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 dopes 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 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 the 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 flash 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 in1 ml 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% H2O2 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 acetylacetone 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 acetylacetone. 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 acetylacetone 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\(_3\)COCHCOCH\(_3\))\(_3\), PVC-Cu(CH\(_3\)COCHCOCH\(_3\))\(_2\), PVC-
Co(CH₃COCHCOCH₃)₃, PVC-Ni(CH₃COCHCOCH₃)₂, PVC-Fe(CH₃COCHCOCH₃)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 Cr(CH₃COCHCOCH₃)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 Fe(acac)₃ film rust colour, Cr(acac)₃ light yellow
colour, Cu(acac)₂ blue colour, Ni(acac)₂ light blue and for Co(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 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 acetylacetone shows carbonyl peaks for both the enol and keto tautomers [12]. Carbonyl shows a doublet at 1723 m$^{-1}$ and 1706 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 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 acetylacetone. A broad OH band is observed for the enol form at 3200 – 2400 cm$^{-1}$. A peak for $–$CH$_3$ bend is observed at 1380 cm$^{-1}$.

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

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Cr(ac ac)$_3$ (cm$^{-1}$)</th>
<th>Fe(ac ac)$_3$ (cm$^{-1}$)</th>
<th>Co(ac ac)$_3$ (cm$^{-1}$)</th>
<th>Ni(ac ac)$_2$ (cm$^{-1}$)</th>
<th>Cu(ac ac)$_2$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$–$ C = O bend</td>
<td>1580</td>
<td>1580</td>
<td>1596</td>
<td>1600</td>
<td>1590</td>
</tr>
<tr>
<td>$–$ C = C Stretch</td>
<td>1475</td>
<td>1520</td>
<td>1490</td>
<td>1406</td>
<td>1475</td>
</tr>
<tr>
<td>$–$CH$_3$ bend</td>
<td>1358</td>
<td>1375</td>
<td>-</td>
<td>1200</td>
<td>-</td>
</tr>
<tr>
<td>$–$ C – O</td>
<td>1000</td>
<td>1095</td>
<td>1050</td>
<td>1095</td>
<td>1050</td>
</tr>
<tr>
<td>$=$C–H</td>
<td>728</td>
<td>775</td>
<td>725</td>
<td>775</td>
<td>776</td>
</tr>
<tr>
<td>Out of plane bend</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr $→$ O</td>
<td>460</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe $→$ O</td>
<td>-</td>
<td>404</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co $→$ O</td>
<td>-</td>
<td>-</td>
<td>404</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni $→$ O</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>556</td>
<td>-</td>
</tr>
<tr>
<td>Cu $→$ O</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>410</td>
</tr>
</tbody>
</table>
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 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 cm\(^{-1}\) show the formation of co-ordination bond of acetylacetonate with the metal atom. This peak is absent in the spectra of acetylacetone.

Some new peaks are observed at 1475 cm\(^{-1}\), 1000 cm\(^{-1}\), 775 cm\(^{-1}\), for the C = C stretch, C – O stretch = C – H out of plane bend, the spectra of Co and Ni acetylacetonate complexes show the presence of water molecules in the complex at 3396 cm\(^{-1}\) and 3340 cm\(^{-1}\) respectively. From the IR data it can be concluded that acetylacetone 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 cm\(^{-1}\) (692 cm\(^{-1}\) and 635 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 cm\(^{-1}\) due to CH\(_2\) scissoring vibration, the CH bending of the – CHCl group at 1331 and 1252 cm\(^{-1}\), the backbone – C-C- stretching at 1097 cm\(^{-1}\), and CH\(_2\) rocking at 959 cm\(^{-1}\). The CH\(_2\) scissors vibration band is attributed to the crystalline component of PVC [13]. The peaks at 2854 cm\(^{-1}\) and 2913 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 cm$^{-1}$ and 1724 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

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Assignment</th>
<th>PVC Films (cm$^{-1}$)</th>
<th>5% Cr(acac)$_3$ – PVC film (cm$^{-1}$)</th>
<th>5% Fe(acac)$_3$ – PVC film (cm$^{-1}$)</th>
<th>5% Co(acac)$_3$ – PVC film (cm$^{-1}$)</th>
<th>5% Ni(acac)$_2$ – PVC film (cm$^{-1}$)</th>
<th>5% Cu(acac)$_2$ – PVC film (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>OH Stretching</td>
<td>-</td>
<td>3452</td>
<td>3452</td>
<td>2908</td>
<td>3380</td>
<td>2904</td>
</tr>
<tr>
<td>2.</td>
<td>$–\text{CH}$-Stretched (symmetric, asymmetric)</td>
<td>2913 2854</td>
<td>2904 -</td>
<td>2896 -</td>
<td>2854 -</td>
<td>2876 -</td>
<td>-</td>
</tr>
<tr>
<td>3.</td>
<td>C=O Stretched band</td>
<td>1773 1724</td>
<td>1712</td>
<td>1704</td>
<td>1722</td>
<td>1725</td>
<td>1718</td>
</tr>
<tr>
<td>4.</td>
<td>$–\text{C}=\text{C}$- Stretch</td>
<td>- - 1566 -</td>
<td>-</td>
<td>1590 -</td>
<td>1590 -</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5.</td>
<td>CH$_2$ Scissoring</td>
<td>1427</td>
<td>1559</td>
<td>1420</td>
<td>1418</td>
<td>1427</td>
<td>1418</td>
</tr>
<tr>
<td>6.</td>
<td>CH bending of CH-Cl group</td>
<td>1331 1252</td>
<td>1333</td>
<td>1310</td>
<td>1335</td>
<td>1331</td>
<td>1324</td>
</tr>
<tr>
<td>7.</td>
<td>Backbone $–\text{C}$-Stretch</td>
<td>1097</td>
<td>1002</td>
<td>1097</td>
<td>1168</td>
<td>1097</td>
<td>1097</td>
</tr>
<tr>
<td>8.</td>
<td>CH$_2$ Rocking</td>
<td>959</td>
<td>712</td>
<td>956</td>
<td>959</td>
<td>959</td>
<td>959</td>
</tr>
<tr>
<td>9.</td>
<td>C-Cl</td>
<td>692 635</td>
<td>650</td>
<td>660</td>
<td>606</td>
<td>660</td>
<td>652</td>
</tr>
</tbody>
</table>

In iron, copper, nickel (acac) doped samples a peak is observed at 1566 – 1519 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 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...
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

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Complexes</th>
<th>( R_f ) Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Cr(ac ac)(_3)</td>
<td>0.75</td>
</tr>
<tr>
<td>2.</td>
<td>Fe(ac ac)(_3)</td>
<td>0.70</td>
</tr>
<tr>
<td>3.</td>
<td>Co(ac ac)(_3)</td>
<td>0.65</td>
</tr>
<tr>
<td>4.</td>
<td>Ni(ac ac)(_3)</td>
<td>0.66</td>
</tr>
<tr>
<td>5.</td>
<td>Cu(ac ac)(_3)</td>
<td>0.67</td>
</tr>
</tbody>
</table>

**CONCLUSION**

In the present work study of effect of doping on the PVC was observed. Different transition metal acetylacetonate complexes like Fe(acac)\(_3\), Cu(acac)\(_2\), Ni(acac)\(_2\), Co(acac)\(_3\) and Cr(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.
References