THE STRUCTURAL AND OPTICAL CHARACTERISTICS OF POLYVINYLPYRROLIDONE DOPED WITH NANO CRYSTAL NAF FILMS

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ABSTRACT

The samples of polyvinylpyrrolidone were doped with nanostructure NaF by using different preparations such as a wet casting, quartz cell and spin-coating techniques with concentrations (0, 2, 4, 6, 8, 10, 12, 14 wt%). The X-Ray diffraction of the samples indicate that the pure PVP are amorphous structure and the doped are polycrystalline for selective concentrations (4, 8, 12, 14) wt% with nano crystal grain size (30.10, 26.00, 22.88, 31.79) nm respectively. It was observed that the amorphousation decreases with increasing NaF concentration. The Fourier Transform Infrared (FTIR) spectrometer measurements show that the stretching vibration in the oxygen containing chain polymer with change the covalent bond distribution with fluoride ion bonds that is the greatest. Increasing UV-vis absorption spectrometer refers to a maximum peak absorbance spectra of different techniques have about (0.5-0.6) values, and there are a high shifting in a casting method. The indirect Egopt of pure and doped PVP films were estimated to be decrease about (3.65, 3.57, 3.55, 3.45, 3.33), and 3.25 eV for indirect allowed transitions, whereas the indirect forbidden band gaps were determined as (3.52, 3.50, 3.41, 3.31, 3.18) and 3.13 eV with increase sodium fluoride contents respectively. All prepared samples appeared near band edge peak absorption at about (300nm) of different deposition, it close to each other for bulk specimens (solution), shifting at higher frequencies.

Keywords: polyvinylpyrrolidone (PVP), doping, structural, optical properties, optical energy gap, concentration, sodium fluoride

INTRODUCTION

Polyvinylpyrrolidone (PVP), commonly called Polyvidone or Povidone, is a water-soluble polymer and other polar solvents made from the monomer N-vinylpyrrolidone[1].

When dry it is a light flaky powder, which readily absorbs up to 40% of its weight in atmospheric water. In solution, it has excellent wetting properties and readily forms films. This makes it good as a coating or an additive to coatings. PVP is a branched polymer, more complicated than linear polymer, though it too lies in a two-dimensional plane and later in a wide variety of applications in medicine, pharmacy, cosmetics and industrial production[2]. It is used as a binder in many pharmaceutical tablets[3]; autopsyes have found that crospovidone does contribute to pulmonary vascular injury in substance abusers[4]. PVP added to iodine forms a complex called povidone-iodine that possesses disinfectant properties[5]. This complex is used in various products like solutions, ointment, pessaries,
liquid soaps and surgical scrubs. PVP is also used in many technical applications: as an adhesive in glue stick and for batteries, ceramics, fibreglass, and in the chemical-mechanical planarization process, an emulsifier and disintegrant for solution polymerization, as a photoresist for cathode ray tubes (CRT) used in aqueous metal quenching for production of membranes, as an aid for increasing the solubility of drugs in liquid and semi-liquid dosage forms (syrups, soft gelatin capsules) and as an inhibitor of as an additive to Doro's RNA extraction buffer as a liquid-phase dispersion enhancing agent in DOSY NMR. PVP binds to polar molecules exceptionally well, owing to its polarity. This has led to its application in coatings for photo-quality ink-jet papers and transparencies. It has also been used in contact lens solutions and in steel-quenching solutions. Other references state that polyvinyl pyrrolidone and its derivatives are fully from mineral synthetic origin. Allergies attributed to these other chemicals may possibly be caused by the PVP instead.

In (2010) Abdul Muniam and Hashim studied the addition of (LiF) to polystyrene on some optical properties. They concluded that the absorption coefficient increasing with increased addition of (LiF), but the energy gap decreasing. In (2010) Mahdi et al. studied the effect of adding (Al₂O₃) on some optical properties of polystyrene. They found that absorption coefficient increasing with increased of added material, while energy gap decreases. Masoud and Faranak (2011) studied highly efficient method for the preparation of N-tert-butyl amides by reaction of nitriles with tert-butyl acetate is described using polyvinylpolypyrrolidone-supported boron trifluoride (PVP-BF₃) at 70°C in good to excellent yields to be complex shows non-corrosive and stable solid catalyst elevated Lewis acid property. M. Nikoorazm, et al. (2011) added nitric acid on polyvinylpolypyrrolidone was found to be an efficient, environmentally friendly, mild nitrating agent for the nitration of substituted phenols in dichloromethane at room temperature with moderate yields. (Noorhanim Ahad, et al.,2012) prepared the polymer electrolytes at different weight percent ratios by solution casting technique. Faisal A., (2013) studied optical properties of doped polyvinyle alcohol with NaI it is found that E_opt decrease with increasing doping. The propose of report is to obtain the better methods of prepared specimens of polyvinylpyrrolidone doped with NaF and studied the structural and optical properties and the nature of bond connections using (FTIR) and the optical energy gaps at different concentration of inorganic materials to use in photoelectric semiconductor industries such as solar cell, IC, bipolar devices.

Experimental

Chemicals were purchased from Fluka, Merck and Aldrich chemical companies. PVP were doped with different sodium florid weight percent (0,2,4,6,8,10,12,14)wt%. It is dissolved in (30ml) distilled water as a solvent to obtain gel solution and mixed by using magnetic stirrer for period (10 min) at (50°C) to obtain a real solution. Part of solution placed in britidish (5cm diameter) using casting technique to preparation films. Each sample was poured in (25cm²) glass basin after being cleaned with deionized water using ultrasonic device. The samples were put in dried oven at (50°C) period 2hr. After dried samples, its thickness becomes about 0.04cm. Other part of solution are placed in quartz cell, and other are pouring on glass substrate to obtain a film by using spin coating technique under (0.1 mbar) vacuum and (3000 t/min.), its thickness is kept around 4.8393µm using Digital Computerized Optical Thin Film Measurement Device (LIMF-10, Lambda Scientific Pty LTD, Germany). The specimens are analyzed using (Computerized XRD, Cu Kα, 40kV, 30mA, Japan). The spectrum of absorption and transmittance have been recorded for wavelengths (190-850)nm by using double beam spectrophotometer data( UV-vis – CECIL 2700 provided by optima 300 plus company) at room temperature. (Computerized FTIR, (Phywe) laser glass Germany (Alpha) BRUKER Company) are also used for pure and some doped PVP films to analyze the bond structure from 400 to 4000cm⁻¹.
Theoretical

To calculate constructively the spacing $d$ between diffracting planes in a few specific directions, determined by Bragg's law [19][20]:

$$2dsin\theta = n\lambda$$

(1)

Where $\theta$ is the Bragg angle, $n$ is any integer, and $\lambda$ is the wavelength of the beam, $\lambda=0.15406$ nm. These specific directions appear as spots on the diffraction pattern called reflections.

The lattice constant can be finding from the equation [21]:

$$a = \frac{n\lambda \sqrt{h^2 + k^2 + l^2}}{2sin \theta}$$

(2)

A shape factor is used in X-ray diffraction and crystallography to correlate the size of sub-micrometer particles, or crystallites, in a solid to the broadening of a peak in a diffraction pattern. In the Scherrer equation [22]:

$$\tau = \frac{K\lambda}{\beta \cos \theta}$$

(3)

where $K$ is the shape factor, denoting the ratio of a particle's major dimension to its minor dimension, $\lambda$ is the X-ray wavelength, $\beta$ is the line broadening at half the maximum intensity (FWHM X/180) in radians, and $\theta$ is the Bragg angle. $\tau$ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size. The dimensionless shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite. The Scherrer equation is limited to nano-scale particles. It is not applicable to grains larger than about 0.1 $\mu$m, which precludes those observed in most metallographic and ceramographic microstructures.

The relationship between incident intensity and the penetrating light intensity is given by equation [23]:

$$I = I_o e^{-\alpha t}$$

(4)

Where $t$ is the thickness of the matter (cm) and $\alpha$ is the absorption coefficient (cm$^{-1}$),

$$\alpha = 2.303 \log \frac{I}{I_o}$$

(5)

where the amount of log $I/I_o$ represents the absorbance (A). The absorption coefficient can be calculated by:

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

(6)

If the amount of absorption is $\alpha \geq 104$ cm$^{-1}$, the electronic transitions are direct. The amount of optical energy gap from this region can be evaluated by the relation [24]:

$$\alpha \ h\nu = A(h\nu - E_g)m$$

(10)

Where $h\nu$ is the photon energy, $A$ is the proportional constant, $E_g$ is the allowed or forbidden energy gap of direct transition and $m$ is a parameter that gives the type of electron transition. Specifically, $m$ is ½, 3/2, 2, and 3 for transitions direct allowed, direct forbidding, indirect allowed and indirect forbidding respectively [25]. The indirect transition, which requires phonon assistance, the absorption coefficient has the following dependence on photon energy [26]:

$$\alpha h\nu = A(h\nu - E_g + E_p)^2 + B(h\nu - E_g - E_p)^2$$

(11)
Where $E_p$ is the energy of the photon associated the transition, $A$ and $B$ are constants, depending on band structure. The optical absorption edge can be correlated to optical gap energy using Tauc’s equation [27]. The variation of $\ln \alpha$ as a function of photon energy is given by:

$$\alpha = \alpha_o \exp \left(\frac{h \nu}{E_u}\right)$$  \hspace{1cm} (12)

Where $E_u$ is the Urbarch energy, it can be evaluated as width of the localized states. The optical band gap can be obtained by extrapolating the linear portion of plot $(\alpha h \nu)^1/n$ versus $h \nu$ to $\alpha = 0$. The refraction index consists of real and imaginary parts ($N = n-ik$), the relation between reflectivity and refractive index is given by the equation [28]:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$  \hspace{1cm} (13)

Where $k$ is the extinction coefficient. The quality ($R+T<1$) at certain wavelength implies the existence of absorbing region. The refractive index can be expressed by the equation [29]:

$$n = \frac{4R-2}{(R+1)}$$  \hspace{1cm} (14)

The extinction coefficient can be calculated by using the equation [30]:

$$k = \frac{\alpha \lambda}{4\pi}$$  \hspace{1cm} (15)

Where $\lambda$ is the wavelength of the incident ray. The relation between the complex dielectric constant and the complex refractive index $N$ is expressed by:

$$\varepsilon = N^2$$  \hspace{1cm} (16)

It can concluded that[31]:

$$(n-ik)^2 = \varepsilon_1 - i\varepsilon_2$$  \hspace{1cm} (17)

The real and imaginary complex dielectric constant can be expressed by the following two equations respectively:

$$\varepsilon_1 = n^2 - k^2, \hspace{1cm} \varepsilon_2 = 2nk$$  \hspace{1cm} (18)

Also the finesses coefficient is given by [23]:

$$F = \frac{4R}{(1-R)^2}$$  \hspace{1cm} (19)

The optical conductivity is related to light speed and can be expressed by the equation [32]:

$$\sigma_{opt} = \frac{\alpha n c}{4\pi}$$  \hspace{1cm} (20)

RESULTS AND DISCUSSION

For analyzing the powder PVP doped with nano crystalline NaF. It observed that the pure PVP is an amorphous and the amorphousness decreases as the NaF content increases. The peak intensity increase with increasing doping concentration with average ratio (42%) as shown in figure 1. The grain size of pure NaF is (57.20 nm) at (200), but these grain sizes are
(30.10, 26.00, 22.88,) nm at (4, 8, 12) wt% respectively, and becomes (31.79 nm) at (14%) because the composition converts to another composite phase. The spacing between diffracting planes is (0.23364) nm, with lattice constant (0.46728) nm of Miller indices (200), (220),(222). The crystallite size is decreased because the effect of polymer chains lead to form NaOH after dissolved in deionized water, but floured ions connect with R+ of polymer, or the ionic bond replaced covalent bonds within polymer chain. The values of crystalline size of PVP doped with NaF nanoparticles is shown in table 1. It was appeared that no shifting in peaks obtained in pure NaF after doping PVP, that means the fluoride ion bonds is the mostly in all material. Figure 2 shows decreasing of grain size, as concentration content increase, this means that the crystalline size of the produced polymer decrease after doping.
Figure 1. X-Ray patterns of NaF doped PVP at (0, 4, 8, 12, 14) wt% and pure NaF samples
Table 1. XRD analysis results PVP doped NaF films

<table>
<thead>
<tr>
<th>NaF(wt%)</th>
<th>Relative Intensity</th>
<th>τ(nm)</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure (200)</td>
<td>‘100%</td>
<td>57.20</td>
<td>0.1471</td>
</tr>
<tr>
<td>NaF (220)</td>
<td>29%</td>
<td>38.24</td>
<td>0.2552</td>
</tr>
<tr>
<td>4 (200)</td>
<td>100%</td>
<td>30.10</td>
<td>0.2794</td>
</tr>
<tr>
<td>(220)</td>
<td>47%</td>
<td>27.76</td>
<td>0.3235</td>
</tr>
<tr>
<td>8 (200)</td>
<td>100%</td>
<td>26.00</td>
<td>0.3235</td>
</tr>
<tr>
<td>(220)</td>
<td>39%</td>
<td>24.45</td>
<td>0.3676</td>
</tr>
<tr>
<td>12 (200)</td>
<td>100%</td>
<td>22.88</td>
<td>0.3676</td>
</tr>
<tr>
<td>(220)</td>
<td>41%</td>
<td>20.37</td>
<td>0.4411</td>
</tr>
<tr>
<td>14 (200)</td>
<td>100%</td>
<td>31.79</td>
<td>0.2647</td>
</tr>
<tr>
<td>(220)</td>
<td>40%</td>
<td>30.55</td>
<td>0.2940</td>
</tr>
</tbody>
</table>

Figure 2. Grain size of crystal against of NaF doping PVP for (200),and(220) indices

Figure 3 shows the low change in FTIR transmission spectrum of PVP doped with NaF films prepared by spin coating, the labeled peaks from 0 to 14wt% correspond to Na-F mode (near over 2000cm⁻¹) stretching vibration in the oxygen containing chain polymer with change in the hydrogenated bond distribution. The integrated intensity is directly proportional to the concentration of polymer bonds with fluoride and sodium ions content. Less than (1900cm⁻¹), the peaks disappear and is more amorphous for pure PVP and glass substrate. The value of wave number is 2971cm⁻¹ for high absorbance; this means that there are mostly ionic bonds instead of hydrogenic and covalent bonds of chain polymer. The two broad absorption bands at 3054, 2971 and 2875cm⁻1 are associated with Na-F stretching modes. Thus, the FTIR result suggests the presence of Na-F bonds. The bonds of OH⁻ radicals are at (3400-3800) cm⁻¹ that is disappeared, because of forming NaOH, above 2800 cm⁻¹, there is H-bond as a result to H₂O solvent. The amorphous formation is formed from 400 to 1900cm⁻¹ that is decreased when the specimen is doping, this means that the fluoride ions occupy sites in the vacancies, and the surface becomes more smoothness, because IR measurements depend upon the smooth surface of material. The PH base is increased with NaF increasing, the peaks is between 2000 to 3000cm⁻¹ because it substitute instead of polymer chains by fluoride ions which does not have hydrogen bonds, that most of them are covalent bonds.
Figure 3. FTIR transmission spectrum of doped PVP films with different concentrations of NaF prepared by spin coating

The influence of the doping polymer on the optical properties can be explained by PVP matrix. The absorption spectral analysis showed that the optical energy band is due to the indirect allowed and forbidden optical transitions. It is shown that the highest shift in absorption wavelength is at wavelengths (226-235) nm. The absorption of light energy by polymeric materials involves transition electron in $n$ to $\pi^*$ orbital from ground state to higher energy states. These transitions need an unsaturated group in the molecule to provide the $\pi$ electron \cite{32}. When polymer coils approach each other, interchange interaction in the outside of different polymer coils may induce the slight increase of absorbance. The shift in the absorption edge from UV to visible region could be attributed to an increase in conjugation length. Figure 4 describes the curves of absorbance are close to each other, or the concentrations of NaF by using quartz cell give a good associative between the polymer chain and sodium fluoride material, such that the interaction at different concentration of solutions would disappear especially in peak point.

Figure 4. The absorbance as a function of wavelength of NaF doped PVP solutions at different concentrations
Figure 5 shows the relationship between the absorbance and wavelength in the case using the spin coating technique. It was observed that the curves was approached at 330nm, but appeared a varied curve at 300nm and generally the absorbance increase at higher doping concentration.

![Absorbance vs Wavelength](image1)

Figure 5. The absorbance as a function of wavelength of NaF doped PVP films at different concentrations prepared by spin coating technique.

Figure 6 shows the optical absorbance as a function of the wavelength of PVP doped with NaF at different concentrations by using casting technique. The shifting in absorbance curves is high at \( \lambda > 309 \text{nm} \), while there is a slight shifting in the intensity at the peak edges. The absorbance is smoothly changed with increasing doping concentration. This is because the filling of sodium and fluoride ions combined with the polymer chains which absorb the incident radiation at the shortest wavelengths by the free electrons. So chemically, a great change in the structure of polymer is occurred \[13, 33\]. The difference among three types of depositions lead to a slight change of absorbance because of different technique, which depend on the circumstances of deposition.

![Absorbance vs Wavelength](image2)

Figure 6. The absorbance as a function of wavelength of NaF doped PVP films at different concentrations prepared by casting technique.
The relationship between the reflectance and wavelength is described in figure 7; there is a low change in the position of peak edge for all samples. The reflectance increases with increasing the additives of sodium and fluorine ions in the film, but the lowering of the curves is slightly decreased as wavelength increase. This result means that there is a clear change in the structure of polymer because of shifting curves at different concentrations of casting deposition.

![Figure 7. The reflectance as a function of wavelength of NaF doped PVP films at different concentrations](image1)

Figure 7. The reflectance as a function of wavelength of NaF doped PVP films at different concentrations

Figure 8 shows an optical transmittance spectrum as a function of incident wavelength of NaF doped PVP films. The transmittance percent decreases with increasing ions concentration, this is because of layer form of ionic bonds between polymer chains and additives that decrease the transmitting of the incident light especially at the shortest wavelengths. The electron in the outer orbits can be travel to the higher energy levels and have occupied vacant positions of energy bands. Thus part of incident light does not penetrate through it. However the undoped PVP have no free electron and the conduction band need photon with high energy, and then it has a high transmittance.

![Figure 8. The transmittance for NaF doped PVP films as a function of wavelength at different concentrations](image2)

Figure 8. The transmittance for NaF doped PVP films as a function of wavelength at different concentrations
The gradient of the absorption coefficient is occurred from high photon energy to the low photon energy that is small. This means that the possibility of electron transition is little, because, the energy is not sufficient to move the electron from the valence band to conduction band \((h\nu<E_g)\). These variations are shown in figure 9. It was observed that at high energy, absorption is a great and the forbidden energy gap is less \(^{[13]}\). It is expected that, indirect transition of electron occur at low absorption coefficient and the electronic momentum is maintained with assistance of photon. The energy of incident photon is greater than the forbidden energy gap \(^{[23]}\).

![Figure 9. The absorption coefficient of NaF doped PVP films as a function of photon energy](image)

Figure 9. The absorption coefficient of NaF doped PVP films as a function of photon energy

Figure 10 shows the relationship between absorption edge \((a\nu)^{1/2}\) for casting material as a function of photon energy, at extended of the curve to the values of \((a\nu)^{1/2}=0\), to get indirect allowed gap transition.

![Figure 10. \((a\nu)^{1/2}\) vs. \(\nu\) plots of NaF doped PVP films for different dopant concentrations with energy gap of allowed indirect transitions](image)

Figure 10. \((a\nu)^{1/2}\) vs. \(\nu\) plots of NaF doped PVP films for different dopant concentrations with energy gap of allowed indirect transitions

From figure 11, it was observed that the values of energy gap decrease with increasing of the weight percentage of added salt. This attributes to the creation of the site levels in forbidden indirect energy gap lead to facilitate the crossing of electron from the valence band to the local levels of conduction band \(^{[33, 34]}\). In other meaning the electronic conduction depends on added impurities.
Figure 11. \((\alpha h)^{1/3} vs. h\nu\) plots of NaF doped PVP films for different dopant concentrations with energy gap of forbidden indirect transitions

Fig.12 shows the values of finesses coefficient against wavelengths at different concentrations of NaF doped PVP. It was observed that \((F)\) values decrease from 335 to 680 nm wavelengths. The position of the peaks spectrum is slightly shifted especially at the greatest concentration of doping. This means that there is a slight change in polymer structure as a result of doping. Also the finesses coefficient increases with increasing in doping percentage because of doped additives lead to changing in reflectance which \((F)\) is dependent on \((R)\), as described in equation (19).

The real dielectric depends on \((n^2)\) and \((k^2)\), but the imaginary depends on \((k)\) and \((n)\).

The real and imaginary dielectric constant \((\varepsilon_1, \varepsilon_2)\) for (PVP-NaF) have been calculated from equation (18), the figures 13 and 14 show the change of these constants with wavelengths. The values of real are high with respect to imaginary dielectric constant.
The real dielectric constant for (PVP-NaF) films as a function of incident wavelength. Figure 13.

The imaginary dielectric constant for (PVP-NaF) films as a function of incident wavelength. Figure 14.

The optical conductivity decreases suddenly after 300nm wavelength as shown in figure 15. It was observed an increase in optical conductivity as increasing in doping percentages. This means that the generation of sodium and flouride ions percentages increases the contribution of electron transitions between the valence and conduction bands, leads to reduction of energy gap as a result of sit level generation. This optical conductivity becomes constant after about 700nm for every concentration. Figure 15.
Figure 16 describes the change in refraction index for (PVP-NaF) as a function of wavelength that have occurred an increase in \( n \) with increasing the doping percentages. This is because of amorphous crystalline substance of the pure polyvinylepolypirodone with low density that increases with added filler. The refraction indexes decreases at the longest wavelengths and increases at the greatest doping concentration, because the transmission of the longest wavelength is more.

![Figure 16. The refraction index of NaF doped PVP films as a function wavelength at different concentrations](image)

The change of extinction coefficient as a function of wavelength is shown in figure 17. It was noted that \( k \) have the lowest value at low concentration, and this attributed to increase the absorption coefficient with increased the doping percentages of salt ions solute in distilled water. The extinction coefficient is high at the longest wavelengths and at high concentrations.

![Figure 17. The extinction coefficient for NaF doped PVP films as a function of wavelength](image)

Figure 18 shows the value of energy gap for the allowed indirect transition that is greater than the forbidden indirect transition for all concentrations, because of the different generation of site levels between valence and conduction bands depends on \( m \) that equal to 2 or 3 .The energy gap is inversely proportional to weight percentage, because the increasing of doping generates a new energy level between valence band and conduction band. These two types of energy gaps are between 3.65 to 3.13eV. It is due to the quantum confinement effect exerted by the nanocrystals.
Figure 18. The dependence of $E_g$ on doping levels for allowed and forbidden indirect transitions

To combine the peak edge points, figure 19 describes the variations between the values of spectra peaks of the optical parameters. It was observed that the edge spectrum peak values of transmittance, refraction index, and reflectance, are constant, while the peak values of extinction coefficient is increased, but the finesse coefficient and absorbance are decreased as doping percentages of NaF increasing. These variations depend upon the type of optical parameter that has a maximum value, in light of the wavelength.

Figure 19. The edge spectrum peaks against doping concentration of NaF

CONCLUSIONS

It was concluded that:

1. The grain size of the crystalline decreases as doping of NaF content increase, and there are converted from doping phase to composite phase of the film.
2. The amorphousation decrease as the doping of polymer increase.
3. The fluoride ion bonds mostly occupy the vacancies between the polymer chains that change the optical parameters.
4. The absorbance, absorption coefficient, extinction coefficient, fineses coefficient, refraction index and reflectance of NaF doped PVP films increase with increasing of doping percentages accept the transmittance.
5. The energy gap of indirect (allowed and forbidden) transition decrease with increasing of doping.
6. The dielectric constant (real, imaginary) increases with increasing doping content.
7. The low percent of NaF doping have high influence on the physical properties and type of bonds in polymer chains.

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