

## Study of Transition Metal Acetylacetonate Doped PVC Films

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### Abstract

PVC is one of the widely used polymers for various applications throughout the world. Various additives are added to modify its properties according to the requirement of a particular product. Doping of the polymer is known to affect its electrochemical properties. In the present work five transition metal acetylacetonate complexes, Tris(acetylacetonato) chromium, Tris(acetylacetonato) cobalt, Bis(acetylacetonato) copper, Bis(acetylacetonato) nickel and Tris(acetylacetonato) iron, were prepared and crystallized. These metal complexes were analysed with IR spectroscopy, and their purity was checked with TLC. PVC was then doped with 5% of these complexes, and casted into films, by slow heating. The film thickness was measured with micrometer. All the films were transparent and had different colours. The structural changes in doped PVC matrix were studied by IR Spectrophotometer. Our experimental investigations show significant changes in the matrix of the doped PVC films. The interpretation of the IR spectra in comparison to the undoped PVC film shows the formation of polyene and alcohol group sequences in doped polymer matrix. Formation of alcoholic group was not observed in the PVC film doped with that the Bis(acetylacetonato) copper. No correlation could be observed between the structural changes in the doped PVC matrix and the periodic position of the metal ions.

**Key Words:** PVC, Polymer doping, metal acetylacetonate, Infrared spectroscopy, PVC films

## **Introduction:**

Polyvinyl chloride is one of the most widely used polymer in the world [1]. Various types of additives are used to prepare finished PVC products [2]. It is common observation that vinyl chloride polymers of nominally identical type often exhibit markedly different heat stabilities. Moreover, the reaction of such polymers to various stabilizers may also be differing considerably, and rankings in order of stability may often vary according to the particular stabilizer employed. The stability of bulk or mass produced polymers is usually marginally superior to that of the best of suspension polymers and this is usually attributed to the presence of small traces of residues from the suspension agents used in polymerization. Residual traces of initiators are also likely to affect thermal stability [3,4]. Trace amounts of some metals such as iron appears to catalyse thermal decomposition considerably. A number of metal chlorides, such as ferric chloride, and those formed by the reactions of stabilizers with liberated hydrogen chloride, catalyse the decomposition. It has been suggested that the effect of cations are to catalyse decomposition of residual peroxides some of the polymer molecules [5]. Plasticizers such as phthalate are used to impart flexibility to PVC [6]. Doping of polymers is used to tailor its electronic properties [7]. PVC being a low cost material, with chemical and biological resistant properties finds wide applications, as sewerage pipes, insulation of electric cables, sheets for the sign boards and for clothes and furniture [8]. Therefore a large number of studies are being carried out to modify PVC to produce it with improved qualities [9,10].

In the present work, different metal acetylacetonate complexes were prepared and PVC films were doped with these complexes. The structural changes resulting in the PVC were studied with spectroscopic methods.

## **Experimental**

### **Materials**

PVC was purchased from local market in powdered form. All the other chemicals were purchased from E.Merck Germany.

### **Synthesis of transition metal acetylacetonate complexes**

The Following transition metal acetylacetonate complexes were prepared. Tris(acetylacetonato) chromium, Tris(acetylacetonato) cobalt. Bis(acetylacetonato) Copper, Bis(acetylacetonato) Nickel and Tris(acetylacetonato) iron. The procedure for the preparation of these complexes is given below

#### **a) Tris(Acetylacetonato) Chromium**

To a (235 ml) conical flask having 8 ml of distilled water, 0.22g of chromium chloride hexahydrate were dissolved. 1.5g of urea were added to this solution in 3 to 4 portions and then 0.48 ml of acetylacetone were added. The flask was covered with a watch glass and heated on a steam bath for 1.5 hour. Upon cooling the product was isolated, filtered and dried. For recrystallization of the complex, 0.2g of dried product was dissolved in 20 ml of cyclohexane. Heated on the steam bath for 4 – 5 minutes. It was cooled filtered and dried in air.

#### **b) Tris(Acetylacetonato) Cobalt**

0.12g of cobalt carbonate were dissolved in 1ml of acetylacetone. This solution was heated to about 90°C on a hot plate with continuous stirring. To this solution, 2.5 ml of 6% H<sub>2</sub>O<sub>2</sub> were

added drop wise over a 30 minute period, while stirring. Stirring was continued for 15 minute. After that the solution was filtered and the precipitates were dried in air. For recrystallization 0.3g of the dried product was dissolved in 10ml of toluene and warmed for 5 minutes on a steam bath. The mixture was filtered and transferred to another flask. The solution was reheated after the addition of 20 ml of hot petroleum ether. The product was cooled and filtered by suction filtration, and washed with 50 ml of pet ether dried in the air.

c) Bis(acetylacetonato) Copper

0.4g of copper (II) chloride dihydrate were dissolved in 2.5 ml of distilled water, in a flask. 0.5 ml of acetylacetonone were added in 1 ml methanol slowly, over a period of 20 minutes with constant stirring. 0.68g of sodium acetate in 1.5 ml of distilled water were added to the above solution. This mixture was heated to 80°C on a hot plate for 15 minute maintaining rapid stirring. This mixture was cooled, filtered and dried in air. For recrystallization 0.2g of product was added in 25 ml methanol. Boiled on a steam bath. Filtered and dried in air.

d) Bis(acetylacetonato) Nickel

Dilute ammonia solution was added in small amount to 3.0 ml of acetylacetonone. This homogeneous mixture was then added slowly with stirring to a solution of 3.5g of nickel nitrate in 50 ml of cold water. The light greenish precipitates appeared immediately on mixing the two solutions. The precipitates were washed with distilled water until the filtrate became colourless and then finally washed with acetone, dried and stored in desiccator.

For recrystallization of the complex the precipitates were dissolved in a required amount of methanol by heating in a water bath. The complex was crystallized out by addition of hot water to the methanol solution. For complete recrystallization mixture was cooled in ice bath. Filtered washed with water followed by acetone and dried. The crystalline shiny precipitates were stored in a desiccator.

e) Tris(acetylacetonato) iron

0.33g of finely ground iron(III) chloride hexahydrate were dissolved in 2.5 ml of distilled water. 0.39 ml of acetylacetonone in 10 ml methanol were added to the iron solution with constant magnetic stirring. To the resulting mixture, solution of 0.51g of sodium acetate in 1.5 ml of distilled water was added with stirring. This mixture was heated to about 80°C using the hot plate and temperature was maintained for 15 minutes. After that cooled the mixture in ice bath and filtered with suction filtration. The precipitates were washed with cold distilled water and dried in air. For recrystallization, 0.2g of the product dissolved in methanol solution was heated on a steam bath, cooled in an ice bath, filtered and dried in the air.

### Preparation of stock solutions

a) Preparation of Polyvinyl Chloride (PVC) solution

Stock solution of PVC was prepared by adding 3.32g PVC pinch by pinch to a conical flask containing 100 ml of Tetrahydrofuran (THF) and stirred for 48 hours at room temperature and the solution was saved.

b) Preparation of Metal Acetylacetonate Complexes

0.2 M stock solutions of all the synthesized complexes were prepared in 15 ml of THF in a conical flask by stirring for 48 hours and the solution was saved.

c) Preparation of PVC solution containing 5% solution of metal complexes

5% solutions of PVC-Cr(CH<sub>3</sub>COCHCOCH)<sub>3</sub>, PVC-Cu(CH<sub>3</sub>COCHCOCH<sub>3</sub>)<sub>2</sub>, PVC-

$\text{Co}(\text{CH}_3\text{COCHCOCH}_3)_3$ ,  $\text{PVC-Ni}(\text{CH}_3\text{COCHCOCH}_3)_2$ ,  $\text{PVC-Fe}(\text{CH}_3\text{COCHCOCH}_3)_3$  were prepared. To prepare these solutions, five dry and clean conical flasks (250 ml) were taken and 8 ml of PVC solution was placed in each flask. To these flasks 0.381 ml, 0.508 ml, 0.373 ml, 0.380 ml, 0.376 ml of 0.1 M solution of metal complexes were added respectively to prepare 5% concentration solution of complexes with PVC respectively. In each case the mixture was stirred for 24 hours.

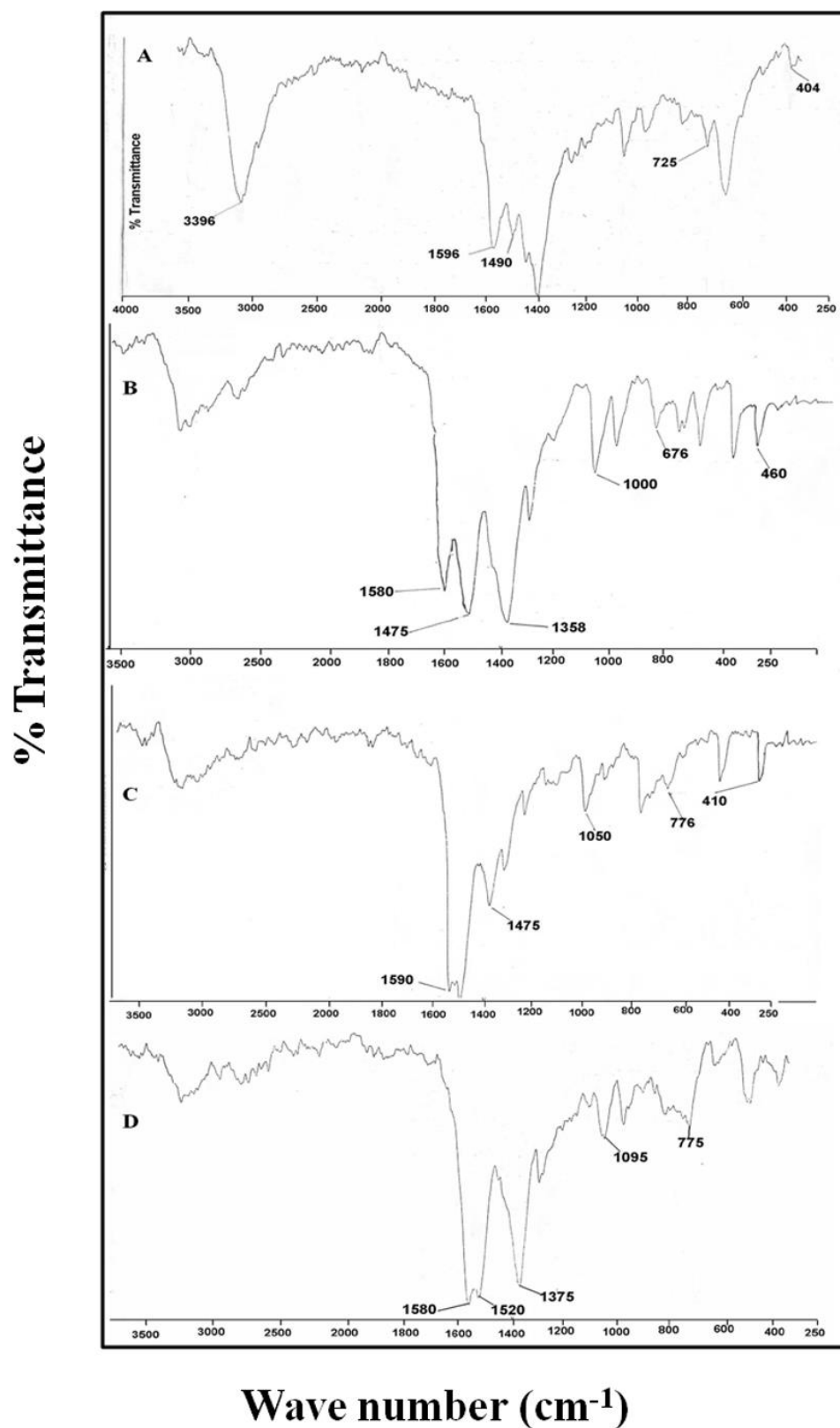
### **Preparation of metal acetylacetonate doped PVC films**

PVC films containing 5% concentration of metal complexes were prepared by solvent evaporation method as follows. Clean and dry petridish (3 cm diameter) was taken and 8 ml of for example  $\text{Cr}(\text{CH}_3\text{COCHCOCH}_3)_3$  – PVC mixture was poured into it. The solvent was evaporated at 40°C in the oven for 4 – 5 hours. Similarly films of other complexes were prepared adopting the same procedure. The films were dried and stored in a desiccator for 24 hours to avoid the moisture.

Purity of metal acetylacetonate complexes were checked by using TLC technique. The solution of metal acetylacetonate complexes were made in dichloromethane. The solutions were spotted on the TLC plates, and were developed using 1.5% solution of methanol in dichloromethane. After developing the plates were dried and the spots were located with UV lamp. The thickness of the films was measured by a micrometer. The structural studies of PVC with and without doping were carried out by IR spectrophotometer.

### **Results and Discussion**

In the present work different transition metal acetylacetonate complexes were prepared. PVC was then doped with these complexes to study changes in PVC matrix. To study the effect of transition metal complexes on the degradation of PVC, films containing different transition metal acetylacetonate complexes (Fe, Ni, Co, Cu, Cr) were prepared. All the films were doped with 5% of transition metal acetylacetonate complexes. The films prepared were of different colours. For  $\text{Fe}(\text{acac})_3$  film rust colour,  $\text{Cr}(\text{acac})_3$  light yellow colour,  $\text{Cu}(\text{acac})_2$  blue colour,  $\text{Ni}(\text{acac})_2$  light blue and for  $\text{Co}(\text{acac})_3$ , light green colour was observed. The thickness of the films varied between 0.08 mm – 0.09 mm. The addition of these complexes brings about structural changes in polymer matrix. These changes in the polymer matrix were studied by IR spectroscopy. IR spectra of all transition metal complexes and film samples have been recorded on IR Spectrophotometer, Hitachi limited Tokyo, Jp, 270-30/60, scanned at full wavelength range 4000 – 250  $\text{cm}^{-1}$ . Tentative assignments have been made on the basis of earlier publications [11]. The spectra of metal

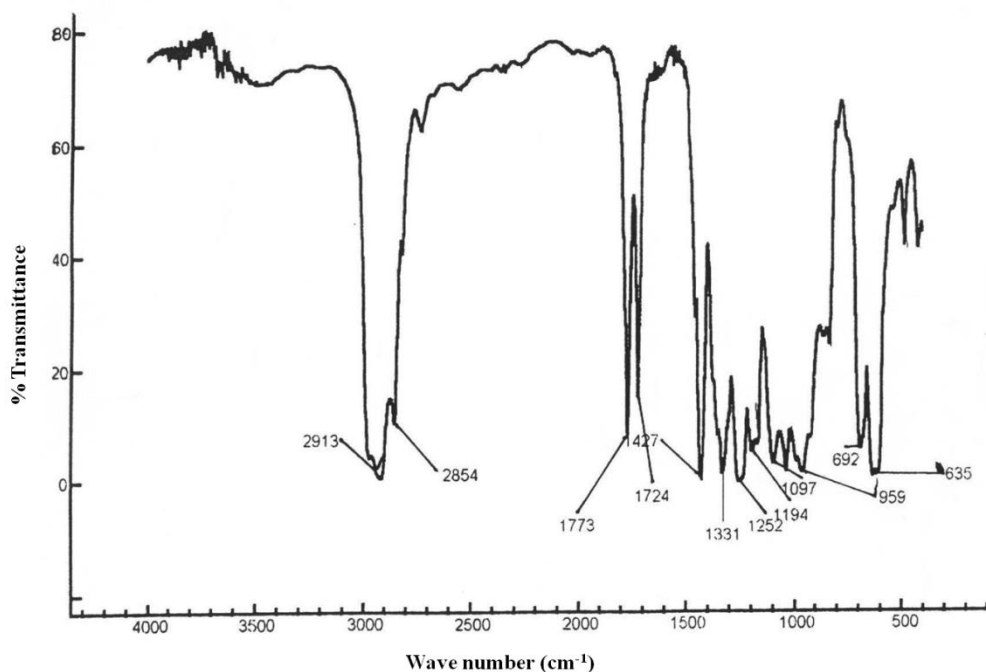


**Figure 1:** IR spectra of metal acetylacetonate complexes. A) Cobalt complex; B) Chromium complex; C) Copper complex; D) Iron Complex

acetylacetonate complexes are shown in Fig. 1 and the doped PVC films are shown in Fig. 3. Results are tabulated in Tables 1 and Table 2. Acetylacetonate exhibits tautomerization which yields an equilibrium mixture of enol and keto tautomers. The IR spectrum of acetylacetonate shows carbonyl peaks for both the enol and keto tautomers [12]. Carbonyl shows a doublet at  $1723\text{ m}^{-1}$  and  $1706\text{ m}^{-1}$  due to the symmetric and asymmetric stretch of the carbonyl group. The carbonyl group in the enol form shows a peak at about  $1622\text{ cm}^{-1}$  and substantially shifted and intensified in comparison to the normal ketone value. The shift is a result of internal hydrogen bonding and resonance in the enol form. This effect introduces single bond character into the enol form. This peak is absent in the spectra of acetylacetonate. A broad OH band is observed for the enol form at  $3200 - 2400\text{ cm}^{-1}$ . A peak for  $-\text{CH}_3$  bend is observed at  $1380\text{ cm}^{-1}$ .

**Table 1:** IR Data of transition metal acetylacetonate complexes

Assignment	Cr(ac ac) <sub>3</sub> (cm <sup>-1</sup> )	Fe(ac ac) <sub>3</sub> (cm <sup>-1</sup> )	Co(ac ac) <sub>3</sub> (cm <sup>-1</sup> )	Ni(ac ac) <sub>2</sub> (cm <sup>-1</sup> )	Cu(ac ac) <sub>2</sub> (cm <sup>-1</sup> )
- C = O bend	1580	1580	1596	1600	1590
- C = C Stretch	1475	1520	1490	1406	1475
-CH <sub>3</sub> bend	1358	1375	-	1200	-
- C - O	1000	1095	1050	1095	1050
=C-H Out of plane bend	728	775	725	775	776
Cr → O	460	-	-	-	-
Fe → O	-	404	-	-	-
Co → O	-	-	404	-	-
Ni → O	-	-	-	556	-
Cu → O	-	-	-	-	410

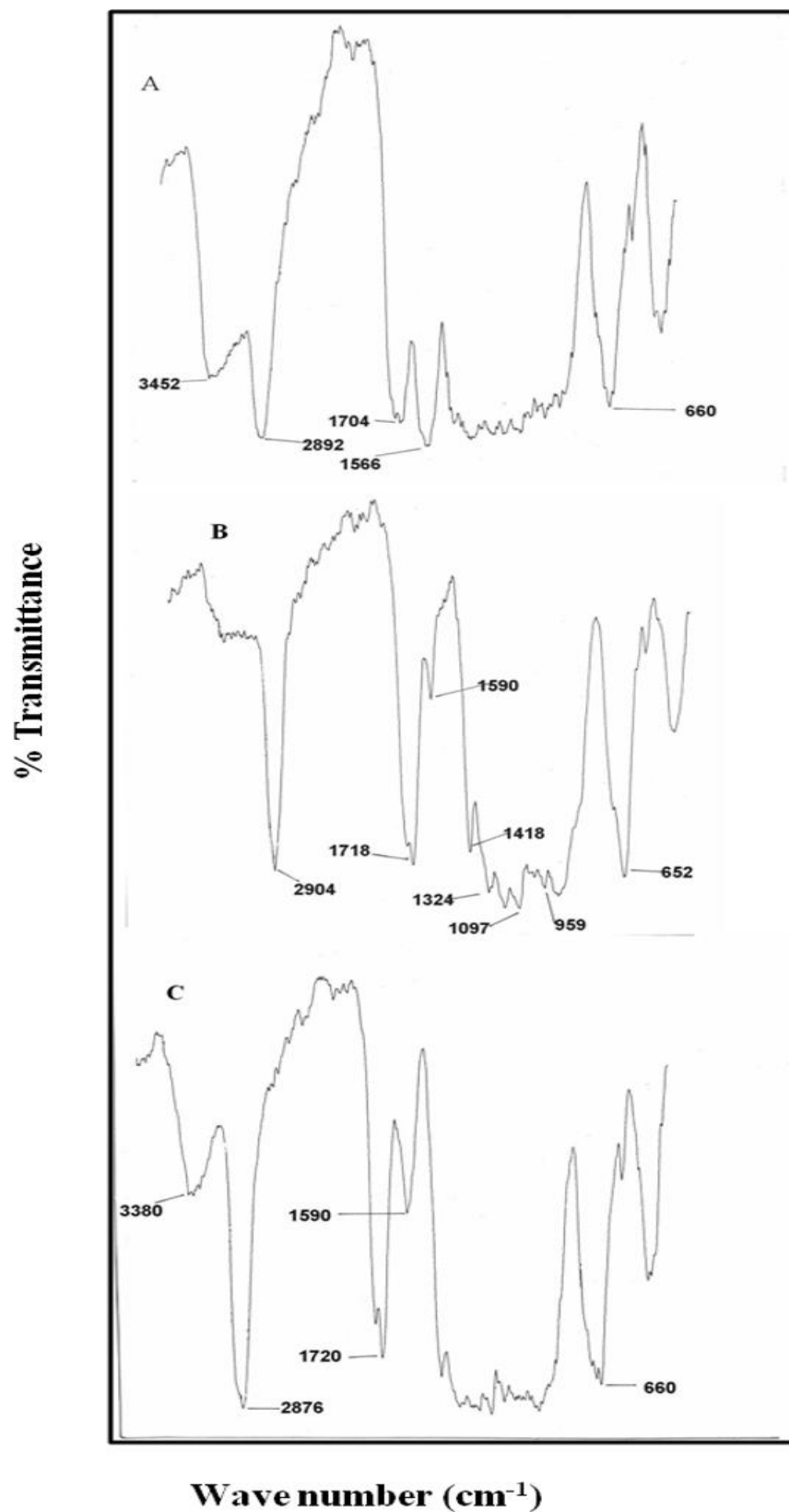


**Figure 2:** IR spectrum of PVC film

In the transition metal acetylacetonate complex the C = O doublet of keto tautomer is lost and a single carbonyl peak is present in the range  $1606 - 1580 \text{ cm}^{-1}$  indicating that now it is present in enolic form. The peak due to -OH group is absent in the transition metal acetylacetonate complexes. A peak is observed in the range between  $404 - 556 \text{ cm}^{-1}$  show the formation of co-ordination bond of acetylacetonate with the metal atom. This peak is absent in the spectra of acetylacetonate.

Some new peaks are observed at  $1475 \text{ cm}^{-1}$ ,  $1000 \text{ cm}^{-1}$ ,  $775 \text{ cm}^{-1}$ , for the C = C stretch, C - O stretch = C - H out of plane bend, the spectras of Co and Ni acetylacetonate complexes show the presence of water molecules in the complex at  $3396 \text{ cm}^{-1}$  and  $3340 \text{ cm}^{-1}$  respectively. From the IR data it can be concluded that acetylacetonate has been coordinated with the metal.

The IR spectrum of undoped PVC film (Fig. 2), shows a doublet like convoluted band profile in the region between  $700$  and  $600 \text{ cm}^{-1}$  ( $692 \text{ cm}^{-1}$  and  $635 \text{ cm}^{-1}$ ) assigned to C-Cl stretching vibration. In addition to this characteristics band structure, the major features of the PVC IR spectrum are a band at  $1427 \text{ cm}^{-1}$  due to  $\text{CH}_2$  scissoring vibration, the CH bending of the -CHCl group at  $1331$  and  $1252 \text{ cm}^{-1}$ , the backbone -C-C- stretching at  $1097 \text{ cm}^{-1}$ , and  $\text{CH}_2$  rocking at  $959 \text{ cm}^{-1}$ . The  $\text{CH}_2$  scissors vibration band is attributed to the crystalline component of PVC [13]. The peaks at  $2854 \text{ cm}^{-1}$  and  $2913 \text{ cm}^{-1}$  are due to the symmetric and



**Figure 3:** IR spectra of metal acetylacetonate doped PVC film. A) Iron acetylacetonate doped film; B) Copper acetylacetonate doped film; C) Nickel acetylacetonate doped film



asymmetric stretching vibrations of the  $-\text{CH}_2$  group. The peaks at  $1773\text{cm}^{-1}$  and  $1724\text{cm}^{-1}$  are attributed to the  $-\text{C}=\text{O}$  group which indicates the presence of some plasticizer like dioctyl phthalate (DOP) in the PVC sample.

**Table 2:** IR Data of PVC and doped PVC films

Sr. No.	Assignment	PVC Films ( $\text{cm}^{-1}$ )	5% $\text{Cr}(\text{ac ac})_3$ – PVC film ( $\text{cm}^{-1}$ )	5% $\text{Fe}(\text{ac ac})_3$ – PVC film ( $\text{cm}^{-1}$ )	5% $\text{Co}(\text{ac ac})_3$ – PVC film ( $\text{cm}^{-1}$ )	5% $\text{Ni}(\text{ac ac})_2$ – PVC film ( $\text{cm}^{-1}$ )	5% $\text{Cu}(\text{ac ac})_2$ – PVC film ( $\text{cm}^{-1}$ )
1.	OH Stretching	-	3452	3452	2908	3380	2904
2.	-CH-Stretched (symmetric, asymmetric)	2913 2854	2904 -	2896 -	2854 -	2876 -	- -
3.	C=O Stretched band	1773 1724	1712 -	1704 -	1722 -	172- -	1718 -
4.	-C=C- Stretch	-	-	1566	-	1590	1590
5.	$\text{CH}_2$ Scissoring	1427	1559	1420	1418	1427	1418
6.	CH bending of CH-Cl group	1331 1252	1333 -	1310 1230	1335 -	1331 -	1324 -
7.	Backbone $-\text{C}-\text{C}-$ Stretch	1097	1002	1097	1168	1097	1097
8.	$\text{CH}_2$ Rocking	959	712	956	959	959	959
9.	C-Cl	692 635	650 -	660 -	606 -	660 -	652 -

In iron, copper, nickel (acac) doped samples a peak is observed at  $1566 - 1519 \text{cm}^{-1}$  (Fig. 3). The appearance of this characteristic peak is due to the formation of polyenes. Thus they act as effective degrading agent and facilitate the dehydrochlorination of PVC.

The degradation reaction can be explained to be a result of complex interactions between metal acetylacetonate complexes and the polymer matrix, thus creating a labile chlorine in the PVC chain [14].

The labile chlorine once produced initiates a zip opening reaction in the PVC chain. A broad band is observed at  $3452 - 3380 \text{cm}^{-1}$  in the IR spectra of chromium, iron, cobalt, nickel, acetylacetonate doped films because of the formation of  $-\text{OH}$  group in PVC matrix. Copper (acac) doped film does not show the formation of alcoholic group. The changes in the PVC

matrix by dopants does not show any relation to the periodic trend of metals.

TLC of the transition metal acetylacetonate complexes was done to establish the purity of the compounds. The plate was viewed under UV light and showed the presence of a single component. So it can be concluded that the compounds are pure.  $R_f$  values were also calculated and are given in Table 3.

**Table 3:**  $R_f$  values of transition metal acetylacetonate complexes

Sr. No.	Complexes	$R_f$ Values
1.	$\text{Cr}(\text{ac ac})_3$	0.75
2.	$\text{Fe}(\text{ac ac})_3$	0.70
3.	$\text{Co}(\text{ac ac})_3$	0.65
4.	$\text{Ni}(\text{ac ac})_3$	0.66
5.	$\text{Cu}(\text{ac ac})_3$	0.67

## CONCLUSION

In the present work study of effect of doping on the PVC was observed. Different transition metal acetylacetonate complexes like  $\text{Fe}(\text{acac})_3$ ,  $\text{Cu}(\text{acac})_2$ ,  $\text{Ni}(\text{acac})_2$ ,  $\text{Co}(\text{acac})_3$  and  $\text{Cr}(\text{acac})_3$  were prepared. PVC was doped with these compounds. The concentration of PVC doped films were kept constant i.e., 5%. It was observed that addition of metal acetylacetonate complexes brings about structural changes in the polymer matrix which were analyzed by IR spectrophotometer. The IR spectrum shows that the doped PVC films are similar to undoped PVC film. However some new peaks were observed in the doped films which show the formation of polyene sequences and OH – group in PVC matrix.

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