

Studies on the thermal stabilization for Polyvinyl chloride by some metal stearates

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Abstract

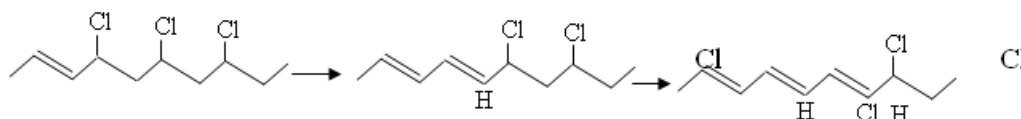
In this study, preparation of some metal stearates derived from stearic acid with metals ; Iron , Cobalt, Nickel, Copper and Zinc . They were used as thermal stabilizers for Polyvinyl chloride. These metal stearates were identified by elemental analysis and infrared spectroscopy. I.R, spectroscopy within the rang $1500-1900\text{ cm}^{-1}$ was used to study the thermal stability for PVC containing prepared metal stearates , and that depending on thin films technique . The variations in the absorption bands intensity of the groups $\text{C}=\text{O}$, $\text{C}=\text{C}$, COO^- at 195°C were studied at different times (15 ,30 ,45 , 60 min) from thermal stress. These variations resulted from the rule of the metal stearates in the stabilizing of polymer . U.V-V.S spectroscopy was used to study the thermal degradation of unstabilized PVC and the reprecipitated PVC from the stabilizers .This study was carried out by the investigation of the polymer resulted from the evolving of HCl from the polymer chain at 275nm and 385 nm corresponding to three and seven conjugated double bonds respectively .The results were indicated that metal stearates and their synergistic mixtures have the ability to stabilize PVC by decreasing the conjugated double bonds in the polymer .

The thermal stability of the unstabilized PVC and PVC containing different metal stearates was investigation by thermogravimetric analysis (TGA). Many functions were calculated such as the decomposition temperature , rate of decomposition ,activation energy ,char content ,and percentage of HCl evolving from the polymer chain . The results indicated that metal stearates was increasing the thermal stability for PVC . TGA was also used to evaluate the synergistic effect for some mixtures of the prepared metal stearates (Zinc stearate with stearates of the Nickel ,Cobalt ,Copper , Iron) , and it was found that these mixtures have high stabilizing ability for the PVC .

Introduction

PVC is commonly used as thermoplastic because of its wide variability of properties allowing its application in rigid and soft products. However, PVC has very poor thermal stability⁽¹⁾. The major chain degradation occurs by the elimination of HCl and simultaneous formation of conjugated double bond

leading to a colour change and also causes the deteriorations of physical, chemical and electrical properties. Dehydrochlorination can occur at only moderately elevated temperatures (about 100 °C). It is catalyzed by the HCl evolved (autocatalysis), and can also be promoted or initiated by other strong acids. The general mechanism of degradation of PVC is shown below^(2,3):



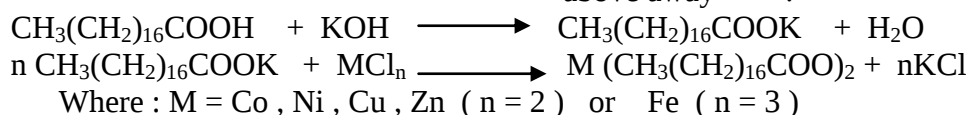
Thermal stability of PVC can be improved using various types of stabilizers which can quench the HCl produced such as metal carboxylates. It is generally accepted that thermal degradation of PVC can be blocked or retarded by metal carboxylates which must perform at least two basic functions; substitute stable group for labile chlorine atoms in PVC chains (allylic or tertiary chlorine atom) and react with HCl generated by the degradation process^(4,5). The most important stabilizers of PVC are different metal carboxylates like Pb-, Cd-, Ba-, Ca-, and Zn-carboxylates and some mono alkyl tin compounds. While thermal stabilizers based on tin and lead are most effective in some cases, they are not used any more since they are poisonous and are substituted by Ca-Zn-stabilizer which are nontoxic^(1,6). Many researchers have tried to study or explain the synergism of mixtures in the thermal stabilization of PVC⁽⁷⁻⁹⁾.

In this thermal stabilizers were prepared derived from stearic acid with Fe, Co, Ni, Cu, and Zn metals, also the role of these metal stearates and their synergistic mixtures on the thermal stabilization of PVC by infrared and ultraviolet visible spectrophotometers as well as thermogravimetric analysis was studied.

Procedures

Preparation of metal stearates

(4 g, 0.014 mole) from stearic acid was dissolved in 100 cm³ of alkaline water (0.14 M) of potassium hydroxide. The mixture was heated and stirred. Potassium salt of stearic acid was formed, after that 100 cm³ of solution from cobalt salt (0.07 M) was added. The formed mixture was also stirred and it was observed formation of precipitated cobalt stearate, filtered and washed with water then with methanol and dried until constant weight was obtained. All the metal stearates have been prepared as in above way^(10,11).



Preparation of stabilized PVC samples

The stabilized PVC samples were prepared by mixing prepared stabilizers with (4 %w/w) PVC. In order to study of synergistic effect of these stabilizers , 0.2 g each of two metal stearates were mixed with 10 g of PVC by grinding the require amount in mortar for 15 minutes ^(11,12).

IR with range (1500 – 1900 cm⁻¹) were recorded for stabilized PVC films (thickness = 0.17 mm) at different periods of exposure to thermal stress at 195 °C . Furthermore , ultraviolet visible spectra at 275 nm and 385 nm were used to study the thermal degradation of unstabilized PVC and reprecipitated PVC from stabilizers ⁽¹³⁾.

Thermogravimetric analysis technique was also evaluated for stabilized PVC

samples with heating rate of 20 °C / min in nitrogen atmosphere (gas flow rate equal 30 ml / min) .

Results and discussion

Identification of metal stearates

Table (1) is illustrated some physical properties of prepared metal stearates . The metal stearates have a wide range of melting points , and that seem to have liquid crystalline properties ^(14,15), The metal stearates were identified by elemental analysis , and the results show that the practical percentage of carbon and hydrogen are equivalent to the theoretical values .

In addition , These metal stearates were also identified by infrared spectra as shown in table (2) and figure (1-6)

Table (1) physical properties and elemental analysis for prepared metal stearates

Compound	Formula	C%	H%	Melting point	Color	Yield (%)
		Theoretical Practical	Theoretical Practical			
Fe Stearate	[Fe(CH ₃ (CH ₂) ₁₄ COO) ₂] H ₂ O	70.16 69.98	11.66 10.93	99-106	Brown powder	94.7
Co Stearate	[Co(CH ₃ (CH ₂) ₁₄ COO) ₂] .2H ₂ O	65.29 65.55	11.25 11.10	86-97	Violet powder	97.7
Ni Stearate	[Ni(CH ₃ (CH ₂) ₁₄ COO) ₂] .2H ₂ O	65.35 65.25	11.26 10.97	92-108	Green powder	91
Cu Stearate	[Cu(CH ₃ (CH ₂) ₁₄ COO) ₂] H ₂ O	66.67 66.35	11.18 11.19	113-119	Blue powder	93.4
Zn Stearate	[Zn(CH ₃ (CH ₂) ₁₄ COO) ₂] . H ₂ O	66.47 66.40	11.15 11.18	173-195	White powder	96.4

Table (2) : I.R spectra for prepared metal stearates

Compound	Str. Vib. O-H (cm^{-1})	Str. Vib. C-H (cm^{-1})	Str. Vib. (antisymm.) COO- (cm^{-1})	Str. Vib. (symm.) COO- (cm^{-1})	Bending vib. COO- (cm^{-1})	Str. Vib. C=O (cm^{-1})	Bending vib. C-H (cm^{-1})
Stearic acid	3400(m)	2930 (m)	-	-	-	1695 (s)	750 (m)
Fe stearate	3451 (m)	2870 (s) 2940 (s)	1540 (s) 1466 (s)	1460 (s)	938 (w)	-	722 (m)
Co stearate	3450 (m)	2860 (s) 2940 (s)	1560 (s)	1460 (s)	910 (w)	-	726 (m)
Ni stearate	3454 (m)	2968 (s) 2937 (s)	1563 (s)	1460 (s) 1435 (s)	938 (w)	-	724 (m)
Cu stearate	3450 (m)	2870 (s) 2940 (s)	1565 (s)	1465 (s) 1425 (s)	925 (w)	-	(m) 725
Zn stearate	3450 (m)	2897 (s) 2940 (s)	1548 (s)	1460 (s) 1400 (s)	925 (w)	-	(m) 725

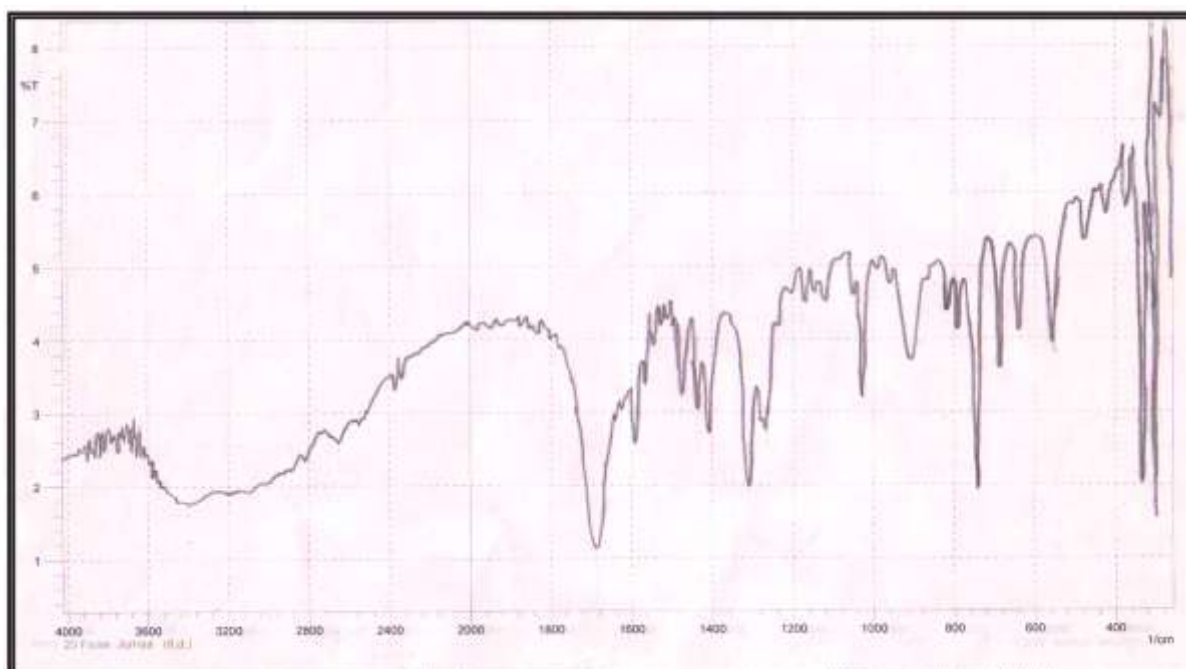


Fig (1): Infrared spectrum for stearic acid

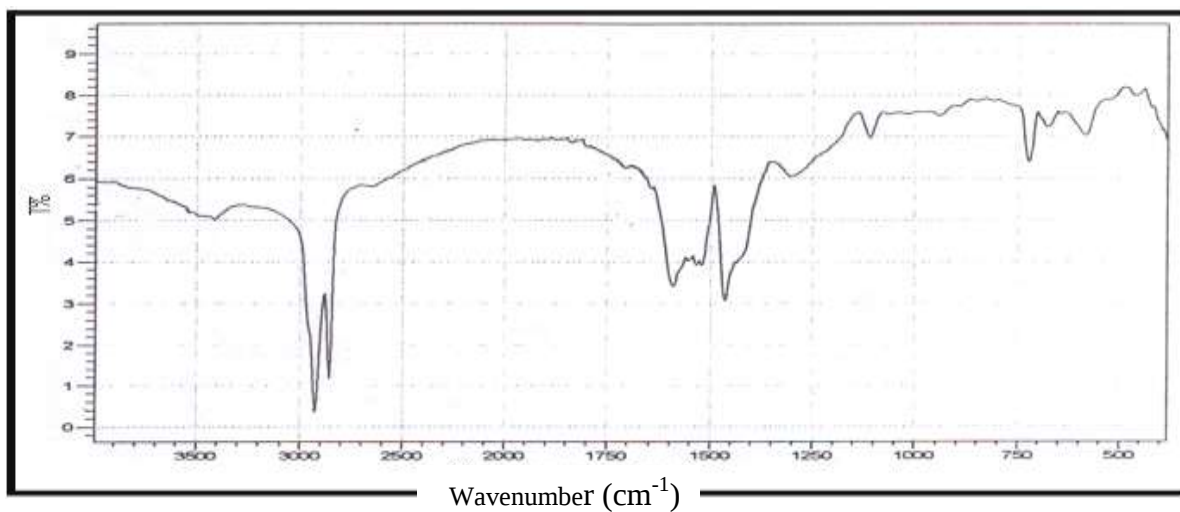


Fig (2): Infrared spectrum for Fe stearate

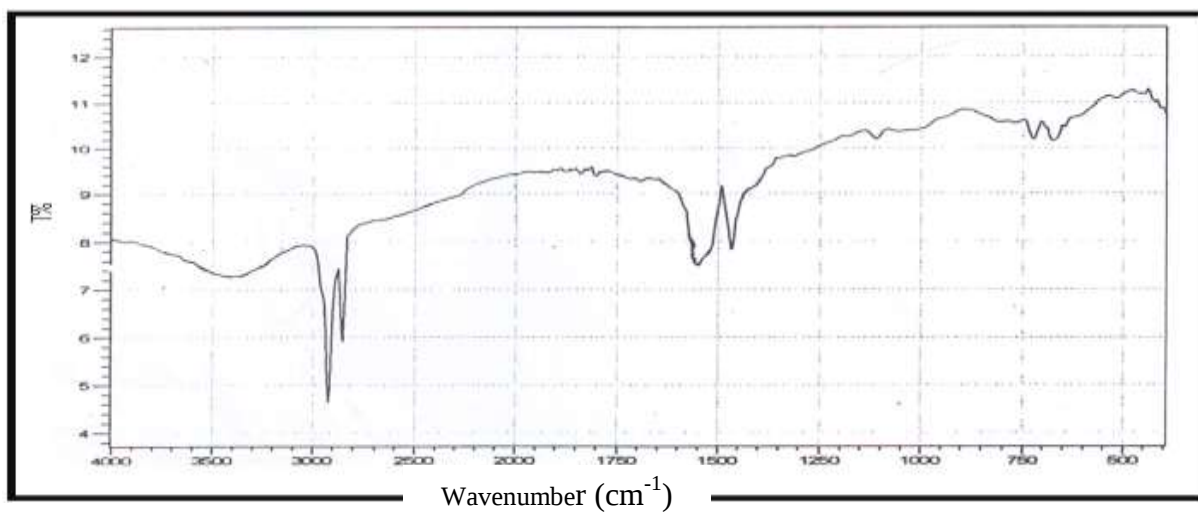


Fig (3): Infrared spectrum for Co stearate

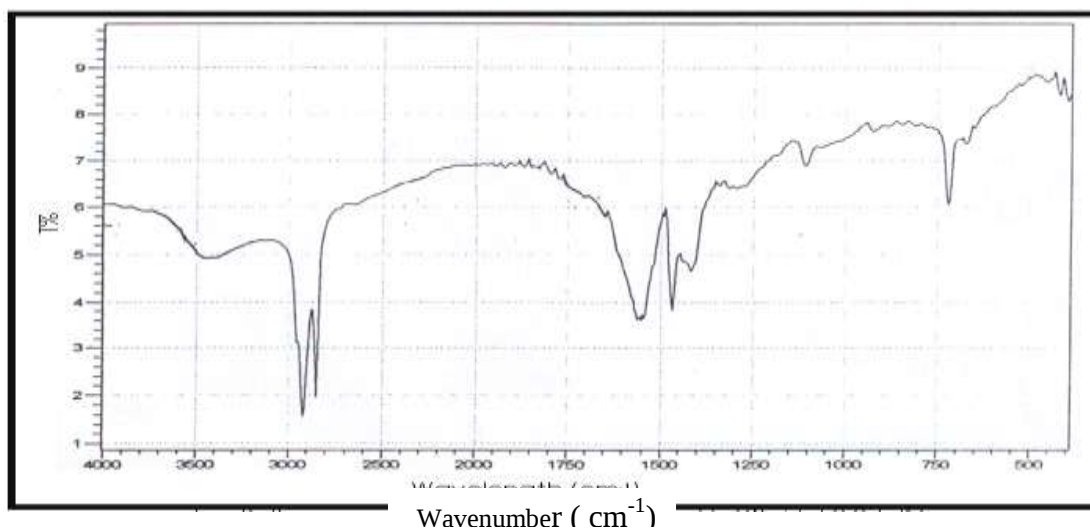


Fig (4): Infrared spectrum for Ni stearate

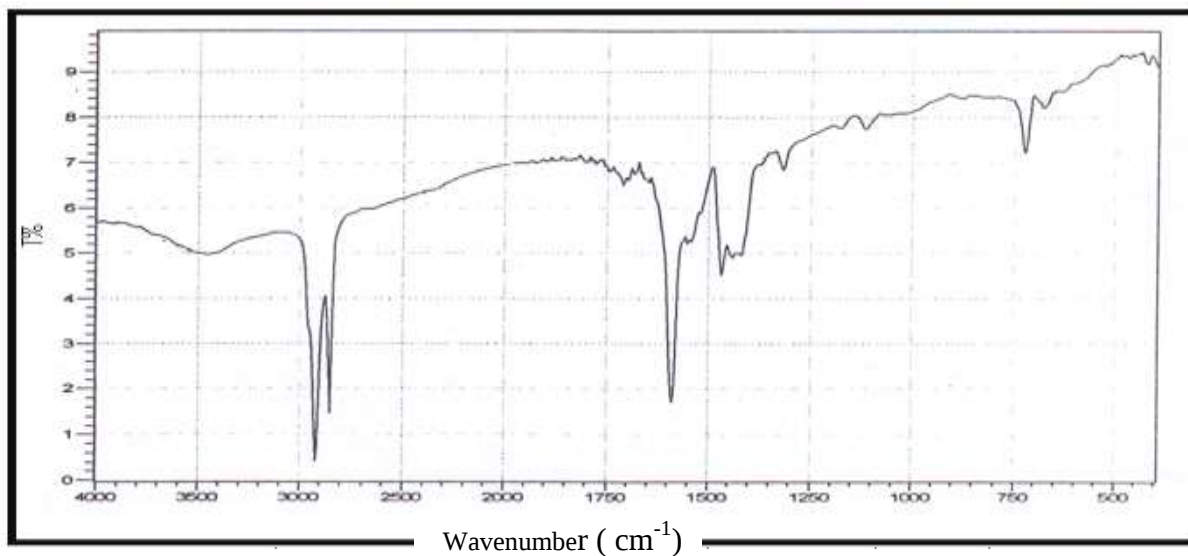


Fig (5): Infrared spectrum for Cu stearate

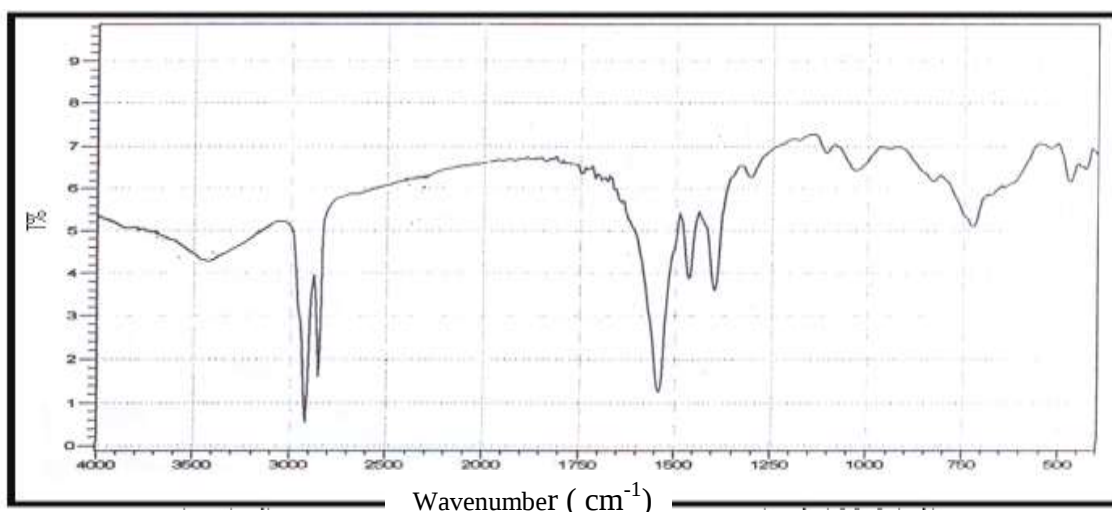


Fig (6): Infrared spectrum for Zn stearate

Infrared spectroscopy was studied for three absorption ranges ; antisymmetrical stretching vibration of COO^- group ($1500 - 1600 \text{ cm}^{-1}$) , stretching vibration of $\text{C}=\text{C}$ group ($1600-1650 \text{ cm}^{-1}$) and stretching vibration of $\text{C}=\text{O}$ group ($1700 - 1750 \text{ cm}^{-1}$) ^(16,17) as shown in figures (7) – (15)

Antisymmetrical stretching vibration of COO^- group in the Nickel, Iron ,Cobalt , Zinc and Copper stearates was appeared in different positions at 1556 , 1575 , 1553 , 1545 and 1560 cm^{-1} respectively because the site of this band is limited in cation attached with fatty acid . The results refer that the absorption of this band was

decreased during the increasing time of thermal stress and to derived conclusions about the consumption of metal stearates because of the reaction of these stearates with hydrogen chloride evolved from PVC chain and formation of fatty acid^(18,19).

The important band lies near 1630 cm^{-1} that belong to C=C bonds . This maximum lies somewhat lower than the characteristic absorption . The band may therefore be that of polyene or a group with double bond bearing chlorine or some other electronegative group in the vicinity . The C=O group , whose wavenumber has been reduced

by interaction with metal chloride , can not be ruled out⁽¹⁷⁾. The results show that imperviously changes in the absorption of this band with increasing degradation time .

On the other hand , the spectral range $1700 - 1750\text{ cm}^{-1}$ is included two bands at 1740 cm^{-1} and 1710 cm^{-1} that may be assumed two oxygen containing decomposition forms appeared during the degradation . The higher band was explained by the bond formation between stearates and the PVC chain to form ester group^(15,18) as shown below :



Where : M = Co , Ni , Cu , Zn

N = Fe

R = $\text{CH}_3(\text{CH}_2)_{16}$

The other band at 1710 cm^{-1} lies in the typical range of ketons or the associated form of fatty acids , even if the formation of the acid due to the stearates reaction with HCl released during the degradation . However , it seems to be that band belong to either the carbonyl group formed on the PVC chain or the carbonyl group to the fatty acid formed by HCl and that in agreement with others^(18,20).

Ultraviolet visible spectroscopy is used to study the thermal degradation of unstabilised PVC and stabilized PVC reprecipitated from metal stearates. This was done by the investigation of the absorption of the polyenes resulted from the losing of HCl from the PVC chain at 275 nm and 385 nm , which are corresponded to three and seven conjugated double bonds respectively^(13,21).

Table (3) and figures (16) , (17) show that the intensity of absorption at 275nm is higher than absorption at 385 nm because the concentration of polyenes contained three conjugated double bonds is great and formed firstly at exposure for thermal stress in comparison with polyenes contained seven conjugated double bonds .

On the other hand , the results indicated that Fe , Co , Ni and Cu stearates have the ability to stabilize PVC by decreasing the conjugated double bonds in the polymer chain , while Zn stearate was acted to increase the intensity of absorption for stabilized PVC in comparison with PVC alone at 275 nm and 385 nm .

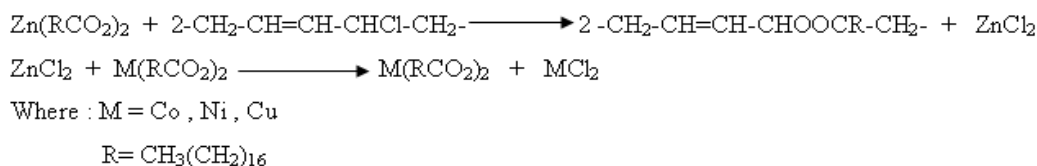
In order to increasing the stabilization efficiency for Zn stearate , the synergistic mixtures were prepared such as Zn-Fe , Zn-Co , Zn-Ni and

Zn-Cu stearates. The results shown in table (3) and figures (18) , (19) indicate that these mixtures have ability to increase the thermal stability of PVC and that is obviously during decreasing the intensity of absorption at 275 nm and 385 nm .

Thermogravimetric analysis was used in the present study to evaluate the thermal stability for PVC containing prepared metal stearates . Several thermal stability parameters were determined such as decomposition temperature , half loss temperature , total hydrogen chloride loss , rate of decomposition , activation energy and char content . The results shown in table (4) and figures (20) – (25) indicate that all metal stearates (except Zn stearate) increase the thermal stability of PVC , and this is

obviously during improvement of all thermal stability parameters . This thermal stability is due to the ability of the metal stearates to reduce the dehydrochlorination of PVC and that means reducing the catalytic effect of hydrogen chloride on the PVC degradation which interact with double bonds of dehydrochlorination chain (13,22) .

To improve the stabilizing rule of Zn stearate , the synergistic effect of Zn stearate mixed with Fe , Co , Ni and Cu stearates was studied . The results shown in table (4) and figures (26) – (29) indicate that thermal stability of PVC stabilized with these mixtures increase in comparison with PVC alone . The stabilization of PVC can be carried out probably according to the following mechanism (3,8,23) :



These equations show that $\text{Zn(RCO}_2\text{)}_2$ have ability to form ester bonding with PVC chain to result MCl_2 which act as lious acid increased the dehydrochlorination , but the presence of $\text{M(RCO}_2\text{)}_2$ leads to the variation of ZnCl_2 into inactive molecule , then the reestrication process take pl

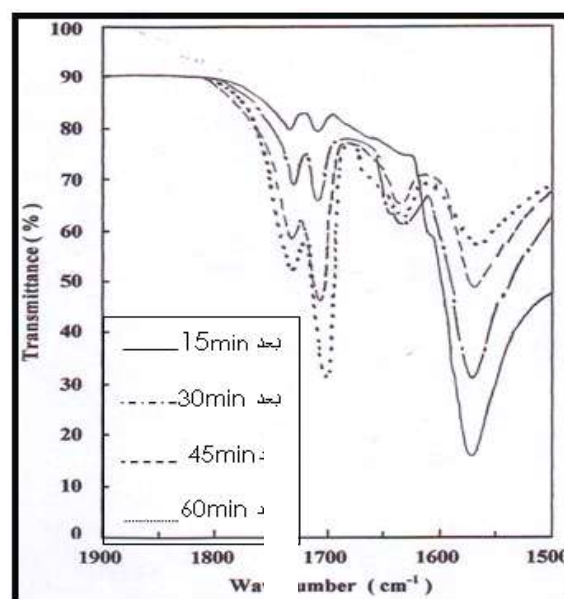


Fig (7): Infrared spectra for PVC films stabilized with Fe stearate in the degradation at 195 °C in air

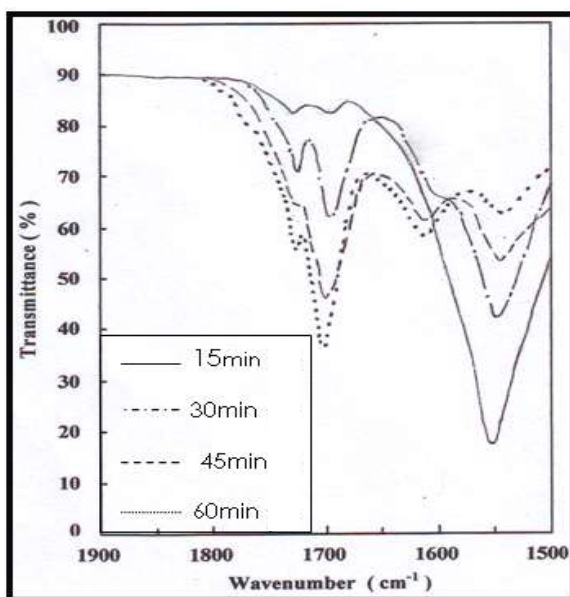


Fig (8): Infrared spectra for PVC films stabilized with Co stearate in the degradation at 195 °C in air

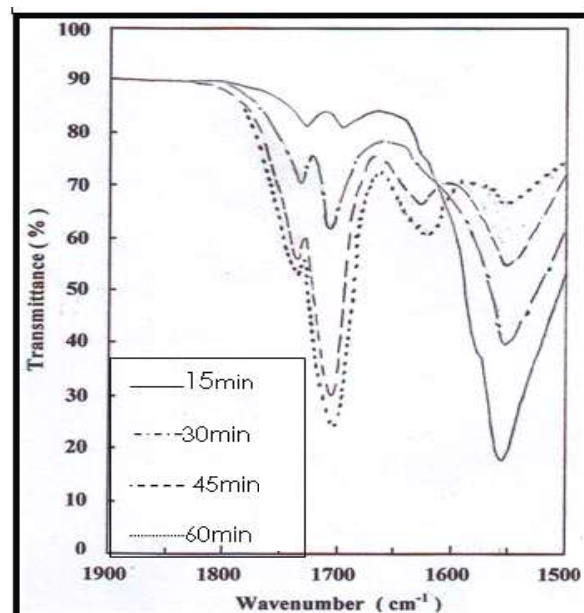


Fig (9): Infrared spectra for PVC films stabilized with Ni stearate in the degradation at 195 °C in air

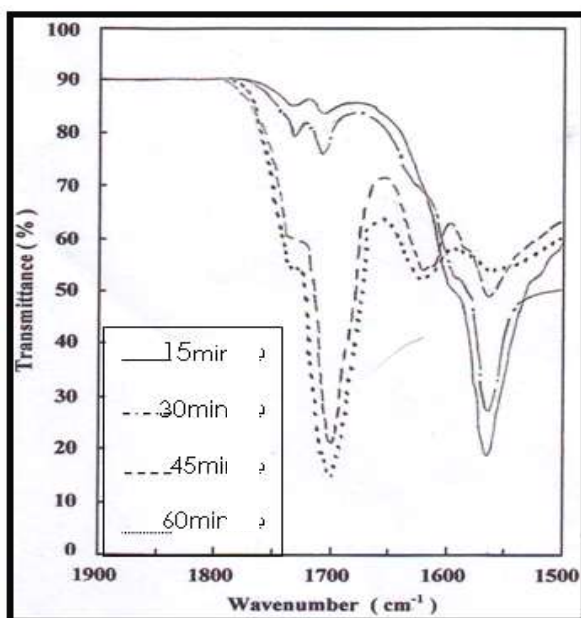


Fig (10): Infrared spectra for PVC films stabilized with Cu stearate in the degradation at 195 °C in air

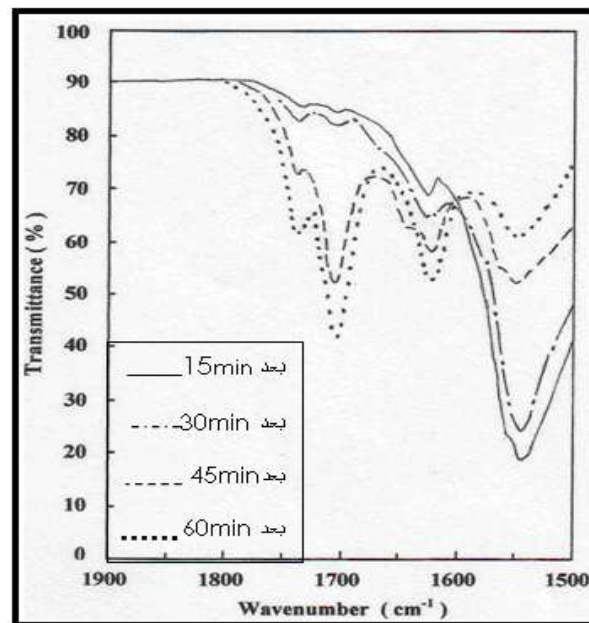


Fig (10): Infrared spectra for PVC films stabilized with Zn stearate in the degradation at 195 °C in air

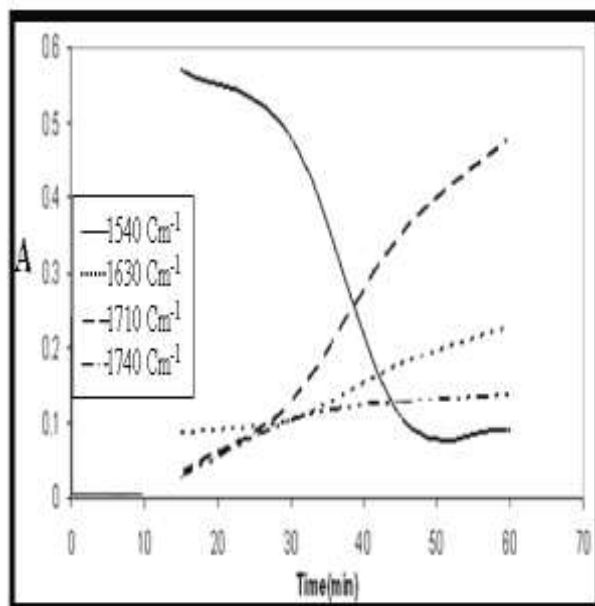


Fig (11): Dependence of the peaks for PVC films stabilized with Fe stearate on the time of thermal degradation at 195 °C in air [$A_i = \log (T1800 / T_i)$]

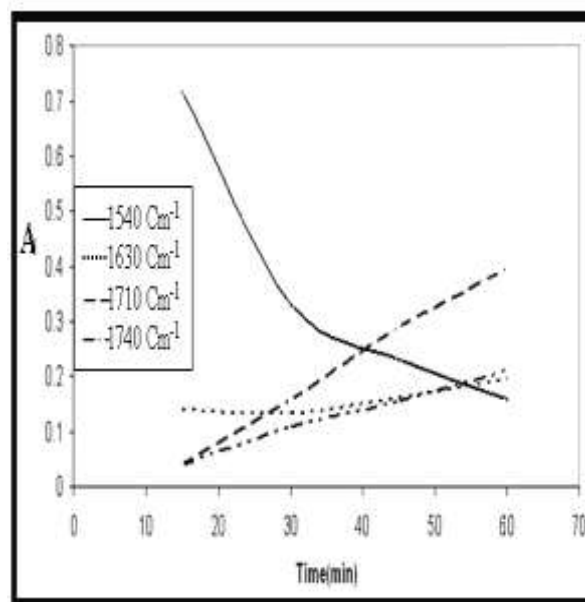


Fig (12): Dependence of the peaks for PVC films stabilized with Co stearate on the time of thermal degradation at 195 °C in air [$A_i = \log (T1800 / T_i)$]

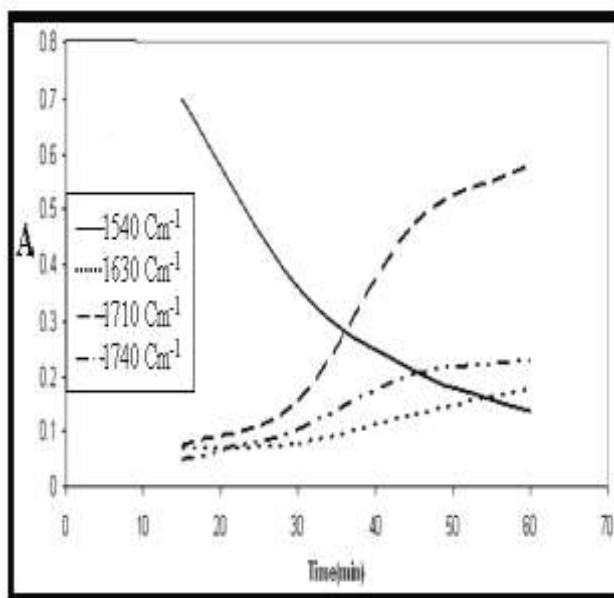


Fig (13): Dependence of the peaks for PVC films stabilized with Ni stearate on the time of thermal degradation at 195 °C in air [$A_i = \log (T1800 / T_i)$]

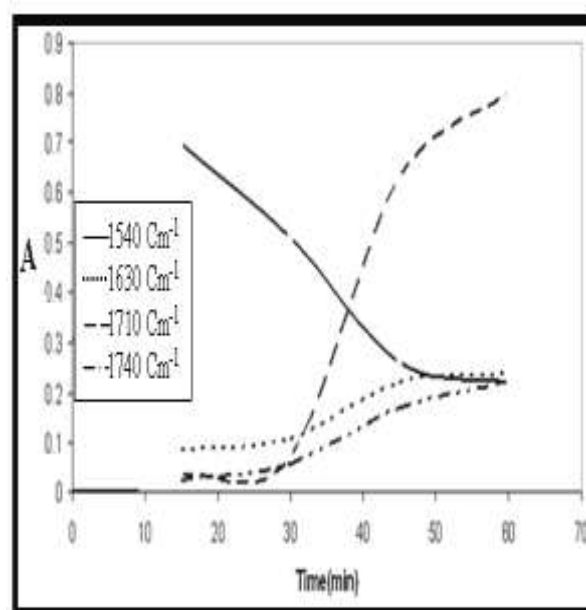


Fig (14): Dependence of the peaks for PVC films stabilized with Cu stearate on the time of thermal degradation at 195 °C in air [$A_i = \log (T1800 / T_i)$]

Table (3): Values of absorbances for unstabilized PVC and PVC reprecipitated from metal stearates at 275 nm and 385 nm

Compound	Absorbance at 385 nm				Absorbance at 275 nm			
	Time of thermal stress (min)				Time of thermal stress (min)			
	15	30	45	60	15	30	45	60
Unstabilized PVC	0.136	0.185	0.232	0.343	0.253	0.398	0.643	0.895
PVC+Fe-stearate	0.111	0.146	0.2	0.281	0.112	0.288	0.596	0.816
PVC+Co-stearate	0.086	0.114	0.177	0.256	0.072	0.25	0.561	0.751
PVC+Ni-Stearate	0.072	0.106	0.167	0.24	0.061	0.234	0.514	0.731
PVC+Cu-stearate	0.092	0.123	0.184	0.265	0.083	0.265	0.58	0.794
PVC+Zn-stearate	0.143	0.188	0.237	0.351	0.264	0.411	0.665	0.899
PVC+Zn-Fe-stearate	0.118	0.16	0.211	0.306	0.176	0.326	0.586	0.843
PVC+Zn-Co-stearate	0.092	0.134	0.183	0.271	0.14	0.282	0.527	0.793
PVC+Zn-Ni-stearate	0.084	0.126	0.173	0.261	0.114	0.246	0.505	0.769
PVC+Zn-Cu-stearate	0.107	0.142	0.2	0.29	0.154	0.3	0.568	0.814

Table (4): Some parameters of thermal stability for PVC stabilized with prepared metal stearates

Compound	Decomposition temperature (°C) from		Total HCl Loss(%)	Rate of Decomp. (w%/min)	Activation energy at 300-350 °C (KJ.mole ⁻¹)
	50% decomp.	DT			
Unstabilized PVC	337.5	286.5	62.0	7.05	131
PVC+Fe-Stearate	352.0	298.0	60.0	5.6	170.66
PVC+Co-Stearate	375.0	313.0	61.1	3.66	249.42
PVC+Ni-Stearate	376.0	325.0	60.1	3.35	270.21
PVC+Cu-Stearate	357.0	304.5	60.0	4.93	190.03
PVC+Zn-Stearate	330.0	267.0	62.9	8.16	129.78
PVC+Zn-Fe-Stearate	349.0	287.5	60.1	7.036	141.34
PVC+Zn-Co-Stearate	357.0	306.0	60.0	6.0	145.5
PVC+Zn-Ni-Stearate	375.0	308.0	60.0	5.7	172.7
PVC+Zn-Cu-Stearate	356.5	300.0	60.0	7.013	142.53

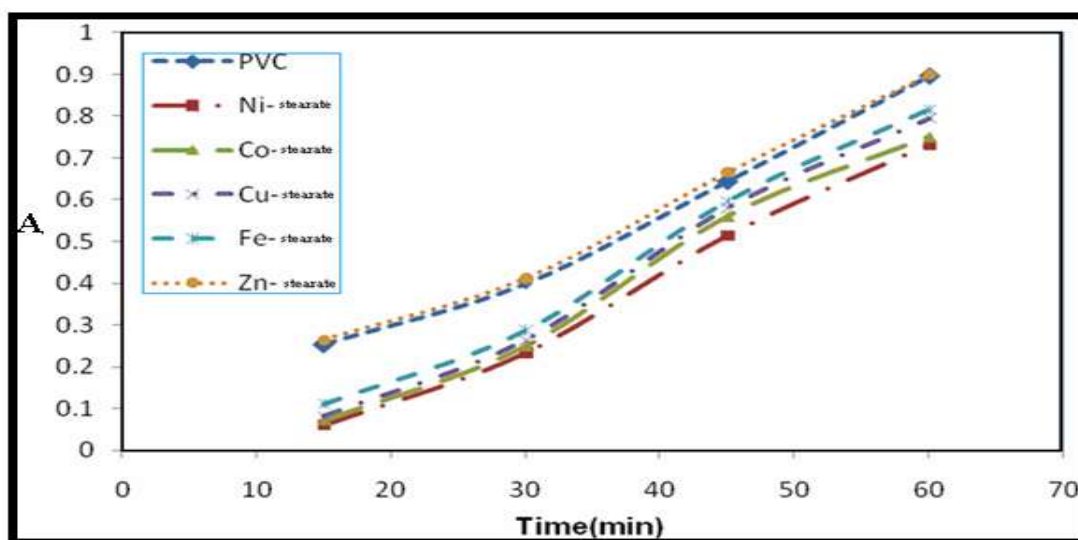


Fig (16): Dependence of absorbance for PVC films stabilized with prepared metal stearates at 275 nm on the time of thermal degradation at 195 °C in air

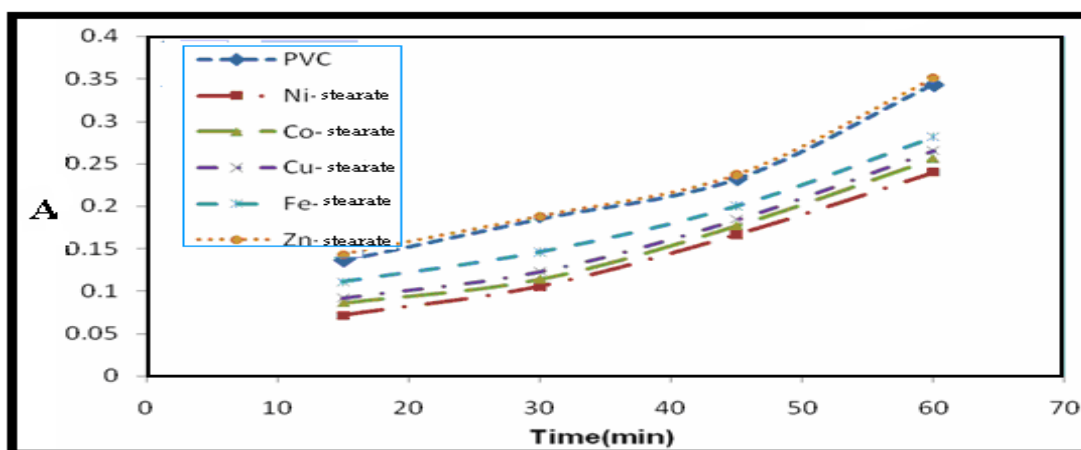


Fig (17): Dependence of absorbance for PVC films stabilized with prepared metal stearates at 385 nm on the time of thermal degradation at 195 °C in air

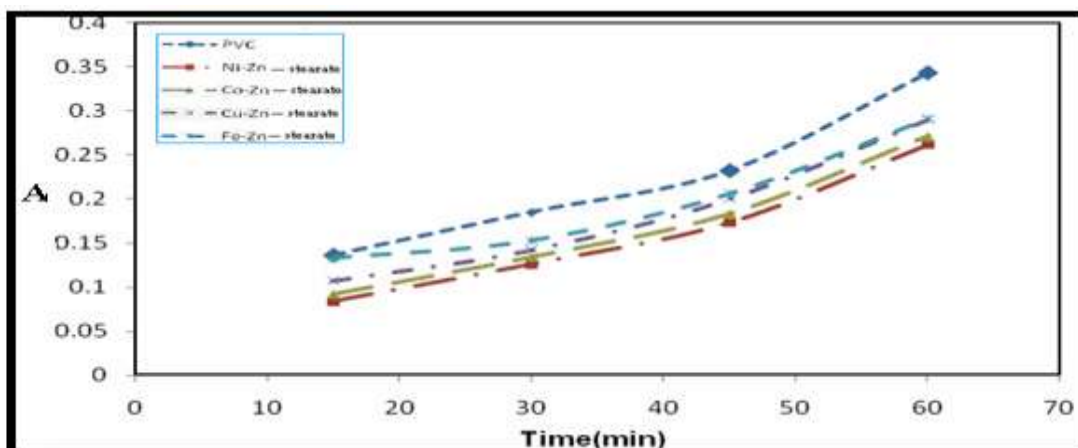


Fig (18): Dependence of absorbance for PVC films stabilized with synergistic mixtures of prepared metal stearates at 275 nm on the time of thermal degradation at 195 °C in air

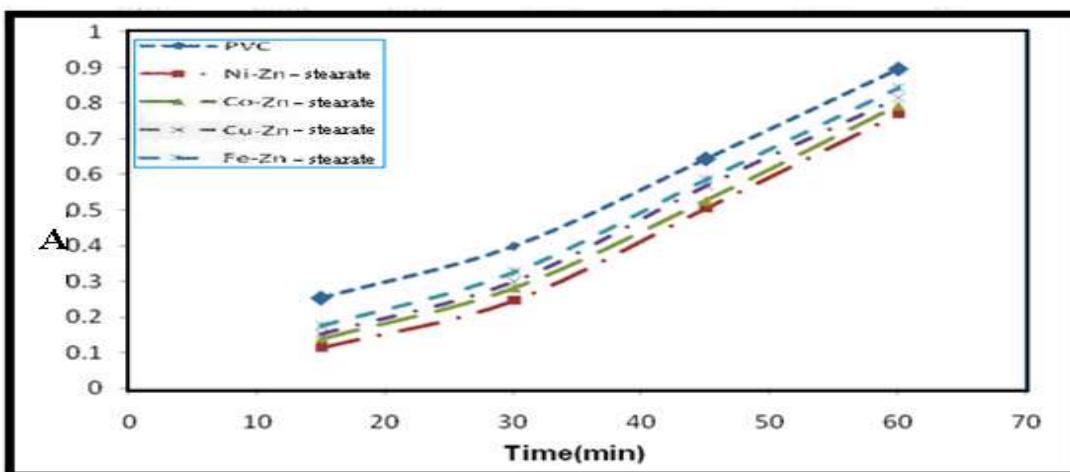


Fig (19): Dependence of absorbance for PVC films stabilized with synergistic mixtures of prepared metal stearates at 385 nm on the time of thermal degradation at 195 °C in air

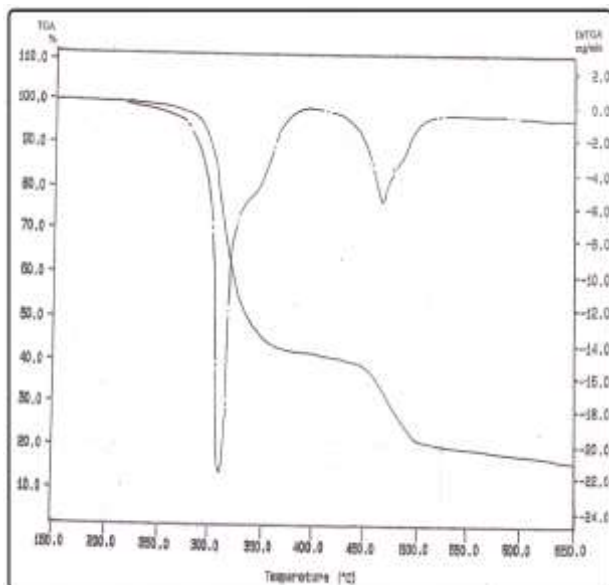


Fig (20): TGA curve for unstabilized PVC

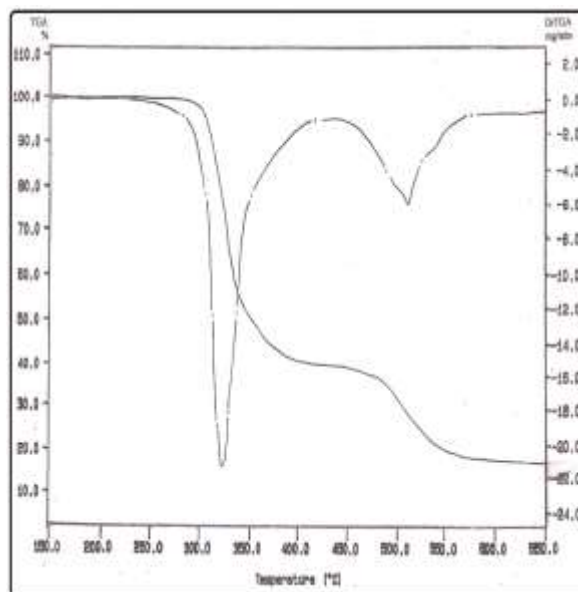


Fig (21): TGA curve for PVC stabilized with Fe stearate

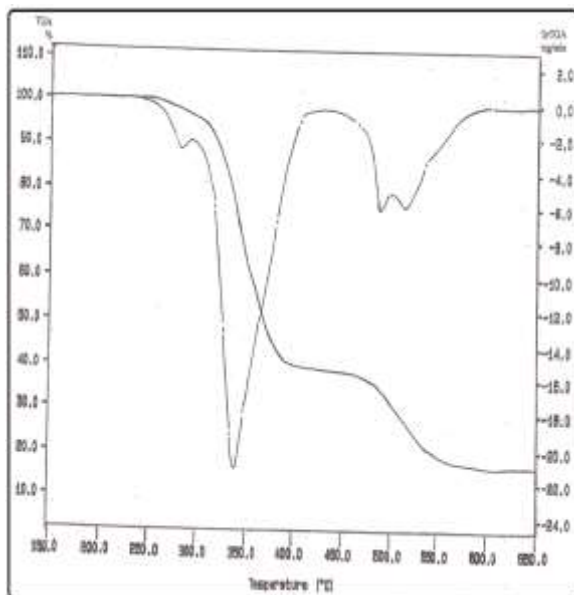


Fig (22): TGA curve for PVC stabilized with Co stearate

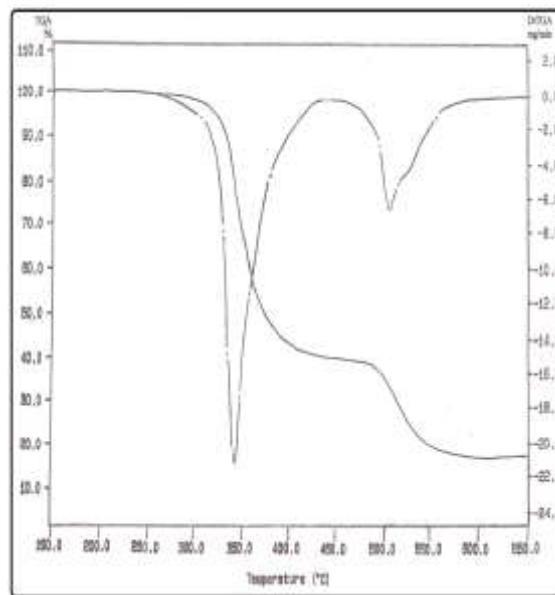


Fig (23): TGA curve for PVC stabilized with Ni stearate

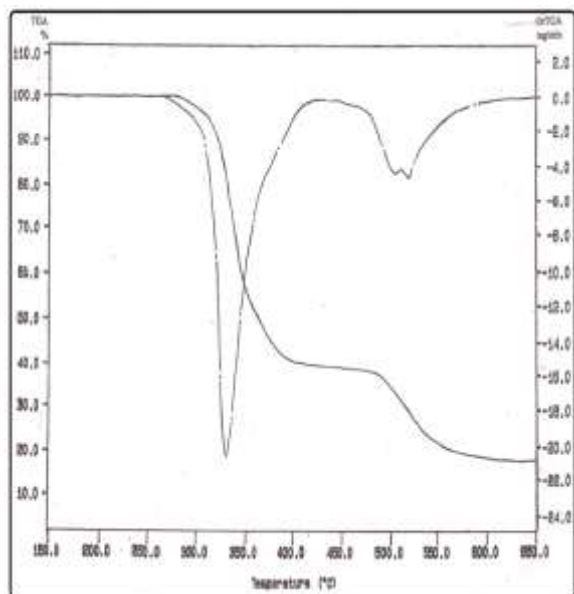


Fig (24): TGA curve for PVC stabilized with Cu stearate

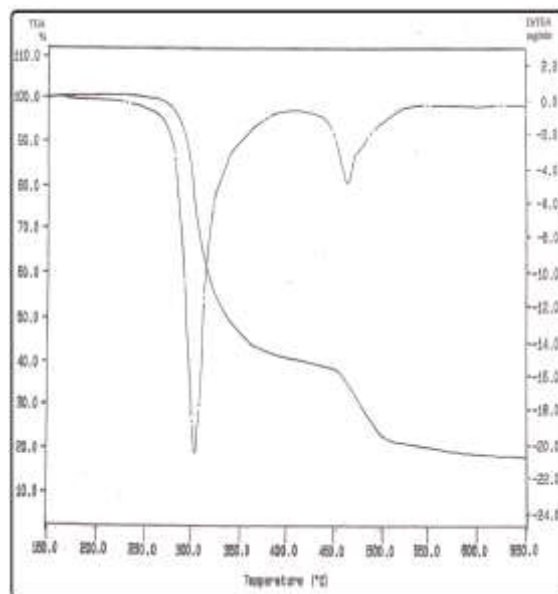


Fig (25): TGA curve for PVC stabilized with Zn stearate

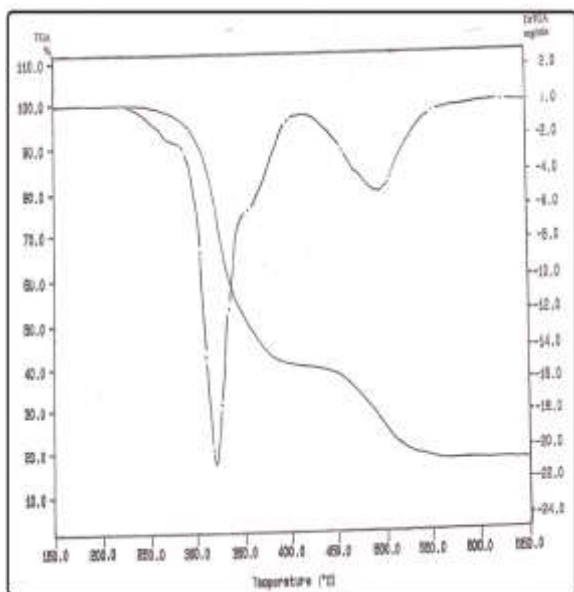


Fig (26): TGA curve for PVC stabilized with Zn-Fe stearate

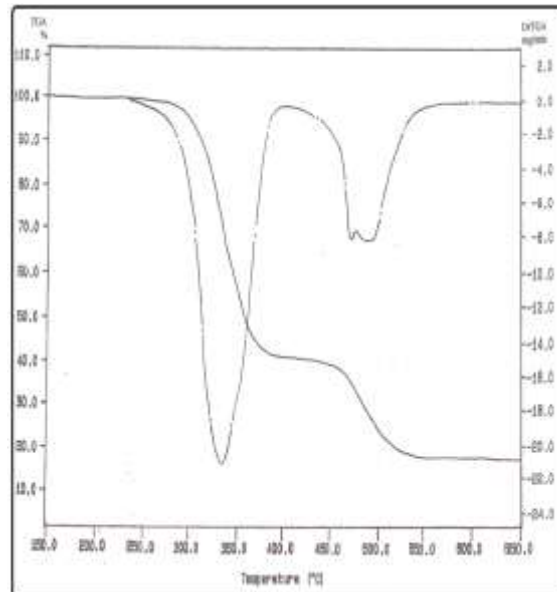


Fig (27): TGA curve for PVC stabilized with Zn-Co stearate

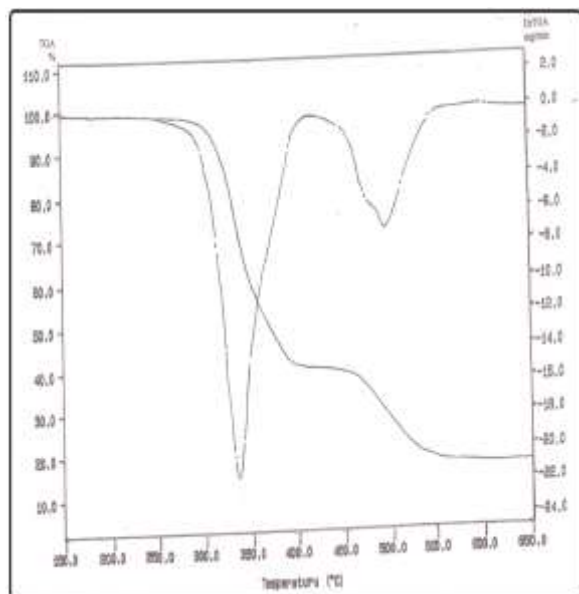


Fig (28): TGA curve for PVC stabilized with Zn-Ni stearate

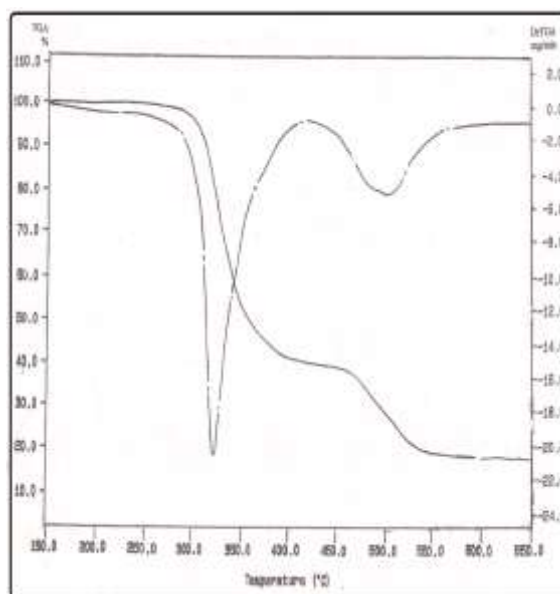


Fig (29): TGA curve for PVC stabilized with Zn-Cu stearate

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دراسة الثبات الحراري لبولي كلوريد الفايثيل بوجود سترات العناصر الفلزية

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الملخص

ضمنت الدراسة تحضير بعض ستيرات الفلز المشتقة من حامض الستريك مع فلزات الحديد والكوبلت والنيكل والنحاس والزنك وقد استخدمت هذه الستيرات كمثبتات حرارية للـ PVC . تم تشخيص ستيرات الفلز المحضرة بواسطة تحليل العناصر ومطيافية الاشعة تحت الحمراء . كما تضمنت الدراسة ايضا استخدام مطيافية الاشعة تحت الحمراء ضمن المدى ١٥٠٠ – ١٩٠٠ سم^{-١} لدراسة الـ PVC المحتوي على ستيرات الفلز وبالاغتماد على تقنية الافلام الرقيقة . حيث درست التغيرات في شدة حزم الامتصاص لمجموعة COO^- , $\text{C}=\text{C}$, $\text{C}=\text{O}$ عند 195°C في اوقات مختلفة (١٥ ، ٣٠ ، ٤٥ ، ٦٠ ، دقيقة من التعرض للاجهاد الحراري . وان تلك التغيرات تكون ناتجة من دور ستيرات الفلز في تثبيت البوليمر . استخدمت مطيافية الاشعة المرئية وفوق البنفسجية في دراسة التفكك الحراري للـ PVC غير المثبت والـ PVC المعاد ترسيبه من المثبتات . حيث تم تقييم البوليمر الناتج من تحرر HCl من سلسلة البوليمر عند الطولين الموجيين ٢٧٥ و ٣٨٥ نم والتي تقابل تكوين ثلاث وسبع اواصر مزدوجة متعاقبة على التوالي . وقد اشارت النتائج ان ستيرات الفلز وامزجتها التعاونية لها القابلية على تثبيت الـ PVC عن طريق تقليل تلك الاواصر المزدوجة المتعاقبة في البوليمر . بالاضافة الى ذلك درس الثبات الحراري للـ PVC المحتوي على ستيرات الفلز وامزجتها التعاونية بواسطة تقنية التحليل الحراري الوزني , وقد حسبت عدة دوال حرارية مثل درجة حرارة التفكك ومعدل سرعة التفكك وطاقة التنشيط ومحتوى التفحم بالاضافة الى النسبة المئوية للـ HCl المتحرر من سلسلة البوليمر . وقد اشارت النتائج بان ستيرات الفلز المحضرة تعمل على زيادة الثبات الحراري للـ PVC .