nearly a constant value at about 50KHz, also it was clear the dielectric loss factor increase with temperature, particularly at lower frequencies at which dielectric loss due to chain motion of polymer is more effective. At higher frequencies, however, the dielectric loss factor is low and remains more or less constant with increasing temperature because the orientation due to chain motion of polymer can not keep phase with the rapidly oscillating electric field

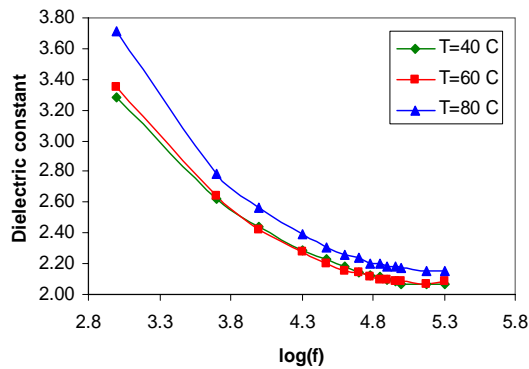


Figure 9: Dielectric constant as a function of frequency, at different temperature.

The increase in ε' with temperature is due to greater freedom of movement of dipole molecular chain at high temperature. As the temperature increases, the dipoles comparatively become free and they respond to the applied electric field [20]. Thus polarization increased and hence dielectric constant is also increased with the increase of temperature.

(Figure 10) shows the variation of dielectric loss factor ε'' with frequency at three different temperatures (e.g. 40, 60 and 80°C).

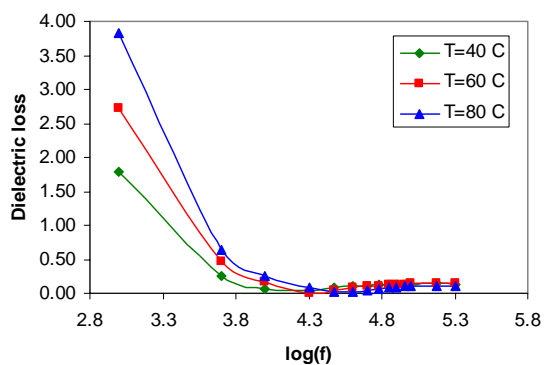


Figure 10: Dielectric loss as a function of frequency, at different temperature.

6. Conclusion

Several conclusions can be drawn on the basis of the experimental data. The optical absorption analysis of PVC thin film indicates

increases, the orientation of dipoles is facilitated and this increases the capacity [8].

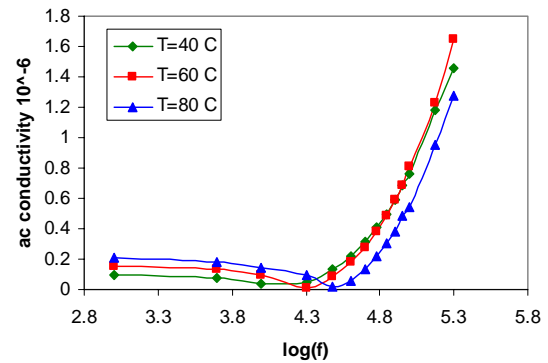


Figure 7: Conductivity as a function of frequency, at different temperature.

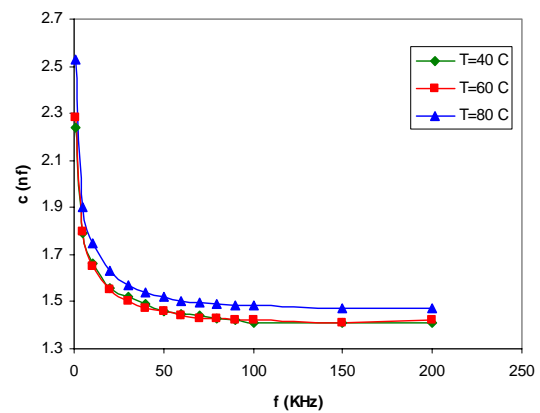


Figure 8: Variation of capacitance C with frequency for PCV at different temperatures.

(Figure 9) shows the variation of dielectric constant ε' with frequency at three different temperatures (e.g. 40, 60 and 80°C). It is observed from the (figure 9) that the dielectric constant continuously decreases with increasing frequency; similar behavior was observed in the case of strong polar polymers [14]. A rapid decrease in dielectric constant may be noticed over the frequency range (1-50)KHz. This may be attributed to the tendency of dipoles in macromolecules to orient themselves in the direction of the applied field in the low frequency range. However, in the high frequency range the rotational motion of the polar molecules of dielectric is not sufficiently rapid for the attainment of equilibrium with the applied field and hence the value of the dielectric constant decreases [18]. Similar effect was observed by Yang and co workers for the VGCNF reinforced polyethylene [19].

The value of ε' increases with temperature at fixed frequency. At lower frequencies this effect is more prominent. Significant decrease of loss

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- that the optical absorption is associated with allowed and forbidden direct transitions i.e. there are no indirect transitions. The variation in optical energy gap after annealing is explained on the basis of changes in the degree of crystallization.
- The experimental results indicate that ϵ' and ϵ'' decrease with increase of frequency which is due to the orientation polarization while increase in ϵ' and ϵ'' with increase of temperature is due to greater freedom of movement of dipole molecular chain of polymers at higher temperature. The variation of ac-conductivity with frequency accounts for the electronic conduction via a hopping process.

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