

Preparation of Chloro Penta Amine Cobalt (III) Chloride and Investigate its Influence on the Structural Properties and Acoustical Parameters of Polyvinyl Alcohol

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Abstract

Chloro penta amine Cobalt (III) Chloride $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was prepared then characterized by FTIR and XRD . The obtained results indicated the formation of Orthorhombic $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ nano particles of ≈ 28.75 nm size .Polymeric films based on polyvinyl alcohol PVA doped with Chloro penta amine Cobalt (III) Chloride $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ at different weight percent ratios were prepared using the solvent cast technique. The structural properties of these polymeric films were examined by XRD, FTIR and SEM studies. The complexation of the additive with the polymer was confirmed by FTIR and SEM studies. The XRD pattern revealed that the amorphousness of PVA polymer matrix increased with raising the $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ content. Ultrasonic pulse technique of variable frequency (25, 30, 35 and 40) kHz were performed to study the influence of ultrasonic frequency on the mechanical properties of PVA/ $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ composite.

Some properties such as ultrasonic velocity, acoustic impedance ,bulk modulus and transmittance and relaxation amplitude were found to be decreasing with frequency while absorption coefficient and compressibility were increasing with frequency .Results showed that ultrasonic wave made degradation to the randomly coiled polymer chains ,when ultrasonic frequency increase there were more degradation that increasing the number of un-tied chains as a result of absorbing composite ultrasonic waves ,for this reason it could be pointed that PVA/ $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ composite as a good ultrasonic absorber. It was found that there was significant relationship between ultrasonic velocity and material properties.

Keywords: polymer composite; solution casting method; acoustical parameters; nanoparticles.

1. Introduction

Composites have good potential for various industrial fields because of their excellent properties such as high hardness, high melting point, low density, low coefficient of thermal expansion, high thermal conductivity, good chemical stability and improved mechanical properties such as higher specific strength, better wear resistance and specific modulus [1]. Polymer

systems are made up of chemical bonds along the polymer chains and physical bonds across the polymer chains, former includes covalent bonds and the latter results from hydrogen bonding, dipolar bonding or van der Waals forces. The type of physical bonding has huge effects on the physical properties of polymers [2].

Ultrasonic technique is one of the basic non-destructive methods for evaluation of materials and structures. A

significant part of every ultrasonic inspection is the way in which the ultrasonic energy is transferred between the transducer and the tested object. [3] Some of mechanical properties of different polymers were carried by some workers using ultrasonic technique [4]. The absorption of ultrasound in polymer systems is governed by local modes of motion and cooperative because of the existence of strong intermolecular interaction within the polymer. Ultrasonic attenuation measurements are a standard method used to assess the effects of material degradation [5]. Al-bermany *et.al*, (2013) [2] prepared CMC/PVA composite films by casting method and studied the mechanical properties of the composites by sound waves. Ultrasonic velocity, compressibility, acoustic impedance and bulk modulus, were measured and calculated at fixed frequency ($f = 2.5$ KHz). Also, the absorption coefficient, transmittance and the reflected pressure ratio of the sound were calculated. The results revealed that, there is considerable relationship between ultrasonic velocity and material properties also the results showed that PVA is affecting on the density and the absorption of the ultrasonic waves by the composites samples.

The effects of various parameters like ultrasound intensity, frequency of ultrasonic waves and polymer concentration have been investigated[6].

Polyvinyl alcohol (PVA) is a semi crystalline polymer whose hydroxyl groups produce inter- and intra-molecular hydrogen bonding [7]. These hydrogen bonding assist in the formation of polymer [8]. Certain physical properties resulting from crystal-amorphous interfacial effects[9].

Coordination compounds or metal complex are metal ions surrounded by ligands. Ligands are either anions or molecules that can donate electrons into the d-orbitals of the metal ion and form a bond. An example of common ligands is chloride ion. The metal ions that form coordination compounds are from a group of metals known as transition metals. These metals have more than one oxidation state. This property allows the transition metals to act as Lewis acids [10]. The metal complex used in this paper is Chloro pentammine cobalt (III) chloride which is a paramagnetic compound [11]. It decomposes upon heating above 150 °C. Its solubility is 0.4 g per 100 ml at 25 °C [12].

In this paper an effort has been made to study the effect of addition of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ on structural, optical properties and acoustical parameters of polyvinyl alcohol by FTIR, XRD, SEM and velocity of sound instrument SV-DH-7A/SVX-7. The results obtained from these measurements have been analyzed and discussed to be utilized in deferent industrial applications.

2. Experimental Work

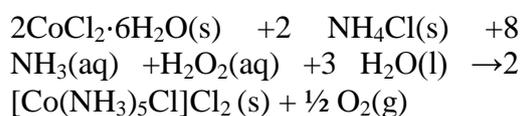
2.1 Preparation of chloro penta amine cobalt (III) chloride

$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

Chloro penta amine Cobalt (III) Chloride $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was prepared by the procedure reported in [13].

1.7 g of Ammonium Chloride NH_4Cl was completely dissolved in ~10 ml of concentrated ammonia NH_3 in a 400 ml beaker. With continuous stirring, 3.3 g of cobalt (II) chloride CoCl_2 was add in small portions. With continued stirring of the resulting brown slurry, 2.7 ml of 30% Hydrogen Peroxide H_2O_2 was added slowly. After the effervescence had stopped, ~10 ml of

concentrated Hydrochloric acid HCl was added slowly. With continued stirring, the mixture heated on a hot plate and maintained at 85°C for 20 minutes. Then, the mixture cooled to room temperature in an ice bath and filtered (using a Buchner funnel). The crystals of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ were washed with 5-6, 5 ml portions of ice water (distilled water cooled in ice) and then 5-6, 5 ml portions of Ethanol $\text{C}_2\text{H}_6\text{O}$. All chemicals used in preparation of chloro penta amine cobalt (III) chloride were purchased from Sigma –Aldrich.



2.2 Sample Preparation

Polyvinyl alcohol (PVA) with molecular weight (30,000-70,000) was purchased from Aldrich. The PVA/ $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ composites films were fabricated by the solvent casting technique. At first a PVA solution was prepared by adding distilled water to solid PVA $(-\text{C}_2\text{H}_4\text{O})_n$ then stirred by magnetic stirrer for 2 h. at 70 °C. The necessary weight fractions of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ were first dispersed in distilled water with a magnetic stirrer for 1 h. then it was added gradually into the polymeric emulsion with continuous stirring and kept under string for 1 h. Finally, the solution was poured on to cleaned Petri dishes and allowed to evaporate slowly at room temperature for a week. After drying, the films were peeled from Petri dishes and kept in vacuum desiccator until use. The thickness of the obtained films was in the range of $\approx 120\text{--}150 \mu\text{m}$.

X-ray diffraction scans were obtained using DX-2700 Diffractometer using Cu $\text{K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 kV and 30 mA, Data

was taken for the 2θ range of 5-50°. Measurements were carried out at room temperature. The diffracted intensity was measured as a function of the reflection angle automatically by the X-ray diffractometer. The various peaks obtained in the diffraction pattern gave the information about the size and interplanar spacing of the compound. A FTIR was recorded on Fourier Transform Infrared spectrophotometer, Shimadzu, model IR-Prestige 21, using KBr pellets. FT-IR spectra of the samples were obtained in the spectral range of $(4000\text{--}400) \text{ cm}^{-1}$. The measurement of velocity (v) was based on the accurate determination of the wavelength (λ) in the medium. Ultrasonic measurements were made by pulse technique of sender-receiver type (SV-DH-7A/SVX-7 velocity of sound instrument) with different frequencies (25, 30, 35 and 40) kHz. The morphology of the films was characterized by scanning electron microscope using Bruker Nano GmbH, Germany, operating at 5 kV accelerating voltage.

3. Theory

Relaxation processes are the primary mechanisms of energy dissipation for an ultrasound beam transverse a substance. These processes involve (a) removal of energy from the ultrasound beam and (b) eventual dissipation of this energy primarily as heat. Ultrasound is propagated by displacement of molecules of a medium into regions of compression and rarefaction. This displacement requires energy that is provided to the medium by the source of ultrasound. As the molecules attain maximum displacement from an equilibrium position, their motion stops, and their energy is transformed from kinetic

energy associated with motion to potential energy associated with position in the compression zone. From this position, the molecules begin to move in the opposite direction, and potential energy is gradually transformed into kinetic energy. The maximum kinetic energy (i.e., the highest molecular velocity) is achieved when the molecules pass through their original equilibrium position, where the displacement and potential energy are zero. Actually, the conversion of kinetic to potential energy (and vice versa) is always accompanied by some dissipation of energy. Therefore, the energy of the ultrasound beam is gradually reduced as it passes through the medium [14].

The existence of sound waves is always restricted to a material medium, the nature and the structure of which determines the particular parameters of their propagation [15]. Sound absorption in a plane harmonic sound wave is characterized by an exponential decrease of amplitude with traveling distance [16].

The absorption coefficient α was calculated from Beer–Lambert law equation [17]:

$$A/A_0 = e^{(-\alpha x)} \dots\dots\dots (1)$$

Where (A_0) is the initially amplitude of the ultrasonic waves, (A) is the wave amplitude after absorption.

The transmittance (T) is the fraction of incident wave at a specified wavelength that passes through a sample was calculated from the following equation [18]:

$$T = I/I_0 \dots\dots\dots (2)$$

The relaxation amplitude of ultrasonic wave is calculated from the following

equation where (f) is the frequency [19]:

$$D = \alpha/f^2 \dots\dots\dots (3)$$

The method of measuring the speed of ultrasound is by measuring the thickness of the sample and the time it takes inside the sample [20]:

$$v = x/t \dots\dots\dots (4)$$

Where (x) is the sample thickness measured by digital vernier; (t) is the time that the waves need to cross the sample.

As known from basic physics the characteristic variables describing the propagation of a monochromatic wave in time and space are frequency f or period T and wavelength λ given by:

$$\lambda = v/f \dots\dots\dots (5)$$

Where, v is the wave propagation velocity (also termed sound velocity or speed of sound) [21].

The acoustic impedance of a medium which is a material property is calculated by the following equation [22]:

$$Z = \rho v \dots\dots\dots (6)$$

Where Z acoustic impedance [$\text{kg}/(\text{m}^2\text{s})$] = [Ray], ρ density of transmitting medium [kg/m^3], and v is sound velocity [m/s] [23].

The bulk modulus B , is defined as the pressure increase needed to decrease the volume; its base unit is the Pascal (Pa.) is calculated by following equation [24]:

$$B = \rho v^2 \dots\dots\dots (7)$$

Compressibility β is a measure of the relative volume change of a fluid or solid as a response to a pressure (or mean stress) change, it was calculated by the following equation [25]:

$$\beta = (\rho v^2)^{-1} \dots\dots\dots (8)$$

4. Results and discussion

4.1 X-ray diffraction (XRD)

A typical XRD pattern for [Co(NH₃)₅Cl]Cl₂ is shown in Figure 1 . It can be seen that many sharp peaks were observed in the X-ray profile. The crystalline nature of synthesized [Co(NH₃)₅Cl]Cl₂ was observed by the various sharp crystalline peaks in the XRD pattern. Figure 1 shows diffraction peaks at 15.8313°, 25.6011°, 32.6249° and 34.8279° corresponding to the (011), (221), (122) and (040) planes [Co(NH₃)₅Cl]Cl₂ which are indexed to Orthorhombic structure according to the literature data of Materials Data, Inc. [26]. The average

particle size could be calculated using the first sphere approximation of Debye–Scherrer formula [27]:

$$D = \frac{0.9\lambda}{b \cos(\theta)} \dots\dots\dots (9)$$

Where D is the average diameter of the crystals, λ is the wavelength of X-ray radiation, and b is the full width at half maximum intensity of the peak (FWHM). The obtained particle size of [Co(NH₃)₅Cl]Cl₂ was around 28.75 nm. The structural parameter such as diffraction angle 2θ (deg.), interplaner d (Å), relative intensity (I/I₀) and full width at half maximum FWHM (deg.) are presented in table 1.

Table 1: Diffraction angle 2θ (deg.), interplaner d (Å), relative intensity (I/I₀) and full width at half maximum FWHM (deg.).

Material	2 θ (deg.)	d(Å)	I/I ₀	FWHM (deg.)
[Co(NH ₃) ₅ Cl]Cl ₂	15.7313	5.59343	100	0.2763
	25.6011	3.47674	60	0.2046
	33.4837	2.6741	36	0.2359
	34.7279	2.5739	43	0.2143

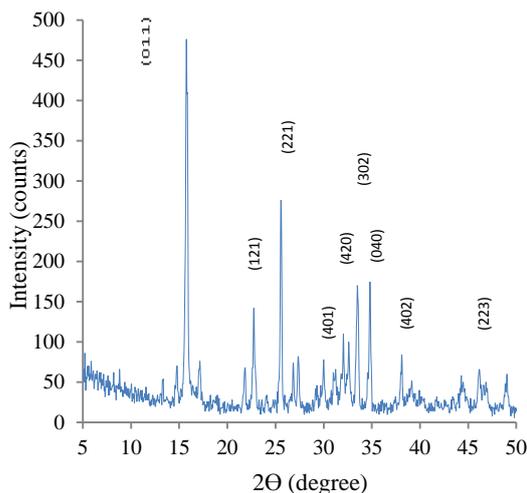


Fig.1: XRD pattern for [Co(NH₃)₅Cl]Cl₂ powder.

PVA is semi-crystalline polymer as indicated from the XRD patterns

illustrated in Figure 2 (pure). The crystalline nature of this polymer was emphasized by the diffraction peaks at 2θ = 19.8°, 41.05° assigned for PVA, with a hallow shoulder at 2θ = 23° representing the amorphous phase in PVA [28]. On a molecular level, the crystalline nature of PVA results from the strong intermolecular interactions between layered PVA chains through hydrogen bonding. Meanwhile, weaker Van Der Waal’s forces operate between double layers. This folded chain structure leads to small ordered regions (crystallites) scattered in unordered amorphous domains [28] as indicated by the XRD pattern shown in Figure 2 (pure) . Moreover, PVA structure enriched with hydroxyl (OH) groups, which are small enough to fit into the lattice without disrupting the

carbon backbones chains [29]. It has been found that the diffraction peak of pure PVA decreases in intensity with addition of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ concentration and also broad nature has been found to be increased. This could be due to the disruption of the PVA crystalline structure by the additive [30] or in other words the interactions between PVA and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ lead to the decrease of the intermolecular interaction between the PVA chains [31]. Similar results have been obtained for the system PVA- H_3PO_4 [32], PVA- LiCF_3SO_3 [33] and PVA-CuI [27]. This is in agreement with Hodge et al. [34] criterion, which established a correlation between the intensity of the peak and the degree of crystallinity. No sharp peaks pertaining to $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ appeared in the PVA/3 wt.% concentration of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ composites, indicating the complete/partial dissolution of the additive in the polymer matrix [30]. Also, figure 2 (6 wt.% and 9 wt.%) shows obvious presence of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ peaks, especially (011) plane (which is used to find the grain size of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ particles), that means a growth of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ crystallite particles in the polymer matrix. Figure 2 (9 wt.%) shows that the peaks belongs to $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ observed with lower intensity. This behavior is similar to other PVA composites [27]. From above, it can be concluded that $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ has retained its structure even though it is being capped with PVA after formation of composites, that agrees with (Aashis S. Roy et.al 2013) [35].

Equation (9) was used to find particle size of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ particles according to the preferred direction plane (011) for PVA / 6 wt.% and 9 wt.% of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ composites

film which were around 44.63 nm and 19.76 nm respectively. The apparent fluctuation of the particle size of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ may be attributed to the particles aggregation in the samples rich with $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ [36].

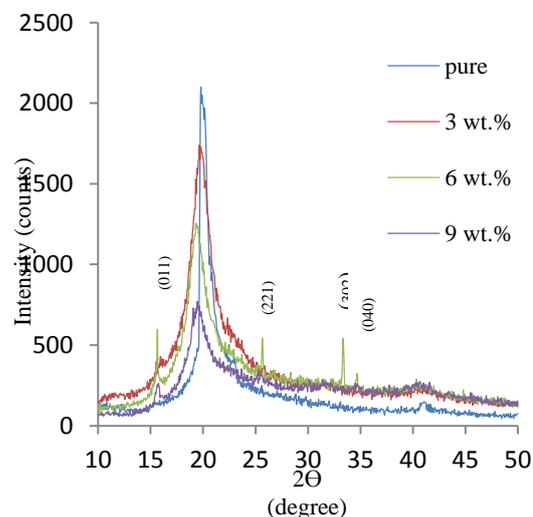


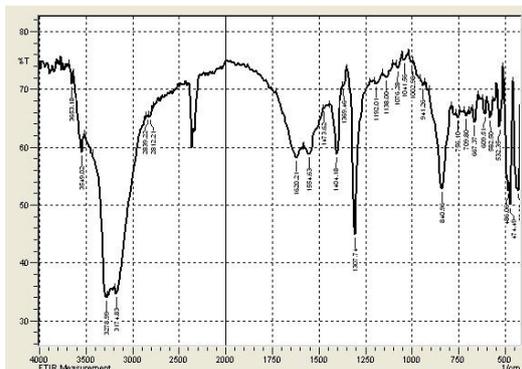
Fig. 2: XRD pattern for PVA/ $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ composites film with different concentrations.

4.2 Fourier transform infrared spectroscopy (FTIR)

FTIR spectroscopy is an important technique for the investigation of polymer structure, as it provides information about the complexation and interactions between the various constituents in the polymer complexes [37].

FTIR was recorded on Fourier Transform Infrared spectrophotometer, Shimadzu, model IR-Prestige 21, using KBr pellets. FTIR spectra of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ show peaks at 3278, 1620, 1307, 840 and 486 cm^{-1} which correspond to the NH_3 stretching vibration, degeneration deformation vibration of NH_3 ligand, symmetric deformation vibration of NH_3 , rocking vibration of NH_3 and Co-NH_3 stretching vibrations respectively. Also Co-Cl peak appeared around 840 cm^{-1} . The FTIR characterization agreed with

Mohd. Hanief Najar and Kowsar Majid (2013) [38] who investigated $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. The only functional group of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ is N-H which was around $3100\text{-}3500\text{ cm}^{-1}$. Figure 3 represents the FTIR spectrum of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. The N-H is between $(3161.34 - 3279.1)\text{ cm}^{-1}$.



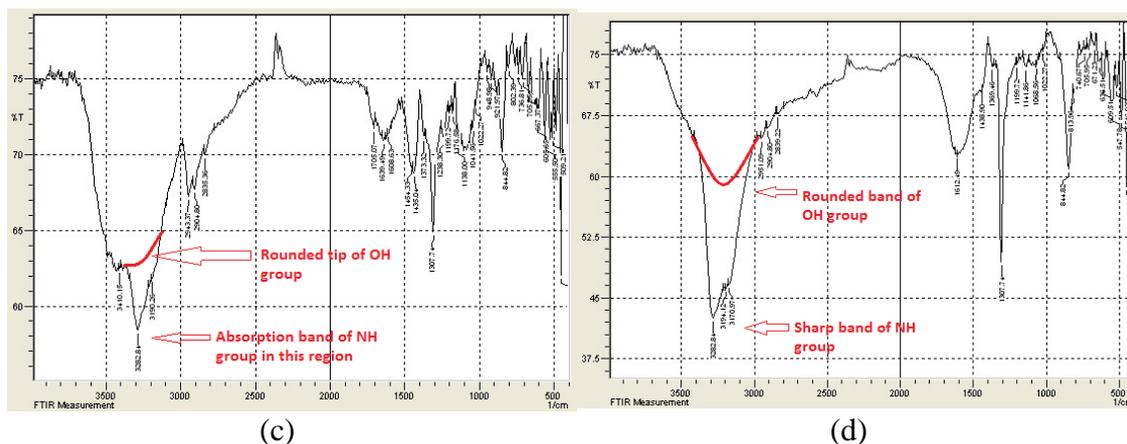


Fig.4: FTIR graph of PVA / $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ composites film with different concentrations (a) pure PVA, (b) 3 wt.% (c) 6 wt.% and (d) 9 wt.%.

4.3 Scanning electron microscope (SEM)

Depending on the amount of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ present in the polymer matrix, the morphology of the PVA/ $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ composite will vary and greatly influence its properties. Scanning electron micrographs of pure PVA, and PVA/ (3, 6, 9) wt. % of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ composites are given in Figure 5 (a, b, c and d) respectively. Very distinguishable changes have been observed from pure PVA, to low, intermediate and high concentrations of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. Pure PVA showed smooth surface of the PVA film. Tiny and very few agglomeration of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ particles was observed in Figure 5 (b), which contained 3 wt.% of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. Thus suggesting that $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ particle can be well dispersed in PVA matrix and the fabricated film can be considered as homogenous and dense with no obvious phase separation. With 6 wt.% concentration of

$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (figure 5 c), an agglomerations with different size (about 4.2-1.8 μm) are appeared, while in PVA/ 9wt.% of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ prepared samples (figure 5d) there are some semi-tori (with different sizes in the range of about 0.178-0.625 μm) appeared as bright spots in all of them with different degrees of roughness. These showed uniform distributed bright spots on the backscattered images shown in the figure 5b,c and d, seem to be agglomerates of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ particles, which increase with increasing the concentration of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. The degree of roughness of the film surface increases with increase of the content of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$. This indicates agglomeration of the $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ in the host matrix and this may confirm the interaction and complexation between the $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and the PVA, also refers to growth of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ particles [40]. These results are in agreement with XRD and FTIR results.

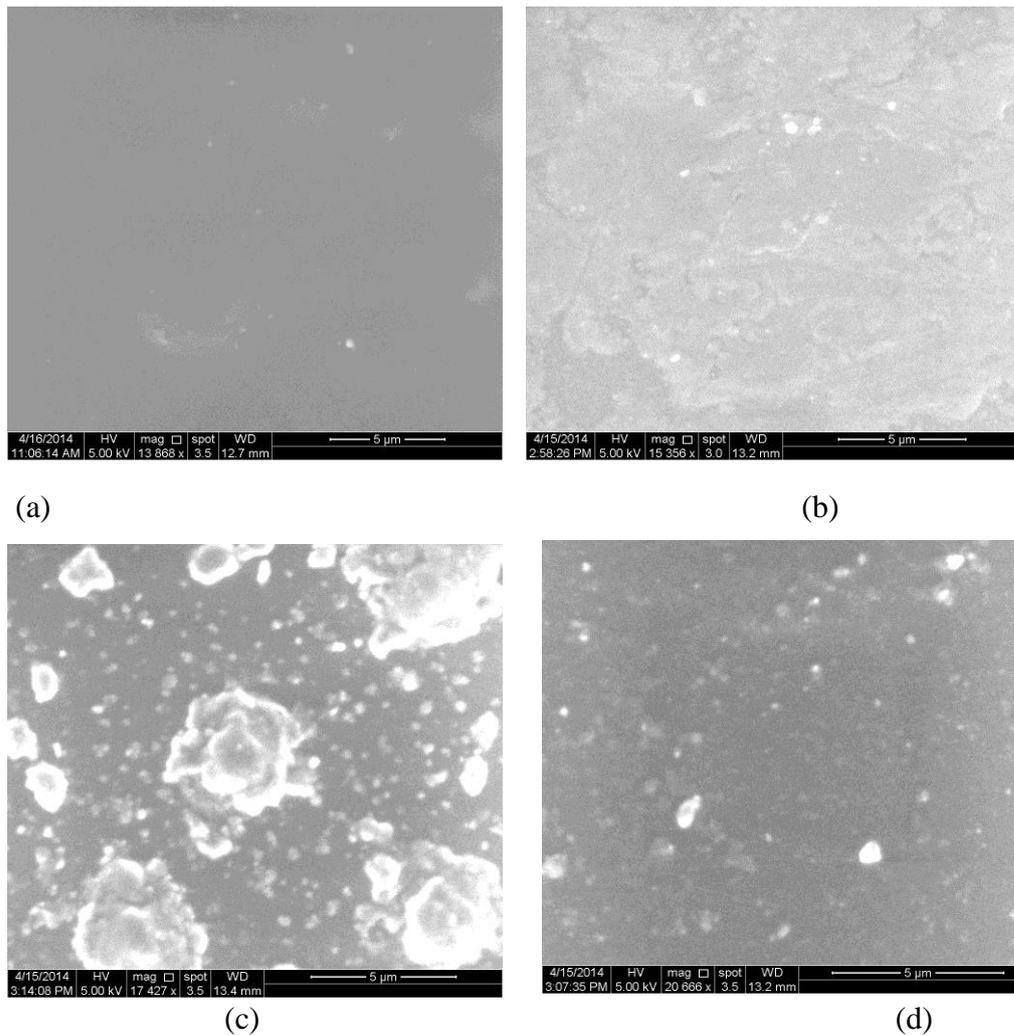


Fig. 5: SEM photographs for PVA/ $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ composite films with different concentration of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$: (a) 0 wt.%,(b) 3wt.%,(c)6wt.% and (d) 9wt.%.

4.4 Acoustical parameters

Since the density is defined as mass per unit volume and the volume is fixed (in this study) ,so the density is increasing with the concentration .Also, the increas of density with concentration is the result of the tight interaction between the metal complex and polymer molecules as shown in figure 6. Ultrasonic velocity (calculated by equation 4) versus concentration of metal complex composites at different ultrasonic frequencies is shown in figure 7. The velocity is decreasing with the increase of concentrations, this could be attributed to the interaction causing association between polymer and metal

complex molecules. During the propagation of ultrasonic wave through the composite, periodical changes are occurring. Because of wave pressure, molecules are flowing into vacancies in the lattice during compression phase and to return to their original positions in the lattice during rarefaction, so when concentration increases the velocity decreases [41]. Also, adding metal complex forms a network between polymer chains acting as restriction of the ultrasonic waves leading to more ultrasound wave attenuation [42] so, Ultrasonic wave velocity decreases with concentration. Figure 7 show that, the velocity is decreasing with frequency. The ultrasonic wave causes degradation in

polymer chains which is attributed to decrease in the number of tie-chains and leads to slight decrease in tensile properties [41]. Since frequency related to energy, degradation increases and number of tie chains are reduced, so, velocity decreased [43].

Polymer molecules absorbed the sound waves according to Lambert-Beer Law which is based on concentration [44] rather than as shown in figure 8 Absorption coefficient is increases with concentration, because the attenuation of the ultrasonic wave is determined mainly by the size, shape, and particles distribution which is attributed to the fact that when metal complex concentration increase there will be more molecules in polymer this lead to more attenuation against wave propagation. The attenuation can be attributed to the friction and heat exchange between the particles and the surrounding medium as well as to the decay of the acoustic wave in the forward direction due to scattering by the particles [45]. This behavior is similar to that given by other researchers for other polymers [46]. As an ultrasound beam penetrates a medium, energy is removed from the beam by absorption, scattering, and reflection. As with x-rays, the term attenuation refers to any mechanism that removes energy from the ultrasound beam. Ultrasound is “absorbed” by the medium if part of the beams energy is converted into other forms of energy, such as an increase in the random motion of the molecules. Ultrasound is “reflected” if there is an orderly deflection of all or part of the beam. If part of an ultrasound beam changes direction in a less orderly fashion, the event is usually described as “scatter” [14], so adding $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ enhancing absorption coefficient of PVA. Also it can be seen from figure 8 that the

absorption coefficient of the ultrasonic waves are increasing with frequency ,because when the frequency increases, the vibration is increasing leading to increase and decrease in pressure relatively to atmospheric pressure . The compression and rarefaction are decreasing by displacement of the molecules from their equilibrium positions so as a result to high frequency, there are more degradation to polymer chains, then increasing in absorption by composite which agrees with decreasing transmittance [47].

Little attenuation occurs in a medium means, this medium is very good transmitter and vice versa [14]. The transmittance is calculated by equation 2, is decreasing with $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ concentration as shown in figure 9. The molecules of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ fill the vacancies between polymer chains and restricted these chains, so ultrasonic wave faces a strong resistance to follow through the composite [48]. Figure 9 clarifies that transmittance are decreasing with frequency. Since frequency related to energy, so, high frequency causes more degradation that introduces un tie chains .Ultrasonic wave transfer as compression and rarefaction, the un tie chains play an important role of dumping the propagation of ultrasonic wave which decreases transmittance [43].

The relaxation amplitude, calculated by equation 3, is found to be increasing with increasing concentration as in figure 10. This is attributed to the displacement of excited molecules which became small, because the moment of inertia of molecules is reduced [48].

Since wavelength is inversely related to the frequency (indicated from equation 5) the wavelength of ultrasonic wave decreases with

frequency as shown in figure 11, also it can be noticed that, the ultrasonic wavelength is decreasing with $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ concentration. This behavior is related to the closeness of the molecules at high concentration so there are more interaction between neighbored molecules and there are more attenuation according to compression and rarefaction of wave propagation by these molecules [2].

The acoustic impedance, calculated by equation 6, is decreasing with concentration as shown in figure 12; this result agreed with other researcher's [49]. From equation (6), acoustic impedance follows the same behavior of ultrasonic velocity because it is more effective than density which has small variation with respect to velocity variation [50]. When concentrations increases, rearrangements of the polymer network is occurs, by breaking chains bonds. It was probably the clusters grew and contacted with each other in the composites resulting in a gradual change from small metal complex clusters to larger clusters with stronger hydrogen bonds which were confirmed by SEM results [51]. Also from figure 12, it can be noticed that, the acoustic impedance is decreasing with frequency because of the polymer chains degradation which is combined with high frequency. This degradation is resisting the transferring of the ultrasonic wave and gave the composite good acoustic impedance [43].

Bulk modulus can be calculated by equation 7. Bulk modulus is decreasing

with the concentration of metal complex as it is shown in figure 13, this is attributed to the fact that metal complex molecules make entanglement interaction to the polymer chains forming a network [52] which can be indicated from the reduction of polymer crystallinity [53]. This result agree with XRD observation, also low concentration of metal complex means more vacancies that coiling polymer chains randomly to be close to each other giving the composite higher Bulk modulus [51]. While the compressibility, as calculated using equation 8, is increasing with increasing concentration shown in figure 14, this is the same behavior found by other researches [42]. This behavior is caused by the propagation of ultrasonic waves which made polymer chains are adjacent to each other which change conformation and configuration of these molecules producing more compression for these molecules [54]. Sequentially with increasing frequency, the compressibility is also increasing. The bulk modulus is inversely related to the compressibility as it clear by the equations (7) and (8) respectively, so Bulk modulus is decreasing with frequency as it is seen in figure 14, this result is in agreement with the fact that the velocity of ultrasound is determined principally by the compressibility of the medium. A medium with high compressibility yields a slow ultrasound velocity, and vice versa [14] and in another hand it agreed with previous result in this study.

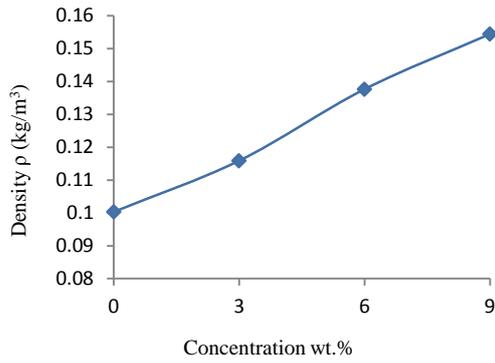


Fig. 6: The variation of density versus the concentration of metal complexes.

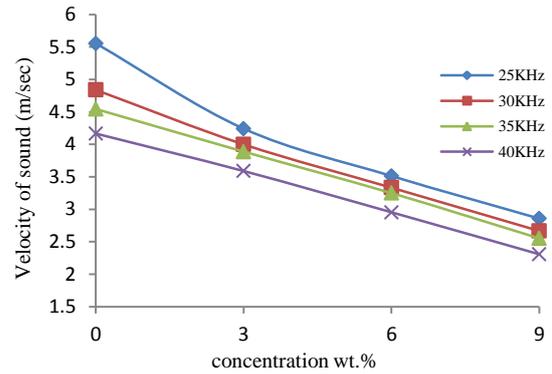


Fig. 7: The variation of ultrasonic velocity versus $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ concentration for PVA/ $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ composites.

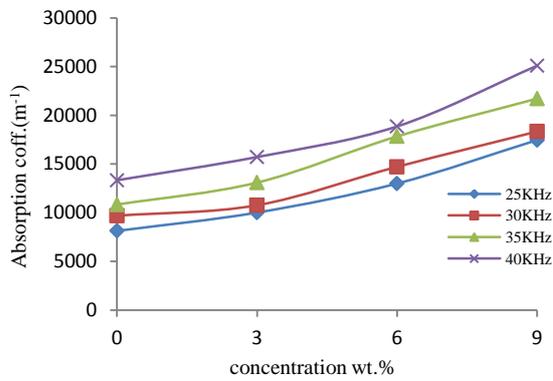


Fig. 8: The variation of absorption coefficient versus $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ concentration for PVA/ $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ composite.

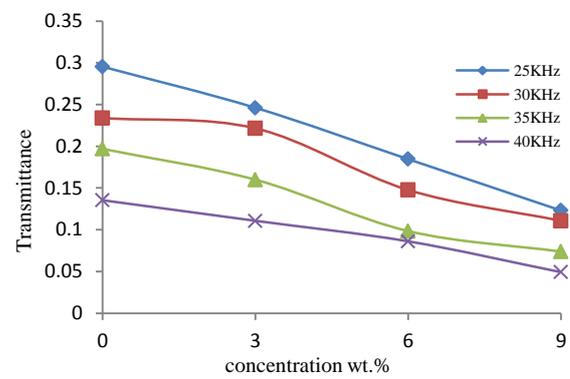


Fig. 9: The variation of transmittance versus $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ concentration for PVA/ $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ composites.

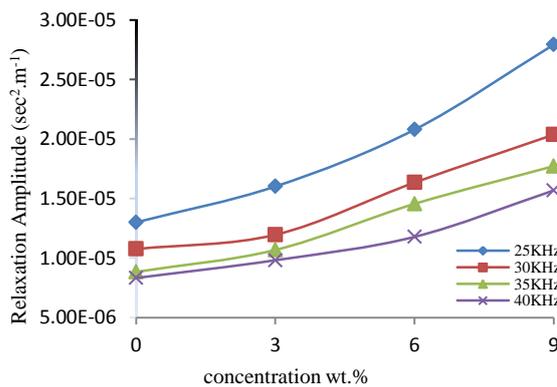


Fig. 10: The variation of relaxation amplitude versus $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ concentration for PVA/ $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ composites.

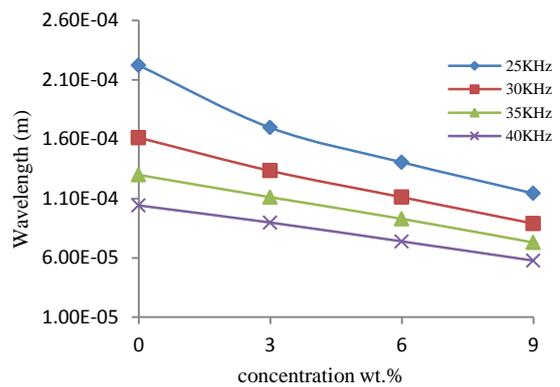


Fig. 11: The variation of wavelength versus $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ concentration for PVA/ $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ composites.

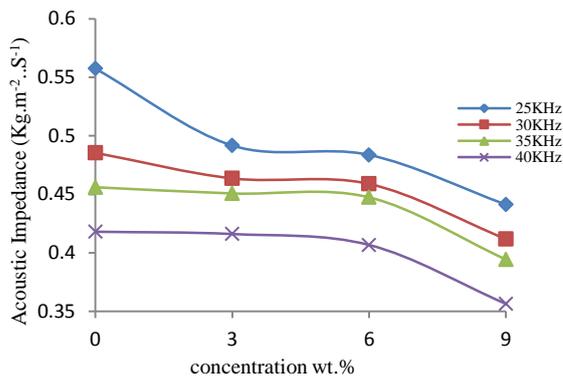


Fig. 12: The variation of acoustic impedance versus $[Co(NH_3)_5Cl]Cl_2$ concentration for PVA/ $[Co(NH_3)_5Cl]Cl_2$ composites.

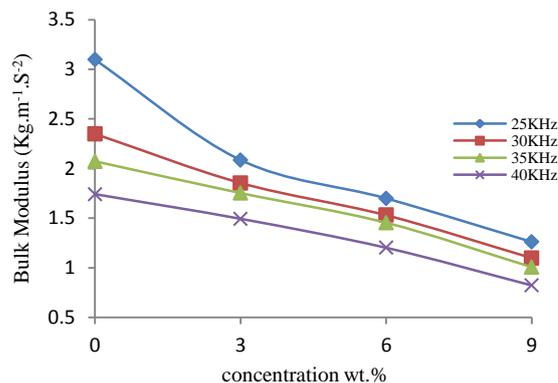


Fig. 13: The variation of Bulk Modulus versus $[Co(NH_3)_5Cl]Cl_2$ concentration for PVA/ $[Co(NH_3)_5Cl]Cl_2$ composites.

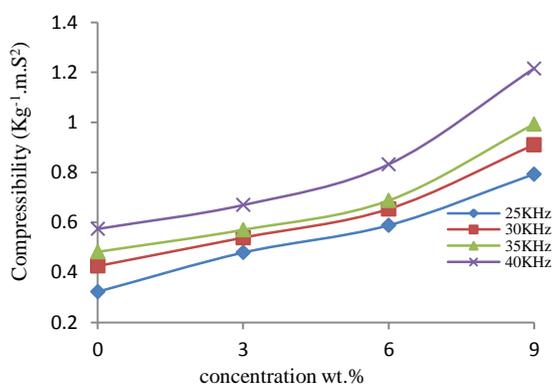


Fig. 14: The variation of Compressibility versus $[Co(NH_3)_5Cl]Cl_2$ concentration for PVA/ $[Co(NH_3)_5Cl]Cl_2$ composites.

5. Conclusions

Polymer films based on PVA with different concentrations of $[Co(NH_3)_5Cl]Cl_2$ were prepared using solvent casting technique. XRD revealed that, the synthesized $[Co(NH_3)_5Cl]Cl_2$ was indexed to Orthorhombic structure. The formation of an intermolecular interaction and complexation between PVA and $[Co(NH_3)_5Cl]Cl_2$ has been confirmed using XRD, FTIR, SEM. The presence of $[Co(NH_3)_5Cl]Cl_2$ leads to decrease the velocity because, $[Co(NH_3)_5Cl]Cl_2$ forms a network between polymer chains acting as restriction of the ultrasonic waves. $[Co(NH_3)_5Cl]Cl_2$

enhances the ultrasonic absorption coefficient of PVA, making PVA/ $[Co(NH_3)_5Cl]Cl_2$ composite a good candidate for coated material to objects that wanted to be observed by sonar or such radars. This study shows there is strong intermolecular interaction which is responsible for increasing compressibility of composite with adding $[Co(NH_3)_5Cl]Cl_2$. PVA/ $[Co(NH_3)_5Cl]Cl_2$ composite can be applied in deferent industries such as reducing sound noise in factories, airplane, coating wall buildings and teaching room.

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