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# Synthesis and Study of Some Optical and Thermal Properties of (PVA-CuCl) Films

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## Abstract

*Films of pure and (CuCl) salt doped (with different concentrations; 2, 4, 6, 8 and 10 wt%) polymer (polyvinyl alcohol (PVA)) were prepared using casting technique. The optical and thermal properties of pure and doped films were studied. The transmission and absorption spectra have been recorded in the wavelength range of (300-1100) nm. The experimental results for (PVA-CuCl) films show that the transmittance decreases with increasing the filler content while the absorbance increases with increasing the filler content. The absorption coefficient, refractive index, extinction coefficient and real and imaginary parts of dielectric constant were found to be increased as filler content concentration increases. Moreover, the results show that the electronic transition is allowed indirect transition, and the energy gap ($E_g$) decreases with increasing the filler content. The experimental results also show that the thermal conductivity decreases with increasing the filler content.*

**Keywords:** Optical properties, thermal properties, polyvinyl alcohol (PVA), copper chloride, composites.

## Introduction

The properties of polymer-mineral reinforced composites are determined by the component properties (particle shape, surface area, surface chemistry, polymer microstructure) and as well as by the processing method and processing conditions. Among of processing methods, injection molding has strong influence on the internal microstructure of polymers and in a consequence on mechanical response of the material[1,2]. Recently, thermo-softening polymers are widely used in various aspects of daily life because of their favorite properties such as good chemical resistance, better mechanical properties, and cost effectiveness. These properties made these types of polymers a good choice for many applications. The use of thermo-softening polymer composites reinforced with natural fillers has been rapidly increasing in many industrial applications[3].

Polyvinyl alcohol (PVA) is a water-soluble synthetic polymer. Due to the characteristics of easy preparation, good biodegradability, excellent chemical resistance and good mechanical properties, PVA has been used in many biomaterial applications[4]. Doping of polymers attracted the scientific and technological researchers, because of their wide applications. The dopant in polymer can change the molecular structure and hence the microstructure as well as the macroscopic properties of the polymer[5].

## Material and Methods

The materials used in this work were powder of polymer (polyvinyl alcohol (PVA)) doped with copper chloride CuCl salt with weight percent (0, 2, 4, 6, 8 and 10) wt%. It was dissolved in (15 ml) of distilled water in glass beaker by using magnetic stirrer for about (45 minute) and placed in Petri dish (5 cm diameter) using casting technique to prepare the films. The thickness of the dried films was (45 μm) measured by digital micrometer. The transmission and absorption spectra for (PVA-CuCl) films were recorded in the wavelength range between 300 and 1100 nm using UV-Visible 1800 spectrophotometer manufactured by Shimadzu, Japanese company. For the purpose of measuring the thermal conductivity for (PVA-CuCl) films, the conventional Lee's Disk method was used.

## Results and Discussion

**Optical Properties:** Figure-1 shows the transmission spectrum for (PVA-CuCl) films with different concentrations of CuCl salt as a function of the wavelength. It is clear that the transmittance increases as the wavelength increases for all the films**.** And also the transmittance decreases with the increasing of the weight percentage of the added CuCl salt. These results are in agreement with other reports[6-8]. This is caused by the added CuCl salt which contains electrons in its outer orbits which can absorb the electromagnetic energy of the incident light and then the electrons are excited to higher energy levels, thus part of the incident light is absorbed by the substance and does not penetrate through it. On the other hand, the pure polyvinyl alcohol films are highly transparent due to the lack of free electrons (i.e. electrons are bonded to atoms), and to break these bonds photons with sufficiently high energy are needed[9].

Figure-2 shows the absorption spectra of (PVA-CuCl) films with different concentrations of CuCl salt as a function of wavelength. It is clear that adding CuCl salt to the polymer (PVA) leads to increase the intensity of the absorbance in the short wavelength region and there is shift in the position of the absorption edge for all amounts of CuCl concentration towards red wavelengths[6-8]. The increase of absorbance with the increase of the weight percentage of the added CuCl salt can be explained by the fact that CuCl salt ions absorbed the incident light on them[9,10].

Figure-3 shows the absorption coefficient of (PVA-CuCl) films with different concentrations of CuCl salt as a function of the wavelength. The absorption coefficient α is calculated using equation[11]:

$$\alpha = 2.303\left(\frac{A}{t}\right) \quad (1)$$

Where A is the absorbance and t is the thickness of the film.

The absorption coefficient is high at high energies, which indicates high possibility of transitions of valance band electrons to the conduction band[9]. It can be noticed that the values of the absorption coefficient are lower than $10^4$ $cm^{-1}$, and this suggests that the type of the electronic transitions are of indirect transition type where the electronic momentum is conserved by the assistance of phonons[12]. It can also be observed that the absorption coefficient increases with increasing the weight percentage of the added CuCl salt.

Figure-4 shows the $(\alpha h\nu)^{1/2}$ vs. $h\nu$ of (PVA-CuCl) films with different concentrations of CuCl salt (Tauc's Plots). The energy gap ($E_g$) for allowed indirect transition can be estimated using equation[13]:

$$\alpha h\upsilon = B\left(h\upsilon - E_g\right)^2 \quad (2)$$

Where B is constant inversely proportional to amorphousity and hυ is the energy of the incident photons.

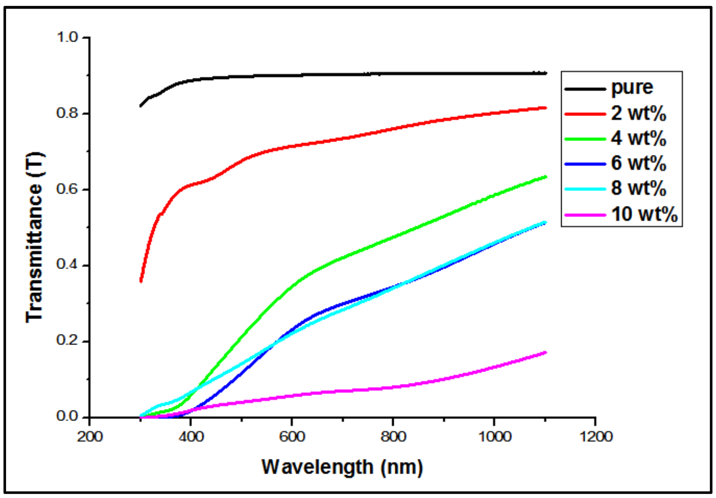


**Figure-1**
**Transmittance spectra of (PVA-CuCl) films with different concentrations of CuCl salt**

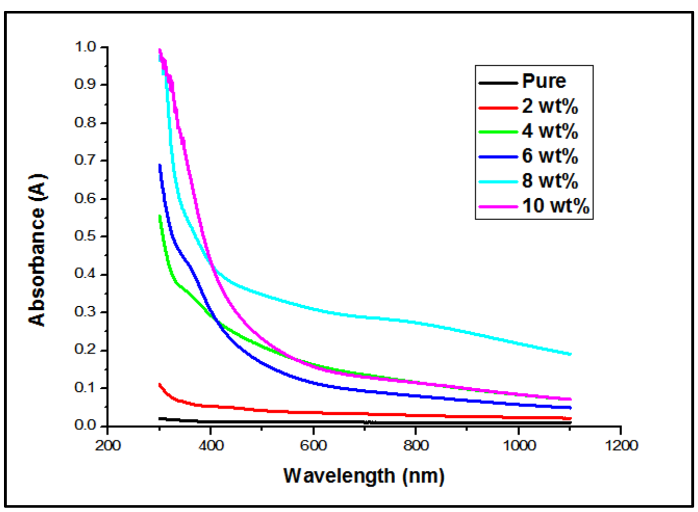


**Figure-2**
**Absorbance spectra of (PVA-CuCl) films with different concentrations of CuCl salt**

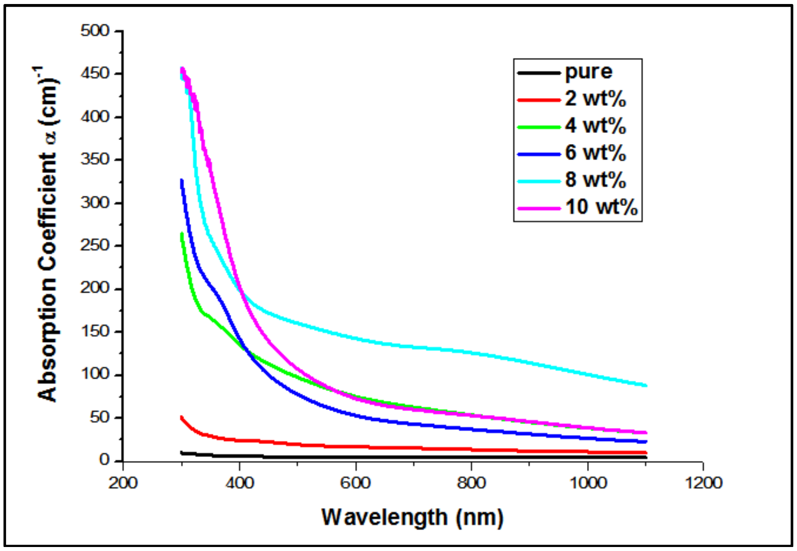


**Figure-3**
**Absorption coefficient of (PVA-CuCl) films as a function of the wavelength**

Plotting a straight line which best fits the linear portion of the curve can lead to the calculation of the energy gap ($E_g$) value which is the intercept of this straight line with the x-axis where the value $(\alpha h\nu)^{1/2}= 0$. The obtained values are shown in table (1). It can be seen that the energy gap values decrease as the weight percentage of the added CuCl salt increases. This is attributed to the creation of onsite levels in the energy gap ($E_g$), the transition in this case occurs in two stages, the transition of electron from the valence band to the localized levels in the forbidden band and to the conduction band as a result of increasing the added weight percentage. This behavior is attributed to the fact that composites are of heterogeneous type (i.e. the electronic conduction depends on added impurities). The increase of the added rate provides electronic paths in the polymer which facilitates the electronic transitions from valance band to conduction band[9,14].

Figure-5 shows the change of refractive index of (PVA-CuCl) films with different concentrations of CuCl salt as a function of wavelength. The refractive index (n) is calculated from equation[15]:

$$n=\sqrt{\frac{4R-k^2}{(R-1)^2}-\frac{(R+1)}{(R-1)}} \qquad (3)$$

Where R is the reflectance and k is the extinction coefficient.

It is clear that the refractive index values increase as the percentage of the added CuCl salt increases.

Figure-6 shows the change of extinction coefficient of (PVA-CuCl) films with different concentrations of CuCl salt as a function of the wavelength. The extinction coefficient (k) is calculated from equation[16]:

$$k = \frac{\alpha\lambda}{4\pi} \qquad (4)$$

Where λ is the photon wavelength.

It is clear that the extinction coefficient is of low values at low concentrations, but it increases with increasing the weight percentage of the added CuCl salt. This is attributed to increased absorption coefficient with increased percentage of added CuCl salt.

**Table-1**
**Energy gap ($E_g$) for the allowed indirect transition of (PVA-CuCl) films with different concentrations of CuCl salt**

| **CuCl (wt%)** | **$E_g$ (eV)** |
|---|---|
| | **Allowed indirect** |
| Pure (PVA) | 5.659 |
| 2 | 3.457 |
| 4 | 2.840 |
| 6 | 2.80 |
| 8 | 2.68 |
| 10 | 2.187 |

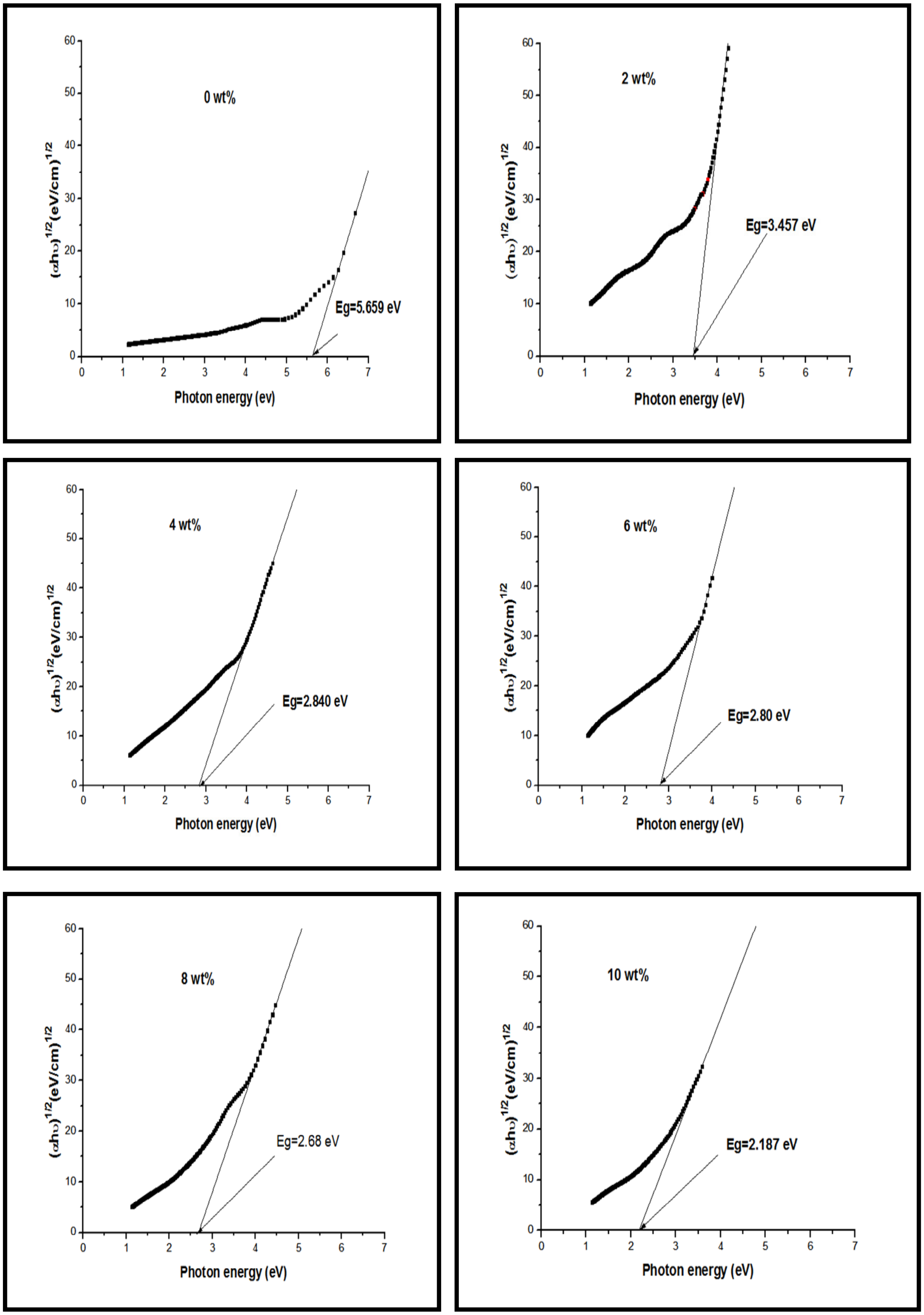


**Figure-4**
**Tauc's plots of the allowed indirect transition of (PVA-CuCl) films**

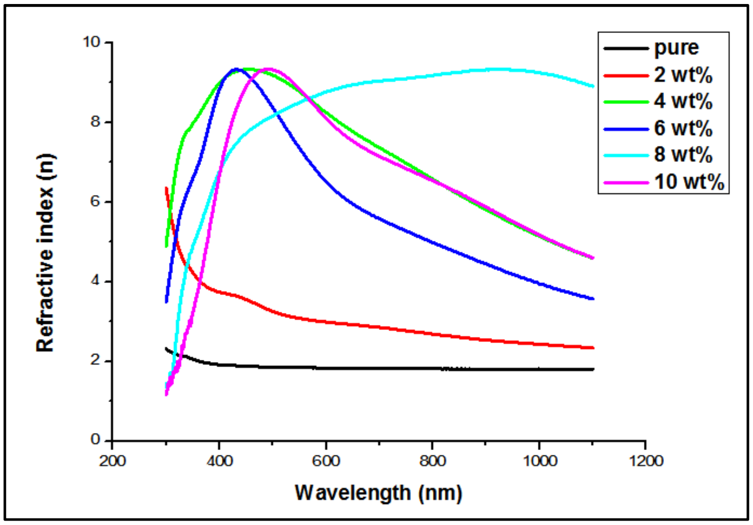


**Figure-5**
**Refractive index of (PVA-CuCl) films as a function of the wavelength**

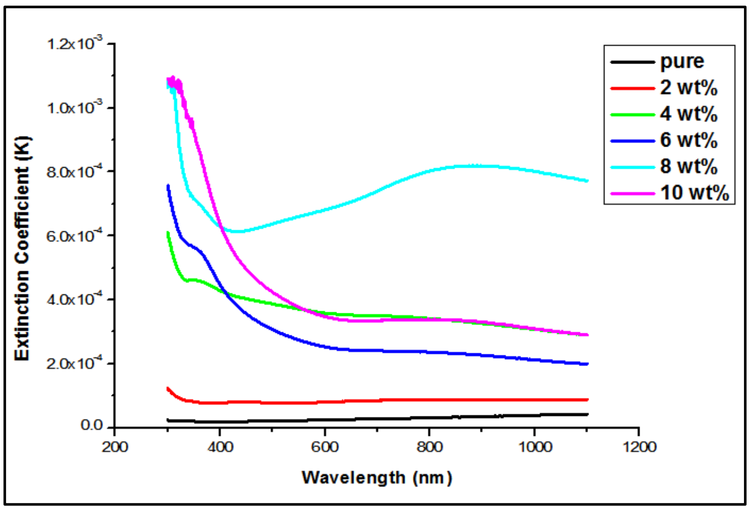


**Figure-6**
**Extinction coefficient of (PVA-CuCl) films as a function of the wavelength**

Figures-7 and 8 show the change of the real and imaginary parts of dielectric constant of (PVA- CuCl) films with different concentrations of CuCl salt as a function of the wavelength. The real and imaginary parts of dielectric constant ($\varepsilon_1$ and $\varepsilon_2$) can be expressed by the following equation[17]:

$$\varepsilon_1 = n^2 - k^2 \quad (5)$$
$$\varepsilon_2 = 2nk \quad (6)$$

It can be seen that the real and imaginary parts of dielectric constant increases with increasing the weight percentage of the added CuCl salt, and this behavior is similar to the behavior of refractive index and the extinction coefficient.

**Thermal Properties:** If the heat transfer depends on the gradient of temperature only then the thermal conductivity (K) can be defined as the quantity of transmitted heat per unit temperature gradient per unit time at steady state condition in a direction perpendicular to the surface of unit area[18]. Using Lee's disk method, the thermal conductivity can be calculated according to equations -7 and 8, respectively[19]:

$$\mathrm{IV} = \pi r^2 e(\mathrm{TA}+\mathrm{TB}) + 2\pi r e\left[\mathrm{dATA} + \frac{\mathrm{ds}}{2}(\mathrm{TA}+\mathrm{TB}) + \mathrm{dBTB} + \mathrm{dcTC}\right] \quad (7)$$

$$\mathrm{K}\left[\frac{\mathrm{TB}-\mathrm{TA}}{\mathrm{ds}}\right] = e\left[\mathrm{TA} + \frac{2}{r}\left(\mathrm{dA} + \frac{\mathrm{ds}}{4}\right)\mathrm{TA} + \mathrm{dsTB}/2r\right] \quad (8)$$

Where V is the potential difference across the heater, I is the current flows through it, e is the energy emitted from the surface (measured by joules), ds, $d_A$, $d_B$ and $d_C$ are the thickness of the sample and the disks A, B and C, respectively; $T_A$, $T_B$ and $T_C$ are the temperature of the disks A, B and C above surrounding temperature[19].

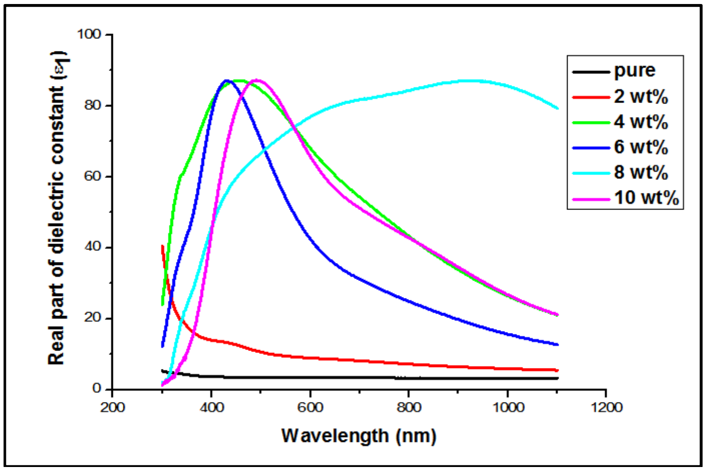


**Figure-7**
**Real part of dielectric constant of (PVA-CuCl) films as a function of the wavelength**

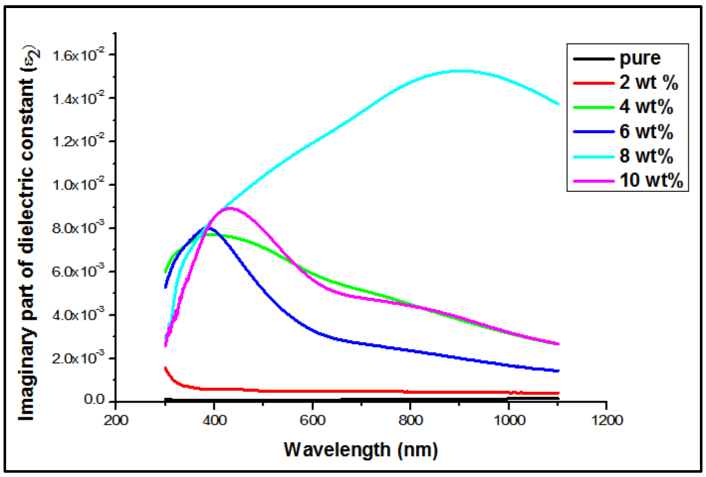


**Figure-8**
**Imaginary part of dielectric constant of (PVA-CuCl) films as a function of the wavelength**

Figure-9 shows the volume thermal conductivity coefficient (K) (W/m.K) of (PVA- CuCl) films as a function of the concentration of CuCl salt. It is well known that the thermal conductivity of composites depends on the matrix material and the filler, so it is expected that the thermal conductivity of the pure (PVA) strongly depends on CuCl salt concentration. The figure shows that the thermal conductivity decreases with increasing the concentration of CuCl salt from 2 wt% to 8 wt%. When increasing the concentration of CuCl salt to (10 wt%), the thermal conductivity increases to the small value of (0.012) for (CuCl) salt[18]. This result suggests that all concentrations of CuCl salt have a comparable impact on the thermal conductivity of these composites films. The decrease in thermal conductivity as the concentration of CuCl salt increases can be attributed to the change from semi crystalline structure of (PVA) to amorphous structure. In fact, the phonons which can move smoothly in the crystal lattice may scatter and take irregular paths with random directions due to the presence of amorphous structure regions, and this leads to decrease in thermal conductivity at the surface and in the semi crystalline bulk of the composite. The increase in the thermal conductivity at (10 wt%) of CuCl concentration can be explained by presence of a threshold value of CuCl concentration; beyond this value an overcompensation by the composite material occurs[18]. Table-2 shows the values of volume thermal conductivity (K) (W/m.K) of (PVA-CuCl) films with concentrations of CuCl salt.

## Conclusion

The absorption coefficient of (PVA-CuCl) films increases with increasing of the filler content (wt%). The absorption coefficient of (PVA-CuCl) films is lower than ($10^4$ $cm^{-1}$); suggesting that the electronic transition is indirect. The energy gap of allowed indirect transition of (PVA-CuCl) films decreases with increasing of filler content (wt%). The real and imaginary parts of dielectric constant, the extinction coefficient and the refractive index increase with increasing of the filler content (wt%). Volume thermal conductivity coefficient K (W/m.k) of (PVA-CuCl) films decreases with increasing of filler content (wt%) until at filler content of (10 wt%).

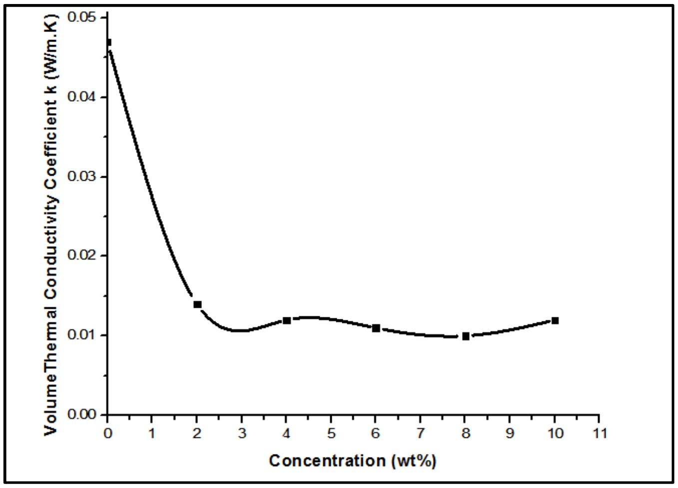


**Figure-9**
**Volume thermal conductivity coefficient k (W/m.K) of (PVA-CuCl) films as a function of the concentration of CuCl salt**

**Table-2**
**Values of volume thermal conductivity coefficient k (W/m.K) of (PVA-CuCl) films with different concentrations of CuCl salt**

| concentration (wt%) | k (W/m.K) |
|---|---|
| Pure (PVA) | 0.047 |
| 2 | 0.014 |
| 4 | 0.012 |
| 6 | 0.011 |
| 8 | 0.010 |
| 10 | 0.012 |

## References


1. Gowariker V.R., Viswanathan N.V. and Sreedhar J., Polymer Science, New Age International (p) Ltd Publishers, New Delhi, **(2005)**

2. Bula K., Jesionowski T. and Borysiak S., Effect of injection molding conditions on composite properties based on PBT with $SiO_2$ and MMt Nanofillers, *Proceedings of the Conference of Multiphase Polymers and Polymer Composites: From Nanoscale to Macro Composites*, Paris-Est, Creteil Uniersity, France, June **(2011)**

3. Singh V., Kulkarni A.R. and Rama T.R., Dielectric properties of alumium-epoxy composites, *J. Appl. polymer Sci*., **90(13)**, 3602-3608**(2003)**

4. Mahsan M., Sheng C., Isa. M., Ghapur E., Ali E. and Razali M., Structural and physical properties of PVA / $TiO_2$ composite, *Malaysia Polymer International Conference*, 486-495 **(2009)**

5. Tawansi A., Migahed M.D. and El-Hamid M.I.A., Electrical conduction of poly (vinyl alcohol) films, *J. Polym. Sci. Part B: Polymer physics*, **24(12)**, 2631-2642 **(1986)**

6. Salman S.A., Bakr N.A. and Mahmood. M.H., Preparation and study of some optical properties of (PVA-Ni($CH_3COO)_2$) composites, *Int. J. Current. Res.*, **6**(**11**), 9638-9643 (**2014**)

7. Hashim A., Ali M. and Rabee B.H., Optical properties of (PVA- CaO) composites, *Am. J. Sci. Res.*, (**69**), 5-9 (**2012**)

8. Abdallh M., Hamood O. and Yousif E., Study the optical properties of Poly (vinyl alcohol) doped Copper Chloride, *J. Al-Nahrain. Univ.*, **16**(**1**), 17-20 **(2013)**

9. El-Dahshan M. E., Introduction to Material Science and Engineering, 2nd Ed., King Saud University Press, Saudi Arabia, **(2002)**

10. Abdul Munaim A. and Hashim A., Electronic transitions For (PS - LiF) composites, 6th Science Conference of College of Science University of Mustansiriah, **(2010)**

11. Mwolfe C., Holouyak N. and Stillman G.B., Physical Properties of Semiconductor, Prentice Hall, New York, **(1989)**

12. Chiad S., Optical and structural properties of ($SnO_2$) doped by fluorine irradiated by gamma rays, M.Sc. Thesis, College of Science for Women, Baghdad University, Iraq**(2005)**

13. Sze S. M. and Kwok K. Ng., Physics of Semiconductor Devices, 3rd Ed., John Wiley and Sons Inc., Hoboken, New Jersey, **(2006)**

14. Gabur K., Preparation and study the electrical and optical

properties of (PS-Ni) composites, M.Sc. Thesis, Babylon University, College of Science, Iraq **(2010)**

**15.** Chopra K. L. and Kaur I., Thin film Device Applications, Plenum Press, New York, **(1983)**

**16.** Berglund R., Graham P. and Miller R., Applications of In-situ FT-IR in pharmaceutical process R and D, *Spectroscopy*, **8(8)**, 31-38 **(1993)**

**17.** Klingshirn C., Semiconductor Optics, Springer-Verlag Berlin Heidelberg, **(1997)**

**18.** Nasar G., Khan M. and Khlil U., Study on structural, mechanical and thermal properties of polymer composites of poly(vinyl alcohol) with inorganic material, *Mocromol. Symp*., **(298)**, 124-129 **(2010)**

**19.** Majied H. A., Study of the mechanical and thermal behavior of mineral wool and carbon black, M.Sc. Thesis, University of Technology- Applied Sciences, Iraq **(2005)**