Effect of Fe, Co and Ni–Laurates on the Thermal Stability of PVC

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Abstract

Metal carboxylates (Fe,Co,Ni–laureates) were prepared and identified by elemental analysis and infrared spectroscopy .

The thermal stability of the PVC absence and presence of these metal carboxylates and their synergistic mixtures was studied by the TGA . It was observed that the values of decomposition temperature and activation energy for PVC samples containing different stabilizer were found to be higher as compared to pure PVC .

Infrared spectroscopy was used to study the stabilizing effects for the metal carboxylates within the range 1500-1900 Cm^{-1} . The spectra were followed for films of stabilized PVC at 245 ºC in the air and in few cases in nitrogen . IR spectroscopy was found to be suitable method to trace the consuming of the metal carboxylates during the degradation via antisymmetrical stretching vibration of the carboxylate group at 1540 Cm^{-1} . The thermal degradation was also studied for stabilized PVC by U.V. spectroscopy at 275 and 385 nm ,and it was found that the metal carboxylates were decreased conjugated double bonds in the polymer .

The general results indicate that these prepared metal carboxylates hinder the degradation and increase the thermal stability of PVC .

الخلاصة

تم تحضير عدد من الكاربوكسيلات الفلزية وهي لورات كل من الحديد والكوبلت والنيكل واستخدمت كمثبتات حرارية لـ PVC . وقد شخصت هذه المثبتات بواسطة جهاز تحليل العناصر ومطيافية الاشعة تحت الحمراء .

تم دراسة الثبات الحراري لـ PVC بوجود الكاربوكسيلات الفلزية المحضرة ومزيجها التعاوني وذلك باستخدام التحليل الحراري الوزني حيث لوحظ بان قيم درجة حرارة التفكك وطاقة التنشيط لنماذج الـ PVC المحتوية على المثبتات ترتفع بالمقارنة مع الـ PVC النقي .

كما استخدمت ايضاً مطيافية الاشعة تحت الحمراء لدراسة التاثير التثبيتي للكاربوكسيلات الفلزية المحضرة عند المدى الطيفي (1500 – 1900 سم-1) على افلام الـ PVC عند 245 م° في الهواء وفي حالات قليلة بوجود النتروجين ، حيث كانت مطيافية الاشعة تحت الحمراء وسيلة ملائمة لمتابعة استهلاك الكاربوكسيلات الفلزية خلال عملية التفكك بواسطة الاهتزاز الاتساعي غير المتماثل لمجموعة الكاربوكسيلات عند 1540 سم-1 . بالاضافة الى ذلك تضمن البحث دراسة التفكك الحراري لنماذج الـ PVC المثبتة بواسطة مطيافية الاشعة فوق البنفسجية عند الطولين الموجيين 275 و 385 نانومتر ، وقد وجد ان الكاربوكسيلات الفلزية المحضرة تقلل من الاواصر المزدوجة التي تتكون في سلسلة البوليمراثناء التفكك .

ان النتائج العامة المستخلصة تشير بان تلك الكاربوكسيلات الفلزية المحضرة تمنع التفكك وتزيد الثبات الحراري لـ PVC .

Introduction

Poly vinyl chloride (PVC) was one of the first thermoplastic developed . When PVC is processed at high temperatures , it is degraded by dehydrochlorination , chain scission , and crosslinking of macromolecules . Free hydrogen chloride (HCl) evolves and discoloration of the resin occurs along with important changes in physical and chemical properties . The evolution of HCl takes place by elimination from the polymer backbone , discoloration results from the formation of conjugated polyene sequences of 5-30 double bonds . Subsequent reactions of highly reactive conjugated polyenes crosslink or cleave the polymer chain , and form benzene and condensed and / or alkylated benzenes in trace amounts depending on temperature and available oxygen (1,2) .

During processing , in addition to thermal dehydrochlorination , the polymer is exposed to thermo-oxidative degradation resulting from oxygen , in addition , mechanical stress may cause chain scission . The main feature in thermo-oxidative degradation is dehydrochlorination as in thermal degradation. The presence of oxygen causes the dehydrochlorination process to accelerate , but the discoloration is not as severe as during thermal degradation (3,4) .

This degradation must be controlled by the addition of stabilizers .the heat stabilizer must prevent the dehydrochlorination reaction by several methods(5-7) . The metal carboxylates are regarded as principal thermal stabilizers for PVC and studied by many workers .The thermal stabilization at 194 ºC in air was studied(8) for PVC samples with the soaps of Eu with lauric and myristic acids .These soaps was shown resistance to PVC degradation .In other study(9), infrared (1500-1900 Cm^{-1}) were studied for PVC films stabilized with (La,Ce, and Nd- palmitate) . At least tow types of oxygen containing products were formed during the degradation and the presence of atmospheric oxygen leading to the formation of carbonyl groups on the chain seems to play an essential role in the degradation .

On the other hand, the synergistic effect of stabilizers blends in the thermal treatment of PVC have been studied for many combinations systems .These Combinations included Ba/Cd , Ba/Zn , Zn/Ca and Cd/Zn stearates(10)in common though other systems like Tb/Ho,Tb/Dy and Dy/Ho-laurates mixtures have also been studied(11). For Ba/Cd stearates mixtures in different molar ratios, it was found that the best ratio was 1:1 to affect the best inhibition of polyene growth while other blends containing higher ratios of Ba stearate practically have no any improvement upon the effect of each stabilizer alone .The effect of rare earth (Ho,Tb and Dy-laurate) on the thermal degradation of PVC showed such a synergistic stabilizing rule in Tb/Ho ,Tb/Dy and Dy/Ho laureates blends .The synergistic effect of La , Eu and Nd laurate, myristate and stearate on the thermal degradation of PVC was studied(12) by the means of thermal analysis (TGA) in the temperature rang 25-600ºC , it was found that these blends reduce the dehydrochlorination of PVC . The rate of decomposition and the activation energy have been calculated by Newkirk method and found that the activation energy of this process was increased in the PVC samples containing the soaps .

The present work is devoted to prepare new metal carboxylates (Fe,Co,Ni–laurates) and to study their stabilizing effect on the PVC by using TGA , IR and U.V. spectroscopy .

Experimental

Materials

* Potassium hydroxide , Methanol , tetrahydrofuran from BDH Company
* Lauric acid , Ferric chloride , Cobalt chloride Nickel chloride from Fluka Company
* Poly vinyl chloride from Petrochemical Company , Basrah , as following characteristics : PVC SCC 676 , K value = 76.5 - 65.5 , Density (g/cm^3) = 0.45 , Ash content = 0

Instruments

* Infrared spectrophotometer model SP3-300 in the college of education
* Uv/Vis spectrophotometer model LKB ULTRSPEC II 4050 in the college of education
* Thermogravimetric analyzer model Perkin-Elmer TGA7 in the recent Qaka'a Company , Baghdad . Thermal measurements were carried out in nitrogen steam with fixed heating rate of 20 ºC /min , with a gas flow rate of 30 ml /min .
* Elemental analyzer model CHN EA1108 in the recent Qaka'a Company , Baghdad

Preparation of metal carboxylates (11)

Fe salt of lauric acid (Fe – laurate) was obtained by dissolving 2.804 g (0.014 mole) lauric acid in 100 ml of 0.14M KOH solution with gentle heating , then 100 ml of 0.0046 M $FeCl_3$ solution was added with stirring and precipitation occurred . The precipitated Fe – laurate was filtered , washed with water then with methanol and dried under vacuum at 50 ºC still constant weight was obtained . Co and Ni – laurate also prepared at the same method and with a stability of used metal salt moles .

Preparation of the stabilized samples(13)

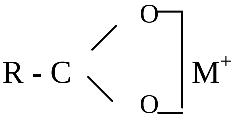
3% w/w samples of prepared metal carboxylates at singly with PVC were prepared by grinding in an agate mortar for 30 min . Then 0.02 g of the mixture was pressed to a constant pressure (10 tons) for 2 min . Then the mixture in the die was heated at 240 ºC for the required period . The mixture was pressed for 5 min at pressure of 2 tons to make a homogenous film , with a thickness of about 0.25mm as measured by a micrometer . In addition to this , the synergistic effect of these metal carboxylates was studied by mixing 1% each of metal carboxylates with PVC .

Results and discussion

Identification of metal carboxylates

The metal carboxylates have a wide range of melting points and that seem to have liquid crystalline properties , for example , the range of melting point of Fe–laurate 104-138 ºC . In addition , the results of elemental analysis show that the practical percentage of carbon and hydrogen are equivalent to theoretical values as shown in table (1) .

The metal carboxylates were also identified by infrared spectra . The important stretching vibration bands of lauric acid and metal carboxylates were shown in figures (1-4) and table (2) . The most striking differences between the spectra of the lauric acid and metal carboxylates are the bands of COOH group since the bands of the aliphatic portion are essentially unchanged from lauric acid to the metal carboxylates . It is expected that the bands due to OH group should disappear in the metal carboxylates . Thus the bands 3000-3300 Cm^{-1} and 933 Cm^{-1} are absent from the spectra of the metal carboxylates . In addition , the band of C=O group at 1090 Cm^{-1} in lauric acid disappear and instead a new band appears at (1520-1550 Cm^{-1}) because of the complete resonance in the carbonyl group that is attached to the metal . For these reasons , the structure of the metal carboxylates should be in the form :



In this case both C-O bonds are identical and have force constant intermediate to those of normal double and single bonds . Accordingly three bands could be appeared to the COO^- group , the asymmetrical stretching vibration (1520-1550Cm^{-1}) , the symmetrical stretching vibration (1420-1435Cm^{-1}) , and the bending vibration (918-925Cm^{-1})(14,15) .

Thermogravimetric analysis (TGA)

Figure (5) shows that the degradation of PVC occur in two steps . The first weight loss in the temperature range 265-374 ºC is due to dehydrochlorination of PVC , while second weight loss which starts at 445 ºC is because of evolution of volatile products which are formed by the cyclization of short polyene linkages (16,17) . Comparison of TG curves of pure PVC ad stabilized PVC shown in figures (6-8) reveal that the metal carboxylates under study increase the temperature at which dehydrochlorination starts . This is indicates that the metal carboxylates reduce the catalytic effect of the evolved hydrochloric acid gas on the PVC degradation . This is confirmed by the thermal parameters calculated in table (3) which shows that the optimal decomposition temperature of pure PVC occurs at 305 ºC , while for stabilized PVC it occurs within the range 315-322 ºC . Also the 50 % decomposition temperature of pure PVC is 332 ºC,while for stabilized PVC it is occurred within the range 343-347 ºC . As a conclusion , all the thermal parameters indicate that the metal carboxyates under study have a good efficiency for stabilizing of PVC .

The synergistic effect of mixed metal carboxylates was also studied for equiweights 1 % . The figure (9) and table (3) show that these mixtures have a considerable stabilizing effect on the decomposition of PVC and this is obviously by the increasing decomposition temperature and activation energy , while the rate of hydrogen chloride liberation was decreased ,and the mechanism of stabilization of these mixtures was explained by many workers(18,19) on the other metal carboxylates .

Infrared and ultraviolet spectroscopy

In order to carried out the quantitative study of IR spectra , it has calculated the absorbances of the bands through the following equation (20) :

$A_i = \log (T_{1800} / T_i)$

Where

A_i : absorbance at wavenumber under study

T_{1800} : the percentage of transmittance at 1800 Cm^{-1}

T_i : the percentage of transmittance at wavenumber under study

The IR spectrum of thermally treated PVC appears bands at 1600 and 1700 Cm^{-1} attributed to C=C and C=O vibration respectively(5) . The intensity of these bands increase with increasing time of heating . This behavior is clear in figure (10) . The band at 1600 Cm^{-1} results as PVC losses hydrogen chloride because of degradation and formation of polyene chains , while the band at 1700 Cm^{-1} is due to the carbonyl group formed on PVC by the action of atmospheric oxygen (15,21) .

IR spectra of stabilized PVC display two new bands at spectral range 1500-1600 Cm^{-1} and 1735 Cm^{-}as well as the bands that explained in pure PVC (20,22). The spectral range 1500-1600 Cm^{-1} contains absorption bands for the antisymmetrical stretching vibration of the COO^{-} group that lies approximately at 1540 Cm^{-1} for all metal carboxylates . It is possible to follow the decrease of this band intensity with increasing time of heating and to derive conclusions about the consumption of metal carboxylates as a result of its reaction with HCl librated of PVC chain and formation of fatty acid as shown in figures (11-13) . The band that appears at 1735 Cm^{-1} may be attributed to ester group formed upon the polymeric chain . It is found that the variation of this band intensity was corresponded with the band at 1700 Cm^{-1} . The changes in the absorption of these bands were quantitively represented in figures (14-16) .

On the other hand , the thermal degradation of PVC in the presence of nitrogen was studied to improve the esterification of polymeric chains . Czako etal (20) was proposed that consumption of metal carboxylates is increased with increasing the degree of esterification , and then the band intensity at 1730 Cm^{-1} is also increased . This is noticed in our study . The content of carboxylates is determined from the band intensity at 1540 Cm^{-1} for example , this band was decreased to 60 % after 40 min of degradation in air for stabilized PVC with Fe-laurate in comparison 54 % in nitrogen for the same sample , while the absorbance of the band at 1730 Cm^{-1} is equal 0.196 and 0.117 respectively as shown in figures (17-19) .

For above , our conclusion is that the band at 1730 Cm^{-1} attributed to ester group in PVC chain . It is also observed that the band intensity at 1700 Cm^{-1} in the presence of nitrogen was decreased to half in comparison with atmospheric oxygen because the nitrogen is prevented oxidation of polymeric chains in PVC .

Ultraviolet spectroscopy is used to study the thermal degradation of pure PVC and the precipitated PVC from the metal carboxylates at 275 and 385 nm corresponded to three and seven conjugated double bonds respectively (10,23) . The results shown in tables (4,5) indicate that these metal carboxylates are decreased the absorbance at 275 and 385 nm in comparison with pure PVC , so that these metal carboxylates and their synergistic mixtures have a good ability for stabilizing of PVC . In addition , the effect of inert nitrogen gas on the thermal degradation of PVC was studied for pure PVC and stabilized PVC with Fe-laurate , it was observed in table (6) the absorbances of pure PVC at 275 and 385 nm was decreased in the presence of nitrogen in comparison with atmospheric oxygen because the atmospheric oxygen forms keto allyl groups in the PVC chain that increase rate of dehydrochlorination and forming the double bonds . The presence of atmospheric oxygen decreases also the efficiency of stabilizer (Fe-laurate) and that attributed to the stabilizer do not receive evaluated HCl from PVC chain considerably .

Table 1: The molecular formula and elemental analysis data for prepared stabilizers

Stabilizer	**Formula**	**Elemental analysis Theoretical Practical**		**Milting point**	**Yield (%)**
		%C	**%H**		
Fe-laurate	$[Fe(CH_3(CH_2)_{10}CO_2)_3]H_2O$	64.40 64.34	10.58 10.52	104-138	95
Co-laurate	$[Co(CH_3(CH_2)_{10}CO_2)_3]H_2O$	64.10 64.16	10.53 10.50	110-142	93
Ni-laurate	$[Ni(CH_3(CH_2)_{10}CO_2)_3]H_2O$	64.12 64.02	10.54 10.45	115-145	90

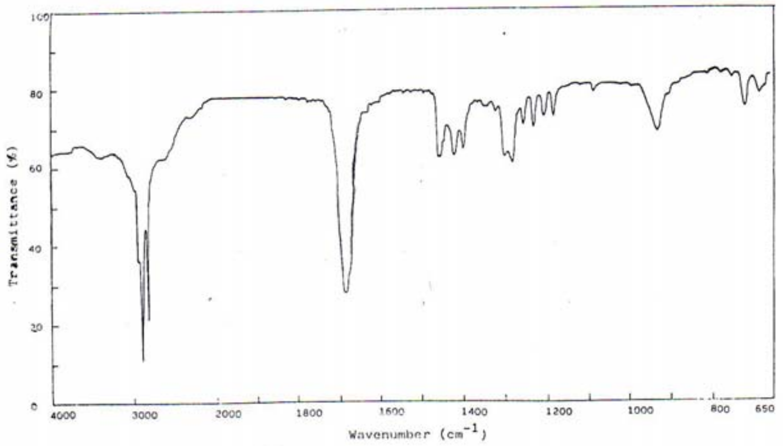


Figure 1 : Infrared spectrum of lauric acid (KBr disc)

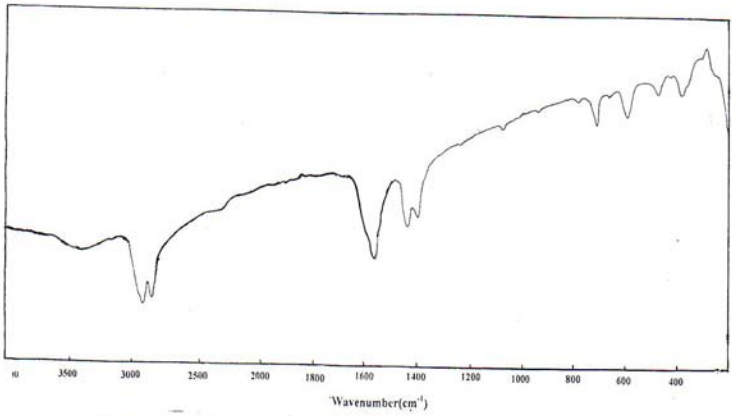


Figure 2 : Infrared spectrum of Fe - laurate (KBr disc)

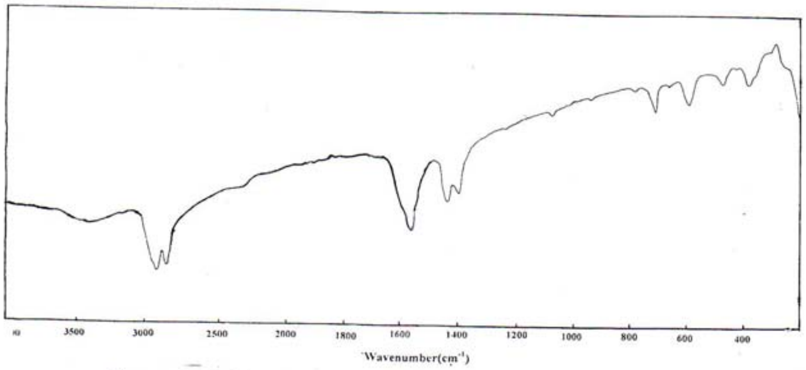


Figure 2 : Infrared spectrum of Fe - laurate (KBr disc)

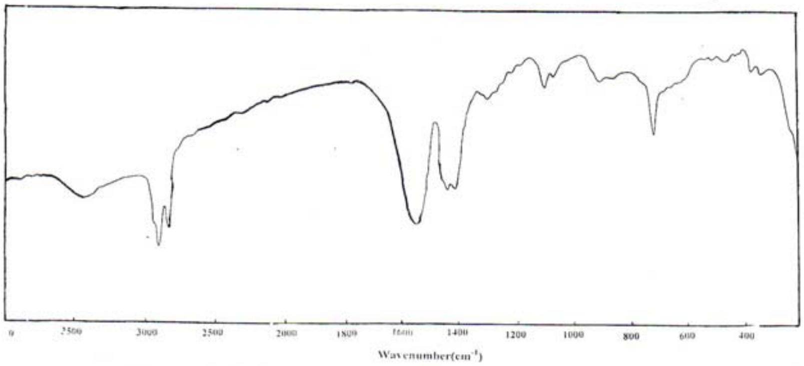
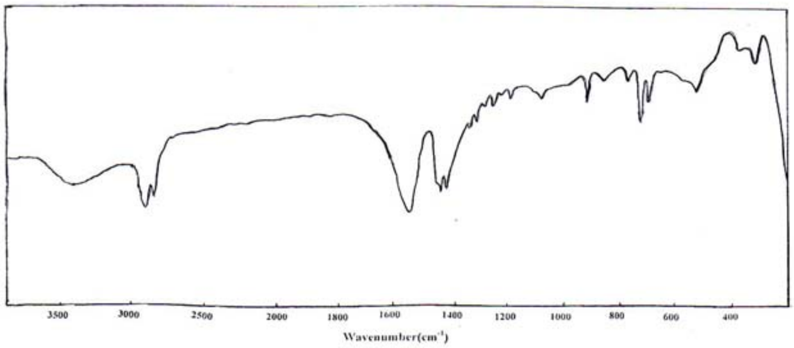


Figure 3 : Infrared spectrum of Co - laurate (KBr disc)



. Figure 4 : Infrared spectrum of Ni - laurate (KBr disc)

Table 2 : Results of infrared spectra of lauric acid and prepared metal carboxylates

Compound	Stretching vibration of O-H (cm^{-1})	Stretching vibration of C-H (cm^{-1})	Stretching vibration of C=O (cm^{-1})	Bending vibration of C-H (cm^{-1})	Bending vibration of O-H (cm^{-1})	Stretching vibration of C-O (cm^{-1})	Stretching vibration (antisymm.) of COO^- (cm^{-1})	Stretching vibration (symm) of COO^- (cm^{-1})	Bending vibration of COO^- (cm^{-1})	Bending vibration (extraplane) of C-H (cm^{-1})
Lauric acid	2645-3300 (S)	2930 (S) 2900 (S) 2825 (S)	1690 (S)	1405 (M) 1525 (M) 1461 (M)	933 (M)	1274 (M) 1246 (M)	-----	-----	-----	720 (M)
Fe-laurate	3400 (M)	2930 (S) 2900 (S) 2825 (S)	-----	-----	-----	-----	1550 (S)	1435 (S)	920 (M)	720 (M)
Co-laurate	3400 (M)	2930 (S) 2900 (S) 2825 (S)	-----	-----	-----	-----	1545 (S)	1425 (S)	918 (M)	720 (M)
Ni-laurate	3400 (M)	2930 (S) 2900 (S) 2825 (S)	-----	-----	-----	-----	1520 (S)	1420 (S)	925 (M)	720 (M)

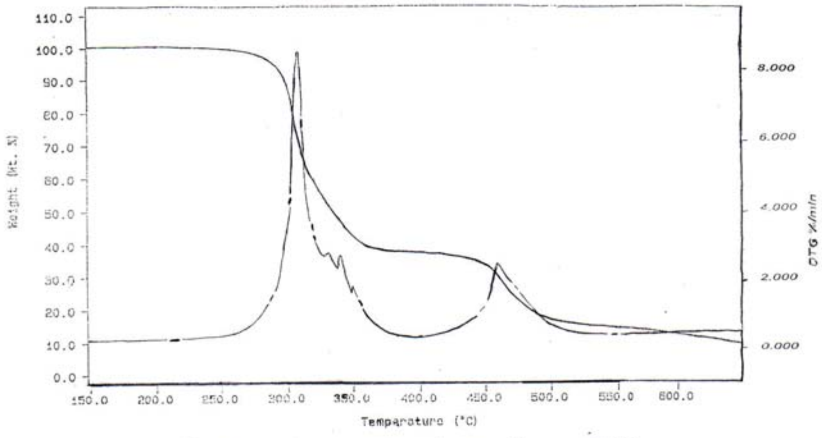


Figure 5 : Thermogravimetric curve for pure PVC

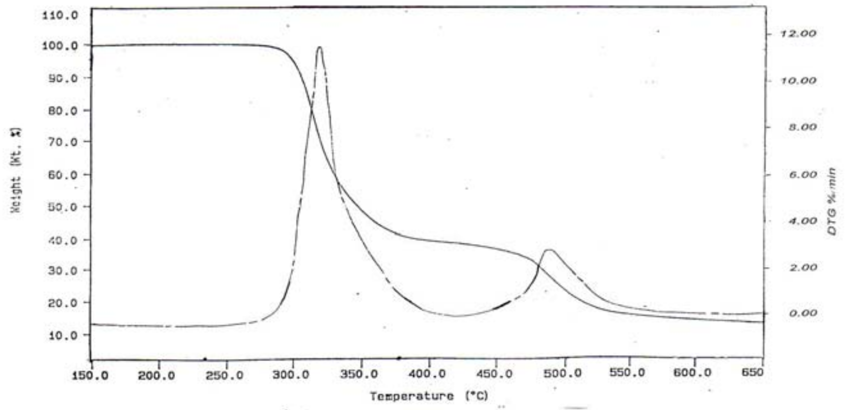


Figure 6 : Thermogravimetric curve for PVC containing 3% Fe - laurate

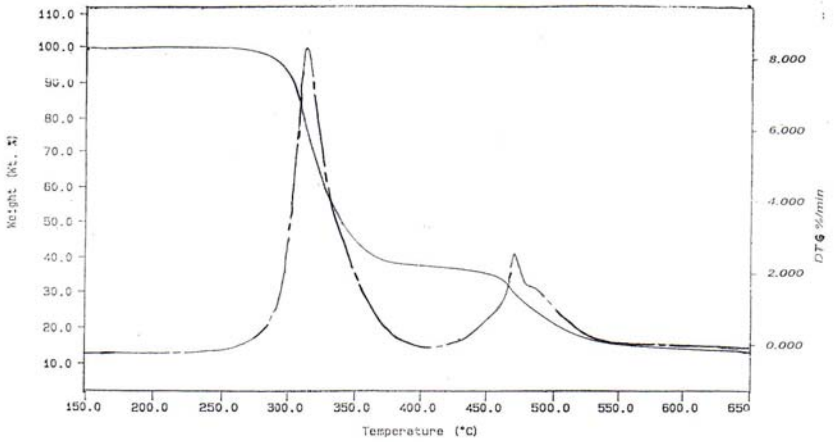


Figure 7 : Thermogravimetric curve for PVC containing 3% Co - laurate

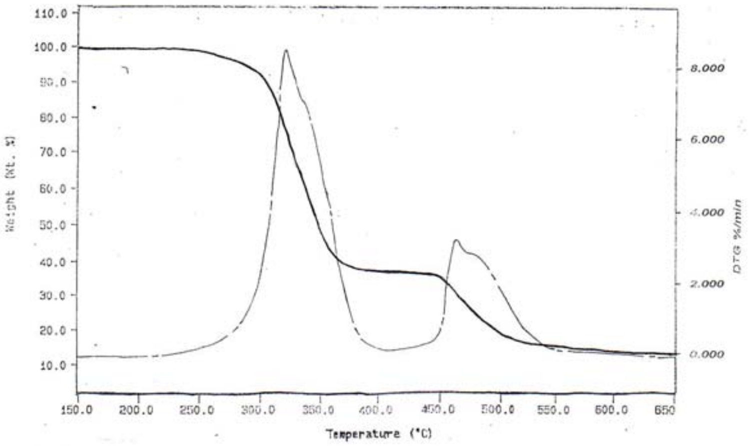


Figure 8 : Thermogravimetric curve for PVC containing 3% Ni - laurate

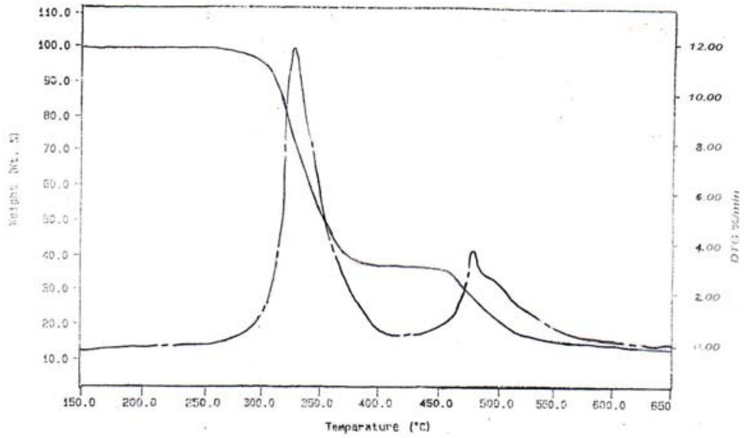


Figure 9 : Thermogravimetric curve for PVC containing synergistic mixture (Fe , Co , Ni – laurate)

Table 3 : Characters of thermal stability for pure PVC and PVC containing prepared metal carboxylates

Compound	Decomposition temperature			50% decomp.	Rate of decomp. at 318 ° C (%/min)	Total HCl loss (%)	Activation energy at (290-320 °C) (Kj.mole^{-1})
	T_i	T_{op}	T_f				
Pure PVC	265	305	374	332	10.32	64	140.82
PVC + Fe-laurate	275	322	402	347	7.92	61	175.66
PVC + Co-laurate	267	315	392	346	8.22	60	168.15
PVC + Ni-laurate	245	320	374	343	8.68	58	155.40
PVC + Fe,Co,Ni-laurate	268	326	404	350	7.35	57	191.96

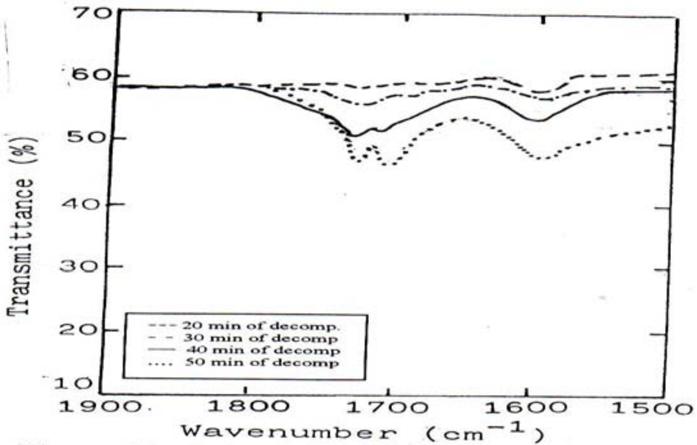


Figure 10 : Infrared spectra of pure PVC films after different times of decomposition at 245 ° C in air

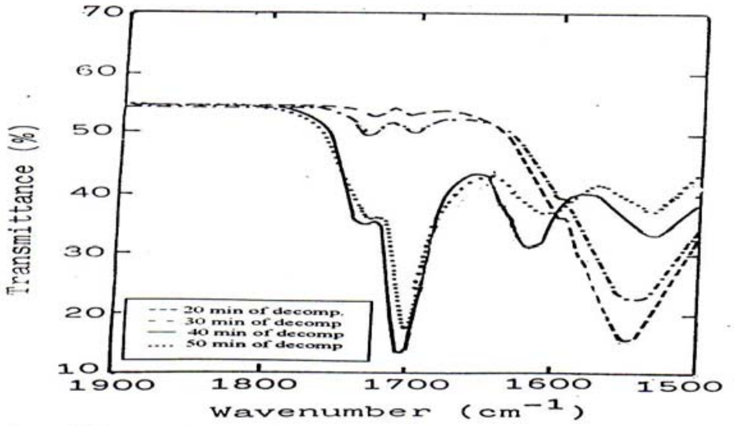


Figure 11 : Infrared spectra of PVC films stabilized with Fe-laurate after different times of decomposition at 245 ° C in air

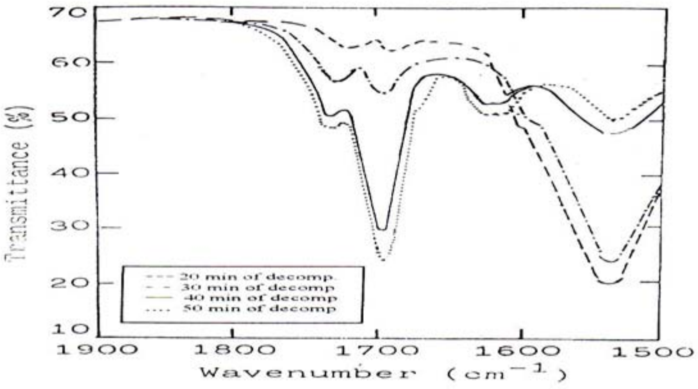


Figure 12 : Infrared spectra of PVC films stabilized with Co-laurate after different times of decomposition at 245 ° C in air

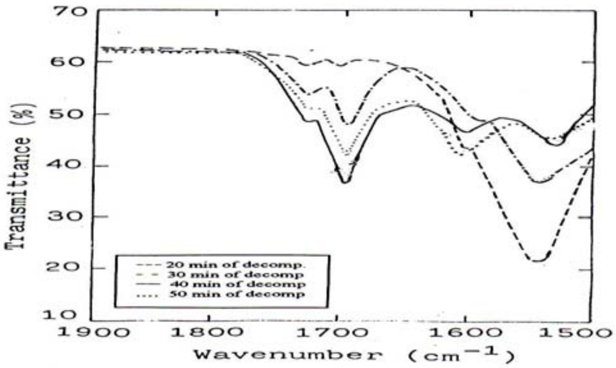


Figure 13 : Infrared spectra of PVC films stabilized with Ni-laurate after different times of decomposition at 245 ° C in air

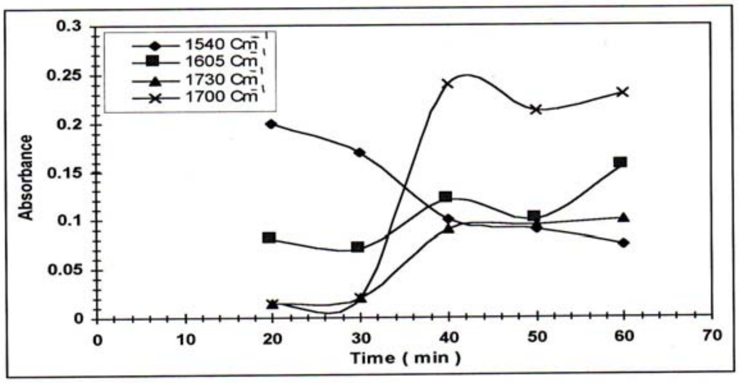


Figure 14 : Variation of the peak absorbances for PVC films stabilized with Fe – laurate after different times of thermal decomposition at 245 ° C in air

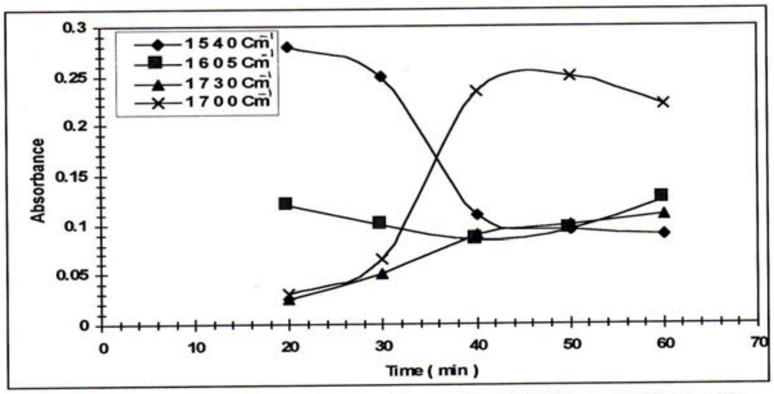


Figure 15 : Variation of the peak absorbances for PVC films stabilized with Co–laurate after different times of thermal decomposition at 245 ° C in air

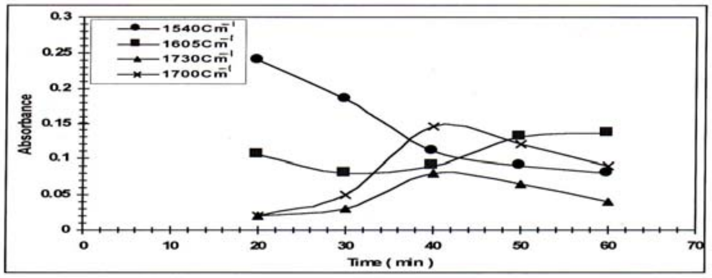


Figure 16 : Variation of the peak absorbances for PVC films stabilized with Ni – laurate after different times of thermal decomposition at 245 ° C in air

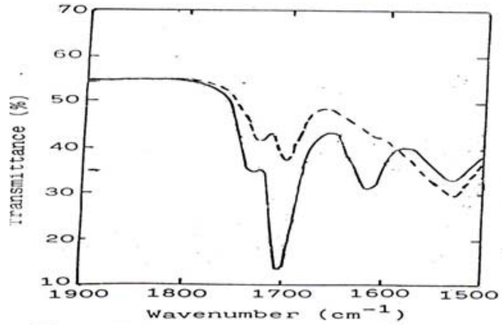


Figure 17 : Infrared spectra of PVC films stabilized with Fe-laurate after 40 min of decomposition at 245 ° C in air —— , and nitrogen -----

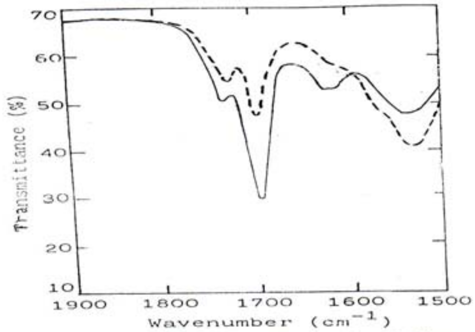


Figure 18 : Infrared spectra of PVC films stabilized with Co-laurate after 40 min of decomposition at 245 ° C in air —— , and nitrogen -----

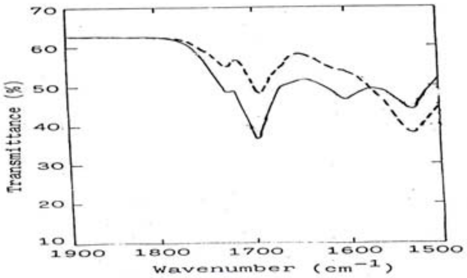


Figure 19 : Infrared spectra of PVC films stabilized with Ni-laurate after 40 min of decomposition at 245 ° C in air —— , and nitrogen -----

Table 4 : Values of absorbance at 275 nm for pure PVC and stabilized PVC in THF solvent

Stabilizer	Absorbance at 275 nm				
	Time of thermal stress (min)				
	20	30	40	50	60
Pure PVC	0.292	0.375	0.533	0.811	0.873
PVC + Fe-laurate	0.138	0.272	0.403	0.701	0.793
PVC + Co-laurate	0.140	0.288	0.491	0.745	0.801
PVC + Ni-laurate	0.163	0.300	0.504	0.773	0.824
PVC + Fe,Co,Ni-laurate	0.095	0.231	0.400	0.651	0.722

Table 5 : Values of absorbance at 385 nm for pure PVC and stabilized PVC in THF solvent

Stabilizer	Absorbance at 385nm				
	Time of thermal stress (min)				
	20	30	40	50	60
Pure PVC	0.127	0.161	0.208	0.273	0.305
PVC + Fe-laurate	0.067	0.124	0.175	0.200	0.251
PVC + Co-laurate	0.083	0.133	0.182	0.222	0.283
PVC + Ni-laurate	0.101	0.142	0.193	0.255	0.300
PVC + Fe,Co,Ni-laurate	0.055	0.120	0.153	0.192	0.225

Table 6 : Values of absorbance at 275 nm and 385 nm for Pure PVC and stabilized PVC with Fe-laurate in the presence of nitrogen

Compound	Absorbance at 275 nm / 285 nm				
	Time of thermal stress (min)				
	20	30	40	50	60
Pure PVC	0.241 0.097	0.298 0.120	0.487 0.188	0.780 0.233	0.802 0.271
PVC + Fe-laurate	0.125 0.063	0.203 0.101	0.363 0.135	0.671 0.161	0.733 0.211

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