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Characterization Effect of Copper Oxide and Cobalt Oxide Nanocomposite on Poly(Vinyl Chloride) Doping Process for Solar Energy Applications

A. N. Abed*, R. N. Abed

Mechanical Engineering Department, Engineering College, Al-Nahrain University, P.O. Box: 64040, Baghdad, Iraq.

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ABSTRACT

The optical properties for pure poly(vinyl chloride) were doped by nanomaterials of CuO and CoO with various concentration ratios has been applied on a glass substrate. The result obtained was shown the thin film coating of CuO and CoO has a high absorptive of solar energy. Optical properties have been measure by the UV-Visible spectra and reflectivity tests in the wavelengths range (200-1200 nm) at room temperature. The transmittance, absorbance, refractive index, extinction factor, and energy gap were used to study different optical properties. Optical energy gap (E_g), absorbance coefficient, reflectance, transmittance, skin depth, optical density. These properties have been increased by doping PVC with nanomaterials. The energy gaps were calculated and their values have been investigated. The energy gap value was found to be a decline from 5.15 eV for pure PVC to 2.2 and 2.1 eV for PVC/CuO and PVC/CoO, respectively of the nanocomposites. The optical data was interpreted and analyzed by phonon theory to assist in the direct transition of electrons, it is clear that the energy gap is influenced by nanomaterials used in doping poly(vinyl chloride), then the present results depend on the optical properties of pure and poly(vinyl chloride) films adopted with nanomaterials. The AFM has been used to determine the surface morphology of the thin films and the distribution of nanoparticles which was inspected in three dimensional images. Prog. Color Colorants Coat. 15 (2022), 235-241© Institute for Color Science and Technology.

1. Introduction

Poly(vinyl chloride) will be the fastest growing material in the world for it uses in many countries because it has light in weight, high conductivity, inexpensive and has tremendous advancement in the last years for the technological applications range include organic light emitting diodes, lithography, electrochemical cells, coatings and sensors. Poly(vinyl chloride) (PVC) is a thermoplastic material which use widely in the world due to its worthy properties in various applications, the most important property high chemical resistance and barrier properties [1, 2]. The optical properties of amorphous semiconductors are the subject to be consider by many modern researches, because. First; the materials are used in optical fibers and reflective coatings. Second, the optical properties due to their electronic structure, atomic structure, and electrical properties [3, 4]. By using solution-casting methods pure poly(vinyl alcohol) has been doped by (KNO_3 and $MgCl_2$) to make thin films to be use at room temperature with a wavelength range of (200-800 nm), optical absorption spectra for thin films were recorded [5]. When the concentrations of nanoparticles for the cobalt oxide and magnesium oxide increase which mixed with polymers, the nanocomposites absorbance (α) is increased with different polymers

*Corresponding author: * abdulrahman.n.abed@nahrainuniv.edu.iq

such as (PVA 0.90-PEG 0.05-PVP 0.05) in different weight percentages. But energy gap is decreases for the polymer by increase the weight percentages of CoO and MgO dopants. These nanocomposites prepared by casting technique have many applications [6]. The nanoparticles of lead monoxide (PbO) is synthesized and mixed with poly(vinyl chloride) (PVC) by using chemical method (sol–gel) to transfer the influences of PbO content to PVC composite and improve the refractive index and the direct optical band gap of the materials [7].

The optical properties of PVC were doped by additives of the 2-amino acetate benzothiazole complexes to improve the behavior of conductivity of PVC. The energy gaps will be as an indicator for conductivity that measured, this means, the energy gap is influenced by type of metal complexes used for doping [8].

The polymers optical properties can be appropriately modified by the dopants which are depending on its structure with host medium. The nano dopants are fast conducting compounds in the crystalline of the doped material, to enhance its optical and electrical performance. The essential understanding of polymer thin films properties is important for the successful use of nanomaterials in present time and future technologies, by using the polymer blends and doping them. The optical properties, thermal, electrical, dielectric, and mechanical can be better achieved. The optical properties of polymers can be tailored to a special requirement by added of appropriate dopant materials to become nanocomposite [9].

The current study revealed that the optical properties can improve the behavior conductivity of PVC which is modified by using nanomaterials and its industrial applications will be increased. Besides the easy processing, low cost and flexibility, they exhibit good optical and electrical properties. The overall performances of the polymeric materials could improve by nano-additives, due to its quantum retention effects, small size, large specific area and a strong interfacial interaction. A thin film optical property gives indication about some significant physical properties, such as band structure and band gap energy. The coating method has progressive for measurements to determine transmittance, extinction factor, absorption coefficient and refractive index. The aim of this research is to prepare successful nanocomposite and investigate the optical properties of pure poly(vinyl chloride) films with different percentages of nanometals.

2. Experimental

2.1. Materials

Structurally, the PVC is similar to polyethylene, but in other words, the carbon in the backbone chain by one of the atoms of hydrogen is replaced with an atom of chlorine, which is produced by free radical, the formula below is show polymerization of vinyl chloride with chlorine instead of hydrogen as shown in Figure 1.

Spin and casting methods were used to produce thin films of nanocomposite materials that precipitated on the glass substrates. The nano-copper oxide (CuO) with average particle size 50 nm and purity 99.9 %, density 6.67 g/cm^3, and the nano-cobalt oxide (CoO) with average particle size of 20 nm and 99.9 % purity, were equipped by Changsha Easchem company /Hunan China, The atomic force microscope is the most powerful tools which have been recognized for the analysis of surface morphologies because three-

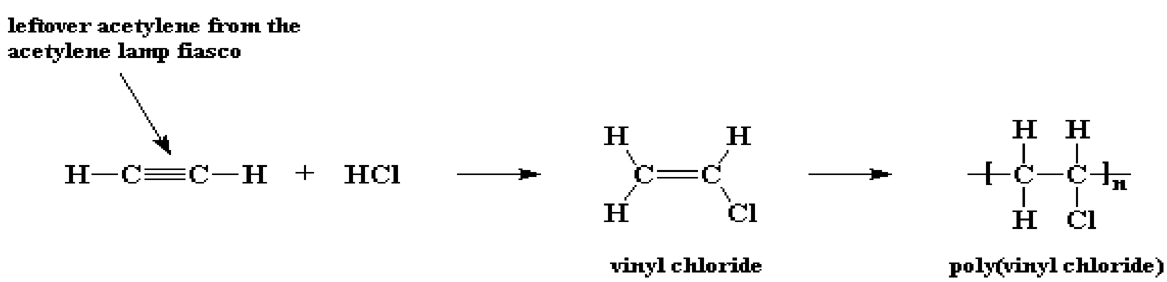

Figure 1: Presentation of polymerization of vinyl chloride with chlorine instead of hydrogen.

dimensional images can be created at angstrom and nano scale. The results for CuO and CoO were confirmed the average particles size 56.43 and 30.69 nm, respectively, as shown in Figure 2.

2.2. Preparation of nanocomposite thin films

The PVC films were intended at room temperature by using solution casting technique and their thickness of (45-60 µm) was inspected by SEM Inspect S50 low vacuum. Firstly, 0.5 g from PVC was dissolved by 10 mL of tetrahydrofuran (THF) to obtain the pure film of PVC. Secondly, the nanomaterials that were added to PVC at a concentration 0.1 g by weight and 2 g from PVC blended with it, and then dissolved by 40 mL THF solution. The dissolution was completed for PVC and THF, but the nanomaterials were suspended in the solution at temperature (60 ^{o}C) for 2 h and stirring in a magnetic stirrer. After the mixing process homogeneous solutions were achieved and then spread on a glass substrate and dried slowly to evaporate the solvent at room temperature for 72 hours.

2.3. Optical properties spectroscopy test

UV-Visible spectrophotometer has been computerizes (SHIMADZU UV-1601 PC), the transmittance and absorbance were registered in wavelength region between (200-1200 nm). In order to detect the effect of doping on the samples, the optical properties were computed for pure and nanocomposites of PVC, in which absorbance (A), transmission (T), refractive index (n), absorption coefficient (α), extinction factor (k), and energy gap (E_g). The results of surface roughness and particle size obtained by atomic force microscopy (AFM) AA2000 equipment.

3. Results and Discussion

3.1. Optical absorption spectra

It is obviously from Figure 3 represent UV-Vis optical absorption spectra of pure PVC and nanocomposites of PVC/CuO and PVC/CoO have different region of sharp absorption for all films. This may be attributed to the interaction between bonds of PVC and nanomaterials, and then rapidly reduce with increase the wavelength [10]. The absorption was increased with different nanometals of (CuO and CoO) respectively after doped films; the incident light is absorbed by free electrons.

3.2. Transmittance spectra

The spectra of transmittance in Figure 4 shows the transmittances for poly vinyl chloride and its nanocomposites were increased with wavelength. After adding nanometals, the transmittance decreased because depending on the type of nanoparticles that added such as (CuO and CoO), respectively. The light measured through the sample will be regard as the ratio of the light passes to the intensity of incident light that fall on the sample, therefore can be calculated from the equation below (Eq. 1) [11]:

$$\boldsymbol{T} = \frac{\boldsymbol{I}}{\boldsymbol{I_o}} \cdots \qquad (1)$$

Where transmitted light is I through a substance and incident light is I_o.

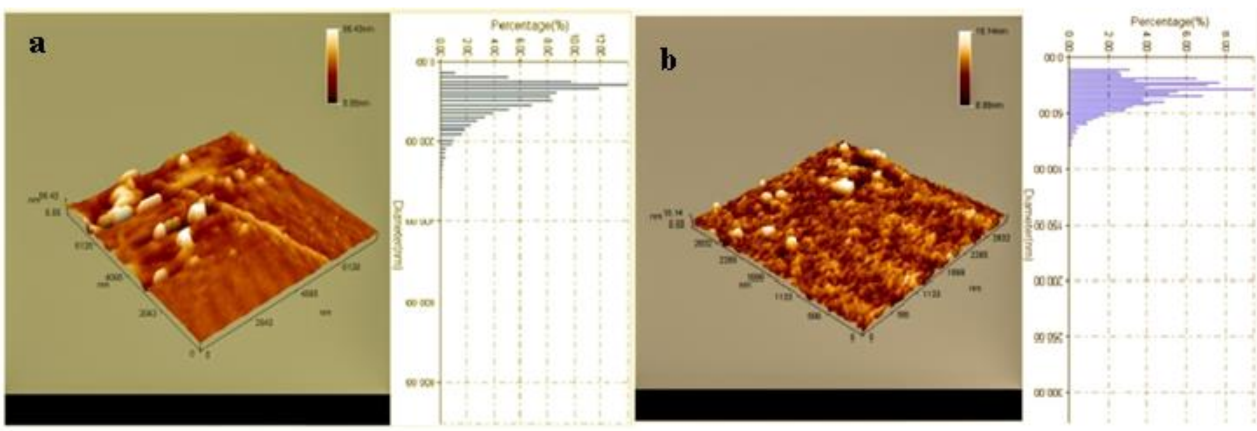

Figure 2: Particles size of a) Copper oxide (CuO) powder and b) cobalt oxide (CoO) powder.

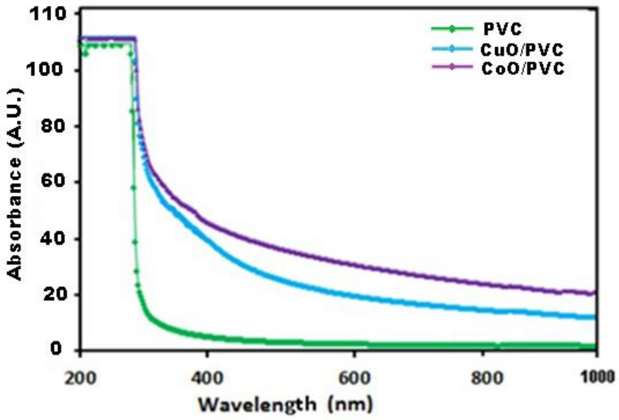

Figure 3: Spectra absorption of pure PVC and nanocomposite PVC samples.

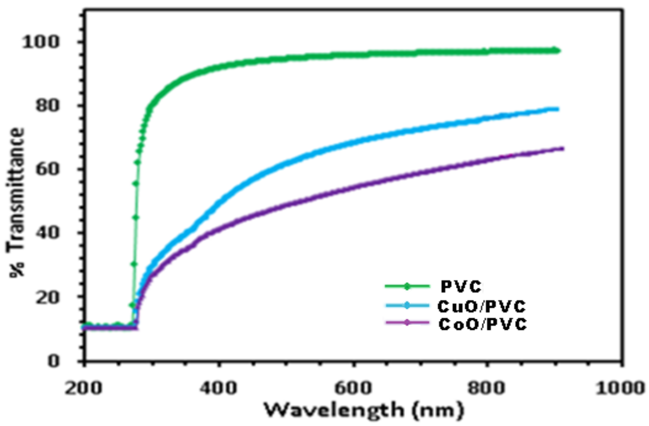

Figure 4: Transmittance of PVC and nanocomposites of PVC.

3.3. Coefficient of absorption

The coefficient of absorption is presented in Figure 5, which shows when the wavelength increases the coefficient of absorption decreasing for all thin films. This behavior of increases absorption with modification of nanoparticles doping for PVC related to increasing the charge carries number which leads to increase the absorbance from higher scale of vibration of basic level state to higher sublevels of first excited single state [6].

The coefficient of absorption (α) calculated by using relation Eq. 2 [10]:

$$\alpha=2.303\times\frac{A}{t} \tag{2}$$

Where A the absorbance; t the thickness of thin film.

3.4. Refractive index

The refractive index of PVC and for its nanocomposites (n) thin films can be determined from the reflectance (R). Figure 6 shows the variation of refractive index with the wavelength for all films before and after doping. It is evident from Figure 6 that the refractive index shows regular variation with the wavelength (200-320 nm) for all samples and the value of refractive index increase to the highest value of wavelength. After doping of PVC samples by (CuO and CoO), respectively, the refractive index was increased, this increasing was attributed to increase the scattering for incident photon which causes to decrease the reflectance for the nanomaterials in photonics and optics losses at interfaces [12, 13].

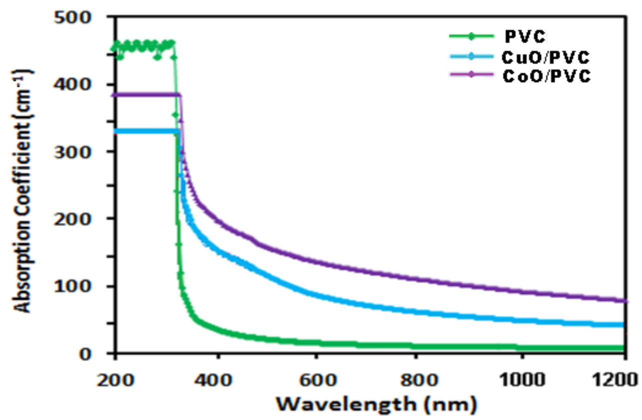

Figure 5: Absorption coefficient for pure PVC and nanocomposite of PVC.

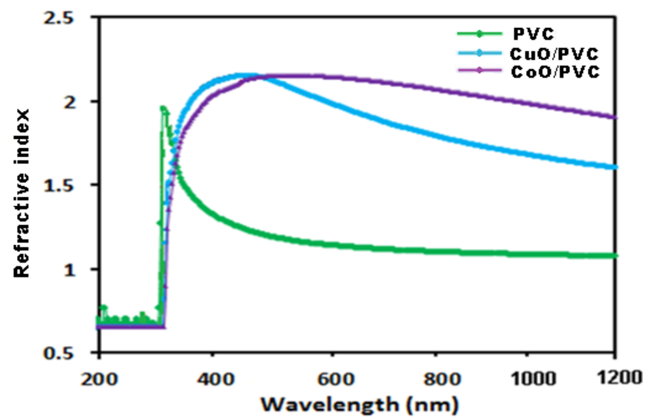

Figure 6: Refractive index for pure PVC and its nanocomposites.

The following equation is represented the refractive index (n) (Eq. 3)[14]:

$$n=\left[\frac{1+R}{1-R}\right]+\sqrt{\frac{4R}{(1-R)^2}-k^2} \quad (3)$$

Where R= reflectance.

3.5. Extinction coefficient

The confirmation of the extinction coefficient (k) on the range of wavelength (200-1200 nm) for pure PVC and its nanocomposites is showing in Figure 7. It is obvious that (*k*) for films demonstrates completely increase in the region (200-350 nm) of wavelengths because the losses in incident wave energy on the molecules. In the other hand, it shows decrease in the value of extinction coefficient on the wavelengths (350-1200 nm). This attribute to assign for growing coating region for films and depending on the absorption coefficient as shown in the equation 4 also depends on the nanomaterials that used for doping PVC [13, 14].

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

3.6. Energy gap

The band gap of the films was calculated by Tauc's relation as display in equation 5 according to inter-band absorption theory.

$$(\alpha h\upsilon)^p=B(h\upsilon-E_g) \quad (5)$$

Where h Planck's constant, B constant, Eg energy band gap, υ the frequency of photon, p an index which could agree various account award to the allowed transition.

The data from experimental results were fitted in the theoretical Equation 5 for various values of p and the best given fitting was obtained for p=2, this behavior for direct transitions is allowed. By plotting (αhν)2 the direct allowed band gap was calculated with the photon energy function(hν) for the thin films as shown in Figures 8-10, respectively, the diagram is straight line and the value of Egis gained by extra piloting linear part of diagram to intercept x-axis of photon energy [10]. It was found that Eg reduces from (5.15) of pure PVC to (2.2 eV) for PVC/CuO and (2.1 eV) for PVC/CoO nanocomposites, respectively. The values of direct allowed of energy gap is illustrated in Table 1. By doping PVC, the differences in mobility gap of the doped PVC can be comprehended for the lowering of E_g of PVC films after adding in different nanometals [10, 13].

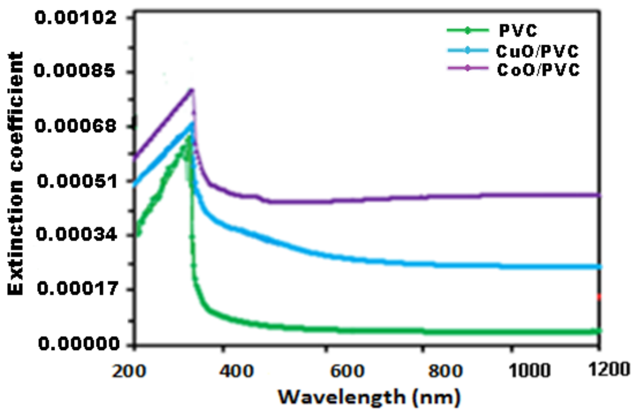

Figure 7: Extinction coefficient for pure PVC and its nanocomposites.

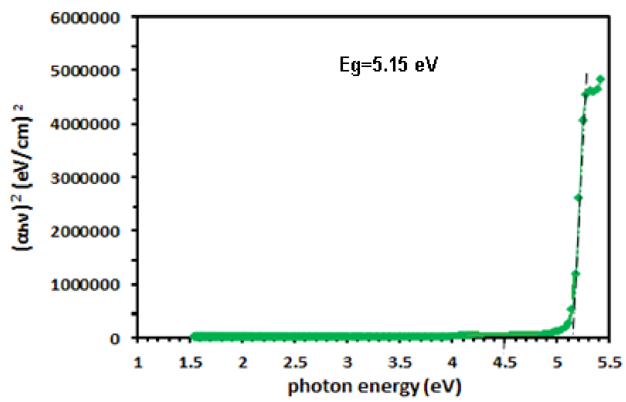

Figure 8: Energy gap for pure PVC before doping.

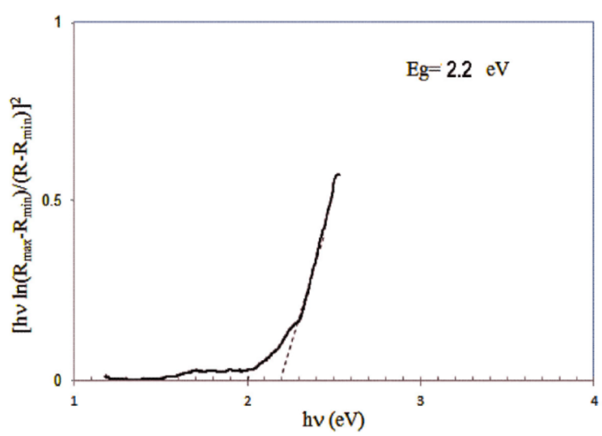

Figure 9: Energy gap for nanocomposite CuO/PVC after doping.

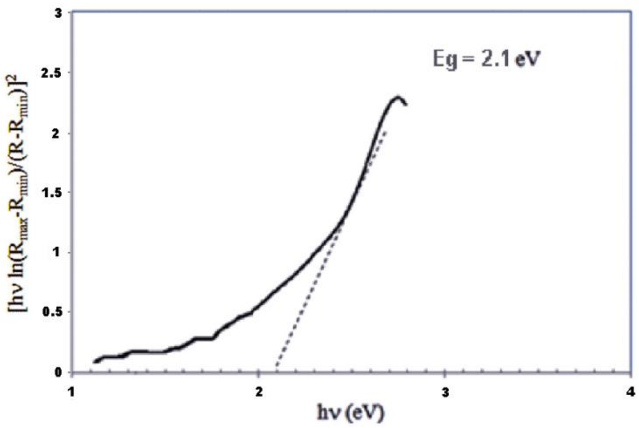

Figure 10: Energy gap for nanocomposite CoO/PVC after doping.

Table 1: Energy gap value for the pure PVC and nanocomposites of PVC.

PVC and Nanocomposite of PVC	Energy gap (eV)
Pure PVC	5.15
CuO/PVC	2.2
CoO/PVC	2.1

3.7. Investigation of surface roughness and homogeneity by (AFM)

Atomic surfaces with high resolution can be inspected the progress for mapping three-dimensional topographical differences in surfaces. The utilization of this device on PVC films and its nanocomposites surface coating is particularly appropriate. The roughness of specimens coating surface and its adhesive to be fixed on the PVC substrate is considered as important parameter for solar energy application. To raise the roughness of specimens coated surface of the solar energy implant, many procedures exist. The topography of specimens coating surface can be revealed atomic force microscopy (AFM), in which represent topography of three-dimension of the coated surfaces with high resolution as shown in Figure 11 a and b. It is clear that specimen coated with copper oxide has higher surface roughness compared to specimen coated with cobalt oxide.

The atomic force microscopy revealed homogeneous distribution of both nanoparticles of copper oxide and nano particles of cobalt oxide on the PVC surface, as it is clear in scans area extracted from atomic force microscope Figure 11 a and b.

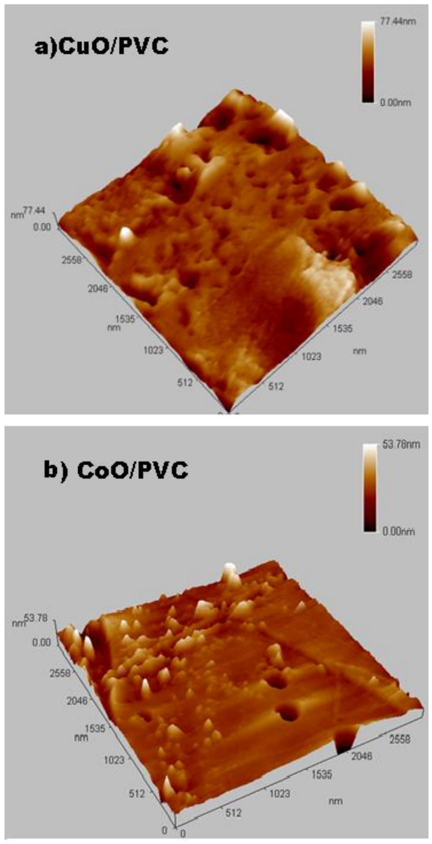

Figure 11: AFM images of nanocomposite a) CuO/PVC and b) CoO/PVC films.

4. Conclusion

The nanocomposites were made in order to determine the effect of nanomaterials (CuO and CoO) content on the optical properties of PVC host. By adding nanomaterials highly enhances UV absorption of PVC host and the decrease in value of energy gap for the poly(vinyl chloride) by doping it to get the best energy gap, the conductivity of PVC can be improved by using various types of dopants. The energy gap values were found to be 5.15 eV for pure PVC and 2.2 eV PVC doped by CuO and 2.1 eV PVC doped with CoO. The optical properties analysis of nanocomposites thin films reviled that the thin films are exhibited decrease in energy and become a semiconductor which will be use to absorb the solar energy. So that nanocomposite will be use as a coating on flat plate collector or in concentrating solar system over the pipes. The absorption coefficient, refractive index, and extinction factor were increased with additive nanometals concentration. AFM analysis exhibited the morphology of the surface for the nanocomposites of PVC which doped by nanomaterials (CuO and CoO).

5. References

1. S. Zhu, Y. Zhang, Y. Zhang, C. Zhang, Effect of $CaCO_3$/$LiCO_3$ on the HCl generation of PVC during combustion, *Polym. Test.*, 2(2003), 539-543.
2. F. Gong, M. Feng, C. Zhao, S. Zhang, M. Yang, Thermal properties of poly(vinyl chloride)/ montmorillonite nanocomposites, *Polym. Degrad. Stab.*, 84(2004), 289-294.
3. M. Youssif, A. Bahgat, A. Ali, Ac magnetic susceptibility technique for the characterization of high temperature superconductors, *Egypt. J. Solid*, 23(2000), 231-250.
4. N. Mott, E. Davis, Electronic process in non-crystalline materials, *2^{nd} Clarendon Press, Oxford*, (1979), 458-465.
5. S. Kramadhati, K. Thyagarajan, Optical properties of pure and doped (KnO_3 & $MgCl_2$) polyvinyl alcohol polymer thin films, *Int. J. Eng. Res. Dev.*, 6(2013), 15-18.
6. I. R. Agool, A. Hashim, Preparation of (PVA-PEG-PVP-MgO, CoO) nanocomposites and study their optical properties, *Int. J. Sci. Res.* (IJSR), 3(2014), 1729-1732.
7. A.M. El Sayed, W.M. Morsi, Dielectric relaxation and optical properties of polyvinyl chloride/lead monoxide nanocomposites, *Polym. Compos.*, 34(2013), 1-9.
8. A. Ahmed, T. Najim, J. Salimon, N. Salih, A. Graisa, Y. Farina, E. Yousif, Optical properties modification of poly(vinyl chloride) using complexes of 2-amino acetate benzothiazole, *ARPN J. Eng. Appl. Sci.*, 5(2010), 43-45.
9. Y. Zare, Recent progress on preparation and properties of nanocomposites from recycled polymers: A review, *Waste Manag.*, 33(2013), 598-604.
10. O. G. Abdullah, D. R. Saber, Optical absorption of polyvinyl alcohol films doped with nickel chloride, *Appl. Mech. Mater*., 110-116(2012), 177-182.
11. K. Grandin, A. Roos, Evaluation of correction factors for transmittance measurements in single beam integrating spheres, *Appl. Opt.*, 33(1994), 6098-6104.
12. T. Estabraq Abdullah, S. M. Hasan, A. M. Naji, Optical properties of PVC-MWCNT Nano composite, *Indian J. pure Appl. Phys.*, 51 (2013). 77-80.
13. R. N. Abed, N. K. Al-Sahib and A. J. N. Khalifa, Optical study to doping carbon with TiO_2 that utilizing in thermal concentration, *Orient. J. Phys. Sci.*, 02 (2017), 109-113.
14. W.A. Jabbar, N.F. Habubi, S.S. Chiad, Optical characterization of silver doped poly(vinyl alcohol) films, *J. Ark. Acad.Sci.*, 64(2010), 101-106.
15. R. N. Abed, A. R. N. Abed, F. A. Khamas, M. Abdallh, E. Yousif, High performance thermal coating comprising (CuO:NiO) nanocomposite/C spectrally selective to absorb solar energy, *Prog. Color Colorants Coat.*, 13(2020), 275-284
16. R. N. Abed, A. R. N. Abed, E. Yousif, Carbon surfaces doped with (Co_3O_4-Cr_2O_3) nanocomposite for high temperature ohoto thermal solar energy conversion via spectrally selective surfaces, *Prog. Color Colorants Coat.*, 14(2021), 301-315.

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